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A Study of Some Metal Cluster Systems Containing Niobium, Tantalum, Molybdenum and Tungsten

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A study of some metal cluster systems containing niobium, tantalum, molybdenum and tungsten

by

William Clifford Dorman

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A study of some metal cluster systems containing niobium, tantalum, molybdenum and tungsten*

William Clifford Dorman

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Four new mixed metal cluster compounds containing tantalum and tungsten, niobium and tungsten, and niobium and molybdenum were prepared and characterized by their electronic spectra, far infrared spectra, magnetic properties, and X-ray diffraction patterns. Tungsten substituted derivatives of $Ta_6Cl_{12}{}^{n+}$ obtained in this work were formulated as $[(C_3H_7)_4N]_{2,3}[(Ta_5WCl_{12})Cl_6]$. Also, new compounds considered to be derivatives of Nb_3Cl_8 were formulated as $Nb_{3-x}M_xCl_8$ (M = Mo, W).

All compounds were prepared by coreducing the appropriate pentahalides, or tungsten hexahalide, with Al in a $NaCl$-$AlCl_3$ melt. After reduction, the reaction ampoules were opened and their contents crushed and extracted, twice with water and a third time with ethanol.

The third extraction of the tantalum-tungsten mixture afforded a solution of the mixed metal clusters. This solution was saturated with anhydrous HCl, and $[(C_3H_7)_4N]_2$

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$[(Ta_5WCl_{12})Cl_6]$ was crystallized from solution, after oxidation with Cl_2, by the addition of excess tetrapropylammonium chloride. Reduction of this compound with zinc in butyronitrile yielded $[(C_3H_7)_4N]_3[(Ta_5WCl_{12})Cl_6]$.

The third extraction of the niobium-tungsten and niobium-molybdenum preparations yielded products free from the salt medium and from any soluble cluster species.

The reaction variables investigated in all preparations were the metal ratios in the starting mixtures, the reaction times and the reaction temperatures.

The electronic spectra, far infrared spectra, and magnetic properties of the $Ta_5WCl_{12}^{n+}$ species were found to be in close agreement with those of the corresponding isoelectronic members of the $Ta_6Cl_{12}^{n+}$ series.

The electronic spectra of the mixed metal clusters of niobium and tungsten were similar to that of Nb_3Cl_8. The niobium-molybdenum substituted compound, however, displays a unique electronic spectrum.

Magnetic data obtained for the tungsten substituted $Nb_{3-x}W_xCl_8$ species show a reduction in moment with increasing substitution of tungsten. The niobium-molybdenum compound was found to be diamagnetic.

The vibrational spectrum of the niobium molybdenum mixed metal compound reveals that this species is not related to the Nb_3Cl_8 cluster type compounds. However, a similar study of the niobium-tungsten phases indicates that the Nb_3Cl_8 structure type is maintained upon substitution of tungsten into the Nb_3Cl_8 phase. These conclusions are confirmed by data obtained from X-ray diffraction studies.

INTRODUCTION

Recently, there has been a tremendous renewed interest in the study of compounds containing metal-metal bonds. It is well known that many of the lower halides of niobium, tantalum, molybdenum and tungsten contain clusters of metal atoms with strong metal-metal interactions. Within this area of interest in these elements, research on metal atom cluster compounds of the type M_6X_{12} and M_6X_8 has also increased. The physical and chemical characterization of compounds containing these cluster species has led to an extension of the knowledge and applicability of them.

The purpose of this investigation was to extend the chemistry of hexanuclear and trinuclear metal atom clusters by preparing some new mixed metal cluster species and subsequently comparing some of the characteristics of the heteronuclear and homonuclear metal cluster compounds.

REVIEW OF PREVIOUS WORK

Synthesis of the Niobium and Tantalum M_6X_{12} Cluster Compounds.- In 1913, Harned (1) first reported a polynuclear compound of niobium obtained from the reduction of $NbCl_5$ with Nb(Hg) at elevated temperatures. From aqueous solution, he obtained crystals formulated as $(Nb_6Cl_{12})Cl_2 \cdot 7H_2O$. This formulation was later verified by an X-ray study on an ethanolic solution of $(Nb_6Cl_{12})^{2+}$. This study by Vaughan *et al.* (2) showed the compound to contain an octahedral arrangement of the niobium atoms. The reduction of niobium pentachloride using cadmium at red heat *in vacuo* has been shown to give increased yields of the hydrate, $(Nb_6Cl_{12})Cl_2 \cdot 8H_2O$, after extraction of the reaction mass with water.

Fleming, Mueller and McCarley (3) have obtained $(Nb_6Br_{12})Br_2 \cdot 8H_2O$ in up to 30% yields by the aluminum reduction of niobium pentabromide in a temperature gradient reaction of 350/280°. The reaction product was extracted with water, and the hydrated cluster was recrystallized from a neutral aqueous solution.

Schäfer and Spreckelmeyer (4) have obtained the oxidized form of the hydrated niobium cluster, $(Nb_6Cl_{12})Cl_3 \cdot 8H_2O$. They found that the $(Nb_6Cl_{12})^{2+}$(aq) can be oxidized by hydrogen peroxide in a hydrochloric acid solution to the $(Nb_6Cl_{12})^{3+}$ (aq) and evaporation yields the brown oxidized salt. This brown compound is paramagnetic as opposed to the dark green reduced parent compound which is diamagnetic (4,5,6).

Schäfer et al. (7) have prepared the pure anhydrous $(Nb_6Cl_{12})Cl_2$ by a high temperature, 800°, equilibration with niobium metal and Nb_3Cl_8. In a similar experiment, Schäfer and workers (8) prepared $(Nb_6F_{12})F_3$ by a high temperature equilibration of niobium and niobium pentafluoride. Both compounds are chemically inert and uniquely the only anhydrous binary halide phases containing the Nb_6X_{12} unit. The oxidation-reduction chemistry of the niobium clusters has been established by McCarley et al. (9), in which the +4 oxidation state of the cluster has been verified. Espenson and McCarley (10) were able to establish the two one-electron oxidations of the corresponding tantalum clusters as outlined in Equations 1 and 2.

$$Ta_6Cl_{12}{}^{2+} + Fe^{3+} = Ta_6Cl_{12}{}^{3+} + Fe^{2+} \qquad (1)$$

$$Ta_6Cl_{12}{}^{3+} + Fe^{3+} = Ta_6Cl_{12}{}^{4+} + Fe^{2+} \qquad (2)$$

Fleming and workers (11) have prepared $K_4(Nb_6Cl_{12})Cl_6$ by equilibrating either $(Nb_6Cl_{12})Cl_2$ or a higher niobium chloride with potassium chloride in a niobium tube at 800°.

The following tetraethylammonium, M, and tetraphenylarsonium, M', salts have been prepared by Fleming, Dougherty, and McCarley (12): $M_X[(Nb_6Cl_{12})Cl_6]$ (X = 2,3), $M'_2[(Nb_6Cl_{12})Cl_4(OH)(H_2O)]$, $M'_3[(Nb_6Cl_{12})Cl_5(OH)]$, and $M'_2[(Nb_6Cl_{12})Cl_5(H_2O)]$. The tetraethyl ammonium salts are prepared by oxidizing ethanol solutions saturated with HCl(g) of $(Nb_6Cl_{12})Cl_2 \cdot 8H_2O$

with oxygen to obtain the 3+ cluster and with chlorine to obtain the 4+ cluster. The appropriate salts immediately crystallize upon addition of excess tetraethylammonium chloride. Addition of M', tetraphenylarsonium chloride, to an aerated methanol-aqueous hydrochloric acid solution of $(Nb_6Cl_{12})Cl_2 \cdot 8H_2O$ yields the 3+ M' complexes. The 4+ M' complexes, in the above mentioned order, were obtained by addition of M' to solutions containing progressively higher concentrations of hydrochloric acid and by oxidation with chlorine gas.

Mackay and Schneider (13) used the same method to prepare $[(Et_4N)]_X[(Nb_6Cl_{12})Cl_6]$ (X = 2,3). To prepare the reduced $[(Et_4N)]_4[(Nb_6Cl_{12})Cl_6]$, the crystallization reaction was carried out under nitrogen to exclude oxygen. The magnetic moment of the 2+ complex, 0.47 B.M., was attributed to some 3+ impurity resulting from a lack of total oxygen exclusion. The 3+ complex was paramagnetic with an effective magnetic moment of 1.615 B.M.

The following complexes were also prepared and studied by Mackay (14): $[(Et_4N)]_2[(Nb_6Cl_{12})X_4(EtOH)_2]$ (X = Cl,Br), $[(Nb_6Cl_{12})(DMSO)_6](ClO_4)_2$, $[(Et_4N)]_2[(Nb_6Cl_{12})Br_6]$, and $[(PyMe)]_2[(Nb_6Cl_{12})I_6]$ (DMSO = dimethylsulfoxide, PyMe = N-methylpyridinium cation). The first two complexes are precipitated from a refluxing ethanolic solution of $(Nb_6Cl_{12})Cl_2 \cdot 8H_2O$ by the addition of excess Et_4NX. If the two terminal chlorides are precipitated by addition of silver perchlorate to the same ethanolic solution of $(Nb_6Cl_{12})Cl_2 \cdot 8H_2O$, the DMSO adduct can be prepared by addition of DMSO to the resulting solution. The pyridinium complexes are prepared in a manner similar to the preparation of the tetraethylammonium salts.

Field and Keppert (15) have reported a series of complexes of the niobium chloride cluster with oxygen donor ligands. If $(Nb_6Cl_{12})Cl_2 \cdot 8H_2O$ in neat DMSO or DMF is diluted with a small amount of isopropanol, the $(Nb_6Cl_{12})Cl_2L_4$ adducts are precipitated (L = DMSO,DMF), (DMF = dimethylformamide). From an ethanolic solution of the hydrated chloride cluster, the triphenylarsine oxide, triphenylphosphine oxide and pyridine-N-oxide adducts can be obtained by evaporating the ethanolic solution to dryness in the presence of the ligand.

Chabrié (16) reported a compound in 1907 which is probably the first reported hexanuclear tantalum cluster compound. By reducing tantalum pentachloride at red heat with sodium amalgam under water aspiration, Chabrié obtained a substance which was partially water soluble and formulated as $TaCl_2 \cdot 2H_2O$.

Chapin (17) reported in a similar reduction with the bromides that one-seventh of the bromide in a solution of his reduced product could be replaced by chloride, iodide, and hydroxide. He gave an insight to the proper formulation of the compounds when he reported the molecular weight of this reduction product to be 2275 in water or propanol. The compounds were reported as $(Ta_6Br_{12})Br_2 \cdot 8H_2O$, and the derivatives as $(Ta_6Br_{12})X_2 \cdot nH_2O$ where X = Cl, I, OH. At the same time, van Haagen reported the synthesis of $(Ta_6Br_{12})Br_2$ by the hydrogen reduction of $TaBr_5$ (18).

In a series of studies beginning in 1922, Lindner et al. (19-22) investigated the lower halides of tantalum, tungsten, and molybdenum. One aspect of their work was the reduction of tantalum pentachloride with lead, aluminum or zinc under nitrogen. After subsequent work-up of the aqueous solutions, a crystalline compound was obtained and formulated as the trimer, $H(Ta_3Cl_7 \cdot H_2O) \cdot 3H_2O$. The formulation of this compound as one of tantalum(II) was contended to be incorrect by Ruff and Thomas (23,24) who indicated it should be formulated as a tantalum(III) complex, $Ta_3Cl_7O \cdot 3H_2O$.

After reduction of tantalum pentaiodide with tantalum, Körösy (25) reported that a lower iodide of tantalum was obtained by evaporating the green aqueous extract to yield green crystals.

However, Alexander and Fairbrother (26) heated tantalum pentaiodide and tantalum together and reported no reaction up to 500°, and in the range of 1000° to 1500° only thermal decomposition of tantalum pentaiodide.

McCarley and Kuhn (27) reported the preparation of $(Ta_6X_{12})X_2$ (X = Cl,Br,I) by reducing the appropriate pentahalide with aluminum in a thermal gradient. The reactions were carried out in Vycor ampules placed in a gradient furnace at an angle such that the reactants occupied the lower end of the tube, the hot zone. The conditions were as follows: for X = Cl, 200°/400°; X = Br, 280°/450°; and 300°/475° for X = I.

In a study of the tantalum pentabromide-tantalum and tantalum pentaiodide-tantalum phase diagrams, McCarley and Boatman (28) reported compounds of the stoichiometry $TaBr_4$, TaI_4, $TaBr_{2.83}$, $TaBr_{2.5}$, $TaBr_{2.33}$, and $TaI_{2.33}$. The expanded formulations of the last three compounds are $[Ta_6Br_{12}]Br_3$ $[Ta_6Br_{12}]Br_2$ and $[Ta_6I_{12}]I_2$. All of the compounds, except the tetrahalides, dissolve in water to give solutions which exhibit electronic absorption spectra indicative and characteristic of the $Ta_6X_{12}{}^{n+}$ ions.

Schäfer et al. (29-32) reported the synthesis of $(Ta_6Cl_{12})Cl_3$, $(Ta_6Br_{12})Br_3$ and $(Ta_6I_{12})I_2$ by utilizing transport techniques. Bauer et al. also reported the preparation of the iodide by reducing tantalum pentaiodide with tantalum in a temperature gradient (33). Schäfer and workers (29,30) could find no crystalline anhydrous chloride of tantalum lower than Ta_6Cl_{15}. Schäfer and Bauer (34) verified the correct formulation of the hydrate $(Ta_6Cl_{12})Cl_2 \cdot 8H_2O$.

Oxidation of the $(Ta_6X_{12})^{2+}$ by the appropriate halogen in aqueous media (X = Cl,Br) yields the corresponding $(Ta_6X_{12})^{4+}$ as reported by McCarley et al. (9). As indicated in reactions 1 and 2, oxidation of the 2+ to the 3+ cluster by iron(III) is quantitative. However, as indicated in (10), a large excess of iron(III) is necessary for the oxidation step from the 3+ cluster to the 4+ as shown in Equation 2.

As reported by McCarley et al. (9), the oxidized sulfate, $(Ta_6Cl_{12})(SO_4)_2$ can be prepared from an aqueous solution that has been acidified with sulfuric acid and oxidized with iron (III) or chlorine. The preparation of the reduced sulfate, $(Ta_6Cl_{12})SO_4$, can be achieved by an ion exchange technique.

Spreckelmeyer and Schäfer (35,36) report the isolation of the hydrates $(Ta_6Cl_{12})Cl_3 \cdot 7H_2O$, $(Ta_6Br_{12})Br_3 \cdot 7H_2O$ and $(Ta_6Br_{12})Br_4 \cdot nH_2O$. Allen and Sheldon (37) reported the synthesis of $[Ta_6Cl_{12}]Cl_2 \cdot 8H_2O$.

$(Ta_6I_{12})I_3$ can be isolated from the oxidation of $(Ta_6I_{12})I_2$ with liquid iodine as reported by Bayer and Schäfer (38). The product remains after the excess iodine is pumped away from the reaction mass.

Starting with a $(Ta_6Cl_{12})Cl_2 \cdot 8H_2O$ ethanolic solution saturated with HCl(g), Mackay and Schneider (39) isolated $[(C_2H_5)_4N]_3[(Ta_6Cl_{12})Cl_6]$ by oxidizing the solution with air, adding excess tetraethylammonium chloride and evaporating the solution under oxygen free conditions.

Spreckelmeyer (40) isolated a number of compounds by dissolving the parent compound, $(M_6X_{12})X_2 \cdot 8H_2O$, in 5N ethanolic hydrogen halide, oxidizing with 30 per cent hydrogen peroxide, and adding neat pyridine which caused crystallization of the pyridinium salts, $[(C_5H_5NH)]_2[(M_6X_{12})Cl_6]$, where M = Ta, Nb; X = Cl, Br; $[(C_5H_5NH)]_2[(Ta_6Cl_{12})Br_6]$ was prepared in a similar manner. These salts were found to be identical to the pyridinium salts isolated by Lindner et al. (21).

Hughes et al. (41) reported a series of oxidized derivatives of $(Ta_6X_{12})^{4+,3+}$. The black crystalline $[(Ta_6Br_{12})Br_4(H_2O)_2]\cdot 3H_2O$ was isolated from a methanol solution of the anhydrous $(Ta_6Br_{12})Br_2$ by oxidizing the solution with bromine water, acidifying with aqueous hydrogen bromide and reducing the volume. Beginning with an aqueous solution of the corresponding $(Ta_6Cl_{12})^{2+}$ and treating in a similar manner, good yields of the red-brown analogous hepta-hydrate, $[(Ta_6Cl_{12})Cl_4(H_2O)_2]\cdot 7H_2O$ were obtained. When a methanol solution of $(Ta_6Cl_{12})^{2+}$ was so treated, the acid hydrate salt of the oxidized cluster, $H_2[(Ta_6Cl_{12})Cl_6]\cdot nH_2O$, was isolated. They also showed that the aqueous solutions of the parent compounds, $(Ta_6X_{12})^{2+}$ X = Cl, Br, could be titrated spectrophotometrically with iron(III) or the appropriate halogen in water, acidified with the corresponding hydrohalic acid and partially evaporated to yield the 3+ hydrates, $[(Ta_6X_{12})X_3(H_2O)_3]\cdot 3H_2O$ where X = Cl, Br.

These same workers also reported the preparation of the compounds with the general formulation, $[(C_2H_5)_4N]_2[(Ta_6X_{12})Y_6]$ where X, Y = Cl, Br. These compounds crystallize from a solution of the parent compound, $(Ta_6X_{12})X_2$, in ethanol by oxidizing with the appropriate halogen, saturating the solution with HY and adding $(C_2H_5)_4NY$. The $[(C_6H_5)_4As]_2[(Ta_6Cl_{12})Cl_6]$ compound can also be prepared in a similar manner. In order to prepare the 3+ cluster compound,

$[(C_2H_5)_4N]_3[(Ta_6Cl_{12})Cl_6]$ it was necessary to start with an ethanol solution of the 3+ hydrated parent compound, $[(Ta_6Cl_{12})Cl_3(H_2O)_3]\cdot 3H_2O$, and rigorously protect the solution from air oxidation until the solid complex had been obtained.

Fleming et al. (42) have reported the preparation of two DMSO adducts, $[(Ta_6Cl_{12})(DMSO)_6](ClO_4)_2$ and $(Ta_6Cl_{12})Cl_3(DMSO)_3$, and $K_4[(Ta_6Cl_{12})Cl_6]$. This tetranegative anion ot the tantalum cluster is formed directly in the aluminum reduction of tantalum pentachloride in the presence of potassium chloride.

Broll, Juze and Schäfer (43) reported the preparation of the series of compounds $A_4[(Nb_6Cl_{12})Cl_6]$ (where A = Na,K, Cs), $K_4[(Nb_6Br_{12})Br_6]$, and $A_4[(Ta_6Cl_{12})Cl_6]$ (where A = Na,K, Cs). The niobium compounds are prepared by a high temperature disproportionation of Nb_3X_8 in the presence of AX, X = Cl, Br and A as outlined above. The same products are obtained if the trimer is reduced with niobium metal in the presence of the alkali-halide. Beginning with either $(Ta_6Cl_{12})Cl_3$ or "$TaCl_3$", and reacting these materials in a similar manner as above, the corresponding tantalum species are obtained.

Juza and Schäfer (44) have used $Na_4[(Nb_6Cl_{12})Cl_6]$ and the corresponding $Na_4[(Ta_6Cl_{12})Cl_6]$ to prepare a mixed phase formulated as $Na_4[(Nb,Ta)_6Cl_{12})Cl_6]$. This was accomplished by the co-reduction as described in (43) of Nb_3Cl_8 with Nb and $TaCl_3$ with Ta in the presence of NaCl at 800°. It was possible to obtain the mixed phase beginning with $(Nb_6Cl_{12})Cl_2$, $(Ta_6Cl_{12})Cl_3$ + Ta and NaCl. A co-reduction of the pentachlorides with cadmium or sodium amalgam also yields the mixed phase.

Schäfer and Spreckelmeyer (45) also report a mixed phase of niobium and tantalum bromide. These workers prepared a solid solution of tantalum and niobium pentabromides by brominating a mixture of the metals in composition ranges from 1:3 to 3:1. The resultant pentabromides were reduced with cadmium metal and the products extracted with water. The cadmium was removed as the sulfide, and the solution was acidified with aqueous hydrogen bromide. At this point the final product crystallized from solution. The electronic absorption spectra of the final product showed that the final solution was not simply a mixture of $(Nb_6Br_{12})^{2+}$ and $(Ta_6Br_{12})^{2+}$. From analytical data the phase was formulated as $[(Ta_{6-x}Nb_xBr_{12}]\cdot 8H_2O$ where x = 1.6 to 2.4. X-ray powder diffraction studies of this phase were very similar to patterns of $[(Ta_6Br_{12})Br_2]\cdot 8H_2O$ and $[(Nb_6Br_{12})Br_2]\cdot 8H_2O$.

All hydrates of the type $[M_6X_{12}]X_2 \cdot nH_2O$ have been verified by Schäfer and Bauer (34) to be the octahydrate, n = 8. For clarity and consistency, all hydrates of the 2+ niobium and tantalum clusters discussed have been recorded as the 8-hydrate.

Meyer also reports (46) a series of mixed metal hexanuclear cluster compounds. From a co-reduction of tantalum pentachloride and molybdenum pentachloride with aluminum, the complexes $M_2[(Ta_4Mo_2Cl_{12})Cl_6]$, $M_x[(Ta_5MoCl_{12})Cl_6]$ (x = 2,3), where M is a tetraalkylammonium cation, can be isolated.

Before beginning a review of the physical characterizations of the hexanuclear clusters of niobium and tantalum, it is interesting to point out here that there are only two violations of the sanctity of the (M_6X_{12}) configuration for the clusters of niobium and tantalum and the well-known (M_6X_8) configuration for the clusters of molybdenum and tungsten. Siepmann et al. (47), in an attempt to oxidize the tungsten(II) chloride cluster, reacted $(W_6Cl_8)Cl_4$ with liquid chlorine at 100° to produce the (M_6X_{12}) moiety in $(W_6Cl_{12})Cl_6$. The other exception is $(Nb_6I_8)I_3$ identified by Bauer et al. (33), Schäfer et al. (7), and Simon et al.

(48) who later confirmed its formulation as $(Nb_6I_8)I_{6/2}$ through single crystal X-ray analysis. Independently Bateman *et al*. (49) also arrived at the same formulation studying crystals prepared by Kust *et al*. (50). $(Nb_6I_8)I_3$ can be prepared by the disproportionation of γ-(Nb_3I_8) (48,49) or by the niobium reduction of the same compound (48). Simon *et al*. (48) and Simon (51) showed that $(Nb_6I_8)I_3$ will absorb hydrogen above 300° at atmospheric pressure to form a hydride of limiting composition $H(Nb_6I_8)I_3$.

Structural Studies.- X-ray structural studies have confirmed the existence of (M_6X_{12}) and (M_6X_8) cluster units in the lower halides of niobium, tantalum, molybdenum, and tungsten. Simon *et al*. (48) and Bateman *et al*. (49) verified the octahedral configuration of the metal atoms in $(Nb_6I_8)I_3$ and showed the compounds to contain (M_6X_8) units. However, these (Nb_6I_8) clusters were distorted from O_h symmetry to C_i. This distortion can be viewed as a displacement of two *trans* Nb atoms about 5° from the ideal C_4 axis and a slight compression. This compression leads to an apical *trans* Nb-Nb distance of 3.96 Å as compared to the other two *trans* distances of 4.08 and 4.06 Å respectively. *Cis* Nb-Ng distances range from 2.72 to 2.94 Å. The Nb-I^b (b = bridge) average distance is 2.87 Å with the range of distances between 2.84 and 2.90 Å. There were three Nb-I^t (t = terminal) distances observed: 2.90, 2.93 and 2.96 Å. The above interatomic distances are listed from Bateman et al. (49). He suggests (49) that the observed distortion is a result of the Jahn-Teller effect due to a single electron occupying a degenerate set of molecular orbitals. Simon et al. (48), whose parameters are in general good agreement with those of Bateman, suggests that the distortion is in part due to the intercluster bridging arrangement in the crystal. Simon (51) has completed the neutron diffraction study on $H(Nb_6I_8)I_3$ and located the proton in the center of the (Nb_6I_8) cluster.

Utilizing diffuse X-ray scattering techniques, Vaughan et al. (2) first determined the presence of the (M_6X_{12}) clusters in the lower halides of tantalum and niobium. These studies on ethanol solutions of $(M_6X_{12})X_2 \cdot 8H_2O$ showed the metal-metal distances in these compounds to be 2.85 Å $(Nb_6Cl_{12})^{2+}$, 2.88 Å $(Ta_6Cl_{12})^{2+}$, and 2.92 Å for the $(Ta_6Br_{12})^{2+}$. In this configuration, the cluster unit is described as an octahedron of metal atoms with a bridging halogen over each edge of the octahedron.

Burbank (52) asserts, from single crystal X-ray studies on $[(Ta_6Cl_{12})Cl_2] \cdot 8H_2O$, that the Ta_6 cluster forms a tetragonally distorted elongated tetragonal bipyramid. From this study, the correct formulation of the compound is $[(Ta_6Cl_{12})$

$Cl_2(H_2O)_4]\cdot 4H_2O$ indicating that the six terminal positions of the Ta_6 cluster are occupied by two chlorines and four water molecules. The other water molecules separate the cluster units into layers within the crystal.

Schäfer et al. (7) have shown by single crystal X-ray studies that $(Nb_6Cl_{12})Cl_2$ contains tetragonally compressed Nb_6 units. The four basal Nb-Nb distances are 2.95_5 Å and the apical to basal Nb-Nb distance is 2.89_5 Å. The compound is best formulated as $(Nb_6Cl^{i}_{10}Cl^{i-a}_{2/2})Cl^{a-i}_{2/2}Cl^{a-a}_{4/a}$, as suggested by Schäfer, where Cl^{i} is an inner bridging cluster chloride, Cl^{i-a} is an inner bridging cluster chloride which is weakly bound to another cluster, Cl^{a-i} is a terminal chloride weakly bound from another cluster and Cl^{a-a} is a normal terminal chloride link between clusters. This configuration does account for all terminal Nb positions to be coordinated to chlorine atoms.

Bauer and workers (33) found that $(Ta_6I_{12})I_2$ was isostructural with $(Nb_6Cl_{12})Cl_2$.

The structure of $(Nb_6F_{12})F_3$ has been reported by Schäfer et al. (8) to contain the (Nb_6F_{12}) cluster configuration with complete three dimensional intercluster bridging such that a better formulation would be $(Nb_6F_{12})F_{6/2}$. $(Ta_6Cl_{12})Cl_3$ is reported to have a similar structure by Bauer and Schnering (53).

Thaxton and Jacobson (54) reported the single crystal study of $H_2[(Ta_6Cl_{12})Cl_6]\cdot 6H_2O$. They found the structure to contain regular octahedral $(Ta_6Cl_{12})Cl_6{}^{2-}$ anion clusters. The Ta-Ta distance was found to be 2.962 Å, the Ta-Cl^b distance was 2.414 Å and the Ta-Cl^t was 2.507 Å. In comparison, Koknat and McCarley (55,56) reported the structures of $[(CH_3)_4N]_2[(Nb_6Cl_{12})Cl_6]$ and $[(CH_3)_4N]_3[(Nb_6Cl_{12})Cl_6]$. In the former, which is the niobium analog to $Ta_6Cl_{18}{}^{2-}$, the Nb-Nb distance was found to be 3.018 Å, Nb-Cl^b 2.425 Å and the Nb-Cl^t distance was 2.457 Å. In the $(Nb_6Cl_{12})Cl_6{}^{3-}$ anion of the latter compound, the important average internuclear distances were Nb-Nb 2.97 Å, Nb-Cl_b 2.43 A and Nb-Cl^t 2.52 Å. In comparison with the structure of $K_4[(Nb_6Cl_{12})Cl_6]$ reported by Simon et al. (57), it was shown that the Nb-Nb distances gradually increase and that the Nb-Cl^t distances decrease upon stepwise removal of two electrons from the $(Nb_6Cl_{12})Cl_6{}^{4-}$ anion. These results are interpreted to mean that the electrons removed in the oxidation process are being taken from bonding orbitals centered primarily on the metal atoms.

Vibrational Spectra.- Infrared spectra have been obtained by Boorman and Straughan (58) on some tantalum and niobium compounds in the region of 20-450 cm^{-1}. Generally, the compounds studied contained the $(M_6X_{12})^{2+}$ unit and exhibited four strong bands in this region. The positions and intensities were said to be characteristic of the 2+ clusters. Mackay and Schneider (39) have reported their infrared study on a series of compounds which include $[(C_2H_5)_4N]_2[(Ta_6Cl_{12})Cl_6]$ and compounds containing anions of the type $(Nb_6Cl_{12})L_6^{n-}$ where L was generally a uninegative anion. The niobium cluster spectra were assigned as either metal-inner chloride, metal-terminal chloride, or metal-metal modes. Five bands in the region 350-140 cm^{-1} were exhibited by the clusters including one at about 140 cm^{-1} assigned as a metal-metal mode. Meyer (59) has examined the vibrational spectra of the tantalum cluster compounds, $K_4[(Ta_6Cl_{12})Cl_6]$ and the hydrates $[(Ta_6Cl_{12})Cl_3]\cdot 6H_2O$, $[(Ta_6Br_{12})Br_3]\cdot 6H_2O$ and $[(Ta_6Cl_{12})Br_3]\cdot nH_2O$. A one to one correspondence in bands between the 2, 3, and 4+ oxidation states exists. There is a band splitting in the 2+ and 4+ compounds. Omitting the split band, there are five bands in the infrared of the tantalum compounds as there are in the niobium (42).

Fleming et al. (42), in a study of compounds of the type $R_n[(M_6X_{12})Y_6]$, where R is a tetraalkylammonium or n-propylammonium cation, reported the vibrational spectra of pure and mixed ligand cluster compounds of niobium and tantalum. They conclude the metal-metal stretching mode is not readily identified. The M-Y stretching modes are only recognizeable when these bands occur outside the immediate wave number range of the $M_6X_{12}^{n+}$ vibrational modes. Only one of the four bands arising from the $M_6X_{12}^{n+}$ vibrational modes, usually the one of highest frequency, undergoes little change in intensity or frequency upon substitution of the Y atoms. Because of less extensive mixing of the normal modes in the $Ta_6X_{12}^{n+}$ compounds, requisite fundamental bands can be identified with greater confidence.

The far infrared spectra of the mixed metal clusters of tantalum and molybdenum, $(Ta_5MoCl_{12})Cl_6^{3-,2-}$ and $(Ta_4Mo_2Cl_{12})Cl_6^{2-}$, as reported by Meyer and McCarley, closely resembles the spectra of the corresponding homonuclear tantalum clusters.

Electronic Spectra.- Allen and Sheldon (60), using a MO bonding scheme proposed by Cotton and Haas (61), reported data on aqueous solutions of $(M_6X_{12})^{2+}$ compounds and assigned all the absorptions to metal-metal transitions. Robin and Kuebler (62) reported the electronic spectra of the tantalum series $(Ta_6X_{12})^{2+}$ (X = Cl,Br). It was later reported by Schneider and Mackay (63) and Fleming and McCarley (64) that they incorrectly interpreted the spectra of $(Ta_6X_{12})^{3+}$ for those of $(Ta_6X_{12})^{4+}$ (X = Cl,Br). Reporting the electronic spectra of some $(Nb_6Cl_{12})^{2+}$ derivatives, Field and Kepert (65) asserted that their data refuted assignments made by Allen and Sheldon (60) and were in line with those published by Robin and Kuebler (62). Fleming and McCarley (64) reported the spectra of several $(Nb_6X_{12})^{n+}$ and $(Ta_6X_{12})^{n+}$ derivatives and also disagreed with the assignments made by Allen and Sheldon. Their assignments were also made according to the molecular orbital bonding scheme of Cotton and Haas (61) but designated several of the transitions as arising from charge transfer bands. The spectral and magnetic data of Field and Kepert (65) indicate the presence of the oxidized cluster, $(Nb_6Cl_{12})^{3+}$, as a contaminant of their solutions of $(Nb_6Cl_{12})^{2+}$ according to Fleming and McCarley. Schneider and Mackay (63) reported the electronic spectra of several $(Nb_6Cl_{12})^{n+}$ derivatives, however, the data for $(Nb_6Cl_{12})Cl_6^{4-}$ have been found to agree with that for, again, the oxidized derivative $(Nb_6Cl_{12})^{3+}$ (64,66). Spreckelmeyer (66) has tabulated data and reviewed the data of several other authors on the electronic absorption spectra of a number of $(M_6X_{12})^{n+}$ species (M = Nb,Ta; X = Cl,Br; n = 2,3,4), $(Ta_6I_{12})^{2+}$ and $(Nb_6F_{12})^{3+}$.

Finding no enhancement of inner chloride exchange upon appropriate irradiation of solutions of $(Nb_6Cl_{12})^{n+}$, van Bronswyk (67) has questioned the assignment as charge transfer bands to some absorptions in the ultraviolet spectra of $(Nb_6Cl_{12})^{n+}$.

Schäfer et al. (68) completed a study of the electronic spectra of a number of cluster compounds including $(Ta_6I_{12})I_2$, $(Ta_6Cl_{12})Cl_3$, $(Ta_6Br_{12})Br_2$, $(Ta_6Br_{12})Br_3$, $[(Ta_6Cl_{12})Cl_2]\cdot 8H_2O$, $[(Ta_6Br_{12})Br_2]\cdot 8H_2O$, $(Nb_6I_8)I_3$, $(Mo_6Cl_8)Cl_4$, and $(Mo_6Br_8)Br_4$. Of these compounds, only those which contain the (M_6X_{12}) configuration had absorption maxima at wavelengths longer than 500 nm. The dihalides of molybdenum and tungsten, discussed later in this work, all show one or more charge transfer bands in the region of 300-360 nm.

Meyer (46), in his characterizations of the new mixed metal cluster compounds $(Ta_{6-x}Mo_xCl_{12})Cl_6^{n-}$ (x = 1,2; n = 2,3) reports a one to one band correspondence in the electronic spectra of the $(Ta_5MoCl_{12})Cl_6$ 3- and 2- anions with the isoelectronic tantalum and niobium cluster compounds, $(Ta_6Cl_{12})Cl_6^{2-}$, $(Ta_6Cl_{12})Cl_6^{3-}$ and $(Nb_6Cl_{12})Cl_6^{2-}$. He does report some difficulty in the interpretation of the spectra of the $(Ta_4Mo_2Cl_{12})Cl_6^{2-}$. This is caused by an apparent appearance of five extra bands in the spectra of this compound not present in any of the isoelectronic series studied. For this reason, the electronic spectra were used mainly as an analytical tool to attest to purity.

Magnetic Studies.- The magnetic properties of some $(Nb_6Cl_{12})^{n+}$ derivatives have been examined and reported by Fleming et al. (12) and Mackay and Schneider (13). They report that the 2+ and the 4+ cluster derivatives are diamagnetic, while the 3+ derivatives are paramagnetic. Schäfer et al. (30) and Allen and Sheldon (37) reported that $(Nb_6Cl_{12})Cl_2$ is diamagnetic and that $(Ta_6Cl_{12})Cl_3$ has an effective paramagnetic moment corresponding to one unpaired electron. Schäfer et al. (32) also reported that $(Ta_6Br_{12})Br_3$ is paramagnetic.

In 1971, Converse and McCarley published (69) a comprehensive study of the magnetic properties of $(M_6X_{12})^{n+}$ derivatives. They found the 2+ and the 4+ derivatives to be diamagnetic and the 3+ derivatives paramagnetic with moments corresponding to one unpaired electron per cluster unit. These workers also published values of the temperature independent paramagnetism of a number of derivatives of the (M_6X_{12}) clusters.

$(Nb_6I_8)I_3$ was found to be paramagnetic by Simon <u>et</u> <u>al</u>. (48) and that the compound has a complicated temperature dependence of the susceptibility. This magnetic behavior could be explained in terms of a doublet-quartet transition. The hydride derivative, $H(Nb_6I_8)I_3$ was found to be diamagnetic by Simon (51).

The magnetic susceptibilities of the mixed-metal cluster compounds, $[(C_2H_5)_4N]_2[(Ta_5MoCl_{12})Cl_6]$, $[(C_2H_5)_4N]_2[(Ta_4Mo_2Cl_{12})Cl_6]$, $[(C_2H_5)_4N]_3[(Ta_5MoCl_{12})Cl_6]$, were reported by Meyer (46). The two compounds which were expected to be diamagnetic $(Ta_5MoCl_{12})Cl_6^{3-}$ and $(Ta_4Mo_2Cl_{12})Cl_6^{2-}$, contain some paramagnetic impurity which was thought not to be a cluster species. This result was indicated by their spectral and analytical data. The paramagnetic cluster compound, $(Ta_5MoCl_{12})Cl_6^{2-}$, showed a reduced effective magnetic moment indicating a diamagnetic impurity, also thought to be other than another cluster species. The data were compared to the isoelectronic series of homonuclear tantalum and niobium clusters.

Synthesis of the Molybdenum and Tungsten M_6X_8 Cluster Compounds.- Investigation of the molybdenum dihalides was begun in 1859 by Blomstrand (70). Repeated volatilizations of molybdenum(III) chlorides and bromides, in a stream of carbon dioxide, produced the corresponding dihalides. Muthmann and Nagel (71) determined the molecular weight of molybdenum(II) chloride in absolute alcohol and found it to correspond to the trimeric formula (Mo_3Cl_6). By evaporation of a strongly acidic hydrochloric acid solution of the dichloride, Rosenheim and Kohn (72) crystallized the acid salt ($Mo_3Cl_6 \cdot HCl \cdot 4H_2O$). They noted, as did Chapin (17) in his study of the reduced tantalum bromides, that only three-sevenths of the chlorine in the compound was ionizable.

In the early 1920's, Lindner (19) began a study of the hexanuclear molybdenum clusters with the synthesis of molybdenum(II) chloride by aluminum reduction of molybdenum(V) chloride. Hellriegel (73) and Senderoff and Brenner (74) found molybdenum metal to be a successful reducing agent in the preparation of the dihalides. Lewis et al. (75) thermally decomposed molybdenum(III) iodide in an oxygen free atmosphere to produce the diiodide. Similarly, the trichlorides and bromides can be disproportionated to produce the corresponding dichloride and bromide, as found by Couch and Brenner (76), and Robinson (77). Lindner et al. (20), and Durand et al. (78) prepared molybdenum(II) bromide directly from the elements at 600°-700°. By reacting molybdenum metal with aqueous hydrogen bromide at 700° under 3000 atmospheres of supporting pressure, Guggenberger and Sleight (79) obtained orange crystals of the dihydrate, $[(Mo_6Br_8)Br_4]\cdot 2H_2O$. Lindner et al. (20) found that molybdenum(II) chloride could be synthesized by passing phosgene over molybdenum metal in a dry atmosphere at 600°.

Matsuzaki et al. (80) followed the disproportionation and hydrogen reduction of several molybdenum halides by a thermogravimetric method. In this study the compounds $MoCl_4$, $MoCl_{3.3}$, $MoCl_{3.0}$, and $MoCl_{2.9}$ were found to disproportionate to $MoCl_2$ at about 390°. The compounds $MoCl_{3.3}$ and $MoCl_{2.9}$ have not been reported elsewhere and their existence needs to be verified.

Three isomers of molybdenum(II) chloride, which do not seem to contain the hexanuclear $(Mo_6Cl_8)^{4+}$ moieties, were prepared by Holste and Schäfer (81). After tempering two of these isomers for 14 days at 350° a yield of about 2% of $(Mo_6Cl_8)Cl_4$ was extracted from each of them. The third isomer provided about 80% of the cluster species after the same treatment.

There are numerous anionic and neutral complexes of the molybdenum dihalides. In the early literature, these complexes were reported as complexes of the trimeric form (Mo_3Cl_6). Lindner (19,22) prepared the acid hydrates,

$H(Mo_3Cl_7 \cdot H_2O)$ and $H(Mo_3Cl_4Br_3 \cdot H_2O)$, by extracting molybdenum dichloride in the appropriate aqueous hydrogen halide. Lindner (19) and Lindner, Kohler and Helwig (20) prepared the pyridinium salts of the hydrates by adding the cation to acidified solutions of the dihalides. Such salts as $(PyH)(Mo_3Cl_7 \cdot H_2O)$ and the analogous bromide were precipitated.

Sheldon (82-85) prepared an entire series of anionic compounds that are derivatives of the acid hydrates. These compounds of the molybdenum clusters were crystallized from the appropriate hydrohalic acid and the general formula $M'_2(Mo_6X_8)Y_6$ where $M' = M(I)^+$, H_3O^+, PyH^+, $(C_6H_5)_3PH^+$, NH_4^+, or R_4N^+: $X = Cl, Br, I$; $Y = Cl, Br, I, OH$. Sheldon arrived at the hexanuclear formulation on the basis of molecular weight data. Conductivity studies showed members of this series of compounds to be 2:1 electrolytes in nitrobenzene. Other members of the above series of compounds have been prepared, in a similar manner, and verified by the following workers: Mackay (14), Cotton _et al_. (86), Clark _et al_. (87), and Hartley and Ware (88). The bromide derivatives were prepared in iodine monobromide by Opalovskii and Samoilov (89).

Rosenheim and Kohn (72) prepared a new series of anhydrous compounds, $(M_6X_8)Y_4$, by the thermal decomposition of the above mentioned acid hydrate salts. Sheldon (83,85), Mackay (14), and Mattes (90) prepared this series where $M = Mo$; $X = Cl, Br, I$; and $Y = Cl, Br, I, OH$. Hogue and McCarley (91) have published a study of this series for M = W.

Using tracer techniques with radioactive chloride and bromide solutions, Sheldon (84) demonstrated that the outer halogens of $(Mo_6Cl_8)X_6^{2-}$ exchange rapidly but no exchange of the internal halogens was observed. Further study (82) showed that while the cluster is completely disrupted by fluoride, thiocyanate and concentrated hydroxide solutions, there is some exchange, maintaining the integrity of the cluster, of internal halogen with hydroxide in dilute solutions (85,92, 93), as demonstrated by the compound $(Et_4N)_2(Mo_6Cl_7(OH))Cl_6$ (94). Schäfer _et_ _al_. (95) has verified the study by Sheldon (85) who, starting with molybdenum(II) chloride, prepared the dibromides and diiodides of molybdenum in melts of the appropriate lithium halide. The study by Schäfer was much more thorough in that he prepared the entire series of compounds $(Mo_6X_4^iX'^i_4)X_4^o$, where X^i, X'^i, X^o = Cl, Br, or I. The investigation of the thermal X^i/X^o exchange demonstrates that the heavier halogen goes from the X^o position into the X^i position. An exception was found by Lesaar and Schäfer (96) in the case of the reaction of $(Mo_6X_8^i)X_4^o$ with melts of HgY_2 at 400° where X = Cl, Br, I; and Y = Cl, Br, I. The compounds $Hg(Mo_6X_8)Y_6$ and $Hg(Mo_6Y_8)Y_6$ are found. X-ray evidence reported by Schnering (97) shows an inversion of the usually observed direction of substitution in $(Mo_6X_8^i)X_4^o$. That is, in these compounds a heavier halogen initially in the X^i position is always substituted by a lighter halogen originating from the X^o positions or the HgY_2 melt.

In his extensive study, Sheldon noted (82) that $(Mo_6Cl_8)Cl_4$ decomposes above 300° in air and 800° *in vacuo*. The cluster is unaffected by boiling lithium iodide trihydrate at 200°, disproportionates slowly in fused lithium chloride at 610°, and in potassium chloride at 770° disproportionates very rapidly (85). The disproportionation products were identified as molybdenum metal and potassium hexachloromolybdate(III).

A variety of methods have been used to synthesize the lower oxidation states of tungsten halides. Higher halides have been reduced with metals, hydrogen and other known reducing agents. Intermediate oxidation states halides have been disproportionated to give the appropriate dihalide, and tungsten metal has been oxidized in controlled halogen atmospheres.

Hill (98) prepared tungsten(II) chloride by the sodium amalgam reduction of tungsten(VI) chloride. It was demonstrated by Lindner and Kohler (99) that aluminum would produce higher yields of the dichloride than would lead, zinc or magnesium when reducing the hexachloride. Murray (100) used aluminum in reducing tungsten(V) bromide to tungsten(II) bromide in a temperature gradient furnace. Hydrogen reduction of tungsten(V) bromide, at 450°, will yield the dibromide as indicated by Emeleus and Gutman (101). McCarley and Brown disproportionated the tetrahalides of tungsten to obtain the corresponding tungsten(II) chlorides and bromides (102).

The reactions of the lower halides have been studied in a variety of aqueous and non-aqueous media. Anionic complexes have been prepared from acidic solutions and neutral complexes from solutions in donor solvents. Oxidation, thermal decomposition and chemical disruption of the halides have also been studied.

Unlike Lindner (19,22), who formulated the chloroacid of molybdenum as a trimer, Hill (98) formulated the chloroacid of tungsten as $(W_6Cl_8)Cl_4 \cdot 2HCl \cdot 9H_2O$. In the same manner as Lindner, Hill extracted the dichloride of tungsten into hydrochloric acid to prepare the chloroacid.

As in the analogous study of molybdenum by Rosenheim and Kohn (72), Lindner and Kohler (99) observed the loss of hydrogen chloride upon heating the hydrated tungsten chloroacid. As was mentioned in the review of work pertaining to the preparation of molybdenum(II) halides, the thermal decomposition of the acid hydrates led to an entire series of pure and mixed anhydrous clusters, $(M_6X_8)Y_4$, where M = Mo; X = Cl, Br, I; Y = Cl, Br, I, Oh, for Sheldon (83,85), Mackay (14) and Mattes (90), and M = W for Hogue and McCarley (91).

Although oxidation of niobium and tantalum clusters is well documented, little success has been found in oxidizing derivatives of molybdenum and tungsten clusters. McCarley and Brown (103) utilized liquid bromine as solvent and reactant to oxidize tungsten(II) bromide to tungsten(III) bromide. Siepmann and Schäfer (104-106) studied the system in more detail and found the compounds W_6Br_{14}, W_6Br_{16}, W_6Br_{18} were all derivatives of the $(W_6Br_8)^{6+}$ cluster. Thermal decomposition of any of the oxidized forms produced $(W_6Br_8)Br_4$. Siepmann et al., as mentioned before, (47) in an attempt to oxidize the tungsten(II) chloride cluster to $(W_6Cl_8)^{6+}$ in liquid chlorine, instead converted the $(W_6Cl_8)^{4+}$ cluster to the $(W_6Cl_{12})^{6+}$ cluster, $(W_6Cl_{12})Cl_6$.

Lindner and Kohler (99) reported that tungsten(II) chloride was hydrolyzed in basic solutions, but was stable in sulfuric acid from which they isolated $(W_3Cl_4)SO_4$, which now should be formulated as $(W_6Cl_8)(SO_4)_2$.

Structural Studies.- The hexanuclear metal clusters have been confirmed by single crystal X-ray determinations. Brosset (107,108) analyzed single crystals of $(Mo_3Cl_4)(OH)_2 \cdot 8H_2O$ and $(Mo_3Cl_4)Cl_2 \cdot 4H_2O$ and found both to contain the $(Mo_6Cl_8)X_4$ groups, where X = chlorine or the oxygen of hydroxide or water. The inner (M_6X_8) cluster consists of a very nearly regular octahedron of molybdenum atoms with an average Mo-Mo distance of 2.63 Å. A chlorine atom is symmetrically located above each of the eight triangular faces of the metal octahedron forming three molybdenum-chlorine bonds at 2.56 Å. The remaining constituents, X, are located directly out from each molybdenum along the C_4 axes at a distance of 2.43 Å for

X = Cl. Brosset (109), from the X-ray radial distribution curves of $H(Mo_3Cl_7 \cdot H_2O) \cdot 3H_2O$ in concentrated ethanol solution, confirmed the formulation of the ions as $(Mo_6Cl_8)Cl_6{}^{2-}$. Vaughan (110), utilizing the radial distribution method, studied a powdered sample of $(NH_4)_2(Mo_6Cl_8)Cl_6 \cdot H_2O$ and also verified the presence of the $(Mo_6Cl_8)Cl_6{}^{2-}$ group having the above mentioned bond lengths. Single crystal studies led Schäfer et al. (111) to formulate molybdenum dichloride as $(Mo_6Cl_8)Cl_{4/2}Cl_2$, with the internal $(M_6X_8)^{4+}$ cluster. The Mo-Mo bond lengths are 2.61 Å and the Mo-Cl distances are 2.47 Å. The four external chlorines, which bridge to four adjacent clusters, have a Mo-Cl distance of 2.50 Å. The non-bridging external halogens, Cl, had a Mo-Cl distance of 2.38 Å.

Siepmann and Schnering (112) performed a single crystal X-ray study of the oxidized tungsten bromide clusters. They found that crystals of (W_6Br_{16}) contained the polynuclear $(W_6Br_8)^{6+}$ cluster and polybromide anions, $Br_4{}^{2-}$. From their study they arrived at the formulation $(W_6Br_8)Br_4(Br_4)_{2/2}$ indicating that the cluster is surrounded by four terminal bromides and two bridging polybromide anions. Bond lengths reported were: $d(W\text{-}W) = 2.64$, $d(W\text{-}Br^i) = 2.58$, $d(W\text{-}Br^o) = 2.58$ Å.

Schäfer et al. (29,111), McCarley and Brown (102), Murray (100) and Clark et al. (87) have shown that anhydrous compounds having the general composition $(M_6X_8)X_{4/2}X_2$ are all isostructural. Sheldon (85) used powder patterns to show that $(Mo_6Br_8)(OH)_4 \cdot 14H_2O$ was isomorphous with the analogous chloride reported in Brosset's (107) single crystal studies. Mackay (14) found that the $Cs_2(Mo_6Cl_8)X_6$, where X = Cl, Br, I, salts were all isomorphous. The haloacids, $H_2(M_6Cl_8)X_6 \cdot 8H_2O$, where M = Mo, W; X = Cl, Br, are also isostructural as found by Clark et al. (87). Their study also showed the bidentate ligand derivatives $(M_6Cl_8)Cl_4$(O-phen)$_2$ for both molybdenum and tungsten to be isomorphous.

Vibrational Spectra.- Recently the far infrared spectra of a number of cluster compounds have been investigated. The hexahaloanions, $(Mo_6X_8)Y_6^{2-}$ have been studied by Mackay (14), Cotton et al. (86), Clark et al. (87), and Hartley and Ware (88). Mackay (14), Clark et al. (87), and Mattes (90) also investigated the spectra of the anhydrous compounds $(M_6X_8)Y_4$. The bidentate ligand adducts of the clusters, $(M_6Cl_8)Cl_2B_2Cl_2$, gave similar spectra to the above hexahaloanions and the anhydrous derivatives as reported by Clark et al. (87) and Walton and Edwards (113). Hogue and McCarley (91) reported a study of compounds containing tungsten halide clusters. Their report contains a comprehensive study of the spectra of these compounds.

Although there are some differences in the assignments, the spectra are similar and the authors base their assignments on octahedral symmetry with two M-X modes, one M-M mode, one M-Y and one X-M-Y mode allowed in the infrared. It is generally agreed that these modes are not purely independent.

Electronic Spectra and Magnetic Studies.- Large amounts of physical data have been recorded for the dihalides of molybdenum and tungsten and their derivatives. Conductivity measurements and molecular weight data have been taken; magnetic susceptibilities and electronic spectra have been interpreted in terms of the configurations of the molecules. Some single crystal X-ray studies have been completed along with some corroborative powder diffraction studies which elucidate the hexanuclear clusters of the metal atoms. Along with the structural data, Raman and infrared spectra have been extended, through normal coordinate analysis, to include similar clusters. Insight into the chemical and physical properties of the hexanuclear metal atom clusters has been gained through theoretical interpretations of the molecular orbitals and the bonding involved.

Nothing surprising is found in the magnetic studies of the dihalides and their derivatives. The pure and mixed anhydrous dihalides of molybdenum and tungsten, $(M_6X_8)Y_4$, where M = Mo, W; X = Cl, Br, I; Y = Cl, Br, I, were found to be diamagnetic by Tjabbes (114), Klemm and Steinberg (115), Sheldon (83,85), Schäfer and Schnering (29), and Schäfer and Siepmann (106). Sheldon (83,94), and Edwards (116) found that derivatives such as the acid hydrates, their non-proton cation analogs and the dihalide tetraamines were also diamagnetic.

It is interesting to note that Brown (117), and Schäfer and Siepmann (106) found the oxidized forms, (W_6Br_{14}), (W_6Br_{16}), and (W_6Br_{18}) were paramagnetic.

The electronic spectra of the molybdenum(II) and tungsten (II) chlorides and bromides have been investigated by several workers. The molybdenum cluster hexahalo anions, anhydrous dihalides and neutral adducts have been studied by Sheldon (82,84,85), Edwards (116), Carmichael and Edwards (118), and Fergusson *et al*. (119). Murray (100) and Schäfer and Siepmann (105,106) studied tungsten(II) bromide. In general, one or more charge transfer bands were observed in the 300-360 nm range, but no indication was found for the ligand field spectra one might expect from a d^4 ion.

Bonding in the M_6X_{12} and the M_6X_8 Cluster Compounds of Niobium, Tantalum, Molybdenum and Tungsten.- The various approaches to the bonding of these cluster compounds have been left to this point in order that the bonding in both the (M_6X_{12}) and the (M_6X_8) clusters could be considered in total. There has been extensive study of the bonding in the M_6 cluster compounds.

Sheldon (82), in discussing the bonding in the hexahalo-anions of molybdenum, described the halogen configuration about each Mo as a tetragonal pyramid. This bonding configuration used the $d_{(x^2-y^2)}sp^3$ hybrid orbitals for Mo-X (internal halogens) and Mo-Y (external or terminal halogens) bonding.

The $d_{(xz,yz)}$ orbitals were then used for metal-metal bonding. The remaining molybdenum electrons were considered to occupy the remaining metal d orbitals. Gillespie (120), expanding on Sheldon's approach, considered repulsions arising between the Mo-X bond electron pairs. He described the structure in terms of a distorted square antiprism of bonding electrons around the metals. He arrived at a description of the bonding in $(Mo_6Cl_8)^{4+}$ and $(Nb_6Cl_{12})^{2+}$ which utilized all of the metal electrons in the bonding. His description, however, did require severely bent localized Mo-X bonds. In view of recently obtained physical data, the above descriptions are not very useful.

Duffy (121) and Crossman et al. (122) proposed the first molecular orbital treatment for the bonding in the $(Mo_6Cl_8)^{4+}$ and the $(Ta_6Cl_{12})^{2+}$ clusters. In each case, the bonding orbitals, formed from hybrid metal orbitals, are just filled with the electrons that are available.

Cotton and Haas (61) used a similar approach, but reserved some of the available orbitals for specific bonding. Metal orbitals used to bond with the internal halogens were $d_{(x^2-y^2)}$, s, $p_{(x,y)}$. The metal $p_{(z)}$ orbital was used for bonding to atoms located externally to the metal cluster on the C_4 axis. LCAO-MO wave functions of the proper symmetry were constructed for the remaining metal d orbitals. The resulting molecular orbital energy level diagram accounted for the diamagnetism, the metal-metal bond order and the relative chemical reactivity of internal and external halogens in the clusters. Metal-halogen interactions were excluded from this calculation. The bonding orbitals for the $(M_6X_{12})^{2+}$ cluster in order of increasing energy were found to be a_{1g}, t_{1u}, t_{2g} and a_{2u}.

Robin and Kuebler (62) have used the LCAO-MO approach including metal-halogen interactions to obtain relative ordering of one electron levels for $(Ta_6Cl_{12})^{2+}$. In order to complete their scheme, experimental electronic spectra were employed to obtain the orbital ordering. The result, then, was consistent with their experimental data. It has since been shown by a comparison of spectra obtained by Espenson and McCarley (10) to Robin and Kuebler's data that their compound reported as $(Ta_6X_{12})^{4+}$ was indeed $(Ta_6X_{12})^{3+}$. In addition, a tetragonal distortion of the Ta_6 cluster and a resulting trapping of integral valence on the metal atoms was proposed to rationalize the tantalum cluster spectra. Coulomb repulsion forces were invoked as providing an internal mechanism for the distortion. This mechanism would lead to a tetragonal compression in the 4+ cluster and a tetragonal elongation in the 2+ cluster.

Kettle (123) employed a forty electron model including metal-halogen interactions to show the similarity in the bonding of the $(Mo_6Cl_8)^{4+}$ and the $(Ta_6Cl_{12})^{2+}$ clusters.

In the former, 24 electrons were used in 12 metal-metal bonding orbitals along the octahedral edges and 16 electrons were used in 8 bonding orbitals in metal-halogen bonds directed normal to the octahedral faces. In the latter, 16 electrons were used in the metal-metal bonding and 24 electrons in the metal-halogen bonding.

Mackay (14) has used the available molecular orbital calculations in conjunction with new spectral and magnetic data to obtain a reordering of the cluster molecular orbitals. A scheme consistent with his spectral data resulted. An important electron spin resonance experiment was also reported by Mackay and Schneider (13) in which they obtained a symmetric resonance with all but six of the expected fifty-five hyperfine lines for an electron delocalized over the Nb_6 unit. The calculated hyperfine interaction constant was about one sixth of that found in the Nb(IV) complexes, $NbCl_5(OCH_3)^{2-}$ and $NbCl_6^{2-}$. This result is used as support for using d orbitals in the metal-metal bonding. They conclude (13) by agreeing with the general approach of Cotton and Haas (61). They also assigned the A_{2u} orbital as the top occupied orbital in the 2+ and 3+ clusters.

Synthesis of Nb_3Cl_8.- The trimeric analog of the $(Nb_6Cl_{12})Cl_4$ has been found by Schäfer and Dohmann (124) to be the lowest stoichiometric compound in the homogeneous composition range $NbCl_{2.67}$-$NbCl_{3.1}$. Compounds within this composition range can be prepared by the thermal decomposition of $NbCl_4$, reduction of $NbCl_5$ with hydrogen and by the following chemical transport reaction:

$$NbCl_{x(s)} + (4-x)NbCl_{5(g)} = (5-x)NbCl_{4(g)}.$$

The Nb_3Cl_8 was found to form most readily in the thermal decomposition of the tetrahalide in a thermal gradient of 500°/20° for three days. Other compositions within the range can be converted to the same composition, Nb_3Cl_8, by annealing at 600° for about 27 days.

Utilizing hydrogen reduction of $NbCl_5$, these workers found the best yields of $NbCl_{2.67}$ to be obtained in reactions between 500° and 600°.

They found that the trimer was not formed in the transport reaction until the temperature gradient hot zone was maintained at a temperature greater than 580°. Further tests, involving the reduction of Nb_3Cl_8 with niobium at 800°, demonstrated the high thermal stability of this compound even after eight days at this temperature.

Structural and Bonding Studies of Nb_3Cl_8.- Schäfer and Dohmann (124) also report a study of the X-ray powder diffraction patterns of various compositions within the above homogeneity range. These patterns are used in a qualitative manner, primarily for the identification of various compositions. Schnering *et al*. (125,126) report, however, the crystal structure parameters from such X-ray data. In a review

(29) of metal-metal bonded systems, Schäfer and Schnering described the bonding of the $NbCl_{2.67}$ composition as a closest packed structure with the niobium atoms occupying 3/4 of the octahedral holes in every other layer in the structure. This bonding arrangement also accounts for the micaceous properties of the compound. The important internuclear distances are as follows: Nb-Nb 2.81Å, Nb-Cl^{tb} 2.42Å (tb refers to the triply bridging chlorine which lies over the plane of the three niobium atoms), Nb-Cl^{pb} 2.46Å (pb indicates the chlorine atoms which bridge the edges of the niobium triangle), Nb-Cl^{b} 2.53Å (Cl^{b} are normal external bridging chlorines between trimers), Nb-$Cl^{'tb}$ 2.64Å ('tb denotes terminal chlorines which are triple bridged). The compound can therefore be formulated $(Nb_3Cl_4)Cl_{6/2}Cl_{3/3}$ which gives the stoichiometry Nb_3Cl_8.

Strause and Dahl (127) have discussed the molecular orbital bonding scheme of compounds of this type having C_{3v} symmetry. Although their scheme is not rigorous, it is practical and can be applied to the bonding in the Nb_3Cl_8 trimer. According to their method, the highest occupied molecular orbital is an a_2 orbital and the next highest an e orbital.

EXPERIMENTAL

Materials.- It was necessary to handle all higher halides of aluminum, niobium, tantalum, molybdenum and tungsten in a dry box maintained with an atmosphere of pre-purified nitrogen at a working dew point of ca. -80°C. The nitrogen was circulated through Linde 4A molecular sieves to maintain this level of purity and dryness. Reactions involving the above types of compounds were generally carried out in evacuated Pyrex or Vycor containers after the necessary preliminary loading and sealing steps had been carried out in the dry box and on a vacuum manifold.

The niobium metal used in this work was supplied by E. I. DuPont de Nemours and Co. in the form of high purity beads or pellets.

Melting grade tantalum powder was purchased from Fansteel Metallurgical Corporation or tantalum sheet was obtained from laboratory stock for use in the generation of $TaCl_5$.

Molybdenum metal, purity reported to be 99.9%, was obtained from the Rembar Corporation as 4x8 inch sheets with a thickness of 15 mil.

Tungsten metal, as 200 mesh powder, 99.9% pure, was obtained from General Electric Co.

Aluminum round of 99.999% nominal purity was obtained from laboratory stock. To maintain the purity, turnings from the aluminum rod were cut with a tungsten carbide bit to prevent iron contamination.

All non-aqueous solvents were of reagent or spectro grade. In some instances it was necessary to use anhydrous and outgassed solvents. Absolute ethanol was outgassed by evacuation at room temperature to remove most of the dissolved gases. The solvent was used after evacuation for the ion exchange work. Absolute ethanol and water used in extraction procedures were purged with pre-purified nitrogen. Other organic solvents were outgassed as described above and stored over Linde 3A Molecular Sieves and used as needed.

Hydrogen chloride and chlorine were obtained in lecture size bottles and were generally used without purification. However, in preparing the higher chlorides of the group V and VI metals, the bottle of chlorine was first cooled to boiling liquid nitrogen temperature and evacuated to _ca_. 10^{-4} Torr. The chlorine was then used without further purification.

All other chemicals, used in synthesis and separations were of reagent grade purity and used as obtained.

Analyses.- Analysis for chlorine was carried out by a potentiometric titration with standard silver nitrate solution in an acidic media. The cluster species were destroyed in strongly basic hydrogen peroxide solution. These solutions were carefully heated to remove excess peroxide and acidified with nitric acid to a pH of _ca_. 5-6. The solutions were then titrated potentiometrically using a standard calomel electrode versus a silver/silver chloride electrode.

Analysis for carbon and hydrogen were determined by the Ames Laboratory Analytical Service Group, Iowa State University of Science and Technology, Ames, Iowa.

Niobium was determined, in the binary halide compounds, gravimetrically as the oxide, Nb_2O_5. Samples were treated in the following manner. Accurately weighed samples were wetted with a few ml of acetone and water and warmed carefully to dryness by suspending the porcelain crucibles containing the samples over a hot plate with a desiccator plate. A few ml of 6N nitric acid were added and the samples again warmed to dryness. The samples were then warmed with concentrated nitric acid to yield a white solid hydrous oxide. The crucibles were then heated overnight at medium heat to insure dryness. The oxide was then obtained by placing the crucibles in a muffle furnace at 550° and heating for several hours.

To insure complete accuracy in analysis, along with a total mass balance, a total oxide on mixed metal clusters was also determined as described above. From either single metal analysis, a cross check on the second metal abundance could be calculated.

Synthesis of Starting Compounds.- High purity aluminum chloride was obtained by resubliming reagent grade aluminum chloride in the presence of a small amount of pure aluminum turnings, under dynamic vacuum at *ca*. 125°. High purity aluminum chloride was also obtained by passing electronic grade (99.99%) hydrogen chloride, obtained from Air Products and Chemicals, Inc., over turnings of the high purity aluminum metal at 300°.

Kuhn (128), using direct chlorination of the metal, has outlined the method for preparation of tantalum pentachloride. As modified by Meyer (46), large amounts (ca. 250 g) of tantalum and molybdenum pentachlorides can be prepared in one reaction. The preparations of Nb(V) and W(VI) chlorides were carried out in the same manner. A Vycor reaction vessel, instead of Pyrex, was used in the synthesis of the tungsten chloride at higher temperatures. It should be mentioned that the tungsten metal, prior to reaction with chlorine, was reduced in a quartz boat in a Vycor reaction tube at 1000° under a stream of hydrogen gas. The reaction temperatures for the synthesis of these halides were as follows: $NbCl_5$, 450°, $TaCl_5$, 450°, $MoCl_5$, 450°, WCl_6, 550°.

X-ray Diffraction Studies.- X-ray powder samples were treated in three ways. X-ray powder patterns were obtained with a 114.59 mm Debye-Scherrer camera or with a Nonius Guinier camera using a tungsten powder internal standard. For the Debye-Scherrer method, finely powdered samples were packed and sealed into 0.2 Lindemann glass capillaries. Samples were exposed to copper K_α radiation for twenty to forty hours. Finely powdered Guinier samples were intimately mixed in Dow-

Corning High Vacuum grease with tungsten powder. These samples were mounted on a mylar window and exposed to copper K_{α} radiation for fifteen to thirty hours. Intensity data, for qualitative comparison only, was collected on a G.E. powder diffractometer. The solid samples were ground to ca. 200 mesh and mounted on a glass microscope slide with Dow-Corning High Vacuum grease.

Diffraction data collected for Nb_3Cl_8 were compared to a computer calculated diffraction pattern for a compound which crystallized in a trigonal space group but solved in hexagonal space group $D^3{}_{3d}$ or $P\bar{3}_{1m}$ with the following unit cell parameters: $a = b = 6.974\text{Å}$, $c = 12.268\text{Å}$, $\alpha = \beta = 90°$, $\gamma = 120°$. $Z = 2$, $\rho = 3.75\ \text{gcm}^{-1}$(126). The computer output lists the calculated θ, 2θ, d-value, hkl and $\sin^2\theta$. The calculated values were compared to experimental data for indexing. A listing of the program is contained in the Appendix.

Vibrational Spectra.- Samples, as solids, were mulled with mineral oil, sealed between polyethylene in a special cell constructed by the Ames Laboratory Shop. All far-infrared spectra were obtained with polyethylene windows on a Beckman IR-11 spectrophotometer in the region 800-70 cm^{-1}.

Electronic Spectra.- Spectra were measured on solutions of cluster containing compounds in a variety of solvents at room temperature with a Cary Model 14 recording spectrophotometer. All solution spectra were obtained in 10 mm fused quartz cells and were measured using a solvent reference. A baseline was recorded for each spectrum so that accurate absorbance values and molar extinction coefficients could be obtained at any desired wavelength.

Electronic spectra were obtained on insoluble solids by reflectance techniques. Samples were ground to <u>ca</u>. 200 mesh, intimately mixed with $MgCO_3$ and mounted in cells covered by a fused optical quartz window. A similar cell containing only $MgCO_3$ was used as a standard reference. The spectra were measured on a Beckman model DU spectrophotometer.

The electronic spectra of the solutions of the tantalum-tungsten mixed metal cluster compounds were very complex, so the spectra were resolved into Gaussian components. A computer program was developed for this purpose by the Ames Laboratory Computer Services Group, Iowa State University of Science and Technology, Ames, Iowa. This program used component peaks defined by an equation from Jørgensen (129) to fit experimental spectra.

$$\varepsilon = \varepsilon_o \exp \frac{-(\nu-\nu_o)^2}{\theta^2} \qquad (3)$$

where: ε = extinction coefficient in ℓ mole^{-1}cm^{-1},

ε_o = extinction coefficient at the absorption maximum,

ν = wavenumber in cm^{-1},

ν_o = wavenumber at the absorption maximum,

$\theta = \delta / \sqrt{\ln 2}$,

δ = absorption half-width at half-height.

A least squares procedure was used to obtain a best fit of calculated Gaussian components to the observed spectra. Input data consisted of observed wavelength and absorbance values, the number of components into which the given region of the spectrum was to be resolved, the estimated ν_o, ε_o, and δ values for each Gaussian component. Up to one hundred observed wavelength-absorbance couples could be read into the computer. The maximum number of components into which the given region of the spectrum could be resolved was five. The computer varied the ν_o, ε_o, and δ parameters two at a time, iterating until a variation of 0.1 percent in each did not improve the fit of the sum of the calculated components to the observed spectrum.

The computer output was the calculated ν_o, ε_o, and δ values for each component and a graphical representation of the fit of the sum of the calculated components to the observed spectrum. A listing of the computer program is given in the Appendix.

Magnetic Susceptibilities.- Magnetic susceptibilities were determined by the Faraday method on a balance constructed by E. T. Maas. Data collected were evaluated by a computer program written by the Ames Laboratory Computer Services Group, Iowa State University of Science and Technology, Ames, Iowa. The computer output was the calculated molar and gram susceptibilities at each temperature determined and a graphical representation of magnetic data versus a temperature variable. A listing of the computer program is given in the Appendix.

Preparation of $[(C_3H_7)_4N]_2[(Ta_5WCl_{12})Cl_6]$.- A typical reaction for the synthesis of this 5-1-2 complex is described below. Tantalum pentachloride and tungsten hexachloride in equimolar amounts, 28.66 g (0.08 moles) $TaCl_5$ and 31.72 g (0.08 moles) WCl_6, and enough aluminum metal to reduce the tantalum(V) and tungsten(VI) to tantalum (2.33) and tungsten (2.33), 4.4 g (0.163 moles) Al, were loaded along with 13.5 g (0.233 moles) NaCl and 31.05 g (0.234 moles) $AlCl_3$ into a flame-outgassed 45 mm x 140 mm Pyrex reaction tube fitted with an 18/9 ball or socket joint. Because of the air sensitivity of the tantalum, tungsten, and aluminum chlorides, the tube was loaded in the dry box. The tube and contents, under a prepurified nitrogen atmosphere, were attached to the vacuum line, and evacuated to ca. 10^{-5} Torr. The reaction vessel was sealed above the reaction tube about 2.5 cm up on the 9 mm connector. The contents were vigorously shaken to insure an intimate mixture. The tube was fitted with a chromel/alumel thermocouple, and mounted in a rocking furnace whose temperature was regulated by the attached thermocouple. While the furnace slowly rocked from an upright position through an angle of *ca*. 100°, the following time-temperature program was followed:

Temperature (°C)	Duration (Hrs)
175	4
250	4
320	72

At the end of this period, the reaction tube was removed from the furnace, allowed to cool, and opened in air taking care to keep the broken glass from the cooled reaction slug. In reactions which provided the highest yields, the cooled melt was black with some solidified salt media having cooled in a clear layer on top of the reaction mass. The products were ground in a mortar and carefully poured into *ca*. 500 ml of an iced solution of 0.1 M HCl. A Teflon coated stirring bar was placed in the solution and the contents stirred for about 1 hour in order to dissolve the $NaAlCl_4$, $AlCl_3$ and some Ta_6Cl_{14}. The solution was centrifuged and the supernate was discarded. The residue was extracted a second time with an iced solution of 0.1 M HCl for *ca*. 6 hours and again the solids were centrifuged from solution. Washing of the residue with cold 0.1 M HCl was continued until a minimum amount of blue color resulted. A 2 hour extraction of the solids with 400 ml of absolute ethanol yielded a very dark opaque solution which was centrifuged, filtered, diluted with water to make the solution 30 per cent water by volume, and thoroughly outgassed. The ethanol-water solution was passed through a column of cation exchange resin (Dowex 50W-X8, 50-100 mesh, in the acid form) and transferred to a 2-liter round bottom flask. The solution was cooled in an ice bath, thoroughly purged with prepurified nitrogen gas and saturated with anhydrous hydrogen chloride at a rate such that the temperature of the solution was maintained below 20°C. An excess of tetrapropylammonium chloride in a minimum amount of ethanol was added to the solution. A blanket of chlorine gas was allowed to stand over the solution in order to insure complete oxidation of the compounds in solution. About six hours later approximately 6.80 g of very fine dark brown crystals were collected on a glass frit, washed with cold absolute ethanol and air dried. These crystals were then vacuum dried at 45°C overnight. Spectral analysis of this compound indicates a consistent oxidation state, peak to peak and peak to valley ratios reproducible to within 0.5%. Anal. Calc. for $[(C_3H_7)_4N]_2[(Ta_5WCl_{12})Cl_6]$: Ta, 43.09; W, 8.76; Cl, 30.40; C, 13.73; H, 2.69. Found: Ta, 42.99^a, 43.45^b; W, 8.90^a, 8.69^b; Cl, 30.55, 30.63; C, 13.87^a; H, 2.86^a; Ta/W, 4.95^a, 5.05^b. (a, results obtained from spectrographic analysis; b, results obtained from colorimetric analysis.)

Preparation of $[(C_3H_7)_4N]_3[(Ta_5WCl_{12})Cl_6]$.- This 5-1-3 compound can be easily obtained by reducing a butyronitrile solution of the 5-1-2 compound, $[(C_3H_7)_4N]_2[(Ta_5WCl_{12})Cl_6]$, with zinc amalgam. Typically 2.286 g (10^{-3} moles) of the

5-1-2 parent compound, $[(C_3H_7)_4N]_2[(Ta_5WCl_{12})Cl_6]$, was dissolved in a minimum volume of butyronitrile, ca. 60 ml, along with 0.225 g ($1.015x10^{-3}$ moles) of tetrapropylammonium chloride in a vacuum line adapted double flask apparatus. Several grams of freshly prepared zinc amalgam was added to the solution and the solution was thoroughly outgassed and sealed. This solution was stirred overnight and then allowed to settle. The solution was then decanted away from the solids into the side arm flask. The butyronitrile in the side arm flask was then distilled back into the main reduction flask and the solution stirred for about 30 minutes. The decantation and distillation steps were repeated until the decanted solution was colorless. The butyronitrile was then distilled away from the crude 5-1-3 compound. The green solid, containing both zinc chloride and the reduction product, was removed from the reduction apparatus and extracted quickly with cold absolute ethanol. The slurry was centrifuged and the residue washed again with ethanol. The 5-1-3 compound, $[(C_3H_7)_4N]_3[(Ta_5WCl_{12})Cl_6]$, was then vacuum dried at 45°C overnight. Electronic spectra of this compound show no indication of the 5-1-2 oxidized analog. Peak to peak and peak to valley analyses of these spectra indicate a compound of constant composition. Anal. Calc. for $[(C_3H_7)_4N]_3[(Ta_5WCl_{12})Cl_6]$: Ta, 39.58; W, 8.04; Cl, 27.92; C, 18.92; H, 3.70. Found: Ta, 39.83; W, 8.12; Cl, 28.82; C, 18.29; H, 3.68.

Preparation of Nb_3Cl_8.- A typical reaction for this synthesis is described as follows: 12.15 g (0.045 moles) $NbCl_5$, 0.95 g (0.035 moles) Al, 4.35 g (0.075 moles) NaCl, and 10.00 g (0.075 moles) $AlCl_3$ were loaded into a flame-outgassed 54 mm x 140 mm Vycor reaction tube fitted with an 18/9 ball or socket joint in the dry box. The tube and contents were attached to the vacuum line, evacuated and sealed as described previously. The ampule was shaken and then fitted with a thermocouple. Again the reaction was carried out in a rocking furnace according to the following time-temperature program:

Temperature (°C)	Duration (Hrs)
175	4
225	2
300	2
375	2
450	6
550	72

At the end of this period, the furnace was allowed to cool slowly over a period of 12 hours without rocking. The tube was then removed from the furnace and opened in air. The reaction mass occurred in two adjoining sections. The first was a layer of very white salt medium on top of the black insoluble reduction product. The products were removed from the tube, ground in a mortar and carefully poured into *ca*. 500 ml of an iced solution of 0.1 M HCl. A Teflon coated stirring

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bar was placed in the solution and the contents were stirred for about 1 hour to insure complete removal of the salt reaction medium. The solution was centrifuged and the supernate discarded. The residue was thoroughly washed with water and again the solids were centrifuged from solution. The residue was then stirred in absolute ethanol for ca. 2 hours. This solution was then centrifuged and the residue washed with ethanol and recentrifuged. The final residue, a very dark green (black?) microcrystalline powder, was then vacuum dried overnight at 45°C. The final dried weight of the compound was ca. 8.45 g and was analyzed for Nb and Cl. Anal. Calc. for Nb_3Cl_8: Nb, 49.56; Cl, 50.44. Found: Nb, 49.55, 49.56; Cl, 50.40, 50.43; Cl/Nb, 2.67.

Preparation of the Niobium-Tungsten Mixed Metal M_3X_8 Phases.- The general procedure for these compounds was the same as for the preceding compound Nb_3Cl_8. Starting mixtures, according to the ratios indicated in Equations 3-6, were sealed in the usual manner in Vycor reaction ampules. The following equations define the stoichiometry with starting amounts indicated:

$$54NbCl_5 + 9WCl_6 + 52Al = 18Nb_3Cl_8 + 3W_3Cl_8 + 52AlCl_3 \qquad (3)$$

For this reaction, 16.27 g (0.06 moles) $NbCl_5$, 3.97 g (.01 moles) WCl_6, 1.56 g (.057 moles Al, 9.0 g (0.154 moles) NaCl and 21.0 g (0.155 moles) $AlCl_3$ were used as the starting mixture.

$$36NbCl_5 + 9WCl_6 + 38Al = 12Nb_3Cl_8 + 3W_3Cl_8 + 38AlCl_3 \qquad (4)$$

As above, 10.80 g (.04 moles) $NbCl_5$, 3.97 g (.01 moles) WCl_6, and 1.14 g (.042 moles) Al were loaded into a Vycor reaction tube. In all of these reactions, the amounts of NaCl and $AlCl_3$ were held constant, 9.0 g (.154 moles) NaCl and 21.0 g (.155 moles) $AlCl_3$.

$$12NbCl_5 + 6WCl_6 + 16Al = 4Nb_3Cl_8 + 2W_3Cl_8 + 16AlCl_3 \qquad (5)$$

The amounts of the starting materials were as follows: 10.80 g (.04 moles) $NbCl_5$, 7.94 g (.02 moles) WCl_6 and 1.44 g (.054 moles) Al.

$$27NbCl_5 + 18WCl_6 + 41Al = 9Nb_3Cl_8 + 6W_3Cl_8 + 41AlCl_3 \qquad (6)$$

For this reaction, 12.16 g (.045 moles) $NbCl_5$, 11.90 g (.03 moles) WCl_6, and 1.85 g (.0684 moles) Al were loaded and sealed in a Vycor reaction tube.

In general, the treatment of each sample from the initial loading in the dry box through extraction was identical to that for the preparation of the Nb_3Cl_8. After each tube was loaded, evacuated and sealed, they were thoroughly shaken and placed in the rocking furnace. The following time/temperature program was followed in each case.

Temperature (°C)	Duration (Hrs)
175	4
225	2
300	2

Temperature (°C)	Duration (Hrs)
375	2
450	6
550	72

At the end of this period, the power was shut off to the furnace and the furnace was allowed to cool slowly over a 12 hour period in an upright position. In each case, the cooled reaction mass occurred in two layers, an insoluble black portion at the bottom of the tube covered by a white layer of salt media. The reaction tubes were opened in air and the reaction products thoroughly ground and poured carefully into ca. 500 ml of iced 0.1 M HCl. This slurry was stirred for about 2 hours to insure complete removal of the salt reaction medium and any species other than the M_3X_8 phase expected. The slurry was centrifuged and the residue washed with iced water. The residue was separated from solution by recentrifuging and the supernate was discarded. The residue was stirred for about 2 hours in absolute ethanol. At the end of this period, the slurry was centrifuged and the supernate discarded. The residue was stirred for about 15 minutes in ethanol and reseparated from solution. The final residues, very dark black microscystalline powders were then vacuum dried overnight at 45°C. In each case, a total analysis was obtained for niobium, tungsten and chlorine. In each case, the reactions appeared quantitative based on the physical observation of the supernatant liquids obtained from the various extraction processes. These liquids showed no species other than the salt medium from the reaction to be present. Anal. From Equation 3 Calc. for $6Nb_3Cl_8/W_3Cl_8$: Nb, 39.73; W, 13.10; Cl, 47.16. Found: Nb, 40.27; W, 13.65; Cl, 45.45. From Equation 4 Calc. for $4Nb_3Cl_8/W_3Cl_8$: Nb, 36.15; W, 17.88; Cl, 45.97. Found: Nb, 36.68; W, 14.9; Cl, 46.32. From Equation 5 Calc. for Nb_2WCl_8: Nb, 28.44; W, 28.14; Cl, 43.41. Found: Nb, 29.72; W, 29.52; Cl, 39.21. From Equation 6 Calc. for $3Nb_3Cl_8/2W_3Cl_8$: Nb, 24.91; W, 32.86; Cl, 42.24. Found: Nb, 24.11; W, 32.99; Cl, 45.40.

Attempted Preparation of the Niobium-Molybdenum Mixed Metal M_3X_8 Phases.- Only one starting mixture was used in the preparation of these phases according to Equation 7.

$$6NbCl_5 + 3MoCl_5 + 7Al = 2Nb_3Cl_8 + 1Mo_3Cl_8 + 7AlCl_3 \qquad (7)$$

As in previous preparations of the M_3X_8 phases, 10.80 g (.04 moles) $NbCl_5$, 5.46 g (.03 moles) $MoCl_5$, 1.26 g (0.046 moles) Al, 9.0 g (.154 moles) NaCl, and 21.0 g (.155 moles) $AlCl_3$ were loaded into the reaction tubes indicated below. The reaction vessels were evacuated and sealed off. The tubes were thoroughly shaken to insure a well mixed reaction medium. The tubes were placed in the rocking furnace and the reactions were allowed to proceed according to the following time/temperature programs:

Temperature	Reaction 1 Pyrex Duration Hrs.	Reaction 2 Vycor Duration Hrs.	Reaction 3 Vycor Duration Hrs.
175	4	4	4
225	2	2	2
275	2	2	2
320	48		
350		2	2
450		6	6
550		72	2
650			72

At the completion of the reaction time, the furnace was allowed to cool slowly in an upright position. The cooled reaction mass was ground in a mortar and poured carefully into an iced solution of .1 M HCl as usual. The solution was stirred for about 2 hours and then centrifuged. The residue was collected and washed thoroughly with cold water to insure complete removal of all aqueous soluble materials. This slurry was recentrifuged and the supernate discarded. The residue was stirred in absolute ethanol for about 1 hour. The solids were again collected and rewashed with ethanol. After centrifuging the samples and collecting the residues, the residues were vacuum dried overnight at 45°C. The residue from reaction 1 at 320°C was a dark scarlet, from reaction 2 at 550°C was a light brown and from reaction 3 at 650°C a dark black. Anal. for Nb_2MoCl_8 Calc: Nb, 32.87; Mo, 16.97; Cl, 50.16. Found for reaction 1: Nb, 33.41; Mo, 16.99; Cl, 51.72. Found for reaction 2: Nb, 34.82; Mo, 17.51; Cl, 50.50. Found for reaction 3: Nb, 39.80; Mo, 17.80; Cl, 44.63.

Attempted Preparation of $Nb_4Mo_2Cl_{11}$.- The procedure for the preparation of this compound is identical to that for the M_3X_8 phases. For this compound, 10.80 g (.04 moles) $NbCl_5$, 5.46 g (.02 moles) $MoCl_5$, 1.71 g (.063 moles) Al, 9.0 g (.154 moles) NaCl and 21.0 g (.155 moles) $AlCl_3$ were loaded, in the dry box, into a Vycor reaction ampule. The ampule was evacuated to about 10^{-5} Torr and sealed in the usual manner. The contents were shaken thoroughly to insure a good mixture and the reaction vessel was placed in the rocking furnace. The following time/temperature program was followed during the course of the reaction:

Temperature (°C)	Duration (Hrs)
175	2
225	2
300	2
375	2
459	6
550	2
650	72

The furnace was placed in an upright position and allowed to cool slowly overnight. The contents were removed from the tube, ground in a mortar and poured very carefully into *ca.*

500 ml of iced 0.1 M HCl. The solution was stirred for about 2 hours and then centrifuged. The supernate was discarded and the remaining residue was washed thoroughly with iced water and recentrifuged. The residue was then stirred for <u>ca</u>. 1 hour in absolute ethanol. This slurry was centrifuged and the residue was washed again with absolute ethanol. The residue was separated from the solution by centrifuging and was dried overnight at 45°C under dynamic vacuum. <u>Anal</u>. Calc. for $Nb_4Mo_2Cl_{11}$: Nb, 38.98; Mo, 20.12; Cl, 40.90. Found: Nb, 37.78; Mo, 19.69; Cl, 39.25.

RESULTS AND DISCUSSION

Synthesis of Tantalum-Tungsten M_6X_{12} Cluster Compounds.- Following the method outlined by Meyer (46), this work represents an extension of the studies of mixed metal M_6X_{12} cluster systems. The basic preparative reaction is described by Equation 8.

$$6TaCl_5 + 6WCl_6 + 12Al \xrightarrow[\substack{50\ m/o\ NaCl \\ 50\ m/o\ AlCl_3}]{320°,\ 3\ days} Ta_6Cl_{15} + W_6Cl_{15} + 12AlCl_3 \qquad (8)$$

Although Schäfer and Spreckelmeyer (45) showed that an intimate mixture of tantalum and niobium bromides could be coreduced to give a mixed tantalum-niobium cluster compound, Meyer (46) has shown that this method gives no yield of cluster compounds when the starting component metals are taken from different groups. Thus the mixed metal clusters reported here and by Meyer (46) were accomplished by reductions in a solvent.

The solvent system sodium chloride-aluminum trichloride was selected because of its wide liquid range with low vapor pressure and variable acidity over the temperature range desired. This solvent system was also chosen because it adds no additional component to the system that was likely to interfere with the reaction or subsequent treatments of the reaction mass.

Aluminum was chosen as the reducing agent because it would add no additional component to the system. It has previously been noted that aluminum will reduce the halides of the group V and VI heavy transition metals to their respective cluster compounds.

Initially it was felt that, from foregoing experimental evidence, two things were true:

1) It appears from the $Ta_4Mo_2Cl_{12}^{4+}$ and $Ta_5MoCl_{12}^{3+,4+}$ that the heavy metal atom governs the cluster configuration, M_6X_{12} or M_6X_8.

2) Tantalum being the most active metal will not approach the 2+ oxidation state closer than 2.33+.

It has been shown by Dorman and McCarley (130), that the reduction of tungsten hexachloride occurs at an appreciable rate only at temperatures in excess of 500°C. However, Meyer (46) has shown that the yield of mixed metal clusters in the tantalum-molybdenum system is significantly reduced at temperatures exceeding 350°C.

Since the homonuclear tantalum cluster begins forming at an appreciable rate at 325°C, a temperature of 320°C was chosen for the reaction conditions. It was thought that this temperature would minimize the formation of the individual tantalum and tungsten clusters while allowing the reduction to proceed at a reasonable rate. The mixed metal cluster was indeed formed at this temperature along with surprising amounts of the pure tantalum and tungsten clusters. It appears that the tantalum cluster is more readily formed if a group VI metal is present in the reduction mixture. The amount of tungsten cluster certainly was shown to be dependent on the amount of tungsten hexachloride used initially. Also the amount of mixed metal cluster formed was closely dependent on the amount of tungsten present initially. Several preliminary reactions in which the ratio of $TaCl_5/WCl_6$ was varied as follows: 5/1, 4/2, 1/1, 1/5, showed only that the 1/1 starting ratio gave significant yields.

Reaction time seemed to have little effect on the yield of the mixed metal tantalum-tungsten cluster. A study of reaction time with a starting ratio of $TaCl_5/WCl_6$ of 1/1 was undertaken. Three reaction times were compared 24 hrs, 48 hrs, and 72 hrs at 320°C. The reaction after 24 hrs showed only $Ta_6Cl_{12}^{2+}$ cluster with no mixed metal cluster and no tungsten cluster. There was a significant amount of unreacted aluminum metal found in the reaction mass after the appropriate extractions. There was only a slight difference in the amounts of cluster species, $Ta_6Cl_{12}^{2+}$, $W_6Cl_8^{4+}$, and $Ta_5WCl_{12}^{3+}$ found in comparing the 48 hour reaction to the 72 hour reaction.

A higher temperature was attempted for a 1/1 starting ratio for a 3 day period. No significant amount of mixed metal cluster was found.

The most effective conditions found were three days at 320°C with a starting ratio of $TaCl_5/WCl_6$ of 1/1. At these conditions a final yield of 48.5% of theoretical based on recrystallized $[(C_3H_7)_4N]_2[(Ta_5WCl_{12})Cl_6]$ was realized.

The reduced product, $[(C_3H_7)_4N]_3[(Ta_5WCl_{12})Cl_6]$, obtained by the zinc reduction of $[(C_3H_7)_4N]_2[(Ta_5WCl_{12})Cl_6]$, could be recovered almost quantitatively from the reduction procedure.

When the coreduction reaction had been completed, the reduction mass contained aluminum chloride, sodium tetrachloroaluminate, tantalum chloride cluster, tungsten chloride cluster and the desired tantalum-tungsten mixed metal chloride cluster. No special problems were presented by any of these contaminants in the process of separation. Most of these contaminants were completely leached out by the water extraction.

A cold solution, it was felt, would keep the final temperature of the extracting solution at about room temperature, i.e. it would off-set the tremendous heat of solution of aluminum chloride and sodium tetrachloroaluminate. By keeping the solution at about room temperature, there appeared to be no loss of mixed metal cluster by hydrolysis. This first water extraction removed the sodium tetrachloroaluminate and the aluminum chloride. This extraction also removed some of the pure tantalum cluster and most of the pure tungsten cluster. A second water extraction served to complete the removal of all the soluble components except some of the tantalum cluster which was slow to dissolve. These two aqueous extractions were completed in about six hours of stirring.

Even though continued aqueous extraction might have removed all of the tantalum cluster, it was felt that prolonged exposure of the tantalum-tungsten cluster to water would increase the probability of loss of yield due to hydrolysis.

It was noted that a second ethanol extraction showed no significant amount of cluster species extracted. After dilution, the ethanol-aqueous solution contained sufficient water to prevent dehydration of the ion exchange resin, and yet this amount of water was not sufficient to promote hydrolysis of the cluster.

Outgassing the ethanol-aqueous solution prevented air bubbles in the column during the ion exchange process. When the ethanol-water solution was passed down the column, a dark ring of tantalum cluster was retained at the top of the column, while the mixed-metal cluster was passed through the column. The mixed-metal cluster apparently exists as a molecular species in these solutions. A solution of the corresponding tantalum-molybdenum mixed metal also will pass through an anion exchange column without loss of the cluster.

Since the spectral data for compounds comparable to this mixed-metal cluster pertain mostly to anionic moieties, the mixed-metal cluster was isolated in the anionic form.

The anation of the mixed-metal cluster was accomplished under oxidizing conditions. The solution was saturated with HCl(g) and oxidized with Cl_2(g). The tantalum-tungsten mixed metal cluster was precipitated under oxidizing conditions

These ethanol-water-HCl solutions were very susceptible to air oxidation. An attempt to separate the reduced species under these conditions would have resulted in a product contaminated with the oxidized form of the cluster. As soon as the solution was oxidized, often the acid hydrate, $[(H_3O)_2][(Ta_4WCl_{18})]\cdot nH_2O$ would separate from solution. This solid could be removed as a dark brown crystalline solid which is soluble in ethanol. As soon as the solution was saturated and oxidized, the tantalum-tungsten mixed metal cluster could be crystallized out of the solution in the presence of excess tetraalklyammonium cation. Normally very little of the 5-1-2 derivative crystallized until the volume of the solution had been reduced by about 30 percent. If additional tetraalkylammonium cation was added over a period of several days while the volume was being reduced, almost all of the mixed metal cluster would be crystallized from the solution to leave an almost colorless solution.

Very pure 5-1-2, $[(C_3H_7)_4N]_2[(Ta_5WCl_{12})Cl_6]$, could be obtained by recrystallizing the crude tetraalklyammonium salt of the 5-1-2 from ethanol saturated with HCl(g) upon addition of a small amount of tetraalkylammonium cation. All characterizations were carried out on this recrystallized compound.

The 5-1-3 analog could be obtained quantitatively by the zinc reduction of the 5-1-2 species in butyronitrile. The 5-1-3 species, in solution, is very susceptible to air oxidation. Therefore, the reduction and separation steps were done *in vacuo*.

The complexes were usually isolated as the tetrapropylammonium salts, although the tetraethylammonium salt of the 5-1-2 analog was isolated.

It should be noted that routine preliminary assessment of the purity of these compounds was performed by spectral analysis and not by elemental analysis. Only those products whose spectra showed little deviation from standard peak to peak and peak to valley ratios were submitted for elemental analysis as relatively pure compounds.

Synthesis of Niobium-Tungsten M_3X_8 Cluster Compounds.- This work represents the first preparation of mixed metal M_3X_8 clusters containing metals from different groups. Several reactions were initially run to prepare mixed metal M_6X_8 or M_6X_{12} clusters containing niobium and tungsten. Since niobium and tungsten will adapt to both cluster configurations, it was felt that a series of cluster compounds containing a substituted metal could be prepared. Starting ratios of $NbCl_5/WCl_6$ of 5/1 and 4/2 with sufficient aluminum to reduce the Nb(V) and W(VI) to 2.5 and 2.67 were reacted according to Equations 9 and 10.

$$15NbCl_5 + 3WCl_6 + 16Al \xrightarrow[\substack{50\ m/o\ NaCl \\ 50\ m/o\ AlCl_3}]{320°,\ 3\ days} 3Nb_5WCl_{12}Cl_3 + 16AlCl_3 \qquad (9)$$

$$12NbCl_5 + 3WCl_6 + 16Al \xrightarrow{d.o.} 3Nb_4W_2Cl_{12}Cl_4 + 16AlCl_3 \qquad (10)$$

When no appreciable amount of cluster species was found in either the aqueous or ethanol extraction supernate, an attempt to prepare a mixed metal M_6X_8 cluster was made with a starting ratio of $WCl_6/NbCl_5$ of 5/1 and sufficient aluminum to prepare $W_5NbCl_8Cl_3$ according to the reaction described by Equation 11.

$$5WCl_6 + NbCl_5 + 8Al \xrightarrow[\substack{50\text{ m/o NaCl} \\ 50\text{ m/o AlCl}_3}]{550°,\ 3\text{ days}} W_5NbCl_8Cl_3 + 8AlCl_3 \qquad (11)$$

The aqueous and ethanol extraction showed only $Nb_6Cl_{12}{}^{3+}$ and $W_6Cl_8{}^{4+}$ and an X-ray powder pattern of the residue remaining after the extractions showed only tungsten metal.

A continued look at the residues remaining after the extractions of the products of the reactions described by Equations 9 and 10 revealed these residues gave powder diffraction patterns very similar to those reported for "$NbCl_3$".

Some preliminary reactions, based on Equation 12, for the reduction of niobium pentachloride alone showed that the lowest composition in the "$NbCl_3$" homogeneity range, $NbCl_{2.67}$, could be obtained by the reduction with aluminum.

$$9NbCl_5 + 7Al \xrightarrow[\substack{50\text{ m/o NaCl} \\ 50\text{ m/o AlCl}_3}]{550°,\ 3\text{ days}} 3Nb_3Cl_8 + 7AlCl_3 \qquad (12)$$

Not only was the reduction stoichiometric but also quantitative at 550°C. When the reduction had been completed, the products were extracted as previously described. In both extractions, no color appeared in the supernate and the product was separated as an insoluble dark green crystalline powder.

As previously described in the experimental section in Equations 3-6, starting ratios of $NbCl_5/WCl_6$ of 6/1, 4/1, 2/1, and 3/2 along with sufficient aluminum to reduce all metal species to the 2.67 oxidation state were reacted in the usual manner at 550°C. In all cases the cooled reaction mass had the same characteristics as those observed during preparation of the parent compound, $NbCl_{2.67}$. That is, there was an insoluble mass of dark black material covered by a layer of white salt medium.

These reductions all behaved similarly during extraction and processing. In one case, extraction of the 2/1 reduction product did give a pale yellow aqueous supernate identified as $W_6Cl_8{}^{4+}$. It was estimated that the colored species was of sufficiently low concentration to be considered insignificant. The final isolated products were dark microcrystalline powders which appeared to be homogeneous under observation with a polarizing microscope, with the 6/1 compound giving the appearance of being more green than the rest of the compounds. As one might expect, the 6/1 ratio compound should be the most like the parent Nb_3Cl_8.

Electronic Spectra of the Tantalum-Tungsten M_6X_{12} Mixed Metal Cluster Compounds.- The determination of the electronic structure of the M_6X_{12} cluster compounds of niobium and tantalum has been the object of several previous studies (5,63, 64,65,67). It was hoped that the substitution of one or more of the metal atoms in the cluster core would alter the electronic spectra of the cluster derivatives in such a way as to facilitate the definite assignment of at least some of the observed bands in the spectra. This was one of the primary objectives of the study initiated by Meyer (46). The electronic spectra of the ions $[Ta_5WCl_{18}]^{3-,2-}$ obtained in this study are compared below with the spectra of $[Ta_6Cl_{18}]^{4-,3-}$ and $[Ta_5MoCl_{18}]^{3-,2-}$, as obtained by Meyer (46).

It should be ascertained whether the spectra are indeed of the ions mentioned or of a dissociated species where solvent has substituted for terminal halide on the cluster. Schneider and Mackay (39,13) studied the conductance of $[(C_2H_5)_4N]_n[(Nb_6Cl_{12})Cl_6]$ (n = 2,3,4) in nitromethane solution and found the compounds to be n:1 electrolytes. These authors also found (13) that the infrared spectra of those compounds in nitromethane solution agreed very well with the data on the solids, further indicating no dissociation of the terminal halogens. Fleming and McCarley (64) compared the electronic reflectance spectra of compounds containing the $[(Nb_6Cl_{12})Cl_6]^{2,3,4-}$ ions to the spectra of these compounds in several solvents and found good agreement between the acetonitrile solution spectra and the reflectance spectra of the 3- and 2- ions. These data are also in good agreement with the nitromethane solution data for the 3- ion as obtained by Schneider and Mackay (13). The data of Fleming and McCarley (64) do indicate that $[Ta_6Cl_{18}]^{4-}$ may be dissociated to some extent in acetonitrile. Meyer (46) found that the mixed metal clusters of tantalum and molybdenum could be recrystallized from acetonitrile without lowering the chlorine to metal ratio. From the foregoing arguments it seems unlikely that the tantalum-molybdenum cluster anions are significantly dissociated in acetonitrile.

It was found in this work that the 5-1-2 compound of tantalum and tungsten was reduced over a period of time in acetonitrile, but not in butyronitrile. It was also found that solutions of the same 5-1-2 ion in ethanol were reduced over a period of time. For this reason, spectral measurements were made in butyronitrile.

The resolved electronic spectra of the three cluster derivatives, $[Ta_6Cl_{18}]^{3-,4-}$, $[Ta_5MoCl_{18}]^{2-,3-}$ and $[Ta_5WCl_{18}]^{2-,3-}$ are shown in Figures 1-7. The data are compared in Figure 8 and summarized in Table 1.

Figure 1 shows the resolved spectrum of the $[(Ta_6Cl_{12}Cl_6]^{4-}$ ion in acetonitrile solution as published by Meyer (46). He reports that attempts to fit the observed spectrum

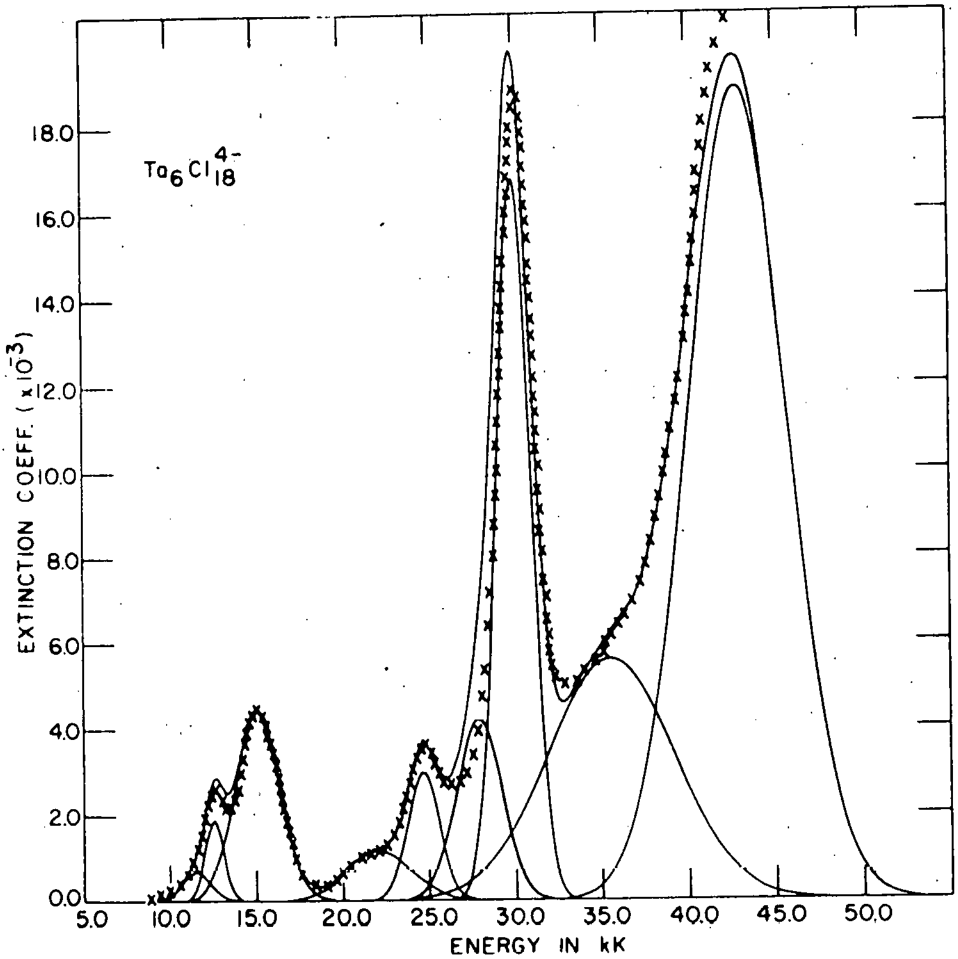


Figure 1. Spectrum of $[(Ta_6Cl_{12})Cl_6]^{4-}$ in acetonitrile showing observed (upper solid line), calculated (XXX) and Gaussian components (lower solid lines)

Figure 2. Spectrum of $[(C_2H_5)_4N]_3[(Ta_5MoCl_{12})Cl_6]$ in acetonitrile showing observed (upper solid line), calculated (XXX) and Gaussian components (lower solid lines)

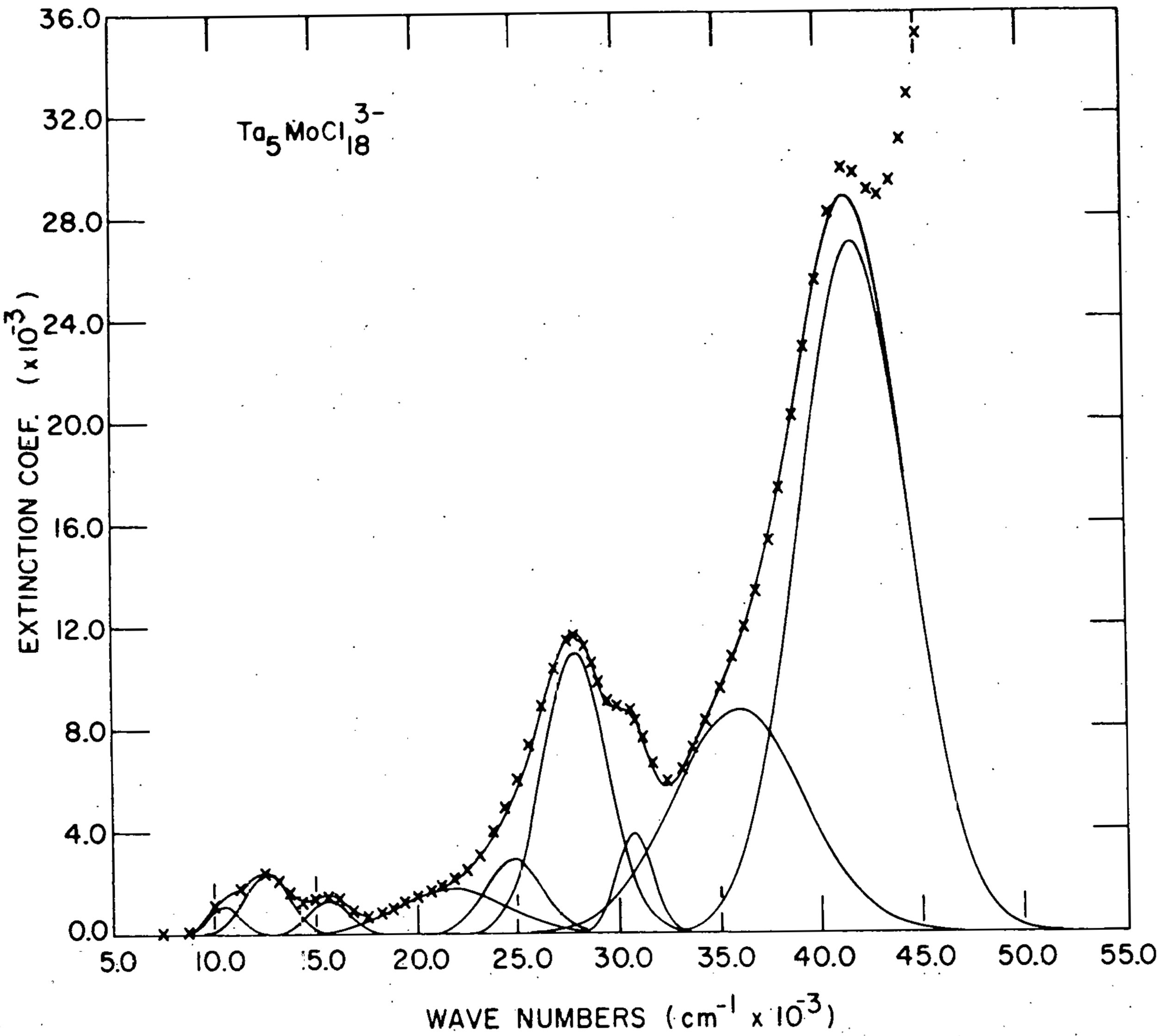
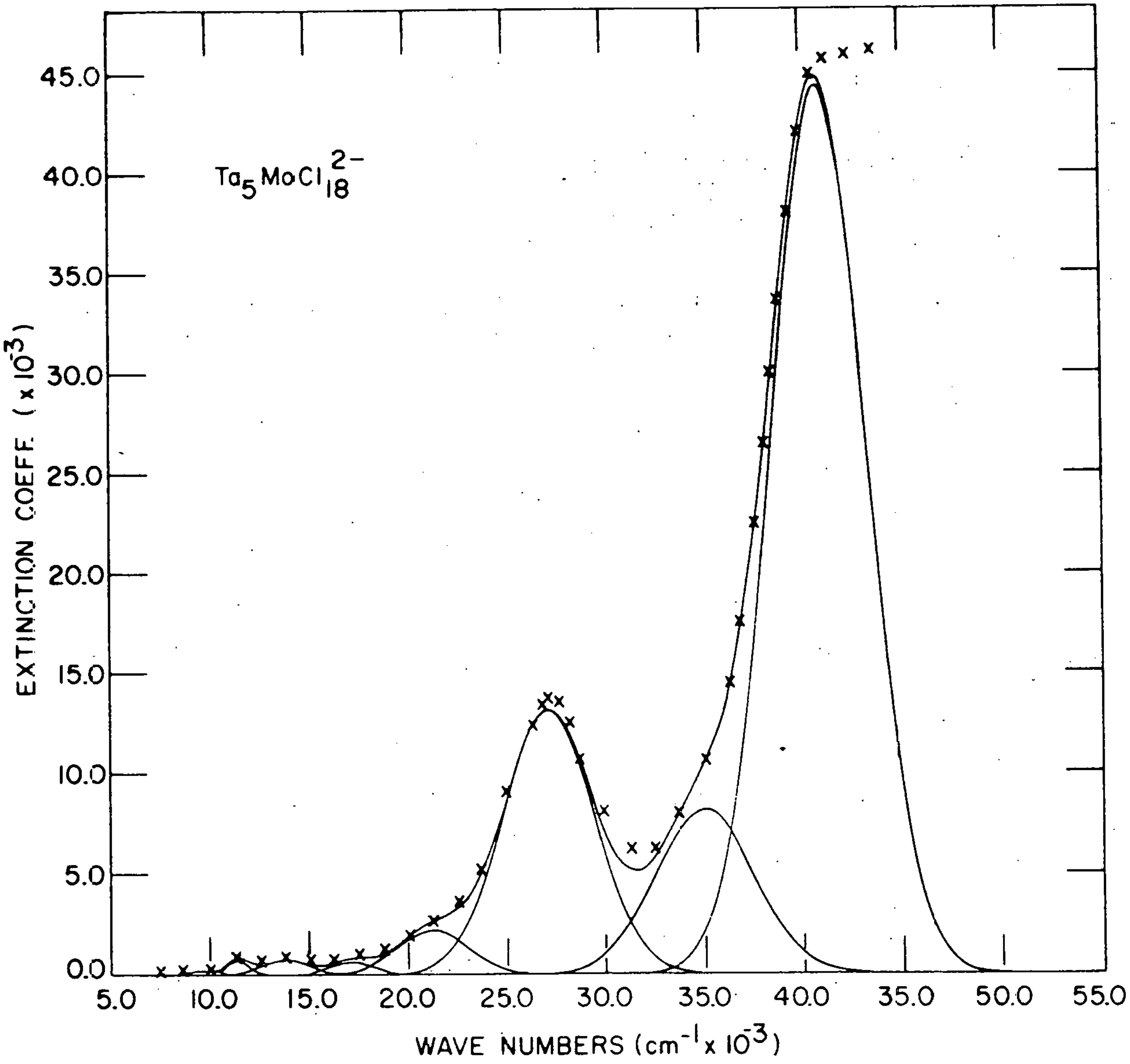

$Ta_5MoCl_{18}^{3-}$
EXTINCTION COEF. $(\times 10^{-3})$
36.0
32.0
28.0
24.0
20.0
16.0
12.0
8.0
4.0
0.0
5.0
10.0
15.0
20.0
25.0
30.0
35.0
40.0
45.0
50.0
55.0
WAVE NUMBERS $(cm^{-1} \times 10^{-3})$

Figure 3. Spectrum of $[(C_4H_9)_4N]_2[(Ta_5MoCl_{12})Cl_6]$ in acetonitrile showing observed (upper solid line), calculated (XXX) and Gaussian components (lower solid lines)


$Ta_5MoCl_{18}^{2-}$
EXTINCTION COEFF. (x 10^3)
45.0
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
5.0
10.0
15.0
20.0
25.0
30.0
35.0
40.0
35.0
50.0
55.0
WAVE NUMBERS (cm^{-1} x 10^{-3})

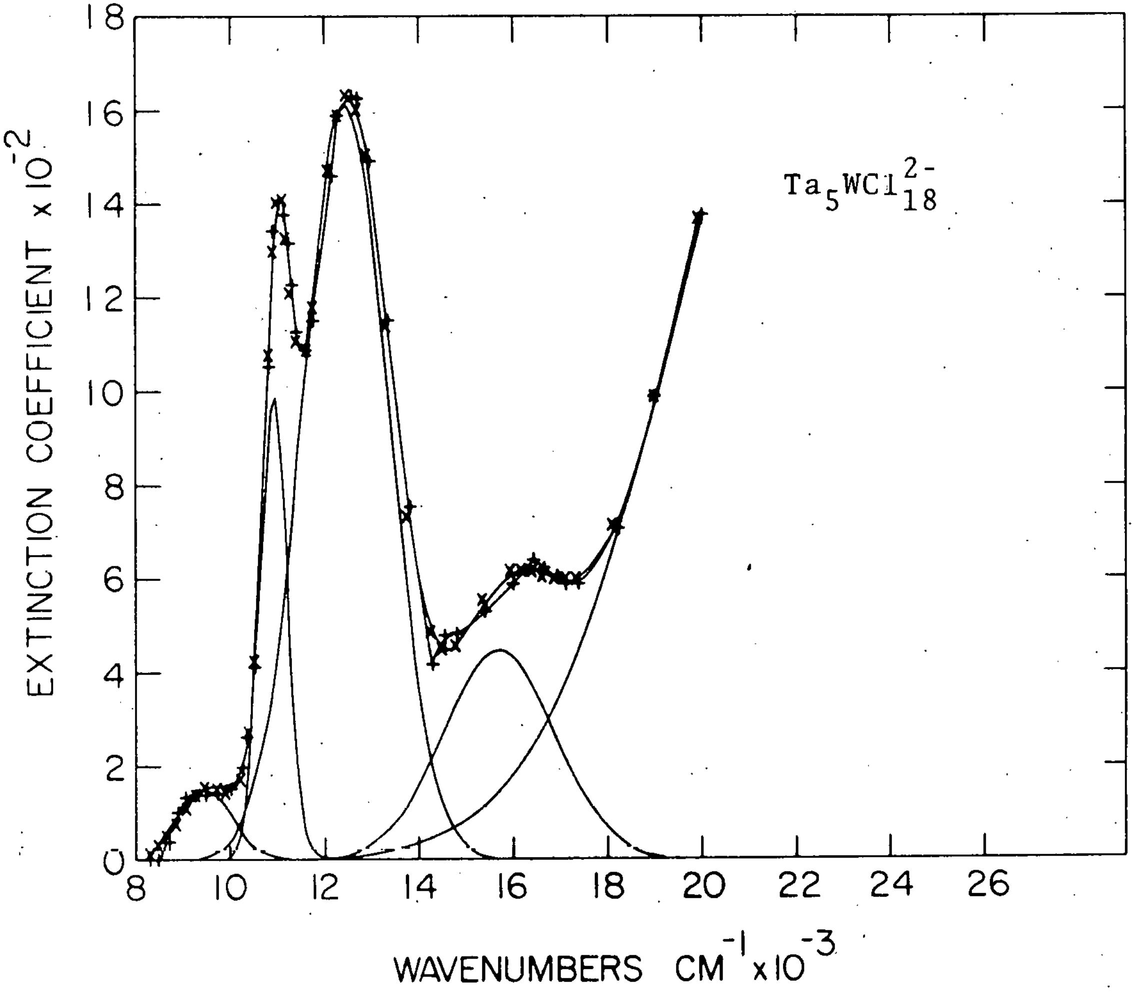


Figure 4. Spectrum of $[(C_3H_7)_4]_2[(Ta_5WCl_{12})Cl_6]$ in butyronitrile showing observed (upper solid line), calculated (XXX) and Gaussian components (lower solid line)

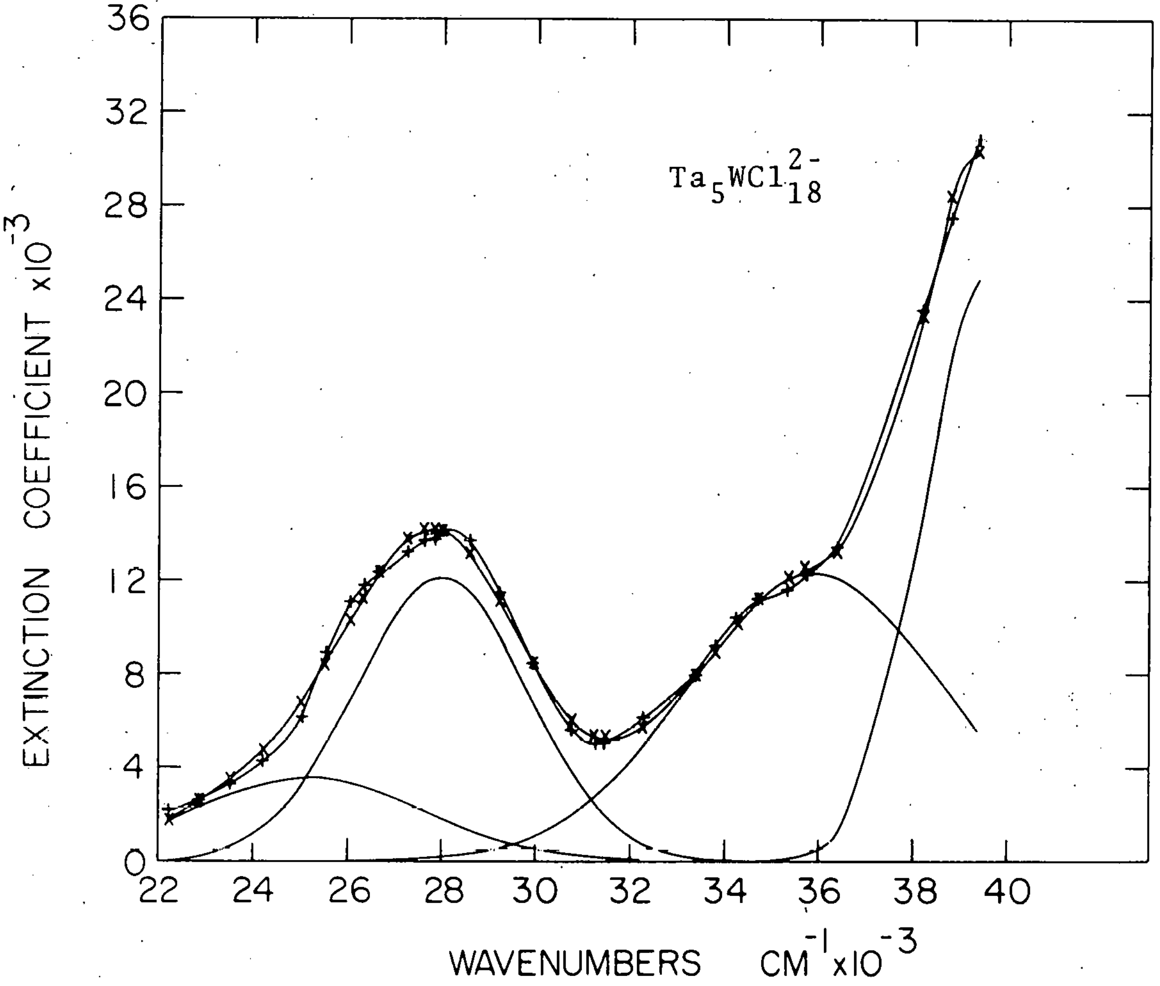


Figure 5. Spectrum of $[(C_3H_7)_4N]_2[(Ta_5WCl_{12})Cl_6]$ in butyronitrile showing observed (upper solid line), calculated (XXX) and Gaussian components (lower solid line)

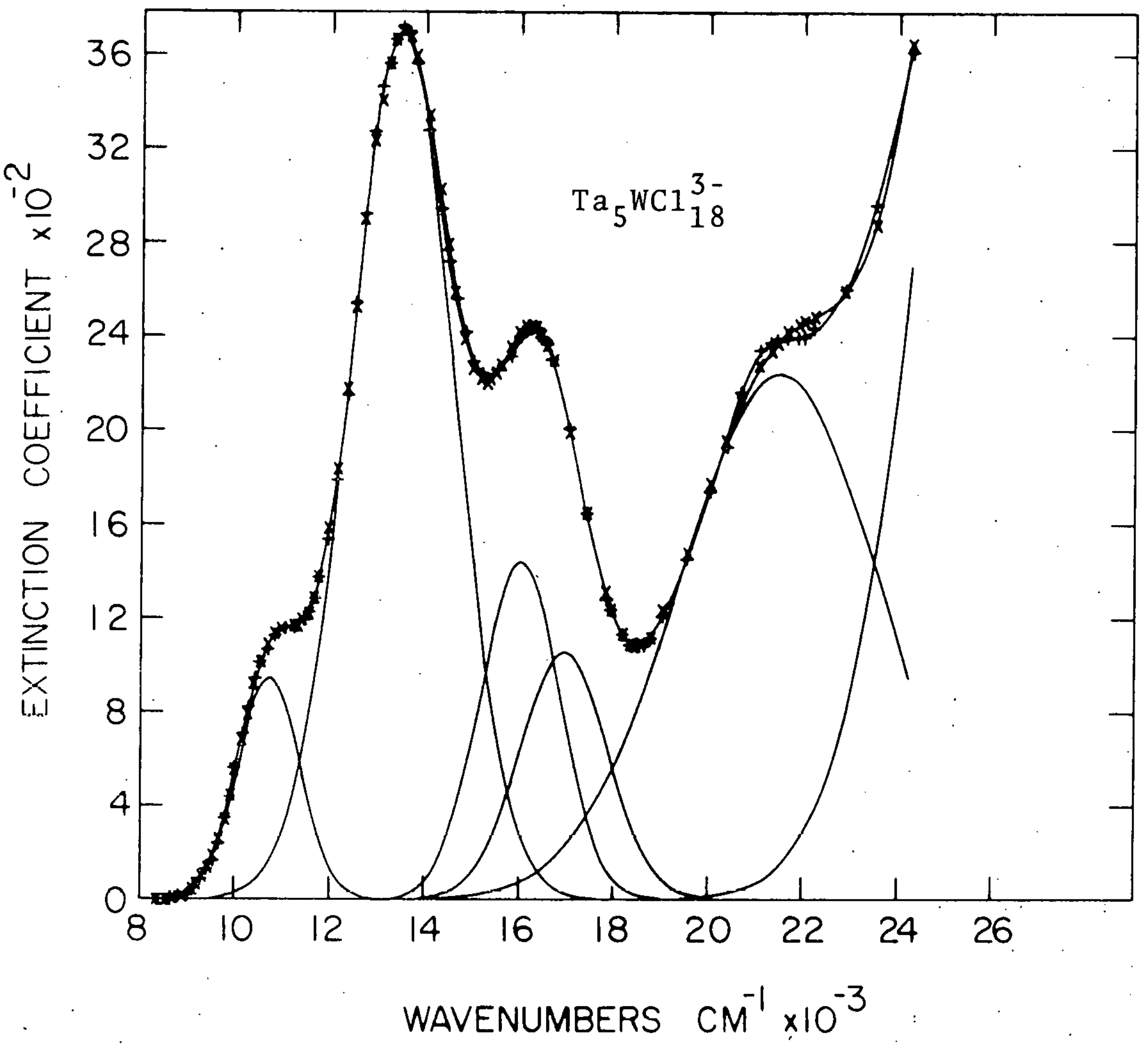


Figure 6. Spectrum of $[(C_3H_7)_4N]_3[(Ta_5WCl_{12})Cl_6]$ in butyronitrile showing observed (upper solid line), calculated (XXX) and Gaussian components (lower solid line)

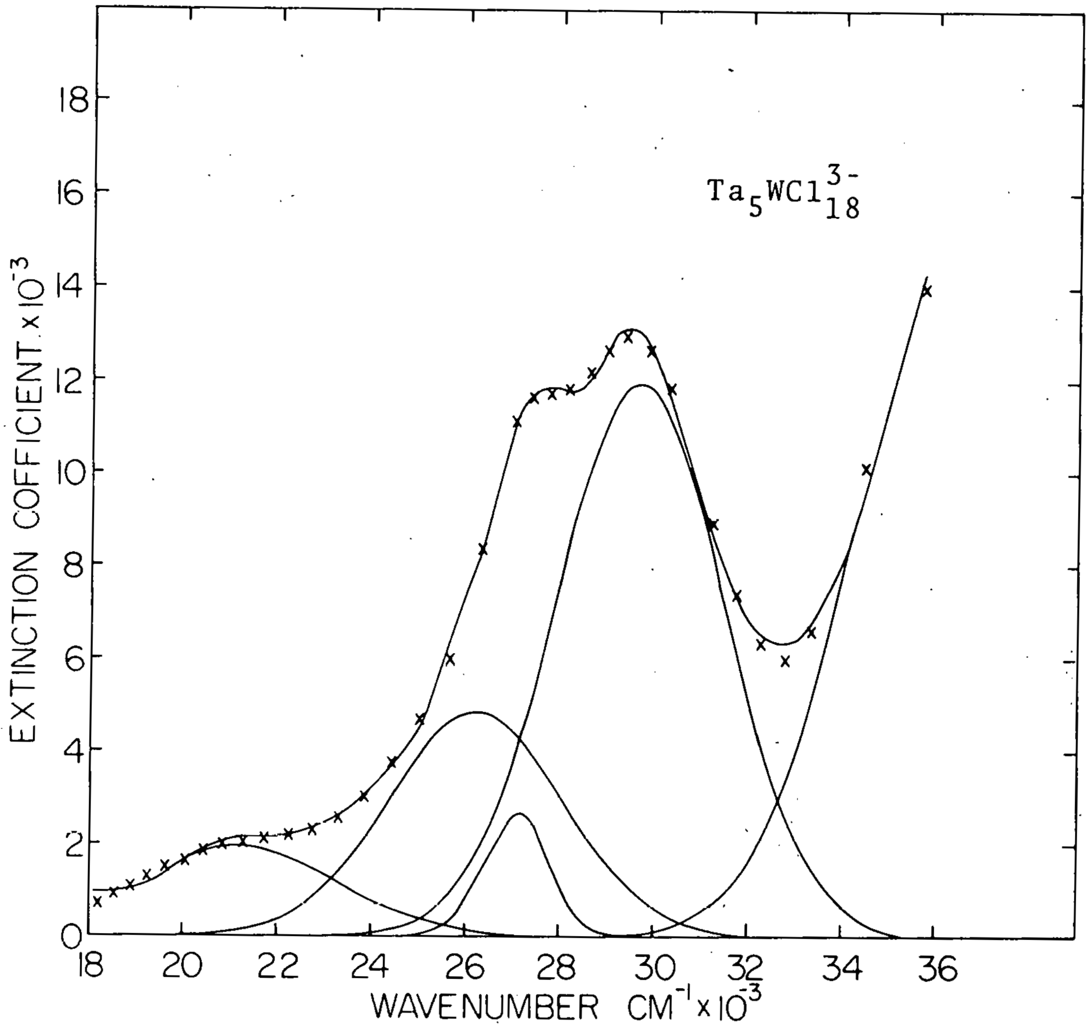


Figure 7. Spectrum of $[(C_3H_7)_4N]_3[(Ta_5WCl_{12})Cl_6]$ in butyronitrile showing observed (upper solid line), calculated (XXX) and Gaussian components (lower solid line)

Figure 8. Comparison of component bands in spectra of

A) $[Ta_6Cl_{18}]^{4-}$ in acetonitrile
B) $[Ta_5MoCl_{18}]^{3-}$ in acetonitrile
C) $[Ta_5WCl_{18}]^{3-}$ in butyronitrile
D) $[Ta_6Cl_{18}]^{3-}$ in ethanol
E) $[Ta_5MoCl_{18}]^{2-}$ in acetonitrile
F) $[Ta_5WCl_{18}]^{2-}$ in butyronitrile

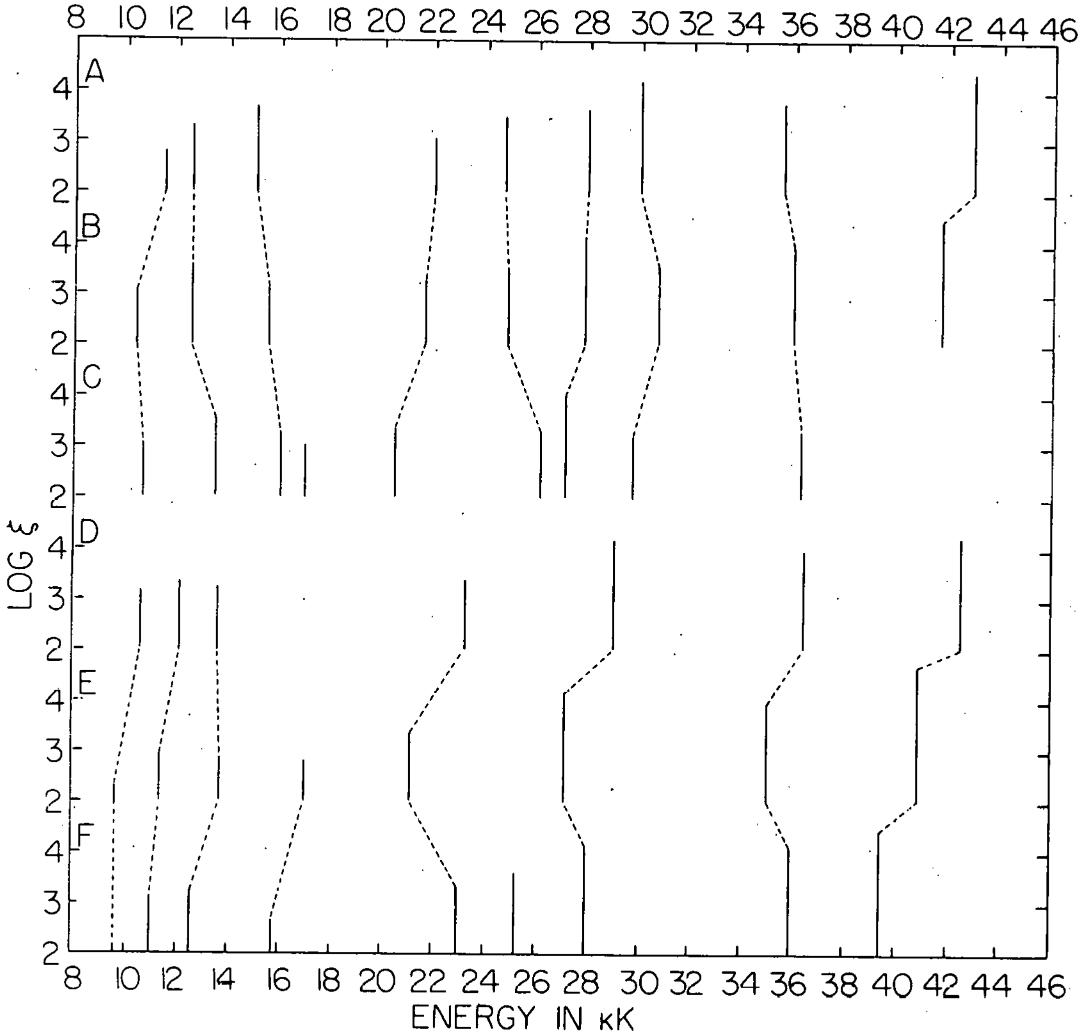

8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
42
44
46
A
B
C
D
E
F
4
3
2
LOG ξ
ENERGY IN κK

Table 1. Electronic absorption data[a]

$[(Ta_6Cl_{18})]^{4-}$		$[(Ta_5MoCl_{18})]^{3-}$		$[(Ta_5WCl_{18})]^{3-}$	
ν^b	ε^c	ν^b	ε^c	ν^b	ε^c
11.49	0.67	10.40	1.10	10.71	.94
12.56	1.91	12.54	2.58	13.48	3.68
15.06	4.46	15.55	1.36	16.01	1.44
---	---	---	---	16.94	1.06
22.0	1.15	21.6	1.76	21.49	2.24
24.7	3.01	24.8	2.88	---	---
27.9	4.23	27.8	10.95	27.08	9.21
30.0	16.86	30.7	3.91	29.68	11.90
35.5	5.61	35.9	8.73	36.29	14.51
42.9	18.9	41.7	27.01	---	---
$[(Ta_6Cl_{18})]^{3-}$		$[(Ta_5MoCl_{18})]^{2-}$		$[(Ta_5WCl_{18})]^{2-}$	
ν^b	ε^c	ν^b	ε^c	ν^b	ε^c
10.6	1.5	9.67	.22	9.55	.15
12.1	2.0	11.37	.74	10.99	.99
13.6	1.7	13.69	.76	12.51	1.61
---	---	17.0	.64	15.75	.449
23.2	2.2	21.1	2.20	22.9	2.13
---	---	---	---	25.17	3.57
29.0	14.5	27.1	13.16	27.98	12.14
36.4	8	35.0	8.23	35.93	12.30
42.5	16	40.8	44.25	39.46	24.91

[a] Absorptions are resolved Gaussian components.

[b] In units of kiloKaysers (1 kK = 1000 cm^{-1}).

[c] In units of liter $mole^{-1}$ cm^{-1} ($x10^{-3}$).

by Gaussian analysis omitting the band at 27.9 kK resulted in much poorer fit. This poorer fit may be due to the non-Gaussian shape of the bands in the spectra.

It was necessary to include an extra absorption band in the analysis of the spectra of the tantalum-tungsten 5-1-2 and 5-1-3, $[(Ta_5WCl_{12})Cl_6]^{2,3-}$, shown in Figures 4 and 7. In order to get a reasonably good fit of the observed spectra, these bands at 16.94 kK in the 5-1-3, Figure 4, and at 25.17 kK in the 5-1-2, shown in Figure 7, were included.

Figure 8 lists the data obtained from the Gaussian analysis of all the spectra. The spectra of all of these cluster compounds should indeed be comparable. Previous discussions have pointed out that the homonuclear clusters maintain nearly perfect octahedra with O_h symmetry even on oxidation. Also Fleming and McCarley (64) have reported that the spectra of the tantalum clusters in solution are qualitatively independent of the solvent. Therefore, if solvation does occur, significant distortion of the metal octahedra does not occur or has no effect on the spectra. The magnetic data for the tantalum and the niobium cluster compounds indicate that these compounds all have similar electronic structures.

Fleming and McCarley have noted (64) that the tantalum cluster bands generally appear at energies from 2 to 8 kK higher than corresponding bands in the niobium clusters. Such a shift is in good agreement with the shifts found in comparing the spectra of hexahalo complexes of $4d^n$ and $5d^n$ metals.

Figure 8 lists the data for these spectra and only the spectra of isoelectronic species are compared. For these isoelectronic compounds, dashed lines connect the bands which are thought to be analogous. The dashed lines do emphasize a few discrepancies in the data presented. For example, in the spectra of the oxidized derivatives, $Ta_6Cl_{18}{}^{3-}$, $Ta_5MoCl_{18}{}^{2-}$, and the $Ta_5WCl_{18}{}^{2-}$, there appears to be a band missing in the energy range 15 to 20 kK in the spectrum of the tantalum cluster. Both the tantalum-molybdenum, spectrum E, and the tantalum-tungsten, spectrum F, suggest that a weak band should be found in this energy range. Spectrum C, $Ta_5WCl_{18}{}^{3-}$, also suggests that this band should also be found in this species, although Meyer (46) does not report a corresponding band in the reduced tantalum-molybdenum cluster. It is interesting to note that Fleming and McCarley (64) do report such a band in the spectra of the $Nb_6Cl_{18}{}^{3-}$.

Other than the band at 25.17 kK in spectrum F, spectra D, E and F show a one to one line correspondence. The spectra of the tantalum and the tantalum-tungsten oxidized derivatives indicate that, in general, there is a much smaller perturbation on the electronic structure by the addition of a tungsten than that caused by the addition of a molybdenum atom in the cluster. The line that appears to be the most shifted with respect to the other oxidized derivatives occurs at 39.46 kK in spectrum F. This line perhaps can be attributed to a charge transfer band in the spectrum. It should be noted that the charge on this cluster species is 4+, $Ta_5WCl_{12}^{4+}$, corresponding to the charge on the $Ta_6Cl_{12}^{4+}$. Fleming and McCarley (64) report a charge transfer band for the tantalum 4+ cluster at 40.3 kK.

The correspondence of the spectra of the reduced species, $Ta_5WCl_{18}^{3-}$, in general, shows a poorer agreement with the other two reduced species, $Ta_6Cl_{18}^{4-}$ and $Ta_5MoCl_{18}^{3-}$. There is a one to one line correspondence in the lower end of the spectrum, except for the band at 16.01 kK discussed earlier, through about 22 kK. The absence of the band at about 24.8 kK is obvious. As can be seen from Figure 3, however, excellent agreement between the calculated spectrum and the observed is obtained without that particular band. The other major difference is that only three bands are observed above 25 kK. This may be due to the solvent cut-off for butyronitrile obscuring the highest charge transfer band which we expect at about 42.5 kK.

In summary, the spectra of the tantalum-tungsten mixed metal clusters compare very closely to the appropriate isoelectronic tantalum cluster derivative. Even though the correspondence is less favorable in the reduced species, there is excellent agreement between observed and calculated spectra. The change from a Ta_6 core to either a Ta_5Mo or Ta_5W core did not result in any profound changes in the spectra of the clusters. As previously stated, it has been hoped that the electronic spectra of these new compounds would provide some new information about the electronic structure of the $M_6X_{12}{}^{n+}$ cluster compounds. The spectra of the tantalum-tungsten cluster species have so far served only to substantiate the identity of the compounds.

Far Infrared Spectra of the Tantalum-Tungsten Mixed Metal M_6X_{12} Cluster Compounds.- The infrared spectra of the 5-1-3 and the 5-1-2 are informative but do not yield more than comparative information. The total reducible representation of the $[(Ta_5WCl_{12})Cl_6]^{n-}$ ion in C_{4v} symmetry is given by the equation below in terms of the irreducible representations it contains.

$$\Gamma_{total} = 14A_1 + 5A_2 + 9B_1 + 6B_2 + 19E$$

Only the A_1 and E modes are infrared active in C_{4v} symmetry. Of the total bands permitted in the vibrational spectrum one expects to see a total of thirty bands in the infrared spectrum. As can be seen from the data in Table 2, none of the four compounds possessing C_{4v} symmetry display more than 11 bands.

Upon close examination of the data in Table 2, it becomes apparent that the far infrared spectra of the mixed-metal clusters closely resemble the spectra of the homonuclear tantalum cluster species given in the table for comparison. Structural studies already discussed have shown that the

Table 2. Far infrared spectra (cm^{-1})[a]

Band No.	Cs^{+} $Ta_6Cl_{18}^{2-}$[b]	$(n\text{-}Bu)_4N^{+}$ $Ta_5MoCl_{18}^{2-}$[b]	$(n\text{-}Pr)_4N^{+}$ $Ta_5WCl_{18}^{2-}$	$(Et_4)N^{+}$ $Ta_6Cl_{18}^{3-}$[b]	$(Et)_4N^{+}$ $Ta_5MoCl_{18}^{3-}$[b]	$(n\text{-}Pr)_4N^{+}$ $Ta_5WCl_{18}^{3-}$
A	---	350 sh	---	----	352 sh	---
B	332VS(F)	336 VS	340 VS	324 VS	326 VS	328 VS
C	290 S(F)	300 S	298 VS	283 VS	290 VS	285 S
D	---	286 W	---	----	---	---
E	253VS(F)	261 VS	256 VS	243 VS	245 VS	238 VS
G	---	202 M	---	---	197 M	204 W
H	---	187 S	189 W	---	---	184 W
I	165 M(F)	171 VW	173 W	171 W	---	172 W
J	153 W	163 W	155 W	153 W	---	154 W
K	141 S(F)	138 M	143 S	140 S	141 M	142 S
L	118 M(F)	122 W	124 W	118 M	123 M	123 M

[a] S = strong, M = medium, W = weak, V = very, sh = shoulder, (F) designates band as fundamental according to reference (91).

[b] Data from reference (46).

tantalum clusters can be considered to have O_h symmetry. The close resemblance of the spectra of the tantalum clusters and the mixed metal clusters indicates that the effective symmetry of the mixed metal clusters approaches O_h. Mattes (90) has noted from his own work and from references (14,87,88) that the far infrared spectra of $M_6X_8Y_6^{2-}$ species (O_h symmetry) and the $M_6X_8Y_4$ (D_{4h}) differ only slightly. Hogue and McCarley (91) also verified this contention in comparing the spectra of $W_6Cl_8Cl_4(CH_3CN)_2$ and $W_6Cl_8Cl_6^{2-}$. There is extensive mixing of the normal modes of vibration in $M_6X_{12}^{n+}$ derivatives (91) and this mixing could serve to moderate the effect of the change of one of the tantalum atoms. This would seem to be especially true in the case of a tungsten substitution where the substitution is more like an isotopic change. If the effective symmetry is O_h, six fundamental bands should be observed in the spectra.

Further examination of the data in Table 2 reveals that six of the bands designated as fundamentals in the spectrum of $Cs_2Ta_6Cl_{18}$ (46) are clearly present in all of the tantalum-tungsten spectra listed. These bands are listed as B, C, E, I, K, and L in the table. The lower energies of the bands B, C, and E in the spectra of the 3+ derivatives is consistent with observations made by Fleming (42), and Mackay and Schneider (39).

Bands A, D, G and H are seen to be unique to the spectra of the mixed metal species, with band G observed in only one tantalum-tungsten derivative, 5-1-2. Band H is observed at 184 cm^{-1} in both tantalum-tungsten compounds, but has a weak intensity.

In general, the 5-1-2 derivative of the tantalum-tungsten compounds agree very closely with the spectra of the $Ta_6Cl_{18}^{2-}$ compound. Bands E and I show the greatest shift, with E moving 10 cm^{-1} to lower energy, and I to 173 cm^{-1}, 8 cm^{-1} higher in energy than the corresponding band in the tantalum compound.

The spectrum of the 5-1-3, tantalum-tungsten derivative, is much like that for the corresponding tantalum derivative, but shows shifts in the common bands from 2 to 5 cm^{-1}.

<u>Magnetic Properties of the Tantalum-Tungsten M_6X_{12} Mixed-Metal Clusters</u>.- The compounds of $Ta_6Cl_{12}^{2+}$, $Ta_5WCl_{12}^{3+}$ and $Ta_5MoCl_{12}^{3+}$, and the compounds of $Ta_6Cl_{12}^{3+}$, $Ta_5WCl_{12}^{4+}$ and $Ta_5MoCl_{12}^{4+}$ are isoelectronic and should have similar magnetic properties. As discussed in the introduction, derivatives of $Ta_6Cl_{12}^{2+}$ are diamagnetic while derivatives of $Ta_6Cl_{12}^{3+}$ are paramagnetic with magnetic moments corresponding to one unpaired electron per cluster unit. Table 3 (and Tables 12 and 13 in the Appendix) summarize the magnetic data obtained on the mixed metal cluster compounds and some comparable data on related compounds. Detailed χ versus T data are listed in the tables in the Appendix.

Table 3 lists the data for $[(C_4H_9)_4N]_2[(Ta_5MoCl_{12})Cl_6]$

Table 3. Magnetic susceptibilities (emu/mole) at room temperature

Compound	$\chi_M x10^6$	$\chi_D x10^{6a}$	$\chi_{tip} x10^{6a}$	μ(obs) B.M.	μ(calc) B.M.	θ (°K)	$\bar{g}$(epr)
$[(C_3H_7)_4N]_2[(Ta_5WCl_{18})]$	209	-1054	500	1.64	1.62	-50	1.868[b]
$[(C_3H_7)_4N]_3[(Ta_5WCl_{18})]$	-377	-1154	500	0.19	--		--
$[(C_2H_5)_4N]_2[(Ta_6Cl_{18})]^c$		-934	497	--	--		--
$[(C_2H_5)_4N]_3[(Ta_6Cl_{18})]^c$		-1054	501	1.67	1.66		1.922
$[(C_2H_5)_4N]_3[(Ta_5MoCl_{18})]^c$		-1066	516	0.76	--		
$[(C_4H_9)_4N]_2[(Ta_5MoCl_{18})]^c$		-1136	626	1.47	1.69		1.958

[a] Data from Reference (131).

[b] Measured by J. L. Templeton of this Laboratory on a powdered sample.

[c] Data from Reference (46).

and $[(C_2H_5)_4N]_3[(Ta_5MoCl_{12})Cl_6]$. The observed moment of the former is 1.47 B.M. as compared to the expected value of 1.69 B.M. for a single-electron paramagnetic compound. The observed moment of the $[(C_2H_5)_4N]_3[(Ta_5MoCl_{12})Cl_6]$, a diamagnetic compound, is 0.76 B.M. These moments show that the two compounds contain significant amounts of magnetic impurities. As discussed by Meyer (46) these impurities may not be simple hexanuclear cluster contaminants.

Figure 9 is a trace of the electron paramagnetic resonance spectrum of $[(C_3H_7)_4N]_2[(Ta_5WCl_{12})Cl_6]$ obtained on a powder sample at room temperature. The data obtained in this experiment are listed in Table 3.

The magnetic data for the tantalum-tungsten derivatives compare very well with those for the homonuclear tantalum clusters. The $\bar{g}$ value for the tantalum-tungsten 5-1-2 cluster, $[(C_3H_7)_4N]_2[(Ta_5WCl_{18})]$, is slightly lower, as is expected, than that for the isoelectronic tantalum cluster, $[(C_2H_5)_4N]_3[(Ta_6Cl_{18})]$. Likewise, the corresponding moments are lower. Further examination of the data in Table 3 shows the very good agreement between the magnetic moment calculated from the epr experiment and the moment calculated from the susceptibility data.

The magnetic data from Table 3 for the 5-1-3, $[(C_3H_7)_4N]_3[(Ta_5WCl_{18})]$, indicated that this compound contains a mole fraction of paramagnetic impurity of about 0.09. Even at this

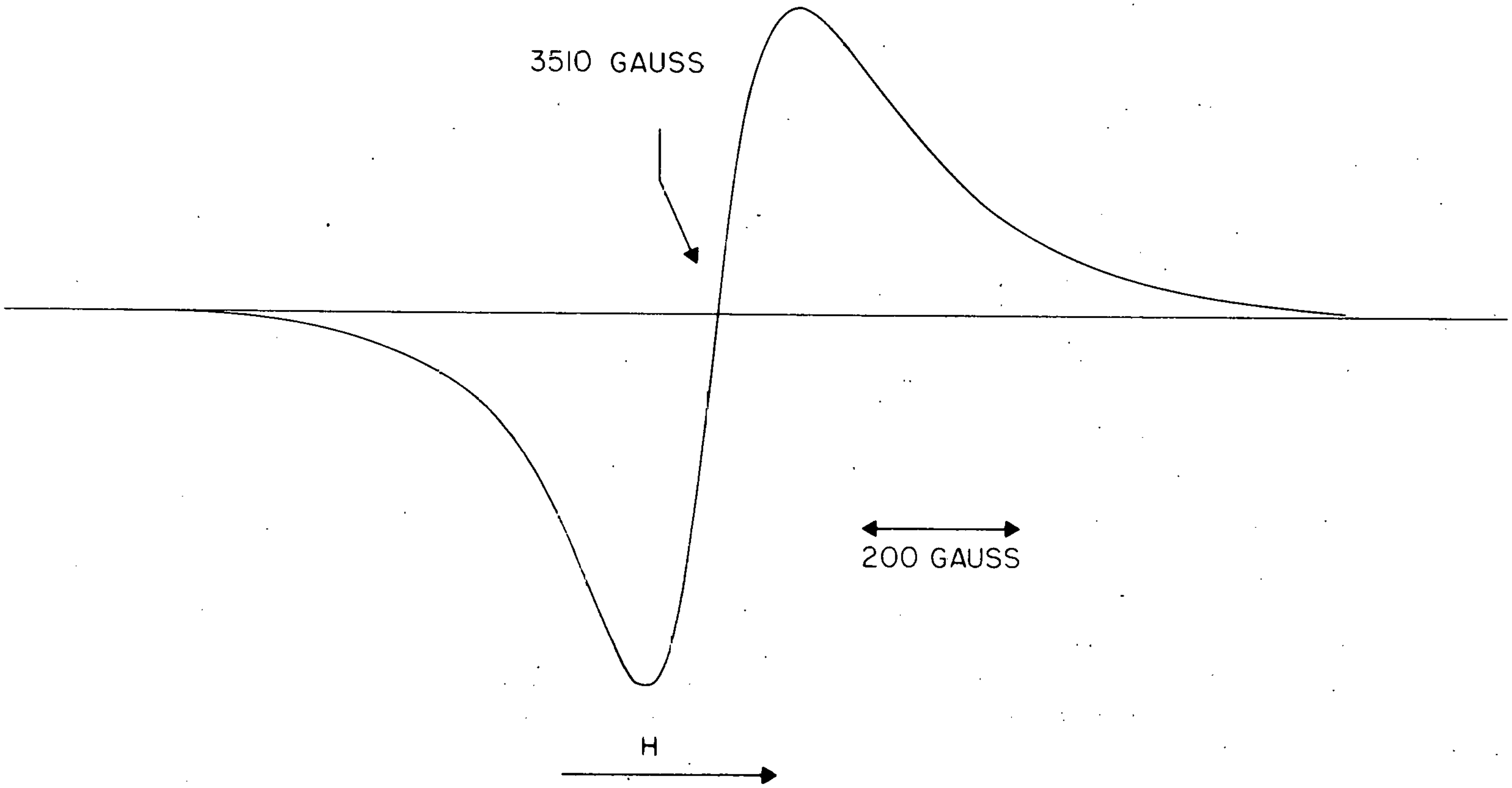


Figure 9. Electron paramagnetic resonance spectrum of $[(C_2H_7)_4N]_2[(Ta_5WCl_{12})Cl_6]$ obtained on solid sample

very low concentration, the contribution of the observed moment is large. Since there is no evidence for the presence of the paramagnetic $[Ta_6Cl_{18}]^{3-}$, it can be concluded that this impurity is $[Ta_5WCl_{18}]^{2-}$, present due to incomplete reduction.

X-ray Diffraction Studies of the Niobium and the Niobium-Tungsten M_3X_8 Species.- In the course of complete reaction work-up, x-ray diffraction studies of final residues were made. It was these diffraction studies that revealed most of the niobium and tungsten in the insoluble residues obtained in attempts to synthesize M_6X_{12} and M_6X_8 mixed metal cluster compounds in the residue as a species that gave a diffraction pattern identified as "$NbCl_3$". It was also noted that the product from the reaction designed to prepare $Nb_4W_2Cl_{12}Cl_4$ had the same stoichiometry as Nb_2WCl_8 and did give the best diffraction patterns. For this reason, Nb_3Cl_8 was prepared in a molten salt medium and the powder diffraction pattern was measured. Table 4 lists the data from this study, along with a computer calculated diffraction pattern for Nb_3Cl_8, the film data collected from a Debye-Scherrer study and data collected on all of the preparations for the substitution of tungsten into the niobium trimer.

Figure 10 points out the general line correspondence and the relative line intensities. As can be seen from the figure, the 2/1 and 3/2 Nb/W preparations give poorer diffraction patterns and reveal a very strong tungsten metal peak at 40.2°.

Table 4. X-ray diffraction data (degrees of 2θ)

Index[a]	Calc[a] Nb_3Cl_8	Film[b] Nb_3Cl_8	Powder[c] Nb_3Cl_8	Int.	6/1[c]	Int
002	14.44	14.24	14.34	541	14.34	307
100	15.17	15.19	15.18	44	15.24	36
					15.98	16
101	16.81	16.85	16.80	20	16.84	20
102	21.00	21.04	20.99	28	21.04	32
110	26.43	26.52	26.47	16	26.52	10
112	30.25	30.48	30.25	18	30.31	14
200	30.61		30.65	22	30.76	17
					32.25	12
104	32.99	32.99	32.96	17	33.07	15
202	34.00	34.05	34.02	100	34.09	100
					35.18	30
105	39.85	39.84	39.74	17	39.9	22
120,210	40.88	40.96	40.94	23	41.02	20
121,211	41.57	41.62	41.56	23	41.62	18
204	42.75	42.81	42.74	61	42.81	64
212,122	43.57		43.53	12	43.66	15
006	44.30	44.27	44.24	29	44.33	20
300	46.65	46.69				
213,123	46.76		46.85	18	46.82	14
301	47.27	47.34	47.22	21	47.33	16
302	49.09	49.15	49.07	13	49.16	15
303	52.02	52.01	52.02	19	52.08	10
220	54.42	54.60	54.47	15	54.54	35
206	54.81		54.78	31	54.86	26
304	55.94	55.97	56.00	10		
222	56.61	56.67	56.62	15	56.66	12
008	60.36	60.23	60.20	28	60.36	18

---

[a] A Fortran IV Program for the intensity calculation of powder patterns 1969, by K. Yvon, W. Jeitschko, and E. Parthé.

[b] Film data collected on a Debye-Scherrer or Guineré camera.

[c] Powder diffraction data collected on a G.E. powder diffractometer and normalized to peak at 34° with I = 100.

Table 4. (Continued)

$4/1^c$	Int	$2/1^c$	Int	$3/2^c$	Int	$W^{\circ c}$	Int
12.73	132						
15.05	252	14.3	170	14.37	172		
15.63	32			15.1	28		
16.68	19						
20.87	28	23.6	64				
32.82	26						
33.88	100	33.7	100	33.7	100		
34.97	11	35.7	64	34.97	64		
39.76	32			35.05	60		
		40.2	375	40.2	140	40.26	100
41.46	17						
42.64	71	42.5	52	42.5	108		
43.03	27	43.5	77	43.7	124		
44.13	33						
46.17	19						
46.62	17						
47.09	16						
48.96	11						
51.88	11						
54.36	24			54.4	44		
54.63	40						
		58.0	34			58.27	15
60.22	16						

Figure 10. X-ray diffraction data (degrees of 2θ)

A. Calculated diffraction pattern for Nb_3Cl_8

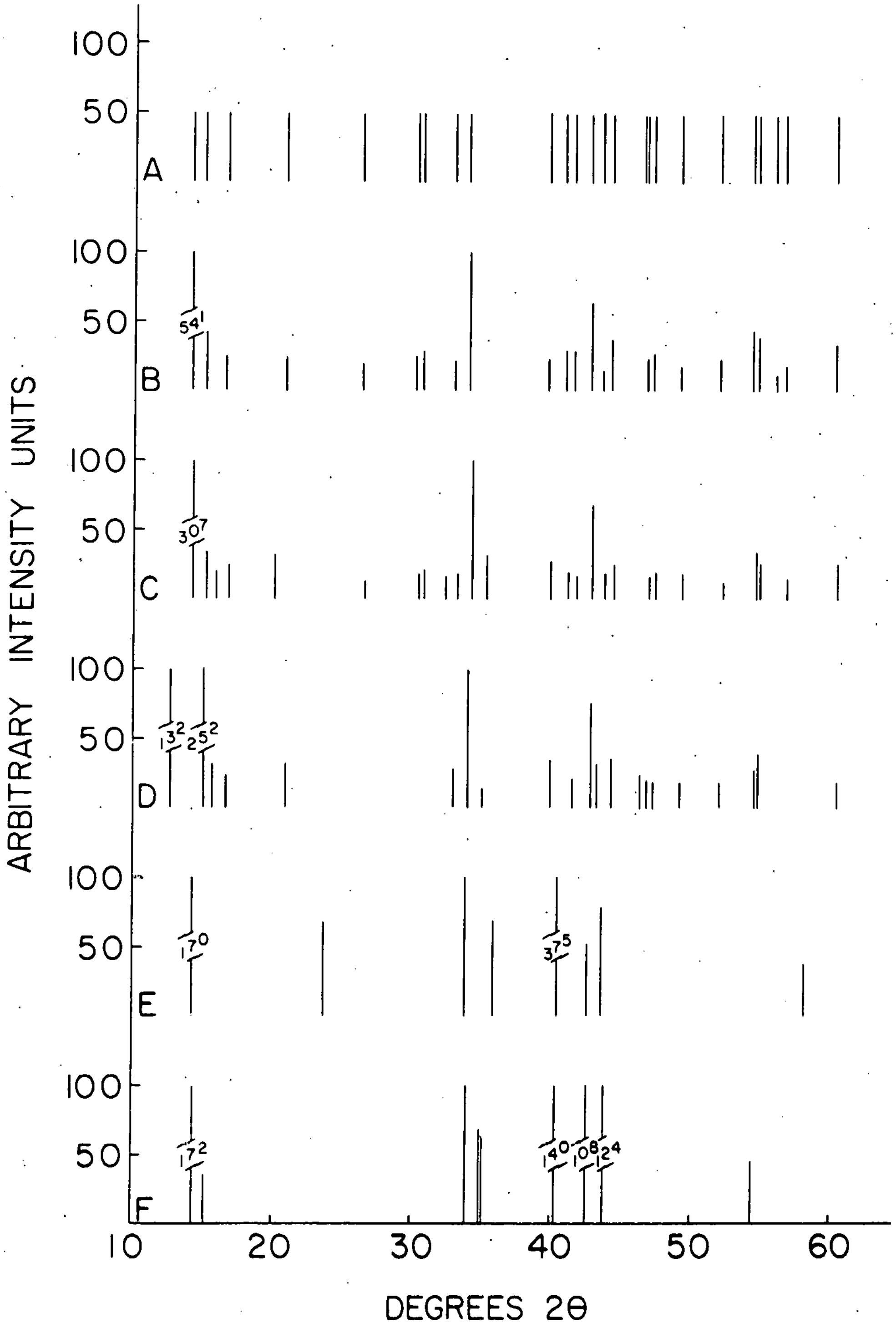
B. Powder diffraction data collected on diffractometer for Nb_3Cl_8

C. Powder diffraction data collected on diffractometer for Nb/W-6/1

D. Powder diffraction data collected on diffractometer for Nb/W-4/1

E. Powder diffraction data collected on diffractometer for Nb/W-2/1

F. Powder diffraction data collected on diffractometer for Nb/W-3/2


ARBITRARY INTENSITY UNITS
100
50
A
100
50
B
541
100
50
C
307
100
50
D
132
252
100
50
E
170
375
100
50
F
172
140
108
124
10
20
30
40
50
60
DEGREES 2θ

In both Table 4 and Figure 10, lines E and F indicate that these two reactions have yielded a mixture of products, i.e. tungsten metal, Nb_3Cl_8, and possibly others. For these reasons, the 2/1 and 3/2 preparations will be eliminated from further discussion.

Examination of the data in Table 4 and comparison of the patterns of the remaining compounds in Figure 10, in general, indicate a one to one line correspondence with the following exceptions. There is a drop in the intensity of the strong line at ca. 15° of about 15% in comparing the Nb_3Cl_8 compound to the 6/1 preparation, and a 30% drop in intensity comparing the 6/1 to the 4/1. There are a few new lines found in comparing the 4/1 and 6/1 preparations with Nb_3Cl_8. The very intense new line at 12.73° in the 4/1 preparation, the lines at 32.25° and 35.18°, and the lines at 32.82° and 34.97° in the 6/1 and 4/1 preparations, respectively, are strong evidence for a phase resulting from the substitution of tungsten into the niobium trimer. The absence of the line which normally occurs at 57° indicates that Nb_3Cl_8 is no longer present.

Except for the strong line in the Nb/W-4/1 preparation at 12.73°, the x-ray diffraction patterns of these mixed metal products strongly support the conclusion that they have the Nb_3Cl_8 structure and may be formulated as solid solutions $Nb_{3-x}W_xCl_8$, with $0 < x < 1$.

Far Infrared Spectra of the Niobium-Tungsten M_3X_8 Mixed Metal Cluster Compounds.- Table 5 lists the data for this series of experiments. Examination of the data indicates further that the compounds obtained from the Nb/W - 2/1 and 3/2 preparations are a mixture of two or more compounds, one being Nb_3Cl_8 or a derivative of that compound. Because of the difficulty in determining their identity, the 2/1 and 3/2 preparations will not be discussed.

Further examination of the data indicates that there has indeed been a substitution made in the niobium trimer. This is substantiated not only by shifts in the bands' positions, but also splitting of one band into two. Examination of the spectra shows further evidence of substitution, i.e. band broadening and distortion, as would be expected by a lowering of the symmetry from C_{3v} to C_s upon going from Nb_3 to Nb_2W clusters.

Maas and McCarley (132) have pointed out that the highest vibrational stretching frequency, a niobium terminal chlorine stretch, for niobium in an oxidation state of 2.67 should be expected at about 310 cm^{-1}. Band D, listed in Table 5, corresponds to this expected value and is more than likely arising from the mode described. Bands A and B, found at 403 and 369 cm^{-1}, respectively, possibly arise from metal-triply bridging chlorine and metal-double bridging chlorine in the Nb_3Cl_8 cluster, and taken together appear to be a unique indicator of the presence of this phase.

Table 5. Far infrared spectra (cm^{-1})

Band No.	Nb_3Cl_8	6/1 Nb/W	4/1 Nb/W	2/1 Nb/W	3/2 Nb/W
A	403 M	402 M	405 M	402 S	403 S
B	369 S	363 S	365 S	363 S	363 S
C	---	---	---	345 S	---
D	301 S	309 S	309 S	305 S	309 S
E	---	281 VS	280 VS	282 VS	280 VS
F	274 VS	270 VS	271 VS	269 VS	270 VS
G	247 M	247 S	247 S	248 VS	248 S
	---	---	---	228 M	229 W
	---	---	---	216 M	216 W
	---	---	---	210 W	---
	---	---	---	208 M	204 W
	---	---	---	197 W	---
H	192 M	191 M	190 M	190 W	190 M
	---	---	---	183 W	---
	---	---	---	179 W	180 M
	---	---	---	173 W	---
I	163 M	164 M	164 M	160 W	---
J	---	---	153 M	155 M	154 M
K	---	145 W	142 W	143 W	143 W
L	131 W	132 W	132 W	135 W	135 W
	---	---	---	124 W	124 W

There is a strong correspondence of bands in comparing the infrared spectra of the Nb_3Cl_8 with the 6/1 and 4/1 preparations, but at the same time there are some very striking differences in the spectra of the 6/1 and 4/1 compounds. Band F, at 274 cm^{-1}, in the parent compound is split into two bands upon substitution, one at 280 cm^{-1} and one at 270 cm^{-1}. There is a shift of band B to lower, and band D to higher energy. Band J, 153 cm^{-1}, appears to be unique in the higher substituted species, i.e. 4/1, 2/1 and the 3/2. Note that both the 6/1 and 4/1 preparations have developed a band at *ca.* 145 cm^{-1}, band K.

A summary of the data in Table 5 and a review of the arguments presented above indicate that the 2/1 and 3/2 preparations are mixtures of compounds. However, the data are also conclusive in that the 6/1 and 4/1 preparations have generated a new niobium-tungsten mixed metal M_3X_8 phase.

Magnetic Susceptibilities of the Niobium and Niobium-Tungsten Mixed Metal Cluster Species.- Dahl has suggested that the highest filled molecular orbital in the M_3X_8 cluster is either an e or an a_2 orbital. In either case, Nb_3Cl_8 is an odd electron system with 7 electrons occupying the metal-metal bonding orbitals and the molecular orbital diagram accounts for the paramagnetism of this member of the M_3X_8 cluster compound. If a tungsten is substituted for one of the niobium atoms in the trimer and if the oxidation state remains unchanged, the molecule would be an even numbered electronic system containing 8 electrons in those metal-metal orbitals and can be either diamagnetic or paramagnetic. If the highest occupied molecular orbital is non-degenerate, additional electron would be the second to be placed in that orbital and the system would be diamagnetic. If the highest occupied molecular orbital is degenerate, the system would be paramagnetic with a spin only value corresponding to two unpaired electrons according to the preceding argument. It was therefore the purpose of this particular study to elucidate some information about the electronic state of the M_3X_8 systems.

Table 6, and Table 14 in the Appendix, summarize the data from this study. The molar susceptibilities were calculated using the apparent molecular weights determined from analytical data. Since X-ray analysis has shown the Nb/W-2/1 and 3/2 preparations to contain tungsten metal, and the electronic and vibrational spectra have shown them to contain the Nb_3Cl_8 phase in a mixture, we will limit the discussion to the pure Nb_3Cl_8, the Nb/W - 6/1, and the Nb/W - 4/1 compounds.

Inspection of the data in Table 6 reveals that the apparent moment does indeed decrease as tungsten is substituted into the niobium trimer. In comparison of the effective moments, it should be noted that there are decreases in moments of 9.9% and 7.9% in comparing the 6/1 to Nb_3Cl_8 and 4/1 to 6/1 respectively. From the foregoing analysis made in

Table 6. Magnetic susceptibilities (emu/mole) at room temperature[a]

Compound	$\chi_M \times 10^6$	$\chi_D \times 10^6$	$\chi_M^{corr} \times 10^6$	$\mu_{(obs)}$ B.M.	$\mu_{(calc)}$ B.M.	θ °K
Nb_3Cl_8	1014	277	1291	1.83	1.83	-25°
6/1	789	287	1076	1.65	--	-30°
4/1	617	283	900	1.52	--	-30°
2/1	268	305	573	1.17	--	-37°
3/2	106	288	394	0.98	--	-42°

[a] μ(obs) calculated from slope of Curie-Weiss plot.

conjunction with the magnetic susceptibility measurements, it is reasonable to conclude that not only is tungsten being substituted into the niobium trimeric compound, Nb_3Cl_8, but also that the additional electron in the compound is paired in a non-degenerate orbital.

Electronic Spectra of Nb_3Cl_8 and the Niobium-Tungsten Mixed metal M_3X_8 Species.- The study of the electronic spectra of this series of compounds was made on the solid compounds by diffuse reflectance technique. It was not the purpose of this study to elucidate the electronic structure of these species, but more to use the information obtained from this experimental technique as a comparative tool or probe into the identity of the substituted species. In general, only the spectra of the Nb_3Cl_8, the 6/1 Nb/W and 4/1 Nb/W reaction products provided useful information.

Magnesium carbonate was used as the reflectance standard and as the sample matrix. The spectra of these compounds were measured over the energy range 10.0 kK to 50.0 kK. In all cases, the absorption drops off in going from low energy to high energy. Table 7 summarizes the data.

The parent compound, Nb_3Cl_8, shows two very well resolved peaks, one at 13.8 kK and the other at 20.0 kK. Upon substitution, the peak at 13.8 kK is seen to shift to lower energies, 13.3 kK, in both the 6/1 and 4/1 preparations. The peak at 20.0 kK, in the spectrum of Nb_3Cl_8, and 15.4 kK, in the spec-

Table 7. Electronic absorption data

Nb_3Cl_8	Nb/W 6/1	Nb/W 4/1	Nb/W 2/1	Nb/W 3/2
13.8 kK	13.3 kK	13.3 kK (sh)	14.3 kK (sh)	14.3 kK (sh)
--	--	15.4 kK (sh)	--	--
20.0 kK	--	--	--	--
--	--	26.6 kK (sh)	--	--

trum of the 4/1 preparation, are unique to their species. The general absorption characteristics of this entire series is very similar. The absorbance was always high at low energies and dropped to very low values at high energies. That particular characteristic and the absorption at about 13.8 kK seemed to be indicative of this series. The spectra of the 2/1 and 3/2 preparations are so poorly resolved that they are barely discernable as being related to this series.

In the case of the 6/1 and 4/1 preparations, it is safe to say upon substitution of tungsten into the niobium trimer, Nb_3Cl_8, there is some perturbation upon the system but that the overall electronic structure basically remains unchanged. The shift of the major peak of Nb_3Cl_8 from 13.8 kK to 13.3 kK in both the 6/1 and 4/1 preparations is strong evidence that the tungsten has been substituted into the trimeric cluster without disruption of the cluster or its basic electronic environment.

Synthesis of the Niobium-Molybdenum Mixed Metal Cluster Compounds.- Because of the apparent success in the preparation of mixed metal M_3X_8 cluster compounds with niobium and tungsten, analogous reactions were attempted, each one starting with a $NbCl_5/MoCl_5$ ratio of 2/1 according to Equation 13.

$$6NbCl_5 + 3MoCl_5 + 7Al \xrightarrow[\substack{50\ m/o\ NaCl\\ 50\ m/o\ AlCl_3}]{} 2Nb_3Cl_8 + 1Mo_3Cl_8 + 7AlCl_3 \qquad (13)$$

Preliminary reactions had shown molybdenum pentachloride to be rapidly reduced by aluminum at temperatures exceeding 450°C. Because it might be possible to prepare niobium-molybdenum mixed metal clusters of more than one type, reactions over a range of temperatures were performed in order to explore the possibility of more than one compound being formed. Following the method outlined by Meyer (46), for formation of mixed-metal M_6X_{12} clusters, a reaction was performed for 3 days at 320°C according to Equation 13'.

$$12NbCl_5 + 6MoCl_5 + 14Al \xrightarrow[\substack{50\ m/o\ NaCl\\ 50\ m/o\ AlCl_3}]{320^\circ,\ 3\ days} 3Nb_4Mo_2Cl_{12}Cl_4 + 14AlCl_3 \qquad (13')$$

For ease of discussion, the products obtained, and this reaction in general, will be referred to as the Nb-Mo-320 reaction.

No special problems were encountered in the work-up of the reaction mass. A very light color was observed in the aqueous extraction and was identified as the $Mo_6Cl_8^{4+}$ cluster species. A slight coloration was also noted in the ethanol extraction and this color was attributed to the formation of $Nb_6Cl_{12}^{3+}$ in the product. Both of these species were found to be in very low concentration and were considered to be an insignificant fraction of the product.

The final product was a dark scarlet powder which appeared to be homogeneous under inspection with a polarizing microscope. The product, it is felt, is not related to the $M_6X_{12}^{n+}$ cluster derivatives because of the solubility differences. It is also believed, on the same basis, that this product is not related to the $M_6X_8^{4+}$ cluster compounds, which are very soluble in both the aqueous and ethanolic media. Further physical evidence, to be discussed below, indicates that the compound can be formulated as Nb_2MoCl_8, but is not necessarily related structurally to the M_3X_8 species.

The second reaction in this series is described below. Equation 13 describes the stoichiometry of the reaction run at 550°C for three days in an effort to prepare the M_3X_8 species, Nb_2MoCl_8. This particular preparation followed the methods outlined for the preparations of Nb_3Cl_8 and the niobium-tungsten mixed metal M_3X_8 compounds.

This preparation, noted as the Nb-Mo-550, deviated from the other preparations as follows: 1) The reduced compound appeared to be soluble in the molten salt media, where it was observed to be evenly dispersed throughout the entire cooled slug. 2) The reduced compound was sensitive to hydrolysis upon prolonged extraction with water. For this second reason, special care had to be taken in the extraction procedure of this product, and both the aqueous and ethanol extractions were carried out using Schlenk techniques. The aqueous wash did indicate the presence of some $Mo_6Cl_8^{4+}$ species and the ethanol solution indicated a very dilute solution of the homonuclear niobium cluster, but both in concentrations deemed insignificant. The final product was a brown powder which appeared to be homogeneous under microscopic examination.

Although the stability of this species is quite different from the previous preparation, subsequent evidence, to be discussed, shows that these two reactions provided very similar products. Again the solubility characteristics indicate that this product is neither an $M_6X_{12}^{n+}$ nor $M_6X_8^{4+}$ derivative. The above mentioned physical evidence also indicates that this compound is correctly formulated as Nb_2MoCl_8, and is identical to that formed in the 320°C preparation above, but again may not be related to the M_3X_8 compounds structurally.

One further set of reaction conditions was investigated. According to the stoichiometry of Equation 13, a reaction was set up and performed in the usual manner for three days at 650°C. The notation for the reaction and the products obtained from this set of conditions is Nb-Mo-650. The product obtained from this preparation was the most analogous to the Nb_3Cl_8 and the niobium-tungsten M_3X_8 species. Since the product was inert and insoluble the extraction procedure for this compound presented no special problems. The final extracted product was a black crystalline residue which appeared homogeneous when viewed under a polarizing microscope. Initially, it was felt that this preparation was the most analogous to the Nb_3Cl_8 and niobium-tungsten M_3X_8 compounds. Further study of this compound revealed that it was a mixture of several products including molybdenum metal.

One additional reaction in the study of the coreductions of niobium and molybdenum pentahalides was set up in an attempt to prepare a compound of the formulation $Nb_4Mo_2Cl_{11}$. This compound would be analogous to Nb_6I_{11}, but would be a 21 electron M_6X_8 cluster instead of a 19 electron cluster. Equation 14 describes the basic preparative reaction.

$$12NbCl_5 + 6MoCl_5 + 19Al \xrightarrow[\substack{50\ m/o\ NaCl \\ 50\ m/o\ AlCl_3}]{650°,\ 3\ days} 3Nb_4Mo_2Cl_{11} + 19AlCl_3 \qquad (14)$$

When the coreduction reaction had been completed, the reaction mass was found to be similar to those which provided compounds having the M_3X_8 structure. A mass of insoluble black material was covered by a layer of the salt medium. This reaction mass was treated in the usual manner, and very much like the M_3X_8 phases, there were no colored effluents from the extractions. The final product was a black, very crystalline residue which appeared homogeneous under microscopic examination. Even though this product resulted from a reaction of different stoichiometry, it was analogous to the product of the Nb-Mo-650 reaction, and is discussed below in that light.

<u>X-ray Diffraction Studies on the Niobium-Molybdenum Mixed Metal Cluster Species</u>.- Table 8 summarizes the data collected on this series of compounds and Figure 11 points out the general line correspondence and relative line intensities.

Examination of the data in Table 8 indicates the Nb-Mo-320 product is a mixture containing some unidentified phase plus a new phase also found in the Nb-Mo-550 preparation. The diffraction data for the product of the Nb-Mo-550 reaction establish that this material is a new compound of unique structure. The table lists data that lead one to conclude that the Nb-Mo-650 and the $Nb_4Mo_2Cl_{11}$, prepared also at 650°C, are mixtures of compounds including molybdenum metal. Little will be said of the latter two high temperature products simply because the data collected do indicate a mixture of products and little can be said of the actual nature of any new species that might be present.

In general, the Nb-Mo-320 gave a very poor diffraction pattern which makes it difficult to make conclusions about the identity of the phases present. However as will be shown later from infrared spectra, one component of the mixture is a phase having the Nb_3Cl_8 structure; the second component appears to be related to the product from the Nb-Mo-550 reaction. The comparison of the Nb-Mo-320 and Nb-Mo-550 powder

Table 8. X-ray diffraction data (line positions in 2θ)

Line No.	Nb/Mo-2/1 320[a]	Int	Nb/Mo-2/1 550[a]	Int	Nb/Mo-2/1 650[b]	Int	$Nb_4Mo_2Cl_{11}$[b]	Int	$\overset{\circ}{\mathrm{Mo}}$	Int
1							12.56	25		
2							13.08	30		
3	14.70	255	13.36	320	14.57	180	14.11	212		
4			15.52	62	15.33	54	14.96	40		
5					16.95	33	16.6	25		
6					21.17	42	20.78	28		
7							26.2	15		
8			31.13	34						
9			31.67	64						
10			32.86	26			32.75	15		
11	34.12	100	33.61	100	34.17	100	33.83	100		
12			34.58	20						
13			35.18	30						
14			36.13	20						
15			37.17	18						
16			37.92	64						

---

[a] Film data collected on Debye-Scherrer or Guinier camera (intensities estimated).

[b] Data collected on G.E. powder diffractometer.

Table 8. (Continued)

Line No.	Nb/Mo-2/1 320[a]	Int	Nb/Mo-2/1 550[a]	Int	Nb/Mo-2/1 650[b]	Int	$Nb_4Mo_2Cl_{11}$[b]	Int	Mo°	Int
17			39.20	22						
18			39.66	32						
19			40.54	16	40.51	111	40.3	45	40.51	100
20			41.37	38	41.74	36	41.37	20		
21			42.82	65	42.91	84	42.58	65		
22	43.94	65	44.01	100			44.05	25		
23			44.48	88	44.45	21				
24			45.70	33						
25					46.9	27	46.6	20		
26			47.25	16	47.4	24	47.0	20		
27			48.78	16						
28			50.27	48						
29			51.24	31						
30			52.30	29						
31	53.47	45	53.33	16						
32	54.46	50	54.30	20	54.6	30	54.28	35		
33					54.9	42	55.55	25		
34							56.4	15		
35					58.7	21			58.60	21
36	59.6	55								
37	61.0	50			60.4	24	60.14	20		
38			62.95	30						

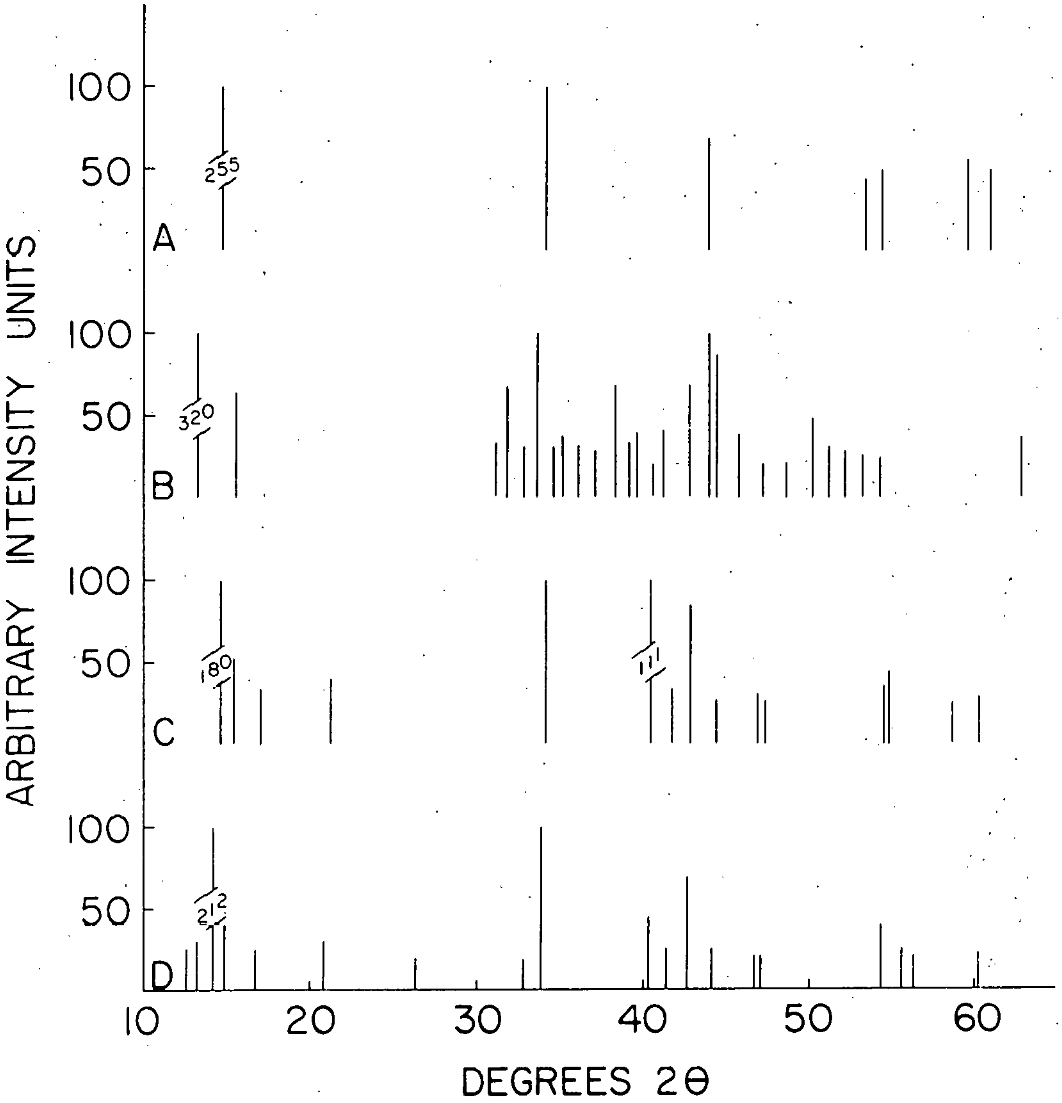
Figure 11. X-ray diffraction data (degrees of 2θ)

A. Diffraction data from Debye-Scherrer study of Nb-Mo-320

B. Diffraction data from Debye-Scherrer study of Nb-Mo-550

C. Powder diffraction data collected on diffractometer for Nb-Mo-650

D. Powder diffraction data collected on diffractometer for $Nb_4Mo_2Cl_{11}$


ARBITRARY INTENSITY UNITS
100
50
A
255
100
50
B
320
100
50
C
180
111
100
50
D
212
10
20
30
40
50
60
DEGREES 2θ

patterns with that of Nb_3Cl_8 is convincing that the new phase formed in these reactions does not have the Nb_3Cl_8 structure type. Although based on its composition the Nb_2MoCl_8 bears an obvious relation to Nb_3Cl_8, and indeed the former may also contain M_3 clusters, clearly the two compounds possess different crystal structures.

Far Infrared Spectra of the Niobium-Molybdenum Mixed Metal Clusters.- The study of the far infrared spectra of these mixed metal cluster compounds was carried out for comparison purposes and not for the purpose of making fundamental mode assignments. Table 9 lists the data collected in this study along with the data for Nb_3Cl_8. Inspection of these data reveals that the spectra of the two high temperature preparations, Nb-Mo-650 and $Nb_4Mo_2Cl_{11}$, show similar features to the spectra listed in Table 5 for Nb/W-2/1 and Nb/W-3/2. These products are shown in this study to be mixtures, one component of which was shown to be molybdenum metal by X-ray diffraction studies. Because of the difficulty in determining the exact identity of these mixtures, they will be eliminated from the discussion pertaining to the vibrational spectra.

Further examination of Table 9 reveals that the spectrum of Nb-Mo-320 bears a strong resemblance to the spectra of both Nb_3Cl_8 and Nb-Mo-550. Bands A and B, indicative of the Nb_3Cl_8 cluster type, are present in the spectra of Nb-Mo-320 but conspicuously absent from the spectrum of Nb-Mo-550. This

Table 9. Far infrared spectra (cm^{-1})

Band No.	Nb_3Cl_8	Nb/Mo-320	Nb/Mo-550	Nb/Mo-650	$Nb_4Mo_2Cl_{11}$
A	403 M	403 S	---	407 S	405 W
B	369 S	369 S	---	---	---
C	---	362 S	355 S	363 S	365 M
D	---	327 S	328 S	---	---
E	301 S	305 VS	304 VS	310 S	309 S
F	---	292 M	---	---	---
G	---	283 VS	---	282 VS	---
H	274 VS	272 VS	---	271 VS	273 VS
I	---	256 M	---	---	---
J	247 M	247 S	243 S	247 S	247 S
K	---	229 S	---	228 W	225 W
L	---	210 M	---	---	---
M	---	204 M	204 M	204 W	204 W
N	---	197 W	197 W	---	---
O	192 M	192 W	191 W	193 M	193 M
P	---	---	179 M	178 M	179 W
Q	---	174 M	173 M	---	173 W
R	163 M	---	---	164 M	165 W
S	---	160 M	159 M	---	159 W
T	---	154 M	155 M	154 W	155 W
U	---	143 W	143 W	143 M	142 M
V	---	135 W	134 W	---	135 W
W	131 W	---	---	---	130 W

evidence, along with other differences in the spectra of these three moieties, leads one to conclude that the Nb-Mo-550 not only is a new compound, but also has a structure unrelated to the Nb_3Cl_8 cluster type.

Magnetic Susceptibilities of the Niobium and Molybdenum Mixed Metal Cluster Species.- The magnetic susceptibilities of the Nb/Mo-2/1-320 and 550 preparations were measured. Table 10 summarizes that data and Table 15 in the Appendix lists the detailed χ versus T data. The data, as is shown in Table 10, obey a Curie-Weiss law with Weiss constants as tabulated. In general, these data show much reduced moments when compared to the corresponding niobium-tungsten species listed in Table 6. The molar susceptibilities listed in Table 10 have been calculated on the basis of the molecular formulation determined from the analytical data.

Table 10. Magnetic susceptibilities (emu/mole) at room temperature

Compound	$\chi_M x10^6$	$\chi_D x10^6$	$\chi_M^{corr} x10^6$	$\mu_{(obs)}$ B.M.	θ
Nb/Mo-2/1 320	428	278	706	1.21	-30°
Nb/Mo-2/1 550	-207	284	77	0.41	-28°

From the foregoing arguments outlined in the section discussing the magnetic properties of the niobium-tungsten compounds, the stoichiometric compound Nb_2MoCl_8 should be diamagnetic. The Nb-Mo-650 and $Nb_4Mo_2Cl_{11}$ preparations were eliminated from this study because preceding data discussed have verified that these compounds are mixtures containing molybdenum metal.

By the method outlined previously, the Nb-Mo-320 preparation shows an apparent moment of 1.21 B.M. This moment can be attributed to 0.45 mole fraction of a paramagnetic species, which is taken to be Nb_3Cl_8 because its presence is verified by the vibrational spectrum. However the Nb_3Cl_8 phase present may contain some molybdenum substituted for niobium, hence the above estimate may be in error. As noted earlier substitution of a group VI metal into the Nb_3Cl_8 cluster should lower the magnetic moment.

The apparent moment of the Nb-Mo-550 compound is only 0.41 B.M., corresponding to a mixture whose major component is diamagnetic and a minor component of a paramagnetic species. Based on the assumption that the minor component is Nb_3Cl_8 an estimate of 0.05 mole fraction is made for this component. It is reasonable to conclude that the formation of the new Nb-Mo compound is initiated even at lower temperatures, 320°C, but is much more readily formed at 550°C. It is also apparent that this same compound undergoes disproportionation to molybdenum metal, a phase having the Nb_3Cl_8 structure, and other species at the higher temperature, 650°C.

Electronic Spectra of the Niobium-Molybdenum Mixed Metal Species.- The electronic spectra of this series of compounds are reported from a study made on the solids by diffuse reflectance spectroscopy. Again, it was the purpose of these experiments to obtain qualitative information in comparing one preparation with another.

The spectra were measured from 10.0 to 50.0 kK using magnesium carbonate as the reflectance standard and as the sample matrix. These spectra fall into two classes, those that compare relatively well to the niobium-tungsten compounds and those that are unique in themselves. The two high temperature species, Nb-Mo-650 and $Nb_4Mo_2Cl_{11}$, demonstrate the usual characteristics of the Nb_3Cl_8 and the Nb_2WCl_8 compounds: i.e. poor resolution and the absorption falling off at higher energies. The Nb-Mo-320 and the Nb-Mo-550 both give the spectra outlined in Figure 12.

Table 11 summarizes the data from this study, and Figure 12 compares the spectra of Nb_3Cl_8, one of the niobium-tungsten substituted compounds, Nb/W-6/1, and the Nb-Mo-550. It seems reasonable to conclude that the spectra of the two high temperature products, Nb-Mo-650 and the $Nb_4Mo_2Cl_{11}$, arise from solid solutions having the Nb_3Cl_8 structure.

Examination of the data in Table 11 shows one very well

Table 11. Electronic absorption data

Nb_3Cl_8	Nb/Mo 320	Nb/Mo 550	Nb/Mo 650	$Nb_4Mo_2Cl_{11}$
13.8 kK	--	--	13.3 kK (sh)	13.3 kK (sh)
--	--	--	--	15.4 kK (sh)
20.0 kK	--	--	--	22.2 kK (sh)
--	26.6 kK	26.6 kK	--	--

resolved single peak at about 26.6 kK for the Nb-Mo-320 and the 550 compounds.

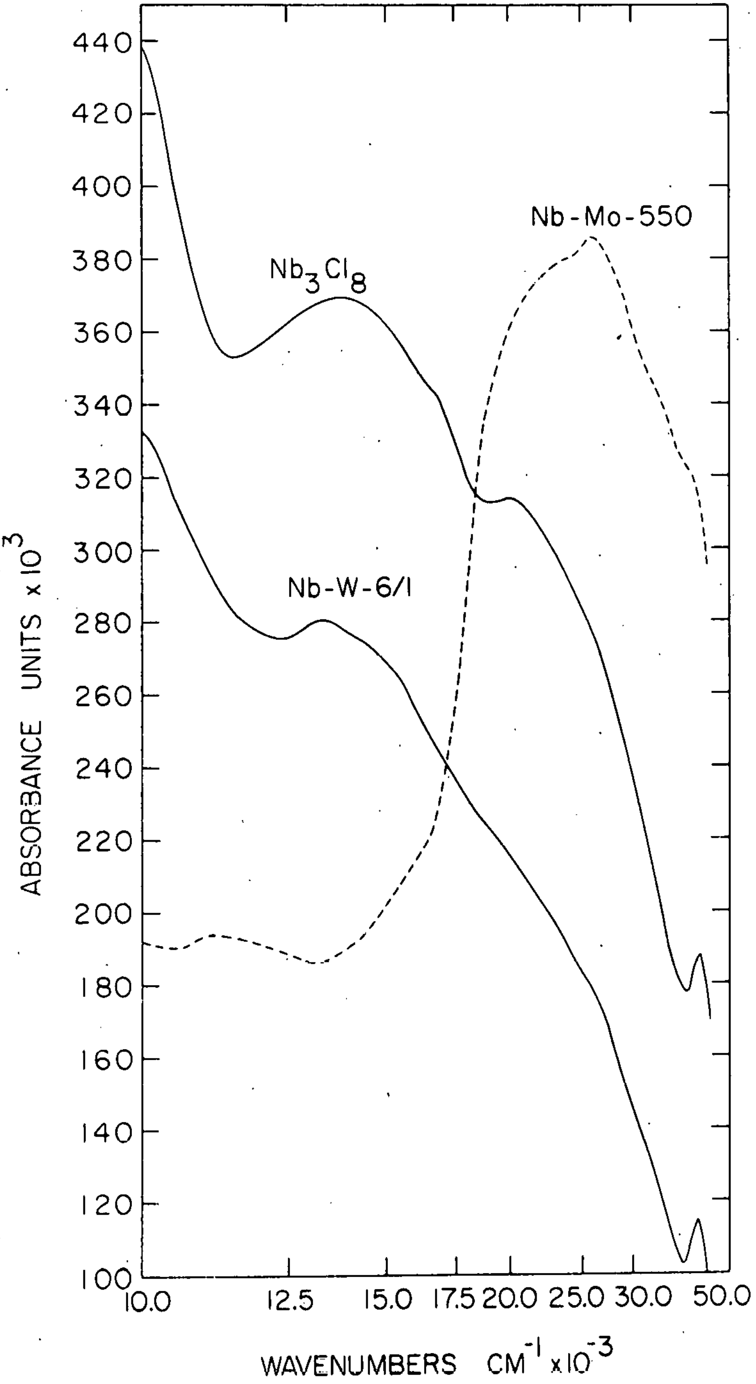


Figure 12. Diffuse reflectance spectra of Nb_3Cl_8, Nb-W-6/1 and Nb-Mo-550(Nb-Mo-320)

CONCLUSIONS

Comparison of the physical properties of the tantalum-tungsten $M_6X_{12}{}^{n+}$ mixed metal cluster compounds with those of the tantalum and tantalum-molybdenum isoelectronic cluster analogs show a very close correlation between all of these compounds. The physical properties of these new mixed metal compounds are as expected. The vibrational and electronic spectra of the new tantalum-tungsten compounds show a very good band correspondence with the appropriate tantalum cluster compound. The magnetic data of the oxidized species, $[(C_3H_7)_4N]_2[(Ta_5WCl_{12})Cl_6]$, proved that this compound is paramagnetic with an observed moment of 1.64 B.M. This moment compares very well with the isoelectronic compound, $[(C_4H_9)_4N]_3[(Ta_6Cl_{12})Cl_6]$, whose moment is observed to be 1.67 B.M. The 5-1-3 compound, $[(C_3H_7)_4N]_3[(Ta_5WCl_{12})Cl_6]$, is diamagnetic as expected. In general, the substitution of a tungsten for a tantalum in the Ta_6 core seems to cause a smaller perturbation of the properties of the core than does the substitution of a molybdenum atom into the core.

As reported by Dorman and McCarley (130), the acidic melts formed by aluminum chloride and sodium chloride are an excellent medium for the preparation of reduced oxidation state metal cluster compounds. The quantitative preparation of the niobium trimeric species, Nb_3Cl_8, further demonstrates the utility of this method.

3

From an examination of the physical evidence obtained on the studies of the substituted niobium trimeric species, it is reasonable to conclude that both attempts to substitute tungsten and molybdenum into the trimer were successful.

The extent of substitution of tungsten into the trimer appears to be limited to ca. 60 mole %. This corresponds to the ratio $2Nb_3Cl_8/3Nb_2WCl_8$. The electronic and vibrational spectra obtained on this series of compounds verifies the substitution into the niobium trimer and the formation of a substituted phase. The magnetic studies and other physical evidence indicate that this new phase can be formulated as $Nb_{3-x}W_xCl_8$ $(0<x<1)$, with the compound of limiting composition Nb_2WCl_8 diamagnetic as expected. X-ray analysis of these preparations also indicate that these new compounds have the Nb_3Cl_8 structure type.

Attempted substitution of molybdenum for niobium in the Nb_3Cl_8 cluster provides a much different result than substitution of a tungsten. Analytical data suggest that the imperical formula for this new mixed metal compound is Nb_2MoCl_8. Vibrational and electronic spectra verify the formation of a new compound and indicate that there are some very large differences between this compound and the Nb_3Cl_8 or $Nb_{3-x}W_xCl_8$ phases. The x-ray diffraction studies of this new compound indicate that the Nb_3Cl_8 structure is not maintained. The reduction in the observed magnetic moment and the net diamagnetic susceptibility suggests that metal-metal bonding or metal cluster formation is important in the compound.

SUGGESTIONS FOR FUTURE WORK

With the completion of this work and the work by Meyer (46), it seems reasonable to assume that the Ta_6 cluster series may not be extended. Meyer (46) reports no substitution ratio of Ta/Mo lower than 4/2. It was found in this work, that only one substitution compound of tantalum and tungsten could be obtained, the Ta_5W.

Extension of this type of compound to include mixtures of niobium and tungsten or molybdenum may be possible. Evidence from this work does indicate a very stable phase formed at higher temperatures in the niobium-tungsten mixtures which will not reduce below the oxidation state 2.67. Limited data on the niobium-molybdenum system are not sufficient to indicate that this system might be extended to include the hexanuclear cluster systems. Work in this area might be particularly fruitful and informative.

By preparing a complete series of substituted M_6 cluster species containing niobium and molybdenum, enough data might be collected to completely elucidate both the electronic structure of these cluster compounds and also provide sufficient information for the complete assignment of the far infrared spectra.

A study of the electronic spectra of the existing series of homonuclear and mixed metal cluster compounds at liquid helium temperatures are needed to clarify which of the observed bands are dipole allowed and which are vibronically activated. This information would be of significant help in assigning the spectral bands to specific electronic transitions. Low temperature far infrared spectra might have sufficiently better resolution to show additional bands or at least provide better data on the existing spectra.

Further assistance in assigning the bands in the far infrared spectra would be provided by the preparation of mixed-halogen derivatives where the terminal chloride atoms have been replaced by other halides or other ions. Preparation of the bromide analogs of these mixed metal cluster species of the type $M_{6-x}M'_xBr_{12}^{n+}$ (M = Ta or Nb; M' = Mo or W) might provide useful information in the assignment of the metal-halogen bands in the vibrational spectra.

A study of the nature of the products contained in the final residues of these reduction reactions should be made. With sufficient reducing agent to reduce all of the species to lower oxidation states and little evidence found to indicate the reduction all the way to metal, it seems likely that there are some interesting possibilities of other mixed metal species present in the residues of these reduction reactions.

The study of the trimeric species of niobium and the substituted trimeric species was only started in this work. Although the coreductions of niobium and tungsten higher halides provided only limited substitution, conditions may be found that would provide the stoichiometric Nb_2WCl_8.

The formulation of the new niobium-molybdenum compound as Nb_2MoCl_8 is shown from analytical data and x-ray data to be reasonable. However, further work should be carried out on this system to elucidate the actual nature of this compound. Vibrational and electronic spectra do indicate that this new species might not necessarily be related to the Nb_3Cl_8 type compounds. Substitution reactions, in attempts to derivatize this compound, may lend new evidence to the identity of this new species.

The experimentation in the molten salt media described in this work will provide a number of new compounds. In some preliminary work, evidence for W(III) and Nb_2^{6+} was found. These systems should be thoroughly investigated along with other difficult-to-prepare reduced species that might lend themselves to preparation in this environment.

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To my wife, for mountains of patience and encouragement, for love and understanding, I want to dedicate this work.

To my children, for all of the lost time, thank you for your understanding.

APPENDIX

INTENSITY CALCULATION FOR POWDER DIFFRACTION PATTERNS

(1969 VERSION)

by K. Yvon, W. Jeitschko and E. Parthe

School of Metallurgy and Materials Science, Laboratory for
Research on the Structure of Matter, University of Pennsylvania,
Philadelphia 19104

```
//STEPONE EXEC FORTG,REGION.FORT=112K,
//             TIME.GO=2,REGION.GO=128K
//FORT.SYSIN  DD  *
C           INTENSITY CALCULATION FOR POWDER DIFFRACTION PATTERNS          YJP0010
C                               (1969 VERSION)                             YJP0020
C           PROGRAM WRITTEN BY K.YVON, W.JEITSCHKO AND E.PARTHE            YJP0030
C              SCHOOL OF METALLURGY AND MATERIALS SCIENCE                  YJP0040
C           LABORATORY FOR RESEARCH ON THE STRUCTURE OF MATTER             YJP0050
C             UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA 19104               YJP0060
     0DIMENSION Q(1500),YH(1500),YK(1500),YL(1500),THETA(1500),SUMA(1500  YJ0070
     1),SUMB(1500),VINT(1500),NA(8),X(48,8),Y(48,8),Z(48,8),AAA(8),AA(8)  YJ0080
     2,BBB(8),BB(8),CCC(8),BTEMP(8),ELEMT(8),PLAY(100),COMPND(20),SP(180 YJP0090
     3),W(180),FOCCU(8),STRU(1500),SFA(30,8),FPLG(1500),FMUL(1500)        YJP0100
 7000 FORMAT(/27H1INTENSITY CALCULATION FOR ,20A4/)                        YJP0110
 7001 FORMAT(/25H1DIFFRACTION PATTERN FOR ,20A4,4H WL=,F8.5/)              YJP0120
 7008 FORMAT (5X,15F5.0)                                                   YJP0130
 7009 FORMAT(15F5.0)                                                       YJP0140
 7010 FORMAT(A4,F6.0,6F10.0)                                               YJP0150
 7011CFORMAT(/46H COEFFICIENTS FOR ATOMIC SCATTERING FACTOR OF A4,5F10.4 YJP0160
     1,/7H BTEMP=F10.5,58H ,OCCUPATION FACTOR (FOCCU) OF THE FOLLOWING P YJP0170
     2OSITIONS IS F10.5,/)                                                 YJP0180
 70120FORMAT(/23H SCATTERING FACTORS OF A4, 34H IN STEPS OF .05*SIN(THET YJP0190
     1A)/LAMBDA,/ 0P15F7.3,/ 0P15F7.3,//7H BTEMP=F10.5,58H ,OCCUPATION F YJP0200
     2ACTOR (FOCCU) OF THE FOLLOWING POSITIONS IS F10.5,8X,/)              YJP0210
 7020 FORMAT(3F10.0)                                                       YJP0220
 7021 FORMAT(1X,A4,1X,3F10.5)                                              YJP0230
 7022 FORMAT(1X,A4,1X,3F10.5,17H   +(1/2 1/2 1/2))                         YJP0240
 7023 FORMAT(1X,A4,1X,3F10.5,29H   +(2/3 1/3 1/3,1/3 2/3 2/3))             YJP0250
 7024 FORMAT(1X,A4,1X,3F10.5,35H   +(1/2 1/2 0,1/2 0 1/2,0 1/2 1/2))       YJP0260
 7025 FORMAT(1X,A4,1X,3F10.5,15H   +(0 1/2 1/2))                           YJP0270
 7026 FORMAT(1X,A4,1X,3F10.5,15H   +(1/2 0 1/2))                           YJP0280
 7027 FORMAT(1X,A4,1X,3F10.5,15H   +(1/2 1/2 0))                           YJP0290
 7049 FORMAT(10X,'   ATOMS IN UNIT CELL: ELEMT(M)  NA(M)*NBRA*FOCCU(M)') YJP0300
 7050 FORMAT(35X,A4,5X,I2,3H  *,I2,3H  *,F6.2)                             YJP0310
 7052 FORMAT (F8.1,4X,100A1)                                               YJP0320
 8001 FORMAT(3H A=F9.5,3H,B=F9.5,3H,C=F9.5,6H,BETA=F9.5,4H,WL=F8.5)        YJP0330
 8002 FORMAT(3H A=F9.5,3H,B=F9.5,3H,C=F9.5,4H,WL=F8.5,9H ANGSTROM)         YJP0340
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8003 FORMAT(3H A=F9.5,3H,C=F9.5,4H,WL=F8.5,9H ANGSTROM)                 YJP0350
8005 FORMAT(3H A=F9.5, 4H,WL=F8.5,9H ANGSTROM)                          YJP0360
80070FORMAT(3H A=F9.5,3H,B=F9.5,3H,C=F9.5,7H,ALPHA=F9.5,6H,BETA=F9.5,7H YJP0370
    1,GAMMA=F9.5,4H,WL=F8.5)                                            YJP0380
80100FORMAT(48H  SIN-SQUARE-THETA-VALUES CALCULATED BETWEEN SL=F7.4,8H  YJP0390
    1AND SH=F7.4,9X,6HKODLP=,I2,9X,6HAGUIN=0PF5.2,6X,6HBGUIN=0PF5.2)    YJP0400
8011 FORMAT(38H DATA CALCULATED FOR LOW LAUE-SYMMETRY)                  YJP0410
8012 FORMAT(39H DATA CALCULATED FOR HIGH LAUE-SYMMETRY)                 YJP0420
8029 FORMAT (20A4)                                                      YJP0430
8031 FORMAT(39H SYMMETRY CENTER AT ORIGIN OF UNIT CELL)                 YJP0440
8842 FORMAT(19H HKO ONLY WITH H=2N)                                     YJP0450
8843 FORMAT(19H HKO ONLY WITH K=2N)                                     YJP0460
8844 FORMAT(19H HKO ONLY WITH H+K=I1,1HN)                               YJP0470
8847 FORMAT (19H OKL ONLY WITH K=2N)                                    YJP0480
8848 FORMAT(19H OKL ONLY WITH L=2N)                                     YJP0490
8849 FORMAT(19H OKL ONLY WITH K+L=I1,1HN)                               YJP0500
8852 FORMAT(19H HOL ONLY WITH H=2N)                                     YJP0510
8853 FORMAT(19H HOL ONLY WITH L=2N)                                     YJP0520
8854 FORMAT(19H HOL ONLY WITH H+L=I1,1HN)                               YJP0530
8857 FORMAT(19H HHL ONLY WITH L=2N)                                     YJP0540
8858 FORMAT(22H HHL ONLY WITH 2H+L=4N)                                  YJP0550
8860 FORMAT(17H HOO ONLY WITH H=I1,1HN)                                 YJP0560
8863 FORMAT(19H OKO ONLY WITH K=2N)                                     YJP0570
8865 FORMAT(17H OOL ONLY WITH L=I1,1HN)                                 YJP0580
8881 FORMAT (49H PRIMITIVE BRAVAISLATTICE.ALL HKL VALUES ALLOWED )      YJP0590
8882 FORMAT (51H BODYCENTERED BRAVAISLATTICE.HKL ONLY WITH H+K+L=2N)    YJP0600
8883 FORMAT (52H RHOMBOHEDRAL BRAVAISLATTICE.HKL ONLY WITH -H+K+L=3N)   YJP0610
8884 FORMAT (54H FACECENTERED BRAVAISLATTICE.H,K,L ALL EVEN OR ALL ODD) YJP0620
8885 FORMAT (47H A-CENTERED BRAVAISLATTICE.HKL ONLY WITH K+L=2N)        YJP0630
8886 FORMAT (47H B-CENTERED BRAVAISLATTICE.HKL ONLY WITH H+L=2N)        YJP0640
8887 FORMAT (47H C-CENTERED BRAVAISLATTICE.HKL ONLY WITH H+K=2N)        YJP0650
8990 FORMAT(/48H DATA CALCULATED FOR A MONOCLINIC STRUCTURE WITH)       YJP0660
8991 FORMAT(/47H DATA CALCULATED FOR A TRICLINIC STRUCTURE WITH)        YJP0670
8992 FORMAT(/51H DATA CALCULATED FOR AN ORTHORHOMBIC STRUCTURE WITH )   YJP0680
8993 FORMAT(/50H DATA CALCULATED FOR A TRIGONAL STRUCTURE WITH       )  YJP0690
8994 FORMAT (/48H DATA CALCULATED FOR A TETRAGONAL STRUCTURE WITH    )  YJP0700
8995 FORMAT(/43H DATA CALCULATED FOR A CUBIC STRUCTURE WITH )           YJP0710
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8996 FORMAT (/47H DATA CALCULATED FOR A HEXAGONAL STRUCTURE WITH )       YJP0720
89980FORMAT( 130H1 H  K  L    THETA  SIN2*1000 INT.SCALED    INTENSITY U YJP0730
    1NSCALED         /F(HKL)/**2        A(HKL)        B(HKL) PHA.ANG. MU YJP0740
    2LT    LPG )                                                         YJP0750
89990FORMAT( 132H1 H  K  L  THETA  2THETA D-VALUE   SIN   SIN2*1000  H   YJP0760
    1K  L   INTENSITY      /F(HKL)/**2       A(HKL)     B(HKL) PHA.ANG.  YJP0770
    2MULT     LPG)                                                       YJP0780
9900 FORMAT(21H SOMETHING WENT WRONG)                                    YJP0790
9997 FORMAT(4I2,2X,7I2,6X,9I2)                                           YJP0800
9998 FORMAT(F10.0,2F5.0,4I2,2X,2F10.0)                                   YJP0810
9999 FORMAT(6F10.0)                                                      YJP0820
90000FORMAT(3I3,2F7.2, F8.4,2X,F6.4, 3PF9.2,1X,3I3,0PF11.1,0PF17.1,      YJP0830
    1 0P2F12.2,0PF8.3,0PF5.0,0PF9.2)                                     YJP0840
9001 FORMAT(3I3,F9.2,3P1F10.2,0PF10.1,0PF22.1,0PF20.1,0P2F14.2,0PF8.3,   YJP0850
    10PF5.0,0PF10.2)                                                     YJP0860
     PI2 = 6.2831853                                                     YJP0870
     E = 2.7182818                                                       YJP0880
     FRTD=4./3.                                                          YJP0890
 999 READ (5,8029,END=997) COMPND                                        YJP0900
     READ 9999,   A,B,C,ALPHA,BETA,GAMMA                                 YJP0910
     READ 9998,WL,SL,SH,NORM,ISCAT,IMAGE,KODLP,AGUIN,BGUIN               YJP0920
    0READ 9997,ISYSTM,IBRAVL,LAUE,ISYMCE,IHKO,IOKL,IHOL,IHHL,IHOO,IOKO,  YJP0930
    1IOOL,NCOMPO,(NA(II),II=1,8)                                         YJP0940
     IF((SH.EQ.0.).OR.(SH.GT.0.999))SH=0.999                             YJP0950
     N = 0                                                               YJP0960
     ICON=0                                                              YJP0970
     VMXINT=0.                                                           YJP0980
     NLINE=0                                                             YJP0990
     IF(LAUE)699,809,699                                                   P1000
 699 DO 700 M=1,NCOMPO                                                   YJP1010
     READ 7010,ELEMT(M),FOCCU(M),AAA(M),AA(M),BBB(M),BB(M),CCC(M),       YJP1020
    1BTEMP(M)                                                            YJP1030
     IF(ISCAT.NE.0) READ 7008,(SFA(I,M),I=1,15)                          YJP1040
     IF(ISCAT.NE.0) READ 7009,   (SFA(I,M),I=16,30)                      YJP1050
     NL=NA(M)                                                            YJP1060
 700 READ 7020,(X(I,M),Y(I,M),Z(I,M),I=1,NL)                             YJP1070
 809 PRINT 7000, COMPND                                                  YJP1080
```

```
      WLSQ4=WL**2/4.                                                    YJP1090
      ASTAR=WLSQ4/A**2                                                  YJP1100
      IF((ISYSTM.EQ.1).OR.(ISYSTM.EQ.2).OR.(ISYSTM.EQ.7))               YJP1110
     1BSTAR=WLSQ4/B**2                                                  YJP1120
      IF(ISYSTM.NE.5) CSTAR=WLSQ4/C**2                                  YJP1130
      BET=BETA*PI2/360.                                                 YJP1140
      SINB2=(SIN(BET))**2                                               YJP1150
      COSB=COS(BET)                                                     YJP1160
      IF(ISYSTM.NE.7)GO TO 201                                          YJP1170
      ALPH=ALPHA*PI2/360.                                               YJP1180
      GAMM=GAMMA*PI2/360.                                               YJP1190
      SV=(ALPH +BET+GAMM)/2.                                            YJP1200
      VOL=2.*A*B*C*SQRT(SIN(SV)*SIN(SV-ALPH)*SIN(SV-BET)*SIN(SV-GAMM))  YJP1210
      AST=(B*C*SIN(ALPH))/VOL                                           YJP1220
      BST=(A*C*SIN(BET))/VOL                                            YJP1230
      CST=(A*B*SIN(GAMM))/VOL                                           YJP1240
      COAST=(COSB*COS(GAMM)-COS(ALPH))/(SIN(BET)*SIN(GAMM))             YJP1250
      COBST=(COS(GAMM)*COS(ALPH)-COSB)/(SIN(GAMM)*SIN(ALPH))            YJP1260
      COGST=(COS(ALPH)*COSB-COS(GAMM))/(SIN(ALPH)*SIN(BET))             YJP1270
  201 ZH=0.                                                             YJP1280
      ZK = 0.                                                           YJP1290
      ZL = 0.                                                           YJP1300
  100 ZH=ZH+1.                                                          YJP1310
      GO TO(1,2,3,4,5,6,7),ISYSTM                                       YJP1320
    1 ZHTEST=(2.0*A*SQRT(SH))/WL                                        YJP1330
      IF(ZH.LE.ZHTEST) GO TO 205                                        YJP1340
      ZH=0.                                                             YJP1350
      ZK=ZK+1.                                                          YJP1360
      ZKTEST=(2.0*B*SQRT(SH))/WL                                        YJP1370
      IF(ZK.LE.ZKTEST) GO TO 1                                          YJP1380
      ZK=0.                                                             YJP1390
      IF(ICON.EQ.0)GO TO 203                                            YJP1400
      ZL=ZL-1.                                                          YJP1410
      GO TO 204                                                         YJP1420
  203 ZL=ZL+1.                                                          YJP1430
  204 ZLTEST=(2.0*C*SQRT(SH))/WL                                        YJP1440
      IF(ABS(ZL).LE.ZLTEST) GO TO 1                                     YJP1450
```

```
      IF(ICON.EQ.1)GO TO 202                                            YJP1460
      ICON=1                                                            YJP1470
      GO TO 201                                                         YJP1480
  205 ATEST=ASTAR*ZH**2/SINB2+BSTAR*ZK**2+CSTAR*ZL**2/SINB2-WLSQ4*2.*ZH* YJP1490
     1ZL*COSB/(A*C*SINB2)                                               YJP1500
      IF(ATEST.GT.SH) GO TO 100                                         YJP1510
      IF((ICON.EQ.0).OR.((ZH.GT.0.9).AND.(ZL.LT.(-0.9))))GO TO 70       YJP1520
      GO TO 100                                                         YJP1530
  202 PRINT 8990                                                        YJP1540
      PRINT 8001,A,B,C,BETA,WL                                          YJP1550
      GO TO 23                                                          YJP1560
    2 ATEST=ASTAR*ZH**2+BSTAR*ZK**2+CSTAR*ZL**2                         YJP1570
      IF(ATEST.LE.SH)GO TO 70                                           YJP1580
      ZH = 0.                                                           YJP1590
      ZK = ZK + 1.                                                      YJP1600
      BTEST=BSTAR*ZK**2+CSTAR*ZL**2                                     YJP1610
      IF (BTEST.LE.SH)GO TO 2                                           YJP1620
      ZK = 0.                                                           YJP1630
      ZL = ZL+1.                                                        YJP1640
      CTEST=CSTAR*ZL**2                                                 YJP1650
      IF(CTEST.LE.SH)GO TO 2                                            YJP1660
      PRINT 8992                                                        YJP1670
      PRINT 8002,A,B,C,WL                                               YJP1680
      GO TO 23                                                          YJP1690
    3 ATEST=FRTD*ASTAR*(ZH**2+ZH*ZK+ZK**2)+CSTAR*ZL**2                  YJP1700
      IF((ZH.EQ.0.).AND.(ZL.EQ.0.)) GO TO 100                           YJP1710
      IF(ATEST.LE.SH)GO TO 210                                          YJP1720
      ZH = 0.                                                           YJP1730
      ZK=ZK+1.                                                          YJP1740
      BTEST=FRTD*ASTAR*ZK**2+CSTAR*ZL**2                                YJP1750
      IF (BTEST.LE.SH)GO TO 3                                           YJP1760
      ZK=0.                                                             YJP1770
      IF(ICON.EQ.0)GO TO 220                                            YJP1780
      ZL=ZL-1.                                                          YJP1790
      GO TO 221                                                         YJP1800
  220 ZL=ZL+1.                                                          YJP1810
  221 CTEST=CSTAR*ZL**2                                                 YJP1820
```

```
    IF(CTEST.LE.SH)GO TO 3                                               YJP1830
    IF(ICON.EQ.1)GO TO 211                                               YJP1840
    ICON=1                                                               YJP1850
    GO TO 201                                                            YJP1860
2100IF((ICON.EQ.0).OR.((ZL.LT.(-0.9)).AND.((ZH.NE.0.).AND.(ZK.NE.0.)))   YJP1870
   1)GO TO 70                                                            YJP1880
    GO TO 100                                                            YJP1890
211 PRINT 8993                                                           YJP1900
    GO TO 71                                                             YJP1910
  4 ATEST=ASTAR*(ZH**2+ZK**2)+CSTAR*ZL**2                                YJP1920
    IF(ATEST.LE.SH)GO TO 70                                              YJP1930
    ZH = ZK+1.                                                           YJP1940
    ZK=ZH                                                                YJP1950
    BTEST=ASTAR*2.*ZH**2+CSTAR*ZL**2                                     YJP1960
    IF (BTEST.LE.SH)GO TO 4                                              YJP1970
    ZH = 0.                                                              YJP1980
    ZK = 0.                                                              YJP1990
    ZL = ZL +1.                                                          YJP2000
    CTEST=CSTAR*ZL**2                                                    YJP2010
    IF(CTEST.LE.SH)GO TO 4                                               YJP2020
    PRINT 8994                                                           YJP2030
    GO TO 71                                                             YJP2040
  5 ATEST = ASTAR*(ZH**2+ZK**2+ZL**2)                                    YJP2050
    IF(ATEST.LE.SH)GO TO 70                                              YJP2060
    ZH = ZK+1.                                                           YJP2070
    ZK=ZH                                                                YJP2080
    BTEST=ASTAR*(2.*ZH**2+ZL**2)                                         YJP2090
    IF (BTEST.LE.SH)GO TO 5                                              YJP2100
    ZH = ZL+1.                                                           YJP2110
    ZK=ZH                                                                YJP2120
    ZL=ZH                                                                YJP2130
    CTEST=ASTAR*3.*ZH**2                                                 YJP2140
    IF(CTEST.LE.SH)GO TO 5                                               YJP2150
    PRINT 8995                                                           YJP2160
    PRINT 8005,A,WL                                                      YJP2170
    GO TO 23                                                             YJP2180
  6 ATEST=FRTD*ASTAR*(ZH**2+ZH*ZK+ZK**2)+CSTAR*ZL**2                     YJP2190
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```
      IF(ATEST.LE.SH)GO TO 70                                            YJP2200
      ZH = ZK+1.                                                         YJP2210
      ZK=ZH                                                              YJP2220
      BTEST=FRTD*ASTAR*3.*ZH**2+CSTAR*ZL**2                              YJP2230
      IF (BTEST.LE.SH)GO TO 6                                            YJP2240
      ZH = 0.                                                            YJP2250
      ZK = 0.                                                            YJP2260
      ZL = ZL+1.                                                         YJP2270
      CTEST=CSTAR*ZL**2                                                  YJP2280
      IF(CTEST.LE.SH)GO TO 6                                             YJP2290
      PRINT 8996                                                         YJP2300
      GO TO 71                                                           YJP2310
    7 ZHTEST=(2.0*A*SQRT(SH))/WL                                         YJP2320
      IF(ZH.LE.ZHTEST) GO TO 206                                         YJP2330
      ZH=0.                                                              YJP2340
      IF(ICON.LT.2)GO TO 212                                             YJP2350
      ZK=ZK-1.                                                           YJP2360
      GO TO 213                                                          YJP2370
  212 ZK=ZK+1.                                                           YJP2380
  213 ZKTEST=(2.0*B*SQRT(SH))/WL                                         YJP2390
      IF(ABS(ZK).LE.ZKTEST) GO TO 7                                      YJP2400
      ZK=0.                                                              YJP2410
      IF((ICON.EQ.0).OR.(ICON.EQ.2))GO TO 208                            YJP2420
       ZL=ZL-1.                                                          YJP2430
      GO TO 209                                                          YJP2440
  208 ZL=ZL+1.                                                           YJP2450
  209 ZLTEST=(2.0*C*SQRT(SH))/WL                                         YJP2460
      IF(ABS(ZL).LE.ZLTEST) GO TO 7                                      YJP2470
      ICON=ICON+1                                                        YJP2480
      GO TO(201,201,201,207),ICON                                        YJP2490
  2060ATEST=WLSQ4*((ZH*AST)**2+(ZK*BST)**2+(ZL*CST)**2+2.*ZK*ZL*BST*CST* YJP2500
     1COAST+2.*ZH*ZL*AST*CST*COBST+2.*ZH*ZK*AST*BST*COGST)               YJP2510
      IF(ATEST.GT.SH) GO TO 100                                          YJP2520
      IF(ICON.EQ.0)GO TO 70                                              YJP2530
     0IF(((ZH.EQ.0.).AND.(ZK.EQ.0.)).OR.((ZK.EQ.0.).AND.(ZL.EQ.0.)).OR.  YJP2540
     1((ZH.EQ.0.).AND.(ZL.EQ.0.)))GO TO 100                              YJP2550
      IF((ICON.EQ.1).AND.(ZL.LT.(-0.9)))GO TO 70                         YJP2560
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      IF(((ICON.EQ.2).AND.(ZK.LT.(-0.9))).AND.(ZH.GT.0.9))GO TO 70      YJP2570
      IF((ICON.EQ.3).AND.((ZH*ZK*ZL).NE.0.))GO TO 70                    YJP2580
      GO TO 100                                                         YJP2590
  207 PRINT 8991                                                        YJP2600
      PRINT 8007,A,B,C,ALPHA,BETA,GAMMA,WL                              YJP2610
      GO TO 23                                                          YJP2620
   70 IF(ATEST.LT.SL) GO TO 100                                         YJP2630
      XH=ZH                                                             YJP2640
      XK=ZK                                                             YJP2650
      XL=ZL                                                             YJP2660
  171 GO TO(90,82,83,84,85,86,87),IBRAVL                                YJP2670
   82 TESTBR=(XH+XK+XL)/2.                                              YJP2680
      GO TO 89                                                          YJP2690
   83 TESTBR=(-XH+XK+XL)/3.                                             YJP2700
      GO TO 89                                                          YJP2710
   84 FACEHK=(XH+XK)/2.                                                 YJP2720
      IF((AINT(FACEHK)-FACEHK).NE.0.)GO TO 100                          YJP2730
   85 TESTBR=(XK+XL)/2.                                                 YJP2740
      GO TO 89                                                          YJP2750
   86 TESTBR=(XH+XL)/2.                                                 YJP2760
      GO TO 89                                                          YJP2770
   87 TESTBR=(XH+XK)/2.                                                 YJP2780
   89 IF((AINT(TESTBR)-TESTBR).NE.0.)GO TO 100                          YJP2790
   90 IF(XL.EQ.0.)GO TO (91,105,104,105,102),IHKO                       YJP2800
   91 IF(XH.EQ.0.)GO TO (92,111,110,111,108),IOKL                       YJP2810
   92 IF(XK.EQ.0.)GO TO (93,117,116,117,114),IHOL                       YJP2820
   93 IF(XH.EQ.XK)GO TO (94,120,122),IHHL                               YJP2830
      IF((XK.EQ.XL).AND.(ISYSTM.EQ.5))GO TO (94,1201,1221),IHHL         YJP2840
   94 IF(XK.EQ.0..AND.XL.EQ.0.)GO TO(95,124,610,124),IHOO               YJP2850
   95 IF(XH.EQ.0..AND.XL.EQ.0.)GO TO(96,128),IOKO                       YJP2860
   96 IF(XH.EQ.0..AND.XK.EQ.0.)GO TO(170,130,130,130,610,130),IOOL      YJP2870
      GO TO 170                                                         YJP2880
  102 FIHKO=XH/2.                                                       YJP2890
  103 IF(AINT(FIHKO)-FIHKO)100,91,100                                   YJP2900
  104 FIHKO=XK/2.                                                       YJP2910
      GO TO 103                                                         YJP2920
  105 HKO=IHKO                                                          YJP2930
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      FIHKO=(XH+XK)/HKO                                                 YJP2940
      GO TO 103                                                         YJP2950
  108 FIOKL=XK/2.                                                       YJP2960
  109 IF(AINT(FIOKL)-FIOKL)100,92,100                                   YJP2970
  110 FIOKL=XL/2.                                                       YJP2980
      GO TO 109                                                         YJP2990
  111 OKL=IOKL                                                          YJP3000
      FIOKL=(XK+XL)/OKL                                                 YJP3010
      GO TO 109                                                         YJP3020
  114 FIHOL=XH/2.                                                       YJP3030
  115 IF(AINT(FIHOL)-FIHOL)100,93,100                                   YJP3040
  116 FIHOL=XL/2.                                                       YJP3050
      GO TO 115                                                         YJP3060
  117 HOL=IHOL                                                          YJP3070
      FIHOL=(XH+XL)/HOL                                                 YJP3080
      GO TO 115                                                         YJP3090
  120 FIHHL=XL/2.                                                       YJP3100
  121 IF(AINT(FIHHL)-FIHHL)100,94,100                                   YJP3110
  122 FIHHL=(2.*XH+XL)/4.                                               YJP3120
      GO TO 121                                                         YJP3130
 1201 FIHHL=XH/2.                                                       YJP3140
      GO TO 121                                                         YJP3150
 1221 FIHHL=(2.*XL+XH)/4.                                               YJP3160
      GO TO 121                                                         YJP3170
  124 HOO=IHOO                                                          YJP3180
      FIHOO=XH/HOO                                                      YJP3190
      IF(AINT(FIHOO)-FIHOO)100,95,100                                   YJP3200
  128 FIOKO=XK/2.                                                       YJP3210
      IF(AINT(FIOKO)-FIOKO)100,96,100                                   YJP3220
  130 OOL=IOOL                                                          YJP3230
      FIOOL=XL/OOL                                                      YJP3240
      IF((AINT(FIOOL)-FIOOL).NE.0.)GOTO 100                             YJP3250
  170 N=N+1                                                             YJP3260
      Q(N)=ATEST                                                        YJP3270
      YH(N)=XH                                                          YJP3280
      YK(N)=XK                                                          YJP3290
      YL(N)=XL                                                          YJP3300
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```
      JJ = N                                                            YJP3310
      J = JJ - 1                                                        YJP3320
      IF((LAUE.EQ.2).OR.(ZH.EQ.XK))GO TO 100                            YJP3330
      GO TO(100,100,100,724,725,724,100),ISYSTM                         YJP3340
  724 IF((ZH.GT.ZK).AND.(ZK.GT.0.))GO TO 731                            YJP3350
      GO TO 100                                                         YJP3360
  725 IF((ZH.GT.ZK).AND.(ZK.GT.ZL))GO TO 731                            YJP3370
      GO TO 100                                                         YJP3380
  731 TEMP=XH                                                           YJP3390
      XH=XK                                                             YJP3400
      XK=TEMP                                                           YJP3410
      GO TO 171                                                         YJP3420
   71 PRINT 8003,A,C,WL                                                 YJP3430
   23 PRINT 8010,SL,SH,KODLP,AGUIN,BGUIN                                YJP3440
      IF((ISYSTM.GT.3).AND.(ISYSTM.LT.7).AND.(LAUE.EQ.1))PRINT 8011     YJP3450
      IF((ISYSTM.GT.3).AND.(ISYSTM.LT.7).AND.(LAUE.EQ.2))PRINT 8012     YJP3460
      IF(IBRAVL.EQ.1)PRINT 8881                                         YJP3470
      IF(IBRAVL.EQ.2)PRINT 8882                                         YJP3480
      IF(IBRAVL.EQ.3)PRINT 8883                                         YJP3490
      IF(IBRAVL.EQ.4)PRINT 8884                                         YJP3500
      IF (IBRAVL.EQ.5)PRINT 8885                                        YJP3510
      IF(IBRAVL.EQ.6)PRINT 8886                                         YJP3520
      IF(IBRAVL.EQ.7)PRINT 8887                                         YJP3530
      IF((IHKO.EQ.2).OR.(IHKO.EQ.4))PRINT 8844,IHKO                     YJP3540
      IF(IHKO.EQ.3)PRINT 8843                                           YJP3550
      IF(IHKO.EQ.5)PRINT 8842                                           YJP3560
      IF((IOKL.EQ.2).OR.(IOKL.EQ.4))PRINT 8849,IOKL                     YJP3570
      IF(IOKL.EQ.3)PRINT 8848                                           YJP3580
      IF(IOKL.EQ.5)PRINT 8847                                           YJP3590
      IF((IHOL.EQ.2).OR.(IHOL.EQ.4))PRINT 8854,IHOL                     YJP3600
      IF(IHOL.EQ.3)PRINT 8853                                           YJP3610
      IF(IHOL.EQ.5)PRINT 8852                                           YJP3620
      IF(IHHL.EQ.2)PRINT 8857                                           YJP3630
      IF(IHHL.EQ.3)PRINT 8858                                           YJP3640
      IF(IHOO.NE.1)PRINT 8860,IHOO                                      YJP3650
      IF(IOKO.NE.1)PRINT 8863                                           YJP3660
      IF(IOOL.NE.1)PRINT 8865,IOOL                                      YJP3670
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      IF(ISYMCE.EQ.1)PRINT 8031                                          YJP3680
   79 IF(LAUE)879,750,879                                                    3690
  879 NBRA = IBRAVL                                                      YJP3700
      IF(IBRAVL.GT.4) NBRA = 2                                           YJP3710
      PRINT 7049                                                         YJP3720
      DO 709 M=1,NCOMPO                                                  YJP3730
      IF(FOCCU(M).EQ.0.)FOCCU(M)=1.0                                     YJP3740
  709 PRINT 7050,ELEMT(M),NA(M),NBRA,FOCCU(M)                            YJP3750
      FBRA = NBRA                                                        YJP3760
      DO 701 M=1,NCOMPO                                                  YJP3770
      IF(ISCAT.EQ.0) PRINT 7011,ELEMT(M),AAA(M),AA(M),BBB(M),BB(M),      YJP3780
     1CCC(M),BTEMP(M),FOCCU(M)                                           YJP3790
      IF(ISCAT.NE.0)PRINT7012,ELEMT(M),(SFA(I,M),I=1,30),BTEMP(M),FOCCU( YJP3800
     1M)                                                                 YJP3810
      NL=NA(M)                                                           YJP3820
      IF(IBRAVL.EQ.1) PRINT 7021,(ELEMT(M),X(I,M),Y(I,M),Z(I,M),I=1,NL)  YJP3830
      IF(IBRAVL.EQ.2) PRINT 7022,(ELEMT(M),X(I,M),Y(I,M),Z(I,M),I=1,NL)  YJP3840
      IF(IBRAVL.EQ.3) PRINT 7023,(ELEMT(M),X(I,M),Y(I,M),Z(I,M),I=1,NL)  YJP3850
      IF(IBRAVL.EQ.4) PRINT 7024,(ELEMT(M),X(I,M),Y(I,M),Z(I,M),I=1,NL)  YJP3860
      IF(IBRAVL.EQ.5) PRINT 7025,(ELEMT(M),X(I,M),Y(I,M),Z(I,M),I=1,NL)  YJP3870
      IF(IBRAVL.EQ.6) PRINT 7026,(ELEMT(M),X(I,M),Y(I,M),Z(I,M),I=1,NL)  YJP3880
  701 IF(IBRAVL.EQ.7) PRINT 7027,(ELEMT(M),X(I,M),Y(I,M),Z(I,M),I=1,NL)  YJP3890
  750 DO 80 N=1,J                                                        YJP3900
      NN = N + 1                                                         YJP3910
      DO 80 M = NN,JJ                                                    YJP3920
      IF((Q(N)-Q(M)).LE.0.)GO TO 80                                      YJP3930
      TEMP=Q(N)                                                          YJP3940
      Q(N) = Q(M)                                                        YJP3950
      Q(M) = TEMP                                                        YJP3960
      TEMP = YH(N)                                                       YJP3970
      YH(N) = YH(M)                                                      YJP3980
      YH(M) = TEMP                                                       YJP3990
      TEMP = YK(N)                                                       YJP4000
      YK(N) = YK(M)                                                      YJP4010
      YK(M) = TEMP                                                       YJP4020
      TEMP = YL(N)                                                       YJP4030
      YL(N) = YL(M)                                                      YJP4040
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      YL(M) = TEMP                                                      YJP4050
   80 CONTINUE                                                          YJP4060
      IF(LAUE)839,801,839                                                  4070
  801 WRITE (6,841)                                                       P4080
  841 FORMAT(53H1 THETA   2-THETA   D-VALUE   H  K  L   SIN2THETA     /)   4090
      DO 805 N=1,JJ                                                        4100
      IH=YH(N)                                                             4110
      IK=YK(N)                                                             4120
      IL=YL(N)                                                             4130
      THETA(N)=57.29578*ATAN(SQRT(Q(N)/(1.-Q(N))))                         4140
      THETA2=2.*THETA(N)                                                   4150
      DVAL=WL/(2.*SQRT(Q(N)))                                              4160
      NLIN=NLIN+1                                                          4170
      IF(NLIN-56)807,806,807                                               4180
  806 WRITE (6,841)                                                        4190
      NLIN=0                                                               4200
  807 WRITE (6,808)THETA(N),THETA2,DVAL,IH,IK,IL,Q(N)                      4210
  808 FORMAT(F7.2,F10.2,F10.4,1X,3I3,F12.5)                                4220
  805 CONTINUE                                                             4230
      GO TO 999                                                            4240
  839 IF(NORM.EQ.1)  PRINT 8999                                         YJP4250
      IF(NORM.NE.1)  PRINT 8998                                         YJP4260
      AGUIN=AGUIN*PI2/360.                                              YJP4270
      DO 200 N = 1,JJ                                                   YJP4280
      THETA(N)=57.29578*ATAN(SQRT(Q(N)/(1.-Q(N))))                      YJP4290
      VV=THETA(N)*0.0174533                                             YJP4300
      SX2=(SIN(VV)/WL)**2                                               YJP4310
      IF(KODLP.EQ.0) PLG=(1.+(1.-2.*Q(N))**2)/(Q(N)*SQRT(1.-Q(N)))      YJP4320
      IF(KODLP.EQ.1) PLG=1.                                             YJP4330
      IF(KODLP.EQ.2) PLG=1./(Q(N)*SQRT(1.-Q(N)))                        YJP4340
     0IF(KODLP.EQ.3) PLG=(1.+((1.-2.*Q(N))**2)*((COS(AGUIN)))**2)/      YJP4350
     1(Q(N)*SQRT(1.-Q(N)))                                              YJP4360
      WW=(2.*THETA(N)-BGUIN)*0.0174533                                  YJP4370
     0IF(KODLP.EQ.4) PLG=(1.+((1.-2.*Q(N))**2)*((COS(AGUIN)))**2)/      YJP4380
     1((SQRT(Q(N)))*COS(WW)*SIN(2.*VV))                                 YJP4390
      GO TO(501,502,503,504,505,506,602),ISYSTM                         YJP4400
  501 IF((YK(N).EQ.0.).OR.((YH(N).EQ.0.).AND.(YL(N).EQ.0.)))GO TO 602   YJP4410
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604 FMULTI = 4.0                                                            YJP4420
    GO TO 530                                                               YJP4430
502 IF(YH(N).EQ.0.)IF(YK(N))610,602,551                                     YJP4440
    IF(YK(N).EQ.0.)GO TO 551                                                YJP4450
    IF(YL(N).EQ.0.) GO TO 604                                               YJP4460
608 FMULTI = 8.0                                                            YJP4470
    GO TO 530                                                               YJP4480
551 IF(YL(N))610,602,604                                                    YJP4490
503 IF((YH(N).EQ.0.).AND.(YK(N).EQ.0.)) GO TO 602                           YJP4500
606 FMULTI = 6.0                                                            YJP4510
    GO TO 530                                                               YJP4520
504 IF((YH(N)-YK(N)).EQ.0.)IF(YH(N))610,602,552                             YJP4530
    IF(YK(N).EQ.0.)GO TO 552                                                YJP4540
    IF(YL(N).EQ.0.)IF(LAUE - 1) 610,604,608                                 YJP4550
    IF(LAUE.EQ.1) GO TO 608                                                 YJP4560
    FMULTI=16.                                                              YJP4570
    GO TO 530                                                               YJP4580
552 IF(YL(N))610,604,608                                                    YJP4590
505 IF((YH(N)-YK(N)).EQ.0.)IF(YL(N))610,612,554                             YJP4600
    IF((YL(N).EQ.0.).AND.(LAUE.EQ.2))IF(YK(N)) 610,606,624                  YJP4610
    IF((YL(N).EQ.0.).AND.(LAUE.EQ.1))IF(YK(N)) 610,606,612                  YJP4620
    IF(((YK(N)-YL(N)).EQ.0.).OR.(LAUE.EQ.1)) GO TO 624                      YJP4630
    FMULTI=48.                                                              YJP4640
    GO TO 530                                                               YJP4650
554 IF(YH(N)-YL(N))610,608,624                                              YJP4660
506 IF((YH(N)-YK(N)).EQ.0.)IF(YH(N))610,602,553                             YJP4670
    IF(YK(N).EQ.0.)GO TO 553                                                YJP4680
    IF((YL(N).EQ.0.).AND.(LAUE.EQ.1)) GO TO 606                             YJP4690
    IF((YL(N).EQ.0.).OR .(LAUE.EQ.1)) GO TO 612                             YJP4700
624 FMULTI = 24.0                                                           YJP4710
    GO TO 530                                                               YJP4720
553 IF(YL(N))610,606,612                                                    YJP4730
602 FMULTI =2.0                                                             YJP4740
    GO TO 530                                                               YJP4750
612 FMULTI = 12.0                                                           YJP4760
530 SUMA(N) = 0.                                                            YJP4770
    SUMB(N)=0.                                                              YJP4780
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      DO 703 M=1,NCOMPO                                                 YJP4790
      SMA=0.                                                            YJP4800
      SMB=0.                                                            YJP4810
      NL=NA(M)                                                          YJP4820
      DO 704 I=1,NL                                                     YJP4830
      ARG=PI2*(YH(N)*X(I,M)+YK(N)*Y(I,M)+YL(N)*Z(I,M))                  YJP4840
      SMA=SMA+COS(ARG)                                                  YJP4850
      IF(ISYMCE.EQ.1)GO TO 704                                          YJP4860
      SMB=SMB+SIN(ARG)                                                  YJP4870
  704 CONTINUE                                                          YJP4880
      FSCAT=AAA(M)*E**(-AA(M)*SX2)+BBB(M)*E**(-BB(M)*SX2)+CCC(M)        YJP4890
      IF(ISCAT.EQ.0) GO TO 702                                          YJP4900
      FL=(SQRT(SX2))/.05 + 1.0                                          YJP4910
      IFL=FL                                                            YJP4920
      FFL=FL-FLCAT(IFL)                                                 YJP4930
      FSCAT=SFA(IFL,M)+(SFA(IFL+1,M)-SFA(IFL,M))*FFL                    YJP4940
  702 FSMOD=FSCAT*FOCCU(M)*E**(-BTEMP(M)*SX2)                           YJP4950
      SUMA(N)=SUMA(N)+SMA*FSMOD                                         YJP4960
      SUMB(N)=SUMB(N)+SMB*FSMOD                                         YJP4970
  703 CONTINUE                                                          YJP4980
      SUMA(N) = FBRA*SUMA(N)                                            YJP4990
      SUMB(N) = FBRA*SUMB(N)                                            YJP5000
      FPLG(N)=PLG                                                       YJP5010
      FMUL(N)=FMULTI                                                    YJP5020
      STRU(N)=SUMA(N)**2+SUMB(N)**2                                     YJP5030
      VINT(N)=PLG*FMULTI*STRU(N)                                        YJP5040
  200 VMXINT=AMAX1(VMXINT,VINT(N))                                      YJP5050
      DO 705 N=1,JJ                                                     YJP5060
  735 IH=YH(N)                                                          YJP5070
      IK=YK(N)                                                          YJP5080
      IL=YL(N)                                                          YJP5090
      DVAL=WL/(2.*SQRT(Q(N)))                                           YJP5100
      THETA2=2.*THETA(N)                                                YJP5110
      PRPINT=VINT(N)*1000./VMXINT                                       YJP5120
      VVV=Q(N)                                                          YJP5130
      SQURQ=(VVV)**0.5                                                  YJP5140
      SUMAN=SUMA(N)                                                     YJP5150
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      SUMBN=SUMB(N)                                                     YJP5160
      PHANG=0.0                                                         YJP5170
      IF((SUMAN.NE.0.).OR.(SUMBN.NE.0.))                                YJP5180
     1PHANG=(ATAN2(SUMBN,SUMAN))*360./PI2                               YJP5190
  712 NLINE=NLINE+1                                                     YJP5200
      IF(NLINE.NE.60)GO TO 711                                          YJP5210
      IF(NORM.EQ.1)  PRINT 8999                                         YJP5220
      IF(NORM.NE.1)  PRINT 8998                                         YJP5230
      NLINE=0                                                           YJP5240
  711 IF(NORM.EQ.1) GO TO 714                                           YJP5250
  7130PRINT 9001,IH,IK,IL,THETA(N),Q(N),PRPINT,VINT(N),STRU(N),SUMA(N), YJP5260
     1SUMB(N),PHANG,FMUL(N),FPLG(N)                                     YJP5270
      GO TO 705                                                         YJP5280
  7140PRINT 9000,IH,IK,IL,THETA(N),THETA2,DVAL,SQURQ,Q(N),IH,IK,IL,     YJP5290
     1PRPINT,STRU(N),SUMA(N),SUMB(N),PHANG,FMUL(N),FPLG(N)              YJP5300
  705 CONTINUE                                                          YJP5310
      IF(IMAGE.EQ.0)GO TO 998                                           YJP5320
      VMXINT=0.                                                         YJP5330
      PRINT 7001,COMPND, WL                                             YJP5340
      DATA STAR, BLANK/1H*,1H /                                         YJP5350
      W(1)=AINT(57.29578 * ATAN(SQRT(SL/(1.-SL))))                      YJP5360
      KK = (AINT(57.29578 *ATAN(SQRT(SH/(1.-SH))) - W(1))* 2. + 1.      YJP5370
      DO 800 K = 1,KK                                                   YJP5380
      SP(K) = 0.                                                        YJP5390
      IF(K.NE.1) W(K) = W(K-1) + 0.5                                    YJP5400
      DO 800 N = 1,JJ                                                   YJP5410
     0IF((THETA(N).GE.W(K)).AND.(THETA(N).LT.(W(K)+0.5))) SP(K)=SP(K)+  YJP5420
     1VINT(N)                                                           YJP5430
  800 VMXINT = AMAX1(VMXINT,SP(K))                                      YJP5440
      DO 804 K = 1,KK                                                   YJP5450
      NSPIEL = (SP(K)*1000.)/(VMXINT*10.0)                              YJP5460
      DO 802 MP = 1,100                                                 YJP5470
  802 PLAY(MP) = BLANK                                                  YJP5480
      IF(NSPIEL.EQ.0) GO TO 804                                         YJP5490
      DO 803 MP = 1,NSPIEL                                              YJP5500
  803 PLAY(MP) = STAR                                                   YJP5510
  804 WRITE(6,7052)W(K),(PLAY(MP),MP=1,NSPIEL)                          YJP5520
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      GO TO 998                                                         YJP5530
  610 PRINT 9900                                                        YJP5540
  998 GO TO 999                                                         YJP5550
  999 CALL EXIT                                                         YJP5560
      END                                                               YJP5570
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GAUSSIAN ANALYSIS PROGRAM

```
//STEPONE EXEC  FORTG,REGION.GO=128K,TIME.GO=8
//FORT.SYSIN  DD *
      COMMON  N,A(64),D(64),PX(64),CY(99),X(99),Y(99),NP,NG
      DIMENSION WLMM(99),ABSU(99),YS(99,6),XL(5),YL(5),GL(5),DL(5),TITLE
     1(19)
      CALL ERRSET (208,0,-1,1)
      READ(5,51)TITLE
1     READ(5,2) NP,NG,C
2     FORMAT(2I10,F10.0)
      IF(NP)4,4,6
4     STOP
6     N=NG*3
      READ(5,7)(A(I),I=1,N)
7      FORMAT(3F10.0)
      READ(5,8)(WLMM(I),ABSU(I),I=1,NP)
8     FORMAT(8(F5.3,F5.3))
      DO 10 I=1,NP
      X(I)=1./WLMM(I)*1.E+7
10    Y(I)=ABSU(I)/C
      CALL FUNFIT(.001,2)
      WRITE(6,51)TITLE
51    FORMAT('1',19A4)
      WRITE(6,48)
48    FORMAT('0'10X'EXTC(MAX)'10X'WLRC(MAX)'12X'DEL(I)')
42    WRITE(6,44)(A(I),I=1,N)
44    FORMAT(3F20.5)
      READ(5,45)XL,YL,GL,DL
45    FORMAT(20A4)
      CALL GRAPH(NP,X,Y,3,1,10.,10.,0.,0.,0.,0.,XL,YL,GL,DL)
      CALL GRAPH(NP,X,CY,4,1,0.,0.,0.,0.,0.,0.,0.,0.,0.,0.)
      DO 50 I=1,NG
      DO 46 J=1,NP
      V=(X(J)-A(3*I-1))/A(3*I)
46    YS(J,I)=A(3*I-2)/EXP(V*V)
   50 CALL GRAPH(NP,X,YS(1,I),0,2,0.,0.,0.,0.,0.,0.,0.,0.,0.,0.)
      WRITE(6,52)
52    FORMAT(1H0,1X10HLAMBDA(MU),2X6HCM(-1),4X5HABSU,3X10HEXTC(OBS) ,10H
```

```
     1EXTC(CALC),5X7HEXTC(I))
      DO 54 I=1,NP
54    WRITE(6,56)WLMM(I),X(I),ABSU(I),Y(I),CY(I),(YS(I,J),J=1,NG)
56    FORMAT(1H0,F6.0,F13.3,F9.3,7F10.2)
      GO TO 1
      END
      SUBROUTINE FUNFIT(DLIM,IP)
      COMMON NP,A(1)
      DIMENSION DA(99)
      CALL FCN(ER)
      PDEL=.1
      SQ2=SQRT(2.)/2.
2     DO 4 I=1,NP
4     DA(I)=A(I)*PDEL
6     IS=1
      ER1=1.E70
      ER2=ER1
      DO 28 I=1,NP
      A(I)=A(I)+DA(I)
      CALL FCN(ER3)
      A(I)=A(I)-DA(I)
      IF(ER3-ER)14,14,10
10    A(I)=A(I)-DA(I)
      CALL FCN(ER4)
      A(I)=A(I)+DA(I)
      IF(ER4-ER3)12,14,14
12    ER3=ER4
      DA(I)=-DA(I)
14    IF(ER3-ER2)16,28,28
16    IF(ER3-ER1)18,20,20
18    I2=I1
      ER2=ER1
      I1=I
      ER1=ER3
      GO TO 28
20    ER2=ER3
      I2=I
```

```
28      CONTINUE
30      COSX=DA(I1)*SQ2
        SINX=DA(I2)*SQ2
        A(I1)=A(I1)+COSX
        A(I2)=A(I2)+SINX
        Y0=ER1
        CALL FCN(Y1)
        Y2=ER2
        A(I1)=A(I1)-COSX
        A(I2)=A(I2)-SINX
        IF(Y1-(Y0+Y2)*.5)31,305,305
305     Z=2.
        GO TO 32
31      C2=(4.*Y1-Y2-3.*Y0)*.5
        C3=Y1-Y0-C2
        Z=-C2/(C3*4.)
        IF(Z)32,38,38
32      GO TO (34,36),IS
34      IS=2
        DA(I2)=-DA(I2)
        A(I2)=A(I2)+DA(I2)
        CALL FCN(ER3)
        A(I2)=A(I2)-DA(I2)
        GO TO 30
36      SINX=0.
        COSX=DA(I1)
        A(I1)=A(I1)+COSX
        ER3=Y0
        GO TO 40
38      SINX=(1.570627*Z-.6432292*Z*Z*Z+.0727102*Z*Z*Z*Z*Z)*DA(I2)
        A(I2)=A(I2)+SINX
        Z=Z-1.
        COSX=(-1.570627*Z+.6432292*Z*Z*Z-.0727102*Z*Z*Z*Z*Z)*DA(I1)
        A(I1)=A(I1)+COSX
        CALL FCN(ER3)
40      IF(ER3-ER)42,44,44
42      ER=ER3
```

```
      A(I2)=A(I2)+SINX
      A(I1)=A(I1)+COSX
      CALL FCN(ER3)
      IF(ER3-ER)42,43,43
43    A(I2)=A(I2)-SINX
      A(I1)=A(I1)-COSX
      WRITE(6,7)(A(I),I=1,9),ER,Z,I1,I2
7     FORMAT(11F10.2,2I5)
      GO TO 6
44    A(I2)=A(I2)-SINX
      A(I1)=A(I1)-COSX
      IF(PDEL-DLIM)70,62,62
62    PDEL=.3*PDEL
      GO TO 2
70    CONTINUE
      CALL PDUMP(I,COSX,4,I,COSX,5)
      RETURN
      END
      SUBROUTINE FCN(ER)
      COMMON  N,A(64),D(64),PX(64),CY(99),X(99),Y(99),NP,NG
      ER=0
      DO 50 I=1,NP
      CY(I)=0.
      DO 40 J=1,NG
      V=(A(3*J-1)-X(I))/A(3*J)
      IF(ABS(V)-13.2)39,39,40
39    CY(I)=CY(I)+A(3*J-2)/EXP(V*V)
40    CONTINUE
      CYY=CY(I)-Y(I)
      ER=ER+CYY*CYY
50    CONTINUE
      RETURN
      END
//GO.FT14F001 DD SPACE=(800,(120,15)),DISP=(,PASS),DSNAME=&SM,UNIT=DISK
//GO.SYSIN  DD  *
//STEP2  EXEC  PLOT,PLOTTER=INCRMNTL
```

MAGNETIC SUSCEPTIBILITY PROGRAM

```
//ST1   EXEC   FORTG
//FORT.SYSIN   DD   *
      DIMENSION D(10),F(10),FC(10),DY(20),YCALC(20),KT(50,5),CHISM(50,5)   00010
     1,X(10),Y(10),RKT(50,5),CHISG(50,5),XL(5),YL(5),GL(5),DL(5)
C     L IS THE NUMBER OF DATA SETS PER RUN.                  DIMEN  9      00100
      READ (5,108)L
      READ (5,100)GC                                                       00030
      READ (5,101)(FC(I),I=1,L)                                            00040
      READ (5,102)(X(I),I=1,L)
C     N IS THE NUMBER OF SAMPLES                              DIMEN  5      00060
      READ (5,107)N
      DO 5 K=1,N                                                           00080
      READ (5,103)                                                         00090
C     M IS THE NUMBER OF TEMPERATURE RUNS FOR EACH SAMPLE.    DIMEN 50      00120
      READ (5,104)WM,WS,WCN,M
      WRITE (6,200)
      WRITE (6,201)GC
      WRITE (6,202)
      WRITE (6,203)(I,FC(I),X(I),I=1,L)
      WRITE (6,103)
      WRITE (6,205)M,WM,WS,WCN
      DO 1 J=1,M                                                           00200
      READ (5,105)KT(J,K),DO1,DO2,CHICN,UCCN,RMD
      DELDO=DO1-DO2                                                        00220
      DRFT=DELDO*GC*RMD                                                    00230
      DOM=(DO1+DO2)/2.                                                     00240
C     FORCE DATA MUST RUN SEQUENTIALLY FROM H DH/DZ=MAX VALUE              00250
      READ (5,106)(D(I),I=1,L)
      DO 2 I=1,L                                                           00270
      F(I)=(D(I)-DOM)*RMD*GC
      IF (FC(I))10,10,2
    2 Y(I)=F(I)/FC(I)
      WRITE (6,206)KT(J,K)
      WRITE (6,207)DO1,DO2,DRFT,RMD
      WRITE (6,208)(I,I=1,L)
      WRITE (6,209)(D(I),I=1,L)
      WRITE (6,219)(F(I),I=1,L)
```

```
      SX=0
      SY=0
      SPXY=0
      SXS=0
      DO 3 I=1,L
      SX=SX+X(I)
      SY=SY+Y(I)
      PXY=X(I)*Y(I)
      SPXY=SPXY+PXY
      XS=X(I)**2
    3 SXS=SXS+XS
      SSX=SX**2
      R=L
      Z=(R*SXS)-SSX
      IF (Z)10,10,13
   13 AA=((SXS*SY)-(SX*SPXY))/Z
      BB=((R*SPXY)-(SX*SY))/Z
      SDYS=0
      DO 4 I=1,L
      YCALC(I)=AA+(BB*X(I))
      DY(I)=Y(I)-YCALC(I)
      DYS=DY(I)**2
    4 SDYS=SDYS+DYS
      SOFY=SQRT(SDYS/(R-1.))
      SOFA=SOFY*SQRT((R*SXS)/((R-1.)*Z))
      SOFB=SOFY*SQRT(R**2/((R-1.)*Z))
      WRITE (6,210)(Y(I),I=1,L)
      WRITE (6,220)(YCALC(I),I=1,L)
      WRITE (6,230)(DY(I),I=1,L)
      WRITE (6,211)SOFY,AA,SOFA,BB,SOFB
      IF (WS)10,10,14
   14 CHISG(J,K)=(AA   /WS)-(CHICN*WCN/WS)
      UCSG=(SOFA   /WS)+(UCCN*WCN/WS)
      CHISM(J,K)=WM*CHISG(J,K)
      UCSM=UCSG*WM
    1 WRITE (6,212)CHISM(J,K),UCSM,CHISG(J,K)
      WRITE (6,215)
```

```
      WRITE (6,103)
      WRITE (6,216)
      WRITE (6,213)
      DO 23 J=1,M
      IF (KT(J,K))5,5,23
   23 RKT(J,K)=1./FLOAT(KT(J,K))
      READ(5,333) JKL
      IF(JKL)6,6,5
    6 READ (5,33)XL,YL,GL,DL
      CALL GRAPH(M,RKT(1,K),CHISM(1,K),3,11,13.0,10.0,0.001,0,0,0,XL,YL,
     1GL,DL)
    5 WRITE (6,214)(J,KT(J,K),CHISM(J,K),RKT(J,K),CHISG(J,K),J=1,M)
   10 STOP
   33 FORMAT(20A4)
  100 FORMAT (F10.4)
  101 FORMAT (6E10.4)
  102 FORMAT (6E10.4)
  103 FORMAT (1X52H                                                    )
  104 FORMAT (F10.1,2F10.4,I3)
  105 FORMAT (I3,7X,2F10.5,2E10.3,F10.3)
  106 FORMAT (9F7.5)
  107 FORMAT (I2)
  108 FORMAT (I2)
  200 FORMAT (102H1MAGNETIC SUSCEPTIBILITIES AT INFINITE FIELD FROM LEAS
     1T SQUARES FIT TO HONDA/OWEN PLOT. FARADAY METHOD/)
  201 FORMAT (9X20H FORCE CONVERSION   1PE15.4,16H DYNES/MILLIGRAM /)
  202 FORMAT (22X7HH DH/DZ15X3H1/H/)
  203 FORMAT ((9X0PI1,1P2E20.3)/)
  205 FORMAT (1H08X19HRUNS                 I10/9X19HMOL WT             F1
     10.2,11H GRAMS/MOLE/9X19HSAMPLE MASS         F10.4,6H GRAMS/9X19HCO
     2NTAINER MASS     F10.4,6H GRAMS//)
  206 FORMAT (4XI3,2X14HDEGREES KELVIN/)
  207 FORMAT (9X10HDD1         F10.4,6H  MG  /9X10HDD2         F10.4,6H  M
     1G  /9X10HDRFT       F10.4,6H DYNES/9X10HRMD        F10.4,5H  MG  /)
  208 FORMAT (15X9(9XI1))
  209 FORMAT (1H08X10H MG        9F10.4)
  219 FORMAT (9X10HDYNES      10F10.4)
```

```
210 FORMAT (1H08X10HY         10(1PE10.3))
220 FORMAT (9X10HYCALC     10(1PE10.3))
230 FORMAT (9X10HDY        10E10.3)
211 FORMAT (1H08X10HSOFY       E15.3//9X10HA          E15.3,5X10HSOFA
   1   E15.3/9X10HB          E15.3,5X10HSOFB      E15.3/)
212 FORMAT (9X10HCHISM     E15.4,5X10HUCSM      E15.3,5X10HCHISG
   1E15.4//)
213 FORMAT (8X2H J10X1HT11X5HCHISM17X3H1/T14X5HCHISG /)
214 FORMAT (9XI2,8XI3,0PE18.4,2PE20.2,0PE20.4 /)
215 FORMAT (1H1)
216 FORMAT (1H0)
333 FORMAT (I2)
    END
```

Table 12. Magnetic susceptibilities (emu/mole)x10^6
$[(C_3H_7)_4N]_2[(Ta_5WCl_{18})]$

T °K	T^{-1}°K^{-1}x10^3	χ_M
77	12.99	2602
78	12.82	2596
80	12.50	2561
85	11.76	2480
90	11.11	2409
95	10.53	2330
100	10.00	2252
110	9.09	2128
120	8.33	2011
130	7.69	1867
140	7.14	1797
150	6.67	1721
160	6.25	1589
180	5.56	1440
240	4.17	1147
260	3.85	1070
300	3.33	963

Table 13. Magnetic susceptibilities (emu/mole)x10^6 $[(C_3H_7)_4N]_3[(Ta_5WCl_{12})Cl_6]$

T °K	T^{-1}°K^{-1}x10^3	$-\chi_M$
77	12.99	102
80	12.50	120
100	10.00	196
120	8.33	269
140	7.14	284
160	6.25	329
180	5.56	348
200	5.00	356
225	4.44	365
250	4.00	362
275	3.64	387
300	3.33	377

Table 14. Magnetic susceptibilities (emu/mole)x10^6

T°K	T^{-1}°K^{-1} x10^3	Nb_3Cl_8 [a,b] χ_M^{corr}	6/1 [a,b] χ_M^{corr}	4/1 [a,b] χ_M^{corr}	2/1 [a,b] χ_M^{corr}	3/2 [a,b] χ_M^{corr}
77	12.99	4152				
78	12.82		3206	2696	1504	
80	12.50		3189	2684		897
85	11.76	3803	3084	2576	1405	
90	11.11	3648	2867	2486	1335	880
95	10.53	3465	2774	2367	1288	
100	10.00	3363	2675	2241	1248	815
110	9.09	3110	2462	2068	1163	759
120	8.33	2874	2284	1889	1087	692
130	7.69	2661	2122	1771	1033	
140	7.14	2505	2021	1677	973	609
150	6.67	2363	2100	1601		
160	6.25	2710	1905	1165	886	566
170	5.88	2097				
180	5.56	2013	1752	1378	816	521
200	5.00	1851	1664	1278	756	486
220	4.55	1693	1403	1227		
225	4.44				700	457
240	4.17	1632	1389	1217		
250	4.00				656	426
260	3.85	1558	1202	1053		
275	3.36				616	404
280	3.57	1421	1115	951		
300	3.33	1291	1076	900	573	394

[a] Niobium-tungsten mixed metal cluster compounds.

[b] χ_D for Nb_3Cl_8 = 277, 6/1 = 287, 4/1 = 283, 2/1 - 305, 3/2 = 288.

Table 15. Magnetic susceptibilities (emu/mole)x10^6

T °K	T^{-1} °K^{-1} x10^3	Nb/Mo-320 χ_M^{corr}[a]	Nb/Mo-550 χ_M^{corr}[b]
77	12.99	1835	189
80	12.50	1773	192
90	11.11	1602	171
100	10.00	1477	156
120	8.33	1281	135
140	7.14	1137	121
160	6.25	1032	110
180	5.56	954	97
200	5.00	893	90
225	4.44	827	83
250	4.00	774	80
275	3.64	747	79
300	3.33	706	77

[a] χ_D = 278.

[b] χ_D = 284.