BNL-22982

CONF-770510-5

Neutron Diffraction Studies of Tetrahedral Cluster Transition Metal Hydride Complexes: $HFeCo_3(CO)_9(P(OCH_3)_3)_3$ and $H_3Ni_4(C_5H_5)_4$

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Abstract: Structures of the tetrahedral cluster transition metal hydride complexes $HFeCo_3(CO)_9(P(OCH_3)_3)_3$ and $H_3Ni_4(C_5H_5)_4$ have been investigated by low-temperature neutron diffraction techniques. Both complexes have approximate C_{3v} symmetry. In $HFeCo_3(CO)_9(P(OMe)_3)_3$ the hydride ligand is found outside the $FeCo_3$ cluster, 0.978(3) Å from the Co_3 face, and essentially on the molecular three-fold axis, triply bridging the cobalt atoms. Mean distances in the cluster are Co-Co 2.489(7), Co-Fe 2.559(2), Co-H 1.734(4) Å. In $H_3Ni_4(Cp)_4$ the three hydride ligands are face-bridging, and their mean displacement from the faces of the cluster is 0.90(3) Å. The H_3Ni_4 core may be envisaged as a distorted cube, with one vertex unoccupied. Mean distances are

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Ni-Ni 2.469(6), Ni-H 1.691(8), H···H 2.316(6) Å. The observed geometries of the two clusters considered here suggest a plausible model for chemisorption of hydrogen on {111} faces of cubic and {001} faces of hexagonal close-packed metals, in which hydrogen atoms are located approximately 1 Å above the centers of triangles of metal atoms.

Introduction

A variety of factors contribute to the great current interest in polynuclear metal hydride complexes. These include the novel geometries found in these systems and their usefulness as models for the bonding of hydrogen to metals, such as may occur in catalysis (1) or hydrogen-storage applications (2). A comprehensive review of the subject of metal hydride complexes, in which polynuclear species are included, has been published by Kaesz and Saillant (3).

Direct location of hydride ligands in metal complexes by X-ray diffraction may be difficult, especially in the case of bridging hydrides commonly occurring in polynuclear systems.[a] X-ray diffraction studies cannot, in any event be expected to provide M-H bond lengths of accuracy much better than ±0.1 Å. Thus, precise information on geometries of metal hydride complexes has depended upon neutron diffraction.[b] In this article we briefly review some results of prior neutron diffraction studies, and present new results for two tetrahedral cluster complexes with face-bridging

[a] Several cases have been reported where the hydride was found successfully. For example, Churchill and DeBoer have located the bridging hydride in $HOs_3(CO)_{10}(CHCH_2PMe_2Ph)$ (4), while we have used a Fourier-averaging technique to locate the face-bridging hydrogen atoms in $H_4Re_4(CO)_{12}$ (5).

[b] The sensitivity of neutron diffraction to light atoms in general and hydrogen in particular is due to the large relative cross sections of these atoms, compared to those for X-ray diffraction. For example $\sigma(H)/\sigma(Os)$ is 0.12 for neutrons and 1.7×10^{-4} for X-rays ($2\theta = 0^{\circ}$). Thus the relative contribution of hydrogen in a structure containing osmium, will be roughly three orders of magnitude greater in neutron than in X-ray diffraction.

hydride ligands: $HFeCo_3(CO)_9(P(OMe)_3)_3$ and $H_3Ni_4(Cp)_4$.[a] These complexes, together with $[HNi_{12}(CO)_{21}]^{3-}$ and $[H_2Ni_{12}(CO)_{21}]^{2-}$ (6), are the only examples of polynuclear transition metal hydrides for which single-crystal neutron diffraction data currently are available.[b]

Prior Neutron Diffraction Work on Transition Metal Hydride Complexes

The first neutron diffraction study of a transition metal hydride complex was that of K_2ReH_9 (8), reported in 1964, which showed that the $[H_9Re]^{2-}$ dianion forms a tri-capped trigonal prism, with a mean Re-H bond distance of 1.68(1) Å. This investigation, together with subsequent X-ray (9) and neutron (10) diffraction studies of $HMn(CO)_5$, demonstrated unequivocally that hydrogen is a stereochemically active ligand in the latter complex and that terminal M-H distances correspond to those expected for normal covalent bonds. More recently, a substantial body of accurate data on terminal and bridging M-H bonds has emerged based on neutron diffraction studies of 18 complexes, listed in Table I. We have published a review covering this work up to 1976 (22), and results for polyhydride complexes are discussed in an accompanying article (23).

The studies of $HMo_2(Cp)_2(CO)_4(PMe_2)$ (17), $HW_2(CO)_9(NO)$ (18), and $HW_2(CO)_8(NO)(P(OMe)_3)$ (19) are of particular significance and provide definitive evidence that M-H-M bridges are best described as closed

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[a] Abbreviations used in this paper are as follows: Me: methyl, Et: ethyl, Cp: cyclopentadienyl, Ph: phenyl.

[b] A neutron powder diffraction study of HNb_6I_{11} has been reported (7). The hydride ligand was located at the center of the octahedral Nb_6 cluster, similar to the situation in the dodecanickel anions mentioned above, where the hydride ligands occur in octahedral sites in the nickel framework.

three-center bonds, with significant metal-metal interaction (18). It is not surprising that such is the case, since any metal orbitals of proper symmetry to interact with H(1s) will also interact with one another, as has been pointed out by Hoffmann (24). In $HW_2(CO)_8(NO)(P(OMe)_3)$ (Figure 1) the W-H-W bridge was found to be slightly asymmetric, with the hydride ligand displaced toward the $W(CO)_5$ group, as could be predicted on electron-counting considerations. It is likely that such asymmetry also exists in $HW_2(CO)_9(NO)$, but the effect could not be measured, since both crystalline forms of this latter complex exhibit disorder with rotation of the molecule about the pseudo two-fold axis passing through the hydrogen atom.

Experimental

A powdered sample of $HFeCo_3(CO)_9(P(OMe)_3)_3$ was supplied by Prof. H. D. Kaesz and Dr. B. T. Huie of the University of California, Los Angeles, and recrystallized from a dichloromethane/diethylether/hexane mixture. Single crystals of $H_3Ni_4(Cp)_4$ were supplied by Prof. J. Müller of The Technical University of Berlin. Large single crystals of both compounds were affixed to aluminum pins and mounted in cryostats on an automated four-circle diffractometer (25,26) at the Brookhaven High Flux Beam Reactor. $HFeCo_3(CO)_9(P(OMe)_3)_3$ was studied at 90 K, and $H_3Ni_4(Cp)_4$ at 81 K. Crystal data and experimental parameters are summarized in Table II.

For $HFeCo_3(CO)_9(P(OMe)_3)_3$, starting phases were calculated based upon the positions of non-hydrogen atoms determined from a prior X-ray analysis (27), and all hydrogen atoms were then located in a difference-Fourier synthesis. Initial refinement was carried out with an automated procedure employing

differential-Fourier syntheses (28), followed by full-matrix least-squares based upon F_o^2, including reflections with $F_o^2 < 0$. Parameters were blocked into groups of ca. 250 and anisotropic thermal factors used for all atoms. Satisfactory convergence was achieved, and all bond distances determined with precision better than 0.004 Å.

For $H_3Ni_4(Cp)_4$, the initial phasing model consisted of the nickel and carbon atoms, at positions determined in an earlier X-ray study (29,30), with cyclopentadienyl hydrogen atoms in calculated positions. The hydride ligands were located in a difference-Fourier synthesis, and the structure refined by least-squares procedures, including only reflections with $F_o^2 > 1.5\sigma(F_o^2)$. The relatively high R-values result from the fact that a large fraction of the reflections were measured to have very low intensity.[a] However, chemically equivalent bond lengths in the H_3Ni_4 core agree to within 0.04 Å. Anisotropic thermal factors refined to quite large values for certain atoms in the Cp rings, as might be expected if the barrier to rotation of the rings in the solid state is assumed to be low.

Results

$HFeCo_3(CO)_9(P(OMe)_3)_3$. This complex is found to possess essentially C_{3v} symmetry, with the geometry shown schematically in Figure 2. Figure 3 illustrates the molecular structure with thermal ellipsoids and gives the atomic numbering scheme. The hydride ligand is located outside the $FeCo_3$ cluster, 0.978(3) Å from the Co_3 face, triply bridging the cobalt atoms. These results confirm the findings of Huie et al. (27), based on their X-ray

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[a] 3478 of a total of 5633 unique reflections were observed with $F_o^2 < 3\sigma(F_o^2)$.

diffraction study at 134 K. The bridging hydride is found essentially on the molecular three-fold axis, as illustrated in Figure 3b. Selected bond distances and angles are presented in Table III.

$H_3Ni_4(Cp)_4$. The structure of $H_3Ni_4(Cp)_4$, shown schematically in Figure 4, consists of a tetrahedral nickel cluster, with each nickel atom π-bonded to a Cp ring. The three hydride ligands are face-bridging, as deduced on the basis of X-ray data (29,30). Figure 5 gives a close-up view of the H_3Ni_4 core, which may be envisaged as a tri-capped tetrahedron, or equivalently as a distorted cube, with alternate corners occupied by nickel and hydrogen atoms and one corner vacant. Selected bond distances and angles are presented in Table IV. The mean displacement of the hydride ligands from the faces of the Ni_4 cluster is 0.90(3) Å.

Discussion

In 1968, an unusual structure for $HFeCo_3(CO)_{12}$ with the hydride ligand located inside the cage, was proposed by Mays (32) on the basis of mass spectral evidence and electron-counting considerations. However, this model was disproved by the X-ray work of Huie et al. on the tris(trimethylphosphite) derivative (27), in which the hydride ligand was located in a difference-Fourier synthesis and shown to bridge the Co_3 face. The present neutron diffraction study has allowed definitive placement of the hydride ligand and yielded more accurate bond distances and angles.

One motivation to carry out a neutron diffraction investigation of $H_3Ni_4(Cp)_4$ was to check the possibility of disorder of the hydride ligands over all four faces of the Ni_4 tetrahedron. The hydrides were not located

from the X-ray data (29,30). Rather, their positions were inferred from the deviations of the structure from strict tetrahedral symmetry. The observed Cp(i)-Cn-Cp(j) angles (Table IV) are distorted from the tetrahedral value, such that Cp(2), Cp(3) and Cp(4) are bent away from Cp(1). The face defined by Ni(2), Ni(3), and Ni(4) therefore could be expected to be vacant. Our neutron results indicate that such is indeed the case, there being no evidence for disorder of the hydride ligands on the nuclear density maps.

The metal clusters in $HFeCo_3(CO)_9(P(OMe)_3)_3$ and $H_3Ni_4(Cp)_4$ contain different numbers of electrons. The former cluster is a closed-shell structure (60 electrons),[a] while the latter contains 63 electrons and is paramagnetic with S = 3/2 (29). This paramagnetism could in principle be detected by neutron diffraction with a polarized beam and external magnetic field. However, such measurements were not undertaken, and the effects of paramagnetism on the observed diffraction intensities were assumed to be small and therefore ignored.

Mean Co-Co and Ni-Ni distances observed in these complexes are very close to interatomic distances as determined at ambient temperatures in cobalt and nickel metals (Co-Co: 2.489(7) Å *vs.* 2.507 Å in α-cobalt (34); Ni-Ni 2.469(6) Å *vs.* 2.492 Å in the metal (35)). The mean M-H bond lengths, as well as hydride displacements from M_3 faces, are less for nickel in $H_3Ni_4(Cp)_4$ than for cobalt in $HFeCo_3(CO)_9(P(OMe)_3)_3$. Although the differences are marginally significant within error limits (Ni-H 1.691(8) Å *vs.* Co-H 1.734(4) Å; displacements from plane: Ni_3 0.90(3) Å *vs.* Co_3 0.978(3) Å), they are

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[a] For a description of the electron-counting procedure as applied to metal clusters, see reference (33).

in the expected direction, since the covalent radius should vary inversely with atomic number within a transition series. However, other effects, such as the number of electrons in the cluster may also influence these dimensions.

The geometries of the two clusters considered here suggest a plausible model for chemisorption of hydrogen on close-packed metals. Thus hydrogen atoms might be placed roughly 1 Å above the centers of triangles of metal atoms, such as occur on {111} or {001} surfaces of ccp or hcp metals, respectively. In this model adjacent hydrogen atoms are roughly 1.4 Å apart and therefore separated well beyond bonding distance.[a] Hydrogen chemisorbed on metals is normally considered to exist as atomic hydrogen, as required by Sievert's law (36).

Acknowledgement

We wish to thank Professors Herbert D. Kaesz and Jorn Müller for generously providing the chemical samples used in this study, and Mr. Joseph Henriques for technical assistance. We are grateful to the National Science Foundation and the Petroleum Research Fund (administered by the American Chemical Society) for financial support through grants CHE-77-00360 and 7800-AC3,6 respectively, and to the W. C. Hamilton Memorial Fund for a Scholarship awarded to RGT. Research at Brookhaven National Laboratory was performed under contract with the U. S. Energy Research and Development Administration and supported by its Division of Basic Energy Sciences.

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[a] The mean H···H distance between hydride ligands in $H_3Ni_4(Cp)_4$ is considerably longer than this (2.316(6) Å).

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Table I. Transition Metal Hydride Complexes Studied by Neutron Diffraction[a]

A. Mononuclear

$HMn(CO)_5$ (10)

$HZnN(Me)C_2H_4N(Me)_2$ (11)

$D_2Mo(Cp)_2$ (12)

$H_3Ta(Cp)_2$ (13)

$K_2^+[H_9Re]^{2-}$ (8)

$H_4Os(PMe_2Ph)_3$ (14)

B. Binuclear

$[Et_4N]^+[HCr_2(CO)_{10}]^-$ (15)

$[(Ph_3P)_2N]^+[HCr_2(CO)_{10}]^-$ (16)

$HMo_2(Cp)_2(CO)_4(PMe_2)$ (17)

$HW_2(CO)_9(NO)$ (18)

$HW_2(CO)_8(NO)(P(OMe)_3)$ (19)

$H_8Re_2(PEt_2Ph)_4$ (20)

$[H_3Ir_2(C_5Me_5)_2]^+BF_4^-$ (21)

C. Polynuclear

$HFeCo_3(P(OMe)_3)_3$

$H_3Ni_4(Cp)_4$

$[(Ph_3P)_2N]_3^+[HNi_{12}(CO)_{21}]^{3-}$ (6)

$[(Ph_3P)_2N]_2^+[H_2Ni_{12}(CO)_{21}]^{2-}$ (6)

HNb_6I_{11} (7)

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[a] Me: methyl, Et: ethyl, Cp: cyclopentadienyl, Ph: phenyl

Table II. Crystal Data and Experimental Parameters

		$HFeCo_3(CO)_9(P(OMe)_3)_3$	$H_3Ni_4(Cp)_4$
Space group		$P2_1/c$	C2/c
Cell parameters	a	15.957(8) Å	28.312(13) Å
	b	10.611(5)	9.234(5)
	c	18.383(9)	14.783(7)
	β	98.70(2)°	103.35(2)°
Cell Volume		3077(3) $Å^3$	3760(3) Å
No. of molecules per unit cell (Z)		4	8
Molecular Weight		858.0	498.2
Calc. density		1.85 g/cm^3	1.76 g/cm^3
Absorption coefficient (μ)[a]		1.54 cm^{-1}	1.94 cm^{-1}
Wavelength		1.1598(1) Å	1.0183(1) Å
Sample volume		31.2 mm^3	12.5 mm^3
Data collection temperature		90.0(4) K	81(1) K
Data collection limit ($\sin\theta/\lambda$)		0.68 $Å^{-1}$	0.68 $Å^{-1}$
No. of reflections used in structure analysis		8229	2656
Final agreement factors[b]		R_F = 0.070 R_{wF} = 0.035	R_F = 0.107 R_{wF} = 0.067

[a] Calculated assuming an incoherent scattering cross-section for hydrogen of 40 barn.

[b] $R_F = \sum\left|F_o - |F_c|\right| / \sum F_o \qquad R_{wF} = \left\{\sum w\left|F_o - |F_c|\right|^2 / \sum wF_o^2\right\}^{\frac{1}{2}}$

Table III. Selected Bond Distances and Angles in $HFeCo_3(CO)_9(P(OMe)_3)_3$[a]

Distances (Å)		Angles (°)	
Co(1)-H	1.742(3)	Co(1)-H-Co(2)	92.1(1)
Co(2)-H	1.731(3)	Co(1)-H-Co(3)	91.7(1)
Co(3)-H	1.728(3)	Co(2)-H-Co(3)	91.5(1)
Mean	1.734(4)	Mean	91.8(2)
Co(1)-Fe	2.563(2)	Fe-Co(1)-H	89.5(1)
Co(2)-Fe	2.556(2)	Fe-Co(2)-H	90.0(1)
Co(3)-Fe	2.558(2)	Fe-Co(3)-H	90.0(1)
Mean	2.559(2)	Mean	89.8(2)
Co(1)-Co(2)	2.501(2)	Fe-Co(1)-Co(2)	60.6(1)
Co(1)-Co(3)	2.489(3)	Fe-Co(1)-Co(3)	60.8(1)
Co(2)-Co(3)	2.477(3)	Fe-Co(2)-Co(1)	60.9(1)
Mean	2.489(7)	Fe-Co(2)-Co(3)	61.1(1)
		Fe-Co(3)-Co(1)	61.0(1)
Mean values		Fe-Co(3)-Co(2)	61.0(1)
Co-P	2.175(4)	Mean	60.9(1)
Co-C (terminal CO)	1.756(4)		
Co-C (bridging CO)	1.953(6)	Co(1)-Fe-Co(2)	58.5(1)
Fe-C	1.798(2)	Co(1)-Fe-Co(3)	58.2(1)
C-O (terminal)	1.147(1)	Co(2)-Fe-Co(3)	58.0(1)
C-O (bridging)	1.165(1)	Mean	58.2(1)
		Mean values	
		P-Co-H	91.6(39)
		C-Co-H (terminal CO)	170.5(14)
		C-Co-H (bridging CO)	83.8(6)
		Co-C-Co	79.2(1)

[a]Standard deviations of mean values are calculated as $\left[\sum(x_i - \bar{x})^2 / n(n-1)\right]^{1/2}$, where n is the number of observations. The resulting deviations are to be regarded as rough estimates of uncertainty, in cases where n = 3.

Table IV. Selected Distances and Angles in $H_3Ni_4(Cp)_4$[a,b]

Distances (Å)		Angles (°)	
Ni(1)-H(1)	1.720(8)	Ni(1)-H(1)-Ni(2)	94.0(4)
Ni(1)-H(2)	1.718(9)	Ni(1)-H(1)-Ni(3)	93.1(4)
Ni(1)-H(3)	1.711(7)	Ni(1)-H(2)-Ni(3)	93.6(4)
Mean	1.716(3)	Ni(1)-H(2)-Ni(4)	93.9(4)
		Ni(1)-H(3)-Ni(2)	94.7(4)
Ni(2)-H(1)	1.684(7)	Ni(1)-H(3)-Ni(4)	93.0(3)
Ni(2)-H(3)	1.674(8)	Mean	93.7(3)
Ni(3)-H(1)	1.674(8)		
Ni(3)-H(2)	1.661(9)	Ni(2)-H(1)-Ni(3)	94.1(4)
Ni(4)-H(2)	1.672(8)	Ni(3)-H(2)-Ni(4)	95.7(4)
Ni(4)-H(3)	1.704(8)	Ni(2)-H(3)-Ni(4)	93.1(4)
Mean	1.678(6)	Mean	94.3(8)
Ni(1)-Ni(2)	2.490(3)	Cp(1)[c]-Cn[d]-Cp(2)	117.5(2)
Ni(1)-Ni(3)	2.464(3)	Cp(1)-Cn-Cp(3)	112.3(2)
Ni(1)-Ni(4)	2.478(3)	Cp(1)-Cn-Cp(4)	112.3(2)
Mean	2.477(8)	Mean	114.0(17)
Ni(2)-Ni(3)	2.458(3)	Cp(2)-Cn-Cp(3)	105.0(2)
Ni(2)-Ni(4)	2.454(3)	Cp(2)-Cn-Cp(4)	103.6(2)
Ni(3)-Ni(4)	2.471(3)	Cp(3)-Cn-Cp(4)	105.1(2)
Mean	2.461(5)	Mean	104.6(5)
H(1)···H(2)	2.317(11)	Overall Mean Values	
H(1)···H(3)	2.305(10)	Ni-H-Ni	93.9(3)
H(2)···H(3)	2.326(9)	H-Ni-H	86.1(6)
Mean	2.316(6)	Ni-Ni-Ni	60.0(2)

(Table IV continued on next page)

(Table IV continued)

	Distances (Å)
Ni(1)-Cp[c](1)	1.758(2)
Ni(2)-Cp(2)	1.761(2)
Ni(3)-Cp(3)	1.763(2)
Ni(4)-Cp(4)	1.764(2)
Mean	1.763(1)
Cn[d]-Cp(1)	3.279(2)
Cn-Cp(2)	3.258(2)
Cn-Cp(3)	3.262(2)
Cn-Cp(4)	3.268(2)
Mean	3.263(3)
Overall Mean Values	
Ni-Ni	2.469(6)
Ni-H	1.691(8)
Ni-Cp	1.762(1)
Cn-Cp	3.267(5)
C-C (Cp rings)	1.408(5)
C-H	1.076(8)

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[a] Standard deviations of mean values calculated as in Table III.

[b] The numbering of Ni(2) and Ni(4), as well as their attached Cp rings, has been interchanged compared to that given in (30). This has been done to ensure that atom numbers increase upon clockwise rotation when viewed along the three-fold axis, with Ni(1) pointing up.

[c] Cp = ring centroid

[d] Cn = Ni_4 centroid

Figure Captions

Figure 1. Schematic view of $HW_2(CO)_8(NO)(P(OMe)_3)$

Figure 2. Schematic view of $HFeCo_3(CO)_9(P(OMe)_3)_3$

Figure 3. Molecular structure of $HFeCo_3(CO)_9(P(OMe)_3)_3$ with thermal ellipsoids drawn to enclose 50 percent probability (31). Methoxy groups have been removed for clarity. (a) View normal to the three-fold molecular axis. (b) View approximately along the three-fold axis.

Figure 4. Schematic view of $H_3Ni_4(Cp)_4$.

Figure 5. The H_3Ni_4 core of $H_3Ni_4(Cp)_4$, drawn with thermal ellipsoids enclosing 50 percent probability. (a) View approximately along the three-fold molecular axis. (b) View approximately normal to the Ni(1)-Ni(2) bond.

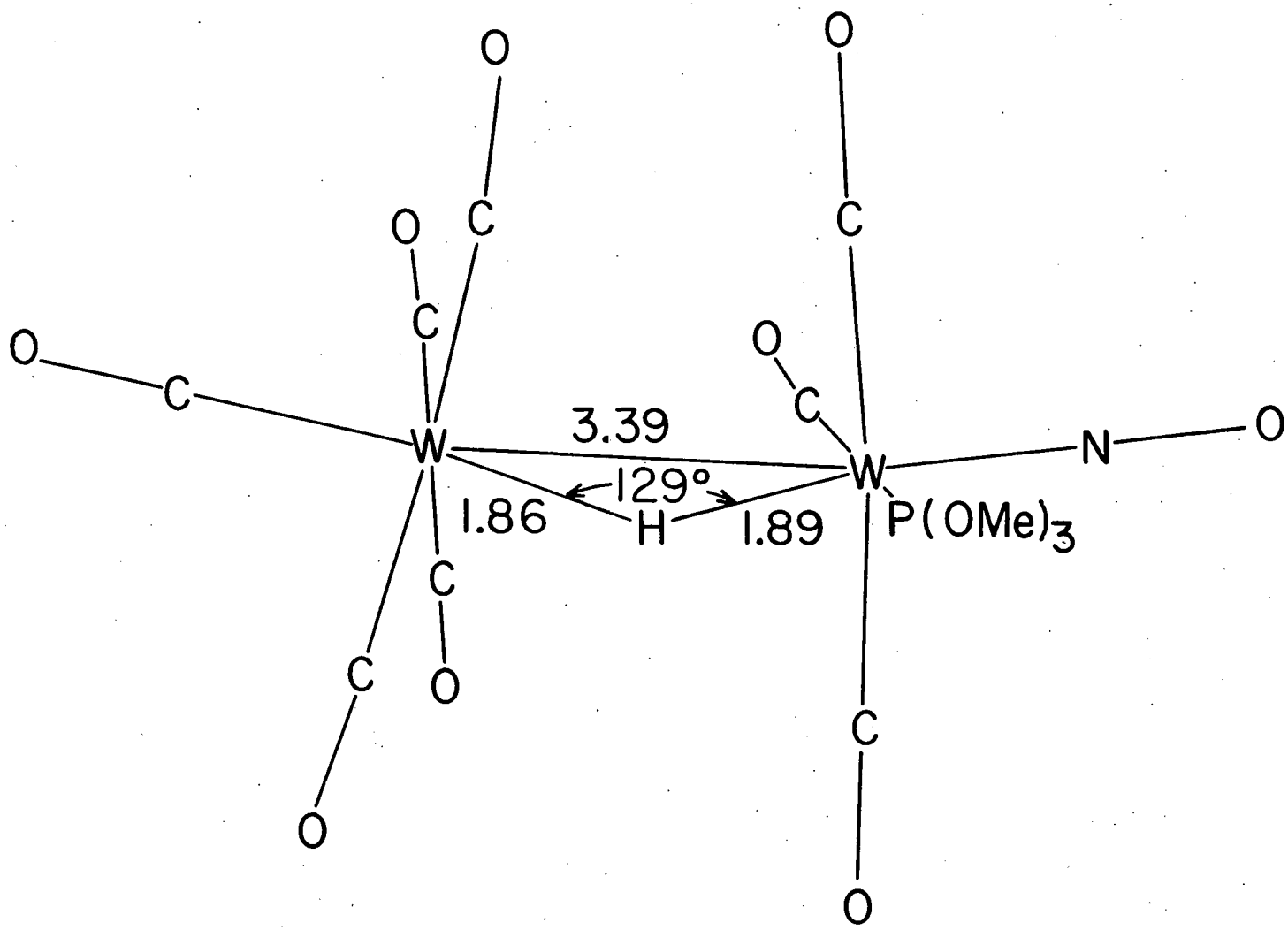

Figure 1
Neg # 11-487-76

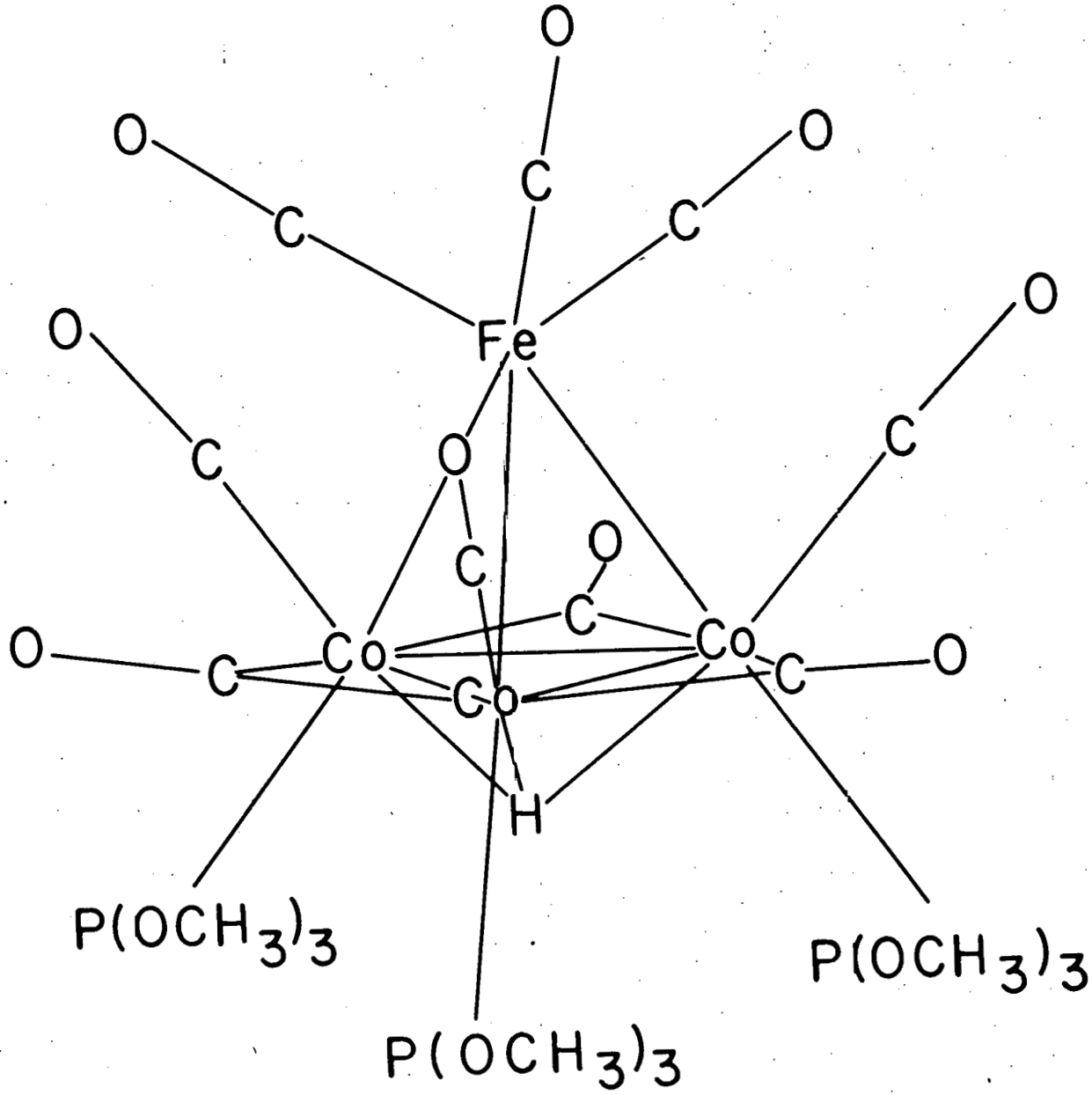

Figure 2
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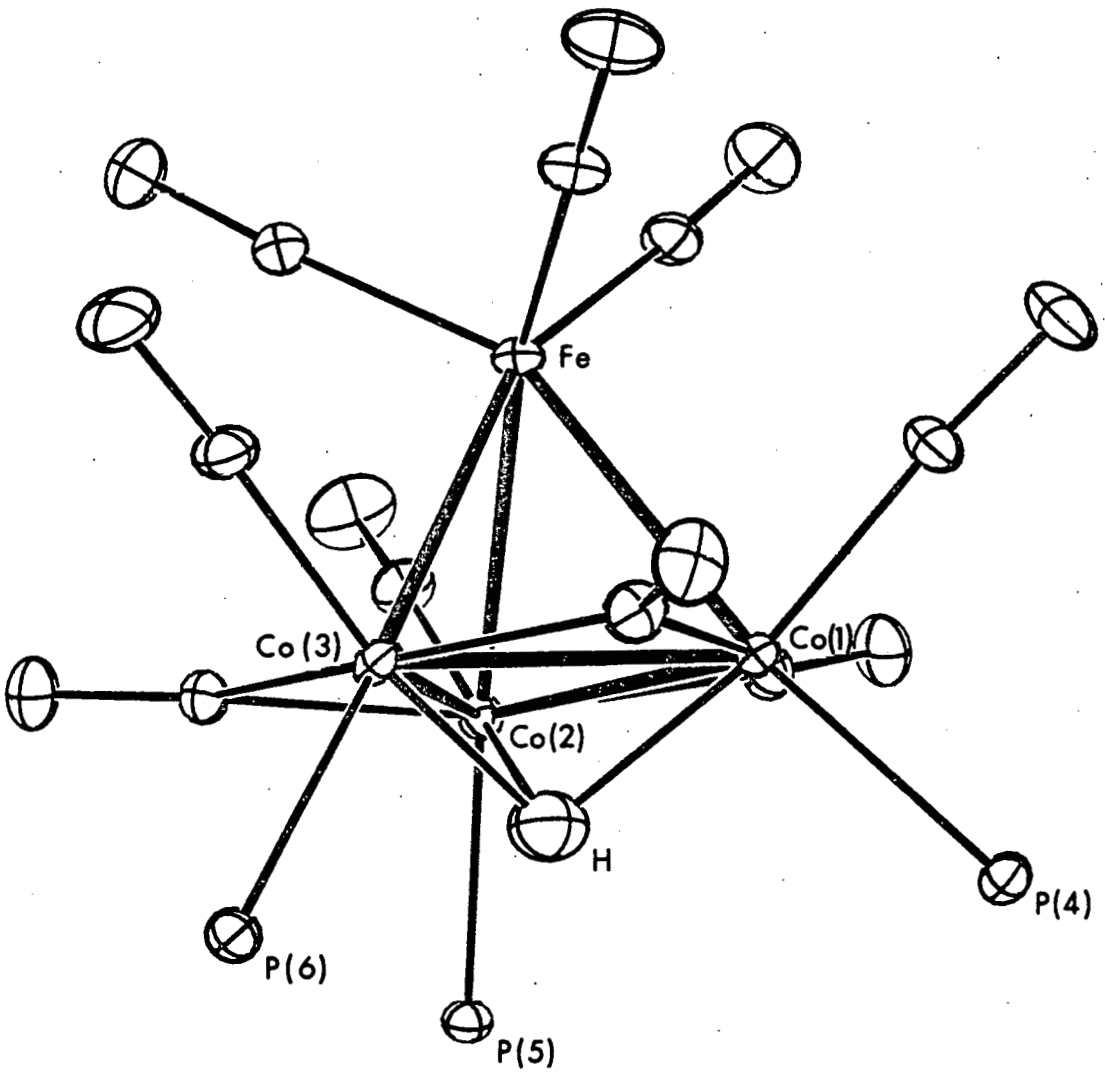


Figure 3a

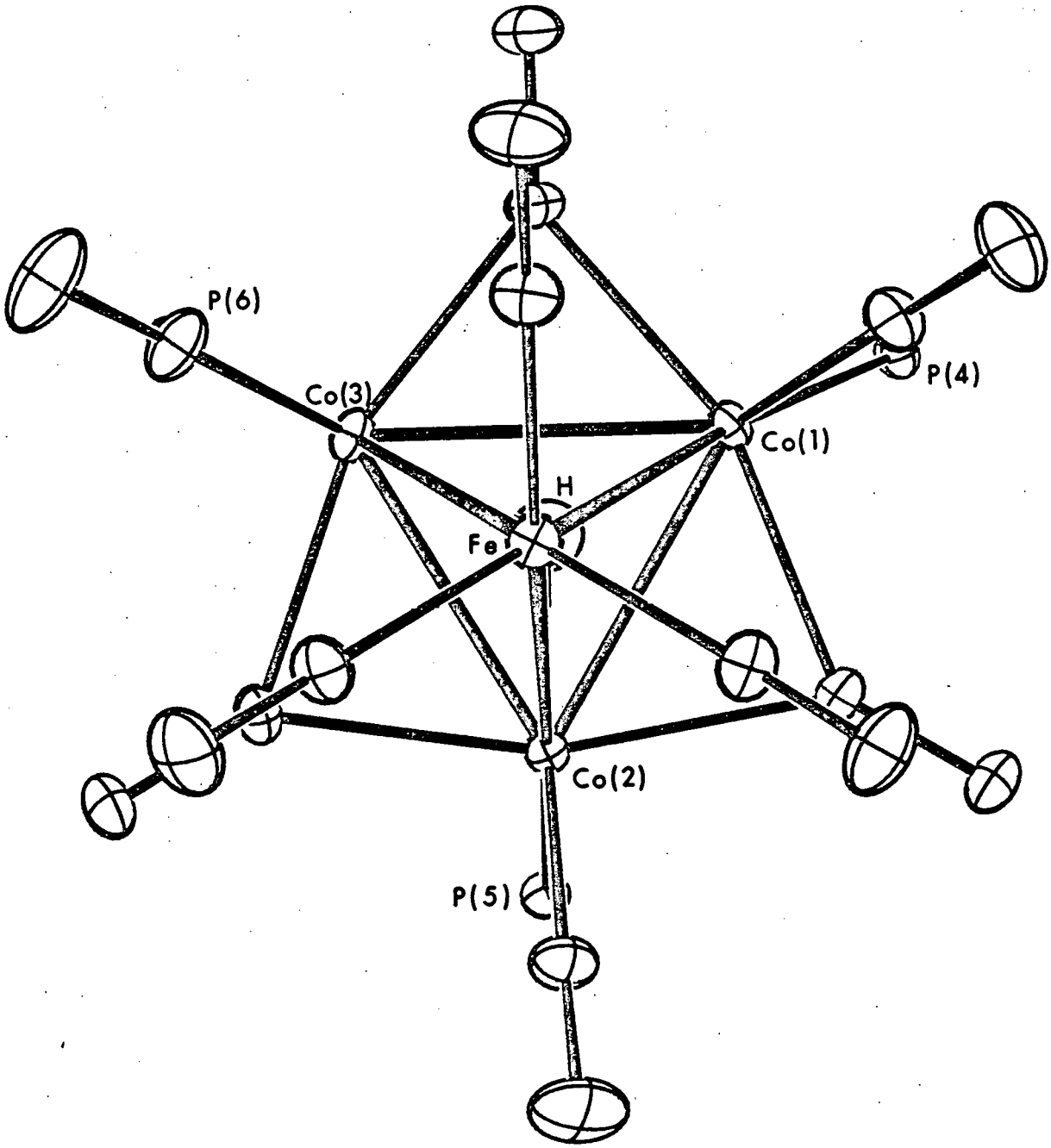


Figure 3b

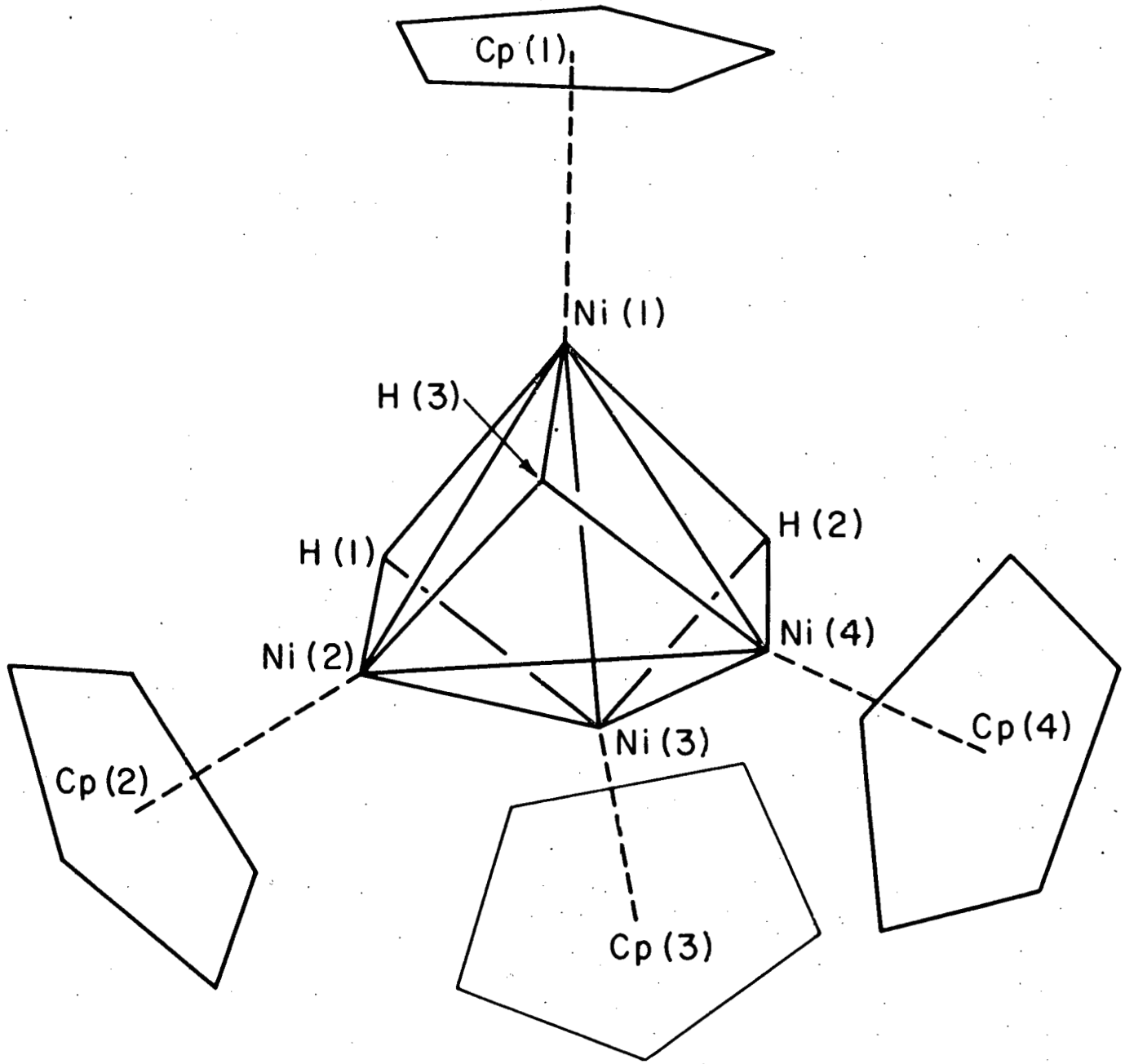
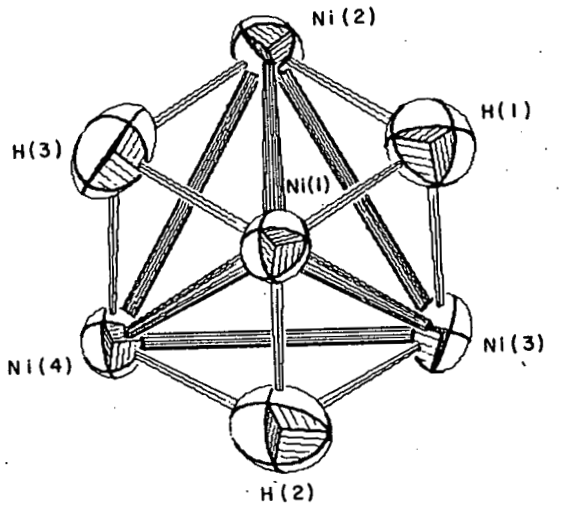
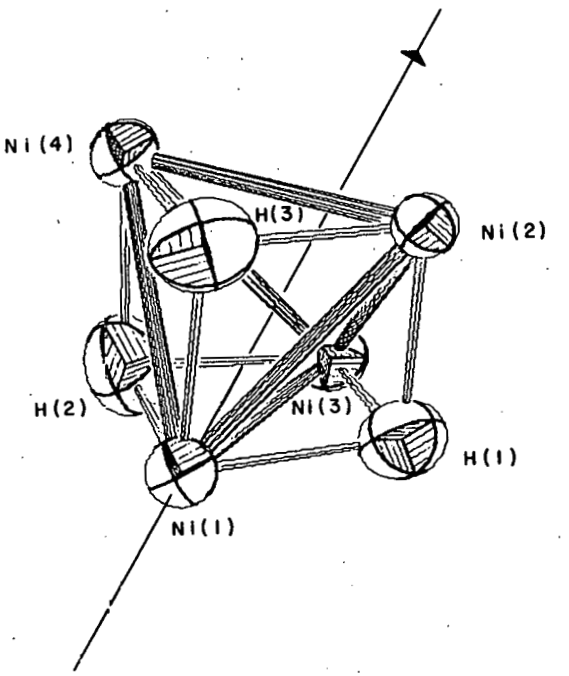


Figure 4
Neg # 6-912-77



(a)



(b)

Figure 5
Neg # 6-1115-77