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AB INITIO MOLECULAR ORBITAL STUDIES OF SOME HIGH TEMPERATARE METAL HALIDE COMPLEXES

by

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ABSTRACT

The use of *ab initio* molecular orbital calculations to aid in the characterization, *i.e.*, structures and energies, of metal halide complexes present in high temperature salt vapors has been investigated. Standard LCAO-SCF methods were used and calculations were carried out using the minimal STO-3G basis set. The complexes included in this study were Al_2F_6, Al_2Cl_6, $AlF_3 \cdot NH_3$, $AlCl_3 \cdot NH_3$, and $AlF_3 \cdot N_2$. The Al_2X_6 complexes are found to have D_{2h} symmetry in agreement with most experimental results. A planar form was found to be considerably higher in energy. The $AlX_3 \cdot NH_3$ complexes are found to have C_{3v} symmetry with a small barrier to rotation about the Al-N axis. The $AlF_3 \cdot N_2$ complex is found to be weakly bound together with a binding energy of -8.2 kcal/mole at the STO-3G level.

INTRODUCTION

There has been considerable interest in the complexes formed in the high temperature vapors (300-500°C) of metal halide compounds having low volatility.[1-3] Vapor density, molecular beam, and mass spectrometric methods have been among the techniques used to help identify the polymeric species present in the high temperature vapors. Information on the structures of these complexes has been obtained using electron diffraction with help from raman, infrared, and microwave spectroscopy. Still, there are many unanswered questions concerning the nature of the complexes.

In order to investigate some of these questions, we have undertaken a study of the use of *ab initio* molecular orbital theory as an aid in the characterization of metal halide complexes present in high temperature molten salt vapors. The complexes considered in this study are: (a) the aluminum halide dimers, Al_2F_6 and Al_2Cl_6; (b) the complexes between an aluminum halide molecule and ammonia, $AlF_3 \cdot NH_3$ and $AlCl_3 \cdot NH_3$; and (c) the complex between aluminum trifluoride and nitrogen, $AlF_3 \cdot N_2$. The structures and energies of these complexes are determined using a minimal basis set. In addition, force constants and electron distributions of several of these complexes are calculated.

Theoretical calculations on these complexes may help to answer questions raised by some of the experimental results such as whether Al_2Cl_6 is distorted from D_{2h} symmetry by rotation about a torsion axis as suggested by a recent electron diffraction study and whether $AlCl_3 \cdot NH_3$ is eclipsed or staggered. Also, these calculations can give information on such things as the structure of the planar form of Al_2Cl_6 and on the strength of the bond between AlF_3 and N_2.

CALCULATIONAL METHODS

In the following study standard molecular orbital methods[4,5] are employed. The type of calculation carried out here is *ab initio* in the sense that it does not use any experimental information (except for the values of fundamental constants). *Ab initio* theories are generally divided into single determinant methods which use a single molecular orbital configuration and more complicated configuration interaction methods in which the wave function is written as the sum of several determinants.

In all the calculations carried out here a spin restricted single determinant method for closed shell molecules (singlets) has been used. In this method pairs of electrons are assigned to spatial molecular orbitals, ψ_i, which are in turn approximated as linear combinations of a set of basis functions ϕ_u,

$$\psi_i = \sum_u c_{ui} \phi_u \qquad (1)$$

The coefficients c_{ui} are then chosen by a variational procedure in which the total energy of the molecule is minimized.

There are various different types of basis sets that are used in *ab initio* single determinant methods. The simplest is the minimal which consists of just enough atomic-orbital type functions to describe the ground state of the corresponding atom (1s for hydrogen; 1s, 2s, $2p_x$, $2p_y$, $2p_z$ for fluorine). Improvements can be made on the minimal basis set by adding more s and p functions. These are generally called extended basis sets. Also these basis sets can be augmented by the addition of *d* or polarization functions. In all the calculations reported in this paper the minimal STO-3G basis set[5] has been used.

The STO-3G basis set uses a set of Slater type functions that are replaced by a least squares-fitted combination of three gaussian functions.

In a study of molecules containing second row atoms Collins *et al.*[6] noted that although the STO-3G basis is small and lacks *d* functions, it does quite well in determining the geometries of molecules containing aluminum atoms. The optimized STO-3G geometries for AlF_3 and $AlCl_3$ in Table I are in very good agreement with the observed geometries. Hence, it is reasonable to expect that the STO-3G basis should do well for the structures of the complexes considered in this paper: Al_2F_6, Al_2Cl_6, $AlF_3 \cdot NH_3$, $AlCl_3 \cdot NH_3$ and $AlF_3 \cdot N_2$.

The structures of these complexes can be described in terms of a set of geometrical parameters which are discussed in the next section. In the geometry optimization procedure used here these parameters are optimized with respect to the total energy. The resulting bondlengths and bond angles are believed to have computational uncertainties of ± 0.01 Å and ± 1°, respectively.

RESULTS AND DISCUSSION

Al_2F_6 and Al_2Cl_6. For Al_2F_6 and Al_2Cl_6 we have considered the two structures illustrated in Fig. 1. Structure I is formed when two tetrahedra share a common edge. The aluminum atoms are located at the center of the tetrahedron and the halide atoms are at the apexes of the tetrahedra. Structure II is similar to I except that it is completely planar.

In the geometry optimization of Al_2Cl_6 (structure I) D_{2h} symmetry was imposed and the two tetrahedra were allowed to distort with the exception that the terminal Al-Cl bondlengths were kept fixed at the STO-3G optimized value for $AlCl_3$ of 2.05 Å. This should be a good approximation since, as is shown later, the terminal Al-F bondlengths in Al_2F_6 do not change significantly upon optimization. The parameters optimized are listed in Table II along with the resulting values. The bridged Al-Cl bondlengths (2.24 Å) in Al_2Cl_6 lengthen by 0.19 Å over their value in the monomer. The terminal ClAlCl bond angles increase only slightly from 120.0° in the monomer to 122.8 in the dimer while the bridged ClAlCl angle decreases to 94.7°.

The D_{2h} symmetry of structure I was tested by rotating the terminal $AlCl_2$ groups about axes (ϕ_1 and ϕ_2 in Fig. 1) containing the bisectors of the terminal ClAlCl angles and the two aluminum atoms. Rotation of the two $AlCl_2$ groups by 5° in the same direction ($+\phi_1$, $+\phi_2$) and in opposite directions ($+\phi_1$, $-\phi_2$) both led to increases in energy. Hence, the D_{2h} symmetry of structure I appears to be a definite minimum in the energy surface.

The geometry optimization of the planar structure of Al_2Cl_6(II) led to the results given in Table II. The energy of structure II is 84.2 kcal/mole above that of structure I indicating considerable unfavorable interaction between the terminal chlorines and the bridged chlorines in the planar configuration. This is also indicated by the decrease in the terminal ClAlCl bond angle from 120.0° in monomer to 103.3 in the dimer.

Experimentally, the structure of Al_2Cl_6 has been studied using electron diffraction by Palmer and Elliot[7] in 1938 and by Akishin, Rambidi and Zasorin[8] in 1959. Both groups concluded that it has D_{2h} symmetry corresponding to structure I in Fig. 1 and the geometries that they determined are in good agreement with the STO-3G results (see Table II). The electron diffraction results for Al_2Cl_6 indicate that the bridge Al-Cl distances increase by 0.15 - 0.18 Å compared to the STO-3G prediction of 0.19 Å. Both theory and experiment indicate that the terminal ClAlCl bond angle in the complex changes very little from the ClAlCl angle of 120° in the monomer. The experimental results indicate that the bridge ClAlCl angle in the complex decreases considerably from what it is in the monomer to a value of 80-87°. The STO-3G calculation gives an angle of 94.7°.

Some experimental results have indicated that there may be some distortion of the D_{2h} symmetry of Al_2Cl_6 by a rotation of one of the $AlCl_2$ groups about an axis (χ in Fig. 1) passing through the two bridged chlorines. To check out this possibility we carried out a STO-3G calculation on structure I with one of the $AlCl_2$ groups rotated by 5° about the χ axis and found that the energy increased. This seems to indicate that the equilibrium structure of Al_2Cl_6 does not have a tendency to distort from its D_{2h} symmetry.

An estimate of the rigidity of twisting about the χ axis in comparison to the other motions may be made by calculating the second derivatives of the Al_2Cl_6 energy with respect to coordinates corresponding to these motions. These derivatives may be approximated by changing each angle by ± 5° and using the formula

$$\partial^2\varepsilon/\partial x^2 = [\varepsilon(x + \Delta) + \varepsilon(x-\Delta) - 2\varepsilon(x)]/\Delta^2 \qquad (2)$$

where x is the coordinate, Δ is the size of the variation in the coordinate, and ε is the energy. For χ, ϕ, and $\Theta = \angle ClAlCl$ the following results (with energy in atomic units and angles in radians) are obtained:

$$\partial^2\varepsilon/\partial\chi^2 = 0.03228$$

$$\partial^2\varepsilon/\partial\phi_1^2 = 0.16770$$

$$\partial^2\varepsilon/\partial\Theta^2 = 0.15744$$

They indicate that the χ coordinate corresponds to a loose motion when compared to the Θ and ϕ coordinates which are more rigid.

Turning now to the Al_2F_6 complex, the geometry of structure I (Fig. 1) was optimized in a similar manner as for structure I of Al_2Cl_6 except that the Al-F bond lengths were included in the optimization procedure. The parameters optimized and their resulting values are given in Table II. The D_{2h} symmetry of this structure was tested in the same manner as in the case of Al_2Cl_6 by twisting the terminal FAlF groups about the Al-Al axis (ϕ_1 and ϕ_2) and about the $F_{br}-F_{br}$ axis (χ). The results indicated that D_{2h} symmetry was again preferred.

The planar Al_2F_6 structure (II in Fig. 1) was also optimized in a similar manner to the Al_2Cl_6 structure. The results are given in Table II. The energy is again considerably higher (69.6 kcal/mole) than structure I.

In other work[9] structures were considered for Al_2F_6 complexes in which the bridge was composed of 0, 1, and 3 fluorines. All of these structures were also found to be less stable than structure I.

The Al_2F_6 geometry has not been measured experimentally, but has been estimated[10,11] by comparing the geometries of AlF_3, $AlCl_3$, and Al_2Cl_6. (See Table II) The only major discrepancy between the STO-3G and the estimated geometries is for the bridge FAlF angle. The STO-3G results indicate that the angle in Al_2F_6 is 80.0°, a decrease from 94.7° in Al_2Cl_6. In contrast, the estimated angle for Al_2F_6 is 90-98°, an increase from 80-87° in Al_2Cl_6. Since fluorine has a smaller van der Waals radius than chlorine it would be expected that the fluorines should be closer together in the bridge. Hence, the STO-3G prediction for the bridge angle in Al_2F_6 is probably more reasonable than the estimated value.

Table III gives complexation energies for Al_2F_6 and Al_2Cl_6 (*i.e.*, the difference between the energy of the complex and the energy of two monomers). The AlF_3 dimer (structure I) has a complexation energy of -112.9 kcal/mole. Correction[12] for differences in vibrational, rotational and translational energies between the complex and two AlF_3 molecules gives an enthalpy of complexation of -109.9 kcal/mole. The $AlCl_3$ dimer (structure I) has a complexation energy of -46.7 kcal/mole and an enthalpy of complex formation of -45.1. Experimentally[10] the enthalpies of complex formation have been measured to be -49.0 kcal/mole for Al_2F_6 and -30.2 kcal/mole for Al_2Cl_6. Hence, the STO-3G basis set overestimates by a considerable amount the interaction energy of these complexes. A larger basis set is probably necessary to obtain reasonable complexation energies.[9] However, the STO-3G basis appears to do adequately when it comes to the geometries of these complexes.

$AlF_3 \cdot NH_3$ and $AlCl_3 \cdot NH_3$. We initially considered ethane-like structures with C_{3v} symmetry for $AlF_3 \cdot NH_3$ and $AlCl_3 \cdot NH_3$ as illustrated in Fig. 2. STO-3G optimized geometries for AlF_3 (Table I), $AlCl_3$ (Table I), and NH_3[13] (r(N-H) = 1.033Å, ∠HNH = 104.2°, E = -55.45542 a.u.) were used as initial guesses for the structures. The geometry and rotational conformation of each complex was determined.

Both staggered and eclipsed forms of $AlF_3 \cdot NH_3$ were optimized. The geometry of the eclipsed form is listed in Table IV. The optimized Al-N bondlength is 1.99Å while the optimized values of the Al-F and N-H bondlengths in the complex remain nearly the same as in the monomers. The optimized geometry of the staggered form is nearly the same as the eclipsed form and is only 0.33 kcal/mole higher in energy. Hence, the barrier to rotation about the Al-N axis is very small.

The possibility that the $AlF_3 \cdot NH_3$ complex does not have C_{3v} symmetry was investigated by relaxing its symmetry to C_s, *i.e.*. a plane of symmetry passing through the Al-N axis, one of the hydrogens and one of the fluorines. It was found that any changes in the geometry away from C_{3v} symmetry led to a higher energy. Hence, the minimum energy structure for $AlF_3 \cdot NH_3$ appears to have C_{3v} symmetry.

In the case of the $AlCl_3 \cdot NH_3$ complex the same parameters as for the $AlF_3 \cdot NH_3$ complex were optimized with the exception that the Al-F and N-H bondlengths were held fixed. This should be a good approximation since they do not change significantly upon optimization for $AlF_3 \cdot NH_3$. Both staggered and eclipsed forms were optimized. In contrast to $AlF_3 \cdot NH_3$, the staggered rotational conformation is lower in energy than the eclipsed form. Again, the difference in energy between the two forms is very small (0.13 kcal/mole). The resulting geometry for the staggered conformation is given in Table IV.

The STO-3G results for $AlCl_3 \cdot NH_3$ are in very good agreement with the electron diffraction study of Hargittai *et al.*[14] as indicated in Table IV. The theoretical results for the similar complex, $AlF_3 \cdot NH_3$, indicate that the assumption of C_{3v} symmetry in the interpretation of the experimental results is valid. The STO-3G results also indicates that there is almost free rotation about the Al-N axis. This may be due to the fact that the interaction between the chlorines and the hydrogens is quite small.

The energies for $AlF_3 \cdot NH_3$ and $AlCl_3 \cdot NH_3$ are given in Table III. The $AlF_3 \cdot NH_3$ complex has a binding energy of -41.3 kcal/mole and that of the $AlCl_3 \cdot NH_3$ is -62.1 kcal/mole. Correction for differences in vibrational, rotational and translational energies between the complex and the AlX_3 and NH_3 molecules is difficult to calculate because many of the vibrational frequencies of the complex have not been reported. However, the correction should be small (∿2-4 kcal/mole) as it was for Al_2F_6 and Al_2Cl_6. Experimentally,[15] the enthalpy of complex formation of $AlCl_3 \cdot NH_3$ has been measured to be -39.9 kcal/mole. Again, as in the case of the $AlCl_3$ dimer, the STO-3G basis set overestimates the interation energy by a considerable amount. However, it does find that $AlCl_3 \cdot NH_3$ is more strongly bound together than Al_2Cl_6 in agreement with the experimental results.

It is interesting to compare the strengths of the various complexes considered so far. In the case of the Al_2X_6 complexes the largest binding energy occurs when X = F, whereas, in the case of the $AlX_3 \cdot NH_3$ complexes the largest binding energy occurs when X = Cl. One explanation for this result can be found in the STO-3G Mulliken population analysis[16] in Table V. The aluminum atom has more of a positive charge on it in $AlCl_3$ than in AlF_3.

Hence, on the basis of a simple electrostatic interaction picture the $AlCl_3 \cdot NH_3$ complex is indeed expected to have a more negative binding energy than $AlF_3 \cdot NH_3$. On the other hand Al_2F_6 has a more negative binding energy than Al_2Cl_6 because there is probably more repulsion between the two bridged chlorines than between the two bridged fluorines due to the fact that the chlorines are larger in size and have more negative charge than the fluorines.

<u>$AlF_3 \cdot N_2$</u>. The possibility that complexes may be formed between $AlCl_3$ and nonpolar gases such as argon and nitrogen is quite intriguing, but no evidence for complexes of that type has yet been found.[17] To investigate this possibility we carried out calculations on the complex between AlF_3 and N_2. The structure considered is illustrated in Fig. 2. STO-3G optimized geometries for AlF_3 (Table I) and N_2[13] (r(N-N) = 1.134Å, E = -107.50065 a.u.) were used as initial guesses for the structure.

Optimization of the geometry of $AlF_3 \cdot N_2$ indicates that N_2 lies on the C_3 axis of the AlF_3 molecule and is pointed towards the aluminum. The resulting geometry is

r(Al-N') = 2.942Å	∠FAlN' = 94.5°
r(Al-F) = 1.605Å	∠AlN'N = 180.0°
r(N'-N) = 1.136Å	

The AlF_3 becomes pyramidal in the complex. The N-N bondlength increases slightly by 0.002Å in the complex. A complex in which the N_2 molecule was situated perpendicular to the C_3 axis was also investigated. It was found to be considerably higher in energy than the complex in which N_2 coincided with the C_3 axis.

The binding energy of the $AlF_3 \cdot N_2$ complex is -8.2 kcal/mole which is on the order of the binding energy of some hydrogen bonded complexes,[18] but considerably smaller than that of most alkali halide complexes. Hence, since most hydrogen bonded complexes are difficult to "see" with such techniques as electron diffraction or infrared spectroscopy, the $AlF_3 \cdot N_2$ complex probably would also be difficult to detect with such techniques. This would also apply to complexes of the other aluminum halides with N_2 such as $AlCl_3 \cdot N_2$.

CONCLUSIONS

The following conclusions from this theoretical study of high temperature salt vapor species can be drawn:

(1) Theoretical calculations can provide useful information concerning the structures and energies of metal halide complexes and may be helpful in the future as an aid in their characterization.

(2) Both Al_2F_6 and Al_2Cl_6 are found to have D_{2h} bridged structures. The energies of both are overestimated by the STO-3G basis while the STO-3G optimized geometries are in good agreement with experimental and estimated geometries.

(3) The STO-3G basis set results indicate that the experimental assumption of C_{3V} symmetry for complexes of the type $AlX_3 \cdot NH_3$ is valid. The barrier to rotation about the Al-N axis is found to be very small.

(4) The $AlF_3 \cdot N_2$ complex is found to have a binding energy of -8.2 kcal/mole. This is on the order of the typical hydrogen bonded complex and not nearly as strong as the other metal halide complexes considered in this study.

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Table 1. STO-3G optimized geometries[a] for AlF_3 and $AlCl_3$ (experimental values in parentheses).

	r(Al-X), Å	XAlX, degrees	Energy, a.u.
AlF_3[b]	1.60 (1.63 ± 0.01)	120. (120)	-533.24983
$AlCl_3$[c]	2.05 (2.06 ± 0.01)	120. (118 ± 1.5)	-1603.02719

[a] C_{3v} symmetry assumed.

[b] Theory: reference 6 (note that the optimized bondlength is incorrectly reported as 1.56 Å in this reference).

Experiment: reference 8.

[c] Theory: this work.

Experiment: E. Z. Zasorin and N. G. Rambidi, Zh. Strukt. Khim, 8, 391 (1967).

Table II. STO-3G optimized geometries[a] for Al_2F_6 and Al_2Cl_6 (experimental results[b,c] in parentheses).

Structure[d]	Parameter[d]	Al_2F_6	Al_2Cl_6
I	r(Al-X)	1.60 (1.63, 1.63)[b]	2.05[e] (2.06, 2.04)[c]
	r(Al-X_{br})	1.72 (1.80, 1.80)	2.24 (2.21, 2.24)
	∠XAlX	124.6° (120°, 116°)	122.8° (118°, 122°)
	∠X_{br}AlX_{br}	80.0° (90°, 98°)	94.7° (80°, 87°)
II	r(Al-X)	1.61	2.05[e]
	r(Al-X_{br})	1.75	2.31
	∠XAlX	104.2°	103.3°
	∠X_{br}AlX_{br}	73.0°	75.5°

[a] The parameters r(Al-X_{br}) and ∠X_{br}AlX_{br} are given for comparison with experiment. The parameters actually optimized were r(X_{br}-X_{br}) and r(Al-Al). Bondlengths are in Å.

[b] For Al_2F_6 the experimental geometries were estimated from the geometries of AlF_3, $AlCl_3$, and Al_2Cl_6. The first set of values is from reference 10 and the second set is from reference 11.

[c] For Al_2Cl_6 the first set of values is from reference 7 and the second set is from reference 8.

[d] Illustrated in Figure 1.

[e] Not optimized.

Table III. STO-3G energies.

Complex	Energy, a.u.	Complexation Energy, a.u.
Al_2F_6(I)	-1066.67961	-112.9
Al_2F_6(II)	-1066.56863	- 43.3
Al_2Cl_6(I)	-3206.12874	- 46.7
Al_2Cl_6(II)	-3205.99466	+ 37.5
$AlF_3 \cdot NH_3$	- 588.77113	- 41.3
$AlCl_3 \cdot NH_3$	-1658.58159	- 62.1
$AlF_3 \cdot N_2$	- 640.76356	- 8.2

Table IV. STO-3G optimized geometries[a] for $AlF_3 \cdot NH_3$ and $AlCl_3 \cdot NH_3$ (experimental results[b] in parentheses).

Geometrical Parameter[c]	$AlF_3 \cdot NH_3$	$AlCl_3 \cdot NH_3$
r(Al-N)	1.99	1.94 (1.996)
r(Al-X)	1.62	2.05[d] (2.10)
r(N-H)	1.03	1.03[d]
∠XAlN	100.1°	101.2° (101.0°)
∠HNAl	112.2°	112.4°
ϕ	0.0°	180.0°

[a] $AlF_3 \cdot NH_3$ is eclipsed and $AlCl_3 \cdot NH_3$ is staggered. Bondlength in Å.

[b] Ref. 14

[c] Defined in fig. 2.

[d] Held fixed at the monomer values.

Table V. Atomic Populations of AlF_3, $AlCl_3$, $AlF_3 \cdot NH_3$, and $AlCl_3 \cdot NH_3$.

	AlX_3		$AlX_3 \cdot NH_3$			
	Al	X	Al	X^a	N	H^a
X=F	11.825	9.392	11.838	9.449	7.494	0.773
X=Cl	11.730	17.423	11.731	17.510	7.503	0.746

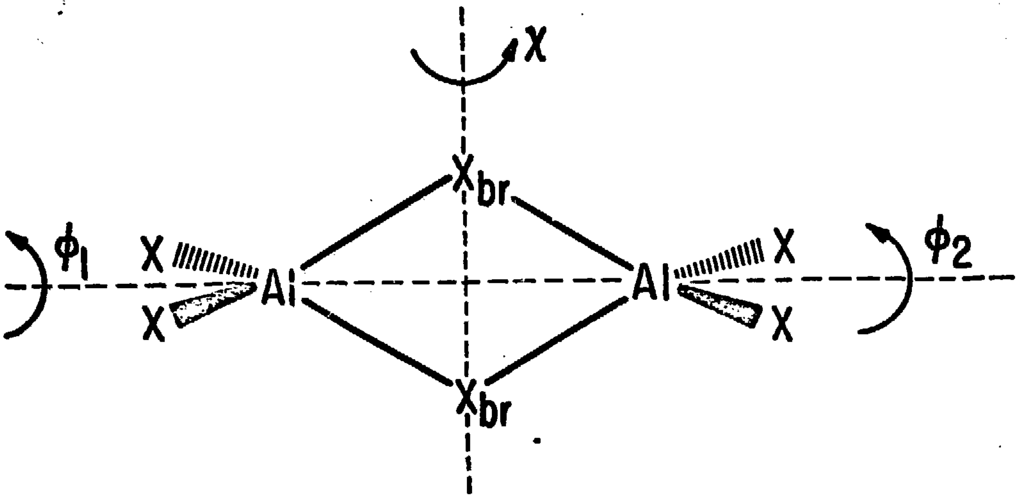
[a] The population of all three atoms in each group are equivalent to the accuracy shown.

Figure Captions

Figure 1. Al_2X_6 structures with X = F or Cl.

Figure 2. Structure of $AlX_3 \cdot NH_3$ (in the figure $\phi = 180°$).

Figure 3. Structure of $AlX_3 \cdot N_2$.



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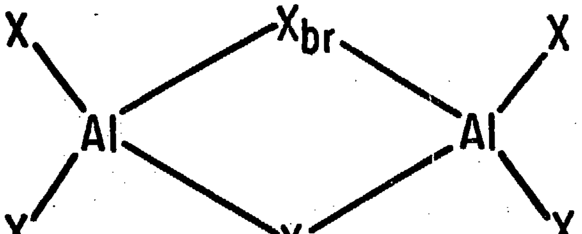

II

Fig. 1

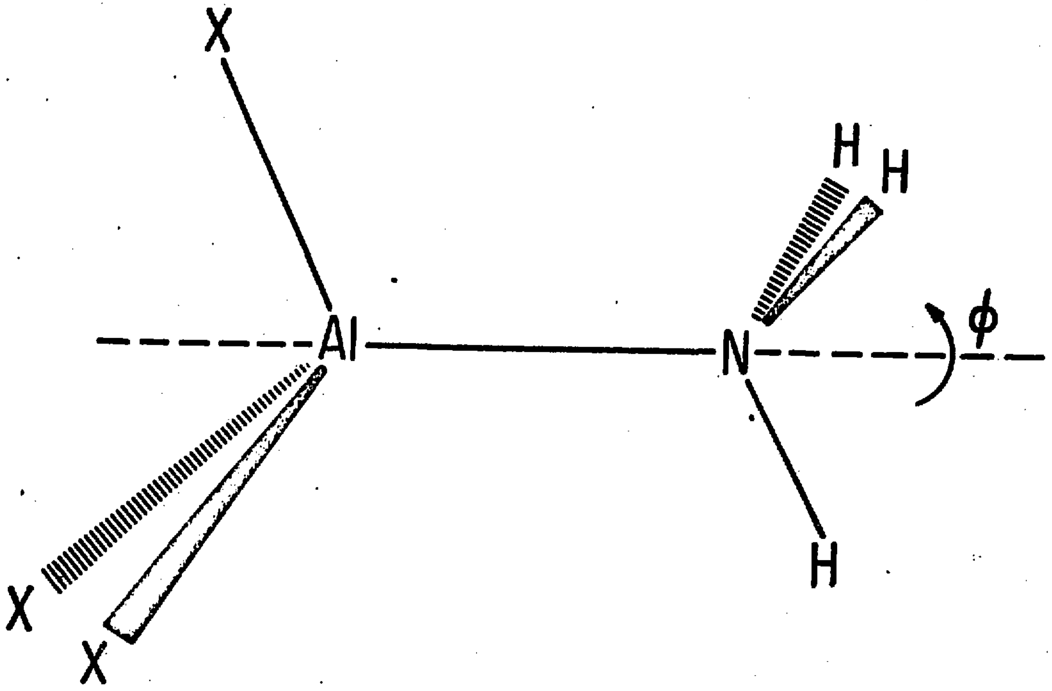

Fig. 2

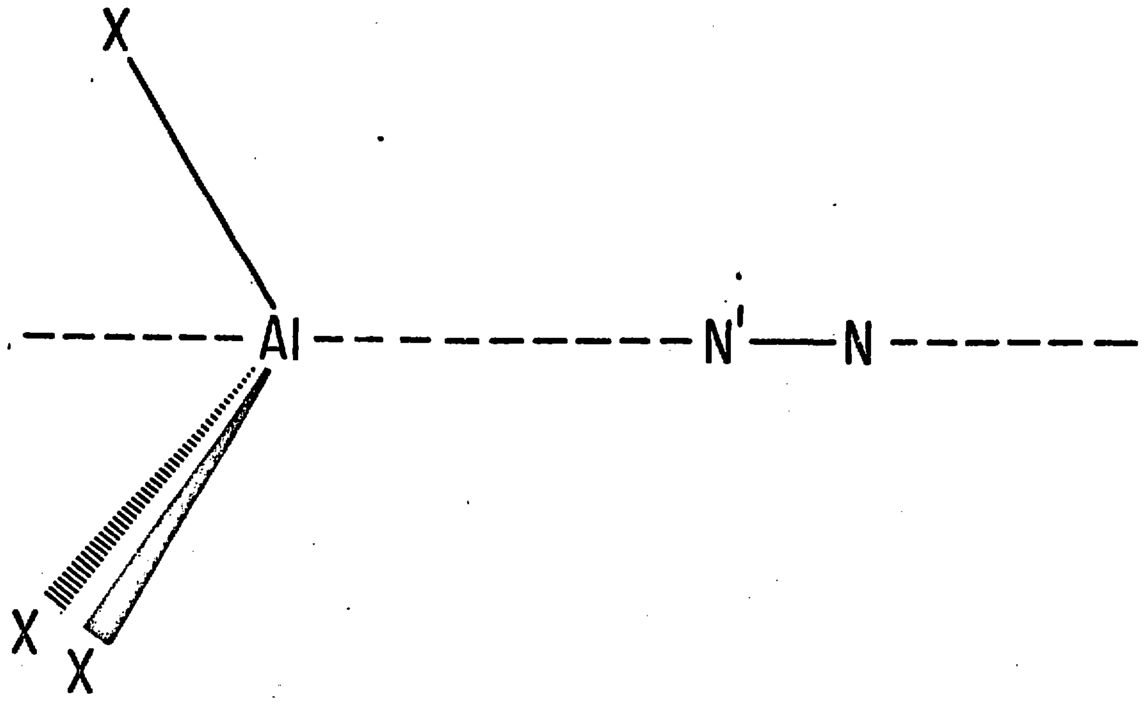

Fig. 3