Inorg. Chem. **1981**, *20*, 1179–1181 **1179**

Contribution from the Department of Chemistry,
University of Texas at Austin, Austin, Texas 78712

Crystal and Molecular Structure of the 1:2 Aluminum Trichloride–Tetrahydrofuran Complex AlCl$_3$·2THF

ALAN H. COWLEY,* MIKE C. CUSHNER, RAYMOND E. DAVIS,* and PAUL E. RILEY

Received July 7, 1980

The crystal structure of AlCl$_3$·2THF, which is formed by dissolution of (Me$_2$N)$_3$SiCl·AlCl$_3$ in THF, has been determined by single-crystal X-ray diffraction techniques with three-dimensional data gathered at −35 °C by counter methods. Colorless, blocky crystals of AlCl$_3$·2THF form in orthorhombic space group *Pbcn* with unit cell constants a = 10.359 (2), b = 9.803 (4), and c = 12.617 (5) Å at −35 °C. Full-matrix least-squares refinement of the structure converged with an R index (on $|F|$) of 0.028 for the 1154 symmetry-independent reflections within the Mo Kα shell defined by $4° < 2\theta < 55°$ which have $I_0/\sigma(I_0) > 2.0$. The molecules possess nearly idealized trigonal-bipyramidal geometry with the Cl atoms at equatorial positions and the THF ligands at axial sites. Perhaps unexpectedly, the THF ligands are well ordered and exhibit an envelope conformation (C_s symmetry) in which a carbon atom forms the "flap" of the envelope. The arrangement of the molecules in the crystal approximates that of a hexagonal closest packed structure.

Introduction

Recently we investigated[1] the reaction of (Me$_2$N)$_3$SiCl with Al$_2$Cl$_6$ and found that (Me$_2$N)$_3$SiCl·AlCl$_3$, a 1:1 N→AlCl$_3$ Lewis acid–base complex, was formed rather than the salt, [(Me$_2$N)$_3$Si]$^+$[AlCl$_4$]$^-$. In searching for a recrystallization solvent for (Me$_2$N)$_3$SiCl·AlCl$_3$, it was discovered that tetrahydrofuran (THF) reacts with this material to afford the 1:2 complex AlCl$_3$·2THF.

The direct interaction of aluminum chloride and THF has been studied by various physical techniques—often with conflicting conclusions. For example, in two ^{27}Al NMR studies of this system[2,3] it was suggested that Al$_2$Cl$_6$ simply dissolves in THF without specific complex formation, while more recently ^{27}Al NMR data[4] have suggested the existence of AlCl$_3$·THF, *cis*-AlCl$_3$·2THF, *trans*-AlCl$_3$·2THF, and [AlCl$_2$(THF)$_4$]$^+$[AlCl$_4$]$^-$. Vibrational spectroscopic data[5] of solid materials possessing 1:1 and 1:2 AlCl$_3$/THF compositions indicate that, while the 1:1 material is a simple adduct, the 1:2 species is ionic, viz., [AlCl$_2$(THF)$_4$]$^+$[AlCl$_4$]$^-$. Conductivity experiments with THF solutions of Al$_2$Cl$_6$ have been interpreted in terms of ionic dissociation equilibria[6] and also of rupture of the THF ring.[7]

The foregoing conflicting results emphasize the necessity for definitive structural data on aluminum trihalide/THF compounds. This paper presents the X-ray crystal structure of one compound of this family, that of AlCl$_3$·2THF.

Table I. Molecular Geometry of AlCl$_3$·2THF[a]

Bond Lengths (Å)

Al–Cl(1)	2.163 (1)	O–C(4)	1.471 (2)
Al–Cl(2)	2.154 (1)	C(1)–C(2)	1.498 (3)
Al–O	1.990 (1)	C(2)–C(3)	1.506 (3)
O–C(1)	1.477 (2)	C(3)–C(4)	1.498 (3)

Bond Angles (Deg)

Cl(1)–Al–Cl(2)	121.0 (1)	Al–O–C(4)	122.9 (1)
Cl(2)–Al–Cl(2)′ [b]	118.0 (1)	C(1)–O–C(4)	108.2 (1)
Cl(1)–Al–O	89.4 (1)	O–C(1)–C(2)	105.3 (2)
Cl(2)–Al–O	89.9 (1)	C(1)–C(2)–C(3)	103.3 (2)
O–Al–O′ [b]	178.9 (1)	C(2)–C(3)–C(4)	102.4 (2)
Al–O–C(1)	120.4 (1)	C(3)–C(4)–O	104.8 (1)

Mean Plane[c] of the THF Ligand

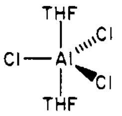
$$0.4109X + 0.8460Y - 0.3397Z - 0.9495 = 0$$

atom	dev from plane, Å	atom	dev from plane, Å
O*	−0.040 (1)	C(4)*	0.025 (2)
C(1)*	0.039 (2)	C(3)	0.584 (2)
C(2)*	−0.025 (2)		

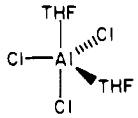
[a] Numbers in parentheses are the estimated standard deviations in the least significant digits. See Figure 1 for identity of the atoms. The average C–H distance is 0.99 ± 0.02 Å, the average H–C–C or H–C–O angle is 110 ± 4°, and the average H–C–H angle is 112 ± 5°. [b] Coordinates of atoms marked with primes are related to the corresponding unprimed atoms of Table IV by the symmetry operation $-x, y, \frac{1}{2} - z$. [c] Orthonormal (Å) coordinate system with axes X, Y, and Z parallel to unit cell vectors a, b, and c. A negative deviation from the plane indicates that the atom with coordinates given in Table IV lies between the plane and the origin of the unit cell.

Results and Discussion

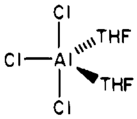
The crystal structure consists of discrete molecules of AlCl$_3$·2THF in which the geometry around aluminum is very close to that of an idealized trigonal bipyramid (see Table I). The molecules possess twofold rotational symmetry with the C_2 axis coincident with the Al–Cl(1) bond (Figure 1). The fact that the trans (diaxial) isomer (**1**) is preferred over the axial–equatorial (**2**) and diequatorial (**3**) isomers is consistent with the generalization that the more electronegative ligands (in this case the oxygen atom of a THF molecule) adopt the axial sites of trigonal-bipyramidal main-group systems. Moreover, structure **1** is the one in which steric interactions between the THF ligands are minimized. A crystal structure analogous to **1** has also been reported for AlCl$_3$·2NHMe$_2$,[9] and, in fact, the trans (diaxial) geometry persists in many other bis(amine) complexes of the group 3A trihalides.[10]



1



2



3

The mean Al–Cl distance in AlCl$_3$·2THF is 2.158 Å, close to the mean value of 2.18 Å found in the crystal structure of AlCl$_3$·2NHMe$_2$.[9] As shown in Table I, the angles about Al are virtually equivalent to the idealized values for a trigonal-bipyramidal complex and do not exhibit the large deviations in the equatorial plane (114–126°) which are observed in AlCl$_3$·2NHMe$_2$. The Al–O distance of 1.990 Å is somewhat

---

(1) Cowley, A. H.; Cushner, M. C.; Riley, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 624.

(2) O'Reilly, D. E. *J. Chem. Phys.* **1960**, *32*, 1007.

(3) Haraguchi, H.; Fujiwara, S. *J. Phys. Chem.* **1969**, *73*, 3467.

(4) Derouault, J.; Granger, P.; Forel, M. T. *Inorg. Chem.* **1977**, *16*, 3214.

(5) Derouault, J.; Forel, M. T. *Inorg. Chem.* **1977**, *16*, 3207 and earlier references cited therein.

(6) Waki, H.; Noboyuki, U.; Yoshio, M.; Nobukito, I. *Nippon Kagaku Zasshi* **1963**, *89*, 1063. Masuki, Y.; Nobukito, I.; Waki, H. *J. Inorg. Nucl. Chem.* **1972**, *34*, 2439.

(7) Evans, G. G.; Gibb, T. R. P., Jr.; Kennedy, J. K.; Del Greco, F. P. *J. Am. Chem. Soc.* **1954**, *76*, 4861.

(8) Muetterties, E. L.; Schunn, R. A. *Q. Rev., Chem. Soc.* **1966**, *20*, 245.

(9) Ahmed, V. A.; Schwarz, W.; Weidlein, J.; Hess, H. *Z. Anorg. Allg. Chem.* **1977**, *434*, 207.

(10) Beattie, I. R.; Gilson, T.; Ozin, G. A. *J. Chem. Soc. A* **1968**, 1092. Beattie, I. R.; Ozin, G. A.; Blayden, H. E. *Ibid.* **1969**, 2535.

0020-1669/81/1320-1179$01.25/0

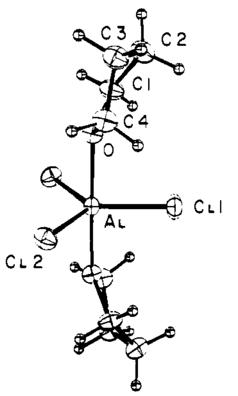


Figure 1. Drawing of the $AlCl_3 \cdot 2THF$ molecule, illustrating the atom numbering scheme. Nonhydrogen atoms are shown as ellipsoids of 30% probability and hydrogen atoms as spheres of radius 0.1 Å.

longer than that found in the dialuminacyclohexadiene complex $Al(Ph)C{=}C(Ph)Al(Ph)C{=}C(Ph) \cdot 2THF$ of 1.907 (3) Å,[11] doubtless a consequence of the higher coordination number (5 vs. 4) in $AlCl_3 \cdot 2THF$.

The THF molecule is disordered in many crystallographic determinations because of the facility of (pseudorotatory) ring-flexing processes.[12-25] Indeed, as recently as 1978, Rietz et al.[24] commented that they were unable to find "an example of a crystal structure in which it (THF) exists with good bond lengths and thermal amplitudes of motion". The crystal structure of $AlCl_3 \cdot 2THF$ is apparently exceptional in that the geometry of the THF rings is rather well defined, although the mean C–C (1.501 Å) and C–O (1.474 Å) distances differ from the corresponding distances (1.538 and 1.430 Å) obtained for the free molecule by gas-phase electron diffraction.[26] Futhermore, as shown in Figure 1, the coordinated THF ligand clearly exhibits an envelope conformation (C_s symmetry, with C(3) as the "flap" atom), which is consistent with the model favored in this electron diffraction study. The reasonable geometry of the THF rings in this crystal structure is probably due to the highly symmetrical packing of $AlCl_3 \cdot 2THF$ molecules in the crystal. As shown in Figure 2, each molecule is surrounded by 12 others in an approximately hexagonal closest packed arrangement. There are, however, no unusually close intermolecular contacts which could help account for the satisfactory geometry of the THF ligands in this crystal structure.

Table II. Calculated and Reported X-ray Diffraction Data for $AlCl_3 \cdot 2THF$

d_{calcd},[a] Å	d_{obsd},[b] Å	d_{calcd},[a] Å	d_{obsd},[b] Å
7.12	12.0	3.26	3.75
6.31	9.80	3.19	3.50
5.39	8.92	3.05	3.19
5.18	8.22	2.89	3.05
4.90	7.31	2.79	2.85
4.72	6.05	2.72	2.77
4.57	5.51	2.65	2.69
4.30	5.24	2.60	2.62
4.18	4.92	2.53	2.54
4.00	4.65	2.46	2.48
3.87	4.34	2.41	2.42
3.71	4.10	2.34	2.38
3.43	3.91		

[a] Computed with structural data obtained in this study. [b] See supplementary Table A of ref 5.

Table III. Crystallographic Summary

Crystal Data at −35 °C[a]

empirical formula	$C_8H_{16}AlCl_3O_2$	d_{calcd}, g cm^{-3}	1.439[b]
fw	277.56	cryst system	orthorhombic
a, Å	10.359 (2)	space group	*Pbcn* (No. 60)
b, Å	9.803 (4)	*Z*	4
c, Å	12.617 (5)	*F*(000), e	576
V, Å^3	1281 (1)		

Data Collection at −35 °C[c]

radiatn (Mo Kα), Å	0.710 69
mode	ω scan
scan range	symmetrically over 1.0° about K$\alpha_{1,2}$(max)
bkgd	offset 1.0° and −1.0° in ω from K$\alpha_{1,2}$(max)
scan rate, deg min^{-1}	variable 2.0–5.0 for the first 60% of data collection, then 4.0–5.0 for the remaining 40% to minimize effects of crystal decay
check rflctns	4 remeasured after every 96 reflections; anal.[d] of these data indicated a smooth decline in intensity of 11% during the 23 h of data collection for which the appropriate corrections were applied
2θ range, deg	4.0–55.0
total rflctns measd	1479
data cryst dimens, mm	0.48 × 0.54 × 0.85
μ(Mo Kα), mm^{-1}	0.76[e]

[a] Unit cell parameters were obtained by least-squares refinement of 30 reflections with $28.1° < 2\theta < 29.8°$. [b] Owing to air/moisture sensitivity an experimental density was not obtained. [c] Syntex $P2_1$ autodiffractometer equipped with a graphite monochromator and a Syntex LT-1 inert-gas low-temperature delivery system. [d] Henslee, W. H.; Davis, R. E. *Acta Crystallogr., Sect. B* 1975, *B31*, 1511. [e] Since the faces of the data crystal were severely eroded as a consequence of the aforementioned decay by the conclusion of data collection, an absorption correction based upon the diffractometer setting angles of the crystal faces was not applied to the intensity data. The estimated range in transmission factors based upon the extreme dimensions of the crystal is 0.43–0.69.

As pointed out in the Introduction, Derouault et al.[5] proposed, on the basis of vibrational spectroscopic data, that the bis(THF) complex of $AlCl_3$ is ionic and of composition $[AlCl_2(THF)_4]^+[AlCl_4]^-$. Derouault et al.[5] also reported an X-ray powder pattern for their product. We have computed the X-ray powder pattern for our compound from the single-crystal data. The computed *d* spacings for our compound are compared with the experimental data of Derouault et al.[5] in Table II. It is clear that the two materials are different. Accepting the vibrational spectroscopic structure assignment, one may infer that $AlCl_3 \cdot 2THF$ and $[AlCl_2(THF)_4]^+[AlCl_4]^-$ possess similar free energies. One way to rationalize the difference between our results and those of Derouault et al.[5] is by recognizing that our product arose from a base competition reaction involving a single $AlCl_3$ unit, i.e., eq 1, whereas

$$(Me_2N)_3SiCl \cdot AlCl_3 + 2THF \rightarrow (Me_2N)_3SiCl + AlCl_3 \cdot 2THF \quad (1)$$

the compound of Derouault et al.[5] was formed in the reaction of THF with the dimer Al_2Cl_6. As first observed by Shore

---

(11) Hoberg, H.; Gotor, V.; Milchereit, A.; Kruger, C.; Sekutowski, J. C. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 539; *Angew. Chem.* **1977**, *89*, 563.
(12) Daly, J. J.; Sheedan, R. P. A. *J. Chem. Soc. A* **1967**, 736.
(13) Krausse, J.; Marx, G.; Schödl, G. *J. Organomet. Chem.* **1970**, *21*, 159.
(14) Ganis, P.; Avitabile, G.; Mechlinski, W.; Schaffner, C. P. *J. Am. Chem. Soc.* **1971**, *93*, 4560.
(15) Brauer, D. J.; Stucky, G. D. *J. Organomet. Chem.* **1972**, *37*, 217.
(16) Brauer, D. J.; Kruger, C. *J. Organomet. Chem.* **1972**, *42*, 129.
(17) Muller, B.; Krausse, J. *J. Organomet. Chem.* **1972**, *44*, 141.
(18) Hodgson, K. O.; Raymond, K. N. *Inorg. Chem.* **1972**, *11*, 171.
(19) Atwood, J. L.; Smith, K. D. *J. Chem. Soc., Dalton Trans.* **1974**, 921.
(20) Brauer, D. J.; Kruger, C. *Inorg. Chem.* **1975**, *14*, 3053.
(21) Gall, R. S.; Schaefer, W. P. *Inorg. Chem.* **1976**, *15*, 2758.
(22) Ely, S. R.; Hopkins, T. E.; DeKock, C. W. *J. Am. Chem. Soc.* **1976**, *98*, 1624.
(23) Reynolds, J. G.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1977**, *16*, 3357.
(24) Rietz, R. R.; Edelstein, N. M.; Ruben, H. W.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1978**, *17*, 658.
(25) Reed, C. A.; Toshio, M.; Scheidt, W. R.; Spartalian, K.; Long, G. *J. Am. Chem. Soc.* **1980**, *102*, 2302.
(26) Geise, H. J.; Adams, W. J.; Bartell, L. S. *Tetrahedron* **1969**, *25*, 3045.

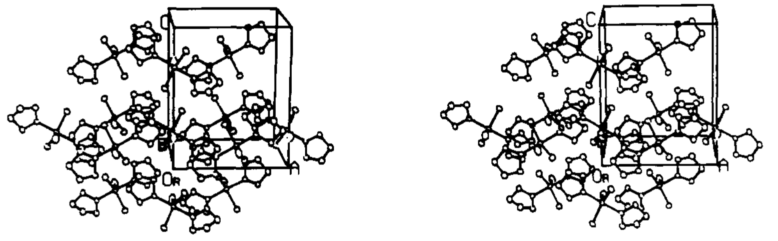


Figure 2. Stereoscopic view of the packing environment about an $AlCl_3 \cdot 2THF$ molecule. Each molecule is within 3.85 Å, ignoring hydrogen atom contacts, of 12 other molecules in an approximately hexagonal closest packed arrangement. Atoms are drawn as ellipsoids of 30% probability; hydrogen atoms have been omitted for the sake of clarity.

Table IV

Fractional Coordinates and Anisotropic Thermal Parameters ($\times 10^3$) for Nonhydrogen Atoms[a]

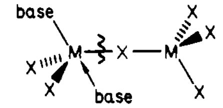
atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(1)[b]	0	−0.10578 (6)	1/4	584 (5)	294 (3)	1080 (6)	0	185 (5)	0
Cl(2)[b]	0.08728 (5)	0.22795 (5)	0.37753 (4)	474 (3)	557 (3)	442 (2)	−49 (2)	−63 (2)	−136 (2)
Al[b]	0	0.11479 (6)	1/4	343 (4)	291 (3)	358 (3)	0	−39 (3)	0
O	0.1667 (1)	0.1128 (1)	0.1717 (1)	34 (1)	46 (1)	36 (1)	−1 (1)	−5 (1)	−3 (1)
C(1)	0.1725 (2)	0.0624 (3)	0.0615 (1)	47 (1)	69 (1)	38 (1)	1 (1)	−1 (1)	−11 (1)
C(2)	0.2976 (2)	−0.0135 (2)	0.0536 (2)	51 (1)	62 (1)	54 (1)	2 (1)	2 (1)	−13 (1)
C(3)	0.3824 (2)	0.0574 (3)	0.1333 (2)	41 (1)	65 (1)	56 (1)	2 (1)	−1 (1)	−6 (1)
C(4)	0.2911 (2)	0.0834 (2)	0.2230 (1)	35 (1)	63 (1)	45 (1)	1 (1)	−7 (1)	−3 (1)

Fractional Coordinates and Isotropic Thermal Parameters ($Å^2$) for Hydrogen Atoms[a]

atom[c]	x	y	z	B	atom[c]	x	y	z	B
H(1,1)	0.163 (2)	0.142 (3)	0.015 (2)	6.2 (6)	H(3,1)	0.448 (2)	0.000 (2)	0.163 (2)	6.6 (6)
H(1,2)	0.098 (2)	0.006 (2)	0.051 (2)	4.9 (5)	H(3,2)	0.417 (2)	0.148 (2)	0.104 (2)	5.5 (5)
H(2,1)	0.333 (2)	−0.011 (3)	−0.020 (2)	7.0 (6)	H(4,1)	0.276 (2)	0.004 (2)	0.272 (1)	4.4 (5)
H(2,2)	0.281 (2)	−0.106 (2)	0.085 (2)	5.4 (5)	H(4,2)	0.318 (2)	0.162 (2)	0.267 (2)	6.4 (5)

[a] See Figure 1 for identity of the atoms. Numbers in parentheses are the estimated standard deviation in the units of the least significant digits for the corresponding parameter. The U_{ij} are the mean square amplitudes of vibration in $Å^2$ from the general temperature factor expression $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. [b] For Cl and Al atoms the anisotropic thermal parameters are given $\times 10^4$. [c] The sequence number of a hydrogen atom corresponds to that of the carbon atom to which it is bound.

and Parry,[27] unsymmetrical cleavage of M_2X_6 systems arises when successive molecules of Lewis base attack the same M atom as illustrated:



Experimental Section

The complex $AlCl_3 \cdot 2THF$ was prepared, as noted at the outset of this paper, by dissolution of $(Me_2N)_3SiCl \cdot AlCl_3$[1] in THF. Crystals of $AlCl_3 \cdot 2THF$ were then obtained as colorless blocks from a diethyl ether solution. Due to the extreme air and moisture sensitivity of the material, all crystallographic manipulations were conducted in an atmosphere of dry N_2. A single crystal was glued to a glass fiber which was affixed to a brass pin and, in turn, to a gonimeter head. The crystal was then transferred to a Syntex $P2_1$ autodiffractometer where it was maintained in a stream of cold (−35 °C), dry N_2. Preliminary experiments with the crystal with the diffractometer indicated the orthorhombic symmetry of space group *Pbcn* (No. 60). Crystal data and data collection details are summarized in Table III. The recorded X-ray intensities were reduced and assigned standard deviations (with $p = 0.02$) as described elsewhere.[28]

The structure was solved by heavy-atom procedures and refined by full-matrix least-squares methods.[29] The function minimized in refinement is $\sum w(|F_o| - |F_c|)^2$, where the weight w is $\sigma(|F_o|)^{-2}$, the reciprocal square of the standard deviation of each observation, $|F_o|$. Neutral-atom scattering factors for Cl, Al, O, C,[30] and H[31] were used in these calculations, and the real ($\Delta f'$) and imaginary ($\Delta f''$) corrections[30] for anomalous scattering of Mo Kα radiation were applied to the Cl and Al scattering curves. Least-squares convergence was attained with use of only those 1154 reflections with $I_0/\sigma(I_0) > 2.0$ for a structure in which all nonhydrogen atoms were refined anisotropically and hydrogen atoms isotropically, with $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.028$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.032$, and standard deviation of an observation of unit weight $= [\sum w(||F_o| - |F_c||)^2/(m - s)]^{1/2} = 1.90$, for $m = 1154$ observations and $s = 97$ variables. Examination of the data at convergence gave no evidence of secondary extinction. A structure factor calculation using the atomic parameters obtained at convergence with all 1479 reflections gathered during data collection gave R and R_w values of 0.039 and 0.035, respectively.

In the final cycle of refinement, the largest shifts in nonhydrogen and hydrogen atom parameters were less than 0.8 and 1.2 times a corresponding estimated standard deviation (esd), respectively. The largest peaks on a final difference electron density map were ~0.1 e $Å^{-3}$.

Atomic positional and thermal parameters, with corresponding esd's as estimated from the least-squares inverse matrix, are presented in Table IV. A tabulation of observed and calculated structure factor amplitudes is available.[32]

Acknowledgment. The authors are grateful to the National Science Foundation (Grant CHE-7910155) and the Robert A. Welch Foundation of generous financial support. We also thank the National Science Foundation for the purchase of the Syntex $P2_1$ diffractometer (Grant GP-37028) and Ms. Katharine Larsen for her valuable assistance.

Registry No. $AlCl_3 \cdot 2THF$, 15615-14-2; $(Me_2N)_3SiCl \cdot AlCl_3$, 72969-27-8.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

---

(27) Shore, S. G.; Parry, R. W. *J. Am. Chem. Soc.* **1958**, *80*, 8.
(28) Riley, P. E.; Davis, R. E. *Acta Crystallogr., Sect B* **1976**, *B32*, 381.
(29) A listing of the principal computer programs used in this study is provided in ref 28.
(30) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.
(31) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.
(32) Supplementary material.