d orital of VO^{2+} and atomic orbitals of Tl^+ or a superexchange mechanism involving bridging ligand groups could account for the magnitude[16] of the scalar coupling.

Strong scalar superhyperfine coupling between the unpaired electron spin of VO^{2+} and magnetic isotopes of Sn has been reported previously in EPR studies of VO^{2+} doped into a host crystal of SnO_2.[17] In the SnO_2 crystal, two sets of superhyperfine couplings were observed. From the crystal structure it was deduced that the strongest couplings (168 G) were from Sn nuclei that were located 3.18 Å from the vanadyl(IV) center between O ligands in the equatorial plane. This geometry maximizes interaction with the unpaired electron in the nonbonding d orbital of the vanadyl ion.[17] If the VO^{2+}–Tl^+ coupling occurs as a result of direct orbital overlap, the relatively large magnitude of the coupling would be most consistent with a geometry in which Tl^+ was positioned peripheral to and between equatorial ligands in the coordination sphere of the VO^{2+}. The carboxylate groups of the substrates and analogues could also act a bridging ligands between VO^{2+} and Tl^+, and the bridging ligand could mediate a superexchange interaction. Furthermore, a bridging carboxylate could also position Tl^+ for direct interaction with the nonbonding d orbital of VO^{2+}. The strong VO^{2+}–Tl^+ superhyperfine coupling is certainly compatible with a very close spacing of the monovalent and the divalent cation sites on the enzyme.

Acknowledgment. This investigation was supported by NIH Grant GM-35752.

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Interaction of $AlCl_3$ with Tetrahydrofuran. Formation and Crystal Structure of $[AlCl_2(THF)_4][AlCl_4]$

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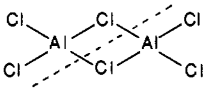
It is well-known that aluminum trichloride forms neutral donor–acceptor complexes with bases through a symmetrical dissociation of the dimer (**1**). Less common is the unsymmetrical



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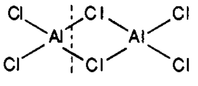

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cleavage (**2**), which produces the ionic species $[AlCl_2(base)_n][AlCl_4]$. We have previously reported complexes of the latter type, which were formed by the reaction of aluminum trichloride with crown ethers in toluene. In the cation, the $AlCl_2^+$ ion fits into the crown cavity (for 15-crown-5[1]) or perches on the crown such that there is a strong interaction with four crown oxygen atoms for 12-crown-4 and 18-crown-6.[2] In the former the chlorine atoms adopt a trans configuration, whereas in the latter a cis geometry is seen. Our studies on bidentate oxygen donors such as dimethoxyethane (DME) showed that the related $[AlCl_2(DME)_2]^+$ was formed.[3] Since these ionic species exhibit interesting two-phase liquid behavior in aromatic solvents,[4] it was of interest to extend the work to bases with only one donor oxygen atom. The $AlCl_3$/THF system was a desirable candidate for study since a number of investigations had already been carried out. The presence of an ionic moiety in the workup of a saturated solution of $AlCl_3$ in THF was deduced from a vibrational spectroscopic study by Derouault and Forel,[5] but Cowley and co-workers found only the molecular $AlCl_3{\cdot}2THF$ in a related system.[6] We report here the isolation and structural characterization of Derouault's compound $[AlCl_2(THF)_4][AlCl_4]$ as the only product of the reaction of stoichiometric quantities of the reactants in toluene.

Table I. Calculated and Reported X-ray Diffraction Data for 1:2 $AlCl_3$/THF Compounds

d_{calcd},[a] Å	d_{obsd},[b] Å	d_{obsd},[c] Å
12.0	7.12	12.0
9.78	6.31	9.80
8.81	5.39	8.92
8.20	5.18	8.22
7.43		
7.29	4.90	7.31
7.16		
6.04	4.72	6.05
5.90		
5.54	4.57	5.51
	4.30	5.24
4.89	4.18	4.92
4.67	4.00	4.65
	3.87	4.34
4.13	3.71	4.10
3.81	3.43	3.91
3.78	3.26	3.75
3.57		
3.54	3.19	3.50
3.51		

[a] Calculated *d* spacings based on the single-crystal data of this study. [b] $AlCl_3{\cdot}2THF$.[6] [c] $[AlCl_2(THF)_4][AlCl_4]$.[5]

Results and Discussion

The species formed upon the interaction of aluminum trichloride with tetrahydrofuran is seen to be dependent upon the state of the $AlCl_3$ and perhaps upon the solvent as well. Derouault and Forel[5] obtained $[AlCl_2(THF)_4][AlCl_4]$ from a THF solution of Al_2Cl_6, while Cowley and co-workers prepared molecular $AlCl_3{\cdot}2THF$ from the dissolution of $(Me_2N)_3SiCl{\cdot}AlCl_3$ in THF. Our approach was different since we sought the ionic complex in the presence of the aromatic solvent. The identity of the title complex has been established by a single-crystal X-ray diffraction study. The compound reported by Derouault and Forel[5] has been shown to be $[AlCl_2(THF)_4][AlCl_4]$ by a comparison of the powder diffraction data reported in the 1977 study with the single-crystal data. The results are given in Table I.

One of the two independent cations is shown in Figure 1. There is no significant difference between the crystallographically independent ions, cations or anions. Important bond lengths and angles are given in Table II. In the cations, the average Al–Cl distance, 2.230 (9) Å, is slightly longer than those found in *cis*-$[AlCl_2(donor)_4]^+$: 2.204 (2) Å in $[AlCl_2(DME)_4]^+$,[3] 2.201 (1) Å in $[AlCl_2(12\text{-crown-}4)]^+$,[2] and 2.18 (1) Å in $[AlCl_2(18\text{-crown-}6)]^+$.[2] The latter values are not significantly different from the 2.200 (3) Å value in the trans cation $[AlCl_2(15\text{-crown-}5)]^+$ in which the aluminum atom is seven-coordinate.[1] In the anions, the Al–Cl distances average 2.10 (2) Å, in keeping with literature values.

Interestingly, the Al–O bonds average 1.94 (1) Å in the title complex, compared to 1.96 (2) Å for the 12-crown-4 analogue.

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0020-1669/87/1326-1466$01.50/0

Table II. Selected Bond Lengths (Å) and Angles (deg) for $[AlCl_2(THF)_4][AlCl_4]$

Al(1)–Cl(1)	2.220 (6)	Al(1)–Cl(2)	2.233 (6)
Al(1)–O(1)	1.93 (1)	Al(1)–O(2)	1.92 (1)
Al(1)–O(3)	1.95 (1)	Al(1)–O(4)	1.95 (1)
Al(2)–Cl(3)	2.227 (6)	Al(2)–Cl(4)	2.241 (6)
Al(2)–O(5)	1.96 (1)	Al(2)–O(6)	1.93 (1)
Al(2)–O(7)	1.92 (1)	Al(2)–O(8)	1.94 (1)
Al(3)–Cl(5)	2.110 (8)	Al(3)–Cl(6)	2.118 (8)
Al(3)–Cl(7)	2.140 (8)	Al(3)–Cl(8)	2.099 (9)
Al(4)–Cl(9)	2.125 (9)	Al(4)–Cl(10)	2.093 (9)
Al(4)–Cl(11)	2.07 (1)	Al(4)–Cl(12)	2.08 (1)
Cl(1)–Al(1)–Cl(2)	179.9 (1)	Cl(1)–Al(1)–O(1)	90.4 (4)
Cl(2)–Al(1)–O(1)	89.7 (4)	Cl(1)–Al(1)–O(2)	90.0 (4)
Cl(2)–Al(1)–O(2)	89.9 (4)	O(1)–Al(1)–O(2)	178.7 (5)
Cl(1)–Al(1)–O(3)	89.8 (3)	Cl(2)–Al(1)–O(3)	90.1 (3)
O(1)–Al(1)–O(3)	89.6 (5)	O(2)–Al(1)–O(3)	89.1 (5)
Cl(1)–Al(1)–O(4)	90.4 (3)	Cl(2)–Al(1)–O(4)	89.6 (3)
O(1)–Al(1)–O(4)	91.3 (5)	O(2)–Al(1)–O(4)	90.0 (5)
O(3)–Al(1)–O(4)	179.1 (5)	Cl(3)–Al(2)–Cl(4)	179.3 (3)
Cl(3)–Al(2)–O(5)	89.9 (3)	Cl(4)–Al(2)–O(5)	90.2 (4)
Cl(3)Al(2)–O(6)	90.0 (3)	Cl(4)–Al(2)–O(6)	89.9 (3)
O(5)–Al(2)–O(6)	179.7 (2)	Cl(3)–Al(2)–O(7)	90.9 (4)
Al(4)–Al(2)–O(7)	89.8 (4)	O(5)–Al(2)–O(7)	90.4 (5)
O(6)–Al(2)–O(7)	89.8 (5)	Cl(3)–Al(2)–O(8)	89.8 (4)
Cl(4)–Al(2)–O(8)	89.5 (4)	O(5)–Al(2)–O(8)	89.9 (5)
O(6)–Al(2)–O(8)	89.9 (5)	O(7)–Al(2)–O(8)	179.3 (5)
Cl(5)–Al(3)–Cl(6)	108.0 (3)	Cl(5)–Al(3)–Cl(7)	110.4 (3)
Cl(6)–Al(3)–Cl(7)	107.4 (3)	Cl(5)–Al(3)–Cl(8)	110.6 (3)
Cl(6)–Al(3)–Cl(8)	109.2 (4)	Cl(7)–Al(3)–Cl(8)	111.1 (4)
Cl(9)–Al(4)–Cl(10)	107.8 (4)	Cl(9)–Al(4)–Cl(11)	110.1 (4)
Cl(10)–Al(4)–Cl(11)	108.9 (4)	Cl(9)–Al(4)–Cl(12)	109.9 (5)
Cl(10)–Al(4)–Cl(12)	110.3 (4)	Cl(11)–Al(4)–Cl(12)	109.9 (4)

The coordination requirements of the crown ether do not appear to make a significant difference in the bond lengths. The THF ligands all adopt the envelope conformation and are arranged around the aluminum in a propeller-like fashion. The best plane of each ring is twisted at an angle of about 60° with respect to the plane of the aluminum and oxygen atoms.

Table III. Crystal Data and Summary of Data Collection for $[AlCl_2(THF)_4][AlCl_4]$

M_r	555.1
space group	$P2_1/n$
cell const	
a, Å	9.023 (2)
b, Å	39.134 (9)
c, Å	15.319 (5)
β, deg	91.22 (3)
cell vol, Å^3	5408
molecules/unit cell	8
T, °C	22
ρ(calcd), g cm^{-3}	1.37
μ(calcd), cm^{-1}	7.25
radiation	graphite-monochromated Mo Kα (λ = 0.71069 Å)
max cryst dimens, mm	0.50 × 0.50 × 0.50
scan width	0.80 + 0.20 tan θ
std reflcns	600, 0,18,0, 008
decay of std	8%
2θ range, deg	2–38
data collcn range	$h,k,\pm l$
no. of reflcns collcd	4507
no. of obsd reflcns	2548
no. of params varied	215
GOF	1.08
R	0.096
R_w	0.088

Experimental Section

Reagent grade Al_2Cl_6 (1.0 g, 3.8 mmol) was added to a solution of 1.3 mL of THF (15 mmol) in 10 mL of toluene in a screw-top tube. The mixture was heated to 100° for 2 h. There was no evidence of a two-phase liquid layering.[4] Upon cooling, a quantitative yield of large, colorless crystals was obtained. When the reaction was run with twice the amount of THF, an identical yield and product were obtained. The compound has good air stability and may be manipulated on the bench for short periods of time without the benefit of a cover gas.

Single crystals of the compound were sealed under N_2 in thin-walled glass capillaries. A well-formed crystal of dimensions 0.5 × 0.5 × 0.5 mm was selected and mounted on a CAD-4 diffractometer. Unit cell parameters as determined by a least-squares refinement of the angular settings of 24 reflections ($2\theta > 25°$) are given in Table III. Data were

Table IV. Final Fractional Coordinates and Equivalent Isotropic Thermal Parameters for $[AlCl_2(THF)_4][AlCl_4]$

atom	x/a	y/b	z/c	U(eq),[a] Å^2	atom	x/a	y/b	z/c	U(eq),[a] Å^2
Al(1)	0.1431 (5)	0.1334 (1)	0.5107 (3)	0.064	C(5)	0.323 (2)	0.0673 (5)	0.507 (1)	0.118
Al(2)	0.1533 (5)	0.1150 (1)	0.0149 (3)	0.066	C(6)	0.309 (2)	0.0331 (6)	0.471 (2)	0.143
Al(3)	0.8313 (6)	0.5117 (2)	0.2370 (4)	0.090	C(7)	0.159 (2)	0.0259 (6)	0.460 (2)	0.142
Al(4)	0.6237 (7)	0.2350 (2)	0.7262 (4)	0.100	C(8)	0.088 (2)	0.0601 (5)	0.451 (1)	0.115
Cl(1)	0.2903 (4)	0.1317 (1)	0.6286 (2)	0.087	C(9)	0.434 (2)	0.1696 (5)	0.469 (1)	0.102
Cl(2)	−0.0048 (5)	0.1349 (1)	0.3920 (2)	0.089	C(10)	0.533 (2)	0.1731 (5)	0.395 (1)	0.105
Cl(3)	0.3103 (5)	0.1360 (1)	0.1153 (2)	0.093	C(11)	0.495 (2)	0.1443 (5)	0.334 (1)	0.099
Cl(4)	−0.0046 (4)	0.0943 (1)	−0.0870 (2)	0.085	C(12)	0.337 (2)	0.1366 (5)	0.346 (1)	0.080
Cl(5)	0.0126 (6)	0.4810 (1)	0.2018 (3)	0.118	C(13)	−0.021 (2)	0.0963 (5)	0.656 (1)	0.103
Cl(6)	0.6371 (6)	0.4814 (2)	0.2277 (4)	0.153	C(14)	−0.173 (2)	0.0857 (6)	0.670 (1)	0.127
Cl(7)	0.8557 (7)	0.5279 (2)	0.3700 (4)	0.155	C(15)	−0.262 (3)	0.1104 (6)	0.631 (2)	0.147
Cl(8)	0.8094 (8)	0.5537 (2)	1.1526 (4)	0.163	C(16)	−0.180 (2)	0.1287 (6)	0.568 (1)	0.112
Cl(9)	0.6382 (8)	0.2201 (2)	0.5933 (4)	0.207	C(17)	−0.023 (2)	0.1569 (5)	0.145 (1)	0.097
Cl(10)	0.7904 (7)	0.2711 (2)	0.7515 (4)	0.141	C(18)	−0.185 (2)	0.1589 (5)	0.166 (1)	0.112
Cl(11)	0.4195 (8)	0.2574 (2)	0.7480 (5)	0.195	C(19)	−0.235 (2)	0.1261 (5)	0.161 (1)	0.126
Cl(12)	0.6526 (9)	0.1927 (2)	0.8069 (6)	0.215	C(20)	−0.147 (2)	0.1066 (6)	0.094 (1)	0.133
O(1)	0.103 (1)	0.1811 (3)	0.5311 (7)	0.077	C(21)	0.464 (2)	0.0909 (5)	−0.027 (1)	0.114
O(2)	0.185 (1)	0.0862 (3)	0.4881 (6)	0.072	C(22)	0.547 (2)	0.0807 (5)	−0.104 (1)	0.112
O(3)	0.312 (1)	0.1461 (2)	0.4403 (6)	0.062	C(23)	0.478 (2)	0.1011 (5)	−0.177 (1)	0.102
O(4)	−0.026 (1)	0.1198 (3)	0.5805 (6)	0.066	C(24)	0.322 (2)	0.1030 (4)	−0.156 (1)	0.077
O(5)	−0.013 (1)	0.1271 (3)	0.0885 (6)	0.074	C(25)	0.152 (3)	0.0373 (6)	0.031 (1)	0.147
O(6)	0.318 (1)	0.1032 (2)	−0.0577 (6)	0.063	C(26)	0.198 (3)	0.0101 (7)	0.090 (1)	0.164
O(7)	0.164 (1)	0.0706 (3)	0.0682 (7)	0.086	C(27)	0.172 (3)	0.0290 (7)	0.171 (2)	0.186
O(8)	0.142 (1)	0.1595 (3)	−0.0405 (6)	0.079	C(28)	0.188 (3)	0.0649 (6)	0.163 (2)	0.160
C(1)	0.073 (3)	0.2080 (6)	0.469 (1)	0.136	C(29)	0.257 (2)	0.1860 (6)	−0.043 (1)	0.131
C(2)	0.109 (3)	0.2407 (8)	0.510 (2)	0.194	C(30)	0.190 (4)	0.2109 (9)	−0.088 (2)	0.263
C(3)	0.079 (3)	0.2327 (8)	0.595 (2)	0.209	C(31)	0.043 (3)	0.2107 (7)	−0.089 (2)	0.199
C(4)	0.100 (3)	0.1993 (6)	0.617 (1)	0.143	C(32)	0.007 (2)	0.1745 (5)	−0.083 (1)	0.117

[a] $U(eq) = (U_{11} + U_{22} + U_{33})$ for the Al and Cl atoms; U(eq) is U for the O and C atoms.

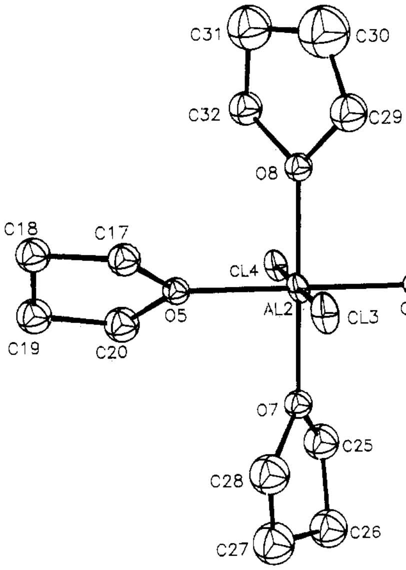

Figure 1. Structure of one of the crystallographically independent cations of $[AlCl_2(THF)_4][AlCl_4]$.

collected in the usual manner.[7] A correction for the crystal decay of 8% was applied. The structure was solved by application of the direct-methods program MULTAN,[8] which revealed the positions of the Al and Cl atoms. The THF molecules were located on subsequent difference Fourier maps.[9] Although the carbon atoms of the THF molecules exhibit high thermal motion, a detailed examination of the difference Fourier maps showed only one maximum. A disordered model for the THF molecules was therefore not attempted. High thermal motion was also noted for the anions, but again a model incorporating disorder was not needed. Due to the paucity of data, only the Al and Cl atoms were assigned anisotropic thermal parameters. The reason for the lack of scatter of the crystal beyond $\theta = 19°$ was apparently the high thermal motion of the THF atoms. Indeed, inclusion of hydrogen atoms even at calculated positions was not deemed worthwhile because of this problem. Refinement converged at $R = 0.096$ and $R_w = 0.088$. Unit weights were used at all stages. Neutral-atom scattering factors were taken from the tabulation of Cromer and Waber.[10] A final difference Fourier showed no residual electron density of consequence. The largest parameter shifts in the final cycle of refinement were less than 0.2 of their corresponding estimated standard deviations. Fractional coordinates and equivalent isotropic thermal parameters are given in Table IV.

Acknowledgment. The authors are grateful to the National Science Foundation for generous financial support.

Supplementary Material Available: Tables containing complete bond lengths and angles (Table A) and thermal parameters (Table B) and figures showing the second cation (Figure S2), both anions (Figures S3 and S4), and a stereoview of the unit cell packing (Figure S5) (8 pages); a table containing observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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Additions and Corrections

1986, Volume 25

Richard D. Adams,* James E. Babin, and Miklos Tasi: Cluster Synthesis. 13. Chemistry of Sulfidoruthenium Carbonyl Clusters. Synthesis and Characterization of the New Unsaturated Clusters $Ru_4(CO)_{11-n}L_n(\mu_4\text{-}S)_2$ (n = 0–2, L = PMe_2Ph).

Page 4515. In column 2, the ^1H NMR spectra for **6** and **7** were incorrectly reported. The ^1H NMR data should read as follows (δ in $CDCl_3$). Tenth line from the bottom: 7.40–7.20 (m, 10 H), 1.78 (d, J_{P-H} = 12 Hz, 12 H). Fourth line from the bottom: 7.41–7.22 (m, 5 H), 1.87 (d, J_{P-H} = 12 Hz, 6 H).—Richard D. Adams