

Crystal and Molecular Structure of Trichlorotris(tetrahydrofuran)scandium(III)

By J. L. Atwood* and K. D. Smith, Department of Chemistry, University of Alabama, Alabama 35486, U.S.A.

The crystal structure of the title compound has been determined by direct methods from X-ray diffractometer data. Crystals are monoclinic plates, space group $P2_1/c$, with $Z = 4$ in a cell with $a = 8.890(4)$, $b = 12.842(6)$, $c = 15.485(6)$ Å, $\beta = 92.24(5)^\circ$. The structure was refined by least-squares techniques to R 0.077 for 1227 unique observed reflections. The substance exists as discrete molecules in which the scandium(III) ion environment is *mer*-octahedral. Mean Sc—O is 2.18, and mean Sc—Cl 2.41 Å.

THE co-ordination chemistry of scandium after being neglected compared to that of other first-row transition elements has now become a subject of considerable attention. Since a review¹ in 1971, the crystal structures of five complexes have been reported.²⁻⁶ These have served to establish the radius of the scandium(III) ion,^{2,6} and to permit the inference of a degree of covalency in a scandium-carbon bond.⁵

Scandium trichloride is known¹ to form complexes of the type $\text{ScCl}_3(\text{L})_n$ (L = neutral oxygen-donor ligand, $n = 1-4$ or 6). In particular, anhydrous ScCl_3 reacts readily with tetrahydrofuran to form the stable (but oxygen- and moisture-sensitive) complex $\text{ScCl}_3(\text{C}_4\text{H}_8\text{O})_3$. Since this substance is often encountered in the synthesis of organometallic derivatives of scandium, and since there have been no other structural studies of a co-ordination compound of scandium trichloride, we have carried out a three-dimensional X-ray characterization.

EXPERIMENTAL

Anhydrous scandium trichloride, obtained by the method of ref. 7, was added to a large excess of tetrahydrofuran with mild (*ca.* 50 °C) heating; pale pink plates of $\text{ScCl}_3(\text{C}_4\text{H}_8\text{O})_3$ were obtained.

Crystal Data.— $\text{C}_{12}\text{H}_{20}\text{Cl}_3\text{O}_3\text{Sc}$, $M = 367.3$, Monoclinic, $a = 8.890(4)$, $b = 12.842(6)$, $c = 15.485(6)$ Å, $\beta = 92.24(5)^\circ$, $U = 1767$ Å³, $D_c = 1.38$, $Z = 4$, $D_m = 1.37$, $F(000) = 768$. Space group $P2_1/c$ from systematic absences. Cu- K_α radiation, $\lambda = 1.542$ Å, $\mu(\text{Cu-}K_\alpha) = 56.6$ cm⁻¹. Crystal dimensions 0.10 × 0.30 × 0.30 mm.

Crystallographic Measurements.—Lattice parameters were obtained by a least-squares refinement of the angular settings of 12 accurately centred reflections. Data were collected on an Enraf-Nonius CAD 4 diffractometer, with graphite-crystal monochromated copper radiation.

Intensities were collected by the ω -2 θ scan technique

¹ G. A. Melson and R. W. Stotz, *Co-ordination Chem. Rev.*, 1971, **7**, 133.

² T. J. Anderson, M. A. Neuman, and G. A. Melson, *Inorg. Chem.*, 1973, **12**, 927.

³ T. J. Anderson, M. A. Neuman, and G. A. Melson, *Abstr.*, Amer. Chem. Soc. Nat. Meeting, Chicago, Illinois, 1973, INOR 140.

⁴ E. Hansson, *Acta Chem. Scand.*, 1972, **26**, 1337.

⁵ J. L. Atwood and K. D. Smith, *J. Amer. Chem. Soc.*, 1973, **95**, 1488.

⁶ K. D. Smith and J. L. Atwood, *J.C.S. Chem. Comm.*, 1972, 593; J. L. Atwood and K. D. Smith, *J.C.S. Dalton*, 1973, 2487.

⁷ R. W. Stotz and G. A. Melson, *Inorg. Chem.*, 1972, **11**, 1720.

⁸ D. J. Wehe, W. R. Busing, and H. A. Levy, ORABS: A Fortran Program for Calculating Single-Crystal Absorption Corrections, Report ORNL TM 229, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1972.

with a take-off angle of 3°. The scan rate was variable and was determined by a fast (20° min⁻¹) prescan. Calculated speeds, based on the net intensity gathered in the prescan, ranged from 7—1° min⁻¹. Background counts were collected for 25% of the total scan time at each end of the scan range. For each intensity the scan range = $A + B \tan \theta$, where $A = 1.00$ and $B = 0.46$. Aperture settings were determined in a like manner with $A = 4$ mm and $B = 4$ mm. Other diffractometer parameters as well as the method of estimating standard deviations of the intensities have been given elsewhere.⁸ One reflection ($\bar{2}11$) was measured every 30 min during data collection, but showed no significant variation in intensity.

One independent quadrant of data was measured out to 2 θ 114°. A total of 1227 unique reflections which had intensities greater than background were collected, and were corrected in the usual manner for Lorentz, polarization, and absorption effects.⁸

Fourier calculations were made with the ALFF⁹ program. Full-matrix least-squares refinement was carried out by use of the Busing and Levy program ORFLS.¹⁰ The function $\sum w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction or anomalous dispersion. Neutral atom scattering factors were taken from ref. 11. Final bond distances, angles, and errors were computed with the aid of the ORFFE¹² program. Crystal structure illustrations were obtained with the program ORTEP.¹³

Structure Determination.—Partial structure solution was accomplished by direct methods,¹⁴ and an electron-density map phased on the scandium, chlorine, and oxygen atoms yielded the positions of the remaining carbon atoms. Several cycles of least-squares refinement with isotropic thermal parameters for all atoms produced R 0.14. Conversion of anisotropic temperature factors and additional cycles of refinement led to a final R of 0.077 and the weighted factor R' of 0.077 ($R' = [\sum w(|F_o| - |F_c|)^2 / \sum (F_o)^2]^{1/2}$, where $w = 1/\sigma^2$). Unobserved reflections

⁹ C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, USAEC Report IS 2625, Ames Laboratory, Iowa State University, Ames, Iowa, 1971.

¹⁰ W. R. Busing, K. O. Martin, and H. A. Levy, ORFLS: A Fortran Crystallographic Least-Squares Program, Report ORNL TM 305, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1962.

¹¹ D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

¹² W. K. Busing, K. O. Martin, and H. A. Levy, ORFFE: A Fortran Crystallographic Function and Error Program, Report ORNL TM 306, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1962.

¹³ C. K. Johnson, ORTEP: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations, Report ORNL 3794, Revised, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1964, p. 70.

¹⁴ G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

were not included. No systematic variation of $w(|F_o| - |F_c|)^2$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was observed. The largest parameter shifts in the final cycle of refinement were $< 0.02\sigma$. A final difference-Fourier map showed several peaks of $0.4 \text{ e}\text{\AA}^{-3}$ in the vicinity of calculated hydrogen-atom positions, but no attempt was made to include them in the refinement. Atomic and thermal parameters are given in Table 1. Observed and calculated structure factor amplitudes are listed in Supplementary Publications No. SUP 20951 (16 pp., 1 microfiche).*

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The molecular structure of trichlorotrakis(tetrahydrofuran)scandium(III) (Figure 1) clearly shows the octahedral environment of the scandium atom. (Bond

light of the suspected high degree of ionicity in the bonds to scandium, it is most reasonably viewed in terms of lattice packing.

Figure 2 illustrates the propeller-like configuration of the tetrahydrofuran groups viewed down the Sc-Cl(1) bond. The packing of four molecules into a unit cell is shown in Figure 3; the non-bonded contacts are typical of a molecular compound of this type.

The mean scandium-oxygen bond distance (2.18 Å) is significantly longer than that found² in tris(acetylacetonato)scandium(III) (2.07 Å) and tris(tropolonato)scandium(III)³ (2.10 Å), but falls on the low side of the range reported for tetra-aquotrakis(oxalato)dis scandium(III) hydrate⁴ (2.18–2.26 Å). The established value of

TABLE 1

Final fractional co-ordinates and thermal parameters * ($\times 10^4$), with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sc	0.7618(2)	0.2436(2)	0.2431(1)	102(3)	67(2)	42(1)	1(2)	8(1)	5(1)
Cl(1)	0.7680(4)	0.4028(3)	0.3252(2)	240(6)	80(3)	64(2)	5(3)	13(3)	-16(2)
Cl(2)	0.9451(3)	0.1608(3)	0.3402(2)	134(4)	104(3)	63(2)	9(3)	-9(2)	19(2)
Cl(3)	0.5756(3)	0.3100(3)	0.1396(2)	160(5)	95(3)	60(2)	11(3)	-15(2)	15(2)
O(1)	0.7562(9)	0.0966(6)	0.1657(5)	236(16)	63(6)	44(5)	6(8)	3(7)	3(4)
O(2)	0.5862(8)	0.1709(6)	0.3129(5)	126(11)	115(8)	50(4)	-33(8)	-5(6)	11(5)
O(3)	0.9390(8)	0.2844(5)	0.1574(5)	150(12)	72(6)	61(5)	7(7)	37(6)	10(4)
C(1)	0.7266(23)	0.0918(11)	0.0725(8)	645(56)	80(12)	31(8)	1(21)	-6(16)	-16(7)
C(2)	0.7572(34)	-0.0211(13)	0.0486(12)	1083(106)	89(15)	71(12)	87(32)	5(28)	-7(11)
C(3)	0.7483(26)	-0.0795(12)	0.1283(12)	673(68)	79(13)	95(13)	13(24)	-36(24)	-20(11)
C(4)	0.7846(20)	-0.0080(9)	0.2020(9)	465(42)	45(9)	67(9)	12(16)	4(15)	6(7)
C(5)	0.5872(15)	0.1644(12)	0.4083(8)	221(25)	177(17)	36(7)	-49(18)	23(10)	12(9)
C(6)	0.4403(18)	0.1193(16)	0.4264(16)	251(31)	264(26)	54(10)	-95(25)	38(14)	-4(13)
C(7)	0.3542(14)	0.1014(12)	0.3478(10)	148(22)	139(15)	102(12)	-30(15)	41(13)	-12(11)
C(8)	0.4497(15)	0.1255(14)	0.2754(9)	166(23)	222(21)	73(10)	-100(19)	-21(12)	24(12)
C(9)	1.0778(14)	0.2235(11)	0.1472(10)	179(22)	125(14)	116(12)	53(15)	97(14)	40(10)
C(10)	1.1455(15)	0.2683(11)	0.0696(10)	209(24)	107(13)	115(12)	25(15)	81(15)	31(10)
C(11)	1.1007(13)	0.3817(10)	0.0685(9)	180(22)	77(10)	83(9)	2(12)	51(11)	0(8)
C(12)	0.9441(13)	0.3799(9)	0.1023(8)	183(21)	75(9)	60(8)	-6(12)	21(10)	15(7)

* Anisotropic thermal parameters defined by: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

distances and angles are listed in Table 2.) The major distortion appears as a lengthening of the Sc-O(1) bond [2.236(8) vs. 2.147(7) and 2.164(7) Å for bonds to other oxygen atoms], apparently brought about by a forcing

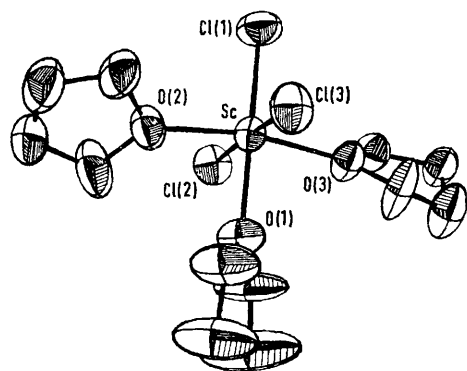


FIGURE 1 Molecular structure: atoms shown as their 40% probability ellipsoids for thermal motion

of the ligands away from Cl(1) such that the angles Cl(1)-Sc-L all fall in the range 92.5(1)–96.7(2)°. The origin of the structural effect could be electronic, but in

* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

TABLE 2

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

(a) Distances			
Sc-Cl(1)	2.406(4)	Sc-O(1)	2.236(8)
Sc-Cl(2)	2.420(4)	Sc-O(2)	2.147(7)
Sc-Cl(3)	2.415(4)	Sc-O(3)	2.164(7)
O(1)-C(1)	1.46(1)	O(1)-C(4)	1.47(1)
O(2)-C(5)	1.48(1)	O(2)-C(8)	1.47(2)
O(3)-C(9)	1.45(1)	O(3)-C(12)	1.50(1)
C(1)-C(2)	1.52(2)	C(2)-C(3)	1.45(2)
C(3)-C(4)	1.49(2)	C(5)-C(6)	1.45(2)
C(6)-C(7)	1.47(2)	C(7)-C(8)	1.43(2)
C(9)-C(10)	1.48(2)	C(10)-C(11)	1.51(2)
C(11)-C(12)	1.51(2)		
(b) Angles			
Cl(1)-Sc-Cl(2)	92.5(1)	Cl(1)-Sc-Cl(3)	93.0(1)
Cl(1)-Sc-O(2)	96.1(2)	Cl(1)-Sc-O(3)	96.7(2)
Cl(2)-Sc-O(1)	87.9(2)	Cl(2)-Sc-O(2)	88.9(2)
Cl(2)-Sc-O(3)	89.9(2)	Cl(3)-Sc-O(1)	86.6(2)
Cl(3)-Sc-O(2)	89.7(2)	Cl(3)-Sc-O(3)	90.2(2)
O(1)-Sc-O(2)	84.3(3)	O(1)-Sc-O(3)	82.9(3)
Cl(1)-Sc-O(1)	179.5(3)	Cl(2)-Sc-Cl(3)	174.4(2)
O(2)-Sc-O(3)	167.2(3)	C(1)-O(1)-C(4)	111.1(9)
O(1)-C(1)-C(2)	104.7(12)	C(1)-C(2)-C(3)	105.6(14)
C(2)-C(3)-C(4)	108.4(14)	C(3)-C(4)-O(1)	104.0(11)
C(5)-O(2)-C(8)	110.5(9)	O(2)-C(5)-C(6)	104.1(11)
C(6)-C(7)-C(8)	110.6(12)	C(6)-C(7)-C(8)	108.1(11)
C(7)-C(8)-O(2)	106.2(11)	C(9)-O(3)-C(12)	109.3(8)
O(3)-C(9)-C(10)	104.4(11)	C(9)-C(10)-C(11)	105.6(11)
C(10)-C(11)-C(12)	103.2(10)	C(11)-C(12)-O(3)	105.1(9)

0.68 Å as the radius of the scandium(III) ion based on the Sc-O distance in the tris(acetylacetonato)-structure seems to be quite valid; one may expect larger Sc-O lengths in complexes of neutral-donor ligands or in those which present detrimental steric factors.

The mean scandium-chlorine bond length (2.41 Å) is quite short compared to the value (2.58 Å) found in the chlorine-bridged dimer $[(C_5H_5)_2ScCl]_2$,⁶ but this is not particularly unusual. In di- μ -chloro-bis[chloro(methyl)aluminium]¹⁵ the Al-Cl(μ) distance is 2.25(1) compared

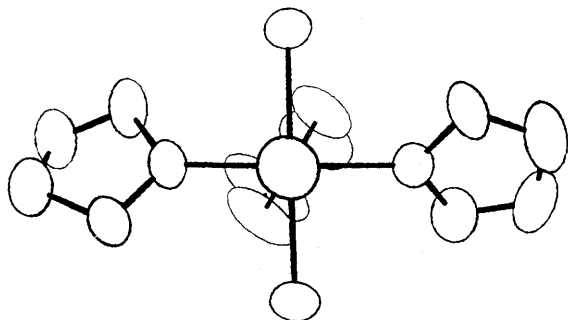


FIGURE 2 Configuration of the tetrahydrofuran rings viewed down the Cl(1)-Sc-O(1) axis

to Al-Cl(terminal) of 2.05(1) Å. This effect is sometimes explained in terms of a weaker donating ability for the bridging halide ion, but recent studies^{16,17} on mono-bridged halide systems such as $PhBrC_3N_2(CN)_2$ and

¹⁵ G. Allegra, G. Perego, and A. Immirzi, *Makromol. Chem.*, 1963, **61**, 69.

$K[Al_2Me_6F]$ show quite normal Br-C and Al-F bond lengths. An explanation of the lengthening of the

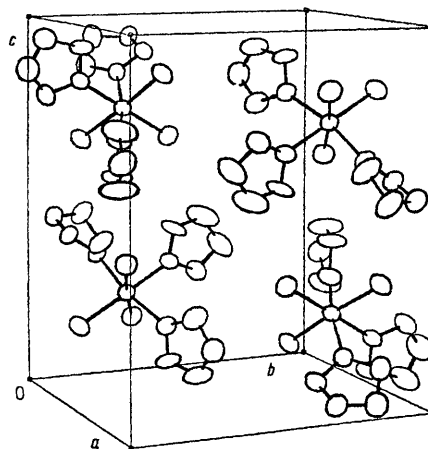


FIGURE 3 Unit-cell packing diagram

bridge-bonds in dibridged halide moieties may therefore lie in ring strain and/or halide-halide repulsion.

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¹⁶ J. L. Atwood and W. R. Newberry, *J. Organometallic Chem.*, 1974, in the press.

¹⁷ J. L. Atwood and W. A. Sheppard, unpublished results.