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The Structure of Trichlorotris(tetrahydrofuran)titanium(III)

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Abstract

$Ti(C_4H_8O)_3Cl_3$, $C_{12}H_{24}Cl_3O_3Ti$, crystallizes in space group $P2_1/c$, with $a = 17{\cdot}63$ (5), $b = 12{\cdot}62$ (2), $c = 15{\cdot}26$ (3) Å, $\beta = 91{\cdot}7$ (2)°, $Z = 8$. Final $R = 0{\cdot}071$ for 2333 observed reflexions. The complex is neutral with octahedrally coordinated Ti^{III} and meridional configuration of the Cl atoms. The two independent molecules in the asymmetric unit are similarly oriented, with the exception of the tetrahydrofuran ligands *trans* to Cl atoms.

Introduction

Clark, Lewis, Machin & Nyholm (1963) determined the space group and cell parameters of the complex. They called attention to the fact that the crystals must contain either four dimers or two sets of four monomers with different orientation of two independent molecules in the asymmetric unit. The magnetic data measured in the temperature range 77–300 K [μ_{eff}(293 K) = 1·82 BM,* $\theta = -37$ K] are in agreement with the monomeric structure and distorted octahedral coordination of the central Ti^{III} atom (Zikmund, Valent, Hrnčiarová & Kohútová, 1969; Zikmund, Kohútová, Handlovič & Mikloš, 1979; see also close values 1·80 BM, Pregaglia, Mazzanti & Morero, 1959; and 1·83 BM, Schläfer & Götz, 1964). A diffuse reflectance spectrum, typical for this coordination, was observed (Clark, Lewis, Machin & Nyholm, 1963; Zikmund & Štepničková, 1969; Zikmund, Kohútová, Handlovič & Mikloš, 1979). From the number of modes active in the infrared it has been concluded that the tetrahydrofuran adduct $Ti(C_4H_8O)_3Cl_3$ adopts the *trans* (C_{2v}) configuration (Clark, 1965).

Investigation of thermal properties did not yield consistent results. Pregaglia, Mazzanti & Morero (1959) observed only formation of $Ti(C_4H_8O)_2Cl_3$, while Kern (1962) and Clark (1968) reported formation of $Ti(C_4H_8O)Cl_3$. Our studies (Zikmund & Štepničková, 1969), however, showed that in the course of thermal decomposition first the monomeric five-coordinate complex $Ti(C_4H_8O)_2Cl_3$ and then the coordination polymer $Ti(C_4H_8O)Cl_3$ are formed.

Experimental

Blue-green prismatic crystals of $Ti(C_4H_8O)_3Cl_3$ were prepared by evaporating a tetrahydrofuran solution of the complex. Because of the extreme reactivity of the Ti^{III} compounds with oxygen and moisture, all reactions and operations were carried out in an atmosphere of dry oxygen-free nitrogen. Suitable crystals were sealed in Lindemann-glass capillaries in an inert atmosphere (Zikmund & Valent, 1969). The capillaries were then coated with lacquer containing a non-coordinating solvent. A suitable crystal was selected by rotation, Weissenberg and precession methods. Intensities were collected on a Syntex $P2_1$ diffractometer with graphite-monochromated Mo $K\alpha$ radiation out to $2\theta = 45°$ in the θ–2θ scan mode. Two check reflexions showed no significant change of intensity. 4103 independent reflexions were recorded; of these, 2333, for which $I_{hkl} > 1{\cdot}96\sigma_I$, were considered to be observed. The data were corrected for Lorentz and polarization effects but not for absorption ($\mu = 0{\cdot}99$ mm^{-1}). Crystal data: $Ti(C_4H_8O)_3Cl_3$; $M_r = 370{\cdot}58$; space group $P2_1/c$; $a = 17{\cdot}63$ (5), $b = 12{\cdot}62$ (2), $c = 15{\cdot}26$ (3) Å, $\beta = 91{\cdot}7$ (2)°; $V = 3393{\cdot}7$ Å^3; $Z = 8$; $D_c = 1{\cdot}45$, D_m (flotation method) = 1·45 Mg m^{-3}; crystal size 0·3 × 0·4 × 0·6 mm.

Structure determination and refinement

A Patterson synthesis was calculated with all reflexions. The distribution of peaks around the origin indicates that the Ti^{III} atoms are octahedrally coordinated, the two independent octahedra have the same orientation and the Cl atoms are in *trans* positions. The distribution of peaks at $y = 0$ and $\frac{1}{2}$ showed that the

Table 1. *Distribution of E^2 by parity groups*

eee	*eoe*	*eoo*	*eeo*	*ooo*	*oee*	*oeo*	*ooe*
2·038	2·141	0·992	0·923	0·487	0·433	0·422	0·409

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* 1 BM ≡ 9·27 × 10^{-24} JT^{-1}.

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octahedra are shifted approximately by **a**/2. Accordingly, the diffractions *hkl* with $h = 2n + 1$ are generally weaker than those with $h = 2n$, Table 1.

Hence it was decided first to solve the fictitious superposition structure with $\mathbf{a}' = \mathbf{a}/2$ corresponding to the subset of diffractions with $h = 2n$ in the same space group $P2_1/c$. The application of *TANFOR* (Drew & Larson, 1968) confirmed the octahedral coordination of $\mathrm{Ti^{III}}$ and showed its correct position out of two possibilities allowed by the Patterson synthesis. The superposition structure could be refined to $R = 0{\cdot}18$. After a few unsuccessful trials to separate the two independent molecules in the true unit cell, *MULTAN* (Main, Woolfson & Germain, 1975) was used with the 426 highest renormalized E values to guarantee the presence of all parity groups. The calculation was stopped when a combination of phases for $h = 2n$ appeared to be identical with that for the superposition structure. The corresponding E map showed the positions of 20 atoms and the next F_o synthesis showed the correct positions of all non-hydrogen atoms.

The isotropic full-matrix least-squares cycles yielded $R = 0{\cdot}13$. Anisotropic block-diagonal least-squares refinement lowered R to 0·09. At this stage H atoms with calculated positional parameters and thermal parameters of corresponding C atoms were included in the refinement. The final R is 0·071 for 2333 observed reflexions, which appears to be satisfactory with respect to experimental difficulties. The final $(F_o - F_c)$ synthesis showed no significant features. The calculations were performed on a Syntex XTL system and a Siemens 4004/150 [Fourier synthesis program *DRF* (Zalkin, 1970); *TANFOR* (Drew & Larson, 1968); NRC crystallographic programs (Ahmed, Hall, Pippy & Huber, 1966)].*

Results and discussion

The analysis confirmed that the complex is neutral. The asymmetric part of the unit cell contains two monomers of trichlorotris(tetrahydrofuran)titanium(III), Fig. 1. Atomic coordinates are listed in Table 2. Both $\mathrm{Ti^{III}}$ atoms are octahedrally coordinated. The Cl atoms are in meridional configuration, their distances from the central atom being very similar, Table 3.

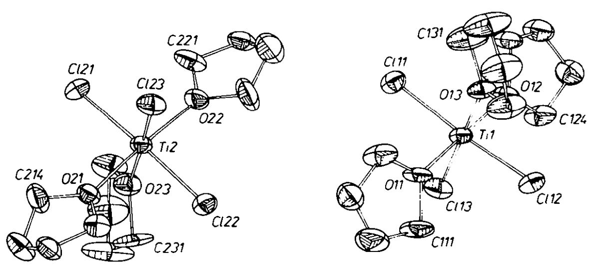

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the two independent molecules at 0·4 probability.

Table 2. *Final positional parameters* (×10⁴) *and equivalent isotropic thermal parameters of non-hydrogen atoms with e.s.d.'s in parentheses*

$B_{\mathrm{eq}} = \frac{4}{3}\sum_i \sum_j \beta_{ij}\,\mathbf{a}_i.\mathbf{a}_j$, where $\beta_{ll} = B_{ll}$ and $\beta_{ij} = \frac{1}{2}B_{ij}$ if $i \neq j$.

	x	y	z	B_{eq} (Å²)
Ti(1)	3811 (1)	2614 (1)	2493 (1)	3·12
Ti(2)	8845 (1)	2555 (1)	2461 (1)	3·13
Cl(11)	4760 (2)	1952 (2)	3470 (2)	4·50
Cl(12)	2859 (2)	3460 (2)	1635 (2)	4·82
Cl(13)	3888 (2)	1133 (2)	1577 (2)	4·96
Cl(21)	9678 (2)	1701 (2)	3450 (2)	4·52
Cl(22)	7960 (2)	3141 (2)	1385 (2)	4·46
Cl(23)	8993 (2)	4191 (2)	3154 (2)	5·11
O(11)	4643 (4)	3421 (6)	1818 (4)	4·46
O(12)	2963 (4)	1881 (5)	3205 (4)	4·14
O(13)	3772 (4)	4035 (5)	3303 (4)	4·08
O(21)	9727 (4)	2873 (5)	1604 (4)	3·83
O(22)	7908 (4)	2186 (6)	3237 (4)	4·34
O(23)	8771 (4)	1049 (5)	1757 (4)	4·95
C(111)	4660 (8)	3512 (12)	858 (7)	6·58
C(112)	5430 (8)	3806 (16)	678 (8)	9·20
C(113)	5844 (7)	4078 (10)	1452 (8)	6·00
C(114)	5326 (7)	3911 (12)	2161 (7)	6·87
C(121)	2925 (6)	1796 (9)	4149 (6)	4·76
C(122)	2314 (7)	1025 (10)	4313 (7)	5·78
C(123)	1807 (6)	1084 (9)	3559 (7)	5·11
C(124)	2322 (7)	1318 (11)	2808 (7)	5·96
C(131)	4036 (10)	4170 (11)	4203 (8)	8·05
C(132)	3929 (11)	5242 (10)	4427 (9)	9·07
C(133)	3821 (9)	5849 (11)	3659 (9)	8·10
C(134)	3583 (10)	5078 (10)	2977 (8)	7·60
C(211)	9783 (6)	3788 (9)	1038 (6)	4·49
C(212)	558 (6)	3761 (9)	659 (7)	4·88
C(213)	773 (7)	2606 (10)	700 (8)	5·97
C(214)	423 (7)	2250 (11)	1547 (8)	6·23
C(221)	7865 (7)	1371 (10)	3903 (7)	5·89
C(222)	7070 (7)	1457 (10)	4235 (7)	5·33
C(223)	6853 (7)	2577 (11)	4093 (9)	6·88
C(224)	7273 (7)	2939 (12)	3298 (9)	7·45
C(231)	8695 (9)	961 (10)	781 (7)	7·35
C(232)	8886 (13)	−115 (12)	586 (8)	10·76
C(233)	8753 (10)	−747 (11)	1314 (9)	8·07
C(234)	8872 (8)	−11 (9)	2083 (7)	5·98

The distances Ti–O are significantly longer for the O atoms that are *trans* to the Cl atoms [2·18 (1) Å] than for the remaining two O atoms [2·08 (1), 2·09 (1) and 2·10 (1), 2·11 (1) Å respectively]. It seems probable that these tetrahydrofuran molecules are released in the first step of the thermal decomposition, leaving $\mathrm{Ti(C_4H_8O)_2Cl_3}$ as the decomposition product, in agreement with the observation of Zikmund & Štepničková (1969).

A similar *trans* effect has been reported for *mer*-$\mathrm{Ti(C_5H_5N)_3Cl_3.C_5H_5N}$ (Collins & Drew, 1972).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35527 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

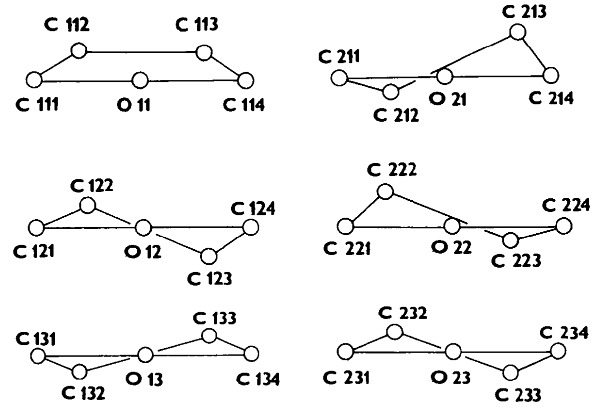

Fig. 2. Schematic drawings of the six tetrahydrofuran rings with different degrees of deformation (viewed from their respective reference planes).

Table 3. *Bond distances* (Å) *and angles* (°) *for the coordination polyhedra*

Ti(1)–Cl(11)	2·360 (3)	Ti(2)–Cl(21)	2·337 (3)
Ti(1)–Cl(12)	2·355 (3)	Ti(2)–Cl(22)	2·352 (3)
Ti(1)–Cl(13)	2·341 (3)	Ti(2)–Cl(23)	2·331 (3)
Ti(1)–O(11)	2·084 (7)	Ti(2)–O(21)	2·100 (7)
Ti(1)–O(12)	2·090 (7)	Ti(2)–O(22)	2·113 (7)
Ti(1)–O(13)	2·181 (6)	Ti(2)–O(23)	2·185 (7)
Cl(11)–Ti(1)–Cl(12)	172·8 (1)	Cl(21)–Ti(2)–Cl(22)	170·9 (1)
Cl(11)–Ti(1)–Cl(13)	92·4 (1)	Cl(21)–Ti(2)–Cl(23)	93·2 (1)
Cl(12)–Ti(1)–Cl(13)	94·8 (1)	Cl(22)–Ti(2)–Cl(23)	95·8 (1)
O(11)–Ti(1)–O(12)	176·9 (3)	O(21)–Ti(2)–O(22)	175·4 (3)
O(12)–Ti(1)–O(13)	92·0 (3)	O(22)–Ti(2)–O(23)	92·7 (3)
O(11)–Ti(1)–O(13)	85·0 (3)	O(21)–Ti(2)–O(23)	84·0 (3)
Cl(13)–Ti(1)–O(13)	177·3 (2)	Cl(23)–Ti(2)–O(23)	176·2 (2)
Cl(12)–Ti(1)–O(13)	84·7 (2)	Cl(22)–Ti(2)–O(23)	84·4 (2)
Cl(11)–Ti(1)–O(13)	88·1 (2)	Cl(21)–Ti(2)–O(23)	86·8 (2)
Cl(11)–Ti(1)–O(12)	91·1 (2)	Cl(21)–Ti(2)–O(22)	91·3 (2)
Cl(12)–Ti(1)–O(12)	88·9 (2)	Cl(22)–Ti(2)–O(22)	86·9 (2)
Cl(13)–Ti(1)–O(12)	90·7 (2)	Cl(23)–Ti(2)–O(22)	91·1 (2)
Cl(11)–Ti(1)–O(11)	89·4 (2)	Cl(21)–Ti(2)–O(21)	91·6 (2)
Cl(12)–Ti(1)–O(11)	90·2 (2)	Cl(22)–Ti(2)–O(21)	89·6 (2)
Cl(13)–Ti(1)–O(11)	92·3 (2)	Cl(23)–Ti(2)–O(21)	92·2 (2)

Table 5. *Deviations Δ* (Å) *of* C(*ij*2) *and* C(*ij*3) *from the reference plane through* O(*ij*), C(*ij*1) *and* C(*ij*4), *the torsion angles τ_{ij}* (°) *around the bond* C(*ij*2)–C(*ij*3) *and the angles φ_{ij}* (°) *of the bond* Ti(*i*)–O(*ij*) *to the respective reference planes for the six tetrahydrofuran rings THF$_{ij}$*

ij	ΔC(*ij*2)	ΔC(*ij*3)	τ_{ij}	φ_{ij}
11	0·336 (19)	0·314 (13)	2·2 (1·8)	3·7
12	0·217 (13)	−0·289 (11)	33·4 (1·2)	7·3
13	−0·139 (19)	0·160 (16)	20·6 (2·0)	2·2
21	−0·082 (11)	0·489 (13)	35·7 (1·1)	−4·4
22	0·374 (12)	−0·089 (13)	30·3 (1·2)	−11·4
23	0·231 (22)	−0·185 (17)	29·1 (2·0)	5·5

Each of the tetrahydrofuran ligands (Table 4) has a different degree of conformation. Only one of the six tetrahydrofuran rings (Fig. 2) has the envelope conformation, the others have a propeller-like form. If the plane through O(*ij*), C(*ij*1) and C(*ij*4) is taken as the reference plane, the deviations of C(*ij*2) and C(*ij*3) from it and the torsion angles τ_{ij} [C(*ij*1)–C(*ij*2)–C(*ij*3)–C(*ij*4)] may serve as a measure of the deformation of rings, Table 5. The bond lengths O–C vary from 1·44 to 1·50 Å, the bond lengths C–C from 1·39 to 1·52 Å. Similar variations in bond lengths for coordinated tetrahydrofuran rings were observed in $Sc(C_4H_8O)_3Cl_3$ (Atwood & Smith, 1974). The angles φ_{ij} between bonds Ti(*i*)–O(*ij*) and the corresponding reference planes are rather small (from 2·2 to 11·4°).

With respect to the bond lengths within coordination polyhedra it seems that packing conditions are mainly responsible for the variation of tetrahydrofuran rings as the most flexible part of the structure.

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Table 4. *Bond distances* (Å) *and angles* (°) *for the tetrahydrofuran rings THF$_{ij}$* [*j is the number of the* O *atom belonging to* Ti(*i*)]

ij	11	12	13	21	22	23
O(*ij*)–C(*ij*1)	1·470 (12)	1·449 (11)	1·446 (14)	1·446 (12)	1·450 (13)	1·496 (12)
C(*ij*1)–C(*ij*2)	1·441 (20)	1·479 (17)	1·410 (19)	1·499 (15)	1·509 (17)	1·433 (20)
C(*ij*2)–C(*ij*3)	1·413 (19)	1·438 (16)	1·409 (19)	1·507 (17)	1·478 (19)	1·392 (20)
C(*ij*3)–C(*ij*4)	1·451 (17)	1·512 (16)	1·476 (20)	1·518 (18)	1·510 (19)	1·506 (18)
C(*ij*4)–O(*ij*)	1·439 (15)	1·453 (14)	1·442 (15)	1·462 (14)	1·473 (16)	1·437 (13)
C(*ij*1)–O(*ij*)–C(*ij*4)	106·7 (8)	108·7 (8)	106·6 (9)	108·8 (8)	110·9 (8)	106·4 (8)
O(*ij*)–C(*ij*1)–C(*ij*2)	104·9 (11)	105·8 (9)	107·6 (12)	107·0 (8)	104·7 (9)	105·2 (11)
C(*ij*1)–C(*ij*2)–C(*ij*3)	111·7 (13)	105·6 (10)	109·5 (13)	103·7 (9)	104·9 (10)	109·3 (14)
C(*ij*2)–C(*ij*3)–C(*ij*4)	105·5 (11)	104·2 (10)	104·9 (13)	102·3 (10)	106·1 (11)	104·2 (13)
C(*ij*3)–C(*ij*4)–O(*ij*)	109·2 (10)	104·8 (9)	107·5 (11)	104·7 (9)	104·4 (10)	107·0 (10)
Ti(*i*)–O(*ij*)–C(*ij*1)	124·5 (6)	127·2 (6)	128·3 (7)	126·1 (6)	127·4 (6)	123·8 (6)
Ti(*i*)–O(*ij*)–C(*ij*4)	128·6 (7)	124·0 (6)	124·5 (7)	124·9 (6)	120·1 (7)	129·4 (6)

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The Structures of the *fac* and *mer* Isomers of Trichlorotris[dimethyl(phenyl)phosphine]iridium(III)

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Abstract

The structure of the *facial* isomer of trichlorotris[dimethyl(phenyl)phosphine]iridium(III) has been determined, and that of the *meridional* isomer has been redetermined. *fac*-[$\mathrm{Ir^{III}Cl_3(PMe_2Ph)_3}$] (1) crystallizes in space group *Ia* with $a = 16{\cdot}198$ (2), $b = 14{\cdot}923$ (2), $c = 22{\cdot}024$ (2) Å, $\beta = 96{\cdot}37$ (2)°, $Z = 8$. *mer*-[$\mathrm{Ir^{III}Cl_3(PMe_2Ph)_3}$] (2) crystallizes in space group $P2_1/n$ with $a = 10{\cdot}814$ (1), $b = 38{\cdot}894$ (3), $c = 13{\cdot}663$ (1) Å, $\beta = 107{\cdot}15$ (1)°, $Z = 8$. The structures were refined to $R = 0{\cdot}025$ [(1), 5471 independent reflections] and 0·031 [(2), 12 556 independent reflections]. Metal–ligand distances in (1) are Ir—Cl 2·456 (2)–2·468 (2) Å (*trans* to P) and Ir—P 2·285 (2)–2·295 (2) Å (*trans* to Cl). Metal–ligand distances in (2) do not differ significantly from those reported earlier but are more precise and reveal the existence of small differences between chemically equivalent bonds due to inequivalence of intramolecular non-bonding interactions. Values from this experiment are: Ir–Cl 2·434 (1)–2·439 (1) Å (*trans* to P) and 2·359 (1)–2·368 (1) Å (*trans* to Cl), Ir—P 2·278 (1)–2·282 (1) Å (*trans* to Cl) and 2·363 (1)–2·384 (1) Å (*trans* to P).

Introduction

Recently, we have carried out a series of X-ray analyses (and in some cases neutron analyses) on the series of complexes $L_3\mathrm{H}_{(3-n)}\mathrm{Cl}_n\mathrm{Ir^{III}}$ (L = $\mathrm{PMe_2Ph}$, $n = 0,1,2,3$). Clearly, metal–ligand bond lengths in such a series are not only a function of the primary ligand type (Cl, H, L). Other determinants include the isomeric arrangement of the ligands (*cis*, *trans*, *mer*, *fac*), the differing steric requirements of differing substituents (Cl or H), and differing bond compression and angle deformations due to changes in non-bonding interactions to the methyl and phenyl substituents of the phosphine ligands (as the $\mathrm{PMe_2Ph}$ configurations alter). The present series of experiments are intended to

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