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Dichlorobis(η^5-isopropylcyclopentadienyl)titanium(IV), [$TiCl_2(C_8H_{11})_2$]

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Abstract. M_r = 333·2, orthorhombic, *Ccmm*, a = 6·808 (4), b = 11·618 (11), c = 20·495 (21) Å, V = 1621·1 Å^3, Z = 4, D_x = 1·365 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 8·6 cm^{-1}, $F(000)$ = 696, T = 295 K, $R_{\rm final}$ = 0·047 for 725 independent observed reflections. The molecules have pseudotetrahedral symmetry at the metal atom, with the isopropylcyclopentadienyl rings eclipsed in projection on the $TiCl_2$ plane. The Ti–ring-carbon-atom distances vary from 2·350 (3) to 2·444 (4) Å, the longest distance being to the carbon atom carrying the substituent alkyl group.

Introduction. The rather limited data presently available suggest that the molecular geometries of bis(η^5-alkylcyclopentadienyl)metal dihalides are determined primarily by the steric requirements of the substituent alkyl groups. Thus in dichlorobis(η^5-methylcyclopentadienyl)titanium(IV), $(MeCp)_2TiCl_2$, the methyl groups eclipse each other directly above and below the $TiCl_2$ group (Peterson & Dahl, 1975), but the corresponding *tert*-butyl compound, $(t\text{Bu}Cp)_2TiCl_2$, has a less symmetrical structure with the more bulky alkyl groups directed away from each other on opposite sides of the molecule (Howie, McQuillan & Thompson, 1984). As these structural features may well affect the reactivity of titanium–aluminium reagent systems derived from these molecules, we were interested to determine the structure of dichlorobis(η^5-isopropylcyclopentadienyl)titanium(IV), $(i\text{Pr}Cp)_2TiCl_2$, in which the steric effect of the alkyl group is intermediate between those of methyl and *tert*-butyl.

Experimental. $(i\text{Pr}Cp)_2TiCl_2$ prepared using the method of Sullivan & Little (1967), deep-red elongated rhombohedral crystals from slowly evaporating dichloromethane.

Single crystal approx. 1·0 × 0·4 × 0·4 mm, Nicolet *P*3 four-circle diffractometer (Mo $K\alpha$), cell parameters from 14 high-angle reflections. Space group *Ccmm* (non-standard setting of *Cmcm*, No. 63). θ–2θ scan technique, variable scan speed, $0 < 2\theta < 50°$, 725 independent reflections, $I > 3\sigma(I)$, measured in one octant of reciprocal space, h 0→8, k 0→13, l 0→24. Four standard reflections showed no sign of deterioration or crystal movement. No absorption correction. Non-hydrogen-atom positions from Patterson and Fourier syntheses, block-diagonal least-squares refinement, all atoms anisotropic, to R = 0·052. Ring hydrogen atoms from difference map, included in refinement with isotropic temperature factors, $R_{\rm final}$ = 0·047. Second difference map showed diffuse areas of electron density (< 0·3 e Å^{-3}) in areas of methyl hydrogen atoms, but no clear indication of hydrogen-atom positions. Temperature factors indicate high thermal vibrational amplitude for methyl carbon atoms. Weighting scheme $w = \{1 + [(|F_o| - 13)/24]^2\}^{-1}$. No reflections discarded. $(\Delta/\sigma)_{\max}$ = 0·15. $\Delta\rho$ in final difference map within +0·3 and −0·3 e Å. Computer programs based on those of Ahmed, Hall, Pippy & Huber (1966), atomic scattering factors from

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International Tables for X-ray Crystallography (1974). Function minimized in least-squares refinement $\sum w(|F_o|-(F_c|)^2$.

Discussion. The calculated atomic coordinates are given in Table 1 and details of bond lengths and angles in Table 2.* The molecular structure is illustrated in Fig. 1.

The (iPrCp)$_2$TiCl$_2$ molecule has the C_{2v} symmetry of the crystal site and the structure is analogous to that of (MeCp)$_2$TiCl$_2$ rather than that of (tBuCp)$_2$TiCl$_2$. The cyclopentadienyl rings are eclipsed in projection on the TiCl$_2$ plane and the substituent isopropyl groups are placed directly above and below the TiCl$_2$ group. This relatively compact arrangement is less likely to present crystal-packing problems than the more cumbersome structure of the *tert*-butyl compound, and there may also be a small electronic contribution in favour of a symmetrical arrangement, where this is possible, of the substituted cyclopentadienyl rings relative to the TiCl$_2$ group.

The ring carbon-atom positions are well defined, with no evidence of the excessive thermal motion occasionally encountered in compounds of this type (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974). The calculated ring C—C distances range from 1·387 (4) to 1·413 (4) Å, with an average of 1·401 Å; within the usual uncertainty limits of 3 × e.s.d. the differences between individual bond lengths are probably not significant. The Ti—C distances, in contrast, vary by 0·094 Å, from Ti—C(3), 2·350 (3), to Ti—C(1), 2·444 (4) Å, indicating a slight displacement of the ring relative to the titanium atom, in such a direction as to increase the separation between the titanium atom and the substituted ring carbon atom. There is no evidence of any directing non-bonded effect to account for this asymmetry in the metal–ring interaction: the closest relevant intermolecular distances are H(4)···Cl′, 2·98 Å, and C(4)···Cl, 3·54 Å, both of which are consistent only with very weak H···Cl or C···Cl van der Waals contacts. Accordingly, we conclude that the displacement of the ring must reflect a small substituent effect of the isopropyl group on the ring π-system. A similar but somewhat larger effect is also observed in the *tert*-butyl compound (Howie *et al.*, 1984).

The isopropyl groups are not significantly displaced from the ring plane [*i.e.* the angle between C(1)—C(4) and the calculated ring plane is less than 1°]. The thermal motion of the methyl groups and, to a lesser extent, of the secondary carbon atom C(4) introduces somewhat larger uncertainties into the isopropyl carbon-atom parameters than those for the ring carbon atoms, and probably accounts for the slightly short calculated C(4)—C(5) distance of 1·483 (7) Å.

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Table 1. *Atomic positional and equivalent isotropic thermal parameters*

(E.s.d.'s in last significant figures are given in parentheses.)

	x	y	z	B_{eq}*(Å^2)
Ti	−0·0141 (1)	0·0000	0·2500	3·05
Cl	0·2269 (1)	0·1475 (1)	0·2500	3·86
C(1)	0·0247 (6)	0·0000	0·1315 (2)	4·43
C(2)	−0·0884 (4)	0·0967 (3)	0·1498 (2)	4·51
C(3)	−0·2626 (4)	0·0605 (3)	0·1782 (2)	4·57
C(4)	0·2247 (7)	0·0000	0·0991 (2)	7·33
C(5)	0·2619 (9)	0·1058 (6)	0·0605 (3)	12·1

* $B_{eq} = \frac{4}{3}(B_{11}a^2 + B_{22}b^2 + B_{33}c^2)$.

Table 2. *Bond lengths* (Å) *and angles* (°)

(E.s.d.'s in last significant figures are given in parentheses.)

Ti—Cl	2·372 (1)	C(4)—C(5)	1·483 (7)
C(1)—C(2)	1·413 (4)	Ti—C(1)	2·444 (4)
C(2)—C(3)	1·387 (4)	Ti—C(2)	2·394 (3)
C(3)—C(3)′	1·406 (5)	Ti—C(3)	2·350 (3)
C(1)—C(4)	1·515 (6)	Ti—Cp(c)	2·068 (4)
Cl—Ti—Cl′	92·5 (1)	C(2)—C(1)—C(4)	127·3 (3)
C(2)—C(1)—C(2)′	105·3 (3)	C(1)—C(4)—C(5)	112·8 (4)
C(1)—C(2)—C(3)	109·7 (2)	C(5)—C(4)—C(5)′	111·9 (4)
C(2)—C(3)—C(3)′	107·7 (3)	Cp(c)—Ti—Cp(c)′	132·9 (3)

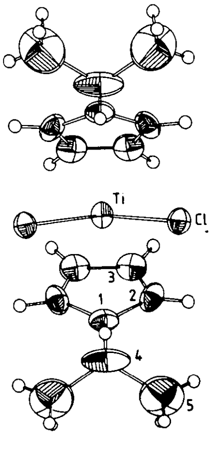

Fig. 1. *ORTEP*II (Johnson, 1976) diagram of ($\eta^5 i$PrCp)$_2$TiCl$_2$. Vibration ellipsoids are drawn at the 30% probability limit; methyl hydrogen atoms are shown in idealized positions.

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* Lists of structure factors, anisotropic thermal parameters, hydrogen-atom coordinates and distances and angles involving hydrogen have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42056 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Hydrogen-Bridged Dimeric Stacked Structure in a Dioximato Complex: (Oxamide oximato)(oxamide oxime)platinum(II) Iodide Dihydrate, $[Pt(C_2H_5N_4O_2)(C_2H_6N_4O_2)]I.2H_2O$

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Abstract. $M_r = 593{\cdot}21$, triclinic, $P\bar{1}$, $a = 7{\cdot}116\ (1)$, $b = 9{\cdot}424\ (2)$, $c = 11{\cdot}848\ (3)$ Å, $\alpha = 71{\cdot}95\ (2)$, $\beta = 89{\cdot}06\ (2)$, $\gamma = 70{\cdot}98\ (2)^\circ$, $V = 711$ Å^3, $Z = 2$, $D_x = 2{\cdot}77$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 115{\cdot}5$ cm^{-1}, $F(000) = 548$, room temperature, final $R = 0{\cdot}049$ for 4720 observed reflections. Strong intermolecular H bridges [O$\cdots$O = 2·74 (2) Å] lead to phane-like deviations of the complex cations from planarity and to pronounced pairing of the complexes in the stacks. The shortest intrastack Pt—Pt separation is 3·241 (5) Å. Further intra- and interstack H bridges involve the water molecules. Pt—N bond lengths are 1·971 (6)–2·006 (6) Å.

Introduction. Dioximato complexes of the d^8 metal ions of the Ni triad are normally planar, forming stacks of equally spaced molecules in the solid state. One of two stacking modes is usually observed (Endres, Keller, Lehmann, Poveda, Rupp & van de Sand, 1977): In the '*M—M* form' the stacking axis is perpendicular to the molecular planes, the metal atoms are in close contact along the stacks, and adjacent complexes of a stack are rotated with respect to each other, probably for steric reasons. Consequently, the unit-cell length along the stacking axis comprises two metal—metal separations. It had been proposed that an attractive metal—metal interaction stabilizes this form (Endres *et al.*, 1977), but recent theoretical work contradicts this assumption (Böhm, 1983), at least for Ni complexes. The highest occupied molecular orbital is considered to be ligand centred, and partial reduction (rather than partial oxidation) may lead to increased electronic conductivity along the stacks (Alvarez & Canadell, 1984). In the '*M—L* form' the stacking direction is inclined to the molecular plane, there are no direct metal—metal contacts, and the unit-cell length equals one metal—metal distance.

The complexes of oxamide oxime ['diaminoglyoxime, oaoH$_2$', HON=C(NH$_2$)—C(NH$_2$)=NOH], however, often differ from this simple behaviour: The mesomeric effect of the free electron pair of the amino groups enhances the basicity of the oxime O atoms, giving them a pronounced capability of forming strong intermolecular H bonds. The amino groups tend to be involved in H bridges as well. Such intermolecular H bridges lead to a rich structural chemistry in the solid state (Endres, 1980, 1982*a*,*b*) and allow the synthesis of new molecular electron conductors (Endres, Bongart, Nöthe, Hennig, Schweitzer, Schäfer, Helberg & Flandrois, 1985). The title compound is another example of the unusual stacking patterns found in oxamide oximato complexes.

Experimental. Preparation: $[Pt(oaoH_2)_2]Cl_2$ (Endres & Schlicksupp, 1980) dissolved in boiling H$_2$O, diluted HI solution added, slow cooling to room temperature, long (≈ 10 mm) dark-red column-like crystals filtered off after three days.

Section of a column, 0·15 × 0·19 × 0·23 mm, mounted on end of glass capillary; lattice parameters from setting angles of 50 reflections (Siemens–Stoe AED2 diffractometer, monochromated Mo $K\alpha$ radiation);

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