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THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS(BISCYCLOPENTADIENYLCHLOROTITANIUM) OXIDE *

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Summary

Bis(biscyclopentadienylchlorotitanium) oxide, $(Cp_2TiCl)_2O$, crystallizes in the enantiomorphic space groups $P3_121$ and $P3_221$ with a 7.742(1), c 27.177(7) Å. In this study only twins were obtained. On the basis of intensity data for 1106 independent reflections, the structure is described in $P3_121$ with final residuals of R_F = 3.27% and R_{wF} = 2.53%. The molecule is very similar to that of the analogous zirconium compound. Mean bond lengths are Cp—Ti(π), 2.09; Cl—Ti, 2.41; and Ti—O, 1.84 Å. The Ti—O—Ti bond angle is 173.8°.

Introduction

A number of quasi-tetrahedral biscyclopentadienyl dimers have been reported in which the metal atoms are linked by a linear or nearly linear oxygen bridge. Among these are the titanium and zirconium compounds with one or two cyclopentadiene (Cp) ligands in each tetrahedral group, with halogen atoms occupying the remaining positions. The structure of $(CpCl_2Ti)_2O$, first described by Allegra et al. [1,2], was recently redetermined by Thewalt and Schomburg [3]. The Ti—O—Ti bridge is linear. On the other hand, Clarke and Drew [4] have shown that the Zr—O—Zr angle in $(Cp_2ClZr)_2O$ is 169°. In this paper the crystal structure of the titanium analogue $(Cp_2ClTi)_2O$ is described, and the molecular structure compared to the structures of similar compounds.

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Experimental

Crystals of $(Cp_2ClTi)_2O$ were obtained by the reaction of biscyclopentadienylchloromethyltitanium Cp_2ClCH_3Ti with traces of water in benzene solution. They were recovered as heavily intergrown, transparent orange hexagonal platelets having $\{0001\}$ and $\{11\bar{2}0\}$ faces. Examination under crossed Nicols showed that all were twins; some contained many crystalline individuals, others only two. One of the latter, measuring 0.5 × 0.2 × 0.06 mm, with individuals of roughly equal volume, was chosen for this study.

X-ray diffraction data were obtained using a fully automated four-circle diffractometer with graphite monochromatized Mo-K_α radiation. Two unique sets were collected with $\langle \Delta I \rangle / \langle I \rangle = 1.4\%$, giving 1106 observed unique reflections ($I > 3\sigma$) out of 1316 unique measurements. No absorption correction was applied. The data were analyzed on a PDP8e computer using programs developed at NRCC.

Unit cell dimensions were determined from Guinier-de Wolff powder diffraction patterns using Cu-K_α radiation and As_2O_3 as an internal standard.

The positions of the Ti and Cl atoms were obtained by direct methods. The remaining non-hydrogen atoms were located by successive refinement and Fourier cycles. The H atoms were introduced at calculated positions, and their positional parameters refined with individual isotropic thermal parameters while the other atoms were refined anisotropically. The final residuals for the observed data are $R_F = 3.27\%$, $R_{WF} = 2.53\%$. The scattering factors for neutral atoms were used [13]. The anomalous scattering was not considered.

Discussion of the crystal structure determination

Since diffraction data from a twin were used to determine the structure of the molecule, some discussion of the crystal structure determination is in order.

The diffraction pattern of the twin displayed the $\bar{3}\frac{2}{m}1$ Laue group in *hP* [5]. Systematic extinctions in $(00l)$ reflections for $l \neq 3n$ showed that the compound belongs to the hexagonal system *hP*. The $\frac{2}{m}$ symmetry in the Laue group could not be due to multiple twinning of crystals belonging to the $\bar{3}$ Laue group because three 2-fold axes could be seen although the sample contained only two individuals. Therefore the only possible space groups for the sample are the enantiomorphs $P3_121$ and $P3_221$ (as for low quartz), and the sample is twinned by merohedry, i.e., is a twin by lattice symmetry [6], the twin law having an optical character [7]. Two twin laws are therefore possible: a reflection in $(11\bar{2}0)$ or one in $(10\bar{1}0)$, respectively the Brazil law and the combined law in low quartz. The combined law would require the superposition of $hk.l$ and $kh.l$ reflections so that the ratio of the intensities of these reflections could only have values in the range limited by the ratios V_I/V_{II} and V_{II}/V_I, V_I and V_{II} being the volumes of the two crystals in the twin. Since some measured intensity ratios were well outside this range (eg, $I(10.11)/I(01.11) > 6000$), the combined law can be discarded. This argument also rules out the presence of Dauphiné twinning, $[0001]_{60°}$, which of course cannot be detected optically.

Hence the twin operation is a reflection in $(11\bar{2}0)$. This operation corresponds to a symmetry element in the Laue class, and only the anomalous dispersion

TABLE 1

ATOMIC POSITIONAL AND THERMAL PARAMETERS FOR $(Cp_2ClTi)_2O$ [a]

Atom	X	Y	Z	$U_{11}(U)$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti	0.90661(9)	0.32364(10)	0.10322(2)	292(4)	281(4)	277(2)	162(2)	2(3)	−23(3)
Cl	1.16450(18)	0.64229(17)	0.07344(3)	624(8)	493(7)	478(6)	59(7)	6(6)	146(6)
O	0.64239(40)	$Y = X$	$Z = 1/2$	216(13)	$U_{22} = U_{11}$	304(15)	89(15)	−5(7)	$U_{23} = -U_{13}$
C(11)	0.55528(55)	0.17067(63)	0.10235(13)	274(23)	552(32)	760(28)	195(24)	−37(21)	−108(27)
C(12)	0.61715(57)	0.28035(64)	0.14538(12)	321(24)	669(32)	405(21)	275(25)	40(19)	−16(22)
C(13)	0.72287(62)	0.47851(64)	0.13297(13)	523(30)	654(35)	505(21)	450(27)	−97(23)	−166(24)
C(14)	0.72431(65)	0.49047(64)	0.08146(13)	564(32)	647(36)	622(24)	469(28)	52(26)	152(26)
C(15)	0.62110(59)	0.29898(64)	0.06210(12)	442(28)	681(34)	473(23)	374(27)	−170(21)	−136(23)
C(21)	0.96764(68)	0.19027(63)	0.02937(12)	732(37)	726(33)	382(18)	485(32)	32(24)	−107(21)
C(22)	1.12723(64)	0.23756(67)	0.06095(14)	550(34)	821(40)	725(28)	462(31)	101(26)	−253(28)
C(23)	1.05777(72)	0.11736(73)	0.10115(13)	1213(51)	1082(47)	461(23)	1033(43)	−174(28)	−262(28)
C(24)	0.85274(78)	−0.00402(64)	0.09561(14)	1228(51)	437(29)	734(28)	578(35)	242(34)	5(25)
C(25)	0.80282(69)	0.04005(66)	0.04983(13)	772(38)	562(32)	649(27)	436(29)	−165(26)	−353(26)
H(11)	0.4988(40)	0.0646(39)	0.1040(8)	20(8)					
H(12)	0.6042(41)	0.2492(40)	0.1756(8)	23(8)					
H(13)	0.7981(46)	0.5798(49)	0.1558(10)	65(12)					
H(14)	0.7755(43)	0.5823(44)	0.0605(9)	44(10)					
H(15)	0.5977(50)	0.2649(50)	0.0244(10)	60(12)					
H(21)	0.9800(56)	0.2568(53)	0.0006(10)	73(12)					
H(22)	1.2366(53)	0.3279(52)	0.0479(10)	84(13)					
H(23)	1.1144(52)	0.1182(53)	0.1326(10)	85(13)					
H(24)	0.7825(52)	−0.0882(52)	0.1217(10)	78(13)					
H(25)	0.6751(56)	−0.0381(60)	0.0312(11)	97(15)					

[a] Hexagonal $P3_121$ (No. 152); oxygen in 3(b), all other atoms in general positions 6(c). Numbers in parentheses are standard deviations. Anisotropic thermal parameters are multiplied by 10^4; isotropic by 10^3. $T = \exp - 2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)$

information is lost in the superposition of the reflections *hk.l* and $h + k\ \bar{k}.l$. Consequently the diffraction data are suitable for crystal structure determination [8]. However the absolute configuration cannot be determined because part of the sample is in $P3_121$ and part in $P3_221$. In the absence of appropriate morphological development, the obverse setting was arbitrarily selected by choosing the axes so that $I(10.1) > I(01.1)$ [9]. The structure is described here in the $P3_121$ space group using the 3(b) and 6(c) positions of the International Tables [10].

Crystal Data

$C_{20}H_{20}Ti_2Cl_2O$, M = 443.08 g mol^{-1}, hexagonal $P3_121$ and $P3_221$, with a 7.742(1), c 27.177(7) Å, U 1411 Å^3, Z = 3, D_c = 1.565 g cm^{-3}.

The atomic positional and thermal parameters are listed in Table 1. *

Discussion of the molecular structure

Bond distances and angles are given in Table 2, and the molecule is illustrated in Fig. 1.

Although the tetracyclopentadienyl zirconium and titanium analogues do not crystallize in the same space group (the Zr compound is monoclinic C2 [4]), the molecular configurations are almost identical. The Ti molecule is more symmetrical, and the oxygen bridge closer to linearity (173.81° vs. 168.3°).

The cyclopentadienyl rings are planar with mean carbon—carbon distances of 1.39 Å (ring 1) and 1.38 Å (ring 2). The minimum and maximum values of 1.344(6) and 1.403(5) Å show less variation than those of the Zr analogue at 1.17(6) and 1.57(6) Å [4].

To facilitate comparison of the configurations about each metal atom in similar molecules, we make use of the convention introduced by Prout et al. [11] in their comprehensive paper on Cp complexes. The molecular parameters are defined in Fig. 2. Data are given in Table 3 for five compounds: $(Cp_2ClTi)_2O$(I); $(Cp_2ClZr)_2O$(II); $(CpCl_2Ti)_2O$(III); Cp_2Cl_2Ti(IV); and Cp_2Cl_2Zr(V). These parameters were calculated using crystal data reported in the references cited except for V, for which the data are taken directly from Prout's analysis.

The configurations in these compounds are so similar that it would be unwise to speculate too extensively on the small differences which appear. However some general features are worth noting.

In each molecule the distortion from tetrahedral symmetry is reflected in an enlarged Φ angle (~130°) and a depressed θ angle (~97°). In the compounds containing two Cp ligands on each metal atom the configuration of the rings is staggered when viewed along the line joining the centroids of the two rings, with the exception of II in which the rings are eclipsed. (Of all the Cp_2XYZr compounds examined by Prout and his co-workers, this is the only compound

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TABLE 2

BOND DISTANCES (Å) AND ANGLES (DEGREES) IN $(Cp_2ClTi)_2O$

Ti—O	1.837(2)	C(11)—C(12)	1.382(5)
Ti—Cl	2.409(1)	C(12)—C(13)	1.372(6)
Ti—Cp(1)	2.084	C(13)—C(14)	1.403(5)
Ti—Cp(2)	2.096	C(14)—C(15)	1.389(6)
		C(15)—C(11)	1.393(5)
Ti—C(11)	2.364(4)	C(21)—C(22)	1.394(6)
Ti—C(12)	2.386(4)	C(22)—C(23)	1.361(6)
Ti—C(13)	2.413(4)	C(23)—C(24)	1.389(6)
Ti—C(14)	2.415(4)	C(24)—C(25)	1.395(6)
Ti—C(15)	2.398(4)	C(25)—C(21)	1.344(6)
Ti—C(21)	2.410(4)	Cp(1)—Ti—Cp(2)	129.61
Ti—C(22)	2.412(4)	Cp(1)—Ti—Cl	105.43
Ti—C(23)	2.406(4)	Cp(2)—Ti—Cl	104.28
Ti—C(24)	2.364(4)	Cp(1)—Ti—O	107.06
Ti—C(25)	2.410(4)	Cp(2)—Ti—O	109.25
		Cl—Ti—O	95.95
		Ti—O—Ti	173.81

Cp refers to the centroid of the cyclopentadienyl ring.

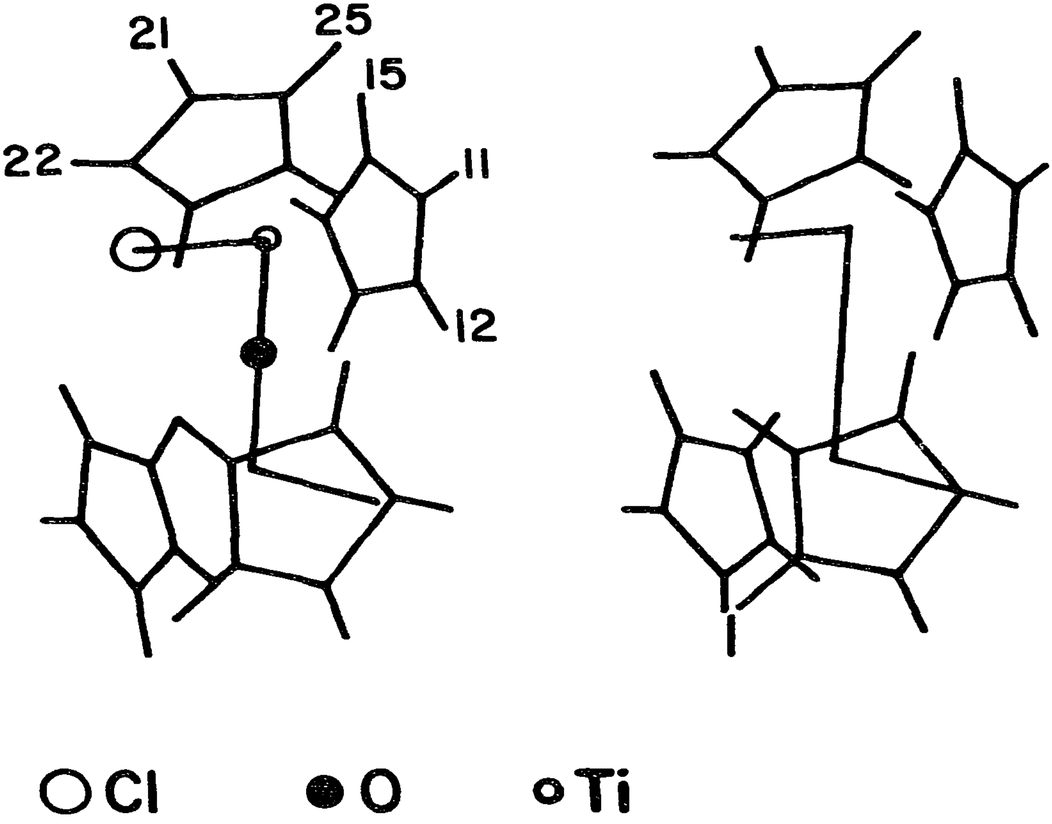

Fig. 1. Stereoscopic representation of $(Cp_2ClTi)_2O$.

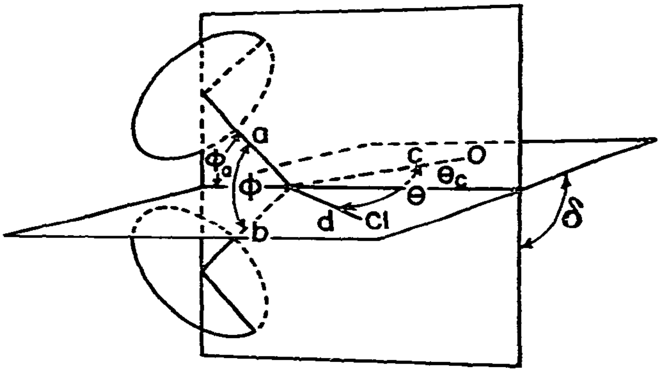

Fig. 2. Definition of the molecular parameters recorded in Table 3. The vertical plane is the Cp(1)—M—Cp(2) plane, where Cp is the centroid of the ring; the horizontal plane is the Cl—M—O plane (after Prout et al. [11]).

in which the rings are eclipsed.) The M—Cp bond length in III (2.01 Å) is significantly shorter than the corresponding distances in I and IV (2.08, 2.06 Å) suggesting a somewhat stronger interaction in mono-Cp groups. The M—Cl distances are also less in III than in the Cp_2Ti-groups by some 0.15 Å. These differences are not apparent in the Zr compounds.

The metal—oxygen distances in both dicyclopentadienyl dimers (I & II) are smaller by ca. 0.25 Å than the sum of the radii of the individual atoms or ions, an observation which led Clarke and Drew [4] to suggest multiple bond character. The M—O bond in the mono-Cp species III is further shortened by 0.06 Å.

The configurations of the two quasitetrahedral groups in I—III relative to each other are illustrated in Fig. 3. The remarkable difference between the mono-Cp and di-Cp species is that the former has a *trans* configuration while the latter

TABLE 3

MOLECULAR DIMENSIONS ABOUT THE METAL ATOM IN $(Cp_2ClTi)_2O$ AND SIMILAR MOLECULES [a]

	Compound	a (M—Cp)	b (M—Cp)	c (M—O)	d (M—Cl)
I	$(Cp_2ClTi)_2O$	2.08	2.10	1.84	2.41
II	$(Cp_2ClZr)_2O$ [b]	2.19	2.22	1.95	2.46
III	$(CpCl_2Ti)_2O$	2.01	2.24	1.78	2.23
IV	Cp_2Cl_2Ti	2.06	2.06	2.36 [c]	2.37
V	Cp_2Cl_2Zr [b]	2.19	2.19	2.44 [c]	2.44

Compound		δ	ϕ	ϕ_a	θ	θ_c	Ring Config.	Ref.
I		91.1	129.6	65.3	95.9	53.0	s [f]	This study
II	Zr(1)	90.2	124.7	63.9	99.3	45.4	e [f]	4
	Zr(2)	90.6	131.9	65.5	96.8	49.3		
III		90.4	117.0 [d]	69.5	102.6	51.7	—	3
IV		90.3	131.0	65.4	94.5 [e]	46.4	s	12
V		89.9	126.0	63.1	97.2 [e]	47.9	s	11

[a] Column headings refer to Fig. 2. Units are Ångstroms and degrees. [b] Average values for non-equivalent metal atoms. [c] M—Cl(2). [d] Cp—Ti—Cl(2); [e] Cl—M—Cl; [f] s = staggered, e = eclipsed configuration of the Cp rings.

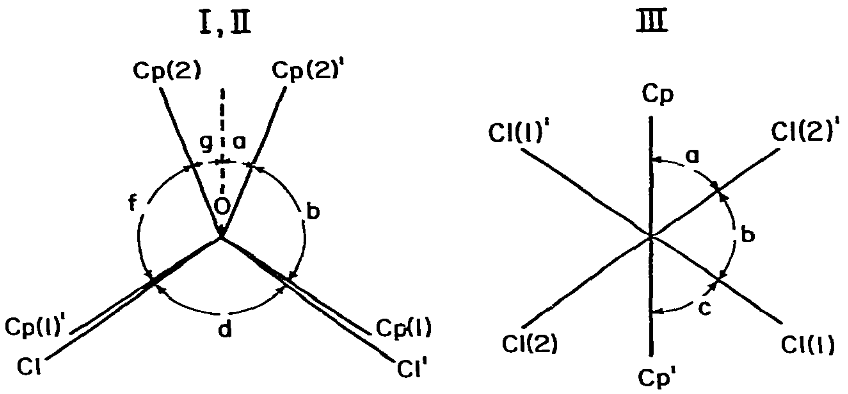

Fig. 3. Molecular configuration in the M—M direction: left, $(Cp_2ClTi)_2O$ (I) and $(Cp_2ClZr)_2O$ (II); right, $(CpCl_2Ti)_2O$ (III). The angles in degrees are:

	a	b	c	d	e	f	g
I	20.5	104.6	2.6	104.6	2.6	104.6	20.5
II	24.0	109.4	1.8	105.4	2.0	106.9	10.5
III	53.5	73.7	52.8				

The angles c and e are respectively taken between Cp(1) and Cl', Cl and Cp(1)'. The primed groups are linked to the second Ti in the molecule.

are eclipsed. The distortions in the Zr compound relative to the Ti compound are indicated in the caption to Fig. 3. In I and II the backbone of the molecule is bent slightly bringing the Cp(1) rings marginally closer to the chlorine atoms at the opposite ends of the molecule, and separating the Cp(2) rings. This slight bend could be due to M—O interactions or long range ligand interactions or both.

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