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THE CRYSTAL AND MOLECULAR STRUCTURE OF μ-OXALATOBIS[DI(η^5-CYCLOPENTADIENYL)TITANIUM]

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Summary

μ-Oxalatobis[di-(η^5-cyclopentadienyl)titanium], $[\mu\text{-}(C_2O_4)\{(\eta^5\text{-}C_5H_5)_2Ti\}_2]$, 0.5 $(C_2H_5)_2O$ crystallises in the orthorhombic space group *Pbcn* with *a* 17.228(13), *b* 12.224(13), *c* 30.309(23) Å and $Z = 12$. The final R was 0.061 (R_w 0.104). The oxalato group acts as a planar tetradentate bridging ligand, with the Ti atoms displaced in a *cis* fashion out of the $C_2O_4^{2-}$ plane. The reason for this displacement is analysed in terms of σ and π interaction between the metal and ligand, and steric contacts between the Cp rings. Comparison with the isoelectronic $[\mu\text{-}\{C_2(N(C_6H_4CH_3\text{-}p))_4\}\{(\eta^5\text{-}C_5H_5)_2Ti\}_2]$ is made.

Introduction

As part of an investigation of the reactions between C_xO_y compounds and derivatives of di(η^5-cyclopentadienyl)titanium (Cp_2Ti, $Cp = \eta^5\text{-}C_5H_5$) or μ-(η^5 : η^5-fulvalene)bis(η^5-cyclopentadienyltitanium) [1,2], which has as its goal the reductive coupling of CO_2 to $C_2O_4^{2-}$, we have prepared and structurally analysed the bridging oxalato complex $[\mu\text{-}(C_2O_4)\{(\eta^5\text{-}C_5H_5)_2Ti\}_2]$ (abbreviated as $[(Cp_2Ti)_2(C_2O_4)]$) which would be the simplest product of such a coupling reaction.

Experimental

$[(Cp_2Ti)_2(C_2O_4)]$ was obtained by dissolving $[(Cp_2TiCl)_2]$ [3] in deoxygenated water, filtering the solution and adding a four-fold molar excess of $K_2C_2O_4$ also dissolved in water. After filtering and drying of the resultant purple precipitate in vacuo at 100°C for 18 h, crystals suitable for X-ray work were obtained by slow evaporation of a solution of the complex in a 2 : 1 mixture of tetrahydrofuran and ether. In solution the paramagnetic complex (g = 1.979) was rapidly decomposed by air; the crystals were only moderately air sensitive. Photographic and diffractometer examination of the crystals readily yielded the space group and cell dimensions; orthorhombic, *Pbcn* with *a* 17.228(13), *b* 12.224(13), *c* 30.309(23) Å, $Z = 12$. Only after the discovery of 0.5 molecules of ether, $(C_2H_5)_2O$, per molecule of $[(Cp_2Ti)_2(C_2O_4)]$ in the crystal could D_x (1.39) be reconciled with D_M (1.44), using the formula $C_{24}H_{25}O_{4.5}Ti_2$, $M = 481.3$. Microanalysis, performed on crystals obtained from

TABLE 1

FRACTIONAL ATOMIC COORDINATES × 10^4 [a]

Atom	*x*	*y*	*z*
Ti(1)	7234(1)	342(1)	369(1)
Ti(2)	4622(1)	2107(1)	4511(1)
C(1)	5899(5)	1681(6)	3903(3)
C(2)	5747(5)	597(6)	4125(3)
O(1)	6484(3)	1748(4)	3666(2)
O(2)	6203(3)	−168(4)	4036(2)
O(3)	5415(3)	2461(4)	3976(2)
O(4)	5167(3)	554(4)	4378(2)
C(10)	7904(6)	−164(9)	4330(3)
C(11)	7592(6)	910(10)	4404(3)
C(12)	7978(6)	1606(8)	4115(4)
C(13)	8502(5)	1042(9)	3867(3)
C(14)	8477(6)	−83(9)	4002(4)
C(15)	6589(6)	17(9)	3008(3)
C(16)	6777(6)	−1011(10)	3181(3)
C(17)	7581(7)	−1099(8)	3198(3)
C(18)	7879(6)	−125(10)	3022(3)
C(19)	7278(7)	533(8)	2920(3)
C(20)	3453(6)	1159(9)	4396(5)
C(21)	3264(6)	2136(13)	4611(4)
C(22)	3451(7)	2991(9)	4306(5)
C(23)	3724(7)	2523(11)	3945(4)
C(24)	3734(6)	1378(11)	3986(4)
C(25)	5243(6)	3543(8)	4889(3)
C(26)	5743(6)	2642(9)	4917(3)
C(27)	5360(6)	1859(9)	5174(3)
C(28)	4649(6)	2227(9)	5301(3)
C(29)	4573(6)	3291(8)	5136(3)
Ti(3)	9064(1)	2013(1)	1739(1)
C(3)	9631(5)	1875(7)	2643(3)
O(5)	8995(3)	1841(5)	2442(2)
O(6)	10260(3)	1888(5)	1950(2)
C(30)	8191(13)	588(16)	1656(6)
C(31)	8315(8)	980(11)	1270(7)
C(32)	9113(11)	783(9)	1161(4)
C(33)	9370(6)	187(9)	1544(5)
C(34)	8749(11)	126(11)	1831(5)
C(35)	9461(7)	3684(9)	1435(5)
C(36)	9308(8)	3894(9)	1873(4)
C(37)	8502(8)	3728(9)	1946(3)
C(38)	8178(6)	3447(9)	1539(4)
C(39)	8766(9)	3414(9)	1237(3)
O(40) [b]	5000	1160(17)	2500
C(41) [b]	4550(18)	2182(36)	2743(9)
C(42) [b]	4559(21)	2887(26)	2367(12)

[a] Estimated standard deviations in parentheses.

[b] Population of these sites set to 3/4.

toluene which were unsuitable for X-ray analysis, agreed excellently with the unsolvated formula.

The crystal used for the intensity determination was of dimensions 0.24 × 0.12 × 0.12 mm. Intensities of 4174 unique reflections ($2\theta < 45°$) were measured using graphite-monochrated MoK_α radiation by a ω—2θ scan at room temperature. 2475 reflections with $I \geqslant 2\sigma(I)$ were used for the structure deter-

TABLE 2

THERMAL PARAMETERS (× 10^3) [a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti(1)	26.6(9)	32.5(9)	32.8(8)	1.0(7)	1.8(7)	1.4(7)
Ti(2)	28.7(9)	27.6(9)	38.6(9)	−0.2(7)	3.9(7)	0.4(7)
C(1)	29(5)	31(5)	32(5)	−5(4)	−1(4)	1(4)
C(2)	36(5)	28(5)	30(5)	−1(4)	−1(4)	−3(4)
O(1)	29(3)	40(3)	42(3)	−3(3)	6(3)	7(3)
O(2)	36(3)	27(3)	48(4)	3(3)	7(3)	0(3)
O(3)	46(4)	31(3)	40(3)	3(3)	8(3)	7(3)
O(4)	37(3)	31(3)	45(4)	0(2)	12(3)	5(3)
C(10)	53(6)	62(7)	54(6)	−10(5)	−23(6)	16(6)
C(11)	32(6)	100(9)	51(6)	6(6)	−10(5)	−28(6)
C(12)	50(6)	37(6)	88(8)	−8(5)	−24(6)	−5(6)
C(13)	27(5)	65(7)	58(7)	−7(5)	5(5)	−4(6)
C(14)	38(6)	69(8)	68(7)	14(5)	−18(5)	−17(6)
C(15)	63(7)	67(7)	49(6)	16(6)	−22(6)	−21(5)
C(16)	77(7)	59(8)	48(6)	−28(6)	12(5)	−21(6)
C(17)	68(9)	46(6)	53(6)	14(6)	1(6)	−16(5)
C(18)	52(6)	71(8)	54(6)	−6(6)	11(5)	−12(6)
C(19)	90(9)	39(6)	47(5)	−4(7)	6(6)	9(5)
C(20)	37(6)	41(8)	103(11)	−12(6)	−18(7)	5(8)
C(21)	28(6)	153(12)	67(8)	12(6)	6(5)	−22(8)
C(22)	59(7)	44(7)	133(12)	20(6)	−31(8)	−4(8)
C(23)	43(8)	107(8)	49(7)	−4(6)	−8(6)	21(6)
C(24)	39(7)	58(11)	73(8)	3(6)	−17(6)	−14(7)
C(25)	64(7)	42(6)	60(7)	−16(5)	12(6)	−3(5)
C(26)	47(6)	60(7)	52(6)	−8(5)	0(5)	−22(5)
C(27)	64(8)	52(8)	61(6)	6(6)	−20(6)	−8(5)
C(28)	75(8)	47(8)	42(5)	−21(6)	8(5)	−9(5)
C(29)	50(6)	61(6)	68(7)	5(5)	28(5)	−3(6)
Ti(3)	28.0(9)	35.2(9)	35.0(9)	−3.5(7)	−3.2(7)	−0.8(7)
C(3)	37(5)	32(5)	29(5)	8(4)	2(4)	2(4)
O(5)	27(4)	57(4)	38(3)	−7(3)	−3(3)	2(3)
O(6)	31(3)	55(4)	36(4)	−2(3)	3(2)	0(3)
C(30)	192(21)	135(15)	105(11)	−125(14)	83(13)	−63(10)
C(31)	84(9)	87(8)	285(18)	58(7)	−134(11)	−129(11)
C(32)	191(20)	58(7)	38(7)	−44(10)	30(9)	−16(6)
C(33)	50(6)	51(7)	127(11)	4(6)	−15(7)	−30(7)
C(34)	96(15)	52(8)	116(11)	4(9)	−10(12)	13(7)
C(35)	61(7)	53(7)	113(11)	−16(6)	20(8)	20(8)
C(36)	106(10)	35(7)	94(9)	−13(6)	−53(8)	3(6)
C(37)	95(9)	49(7)	55(7)	20(6)	−6(6)	−8(5)
C(38)	58(6)	47(7)	72(8)	14(5)	−17(6)	−5(6)
C(39)	107(13)	43(6)	49(6)	22(8)	−3(8)	9(5)
O(40)	135(20)	184(16)	105(14)	0	−31(14)	0
C(41)	242(28)	105(51)	125(21)	29(32)	94(20)	−52(29)
C(42)	288(37)	321(31)	159(28)	164(26)	−37(25)	43(23)

[a] T.F. = $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. Estimated standard deviations in parentheses.

mination. No absorption correction was applied since $\mu = 0.77$ mm^{-1}.

The structure solution using the NRC [4] and XRAY 76 [5] programmes, and with scattering factors (corrected for the real and imaginary parts of the anomalous dispersion) taken from International Tables [6] proceeded normally to an R_1 ($\Sigma|\Delta F|/\Sigma|F_o|$) of 0.10. At this stage a difference synthesis revealed the presence of atoms extraneous to the $[(Cp_2Ti)_2(C_2O_4)]$, of which there are two molecules in the asymmetric unit, one in a general position and one with a two-fold axis of symmetry in the centre of the C—C bond of the C_2O_4 ligand, perpendicular to the C_2O_4 plane. After several rounds of refinement and difference syntheses it was concluded that the extraneous atoms could best be described as one-half of a molecule of ether, $(C_2H_5)_2O$ per $[(Cp_2Ti)_2(C_2O_4)]$ unit. This description is however only approximate, and the rather high final R values are in part due to the inadequacy of the description. Final refinement, with fixed positional and isotropic thermal parameters for the hydrogen atoms, a fixed occupancy of 0.75 for the $(C_2H_5)_2O$ molecule, and anisotropic thermal parameters for all other atoms converged to $R_1 = 0.061$ and R_2 [= $(\Sigma w|\Delta F|^2/\Sigma w|F_o|^2)^{1/2}$] = 0.104. Refinement minimised $\Sigma w(\Delta F)^2$, with $w = 1/(\sigma(F)^2 + kF^2)$ (a value of 0.005 for k was determined from measurement of the standards). There were no significant trends in the data analysed as a function of $|F_o|$ and sin θ. The estimated error in an observation of unit weight was 0.84 electrons. A final difference map had a highest positive peak of 0.81 e Å^{-3} at a distance of 0.75 Å from C(13) and a lowest negative peak of

TABLE 3

BOND DISTANCES (Å) [a]

Bond	Distance	Bond	Distance
Ti(1)—O(1)	2.167(6)	C(25)—C(26)	1.39(1)
Ti(1)—O(2)	2.150(6)	C(26)—C(27)	1.42(2)
Ti(2)—O(3)	2.175(6)	C(27)—C(28)	1.40(2)
Ti(2)—O(4)	2.158(6)	C(28)—C(29)	1.41(1)
C(1)—O(1)	1.253(9)	C(29)—C(25)	1.41(1)
C(1)—O(3)	1.250(10)	Ti(3)—O(5)	2.146(6)
C(1)—C(2)	1.543(11)	Ti(3)—O(6)	2.166(6)
C(2)—O(2)	1.245(9)	C(3)—O(5)	1.237(10)
C(2)—O(4)	1.251(10)	C(3)—O(6′)	1.242(10)
C(10)—C(11)	1.41(2)	C(3)—C(3′)	1.535(11)
C(11)—C(12)	1.43(2)	C(30)—C(31)	1.19(3)
C(12)—C(13)	1.38(1)	C(31)—C(32)	1.54(3)
C(13)—C(14)	1.38(2)	C(32)—C(33)	1.41(2)
C(14)—C(10)	1.37(1)	C(33)—C(34)	1.37(2)
C(15)—C(16)	1.36(2)	C(34)—C(30)	1.19(3)
C(16)—C(17)	1.39(2)	C(35)—C(36)	1.36(2)
C(17)—C(18)	1.37(2)	C(36)—C(37)	1.43(2)
C(18)—C(19)	1.40(2)	C(37)—C(38)	1.36(2)
C(19)—C(15)	1.37(2)	C(38)—C(39)	1.38(2)
C(20)—C(21)	1.40(2)	C(39)—C(35)	1.43(2)
C(21)—C(22)	1.44(2)		
C(22)—C(23)	1.35(2)		
C(23)—C(24)	1.33(2)		
C(24)—C(20)	1.37(2)		

[a] Estimated standard deviations in parentheses.

TABLE 4

BOND ANGLES (°)[a]

Atoms	Angle	Atoms	Angle
O(1)—Ti(1)—O(2)	75.8(2)	C(24)—C(20)—C(21)	108.7(1.0)
Ti(1)—O(1)—C(1)	114.9(5)	C(20)—C(21)—C(22)	104.7(1.0)
O(1)—C(1)—C(2)	116.1(7)	C(21)—C(22)—C(23)	107.2(1.1)
O(1)—C(1)—O(3)	126.3(7)	C(22)—C(23)—C(24)	110.4(1.1)
O(3)—C(1)—C(2)	117.6(7)	C(23)—C(24)—C(20)	109.1(1.0)
C(1)—C(2)—O(2)	116.6(7)	C(29)—C(25)—C(26)	107.5(9)
C(1)—C(2)—O(4)	115.7(7)	C(25)—C(26)—C(27)	108.0(9)
O(2)—C(2)—O(4)	127.7(7)	C(26)—C(27)—C(28)	108.3(9)
Ti(1)—O(2)—C(2)	115.3(6)	C(27)—C(28)—C(29)	107.3(9)
O(3)—Ti(2)—O(4)	75.9(2)	C(28)—C(29)—C(25)	108.8(9)
Ti(2)—O(3)—C(1)	113.5(5)	O(5)—Ti(3)—O(6)	75.1(2)
Ti(2)—O(4)—C(2)	115.4(5)	Ti(3)—O(5)—C(3)	116.2(5)
C(14)—C(10)—C(11)	109.0(9)	Ti(3)—O(6)—C(3′)	115.7(5)
C(10)—C(11)—C(12)	107.0(9)	O(5)—C(3)—O(6′)	127.7(8)
C(11)—C(12)—C(13)	105.9(9)	O(5)—C(3)—C(3′)	116.3(7)
C(12)—C(13)—C(14)	110.9(9)	O(6)—C(3)—C(3′)	116.0(7)
C(13)—C(14)—C(10)	107.1(9)	C(34)—C(30)—C(31)	118(2)
C(19)—C(15)—C(16)	109.7(1.0)	C(30)—C(31)—C(32)	108(2)
C(15)—C(16)—C(17)	107.6(9)	C(31)—C(32)—C(33)	97(1)
C(16)—C(17)—C(18)	107.7(9)	C(32)—C(33)—C(34)	108(1)
C(17)—C(18)—C(19)	108.6(9)	C(33)—C(34)—C(30)	109(2)
C(18)—C(19)—C(15)	106.5(9)	C(39)—C(35)—C(36)	107(1)
		C(35)—C(36)—C(37)	108(1)
		C(36)—C(37)—C(38)	107(1)
		C(37)—C(38)—C(39)	109(1)
		C(38)—C(39)—C(35)	107(1)

[a] Estimated standard deviations in parentheses.

—0.58 e Å^{-3} at 0.43 Å from C(30) (two C atoms of ring F (see below)).

Examination of the terms in the thermal ellipsoids, and of an ORTEP plot of the molecules, showed that the C atoms of one of the six independent rings (atoms C(30)—C(34), Ring E) had large oscillations in the plane of the ring and

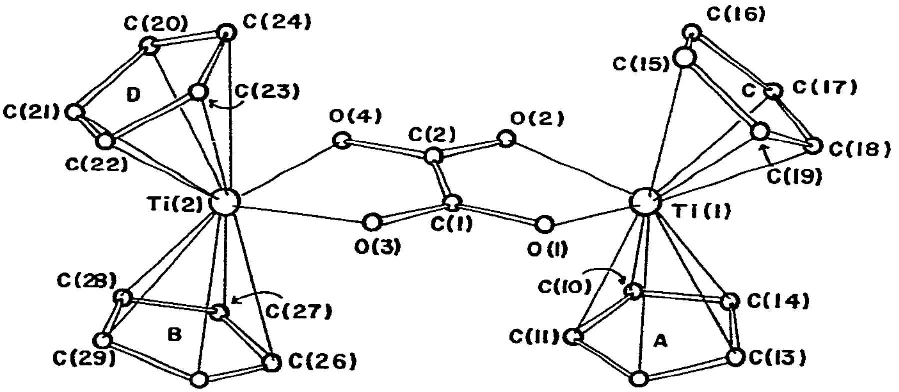

Fig. 1. The molecule of [(Cp$_2$Ti)$_2$(C$_2$O$_4$)] which lies in a general position. Hydrogen atoms have been omitted for clarity.

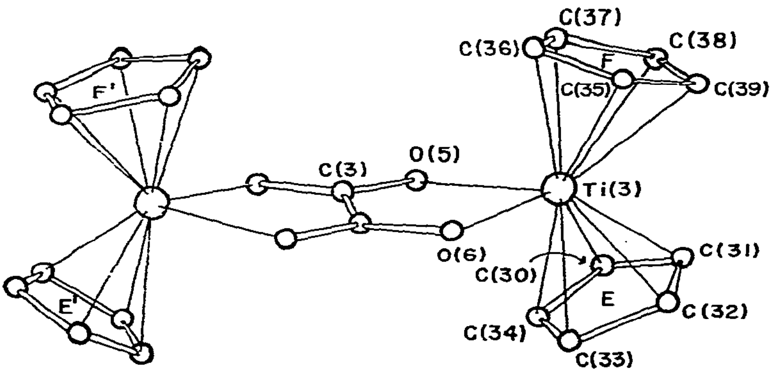

Fig. 2. The molecule of $[(Cp_2Ti)_2(C_2O_4)]$ which has a crystallographic two-fold axis passing through the centre of the C—C bond of the C_2O_4 ligand, perpendicular to the C_2O_4 plane. Hydrogen atoms have been omitted for clarity.

C—C bond distances which differed significantly from those in the other rings (see Table 1 and Figure 2). It is clear that this ring is partially disordered. Because of the limited amount of data available and the already unsatisfactory partial presence of a disordered ether molecule of crystallisation it was decided that a more detailed description of the disorder was impossible. The final atomic coordinates and thermal parameters are given in Tables 1 and 2, and bond lengths and angles in Tables 3 and 4 *. The numbering scheme is shown in Figs. 1 and 2.

Results and discussion

The crystal consists of discrete molecular units of $[((\eta^5\text{-}C_5H_5)_2Ti)_2(C_2O_4)]$ with $(C_2H_5)_2O$ molecules occupying the cavity formed by four $[(Cp_2Ti)_2\text{-}(C_2O_4)]$ units packed approximately at the corners of a square with the C—C bond of the C_2O_4 ligand perpendicular to the square plane. There are two independent molecules of $[(Cp_2Ti)_2Ti(C_2O_4)]$ in the unit cell, one in a general position and one with a crystallographic two fold axis passing through the centre of the C—C bond of the C_2O_4 ligand. The two halves of the bridged molecule in the general position show no significant differences from one another, nor from the independent half of the molecule lying on the two-fold axis, if the apparently disordered Cp ring E in this latter molecule is ignored. All the non-disordered Cp rings are planar and their distances and angles are identical within experimental error. The C_2O_4 bridging ligand is planar within experimental error. It is therefore reasonable to average the dimensions of five Cp rings, and $1.5[Ti(\mu\text{-}(C_2O_4))Ti]$ units. The results of such an averaging are collected in Table 5. These average values will be used in further discussion.

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* Supplementary material has found deposited with NAPS. Order from NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance, in U.S. funds only \$ 5.00 for photocopies of \$ 3.00 for microfiche. Outside the U.S. and Canada add postage of \$ 3.00 for photocopy and \$ 1.00 for microfiche.

TABLE 5

AVERAGE BOND DISTANCES (Å) AND ANGLES (°) IN $[(Cp_2Ti)_2(C_2O_4)]$

Ti—O	2.157(6)	6 [a]	O—Ti—O	75.8(2)	3 [a]
C—O	1.256(10)	6	Ti—O—C [b]	114.7(5)	6
C—C [b]	1.523(11)	2	O—C—C [b]	116.7(7)	6
Ti—Cp [c]	2.058(4)	5	O—C—O [b]	126.5(7)	3
Ti—C	2.374(11)	25	C—C—C [d]	108.1(9)	25
C—C [d]	1.390(17)	25	Cp—Ti—Cp [c]	135.4(3)	2

[a] Numbers in this column are the number of independent determinations which have been averaged.

[b] Distances or angles in the $Ti(\mu\text{-}C_2O_4)Ti$ unit.

[c] Cp refers to the centroid of the η^5-cyclopentadienyl ring.

[d] Distances or angles in the Cp rings.

The C—C and C—O bond distances and the O—C—O angle in the oxalato group are normal for this ligand acting as a tetradentate bridge [7]. Similarly the Ti—ring carbon distances and C—C and C—C—C distances and angles within the rings agree with other determinations of the structures of Cp_2Ti^{III} complexes [8—12].

There are a number of points of comparative interest within the structure. The Ti atoms are displaced an average of 0.297 Å (Ti(1) 0.318; Ti(2) 0.348; Ti(3) 0.225 Å) out of the plane of the C_2O_4 ligand, in a *cis* fashion. This distortion in fact results in H—H non-bonded contacts between rings A and B in the general position molecule of 2.50 Å, and a similar contact of 2.52 Å between rings F and F′ in the molecule on the two-fold axis. All other H—H non-bonded contacts (which are the shortest contacts in the crystal) are close to 2.70 Å. The *cis* folding of the molecule therefore produces unusually close contacts, whereas a *trans* folding, or a completely planar structure would not do so. We therefore conclude that the electronic structure of the molecule is responsible for the folding. Hoffmann and Lauher [13] have analysed the observed [12,14—17] displacements of the Cp_2M moiety from the plane of bidentate ligands (ω angles of up to 46° in their notation) in terms of π interaction between the ligand and the Cp_2M fragment. In the present case the ω angles are 11.89° and 10.86° in the general position molecule and 7.62° in the molecule on the two-fold axis. In Fig. 3 the orbitals involved in the bonding between $C_2O_4{}^{2-}$ and Cp_2Ti are sketched, the Cp_2Ti fragment orbitals being taken from Hoffmann and Lauher [13] and the $C_2O_4{}^{2-}$ orbitals being obtained from an INDO/2 calculation using programmes designed by Zerner [18,19]. It is seen that three electrons (one from Ti^{III} and two from the ligand) must be accommodated in the two a_1 molecular orbitals, one of which forms a σ-bond. The unpaired electron has a repulsive interaction with the ligand, but neither this nor the σ overlap is affected by folding, since the filled a_1 orbital on the ligand lies essentially completely in the y direction, which is the axis of folding. The overlap of the b_2 orbitals forming the second σ-bond will be decreased by folding. However, such folding will result in a stabilising interaction between the single electron in an a_1 orbital and the ligand LUMO b_1 orbital, both of which transform as a in the C_s symmetry of the folded molecule. Note that *cis* folding (i.e. the Ti atoms on the same side of $C_2O_4{}^{2-}$ plane) is required by the sym-

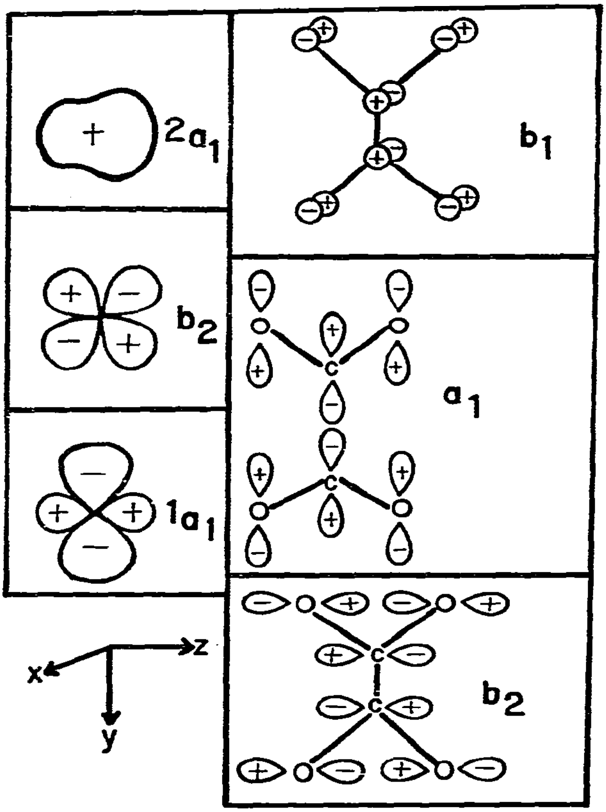

Fig. 3. Schematic diagram of the orbitals involved in bonding between $C_2O_4^{2-}$ and Cp_2Ti^+. In the isolated $C_2O_4^{2-}$ orbitals b_2 and a_1 are occupied, b_1 is unoccupied. In the isolated Cp_2Ti^+ the odd electron would occupy $1a_1$.

metry of the $C_2O_4^{2-}$ LUMO orbital. That the molecule folds indicates that the π-interaction is very important. However, folding is only possible as far as the non-bonded ring contacts will allow, and a compromise between electronic advantage and steric strain is reached.

The average Ti—O distance, 2.157(6) Å, and the O—Ti—O angle, 75.80(21)° are in the ranges to be expected for these parameters based on radii and bite-angle considerations. Only one other Cp_2Ti^{III} complex having Ti—O bonds appears to have been structurally analysed, and in this, $[(Cp_2Ti)_4(CO_3)_2]$, the reduced bite-angle of the CO_3 ligand produces an O—Ti—O angle of 61.3(1)° and a Ti—O distance of 2.128(3) Å [8]. For two monodentate ligands O-bonded to Cp_2Ti^{III} and O—Ti—O angle of about 85°C and a Ti—O distance of circa 2.19 Å would be expected.

It is interesting to compare the present structure with that of $[(Cp_2Ti)_2(C_2(NC_6H_4CH_3\text{-}p)_4]$ [9]. The bridging $C_2(NC_6H_4CH_3\text{-}p)_4$ ligand is isoelectronic with C_2O_4, and its titanium complex can be regarded as a model for the reductive coupling of CO_2 to $C_2O_4^{2-}$, since it was obtained in the reaction between $Cp_2Ti(CO)_2$ and $p\text{-}CH_3C_6H_4\text{—}N\text{=}C\text{=}NC_6\text{—}H_4CH_3\text{-}p$ [9]. The Ti—N distances, 2.176(2) and 2.173(2) Å, differ from the average Ti—O distance in $[(Cp_2Ti)_2(C_2O_4)]$, 2.157(6) Å, by exactly the difference in the covalent radii of N and O, and the N—Ti—N angle of 73.6(1)° is very similar to the O—Ti—O angle (75.8(2)°). However, the average Ti—Cp distances and Cp—Ti—Cp angles (2.058(4) Å and 135.4(3)° for $[(Cp_2Ti)_2(C_2O_4)]$ and 2.095(4) and 131.6(2)° for $[(Cp_2Ti)_2(C_2(NC_6H_4CH_3\text{-}p)_4])$ are significantly different and appear to indicate that C_2O_4 is a better σ and/or π donor than $C_2(NC_6H_4CH_3\text{-}p)_4$ in these complexes. This is probably due to the removal of electrons from the nitrogen atoms by delocalisation into the tolyl rings in $C_2(NC_6H_4CH_3\text{-}p)_4$.

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