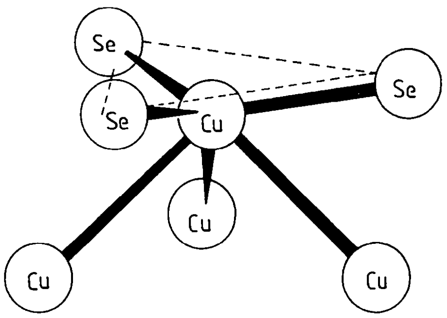

Fig. 2. Coordination of one Cu atom in the $[Cu_8(i\text{-mns})_6]^{4-}$ complex anion.

observed and the Se atoms form an equilateral triangle with the Cu atom nearly in the plane (av. = 0·73 Å; Fig. 2). The average Cu—Se bond is longer by 0·13 Å than the mean Cu—S value in $(Et_4N)_4[Cu_8(i\text{-mnt})_6]$ (Hanhui & Xiufen, 1989). However, this lengthening is expected on the basis of the different covalent radii of Se and S (1·17 and 1·04 Å, respectively) (Pauling, 1960). The selenolate ligands are directed perpendicular to the rectangular faces of the Cu_8 cube and are bridged to each of two parallel Cu—Cu edges. The values for the Se—C bonds lie in the narrow range 1·89–1·95 Å, which agrees well with the values published before, and seems to be normal for a Se—C(sp^2) distance (Bonamico & Dessy, 1971). Although bond lengths for C(2)—C(3) and C(2)—C(4), are close to 1·42 Å which is the value for a C_{sp^2}—C_{sp} bond with a bond order of 4/3 (Bent, 1961), the values for the central C—C bond vary considerably. In *i*-mns (1) and *i*-mns (2) the values are 1·37 and 1·33 Å, respectively, which are close to localized C—C double bonds without any resonance contribution, while in *i*-mns (3) a typical mesomeric value of 1·42 Å is observed (Bent, 1961). Similar differences in bond lengths for diselenolate ligands *i*-mns have been mentioned recently for the structure of $(Et_4N)[TcO\{Se_2C{=}C(CN)_2\}_2]$ (Bandoli, Mazzi, Abram, Spies & Münze, 1987), while in $[As(C_6H_5)_4]_2[Ni^{IV}\{Se_2C{=}C(CN)_2\}_3]$ the value for three crystallographically different ligands is 1·36 (3) Å (Kaiser, Dietzsch, Richter, Golič & Šiftar, 1980).

References

Bandoli, G., Mazzi, U., Abram, U., Spies, H. & Münze, R. (1987). *Polyhedron*, **6**(7), 1547–1550.
Bent, H. A. (1961). *Chem. Rev.* **61**, 275–311.
Bonamico, M. & Dessy, G. (1971). *J. Chem. Soc. A*, pp. 264–266.
Dietrich, H., Storck, W. & Manecke, G. (1981). *Makromol. Chem.* **182**, 2371–2398.
Fackler, J. P. Jr & Coucouvanis, D. (1966). *J. Am. Chem. Soc.* **88**, 3913–3920.
Hall, S. R. & Stewart, J. M. (1988). Editors. *XTAL*2.4 *Users Manual*. Univs. of Western Australia, Australia, and Maryland, USA.
Hanhui, Z. & Xiufen, Y. (1989). *Jiegou Huaxue*, **8**(2), 132–135.
Hollander, F. J. & Coucouvanis, D. (1977). *J. Am. Chem. Soc.* **99**, 6268–6280.
Jensen, K. A. & Henriksen, L. (1970). *Acta Chem. Scand.* **24**, 3213–3229.
Kaiser, J., Dietzsch, W., Richter, R., Golič, L. & Šiftar, J. (1980). *Acta Cryst.* B**36**, 147–150.
Keller, E. (1990). *SCHAKAL*88B/V16. Univ. of Freiburg, Germany.
McCandlish, L. E., Bissell, E. C., Coucouvanis, D., Fackler, J. P. Jr & Knox, K. (1968). *J. Am. Chem. Soc.* **90**, 7357–7359.
Pauling, L. (1960). *Nature of the Chemical Bond*, 3rd edition. Ithaca: Cornell Univ. Press.
Sheldrick, G. M. (1976). *SHELX*76. A program for crystal structure determination. Univ. of Cambridge, England.
Sheldrick, G. M. (1986). *SHELXS*86. Program for solution of crystal structures. Univ. of Göttingen, Germany.

Acta Cryst. (1991). C**47**, 2043–2047

Bis(cyclopentadienyl)bis(*m*-methoxybenzoato)titanium(IV)

By B. Bracke, Y. Dang,* A. T. H. Lenstra and H. J. Geise†

University of Antwerp (*UIA*), *Department of Chemistry*, *Universiteitsplein* 1, *B*-2610 *Wilrijk*, *Belgium*

(*Received* 5 *November* 1990; *accepted* 2 *April* 1991)

Abstract. $[Ti(C_8H_7O_3)_2(C_5H_5)_2]$, $M_r = 480{\cdot}4$, monoclinic, $P2_1/n$, $a = 15{\cdot}739\,(5)$, $b = 7{\cdot}466\,(1)$, $c = 20{\cdot}286\,(5)$ Å, $\beta = 97{\cdot}21\,(2)°$, $V = 2364{\cdot}9\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}349$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}39$ mm^{-1}, $F(000) = 1000$, room temperature, $wR = 0{\cdot}047$, $R = 0{\cdot}043$ for 1308 observed $[I \geq 3\sigma(I)]$ reflections from 3731 measured, and 298 variables. The geometries of the two cyclopentadienyl moieties do not differ significantly. The same holds for the benzoato ligands. Moreover, they follow closely the

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* Present address: University of California, Department of Chemistry, Berkeley, CA 94720, USA.

† Author to whom correspondence should be addressed.

0108-2701/91/102043-05$03.00

Table 1. *Fractional coordinates and equivalent isotropic temperature parameters* (Å^2) *with e.s.d.'s in parentheses*

$$B_{\rm iso} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	$B_{\rm iso}$
Ti	−0·06898 (7)	0·1884 (1)	0·34398 (4)	4·35 (2)
C1	−0·2102 (4)	0·2505 (8)	0·3611 (4)	7·8 (2)
C2	−0·1738 (4)	0·1659 (8)	0·4166 (3)	9·7 (2)
C3	−0·1112 (4)	0·274 (1)	0·4461 (3)	8·6 (2)
C4	−0·1116 (4)	0·4272 (8)	0·4089 (3)	7·7 (2)
C5	−0·1721 (4)	0·4119 (9)	0·3567 (3)	8·0 (2)
C6	−0·1224 (4)	−0·1022 (8)	0·3218 (3)	6·6 (2)
C7	−0·0567 (4)	−0·1096 (7)	0·3747 (3)	6·6 (2)
C8	0·0188 (4)	−0·0691 (8)	0·3498 (4)	7·9 (2)
C9	0·0001 (4)	−0·0336 (9)	0·2847 (3)	8·2 (2)
C10	−0·0852 (5)	−0·0547 (9)	0·2672 (3)	8·4 (2)
C11	−0·0981 (4)	0·3969 (8)	0·2080 (3)	5·4 (2)
C12	−0·0309 (4)	0·4973 (8)	0·1806 (3)	5·5 (2)
C13	−0·0494 (5)	0·596 (1)	0·1230 (3)	9·2 (2)
C14	0·0144 (5)	0·691 (1)	0·0989 (3)	11·8 (2)
C15	0·0961 (5)	0·685 (1)	0·1273 (3)	10·4 (2)
C16	0·1138 (4)	0·5855 (9)	0·1848 (3)	7·4 (2)
C17	0·0503 (4)	0·4944 (8)	0·2103 (3)	5·7 (2)
C18	0·0989 (4)	0·2832 (8)	0·4290 (2)	5·0 (2)
C19	0·1680 (3)	0·4227 (8)	0·4300 (2)	4·7 (2)
C20	0·1642 (4)	0·5629 (8)	0·3868 (3)	5·7 (2)
C21	0·2296 (4)	0·6877 (9)	0·3883 (3)	7·5 (2)
C22	0·2991 (4)	0·6655 (9)	0·4331 (3)	7·8 (2)
C23	0·3057 (4)	0·5250 (9)	0·4776 (3)	6·6 (2)
C24	0·2393 (4)	0·4029 (8)	0·4762 (3)	5·7 (2)
C25	0·2610 (5)	0·676 (1)	0·1996 (4)	11·9 (3)
C26	0·3920 (5)	0·386 (1)	0·5663 (4)	11·8 (3)
O1	−0·0710 (3)	0·3142 (6)	0·2627 (2)	7·2 (1)
O2	−0·1708 (3)	0·3884 (7)	0·1835 (2)	9·5 (2)
O3	0·0433 (2)	0·2896 (5)	0·3773 (2)	5·3 (1)
O4	0·0988 (3)	0·1763 (6)	0·4741 (2)	8·0 (1)
O5	0·1946 (3)	0·5747 (7)	0·2187 (2)	10·6 (2)
O6	0·3806 (3)	0·5181 (7)	0·5188 (2)	10·0 (2)

trends found in the monoclinic and orthorhombic forms of bis(benzoato)bis(η-cyclopentadienyl)titanium(IV). In contrast, the two Z—Ti—O—C═O moieties (where Z denotes the center of mass of a cyclopentadienyl ligand) have different geometries (bond lengths, valence and torsion angles), and follow the trend of the orthorhombic titanocene. The situation can be explained by Ti—O1 having considerable double-bond character and Ti—O3 having predominantly single-bond character. Hence, an asymmetric OC—O═Ti—O—CO group is (i) not unique to orthorhombic titanocene and (ii) possibly not confined to the solid state.

Introduction. The crystal structure of the title compound (see Fig. 1) was investigated as part of a series aimed at the determination of structure–activity relationships in bis(substituted benzoato)titanocenes by X-ray diffraction, IR, NMR and mass spectrometry (Dang, Geise, Dommisse, Esmans & Desseyn, 1990; Dang, Geise, Dommisse, Nouwen & Gelan, 1990; Dang, Geise, Esmans, Claereboudt & Claeys, 1991). Previous X-ray analyses of bis(cyclopentadienyl)bis(benzoato)titanium(IV) had revealed a monoclinic form (Hoffman, Chester & Fay, 1983) and an orthorhombic form (Döppert, Klein & Thewalt, 1986). Both structures were interpreted as proof of an 18-electron configuration around titanium, but have significantly different geometries, particularly noticeable in the Ti—O bonds. In the orthorhombic form two different Ti—O lengths [1·995 (3) and 1·894 (4) Å] are observed, implying one Ti—O bond with normal single-bond character and the O atom contributing one electron to the Ti coordination and another Ti—O bond with considerable double-bond character and the O atom contributing three electrons. In contrast, the monoclinic form has two Ti—O bonds of almost equal length [1·922 (7) and 1·930 (5) Å], implying intermediate bonding character in which each oxygen contributes two electrons. In the ^{13}C NMR and mass spectra of this class of complexes we had found indications (Dang, Geise, Dommisse, Esmans & Desseyn, 1990: Dang, Geise, Dommisse, Nouwen & Gelan, 1990) that the asymmetrical —O—Ti═O— bonding situation is favoured by an effect known as localized π polarization (*e.g.* Bromilow, Brownlee, Craik, Fiske, Rowe & Sadek, 1981). It was argued (Dang, Geise, Dommisse, Esmans & Desseyn, 1990) that the effect can be brought about in titanocene benzoates by substituents with inductively electron-withdrawing properties and that mesomeric donating properties may be tolerated provided the substituent

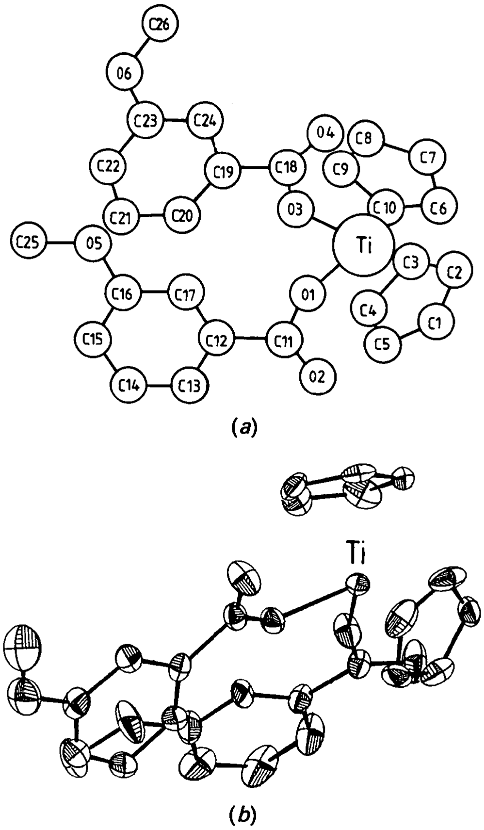

Fig. 1. (*a*) Structural formula and atomic numbering scheme of the title compound, (*b*) *ORTEP* view.

Table 2. *Bond distances (Å), valence angles (°) and selected torsion angles (°) in the title compound and in two forms of the unsubstituted analogue with e.s.d.'s in parentheses*

	This work	Döppert (1986)	Hoffman (1983)		This work	Döppert (1986)	Hoffman (1983)
Benzoato ligands							
C12—C13	1·382 (8)	1·392 (5)	1·390 (15)	C19—C20	1·363 (8)	1·386 (5)	1·397 (9)
C13—C14	1·38 (1)	1·383 (6)	1·397 (24)	C20—C21	1·386 (8)	1·391 (6)	1·377 (12)
C14—C15	1·34 (1)	1·380 (6)	1·369 (16)	C21—C22	1·341 (9)	1·385 (6)	1·370 (13)
C15—C16	1·38 (1)	1·396 (6)	1·340 (22)	C22—C23	1·379 (9)	1·402 (7)	1·369 (13)
C16—C17	1·365 (9)	1·382 (6)	1·370 (22)	C23—C24	1·385 (9)	1·372 (6)	1·363 (11)
C17—C12	1·342 (8)	1·392 (5)	1·381 (10)	C24—C19	1·376 (7)	1·404 (5)	1·396 (9)
C11—C12	1·464 (9)	1·494 (5)	1·509 (19)	C18—C19	1·506 (8)	1·504 (5)	1·497 (9)
C11—O1	1·295 (7)	1·275 (5)	1·299 (12)	C18—O3	1·280 (6)	1·300 (4)	1·308 (8)
C11—O2	1·191 (7)	1·208 (5)	1·204 (10)	C18—O4	1·215 (6)	1·205 (6)	1·206 (10)
C16—O5	1·371 (7)	—	—	C23—O6	1·359 (7)	—	—
C25—O5	1·385 (7)	—	—	C26—O6	1·373 (9)	—	—
C13—C12—C17	118·5 (9)	118·8 (8)	119·1 (11)	C20—C19—C24	119·1 (6)	119·1 (6)	118·5 (6)
C12—C13—C14	119·5 (8)	120·6 (8)	118·6 (8)	C19—C20—C21	122·0 (6)	120·7 (6)	120·6 (7)
C13—C14—C15	122·4 (8)	119·9 (7)	120·6 (14)	C20—C21—C22	118·1 (6)	119·8 (6)	119·7 (8)
C14—C15—C16	117·4 (9)	120·4 (8)	120·1 (17)	C21—C22—C23	121·7 (7)	119·9 (7)	120·2 (8)
C15—C16—C17	120·6 (9)	119·1 (8)	120·9 (10)	C22—C23—C24	119·6 (7)	120·1 (7)	121·2 (7)
C16—C17—C12	122 (1)	121·1 (8)	120·5 (10)	C23—C24—C19	119·4 (6)	120·4 (7)	119·8 (7)
O1—C11—O2	121·9 (8)	123·1 (7)	124·0 (13)	O3—C18—O4	125·3 (6)	124·7 (6)	124·7 (7)
O1—C11—C12	113·3 (7)	114·0 (7)	114·1 (7)	O3—C18—C19	113·8 (6)	114·6 (6)	112·6 (6)
O2—C11—C12	124·8 (8)	122·8 (8)	121·9 (11)	O4—C18—C19	121·0 (6)	120·7 (6)	122·7 (6)
C11—C12—C13	120·7 (9)	120·3 (7)	121·9 (9)	C18—C19—C20	123·4 (6)	121·9 (6)	122·7 (6)
C11—C12—C17	120·9 (8)	120·8 (8)	119·0 (7)	C18—C19—C24	117·4 (6)	119·0 (6)	118·7 (6)
O5—C16—C15	123 (2)	—	—	O6—C23—C22	114·8 (9)	—	—
O5—C16—C17	117 (2)	—	—	O6—C23—C24	125·5 (8)	—	—
C16—O5—C25	120·9 (8)	—	—	C23—O6—C26	119·1 (7)	—	—
O1—C11—C12—C13	− 178·7 (5)	− 175·2 (5)	− 184·7 (8)	O3—C18—C19—C20	11·4 (8)	10·3 (8)	13·6 (9)
O1—C11—C12—C17	1·9 (8)	7·4 (8)	− 2·7 (7)	O3—C18—C19—C24	− 166·8 (5)	− 169·6 (6)	− 166·9 (8)
O2—C11—C12—C13	1·7 (9)	6·3 (9)	− 3·0 (8)	O4—C18—C19—C20	− 169·1 (5)	− 170·2 (6)	− 165·2 (8)
O2—C11—C12—C17	− 177·5 (6)	− 171·2 (6)	− 180·9 (8)	O4—C18—C19—C24	12·6 (8)	9·9 (7)	14·3 (9)
C15—C16—O5—C25	5·0 (9)	—	—	C22—C23—O6—C26	177·9 (6)	—	—
C17—C16—O5—C25	− 174·1 (6)	—	—	C24—C23—O6—C26	− 3·7 (9)	—	—
Cyclopentadienyl ligands							
C1—C2	1·35 (1)	1·398 (8)	1·393 (10)	C6—C7	1·395 (9)	1·475 (8)	1·378 (12)
C2—C3	1·36 (1)	1·352 (9)	1·386 (19)	C7—C8	1·384 (9)	1·412 (8)	1·394 (13)
C3—C4	1·37 (1)	1·356 (7)	1·385 (16)	C8—C9	1·34 (1)	1·313 (8)	1·390 (12)
C4—C5	1·337 (9)	1·310 (7)	1·369 (14)	C9—C10	1·354 (9)	1·343 (7)	1·385 (15)
C5—C1	1·356 (9)	1·473 (8)	1·393 (19)	C10—C6	1·363 (9)	1·305 (8)	1·348 (11)
C5—C1—C2	109·1 (8)	104·4 (8)	107·9 (10)	C10—C6—C7	106·4 (8)	106·5 (8)	109·9 (7)
C1—C2—C3	107·2 (7)	106·9 (6)	107·3 (10)	C6—C7—C8	107·4 (9)	103·6 (8)	106·5 (6)
C2—C3—C4	107·7 (7)	111·7 (7)	108·3 (8)	C7—C8—C9	108·2 (9)	108·4 (8)	107·9 (8)
C3—C4—C5	108·6 (8)	108·4 (7)	108·5 (12)	C8—C9—C10	108·8 (9)	110·5 (8)	107·3 (7)
C4—C5—C1	107·6 (9)	108·5 (8)	108·0 (8)	C9—C10—C6	109·4 (8)	111·0 (8)	108·3 (7)
Titanium coordination							
Ti···C1	2·341 (7)	2·343 (8)	2·337 (6)	Ti···C6	2·352 (7)	2·351 (5)	2·381 (13)
Ti···C2	2·353 (7)	2·348 (4)	2·369 (5)	Ti···C7	2·315 (6)	2·329 (6)	2·338 (15)
Ti···C3	2·345 (7)	2·348 (5)	2·381 (7)	Ti···C8	2·364 (7)	2·378 (7)	2·374 (18)
Ti···C4	2·365 (6)	2·379 (6)	2·381 (12)	Ti···C9	2·391 (7)	2·371 (7)	2·391 (20)
Ti···C5	2·366 (7)	2·369 (5)	2·384 (9)	Ti···C10	2·386 (7)	2·353 (8)	2·393 (11)
Ti—*Z*1*	2·045 (8)	2·045 (7)	2·057 (7)	*Z*1—Ti—*Z*2	132·4 (9)	132·5 (3)	131·7 (5)
Ti—*Z*2*	2·057 (9)	2·048 (6)	2·065 (17)	*Z*1—Ti—O1	108·0 (7)	108·7 (2)	106·5 (5)
Ti—O1	1·895 (4)	1·894 (4)	1·922 (7)	*Z*1—Ti—O3	105·6 (8)	105·2 (2)	107·7 (7)
Ti—O3	1·962 (4)	1·995 (3)	1·930 (5)	*Z*2—Ti—O1	104·4 (7)	104·2 (3)	107·1 (7)
				*Z*2—Ti—O3	107·6 (8)	107·3 (2)	105·0 (7)
				O1—Ti—O3	91·3 (2)	91·5 (1)	91·4 (3)
				Ti—O1—C11	161·8 (5)	168·7 (3)	148·6 (4)
				Ti—O3—C18	139·5 (4)	135·2 (3)	147·9 (7)

* *Z*1 is the center of mass of the ring consisting of atoms C1 through C5, *Z*2 the center of mass of the ring consisting of atoms C6 through C10.

is suitably positioned. This renders the title compound, carrying an *m*-OCH_3 substituent on the benzoato ligand, of interest for further investigation.

Experimental. The title compound was synthesized as described by Dang, Geise, Dommisse, Esmans & Desseyn (1990). A suitable single crystal was obtained by slow evaporation of a benzene solution. Crystal size 0·3 × 0·3 × 0·1 mm. Unit-cell dimensions deduced from 25 high-order reflections ($12 \leq \theta \leq 15°$). Space group inferred from systematic extinctions. Enraf–Nonius CAD-4 diffractometer, $\omega/2\theta$ scan mode, scan angle $(0{\cdot}7 + \tan\theta)°$, aperture of detection unit $(2 + \tan\theta)$ mm. Mo radiation monochromatized by pyrolytic graphite; three intensity control reflections monitored every 2 h showed no drift; three orientation control reflections monitored every 50 reflections showed no angular deviations.

Maximum Bragg angle $\theta = 27°$, 3731 independent measurements of which 1308 reflections considered observed $[I > 3\sigma(I)]$; $0 \le h \le 20$, $0 \le k \le 9$, $-25 \le l \le 25$. No absorption correction applied ($\mu = 0{\cdot}39\ \text{mm}^{-1}$). Structure solved using *DIRDIF* (Prick, 1979) starting from the positional parameters of Hoffman *et al.* (1983). H atoms introduced at calculated positions. Full-matrix least-squares refinements (on *F*) of positional and anisotropic displacement parameters of non-H atoms, H atoms in calculated positions with a fixed isotropic temperature parameter $B = 4{\cdot}0\ \text{Å}^2$. $w = 1/\sigma^2(F_o)$. No extinction coefficient refined. Convergence reached at $R = 0{\cdot}043$, $wR = 0{\cdot}047$, $S = 1{\cdot}71$, $(\Delta/\sigma)_{\max} = 0{\cdot}52$, 298 variables. Noise level in final difference Fourier map between $-0{\cdot}22$ and $+0{\cdot}19\ \text{e Å}^{-3}$. Atomic scattering functions from *International Tables for X-ray Crystallography* (1974, Vol. IV). Enraf–Nonius *SDP* (Frenz, 1978) employed. Refined parameters* are in Table 1, and the atomic numbering scheme is shown in Fig. 1.

Discussion. The high atomic displacement parameters (Table 1) account for the large number of intensities below the $I/\sigma(I) = 3$ threshold (2/3 of total), and this in turn leads to the low observation:parameter ratio (4·4:1) and the relatively high e.s.d.'s. The largest displacement parameters are observed in the methoxy substituents and the cyclopentadienyl ligands and could be due to local disorder. However, the final difference Fourier map has a low noise level and the largest anisotropic Gaussian displacement parameters (AGDP) of the carbons are in directions tangential to the ring. Dunitz, Schomaker & Trueblood (1988), who studied ferrocene (Seiler & Dunitz, 1987), pointed out that such AGDP's are consistent with a librational movement of the ring about the local fivefold axes. Therefore, we believe that the high displacement parameters are a consequence of the librational rigid-body movement of the cyclopentadienyl ligands, which could not be incorporated in the standard anisotropic refinement. This may harm the accuracy with which one can determine the cyclopentadienyl geometry and its position with respect to the $\text{Ti(OOCC}_6\text{H}_4X)_2$ moiety. Nevertheless, comparison of the geometrical details of the title compound with those of the two forms of the unsubstituted bis(cyclopentadienyl)bis(benzoato)titanium(IV) shows great similarity (see Table 2, cyclopentadienyl ligand, Ti···C distances in titanium coordination). Further inspection of Table 2 (benzoato ligands) shows that each methoxy group is virtually coplanar with its phenyl ring. The two corresponding exocyclic O—C(phenyl)—C(phenyl) angles are different, the larger one being on the side where the methyl carbon eclipses the C(phenyl). The same trend is seen in the structures of, for example, *p*-nitroanisol (Talberg, 1979) and *trans,trans*-1,4-bis[2-(3,4,5-trimethoxyphenyl)vinyl]benzene (Verbruggen, Yang Zhou, Lenstra & Geise, 1988). All other benzoato structural particulars, *i.e.* bond lengths, valence angles, planarity of phenyl ring and the twisting of COO groups, follow closely the trends described by Hoffman *et al.* (1983).

In the titanium coordination (Table 2) the centers of mass (*Z*) of the cyclopentadiene ligands and the coordinated O atoms form a distorted tetrahedron with the angles *Z*—Ti—*Z* (132·4°) and O—Ti—O (91·3°) in the range normal for $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}X_2$ derivatives. So far the three compounds reveal little diversity. The differentation is restrained to the immediate vicinity of the Ti—O bonds. In the orthorhombic bis(benzoato)bis(cyclopentadiene)titanium(IV) and the title compound the two Ti—O bond distances differ significantly: the short one (1·895 Å) is associated with a large Ti—O—C angle (161·8°), whereas the long one (1·962 Å) is associated with the relatively small Ti—O—C angle (139·5°). Following the explanation of Hoffman *et al.* (1983) and Döppert *et al.* (1986) (see *Introduction*), we conclude that Ti—O1 has predominantly double-bond and Ti—O3 predominantly single-bond character. The asymmetric OC—O=Ti—O—CO situation is therefore (i) not unique to the orthorhombic form of the unsubstituted benzoato titanocene and (ii) possibly not confined to the solid state because of the link between asymmetric geometry and mass spectroscopic behaviour.

Finally, Newman projections (Fig. 2) reveal in both *Z*—Ti—O—C=O regions the same eclipsing of the Ti—O bond with the C=O bond, and a small

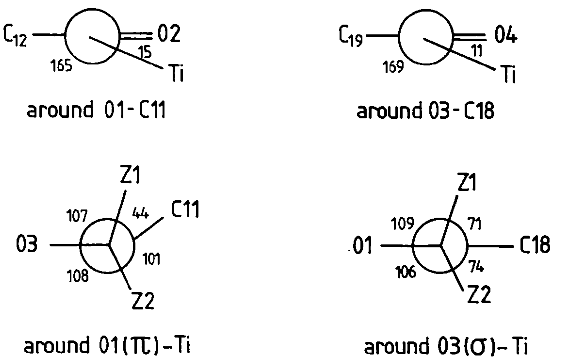

Fig. 2. Newman projections of the *Z*—Ti—O—C=O regions in the title compound. The predominantly double-bonded Ti—O is designated as O(π)—Ti, and the predominantly single-bonded Ti—O as O(σ)—Ti.

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* Lists of structure factors, H-atom positions and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54120 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

but distinct difference in the Z—Ti—O—C conformations. The conformation of O1=Ti—O3—C18 is antiperiplanar, whereas that of O3—Ti=O1—C11 is almost anticlinal.

BB thanks the Belgian Organization IWONL for a predoctoral grant and YD thanks the Antwerp Provincial Authorities for financial support. This text presents research results of the Belgian Program on Interuniversity Attraction Poles initiated by the Belgian State – Prime Minister's Office – Science Policy Programming. The scientific responsibility, however, remains with the authors.

References

BROMILOW, J., BROWNLEE, T. R. C., CRAIK, D. J., FISKE, P. R., ROWE, J. E. & SADEK, M. (1981). *J. Chem. Soc. Perkin Trans.* 2, pp. 753–762.

DANG, Y., GEISE, H. J., DOMMISSE, R., ESMANS, E. & DESSEYN, H. O. (1990). *J. Organomet. Chem.* **381**, 333–348.

DANG, Y., GEISE, H. J., DOMMISSE, R., NOUWEN, J. & GELAN, J. (1990). *J. Chem. Soc. Perkin Trans.* 2, pp. 1785–1790.

DANG, Y., GEISE, H. J., ESMANS, E., CLAEREBOUDT, J. & CLAEYS, M. (1991). To be published.

DÖPPERT, K., KLEIN, H.-P. & THEWALT, U. (1986). *J. Organomet. Chem.* **303**, 205–211.

DUNITZ, J. D., SCHOMAKER, V. & TRUEBLOOD, K. N. (1988). *J. Phys. Chem.* **92**, 856–867.

FRENZ, B. A. (1978). *The Enraf-Nonius CAD4 SDP-A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution.* In *Computing in Crystallography*, edited by H. SCHENK, R. OLTHOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI. Delft Univ. Press.

HOFFMAN, D. M., CHESTER, N. D. & FAY, R. C. (1983). *Organometallics*, **2**, 48–52.

PRICK, P. A. J. (1979). PhD Thesis, Univ. Nijmegen, The Netherlands.

SEILER, P. & DUNITZ, J. D. (1987). *Acta Cryst.* **B35**, 1068–1074.

TALBERG, H. J. (1979). *Acta Chem. Scand. Ser. A*, **33**, 289–296.

VERBRUGGEN, M., YANG ZHOU, LENSTRA, A. T. H. & GEISE, H. J. (1988). *Acta Cryst.* **C44**, 2120–2123.

Acta Cryst. (1991). C**47**, 2047–2052

Two Isomeric Chromium(III) Complexes with 1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol in One Structure: $[Cr^{III}(C_6H_{14}N_3O_3)(C_6H_{15}N_3O_3)][Cr^{III}(C_6H_{15}N_3O_3)_2]_2(SO_4)_4.30H_2O$

BY HELMUT W. SCHMALLE

Anorganisch-Chemisches Institut der Universität Zürich, Winterthurerstrasse 190, *CH*-8057 *Zürich, Switzerland*

AND KASPAR HEGETSCHWEILER* AND MICHELE GHISLETTA

Laboratorium für Anorganische Chemie, ETH-Zentrum, CH-8092 *Zürich, Switzerland*

(*Received* 15 *February* 1991; *accepted* 18 *April* 1991)

Abstract. $[Cr^{III}(C_6H_{14}N_3O_3)(C_6H_{15}N_3O_3)][Cr^{III}(C_6H_{15}N_3O_3)_2]_2(SO_4)_4.30H_2O$, M_r = 2142·9, triclinic, $P\bar{1}$, a = 10·977 (6), b = 12·754 (2), c = 16·370 (5) Å, α = 94·96 (2), β = 103·22 (4), γ = 94·43 (3)°, V = 2212 (4) Å^3, Z = 1, D_x = 1·608 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 0·56 mm^{-1}, $F(000)$ = 1139, T = 295 K. The structure was determined by single-crystal X-ray diffraction using 7777 unique reflections and refined by block-diagonal-matrix least-squares calculations to R = 0·063 with 6078 observed $[I > 3\sigma(I)]$ unique reflections. The unit cell contains two $Cr(N_3O_3)$ and one $Cr(O_6)$ coordinating complexes of 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol, four sulfate groups and 30 water molecules. The average Cr—O distance in the $Cr(O_6)$ complex is 1·983 (4) Å, and 1·943 (3) Å in the $Cr(N_3O_3)$ complex, the average Cr—N distance is 2·089 (5) Å. The structure is predominantly stabilized by hydrogen bonds of the types N—H···O and O—H···O.

Introduction. 1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol (TACI, $C_6H_{15}N_3O_3$) and its methylated derivatives represent a new class of interesting ligands with high affinity for Fe^{III} (Hegetschweiler, Erni, Schneider & Schmalle, 1990) and have recently been considered for the treatment of Cooley's anaemia (Schneider, Erni & Hegetschweiler, 1989). Owing to the chair–chair interconversion (I) and the possible coordination of the atoms in the ax-eq-ax or ax-ax-ax sequence (II), TACI provides four different metal binding sites [O(2), O(4), O(6)], [N(1), N(3), N(5)] and *e.g.* [N(1), O(2), O(6)] and [O(4), N(3),

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* Author to whom correspondence should be addressed.

0108-2701/91/102047-06$03.00