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The Geometry of Bis(η^5-cyclopentadienyl) Metal Diligand Complexes: Structure of Mo(Cp)₂(benzoate)₂

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Abstract. Dibenzoatobis(η^5-cyclopentadienyl)molybdenum(IV), [Mo(C₅H₅)₂(C₇H₅O₂)₂], $M_r = 468.34$, monoclinic, $P2_1/n$, $a = 22.530\,(6)$, $b = 7.648\,(1)$, $c = 12.307\,(3)$ Å, $\beta = 103.76\,(2)°$, $V = 2059.8\,(8)$ Å³, $Z = 4$, $D_x = 1.51$ g cm⁻³, $\lambda(Mo\,K\alpha) = 0.71069$ Å, $\mu = 5.82$ cm⁻¹, $F(000) = 952$, $T = 293$ K. Final $R(F) = 0.0353$, $wR = 0.044$ for 2049 observed diffractometer reflexions. The Mo atom has the usual distorted tetrahedral geometry comprising the Mo–Cp (Cp = η^5-C₅H₅) ring normals [Mo···Cp = 1.970, 1.975 (8) Å] and two Mo–O bonds [Mo–O 2.102, 2.113 (4) Å] to the monodentate benzoates. The Cp/Cp conformation is staggered and the Cp–Mo–Cp and O–Mo–O angles are 133.3 (4) and 72.3 (2)° respectively. The geometry of this molecule is compared with that of the corresponding Ti complex, and the importance of steric factors in both molecules is assessed.

Introduction. The structure determination of the title complex has been completed as part of a continuing study of structural and thermodynamic properties of molybdenum dicyclopentadienyl complexes (Calhorda, Carrondo, Dias, Domingos, Martinho Simões & Teixeira, 1986).

Experimental. Crystals prepared at the Centro de Quimica Estrutural (Teixeira, 1986). Laue symmetry and systematic absences consistent with $P2_1/n$; 2862 independent hkl intensities were measured (range of hkl: $h\,0{\to}24$, $k\,0{\to}8$, $l\,-13{\to}13$), 813 unobserved with $F_o < 3\sigma(F_o)$, θ–2θ scans, $\theta_{max} = 23°$. CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Unit-cell parameters refined from 25 reflexions, $9 < \theta < 15°$. $4\overline{1}4$, $30\overline{7}$, $\overline{7}07$ used as standards, intensities showed no decay throughout data collection. Mo position from sharpened Patterson synthesis map, O and C positions from subsequent difference Fourier synthesis. Full-matrix least-squares refinement with SHELX (Sheldrick, 1976), isotropic temperature factors, gave $R = 0.10$. Anisotropic refinement reduced R to 0.048. H atoms included at calculated positions, C–H distance 1.08 Å, refined isotropically. Final

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($\text{Å}^2 \times 10^3$) *for* $[Mo(O_2CC_6H_5)_2(\eta^5\text{-}C_5H_5)_2]$

	x	y	z	U_{eq}
Mo	1434 (1)	1629 (1)	502 (1)	40·7 (2)
O(11)	940 (2)	2844 (4)	−981 (3)	46 (1)
C(1)	382 (3)	2617 (8)	−1500 (4)	52 (2)
O(12)	37 (2)	1510 (7)	−1312 (4)	99 (2)
C(11)	156 (3)	3943 (8)	−2412 (4)	53 (2)
C(12)	524 (3)	5348 (3)	−2543 (5)	69 (3)
C(13)	298 (5)	6578 (12)	−3367 (7)	112 (5)
C(14)	−280 (6)	6371 (17)	−4037 (8)	141 (6)
C(15)	−642 (4)	4983 (18)	−3905 (7)	117 (5)
C(16)	−421 (3)	3779 (11)	−3100 (5)	77 (3)
O(21)	2035 (2)	3322 (5)	−54 (3)	57 (2)
C(2)	2614 (3)	3625 (7)	339 (5)	53 (2)
O(22)	2934 (2)	3028 (7)	1189 (3)	79 (2)
C(21)	2862 (3)	4820 (8)	−418 (4)	56 (2)
C(22)	3485 (3)	4852 (11)	−356 (5)	82 (3)
C(23)	3696 (4)	5931 (13)	−1106 (7)	97 (4)
C(24)	3318 (5)	6981 (10)	−1843 (8)	96 (4)
C(25)	2710 (5)	6951 (9)	−1891 (7)	92 (4)
C(26)	2475 (3)	5871 (8)	−1177 (6)	72 (3)
C(31)	1712 (3)	−1156 (8)	1097 (5)	71 (3)
C(32)	1137 (3)	−1296 (8)	280 (7)	77 (3)
C(33)	1245 (5)	−766 (10)	−726 (6)	90 (4)
C(34)	1839 (4)	−239 (9)	−556 (6)	82 (4)
C(35)	2139 (3)	−501 (8)	557 (6)	70 (3)
C(41)	1658 (4)	2305 (10)	2383 (5)	77 (3)
C(42)	1123 (4)	1384 (9)	2120 (6)	81 (4)
C(43)	689 (3)	2294 (12)	1380 (7)	81 (3)
C(44)	960 (4)	3888 (10)	1193 (5)	82 (3)
C(45)	1550 (4)	3878 (8)	1835 (6)	73 (3)

E.s.d.'s given in parentheses refer to the least significant digit. The equivalent isotropic mean-square coefficient is

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta).$$

phenyl rings are pointing away from the space occupied by the Cp rings, but, as a result, are directed towards each other. Bond lengths and angles involving the Mo atom are in close agreement with those in most other MoCp$_2$L$_2$ complexes involving oxygen-(or nitrogen-)-bonded ligands (Calhorda, Carrondo, Dias, Duarte, Gomes da Costa & Hursthouse, 1986). It is also pertinent to note that the angle parameters are close to those predicted by Lauher & Hoffman (1976) for a d^2 complex, but with the O—Mo—O angle $\sim6°$ less than the values suggested.
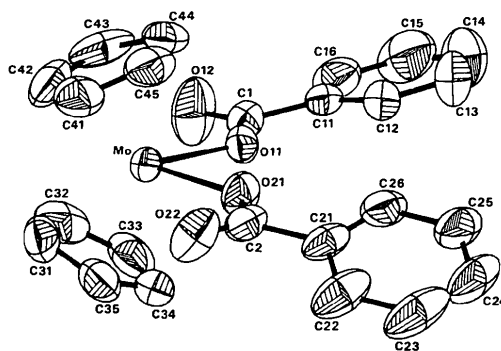

Fig. 1. Molecular structure of the title compound with 30% probability thermal ellipsoids, showing the atom-labeling scheme.

refinement gave $R(F) = 0·0353$, $wR(F) = 0·044$, weighting scheme $w = 1·76/[\sigma^2(F_o) + 0·00053F_o^2]$. Final difference map had no peaks of magnitude greater than 0·35 e Å^{-3}, maximum shift/e.s.d. = 0·094. Atomic scattering factors for Mo, C, O from Doyle & Turner (1968), for H from Stewart, Davidson & Simpson (1965). Anomalous-dispersion corrections (f', f'') for Mo from Cromer & Liberman (1970). No corrections for absorption or secondary extinction. Drawing made with *SNOOPI* (Davies, 1983). The final atomic coordinates and equivalent isotropic temperature factors are given in Table 1.*

Discussion. The structure of the molecule is shown in Fig. 1, along with the atom-numbering scheme. Bond lengths and angles are given in Table 2. The metal has the usual bent MCp$_2$ structure, in which the two Cp rings have a mutually staggered conformation, and is also bonded to one O from each of two monodentate benzoate ligands. The latter are arranged so that the

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43633 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected bond lengths* (Å) *and bond angles* (°)

Mo–O(11)	2·113 (4)	Mo–O(21)	2·102 (4)
O(11)–C(1)	1·281 (8)	O(21)–C(2)	1·300 (8)
O(12)–C(1)	1·208 (8)	O(22)–C(2)	1·210 (8)
C(1)–C(11)	1·508 (9)	C(2)–C(21)	1·505 (9)
C(11)–C(12)	1·389 (10)	C(21)–C(22)	1·386 (10)
C(12)–C(13)	1·388 (11)	C(22)–C(23)	1·403 (13)
C(13)–C(14)	1·375 (17)	C(23)–C(24)	1·350 (14)
C(14)–C(15)	1·372 (17)	C(24)–C(25)	1·359 (14)
C(15)–C(16)	1·357 (14)	C(25)–C(26)	1·399 (11)
C(16)–C(11)	1·379 (10)	C(26)–C(21)	1·375 (11)
Mo–C(31)	2·291 (7)	Mo–C(41)	2·308 (8)
Mo–C(32)	2·333 (7)	Mo–C(42)	2·271 (7)
Mo–C(33)	2·349 (8)	Mo–C(43)	2·259 (8)
Mo–C(34)	2·266 (8)	Mo–C(44)	2·298 (7)
Mo–C(35)	2·265 (7)	Mo–C(45)	2·348 (8)
Mo–Cp$_1$*	1·970 (8)	Mo–Cp$_2$*	1·975 (8)
C(31)–C(32)	1·443 (12)	C(41)–C(42)	1·366 (12)
C(32)–C(33)	1·379 (13)	C(42)–C(43)	1·358 (13)
C(33)–C(34)	1·366 (13)	C(43)–C(44)	1·406 (13)
C(34)–C(35)	1·390 (11)	C(44)–C(45)	1·375 (13)
C(35)–C(31)	1·385 (11)	C(45)–C(41)	1·373 (12)
O(11)–Mo–O(21)	72·3 (2)	Cp$_1$–Mo–Cp$_2$	133·3 (3)
Mo–O(11)–C(1)	128·6 (4)	Mo–O(21)–C(2)	131·0 (4)
O(11)–C(1)–C(11)	113·4 (6)	O(21)–C(2)–C(21)	111·4 (6)
O(11)–C(1)–O(12)	126·8 (7)	O(21)–C(2)–O(22)	126·4 (6)
O(12)–C(1)–C(11)	119·8 (7)	O(22)–C(2)–C(21)	122·2 (7)
C(1)–C(11)–C(12)	120·2 (7)	C(2)–C(21)–C(22)	119·8 (8)
C(1)–C(11)–C(16)	119·8 (8)	C(2)–C(21)–C(26)	120·4 (7)
C(12)–C(11)–C(16)	120·0 (7)	C(22)–C(21)–C(26)	119·8 (8)
C(11)–C(12)–C(13)	119·0 (9)	C(21)–C(22)–C(23)	118·1 (10)
C(12)–C(13)–C(14)	119·3 (12)	C(22)–C(23)–C(24)	122·2 (10)
C(13)–C(14)–C(15)	121·5 (11)	C(23)–C(24)–C(25)	119·2 (9)
C(14)–C(15)–C(16)	119·2 (11)	C(24)–C(25)–C(26)	120·7 (11)
C(15)–C(16)–C(11)	120·9 (11)	C(25)–C(26)–C(21)	119·9 (9)

* Cp$_1$, Cp$_2$ represent the ring normals from Mo to the cyclopentadienyl rings.

In addition to establishing further data for our specific study of Mo complexes, the determination of this structure also allows us to make an interesting comparison with the analogous d^0 titanium(IV) complex, the structure of which has been reported by Fay *et al.* (Hoffman, Chester & Fay, 1983) along with the results of some EHMO calculations.

The comparison of the two structures is most conveniently made by reference to parameters introduced by Fay *et al.* and shown in Fig. 2; actual values are given in Table 3. The differences between φ and d_2 values for the two structures are consistent with theoretical predictions [although the O—Ti—O angle of 91·4° is considerably smaller than the value predicted by Lauher & Hoffmann (1976)]. The values of d_1 and θ are associated with a particular difference between the two molecules, arising out of the differing d-orbital population. In terms of normal Cp—M interactions and O$\rightarrow$$M$ σ bonding only, the metal atom has an 18-electron configuration in the Mo complex but a 16-electron configuration in the Ti complex. Fay *et al.* showed quite clearly, *via* EHMO calculations, that the Ti atom increased its electron count *via* Ti$\leftarrow$O π bonding, with in-plane p orbitals on the carboxylate oxygen interacting strongly with an orbital of a_1 symmetry on the Ti atom. This feature explains the shortening of the Ti—O bond and the rather large value for θ, the Ti—O—C angle, but it is worth noting that the calculations showed that the π bonding would have been maximized at a θ value of 180°. Bearing in mind the fact that the EHMO calculations were made on the simpler model compound TiCp$_2$(O$_2$CH)$_2$, we suspected that the angle θ actually adopted may also be influenced by steric factors, especially involving the phenyl rings on the benzoates. Accordingly, we have made some assessment of the steric situation by examining quantitatively various intramolecular non-bonded interactions, for both Ti and Mo molecules, using our PE calculation program *EENY2* (Backer-Dirks, 1983). A full presentation of our results is beyond the scope of this paper, but they may be summarized as follows. For both molecules, the structures as found give large positive energies ($U_{sum} = 218·4$, 110·4 kJ mol^{-1}) and from our experience (most structures give U_{sum} values of 0 ± 20 kJ mol^{-1}, where U_{sum} is calculated omitting all

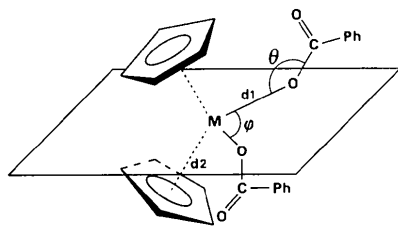**Table 3.** *Comparison of selected geometry parameters in molecules of* $M(Cp)_2(benzoate)_2$, $M = Ti, Mo$

	Ti	Mo
d_1 (Å)	1·926 (9)	2·107 (6)
d_2 (Å)	2·062 (18)	1·973 (11)
φ (°)	91·4 (3)	72·3 (2)
θ (°)	148·3 (8)	129·8 (6)

1,3 interactions) this suggests strong intermolecular crowding. When the structures were allowed to change, by varying the torsion angles M—O—C—C and O—C—C$_\alpha$(Ph)—C$_\beta$(Ph) (*i.e.* the twists of the phenyl rings) and M—O—C bond angles, new minima were obtained at considerably lower U_{sum} values. Most significantly, the M—O—C angles changed to 175·1° (for Ti) and 158·6° (for Mo). The implications are, therefore, that there are no intramolecular steric reasons why, in the Ti complex, the Ti—O—C angle should not approach much closer to the preferred value of 180°, and that in the Mo complex there is a preference for the Mo—O—C angle to adopt a value similar to that found in organic ethers, *etc.*

One major reason for the adoption of the structures as found, identified in our calculations, are intramolecular steric interactions between the phenyl rings, and since the minimizations showed that these can be reduced, then we presume that the particular phenyl ring orientations found are subject also to crystal-packing requirements.

It would seem, therefore, that the values found for the Mo—O—C angles and other parameters in the molecular geometries are a delicate compromise between electronic and both intra- and intermolecular steric energy requirements. These calculations, simple as they are, point to the ill-advisability of over-simplifying the models used for many types of theoretical calculations, where it is quite routine to replace outer ligand groups by H atoms or other small ligands in order to reduce the number of atoms to be handled.

Fig. 2. Definition of parameters d_1, d_2, φ, and θ.

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The Structure of Carbonatobis(di-2-pyridylamine)cobalt(III) Perchlorate

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Abstract. $[Co(C_{10}H_9N_3)_2(CO_3)]ClO_4$, $M_r = 560\cdot8$, monoclinic, $P2_1/n$, $a = 10\cdot983$ (3), $b = 13\cdot640$ (2), $c = 15\cdot548$ (3) Å, $\beta = 93\cdot23$ (1)°, $V = 2325\cdot5$ (9) Å³, $Z = 4$, $D_m = 1\cdot62$ (1), $D_x = 1\cdot60$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 0\cdot904$ mm⁻¹, $F(000) = 1144$, room temperature, $R = 0\cdot094$ for 2039 reflections. The cation possesses a pseudo-octahedral structure with a bidentate carbonato ligand. The bond lengths and angles are normal, but some short non-bonded distances suggest interligand repulsion. Hydrogen bonds occur between the secondary amine groups and (i) the carbonate ligand of a neighbouring cation and (ii) the partially disordered perchlorate anion.

Introduction. The bidentate ligand di-2-pyridylamine [dipyam, (1)] is unusual in forming an η^2 dioxygen complex $[Co(dipyam)_2O_2]^+$ on treatment with hydrogen peroxide (Johnson & Geldard, 1978). An attempt to grow crystals containing this complex yielded the perchlorate salt of the carbonato complex. The crystal structure of this compound is reported, and allows comparison of the structural properties of the ligand dipyam with the analogous 2,2′-bipyridyl [bpy, (2)] and 1,10-phenanthroline [phen, (3)] cobalt (III) carbonato complexes (Niederhoffer, Martell, Rudolf & Clearfield, 1982).

dipyam,(1)   bpy,(2)   phen,(3)

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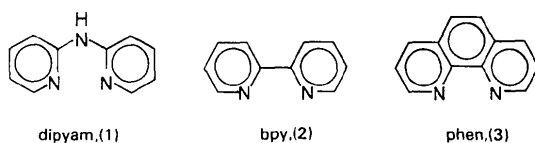
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Experimental. Preparation of crystals: di-2-pyridylamine (previously recrystallized from ethanol), 0·54 g, and cobalt(II) perchlorate hexahydrate, 0·36 g, were dissolved in 150 ml of ethanol:water (2:1) and filtered into a clean flask. 7 ml of 30% hydrogen peroxide were added, and the flask placed in a dewar filled with warm water at 323 K. Over a period of four weeks, red crystals were slowly deposited. Density was measured by flotation.

A parallelepiped $0\cdot18 \times 0\cdot15 \times 0\cdot30$ mm was measured using a Philips PW 1100 diffractometer, $\omega/2\theta$ scan, scan width $1\cdot1°$, scan speed $1\cdot8°$ min⁻¹. Graphite-monochromated Mo $K\alpha$ radiation. 3123 reflections measured $(6 < 2\theta < 44°;$ $h = -11,$ 11; $k = 0,$ 14; $l = 0,$ 16). 2717 unique reflections $(R_{int} = 0\cdot017)$ of which 649 were taken as unobserved $[|F_o| \le 4\sigma(F_o)$ and $|F_o| \le 8\cdot0]$. Two standard reflections measured every 90 min showed a variation of less than $1\cdot8$ $\sigma(I)$, and no correction for change in intensity was applied. Cell parameters from least-squares refinement of 30 centred reflections $(19 \le 2\theta \le 30°)$. Data corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). All other calculations used a local version of *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) and *ORTEP*II (Johnson, 1976). Scattering factors from *International Tables for X-ray Crystallography* (1974). Least-squares refinement on $|F|$ (block matrix, four blocks) with all H atoms in calculated positions gave final values $R = 0\cdot094$, $wR = 0\cdot135$, $S = 3\cdot08$ for 2039 reflections with $w = 1$ for $|F_o| \le 48$, $w = (48/|F_o|)^2$ for $|F_o| > 48$. $(\Delta/\sigma)_{max} = 0\cdot931$. The final difference