Crystal Structure of μ-[Di-(2-methoxyethyl) ethercadmio]-bis(pentacarbonylmanganese)(2 *Cd–Mn*) †

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Crystals of the title compound are monoclinic with $a = 10{\cdot}161(10)$, $b = 23{\cdot}010(20)$, $c = 9{\cdot}718(9)$ Å, $\beta = 91{\cdot}80(2)^\circ$, $Z = 4$, space group $P2_1/n$. The structure was solved by Patterson and Fourier methods from 2191 counter intensities and refined by least-squares to R 4·31%. The cadmium atom is co-ordinated by the terdentate ether molecule and two pentacarbonylmanganese groups in a very distorted trigonal bipyramidal arrangement. There is considerable distortion of the octahedral manganese co-ordination. The molecule has approximate mirror symmetry.

We have previously reported the crystal structure of μ-(2,2′:6′,2″-terpyridylcadmium)-bis(pentacarbonylmanganese)(2 *Cd–Mn*), (terpy)Cd[Mn(CO)$_5$]$_2$, (I), which contains cadmium in a very distorted trigonal bipyramidal co-ordination.[1] This compound was prepared from cadmium, dimanganese decacarbonyl, and terpyridyl, *via* the intermediate (diglyme)Cd[Mn(CO)$_5$]$_2$ (II) {diglyme = di-(2-methoxyethyl) ether, (MeO·[CH$_2$]$_2$·)$_2$O}.[2] (II) is the only one of this series of addition complexes to contain an oxygen-donor Lewis base. Indeed such oxygen-donors are much rarer than nitrogen-donor ligands, and there appears to be only one previously reported structure containing a chelating diglyme ligand.[3] We have determined the structure of (II) for comparison with that of the derivative (I).

EXPERIMENTAL

Crystal Data.—C$_{16}$CdH$_{14}$Mn$_2$O$_{13}$, $M = 636{\cdot}6$, Monoclinic, $a = 10{\cdot}161(10)$, $b = 23{\cdot}010(20)$, $c = 9{\cdot}718(9)$ Å, $\beta = 91{\cdot}80(2)^\circ$, $U = 2256{\cdot}3$ Å^3, $D_c = 1{\cdot}874$, $Z = 4$, $D_m = 1{\cdot}92$ (by flotation), $F(000) = 1248$. Space group $P2_1/n$ (from absences). Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å; μ(Mo-K_α) = 22·4 cm^{-1}.

A sample of crystals, with a powdery coating due to surface decomposition, was used for determination of cell dimensions, space group, and density. Further material was prepared by the method of ref. 2, and recrystallised by cooling ethanol solutions to −32 °C overnight. Crystals were irregular in shape, and there were no preferred cleavage planes. Decomposition took place in air; crystals used for intensity measurements were sealed under dry nitrogen in Lindemann glass capillaries. Unit-cell dimensions were obtained from the ω settings of several carefully centred axial reflexions with crystals mounted about a and b on a Stoe STADI 2 two-circle computer-controlled diffractometer operating on equi-inclination Weissenberg geometry. The space group $P2_1/n$ is equivalent to the standard $P2_1/c$ if different axes are chosen, but this involves an angle β of *ca.* 130°, which is less convenient.

Intensities were collected in the ω-scan mode with Mo-K_α radiation and a graphite monochromator. The diffracted beams were received by a scintillation counter equipped with pulse-height discriminator. A pre-scan of 1 s was made at the centre of the scan range of each reflexion, and used to set step counting time and attenuation filters in order to achieve an approximate constant count method.[4] A variable-range parameter enabled the ω-scan range to be adjusted to allow for the greater width of low-order reflexions of upper layers. The intensities of reflexions with $2\theta < 100^\circ$ were measured from the layers 0—9hkl and h0—6l. Several standard reflexions were monitored after each layer: crystal decomposition was slight and no corrections were made. Reflexions for which the integrated intensity was $< 3\sigma$ (based on counting statistics) were rejected, and a background imbalance test was also applied.[5] Because of the irregular shapes of the crystals, and the reasonably small absorption coefficient, no absorption correction was made. 2191 Independent reflexions were assigned non-zero intensity, and placed on the same scale through common reflexions.[6]

A Patterson map was interpreted to give co-ordinates for the three metal atoms, which were used to phase a Fourier synthesis. About half the carbon and oxygen atoms were located; the rest were revealed in a subsequent weighted difference synthesis.[7] With an overall temperature factor U of 0·04 Å^2, R was 22·1%. For the first two cycles of full-matrix least-squares refinement, all atomic co-ordinates and the overall scale factor were allowed to vary, and there were six isotropic temperature factors: one for each metal atom, one for the carbonyl carbon atoms, one for the carbonyl oxygen atoms, and one for the diglyme atoms. R dropped to 8·27%. With anisotropic temperature factors for the metal atoms, and individual isotropic otherwise, further refinement gave R 4·97%. At this stage a difference-Fourier synthesis contained peaks at positions corresponding to most of the hydrogen atoms, but there were many other peaks of comparable size (*ca.* 0·5 eÅ^{-3}), especially in the neighbourhood of the metal atoms and carbonyl groups, The hydrogen atom positions were therefore not refined, but calculated, the CH$_2$ hydrogen atoms being placed so that the four C–C–H and O–C–H angles were equal in each case and the H–C–H angle was 109·47°; the methyl hydrogen atoms were staggered with respect to the nearest O–Cd bond, and all C–H distances were 1·0 Å. In subsequent refinement cycles, the shifts calculated for each carbon atom were also applied to the hydrogen atoms bonded to it, so that each C–H bond maintained a constant direction and length. Three isotropic temperature factors

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† Reprints not available.

[1] W. Clegg and P. J. Wheatley, *J.C.S. Dalton*, 1973, 90.

[2] A. T. T. Hsieh and M. J. Mays, *J. Chem. Soc.* (*A*), 1971, 729.

[3] K. O. Hodgson and K. N. Raymond, *Inorg. Chem.*, 1972, **11**, 3030.

[4] R. C. G. Killean, *Acta Cryst.*, 1967, **23**, pp. 54, 1109.

[5] H. C. Freeman, J. M. Guss, C. E. Nockolds, R. Page, and A. Webster, *Acta Cryst.*, 1970, **A26**, 149.

[6] A. D. Rae and A. B. Blake, *Acta Cryst.*, 1966, **20**, 586.

[7] G. H. Stout and L. H. Jensen, '*X*-Ray Structure Determination: A Practical Guide,' MacMillan, New York and London, 1968, p. 360.

were refined for hydrogen: one for each set of three methyl hydrogen atoms, and one for all the methylene hydrogen atoms. The reflexions 021 and 120, which appeared to be suffering from extinction, were not allowed to contribute further to refinement.

TABLE 1

(*a*) Fractional atomic co-ordinates (× 10^4) and mean square amplitudes of vibration (Å^2 × 10^3) for the non-hydrogen atoms

Atom	x/a	y/b	z/c	U
Cd	2077(1)	1443(1)	2235(1)	
Mn(1)	2616(1)	626(1)	4188(1)	
Mn(2)	2371(1)	2608(1)	2026(1)	
C(1)	3005(9)	139(4)	5571(9)	58(2)
O(1)	3255(7)	−180(3)	6478(7)	86(2)
C(2)	1097(9)	301(4)	3632(9)	56(2)
O(2)	122(7)	59(3)	3304(7)	83(2)
C(3)	1695(9)	1134(4)	5186(9)	59(2)
O(3)	1065(8)	1450(3)	5844(8)	88(2)
C(4)	4062(11)	1069(5)	4358(10)	69(3)
O(4)	5031(9)	1341(4)	4459(8)	102(3)
C(5)	3370(10)	211(5)	2882(10)	66(3)
O(5)	3809(8)	−91(4)	2051(8)	94(2)
C(6)	2623(11)	3359(5)	1850(11)	72(3)
O(6)	2828(8)	3858(4)	1663(8)	97(2)
C(7)	1791(9)	2449(4)	297(9)	59(2)
O(7)	1415(7)	2368(3)	−836(8)	85(2)
C(8)	710(10)	2714(4)	2509(10)	66(3)
O(8)	−386(8)	2809(4)	2805(8)	94(2)
C(9)	2840(9)	2516(4)	3813(10)	59(2)
O(9)	3127(7)	2474(3)	4978(7)	80(2)
C(10)	4031(10)	2431(4)	1559(9)	60(2)
O(10)	5111(8)	2334(3)	1270(7)	82(2)
C(11)	−1372(12)	1474(5)	2995(12)	91(3)
O(11)	−476(6)	1376(3)	1956(6)	68(2)
C(12)	−993(11)	1032(5)	873(10)	76(3)
C(13)	−131(11)	1045(6)	−289(12)	92(4)
O(12)	1184(6)	925(3)	93(6)	62(2)
C(14)	2004(11)	916(6)	−1056(11)	89(3)
C(15)	3335(12)	783(6)	−729(12)	92(4)
O(13)	3844(6)	1122(3)	366(6)	60(2)
C(16)	5221(11)	1013(5)	582(11)	80(3)

(*b*) Anisotropic vibrational amplitudes (Å^2 × 10^4), in the form $\exp -2\pi^2(h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12} + \cdots)$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cd	453(4)	350(3)	394(3)	−4(3)	−15(2)	−25(3)
Mn(1)	462(7)	365(7)	428(7)	−2(6)	11(5)	21(6)
Mn(2)	549(9)	361(7)	461(7)	−20(6)	−33(6)	−7(6)

(*c*) Calculated fractional co-ordinates (× 10^4) and isotropic vibrational amplitudes (Å^2 × 10^3) for the hydrogen atoms

Atom	x/a	y/b	z/c	U
H(11a)	−2712	1675	2603	48(17)
H(11b)	−1634	1093	3397	
H(11c)	−950	1721	3731	
H(12a)	−1885	1181	584	68(12)
H(12b)	−1072	621	1199	
H(13a)	−179	1441	−713	
H(13b)	−442	749	−980	
H(14a)	1974	1308	−1499	
H(14b)	1650	619	−1720	
H(15a)	3871	852	−1559	
H(15b)	3397	364	−460	
H(16a)	5696	1111	−274	90(24)
H(16b)	5361	594	810	
H(16c)	5569	1259	1360	

Up to this point, the weighting scheme used was $w^{-1} = a + |F_o| + b|F_o|^2$, with $a = 2F_{\text{min.}}$ and $b = 2/F_{\text{max.}}$[8] Weights based on counting statistics were now introduced, so that $w = W/(a + |F_o| + b|F_o|^2)$, with a and b set at 15·17 and 0·005 respectively, on the basis on an analysis of the variance in ranges of $F_o/F_{\text{max.}}$. W is the sum of the counting statistics weight for all equivalent reflexions which were averaged in the data reduction to obtain the observed structure factor F_o. With this scheme, the analysis of the variance was more even than with the previous weighting scheme. The final R was 4·31%, and the largest shift-to-σ ratio in the last cycle was 0·022. 147 Parameters were refined in all. Complex neutral scattering factors were used.[9]

RESULTS AND DISCUSSION

The results are summarised in Tables 1—4. Final atomic co-ordinates and temperature factors are given in Table 1, bond lengths and angles in Tables 2 and 3, and shortest non-bonded contacts in Table 4. In all these Tables estimated standard deviations are given in parentheses. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20889 (15 pp., 1 microfiche).* Reflexions not contributing to the refinement are marked with an asterisk. The labelling of the atoms is shown in Figure 1. The direction of view is inclined at 15° to the normal of the Mn–Cd–Mn plane (*cf.* Figure 1 of ref. 1). Each hydrogen or carbonyl oxygen atom has the same number as the carbon atom to which it is bonded.

TABLE 2

Bond lengths (Å)

Cd–Mn(1)	2·714(2)	Cd–O(11)	2·603(7)
Cd–Mn(2)	2·707(2)	Cd–O(12)	2·541(7)
		Cd–O(13)	2·696(7)
Mn(1)–C(1)	1·785(11)	Mn(2)–C(6)	1·755(12)
Mn(1)–C(2)	1·783(11)	Mn(2)–C(7)	1·801(11)
Mn(1)–C(3)	1·798(11)	Mn(2)–C(8)	1·781(11)
Mn(1)–C(4)	1·789(12)	Mn(2)–C(9)	1·799(11)
Mn(1)–C(5)	1·781(11)	Mn(2)–C(10)	1·806(11)
C(1)–O(1)	1·169(11)	C(6)–O(6)	1·182(13)
C(2)–O(2)	1·172(11)	C(7)–O(7)	1·169(11)
C(3)–O(3)	1·173(11)	C(8)–O(8)	1·179(12)
C(4)–O(4)	1·168(12)	C(9)–O(9)	1·164(11)
C(5)–O(5)	1·165(11)	C(10)–O(10)	1·163(11)
C(11)–O(11)	1·398(13)	C(16)–O(13)	1·429(13)
O(11)–C(12)	1·407(12)	O(13)–C(15)	1·406(13)
C(12)–C(13)	1·451(16)	C(15)–C(14)	1·412(16)
C(13)–O(12)	1·402(13)	C(14)–O(12)	1·413(12)

The co-ordination of the cadmium is best described as a very distorted trigonal bipyramid, and a comparison with the structure of (I) [1] shows how similar are the environments of cadmium in the two compounds. The two axial bonds Cd–O(11) and Cd–O(13) enclose an angle of 126·6°. This angle would be substantially larger if the diglyme ligand were planar (excluding the hydrogen atoms) instead of puckered, but this would also markedly increase repulsive intramolecular interactions between hydrogen atoms on adjacent carbon

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[8] D. W. J. Cruickshank, in 'Computing Methods in Crystallography,' ed. J. S. Rollett, Pergamon, Oxford, 1965, p. 114.

[9] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104; D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

TABLE 3

Bond angles (°)

Mn(1)–Cd–Mn(2)	135·9(1)	O(11)–Cd–Mn(1)	102·1(2)
O(12)–Cd–Mn(1)	107·9(2)	O(11)–Cd–Mn(2)	99·4(2)
O(12)–Cd–Mn(2)	116·1(2)	O(13)–Cd–Mn(1)	99·1(2)
O(11)–Cd–O(12)	63·8(3)	O(13)–Cd–Mn(2)	98·2(2)
O(12)–Cd–O(13)	63·1(3)	O(11)–Cd–O(13)	126·6(3)
Cd–Mn(1)–C(1)	175·1(4)	Cd–Mn(2)–C(6)	177·5(5)
Cd–Mn(1)–C(2)	85·7(4)	Cd–Mn(2)–C(7)	80·5(4)
Cd–Mn(1)–C(3)	80·3(4)	Cd–Mn(2)–C(8)	90·5(4)
Cd–Mn(1)–C(4)	79·5(4)	Cd–Mn(2)–C(9)	80·6(4)
Cd–Mn(1)–C(5)	87·4(4)	Cd–Mn(2)–C(10)	84·3(4)
C(1)–Mn(1)–C(2)	97·7(5)	C(6)–Mn(2)–C(7)	98·9(5)
C(1)–Mn(1)–C(3)	96·2(5)	C(6)–Mn(2)–C(8)	91·9(6)
C(1)–Mn(1)–C(4)	97·3(5)	C(6)–Mn(2)–C(9)	100·1(6)
C(1)–Mn(1)–C(5)	96·3(5)	C(6)–Mn(2)–C(10)	93·3(6)
C(2)–Mn(1)–C(3)	88·6(5)	C(7)–Mn(2)–C(8)	89·4(5)
C(3)–Mn(1)–C(4)	91·2(5)	C(8)–Mn(2)–C(9)	89·2(5)
C(4)–Mn(1)–C(5)	90·1(6)	C(9)–Mn(2)–C(10)	89·7(5)
C(5)–Mn(1)–C(2)	86·9(5)	C(10)–Mn(2)–C(7)	90·0(5)
C(2)–Mn(1)–C(4)	165·0(5)	C(7)–Mn(2)–C(9)	161·1(5)
C(3)–Mn(1)–C(5)	167·2(5)	C(8)–Mn(2)–C(10)	174·8(6)
Mn(1)–C(1)–O(1)	179·7(8)	Mn(2)–C(6)–O(6)	176·2(11)
Mn(1)–C(2)–O(2)	176·2(10)	Mn(2)–C(7)–O(7)	177·5(10)
Mn(1)–C(3)–O(3)	177·8(9)	Mn(2)–C(8)–O(8)	177·0(10)
Mn(1)–C(4)–O(4)	177·7(10)	Mn(2)–C(9)–O(9)	177·9(10)
Mn(1)–C(5)–O(5)	175·4(10)	Mn(2)–C(10)–O(10)	177·9(10)
C(11)–O(11)–C(12)	113·3(9)	C(16)–O(13)–C(15)	110·4(9)
O(11)–C(12)–C(13)	110·5(10)	O(13)–C(15)–C(14)	112·1(10)
C(12)–C(13)–O(12)	112·5(10)	C(15)–C(14)–O(12)	114·2(11)
C(13)–O(12)–C(14)	111·9(9)		
Cd–O(11)–C(11)	125·7(7)	Cd–O(13)–C(16)	128·2(7)
Cd–O(11)–C(12)	117·3(7)	Cd–O(13)–C(15)	115·2(7)
Cd–O(12)–C(13)	115·9(7)	Cd–O(12)–C(14)	116·7(7)

TABLE 4

Shortest non-bonded distances (Å) of various types

Type	Atoms	Distance
Intramolecular		
H · · · H (same C atom)	All of this type	1·663
H · · · H	H(14a) · · · H(15a)	2·196
O(CO) · · · H	O(10) · · · H(16c)	2·517
O(CO) · · · O(CO)	O(3) · · · O(9)	3·279
	O(4) · · · O(9)	3·295
C(CO) · · · C(CO)	C(2) · · · C(5)	2·451
	C(2) · · · C(3)	2·502
O(CO) · · · C(diglyme)	O(8) · · · C(11)	3·238
O(CO) · · · O(diglyme)	O(10) · · · O(13)	3·183
C(CO) · · · O(diglyme)	C(10) · · · O(13)	3·230
C(CO) · · · C(diglyme)	C(5) · · · C(16)	3·493
Cd · · · C(CO)	Cd · · · C(4)	2·967
Cd · · · O(CO)	Cd · · · O(4)	3·650
Intermolecular		
H · · · H	H(15b) · · · H(16b$^{\mathrm{I}}$)	2·567
O(CO) · · · H	O(1) · · · H(11b$^{\mathrm{II}}$)	2·673
O(CO) · · · O(CO)	O(3) · · · O(10$^{\mathrm{III}}$)	2·993
	O(7) · · · O(10$^{\mathrm{IV}}$)	3·147
	O(8) · · · O(9$^{\mathrm{IV}}$)	3·161
O(CO) · · · C(diglyme)	O(5) · · · C(16$^{\mathrm{I}}$)	3·489

The Roman numeral superscripts refer to transformation of co-ordinates of the second atom as follows:

I $1 - x, -y, -z$ II $-x, -y, 1 - z$
III $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ IV $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$

atoms. The actual shape adopted by the ligand produces a staggered conformation about the C(12)–C(13) and C(14)–C(15) bonds. One very important difference between the structures of (I) and (II) on the one hand, and dichloro(terpyridyl)zinc (also described as distorted trigonal bipyramidal [10]) on the other is the large difference between the two N(2)–Zn–Cl angles in (terpy)ZnCl$_2$. This has also been noted in (terpy)CoCl$_2$,[11] and (paphy)-CoCl$_2$ [12] (paphy = pyridine-2-carbaldehyde-2-pyridylhydrazone, a terdentate ligand not greatly dissimilar from terpyridyl), and, chiefly as a result of this, Gerloch [12] and Goldschmied and Stephenson [11] have interpreted the structures of these three compounds as closer to square pyramidal than trigonal bipyramidal. It appears, however, from the bond lengths and angles, that distorted trigonal bipyramidal is the better description of the co-ordination of cadmium in (I) and (II), but it should be noted that the two ideal extremes are not very different in energy or even in geometry.

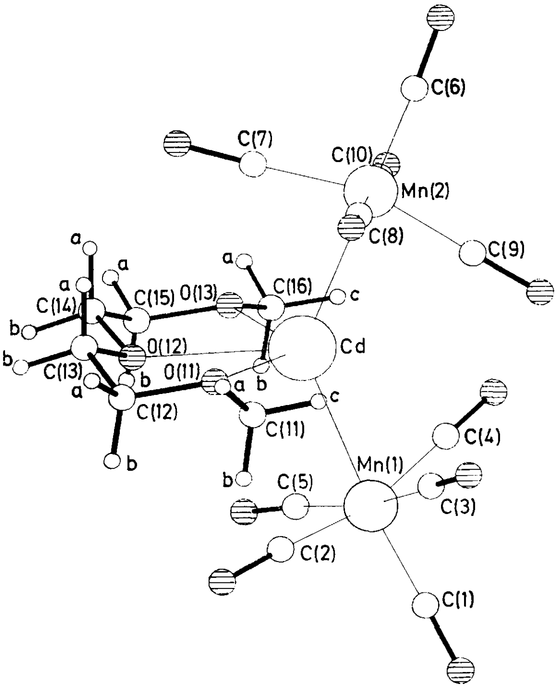

FIGURE 1 View of one molecule showing the labelling of the atoms

Within the diglyme ligand, all C–O distances are essentially equal, and the mean (1·409 Å) is a little smaller than the standard value for saturated alcohols and ethers (1·426 Å).[13] The two C–C distances are considerably shorter than the normal value (1·54 Å). This shortening is probably not real, but the result of libration,[14] for which no corrections have been made.

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[10] F. W. B. Einstein and B. R. Penfold, *Acta Cryst.*, 1966, **20**, 924.

[11] E. Goldschmied and N. C. Stephenson, *Acta Cryst.*, 1970, **B26**, 1867.

[12] M. Gerloch, *J. Chem. Soc.* (*A*), 1966, 1317.

[13] *Chem. Soc. Special Publ.*, No. 18, 1965.

[14] D. W. J. Cruickshank, *Acta Cryst.*, 1956, **9**, 757; 1961, **14**, 896.

Of the three Cd–O bonds, the central one is the shortest. This is in contrast to the K–O distances in [diglymeK][Ce(C$_8$H$_8$)$_2$],[3] where the central bond is 0·051 Å longer than the other two, which are equal by crystallographic symmetry; however, it resembles the situation in terpyridyl complexes.[1,10,11,15] It seems that this shortening of the central bond is a consequence of the distorted trigonal bipyramidal or square pyramidal co-ordinations, as has been suggested for (terpy)ZnCl$_2$.[10] Manipulation of molecular models shows that any attempt to increase the axial–axial angle must reduce the length of the central bond. So there is a conflict between the requirements of the cadmium co-ordination on the one hand, and the bonding and non-bonding interactions within the ligand on the other.[1] The Cd–O(11) and Cd–O(13) bond lengths are significantly different, and this can probably be ascribed to packing forces: O(13) is involved in two of the shortest non-bonded intramolecular contacts (see Table 4), while the nearest neighbours to O(11) outside the diglyme ligand are to C(2) (3·340) and C(8) (3·344 Å).

The Cd–Mn bond lengths (not significantly different) in (II) are somewhat shorter than in (I).[1] The Cd–O bond lengths are all longer than the Cd–N lengths. This suggests weaker Cd–O than Cd–N bonds, and is in keeping with the observation that terpyridyl displaces diglyme from (I),[2] with the greater air-sensitivity of the diglyme complex, and with the rarity of oxygen-donor ligands in general.

The co-ordination of the two manganese atoms is greatly distorted from ideal octahedral, but the pattern is not a simple alternating one as in (I). Similar gross distortions are noted in the complexes of Cd[Mn(CO)$_5$]$_2$ with the bidentate ligands 2,2′-bipyridyl and 1,10-phenanthroline,[16] and smaller distortions, almost invariably involving a displacement of the equatorial carbonyl groups away from the axial, have been observed in a large number of manganese carbonyl derivatives XMn(CO)$_5$,[17] and also in carbonyl complexes of other transition metals.[18] That the effect is not due solely to intermolecular (crystal packing) forces is demonstrated by gas-phase electron diffraction studies,[19] and its consistent nature suggests an intramolecular electronic cause. Evidence for this has been found in interpretation of molecular orbital and force constant calculations,[20] and of mass spectral fragmentation

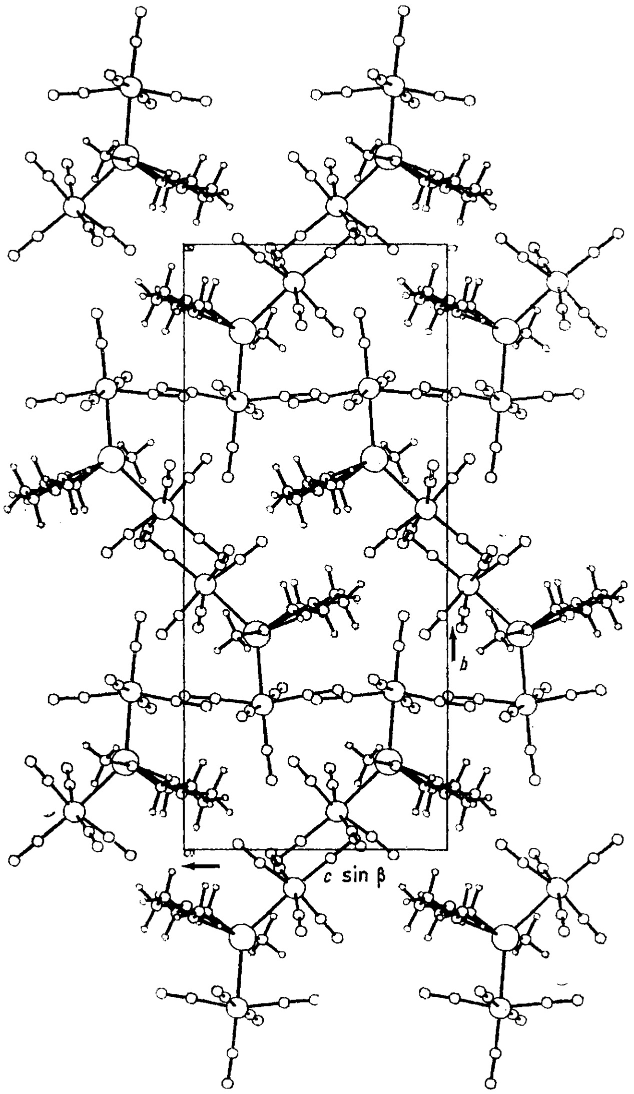

FIGURE 2 The packing illustrated by a projection down the *a* axis

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patterns.[21] Considering the evidence as a whole, it seems that the fundamental cause of the distortion of the manganese co-ordination is a direct X–C(eq) interaction. The simple ' umbrella ' pattern expected is then modified by inter- and intra-molecular forces of the van der Waals type. Consequently, the distortions are most severe [with widely varying X–Mn–C(eq) angles in the same structure] for those compounds with the least-simple X groups, such as (I) and (II).

There is no crystallographic requirement for any molecular symmetry in (II), but there is approximate mirror symmetry (C_s) about the equatorial plane [O(12), Mn(1), Mn(2)]. The crystal packing is shown in projection down the *a* axis in Figure 2.

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