Crystal Structures of μ-[2,2′-Bipyridylcadmium]-bis(pentacarbonylmanganese)(2*Cd–Mn*) and μ-[1,10-Phenanthrolinecadmium]-bis(pentacarbonylmanganese)(2*Cd–Mn*) †

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Crystals of the title compounds [bipyridyl complex (III), phenanthroline complex (IV)] are monoclinic with $Z = 4$, space group $P2_1/n$; (III): $a = 14{\cdot}429(15)$, $b = 15{\cdot}805(16)$, $c = 10{\cdot}423(10)$ Å, $\beta = 94{\cdot}62(2)°$; (IV): $a = 14{\cdot}574(15)$, $b = 16{\cdot}258(16)$, $c = 10{\cdot}453(10)$ Å, $\beta = 96{\cdot}87(2)°$. The structures were solved from diffractometer data by Patterson and Fourier methods and refined by least squares to R 5·27 (2041 reflexions) and 5·76% (1431 reflexions) respectively. The two structures are closely similar: the cadmium atom is co-ordinated by two nitrogen and two manganese atoms in a distorted tetrahedral arrangement, and there is considerable distortion of the octahedral manganese co-ordination. Both molecules have approximate C_2 symmetry.

THE compound cadmiumbis(pentacarbonylmanganese), $Cd[Mn(CO)_5]_2$, forms adducts with a variety of Lewis bases.[1] We have previously reported two of these, both containing terdentate ligands and, consequently, five-co-ordinate cadmium atoms: (terpy)$Cd[Mn(CO)_5]_2$, (I),[2] and (diglyme)$Cd[Mn(CO)_5]_2$, (II).[3] Most of the known

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† Reprints not available.

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

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

[3] W. Clegg and P. J. Wheatley, *J.C.S. Dalton*, 1974, 424.

adducts, however, are with uni- or bi-dentate ligands, and are likely to contain four-co-ordinate cadmium. For the bidentate ligands 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen), it is clear that the co-ordination of the cadmium must be considerably distorted from the ideal tetrahedral, because the N–Cd–N angle cannot reach 109·5°. We have determined the structures of these two adducts [(III) and (IV) respectively] to obtain more information on the metal–metal bonding and the co-ordination of the metal atoms.

EXPERIMENTAL

(bipy)Cd[Mn(CO)$_5$]$_2$, (III)

Crystal Data.—$C_{20}CdH_8Mn_2N_2O_{10}$, $M = 658{\cdot}6$, Monoclinic, $a = 14{\cdot}429(15)$, $b = 15{\cdot}805(16)$, $c = 10{\cdot}423(10)$ Å, $\beta = 94{\cdot}62(2)°$, $U = 2369{\cdot}3$ Å^3, $D_c = 1{\cdot}846$, $Z = 4$, $D_m = 1{\cdot}83$ (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) = 20·4 cm^{-1}.

On preparation,[1] the compound crystallises as orange parallelepipeds, with dimensions typically in the ratio 1 : 2 : 6, the longest dimensions being along [10$\bar{1}$] and the shortest along c^*. Crystals were mounted about [10$\bar{1}$] and [101] for unit-cell and intensity measurements, which were made on a Stoe STADI 2 two-circle computer-controlled diffractometer operating on equi-inclination Weissenberg geometry, with Mo-K_α radiation and a graphite monochromator. Cell dimensions were obtained by a least-squares fit of observed and calculated ω settings for all zero-layer reflexions about each oscillation axis.[4] Intensities were collected in the ω-scan mode with 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 attentuation filters in order to achieve an approximate constant count mode.[5] The intensities of reflexions with $2\theta < 100°$ were measured from the layers $h0$—$16l$ and lkl—$6 + l,k,l$. Crystal decomposition was monitored by measuring 10 standard reflexions after each layer: the decay was small until after the h,12,l layer for the first crystal; higher layers were not used for structure solution and refinement. No other corrections were made for decomposition, or for absorption. Reflexions for which the integrated intensity was $< 3\sigma$ (based on counting statistics) were rejected, and a background imbalance test was also applied.[6] 2041 Independent reflexions were assigned non-zero intensity, and placed on the same scale through common reflexions.[4,7]

A Patterson map was solved for the metal atoms, which were used to phase a Fourier synthesis. The majority of the non-hydrogen atoms could be found, and the rest were located in a subsequent weighted difference synthesis.[8] With an overall temperature factor U of 0·05 Å^2, R was 22·5%. Refinement was by full-matrix least squares, and more temperature factors were introduced at each stage, until R was 5·80% with all atomic temperature factors isotropic except for the three anisotropic metal atoms. Hydrogen atoms were introduced at positions 1·0 Å from the corresponding carbon atoms, and lying on the C–C–C and C–C–N external bisectors. In subsequent refinement cycles the shifts calculated for each carbon atom were applied also to the hydrogen atom bonded to it, so that each C–H bond maintained a constant direction and length; there was one overall isotropic temperature factor for the hydrogen atoms. Three reflexions which appeared to be suffering from extinction were not allowed to contribute to further refinement. The final R was 5·27%, and the largest shift/σ ratio in the last cycle was 0·074. Weights calculated from counting statistics were used throughout. Complex neutral scattering factors were used.[9] 157 Parameters were refined in all.

(phen)Cd[Mn(CO)$_5$]$_2$, (IV)

Crystal Data.—$C_{22}CdH_8Mn_2N_2O_{10}$, $M = 682{\cdot}6$, Monoclinic, $a = 14{\cdot}574(15)$, $b = 16{\cdot}258(16)$, $c = 10{\cdot}453(10)$ Å, $\beta = 96{\cdot}87(2)°$, $U = 2459{\cdot}0$ Å^3, $D_c = 1{\cdot}844$, $Z = 4$, $D_m = 1{\cdot}83$ (by flotation), $F(000) = 1328$. Space group $P2_1/n$ (from absences). Mo-K_α radiation; μ(Mo-K_α) = 19·7 cm^{-1}.

Crystals from ethanol were orange plates, similar to those of (III) but thinner. The crystal axes bear the same relationship to the crystal habit in both compounds. Unit-cell dimensions and intensities were measured by the same methods as for (III), the layers used being $h0$—$11l$, lkl, $2 + l,k,l$, and $4 + l,k,l$. Absorption and decomposition corrections were not applied; there were 1431 independent non-zero structure factors.

Structure solution and refinement followed the same plan as for (III). The value of R was 25·2% before refinement (overall U 0·05 Å^2), 6·21% before introduction of hydrogen atoms, and 5·76% finally. The largest shift/σ ratio in the last cycle was 0·012. Five reflexions were omitted in the last stages of refinement because of the suspected effects of extinction. The weighting scheme was $w = W/(a + |F_o| + b|F_o|^2)$; W is the sum of the counting statistics weights for all equivalent reflexions which were averaged in the data reduction to obtain the observed structure factor F_o; a and b were $2F_{\text{min.}}$ and $2/F_{\text{max.}}$ respectively. 165 Parameters were refined in all.

RESULTS AND DISCUSSION

The results are summarised in Tables 1—5 for (III) and 6—10 for (IV). Estimated standard deviations are given in parentheses. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20922 (22 pp., 1 microfiche).* Reflections not contributing to the refinement are marked with an asterisk. The labelling of the atoms is shown in Figures 1 and 2; in both Figures the direction of view is inclined at 15° to the normal of the Mn–Cd–Mn plane (*cf.* Figure 1 of refs. 2 and 3). Each hydrogen or oxygen atom has the same number as the carbon atom to which it is bonded. The packing for the two structures is very similar, and is shown for (III) in Figure 3.

The cadmium co-ordinations in the two compounds are almost identical, a tetrahedral arrangement distorted by considerable reduction of the N–Cd–N angle and expansion of the Mn–Cd–Mn angle. The former effect is due to the geometrical limitations of the bidentate

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

[4] W. Clegg and G. M. Sheldrick, unpublished work.

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

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

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

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

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

ligand; the latter to the bulky $Mn(CO)_5$ groups. The only significant difference between the two co-ordination geometries is in the Mn–Cd–Mn angle. Bond angles are much more susceptible to intra- and inter-molecular forces than are bond lengths, and this not very great difference could be produced by the slightly different packing in the two structures due to the extra two carbon atoms in (IV).

TABLE 1

(III): (*a*) Fractional atomic co-ordinates ($\times 10^4$) and isotropic vibrational amplitudes (Å$^2 \times 10^3$) for the non-hydrogen atoms

Atom	x/a	y/b	z/c	U
Cd	743(1)	2509(1)	2917(1)	
Mn(1)	2391(1)	3129(1)	2335(1)	
Mn(2)	16(1)	987(1)	2312(1)	
C(1)	3482(9)	3483(8)	1890(11)	76(3)
O(1)	4185(7)	3713(6)	1560(9)	103(3)
C(2)	1702(11)	3963(10)	1725(14)	102(5)
O(2)	1217(9)	4530(8)	1330(11)	138(4)
C(3)	2120(8)	2565(8)	866(11)	65(3)
O(3)	1976(7)	2177(6)	−55(9)	99(3)
C(4)	2745(8)	2176(7)	3137(11)	65(3)
O(4)	2992(6)	1561(6)	3662(8)	92(3)
C(5)	2423(9)	3623(9)	3892(12)	82(4)
O(5)	2475(7)	3903(6)	4932(9)	101(3)
C(6)	−518(9)	−3(9)	1895(12)	83(4)
O(6)	−883(7)	−647(7)	1659(9)	107(3)
C(7)	−979(10)	1419(9)	2996(12)	83(4)
O(7)	−1652(8)	1686(7)	3400(10)	120(3)
C(8)	−274(9)	1586(8)	882(11)	76(3)
O(8)	−432(6)	1978(6)	−78(9)	94(3)
C(9)	1104(8)	685(7)	1760(11)	67(3)
O(9)	1836(7)	515(6)	1415(8)	92(3)
C(10)	543(8)	771(7)	3915(11)	66(3)
O(10)	908(6)	626(5)	4902(8)	85(2)
N(1)	−441(6)	3542(6)	2784(8)	64(2)
C(11)	−880(9)	3789(8)	1681(12)	78(3)
C(12)	−1619(9)	4365(9)	1607(13)	87(4)
C(13)	−1881(12)	4643(10)	2688(15)	112(5)
C(14)	−1498(10)	4382(9)	3857(14)	97(4)
C(15)	−733(8)	3837(7)	3884(10)	63(3)
N(2)	414(6)	2959(6)	4980(8)	61(2)
C(16)	−242(8)	3540(7)	5079(10)	64(3)
C(17)	−425(10)	3862(9)	6311(13)	95(4)
C(18)	91(12)	3566(11)	7342(16)	120(5)
C(19)	708(10)	2991(10)	7298(14)	95(4)
C(20)	899(9)	2667(8)	6044(12)	83(4)

(*b*) Anisotropic vibrational amplitudes * (Å$^2 \times 10^4$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cd	503(4)	519(5)	522(4)	26(4)	91(3)	41(4)
Mn(1)	482(10)	416(10)	560(10)	37(8)	123(7)	−27(8)
Mn(2)	424(9)	488(11)	495(9)	−14(8)	91(7)	6(8)

* In the form: $\exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12} + \cdots)]$.

(*c*) Calculated fractional co-ordinates ($\times 10^4$) for the hydrogen atoms

Atom	x/a	y/b	z/c
H(11)	−664	3559	863
H(12)	−1926	4559	763
H(13)	−2418	5044	2673
H(14)	−1737	4588	4671
H(17)	−920	4295	6405
H(18)	−15	3814	8201
H(19)	1054	2764	8094
H(20)	1391	2229	5961

$U = 0{\cdot}119(21)$ Å^2.

Comparison of the Cd–N and Cd–Mn bond lengths in (I), (III), and (IV) suggests that the effective increase in the covalent radius of cadmium in changing from four- to five-fold co-ordination is *ca.* 0·1 Å. This seems to be in keeping with the general observation that the covalent radius of an atom increases with co-ordination number,[10] but the situation is complicated by the possibility of multiple bonding between the metal atoms, the degree of which may be different with different co-ordinations

TABLE 2

(III): Bond lengths (Å)

Cd–Mn(1)	2·686(3)	Cd–N(1)	2·358(10)
Cd–Mn(2)	2·680(3)	Cd–N(2)	2·349(9)
Mn(1)–C(1)	1·767(15)	Mn(2)–C(6)	1·782(15)
Mn(1)–C(2)	1·740(17)	Mn(2)–C(7)	1·789(16)
Mn(1)–C(3)	1·788(13)	Mn(2)–C(8)	1·787(13)
Mn(1)–C(4)	1·778(13)	Mn(2)–C(9)	1·780(14)
Mn(1)–C(5)	1·798(15)	Mn(2)–C(10)	1·812(12)
C(1)–O(1)	1·157(15)	C(6)–O(6)	1·163(15)
C(2)–O(2)	1·190(17)	C(7)–O(7)	1·168(16)
C(3)–O(3)	1·143(13)	C(8)–O(8)	1·183(13)
C(4)–O(4)	1·158(13)	C(9)–O(9)	1·175(14)
C(5)–O(5)	1·168(14)	C(10)–O(10)	1·141(12)
N(1)–C(11)	1·326(14)	N(2)–C(20)	1·344(15)
C(11)–C(12)	1·399(18)	C(20)–C(19)	1·450(20)
C(12)–C(13)	1·294(19)	C(19)–C(18)	1·276(21)
C(13)–C(14)	1·363(19)	C(18)–C(17)	1·341(19)
C(14)–C(15)	1·392(18)	C(17)–C(16)	1·425(17)
C(15)–N(1)	1·336(14)	C(16)–N(2)	1·330(14)
C(15)–C(16)	1·460(15)		

TABLE 3

(III): Bond angles (°)

Mn(1)–Cd–Mn(2)	127·7(2)	N(1)–Cd–N(2)	69·2(4)
Mn(1)–Cd–N(1)	112·7(3)	Mn(1)–Cd–N(2)	110·2(3)
Mn(2)–Cd–N(1)	109·8(3)	Mn(2)–Cd–N(2)	112·5(3)
Cd–Mn(1)–C(1)	176·5(5)	Cd–Mn(2)–C(6)	177·4(5)
Cd–Mn(1)–C(2)	82·4(6)	Cd–Mn(2)–C(7)	82·8(5)
Cd–Mn(1)–C(3)	82·8(5)	Cd–Mn(2)–C(8)	77·4(5)
Cd–Mn(1)–C(4)	79·1(5)	Cd–Mn(2)–C(9)	88·8(5)
Cd–Mn(1)–C(5)	85·0(5)	Cd–Mn(2)–C(10)	79·9(5)
C(1)–Mn(1)–C(2)	99·2(8)	C(6)–Mn(2)–C(7)	95·0(7)
C(1)–Mn(1)–C(3)	94·1(6)	C(6)–Mn(2)–C(8)	101·2(6)
C(1)–Mn(1)–C(4)	99·4(7)	C(6)–Mn(2)–C(9)	93·5(7)
C(1)–Mn(1)–C(5)	98·1(7)	C(6)–Mn(2)–C(10)	101·6(6)
C(2)–Mn(1)–C(3)	89·2(7)	C(7)–Mn(2)–C(8)	89·4(7)
C(3)–Mn(1)–C(4)	90·8(6)	C(8)–Mn(2)–C(9)	91·5(6)
C(4)–Mn(1)–C(5)	87·6(7)	C(9)–Mn(2)–C(10)	86·1(6)
C(5)–Mn(1)–C(2)	88·5(7)	C(10)–Mn(2)–C(7)	89·7(6)
C(2)–Mn(1)–C(4)	161·3(8)	C(7)–Mn(2)–C(9)	171·1(7)
C(3)–Mn(1)–C(5)	167·8(7)	C(8)–Mn(2)–C(10)	157·2(6)
Mn(1)–C(1)–O(1)	177·9(11)	Mn(2)–C(6)–O(6)	177·7(14)
Mn(1)–C(2)–O(2)	178·5(16)	Mn(2)–C(7)–O(7)	177·1(13)
Mn(1)–C(3)–O(3)	176·9(12)	Mn(2)–C(8)–O(8)	177·5(13)
Mn(1)–C(4)–O(4)	178·7(12)	Mn(2)–C(9)–O(9)	177·4(12)
Mn(1)–C(5)–O(5)	176·0(12)	Mn(2)–C(10)–O(10)	177·2(11)
N(1)–C(11)–C(12)	123·3(13)	N(2)–C(20)–C(19)	119·9(13)
C(11)–C(12)–C(13)	116·6(14)	C(20)–C(19)–C(18)	117·8(15)
C(12)–C(13)–C(14)	123·2(17)	C(19)–C(18)–C(17)	124·4(18)
C(13)–C(14)–C(15)	118·2(15)	C(18)–C(17)–C(16)	117·8(15)
C(14)–C(15)–N(1)	120·0(11)	C(17)–C(16)–N(2)	120·1(11)
C(15)–N(1)–C(11)	119·9(11)	C(16)–N(2)–C(20)	118·6(11)
Cd–N(1)–C(11)	123·2(9)	Cd–N(2)–C(20)	121·5(9)
Cd–N(1)–C(15)	117·9(8)	Cd–N(2)–C(16)	118·6(7)
N(1)–C(15)–C(16)	117·1(11)	N(2)–C(16)–C(15)	117·0(11)
C(14)–C(15)–C(16)	122·9(12)	C(17)–C(16)–C(15)	122·8(12)

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[10] L. Pauling, 'Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 3rd edn., 1960, pp. 221—264.

TABLE 4

(III): Shortest non-bonded distances (Å) of various types

(a) Intramolecular

Type	Atoms	Distance
H ··· H	H(14) ··· H(17)	2·128
O ··· H	O(8) ··· H(11)	2·715
O ··· O	O(3) ··· O(9)	3·057
	O(4) ··· O(9)	3·220
	O(3) ··· O(8)	3·486
C(CO) ··· C(CO)	C(9) ··· C(10)	2·451
	C(2) ··· C(5)	2·469
O ··· C(bipy)	O(5) ··· C(20)	3·280
	O(2) ··· C(11)	3·293
O ··· N	O(2) ··· N(1)	3·324
	O(5) ··· N(2)	3·331
C(CO) ··· N	C(5) ··· N(2)	3·365
Cd ··· C(CO)	Cd ··· C(8)	2·878
Cd ··· O	Cd ··· O(8)	3·532
(b) Intermolecular		
O ··· H	O(3) ··· $H(19^{\mathrm{I}})$	2·436
	O(5) ··· $H(14^{\mathrm{II}})$	2·657
C(CO) ··· H	C(6) ··· $H(13^{\mathrm{III}})$	3·049
O ··· O	O(5) ··· $O(9^{\mathrm{IV}})$	3·110
	O(1) ··· $O(6^{\mathrm{IV}})$	3·121
O ··· C(bipy)	O(1) ··· $C(20^{\mathrm{V}})$	3·372
O ··· C(CO)	O(1) ··· $C(6^{\mathrm{VI}})$	3·148

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

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

TABLE 5

(III): Least-squares planes

(a) Deviations (Å × 10^3) from planes

Plane (1): Cd Mn(1) Mn(2)

Plane (2): N(1), C(11)—(15)

Cd −159, N(1) 7, C(11) −17, C(12) 4, C(13) 17, C(14) −26, C(15) 14, C(16) 20

Plane (3): N(2), C(16)—(20)

Cd 138, C(15) 23, N(2) 7, C(16) −4, C(17) −8, C(18) 17, C(19) −12, C(20) 0

Plane (4): N(1), C(11)—(20)

Cd −30, N(1) 56, C(11) 49, C(12) 22, (C13) −29, C(14) −93, C(15) −4, N(2) −55, C(16) −16, C(17) 44, C(18) −29, C(19) 1, C(20) −53

Root-mean-square deviations: (1) 0, (2) 16, (3) 10, (4) 49

(b) Equations of the planes

(1): $0{\cdot}4310X - 0{\cdot}3738Y + 0{\cdot}8213Z = 1{\cdot}4042$
(2): $0{\cdot}6374X + 0{\cdot}7672Y - 0{\cdot}0712Z = 3{\cdot}6727$
(3): $0{\cdot}6823X + 0{\cdot}7167Y - 0{\cdot}1445Z = 3{\cdot}0074$
(4): $0{\cdot}6608X + 0{\cdot}7425Y - 0{\cdot}1095Z = 3{\cdot}3582$

(c) Dihedral angles (°)

(1)–(2)	94·02	(1)–(3)	95·31
(1)–(4)	94·74	(2)–(3)	5·72
(2)–(4)	2·93	(3)–(4)	2·78

of cadmium. In order to assess the degree of multiple bonding, it is necessary to compare the metal–metal bond lengths with the sums of the covalent radii for the metals. The radius for tetrahedral cadmium is 1·48 Å.[10] There is considerable difficulty in estimating a covalent radius for octahedrally co-ordinated manganese. Estimates vary from 1·15—1·46 Å;[11,12] a value of *ca.* 1·38 Å seems to be favoured. If this is correct, the metal–metal bond in $Mn_2(CO)_{10}$ [13] is longer than twice the radius: this has been explained variously in terms of electrostatic repulsion[13] or rehybridisation to give greater *p* and

TABLE 6

(IV): (a) Fractional atomic co-ordinates (×10^4) and isotropic vibrational amplitudes (Å^2 × 10^3) for the non-hydrogen atoms

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*
Cd	961(1)	2358(1)	3013(1)	
Mn(1)	2589(2)	2930(2)	2426(2)	
Mn(2)	61(2)	953(2)	2391(2)	
C(1)	3650(13)	3305(11)	2033(17)	69(5)
O(1)	4340(9)	3562(9)	1700(12)	96(4)
C(2)	1872(14)	3700(13)	1658(19)	88(6)
O(2)	1382(10)	4222(10)	1126(14)	108(5)
C(3)	2352(11)	2284(10)	1003(16)	65(5)
O(3)	2215(8)	1888(8)	130(12)	84(4)
C(4)	2946(11)	2037(11)	3314(16)	60(5)
O(4)	3188(9)	1470(8)	3965(12)	84(4)
C(5)	2616(11)	3468(11)	3926(17)	65(5)
O(5)	2653(8)	3769(8)	4932(13)	84(4)
C(6)	−607(13)	83(13)	1969(18)	82(6)
O(6)	−1061(10)	−515(10)	1671(14)	111(5)
C(7)	−880(15)	1444(13)	3067(20)	91(6)
O(7)	−1480(12)	1757(11)	3485(16)	128(5)
C(8)	−134(12)	1546(11)	987(18)	72(5)
O(8)	−237(9)	1957(9)	53(14)	96(4)
C(9)	1084(13)	555(12)	1884(18)	76(6)
O(9)	1773(11)	293(9)	1599(13)	107(5)
C(10)	588(12)	711(11)	3981(18)	73(5)
O(10)	946(9)	534(8)	4984(14)	95(4)
N(1)	−171(8)	3415(8)	3024(12)	55(4)
C(11)	−670(12)	3713(11)	2003(17)	71(5)
C(12)	−1362(14)	4326(12)	2051(20)	85(6)
C(13)	−1504(13)	4575(12)	3219(19)	81(6)
C(14)	−1018(12)	4304(11)	4334(17)	68(5)
C(15)	−335(11)	3685(10)	4196(15)	55(4)
N(2)	784(8)	2739(7)	5131(12)	59(4)
C(16)	180(11)	3347(10)	5288(15)	57(5)
C(17)	66(12)	3629(12)	6553(18)	75(5)
C(18)	597(14)	3283(13)	7537(21)	97(7)
C(19)	1227(14)	2688(13)	7425(20)	92(6)
C(20)	1296(12)	2421(14)	6175(17)	81(5)
C(21)	−1108(15)	4546(13)	5634(21)	93(6)
C(22)	−643(12)	4260(12)	6588(19)	79(6)

(b) Anisotropic vibrational amplitudes * (Å^2 ×10^4)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cd	474(7)	464(10)	539(8)	1(7)	89(5)	42(6)
Mn(1)	396(15)	396(15)	500(17)	−27(12)	60(12)	−4(11)
Mn(2)	401(16)	442(17)	555(18)	−2(13)	105(12)	−27(12)

* In the form: $\exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12} + \cdots)]$.

(c) Calculated fractional co-ordinates (× 10^4) for the hydrogen atoms

Atom	*x*/*a*	*y*/*b*	*z*/*c*
H(11)	−559	3490	1143
H(12)	−1722	4551	1254
H(13)	−1998	4993	3295
H(18)	512	3467	8428
H(19)	1622	2455	8187
H(20)	1751	1979	6035
H(21)	−1573	4979	5774
H(22)	−746	4476	7456

$U = 0{\cdot}093(25)$ Å^2.

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TABLE 7

(IV): Bond lengths (Å)

Cd–Mn(1)	2·687(4)	Cd–N(1)	2·382(14)
Cd–Mn(2)	2·675(4)	Cd–N(2)	2·342(14)
Mn(1)–C(1)	1·757(20)	Mn(2)–C(6)	1·744(22)
Mn(1)–C(2)	1·761(23)	Mn(2)–C(7)	1·802(25)
Mn(1)–C(3)	1·821(18)	Mn(2)–C(8)	1·750(20)
Mn(1)–C(4)	1·768(19)	Mn(2)–C(9)	1·764(21)
Mn(1)–C(5)	1·791(20)	Mn(2)–C(10)	1·789(20)
C(1)–O(1)	1·179(20)	C(6)–O(6)	1·196(22)
C(2)–O(2)	1·201(22)	C(7)–O(7)	1·142(23)
C(3)–O(3)	1·116(17)	C(8)–O(8)	1·178(19)
C(4)–O(4)	1·173(19)	C(9)–O(9)	1·162(21)
C(5)–O(5)	1·155(18)	C(10)–O(10)	1·150(19)
N(1)–C(11)	1·310(19)	N(2)–C(20)	1·350(20)
C(11)–C(12)	1·423(25)	C(20)–C(19)	1·393(24)
C(12)–C(13)	1·326(25)	C(19)–C(18)	1·348(27)
C(13)–C(14)	1·362(23)	C(18)–C(17)	1·335(25)
C(14)–C(15)	1·435(22)	C(17)–C(16)	1·428(22)
C(15)–N(1)	1·350(18)	C(16)–N(2)	1·346(19)
C(14)–C(21)	1·436(24)	C(17)–C(22)	1·459(25)
C(15)–C(16)	1·401(21)	C(21)–C(22)	1·229(24)

TABLE 8

(IV): Bond angles (°)

Mn(1)–Cd–Mn(2)	131·4(2)	N(1)–Cd–N(2)	69·5(5)
Mn(1)–Cd–N(1)	112·4(4)	Mn(1)–Cd–N(2)	108·9(4)
Mn(2)–Cd–N(1)	107·3(4)	Mn(2)–Cd–N(2)	110·5(4)
Cd–Mn(1)–C(1)	179·6(6)	Cd–Mn(2)–C(6)	175·4(7)
Cd–Mn(1)–C(2)	81·8(8)	Cd–Mn(2)–C(7)	84·3(8)
Cd–Mn(1)–C(3)	84·3(6)	Cd–Mn(2)–C(8)	76·1(7)
Cd–Mn(1)–C(4)	78·9(6)	Cd–Mn(2)–C(9)	88·8(7)
Cd–Mn(1)–C(5)	84·1(6)	Cd–Mn(2)–C(10)	79·5(7)
C(1)–Mn(1)–C(2)	97·9(10)	C(6)–Mn(2)–C(7)	91·8(10)
C(1)–Mn(1)–C(3)	95·5(9)	C(6)–Mn(2)–C(8)	101·9(10)
C(1)–Mn(1)–C(4)	101·3(9)	C(6)–Mn(2)–C(9)	95·3(10)
C(1)–Mn(1)–C(5)	96·2(9)	C(6)–Mn(2)–C(10)	102·8(9)
C(2)–Mn(1)–C(3)	89·6(9)	C(7)–Mn(2)–C(8)	91·7(10)
C(3)–Mn(1)–C(4)	88·3(8)	C(8)–Mn(2)–C(9)	90·5(9)
C(4)–Mn(1)–C(5)	88·1(9)	C(9)–Mn(2)–C(10)	85·1(9)
C(5)–Mn(1)–C(2)	90·1(10)	C(10)–Mn(2)–C(7)	89·7(10)
C(2)–Mn(1)–C(4)	160·8(10)	C(7)–Mn(2)–C(9)	172·0(10)
C(3)–Mn(1)–C(5)	168·3(9)	C(8)–Mn(2)–C(10)	155·3(9)
Mn(1)–C(1)–O(1)	176·3(17)	Mn(2)–C(6)–O(6)	179·5(19)
Mn(1)–C(2)–O(2)	179·5(19)	Mn(2)–C(7)–O(7)	179·4(21)
Mn(1)–C(3)–O(3)	179·3(16)	Mn(2)–C(8)–O(8)	177·8(17)
Mn(1)–C(4)–O(4)	176·2(16)	Mn(2)–C(9)–O(9)	177·4(18)
Mn(1)–C(5)–O(5)	175·6(16)	Mn(2)–C(10)–O(10)	177·5(18)
N(1)–C(11)–C(12)	123·8(19)	N(2)–C(20)–C(19)	122·9(20)
C(11)–C(12)–C(13)	115·9(20)	C(20)–C(19)–C(18)	115·6(20)
C(12)–C(13)–C(14)	124·5(21)	C(19)–C(18)–C(17)	125·0(23)
C(13)–C(14)–C(15)	115·9(18)	C(18)–C(17)–C(16)	117·2(20)
C(14)–C(15)–N(1)	121·4(15)	C(17)–C(16)–N(2)	119·9(15)
C(15)–N(1)–C(11)	118·5(15)	C(16)–N(2)–C(20)	119·3(16)
C(14)–C(15)–C(16)	120·3(16)	C(17)–C(16)–C(15)	121·2(17)
C(15)–C(14)–C(21)	115·5(17)	C(16)–C(17)–C(22)	114·3(17)
C(14)–C(21)–C(22)	124·1(23)	C(17)–C(22)–C(21)	124·7(22)
Cd–N(1)–C(11)	125·4(12)	Cd–N(2)–C(20)	123·3(13)
Cd–N(1)–C(15)	115·9(11)	Cd–N(2)–C(16)	117·2(11)
N(1)–C(15)–C(16)	118·4(15)	N(2)–C(16)–C(15)	118·9(16)
C(13)–C(14)–C(21)	128·6(19)	C(18)–C(17)–C(22)	128·6(20)

d character to the orbitals forming the metal–metal bond.[12]

If the values 1·38 Å for octahedral manganese and 1·48 Å for tetrahedral cadmium are used, a single Cd–Mn bond in (III) or (IV) would be 2·86 Å; for (I) and (II) the single bond would probably be somewhat longer because of the higher co-ordination number of cadmium.

TABLE 9

(IV): Shortest non-bonded distances (Å) of various types

Type	Atoms	Distance
(*a*) Intramolecular		
H ··· H	H(12) ··· H(13)	2·331
O ··· H	O(10) ··· H(20)	2·792
O ··· O	O(3) ··· O(9)	3·120
C(CO) ··· C(CO)	C(9) ··· C(10)	2·402
	C(4) ··· C(5)	2·476
O ··· C(phen)	O(5) ··· C(20)	3·319
	O(2) ··· C(11)	3·335
O ··· N	O(5) ··· N(2)	3·225
C(CO) ··· N	C(5) ··· N(2)	3·306
Cd ··· C(CO)	Cd ··· C(8)	2·822
Cd ··· O	Cd ··· O(8)	3·429
(*b*) Intermolecular		
O ··· H	O(3) ··· H(19^{I})	2·303
	O(5) ··· H(21^{II})	2·625
C(CO) ··· H	C(3) ··· H(19^{I})	3·021
	C(5) ··· H(21^{II})	2·982
O ··· O	O(5) ··· O(9^{III})	3·119
O ··· C(phen)	O(3) ··· C(19^{I})	3·284
O ··· C(CO)	O(9) ··· C(5^{IV})	3·164

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

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

TABLE 10

(IV): Least-squares planes

(*a*) Deviations (Å $\times 10^3$) from planes

Plane (1): Cd, Mn(1), Mn(2)

Plane (2): N(1), C(11)—(15)

Cd −88, N(1) 6, C(11) −6, C(12) 7, C(13) −9, C(14) 9, C(15) −7, C(16) 32, C(21) −12

Plane (3): N(2), C(16)—(20)

Cd 113, C(15) 37, N(2) −7, C(16) 13, C(17) −7, C(18) −4, C(19) 10, C(20) −5, C(22) −51

Plane (4): C(14), C(15), C(16), C(17), C(21), C(22)

Cd −15, N(1) 39, C(13) −23, C(14) 0, C(15) 9, N(2) −70, C(16) −13, C(17) 8, C(18) 10, C(21) −6, C(22) 2

Plane (5): N(1), N(2), C(11)—(22)

Cd 9, N(1) 46, C(11) 19, C(12) −2, C(13) −36, C(14) −6, C(15) 13, N(2) −48, C(16) −1, C(17) 18, C(18) 29, C(19) 16, C(20) −36, C(21) −13, C(22) 1

Root-mean-square deviations: (1) 0, (2) 7, (3) 8, (4) 8, (5) 26

(*b*) Equations of the planes

$$\begin{aligned}
(1)&:\ 0{\cdot}4652X - 0{\cdot}4324Y + 0{\cdot}7724Z = 1{\cdot}2929\\
(2)&:\ 0{\cdot}6810X + 0{\cdot}7199Y - 0{\cdot}1342Z = 3{\cdot}3943\\
(3)&:\ 0{\cdot}7062X + 0{\cdot}6890Y - 0{\cdot}1632Z = 3{\cdot}0234\\
(4)&:\ 0{\cdot}6920X + 0{\cdot}7080Y - 0{\cdot}1411Z = 3{\cdot}2703\\
(5)&:\ 0{\cdot}6974X + 0{\cdot}7028Y - 0{\cdot}1401Z = 3{\cdot}2372
\end{aligned}$$

(*c*) Dihedral angles (°)

(1)–(2)	95·63	(1)–(3)	95·48
(1)–(4)	95·35	(1)–(5)	95·03
(2)–(3)	2·83	(2)–(4)	1·01
(2)–(5)	1·40	(3)–(4)	1·86
(3)–(5)	1·62	(4)–(5)	0·43

The Cd–Mn bonds in all four complexes are, in fact, substantially shorter than this [means: (I) 2·780, (II) 2·711, (III) 2·683, and (IV) 2·681 Å], so it seems clear that multiple bonding is significant.

In none of the four complexes is there a significant difference between axial and equatorial Mn–C bond lengths, though for each compound the Mn–C(ax) distances are less than the mean Mn–C(eq) without exception. A significant difference has been claimed in some XMn(CO)$_5$ compounds,[13,14] and in many others a difference has been noted but is not significant in itself.[15] It seems that, although for most such compounds these differences are not individually significant, the general trend is a shortening of the axial relative to the equatorial bonds. This indicates a somewhat stronger bond for the axial position, with greater back-donation from metal to carbonyl, the X group being generally a weaker π-acceptor than CO. These conclusions are supported by molecular orbital calculations on manganese carbonyl hydrides.[16] This *trans*-influence[17] is commonly observed in transition-metal co-ordination complexes,[18] and is the result of competition by the ligands for the metal orbitals.

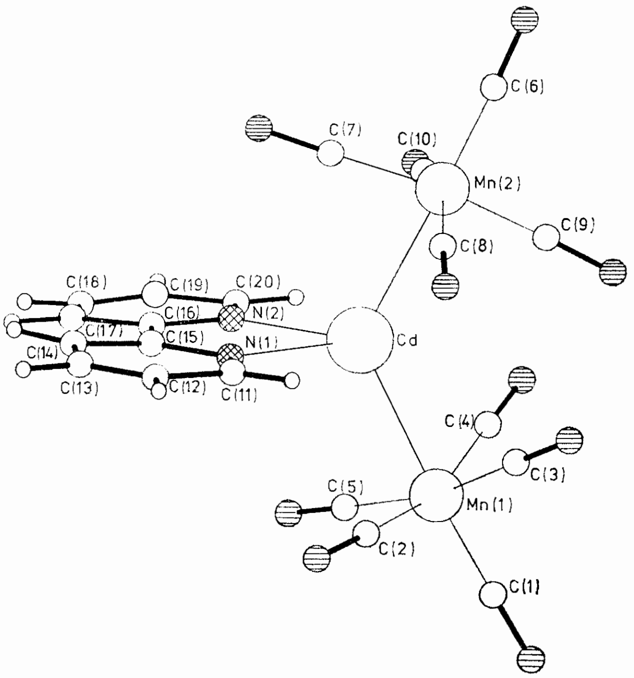

FIGURE 1 View of one molecule of (III) showing the labelling of the atoms

The severe angular distortion of the manganese co-ordination has already been noted in the structures of (I) and (II), and discussed.[3]

In the crystal structure of bipyridyl[19] the molecule is planar. In (III), each of the two pyridyl rings is planar (see Table 5), but they are not coplanar, being twisted relative to one another by several degrees about the C(15)–C(16) bond. As a result, the Cd–N(1) and Cd–N(2) bonds lie significantly out of the planes of the two rings, the angles of inclination being 3·9 and 3·4° respectively, while the displacement of the cadmium atom from the mean plane of the whole ligand is insignificant. These twisting distortions of the ligand are similar to, but smaller than, those observed in (I),[2] and can be ascribed to the same factors, *viz*. (i) the attempt to approach tetrahedral co-ordination, thus maximising overlap between cadmium and nitrogen orbitals; (ii) the need to maintain reasonable covalent distances within the ligand; (iii) packing forces in the crystal, particularly the short intramolecular H(14) · · · H(17) distance of 2·128 Å. In-plane distortions at C(15) and C(16) are observed, as in (I), the internal angles being 117·0 and 117·1°, and the external 122·8 and 122·9°.

The least-squares planes calculated for (IV) (Table 10) are similar to those for (III) (Table 5), but the root-mean-square deviations are rather lower, particularly for the plane of the whole ligand. Doubtless this is due to the greater rigidity of the fused ring system. The dihedral angles between pairs of planes are also smaller for the phenanthroline ligand, and, moreover, the displacement

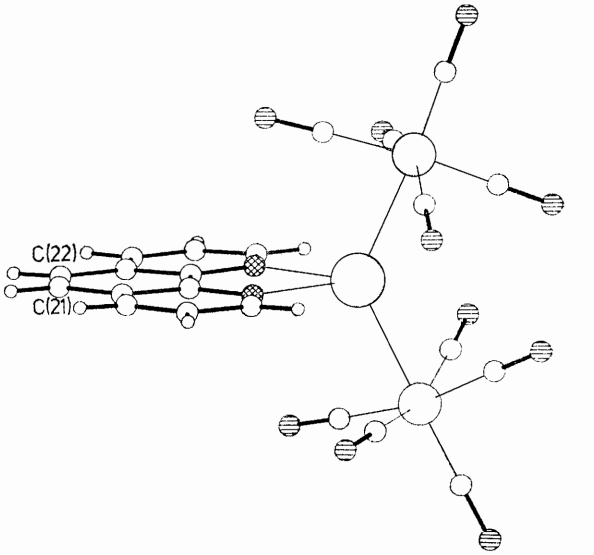

FIGURE 2 View of one molecule of (IV) showing the labelling of the two extra carbon atoms

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of the cadmium atom from the planes of the two outermost rings is smaller, the angles of inclination of the Cd–N bonds to these rings being 2·1 and 2·8°. One important difference between the two ligands is the absence of any particularly short intramolecular H ··· H distances in (IV): the H(13) ··· H(21) and H(18) ··· H(22) distances are greater than those between hydrogen atoms belonging to the same ring.

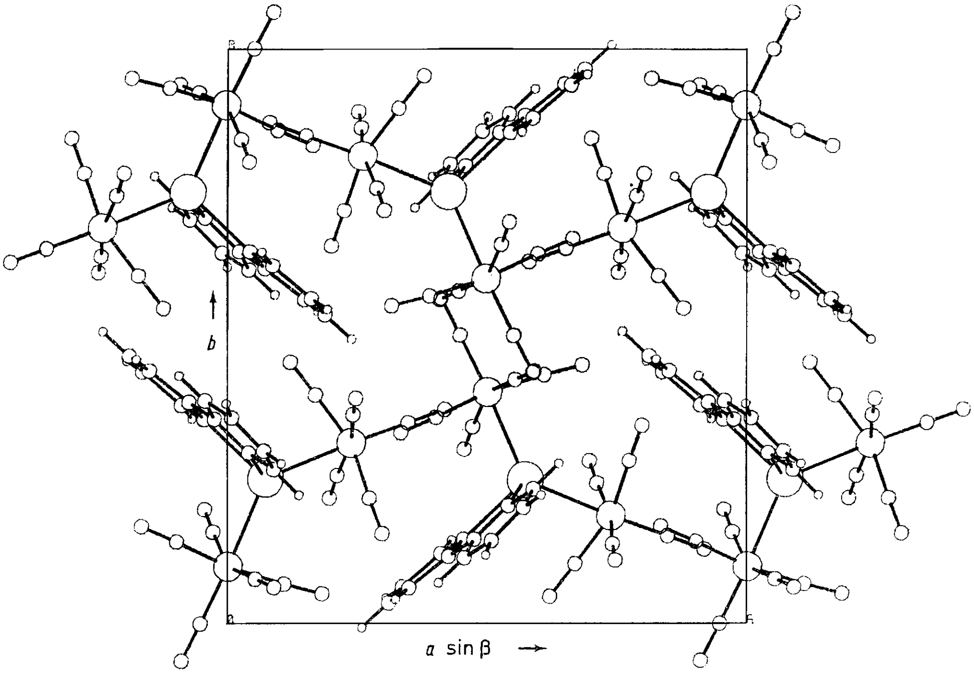

FIGURE 3 The packing, illustrated by a projection of (III) down the *c* axis

In both structures the ligand bonds furthest from the cadmium atom are rather shorter than expected [even allowing for the predicted greater double-bond character of the C(21) ··· C(22) bond in (IV)]. As for (II),[3] this is probably not real, but a result of thermal motion, for which no corrections have been made.[20]

The molecules (III) and (IV) have approximate C_2 symmetry, the ' axis ' bisecting the Mn–Cd–Mn angle. This is similar to the approximate symmetry of (I).[2]

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