Crystal Structure of μ-(2,2′:6′,2″-Terpyridylcadmium)-bis(pentacarbonylmanganese)(2*Cd–Mn*) †

By **W. Clegg** and **P. J. Wheatley,*** Department of Physical Chemistry, Lensfield Road, Cambridge CB2 1EP

Crystals of the title compound are monoclinic with a = 9·158, b = 18·895, c = 16·960 Å, β = 111·38°, Z = 4, space group $P2_1/c$. The structure was solved by Patterson and Fourier methods from 3502 visually estimated intensities and refined by least-squares techniques to R 9·11%. The co-ordination of cadmium is very distorted trigonal bipyramidal and there is considerable distortion of the octahedral manganese co-ordination. The molecule has approximate C_2 symmetry.

We have previously reported the crystal structure of mercuriobis(pentacarbonylmanganese), $Hg[Mn(CO)_5]_2$.[1] Spectroscopic evidence suggests that the corresponding cadmium and zinc compounds have a similar structure, with linear two-co-ordinate Group IIb metal atoms,[2,3] but their instability precludes a crystal-structure determination. The cadmium and zinc compounds form adducts with a variety of Lewis bases.[3] The potential terdentate nature of the terpyridyl molecule suggested a five-co-ordinate cadmium atom in the addition complex μ-(2,2′ : 6′,2″-terpyridylcadmium)-bis(pentacarbonylmanganese) (I). Previously reported five-co-ordinate cadmium complexes[4-6] involve one ' long bond ' in the co-ordination sphere, and, indeed, in one case the co-ordination has been described in

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† Reprints not available.

[1] W. Clegg and P. J. Wheatley, *J. Chem. Soc.* (*A*), 1971, 3572.

[2] A. T. T. Hsieh and M. J. Mays, ' International Review of Science,' vol. 6, Butterworth, London, 1972.

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

[4] A. Domenicano, L. Torelli, A. Vaciago, and L. Zambonelli, *J. Chem. Soc.* (*A*), 1968, 1351.

[5] E. Corao and S. Baggio, *Inorg. Chim. Acta*, 1969, **3**, 617.

[6] L. Cavalca, A. Chiesi Villa, A. Mangia, and C. Palmieri, *Inorg. Chim. Acta*, 1970, **4**, 463.

different ways.[5,6] Terpyridylcadmium chloride is likely to contain a five-co-ordinate cadmium atom, but the structure has not actually been solved.[7] We have determined the structure of (I) in order to confirm the suspected co-ordination. A preliminary report has already appeared.[8]

EXPERIMENTAL

Crystal Data.—$C_{25}H_{11}CdMn_2N_3O_{10}$, $M = 735{\cdot}7$, Monoclinic, $a = 9{\cdot}158(15)$, $b = 18{\cdot}895(26)$, $c = 16{\cdot}960(17)$ Å, $\beta = 111{\cdot}38(9)$, $U = 2732{\cdot}9$ Å^3, $D_c = 1{\cdot}787$, $Z = 4$, $D_m = 1{\cdot}82$ (by flotation), $F(000) = 1440$. Space group $P2_1/c$ (from absences). Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) $= 148{\cdot}2$ cm^{-1}.

A sample of crystals was provided by Dr. M. J. Mays and Dr. A. T. T. Hsieh; further material was prepared by their method.[3] The compound crystallizes as bright red needles elongated along *a*. The best crystals show faces of the forms {021}, {010}, and {100}. Crystals used for intensity measurements had dimensions 0·1—0·2 mm. Decomposition occurred in the *X*-ray beam, so that the intensities were visibly reduced after about 120 h exposure. For this reason five different crystals had to be used to collect intensities.

Cell dimensions were obtained by the α-doublet splitting method ($\lambda = 1{\cdot}54051$ and $1{\cdot}54433$ Å for Cu-$K_{\alpha 1}$ and Cu-$K_{\alpha 2}$).[9a] Intensities were collected from equi-inclination Weissenberg photographs of the 0—8*kl* and *h*0—17*l* layers and estimated visually. Lorentz and polarization corrections were applied, and absorption corrections were made by a method which approximates the crystal shape to a pseudo-ellipsoid.[9b] 3506 independent reflexions were assigned non-zero intensity, and placed on the same scale through common reflexions.

A Patterson map was interpreted to give co-ordinates for the metal atoms. A high concentration of peaks close to the planes $u,v,0$ and $u,v,\frac{1}{2}$ was noted; this is not explained by the space-group symmetry, but indicates that several atoms have z/c close to $\pm 0{\cdot}25$. It was subsequently found that about 30% of the scattering power lies in these positions. A Fourier synthesis phased on the metal atoms revealed all but five of the non-hydrogen atom positions, and those remaining were located from a weighted difference Fourier synthesis.[10] At this stage, with an overall temperature factor U 0·07 Å^2, R was 33·3%.

Refinement began with six isotropic thermal factors: the three metal atoms individually, the ten oxygen atoms, the ten carbonyl carbon atoms, and the atoms of the terpyridyl ligand. Four cycles of full-matrix least-squares refinement reduced R to 11·41%. With anisotropic temperature factors for the metal atoms, and individual isotropic otherwise, further refinement gave R 9·52%. A difference Fourier synthesis showed peaks at all the positions expected for the hydrogen atoms, with heights in the range 0·46—0·86 eÅ^{-3}, but there were many other peaks of comparable size especially in the neighbourhood of the metal atoms. Therefore the hydrogen atoms were placed in calculated positions, new positions being obtained before each subsequent cycle. One overall isotropic temperature factor was refined for the hydrogen atoms. At this stage four reflexions which appeared to be suffering from extinction were rejected. The final value of R was 9·11%, and the largest shift to σ ratio for the last cycle was 0·01. 181 parameters were refined in all.

The weighting scheme was $w = (a + |F_o| + b|F_o|^2)^{-1}$ with a and b set equal to $2F_{\text{min.}}$ and $2/F_{\text{max.}}$; an analysis of the variance showed this to be satisfactory. The final values were $a = 11{\cdot}8$, $b = 0{\cdot}0062$. Complex neutral scattering factors were used.[11]

RESULTS AND DISCUSSION

The results are summarized in Tables 1—5. The atomic co-ordinates and thermal parameters are given in Table 1 and the bond lengths and angles in Tables 2 and 3. Table 4 gives the shortest non-bonded contacts. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20559 (21 pp., 1 microfiche).* The labelling of the atoms is shown in Figure 1. Each oxygen or hydrogen atom has the same number as the carbon atom to which it is bonded.

The co-ordination of the cadmium atom is best described as very distorted trigonal bipyramidal and is similar to that of the zinc atom in terpyridylzinc chloride.[12] The equatorial positions are occupied by Mn(1), Mn(2), and N(2), the axial by N(1) and N(3). Two major distortions are evident: (i) deviations of the equatorial angles from 120°, due to the large size of the $Mn(CO)_5$ groups, and (ii) considerable displacement of the nitrogen atoms from the ideal axial positions, due to the restrictions imposed by the terpyridyl ligand geometry. The two Cd–Mn bond lengths are significantly different, and this is probably due to packing forces. The mean (2·780 Å) is considerably greater than the Hg–Mn length (2·806 Å), in $Hg[Mn(CO)_5]_2$.[1] Even allowing for the effect of the 'lanthanide contraction,' this supports the view[3] that the metal–metal bond is weakened on adduct formation. The shortest intermolecular distance involving cadmium is >4·5 Å.

Since the hydrogen atom positions were calculated (by projecting outwards through the carbon atoms from the centroids of the three rings of the terpyridyl ligand) and not located directly from the diffraction data, conclusions concerning possible hydrogen bonding, based on intermolecular contacts alone, could be false. However, there are three pieces of evidence for the presence of such hydrogen bonding in this structure: (i) three of the intermolecular O · · · H distances were observed to be short (<2·6 Å), (ii) the three hydrogen atoms involved, H(13), (18), and (23), are all positioned *para* to the three nitrogen atoms, so that the polarization of the C–H bonds is enhanced, and (iii) the three carbonyl groups involved, (2), (4), and (6), have the longest C–O distances of the ten, as would be expected if hydrogen bonding is present. The total evidence suggests weak O · · · H

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[7] D. E. C. Corbridge and E. G. Cox, *J. Chem. Soc.*, 1956, 594.

[8] W. Clegg and P. J. Wheatley, *J.C.S. Chem. Comm.*, 1972, 760.

[9] (*a*) N. W. Alcock and G. M. Sheldrick, *Acta Cryst.*, 1967, **23**, 35; (*b*) G. M. Sheldrick, unpublished work.

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

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

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

TABLE 1

(*a*) Fractional atomic co-ordinates (×10^4) and isotropic vibrational amplitudes (Å^2 × 10^3) for the non-hydrogen atoms (standard deviations are given in parentheses in this and subsequent Tables)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*
Cd	−733(1)	1353(1)	2498(1)	
Mn(1)	−1921(2)	939(1)	3707(1)	
Mn(2)	1371(3)	2419(1)	2474(1)	
C(1)	−2730(21)	648(9)	4460(11)	90(5)
O(1)	−3304(17)	439(8)	4910(9)	121(4)
C(2)	−3517(22)	784(10)	2753(12)	94(5)
O(2)	−4620(19)	651(8)	2143(10)	131(5)
C(3)	−2591(19)	1852(9)	3729(10)	84(4)
O(3)	−2965(17)	2419(8)	3766(9)	121(4)
C(4)	43(18)	1179(8)	4374(9)	73(4)
O(4)	1326(16)	1343(7)	4820(8)	104(4)
C(5)	−1239(22)	48(10)	3592(12)	96(5)
O(5)	−755(20)	−504(9)	3562(11)	141(5)
C(6)	2731(23)	3095(10)	2570(12)	99(5)
O(6)	3670(20)	3559(9)	2648(10)	133(5)
C(7)	1422(23)	1842(11)	1639(12)	101(5)
O(7)	1498(18)	1470(8)	1116(10)	123(5)
C(8)	−170(22)	2866(10)	1651(12)	95(5)
O(8)	−1162(19)	3166(8)	1119(10)	128(5)
C(9)	633(17)	2711(8)	3278(9)	71(4)
O(9)	206(14)	2905(6)	3785(8)	96(3)
C(10)	2855(20)	1900(9)	3231(11)	85(4)
O(10)	3869(18)	1601(8)	3761(9)	119(4)
N(1)	−3113(13)	1868(6)	1422(7)	70(3)
C(11)	−3822(19)	2446(8)	1607(10)	81(4)
C(12)	−5199(20)	2701(10)	1076(11)	90(5)
C(13)	−5935(23)	2368(10)	337(12)	99(5)
C(14)	−5252(19)	1766(9)	133(11)	86(4)
C(15)	−3803(16)	1532(7)	714(9)	65(3)
N(2)	−1684(12)	699(5)	1192(6)	57(2)
C(16)	−3018(16)	891(7)	551(8)	63(3)
C(17)	−3617(18)	514(8)	−189(10)	77(4)
C(18)	−2386(18)	−94(8)	−281(10)	78(4)
C(19)	−1518(17)	−304(8)	361(9)	77(4)
C(20)	−930(15)	107(7)	1100(8)	63(3)
N(3)	899(13)	297(6)	2498(7)	69(3)
C(21)	527(15)	−72(7)	1783(8)	59(3)
C(22)	1515(16)	−598(7)	1711(9)	68(3)
C(23)	2898(19)	−751(9)	2387(9)	79(4)
C(24)	3249(19)	−384(8)	3110(10)	80(4)
C(25)	2172(18)	141(8)	3158(11)	82(4)

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

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cd	499(5)	579(5)	495(4)	−27(4)	112(3)	−21(4)
Mn(1)	521(11)	781(14)	545(12)	8(10)	138(9)	−91(10)
Mn(2)	600(13)	638(13)	753(14)	−80(11)	256(11)	−87(10)

* The anisotropic temperature factor takes the form: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13})]$.

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

Atom	*x*/*a*	*y*/*b*	*z*/*c*
H(11)	−3279	2704	2171
H(12)	−5725	3156	1227
H(13)	−7032	2566	−86
H(14)	−5820	1496	−448
H(17)	−4664	679	−689
H(18)	−3278	−402	−853
H(19)	−936	−775	288
H(22)	1234	−885	1145
H(23)	3690	−1158	2346
H(24)	4314	−506	3629
H(25)	2401	427	3713

$U = 0{\cdot}44(12)$ Å^2

TABLE 2

Bond lengths (Å)

Cd–Mn(1)	2·760(4)	Cd–N(1)	2·475(14)
Cd–Mn(2)	2·799(5)	Cd–N(2)	2·405(12)
		Cd–N(3)	2·493(14)
Mn(1)–C(1)	1·781(21)	Mn(2)–C(6)	1·749(22)
Mn(1)–C(2)	1·765(21)	Mn(2)–C(7)	1·802(21)
Mn(1)–C(3)	1·836(20)	Mn(2)–C(8)	1·793(21)
Mn(1)–C(4)	1·799(19)	Mn(2)–C(9)	1·814(17)
Mn(1)–C(5)	1·829(22)	Mn(2)–C(10)	1·785(19)
C(1)–O(1)	1·144(21)	C(6)–O(6)	1·201(23)
C(2)–O(2)	1·180(23)	C(7)–O(7)	1·154(22)
C(3)–O(3)	1·134(20)	C(8)–O(8)	1·167(21)
C(4)–O(4)	1·183(20)	C(9)–O(9)	1·127(17)
C(5)–O(5)	1·143(22)	C(10)–O(10)	1·175(20)
N(1)–C(11)	1·364(19)	N(2)–C(16)	1·356(18)
C(11)–C(12)	1·344(23)	C(16)–C(17)	1·371(20)
C(12)–C(13)	1·343(23)	C(17)–C(18)	1·392(21)
C(13)–C(14)	1·401(24)	C(18)–C(19)	1·358(22)
C(14)–C(15)	1·405(22)	C(19)–C(20)	1·404(20)
C(15)–N(1)	1·301(17)	C(20)–N(2)	1·354(17)
N(3)–C(21)	1·331(16)	C(23)–C(24)	1·342(20)
C(21)–C(22)	1·379(19)	C(24)–C(25)	1·422(22)
C(22)–C(23)	1·394(21)	C(25)–N(3)	1·322(19)
C(15)–C(16)	1·485(20)	C(20)–C(21)	1·452(19)

TABLE 3

Bond angles (°)

Mn(1)–Cd–Mn(2)	132·4(2)	N(1)–Cd–Mn(1)	100·3(4)
N(2)–Cd–Mn(1)	115·5(3)	N(1)–Cd–Mn(2)	97·6(4)
N(2)–Cd–Mn(2)	112·1(3)	N(3)–Cd–Mn(1)	99·9(4)
N(1)–Cd–N(2)	66·2(5)	N(3)–Cd–Mn(2)	99·2(4)
N(2)–Cd–N(3)	66·7(4)	N(1)–Cd–N(3)	132·9(5)
Cd–Mn(1)–C(1)	177·9(7)	Cd–Mn(2)–C(6)	174·2(7)
Cd–Mn(1)–C(2)	77·6(7)	Cd–Mn(2)–C(7)	78·0(7)
Cd–Mn(1)–C(3)	88·5(6)	Cd–Mn(2)–C(8)	90·0(7)
Cd–Mn(1)–C(4)	79·7(6)	Cd–Mn(2)–C(9)	76·2(6)
Cd–Mn(1)–C(5)	86·5(7)	Cd–Mn(2)–C(10)	86·6(6)
C(2)–Mn(1)–C(3)	90·2(9)	C(7)–Mn(2)–C(8)	84·9(9)
C(3)–Mn(1)–C(4)	90·8(8)	C(8)–Mn(2)–C(9)	92·2(8)
C(4)–Mn(1)–C(5)	89·9(8)	C(9)–Mn(2)–C(10)	91·3(8)
C(5)–Mn(1)–C(2)	87·2(9)	C(10)–Mn(2)–C(7)	90·1(9)
Mn(1)–C(1)–O(1)	176·3(18)	Mn(2)–C(6)–O(6)	179·1(20)
Mn(1)–C(2)–O(2)	175·8(18)	Mn(2)–C(7)–O(7)	178·1(19)
Mn(1)–C(3)–O(3)	177·8(18)	Mn(2)–C(8)–O(8)	179·1(19)
Mn(1)–C(4)–O(4)	179·0(15)	Mn(2)–C(9)–O(9)	178·2(15)
Mn(1)–C(5)–O(5)	176·4(20)	Mn(2)–C(10)–O(10)	175·3(16)
N(1)–C(11)–C(12)	122·8(17)	N(3)–C(25)–C(24)	121·6(16)
C(11)–C(12)–C(13)	119·2(19)	C(25)–C(24)–C(23)	118·2(17)
C(12)–C(13)–C(14)	119·5(20)	C(24)–C(23)–C(22)	119·2(17)
C(13)–C(14)–C(15)	118·4(17)	C(23)–C(22)–C(21)	120·4(15)
C(14)–C(15)–N(1)	120·7(14)	C(22)–C(21)–N(3)	119·9(13)
C(15)–N(1)–C(11)	119·4(14)	C(21)–N(3)–C(25)	120·6(14)
Cd–N(1)–C(11)	120·7(11)	Cd–N(3)–C(25)	121·5(11)
Cd–N(1)–C(15)	119·3(10)	Cd–N(3)–C(21)	117·7(10)
C(14)–C(15)–C(16)	121·6(14)	C(22)–C(21)–C(20)	122·6(13)
N(1)–C(15)–C(16)	117·7(13)	N(3)–C(21)–C(20)	117·4(12)
N(2)–C(16)–C(17)	122·5(14)	C(15)–C(16)–C(17)	122·3(14)
C(16)–C(17)–C(18)	118·8(16)	C(15)–C(16)–N(2)	115·1(12)
C(17)–C(18)–C(19)	119·6(16)	Cd–N(2)–C(16)	121·3(9)
C(18)–C(19)–C(20)	119·6(16)	Cd–N(2)–C(20)	120·1(9)
C(19)–C(20)–N(2)	120·9(13)	C(21)–C(20)–N(2)	117·3(12)
C(20)–N(2)–C(16)	118·5(12)	C(21)–C(20)–C(19)	121·7(13)
C(1)–Mn(1)–C(2)	100·6(8)	C(6)–Mn(2)–C(7)	107·0(9)
C(1)–Mn(1)–C(3)	92·6(8)	C(6)–Mn(2)–C(8)	93·4(9)
C(1)–Mn(1)–C(4)	102·1(7)	C(6)–Mn(2)–C(9)	99·0(8)
C(1)–Mn(1)–C(5)	92·3(8)	C(6)–Mn(2)–C(10)	90·3(8)

interactions.[13] The three C–H···O angles are 136 [H(13)], 148 [H(18)], and 147° [H(23)].

The mean C–O bond length (excluding those groups

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[13] D. J. Sutor, *Nature*, 1962, **195**, 68.

involved in hydrogen bonding) is 1·148 Å, and the mean Mn–C bond length for the same seven carbon atoms is 1·807 Å. The idealized co-ordination about each manganese atom is octahedral. In general $Mn(CO)_5X$ compounds have X–Mn–C(eq) angles less than 90°,[1,8,14-16] and this effect seems to have been due to packing forces in the crystal. [In the vapour phase $Mn(CO)_5H$ also shows this distortion,[17] but here too the cause appears to be steric, H being considerably smaller than CO.] In the structure of (I), the distortions are the largest we have noted in such compounds. The Cd–Mn–C angle lies in the range 76·2—79·7° for C(2), (4), (7) and (9), and in the range 86·5—90·0° for C(3), (5), (8), and (10), so that the deviations from 90° are alternately small (<5°) and large (>10°). This pattern is consistent with the proposition that packing forces are responsible for the distortion, for, in this way, adjacent equatorial carbonyl groups are pushed apart. The result is a quite densely packed structure. This is demonstrated to some extent by the distances in Table 4. Figure 2 illustrates the packing as seen in projection down *a*. The large proportion of the scattering material close to $z/c = \pm 0{\cdot}25$ can also be seen.

TABLE 4

Shortest non-bonded distances (Å) of various types

Type	Atoms	Distance
Intramolecular		
H · · · H	H(14) · · · H(17)	1·998
	H(19) · · · H(22)	2·001
O · · · H	O(10) · · · H(25)	2·578
	O(3) · · · H(11)	2·670
O · · · O	O(3) · · · O(9)	3·035
	O(4) · · · O(9)	3·395
	O(4) · · · O(10)	3·455
C(CO) · · · C(CO)	C(7) · · · C(8)	2·428
	C(2) · · · C(5)	2·478
O · · · C(terpy)	O(10) · · · C(25)	3·148
O · · · N	O(5) · · · N(3)	3·136
N · · · C(CO)	N(1) · · · C(2)	3·168
C(CO) · · · C(terpy)	C(10) · · · C(25)	3·375
Cd · · · C(CO)	Cd · · · C(2)	2·940
Cd · · · O	Cd · · · O(9)	3·568
Intermolecular		
H · · · H	H(11) · · · H(23$^{\mathrm{I}}$)	2·380
O · · · H	O(2) · · · H(18$^{\mathrm{II}}$)	2·376
	O(6) · · · H(23$^{\mathrm{III}}$)	2·472
	O(4) · · · H(13$^{\mathrm{IV}}$)	2·522
	O(7) · · · H(19$^{\mathrm{V}}$)	2·601
	O(9) · · · H(22$^{\mathrm{I}}$)	2·663
C(CO) · · · H	C(9) · · · H(13$^{\mathrm{IV}}$)	2·867
O · · · O	O(5) · · · O(8$^{\mathrm{VI}}$)	2·999
	O(5) · · · O(6$^{\mathrm{VI}}$)	3·236
O · · · C(terpy)	O(9) · · · C(22$^{\mathrm{I}}$)	3·198
O · · · C(CO)	O(5) · · · C(8$^{\mathrm{VI}}$)	3·248

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

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

TABLE 5

Least-squares planes in terms of orthogonal axes *a*, *b*, and *c**, deviations from these planes (Å × 10³), and dihedral angles between the planes

Atom	Δ_1	Δ_2	Δ_3	Δ_4	Δ_5
Cd	−14 *	−52 *	−270 *	−99 *	370 *
Mn(1)	0				
Mn(2)	0				
N(1)		98	8		
C(11)		65	−8		
C(12)		7	3		
C(13)		−47	3		
C(14)		−38	−3		
C(15)		37	−2	−60 *	
N(2)	0	8		3	
C(16)		28	−32 *	−8	
C(17)		16		3	
C(18)		−36		7	
C(19)		−87		−11	
C(20)		−44		6	−25 *
N(3)		−131			20
C(21)		−13		70 *	−5
C(22)		138			−7
C(23)		158			5
C(24)		13			9
C(25)		−171			−22
Mean deviations	0	63	5	6	11

Equations of the planes

(1) $-0{\cdot}6687X + 0{\cdot}6440Y - 0{\cdot}3717Z = 1{\cdot}6752$
(2) $0{\cdot}7153X + 0{\cdot}5757Y - 0{\cdot}3961Z = -1{\cdot}6241$
(3) $0{\cdot}6842X + 0{\cdot}5815Y - 0{\cdot}4401Z = -1{\cdot}4963$
(4) $0{\cdot}7400X + 0{\cdot}5428Y - 0{\cdot}3972Z = -1{\cdot}7210$
(5) $0{\cdot}6622X + 0{\cdot}6716Y - 0{\cdot}3324Z = -1{\cdot}4323$

Dihedral angles (°)

(1)–(2)	87·73	(3)–(4)	4·60
(2)–(3)	3·11	(3)–(5)	8·15
(2)–(4)	2·36	(4)–(5)	9·40
(2)–(5)	7·27		

* These atoms were not used in the least-squares calculations, nor in the calculation of the mean deviations.

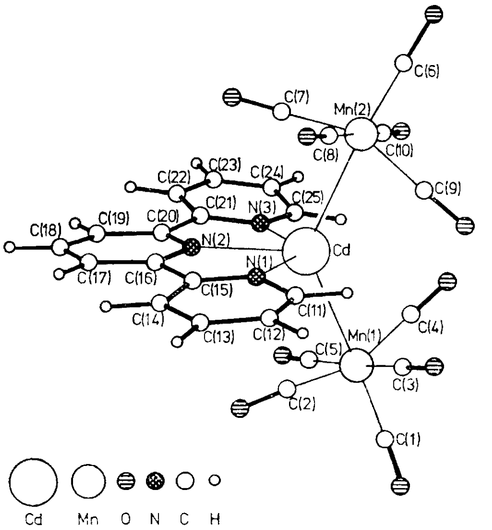

FIGURE 1 View of one molecule showing the labelling of the atoms. The direction of view is inclined at 15° to the normal to the Mn–Cd–Mn plane

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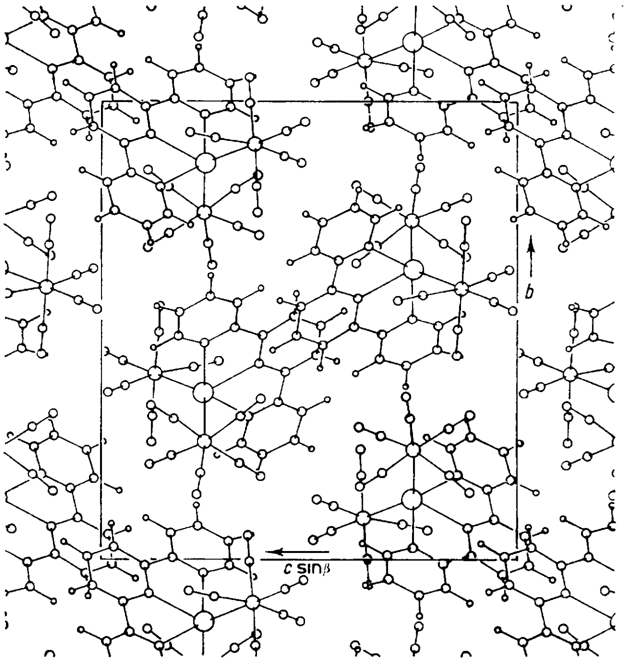

FIGURE 2 Projection of the structure down *a*. The unit cell is outlined

Several least-squares planes were calculated for the terpyridyl ligand, as well as the equatorial plane. The results are given in Table 5. The three rings, each in a well-defined plane, are not strictly coplanar. Moreover, the cadmium atom lies significantly out of planes (**3**) and (**5**) (the two outer rings). These ' twisting ' distortions of the ligand are probably the result of packing forces, including two short H · · · H contacts within the ligand (see Table 4), and the attempt of the nitrogen atoms to occupy one equatorial and two axial positions of the cadmium co-ordination, attaining good overlap between nitrogen and cadmium orbitals while maintaining reasonable covalent distances within the terpyridyl ligand. The mean C–C length within the three rings is 1·380 Å, and the mean N–C length is 1·338 Å, compared with the values 1·394 and 1·340 Å in pyridine.[18]

The molecule has approximate C_2 symmetry about the Cd–N(2) bond.

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