X-Ray Crystal Structure of Bis(pentacarbonylmanganese)-2,2′:6′,2″-terpyridylcadmium $C_{15}H_{11}N_3Cd[Mn(CO)_5]_2$

By W. CLEGG and P. J. WHEATLEY*

(*Department of Physical Chemistry, Lensfield Road, Cambridge* CB2 1EP)

Summary X-Ray diffraction analysis of bis(pentacarbonylmanganese)-2,2′:6′,2″-terpyridylcadmium reveals distorted trigonal bipyramidal co-ordination of cadmium and considerable distortion of the octahedral co-ordination around manganese.

ALTHOUGH many structures of complexes containing main-group-metal to transition-metal bonds have been reported, few have contained Group IIB metals and none, as far as we know, cadmium. We have determined the structure of the title compound† in order to elucidate the co-ordination of the metal atoms.

Crystal data: $C_{25}CdH_{11}Mn_2N_3O_{10}$, $M = 735{\cdot}7$, monoclinic, $a = 9{\cdot}158(15)$, $b = 18{\cdot}895(26)$, $c = 16{\cdot}960(17)$ Å, $\beta = 111{\cdot}38(9)°$, $Z = 4$. Space group $P2_1/c$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å, $\mu = 148{\cdot}2$ cm^{-1}, 3506 independent reflexions were recorded by Weissenberg photography, estimated visually, and corrected for absorption. The structure was solved by Patterson and Fourier techniques, and refined by full matrix least squares to $R = 9{\cdot}11\%$. The hydrogen

† Provided by Dr. M. J. Mays and Dr. A. T. T. Hsieh; further material was prepared by their method [*J. Chem. Soc.* (*A*), 1971,729].

atom positions were calculated and used in structure factor calculations, but not refined. Thermal parameters were anisotropic for the metal atoms and isotropic otherwise; one overall parameter was refined for the hydrogen atoms.

TABLE

Bond lengths (Å)		*Angles* (°)	
Cd–Mn	2·760, 2·799	Mn–Cd–Mn	132·4
Cd–N	2·475, 2·405, 2·493	Mn–Cd–N(2)	115·5, 112·1
Mn–C(mean)	1·796	N(1)–Cd–N(2)	66·2
C–O(mean)	1·161	N(2)–Cd–N(3)	66·7

Manganese co-ordination:

Cd–Mn(1)–C(eq.)	77·6, 88·5, 79·7, 86·5
Cd–Mn(2)–C(eq.)	78·0, 90·0, 76·2, 86·6

Some bond lengths and angles are given in the Table. The co-ordination around cadmium is very similar to that of the zinc atom in terpyridylzinc chloride,[1] described best as a distorted trigonal bipyramid. One of the nitrogen atoms and the two manganese atoms occupy the equatorial positions. Deviations of the equatorial angles from 120° are presumably due to the large size of the $Mn(CO)_5$ groups. Previously reported five-co-ordinate cadmium complexes[2] involve one "long bond" in the co-ordination sphere. It has been claimed that terpyridylcadmium chloride has a five-co-ordinate cadmium, but the structure has not actually been solved.[3]

In compounds of the type $Mn(CO)_5X$, it has been found that the X-Mn-C(equatorial) angles are generally less than 90°, usually in the range 82—88°.[4] In this compound the angles lie in two distinct ranges, 86·5—90·0°, and 76·2—79·7°. This is the largest distortion we have noted in such compounds. A preliminary survey of the inter- and intramolecular non-bonded distances indicates that these large distortions may be due to the efficient packing of the molecules.

Three of the intermolecular distances between oxygen and hydrogen atoms are quite short, 2·38, 2·47, and 2·52 Å. The three hydrogen atoms involved are those in the positions *para* to the nitrogen atoms. This may indicate weak C–H · · · O interactions.[5]

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