

Review

# Organometallic and carbonyl compounds of cadmium: analysis of crystallographic and structural data

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## Abstract

This review draws together the structural information presently available for almost 40 organocadmium and carbonyl derivatives. The cadmium oxidation state varies from 0 to +2. There is only one example of Cd(I), which is in a distorted tetrahedral environment. The oxidation state of +2 is most abundant, with Cd(II) found in digonal, trigonal planar, tetrahedral and five-coordinate (mostly trigonal-pyramidal) environments. The nuclearity ranges from one to seven, and one example each of nine and 13 metal atoms. Correlations are drawn between bond lengths and bond angles, and comparisons made with the corresponding zinc and mercury analogues.

**Keywords:** Cadmium; Carbonyl; Group 12; Crystal structure; Organometallic; Review

## 1. Introduction

The chemistry of cadmium compounds has been an active area of research for a considerable time. Crystallographic structural determinations have been carried out for over 600 coordination complexes of cadmium [1], and over 90 complexes of cadmium with one or more different metal atoms [2]. There has also been much interest in the organometallic derivatives of cadmium, and this review classifies and analyses the structural data for almost 40 such derivatives, published up to the end of July 1994. The data is presented in the order of increasing degree polymerisation, increasing coordination number around the cadmium atom, increasing complexity of the coordination sphere, and increasing atomic number of the principal coordinating ligand.

## 2. Monomeric cadmium derivatives

The crystallographic and structural data for monomeric organocadmium compounds are given in Table 1. They are mostly all either yellow or colourless.

There are four examples in which cadmium(II) is two coordinate, and both bonds are to a carbon atom from an organic ligand. The Cd–C bond distances range from 211.0(3) to 217.2(3) pm (mean value of 214.7 pm) for the first three compounds. These are linear (C–Cd–C = 180°) [3,4] or near linear (C–Cd–C = 173.9(1)°) [5]. The fourth derivative [6] has longer Cd–C distances at 231.0(21) and 237.3(13) pm, with a very unusual bent angle of 76.1(6)° for the digonal C–Cd–C arrangement. However, there are also another two carbon atoms of the respective ligands located at distances of 291.1 and 296.0 pm, which together with the 2,2,4,4-tetraphenyl-1H-2λ<sup>5</sup>-, 4λ<sup>5</sup>-benzodiphosphepinid (C<sub>33</sub>H<sub>27</sub>P<sub>2</sub>) ligands are responsible for this discrepancy.

In another eight derivatives [7–13] each cadmium(II) atom is in a tetrahedral arrangement with differing degrees of distortion. In the first, a pseudo-tetrahedral coordination about the Cd(II) atom is created by three nitrogen atoms of HB(3-<sup>i</sup>Bu-5-Mepz)<sub>3</sub> and by the carbon atom of a methyl (Me) group, giving a CdN<sub>3</sub>C chromophore. In the remaining seven derivatives, a CdN<sub>2</sub>C<sub>2</sub> chromophore is built up from two unidentate pyridine molecules and two unidentate cyclopentadienyl (cp) ligands [8], or by two chelating ligands which utilize both N and C donor sites [9,12], or by one N-chelating ligand plus two unidentate C donor ligands [10,11,13]. The mean Cd–L bond distance increases in

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the order: 216.4 pm (unidentate-C) < 231.1 pm (tridentate-N) < 233.5 pm (unidentate-N) < 256.4 pm (bidentate-N). For the hetero donor ligands (C plus N) the mean Cd–L distances are 221.2 pm (C) and 254.4 pm (N).

There are two different bidentate N-donor ligands, *N,N,N',N'*-tetramethylethylenediamine (Me<sub>4</sub>en) and 2,2'-bipyridyl (2,2'-bpy), which have different bite angle dimensions. The effect of both steric and electronic factors can be observed in the variation of the N–Cd–N bond angles. For the five-membered metallocycles, the mean N–Cd–N bond angle is 71.4° for Me<sub>4</sub>en and 64.5° for 2,2'-bpy. The former is a typical saturated

σ-donor, while the latter is unsaturated and also a π-donor. There is an interdependence between the N–Cd–N bond angles and the Cd–N bond distances. When the bond elongates the intrametallo-cyclic ring opens, and vice versa. The Cd–N and N–Cd–N values for the two ligands are: 260.6 pm and 71.4° (Me<sub>4</sub>en), vs. 252.2 pm and 64.5° (2,2'-bpy).

### 3. Bi- and oligomeric cadmium derivatives

The crystallographic and structural data for the oligomeric organocadmium derivatives are given in

Table 1  
Crystallographic and structural data for monomeric organocadmium compounds<sup>a</sup>

Compound <sup>b</sup> (colour)	Crystal class <sup>c</sup> Space group Z	a (pm) b (pm) c (pm)	β (deg)	Chromophore	Cd–L (pm)	L–Cd–L (deg)	Reference
Cd(vsi) <sub>2</sub> (colourless)	m P2 <sub>1</sub> /n 2	915.1(1) 1773.0(4) 1054.8(2)	103.57(1)	CdC <sub>2</sub>	C <sup>d</sup> 217.2(3,0)	C,C <sup>d</sup> 180	[3]
Cd(C(SiMe <sub>3</sub> ) <sub>2</sub> · (SiMe <sub>2</sub> OMe)) <sub>2</sub> (white)	m C2/c 4	1689.6(13) 935.2(5) 2387.9(8)	114.22(4)	CdC <sub>2</sub>	C 215.9(6,0)	C,C 180	[4]
Cd(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> (colourless)	m P2 <sub>1</sub> /n 4	1203.0(1) 779.2(1) 1371.1(1)	108.94(1)	CdC <sub>2</sub>	C 211.0(3,1)	C,C 173.9(1)	[5]
Cd(C <sub>11</sub> H <sub>17</sub> P <sub>3</sub> ) <sub>2</sub> (colourless)	m P <sub>2</sub> /c 4	1480.4(13) 1269.3(7) 2464(3)	140.12(4)	CdC <sub>2</sub>	C 231.0(21) 237.3(13)	C,C 76.1(6)	[6]
Cd(HB(3- <i>i</i> Bu-5-Mepz) <sub>3</sub> )Me (colourless)	c I $\bar{4}$ 3d 16	2274.7(2)		CdN <sub>3</sub> C C <sub>Me</sub>	N 231.1(7,0) C <sub>Me</sub> 207.4(19)	N,N 85.2(4,0) N,C 128.6(2,0)	[7]
Cd(bpy) <sub>2</sub> (η <sup>1</sup> -cp) <sub>2</sub> (yellow)	m P2 <sub>1</sub> /n 4	1279(1) 1009.3(4) 1478(1)	107.20(8)	CdN <sub>2</sub> C <sub>2</sub>	N <sub>py</sub> 233.5(3,26) C <sub>cp</sub> 233.0(5,23)	N,N 96.4(1) C,C 129.1(2) N,C 106.0(2,3.3)	[8]
Cd(2-(Me <sub>3</sub> Si) <sub>2</sub> CC <sub>3</sub> H <sub>4</sub> N) <sub>2</sub> (colourless)	m P2 <sub>1</sub> /c 8	2445(2) 1656(2) 1660(1)	107.82(6)	CdN <sub>2</sub> C <sub>2</sub>	N 249 C 227	N,N 124.4 C,C 174.3 N,C 105.6	[9]
Cd(Me <sub>4</sub> en)(Me) <sub>2</sub> (colourless)	or Cmca 8	1119.6(2) 1217.9(2) 1796.9(3)		CdN <sub>2</sub> C <sub>2</sub>	N 257.1(14,5) C <sub>Me</sub> 219.4(12,0)	N,N 71.5(5) <sup>e</sup> C,C 154.0(3) N,C 100.5(4,2)	[10]
Cd(Me <sub>4</sub> en)(Me <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> (colourless)	m C2/c 4	1760.4(5) 948.4(3) 1275.8(3)	106.07(2)	CdN <sub>2</sub> C <sub>2</sub>	N 264.2(5,0) C 216.0(4,0)	N,N 71.2(2) <sup>e</sup> C,C 157.0(6) N,C 102.0(2)	[10]
[Cd(bpy)(Me <sub>3</sub> SiCH <sub>2</sub> ) <sub>2</sub> · ½bpy] (yellow)	m P2 <sub>1</sub> /c 4	887.4(4) 947.0(5) 3245(1)	92.01(4)	CdN <sub>2</sub> C <sub>2</sub>	N 252.5(35,5) C 214(6,5)	N,N 65(1) <sup>e</sup> C,C 156(2) N,C 100(2,9)	[11]
Cd(dmab) <sub>2</sub> (yellow)	or P $\bar{4}$ n2 4	1248.0(5) 1248.0(5) 1300.3(5)		CdN <sub>2</sub> C <sub>2</sub>	N 259.8(9) C 215.4(8,0)	N,N 116.12(14) C,C 174.3(1) N,C 114.6(1,7,4)	[12]
Cd(bpy)(Me) <sub>2</sub> (yellow)	or Pbcu 8	1571.0(11) 1178.4(12) 1354.0(10)		CdN <sub>2</sub> C <sub>2</sub>	N 251.9(14,16) C 216.2(25,10)	N,N 64.0(5) <sup>e</sup> C,C 148.4(8) N,C 103.4(8,6,5)	[13]

<sup>a</sup> Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses is the e.s.d., and the second is the maximum deviation from the mean.

<sup>b</sup> vsi = (Me<sub>3</sub>Si)<sub>2</sub>(CH<sub>2</sub>=CHMe<sub>2</sub>Si)C; bpy = bipyridine; dmab = 2-((dimethylamino)methyl)phenyl(-).

<sup>c</sup> M = monoclinic; c = cubic; or = orthorhombic.

<sup>d</sup> The chemical identity of the coordinated atom or ligand is specified in these columns.

<sup>e</sup> Five-membered metallo-cyclic ring.

Table 2  
Crystallographic and structural data for dimeric to polymeric organocadmium compounds<sup>a</sup>

Compound <sup>b</sup> (colour)	Crystal class <sup>c</sup> space group Z	a (pm) b (pm) c (pm)	Chromophore	$\alpha$ (deg) $\beta$ (deg) $\gamma$ (deg)	Cd-L (pm)	Cd-Cd (pm) Cd-L-Cd (deg) $\mu$ L-Cd- $\mu$ L (deg)	L-Cd-L (deg)	Reference
$[\text{Cd}(\text{Me}_3\text{Si})_2\text{N}]_2$ ( $\eta^5\text{-cp}^*$ ) <sub>2</sub> (yellow)	m P2 <sub>1</sub> /a 4	1602.7(2) 1562.2(1) 1622.8(1)	CdN <sub>2</sub> C	93.269(8)	$\mu$ N <sup>d</sup>	322.79(6) 89.5(2,2) 90.5(2,3)	N,C <sup>d</sup> 125.7(2,3) 143.8(2,1)	[14]
$[\text{Cd}(\text{tpsi})\text{Cl}]_2$ (colourless)	m P2 <sub>1</sub> /n 4	1504.8(6) 1824.8(9) 2080.7(21)	CdCl <sub>2</sub> C	108.29(6)	C <sup>sp</sup> $\mu$ Cl C	not given 94.1(1,3) 86.0(1,0)	Cl,C 136.7(1,7,6)	[15]
$[\text{Cd}(\text{C}(\text{SiMe}_3\text{Ph})_3\text{Br})_2]$	m P2 <sub>1</sub> /n 4	1499.6(4) 1827.4(2) 2099.3(2)	CdBr <sub>2</sub> C	109.15(2)	$\mu$ Br C	not given 92.71(4) 87.15(4)	Br,C 128.6–144.0(2)	[16]
$[\text{Cd}(\text{C}_6\text{F}_5\text{Me}_2\text{Ph})_3]$ Br(H <sub>2</sub> O) <sub>2</sub> ·thf	tr P $\bar{1}$ 1	1107.4(6) 1187.6(7) 1224.6(5)	CdBr <sub>2</sub> OC	82.86(2) 84.64(2) 71.07(2)	$\mu$ Br H <sub>2</sub> O C	not given 88.5(1) 91.5(1)	Br,O 92.1(6) 127.3(7) 116.7(7)	[16]
$[\text{Cd}(\mu_3\text{-O})\text{f}^-]$ (C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> ·(tcf) <sub>2</sub> (colourless)	tr P $\bar{1}$ 2	1278.8(6) 1382.1(6) 1388.9(5)	CdO <sub>3</sub> C	63.30(2) 83.30(5) 87.19(5)	C $\mu_3$ HO	212.7(9,7) 99.6(2,1,5) 79.5(2,1,4)	not given C,C 173.0(8)	[17]
$\text{Cd}(\text{Me})_2(\text{dox})_2$ (colourless)	or Phcm 4	428.4(4) 1477.0(12) 1317.0(11)	CdC <sub>2</sub> (O <sub>2</sub> )		C <sup>Me</sup> O	209(2) 281.5(18,30)	C,C	[18]

<sup>a</sup> Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses is the e.s.d., and the second is the maximum deviation from the mean.

<sup>b</sup> tpsi = (th<sub>2</sub>MeSi)<sub>3</sub>C; thf = tetrahydrofuran; tof = toluene.

<sup>c</sup> tr = triclinic.

<sup>d</sup> The chemical identity of the coordinated atom or ligand is specified in these columns.

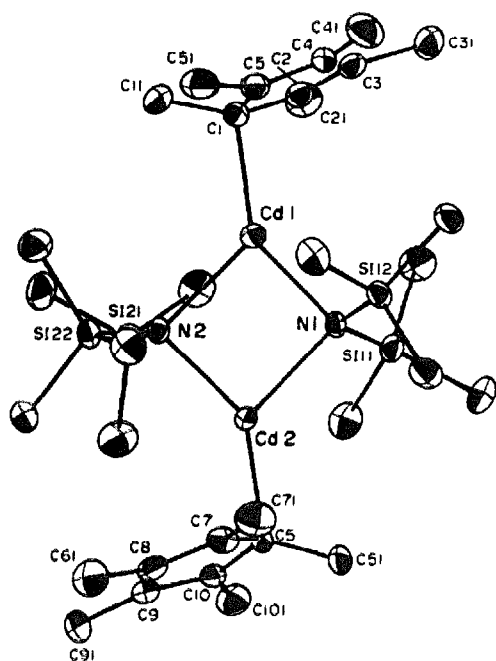


Fig. 1. Structure of  $[\text{Cd}((\text{Me}_3\text{Si})_2(\eta^1\text{-cp}^*))_2]$  [14].

Table 2. Four of the structures are of dimers [14–16]. The structure of the yellow compound  $[\text{Cd}(\text{Me}_3\text{Si})_2\text{N}_2(\eta^1\text{-cp}^*)]_2$  [14] ( $\text{cp}^*$  = pentamethylcyclopentadienyl), shown in Fig. 1, contains the near-planar asymmetric  $\text{Cd}_2\text{N}_2$  ring in which the  $\text{Cd}(1)\text{-N}(1)$  and  $\text{Cd}(2)\text{-N}(2)$  average distance is 7.5 pm smaller than the  $\text{Cd}(1)\text{-N}(2)$  and  $\text{Cd}(2)\text{-N}(1)$  average distance. The  $C_2$  axis perpendicular to the  $\text{Cd}_2\text{N}_2$  plane is not crystallographically imposed. Each  $\text{Cd}(\text{II})$  atom is also coordinated to an  $\eta^1\text{-cp}^*$  ligand with a mean  $\text{Cd}\text{-C}$  bond distance of 222.2(6) pm, creating a distorted trigonal plane ( $\text{CdN}_2\text{C}$ ) about each  $\text{Cd}(\text{II})$  atom. In the other three dimers a pair of chlorine [15] or bromine [15,16] atoms serve as bridges. In two of these, each  $\text{Cd}(\text{II})$  atom is in a distorted trigonal planar environment  $\text{CdX}_2\text{C}$  ( $X = \text{Cl}$  [15] or  $\text{Br}$  [16]). In the other both  $\text{Cd}(\text{II})$  atoms are tetrahedrally coordinated  $\text{CdBr}_2\text{OC}$  [16]. The mean  $\text{Cd}\text{-L}(\text{bridge})$  bond distance in the three-coordinate derivatives increases with the covalent radius of the donor atom in the sequence: 229.4 pm (N, 75 pm) < 253.2 pm (Cl, 99 pm) < 263.6 pm (Br, 114 pm). The  $\text{Cd}\text{-Br}(\text{bridge})$  bond distance in the four-coordinate derivative is 266.3 pm, about 2.7 pm longer than that of the three-coordinate derivative. The mean  $\text{Cd}\text{-C}$  bond distance of the three-coordinate derivatives (220.3 pm) is somewhat longer than that found in two-coordinate derivatives (219.5 pm), and both are longer than that of the four-coordinate derivative (217 pm).

The structure of  $[\text{Cd}(\mu_3\text{-OH})(\text{C}_6\text{F}_5)]_4$  [17] ( $\text{C}_6\text{H}_5$  = pentafluorophenyl) is shown in Fig. 2, where it can be seen that the cluster is of a cubane type with the

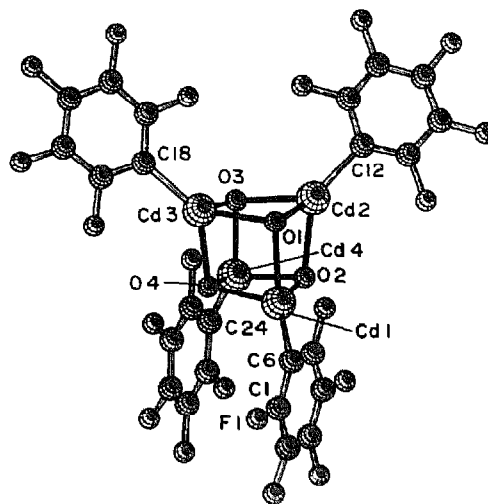


Fig. 2. Structure of  $[\text{Cd}(\mu_3\text{-OH})(\text{C}_6\text{F}_5)]_4$  [17].

cadmium and oxygen atoms occupying the eight corners.

The final structure [18] is an example where a cadmium is bonded to two Me groups ( $\text{Cd}\text{-C} = 209(2)$  pm) and two oxygen atoms ( $\text{Cd}\text{-O}(1) = 288(2)$  pm and  $\text{Cd}\text{-O}(4) = 275(2)$  pm) which are from different 1,4-dioxane (dox) molecules. This gives rise to an unusual one-dimensional polymeric structure, as shown in Fig 3.

#### 4. Heterometallic cadmium derivatives

The data for the heterometallic structures are given in Table 3. There is one example containing two metal atoms,  $\text{Me}_2\text{CdZn}(\text{Et}_2\text{NCSe}_2)_2$  [19], in which each of the diselenocarbamate groups chelates one metal atom and bridges to the other. Each metal atom is four-coordinate with a tetrahedral arrangement distorted towards a trigonal pyramid (chromophore  $\text{CdSe}_3\text{C}$ ). The  $\text{M}\text{-Se}(\text{terminal})$  bond distance of 257.5(4) pm is about 13.7 pm shorter than the  $\text{M}\text{-Se}(\text{bridge})$  distance, with an  $\text{M}\text{-Se}\text{-M}$  bridge angle of 87.1°.

Five derivatives [20–23] contain one cadmium with two other metal atoms. In four of these, with a general formula of  $[\text{LCd}\{\text{Mn}(\text{CO})_5\}_2]_n$ , the cadmium atom is

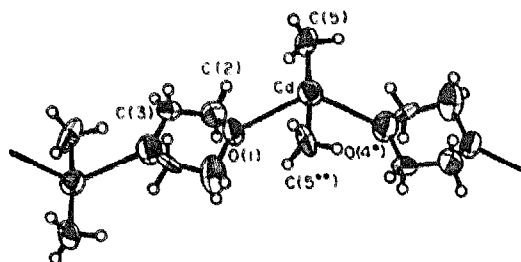


Fig. 3. Structure of  $[\text{Cd}(\text{Me})_2(\text{dox})_2]_n$  [18].

coordinated by a tridentate ligand [20,22] or a bidentate ligand [21] together with two pentacarbonylmanganese groups in a distorted trigonal-bipyramidal or tetrahedral arrangement respectively. The Cd–Mn bond distances range from 270.6(2) pm to 280.0(5) pm (mean value 274.5 pm) in the five-coordinate cadmium derivatives [20,22]. In the two four-coordinate derivatives [21] the Cd–Mn bond distances are 267.5(4) pm and 268.7(4) pm (mean 268.2 pm). It is noted that the mean Mn–C(carbonyl) bond distance of 179.2 pm in the former set is about 1.3 pm longer than the value of 177.9 pm of the latter set, despite the otherwise identical chromophore of the manganese atom ( $\text{MnC}_5$ ).

The structure of  $\{\text{Cd}[(\text{MeO})_3\text{Si}(\text{CO})_3\text{Fe}(\mu\text{-Ph}_2\text{Ppy})_2]\}_2$  [23] (Ph = phenyl, py = pyridine) possesses a crystallographically imposed  $C_2$  axis, as shown in Fig. 4, which passes through the Cd atom and relates the atoms Fe and N to  $\text{Fe}^*$  and  $\text{N}^*$  respectively. The geometry about the Cd atom is that of a flattened tetrahedron, with a Cd–Fe distance of 269.7(5) pm and a Cd–N distance of 249.3(3) pm.

There are eight clusters [23–29] with four metal atoms. A triclinic structure [23] contains a central four-membered ring of alternating Cd and Br atoms, with two  $\text{FeC}_3\text{PSi}$  moieties bonded to each cadmium via the iron atom (Cd–Fe = 254.0(3) pm), which completes a trigonal planar arrangement about the cadmium atoms.

The structure of monoclinic  $[\text{CdFe}(\text{CO})_4]_4$  [24] consists of a nearly planar, centrosymmetric, eight-membered ring of alternating Cd and *cis*- $\text{Fe}(\text{CO})_4$  units. The geometry deviates from  $D_{4h}$  square symmetry, one pair of opposite Fe–Cd–Fe angles have the value  $170.25(5)^\circ$  and the other pair  $189.85(5)^\circ$ . The Cd–Fe bond distance is 256.2(3) pm.

Two derivatives have the general formula  $[(\text{CO})_3\text{Fe}(\text{RO})_3\text{Si}(\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{Ph})\text{CdCl}_2]_2$ , where R is Me or ethyl (Et) [25]. There is a centre of inversion in the molecule, which implies a planar  $\text{Cd}(\mu\text{-Cl})_2\text{Cd}$  system

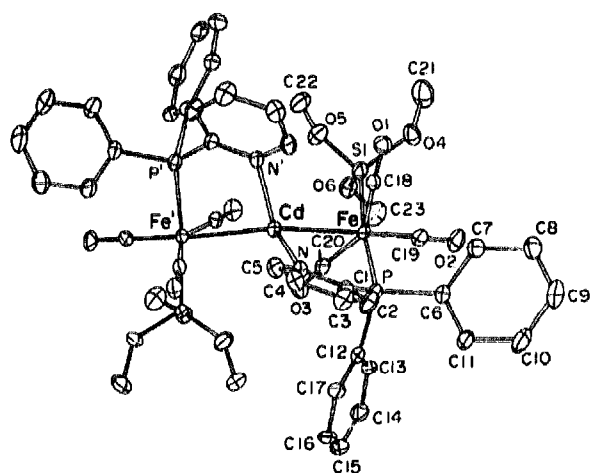


Fig. 4. Structure of  $\text{Cd}[(\text{MeO})_3\text{Si}(\text{CO})_3\text{Fe}(\mu\text{-Ph}_2\text{Ppy})_2]_2$  [23].

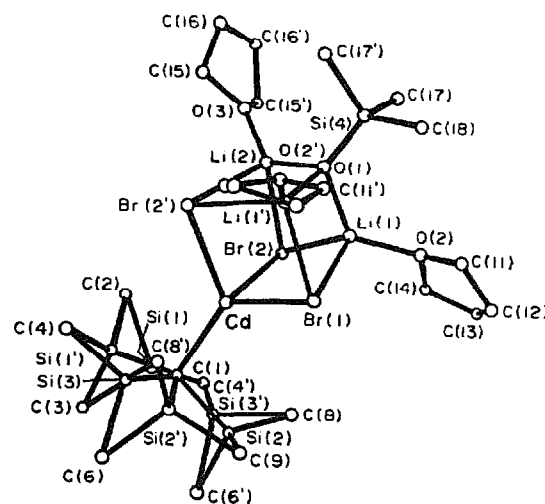


Fig. 5. Structure of  $[\text{Li}(\text{thf})_3]_3\text{Cd}[(\text{Me}_3\text{Si})_3\text{C}](\text{Me}_3\text{SiO})\text{Br}_3$  [28].

and two identical Cd–Fe units with Cd–Fe bond distances of 260(1) pm (R = Me) and 258.5(4) pm (R = Et).

Another derivative with an imposed crystallographic  $C_2$  symmetry [26] consists of two Fe–Cd dinuclear units with Cd atoms joined by double, almost symmetrical, chloride bridges (Cd–Cl = 254.6(3) and 257.0(4) pm). The two  $\text{CdCl}_2$  triangles of the  $\text{Cd}(\mu\text{-Cl})_2\text{Cd}$  system make a dihedral angle of  $165.3(1)^\circ$ . The iron and cadmium centres are linked by a  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$  bridge and a Cd–Fe bond (262.4(2) pm).

A light yellow complex [27] consists of iodide-bridged  $\text{Et}_4\text{Sb}_2\text{Cd}_2\text{I}_4$  units which have  $\text{CdI}_2$  bonded moieties bonded to each antimony atom. The Cd–Sb and Sb–Sb distances are 282.2(2) and 278.4(2) pm respectively. The structure of a heterotetranuclear derivative [28] is shown in Fig. 5. The neutral cluster has a structure based on a  $\text{CdLi}_3\text{Br}_3\text{O}$  cube. Another tetranuclear structure,  $[\text{CdCl}_2(\text{as-4C}_2\text{N})\text{PPCr}(\text{CO})_4]_2$  [29], contains a central  $\text{Cd}(\mu\text{-Cl})_2\text{Cd}$  unit which is connected from both sides by  $\text{CrC}_4\text{P}_2$  moieties via two N-donor atoms of the as-4C<sub>2</sub>N ligand. A trigonal-bipyramidal coordination about each Cd(II) atom is completed by a terminal chlorine atom ( $\text{CdCl}_3\text{N}_2$ ).

A red cluster containing five metal atoms ( $\text{CdFe}_4$ ) [25] has a  $C_2$  axis in the molecule which passes through the Cd atom. The coordination about the Cd(II) centre has the geometry of a flattened tetrahedron ( $\text{CdO}_2\text{Fe}_2$ ) with a Cd–Fe bond distance of 261.2(1) pm.

A hexanuclear structure  $[(2,2'\text{-bpy})\text{CdFe}(\text{CO})_4]_3$  [30] consists of near-planar six-membered rings of alternating *cis*- $\text{Fe}(\text{CO})_4$  and (bpy)Cd units. The ring is distorted from the ideal  $D_{3h}$  to approximate  $C_2$  symmetry by compression along a  $C_2$  axis in the plane of the ring. All Cd–Fe distances are equal at 264.0(7) pm, and the Cd–Fe–Cd angles vary from  $138.81(15)^\circ$  to

Table 3  
Crystallographic and structural data for heterometallic organocadmium compounds <sup>a</sup>

Compound <sup>b</sup> (colour)	Crystal class <sup>c</sup> space group Z	a (pm) b (pm) c (pm)	$\alpha$ (deg) $\beta$ (deg) $\gamma$ (deg)	Chromo- phore	Cd-L (pm)	L-Cd-L (deg)	Reference		
$\text{Me}_2\text{CdZn}^{\text{II}}(\text{Et}_2\text{NCSe}_2)_2$ (colourless)	m	682.4(3)		$\text{MSe}_3\text{C}$	$\mu\text{Se}^{\text{d}}$	271.2(4,30)	[19]		
	$P2_1/n$ 2	1401.3(4) 1103.1(3)	93.70		Se $\text{C}_{\text{Me}}$	$\mu\text{Se}, \mu\text{Se}^{\text{d}}$ $\mu\text{Se}, \text{Se}$ $\mu\text{Se}, \text{C}$ Se, C		80.3(4,5.2) 123.2(3,8.7) 134.9(3) 87.1 <sup>e</sup>	
$((\text{diglyme})\text{Cd}[\text{Mn}(\text{CO})_5]_2)$ (orange)	m	1016.1(10)		$\text{CdO}_3\text{Mn}_2$  $\text{MnC}_5$	O	254.1(7)	[20]		
	$P2_1/n$ 4	2301.0(20) 971.8(9)	91.80(2)		Mn	265.0(7,47) 271.0(2,4)		O, O Mn, Mn O, Mn	63.5(3,4) 126.6(3) 135.9(1)
					OC	178.8(11,33)		C, C	103.8(2,12.3) 92.9(6,7.2) 167.0(6,7.8)
$((\text{bpy})\text{Cd}[\text{Mn}(\text{CO})_5]_2)$ (orange)	m	1442.9(15)		$\text{CdN}_2\text{Mn}_2$  $\text{MnC}_5$	N	235.4(9,5)	[21]		
	$P2_1/n$ 4	1580.5(16) 1042.3(10)	94.62(2)		Mn	268.3(3,3)		N, N Mn, Mn N, Mn	69.2(4) <sup>f</sup> 127.7(2) 111.3(3,1.5)
				OC	178.2(16,42)	C, C	93.4(7,8.2) 164.4(7,7.2)		
$((\text{phen})\text{Cd}[\text{Mn}(\text{CO})_5]_2)$ (orange)	m	1457.4(15)		$\text{CdN}_2\text{Mn}_2$  $\text{MnC}_5$	N	236.2(14,20)	[21]		
	$P2_1/n$ 4	1625.8(16) 1045.3(10)	96.87(2)		Mn	268.1(4,6)		N, N Mn, Mn N, Mn	69.5(5) <sup>f</sup> 131.4(2) 109.8(4,2.6)
				OC	177.5(22,46)	C, C	93.5(9,9.3) 164.1(9,7.0)		
$((\text{terpy})\text{Cd}[\text{Mn}(\text{CO})_5]_2)$ (red)	m	915.8(15)		$\text{CdN}_3\text{Mn}_2$  $\text{MnC}_5$	N	245.8(14,53)	[22]		
	$P2_1/c$ 4	1889.5(26) 1696.0(17)	111.38(9)		Mn	278.0(5,20)		N, N Mn, Mn N, Mn	66.5(5,3) <sup>f</sup> 132.9(5) 132.4(2)
				OC	179.5(22,41)	C, C	104.1(4,11.4)		
$[\text{Cd}\{(\text{MeO})_3\text{Si}(\text{CO})_3 \cdot \text{Fe}(\mu\text{-Ph}_2\text{Ppy})_2\}]_2$	m	2968.4(8)		$\text{MnC}_5$ $\text{CdN}_3\text{Fe}_2$  $\text{FeC}_3\text{PSi}$	OC	179.5(22,41)	[23]		
	$C2/c$ 4	1004.3(3) 2098.8(6)	91.87(2)		N	249.3(3)		N, N	93.4(9,13.6) 80.7(1)
					Fe	269.70(5)		Fe, Fe N, Fe	143.45(3) 101.8(1,12.7)
				OC	175.8(5,10)	C, C	104.9(2,7)		
				P	221.8(1)		146.9(2)		
				Si	228.6(1)	C, P C, Si P, Si	94.9(1,4,3) 84.3(1,1,9) 173.21(5)		
$[(\text{Ph}_3\text{SiXPh}_2\text{HPXCO}_3) \cdot \text{FeCd}(\mu\text{-Br})_2]$	tr	1048.9(5)	75.51(3)	$\text{CdBr}_2\text{Fe}$  $\text{FeC}_3\text{PSi}$	$\mu\text{Br}$	260.4(2)	[23]		
	$P\bar{1}$ 1	1269.6(4) 1515.5(7)	86.58(5) 72.94(5)		Fe	268.9(2) 254.0(3)		Br, Br Br, Fe	90.9 127.58(8) 139.9
					OC	174(3,4)		C, C	102.4(8,4,3)
				P	223.7(5)		151(1)		
				Si	236.4(5)	C, P C, Si P, Si	94.3(6,8,0) 84.4(5,2,5) 172.5(2)		
$[\text{CdFe}(\text{CO})_4]_3 \cdot 2\text{Me}_2\text{CO}$	m	629.2(4)		$\text{CdFe}_2$  $\text{FeC}_4$	Fe	256.3(2,4)	[24]		
	$P2_1/n$ 2	1056.6(6) 2602.4(11)	97.80(3)		OC	177.9(10,10)		Fe, Fe C, C	170.2(1,0) 189.85(5) 98.2(4,2,2)
							154.7(4,2)		
$[(\text{CO})_3\text{Fe}(\text{EtO})_3\text{Si} \cdot (\text{Ph}_2\text{PCH}_2\text{C(O)Ph})\text{CdCl}]_2 \cdot \text{PhCl}$ (yellow)	m	2245.5(3)		$\text{CdO}_2\text{Cl}_2\text{Fe}$  $\text{FeC}_3\text{PSi}$	O	246.5(5,51)	[25]		
	$C2/c$ 4	1768.0(2) 1662.7(4)	90.80(4)		$\mu\text{Cl}$	254.3(2,31)		O, O Cl, Cl	157.5(2) 90.93(8)
					Fe	260.1(1)		O, Fe Cl, Fe	76.6, 95.1(1) 121.4, 146.6(1)
				OC	177(1,0)	P, Cd	94.98(6)		
				P	222.7(1)				
				Si	230.2(2)				
$[(\text{CO})_3\text{Fe}(\text{EtO})_3\text{Si} \cdot (\text{Ph}_2\text{PCH}_2\text{C(O)Ph})\text{CdCl}]_2$ (yellow)	m	2539.2(5)		$\text{CdO}_2\text{Cl}_2\text{Fe}$  $\text{FeC}_3\text{PSi}$	O	258(1,12)	[25]		
	$C2/c$ 4	1855.4(6) 1628(1)	120.73(3)		$\mu\text{Cl}$	254.2(4,35)		Cl, Cl O, Fe	87.7(1) 74.2, 93.5(2)
					Fe	258.5(4)		Cl, Fe	122.1, 148.8(1)
					OC	174(2,2)		P, Cd	94.0(2)
				P	222.1(4)				
				Si	230.4(5)				

148.40(15)°, and the Fe–Cd–Fe angles vary from 94.78(14)° to 102.04(16)°.

The structure of the heptanuclear  $[\text{Fe}_6\text{Cd}(\text{CO})_{22}]^{2-}$  anion [31] reveals two  $\text{Fe}_3$  units coordinated to a central

cadmium atom, which is thus surrounded by four iron atoms in a rather unsymmetrical coordination with a mean Cd–Fe bond distance of 274.3(2) pm. The mean Fe–Fe bond distance (266.6(3) pm) is about 7.7 pm

Table 3 (continued)

Compound <sup>b</sup> (colour)	Crystal class <sup>c</sup> space group <i>Z</i>	<i>a</i> (pm) <i>b</i> (pm) <i>c</i> (pm)	$\alpha$ (deg) $\beta$ (deg) $\gamma$ (deg)	Chromo- phore	Cd–L (pm)	L–Cd–L (deg)	Reference		
[[ $(\text{MeO})_3\text{Si}(\text{CO})_3\text{Fe} \cdot (\mu\text{-dppm})\text{Cd}(\mu\text{-Cl})_2$ ]	or	2349.8(9)		CdCl <sub>2</sub> PFe	$\mu\text{Cl}$	255.8(4,12)	Cl,Cl	[26]	
	<i>Pbcn</i> 4	1685.6(8) 1822.0(8)			P Fe	279.6(4) 262.4(2)	Cl,P Cl,Fe P,Fe	102.2(1,2,0) 132.3(1,2) 95.5(1) 92.6(1) <sup>g</sup>	
Et <sub>3</sub> Sb <sup>II</sup> Cd <sub>2</sub> I <sub>4</sub> (light yellow)	tr	817.9(2)	77.80(2)	CdI <sub>2</sub> Sb	OC	175.9(16,16)	C,C	[27]	
	$P\bar{1}$	891.3(2)	85.13(2)		P	225.1(4)	C,P		102.1(7,3) 96.9(5,7.1)
	2	1622.0(2)	79.23(2)		Si	228.6(5)	C,Si		83.4(5,2.5)
					Sb	275.1(2,16)	I,I		122.0(1,2,0) 117.2(1,9,0) 193.1(9,8)
[[ $(\text{Li}(\text{thf}))_3\text{Cd} \cdot \{(\text{Me}_3\text{Si})_3\text{C} \cdot (\text{Me}_3\text{SiO})\text{Br}_3\}$ ]	or	2387.5(5)		CdBr <sub>3</sub> C	$\mu_3\text{Br}$	271.8(1,1)	Br,Br	[28]	
	<i>Pnam</i> 4	1226.1(6) 1499.0(5)			C	219.9(10)	Br,C	122.5(1,2,0) 82.1(3,2,1) <sup>c</sup>	
[CdCl <sub>2</sub> ( <i>ns</i> -4C2N) · PPCr <sup>IV</sup> (CO) <sub>4</sub> ] <sub>2</sub>	tr	1209.4(4)	90.88(1)	CdCl <sub>3</sub> N <sub>2</sub>	$\mu_3\text{O}$	185(2,4)	Br,Br	97.9(8,3,1)	
	$P\bar{1}$	1423.5(3)	95.77(1)		$\mu_3\text{Br}$	256.2(14,6)	O,O	129.5(8,5) 63.5(7,6) <sup>h</sup>	
	1	1089.5(2)	83.04(1)		O	266(2)			
					OC	197(3,2)			
[Cd{Fe[(MeO) <sub>3</sub> Si] · (Ph) <sub>2</sub> PCH <sub>2</sub> CO} · (C <sub>3</sub> H <sub>4</sub> )Fe(cp)} <sub>2</sub> (red)	tr	1209.4(4)	90.88(1)	CrC <sub>4</sub> P <sub>2</sub>	$\mu\text{Cl}_{\text{eq}}$	251.4(2)	$\mu\text{Cl}_{\text{eq}}, \text{Cl}_{\text{eq}}$	[29]	
	$P\bar{1}$	1423.5(3)	95.77(1)		Cl <sub>eq</sub>	241.9(2)	$\mu\text{Cl}_{\text{eq}}, \text{N}_{\text{eq}}$	126.1(1) 88.0, 126.3(2)	
	1	1089.5(2)	83.04(1)		N <sub>eq</sub>	233.0(6)	Cl <sub>eq}, N<sub>eq</sub></sub>	107.2(2)	
					$\mu\text{Cl}_{\text{np}}$	233.0(6)	$\mu\text{Cl}_{\text{np}}, \text{N}_{\text{np}}$	159.4(1)	
[[ $(\text{bpy})\text{CdFe}(\text{CO})_4$ ] <sub>1</sub> · $\frac{1}{3}\text{C}_6\text{H}_3\text{Cl}_3$	tr	1205.4(5)	90.60(2)	CdO <sub>2</sub> Fe <sub>2</sub>	N <sub>np</sub>	242.9(5)	N,N	177.6(2) <sup>f</sup>	
	$P\bar{4}$	1443.9(4)	91.56(3)		OC	not given	P,P	69.1(1) <sup>i</sup>	
	2	2662.3(7)	97.54(3)		P	237.6(2,3)			
					O	254.1(5,0)	O,O	111.8(3)	
(ppn) <sub>2</sub> [Fe <sub>6</sub> Cd(CO) <sub>22</sub> ]	tr	1205.4(5)	90.60(2)	CdO <sub>2</sub> Fe <sub>2</sub>	Fe	261.2(1,0)	Fe,Fe	[25]	
	$P\bar{1}$	1443.9(4)	91.56(3)		OC	176.9(7,15)	O,O	160.08(4)	
	1	2662.3(7)	97.54(3)		P	225.3(2)	Fe,Fe	76.7, 115.1(4)	
					Si	228.9(2)	O,Fe		
[[ $(\text{GePh}_3)_2\text{Cd} \cdot \text{Ni}(\text{cp})_2\text{Cd}$ ]	tr	1205.4(5)	90.60(2)	FeC <sub>3</sub> PSi	OC	176.9(7,15)			
	$P\bar{4}$	1443.9(4)	91.56(3)		P	225.3(2)			
	2	2662.3(7)	97.54(3)		Si	228.9(2)			
					not given				
[[ $(\mu_3\text{-Co}(\text{CO})_3$ )] <sub>3</sub> · Cd <sup>I</sup> · { $\mu_3\text{-}[(\text{CO})_9\text{Co}_3 \cdot (\mu_3\text{-CCO}_2)]_3 \cdot (\text{thf})_3$ }]	tr	1205.4(5)	90.60(2)	FeC <sub>10</sub> CdN <sub>2</sub> Fe <sub>2</sub>	N	237.3(18,46)	N,N	[30]	
	$P\bar{4}$	1443.9(4)	91.56(3)		Fe	264.0(5,10)	Fe,Fe	142.3(1,6,1)	
	2	2662.3(7)	97.54(3)		OC	173(3,7)	N,Fe	105.5(5,6,9)	
					Fe	274.3(2,10)	Fe,Fe	92.8–141.8(15) 57.9(1,1)	
[[ $(\mu_3\text{-Co}(\text{CO})_3$ )] <sub>3</sub> · Cd <sup>I</sup> · { $\mu_3\text{-}[(\text{CO})_9\text{Co}_3 \cdot (\mu_3\text{-CCO}_2)]_3 \cdot (\text{thf})_3$ }]	tr	1205.4(5)	90.60(2)	FeC <sub>4</sub> CdFe <sub>4</sub>	OC	173(3,7)	C,C	[31]	
	$P\bar{1}$	1443.9(4)	91.56(3)		Fe	274.3(2,10)	Fe,Fe		
	1	2662.3(7)	97.54(3)		OC	not given	Cd,Fe	61.1(1,3)	
					OC	not given	Fe,Fe	60.0(1,7)	
[[ $(\mu_3\text{-Co}(\text{CO})_3$ )] <sub>3</sub> · Cd <sup>I</sup> · { $\mu_3\text{-}[(\text{CO})_9\text{Co}_3 \cdot (\mu_3\text{-CCO}_2)]_3 \cdot (\text{thf})_3$ }]	tr	1205.4(5)	90.60(2)	NiC <sub>10</sub> Ge	$\mu\text{OC}$	266.6(3,20) <sup>j</sup>			
	$P\bar{1}$	1443.9(4)	91.56(3)		Ni	247.5(2,0)	Ni,Ni	180	
	2	2662.3(7)	97.54(3)		Ge	258.7(2)	Ge,Ni	170.31(8)	
					Ni	245.9(2)			
[[ $(\mu_3\text{-Co}(\text{CO})_3$ )] <sub>3</sub> · Cd <sup>I</sup> · { $\mu_3\text{-}[(\text{CO})_9\text{Co}_3 \cdot (\mu_3\text{-CCO}_2)]_3 \cdot (\text{thf})_3$ }]	tr	1205.4(5)	90.60(2)	GeC <sub>3</sub> Cd GeC <sub>3</sub> Ni	C <sub>cp</sub>	207(2)	Ge,Cd	86.46(8)	
	$P\bar{1}$	1443.9(4)	91.56(3)		Ge	230.8(3)			
	2	2662.3(7)	97.54(3)		C <sub>ph</sub>	196(2,5)	C,Cd	112.8(5,2,9)	
					C <sub>ph</sub>	195(2,1)	C,Ni	115.7(5,3,9)	
[[ $(\mu_3\text{-Co}(\text{CO})_3$ )] <sub>3</sub> · Cd <sup>I</sup> · { $\mu_3\text{-}[(\text{CO})_9\text{Co}_3 \cdot (\mu_3\text{-CCO}_2)]_3 \cdot (\text{thf})_3$ }]	tr	1205.4(5)	90.60(2)	CdO <sub>3</sub> CdC <sub>5</sub>	Co	257.3(17)	not given	[33]	
	$P\bar{1}$	1443.9(4)	91.56(3)		O	not given			
	2	2662.3(7)	97.54(3)		O	not given			
					O	not given			

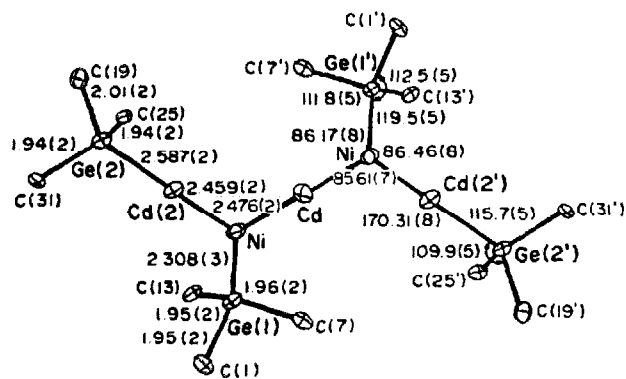


Fig. 6. View of the heterometallic chain of  $[(\text{GePh}_3)_2\text{CdNi}(\text{cp})]_2\text{Cd}$  [32].

shorter than the Cd–Fe distance. The molecule  $[(\text{GePh}_3)_2\text{CdNi}(\text{cp})]_2\text{Cd}$  [32] is shown in Fig. 6. It contains the longest chain of metal atoms (nine) found in cadmium chemistry. The major bond distances and bond angles for the cluster are also given in the figure.

The structure of a cluster with 13 metal atoms ( $\text{Cd}_3\text{Co}_{10}$ ) is shown in Fig. 7, in which parts of the metal cluster play the role of ligands [33]. The structure has a triangular  $\text{Cd}_3$  core capped with  $\text{Co}(\text{CO})_3$  moieties and edge-bridged with three cluster carboxylate ligands.

## 5. Summary

Almost 40 organocadmium and carbonyl derivatives are gathered in this review. The cadmium oxidation state varies from zero through +1 to +2. There is only one example of  $\text{Cd}(\text{I})$ , and this is found in a distorted tetrahedral environment [33]. The oxidation state of +2 is most abundant.  $\text{Cd}(\text{II})$  is found in digonal, trigonal planar, tetrahedral and five-coordinate (mostly trigonal-bipyramidal) environments. The number of metal atoms commonly ranges from one to seven, with one, three and four the most prevalent. There is one example each with nine and 13 metal atoms.

The mean  $\text{Cd-L}$  bond distances vary with degree of coordination. For the three-coordinate derivatives the values follow the order 220.3 pm (CL) < 275.1 pm (I);

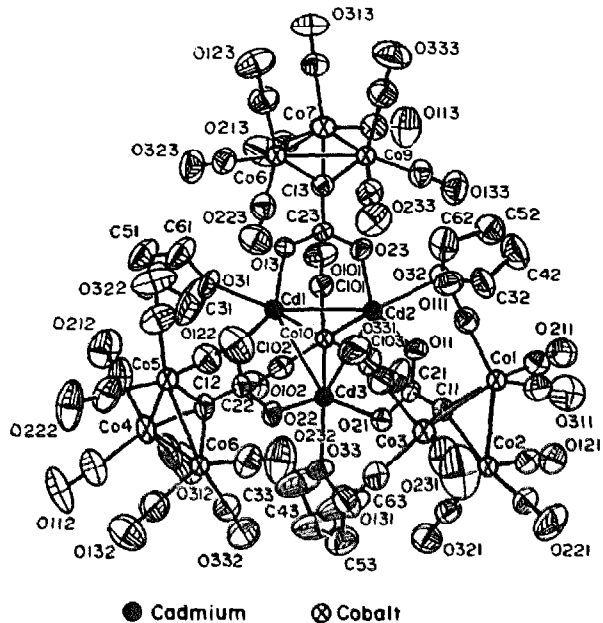


Fig. 7. Structure of  $[\mu_3\text{-Co}(\text{CO})_3]_3\text{Cd}_3[\mu\text{-(CO)}_9\text{Co}_3(\mu_3\text{-CCO}_2)_3] \cdot (\text{thf})_3$  [33].

and 229.4 pm (NL) < 253.2 pm (Cl) < 264.1 pm (Br) for the bridging ligands. For the tetrahedral examples the sequence is: 214.6 pm (CL) < 231.0 pm (tridentate NL) < 233.5 pm (NL) < 238.0 pm (OL) < 247.8 pm (bidentate NL) < 257.5 pm (bidentate SeL). The mean  $\text{Cd-}\mu_3\text{L}$  bond distances are 224.3 pm (OH) and 271.8 pm (Br). The latter value is somewhat longer than the corresponding  $\text{Cd-}\mu\text{Br}$  distance of 266.3 pm.

In the examples with bidentate chelating N-donor ligands the N–Cd–N angles of the five-membered metallocyclic rings are smaller when L is an unsaturated compound (2,2'-bpy, 1,10-phenanthroline (phen), mean value  $67.5^\circ$ ), compared with those of the saturated compounds (ethylenediamine etc., mean value  $73.5^\circ$ ). This is probably due to electronic effects involving the ligand L.

In the series of heterometallic carbonyl and organometallic compound of cadmium the mean  $\text{Cd-M}$  bond distance relates to the atomic radius of the heterometal atom M, for example: 246.7 pm (Ni, 124 pm) < 257.3 pm (Co, 125 pm) < 262.3 pm (Fe, 126 pm) < 269.1 pm (Mn, 135 pm). A similar effect is

<sup>a</sup> Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses is the e.s.d., and the second is the maximum deviation from the mean.

<sup>b</sup> diglyme = di-(2-methoxyethyl)ether; terpy = 2,2':6',2''-terpyridyl; dppm = bis(diphenylphosphine)methane; ppp =  $[\text{N}(\text{PPh}_2)_2]^+$ .

<sup>c</sup> tg = tetragonal.

<sup>d</sup> The chemical identity of the coordinated atom or ligand is specified in these columns.

<sup>e</sup> The Cd–L–M angle.

<sup>f</sup> Five-membered metallocyclic ring.

<sup>g</sup> The Cd–L–Cd angle.

<sup>h</sup> The M–L–M angle.

<sup>i</sup> Four-membered metallocyclic ring.

<sup>j</sup> The M–M distance.

<sup>k</sup> The Cd–Cd distance.



noted for the non-transition metal atoms: 258.7 pm (Ge, 137) < 282.2 pm (Sb, 159). There is only one example [33] in which the Cd(I)–Cd(I) distance (298.0 pm) is less than 300 pm which is taken as a limit for metal–metal bonding.

This review, together with its precursors for zinc [34–36] and mercury [37–39], represents the first overview of structural data for a non-transition metal subgroup. Despite increasing availability of retrieval systems for scientific data, it is usually time consuming and expensive to gather together related series of compounds for comparison. This review attempts to draw together the structural information presently available for organocadmium compounds, and to present the data in a systematic manner.

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