CADMIUM HETEROMETALLIC COMPOUNDS: CLASSIFICATION AND ANALYSIS OF CRYSTALLOGRAPHIC AND STRUCTURAL DATA

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Cadmium chemistry is an important area of research from both an industrial and environmental point of view. This review surveys the structural determination of almost ninety heterometallic complexes of cadmium. The cadmium atom is found mostly in the oxidation state of +2, but there are also examples of +1 and zero. The coordination numbers observed range from two to eight, with six occurring most frequently. The heterometal atoms include both transition and non-transition metals. A range of derivatives from dimers to polymers contain two or more metal atoms, however, there appears to be no evidence to suggest the existence of a direct Cd-Cd metal bond.

CONTENTS

0. ABBREVIATIONS

ac	acetate
(as-4C2N)PP	product of reaction of $Me_2N(CH_2)_2NH_2$ and 1,1-bis(diphenylphosphine)ethene
bn	butanediamine

bpy	bipyridyl
Bu	butyl
cdta	trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetate
$C_4H_8O_2$	1,4-dioxane
cp	cyclopentadienyl
crot	crotonate
diglyme	di-(2-methoxyethyl)ether
dppm	bis(diphenylphosphine)methane
edta	ethylenediaminetetraacetate
egta	ethylenedioxybis(ethylenenitrilo)tetraacetate
en	ethylenediamine
Et	ethyl
$EtCO_2$	propionate
hd	hexanediamine
hfacac	hexafluoroacetylacetonate
m	monoclinic
Me	methyl
mea	2-aminoethanol
Mepy	methylpyridine
mtn	N-methyl-1,3-diaminopropane
nd	nonadiamine
od	octanediamine
or	orthorhombic
pd	pentanediamine
PhCOS	thiobenzoate
phen	1,10-phenanthroline
py	pyridine
qu	quinoline
terpy	2,2':6',2"-terpyridyl
tg	tetragonal
thf	tetrahydrofuran
tld	toluidine
tol	toluene
tr	triclinic
ttftch	1,3,5-tris(trifluoromethyl)-1,3,5-trioxy-cyclohexane(-3)

1. INTRODUCTION

Over the last thirty years studies on the reactivity of various metal derivatives with cadmium salts have been carried out by a number of research groups. In many cases, isolable compounds have been obtained which yielded crystallographic structural data. There have been annual reviews of cadmium chemistry [1], and we have recently completed a review and classification of over six hundred cadmium coordination and organometallic structures [2]. This present review covers the structures of cadmium compounds that contain at least one other metal atom, published up to the end of 1993 and including some 1994 data from journals specific to inorganic chemistry.

One of the aims of this survey is to compare and contrast the structural behaviour of heteronuclear compounds of the Group 2B metals, zinc [3], cadmium and mercury [4]. About ninety cadmium compounds have been examined and the structures classified according to nuclearity. Within each subgroup, the derivatives are referenced in order of decreasing ratio of cadmium atoms and increasing number of heterometal units. Factors relevant to the stereochemical interactions around these metals are discussed.

2. HETERODIMERIC COMPOUNDS

There are two heterobimetallic cadmium derivatives for which the crystallographic and structural data are listed in Table 1A. The other metal atom in both cases is another Group 2B metal. In $Me_2CdZn(Et_2NCSe_2)_2$ [5] each diselenocarbamate unit chelates one metal atom and bridges to the other, as shown in Figure 1

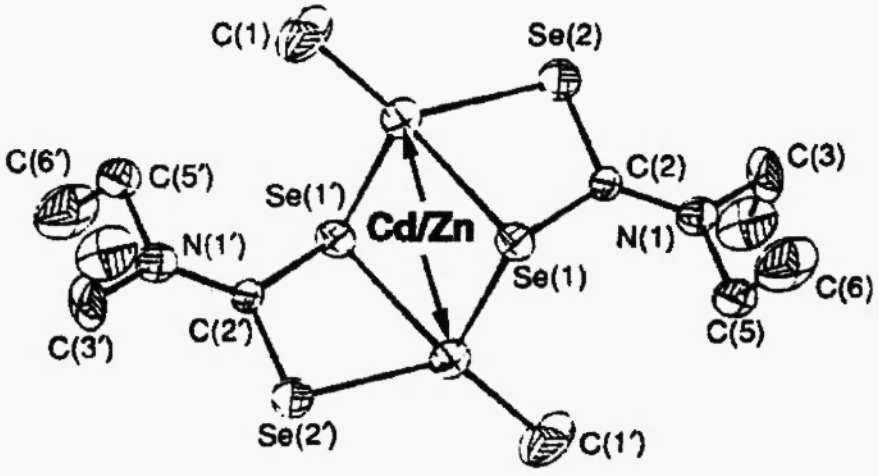

FIGURE 1. Structure of $Me_2CdZn(Et_2NCSe_2)_2$ [5]

Each metal atom is four coordinate, almost tetrahedral but with distortion towards a trigonal bipyramid. The other derivative [6] has an almost planar [Cd(μ-I)$_2$Hg] ring, with the metals being four coordinate CdI_4 and HgI_2P_2, respectively. The former is a slightly distorted tetrahedron while the latter is highly irregular. In particular, the P-Hg-P angle of 152.8(1)° may be attributable to the strong s-donor abilities of triphenylphosphine coupled with the tendency of mercury(II) to adopt linear coordination [2]. The mean Cd-I(bridge) bond distance of 287.4(1) pm is about 19.3 pm shorter than that of the Hg-I(bridge) distance of 306.7(1) pm (Table 1A).

3. HETEROTRIMERIC COMPOUNDS

The structural and crystallographic data for nine heterotrimetallic derivatives of cadmium are given in Table 1B. The orange yellow compound $(NMe_4)\{Na[Cd(PhCOS)_3]_2\}$ [7] has at the centre a sodium atom, and the two cadmium atoms are part of the ligand system around it. This is illustrated in Figure 2. The anion has a crystallographically imposed centre of symmetry, with the Na(I) atom sitting at the inversion centre. It is bonded to each of the PhCOS ligands via oxygen which gives it a distorted octahedral NaO_6 environment. Each Cd(II) atom is S-bonded to three thiobenzoate ions and also interacts weakly with three oxygen atoms at distances of 265.9 to 282.8(5) pm. The Cd-Na separation is 355.7(1) pm and does not involve any direct metal-metal bonding.

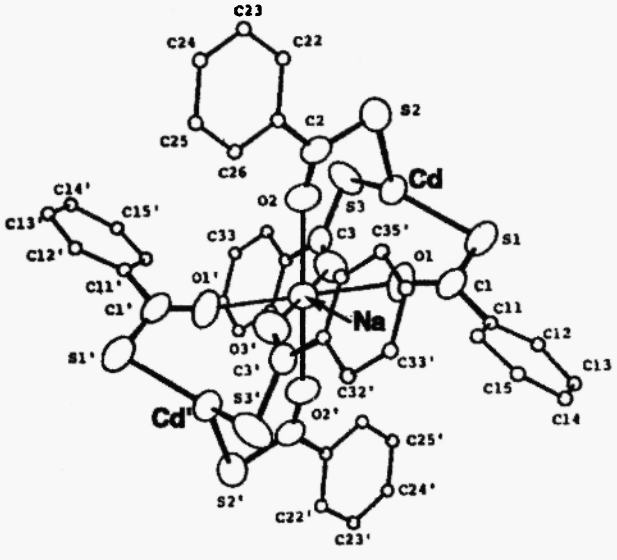

FIGURE 2. Structure of $\{Na[Cd(PhCOS)_3]_2\}^-$ [7]

There are four orange-red derivatives of composition $LCd[Mn(CO)_5]_2$ [8-10] in which cadmium is the central atom and the two $Mn(CO)_5$ moieties are part of the ligand

system. In two of these [8,10] the cadmium atom is coordinated by a terdentate ether [8], or terpyridyl [9] molecule (Cd-O range from 254.1(7) to 269.6(7) pm [8] and Cd-N range from 240.5(12) to 249.3(14) pm [9]), and two $Mn(CO)_5$ units (Cd-Mn, 270.7(2) and 271.4(2) pm [8] and 276.0 and 279.9(5) pm [9]) in a very distorted trigonal bipyramidal arrangement. There is considerable distortion of the octahedral manganese coordination (MnC_5Cd) as seen in Table 1B. Two structures $LCd[Mn(CO)_5]_2$ (L is 2,2'-bipyridyl or 1.10-phenanthroline [9]) are very similar. The cadmium atom is coordinated by two nitrogen atoms of L and two manganese atoms creating a distorted tetrahedral arrangement. Again, there is considerable distortion of the octahedral manganese coordination. In another example [11] the bridging ligand is 2-(diphenylphosphino)pyridine. The geometry about the cadmium centre is a flattened tetrahedron, with the Fe-Cd-Fe angle of 143.44(3)°, N-Cd-N angle of 80.7(1)° and N-Cd-Fe angle of 89.05(7)°. When the Cd-Fe bond is ignored, the geometry about the Fe atom is trigonal bipyramidal.

The derivative $CdZn_2(crot)_6(qu)_2$ [12] has a central cadmium(II) atom octahedrally coordinated (CdO_6) and linked to each zinc(II) atom by three crotonate bridges. Two of these bridges are syn-syn bidentate, and the third is monodentate (monatomic), bridging through only one oxygen. Each zinc(II) atom is a distorted tetrahedral coordinated (ZnO_3N) environment.

In the remaining two colourless derivatives of composition $[Cd\{M(Bu^tO)_3\}_2]$, where M is Ge or Sn [13], the central cadmium(II) atom is sixfold coordinated by oxygen while the other metal (M) have three oxygen neighbours. The oxygen atoms are further bonded to the tert-butyl groups which surround the whole MO_3CdO_3M frame. The Cd-M distances are 298.4(3) pm (Cd-Ge) and 312.1(3) pm (Cd-Sn), respectively.

4. HETEROTETRAMERIC COMPOUNDS

There are nine derivatives each containing four metal atoms, and the relevant data are shown in Table 1C. In $[(Ph_3)Si)(Ph_2HP)(CO)_3FeCd(\mu\text{-}Br)]_2$ [11], two cadmium atoms are doubly bridged by bromine atoms and also each is bonded to an iron atom at a Cd-Fe distance of 254.0(3) pm. The iron atoms are each six coordinate $\{FeC_3PSiCd\}$. The Cd..Cd distance of 371 pm excludes a direct homonuclear metallic bond.

The molecular structure of $[CdFe(CO)_4]_2$ [14] consists of a nearly planar, centrosymmetric eight membered ring of alternating Cd and cis-$Fe(CO)_4$ units. The deviation from D_{4h} symmetry is primarily observed in the trans Fe-Cd-Fe angles, one pair of which is at 170.25(5)°, while the other is at 189.85(5)°. The Cd-Fe distances are equivalent at 256.2(3) pm each. The major distortion from octahedral symmetry about the $Fe(CO)_4$ groups is a bending of the axial carbonyl ligands towards the ring centroid and away from the direction perpendicular to the plane containing the metal atoms (C-Fe-C mean value of 154.7(4)°).

in another two examples [15] there is a centre of inversion which implies a planar $Cd(\mu\text{-}Cl)_2Cd$ system and two identical Cd-Fe units. The Cd-Fe distance is 258.5(4) pm in one case and 260.1(1) pm in the other. Another complex [16] has an imposed C_2 symmetry, with two cadmium atoms joined by a nearly symmetrical double bridge of chlorine atoms. The two Cd-Fe bond distances are 262.4(2) pm, which indicates metal-metal bonding.

The structure of a blue complex containing pairs of Cd(II) and Cu(II) atoms is shown in Figure 3. The metal atoms are linked by bridging oxygen atoms of the μ_3-ttftych(-3) ligands. Each copper atom has distorted square-planar coordination geometry, and each cadmium has a distorted octahedral environment.

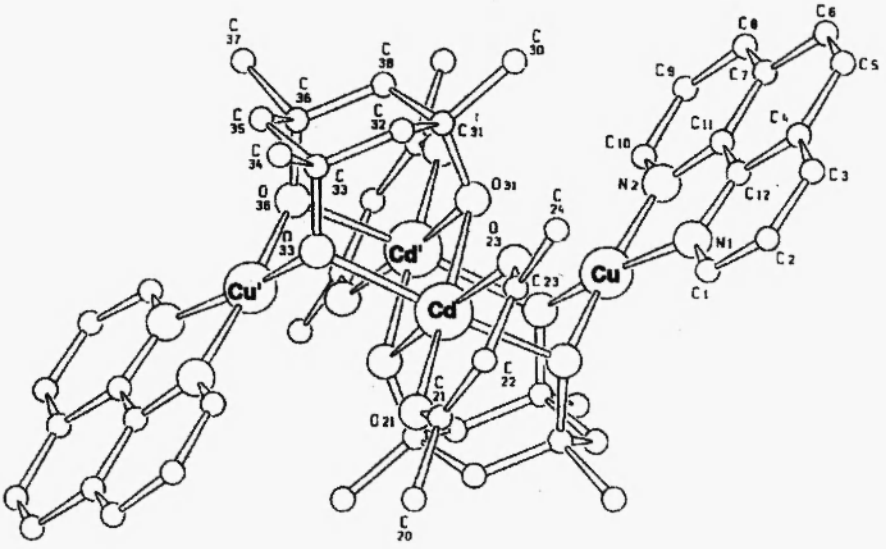

FIGURE 3. Structure of $[Cu_2(phen)_2(ttftch)_2Cd_2(hfacac)_2]$ [17]

The structure of light yellow $Et_4Sb_2Cd_2I_4$ [18] consists of the Cd(1)-Sb(1)-Sb(2)-Cd(2) chain, with Cd(1)-Sb(1)-Sb(2) and Sb(1)-Sb(2)-Cd(2) angles of 119.0(1)° and 122.1(1)°, respectively. The Cd-Sb and Sb-Sb distances are 282.2(2) and 278.4(2) pm, respectively. Antimony and two iodine atoms form a trigonal planar arrangement around cadmium, and there are also two weak bonds to the iodine atoms of adjacent units, giving a distorted trigonal bipyramidal coordination around the cadmium (mean Cd-I distance of 322.6 pm). The distibine units exhibit a skew configuration of the ethyl substituents.

In one final example [19] a cage structure is observed. Each metal atom in the cage is tetrahedrally coordinated.

5. HETEROOLIGOMERIC COMPOUNDS

Crystallographic and structural data for the heterooligomeric compounds are given in Table 1D. There is only one example [15] which contains five metal atoms ($CdFe_4$), the structure of which is shown in Figure 4. There is a C_2 axis in the molecule which passes through the Cd atom. The coordination about the Cd(II) centre is flattened tetrahedral. The Cd-Fe distance of 261.2(1) pm indicates a significant degree of bonding.

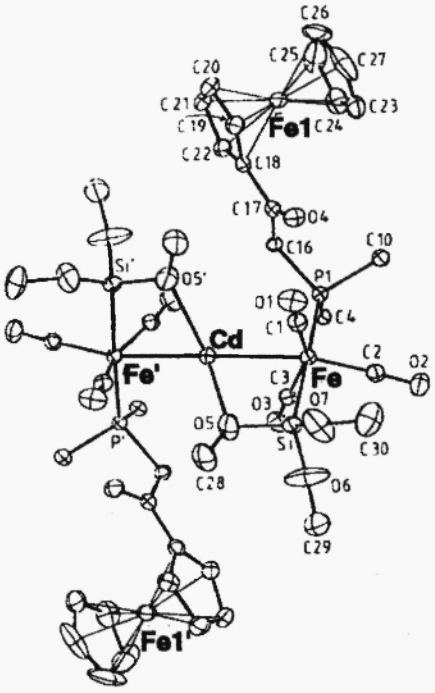

FIGURE 4. Structure of $\{Cd[Fe\{MeO)_3Si\}(Ph_2PCH_2CO)(C_5H_4)Fe(cp)]_2\}$ [15]

There are two derivatives which contain six metal atoms, Cd_3Fe_3 [20] and Cd_2Zr_4 [21]. The former consists of nearly planar rings of alternating cis-$Fe(CO)_4$ and (bpy)Cd units. The ring is distorted from 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 equivalent within experimental error (264.0(5) pm). The Cd-Fe-Cd angles vary from 138.81(15)° to 148.40(15)° and the Fe-Cd-Fe angles vary from 94.78(14)° to 102.04(16)°. The structure of the second compound [21] is shown in Figure 5. It is a centrosymmetric dimer composed of two triangular $[CdZr_2(\mu_3\text{-}OPr^i)_3(\mu\text{-}OPr^i)_2](OPr^i)_4]^+$ units linked by two chloride bridges. In each of these units cadmium interacts with a face-shared bioctahedral $Zr_2(OPr^i)_9^-$ moiety via two terminal and two bridging OPr^i groups of the unit. This leads to octahedral geometry at both cadmium(II) and zirconium(IV). The distortion around the cadmium is substantial, the geometry approaching that of bicapped

tetrahedral. The Cd-Zr and Zr-Zr distances of 335.3(1) and 331.3(1) pm, respectively, preclude any metal-metal bonding.

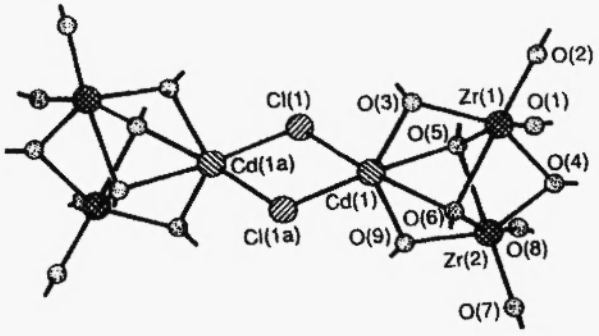

FIGURE 5. Structure of $\{Cd[Zr_2(Pr'O_9](\mu\text{-}Cl)\}_2$ [21]

There is one heptameric example ($CdFe_6$), and the structure is shown in Figure 6. The coordination of two Fe_3 units to a central cadmium atom is revealed, giving a rather unsymmetrical arrangement of four Fe atoms around the cadmium. The mean Cd-Fe bond distance is 274.3(2) pm, and the mean Fe-Fe distance is even shorter at 266.6(3) pm.

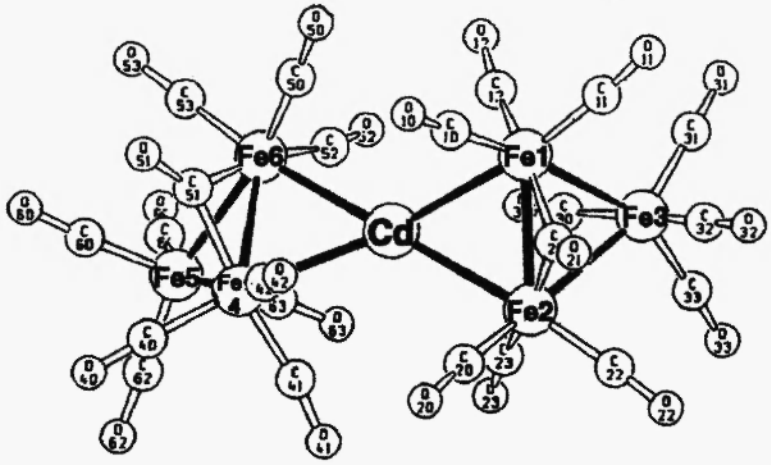

FIGURE 6. Structure of $[Fe_6Cd(CO)_{22}]^{2}$ [22]

A white heterooctanuclear cluster (Cd_4Sn_4) [23] is shown in Figure 7. The molecular unit includes a planar 8-membered ring of four cadmium atoms linked in pairs by single oxygen atoms of two acetate anions, each of which is also chelated to one or other of the cadmium atoms being bridged. The ring is completed by two oxo-groups, each linking a

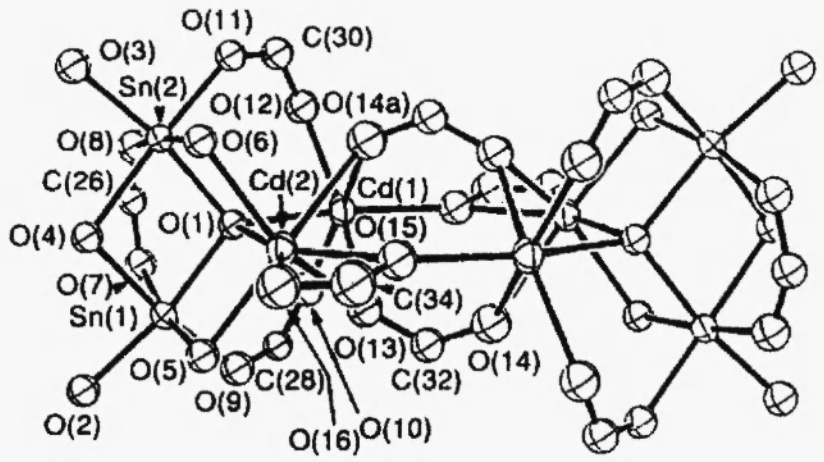

FIGURE 7. Structure of $[Cd_4Sn_4(\mu_4\text{-}O)_2(ac)_{10}(Bu^tCH_2O)_{10}]$ [23]

pair of cadmium atoms on opposite sides of the ring. Pairs of tin atoms are also bonded to the oxo groups, making them four coordinate.

The structure of a nine-member cluster ($Cd_3Ni_2Ge_4$) [24] is shown in Figure 8. The most interesting feature is the presence of metal-metal bonds which are not reinforced by bridging ligands. The nickel atom has a "piano-stool" coordination and an 18-electron shell. However, the Ge-Ni-Cd and Cd-Ni-Cd angles between the stool legs are decreased to about 86° (ideal 90°) due to the steric requirements of the cyclopentadienyl ligand. Each cadmium atom is digonal (Cd(1) linear and Cd(2) almost linear) with the Ni-Cd(2)-Ge angle of 170.3°.

Finally, there is a cluster with three cadmium and ten cobalt atoms [25]. A triangular Cd_3 core is capped with a $Co(CO)_3$ fragment and edge-bridged with three cluster carboxylate ligands. The mean Cd-Co and Cd-Cd distances are 257.3(1) and 298.0(1) pm, respectively.

The data of Table 1 indicates heterobi- to heterononameric and one heterotridecameric cluster arrangements. Cadmium is found in O and +2 oxidation states, with the latter being by far the most common, and one example of +1 [25]. The coordination sphere about cadmium ranges from two to six coordinate, with one example of seven coordination. The hetero-metal partners are usually non-transition metals, but transition metals are also included. The shortest Cd-M distance in this series is Cd-Ni at 245.9(2) pm [24], and the shortest M-M distance is found in the same cluster, Ni-Ge at 230.8(3) pm [24].

TABLE 1. Crystallographic and Structural Data for Dimeric, Trimeric, Tetrameric and Oligomeric Heterometallic Cadmium Compounds[a]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] ß [°] γ [°]	Chromophore	M-L [pm]	M-M [pm] M-L-M [°]	L-M-L [°]		Ref
A. DIMERIC									
Me_2CdZn^{II}-	m	682.4(3)		MSe_3C	μSe[b] 271.2(4,30)		$\mu Se,\mu Se$[b]	92.9(4)	5
	$P2_1/n$	1401.3(4)	93.70		Se 257.5(4)	87.1	μSe,Se	80.3(4,5.2)	
$(Et_2NCSe_2)_2$	2	1103.1(3)			C_{Me} 202.1(10)		μSe,C	123.2(3,8.7)	
							Se,C	134.9(3)	
(colourless)									
$I_2Cd(\mu\text{-}1)_2$-	m	1069.4(5)		CdI_4	I 270.5(2,0)		I,μI	109.9(1,8.7)	6
	$P2_1/c$	1379.4(7)	96.25(5)		μ1 287.4(1,8)	87.3(1,0)	μI,μI	96.3(1)	
$Hg^{II}(PPr_3)_2$	?	2241.5(9)		$Hg_2P_2I_2$	P 241.7(4,7)		P,P	152.8(1)	
					μI 306.7(1,11)		I,1	88.6(1)	
(colourless)							P,1	99.6(1,3.2)	
B. TRIMERIC									
$(NMe)_4\{Na[Cd$-	tr	1102.6(1)	94.32(1)	CdS_5	S 248.9(2,4)	355.7(1)[c]	S,S	118.3(1,7.6)	7
	Pī	1188.6(2)	113.25(1)	(O_3)	252.1(2)				
$(PhCOS)_3]_2\}$	1	1090.6(1)	71.53(1)		O 274.9(5,90)				
				NaO_6	O 230.3(4,0)		O,O	90.0(2,11.3)	
(orange yellow)					245.1(5,20)				
{(diglyme)Cd-	m	1016.1(10)		CdO_3Mn_2	O 254.1(7)		O,O	63.5(3,4)	8
	$P2_1/n$	2301.0(20)	91.80(2)		265.0(7,47)			126.6(3)	
$\{Mn(CO)_5]_2\}$	4	971.8(9)			Mn 271.0(2,4)		Mn,Mn	135.9(1)	
							O,Mn	103.8(2,12.3)	
(orange)				MnC_5	OC 178.8(11,33)		C,C	92.9(6,7.2)	
								167.0(6,7.8)	
{(2,2'-bpy)Cd-	m	1442.9(15)		CdN_2Mn_2	N 235.4(9,5)		N,N	69.2(4)[d]	9
	$P2_1/n$	1580.5(16)	94.62(2)		Mn 268.3(3,3)		Mn,Mn	127.7(2)	
$[Mn(CO)_5]_2\}$	4	1042.3(10)					N,Mn	111.3(3,1.5)	
				MnC_5	OC 178.2(16,42)		C,C	93.4(7,8.2)	
(orange)								164.4(7,7.2)	

Table 1 Continued 2

{(phen)Cd- $[Mn(CO)_5]_2$} (orange)	m $P2_1/n$ 4	1457.4(15) 1625.8(16) 1045.3(10)	96.87(2)	CdN_2Mn_2 MnC_5	N Mn OC	236.2(14,20) 268.1(4,6) 177.5(22,46)		N,N Mn,Mn N,Mn C,C	69.5(5)[d] 131.4(2) 109.8(4,2.6) 93.5(9,9.3) 164.1(9,7.9)	9
{(terpy)Cd- $[Mn(CO)_5]_2$} (red)	m $P2_1/c$ 4	915.8(15) 1889.5(26 1696.0(17	111.38(9)	CdN_3Mn_2 MnC_5	N Mn OC	245.8(14,53) 278.0(5,20) 179.5(22,41)		N,N Mn,Mn N,Mn C,C	66.5(5,3)[d] 132.9(5) 132.4(2) 104.1(4,11.4) 93.4(9,13.6)	10
{Cd[$(MeO)_3Si$}- $(CO)_3Fe$- $(\mu$-$Ph_2Ppy)]_2$}	m C2/c 4	2968.4(8) 1004.3(3) 2098.8(6)	91.87(2)	CdN_2Fe_2 FeC_3PSi	N Fe OC P Si	249.3(3) 269.70(5) 175.8(5,10) 221.8(1) 228.6(1)		N,N Fe,Fe N,Fe C,C C,P C,Si P,Si	80.7(1) 143.45(3) 101.8(1,12.7) 104.9(2,7) 146.9(2) 94.9(1,4.3) 84.3(1,1.9) 173.2(5)	11
$CdZn^{II}_2(crot)_6$- $(qu)_2$ (colourless)	m $P2_1/c$ 2	1074.02(5) 1187.31(5) 1783.51(7)	98.966(4)	CdO_6 ZnO_3N	μO O μO O N	231,4(2,0) 224.2(3,30) 196.3(2) 194.6(3,6) 202.2(3)	103.2(1)	O,O O,O O,N μO,N	89.3(1,4) 107.5(1,5.1) 101.8(1,6) 129.4(1)	12
[Cd{Ge^{II}- $(Bu^tO)_3\}_2$] (colourless)	or Pnma 4	1995.6(15) 1693.2(13) 984.5(7)		CdO_3 GeO_3	μO μO	233(1) 189,3(9)	298.4(3)[c]	O,O O,O	66.8(3) 85.1(3)	13
[Cd{Sn^{II}- $(Bu^tO)_3\}_2$] (colourless)	or Pnma 4	1099.1(13) 1772.7(11) 997.6(9)		CdO_6 SnO_3	μO μO	234(1) 208.0(9)	312.1(3)[c]	O,O O,O	70.5(2) 81.1(2)	13

Table 1 Continued 3

C. TETRAMERIC

[(Ph$_3$Si)-	tr	1048.9(5)	75.51(3)	CdBr$_2$Fe	μBr	260.4(2)	371[e]	Br,Br	90.9	11
	Pi	1268.6(4)	86.58(5)			268.9(2)		Br,Fe	127.58(8)	
(Ph$_2$HP)(CO)$_3$Fe-	1	1515.5(7)	72.94(5)		Fe	254.0(3)			139.9	
				FeC$_3$PSi	OC	174(3,4)		C,C	102.4(8,4.3)	
Cd(μ-Br)]$_2$					P	223.7(5)			151(1)	
					Si	236.4(5)		C,P	94.3(6,8.0)	
								C,Si	84.4(5,2.5)	
								P,Si	172.5(2)	
[CdFe(CO)$_4$]$_2$	m	629.2(4)		CdFe$_2$	Fe	256.3(2,4)		Fe,Fe	170.2(1,0)	14
	P2$_1$/n	1056.6(6)	97.80(3)						189.85(5)	
	2	2601.4(13)		FeC$_4$	OC	177.9(10,10)		C,C	98.2(4,2.2)	
									154.7(4,2)	
[(CO)$_3$Fe-	m	2539.2(5)		CdO$_2$Cl$_2$Fe	O	258(1,12)		Cl,Cl	88.7(1)	15
	C2/c	1855.4(6)	120.73(3)		μCl	254.2(4,35)		O,Fe	74.2, 93.5(2)	
{(EtO)$_3$Si}-	4	1628(1)			Fe	258.5(4)		Cl,Fe	122.1, 148.8(1)	
				FeC$_3$PSi	OC	174(2,2)		P,Cd	94.0(2)	
{Ph$_2$PCH$_2$C(O)Ph}-					P	222.1(2,2)				
					Si	230.4(5)				
CdCl]$_2$										
(yellow)										
[(CO)$_3$Fe-	m	2245.5(3)		CdO$_2$Cl$_2$Fe	O	246.5(5,51)		O,O	157.5(2)	15
	C2/c	1768.0(2)	90.80(4)		μCl	254.3(2,31)		Cl,Cl	90.93(6)	
{(MeO)$_3$Si}-	4	1662.7(4)			Fe	260.1(1)		O,Fe	76.6, 95.1(1)	
								Cl,Fe	121.4, 146.6(1)	
{Ph$_2$PCH$_2$C(O)Ph}-				FeC$_3$PSi	OC	177(1,0)		P,Cd	94.98(6)	
					P	222.7(1)				
CdCl]$_2$.PhCl					Si	230.2(2)				
(yellow)										
[{(MeO)$_3$Si}-	or	2349.8(9)		CdCl$_2$PFe	μCl	255.8(4,12)		Cl,Cl	86.4(1)	16
	Pbcn	1685.6(8)			P	279.6(4)	92.6(1)	Cl,P	102.2(1,2.0)	
(CO)$_3$Fe-	4	1822.0(8)			Fe	262.4(2)		Cl,Fe	132.3(1,2)	
								P	95.5(1)	
(μ-dppm)-				PeC$_3$PSi	OC	175.9(16,16)		C,C	102.1(7,3)	
					P	225.1(4)		C,P	96.9(5,7.1)	
Cd(μ-Cl)]$_2$					Si	228.6(5)		C,Si	83.4(5,2.5)	

Table 1 Continued 4

[$CdCl_2$-	tr	1209.4(4)	90.88(1)	$CdCl_3N_2$	μCl_{eq} 251.4(2)		$\mu Cl_{eq},\mu Cl_{eq}$ 126.1(1)		30
	Pī	1423.5(3)	95.77(1)		Cl_{eq} 241.9(2)		$\mu Cl_{eq},N_{eq}$ 88.0,		
(as-4C2N)PP-	1	1089.5(2)	83.04(1)		N_{eq} 233.0(6)		126.3(2)		
					μCl_{ap} 253.0(2)		$\mu Cl_{ap},N_{ap}$ 159.4(1)		
$Cr(CO)_4]_2$					N_{ap} 242.9(5)		N,N 77.6(2)[d]		
				CrC_4P_2	OC not given		94.9(1)		
					P 237.6(2,3)		P,P 69.1(1)[g]		
[$Cu^{II}_2(phen)_2$-	tr	1223.8(2)	92.95(3)	CdO_3	μO 226.6(3,2)	335.5[c]	$\mu O,\mu O$ 82.8(1,1.3)		17
	Pī	1270.7(5)	104.45(2)		232.0(3,8)	349.3[e]	161.1(1)		
$(ttftch)_2Cd_2$-	1	1185.3(3)	63.41(2)		O 229.8(3,4)	573.1[f]	$\mu O,O$ 98.2(2,6.9)		
							173.7(2,1.0)		
$(hfacac)_2]$.				CuO_2N_2	μO 192.7(3,1)		O,O 91.0(1)		
					N 200.0(3,2)		N,N 82.0(1)[d]		
2MeCN							O,N 93.3(1,1)		
(blue)									
$Et_4Sb^{II}_2Cd_2I_4$	tr	817.9(2)	77.80(2)	CdI_2Sb	I		I,I 122.0(1,2.0)		18
	Pī	891.3(2)	85.13(2)		275.1(2,16)		I,Sb 117.2(1,9.0)		
(light yellow)	2	1622.0(2)	79.23(2)	SbC_2Sb	Sb 282.2(2,1)		C,C 103.1(9,8)		
					EtC				
					217.4(24,5)				
					Sb 278.4(2)				
[{Li(thf)}$_3$-	or	2387.5(5)		$CdBr_3C$	μ_3Br 271.8(1,1)		Br,Br 92.7(1,8)		19
	Pnam	1226.1(6)			C 219.9(10)	82.1(3,2.1)	Br,C 122.5(1,2.0)		
Cd{$(Me_3Si)_3C$}-	4	1499.0(5)		LiO_2Br_2	μ_3O 185(2,4)		Br,Br 97.9(8,3.1)		
					μ_3Br 256.2(14,6)	63.5(7,6)	O,O 129.5(8,5)		
$(Me_3SiO)Br_3$]					266(2)				
					197(3,2)				
(colourless)									
D. OLIGOMERIC									
{Cd[Fe{$(MeO)_3$	or	1901.0(4)		CdO_2Fe_2	O 254.1(5,0)		O,O 111.8(3)		15
	Pbcn	1176.6(5)			Fe 261.2(1,0)		Fe,Fe 160.08(4)		
Si}(Ph_2PCH_2CO)	4	2699.8(7)					O,Fe 76.7, 115.1(4)		
				FeC_3PSi	OC 176.9(7,15)		P,Cd 98.54(5)		
$(C_5H_4)Fe(cp)_2$}					P 225.3(2)				
					Si 228.9(2)				
				FeC_{10}	not given				

Table 1 Continued 5

[(2,2'-bpy)Cd-$Fe(CO)_4]_3$·$\frac{1}{4}C_6H_3Cl_3$	tg P4 2	2904.9(10 - 1324.1(5)		CdN_2Fe_2	N 237.3(18,46) Fe 264.0(5,10)		N,N Fe,Fe N,Fe	68.9(7,6)[d] 142.3(1,6.1) 105.5(5,6.9)	20
				FeC_{15}	OC 173(3,7)		C,C	92.8 - 141.8(15)	
$\{Cd[Zr^{IV}_2(Pr^iO)_9]$ $(\mu\text{-Cl})\}_2$ (colourless)	m $P2_1/n$ 2	1251.2(1) 1946.2(3) 1642.5(1)	93.25(1)	CdO_4Cl_2	μ_3O 240.2(4,42) μO 235.7(4,5) μCl 255.8(2,4)	335.3(1,2)[c] 331.3(1)[f]	O,O O,Cl	71.2(1,2) 134.3(1) 106.5(1,1.3) 171.0(1,4)	21
				ZrO_6	μ_3O not given μO not given θ not given				
$(ppn)_2[Fe_5$- $Cd(CO)_{22}]$	tr M 1	1205.4(5) 1443.9(4) 2662.3(7)	90.60(2) 91.56(3) 97.54(3)	$CdFe_4$	Fe 274.3(2,10)		Fe,Fe	57.9(1,1)	22
				FeC_4	μOc not given OC not given	266.6(3,20)[f]	Cd,Fe Fe,Fe	61.1(1,3) 60.0(1,7)	
$[Cd_4Sn^{IV}_4$ $(\mu_4\text{-O})_2(ac)_{10}$ $(Bu^tCH_2O)_{10}]$ (white)	m C2/c 4	2531.6(15) 1507.6(7) 2822.1(10)	98.16(4)	CdO_6	μ_4O not given μO_{ac} 225.6(20) O_{ac} 230.1(20)	μ_3O 124.5(1) μ_3 90.3(7)	O,O	166.8(6)[h]	23
				CdO_7	μ_4O not given μO_{ac} 234.6(18) O_{ac} 231.0(18)	128.7(8)	O,O	54.7(7)[g] 82.4, 106.4 148.9(6)	
				SnO_5	μ_4O not given μO 206.9(16,35) O_{ac} 212.5(17,61) O 196.5(19)	μ_3O 103.4(7) μ_3 97.7(7)	O,O	87.5(6)	
[{$(GePh_3)_2Cr$- $Ni(cp)\}_2Cd]$	m $P2_1/n$ 2	1332.4(7) 1883(1) 1486(1)	90.55(5)	$CdNi_2$	Ni 247.5(2,0)		Ni,Ni	180	24
				CdGeNi	Ge 258.7(2) Ni 245.9(2)		Ge,Ni	170.31(8)	
				$NiC_{10}Ge_2$	C_{cp} 207(2) Ge 230.8(3)		Ge,Cd	86.46(8)	
				GeC_3Cd	C_{Ph} 196(2,5)		C,Cd	112.8(5,2.9)	
				GeC_3Ni	C_{Ph} 195(2,1)		C,Ni	115.7(5,3.9)	

Table 1 Continued 6

$\{[\mu_3\text{-}Co(CO)_3]\text{-}Cd^I{}_3\{\mu\text{-}[(CC)_9Co_3(\mu_3\text{-}CCO_2)]\}_3\text{-}(thf)_3\}$	tr	1261.5(1)	100.04(1)	CdO_3	O	not given	257.3(1,7)[c]	not given	25
	Pī	1269.0(2)	90.33(1)	CoO_3	O	not given	298.0(1,3)[e]		
	2	2548.7(2)	117.60(1)	CoC_5	O	not given			
					μ_3C	not given			

Footnotes:
a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.
b. The chemical identity of the coordinated atom or ligand is specified in these columns.
c. The Cd-M distance.
d. Five member metallocyclic ring.
e. The Cd-Cd distance.
f. The M-M distance.
g. Four member metallocyclic ring.
h. Sn-μ_4O-Cd = 124.3(8)°; Sn-O-Cd = 102 9(7,1)°.

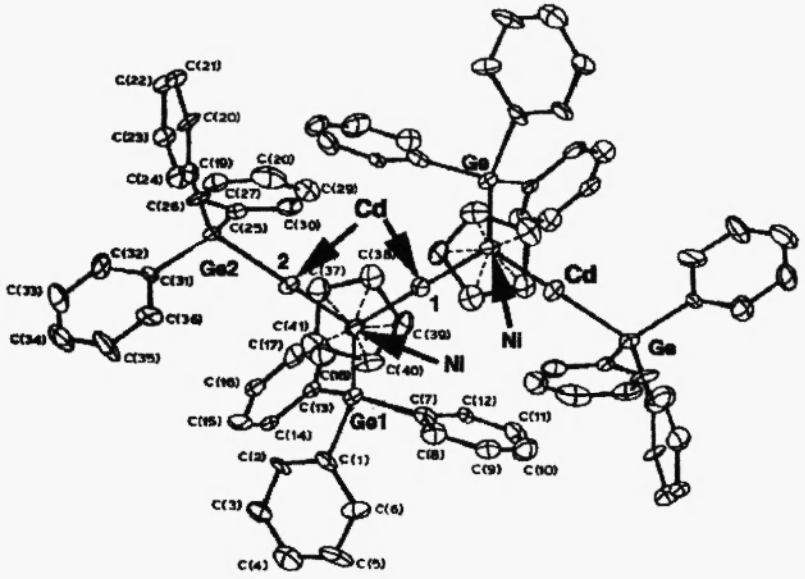

FIGURE 8. Structure of [{$(GePh_3)_2CdNi(cp)_2Cd$] [24]

6. HETEROPOLYMERIC COMPOUNDS.

Crystallographic and structural data for almost sixty heteropolynuclear cadmium derivatives are listed in Table 2. The structure of $Li_2Cd(EtCO_2)_4$ [26] consists of a central sheet with only cadmium(II) and oxygen atoms. Organic moieties are found outside of and between the sheets. The Cd(II) atom is on a crystallographic centre of symmetry and is bonded to six propionate oxygen atoms. Each lithium has a distorted LiO_4 tetrahedral environment, and are joined in pairs by oxygen atoms to form unsymmetrical Li_2O_2 parallelograms.

There are four derivatives which contain hexa- or heptadentate ligands [27,31-33]. The structure of $[(H_2O)_6Mg(edta)(H_2O)Cd].3H_2O$ [27] consists of ions linked by hydrogen bonds. There are two independent sets of Mg(II) atoms located on inversion centres separated by 0.5a and displaying a distorted octahedral coordination. The Cd(II) atom is coordinated to a water molecule and a hexadentate edta ligand, giving a pentagonal bipyramidal environment.

A second derivative, $[Cd(edta)Mn(H_2O)_4].2H_2O$ [31] consists of infinite chains of Mn(II) and Cd(II) coordination polyhedra running parallel to the x-axis. The Mn(II) atom displays octahedral coordination, being linked to four water molecules and two oxygen atoms of two edta ligands. The Cd(II) atom is heptacoordinated (pentagonal bipyramid) with four oxygen atoms and two nitrogen atoms of one edta ligand, and one O atom of a second

edta ligand. These ligands act as bridges between the Mn..Cd and Cd..Cd metal atoms. Each Cd coordination polyhedron is bridged to another Cd and two Mn coordination polyhedra, while the two Mn(II) atoms act as bridges between two Cd coordination polyhedra. A similar structure was observed for $[Cd(cdta)Mn(H_2O)_4]$ [32], where the heptadentate cdta ligand serves as a bridge. The coordination about Cd and Mn is pentagonal-bipyramidal and pseudo-octahedral, respectively.

Considerable attention in cadmium chemistry has been given to "Hoffmann-type" clathrates of the composition $Cd(LN)_xNi(CN)_4.nG$ (where x = 1 or 2, and G is guest molecule(s)). The structures of these essentially yellow clathrates are complex [35-63]. For example, in the orange derivative $Cd(2,2'\text{-bpy})Ni(CN)_4$ [45], the $Ni(CN)_4^{-2}$ ion bridges four Cd(II) atoms to form an infinite two-dimensional folded network stacking along the b-axis. The 2,2'-bipyridine ligands chelate to the Cd(II) atoms alternately above and below the folded network. In $Cd(en)Ni(CN)_4.2C_6H_6$ [46] the Cd(II) and Ni(II) atoms are linked crosswise with the cyanide groups on the (001) plane to form the layers of the polymeric metal cyanide complex $[CdNi(CN)_4]_n$ which are stacked along the c-axis. Each ethylenediamine molecule bridges between two cadmium atoms in the adjacent layers to make a three-dimensional host lattice. The benzene molecules are enclathrated in the cavities formed by the host lattice.

In this series a pseudo-octahedral coordination about each Cd(II) atom is built up by four N atoms of the CN groups, and by two N atoms of the respective ligands. An almost square-planar environment about each Ni(II) atom consists of four C atoms of the CN groups. It is noted that the "soft" Cd(II) atom takes the "hard" N-atom, while the borderline Ni(II) atom takes the "soft" C atom of the cyanide groups. The Cd-N(cyanide) bond distances range from 223.6 to 245.4 pm (mean 235.4 pm). The mean value of 235.4 pm is about 3.1 pm longer than that found in the homonuclear cadmium derivatives [2]. The Cd-N(monodentate amine) and Cd-N(bidentate amine) distances range from 227.0 to 236.5 pm (mean 232.6 pm) and from 224.5 to 247.4 pm (mean 232.0 pm), respectively. The mean values of 234 and 239 pm found in the homopolynuclear cadmium derivatives [2] are, by contrast, longer than those in the present derivatives.

There is a relationship between the mean Cd-N(chelate) distance and the N-Cd-N intrametallocyclic, five-membered, ring angle. When the distance increases, the angle opens. The data for heteropolynuclear versus homopolynuclear cadmium derivatives are 232 pm and 72.6° versus 239 pm and 74.8°, respectively.

In a dark red derivative [64], shown in Figure 9, palladium centres are square-planar. All porphyrin moieties are equivalent, and all four pyridyl units of the porphyrin are bound to essentially octahedral cadmium centres, which are coordinated by two trans monodentate nitrate ligands, two water molecules and two pyridyl units. Infinite linear strips, consisting of porphyrins interconnected by linear cadmium atoms, are indicated in Figure 9b.

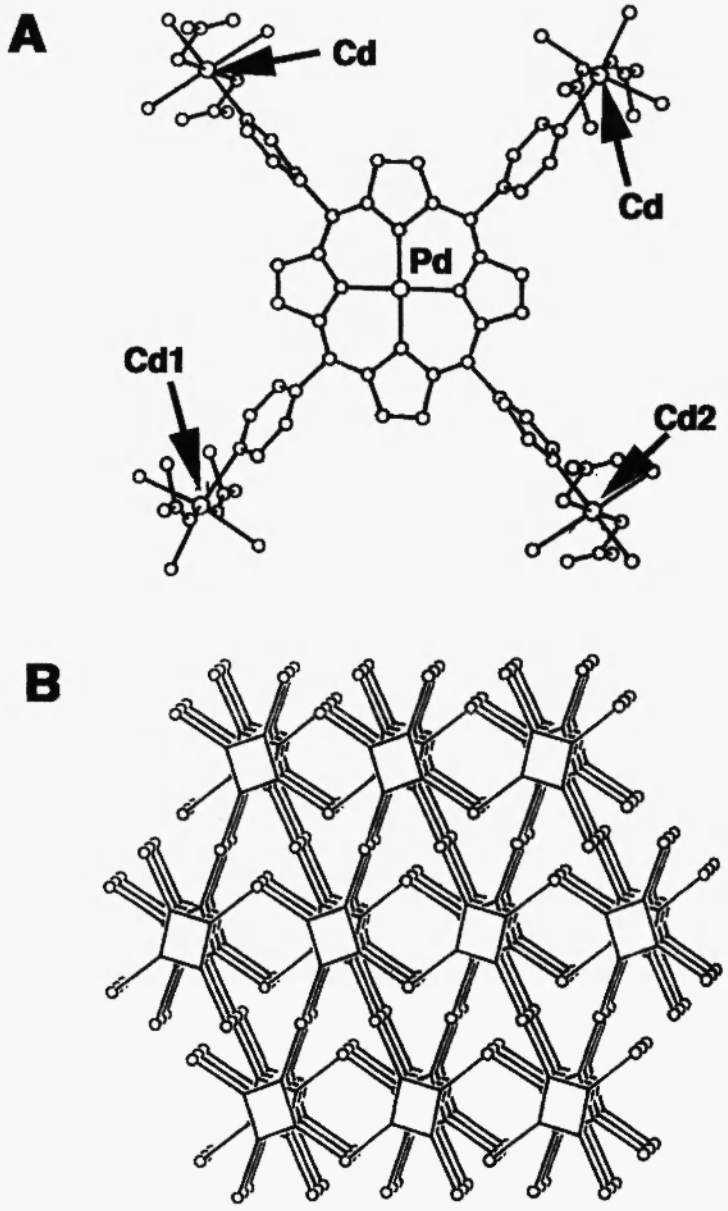

FIGURE 9. Structure of Pd(py-porph).2Cd(NO$_3$)$_2$.H$_2$O [64]

All metal atoms of one strip are coplanar, but deformations within each $Cd_4Pd.py.porph$ moiety lead to the individual macrocyclic $C_{20}N_4Pd$ systems being significantly inclined (6°) to the plane of the strip.

TABLE 2. Crystallographic and Structural Data for Heteropolymeric Cadmium Compounds[a]

COMPOUND (colour)	Cryst. Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	Cd-L		L-Cd-L [°]		Ref
						[pm]			
$Li_2Cd(EtCO_2)_4$	tr	752.6(1)	94.85(2)	CdO_5	O^b	231.6(1,8)	O,O^b	90.0(1,4.6)	26
	P$\bar{1}$	1129.6(2)	98.04(2)		O	226.2(2,0)		108.7(1,1.3)[c]	
(colourless)	1	492.5(1)	78.97(2)	LiO_4	μO	192.5(4,35)	O,O	109.5(3,18.1)	
						204.5(4)		88.7(2)[d]	
$[(H_2O)_6Mg(edta)(H_2O)Cd].$	tr	2059.4(4)	102.25(3)	CdO_5N_2	O_{eq}	242.7(8,31)	O_{eq},O_{eq}	97.0(4,9.6)	27
	P$\bar{1}$	775.5(2)	102.01(3)		N_{eq}	239.8(8,16)	O_{eq},N_{eq}	71.2(2,6)[e]	
$3H_2O$	2	761.9(2)	82.52(4)		H_2O_{eq}	224.5(9)		98.0(3,4.4)	
(colourless)					O_{ap}	235.3(9,17)		148.6(4)	
							O_{ap},O_{ap}	165.1(2)	
				MgO_6	H_2O	207.7(15,41)			
				MgO_6	H_2O	208.1(17,43)			
$[CdCa(ac)_4(H_2O)_2].4H_2O$	tg	1137.4		CdO_8	μO	267.7(8,0)	μO,μO	66.3(2)	28
	I4/m	–			H_2O	228.9(7,0)	O,O	90.7(2)	
(colourless)	4	1608.4		CaO_6	μO	230.5(9,0)	μO,μO	78.8(3)	
					O	235.6(9,10)		101.2(3)	
$[Ba_2Cd(SCN)_6(H_2O)_4].3H_2O$	m	943.6(3)		CdS_6	S	268(1) x2	S,S	90.0(1,3.8)	29
	$P2_1/c$	1469.7(3)	109.02(7)			272(1,1)		180.0(2,0)	
(colourless)	4	1827.1(6)		OdS_6	S	269(1,1)	S,S	90.0(1,1.8)	
						275(1) x2		180.0(2,0)	
				BaN_5O_4	N	294(1,19)			
					H_2O	281(1,15)			
$[Cl(edta)Mn^{II}(H_2O)_4].2H_2O$	tr	1085.2(3)	96.44(4)	OlO_5N_2	O_{eq}	235.8(4,118)	O_{eq},O_{eq}	80.4(2,10.0)	31
	P$\bar{1}$	1053.5(3)	103.35(3)		H_{eq}	242.0(5,4)	N_{eq},N_{eq}	75.4(2)[e]	
(colourless)	2	923.3(2)	102.83(3)		O_{ap}	232.4(4,17)	O_{eq},N_{eq}	69.7(1)[e]	
								130.6(1,1.3)	
								152.4(2)	
							O_{ap},O_{ap}	167.9(2)	
				MnO_6	O	218.4(4,21)	O,O	90.0(2,5.7)	
					H_2O	221.0(5,51)		172.8(2,1.3)	
$[CdMn^{II}(cdta)(H_2O)_4].3H_2O$	m	1123.3(9)		CdO_5N_2	μO	233.9(9,1)	O,O	70.8 - 165.9(3)	32
	$P2_1/n$	933.8(8)	103.10(7)		O	233.1(9,21)	N,N	76.5(4)[e]	
(colourless)	4	2252.8(10)			N	240.6(10,3)	O,H	70.7(3,1.1)[e]	
								94.5 - 152.6(3)	
				MnO_6	μO	222.1(9,17)	O,O	88.3(4,16.8)	
					H_2O	219.0(10,36)		161.7(3)	
								176.8(3,9)	

Table 2 Continued 2

$CdMn^{II}(egta)(H_2O)_8$	m	1547(3)		CdO_3	not given			33
	$P2_1/c$	963.3(9)	108.2(1)					
(white)	4	1886(3)		MnO_6	not given			
$Cd[Fe(CN)_5NO].3H_2O$	m	742.5(2)		CdN_5O	CN 231.4(3,35)	N,N	91.1(1,2.6)	34
	$P2_1/n$	1496.3(2)	91.64(2)		H_2O 233.5(2)		175.4(1,1.2)	
	4	1084.8(3)				N,O	87.8(1,5.0)	
							170.5(1)	
				FeC_5N	NC 194.2(3,9)	C,C	87.6(1,2.9)	
					ON 166.7(3)		171.9(1)	
						C,N	94.5(1,1.8)	
							177.2(1)	
$\{Cd(NH_3)_2Ni(CN)_4\}.2C_6H_6$	tg	757.5(6)		CdN_6	H_3N 231(2)	not given		35
	P4/m	-			CN 234(2)			
(yellow)	1	831.7(5)		NiC_4	NC 185(2)			
$[Cd(NH_3)_2Ni(CN)_4].2C_4H_3O_2$	tg	758.6(9)		CdN_6	H_3N 232	not given		36
	P4/m	-			CN 235			
(yellow)	1	808.2(6)		NiC_4	CN 181			
$[Cd(Me_2NH)_2Ni(CN)_4].o\text{-tld}$	or	2632(1)		CcN_6	not given			37
	Pmma	761.4(9)						
	4	1036.4(1)		NiC_4	not given			
$[Cd(Me_2NH)_2Ni(CN(_4].m\text{-tld}$	m	1466.7(7)		CdN_6	not given			37
	P2/m	761(1)	115.52(6)					
	2	1036.9(8)		NiC_4	not given			
$[Cd(Me_2NH)_2Ni(CN(_4].p\text{-tld}$	tr	1461(2)	94.2(1)	CdN_6	not given			37
	Pī	761(2)	118.2(1)					
	2	1063(1)	89.9(1)	NiC_4	not given			
$[Cd(Me_2NH)_2Ni(CN(_4].\frac{1}{2}C_6H_6$	m	1541.8(7)		CdN_6	not given			38
	$P2_1/a$	1410.0(6)	96.56(5)					
	4	756.6(1)		NiC_4	not given			
$CdNi(CN)_4(4\text{-}Clpy)(NH_3)$	or	1249.0(3)		CdN_5	H_3N 227(2)	N,N	90(2,5)	39
	$Ima2_1$	1423.8(8)			N_{Py} 234(2)			
(yellow)	4	770.5(5)			CN 236.5(50,15)			
				NiC_4	NC 181.5(50,85)	C,C	90(3,8)	
$[CdNi(CN)_4(2\text{-}NH_2\text{-}3Mepy)\text{-}$	or	1353.5(1)		CdN_6	H_3N 231.7(6)	N,N	90.0(2,2.7)	40
	$Pna2_1$	1360.7(1)			N_{Py} 236.5(4)		179.4(2,2)	
$(NH_3)]$	4	764.5(1)			CN 235.7(17,59)			
(white)				NiC_4	NC 186.9(16,34)	C,C	90.0(8,1.5)	

Table 2 Continued 3

$[ClNi(CN)_4(2\text{-}NH_2\text{-}3Mepy)\text{-}(NH_3)]$ (white)	or Pnma 4			CdN_6 NiC_4	H_2N N_{py} CN NC	231.0(3) 236.5(3) 236.3(2,3) 186.5(2,2)			41
$Cd(py)_2Ni(CN)_4$ (yellow)	m C2/m 2	1588.1(4) 754.0(6) 709.7(9)	106.50(5)	CdN_4 NiC_4	N_{py} CN NC	232 233 180	N,N	88.3	42
$[Cl(men)Ni(CN)_4].pyrrole$ (yellow)	or $Pna2_1$ 4	1469.1(1) 1588.1(1) 757.5(1)		CdN_4 NiC_4	N_{mea} CN NC	229.5(6) 237(7,45) 186.5(7,20)	N,N C,C	90.0(2,5.7) 90.0(3,3)	43 44
$[Cd(mea)Ni(CN)_4].C_4H_4S$	or $P2_12_12_1$ 4	1458 1634 759		CdN_6 NiC_4					43
$[Cd(mea)Ni(CN)_4].2C_5H_6$	tg P4/mmm 1	752.9(1) – 809.4(1)		CdN_6 NiC_4	N_{mea} CN NC	231(1) 234.6(4) 186.5(4)	N,N not given	90.0(3,8.9)	43 44
$Cd(2,2'\text{-}bpy)Ni(CN)_4$ (orange)	m C2/c 4	679.0(1) 1723.8(1) 1246.4(1)	91.14(1)	CdN_6 NiC_4	N CN NC	233.6(3,0) 227.3(3,0) 239.2(3,0) 186.3(3,7)	N,N C,C	70.4(1)* 93.2(1,10.4) 165.1(2,2.8) 90.0(1,2)	45
$[Cl(en)Ni(CN)_4].2C_5H_5$ (pale yellow)	tg P4/m 1	767.5(3) – 1805.6(10)		CdN_6 NiC_4	N_{en} CN NC	226(4,0) 239(2) 186(2,0)	not given		46
$Cd(en)Ni(CN)_4$ (yellow)	or Pbna 4	1019.8(3) 1122.9(2) 903.8(2)		CdN_6 NiC_4	N_{en} CN NC	231.8(5,0) 230.9(5,0) 237.8(7,0) not given	N,N	70.4(2)* 99.2(2)	47
$[Cd(en)Ni(CN)_4].2pyrrole$ (yellow)	or Pmmm 1	761.8(3) 764.1(10) 786.1(4)		CdN_6 NiC_4	N_{en} CN NC	225(3) 240 187(1)	not given		48
$[d(en)_2Ni(CN)_4].2PhNH_2$ (yellow)	m $P2_1/c$ 2	992.4(2) 1054.5(3) 1251.0(1)	107.63(1)	CdN_5 NiC_4	N_{en} CN NC	232.9(5,16) 245.4(5,0) 186.0(7,11)	N,N C,C	77.6(2)* 89.6(2,1.6) 88.3(3)	49
$[\{Cd(en)\}_2(en)\{Ni(CN)_4\}_2]$ .4PhOH (yellow)	tr Pī 1	1186.8(1) 1303.0(1) 771.13(6)	105.956(7 94.951(8) 91.584(9)	CdN_6 NiC_4 NiC_4	N_{en} CN NC NC	233.8(4,13) 236.6(4,53) 186.2(4,7) 186.9(5,0)	N,N C,C C,C	76.2(2)* 90.4(2,10.3) 170.3(2,2.5) 90.6(2) 89.2(2)	49

Table 2 Continued 4

[Cd(1,2-pn)Ni(CN)$_4$]G[g]	or	-1400		CdN_6	not given				50
	Pnma	~2670							
(yellow)	8	- 760		NiC_4	not given				
[Cd(1,2-pn)Ni(CN)$_4$]G[g]	m	-1400		CdN_5	not given				50
	A2/a	-2680							
(yellow)	4	- 760	~90.0	NiC_4	not given				
[Cd(1,2-pn)Ni(CN)$_4$].	tg	757.5(2)		CdN_5	N not given				51
	P422	-			CN 235(2)				
1⅓pyrrole (yellow)	1	774.2(2)		NiC_4	NC 184.0(6)				
[Cd(1,2-pn)Ni(CN)$_4$].	tg	757.0(2)		CdN_5					51
	P4/mmm	-							
1¼pyrrole (yellow)	1	774.1(4)		NiC_4					
[Cd(mtn)Ni(CN)$_4$].½C_6H_{12}	tg	1420.9(2)		CdN_6	N 235.8(5,0)	N,N	90.0(2,8.6)		52
	P4/mbm	-			CN 233.0(5,8)				
(yellow)	4	787.6(1)		NiC_4	NC 186.9(5,4)	C,C	91.7(2)		
[Cd(1,4-bn)Ni(CN)$_4$].	m	784.0(4)		CdN_5	N 232.3(5)	N,N	90.4(1,1.7)		53
	P2/m	763.4(2)	90.15(6)		CN 253.3(4)				
pyrrole (yellow)	1	706.0(2)		NiC_4	NC 184.8(4)	C,C	90.0(2,7)		
[Cd(1,4-bn)Ni(CN)$_4$].	tr	977.4(3)	90.41(4)	CdN_5	N 229(1,2)	N,N	90.0(3,4.5)		53
	P1	1391.8(8)	90.43(5)		CN 237.6(9,23)				
1½aniline (yellow)	2	771.5(4)	93.18(4)	NiC_4	NC 185(1)	C,C	90.0(3,4.0)		
[Cd(1,4-bn)Ni(CN)$_4$].	m	986.0(5)		CdN_5	N 229.4(7,21)	N,N	90.0(2,4.0)		53
	$P2_1/m$	1526.7(6)	113.92(4)		CN 236.4(5,11)				
Me_2aniline (yellow)	2	730.9(4)		NiC_4	NC 187.2(5,1)	C,C	90.0(2,8)		
[Cd(1,4-bd)Ni(CN)$_4$].	tr	980.6(3)	89.71(2)	CdN_5	N_{bd} 226.8(7,26)[h]	not given			54
	P1	1438.8(3)	89.96(2)		CN 238.1(5,14)[h]				
o-toluidine (yellow)	2	772.5(2)	98.12(2)	NiC_4	NC not given	not given			
[Cd(1,4-bd)Ni(CN)$_4$].	m	979.5(2)		CdN_5	N_{bd} 228.6(6,5)	N,N	90.1(2,4.1)		55
	$P2_1/m$	1501.0(2)	105.56(1)		CN 236.2(4,4)				
2,5-xylidine (yellow)	2	712.5(1)		NiC_4	NC 185.8(4,8)	C,C	90.0(2,7)		
[Cd(1,5-pd)Ni(CN)$_4$].	tg	748.5(7)		CdN_5	N_{bd} 226.8(7,26)[h]	not given			54
	P4/mmm	-			CN 238.1(5,4)[h]				
o-toluidine	1	1006(3)		NiC_4	NC not given				
[Cd(1,5-pd)Ni(CN)$_4$].	or	1225.4(6)		CdN_5	N_{bd} 226.8(7,26)[h]	not given			54
	Pbam	2062(1)			CN 238.1(5,4)[h]				
m-toluidine	4	780.4(1)		NiC_4	NC not given				

Table 2 Continued 5

[Cd(1,6-hd)Ni(CN)$_4$].	m	954.1(2)		CdN_6	N_{hd}	232.3(5)	N,N	90.3(1)	54
	$P2_1/m$	756.9(2)	100.3(1)		CN	235.7(3)			56
o-toluidine (yellow)	1	719.9(1)		NiC_4	NC	186.1(3)			
[Cd(1,6-hd)Ni(CN)$_4$].m-tld	tr	972.6(2)	89.56(1)	CdN_6	N_{hd}	232.3(3,2)	N,N	90.0(2,1.0)	57
	P$\bar{1}$	759.8(1)	98.81(1)		CN	235.3(2,1)			
(yellow)	1	717.7(1)	84.30(1)	NiC_4	NC	185.6(2,2)	C,C	90.4(2)	
[Cd(1,6-hd)(p-tld)-	m	1210.7(3)		CdN_6	N_{hd}	230.1(4,0)	N,N	90.0(2,5.2)	57
	$P2_1/n$	1011.7(2)	113.67(2)		N_{tld}	247.4(3,0)			58
Ni(CN)$_4$] (yellow)	2	1247.1(3)			CN	234.2(3,0)			
				NiC_4	NC	185.9(3,4)	C,C	87.6(2)	
[Cd(1,6-hd)Ni(CN)$_4$].	m	954.0(2)		CdN_6	N_{hd}	231.0(4,0)	N,N	90.0(2,1.6)	58
	$P2_1/m$	761.1(1)	100.95(1)		CN	234.4(3,0)			
p-tld (yellow)	1	712.0(1)		NiC_4	NC	185.7(3,0)	C,C	90.1(2)	
[Cd(1,6-hd)Ni(CN)$_4$].	m	962.8(2)		CdN_6	N_{hd}	231.4(3,0)	N,N	90.0(2,1.7)	58
	$P2_1/m$	761.3(1)	100.01(1)		CN	234.5(2,0)			
2,4-xylidine (yellow)	1	712.2(1)		NiC_4	NC	185.0(2,0)	C,C	90.2(1)	
[Cd(1,8-od)Ni(CN)$_4$].	m	1134.8(3)		CdN_6	N_{od}	230.6(4,0)	N,N	90.0(1)	59
	$P2_1/m$	765.2(8)	106.07(2)		CN	235.7(4,0)		180.0	
toluene (yellow)	1	704.2(1)		NiC_4	NC	185.9(4,0)	C,C	90.2(2)	
[Cd(1,8-od)Ni(CN)$_4$].	tr	1152(1)	88.93(4)	CdN_6	N_{od}	226.8(7,26)[h]	not given		54
	P$\bar{1}$	763.2(3)	109.71(5)		CN	238.1(5,44)[i]			
p-toluidine (yellow)	1	703.9(4)	82.81(9)	NiC_4	NC	not given			
[Cd(1,8-od)Ni(CN)$_4$].o-	m	1151.3(4)		CdN_6	N_{od}	226.8(7,26)[h]	not given		54
toluidine	$P2_1/m$	762.6(1)	109.63(3)		CN	238.1(5,44)[i]			
	1	710.1(1)		NiC_4	NC	not given			
(yellow)									
[Cd(1,8-od)Ni(CN)$_4$].	m	1147.0(2)		CdN_6	N_{od}	229.4(3)	N,N	90.0(2,3.3)	60
	$P2_1/m$	778.2(1)	105.29(1)		CN	235.4(3)			
hexanoi (yellow)	1	694.5(1)		NiC_4	NC	185.6(2)	C,C	91.6(2)	
[Cd(2,9-nd)$_2$Ni(CN)$_4$].	m	2917.0(2)		CdN_6	N_{nd}	234(2)	N,N	90.0(6,9.3)	61
	$P2_1/c$	905.13(5)	107.935(6		CN	238(2)			
2,3-xylidine (yellow)	4	1715.1(1)		NiC_4	NC	176(4)	C,C	90.0(-,3.0)	
						185(2)			
[Cd(2,9-nd)$_2$Ni(CN)$_4$].	m	2859(1)		CdN_6	N_{nd}	235.7(3,2)	not given		62
	C2/c	908.7(8)	106.08(4)		CN	239.4(3,0)			
2,4-xylidine (yellow)	4	1723.9(7)		NiC_4	NC	not given			

Table 2 Continued 6

$[Cd(2,9\text{-nd})_2Ni(CN)_4]$·	tr	1511.8(3)	91.50(2)	CdN_6	N_{nd}	233(1,0)	N,N	90.0(3,6.7)	63
	Pī	1404.8(4)	131.66(3)		CN	234(1,2)			
o-xylene	2	732.5(1)	107.50(2)	NiC_4	NC	186(1,1)	C,C	90.0(4,1.8)	
(yellow)									
$Pd(pyporph).2Cd(NO_3)_2$·	m	1652.0(9)		CdO_4N_2	O_2NO	not given	N,N	103(1)	64
	C2/c	3460(1)	112.40(6)		H_2O	not given			
H_2O	4	936.1(8)			N	not given			
(red)				PdN_4	N	not given	N,N	90	
$[Cd(H_2O)_3Cu^I(CN)_3]$.MeCN	m	1360.1(3)		CdN_6	CN	223.6(6)	not given		65
	C2/m	862.9(2)	107.90(2)			224.1(9)			
(colourless)	4	995.8(3)		CuC_4	μC	207.5(9)	μC,μC	107.3(4)	
						220(1)	C,C	114.5(3)	
					NC	194.4(6)	μC,C	108.6(3,3.2)	
								72.7(3)[d]	
$[CdCu^I_2(CN)_7][H_5(H_2O)_{14}]$	c	1294.01(9)		CdN_6	CN	not given			66
	$Pa\bar{3}$								
(colourless)	4			CuO_3C	not given				
$[Cd(4\text{-Mepy})_2\{Ag^I(CN)_2\}_2]$·	or	2599.0(9)		CdN_6	CN	not given			67
	Ibca	2694.5(15)			N_{py}	not given			
4-Mepy	16	1400.1(6)		AgC_2	NC	not given			
(colourless)									
$[Cd(4\text{-Mepy})_4\{Ag_2(CN)_3\}]$	m	1197.4(7)		CdN_6	not given				67
	C2/m	1907.8(11)	108.55(5)						
$[Ag(CN)_2]$	2	763.4(4)							
(colourless)									
$[Cd(NH_3)_2Hg(CN)_4].2C_6H_6$	tr	853.4(5)	90.5(1)	CdN_6	H_3N	238(-,3)	not given		68
	Pī	853.7(5)	89.2(1)		CN	234.5			
	2	1461.9(8)	89.3(1)	HgC_4	NC	220(-,1)			

Footnotes: a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.
b. The chemical identity of the coordinated atom or ligand is specified in these columns.
c. Cd-L-M bridge angle.
d. M-L-M bridge angle.
e. Five member metallocyclic ring.
f. Four member metallocyclic ring.
g. There are different aliphatic guest molecules. The parameters for monoclinic range are: a = 1389.7(6) - 1411.6(5) pm, b = 2683.9(4) - 2702.6(3) pm, c = 757.6(4) - 761.2(1), and γ = 88.88(3)° - 91.74(1)°: for orthorhombic, a = 1391.6(3) - 761.2(1) pm, b = 2663.8(2) - 2719.2(3), and c = 758.6(2) - 769.8(2) pm. h. For all six derivatives [54], only average values are given for: Cd-N(NC), range from 233.7(5) to 242.6(5) pm; and Cd-N(amine), range from 224.2(6) - 229.4(8) pm.

7. CONCLUSIONS

Almost ninety heterometallic cadmium compounds have been characterized by X-ray diffraction spectroscopy. Examples are found of heterobi- (2), -tri- (9), -tetra- (8), -penta- (1), -hexa- (2), -octa- (1), -nona- (1), -trideca- (1) and heteroploymeric (58) derivatives. Cadmium is found in the oxidation states of +1 and zero, but by far the most common is the oxidation state of +2. The geometries observed range from two to eight coordinate with the pseudo-octahedral, six coordination, predominating.

The shortest Cd-M bond distances for non-transition and transition metal partners are 230.8(2) pm (Ge) [24] and 245.9(2) pm (Ni) [24]. The shortest Cd-Cd bond observed is 298.0(3) pm [25]. Table 3 summarises Zn-M [3], Cd-M and Hg-M [2] distances in their respective heterometallic clusters, excluding any value which exceeds 300 pm. It should be noted that only the heterometals found with cadmium are included in Table 3. There are, in fact, more such examples in both zinc and mercury chemistry, three hundred and fifty (zinc) [3] and over two hundred (mercury) [71]. Comparing all three metals, the shortest bond to a non-transition metal is found with cadmium, Cd-Ge (above), while the shortest to a transition metal is found with zinc (Zn-Co = 229 pm).

TABLE 3. Summary of the Zn-M, Cd-M and Hg-M Distances[a]

METAL ATOM	Covalent Radius [pm]	Zn-M [pm] ref 3	Cd-M [pm] this study	Hg-M [pm] ref 71
Fe	120	255(1,3)	262(8,13)	265(14,31)
Ni	120		247(1,0)	255(11,13)
Co	126	254(25,24)	257	256(8,11)
Ge	137		298	251(3,2)
Mn	146		271(3,9)	262(4,4)
Cd	154		298	
Sb	159		282	

Footnotes: [a] The first number in parenthesis is the difference between the shortest value and the mean, and the second is the difference between the highest value and the mean.

This review is part of a series which includes zinc coordination compounds (over 500) [69], organozinc compounds (about 50) [3], cadmium coordination and organometallic compounds (over 600) [2], mercury coordination compounds (over 550) [70] and organomercury compounds (about 350) [71]. This represents an overview of structures in a non-transition metal subgroup, the zinc subgroup. In all of these reviews, there is a variation in the ease of availability and the completeness of the data. Some authors have not included bonding parameters about the central metal atom, metal-metal distances, bridge angles, or an adequate description or naming of ligands. It is hoped that this survey will help to correlate the chemistry of these related metal elements, and stimulate further interest in their chemistry.

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