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12. ZINC AND CADMIUM

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CONTENTS

INTRODUCTION

This review covers, essentially, the material in volumes 92 and 93 of Chemical Abstracts, although coverage through 1980 in J. Chem. Soc., Dalton Trans., J. Chem. Soc., Chem. Commun., J. Am. Chem. Soc. and Inorg. Chem. has been attempted. Zinc and cadmium have been considered together since many of the references deal with compounds of both elements, and two separate reviews would have involved considerable redundancy of information. As last year, much of the reported chemistry is routine and has not been reported in detail. In general, it is not explicitly stated if a similar complex of the other element has also been reported, and the reader is advised to check the relevant section, although, of course, the reference number may be of help. Papers describing the biochemistry of zinc and cadmium have not been included in this review.

ZINC

12.1 ZINC(II)

12.1.1 Halide complexes

The mixed fluorohalides, ZnFX (X = Cl or Br) have been prepared and their vibrational spectra studied [1]. The thermal conductivity of aqueous ZnI_2 [2] and the solubility of $ZnCl_2$ in dmf [3] have been investigated. A review discussing ZnF_2, its hydrates, and some fluorozincates, has appeared [4].

The mixed halide complexes, $H[ZnClX_2].2Et_2O$ (X = Cl,Br, or I) react with $PhNH_2$ to give complexes formulated as $[PhNH_2...H...H_2NPh][ZnX_2Cl(PhNH_2)]$ [5].

The Raman and ^{87}Rb NMR spectra of $Rb_2[ZnCl_4]$ [6,7] and $Rb_2[ZnBr_4]$ [8,9,10] have been reported. High-resolution solid-state ^{13}C NMR spectra of $[Me_4N]_2[ZnCl_4]$ [11] and ^{35}Cl NQR spectra of $K_2[ZnCl_4]$ [12] have also been reported. The complexes $L_2[ZnX_4]$ (X = Cl,Br, or I) have been prepared [13].

The macrocyclic complex $[NiL]^{2+}$ (L = 2,9-Me_2-3,10-Ph_2-[14]-1,3,8,10-tetraene-1,4,8,11-N_4) has been precipitated as its tetrachlorozincate salt, in an investigation of the mechanism of the template reaction leading to its formation [14], and the extraction of Zn(II) from aqueous HCl by tributyl phosphate [15] or long-chain amines [16] has been studied.

12.1.2 Pseudohalide complexes

The tetraalkylphosphonium salts, $[R_4P][Zn(CN)_3]$, have been described, and provide some of the few examples of compounds containing the $[M(CN)_3]^-$ ion [17].

The extraction of Zn(II) from aqueous media containing thiocyanate, by Aliquat 33, has been studied [18].

12.1.3 Complexes with oxygen donor ligands

12.1.3.1 Aqueous chemistry and complexes with inorganic oxoanions

There have been many studies of mixed oxides containing zinc or cadmium reported this year. These were not considered to be representative of coordination compounds with oxygen donor ligands and were, therefore, specifically excluded from this review. This review is limited to a consideration of species present in solution, and to distinct chemical species in the solid state.

A new method for the study of ion-pairs in solution, using high-field conductiometric techniques, has been applied to methanolic solutions of $ZnSO_4$ [19]. Glassy solutions of ZnX_2 (X = halide) in water have been studied by Raman spectroscopy and the results indicate the presence of the tetrahedral ions, $[ZnX_{4-n}(H_2O)_n]^{(2-n)-}$ [20,21]. A comparison of ΔH_{solv} for solutions of $Zn[NO_3]_2$ and its hydrate in mixed water-dmso solvents has been made and a value for $\Delta H_f[Zn(NO_3)_2]$ obtained [22]. The binary system $ZnCl_2$-H_2O [23] and the ternary systems $[NH_4][ClO_4]$-$Zn[ClO_4]_2$-H_2O [24] and $ZnCl_2$-ZnO-H_2O [25] have been investigated. In the latter system, an equilibrium exists between ZnO, $ZnCl_2.4Zn(OH)_2.H_2O$, β-Zn(OH)Cl, and α-$ZnCl_2$. The thermal decompositions of $ZnSO_4.7H_2O$ [26] and $[Zn_5(OH)_8Cl_2(H_2)]$ [27] have been studied. A new zincate species, $Na_2[ZnO_2]$, has been characterised in the solid phase of NaOH-ZnO [28].

The extraction of Zn(II) from aqueous solution continues to attract attention and the use of 1,3-diketones [29], 1,3-diketones and trioctyphosphine oxide [30], and tributyl phosphate [31,32] as extractants have been studied. The treatment of aqueous solutions containing Zn(II) or Pb(II) with crown ethers, results in the preferential complexation of Pb(II), to give a complex which is readily transported across the $CHCl_3$-H_2O interface, and the method appears to have potential for the separation of these two metals [33]. Polyethers have also been used for the extraction of zinc from aqueous media containing thiocyanate, and the distribution of the metal between the two phases has been shown to depend upon the solvent and any other cations which may be present [34].

Several complexes of Zn(II) with phosphate anions have been described. The compound $KZn_2H[PO_4]_2.2.5H_2O$ dehydrates readily at room temperature, to give the anhydrous compound, from which the novel materials $KZn_4[PO_4]_3$, $KZn[PO_4]$, and $K_x[NH_4]_{1-x}Zn[PO_4]$ have been prepared [35]. Difluorophosphoric acid, $HOP(O)F_2$, reacts with $ZnCl_2$ to give the complex $[Zn(PO_2F_2)_2].2HOP(O)F_2$, in which the ligands coordinate to the metal through their terminal oxygen atoms [36]. A number of Zn(II)-pyrophosphate complexes have been prepared [37] and the compounds $[NH_4]_4Zn_3[P_3O_{10}]_2.9H_2O$, $Zn_5[P_3O_{10}]_2.16H_2O$, and $[NH_4]Zn_2[P_3O_{10}].7H_2O$ [38] have been isolated. The crystal structure of the last compound has been reported [39]. The formation of complexes with polymerised triallyl phosphate has been described [40] and the thermal decomposition of $[Zn(H_2PO_4)_2].2H_2O$ [41] and $[Zn_2P_2O_7].5H_2O$ [42] has been analysed.

The properties of the complexes $Zn[CrO_4]$ and $Zn[CrO_4].3.5Zn(OH)_2.H_2O$ have been investigated; their reduction by CO (formed *in situ* from the decomposition of zinc oxalate) leads to the formation of species containing catalytically active Cr(V) and Cr(III) centres [43,44]. The preparations of $Zn[CO_3]$, from the reaction of zinc oxalate with CO_2 [45], and $K_2Zn_2[MoO_4]_3$, from the reaction of $K_2Mo_2O_7$ and ZnO [46], have been described.

12.1.3.2 Complexes with carboxylic acids and related ligands

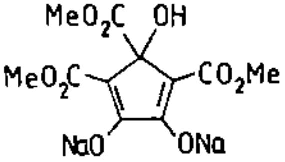
The majority of carboxylic acids studied possess, in addition to oxygen, other atoms which may act as donors, and it is not always evident which manner of coordination the ligand adopts. The policy adopted in this review, and also in that for mercury, is to include all complexes of carboxylic acids, except those in which the ligand contains a heterocyclic ring or a sulphur atom, in this section. Thus, amino acids and H_4edta derivatives will be treated here, despite the fact that there is strong evidence that, in many cases, such species act as *N*, as well as *O*, donor ligands.

A determination of the crystal structure of $Zn(O_2CMe)_2$ has shown the metal to be in $\{ZnO_4\}$ tetrahedra, which are connected by bridging ethanoate groups [47]. The pyrolysis of $Zn(O_2CMe)_2.2H_2O$ gives, initially, the anhydrous compound, which, on further heating, melts and then decomposes to give ZnO, $(MeCO)_2O$, and Me_2CO [48]. The solubility of $Zn(O_2CMe)_2$ in mixed alcohol-hexane solvent systems has been studied and the results used to propose a model for the solvation shell of the metal ion in such solvent systems [49]. The reaction of $Zn(O_2CMe)_2$ with $[UO_2][O_2CMe]_2$ in $MeCO_2H$ gives the double salt, $Zn[(UO_2)_2(O_2CMe)_6].8H_2O$ [50], whilst the crystallisation in the presence of $Mn(O_2CMe)_2$ at 60° gives $Zn(O_2CMe)_2.Mn(O_2CMe)_2.2H_2O$ [51].

Zinc complexes of RCO_2H ($R = C_2H_5$–C_9H_{19}) [53], $ArOCH_2CO_2H$ [54], 1,2,4-benzenetricarboxylic acid [55], and orotic acid [56] have been described. The thermochemical behaviour of the complexes $[Zn(O_2CR)_2]$ (R = Et,Pr,Bu, or pentyl) [57], $[Zn(ox)(H_2O)_2]$ [58], $[Zn(ox)_2].2H_2O$ [59], and $[Zn(salH)_2].2H_2O$ ($salH_2$ = salicylic acid) [60,61] have been investigated; the thermal decomposition of the salicylic acid complex produces [Zn(sal)], PhOH, CO_2, and H_2sal [61]. It has been proposed that the higher zinc carboxylates exhibit an enantiomeric polymorphism on the basis of the X-ray diffraction characteristics of the materials at elevated temperatures [62].

Amino-acid complexes of zinc have also attracted some attention and compounds containing $H_2NCH_2CH_2CO_2H$ [63], DL-serine [64], *N*-arylglycines [65], and phenylalanine [66] as ligands have been reported. The condensation of anthranilic acid with aldehydes produces Schiff bases and a number of zinc complexes of these iminecarboxylic acids have been described [67,68]. The Schiff base from the condensation of alanine with 2-hydroxyacetophenone forms a complex, [ZnL], the bromination of which has been studied; bromination with *N*-bromosuccinimide or 1,4-dioxan-Br_2 occurs on the phenyl ring [69].

The $-N(CH_2CO_2H)_2$ functionality is encountered in many ligands (*e.g.* H_4edta), and complexes of zinc with $(H_2NCOCH_2)N(CH_2CO_2H)_2$ and $(H_2NCOCH_2CH_2)N(CH_2CO_2H)_2$ [70], $(HO_2CCH(OH)CH_2)N(CH_2CO_2H)_2$ [71], DL-$(HO_2CCH_2)_2NCH_2CH(CO_2H)N(CH_2CO_2H)_2$ [72], $(HONHCOCH_2)N(CH_2CO_2H)_2$ [73], and $(2\text{-}HOC_6H_4CH_2)N(CH_2CO_2H)_2$ [74] have been reported. The stability of ternary complexes containing Zn(II), $N(CH_2CO_2H)_3$, and either 1-hydroxy-2-naphthoic or 2-hydroxy-1-naphthoic acid has been investigated [75]. The preparation of zinc complex of the ligand (1) has also



(1)

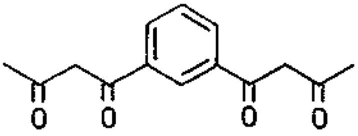
been described [76].

12.1.3.3 *Complexes with amides and related ligands*

The five-coordinate malonamide complexes $[ZnLCl_2(H_2O)]$, $[ZnL(SO_4)]$, and $[ZnL_2(NO_3)][NO_3]$ (L = $H_2NOCCH_2CONH_2$) have been prepared [77,78] and the complexes $[Zn(tmu)_2X_2]$ (X = Cl, Br, or I), in which the ligand is coordinated through oxygen [79], have been reported. Other complexes which have been described include: $[ZnL_2X_2]$ (L = acrylamide; X = Cl or SCN) [80], $[ZnL_4(NO_3)_2]$ (L = $PhCONH_2$) [81], $[ZnL_6][BF_4]_2$ (L = caprolactam) [82], $[ZnL][NO_3]_2$ (L = $H_2NNHCOCONHNH_2$) [83] and $[Zn(dma)Cl_2]$ [84]. Also, zinc complexes with the following amide ligands have been reported: $H_2NCONHCONH_2$ [85], $PhCH{=}CHCONHNH_2$ [86], $PhCH_2CONHOH$ [87], *N*-methylformamide [88], and urea [89,90]. An analysis of the vibrational spectra of the oxamide complexes, $K_2[ZnL_2]$ {L = $(CONH_2)_2$ or $(COND_2)_2$} has been presented [91].

12.1.3.4 *Complexes with ketones and ethers*

Complexes of zinc with $ArCOCH_2COMe$ [92] 5-chloro-2-hydroxy-4-methylacetophenone [52] and (2) [93] have been prepared, as have several compounds in which



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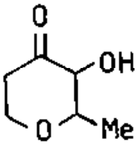

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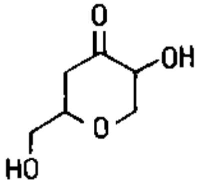

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zinc is bonded to pyran derivatives, including $[ZnL_3(XCN)_2]$ (L = 2,6-dimethyl-4-pyrone; X = S or Se) [94] and $[ZnL_2]$ {HL = (3) or (4)} [95].

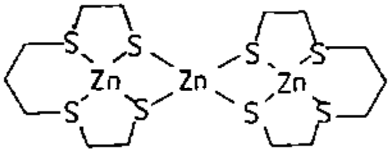
The compound $ZnAlCl_5.Et_2O$ has been investigated and assigned the structure $[Cl_2Zn(\mu\text{-}Cl)AlCl_2(OEt_2)]$ on the basis of its vibrational spectrum [96]. The preparation of $[ZnL_6][InCl_4]$ (L = 1,4-dioxan) has been described [97].

12.1.4 Complexes with sulphur or selenium donor ligands

12.1.4.1 Complexes with thiols, thiones and thioethers

The novel species obtained from the reaction of zinc(II) salts with thiophenol have been further investigated and complexes of formula $[Zn_4(SPh)_8(ROH)]$ have been isolated from the interaction of $Zn[CO_3]$ and PhSH in ROH [98]. A crystallographic study of these species has shown that they should be formulated *catena*-(μ-SPh){(μ-SPh)$_6$Zn$_4$(ROH)(SPh)} and that they form one-dimensional polymeric crystals with one intercluster bridging PhS unit [98]. A crystal structure of the complex $[Me_4N][ClZn_4(\mu\text{-}SPh)_{12}(ZnSPh)_4]$, formed from $Zn(NO_3)_2$, PhSH, Pr_3N and $[Me_4N]Cl$, has also been reported [99].

The reaction of zinc ethanoate with 1,4,8,11-tetrathiaundecane gives the trimetallic complex, (5), which transmetallates on treatment with $[Ni(H_2O)_6]^{2+}$ to give the corresponding trinickel(II) complex [100]. $RS(CH_2)_nNR_2$ and $RSO(CH_2)_nNR_2$ have been used for the extraction of zinc from aqueous solutions of $ZnCl_2$ or $ZnSO_4$ [101].



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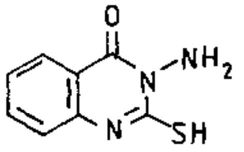
A large number of complexes with heterocyclic mercapto compounds have been described and the ligands studied include: 3-(diphenylaminomethyl)-5-(2-hydroxyphenyl)-2-mercapto-1,3,4-oxadiazole [102], 2-thiouracil [103], 2-mercapto-4,6-dimethylpyrimidine [104], 1-amino-2-mercapto-5-trifluoromethyl-1,3,4-triazole [105], 1-benzylidineamino-3-ethyl-5-mercapto-1,2,4-triazole [106], 1-methyl-2-mercaptoimidazole [107], and 3-amino-2-mercaptoquinazol-4-one [108]. In many cases it is not clear how the ligand is coordinated but, for $[ZnL_4][NO_3]_2.H_2O$ (L = 1-methyl-2-mercaptoimidazole) [107], $[ZnL_2]$ {HL = (6)} [108], $[Zn(HL)_2X_2]$ and $[ZnL_2].LH$ (HL = 2-mercapto-4,6-dimethylpyrimidine; X = Cl,Br, or I) [104], it has been demonstrated that the metal is present in



(6)

$\{ZnS_4\}$, $\{ZnN_2S_2\}$, and $\{ZnN_2X_2\}$ polyhedra respectively.

A number of complexes of the type $[R_4N][ZnL_2]$ (R_4N = Et_4N, or $Me_3NCH_2CH_2OH$; H_2L = 7-nitroquinoxaline-2,3-dithiol, 6,7-dinitroquinoxaline-2,3-dithiol, or 6,7-benzoquinoxaline-2,3-dithiol) have been described [109]. $[ZnL_2]$ (HL = 1,2-dicyanoethene-1,2-dithiol) reacts with MeI to give free 1,2-dicyano-1,2-bis(methylthio)ethene [110].

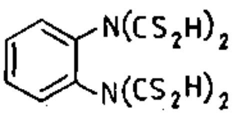
Thioethers have attracted some attention as ligands and the bimetallic complex $[Zn_2L]$ $\{H_4L = HO_2CCH_2CH(CO_2H)SCH(CO_2H)CH_2CO_2H\}$ [111], and complexes with $(HO_2CCH_2)_2S$ [112], Me_2S and MeSSMe [113] and $[HO_2C(CH_2)_nS]_2$ (n = 1 or 2) [114] have been described.

Complexes of zinc with amino acids such as cysteine [115,116] and D-penicillamine [116] have been reported, and polynuclear species identified.

12.1.4.2 Complexes with thioacids, thioamides and related compounds

The majority of the work on this type of ligand has concentrated on thioamides and their derivatives, although a few complexes of thioacids have been reported.

Zinc(II) complexes of thiomalic acid [112,117], $ArCS_2H$ [118], $EtOCS_2H$ [119], (7) [120], and $HS_2CNHCSNH_2$ [121] have been described. On heating [ZnL]



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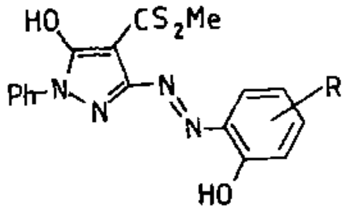


(8)

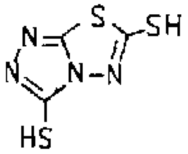
$\{H_2L$ = (7)$\}$ in air, ZnO is formed [120]. The pyrazolone derivatives, (8), give intensely coloured complexes with zinc(II) ions and have been advocated as reagents for the colourimetric determination of the metal [122].

The ligand exchange of $[Zn(tmtu)_4]^{2+}$ with excess tmtu in CD_2Cl_2 has been studied by ^1H NMR spectroscopy and the reaction shown to first order in the complex [123]. Zinc complexes with the thioamides, $R_2C{=}NNHCSNH_2$ [124],

$H_2NCSNHNHCSNH_2$ [125] [$\{H_2C{=}CHCH_2NHCSNH\}_2$] [126], $H_2NCSNHNH_2$ [127], the vinylogous thioamide $PhCSCH{=}CHNR_2$ [128], and with thiocarbamates [129], ethylenethiourea [130], and dithiocarbazates [131] have been reported. A ^1H NMR investigation of the configuration of Zn(II) $R_1R_2C{=}NNHCS_2Me$ and $R_1R_2C{=}NNHCSNH_2$ complexes in solution has been made and the configuration shown to depend upon the nature of the two R groups; with R_1 = Ar and R_2 = H, only one conformer, with the aldehydic hydrogen *syn* to the N-N bond, was present, but a mixture of *syn* and *anti* conformers was present with the compounds derived from ketones [132]. A study of the vibrational spectrum of a polymeric zinc–dithiooxamide complex has also been made [144,145].

12.7.4.3 Complexes with sulphur heterocycles

The interest in zinc(II) complexes of sulphur-containing heterocycles continues and complexes with 2-amino-5-methyl-1,3,4-thiadiazole [133], 2-amino-5-phenyl-1,3,4-thiadiazole [134] and 2-amino-5-(2-hydroxyphenyl)-1,3,4-thiadiazole [135] have been reported. The five-coordinate species [Zn(benzacH) L] (L = benzothiazole) [136] and complexes of the novel ligand (9) have also been described [137]. Zinc ethanoate behaves similarly to mercury(II) ethanoate on reaction with 2-(2-pyridyl)benzothiazole and gives complexes of a ring-opened ligand [138]. A number of complexes of zinc with benzothiazole and other sulphur-containing ligands have been described and the crystal structure of $[NBu_4][\{Zn(S_2CNMe_2)_2\}_2(\mu\text{-}O_2CMe)]$, which contains a square-pyramidal $\{ZnS_4O\}$ unit, has been reported [139].



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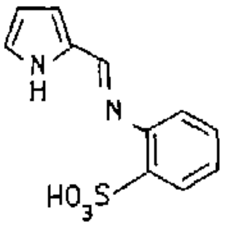
12.7.4.4 Complexes with sulphonic acids and related ligands

Zinc complexes of the ligands (10) and (11) [140,141] and a number of



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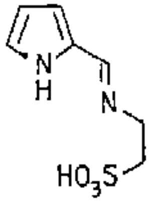


(11)

sulphonamides [142,143,146] have also been described.

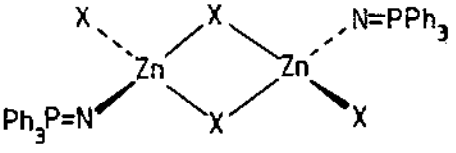
12.1.5 Complexes with nitrogen donor ligands

12.1.5.1 Complexes with amines and related ligands

The majority of complexes with this type of ligand are with diamines, Schiff bases, or amino acids (See 12.1.3.2) but a few compounds with monodentate nitrogen donor ligands have been reported.

A series of violet, air-stable, heteropolynuclear complexes, $[Ni_nZn_m(N_2H_4)_{3(n+m)}][SO_4]_{(n+m)}$ (n = 1, m = 1-4; m = 1, n = 1-4) have been isolated from the $ZnSO_4$-$NiSO_4$-N_2H_4 system [147]. The, presumably tetrahedral, compounds, $[ZnL_2]X_2$ {L = $(HOCH_2CH_2)_2NH$; X = Cl,Br, $[NO_3]$, $[NCS]$ or $[ClO_4]$} have been prepared [148] and stability constants for the formation of the zinc complexes of $RNHCH_2CH_2OH$ reported [149].

A number of zinc(II) azobenzene complexes have been prepared [150]. The complex $[ZnL_2]I_2$ {L = $Me_2CHN{=}CMeCH{=}C(OH)R$} has been investigated by ^1H NMR and IR spectroscopy and a *trans* tetrahedral coordination about the metal proposed [151]. Alcoholysis of $Ph_3P{=}NSiMe_3$ in the presence of ZnX_2 (X = halide), results in the formation of $Ph_3P{=}NH$ complexes, which are thought to have the halide-bridged structure (12) [152].



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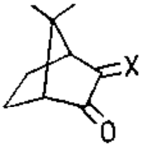
Complexes of zinc with 1,2-diamines continue to be of interest, and the $ZnCl_2$-en system has been reinvestigated [153]. X-ray diffraction and Raman spectroscopy have been applied to the study of zinc-en complexes in aqueous solution; $[Zn(en)_2]^{2+}$ and $[Zn(en)_3]^{2+}$ have the expected tetrahedral and octahedral geometries, respectively [154]. The ternary complexes formed between Zn(II) and the ligands en, 1,2-pn, gly, $Me_2N(CH_2)_2NH_2$, and $MeNH(CH_2)_2NHMe$ have been investigated [155,156].

Aqueous solutions containing Zn(II) and H_4L (H_4L = $[\{(MeCHOHCH_2)_2NCH_2-\}_2]$) have been investigated potentiometrically and shown to contain the complexes $[M(H_4L)]^{2+}$, $[M(H_3L)]^+$, and $[M(H_2L)]$ [157]. A crystal structure of the compound $[\{HZn(MeNCH_2CH_2NMe_2)\}_2]$ has been reported [158].

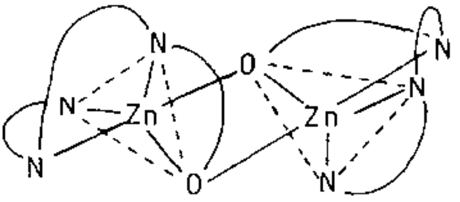
The formation of 1,2-pn and 1,3-pn complexes of zinc has been studied, and the simple 1:1 and 1:2 complexes, as well as a 1:1:1 ternary species, have been detected in solution. It was shown that 1,2-pn, which gives a five-membered chelate ring, is a better ligand for Zn(II) than 1,3-pn [159]. The polarographic reduction of a number of Zn(II)-1,3-pn complexes in a range of solvents has also been investigated [160]. The reaction of (13) with 1,3-pn in the presence of



(13; X = O)
(14; X = $N(CH_2)_3NH_2$)

Zn^{2+} ions results in the formation of $[ZnL_2]^{2+}$ {L = (14)}, rather than the expected macrocycle [161].

The bidentate ligands [$(Ph_3P)(ArNC)Pt(MeOC{=}NAr)_2$] act as N_2 donors and the heteropolynuclear species [$ZnBr_2L$] has been reported [162]. Zinc complexes with the potentially tridentate ligands, [$(MeNH)_3CR$] (R = H,Me, or Et), have been described [163], as have the complex ions $[ZnL]^{2+}$ (L = tach, 1,5,9-triazanonane, or $(H_2NCH_2)_3CMe$) [164]. In the latter cases it has been shown that the rigidity of the ligand plays an important rôle in coordination, and this is reflected in the thermodynamics of complex formation. The tripod-like ligand, $(Et_2NCH_2CH_2)_2N(CH_2CH_2OH)$, has been shown to give dimeric, five-coordinate complexes as in the cation, (15), of the compound $[Zn_2L_2][ClO_4]_2$ [165].



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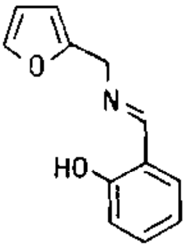

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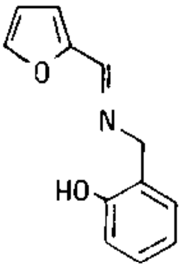

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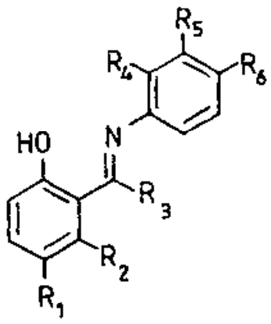
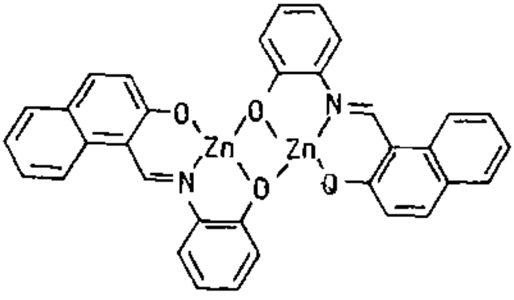


	R_1	R_2	R_3	R_4	R_5	R_6
(18)	benzo		H	OH	H	H
(20)	benzo		H	Me	H	NO
(21)	benzo		H	H	OMe	H
(22)	H	H	Ph	Me	H	H
(23)	H	H	H	H	H	H
(24)	Cl	H	Me	H	H	H
(25)	Me	H	Me	H	H	Me

The interest in the complexes of substituted salicylideneimines continues, and the Schiff base from 2-aminomethylfuran and salicylaldehyde forms a zinc(II) complex which has been shown, by ^{1}H NMR and IR spectroscopy, to contain the ligand in the form (16), rather than as a 2-furylimine (17) [166]. The complex $[Zn_2L_2]$ $\{H_2L$ = (18)$\}$ has been described and considered to have the structure (19) [167]. Reports of complexes with the ligands (20) [168], (21) [169], (22) [170], (23) [171], (24) [172], and (25) [173] have also appeared.

A variable temperature ^{1}H NMR study of the complexes $[ZnL_2]$ $\{HL$ = (26) or (27)$\}$ in solution has indicated that they are dynamic, interconverting between the Λ and Δ enantiomers [174].



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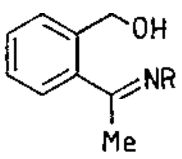


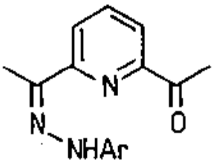
(26; R = Me)
(27; R = CHMe$_2$)

12.1.5.2 Complexes with pyridine and quinoline ligands

The zinc(II)-pyridine system has been further investigated polarographically [175] and complexes with a number of substituted pyridines have been prepared in an attempt to determine the importance of back-donation in the M–N bonding of such systems [176]. The reaction of Zn(ox) with pyridine has been studied and the complex [Zn(ox)(py)$_2$] characterised [177]. Thermal decomposition of [(CF$_3$)$_2$Zn(py)$_2$] leads to CF$_3$H instead of the expected perfluorocyclopropane [178]. The ^{14}N NQR spectra of the complexes [Zn(py)$_4$(NO$_3$)$_2$], [Zn(py)$_3$(NO$_3$)$_2$], and [Zn(py)$_2$X$_2$] (X = Cl,Br,I,NCS, or NO$_3$) have been reported [179]. The halogenation of a number of zinc(II)-pyridine complexes has been investigated and the bromination of [ZnX$_2$L$_2$] (L = 4-methylquinoline or 2,6-dimethylpyridine; X = Cl or Br) shown to give only [LH]$_2$[MX$_2$Y$_2$] (X = Cl or Br; Y = Br) [236]. In no case was any ring-brominated product obtained. An investigation of the ZnX$_2$–2-Mepy (X = Cl or Br) system in C_6H_6, C_6H_5Cl or EtO$_2$CMe has been made and the results interpreted in terms of the formation of the corresponding [Zn(2-Mepy)$_2$X$_2$] complex [180]. A zinc complex with 2-(2-pyridyl)ethanol has also been described [181].

Complexes with pyridine aldehydes and ketones are of interest and the ligand bis(2-pyridyl)ketone has been the subject of several investigations. The type of coordination adopted with this compound appears to depend upon the counter ion, since [ZnL(N$_3$)$_2$] is four coordinate whilst [ZnL$_2$(NCE)$_2$] (E = S or O) are six coordinate with the ketone acting as an N_2 donor in each case [182]. Of the complexes [ZnLX$_2$] (X = Cl,Br, or I), only the iodide ionises in dmf, apparently indicating the halide ions are strongly coordinated [183]. 3-Pyridinealdehyde is also of interest as a ligand and complexes with the parent compound [184] and its thiosemicarbohydrazone [185] have been reported. The condensation of 2-pyridinealdehyde with tach, and 2-pyridinealdehyde or 2-acetylpyridine with 1,1,1-tris(aminomethyl)ethane, results in the formation of tridentate ligands (L) which form the corresponding [ZnL]$^{2+}$ complexes. These complexes have been shown to be chiral, undergoing rapid racemisation in solution [186].

The reaction of Zn(O$_2$CMe)$_2$.nH$_2$O with **(28)** in BzOH results in the formation of monomeric five-coordinate complexes [187]. Surprisingly, the template reaction of ArCONHNH$_2$ with 2,6-diacetylpyridine in the presence of Zn(II) ions does not appear to have been investigated. The formation of zinc complexes with



(28)

2-HO_2Cpy [188], 2,6-$(HO_2C)_2$py [188,189], 2,6-$(HO_2CCH_2)_2$py [190], 3-H_2NCOpy [191], and 2,3-$(HO_2C)_2$py [189] has been described. The vibrational spectra of $[ZnL_2L'_2]$ (LH = 2-pyridinecarboxylic acid *N*-oxide; L' = H_2O or D_2O) indicate coordination through the *N*-oxide oxygen and the carboxylate group [192]. In contrast, the complexes with 3-pyridinecarboxylic acid *N*-oxide and pyridine-4-carboxylic acid *N*-oxide are polymeric multinuclear species [193]. Crystal structures of $[ZnL_4(NCS)_2]$ (L = 3-pyridine-*N*,*N*-diethylcarboxamide) [194] and $[ZnL_2(H_2O)_2(HCO_2)_2]$ (L = 3-pyridinecarboxamide) [195] have been reported.

2-Hydroxyarylhydrazinopyridine {2-HOArNHNHpy (Ar = 2-hydroxy-1-naphthyl or 2,4-dihydroxyphenyl)} complexes of zinc have been investigated, and the metal-ligand vibrations reported [196]. The mass spectrum of the Zn(II) complex (Ar = 10-hydroxy-9-anthryl) is of interest is that it contains an ion corresponding to Zn^+ [197]. Zinc(II) complexes of the Schiff bases from 2-aminopyridines and salicylaldehydes have been prepared and are reported to involve a tetrahedral geometry about the metal [237].

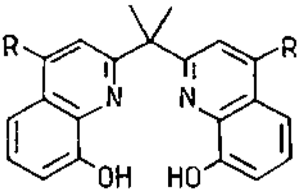
Crystal structures have been reported for the complexes $[Zn(dien)L]^{2+}$ {L = bis(2-pyridyl)amine}, in which the five coordinate zinc atom adopts a trigonal bipyramidal configuration [198], and $[Zn(3\text{-}O_3Spy)_2(H_2O)_4]$, in which the two 3-pyridinesulphonic acid ligands adopt the axial positions of an octahedral $\{ZnO_4N_2\}$ unit [199]. The reaction of $ZnEt_2$ with $LiAlH_4$ in ether results in the formation of a moderately stable form of ZnH_2, which reacts with pyridine to give complexes containing coordinated 1,4-dihydropyridines. The complexes $[L_2ZnL'_2]$ (HL = 1,4-dihydropyridine; L'_2 = $(py)_2$ or tmen) have been characterised and used for the reduction of carbonyl compounds [200,201].

Work on complexes of the classic diimine ligands continues and ^1H NMR studies of solutions of $[Zn(bipy)]^{2+}$ and $[Zn(phen)]^{2+}$ have been reported. These complexes show little tendency, unlike the free ligands, to stack in solution [202]. The electrolysis of alkyl or aryl halides in MeCN-benzene at a zinc electrode in the presence of bipy results in the formation complexes of the type [RZnX(bipy)] (R = Me,CF_3,Et,CH_2=$CHCH_2$,Ph,C_6F_5, or Bz; X = halide). This provides a route to arylzinc complexes, since aryl halides do not normally react with metallic zinc. Oxidation of [RZnX] in the presence of RX and $[R'_4N]X$ had resulted in the formation of $[R'_4N][RZnX_2]$ and these are the first examples of compounds containing the $[RZnX_2]^-$ anion [203]. The system $[Zn(phen)_3]^{2+}$-AMP has been studied, and shown to possess strongly Pfeiffer-active optical activity [204].

The luminescence spectrum of $[Zn(bipy)_3]^{2+}$ and 77 K has been reported [205], and is of particular interest since it has been recently claimed that anomalies in the fluorescence and vibrational spectra of aqueous solutions of bipy are due to the leaching of Zn^{2+} ions from the glassware to give a highly fluorescent zinc-bipy complex [206]. The anomalies had previously been interpreted [207] as evidence for the formation of a covalent hydrate of the diimine; such species must now be regarded as hypothetical in the absence of any further evidence for their existence.

Quinoline complexes have not been so widely studied as those with pyridine ligands, but a few compounds have been described. The reaction of $[ZnL_2(H_2O)]$ (HL = 1-chloro-2,4-pentanedione) with quinoline gives the five coordinate species $[ZnL_2(quin)]$ [238]. Similar reactions occur with isoquinoline, quinaldine and 4-methylpyridine. The complexes $[Zn(amq)X_2]$ (X = Cl,Br, or I) and $[Zn(amq)_2][ClO_4]_2$ are tetrahedral, in contrast to some other zinc(II)-amq complexes which have been described [208]. A ^{13}C NMR investigation of the ligands 8-HO-quin and 4-Me-8-HO-quin, and the complex $[ZnL_2]$ (HL = 4-Me-8-HO-quin) in dmso-d_6 has demonstrated the complex to have a weakly ionic Zn–O interaction, with most of the negative charge localised on the oxygen [209].

Polymeric complexes, $[ZnL(H_2O)_2]_n$ with bis(8-hydroxy-5-quinolinyl)-4,4'-bisazobiphenyl (LH_2) have been prepared, and the ligand shown to coordinate through the quinoline nitrogen and the oxygen atom [210]. The reaction of [NiL] {H_2L = **(29)**} with ammonium persulphate, pyruvic acid and $AgNO_3$ gives **(30)**, which acts as an N_2O_2 donor to a number of transition metals. The complexes [ZnL] {H_2L = **(29)** or **(30)**} have been prepared, and their electronic spectra reported [211].

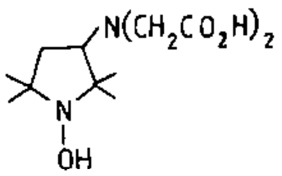


(29; R = H)
(30; R = O_2CMe)

The complex $[ZnL_2(NCS)_2]$ (L = benzoquinoline) has been prepared and the NCS ligands shown to be *N* bonded, in contrast to those in the corresponding Hg(II) or Cd(II) complexes [212]. The complexes $[ZnL_2Q_2]$ (HL = $PhCO_2H$; Q = quin, or isoquinoline) have also been reported and shown to involve octahedral coordination at the zinc(II) atom, with a bidentate carboxylate group [234].

12.1.5.3 Complexes with other heterocyclic ligands

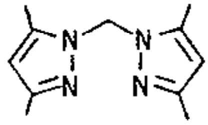
Although no complexes of pyrrole itself have been reported this year (but see next section for macrocyclic ligands containing this group), the pyrrolidine complex $ZnL.MeCO_2H$ {L = (31)} has been described [213]. Treatment of $Zn(acac)_2$]



(31)

with a mixture of imidazole and tetramethylimidazole results in the formation of $[Zn(imid)_2]$ and a determination of the crystal structure of this compound has revealed that it consists of tetrahedral $\{ZnN_4\}$ units, connected by bridging imidazole groups [214]. NMR studies have been made on a number of zinc complexes of elaborate imidazole derivatives [215].

Reactions of the bidentate ligand, bis(3,5-dimethyl-1-pyrazolyl)methane (32),



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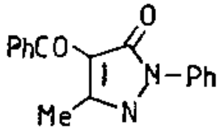


(33)

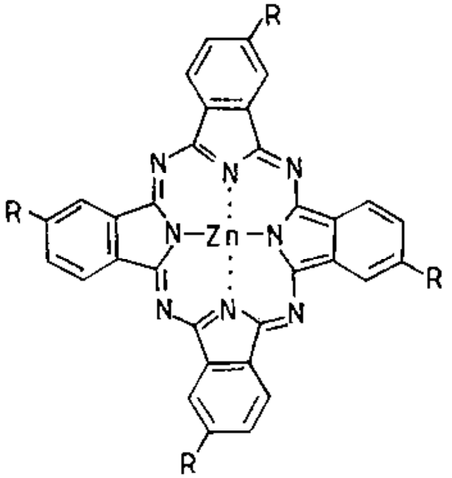
have been investigated, and the complexes $[ZnLX_2]$ (X = Cl or Br) and $[ZnL_2]X_2$ ($X = NO_3$ or ClO_4) have been prepared [216]. The extraction of zinc from aqueous solution by 4-benzoyl-3-methyl-1-phenyl-5(4H)-pyrazolone (33) or $(BuO)_3P$ dissolved in benzene has been studied [217].

Zinc complexes with imidazole [218], 1,2-dimethylimidazole [219], (33) [220], 1,2,4-triazole [221], 5-cyanotetrazole [222], benzimidazole [223], 4-amino-1,2,4-triazole [224], and 2-amino-5-phenyl-1,3,4-oxadiazole [233] have also been reported. A crystal structure of $[ZnL_2(SCN)_2]$ (L = 1,2,4-triazole) has revealed it to consist of $\{ZnN_6\}$ octahedra linked by a 2,4-bridging triazole group [235]. The five coordinate benzotriazole complexes $[ZnL_3X_2]$ ($X = N_3$ or NCO) and the octahedral species $[ZnL_4(NCS)_2]$ have been described [182]. The octahedral complex $[Zn(HL)_2(H_2O)_2]Cl_2.2H_2O$ (HL = 2-hydrazino-6-methyl-4(3H)-pyrimidone) has also been described; one of the chloride ions is hydrogen bonded to the ring NH and the zinc atom is coordinated to a ring nitrogen and the terminal NH_2 group [225].

The interaction of nucleosides and nucleotides with zinc(II) ions is of obvious biological significance and much work has been done to elucidate the nature of the interaction. Complexes formed between ATP and Zn^{2+} are of particular importance, since the presence of this metal ion accelerates the hydrolysis of the polyphosphate, thus the complexes provide models for ATP transport and biological phosphate transfer. A crystal structure of $[Zn(H_2ATP)(bipy)]_2.4H_2O$ has been reported, in which the zinc ions are in $\{ZnO_4N_2\}$ octahedra, with two bridging -OPO- units [226]. The adenine complex $[ZnL][ClO_4].EtOH.H_2O$ (HL = adenine) has been prepared, by the reaction of $Zn[ClO_4]_2$ with adenine in ethanolic triethyl orthoformate, and the method is claimed to be advantageous over those involving aqueous conditions [227,228]. Zinc(II) nucleoside complexes have been investigated by ^{13}C NMR [229] and, in aqueous NaCl, by ^{35}Cl NQR spectroscopy [230]. Zinc complexes with 2-hydrazino-3-methylquinoxaline [231], and 9-methylhypoxanthine [232] have also been described.

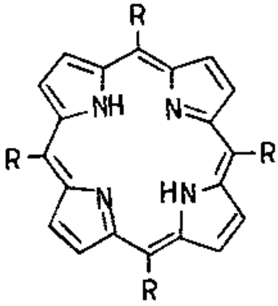
12.1.5.4 Complexes with macrocyclic ligands

The majority of complexes, involving zinc co-ordinated to a macrocyclic ligand, reported this year are based on the porphyrin or phthalocyanine ring system, and such complexes are being intensitively investigated as photocatalysts for the photoreduction of water and/or organic compounds. The results of CNDO/2 calculations for [Zn(Pc)] have been reported, and compared with the PPP and EHMO calculations for the same species [239]. The electrochemical oxidation of zinc tetra-4-*tert*-butylphthalocyanine **(34)** in nitrobenzene or 1,2-dichlorobenzene has been reported [240]. In cationic mycelles, the anionic phthalocyanine, $Na_4[ZnL]$ $\{H_4L$ = **(35)**$\}$, in the presence of cysteine, has been shown to sensitise the photoreduction of the 1,1'-dimethyl-4,4'-bipyridinium dication (methyl viologen, Paraquat) although, in the presence of a surfactant, [Zn(Pc)] was more



(34; R = CMe_3)
(35; R = SO_3H)

effective [241]. Zinc napthalocyanine has been prepared in low yield (18%) by the template reaction of $Zn(O_2CMe)_2$, urea, and 2,3-naphthalenedicarboxylic acid [242]. Most of the work investigating the ability of porphyrins to act as photosensitisers utilises the readily available *meso*-tetraphenylporphyrin (**36**),

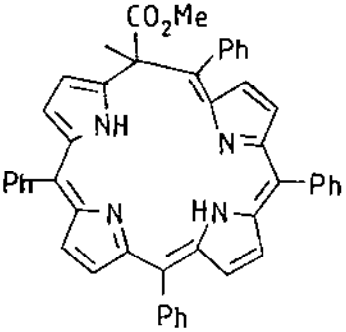


(**36**; R = Ph)
(**37**; R = 4-$HO_3SC_6H_4$)
(**38**; R = 4-(1-methylpyridinium)
(**39**; R = 4-$Me_3NC_6H_4$)

although various anionic and cationic derivatives are now being investigated. Many workers have used the 1,1'-dimethyl-4,4'-bipyridinium dication as an electron acceptor and the photoreduction of this species in the presence of [ZnL] {H_2L = (**36**) or (**37**)} has been investigated [243]. Various chemical mixtures have been utilised for the photoreduction of water and these include, $[ZnL]^{4-}$ {H_6L = (**37**)}/Pt/H_2O [244], $[ZnL]^{4+}$ {$[H_2L]^{4+}$ = (**38**)}/Pt/H_2O [244], and [ZnL] {H_2L = (**36**)}/edta/$[MV]^{2+}$/H_2O [245]. The reversible photooxidation of [ZnL] {H_2L = (**35**)} has been shown to provide a photocatalytic method for the reduction of quinones [246,247]. SnO_2 semiconducting electrodes are photosensitised by zinc porphyrin complexes but the zinc species is consumed in a competing dimerisation reaction [248]. Related investigations have involved studies of the electronic, fluorescence, and phosphorescence spectra [249] and the polarised absorption and linear dichroism spectra [250] of zinc porphyrins. The radical cations of zinc(II) porphyrins may be prepared from the parent complex [ZnL], by reaction with Fe(III) [251], or by oxidation of a triplet state with Eu(III) [252]; it photodisproportionates to [ZnL] and $[ZnL]^{2+}$ [251].

The formation of porphyrin complexes by the reaction of H_2L {(**35**) or (**39**)} with Zn^{2+} has been investigated. In the case of (**35**), an activated complex $[H_2L^{*}...Zn(H_2O)_6]^{2+}$ was implicated as an intermediate [253], whilst the reaction of (**39**) with Zn^{2+} was first order in each reactant, and faster than the corresponding reaction of (**36**) [254]. The formation of a zinc 'nitrotetrabenzoporphyrin' has also been reported [255]. The formation of cobalt(II) porphyrins by metal exchange of [ZnL] with $CoCl_2$ in Field Desorption mass spectrometry has been reported [256]. A number of NMR studies of zinc porphyrin complexes have been made [257,258].

Several reactions of zinc porphyrins have been reported and are of interest as methods for modifying the ligand. Thus, the reduction of [ZnL] {H_2L = **(35)**} with $MeCHN_2CO_2Me$, followed by demetallation, has resulted in the formation of the homoporphyrin **(40)** and the *N*-alkylated species **(41)** [259]. Vilsmieir



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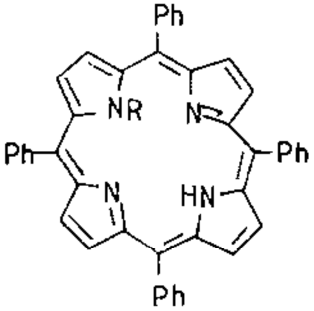

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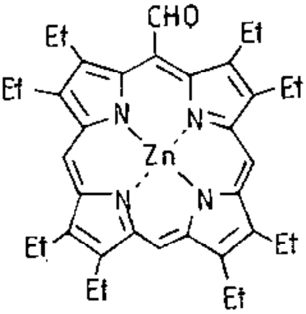

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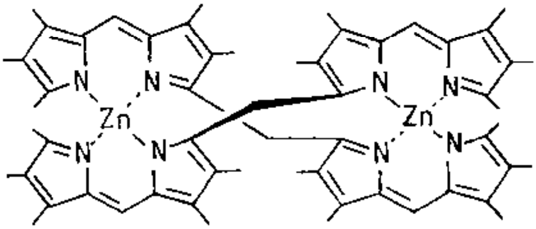

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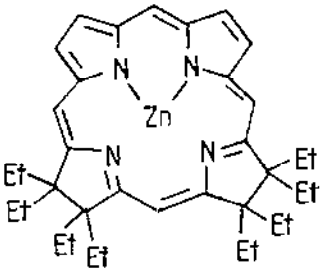


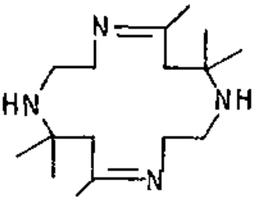
(44)

formylation of zinc octaethylporphyrin gives **(42)** [260]. A crystal structure of a dinuclear zinc complex of the porphin precursor, 1,2,3,7,8,12,13,17,18,19-decamethylbiladiene-*a*,*c* **(43)** has been described [261] and the octaethylisobacteriochlorin complex (44) has been studied as a model for siroheme enzymes [262]. The synthesis of zinc tetra-2,3-naphthoporphine by a template reaction has been described [263].

A zinc complex of [18]ane-1,4,7,10,13,16-N_6 has been reported, [264] and the metal exchange of Cu(II) for Zn(II) in a range of cyclic polyamine complexes, $[ZnL]^{2+}$ (L = [12]ane-1,4,7,10-N_4, [13]ane-1,4,7,10-N_4, [14]ane-1,4,8,11-N_4 or [15]ane-1,4,8,11-N_4) in aqueous solutions buffered by ethanoate has been investigated [265]. The metal exchange reaction was thought to involve a ligand dissociation:

$$[ZnL]^{2+} + MeCO_2H \longrightarrow [Zn(O_2CMe)]^+ + HL^+$$

as already proposed for the metal exchange reactions of porphyrins in dmf. The formation of the complex ions $[ZnL(H_2O)_x]^{2+}$ and $[ZnL(OH)]^+$ {L = 5,7,7,12,14,14-Me_6-[14]-4,11-diene-1,4,8,11-N_4 (45)} has been described [266].



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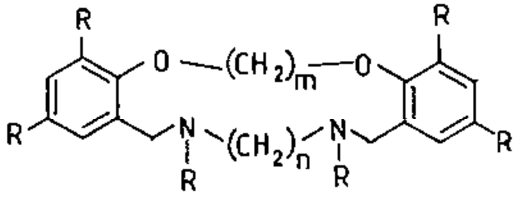


(46)

A number of mixed donor macrocycles of the type (46) have been prepared (n = 2, m = 2; n = 3, m = 2,3 or 4) and their zinc complexes have been characterised. A determination of the crystal structure of the complex $[ZnLI_2]$ (L = 8,12-Me_2-5,6:14,15-Bzo_2-[14]-5,14-diene-8,12-N_2(1,4-O_2) has indicated that only the nitrogen atoms are coordinated to the metal [267]. Lewis *et al.* have described a number of zinc complexes of macrocycles incorporating 2,2'-bipyridine or 1,10-phenanthroline subunits (see Mercury, Section 13.2.7) [268, 269,270].

12.1.6 Complexes with phosphorus or arsenic donor ligands

The reactions of $[Zn(dmso)_6]^{2+}$ with a range of tertiary amines, phosphines, or arsines have been investigated; complexes with Bu_3N and Bu_3P were characterised, and were found to be more stable in water than the dmso complex [231].

12.2 ZINC(I)

Very few complexes of zinc(I) are known but the pulse radiolysis of aqueous solutions of $[Zn([14]ane\text{-}1,4,8,11\text{-}N_4)]^{2+}$ has been shown to produce $[ZnL]^+$ [271].

CADMIUM

12.3 CADMIUM(II)

12.3.1 Halide complexes

A study of the vibrational spectra of CdF_2 and CdFX (X = Cl or Br) has been made, the mixed-halo species being prepared by mixing equimolar amounts of CdF_2 and CdX_2 in the vapour phase. The fluorohalides have been characterised as molecular species for the first time [1]. The solubility of $CdCl_2$ or $CdBr_2$ in dmf [3], and of $CdBr_2$ in water [272] have been determined and the thermal conductivity of aqueous solutions of $CdCl_2$ and $CdBr_2$ has been measured [2]. A determination of the crystal structure of $Cs[CdBr_3]$ has been reported and the metal shown to exist in trigonally distorted $\{CdBr_6\}$ octahedra [273]. The Raman spectra of $Rb[CdX_3]$ (X = Cl or Br) [274] and $[Pr_4N]_2[CdX_3Y]$ (X = Br or I; Y = Cl,Br, or I) have been reported and the latter anions, like $[CdCl_3X]^{2-}$, shown to have a *pseudo*tetrahedral geometry [275].

A number of 1-cetyl-3-methylpyridinium (A^+) salts, $A_2[CdX_4]$ and $A[CdX_3]$ (X = Cl,Br, or I) have been characterised [13], as have the tetrachlorocadmate(II) compounds, $[LH]_2[CdCl_4]$ (L = $4\text{-}NH_2C_6H_4SO_2NH_2$ or $4\text{-}NH_2C_6H_4SO_2NHCOMe$) [276]. The extraction of $Li_2[CdI_4]$ from water by methyl *iso*-butyl ketone (L) has been investigated, and the organic layer shown to contain $CdI_2.4L$ and $Li_2[CdI_4].10L$ [277]. ^{115m}Cd has been used as a tracer to follow the extraction of cadmium from aqueous HCl solutions by tributyl phosphate [278].

The compounds MCd_5Cl, $MCdCl_3$, M_2CdCl_4, $M_3Cd_2Cl_7$ (M = Cs,Rb), $CsCdCl_5$, Rb_4CdCl_6 and $Rb_4Cd_3Cl_{10}$ have been reported as components of MCl–$CdCl_2$ melts [279].

12.3.2 Pseudohalide complexes

A crystal structure determination of $Cd(NCS)_2$ has been reported and the metal shown to be in an N_2S_4 environment [280]. The complex $A_2[Cd(SCN)_4]$ (A = 1-cetyl-3-methylpyridinium) has been prepared [13] and the related species, $[R_4N]_2[Cd(SCN)_4]$, are extracted from aqueous solutions containing Cd^{2+} and $[SCN]^-$

by solutions of quaternary ammonium salts in organic solvents [281].

The thermal decomposition of $[Ph_2I]_2[Cd(CN)_4]$ has been investigated [282]. The interaction of $[R_4P]^+$ with aqueous Cd^{2+} and $[CN]^-$ results in the formation of the complexes $[R_4P][Cd(CN)_3]$, examples of solid complexes containing the rare $[M(CN)_3]^-$ anion [17].

12.3.3 Complexes with oxygen donor ligands

12.3.3.1 Complexes with inorganic oxoanions

For the reasons given at the beginning of Section 12.1.3.1, this review will not attempt to cover the mixed oxides of cadmium which have been reported.

Phases formed in the ternary systems $Eu[ClO_4]_2$–$Cd[ClO_4]_2$–H_2O [283] and $CdSO_4$–H_2O–H_2SO_4 [284] have been studied. The thermal decomposition of $CdSO_4.2HCl$ has been investigated and the compound shown to lose 93% of the HCl between 343 and 523 K [285]. A Raman spectroscopic study of the complex $[NH_4]_2[Cd_2(SO_4)_3]$ has been reported [286]. The reaction of [Cd(ox)] with CO_2 at elevated temperatures has been shown to produce $Cd[CO_3]$ [45].

Only a few phosphate complexes of cadmium(II) have been reported this year, including the ternary species $[Cd(edta)(P_2O_7)]^{6-}$ which was detected potentiometrically in mixtures of Cd^{2+}, H_4edta, and $[P_2O_7]^{2-}$ [287], and $[Cd_3(P_6O_{18})].16H_2O$. The latter species is formed in the reaction of $Cd[ClO_4]_2$ with ethanolic $H_6P_6O_{18}$ and it dehydrates readily to give $Cd[PO_3]$ [360]. The extraction of cadmium from aqueous solution of cadmium(II) salicylate by tributyl phosphate in cyclohexane has been studied [32].

The methanesulphonic acid complex, $[Cd(MeSO_3)_2]$, has been prepared by the reaction of $CdCl_2$ with $MeSO_3H$ [288] and a crystal structure of $Cd(O_3SCH_2SO_3).3H_2O$ has shown the metal to be seven coordinate, in a distorted pentagonal bipyramidal environment [289]. The reaction of $Cd(O_2CMe)_2$ with $[OH]^-$ in the presence of other anions (F^-, $[S_2O_3]^{2-}$ or $[HCO_2]^-$) has been investigated and the products shown to include [Cd(OH)X] (X = F or HCO_2]) or $[Cd_4(OH)_6(S_2O_3)]$, as well as $Cd(OH)_2$ [290].

12.3.3.2 Complexes with carboxylic acids and related ligands

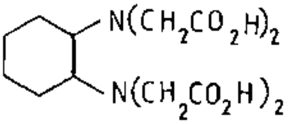
The policy adopted for this section has been to include all the cadmium(II) complexes of carboxylic acids, except those involving ligands which contain either a sulphur atom or a nitrogen heterocyclic ring.

On pyrolysis, $Cd(O_2CMe)_2.2H_2O$ behaves similarly to the corresponding zinc compound giving, ultimately, CdO, Me_2CO, and $(MeCO)_2O$ [48]. A number of ternary complexes containing ethanoate have been reported and the systems investigated include $Cd(O_2CMe)_2$–H_2O–Cl^- [291] and $Cd(O_2CMe)_2$–H_2O–$EtCO_2^-$ [292]. The solubility of $Cd(O_2CMe)_2$ in mixed alcohol-hexane solvents has been investigated and a model for the solvation shell of the metal in such systems has been proposed [49]. A complex, $BaCd(HCO_2)_4.2H_2O$, has been characterised in the $Cd(HCO_2)_2$-$Ba(HCO_2)$-H_2O system [293].

Other carboxylic acids, the interactions of which have been studied with cadmium(II), include 1,2,4-benzenetricarboxylic acid [55], 2,3-dihydroxypropanoic acid [294], citric acid [295], trihydroxyglutaric acid [295], salicylic acid [295], humic acid [296], 2-furancarboxylic acid [297], gluconic acid [298], and 4-hydroxybenzoic acid [299]. A crystal structure of a complex with the latter ligand, $[Cd(H_2O)_5L]L.H_2O$, has been reported [299]. The formation of ternary complexes of cadmium(II) with thiosulphate and itaconate, adipate, or phthalate have been reported and several complexes were isolated [316].

Amino acid complexes of cadmium have not been as widely investigated as those of zinc but compounds with L-glutamic acid [300] and phenylalanine [66] have been described. Mixed-ligand complexes with glycinate and bicinate [301] and citric acid and L-histidine [302], have been reported. Determinations of the crystal structures of $[Cd(gly)_2X_2]$ (X = Cl or Br) have shown the two compounds to be isomorphous and to involve an octahedral environment about the metal; the amino group is hydrogen bonded to a carbonyl group and a halide ion [303]. A number of amino acid and peptide complexes of cadmium(II) have been investigated by ^{14}NQR spectroscopy [315].

Iminodiethanoate complexes continue to be of interest and the ligands investigated include: $(H_2NOOCH_2)N(CH_2CO_2H)_2$ and $(H_2NOOCH_2CH_2)N(CH_2CO_2H)_2$ [70], $(HO_2CCH(OH)CH_2)N(CH_2CO_2H)_2$ [71], H_4edta [304], DL-$(HO_2CCH_2)_2NCH_2CH(CO_2H)N(CH_2CO_2H)_2$ [72], $(MeO_2CCH_2)_2NCH_2CH_2N(CH_2CO_2Me)_2$ [305], and $\{(HO_2CCH_2)_2NCH_2CH_2NHCH_2CH_2NH$-$CH_2CH_2\}_2NH$ [306]. The kinetics of the reaction of [PbL] $\{H_4L = (HO_2CCH_2)_2NCH_2$-$CH_2OCH_2CH_2OCH_2CH_2N(CH_2CO_2H)_2\}$ with Cd^{2+} have been investigated and the product shown to be $[CdHL]^-$ [307]. The natural abundance ^{15}N NMR spectrum of $[CdL]^{2-}$ $\{H_4L$ = **(47)**$\}$ has been reported and satellite peaks due to coupling of ^{15}N to



(47)

the ^{111}Cd and ^{113}Cd nuclei detected [308].

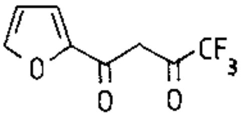
12.3.3.3 Complexes with amides and related ligands

The malonamide (L) complex $[CdCl_2L_2]$.MeOH has been prepared in which the coordination about the metal is octahedral, with the malonamide acting as a bidentate N_2 donor and the chlorine atoms mutually *cis* [309]. This compound differs from the related, but five-coordinate, zinc complexes which have also been reported [77,78]. The complexes [Cd(tmu)X_2] (X = Cl,Br or I) have been reported and, like the zinc complexes, the ligand shown to be coordinated through oxygen [79].

Complexes involving cadmium(II) have also been reported for the ligands: PhCH=CHCONHNH$_2$ [86], H_2NCONHCONH$_2$ [85], PhCH$_2$CONHOH [87], 4-MeC$_6$H$_4$N(OH)COAr [310], and acrylamide [80]. The thermal decomposition of [CdL$_2$X$_2$] (X = Cl or MeCO$_2$; L = MeNHCHO) [88] and [Cd(dma)Cl$_2$] [84] has been investigated. The complexes [Cd(MeSO$_3$)$_2$L] (L = dmf or tmu) have been prepared by the reaction of [Cd(MeSO$_3$)$_2$] with dmf or tmu, respectively [288].

12.3.3.4 Complexes with ketones and ethers

Very few complexes containing ketone ligands have been reported this year but a determination of the crystal structure of [NH$_4$][CdL$_3$] {HL = **(48)**} has shown



(48)

the ligand to be bidentate, with the geometry of the anion distorted towards a trigonal prism [311]. Complexes with ArCOCH$_2$COMe (Ar = 4-MeC$_6$H$_4$ or 4-FC$_6$H$_4$) [92] and 5-chloro-2-hydroxy-4-methyl-acetophenone [312] have also been described.

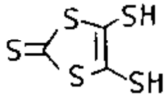
The ^{35}Cl, ^{81}Br and ^{127}I NQR spectra of a number of CdX$_2$-polyether complexes have been reported and the details indicate that the compounds are dimeric in solution, with symmetrical halogen bridges between the metal atoms [313]. The complex [(CF$_3$)$_2$Cd(glyme)] has been prepared, by the metathesis reaction of (CF$_3$)$_2$Hg with [CdMe$_2$] in glyme, and has been shown to be a useful intermediate for the preparation of other trifluoromethyl compounds (*e.g.* R$_4$Ge, R$_4$Sn and R$_3$P) [314].

12.3.4 Complexes with sulphur or selenium donor ligands

12.3.4.1 Complexes with thiols, thiones and thioethers

A number of [Cd(SR)$_2$] complexes with alkanethiols have been prepared [317]. The ligand **(49)**, formed from the reaction of CS$_2$ with alkali metals in dmf, gives an anionic cadmium complex, [Bu$_4$N]$_2$[CdL$_2$] {H$_2$L = **(49)**}. .

The reaction of **(50)** with metal salts results in dealkylation and the formation of the trimetallic species, **(51)**. Thus the reaction of **(50)** with Cd(O$_2$CMe)$_2$ results in the formation of **(51**; $M_1 = M_2$ = Cd; X = 2Br**)**. A



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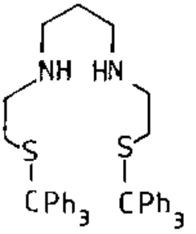

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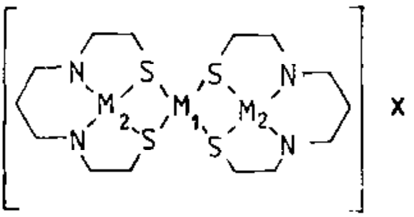
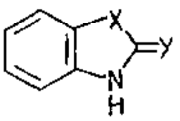


(51)

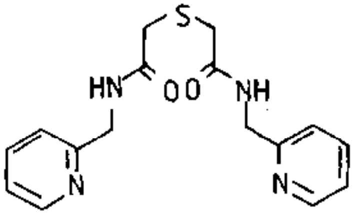
heteropolynuclear species, (51; M_2 = Ni; M_1 = Cd; X = [$CdBr_4$]) results from the reaction of (51; M_1 = M_2 = Ni; X = 2Br) with $Cd(O_2CMe)_2$ [318].

Ligands containing heterocyclic and mercapto groups continue to be of interest and cadmium(II) complexes with 1-amino-2-mercapto-5-trifluoromethyl-1,3,4-triazole [105], 1-benzyl-2-ethyl-5-mercapto-1,3,4-triazole [107], 3-amino-2-mercaptoquinazol-4-one [108], 2-thiouracil [103], and 4,6-dimethyl-2(1H)-pyrimidinethione [104,319] have been reported. With the latter ligand (HL), the complexes {$Cd(HL)_2X_2$} (X = Cl,Br,I or tfa), [$Cd(HL)_3$][ClO_4]$_2$.$2H_2O$, and [CdL_2] have been prepared; the [$Cd(HL)_2X_2$] compounds are polymeric, with a halogen-bridged structure, and differ from the corresponding zinc(II) and mercury(II) complexes, which are tetrahedral monomers [104]. The complexes [CdL_2Cl_2] with the mercapto and selenide ligands (L) (52)-(56) have been reported [320].



	Y	X
(52)	S	NH
(53)	S	S
(54)	Se	NH
(55)	Se	O
(56)	Se	S

Cadmium(II) complexes with a number of dimercaptodicarboxylic acids [321] and thioethers have been described; the ligands employed include: $HO_2CCH_2SSCH_2CO_2H$ and $HO_2CCH_2CH_2SSCH_2CH_2CO_2H$ [114], Me_2S and MeSSMe [113], (57) [322] and $HO_2CCH_2CH(CO_2H)SCH(CO_2H)CH_2CO_2H$ [111]. The complex [$CdLCl_2$] {L = (57)} has been shown to involve a square planar geometry at the metal [322].



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12.3.4.2 Complexes with thioacids, thiamides and related ligands

Complexes of cadmium(II) with (7) [120] and $HS_2CNHCSNH_2$ [121] have been reported. The reactions of [Cd(acac)$_2$] with the anions of Et_2NCS_2H, 3-morpholinedithiocarboxylic acid, or 2-piperidinedithiocarboxylic acid (HL) have been investigated and, in each case, the product was shown to be the corresponding [Cd(acac)L] complex [323]. A number of ternary complexes, [CdL$_2$Q] (Q = bipy or phen; HL = $EtOCS_2H$) have been prepared, including compounds labelled with ^{115m}Cd [119]. The reaction of [CdL$_2$] (HL = diethyldithiocarbamic acid) with a number of other ligands has been studied and the complexes [CdL$_2$Q] (Q = 3-Mepy, quin or morpholine) have been characterised [324].

The preparation of cadmium(II) complexes with thiourea [325,326,327], ethylenethiourea [130], thiosemicarbazide [127], PhNHNHCSNHNHPh [328], dithiooxamide [329], and [{CH_2=$CHCH_2NHCSNH$-}$_2$] [126] have been reported. The thiourea ligands in [Cd(O_2CMe)$_2$(tu)$_2$] and [Cd(tu)$_n$][ClO_4] (n = 4 or 6) are bonded through their sulphur atom; the former complex has a tetrahedral S_2O_4 arrangement, with a more distant interaction with two other oxygen atoms giving the metal atom a bicapped tetrahedral geometry [327], whilst in the latter two complexes the perchlorate counter ion is hydrogen bonded to the amino groups of the ligand [326].

The formation of cadmium(II) complexes of the ligands R_1R_2C=$NNHCS_2Me$ and R_1R_2C=$NNHCSNH_2$ have been studied by ^1H NMR and the behaviour found shown to be similar to that of the corresponding zinc complexes (see Section 12.1.4.2) [132]. The complexes [CdLX$_2$] (X = Cl,Br or NCS) and [CdL$_2$][ClO_4]$_2$ (L = EtMeC=$NNHCSNH_2$ have also been investigated and have been shown to involve tetrahedral cadmium(II) [330].

12.3.4.3 Complexes with sulphur heterocycles

The complexes [Cd(HL)$_2$] and [CdL(H_2O)$_2$] {H_2L = (9)} have been described and are thought to have a tetrahedral geometry at the metal, with the ligands HL or L acting as *NS* donors [137]. Other related complexes which have been described include: [CdL$_2$(py)$_2$][SO_4] (L = 2-amino-5-phenyl-1,3,4-thiadiazole) [134] [CdL$_2$Br$_2$] (L = 4-amino-2,1,3-benzothiadiazole) [331], and complexes of

Cd(II) with 2,1,3-benzothiadiazole and 4-hydroxy-2,1,3-benzothiadiazole [332].

12.3.4.4 Complexes with sulphonic acids

A number of sulphonic acid complexes of cadmium(II) have been mentioned in Section 12.3.3.1 and complexes with the ligands (10) and (11) have also been described [140,141]. The complexes $[CdL_2Cl_2]$ (L = $4\text{-}H_2NC_6H_4SO_2NHR$; R = H or O_2CMe) are formed in the reaction of L with $CdCl_2$ in $MeOH\text{-}Me_2CO$, and react with HCl to give $[LH]_2[CdCl_4]$ [146].

12.3.5 Complexes with nitrogen donor ligands

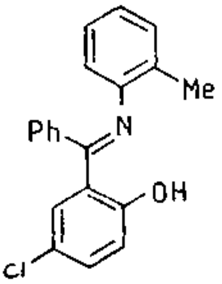
12.3.5.1 Complexes with amines and related ligands

A Raman study of the compounds $[Cd(NH_3)_6]X_2$ (X = Cl,Br, or I) has been reported [333] and the complexes $[Cd(PhNH_2)X_2]$ (X = Cl or Br), and their deuterated derivatives, have been reinvestigated and shown to be octahedral [334]. This latter study clarified some of the confusion present in the earlier literature concerning these compounds. Another aniline complex, $3CdCl_2.4L$, has been studied and it has been shown that there are two types of octahedral environment in which the cadmium atoms are found, one comprising a $\{CdCl_5\}$ unit and the other a $\{CdCl_4N_2\}$ unit [335].

Cadmium(II) complexes of the ethanolamine derivatives $MeNHCH_2CH_2OH$ and $EtNHCH_2CH_2OH$ [149] have been reported. Complexes of diamines have been widely investigated, and several workers have studied the Cd(II)-en system [336-341]. An X-ray spectroscopic study of aqueous solutions of cadmium-en complexes has shown that, like their zinc(II) counterparts, the ions $[Cd(en)_2]^{2+}$ and $[Cd(en)_3]^{2+}$, respectively involve a tetrahedral and an octahedral geometry at the metal atom [336]. Much of the interest in the en complexes has centred upon the ability of $\{Cd(en)\}^{2+}$ salts to form clathrate compounds. The compounds $\{Cd(en)\}\{Pd(CN)_4\}$ and $\{Cd(NH_3)_2\}\{Pd(CN)_4\}$ each accept two guest molecules of phenol, benzene, or thiophen [336,339] and the thermal decomposition of these species, and of the related complex $\{Cd(en)\}\{Ni(CN)_4\}.C_6H_6$ has been studied [338,339]. The compound $\{Cd(en)Cd(CN)_4\}.2C_6H_6$ is of interest, since the en ligand has shown to be bridging, although on heating to 100 °C it loses benzene to form $\{Cd(en)\}\{Cd(CN)_4\}$ [340].

The interaction of Cd^{2+} with $MeNH(CH_2)_3NH_2$ [342], dien, $H_2N(CH_2)_2N(CH_2)_3NH_2$, or $H_2N(CH_2)_3NH(CH_2)_3NH_2$ [343] has been investigated and, in each case, a 1:1 complex was formed; $\{Cd(dien)Cl_2\}$ exists as polymeric chains of octahedral units connected by halide bridges, whereas the complexes with the other ligands contain dimeric species [343]. The kinetics of the ligand exchange reaction between $[Cu(edta)]^{2-}$ and $[Cd(trien)]^{2+}$ have been investigated [344].

Imine complexes of cadmium(II) have not been as widely investigated as those of zinc(II), but complexes of the former with the ligands (23) [171], (24) [172], (25) [173] and (58) [345], have been reported. The diimines (59) and (60), formed by the condensation of benzil with en or 1,2-diaminobenzene respectively, have been shown to form the tetrahedral complexes [CdL] [346].



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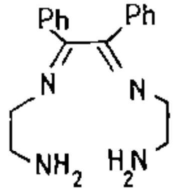

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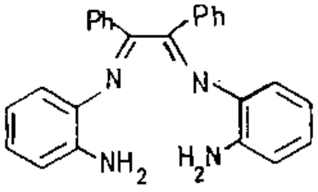

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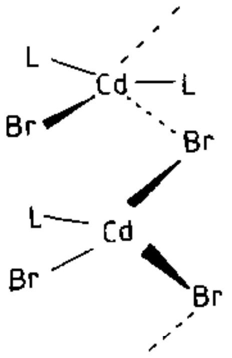
The alcoholysis of $Ph_3P{=}NSiMe_3$ in the presence of CdX_2 (X = Cl,Br or I) results in the formation of the complexes $[Cd_2Cl_4L_2]$, $[Cd_2Br_4L_3]$, and $[Cd_2I_4L_4].2CHCl_3$ (L = $Ph_3P{=}NH$), respectively; the structure of $[Cd_2Cl_4L_2]$ was thought to be similar to that of the corresponding zinc complex, whilst $[Cd_2Br_4L_3]$ and $[Cd_2I_4L_4]$ were thought to have the structures (61) and (62), respectively [152]. The formation of the complexes $[CdX_2L]$ (X = Br or I; L = $[(Ph_3P)(ArNC)Pt(MeOC{=}NAr)_2]$) and $[CdI_2L]$ (L = $[(dppe)Pt(MeOC{=}NR)_2]$) has been



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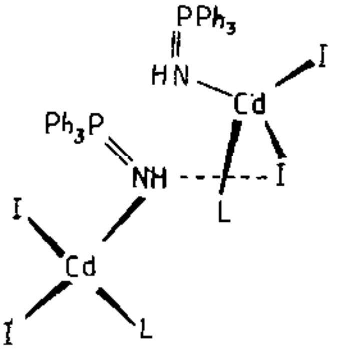


(62)

described and the ligand is considered to act as a bidentate N_2 donor [162].

12.3.5.2 Complexes with pyridine and quinoline ligands

The cadmium(II)-pyridine system has been further studied [347,348], and the ^{14}N NQR spectra of the complexes [$Cd_2(py)_3(NO_3)_4$], [$Cd(py)_2Cl_2$], and [$Cd(py)_3(NO_3)_2$] [349] have been reported. The interaction of cadmium(II) with 3-Mepy, 4-Mepy, 4-Etpy, 3,4-Me$_2$py, and 3-Et-4-Mepy have been studied and the rôle of back donation in the formation of the Cd-N bond has been discussed [176]; an octahedral complex [CdL_6]$^{2+}$ was formed with all the ligands except 3-Et-4-Mepy. The chlorination of ethanolic solutions of [CdL_2X_2] or [$CdLX_2$] (L = py, quin, isoquinoline, 3,5-Me$_2$py or 4-Mepy; X = Cl or Br) has been studied and, like the corresponding zinc compounds, the only products identified were the halocadmate salts, [LH]$_2$[CdX_2Cl_2] and [LH][CdX_2Cl] [350].

Cadmium(II) complexes with 2-(2-pyridyl)ethanol [181], 4-pyridinecarboxylic acid *N*-oxide [351], 3-pyridinecarboxylic acid [352] and 3-pyridinealdehyde [184] have also been described. The compounds [CdL_2I_2] and [$CdLX_2$] (X = Cl or Br; L = bis(2-pyridyl)ketone) are all monomeric non-electrolytes in which the ligand acts as an N_2 donor [183]. Complexes of **(28**; Ar = Ph or 2-thienyl) have been reported but, as in the case of the corresponding zinc complexes, no template reactions have been described [187].

Cadmium complexes of the azo compounds, bis(8-hydroxy-5-quinolinyl)-4,4'-bisazobiphenyl [210] and 2-ArNHNHpy (Ar = 10-hydroxy-9-anthryl) [197] have been reported. The complexes [$Cd(amq)X_2$] (X = Cl,Br, or I) and [$Cd(amq)_2$][ClO_4]$_2$ [208] have been described, as has [$Cd(amq)_2(SCN)_2$] [212]. In the latter compound the thiocyanate is *S* coordinated, in contrast to the corresponding zinc complex in which it is *N* bonded to the metal.

The polarographic behaviour of Cd(II)-bipy complexes in aqueous dmf in the presence of [ClO_4]$^-$ has been investigated [353].

12.3.5.3 Complexes with other heterocyclic ligands

The pyrrolidine complex, CdL.HO$_2$CMe {L = **(31)**}, has been reported [213] and a number of cadmium(II) complexes with imidazoles have been prepared [218,354]. The crystal structure of [Cd(glygly)(imid)Cl] has been reported [315] and shown to involve dimeric units with a distorted octahedral geometry about each metal atom; this complex has also been studied in a ^{13}C NMR investigation of a range of nucleoside and peptide complexes of cadmium(II) [355].

The extraction of cadmium(II) from aqueous solution by benzene solutions of tributyl phosphate and the ligand **(33)** has been studied [217]. Cadmium(II) complexes with 1,2,4-triazole [221], **(32)** [216], benzimidazole [223], 4-amino-1,2,4-triazole [224], 9-methylhypoxanthine [232], and 2-amino-5-phenyl-1,3,4-oxadiazole [233] have been reported.

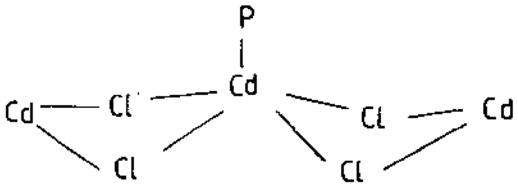
12.3.5.4 *Complexes with macrocyclic ligands*

The study of cadmium complexes of macrocyclic ligands is not as popular as that of the corresponding zinc complexes, but the increasing realisation that cadmium macrocycles undergo facile metal exchange promises to remedy this situation in the near future. The crystal structure of [Cd(TPP)(dioxan)$_2$] and its ^{113}Cd NMR characteristics have been reported [358]. The metal exchange reactions of [Cd(TPP)] with $CoCl_2$ or LiCl in Field Desorption mass spectroscopy resemble those of the corresponding zinc complex [256].

Cadmium complexes of the macrocycles (**46**; $n = 3$, $m = 2,3$ or 4), [267], [18]ane-1,4,7,10,13,16-N$_6$ [264], and [14]ane-1,4,8,11-N$_4$ [308] have been reported. The ^{15}N NMR spectrum of [Cd([18]ane-1,4,7,10,13,16-N$_6$)][NO$_3$]$_2$ has been described and shows satellite peaks due to coupling to ^{111}Cd and ^{113}Cd nuclei; the spectrum shows sets resonances due to two conformations of the cation, one corresponding to a planar and one to a trigonal bipyramidal structure [308].

12.3.6 *Complexes with phosphorus or arsenic donor ligands*

The five coordinate complex {$CdCl_2(PhMe_2P)$}$_n$ has been reported, and shown to have the structure (**63**) [356]. The reactions of $[Cd(dmso)_6]^{2+}$ with R_3N, R_3P, and R_3As parallel those of $[Zn(dmso)_6]^{2+}$, and a number of complexes with these ligands have been prepared [357].



(**63**)

12.4 CADMIUM(I)

Cadmium(I) is a very unstable species but more examples of it are known than of zinc(I). In general, Cd^+ has been produced by pulse radiolysis of solutions of cadmium(II) complexes [358,271] and the complex $[CdL]^+$ (L = [14]ane-1,4,8,11-N$_4$) has been prepared by this means [271]. It is thought that the initial step in the pulse radiolysis is the decomposition of water to hydrated electrons and $[OH]^{\bullet}$, and that it is the former species which reduces the Cd(II) to Cd(I).

^{113}Cd NMR relaxation data indicate that the addition of cadmium metal to CdI_2 results in the formation of Cd_2^{2+} and Cd^+, with the monomeric species having a half life of about 10 ps [359].

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