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1. ZINC AND CADMIUM

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CONTENTS

ZINC

CADMIUM

INTRODUCTION

This review is essentially a continuation of the 1980 Review of zinc and cadmium published in this journal in 1982 [1]. The format adopted is similar to that of the previous review, and the same criteria over content have been adopted. No attempt has been made to include coverage of the numerous reports of applications of the oxides and sulphides of these elements, which are of more concern to the physical chemist or the physicist.

I should like to thank Dr. Olga Kennard and Dr. Sharon Bellard for their help in obtaining structural data from the Cambridge Crystallographic Data Centre.

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1.1 ZINC(II)

1.1.1 Halide and psudohalide complexes

Photoelectron spectra of ZnF_2 in the vapour phase have been recorded using pseudo-molecular beam techniques, and it is proposed that the valence shell configuration is:

$$\text{Zn} \qquad (\pi_g)^4\ (\delta_g)^4\ (\sigma_g)^2$$

$$\text{F} \qquad (\sigma_g)^2\ (\pi_u)^2\ (\sigma_u)^2\ (\pi_g)^4$$

This differs from the configurations assigned to the other Group IIB dihalides, but closely resembles those of the IIA dihalides [2]. Molten zinc chloride has a remarkably high viscosity at its melting point (318° C) and an X-ray diffraction study at 323° C has revealed that the liquid consists of $[ZnCl_4]^{2-}$ and Zn^{2+} ions, rather than molecular $ZnCl_2$ [3]. The conductivity of $ZnCl_2$-LiCl melts has been investigated [4].

An EXAFS study of solutions of $ZnBr_2$ in EtOAc has indicated that quasi-solid clusters, resembling the crystal environment, persist even in dilute (0.05M) solution [5]. The formation of chloride complexes of zinc in methanol-nitromethane mixtures or in aqueous methanol has been investigated [6]. A polarographic study of the Zn^{2+}-F^--NO_3^--urea system has been made, and the stability of $[ZnF]^+$ shown to increase with increasing urea concentration [7]. The equilibrium:

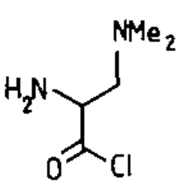
$$[ZnBr]^+ \rightleftharpoons Zn^{2+} + Br^-$$

has been investigated, and a value for ΔH_{ion} of 1331±100 cal mol^{-1} derived [8].

The formation of halide and pseudohalide complexes has been investigated by a number of groups [9-13]. Although Zn^{2+}-$[SCN]^-$ mixtures appear to give the tetrahedral ion $[Zn(NCS)_4]^{2-}$ [11], there is little evidence for the formation of the tetrachlorozincate(II) ion under similar conditions, the major species present in the Zn^{2+}-Cl^- system in dmso being the 1:1, 1:2 and 1:3 complexes [10]. Complexes with the pseudohalide ions $[N(CN)_2]^-$, $[C(CN)_3]^-$ and $[ONC(CN)_2]^-$ have been investigated in a range of non-aqueous solvents [12,13].

The Zn^{2+}-Cl^- system has also been investigated in thf and 1,2-dme, and, once again, there is little evidence for the formation of the $[ZnCl_4]^{2-}$ ion, the major solution species being $[ZnCl_3]^-$ [14]. The hydrazinium salt $[N_2H_5][ZnF_3]$ has also been reported [15]. The novel derivatives $[HZnI_3.L_3]$ (L = Et_2O, py, $PhNH_2$) and $[H_2ZnI_4.L_4]$ (L = Et_2O or $PhNH_2$) have been described, and their structures discussed in detail [16].

Single crystal structural analyses of $K_2[ZnF_4]$ and $K_3[Zn_2F_7]$ have been reported [17]. Although the $[ZnF_4]^{2-}$ ion is perfectly tetrahedral, the $[Zn_2F_7]^{3-}$ ion shows a shortening of the terminal Zn-F bonds. Most of the interest in the $[ZnCl_4]^{2-}$ ion has centred upon its ability to precipitate complex cations from aqueous solution, but Busch has recently pointed out that the water sensitivity of the ion, combined with the fact that the zinc may interfere in later transmetallation reactions, render it inferior to $[PF_6]^-$ as a precipitant [18]. The Vilsmeier-Hack reaction of active methylene compounds with $POCl_3$-dmf is a useful formylation method, and dimethyliminium species have long been proposed as intermediates. Sargeson and his co-workers have now shown that the reaction of $[Co(trien)(gly)]^{2+}$ with $POCl_3$-dmf leads to the ion $[Co(trien)L]^{3+}$ (L = 1), which was characterised by a single crystal structural analysis of the salt $[Co(trien)L][ZnCl_4]Cl.H_2O$ [19]. The macrocyclic complex



(1)

$[CuL][ZnCl_4]$ (L = 3,10-Me_2-2,9-Ph_2-[14]-1,3,8,10-tetraene-1,4,8,11-N_4) has been reported [20], as has a crystal structure of the complex ±-$[Ru(en)_3][ZnCl_4]$ [21]. A number of solid complexes containing the $[Zn(NCS)_4]^{2-}$ anion have been described [22].

The extraction of the Group IIB metals from aqueous solution is of obvious commercial importance and continues to be investigated [23-27]. The precise species which is extracted depends on the pH, but both Aliquat 336 and trin-n-butyl phosphate extract $[ZnCl_3]^-$ from LiCl solution and $[ZnCl_4]^{2-}$ from acidic media.

1.1.2 *Complexes with oxygen donor ligands*

1.1.2.1 *Inorganic molecules and ions*

Ab initio MO calculations have been reported for the species $[Zn(OH_2)_6]^{2+}$, $[Zn(OH)_2]$ and $[Zn(OH)_4]^{2-}$ [28,29] . The hexaaquozinc(II) ion was calculated to possess regular octahedral symmetry, whilst in the other species the Zn-O bond angles and bond lengths were calculated to be a function of the number of hydroxy groups bonded to the metal. An X-ray diffraction study of aqueous $Zn(NO_3)_2$ has been reported, and, as expected, a coordination number of six, almost independent of concentration, was found [30]. A wide-line ^1H NMR study of $[Zn(OH_2)_6][ClO_4]_2$ over the 4.2-363 K temperature range also confirms the basic octahedral symmetry of the cation, although some reorientation of the water molecules does occur [31]. A Raman study of $[Zn(OH_2)_6][MF_6]$ (M = Si or Ti) has been reported, and the symmetrical Zn-O stretching frequency has been unequivocally identified for the first time [32]. Although the $[Zn(H_2O)_6]^{2+}$ ion persists at most concentrations of aqueous solutions of zinc salts, the *total* hydration number is concentration dependent, and a study of aqueous zinc sulphate has revealed that the *total* number of water molecules associated with the $Zn(SO_4)$ decreases linearly with $lg[ZnSO_4]$ [33]. The formation of outer-sphere complexes between $[Zn(OH_2)_6]^{2+}$ and fluoride has been investigated [34]. The reaction of zinc nitrate with aqueous ammonia has been shown to result in the formation of basic nitrates, $4Zn(OH)_2.Zn(NO_3)_2.2H_2O$ and $9Zn(OH)_2.Zn(NO_3)_2$ and ZnO [35].

Other systems which have been investigated are $Mn(SO_3)$-$Zn(SO_3)$-H_2O [36], $Zn(SO_4)$-$Na_2(SO_4)$-H_2O [37], $Zn(NO_3)_2$-$Na(NO_3)$-H_2O [38], $Zn(SO_3)$-H_2O [39] and $Zn(NO_3)_2$-H_2O [40].

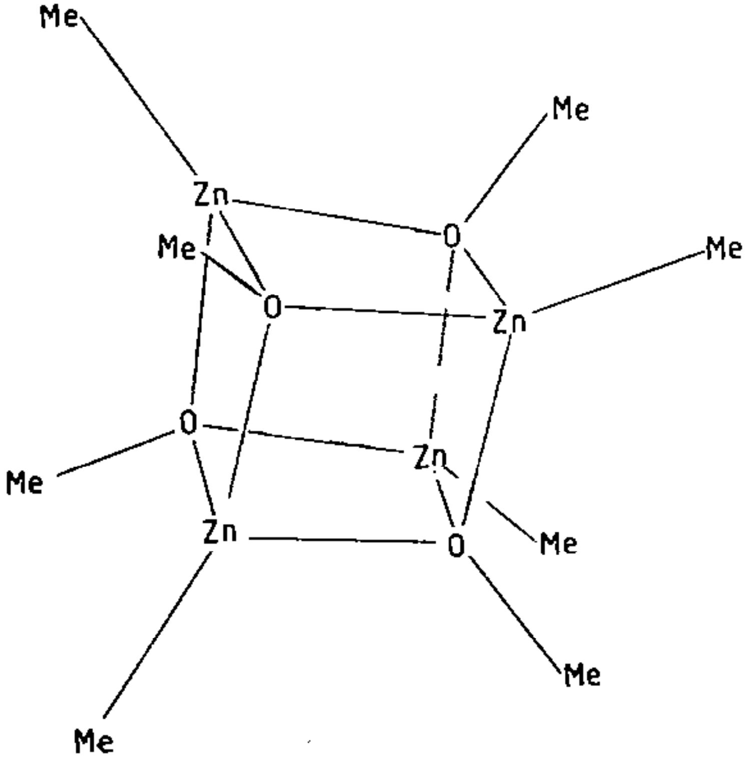
1.1.2.2 Simple organic ligands

The formation of solvated species in a range of organic solvents, in particular dmso, has been investigated. The complex $[Zn(dmso)_6][F_3CSO_3]_2$ is prepared by the reaction of ZnO with trifluoromethanesulphonic acid in dmso, and shows similar properties to $[Hg(dmso)_6][F_3CSO_3]_2$ (See Mercury in this volume) [41]. The electrochemical behaviour of zinc(II) in dmso has been investigated (E° Zn/Zn^{2+} −1.806 V, *c.f.* −1.562 V in water) [42]. The formation of dmso complexes of $Zn(NO_3)_2$ and $ZnCl_2$ has been reported [43], and a number of dihexyl sulphoxide complexes, $[ZnL_x(NO_3)_2]$ have been described [44]. The reaction of $ZnCl_2$ with $SbCl_5$ in nitromethane results in the formation of the complex $[Zn(O_2NMe)_6][SbCl_6]_2$, in which the $MeNO_2$ ligands are very labile [45]. Electronic and vibrational spectroscopic studies of solutions of zinc(II) salts in hmpa indicate the formation of octahedral species [46]. The hexakismethanol salt $[Zn(HOMe)_6][NO_3]_2$ is formed from the reaction of $[Zn(OH_2)_6][NO_3]_2$ with 2,2-dimethoxypropane [47]. A crystal structure of the tetrameric methylzinc(II) derivative $[\{MeZn(OMe)\}_4]$ has revealed the structure to be (2)[48].

Heterocyclic *N*-oxides continue to be of interest as ligands, and a crystal structure of the complex $[ZnL_6][ClO_4]_2$ (L = 4-methylpyridine *N*-oxide) has been reported [49]. The metal is in a near-octahedral O_6 environment, with an average Zn-O distance of 2.114 Å. Complexes of 2,4,6-trimethylpyridine *N*-oxide with zinc nitrate and zinc perchlorate have also been described [50]. The complexes $[ZnL(NO_3)_2]$ and $[Zn_2L_3(NCS)_4]$ (L = 4,4'-bipyridine *N,N'*-dioxide) have been reported, and the metal is thought to be in an octahedral environment in each [51]. Benzo[c]cinnoline *N,N'*-dioxide is reported to form both 1:1 and 1:2 complexes with $ZnBr_2$ [52].

1.1.2.3 Phosphine oxides

The solvent extraction of zinc, cadmium and mercury from aqueous solution is an important process, and phosphine oxides are frequently used as complexing agents. A crystal structure of the complex $[ZnCl_2(OPPh_3)_2]$ has been reported, and the metal is seen to be in a near tetrahedral O_2Cl_2 environment (3) [53]. The structure of



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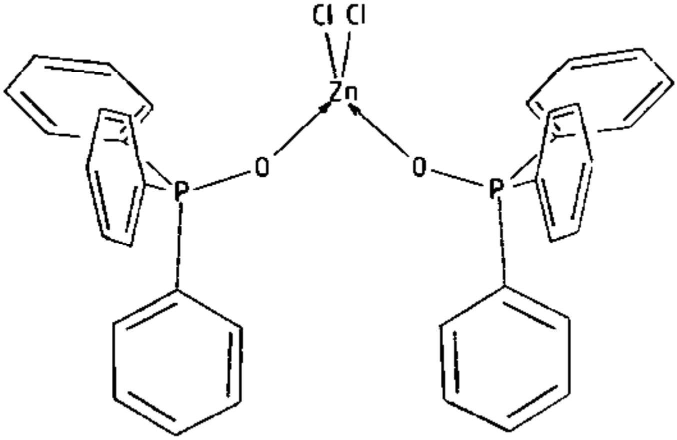


(3)

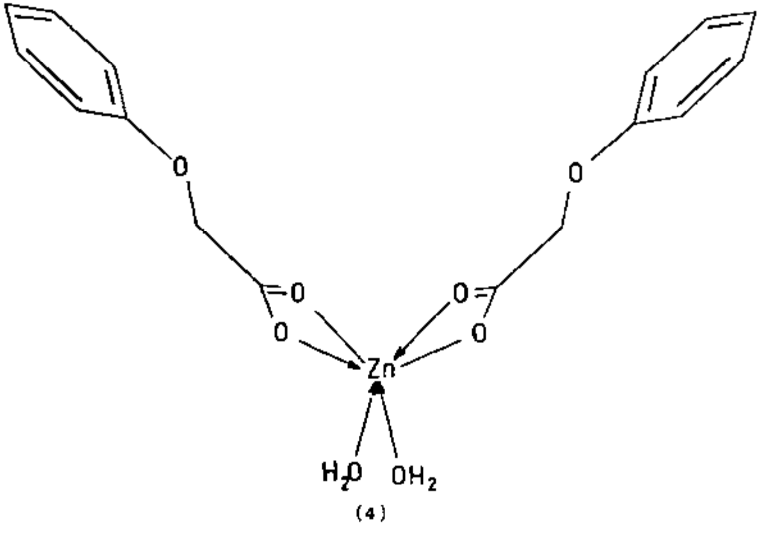
The structure of [$Zn(H_3NCH_2P(Me)O)Cl_2$] has also been reported, and the compound forms polymeric -P-O-Zn-O-P- chains, with the metal in a pseudotetrahedral O_2Cl_2 environment (Zn-O 1.95 Å, Zn-Cl 2.24 Å) [54]. The complexes [$Zn(Et_3PO)_2Cl_2$] and [$Zn(Bu_3PO)_2Cl_2$] have been reported [55]. Ligand exchange processes in a number of phosphine oxide complexes have been investigated by ^{31}P NMR, and it is proposed that the ligand exchange of [$Zn(Ph_3PO)_4$]$^{2+}$ in CD_2Cl_2 proceeds *via* a dissociative mechanism, since the rate of exchange is independent of [Ph_3PO] [56]. Complexes of $(Me_2N)_3PO$, $(MeO)_3PO$ and $(MeO)_2MePO$ have been similarly investigated [57].

The extraction of zinc from aqueous solution by trioctylphosphine oxide has been investigated by a number of workers [58-60].

1.1.2.4 *Carboxylic acids and related ligands*

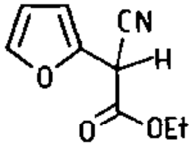
The crystallisation behaviour of the system $Zn(HCO_2)_2$-H_2O-$Mg(HCO_2)_2$ has been studied [61]. An infrared spectroscopic study of the compounds $Zn(OAc)_2.2H_2O$, $Zn(OAc)_2.2D_2O$ and $Zn(OAc)_2$ has been made, and the bands due to the librational modes of the crystallisation water identified, as were those of the Zn-O vibrational modes [62]. The solubility of $Zn(OAc)_2$ in AcOH-dmso mixtures has been studied, and species formulated as $Zn(OAc)_2.(4-n)AcOH.n$ dmso (n = 1 or 2) were identified [63]. The absorption spectra of alcoholic solutions of $Zn(OAc)_2$ are consistent with the formation of solvated species [64]. The mixed crystal $Zn(OAc)_2.Ba(OAc)_2.2H_2O$ has been characterised [65]. A number of mixed carboxylate complexes have been prepared [66].

Two groups have investigated the zinc complexes of phenoxyacetic acid, and confirm that there is no evidence for the coordination of the phenolic oxygen group to the metal [67,68]. Crystal structures of the isostructural complexes [$Zn(OH_2)_2L_2$] (LH = phenoxyacetic acid or 4-chlorophenoxyacetic acid) have been reported, and the metal has been shown to be in a distorted octahedral O_6 environment (4) [67]. Complexes



(4)

with $MeCOCO_2H$ [69], salicylic acid [70], fluorescein [71], cyanoacetic acid [72], 3,5-dinitrosalicylic acid [73]and (5) [74] have been described. A crystal structural analysis of $[Zn(py)_2L_2].2py$ (LH = 4-hydroxybenzoic acid) has shown the metal to be in a tetrahedral O_2N_2 environment (6) [75].



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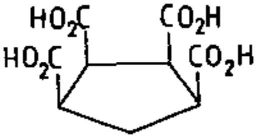

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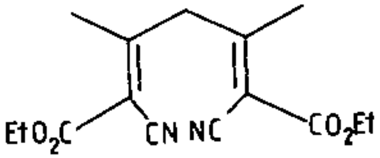

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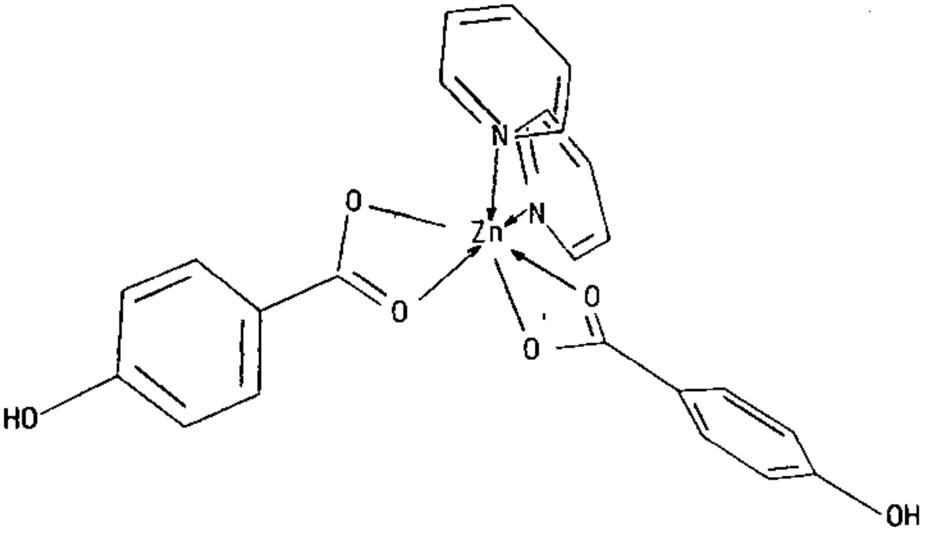


(6)

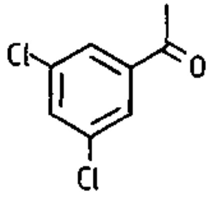
A ^1H NMR study of hydrated zinc acetate has been made, and a comparison with the corresponding cadmium species reveals that the geometry of the crystal is dictated by the number of water molecules and the anion, rather than by the cation [76]. Zinc complexes with a number of dicarboxylic acids have been described [77-84].

Ternary complexes with citric acid and a range of dicarboxylic acids have been described [84], as has a 1:1 complex with (7) [85]. The tetradentate ligand (8) is formed in the reaction of acacH with ethyl cyanoacetate, and forms tetrahedral zinc complexes $[ZnLX_2]$ (X = Cl, SCN or ClO_4) in which it acts as an *N,N',O,O'*-donor [86]

1.1.2.5 Diketonate and other ligands

The reaction of [Zn(acac)$_2$] with azaheterocycles has been shown to result in the formation of five-coordinate species [Zn(acac)$_2$L] (L = quinoline, isoquinoline or morpholine) [87]. An intensive study of the vibrational (IR) spectrum of [Zn(acac)$_2$] and its ^{18}O, ^{68}Zn and ^{64}Zn labelled derivatives has been made, and the bands assigned on the basis of the isotopic shifts assuming C_{4v} localised symmetry [88]. Further examples of the rare β-diketone (as opposed to β-diketonate) ligand have been found, and the complexes [Zn(acacH)$_3$][InCl$_4$] and [Zn(MeCOCH$_2$CO$_2$Et)$_3$][InCl$_4$] have been described [89]. Complexes of zinc with CF$_3$COCH$_2$COMe [90], CF$_3$COCH$_2$COCF$_3$[90]and PhCOCH$_2$COCF$_3$ [91] have been reported.

Salicylaldehyde complexes continue to be of interest, and coordination polymers are formed in the reaction of [ZnL$_2$] (LH = salicylaldehyde) with 1,2-diaminobenzene or 4,4'-diaminobiphenyl [92]. Related ligands which have been studied include (9) [93], (10) [94], (11) [95], (12) [96] and (13) [97]. 8-Hydroxyquinoline *N*-oxide is normally deprotonated in its complexes, but a series of compounds, including [Zn(LH)$_4$(OH$_2$)$_2$][ClO$_4$]$_2$.2H$_2$O, have been described [98]. The zinc is in an octahedral O_6 environment, with the ligand coordinated *only* through the phenolic hydroxy group. The complex [ZnL$_3$][SbCl$_6$]$_2$ (L = 14) has been described; the ligand is a bidentate O_2 donor [99].



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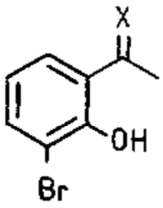
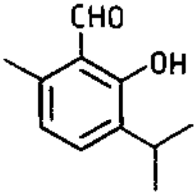


X = NOH, O, NNH$_2$

(10)



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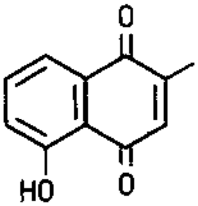

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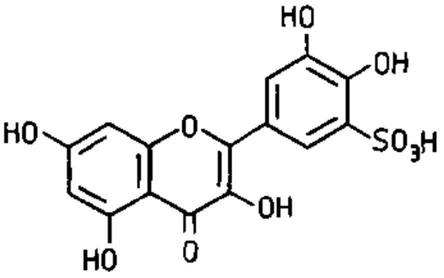

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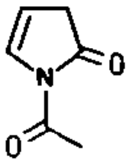
The reaction of catechol, 2,2'-dihydroxybiphenyl or 2,2'-dihydroxy-1,1'-binaphthyl



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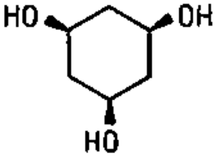


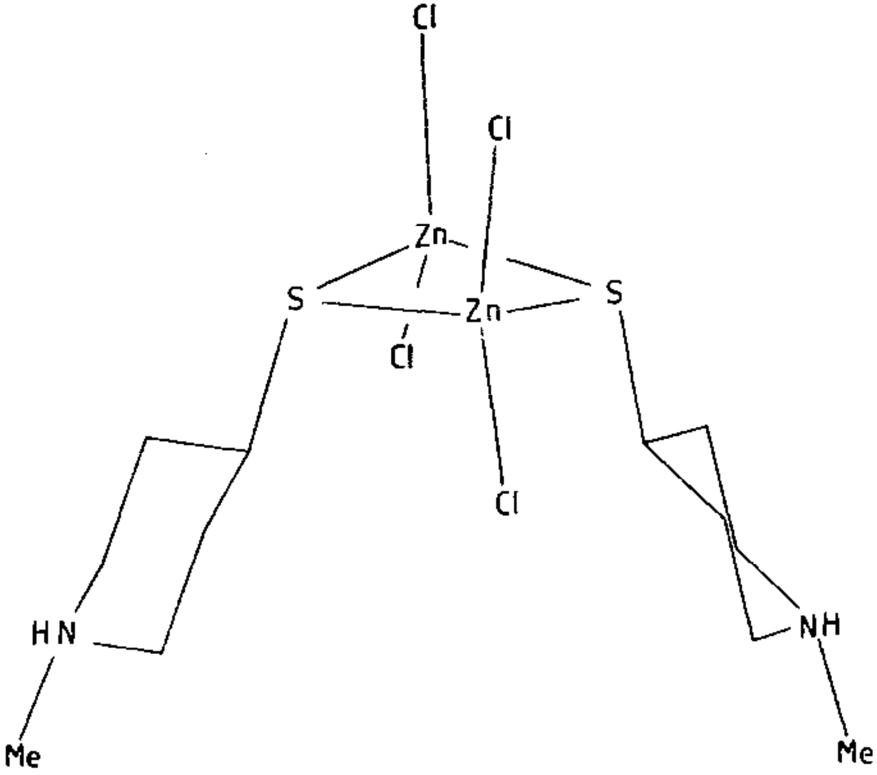
(15)

with $[Et_2Zn]$ gives [ZnL] and ethane [100]. The complexes $[ZnL_2X_2]$ (X = OTs, $MeSO_3$ or NO_3; L = 15) have been reported [101].

1.1.3 Complexes with sulphur donor ligands

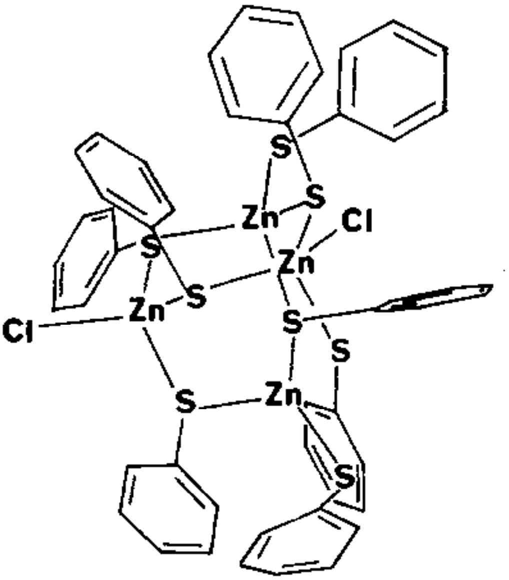
1.1.3.1 Thiols and thioethers

The reaction of $ZnCl_2$ with 4-mercapto-1-methylpiperidinium chloride (H_2L Cl) results in the formation of $[(ZnLCl_2)_2]$. H O, which has been shown by a crystal structural analysis to have the Zwitterionic structure (16) [102].



(16)

It is now well established that thiophenol reacts with zinc salts to give zinc-sulphur clusters, and a further example, $[Me_4N]_2[(\mu\text{-}SPh)_6(ZnSPh)_2(ZnCl)_2]$ (17) has been characterised crystallographically. The adamantane-like structure observed in $[(\mu\text{-}SPh)_6(ZnSPh)_4]^{2-}$ is seen to persist in the anion (17) [103]. Ternary complexes of zinc with α,α'-diimines and MeCHSHCONHPh have also been described [104]. Complexes with 5-thiopyrazolone [105], 1-methylimidazoline-2(3*H*)-thione [106], 2,5-dimercapto-1,3,4-thiadiazole [107], 5-mercapto-3-phenyl-1,3,4-thiadiazoline-2-thione [107], 1-(2'-pyridyl)-1,2,4-triazole-5-thiols [108], 6-mercaptopurine [109] and thioguanine [109]. The Schiff base complex (18) forms a 1:1 complex with *p*-chloranil, which has been intensively investigated [110]. There is evidence for both a π-π* interaction of the aromatic rings with the complex, and a local donor-acceptor interaction of the metal with the chloro- substituent.



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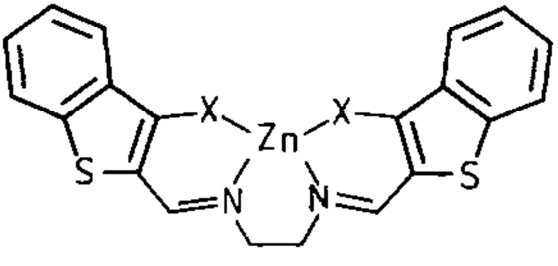
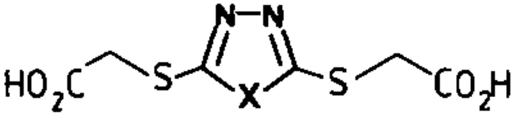


X = O, S or Se

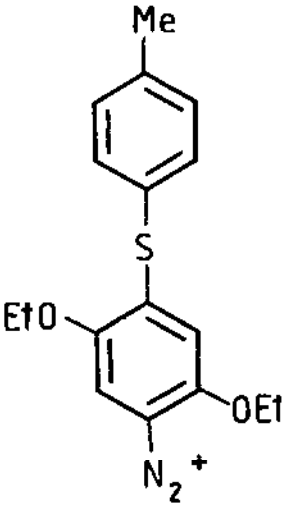
(18)

Zinc complexes of the thiocarboxylic acids, $(HO_2CCH_2CH_2)_2S$ [111], $HO_2CCH_2SCH_2CHNH_2CO_2H$ [112], $HO_2CCH_2CH_2SCH_2CHNH_2CO_2H$ [112], (19) and (20) [113] have been reported, although it is quite likely that the sulphur atom is not coordinated to the metal. A zinc complex of the diazonium cation (21) has been reported, and is claimed to be useful as a high-speed light-sensitive compound [114]. The complex $[ZnL(CN)_2]$ (L = bis(2-pyridyl)disulphide) has been prepared, but the ligand is coordinated to the metal *via* nitrogen, to give a *cis* pseudo-octahedral environment about the metal [115].



(19) X = S

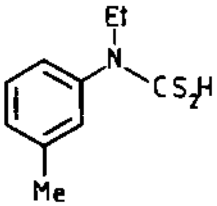
(20) X = NNH_2



(21)

1.1.3.2 Thioacids, thioamides and related compounds

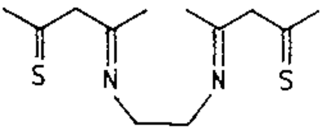
Although no complexes with dithioacids have been reported this year, the compound $[ZnL_2]$ (HL = 22) has been described [116]. Complexes with dithiooxamide [117],



1-amidino-2-thiourea [118], 2-thiopicolinanilide [119] and dialkyl 3-thiobenzoylureas [120] have been described. The formation of transition metal dithiocarbamates continues to be of interest, and a number of zinc complexes of these ligands have been studied [121-123]. Thiosemicarbazides are also widely studied as ligands, and complexes with thiosemicarbazide [124], bisthiosemicarbazones (23) [125], $H_2NCSNHNHCSNH_2$ [126]and $H_2NNHCSNHN{=}CHR$ [127]have been reported. The electrolysis of (24) at a zinc electrode results in the formation of [ZnL] (H_2L = 24) [128]. Zinc

$(MeNHCSNHN{=}CHCH\ )\ R$

(23)



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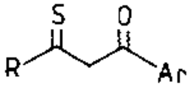


(25) R = MeS; (26) R = Ar

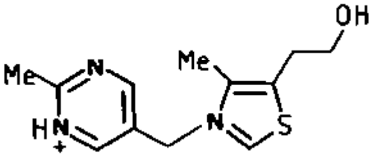
complexes of the related ligands (25) and (26), which act as *SO* donors have been described [129,130].

1.1.3.3 Phosphine sulphides and selenides

The zinc complexes $[ZnLI_2]$ (L = Ph_3PSe, $Ph_2P(S)CH_2CH_2CH_2P(S)Ph_2$or its selenium analogue) have been described [131]. Infra-red and Raman spectroscopic studies of the ligand tetraallyldiphosphine disulphide and its zinc complex $[ZnLCl_2]$ have been reported [132]. The extraction of zinc from acidic perchlorate medium by CCl_4 or heptane solutions of dibutyldithiophosphoric acid has been investigated: the metal is extracted as the complex $[Zn\{S_2P(OBu)_2\}]$ [133].

1.1.3.4 Sulphur and selenium heterocycles

The interaction of metal ions with Vitamin B_1 (thiamine hydrochloride,27), continues to be of interest, and a combination of infra-red, ^1H and ^{13}C NMR techniques have been applied to the study of the zinc complex, and it has been demonstrated that the metal is bonded to N3' of the pyrimidine ring, and not to the sulphur atom [134,135]. The hydrolysis of the Schiff base (28) is catalysed by the complex $[Zn(im)_2L]^+$ (LH =28) [136]. The formation of zinc complexes of sulphathiazole has been investigated [137]. The complexes $[ZnL_2Br_2]$ (L = benzothiazole, 2-methylbenzothiazole, 2,5,-dimethylbenzothiazole or 2,6-dimethylbenzothiazole) [138], $[ZnL_2].2H_2O$ and $[ZnL_2L'_2]$ (HL = 29; L' = 2-methylbenzimidazole) [139]have been described. Complexes of zinc with (30) [140], (31) [141]and (32) [142] have been described.



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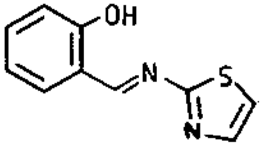

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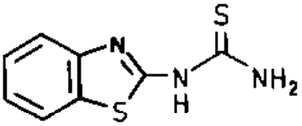

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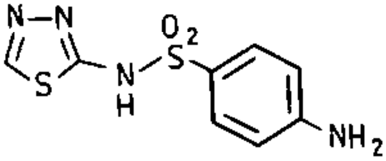

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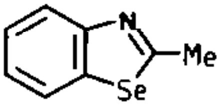

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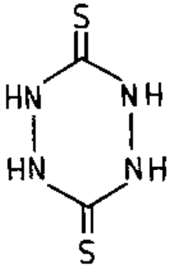

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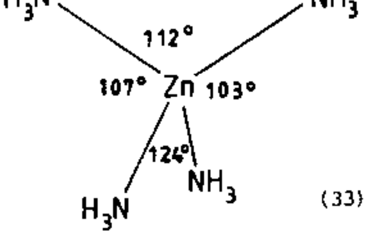
1.1.4 Complexes with nitrogen donor ligands

1.1.4.1 Amines

A crystal structure of $[Zn(NH_3)_4][I_3]_2$ has been reported: the metal is in a tetrahedral N_4 environment, and the triiodide ion is nearly linear (33) [143].



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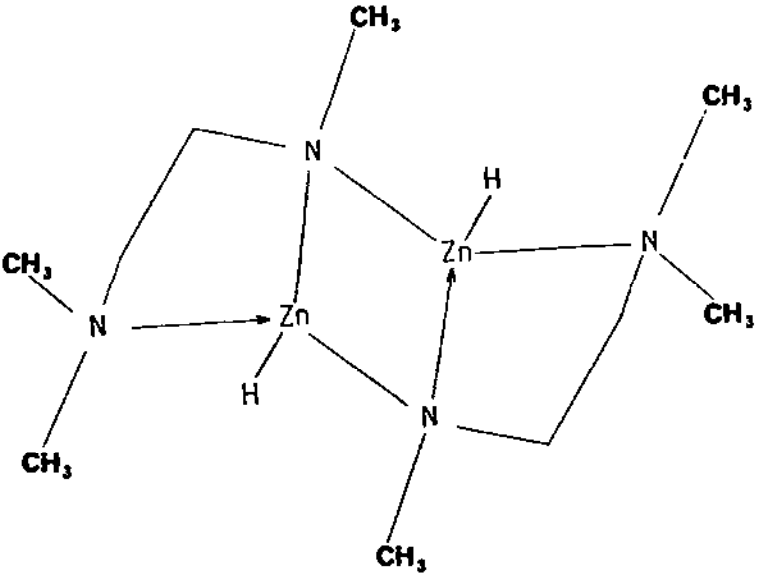
The interest in zinc-ammine complexes as host molecules continues, and the clathrate complex $[Zn(NH_3)_4][Ni(CN)_4].0.1PhOH.H_2O$ has been described [144]. Ternary complexes of bis(diethyl malonato)zinc(II) with diethylamine or dimethylamine have been reported [145]. Hydrazine complexes continue to be investigated, and the complexes $[Zn(N_2H_4)_2F_2]$ [146] and $CuZn(N_2H_4)_4X_4$ (X = Cl or Br) [147] have been prepared. $[Zn(N_2H_4)_2F_2]$ is air-stable, but is rapidly hydrolysed to $[N_2H_5]^+$ complexes. The hydrazine is thought to act as a bidentate bridging ligand in this complex, and it is suggested that there may be significant N-F interactions in the solid state.

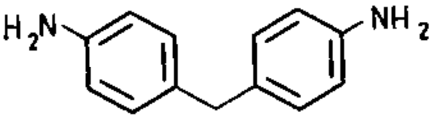
The stability constants for the formation of Zn-en complexes in dmf have been determined, and the complex ions formed shown to be more stable than the corresponding species in an aqueous environment [148]. Ternary complexes of zinc with en and adipic acid [149] and en or 1,2-pn with 5-sulphosalicylic acid [150] have been described. The complexes $[ZnL_2]^{2+}$ and $[ZnL_3]^{2+}$ (L = *meso*-2,3-diaminobutane) have been characterised [151]. Dimesitylzinc has been shown to react with tmeda to give $[R_2Zn(tmeda)]$ [152]. X-Ray and neutron diffraction studies of the hydrido complex $[HZn(MeNCH_2CH_2NMe_2)]$ have been reported [153]. The compound is dimeric, and has the structure shown in (34): each zinc atom has a terminal hydride bonded to it, and is also bonded to three nitrogen atoms, to give an N_3H environment [153]. The formation



(34)

of zinc complexes of triethylenetetramine in aqueous methanol has been investigated

[154]. The complexes $[ZnLX_2]$ (L = 35; X = Cl, Br, NO or NCS) are polymeric, with 35 acting as a bridging bidentate ligand [155].



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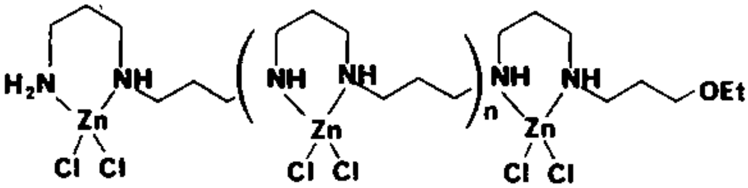
Complexes with a number of bistetrazoles have been reported, in which the two heterocyclic moieties are linked by polyethyleneimino chains [156]. The reaction of $ZnCl_2$ with trimethyleneimine has been shown to result in the formation of the complex $[ZnL_2Cl_2]$, which reacts with HCl or NH_3 to give $L_2[ZnCl_4]$ or $[Zn(NH_3)_4]Cl_2$ respectively (L = trimethyleneimine) [157]. The reaction of $[ZnL_2Cl_2]$ with Et_2NH at 120°C led to the complexes $[Zn\{H_2NCH_2CH_2CH_2(NHCH_2CH_2CH_2)_nNET_2\}]$ (n = 0,1 or 2), whilst the higher oligomers (36) were obtained with ethanol.



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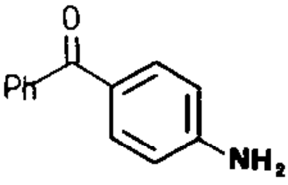
Zinc complexes of a series of diaminobenzenes have been investigated, and it appears that 1,2-diaminobenzene acts only as a monodentate ligand [158,159] . The interaction of ethanolamine with zinc has been studied electrochemically [160] . Complexes with the ligands (37) [161] , (38) [162] and (39) [163]have been reported.



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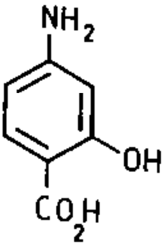

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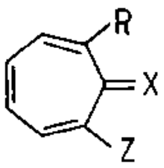
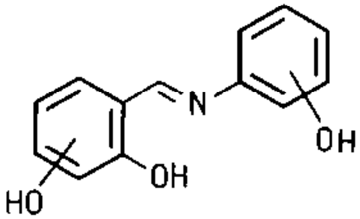


R	X	Z
H or Me	O	NMe
H	S	O
H	S	NMe or NPr

(39)

1.1.4.2 Schiff bases, hydrazones and oximes

The Schiff bases derived from salicylaldehyde continue to be of interest as bidentate *NO* donors, and a number of zinc complexes of such ligands have been described this year. The condensation of dihydroxybenzaldehydes with aminophenols in the presence of Zn^{2+} ions results in the formation of [$ZnLCl_2$] (L = 40) [164]. The complex [ZnL] (H_2L = 41) has been shown to be polymeric [165]. A charge-transfer complex [ZnLQ] (H_2L = 42; Q = ρ-chloranil) has been characterised, and a weak π-π^* interaction between the ZnL and Q moieties demonstrated [166]. A related complex, [ZnL] (H_2L = 43) is formed from the template condensation of HCN tetramer, $H_2N(NC)C{=}C(CN)NH_2$ with salicylaldehyde in the presence of $ZnCl_2$ [167]. In the absence of the zinc salt, unsymmetrical mono-Schiff bases are obtained.



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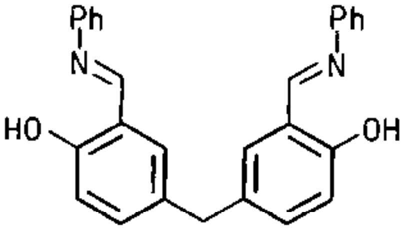

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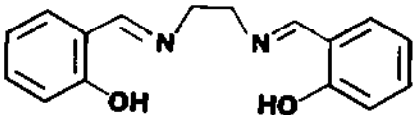

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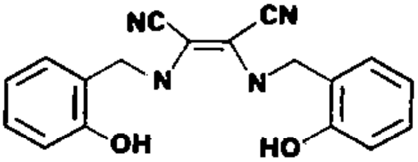

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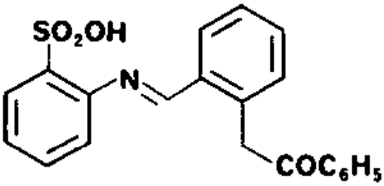
Zinc complexes of Schiff bases derived from histidine and pyridoxal have been investigated as models for the reactions of Vitamin B_6 analogues [168]. Complexes of (44) and (45) with zinc have been reported [169]. 4-Amino-2,6-di-*tert*-butylphenol reacts normally with salicylaldehydes to form Schiff bases, and complexes of the type $[ZnL_2]$ (HL = 46) have been isolated, and shown to generate radical species on treatment with PbO_2 [170]. In contrast, reaction with bis(diketonato)zinc(II) complexes leads not to the Schiff bases, but to the monoiminoquinone complexes (47) [171].



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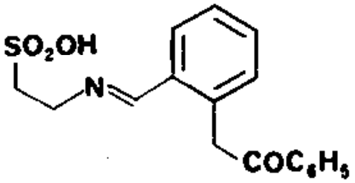

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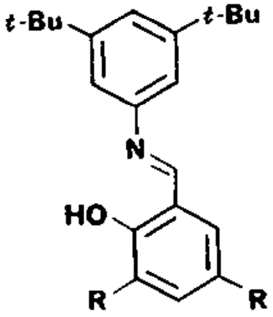

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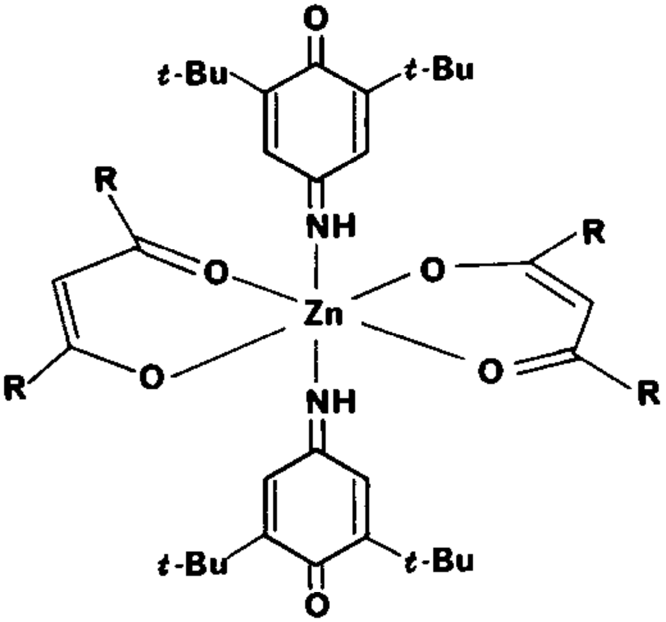

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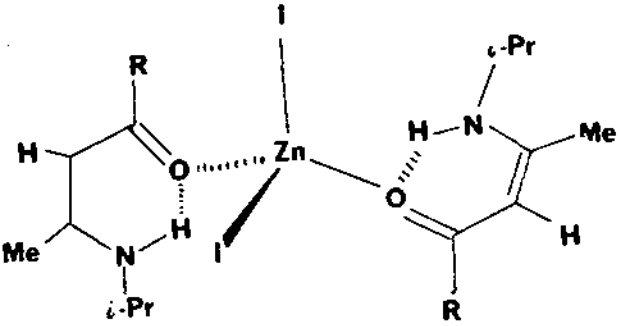

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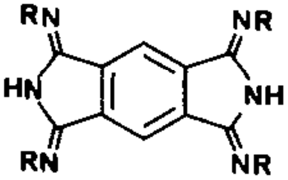
A crystal structure of the Schiff base complex (48) has been reported [172], and it is seen that the complex possesses a distorted C_2 symmetry, with a *trans* arrangement of the ligands. Zinc complexes of a number of bulky polydentate ligands which are structurally related to phthalocyanines have been reported by Gagne [173].



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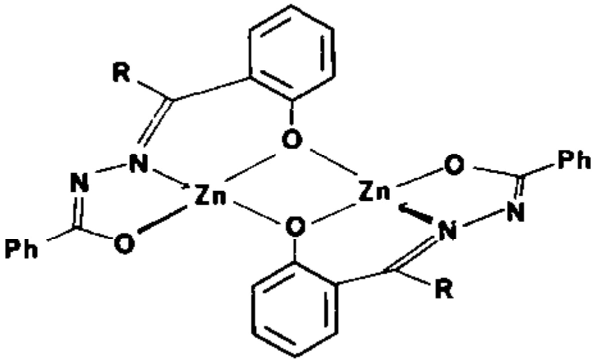
Zinc complexes of salicylaldehyde semicarbazone [174,175], and cinnamaldehyde semicarbazone [174] have been described. The dimeric complex (50), with the benzoylhydrazone of salicylaldehyde [176], and complexes with furfuraldehyde benzoylhydrazones [177] have also been reported.



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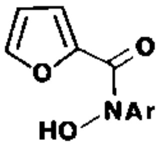
Complexes with 2-hydroxynaphthaldoxime [178,179] and salicylaldoxime [180] have been described, and these ligands may be of use as reagents for the extraction of Group IIb metals from aqueous solution. The reaction of zinc salts with hydroxamic acids (51) has been studied [181].



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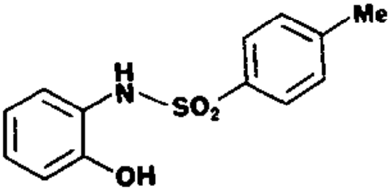
1.1.4.3 *Amides, imides and hydrazides*

The 2:1 complexes of *N,N*-dimethyl and *N,N*-diethylacetamide with ZnX_2 (X = halide) have been investigated, and the ligands shown to coordinate to the metal *via* the oxygen atom of the amide grouping, to give a tetrahedral ZnO_2X_2 unit [182,183]. Complexes of *N*-*tert*-butyl and *N*-2-(2-methylbutyl)acrylamide have also been reported [184]. The first oxamic acid complex, $K_2[Zn(O_2CCONH)_2]$ has been reported, and is thought to show an octahedral geometry about the metal [185].

The hippuric acid complex $[ZnL_2].4H_2O$ (HL = $PhCONHCH_2CO_2H$) has been described [186]. Zinc complexes of diacetamide, $CH_3CONHCOCH_3$ [187] and (52) [188] have been described.



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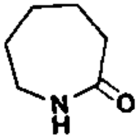
Complexes with urea and its derivatives have been widely investigated, and the compounds reported this year include the zinc complexes $[ZnL_4(H_2O)_2][ClO_4]_2$ [189], $[ZnL_6][ClO_4]_2$ [189] (L = urea), $[ZnL_2X_2]$ (L = $PhNHCONH_2$; X + Cl, Br or NO_3) [190] and $[ZnL_6]X_2$ (L = *N,N'*-bis-*tert*-butylurea; X = ClO_4 or NO_3) [191].

In the complexes $[ZnL_2X_2]$, $[ZnL_8I_2]$, $[ZnL_4(NCS)_2]$ (L = 53 ; X = Cl or Br), $[ZnL_2X_2]$ and $[ZnL_3(NCS)_2]$ (L = 54 ; X = Cl, Br or I) the lactams are coordinated to the metal through the amide oxygen atom [192]. Polymeric complexes with polyimide ligands (55) have also been described [193]. A crystal structural analysis of the complex



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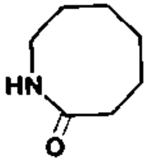

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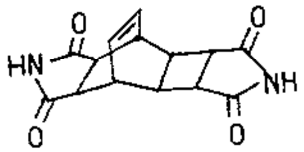

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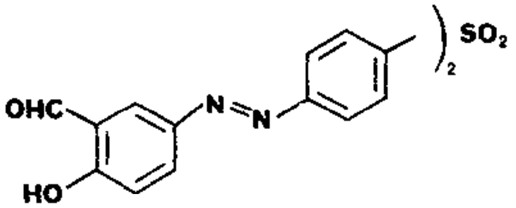
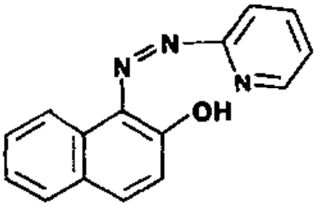


(56)

[Zn(MeCONHNH$_2$)$_3$][S$_2$O$_6$].2.5H$_2$O has been reported [194]. Zinc complexes of both H$_2$NCONHNHCONH$_2$ [195] and H$_2$NCON=NCONH$_2$ [196]have been described, and in each case the 1:1 complex [ZnL] is polymeric, with the ligand acting as a bridging tetradentate N_2O_2 donor.

1.1.4.4 Azo compounds

Zinc complexes of the bisazo compound (56) have been prepared, and are thought to be octahedral and polymeric [197]. Zinc complexes of the azonaphthol derivatives (57) and (58) have been studied [198-200]. The triazine complexes [ZnL$_2$] and



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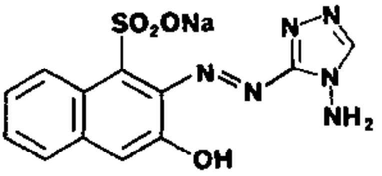

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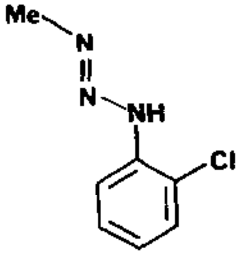


(59)

[ZnL$_2$(bipy)] (Hl = 59) have been reported, and shown to adopt a pseudo-octahedral configuration, in which the metal interacts with the ortho chloro substituent [201]. The complex [ZnL$_3$][InCl$_4$] (L = NCCMe$_2$N=NCMe$_2$CN) [202] has also been described.

1.1.4.5 Amino acids

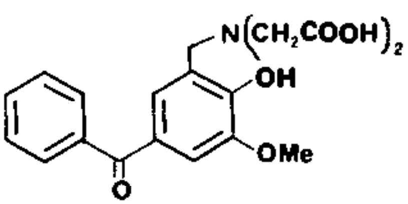
Most studies of zinc complexes of amino acids have concentrated upon naturally occurring ligands, but some other amino acids have been investigated. Complexes with 3- and 4-aminobenzoic acids have been reported [203,204], and a crystal structure of $[ZnL_2].1.5H_2O$ (HL = 4-aminobenzoic acid) has shown that the compound is polymeric, with the metal in a distorted N_2O_2 environment [204]. 1:1 and 1:2 complexes with 4-aminohippuric acid have also been described [205,206].

Numerous studies of the interaction of zinc ions with biologically important amino acids have been made, and complexes with glycine [207-210], alanine [209,211], β-alanine [209], norleucine [208], phenylalanine [209], proline [212], methionine [207], serine [211], histidine [208], asparaginine [213], adrenaline [214], noradrenaline [214], terizidone [215], *S*-ethyl-L-cysteine [216], *S,S'*-methylenebis(L-cysteine) [217], ornithine, lysine, 2,4-diaminobutyric acid and 2,3-diaminopropionic acid [218] have been reported.

Reactions with peptides provide better model for the interaction of zinc ions with proteins, however, and complexes with *N*-acetylglycine [210], *N*-benzoylglycine [210], *N*-benzoylglycyl-L-leucine [219], *cyclo*(L-histidyl-L-histidyl) [220], *N*-benzoyl-L-leucine [221] and *N*-benzoyl-L-phenylalanine [221] have been described.

1.1.4.6 Iminodiacetic acid derivatives

The binuclear complex $Zn_2(edta).H_2O$ has been characterised for the first time [222]. The formation of zinc complexes of H_4edta [223], $HN(CH_2CO_2H)$ [154], $N(CH_2CO_2H)$ [154], $((HO_2CCH_2)_2NCH_2CH_2)_2NCH_2CO_2H$ [224], (60) [225] and xylenol orange (61) [226,227] has been studied. ^1H NMR studies of the Zn^{2+}-$HN(CH_2CO_2H)_2$ system have shown that 2:1 complexes are formed in aqueous solution, and that a variety of intra- and intermolecular exchange processes occur [228]. Amide deprotonation is normally observed in copper(II), nickel(II) or cobalt(II) complexes of amides, but it has now been demonstrated that $[Zn(LH)_2]^{2-}$ ($H_3L = H_2NCOCH_2N(CH_2CO_2H)_2$) may be further deprotonated, and that equilibria:



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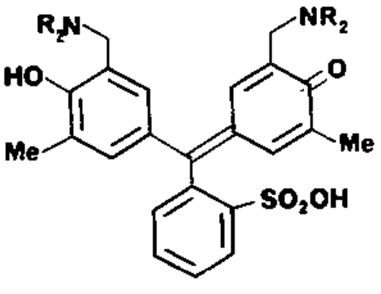


(61)

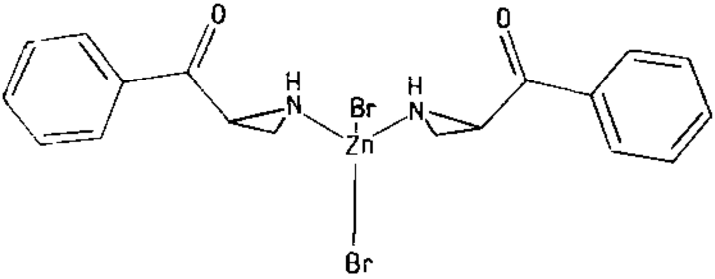
$$[Zn(HL)_2]^{2-} \rightleftharpoons [ZnL(HL)]^{3-} + H^+$$

$$[ZnL(HL)]^{3-} \rightleftharpoons [ZnL_2]^{4-} + H^+$$

are established. The ability of the d^{10} zinc(II) ion to promote such equilibria suggests that a major requirement for deprotonation of an amide is a positively charged centre, since the d^{10} ion may not increase the ligand field stabilisation [229].

1.1.4.7 Heterocycles

A crystal structure of the complex $[ZnL_2Br_2]$ (L = benzoylaziridine) has shown the metal to be in a tetrahedral N_2Br_2 environment (62) [230]. The complex $[ZnL_2(phen)]$ (HL = 63) has been shown to be a homogeneous catalyst for the oxidation of cumene [231]. Complexes of (64) and (65) have also been reported [232,233].



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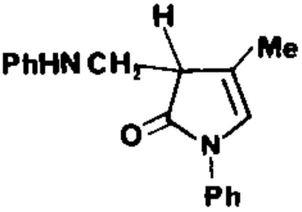
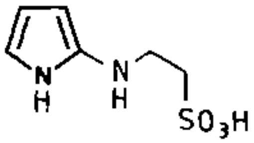


(63)

N-Acetylpyrazole reacts with zinc ions to form a tris complex, and the salt $[ZnL_3][BF_4]_2$ (L = *N*-acetylpyrazole) has been isolated [234]. The ligand is coordinated to the metal through nitrogen and the acetyl oxygen atom, and the acetyl group is found to exist as the enol tautomer. A similar mode of bonding is adopted in the



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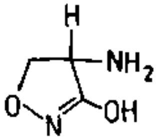
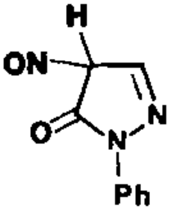


(65)

tris(*N*-carbamoylpyrazole)zinc(II) ion, which has also been isolated as its BF_4 salt [235]. The complexes $[ZnL_2X_2]$ (L = 66 ; X = Cl, Br or NO_3) have been prepared and investigated as potential fungicides: the metal is probably in a distorted octahedral environment [236,237]. Octahedral complexes of zinc with the pyrazolone (67) have also been reported [238,239]. The 2:1 complex of Zn(OAc) with (68) has been investigated by multinuclear (^{15}N, ^{13}C and ^{1}H) NMR techniques [240]. Complexes



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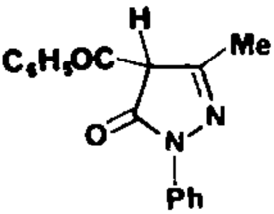

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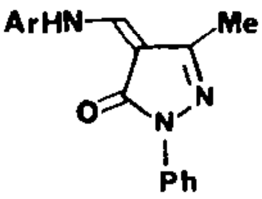
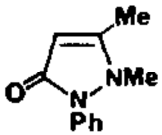


(68)

with antipyrine (69) and related compounds have been described [241], as have a series of complexes with bispyrazoles, $[ZnL][ClO_4]_2$ (L = 70) [242].



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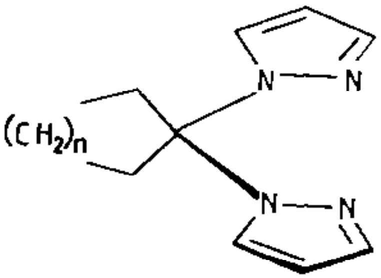

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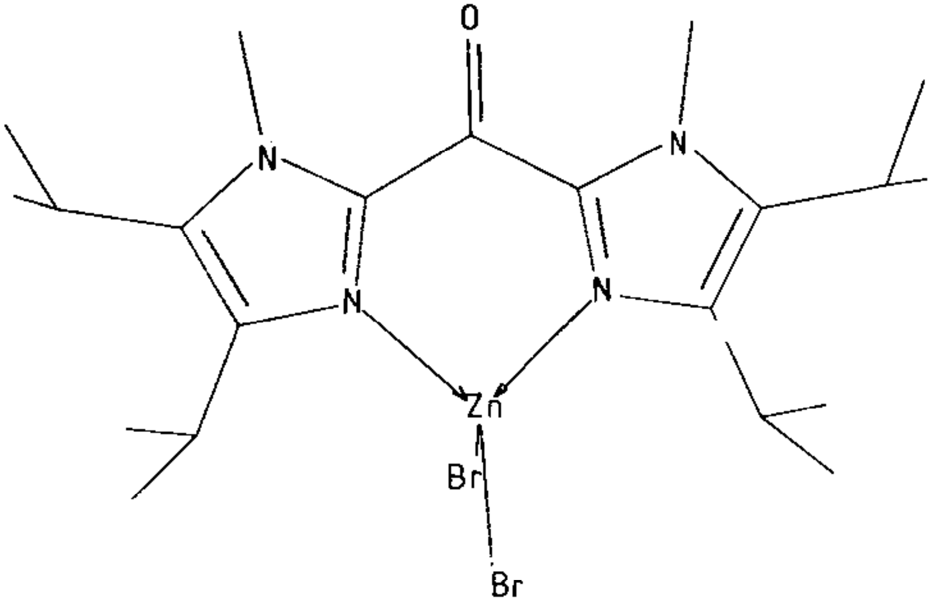
An infra-red spectroscopic study of the imidazole complexes $[Zn(imidH)_6][NO_3]_2$, $[Zn(imidH)_4(NO_3)_2]$ and $[Zn(imidH)_4][ClO_4]_2$ and their deuterated analogues has been made [243]. The reaction of 1-methylimidazole-^{15}N with $Zn(NO_3)_2$ in aqueous solution has been studied by ^{15}N NMR [244]. A crystal structure of the bisimidazolyl ketone complex (71) has been made, and the metal shown to be in an approximately tetrahedral environment [245]. Imidazoline-1-oxyl complexes continue to be studied, and the ligand in $[ZnL_2]$ (HL = 72) has been shown to be coordinated *via* the oxygen atom of the carbonyl group and a deprotonated hydroxy group [246]. A crystal structural analysis of the complex $[ZnL_2(H_2O)_2]$ (HL = 73) has been reported, and the metal shown to be coordinated to two water molecules, the carboxylate group and the imino nitrogens of the imidazoline residues, to give an $N_2O_2O'_2$ environment [247]. The oxadiazole complexes $[ZnL_2]$ (HL = 74) have been reported [248].



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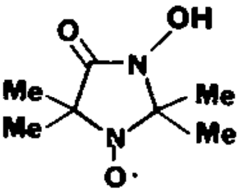

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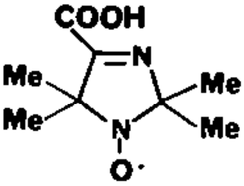
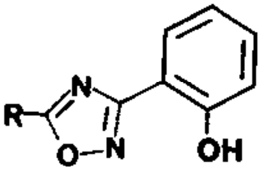


(73)

Complexes of zinc(II) with 4-ethyl-1,2,4-triazole [249], 4-n-butyl-1,2,4-triazole [250] and 1,2,4-triazoledione (urazole) [251] have been investigated. The Schiff base (75) is readily hydrolysed in the presence of metal ions, and the complex $[Zn(imidH)_2L_2]$ (HL = 75) has been shown to be an effective catalyst for this hydrolytic reaction [252]. The complex $[ZnL][ClO_4]_2$ (76) has been reported [253].



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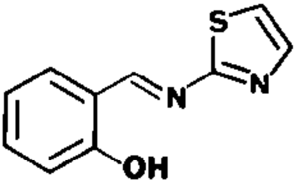

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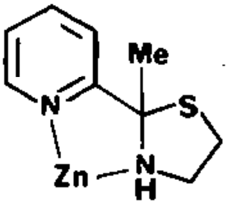
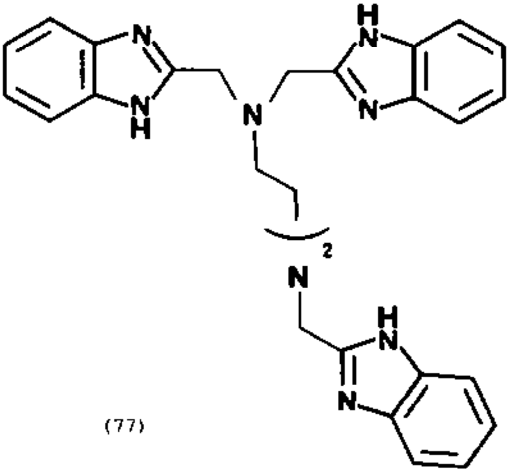


(76)

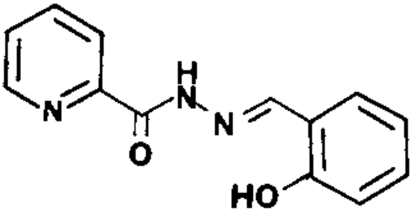
Complexes with 1,2-dimethylbenzimidazole have been described, and there is evidence that the ligand may act as both a monodentate and bidentate *N* donor [254]. The ligand (77) is prepared by the condensation of 1,2-diaminobenzene with diethylenetetraminepentaacetic acid, and a crystal structure of the complex $[Zn_2LCl_4(H_2O)_2]$ has been reported [255]. A number of complexes with 2-hydrazinobenzimidazole [256], 2-hydrazinobenzoxazole [256] and 2-(2'-hydroxyphenyl)benzoxazole [257] have also been described.



(77)

A wide range of pyridine complexes have been investigated, and the ^{13}C NMR chemical shifts of the ligand carbon atoms in such complexes have been correlated with the polarising ability of the metal ion [258]. Ternary complexes with diethyl malonate and pyridines have been described [145]. The extraction of Group IIB metals from aqueous solution by 3-methylpyridine [259], 4-methylpyridine [259], 3,5-dimethyl-pyridine [260], and 2-hexylpyridine [261] has also been investigated. The complex $[Zn(bipy)R_2]$ (R = mesityl) is formed in the reaction of dimesitylzinc with bipy [152].

Zinc complexes of pyridine aldehydes are models for the activated complex formed in the reduction of acetaldehyde by NADH in the presence of the zinc containing alcohol dehydrogenase enzymes, and complexes with 2- and 4-pyridine aldehydes have been studied [262,263]. Nicotinic acid [264,265], nicotinamide [264,266], isonicotinamide [264] and 2-aminonicotinic acid [267] have been investigated as ligands, and it is now evident that these compounds normally act as monodentate ligands, coordinating to the metal through the ring nitrogen atom. A crystal structural analysis of the complex $[ZnL_2(acac)_2]$ (L = nicotinic acid) has confirmed this [265]. Binuclear complexes with $[Co(NH_3)_5L]^{2+}$ (HL = nicotinic or picolinic acid) have been reported [268]. The reaction of picolinoylhydrazide with salicylaldehdye results in the formation of the ligand (78), which may act as a bi-, ter- or quaterdentate donor, and a number of zinc complexes have been prepared [269]. The terdentate ligand, β-(2-pyridyl)alanine forms zinc complexes with a considerable degree of enantioselectivity [270]. Zinc complexes of a range of pyridone defleecing agents have been described [271]. A number of pyridoxamine (79) complexes have been reported [272,273] and a crystal structural analysis of the complex $[ZnL_2(OH_2)_2]$ (HL = 79) (80) has been performed [273].



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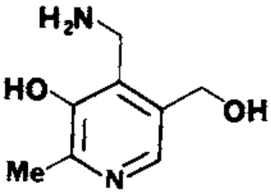

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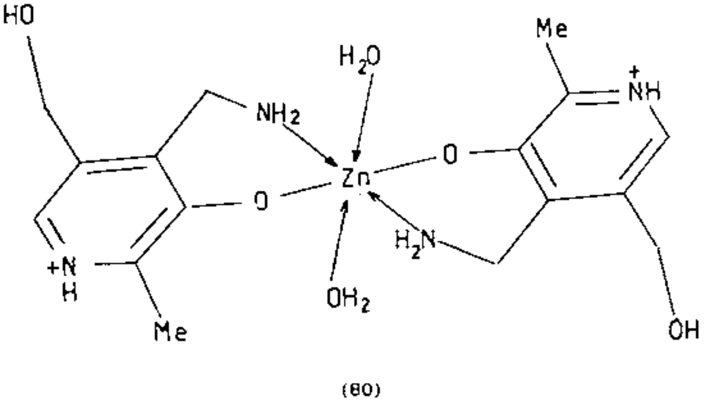
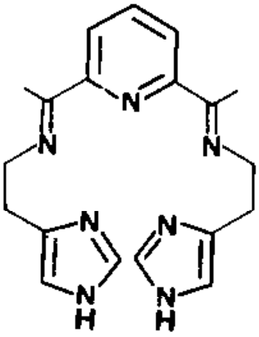


(80)

Zinc complexes of 2-pyridyl azo compounds [274], oximes [275] and sulphonamides [276] have also been described. A crystal structure of $[ZnL][ClO_4]_2$ (L = 81) has been reported, and the ligand shown to be quinquedentate [277]. The related ligand (82) forms a pentagonal-bipyramidal zinc complex $[ZnL][ClO_4]_2$, which is obtained by a metal exchange reaction of $[BaL][ClO_4]_2$ with $Zn[ClO_4]_2$[278]. A zinc complex of the carcinostatic antibiotic streptonigrin has been described [279]. A 2:1 complex of $ZnCl_2$ with morpholine hydrochloride has been reported [280].



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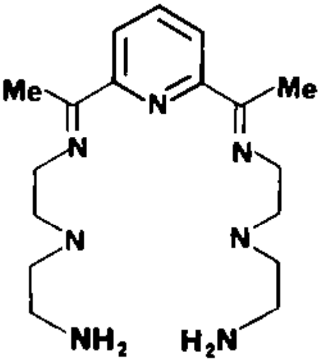
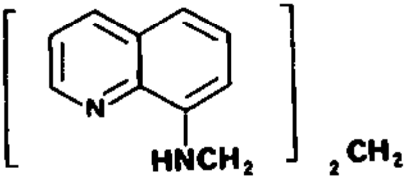


(82)

The complexes $[ZnL][ClO_4]_2$ (L = 83) [281], $[ZnL_2(NCS)_2]$ (L = benzo{f}quinoline) [282] and $[ZnLCl_2]$ (L = 2,4,6-tris(2-pyridyl)-1,3,5-triazine [283] have been described.



(83)

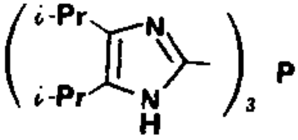
1.1.5 Complexes with phosphorus donor ligands

Complexes of zinc with cytosine [284], adenosine triphosphate [285-287] and other purines [288] have been investigated, and a crystal structure of the complex $[\{Zn(bipy)(H_2ATP)\}_2].4H_2O$ [286] has been described.

1.1.5 Complexes with phosphorus donor ligands

Complexes of the phosphine (84) have been investigated as models for the active site of carbonic anhydrase enzymes [289], and a crystal structure of the complex

[ZnLCl]Cl.2dmf (85) has been reported [290]; the ligand acts as an N_3 donor, and the metal is in a pseudotetrahedral N_3Cl environment. The heterobinuclear complexes $[(py)_4M(NCSe)_2Zn(SCN)_2(PPh_3)_2]$ and $[(bipy)_2M(NCSe)_2Zn(SCN)_2(PPh_3)_2]$ (M = Co or Ni)[291] $NaZn(P_3O_6N_3H_3).7H_2O$ and $Na_4Zn(P_3O_6N_3H_3).12H_2O$ [292] have also been described.



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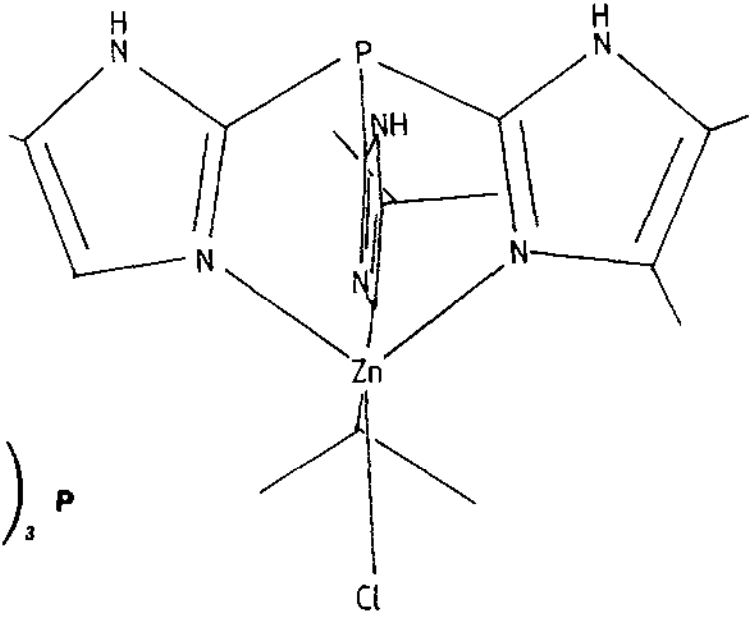

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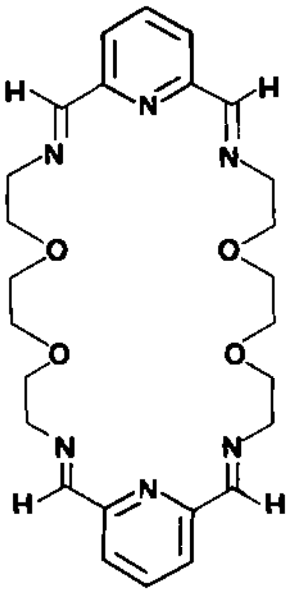
1.1.6 *Macrocyclic complexes*

Zinc complexes of a number of saturated tetraaza macrocycles and their open-chain analogues have been investigated [293-295], and it has been confirmed that the macrocyclic complexes are more stable than the non-cyclic complexes, whatever reference for stability is taken. It was concluded that the stability is due to a favourable enthalpy term, although it has been noted that comparative studies mean little unless the coordination geometry is well-characterised, and strictly comparable [293]. The complexes $[ZnLX_2]$, $[ZnBr(py)L]_2[ZnBr_4]$(L = [14]ane-1,4,8,11-N_4; X = Cl or Br), $[ZnBr_2L]$ (L = [15]ane-1,4,8,12-N_4, [16]ane-1,5,9,13-N_4, 1,4,8,11-Me_4-[14]-ane-1,4,8,11-N_4) and $[ZnBr(EtOH)L]_2[ZnBr_4]$ (L= 1,4,8,11-Me_4-[14]-ane-1,4,8,11-N_4) have been prepared, and their solution properties studied [294]. The transamination of open-chain ligands may be used in the preparation of macrocyclic complexes, and the template condensation of the zinc complex of 2,6-diacetylpyridine bispropylimine with 3,6-dioxaoctane-1,8-diamine results in the formation of the complex $[ZnL]^{2+}$ (L =86) [296]



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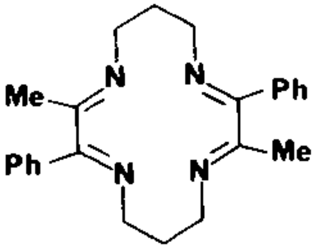


(87)

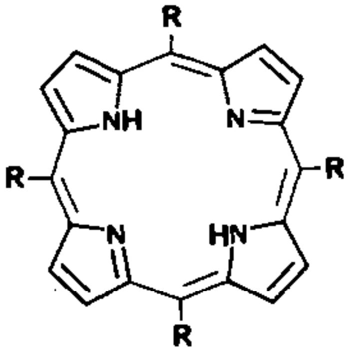
The complex $[CuL][ZnCl_4]$ (L = 3,10-Me_2-2,9-Ph_2-[14]-1,3,8,10-tetraene-1,4,8,11-N_4, 87) undergoes a transmetallation reaction on treatment with zinc metal to give the five-coordinate complex $[ZnLCl]^+$, which may be isolated as its PF_6 salt [20]. It is interesting to note that the complex could not be prepared using zinc as the template metal. The complex ion $[CoL]^{2+}$ reacts with molecular oxygen to form $[LCo(O\text{-}O)CoL]^{4+}$, and this is also the product of the reaction of $[ZnL]^{2+}$ (L = 5,7,7,12,14,14-Me_6-1,4,8,11-N_4-[14]-4,11-diene) with aqueous cobalt(II) ions [297].

Zinc tetrasulphophthalocyanine is an attractive choice for the chromophore in multi-component systems for the photoreduction of water, but recent studies have shown that only low yields of photoproducts are obtained, and that porphyrin-based chromophores are more efficient [298,299]. A number of workers have studied zinc tetraphenylporphyrin complexes, and an intensive study of the luminescence properties of [ZnTPP] has been reported [300]. The formation of the five-coordinate axial complexes [ZnTPP(L)] has been studied electrochemically, and thin-layer spectro-electrochemical techniques have been used to demonstrate that the process:

$$[\mathrm{ZnTPP(L)}] \rightleftharpoons [\mathrm{ZnTPP(L)}]^+$$

to be electrochemically and spectrochemically reversible [301,302]. The effect of substitution of the phenyl groups of the TPP ligand has been investigated [303]. The metallation of $TPPH_2$ in D_2O or H_2O has been studied, and the rate difference

k_H/k_D = 2.3 shown to be due to differences in the concentration of OH and OD complexes, and not due to intrinsic differences in the reactivity of TPPH and TPPD [304]. Metal exchange reactions of manganese(II) porphyrins with zinc have been studied [305]. The synthesis and properties of porphyrins bearing cationic or anionic substituents continues to be an area of active interest, and zinc complexes of the ligands (88) – (91), tetrabenzoporphine and octamethylporphine have been studied [306-310]. The reaction of *meso*-(dimethylaminomethyl)ætioporphyrin with alcohols, ROH, in the presence of $Zn(OAc)_2$ gives good yields of the complexes (92) [311]. A crystal structure of the complex [ZnL(py)] (L = isobacteriochlorin) has been reported; the metal is in a distorted square-planar environment [312]. The structure of the zinc complex of 1,2,3,7,8,12,13,17,18,19-decamethylbiladiene-ac has been reported in detail [313], and a number of donor-acceptor complexes of zinc tetrapyrrole species with 1,3,5-trinitrobenzene have been described [314].



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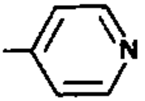

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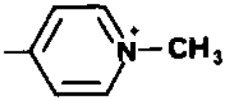

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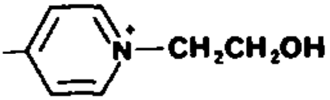

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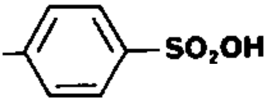

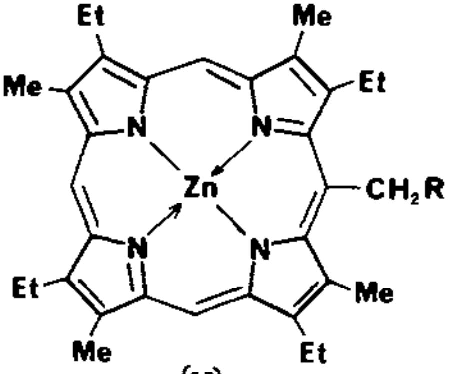

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1.2 CADMIUM(II)

1.2.1 Halide and pseudohalide complexes

The photoelectron spectrum of CdF_2 has been recorded, and the results are very similar to those reported for ZnF_2 (Section 1.1.1) [2]. An electron diffraction study of $CdBr_2$ has also been made, and it is concluded that the equilibrium structure corresponds to a linear Br-Cd-Br molecule, with a Cd-Br distance of 2.372 Å and a Br-Br distance of 4.694 Å [315]. Raman and infra-red spectroscopic studies of $CdCl_2$ have also been reported [316].

The solubility of cadmium halides in dmso containing $[NH_4][ClO_4]$ [9], aqueous hydrofluoric acid [317] and water [318,319] has been investigated. The equilibrium

$$[Cd(H_2O)_n]^{2+} + Cl^- \rightleftharpoons [Cd(H_2O)_{n-1}Cl]^+$$

has been studied potentiometrically, and lg K' for the equilibrium in aqueous glycol or glycerol is calculated to be 3.0 ±0.06 [319]. A polarographic study of the Cd^{2+}-$Na[SCN]$- $Na[ClO_4]$-ROH-H_2O system has been reported [320]. The complex species $[Cd(SCN)_2]$ and $[Cd(SCN)_3]^-$ have been investigated, and it is thought that the thiocyanate is coordinated to the metal *via* sulphur in dmso solution, but that in aqueous solution it is coordinated through the nitrogen atom [11]. The formation of cadmium complexes of the pseudohalide ions $[N(CN)_2]^-$, $[C(CN)_3]^-$, $[NCSe]^-$, $[NCS]^-$, $[ONC(CN)_2]^-$, as well as chloride, bromide and iodide in a range of non-aqueous solvents has been investigated [12,13,321].

The $Cd_3(PO_4)_2$-CdF_2 system has been examined, and evidence is presented for the formation of $Cd_{10}(PO_4)_6F_2$ and $Cd_4(PO_4)_2F_2$ [322].

The interaction of $CdCl_2$ with $[NH_4]Cl$ or LiCl in thf or 1,2-dme has been studied: there is no evidence for the formation of $[CdCl_4]^{2-}$ in these solvents, the only products being $Li[CdCl_3]$ or $[NH_4][CdCl_3]$ [14]. A number of etherate, pyridine or aniline complexes of the acids $HCdI_3$, H_2CdI_4, $HCdCl_2I$ and $H_2CdI_2Cl_2$ have been reported [16,323]. The complexes $[MeAr_2AsR]_2[CdI_4]$ are formed in the reaction of CdI_2 with $[MeAr_2AsR]I$ [324]. A large number of cadmium(II)-halide complexes have been studied by NMR techniques (Section 1.2.7) [325].

The extraction of cadmium from acidic aqueous chloride medium by Aliquat 336 [23,24] and by tributyl phosphate [25-27] has been investigated.

1.2.2 Complexes with oxygen donor ligands

1.1.2.1 Inorganic molecules and ions

The dehydration of $Cd(NO_3)_2.4H_2O$ by P_2O_5 has been shown to yield the anhydrous salt, which readily forms complexes with solvents such as MeOH, dmso or dmf [325]. The solubilities of $Cd[SO_3]$ and $Cd[SO_4]$ in water has been studied [326] and the crystal structure of $Cd[SO_4]$ has been redetermined [327]. The cadmium atom in $Cd[SO_4]$ is in a very distorted CdO_4 tetrahedron, with the O-Cd-O angles varying from 88.1 to 142.7°.

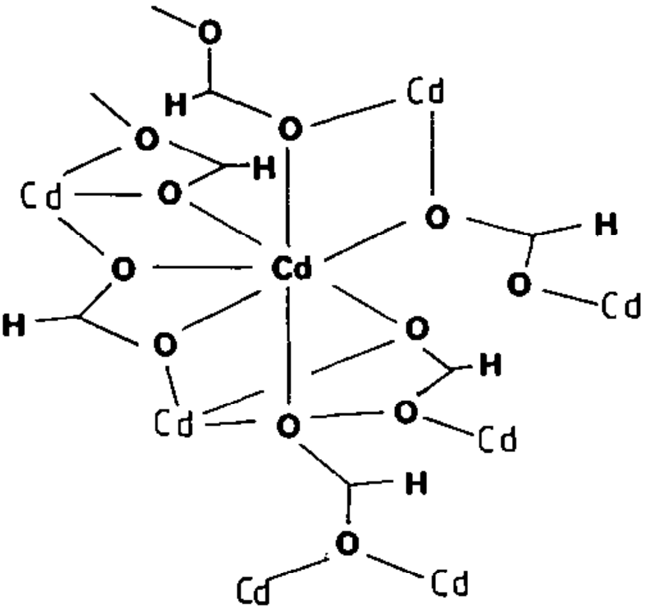
1.1.2.2 Simple organic ligands and phosphine oxides

The polymeric complexes $[CdL(NO_3)_2]$ and $[CdL_2(NCS)_2]$ (L = 4,4'-bipyridine 1,1'-dioxide) have been described, and are thought to possess an octahedral structure [51]. A related complex, $[CdLCl_2]$ (L = benzo[c]cinnoline *N,N'*-dioxide) has also been described [52]. The extraction of cadmium from aqueous chloride media by trioctylphosphine oxide has been studied [59] , and the complex $[Cd(Et_3PO)_2Cl_2]$ has been described [55].

1.2.2.3 Carboxylic acids

There has been a remarkable amount of interest in the cadmium-formate system, and a crystal structure of $Cd(HCO_2)_2$ has been reported. The formate ion acts as a bridging ligand, and the metal ion is seven-coordinate, (93) [328]. The complexes $NaCd(HCO_2)_3$ [329], $KCd(HCO_2)_3$ [330], $K_3Cd(HCO_2)_5$ [330], $[NH_4]Cd(HCO_2)_3$ [331,332], $CdBa(HCO_2)_4.2H_2O$ [331] and $LiCd(HCO_2)_3$ [332] have been characterised as components of the appropriate $Cd(HCO_2)_2$-$M(HCO_2)_x$ systems. The formation of mixed acetate-formate complexes has been investigated [333]. An infra-red study the complexes $Cd(OAc)_2.2H_2O$ and $Cd(OAc)_2.2D_2O$ has been made, and a full analysis of the spectrum reported [62]. A spectroscopic study of the solvation of $Cd(OAc)_2$ in alcoholic solvents has been made [64]. Cadmium complexes of a number of other carboxylic acids have also been studied [66]. The thermodynamics of the complexation of cadmium with cyanoacetic acid [72] and 2-oxopropanoic acid have been investigated [69]. The crystal structure of $[CdL_2(py)_3py]$ (LH = 4-hydroxybenzoic acid) has been reported, and the metal shown to be in an octahedral environment [334,335]. One of the carboxylate anions is bidentate, but the other is monodentate and hydrogen-bonded to one of the pyridine molecules: the remaining three pyridine molecules are coordinated to the metal. A cadmium complex of β-resorcylic acid has been reported [336].

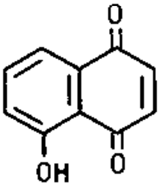
Complexes of dicarboxylic acids have been widely investigated, and cadmium derivatives of oxalic acid [76,337], phthallic acid [82,338,339], succinic acid [339], malonic acid [339], tartaric acid [339], isophthallic acid [82], terephthallic acid [82], itaconic acid [80] and maleic acid [78] have been described. A 1:1 complex of Cd^{2+} with (7) has also been reported [85].



(93)

1.2.2.4 Diketonate and related ligands

A polarographic study of the Cd^{2+}-acacH system has been reported, and values of lg β 4.28, ΔH -11.897 kcal mol^{-1}, ΔG -5.74 kcal mol^{-1} and ΔS -0.02 cal mol^{-1} K^{-1} calculated for the 1:1 complex [340]. The stability constants for cadmium complexes of 3,5-dichloro-2-hydroxyacetophenone [93] and 2-hydroxy-3-isopropyl-6-methylbenzaldehyde [95] have also been reported. The condensation of $[CdL_2]$ (LH = salicylaldehyde) with diamines has been shown to lead to condensation polymers [92]. Cadmium complexes of juglone (94) [341] and 2-methyljuglone (12) [96], fluorescein [71] and some dihydroxy compounds have been described [100].



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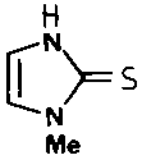
1.2.3 Complexes with sulphur donor ligands

1.2.3.1 Thiols

Ternary complexes of cadmium with 2,2'-bipyridine and 2-mercaptopropionanilide have been described [104], as has a ^{113}Cd NMR study of $[Cd_{D}(SCH_2CH_2OH)_{16}]^{4+}$ [342]. The tetrahedral complex $[Cd(LH)_4][NO_3]_2$ (LH = 95) [106] has been reported, as have complexes of the triazolinethione (96) [108], $(HO_2CCH_2CH_2)_2S$ [111], (19) [113] and (20) [113].



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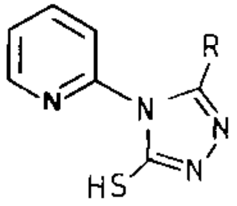

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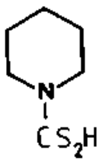
1.2.3.2 Thioacids, thioamides and related ligands

The polymeric complexes $[CdL_2]$ and the pentacoordinate species $[CdL_2Q]$ (LH = 97 or 98; Q = pyridines) have been described, as have complexes with (22) [116], $(HS_2CNHCH_2)_2$ [121] and Et_2NCS_2H [122].



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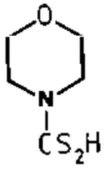
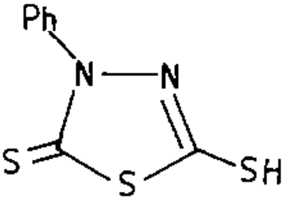


(98)

A number of complexes with thiourea [344,345], $MeCSNH_2$ [345], dithiobiuret [346], thiosemicarbazide [124], (23) [125], $H_2NNHCSNHN{=}CHR$ [127], $ET_2NCONHCSPh$ [120] and (32) [142]. Complexes described include $[CdLCl_2].2H_2O$ ($L = H_2NNHCSNHN{=}CHR$) [127], $[CdL(H_2O)_2]$ (LH = 32) [142], $[Cd(H_2NCSCSNH_2)X_2]$ (X = NCS or Cl) [117] and $[Cd(tu)_x(SCN)]^+$ (x = 1 or 2) [345]. The dithiobiuret complexes $Cd_2L_3Cl_4$, CdL_2Br_2, CdL_2I_2, $CdL_2(ClO_4)_2$, $CdL_4(NO_3)_2$ and $CdL_3(SO_4)H_2O$ (L = dithiobiuret) have been reported, and it is suggested that only one of the sulphur atoms is coordinated to the metal [346].

1.2.3.3 Sulphur and selenium heterocycles

Cadmium complexes of thiamine (Vitamin B_1, 27) have been described, and, in general resemble those reported for zinc (Section 1.1.3.4) [134,135]. Complexes with sulphathiazole [137], (29) [139], (30) [140], (31) [141] and (99) [107] have also been described, and resemble the corresponding zinc complexes.



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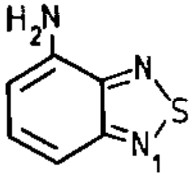

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A number of naphtho[1,2-c]-1,2,5-thiadiazole, naphto[1,2-c]-1,2,5-selenadiazole and naphtho[1,2-c]-1,2,5-oxadiazole complexes have been described [347,348], and a crystal structural analysis of $[CdL_2Br_2]$ (L = 100) has been described [348]. The ligand is in the tautomeric form depicted, and is coordinated to the metal through N_1 to give an octahedral, polymeric complex.

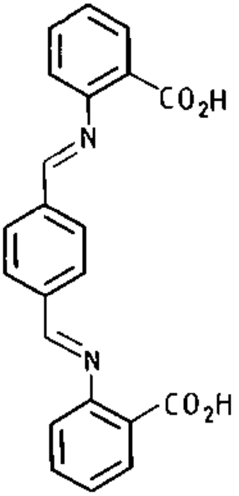
1.2.4 Complexes with nitrogen donor ligands

1.2.4.1 Amines

The Cd^{2+}-en system continues to be of interest, and a detailed study of the vibrational spectra (infra-red and Raman) of $[Cd(en)(NO_2)_2]$ and its deuterated derivative has been reported [349]. The formation of en complexes in aqueous acid [350] and dmf has also been studied [148]. Ternary complexes of en and succinic acid [351] and pn and oxalate [352] have been described, as have pn complexes in aqueous HCONH [353] and *meso*-2,3-diaminobutane complexes [151]. The clathrate complexes $[Cd(dl\text{-}1,2\text{-}pn)][Ni(CN)_4]$.1.5L (L = pyrrole, thiophen or benzene) have been prepared, as have $[Cd(dl\text{-}1,2\text{-}pn)][Cd(CN)_4]$.1.5PhH and $[Cd(dl\text{-}1,2\text{-}pn)][Hg(CN)_4]$.1.5PhH [354]. Complexes $[CdLX_2]$ (L = 35) [155], (36) (M = Cd) [157] and with (37) [161] and (38) [162] have been reported, and closely resemble the zinc complexes of these ligands.

1.2.4.2 Schiff bases, hydrazones and oximes

The ligand (101) is formed in the condensation of 2-aminobenzoic acid with terephthalaldehyde, and forms the poymeric octahedral complex $[CdL(H_2O)_2]$ on treatment with cadmium salts in dmf [355]. Cadmium complexes of (44) and (45) have also been described [169]. Salicylaldehyde semicarbazone is a bidentate *NO* donor , and forms

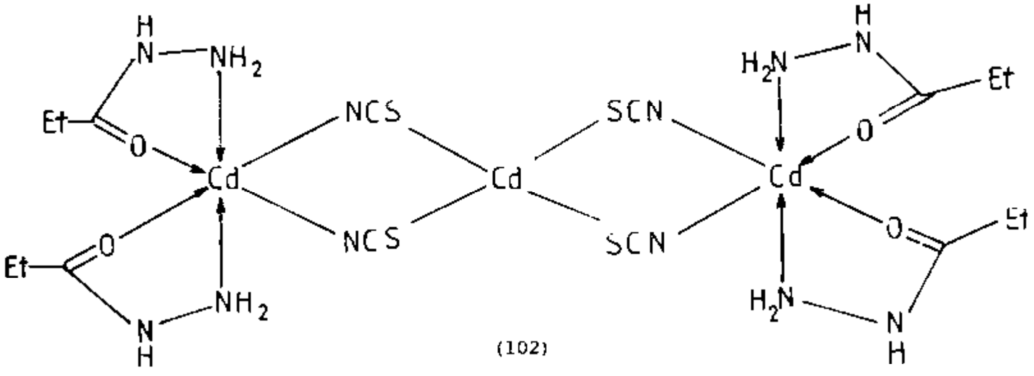


(101)

the octahedral complex $[CdL_2(H_2O)_2]$ [175,356]. Complexes with salicylaldehyde benzoylhydrazone [176] and salicylaldoxime [180] have also been reported. $[CdL_4X_2]$ and $[CdL_4][ClO_4]_2$ (L = $H_2NC(=NH)NHCN$) [357] and $[CdL_2]$ (LH = $HON=C(CN)CONH_2$) [358] have been described.

1.2.4.3 Amides, imides and hydrazides

The complexes $[CdLCl_2]$ (L = dma) [182], $[CdX_2L_2]$ (X = Br or I; L = Et_2NCOMe) [183], $[CdL_2].4H_2O$ (L = $PhCONHCH_2CO_2H$) [186], $[CdL_2X_2]$ (X = Cl, Br or I; L = MeCONHCOMe) [187], $[CdL(NH_3)].H_2O$ and $[CdL]. 3H_2O$ (LH_2 = 55) [193], and compounds with (52) [188], *N*-substituted acrylamides [184] and oxamic acid [185] have been reported. A crystal structural analysis of the complex $[L_2Cd(NCS)_2Cd(SCN)_2CdL_2]$ (L = propionic acid hydrazide) has been reported, and the complex shown to have the structure (102) [359].



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1.2.4.4 Azo compounds

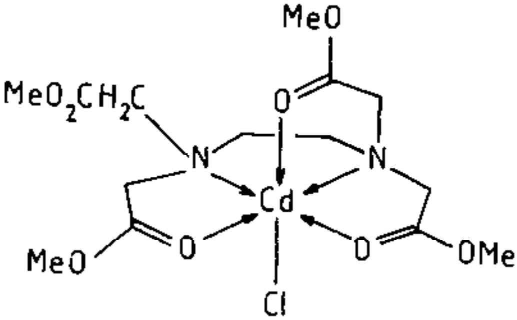
Cadmium complexes of (57) [198] , (58) [200] and (59) [201] have been reported

1.2.4.5 Amino acids

Cadmium complexes with glycine [208-210,360-362], alanine [209,362], norleucine [208], phenylalanine [209], proline [363], serine [364], histidine [208], asparaginine [213], leucine, tyrosine, norvaline, arginine, and tryptophan [364], valine [365], ornithine [366], lysine [367], glycylglycine [368], 4-aminohippuric acid [205], terizidone [215], *S* -ethyl-L-cysteine [216], and a number of other peptides [219,221] have been described.

1.2.4.6 Iminodiacetic acid derivatives

Iminodiacetic acid forms cadmium complexes [CdL] and $CdL_2^{\ 2-}$ (lg K_1 = 5.8, lg K_2 = 4.95) [369], and *N*-methyliminodiacetic acid forms analogous complexes [370]. An ultrasonic study of the $Cd(SO_4)$-edtaH_4 system has been reported [371]. The cadmium complex [CdLCl]Cl.H_2O (L = tetramethyl ethylenediaminetetraacetate) has been prepared, and it is proposed that the complex has the octahedral structure (103) [372]. A number of complexes with (104) [373] and xylenol orange (61) [226,227] have also been described.



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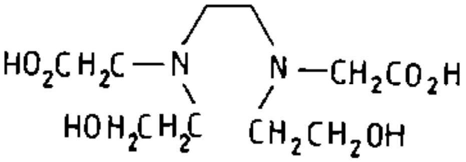


(104)

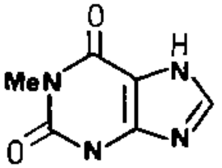
1.2.4.7 Heterocycles

Cadmium complexes of (64) [232] , *N* -acetylpyrazole [234,235] and antipyrine [241] have been described, and generally resemble the zinc complexes of these ligands which have been discussed earlier. A potentiometric study of the formation of cadmium-imidazole complexes has been reported and a number of species, including $[CdL]^{2+}$, $[CdL_2]^{2+}$, $[CdL_3]^{2+}$, $[CdL_4]^{2+}$ and $[Cd(OH)L]^{+}$, have been characterised [374]. Ternary Cd^{2+}-imidazole-tartrate complexes have been investigated [375,376], and a ^{15}N NMR study of the complexation of 1-methylimidazole-$^{15}N_2$ with $Cd(NO_3)_2$ has been made [244]. Complexes with (72) [246], 2-(2'-hydroxyphenyl)benzoxazole [257] and benzimidazole [377] have been prepared.

A study of the ^{13}C NMR chemical shifts in cadmium-pyridine complexes has been made, and a good correlation between the calculated pK_a value of the ligand and δ was observed [258]. The formation of cadmium complexes of picolines [259,378], and 2,2'-bipyridine [379,380] have been studied, as have ternary complexes with bipy and tropolones [381] and 1,10-phenanthroline and bromopyrogallol red [382]. Pyridine-4-aldehyde acts as a monodentate *N*-donor ligand, and a number of cadmium complexes have been reported [263]. A range of binary and ternary complexes of nicotinic acid and nicotinamide have been described [264,383] and crystal structural analyses of $[CdL_2(H_2O)_2(HCO_2)_2]$ (L = nicotinamide) [384] and $[CdL_2(H_2O)_2(OAc)_2]$ (L = *N,N*-diethylnicotinamide) [385] have been reported. Both complexes are octahedral, with the amides coordinated to the metal through nitrogen (Cd-OAc 2.281 Å; Cd-N 2.376 Å; Cd-OH 2.299 Å). Complexes of 2-aminonicotinic acid [267], 2-pyridylacetic acid [386] and 4-(2-pyridylazo)resorcinol [274] have also been described.

Cadmium complexes with 5,7-diiodo-8-hydroxyquinoline [387], 5-chloro-7-iodo-8-hydroxyquinoline [388] and benzo[f]quinoline [282] have been reported.

Theophylline (105) is frequently used as a substitute for guanine (106) in model systems, and the complexes $[CdL_2(RNH_2)_2(H_2O)_2]$ (L = 105) have been described [389].



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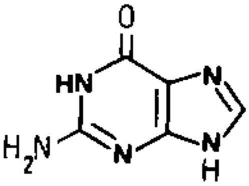
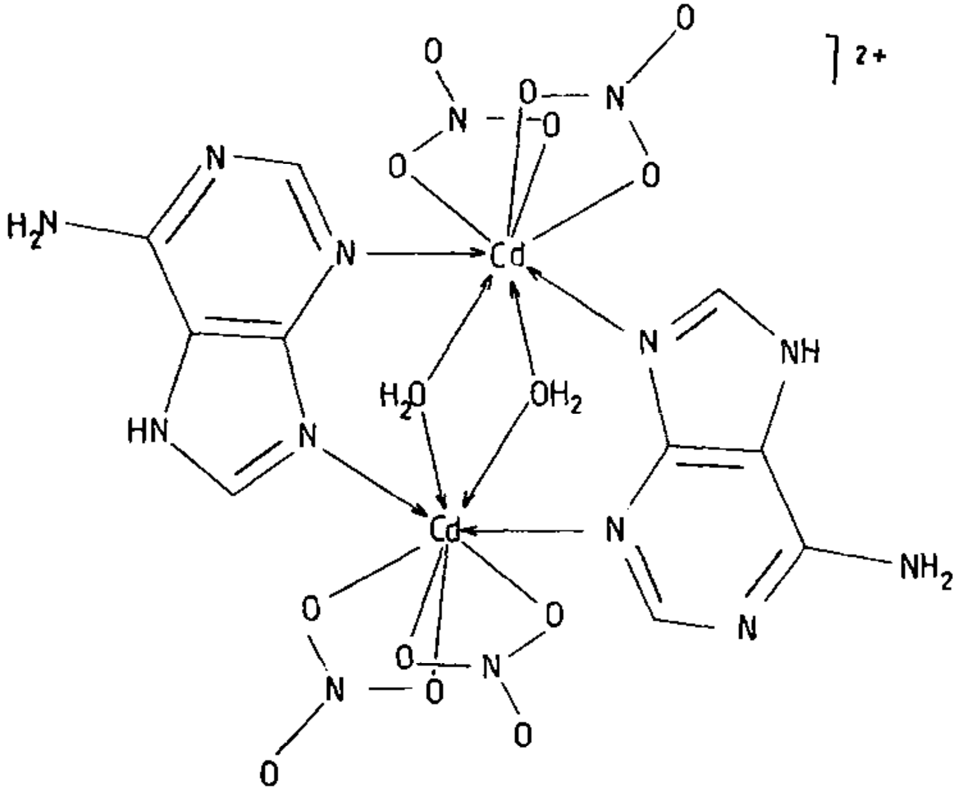


(106)

A crystal structural analysis of the dimeric adenine complex $[\{LCd(NO_3)_2(H_2O)\}_2][NO_3]_2$ (L = adenine) has been reported, and the compound shown to have the structure (107); the Cd-Cd distance is 3.616 Å, which indicates that there is little significant metal-metal interaction [390]. The formation of $Cd(ATP)^{2-}$ complexes has been studied by ^1H NMR, and it has been shown that there is a marked tendency to form dimeric intermolecularly ion-bridged structures [285].



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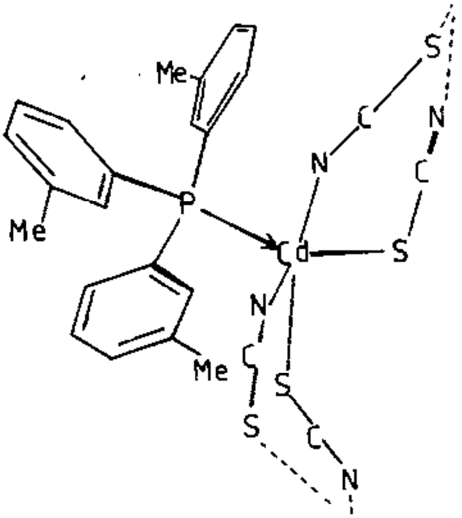
1.2.5 Complexes with phosphorus donor ligands

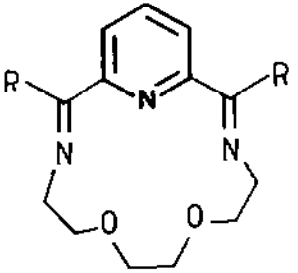
A number of complexes [$CdX_2(R_3P)_2$] ($X = Cl$, Br or I) have been prepared by the reaction of R_3P with CdX_2, and are thought to have a pseudotetrahedral C_{2v} skeletal symmetry. Investigation by ^{31}P NMR spectroscopy has established that the complexes undergo fast phosphine exchange at room temperature, but the limiting low temperature spectra correspond to the frozen out species, and show satellites due to coupling to ^{111}Cd and ^{113}Cd nuclei ($I = \frac{1}{2}$) [391]. In contrast, [$Cd(PR_3)(SCN)_2$] is fluxional even at 183 K, and a polymeric trigonal bipyramidal structure is proposed [392]. This has been confirmed by a crystal structural analysis of [(p-tol P)$Cd(SCN)_2$] (108) [392]. The complexes [$(py)_4M(NCSe)_2Cd(SCN)_2(PPh_3)_2$], [$(bipy)_2M(NCSe)_2Cd(SCN)_2(PPh_3)_2$] (M = Co or Ni) [291] , $NaCd(P_3O_6N_3H_3).4H_2O$ and $Cd_3(P_3O_6N_3H_3)_2.11H_2O$ [292] have been reported.



(108)

1.2.6 Macrocyclic complexes

The template condensation of 2,6-diacetylpyridine with 3,6-dioxaoctane-1,8-diamine in the presence of Cd^{2+} results in the formation of complexes of the 1+1 macrocycle (109) (*cf.* Section 1.1.6) [296]. The macrocyclic complexes $[CdL(NCS)_2]$ (L = 110;



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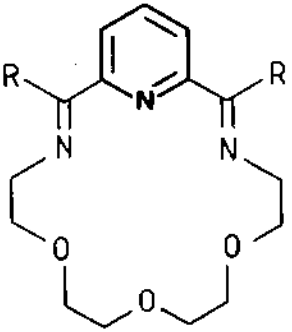

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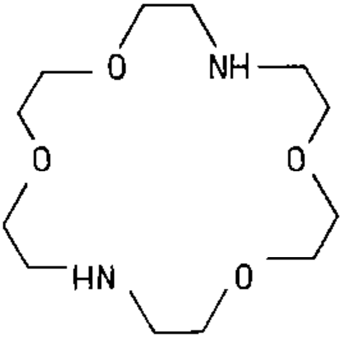
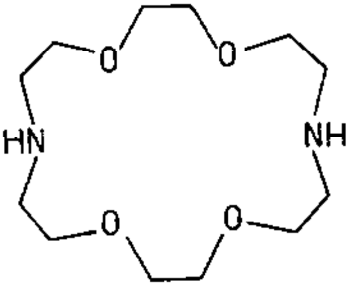


(111)

R = H or Me) have been prepared by template condensations or by metal exchange reactions [393], and the compound [CdLI]I (L = 111) has also been described [394]. Cadmium complexes of the Kryptands (112)-(116) have been investigated, and both $[CdL]^{2+}$ and the binuclear complexes $[Cd_2L]^{4+}$ are formed [395,396]. Cadmium complexes of a number of porphyrins have also been investigated [303,309,397].



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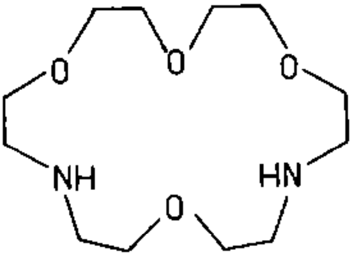

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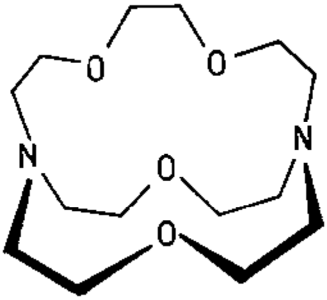

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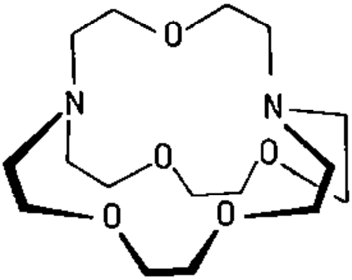

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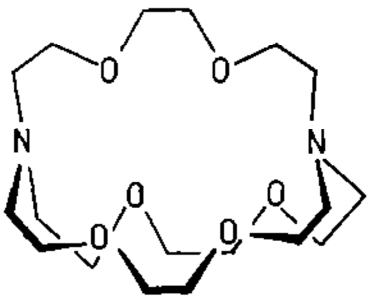

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1.2.7 ^{111}*Cd and* ^{113}*Cd NMR spectroscopy*

Cadmium NMR spectoscopy has been applied to a number of chemical problems this year, and Colton has reported ^{113}Cd NMR data for a very comprehensive selection of tetrahalocadmate(II) ions, and has also investigated the equilibria which are established in solutions containing cadmium and several different halide ions [324]. Colton has also investigated a range of $[CdX_2(PBu_3)_2]$ and $[Cd_2X_4(PBu_3)_3]$ complexes, together with mixed cadmium-mercury phosphine complexes [398]. The formation of edtaH$_4$ complexes has been studied by ^{113}Cd NMR, and, on the basis of the spectroscopic results, a number of solution equilibria were proposed [399]. Biochemical applications of ^{113}Cd NMR include the study of cadmium substituted horse-liver alcohol dehydrogenase [400] and cadmium substituted carbonic anhydrase [401].

Extremely promising results are being obtained from the application of magic angle spinning techniques to the ^{113}Cd NMR study of solid cadmium compounds [402-4] and further developments of this method should be of considerable interest.

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