

## 1. ZINC AND CADMIUM

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### INTRODUCTION

This review is a continuation of the 1981 review of zinc and cadmium published in this journal in 1983 [1]. This year zinc and cadmium are treated together, since the similarity in their coordination chemistry does not appear to merit separate treatment. The format is otherwise similar to that adopted in previous years, and little attempt has been made to cover reports covering the applications of the metal oxides, sulphides or halides.

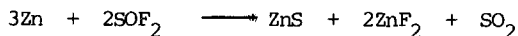
I should like to thank Dr O. Kennard and Dr S. Bellard for their help in obtaining structural data from the Cambridge Crystallographic Data Centre.

## 1.1 ZINC AND CADMIUM(II)

### 1.1.1 Halide and pseudohalide complexes

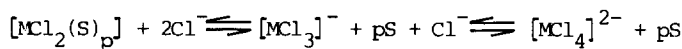
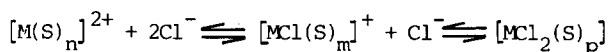
The ionisation spectra of  $\text{ZnCl}_2$  and  $\text{CdCl}_2$  have been determined, and compared with the calculated ionisation potentials [2]. The spectra consist of three groups of energies; the first is due to the metal outer valence s orbitals and the chlorine p orbitals, the second to the metal d orbitals, and the third to the chlorine inner s orbitals. The magnetic screening of the  $^{19}\text{F}$  nuclei in the complexes  $\text{ZnF}_2 \cdot x\text{H}_2\text{O}$  ( $x = 4, 7$  or  $10$ ) and  $\text{ZnF}(\text{OH})$  has been calculated from  $^{19}\text{F}$  NMR studies [3]. Two studies have discussed the

structure of  $\text{Cd}(\text{SCN})_2$  in the solid state, and reach general agreement that a polymeric structure is adopted, with thiocyanate ions bridging octahedral  $\text{Cd}(\text{SCN})_6$  units [4,5]. Molten zinc chloride is a viscous liquid with a low electrical conductivity, and has attracted some attention as a model for the liquid state. This year a number of apparently conflicting reports have appeared, describing the liquid state in non-compatible schemes. A neutron diffraction study of isotopically enriched molten zinc chloride suggests that metal-halide ion interactions are minor, and that the structure should be regarded as a mixture of zinc and chloride ions [6]. In contrast, an X-ray diffraction study at 330, 430 and 530° C has suggested that the liquid phase closely resembles a loosely distorted  $\alpha$ ,  $\beta$  or  $\gamma$   $\text{ZnCl}_2$  structure, with corner sharing  $\text{ZnCl}_4$  units; there are four close Zn-Cl contacts at 2.30 Å at each temperature [7]. Raman studies of  $\text{ZnCl}_2$ -KCl melts are in accord with the presence of  $\{\text{ZnCl}_2\}_n$ ,  $[\text{ZnCl}_4]^{2-}$  and other unidentified species [8]. The molten  $\text{CdCl}_2$ -KCl system has also been studied over the range 0-100 mol%  $\text{CdCl}_2$  at 857 K [9]. Related reports have described studies on the molten  $\text{MnF}_2$ - $\text{ZnF}_2$  system [10,11],  $\text{ZnCl}_2$ - $\text{CuCl}_2$  [12],  $\text{CdCl}_2$ - $\text{AgCl}$  [13] and  $\text{CdCl}_2$ - $\text{PbCl}_2$  [14] systems. The  $\text{AgCl}$ - $\text{CdCl}_2$  system is of some interest, in that vapour pressure measurements show it to exhibit a negative deviation from Raoult's Law [13]. The ternary system  $\text{CdCl}_2$ - $\text{LiCl}$ - $\text{NaCl}$  has been investigated, and a range of chlorocadmiate species characterised [66]. A number of studies in which metal nitrates have been used as solvents have been reported, and the association constants for the formation of  $[\text{CdCl}]^+$  and  $\text{CdCl}_2$  in  $\text{KNO}_3$ - $\text{Ba}(\text{NO}_3)_2$  eutectic mixtures have been determined electrochemically [15]. The same species have also been detected and characterised in aqueous  $\text{Cd}(\text{NO}_3)_2$ - $[\text{NH}_4][\text{NO}_3]$  melts [16]. The dissolution of  $\text{CdO}$  in molten  $\text{LiF}$ ,  $\text{KF}$  and  $\text{Na}_3[\text{AlF}_6]$  has been studied; various fluoro complexes are formed [17]. The interaction of  $\text{CdF}_2$  with  $\text{AsF}_5$  in anhydrous  $\text{HF}$  at room temperature results in the formation of a complex of stoichiometry  $\text{CdF}_2 \cdot 2\text{AsF}_5$  [18]; the compound  $2\text{ZnF}_2 \cdot 3\text{AsF}_5$  is prepared in a similar manner [63]. The reaction of metallic zinc with thionyl fluoride has been shown to result in the formation of  $\text{ZnF}_2$  and  $\text{ZnS}$ :

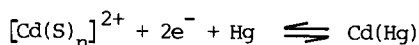
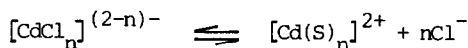


whilst zinc oxide reacts to form pure  $\text{ZnF}_2$  (and  $\text{SO}_2$ ) [64].

The solution chemistry of zinc and cadmium halides continues to be a topic of active interest, and numerous studies involving the related equilibria:



have been reported. Extensive X-ray diffraction studies on cadmium-iodo complexes in aqueous and dmsO solution have confirmed the nature of the solution species. In water the complexes present include  $[Cd(H_2O)_6]^{2+}$  (Cd-O, 2.292 Å; *c.f.* Cd-O in crystalline  $[Cd(H_2O)_6][ClO_4]_2$ , 2.292 Å),  $[Cd(H_2O)I]^{+}$  (Cd-I, 2.80 Å; Cd-O, 2.30 Å),  $[CdI_4]^{2-}$  (Cd-I, 2.79 Å) and traces of  $[CdI_3]^{-}$  and  $[CdI_2(S)_p]$ . In dmsO, the characterised species included  $[Cd(dmsO)_6]^{2+}$  (Cd-O, 2.292 Å; *c.f.* Cd-O in crystalline  $[Cd(dmsO)_6][ClO_4]_2$ , 2.291 Å),  $[CdI_2(dmsO)_x]$  (Cd-I, 2.75 Å),  $[CdI_3]^{-}$  (Cd-I, 2.773 Å,  $\angle I-Cd-I$ , 112°) and  $[CdI_4]^{2-}$  (Cd-I, 2.790 Å). The  $[CdI_3]^{-}$  and  $[CdI_4]^{2-}$  ions possessed the same structures in each solvent (trigonal and tetrahedral respectively), and showed no evidence for the additional coordination of solvent molecules within the first coordination shell [19]. These results are confirmed in studies on the  $ZnBr_2$ -MeOH and  $LiBr$ - $ZnBr_2$ -MeOH systems, which show a coordination number of four about the metal in each case (presumably  $[ZnBr_2(MeOH)_2]$  and  $[ZnBr_4]^{2-}$ ) with only trace amounts of  $[ZnBr_3]^{-}$  [20]. A study of the formation of chloro complexes in dmsO solutions of zinc perchlorate has also been described [65]. An EMF method has been utilised in the study of the interaction of  $ZnCl_2$  with chloride ion in methanol. It is found that  $K_1$  ( $7.76 \times 10^3$  M) is less than  $K_2$  ( $1.74 \times 10^4$  M), which is interpreted in terms of passing from an octahedral  $[ZnCl(MeOH)_5]^{+}$  species to a tetrahedral  $[ZnCl_2(MeOH)_2]$  complex [21]. Related studies have shown that the solubility of cadmium halides in water decreases with increasing pressure [22,23]. Anionic  $[ZnCl_3]^{-}$  and  $[ZnCl_4]^{2-}$  species are present in zinc-chloride battery electrolyte, and are responsible for the observed negative transference numbers for zinc in aqueous acidic chloride medium [24]. In neutral chloride medium, two simultaneous processes:

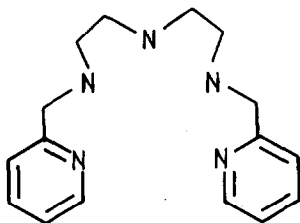


occur in the polarographic reduction of cadmium(II) [25]. The formation of zinc and cadmium chloro complexes in hydrochloric acid media has also been investigated [26]. The electrochemical behaviour of chlorinated aqueous zinc chloride solutions has also been studied [27].

Aqueous solutions containing cadmium and thiocyanate have been shown to contain the species  $[\text{Cd}(\text{SCN})_n(\text{H}_2\text{O})_x]$  ( $n = 1-4$ ); there is no evidence for the formation of polynuclear complexes, although both S and N bonded thiocyanate are present [4]. The tertiary and quaternary complexes  $[\text{Cd}(\text{SCN})(\text{NO}_2)]$ ,  $[\text{Cd}(\text{SCN})_2(\text{NO}_2)]^-$ ,  $[\text{Cd}(\text{SCN})(\text{NO}_2)_2]^-$  and  $[\text{Cd}(\text{SCN})\text{Cl}(\text{NO}_2)]^-$  have been characterised by polarographic methods [28,29]. A range of complexes with halide and pseudohalide ions ( $\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ,  $\text{NCS}$ ,  $\text{NCSe}$ ,  $\text{N}(\text{CN})_2$ ,  $\text{C}(\text{CN})_3$  and  $\text{ONC}(\text{CN})_2$ ) have been characterised for zinc in *dma* [30] and cadmium in *dms*<sub>o</sub>, *dmf*, *MeOH* and *MeCN* [31]; complexes with 1-4 pseudohalide ligands have been described.

The rotational motion of the ammonium ions in ammonium trifluorozincate has been studied over the temperature range 298-1 K by  $^1\text{H}$  NMR methods [32]. Halogen NQR studies of  $[\text{MX}_4]^{2-}$  and  $[\text{MX}_3]^-$  salts ( $\text{M} = \text{Cd}$  or  $\text{Zn}$ ;  $\text{X} = \text{Cl}$ ,  $\text{Br}$  or  $\text{I}$ ) have been reported [33]. Much of the interest in the Group IIB tetrahalometallate salts have centred on the dynamic behaviour and the phase transitions which they exhibit, and studies of  $[\text{R}_4\text{N}]_2[\text{ZnCl}_4]$  ( $\text{R} = \text{tetradecyl}$  [34],  $\text{H}$  [35-37],  $\text{Me}$  [38]),  $[\text{Me}_4\text{N}]_2[\text{ZnCl}_4]$  [39],  $\text{Rb}_2[\text{ZnCl}_4]$  [40-43],  $\text{K}_2[\text{ZnCl}_4]$  [42],  $\text{Rb}_2[\text{ZnBr}_4]$  [42] and  $[\text{RNH}_3]_2[\text{CdCl}_4]$  ( $\text{R} = \text{Me}$  [44] or  $n\text{-Pr}$  [45]), using a variety of techniques have been described.

A number of X-ray structural studies of tetrahalometallate complexes have also been described. In  $[\text{Co}(\text{L})\text{Cl}][\text{ZnCl}_4]$  ( $\text{L} = 1$ ), the anion is in



(1)

in a distorted tetrahedral configuration, with  $\text{Zn-Cl}(\text{average})$ , 2.263 Å [46], whereas a more regular tetrahedral geometry is observed in  $[\text{ZnL}_2(\text{H}_2\text{O})][\text{ZnCl}_4]$  ( $\text{L} = 8\text{-aminoquinoline}$ ),  $\text{Zn-Cl}(\text{average})$ , 2.2 Å [47]. The anion in  $[\text{W}_3\text{O}_2(\text{OAc})_6(\text{H}_2\text{O})_3][\text{ZnBr}_4]$  is tetrahedral, with  $\text{Zn-Br}(\text{average})$ , 2.41 Å [48]. Other complexes reported include  $[\text{CdL}_4][\text{ZnX}_4]$  ( $\text{L} = \text{PhNH}_2$ , 2,3 or 4- $\text{MeC}_6\text{H}_4\text{NH}_2$ ;

X = Cl, Br or I) [49]. The complexes  $[R_4N]_2[ZnCl_4] \cdot xPhH$  ( $R_4N$  = tri-n-octylammonium or tricaprylmethylammonium) are extracted from aqueous chloride medium by benzene solutions of tri-n-octylamine or tricaprylmethylammonium chloride; on heating they decompose to zinc chloride [50]. The thermal decomposition of  $[Ph_2I]_2[M(CN)_4]$  ( $M$  = Cd or Zn) has been shown to result in the formation of phenylisocyanide complexes [51]. A multinuclear NMR study ( $^{13}C$  and  $^{15}N$ ) of  $^{13}C$  N enriched cyanocomplexes has been reported ( $[Zn(CN)_4]^{2-}$ ,  $J_{C,N}$  8.9 Hz,  $\delta^{13}C$  -19.0,  $\delta^{15}N$  -101.4;  $[Cd(CN)_4]^{2-}$ ,  $J_{C,N}$  7.7 Hz,  $\delta^{13}C$  -16.5,  $\delta^{15}N$  -97.8;  $\delta^{13}C$  w.r.t. KCN,  $\delta^{15}N$  w.r.t.  $NaNO_3$ ) [52].

A number of complex halides have been structurally characterised, including  $KCdF_3$  [53],  $RbZnCoF_6$  [54],  $CsZnAlF_6$  [54],  $Cd_2MgCl_6 \cdot 12H_2O$  [55],  $Cd_2NiCl_6 \cdot 12H_2O$  [56] and  $KCd_3Cl_7 \cdot 4H_2O$  [57].

The extraction of Group IIB metals from aqueous medium continues to be of interest, and a number of studies have been reported this year. The metals may be extracted from aqueous acidic chloride medium by tri-n-butyl phosphate [58,59] or tri-n-octylmethylammonium chloride [60], or from thiocyanate medium by tetra-n-octylammonium thiocyanate [61] or tri-n-butyl phosphate [62]; in the latter case the extracted species is  $Cd(SCN)_X \cdot 4L$  ( $L$  = tri-n-butyl phosphate). A number of other studies involving the extraction of Group IIB metal ions from aqueous solution have been reported [67,68].

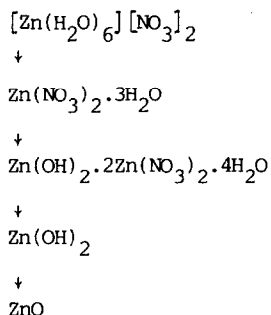
The halometallate complexes  $HCdBr_3 \cdot 3L$  ( $L$  =  $Et_2O$  or  $py$ ),  $HCdBr_2 \cdot 1.3L$  ( $L$  =  $Et_2O$ ,  $py$  or  $PhNH_2$ ) and  $H_2CdBr_4 \cdot L$  ( $L$  =  $ArNH_2$ ) have also been reported [69].

### 1.1.2 Complexes with oxygen donor ligands

#### 1.1.2.1 Inorganic molecules and ions

There have been numerous studies of the  $M^{2+}$ -solvent interaction reported recently, and, whilst the majority of these have been concerned with solution behaviour, a number of reports describing the solid state have also appeared. The dehydration of  $Zn(SO_4) \cdot 7H_2O$  to  $Zn(SO_4) \cdot 6H_2O$  has been studied by optical microscopy and X-ray diffraction methods [70]. The magnetic susceptibilities of  $Zn(SO_4) \cdot nH_2O$  ( $n$  = 0-7) have been shown to differ from those calculated using an additive law; better correlation is obtained on considering a temperature independent Van Vleck polarising magnetism term ( $\chi_p$ ) [71]. The lattice dynamics of  $[Zn(H_2O)_6][ClO_4]_2$  have been investigated by  $^1H$  NMR (4.2 - 363 K) and vibrational spectroscopic methods [72,73]; monitoring the IR active librational modes of the coordinated water revealed phase transitions at 284, 256.5 and 233 K. A  $^1H$  NMR study has also revealed that the water-perchlorate hydrogen-bonding interaction in  $[M(H_2O)_6][ClO_4]_2$  ( $M$  = Zn or Cd) is significantly weaker for the cadmium compound [74]. The thermal

decomposition of  $[M(H_2O)_6][NO_3]_2$  has been shown to follow the pathway: [75]



X-ray diffraction studies of aqueous  $CdSO_4$  solutions have clearly demonstrated the formation of *O*-sulphato complexes [76-78]. These are of the general form  $[Cd(H_2O)_{6-n}(OSO_3)_n]^{(2-2n)+}$ , and appear to be the major species present in concentrated solutions. These results are fully in accord with tensimetric studies of the cadmium and magnesium sulphate aqueous systems, which indicate an increased interionic attraction at elevated temperatures [79]. In contrast, the X-ray diffraction studies on cadmium perchlorate solutions show no evidence for the coordination of the perchlorate ion to the metal, the only cationic species present being  $[Cd(H_2O)_6]^{2+}$  ( $Cd-O$ , 2.292 Å, *c.f.*  $Cd-O$ , 2.292 Å in solid  $[Cd(H_2O)_6][ClO_4]_2$ ) [78]. The formation of  $[Zn(H_2O)_{6-n}(MeOH)_n]^{2+}$  complexes in aqueous methanol has been studied using a polarographic method [80]. Solutions of cadmium nitrate in mixed aqueous solvents (dioxane, methanol or glycol) have been studied, and the interaction of the  $Cd^{2+}-NO_3^-$  ion-pair (complex?) with the solvent has been investigated [81]. The transport behaviour of  $Cd(NO_3)_2-MnCl_2-H_2O$  melts [82], and a small angle neutron scattering study of  $D_2O$  solutions of zinc chloride [83] have also been reported.

The zinc ion catalysed aqutation of *cis*- $[Cr(H_2O)_2L_2]^+$  ( $HL = CH_2(CO_2H)_2$ ) has been shown to obey a rate law of the type:

$$k_{obs} = k_H[H^+] + k_{cat}[Zn^{2+}]$$

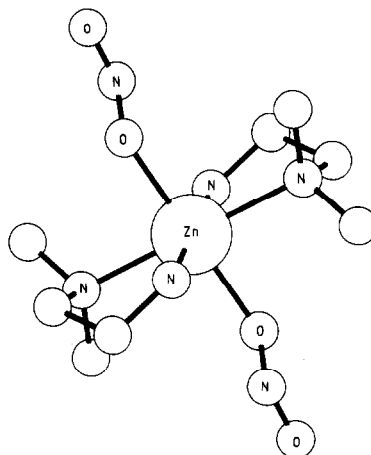
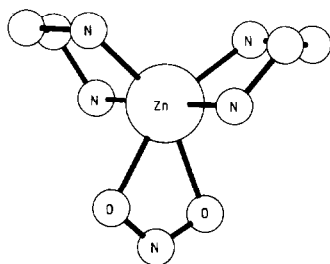
although other transition metal ions are more effective catalysts [84].

Studies of the  $Rb_2(SO_4)-Cd(SO_4)-H_2O$  [85],  $Sm(ClO_4)_3-Cd(ClO_4)_2-H_2O$  [86],  $Cd(ClO_4)_2-NH_4(ClO_4)-H_2O$  [87],  $Cd(SO_4)-[NH_4]_2SO_4-H_2O$  [87],  $Cd(ClO_4)_2-Zn(ClO_4)_2-Ce(ClO_4)_4-H_2O$  [88] and  $Zn(SO_4)-ZnCl_2-H_2O$  [89] systems have been described.

In  $Cd_2(OH)_2(SO_4)$ , the metal is in a highly distorted  $CdO_6$  environment [90], whereas in  $Cd(BrO_3)_2 \cdot 2H_2O$  the metal is in a seven-coordinate

$cdO_7$  environment [91]. The thermal decomposition of the latter compound has also been investigated [92].

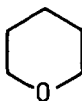
The formation of hydroxy complexes of zinc and cadmium has been studied using anodic stripping voltammetric techniques, and the stability constants for the complexes determined (Zn:  $\lg \beta_1$ , 5.91,  $\lg \beta_2$ , 11.10; Cd:  $\lg \beta$ , 3.69,  $\lg \beta_2$ , 6.49) [93]. It has been shown that the addition of alkali to aqueous solutions of zinc nitrate results in the formation of basic salts rather than pure zinc hydroxide; thus carbonate precipitates  $ZnCO_3 \cdot xZn(OH)_2 \cdot yH_2O$ , ammonia  $Zn_2(NO_3)_2 \cdot xZn(OH)_2 \cdot yNH_3 \cdot zH_2O$  and sodium hydroxide  $Zn(NO_3)_2 \cdot xZn(OH)_2$  or  $Zn(NO_3)_2 \cdot xZnO \cdot yZn(OH)_2$  [94]. The crystal structures of the nitrito complexes  $[Zn(en)_2(NO_2)] [NO_2]$  and  $[Zn(tmen)_2(NO_2)_2]$  have been described [95]. In  $[Zn(en)_2(NO_2)] [NO_2]$  (2), the coordinated nitrite acts as a chelating  $O_2$  donor (Zn-O, 2.240 Å), whereas in  $[Zn(tmen)_2(NO_2)_2]$  (3) it acts as a monodentate monodentate  $O$  donor (Zn-O, 2.221 Å).



Other relevant reports include a study of the  $\text{Cd}(\text{NO}_3)_2\text{-In}(\text{NO}_3)_3\text{-Na}_2\text{WO}_4$  system, which precipitates a mixture of cadmium and indium tungstates [96], the  $\text{Cd}^{2+}\text{-NO}_3^-\text{-N}_3^-$  and  $\text{Cd}^{2+}\text{-NO}_3^-\text{-SCN}^-$  systems [97], an investigation of the phase transitions in  $(\text{K}_x\text{Tl}_{1-x})\text{Cd}_2(\text{SO}_4)_3$  [98], and of the decomposition of  $\text{Zn}(\text{SO}_4)$  in a self generated atmosphere to give  $\text{ZnO} \cdot 2\text{Zn}(\text{SO}_4)$  [99]. The crystal structure of  $\text{Cd}_3[\text{Cr}(\text{CN})_6] \cdot 14\text{H}_2\text{O}$  has been reported; the cyanide ligands bridge the two different metals [100]. Zinc metal dissolves in potassium pyrosulphate,  $\text{K}_2\text{S}_2\text{O}_7$ , to give zinc sulphate and  $\text{SO}_2$  [101].

#### 1.1.2.2 Simple organic ligands

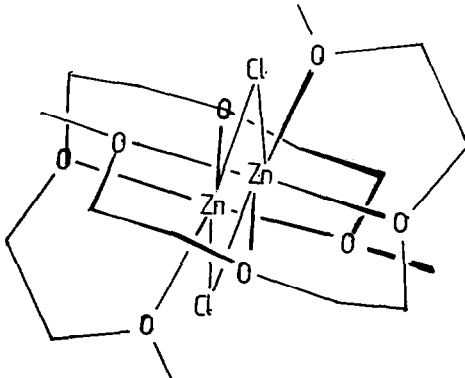
The crystal structure of  $[\text{Zn}(\text{dmsO})_6][\text{ClO}_4]_2$  has been reported; the metal is in an octahedral  $\text{ZnO}_6$  environment, with an average Zn-O distance of 2.110 Å. Complementary solution studies reveal the persistence of the  $[\text{Zn}(\text{dmsO})_6]^{2+}$  cation in dmsO solution, with Zn-O distances of 2.127 Å [102]. Tetrahydropyran (4) reacts with  $[\text{Zn}(\text{H}_2\text{O})_6][\text{ClO}_4]_2$  in triethyl orthoformate to form  $\text{ZnL}(\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}$ ; the complex is a 2:1 electrolyte, and is thus formulated  $[\text{ZnL}(\text{H}_2\text{O})_5][\text{ClO}_4]_2$  ( $\text{L} = 4$ ) [103]. A number of complexes with



(4)

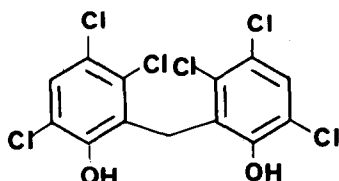
polyethers have been reported, including  $[\text{ZnL}_2][\text{SbCl}_6]_2$  ( $\text{L} = (\text{MeOCH}_2\text{CH}_2)_2\text{O}$ ),  $[\text{ZnL}][\text{SbCl}_6]_2$  ( $\text{L} = (\text{MeOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2)_2$ ) [104], and  $[\text{Zn}_2\text{L}_2\text{Cl}_2][\text{SbCl}_6]_2$  ( $\text{L} = (\text{MeOCH}_2\text{CH}_2\text{OCH}_2)_2$ ) [105]. By analogy with the cobalt complex, for which an X-ray structural determination has been reported, the  $[\text{Zn}_2\text{L}_2\text{Cl}_2]^{2+}$  cation is thought to possess the dichloro-bridged structure (5).

(5)





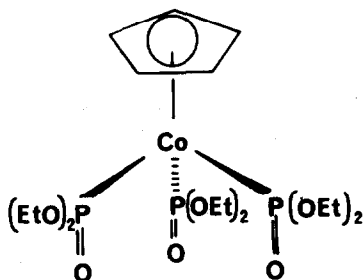
Salts of  $[\text{ZnL}_6]^{2+}$  (L = pyridine *N*-oxide) have been shown to undergo facile solid state reactions with alkali metal halides, an observation of obvious relevance to those recording the infrared spectra of these and related compounds [106]. Zinc complexes with the chelating ligand 2-pyridinecarboxylic acid *N*-oxide have been reported [107]. Zinc and cadmium complexes of hexachlorophene (6) have been described, and their stability constants determined [108].



(6)

#### 1.1.2.3 Phosphine oxides

Crystal structural analyses of the complexes  $[\text{ZnBr}_2(\text{Ph}_3\text{PO})_2]$  (Zn-O, 1.965, 1.970 Å; Zn-Br, 2.354, 2.357 Å) and  $[\text{ZnCl}_2(\text{Ph}_3\text{PO})_2]$  (Zn-O, 1.967 Å; Zn-Cl, 2.187 Å) have been reported; both complexes show near-tetrahedral geometries about the metal [109]. Zinc and cadmium complexes of the novel tripod ligand (7) have also been described [110]. A  $^{113}\text{Cd}$  NMR study of  $^{113}\text{Cd}$  enriched phosphine oxide complexes has been reported [111]. Cadmium

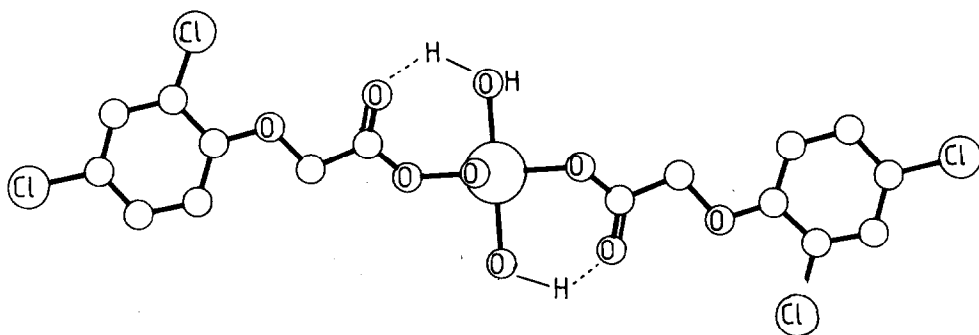


(7)

metal reacts with  $(\text{EtO})_2\text{P}(\text{O})\text{CF}_2\text{Br}$  to form  $\text{BrCdCF}_2\text{P}(\text{O})(\text{OEt})_2$ , which finds some application in organic synthesis; reaction with allyl bromide results in the formation of  $\text{CdBr}_2$  and  $(\text{EtO})_2\text{P}(\text{O})\text{CF}_2\text{CH}_2\text{CH}=\text{CH}_2$  [112].

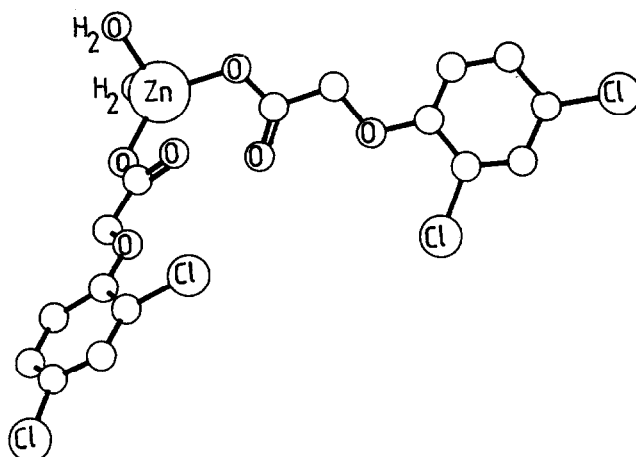
#### 1.1.2.4 Carboxylic acids and related ligands

The crystallisation of magnesium and cadmium formates from water has been investigated, and the formation of mixed crystals demonstrated [113]. In the  $\text{Cd}(\text{HCO}_2)_2 \cdot \text{M}(\text{HCO}_2)_2 \cdot \text{H}_2\text{O}$  systems ( $\text{M} = \text{Li}, \text{Na}, \text{K}$  or  $\text{NH}_4$ ), phases corresponding to  $\text{M}\text{Cd}(\text{HCO}_2)_3$  and  $\text{K}_3\text{Cd}(\text{HCO}_2)_5$  are formed [114]. Hydrated zinc and cadmium acetates are dehydrated to  $\text{M}(\text{OAc})_2$  on heating with 2,2'-dimethoxypropane [115]. A Raman and infrared spectroscopic study of  $\text{Zn}(\text{OAc})_2$  and  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  has been described; in the latter compound the metal is in an octahedral environment, with *trans*-diaxial water ligands and bidentate chelating acetate groups, and in the former compound the metal is in a pseudo-tetrahedral environment [116]. An infrared study of the zinc and cadmium complexes of straight chain monocarboxylic acids ( $\text{C}_6$ - $\text{C}_{18}$  inclusive) has been reported [118]. The diffusion of zinc acetate in water has been investigated by the porous disc method [117]. A crystal structure of the complex tetraaquabis-(2,4-dichlorophenoxyacetato)zinc(II)diaquabis(2,4-dichlorophenoxyacetato)zinc(II) has been reported, in which two distinct metal environments occur. In the  $[\text{Zn}(\text{H}_2\text{O})_4\text{L}_2]$  ( $\text{HL} = 2,4$ -dichlorophenoxyacetic acid) molecule (8) the metal is in an octahedral  $o_6$  environment, with a *trans*-diaxial arrangement of monodentate carboxylate groups ( $\text{Zn}-\text{OH}_2$ , 2.098 Å;  $\text{Zn}-\text{O}$ , 2.071, 2.121 Å) and hydrogen-bonding between coordinated water molecules and uncoordinated oxygens of the carboxylates in the same molecule.



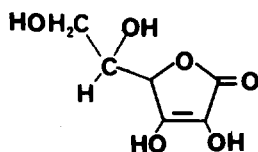
(8)

In  $[\text{Zn}(\text{OH}_2)_2\text{L}_2]$  the metal is in a tetrahedral environment (9) ( $\text{Zn}-\text{OH}_2$ , 2.002 Å;  $\text{Zn}-\text{O}$ , 1.915, 1.956 Å) [119].



(9)

A number of complexes with hydroxycarboxylic acids have been described, including  $[\text{ZnL}]^-$  ( $\text{H}_3\text{L}$  = ascorbic acid, 10) [120],  $[\text{CdCl}(\text{L})]^{2-}$ ,  $[\text{CdCl}_2\text{L}]^{3-}$  and  $[\text{CdClL}_2]^{5-}$  ( $\text{H}_3\text{L}$  = citric acid,  $(\text{HO}_2\text{CCH}_2)_2\text{C}(\text{OH})\text{CO}_2\text{H}$ ) [121]. Complexes



(10)

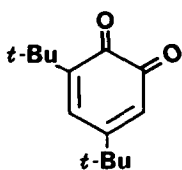
gluconic acid,  $\text{HOCH}_2(\text{CHOH})_4\text{CO}_2\text{H}$  [122] and glycollic acid,  $\text{HOCH}_2\text{CO}_2\text{H}$  [123] have also been described.

A number of oxalate complexes have been investigated, including the heteronuclear species  $\text{MTiL}_2\text{O} \cdot 4\text{H}_2\text{O}$  ( $\text{M} = \text{Cd}$  or  $\text{Zn}$ ;  $\text{H}_2\text{L}$  = oxalic acid) [124] and  $\text{MZrL}_2\text{O} \cdot n\text{H}_2\text{O}$  ( $\text{M} = \text{Zn}$ ,  $n = 6$ ;  $\text{M} = \text{Cd}$ ,  $n = 4$ ;  $\text{H}_2\text{L}$  = oxalic acid) [125]. The thermal decomposition of these compounds, and also of  $\text{CdL}_2 \cdot 3\text{H}_2\text{O}$  ( $\text{H}_2\text{L}$  = oxalic acid) [126] has been studied. A spectroscopic study (infrared,

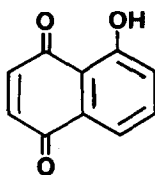
electronic and X-ray) study of anhydrous zinc oxalate has been reported; it is suggested that a polymeric structure containing tetradentate oxalate and octahedral zinc ions is adopted [127]. Complexes with a number of other polycarboxylic acids, including malonic [128-130], succinic [128,131], maleic [128], malic [128] and citric acids [128] have also been described. Crystal structures of  $[\text{Zn}(\text{H}_2\text{O})\text{L}]$  ( $\text{H}_2\text{L}$  = malonic acid,  $\text{CH}_2(\text{CO}_2\text{H})_2$ ) [130] and  $[\text{Cd}(\text{H}_2\text{O})_2\text{L}]$  ( $\text{H}_2\text{L}$  = succinic acid,  $(\text{HO}_2\text{CCH}_2)_2$ ) [131] have been reported. In the former compound the metal is in an octahedral  $D_{4h}$  environment, and a sheet type polymer is formed, whereas in the latter compound the metal is in an approximately pentagonal bipyramidal environment, with succinate ions bridging adjacent metal centres. The complexes  $[\text{M}_2\text{L}]$  ( $\text{M}$  = Zn or Cd;  $\text{HL}$  = pentamethyl cyclopentadienepentacarboxylate) are air-stable and readily prepared from  $\text{HL}$  [178]. The ligand is thought to be coordinated to the metals *via* the carbonyl oxygen atoms. Binuclear complexes  $[\text{M}_2\text{L}]$  ( $\text{H}_4\text{L}$  = 1,2,4,5-benzenetetracarboxylic acid, pyromellitic acid;  $\text{M}$  = Zn or Cd) have been prepared [373].

#### 1.1.2.5 Diketonate and related ligands

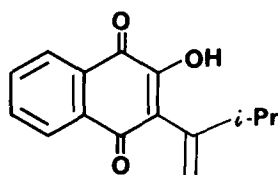
An electron diffraction study of  $[\text{Zn}(\text{acac})_2]$  has been reported. The Zn-O distances of  $1.942 \pm 0.006$  Å correlate reasonably well with those determined from an X-ray structural study of the crystalline solid (Zn-O, 1.999 Å) and are shorter than those observed in the solid state structure of the monohydrate (Zn-O, 2.02 Å) [132]. Zinc complexes of  $\text{CH}_3\text{COCO}_2\text{H}$ ,  $\text{CH}_3\text{COCH}_2\text{CO}_2\text{H}$  and  $\text{CH}_3\text{CH}_2\text{COCO}_2\text{H}$  have been described [133]. The electrochemical properties of complexes of 1,2-benzoquinones have been investigated [134,135] and the complex  $[\text{ZnL}_2]$  ( $\text{H}_2\text{L}$  = 4,6-bis-*tert*-butyl-1,2-benzoquinone, 11) has been shown to possess a less negative reduction potential (to the semiquinone)



(11)



(12)



(13)

than the free ligand [135]. Zinc complexes of the 1,2-benzosemiquinones have been characterised [136]. Complexes with juglone (12) [137] and lapachol (13) [138,210] have also been described.

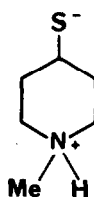
### 1.1.3 Complexes with sulphur and selenium donor ligands

#### 1.1.3.1 Thiols, thioethers and heterocyclic thiols

The electrochemical oxidation of anodic zinc or cadmium into acetonitrile solutions containing RSH or  $R_2S_2$  provides an excellent route to the polymeric  $M(SR)_2$  compounds [139]. This is in contrast to the behaviour when  $Et_3N$  is also present in the solution, in which case the isolated product is the cubane species,  $[Et_3NH]_2[Zn_4(SR)_{10}]$  [140]. A number of multinuclear NMR studies ( $^1H$ ,  $^{13}C$ ,  $^{67}Zn$ ,  $^{113}Cd$ , and  $^{77}Se$ ) of the  $[ML_4]^{2-}$  ( $M = Cd$  or  $Zn$ ;  $HL = RSH$ ) and  $[ML_2]^{2-}$  ( $M = Zn$  or  $Cd$ ;  $H_2L =$  chelating dithiol) species, including the mixed ligand complexes  $[Cd(SPh)_n(SePh)_{4-n}]^{2-}$ , have been reported [141-143]. Cadmium has been shown to form a range of polynuclear complexes with  $HSCH_2CH_2OH$  [144]. The complexes  $[ML_2]$  ( $M = Zn$  or  $Cd$ ;  $HL =$  antimony hydrogen bis(thioglycollate) [145];  $M = Zn$ ;  $HL =$  5-butylthio-8-mercaptoquinoline [146];  $M = Zn$  or  $Cd$ ;  $HL =$  8-mercaptoquinoline [147]) and  $[ZnL'L']$  ( $L =$  bipy or phen;  $H_2L' = HSCH_2CHNH_2CO_2H$ ) [148] have been described. The crystal and molecular structure of  $[ZnL_2]$  ( $HL =$  5-butylthio-8-mercaptoquinoline, 14) has been reported; the metal is in a distorted tetrahedral  $N_2S_2$  environment [146].



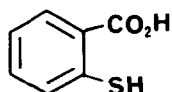
(14)



(15)

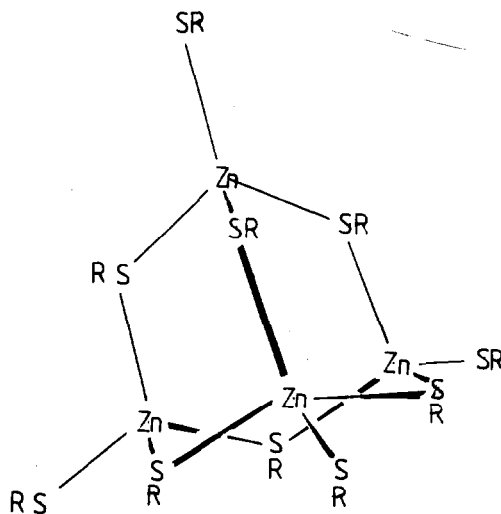
A range of polynuclear complexes of the zwitterionic ligand 1-methyl-4-mercaptopiperidine (15) of zinc and cadmium have been described [149,150]. The reaction of  $[Hg(HL)_2]$  ( $HL =$  2-mercaptobenzoic acid, 16) with cadmium

nitrate leads to the novel  $\text{CdHgL}_2$  species, in which the cadmium is bonded to the carboxylate oxygen atom, and the mercury to the thiolate sulphur [131].



(16)

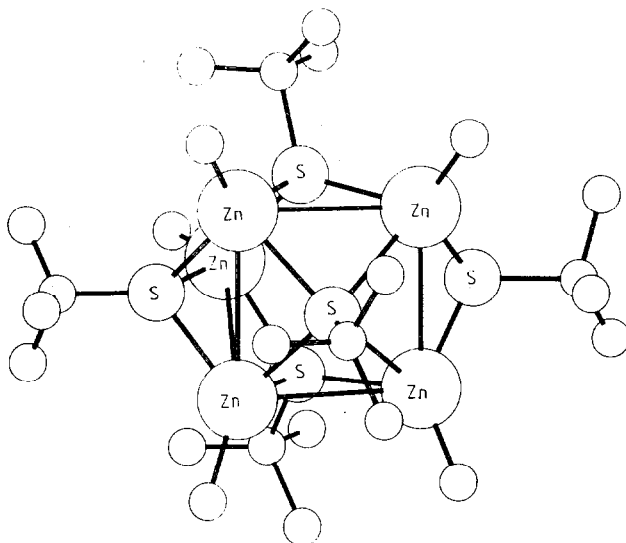
The formation of heteronuclear clusters in thiolate complexes is well-established, and a number of papers dealing with this subject have appeared this year. A crystal structure of  $[\text{Et}_3\text{NH}]_2[\text{Zn}_4(\text{SPh})_{10}]$ , prepared by the electrolytic oxidation of anodic zinc into an acetonitrile solution containing thiophenol and triethylamine, has been described; the anion adopts the adamantane like structure (17), with little evidence for metal-metal bonding, Zn-Zn, 3.98 Å ; Zn-S(bridging), 2.371 Å ; Zn-S(terminal) 2.291 Å [140]. The



(17)

same anion geometry is observed in the crystal structure of the complex  $[\text{Me}_4\text{N}]_2[\text{Fe}_4(\text{SPh})_{10}] \cdot \text{C}_3\text{H}_7\text{CN}$  [152]. The  $[\text{Zn}_4(\text{SPh})_{10}]^{2-}$  cluster anion has also been prepared by the reaction of  $\text{NaSPh}$  with  $\text{ZnCl}_2$ , and  $^1\text{H}$  NMR studies have revealed a rapid SPh(bridging)-SPh(terminal) interconversion, which is thought

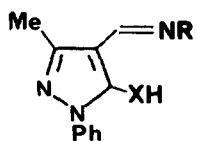
to occur *via* opening of the cluster by successive breaking of two bridging Zn-S bonds [152]. A rapid metal exchange reaction in the mixed-metal clusters  $[M_{4-n}Zn_n(SPh)_{10}]^{2-}$  ( $M = Cd, Co$  or  $Fe$ ) and  $[Co_{4-n}Cd_n(SPh)_{10}]^{2-}$  was also detected. A crystal structural analysis of the pentanuclear cluster  $[(MeZn)_5(^tBuS)_5]$  (18) has also been reported; once again there is little evidence for direct Zn-Zn or S-S interactions [153]. The structure is



(18)

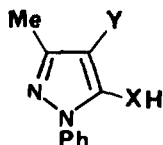
clearly based upon a square pyramid of zinc atoms.

A number of zinc complexes of aminothioethers  $(RCH_2NHCH_2CH_2)_2S$  ( $R = 2$ -pyridyl or  $CH_2NH_2$ ) have been prepared [154]. An EXAFS study of zinc complexes of porphyrins bearing thioether 'tails' has been reported; there is little evidence for a strong axial Zn-S interaction [155]. A number of zinc complexes have been investigated for their inhibitory activity upon the oxidation of ethylbenzene; complexes tested were of the  $[ZnL_2]$  type ( $HL = 19$  or  $20$ ), in which the ligands are coordinated to the metal through the imine nitrogen and the deprotonated thiol, selenol or hydroxy group [156]. Other complexes described include the pyrazole derivatives  $[ZnL_2]$  ( $HL = 21$  or  $22$ ) [157,158] and the imidazole complexes  $[ZnL_2X_2]$ ,  $[ZnL_4]Y_2$  ( $L = 23$  or  $24$ ;  $X =$  halide or  $SCN$ ;  $Y = ClO_4$  or  $NO_3$ ) [159,160]. The  $[ZnL_4][ClO_4]_2$  ( $L = 23$  or  $24$ )



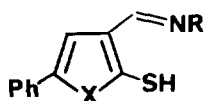
$X = O, S \text{ or } Se$

(19)

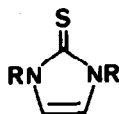


21;  $X = S$ ,  $Y = N=NPh$

22;  $X = Se$ ,  $Y = CH_2NR$



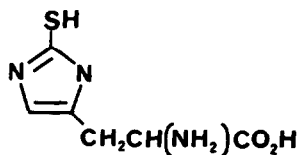
(20)



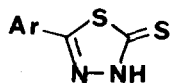
23;  $R = H$

24;  $R = Me$

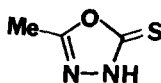
complexes are probably pseudotetrahedral with predominant bonding to the metal through sulphur, although there is some evidence for weak Zn-N interactions in complexes of 23. The metal binding properties of thiolhistidine (25) have been investigated, and the cadmium and zinc complexes described [161]. Compounds have also been described in which 1,3,4-oxadiazole-2-thiones (26) [162], 1,3,4-thiadiazole-2-thiones (27) [163] and 1,2,3,4-thiatriazole-5-thiones (28) [164] act as ligands.



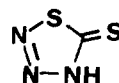
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(26)



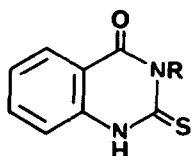
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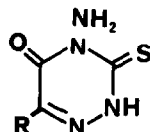
(28)



A number of mercapto derivatives of six-membered ring heterocycles have been reported as forming zinc or cadmium complexes, and species described this year include  $[M_2L_2Cl_2]$  ( $M = Zn$  or  $Cd$ ;  $HL = 29$ ) [165] and  $[ML_2]$  ( $M = Zn$  or  $Cd$ ;  $HL = 30$ ) [166]; the latter ligand is thought to act as a bidentate  $N,S$  donor, through the thione and the amino nitrogen atoms.

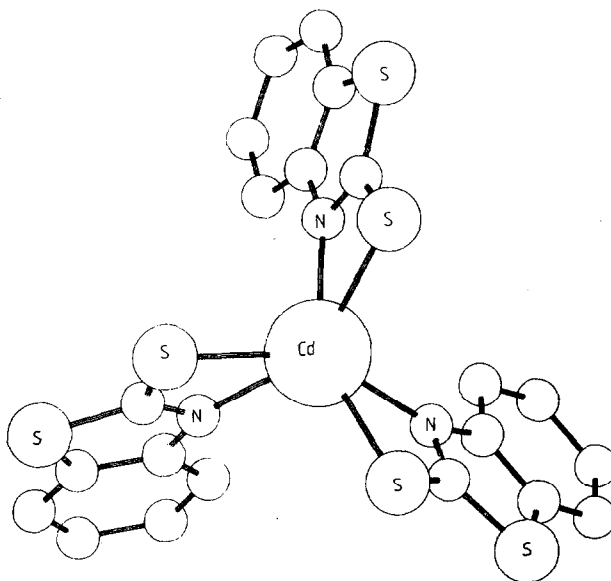


(29)



(30)

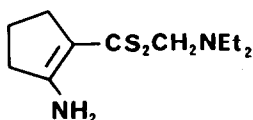
A range of zinc and cadmium complexes of *N*-aminorhodanine (*N*-amino-4-hydroxythiazole-2(3*H*)-thione) have been described [372]. A crystal structural analysis of the complex  $[NEt_4][CdL_3]$  ( $HL =$  benzothiazole-2(3*H*)-thione) (31) has been reported; the anion possesses strict  $C_3$  symmetry with the ligand acting as a bidentate  $NS$  donor ( $Cd-S$ , 2.667 Å;  $Cd-N$ , 2.474 Å) [173]



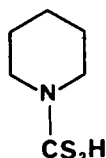
(31)

### 1.1.3.2 Thioacids, thioamides and related compounds

A number of reports describing complexes of ethylxanthates,  $\text{EtOCS}_2\text{H}$ , have been published. Zinc sulphate reacts with  $\text{EtOCS}_2\text{K}$  to give the complex  $[\text{ZnL}_2]$ , in which the ligand acts as a bidentate  $O, S'$  donor [167]; related binuclear complexes including  $[\text{MZnL}_4]$ ,  $[\text{M}(\text{py})_2\text{ZnL}_4]$  and  $[\text{ML}'_3][\text{ZnL}_4]$  ( $\text{L}' = \text{bipy}$  or  $\text{phen}$ ) have also been described [168]. The unusual complex  $[\text{CdL}_2]$  ( $\text{HL} = 32$ ) has also been reported [169].

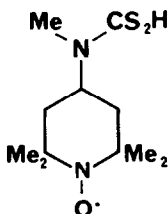


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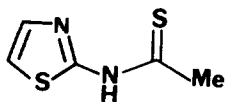


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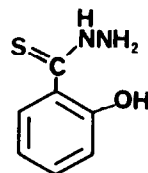
Numerous examples of dithiocarbamate complexes are known, and several papers discussing Group IIB compounds have appeared. The exchange reactions between  $[\text{ZnL}_2]$  ( $\text{HL} = \text{Et}_2\text{NCS}_2\text{H}$ ) and  $\text{Zn}^{2+}$  (solv) have been studied in dioxane or dmf [170], dmsO [171] or a chloroform-water two-phase system [172]. A detailed study of the reactions of  $[\text{CdL}_2]$  ( $\text{HL} = \text{Et}_2\text{NCS}_2\text{H}$ ) with halogens, and of the reactions of iodo-derivatives with Lewis bases has been described [173]. A crystal structure of the complex  $[\text{NBU}_4][\text{CdL}_3]$  (33) ( $\text{HL} = \text{Et}_2\text{NCS}_2\text{H}$ ) has shown the metal to be in an octahedral geometry intermediate between octahedral and trigonal prismatic, with each dithiocarbamate acting as a non-symmetrical  $S_2$  chelate ( $\text{Cd-S}$ , 2.655–2.755 Å) [173]. A number of heteronuclear dithiocarbamate complexes  $[\text{MCDL}_4]$  ( $\text{M} = \text{VO}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$  or  $\text{Zn}$ ;  $\text{HL} = \text{Et}_2\text{NCS}_2\text{H}$  or 34) in which the cadmium is in a tetrahedral  $S_4$  environment have been described [174]. The complexes  $[\text{CdL}_2\text{Cl}_2]$  ( $\text{L} = \text{H}_2\text{NCS}_2\text{Me}$ ) [175] and  $[\text{ZnL}_2]$  ( $\text{HL} = 35$ ) [176], the latter compound incorporating a paramagnetic ligand, have been prepared.



(35)

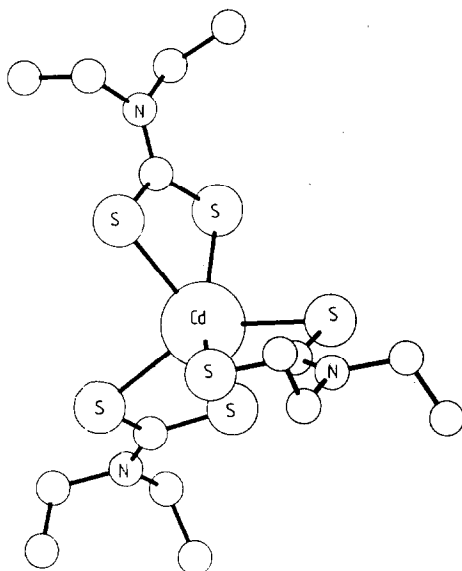


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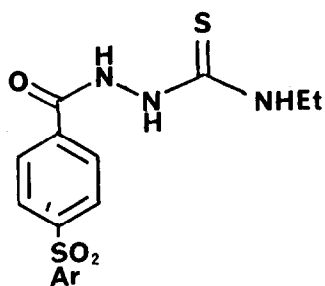
(37)

Complexes of  $O,O'$ -diethylphosphonyldithiocarbamate with zinc and cadmium have also been reported [177].

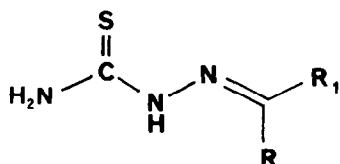



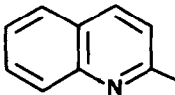
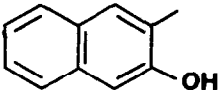
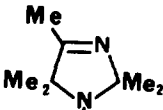
(33)

A crystal structural analysis of the complex  $[ \{ 2\text{CdCl}_2 \cdot \text{L} \}_n ]$  has been described ( $\text{L} = \text{Bu}_2\text{NSCCH}_2\text{O}(\text{CH}_2)_2\text{OCH}_2\text{CSNBu}_2$ ), and the metal shown to exist in two separate environments, one trigonal bipyramidal and one octahedral [179]. In the thioamide complexes  $[\text{ML}_2\text{X}_2]$  ( $\text{M} = \text{Zn}$  or  $\text{Cd}$ ;  $\text{L} = 36$ ;  $\text{X} = \text{Cl}$  or  $\text{Br}$ ) the ligand is thought, on the basis of multinuclear NMR studies, to act as a monodentate donor through the ring nitrogen atom [180]. The complex  $[\text{ZnL}_2(\text{OAc})_2]$  ( $\text{L} = \text{H}_2\text{NCSNH}_2$ ) has been characterised as a component of the  $\text{Zn}(\text{OAc})_2 \cdot \text{L} \cdot \text{H}_2\text{O}$  system [181]; related complexes of *N*-phenyl-*N'*-(4-bromophenyl)thiourea  $[\text{ML}_2\text{X}_2]$  ( $\text{M} = \text{Cd}$  or  $\text{Zn}$ ;  $\text{X} = \text{Cl}$ ,  $\text{NCS}$  or  $\text{OAc}$ ) and  $[\text{ML}_4\text{X}_2]$  ( $\text{M} = \text{Zn}$  or  $\text{Cd}$ ;  $\text{X} = \text{Cl}$ ,  $\text{NCS}$  or  $\text{NO}_3$ ), have also been prepared [182]. A tetrahedral chloro-bridged complex  $[\text{L}_2(\text{Cl})\text{Cd}(\mu\text{-Cl})_2\text{CdL}_2(\text{Cl})]$  ( $\text{L} = \text{N}$ -phenyl-*N'*-(4-bromophenyl)thiourea) is also known [182]. The thiohydrazide compounds,  $[\text{ML}_2] \cdot n\text{H}_2\text{O}$  ( $\text{M} = \text{Zn}$  or  $\text{Cd}$ ;  $\text{HL} = 37$ ;  $n = 1$  or  $2$ ) and  $[\text{M}(\text{HL})_2\text{Cl}_2]$  ( $\text{M} = \text{Cd}$ ;  $\text{HL} = 37$ ) have been reported [183], as have  $[\text{ZnL}_2\text{Cl}_2]$  ( $\text{L} = \text{H}_2\text{NNHCSNH}_2$ ) [184] and  $[\text{CdL}(\text{H}_2\text{O})_2]$  ( $\text{H}_2\text{L} = 38$ ) [185]. Complexes of thiosemicarbazones continue to attract attention, and the compounds  $[\text{M}(\text{HL})_2\text{X}_2]$  ( $\text{M} = \text{Zn}$  or  $\text{Cd}$ ;  $\text{HL} = 39$ ;  $\text{X} = \text{Cl}$  or  $\text{NO}_3$ ) [186],  $[\text{ML}_2]$  ( $\text{M} = \text{Zn}$  or  $\text{Cd}$ ;  $\text{HL} = 40$  [187];  $\text{HL} = 41$  [188]) and  $[\text{MLL}']$  ( $\text{M} = \text{Zn}$  or  $\text{Cd}$ ;  $\text{H}_2\text{L} = 42$ ;  $\text{L}' = \text{H}_2\text{O}$  or  $\text{NH}_3$ ) [189] have been described. In most cases the ligands act as bidentate *NS* donors. The novel paramagnetic imidazoline oxyl complexes  $[\text{ML}_2]$  ( $\text{M} = \text{Zn}$  or  $\text{Cd}$ ;  $\text{HL} = 43$ ) exhibit an unusual electron exchange phenomenon between the two ligands [190]. Dithiobiuret may act as a monodentate *S* donor

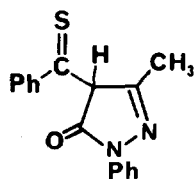


(38)



	R	R <sub>1</sub>
39;	Ph	Me
40;		H
41;		H
42;		H
43;		H

in  $[\text{ZnL}_2\text{X}_2]$  ( $\text{L} = \text{H}_2\text{NCSNHCSNH}_2$ ;  $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ) or as a bidentate  $SS'$  donor in  $[\text{ZnL}_2]\text{X}_2$  ( $\text{L} = \text{H}_2\text{NCSNHCSNH}_2$ ;  $\text{X}_2 = (\text{NO}_3)_2, (\text{ClO}_4)_2$  or  $\text{SO}_4$ ) [191]. The use of the thiourea derivative  $\text{PhNHCSNHCSPh}$  in the extraction of zinc and cadmium is limited by the competing hydrolysis of the ligand [192]. A large number of monothio 1,3-dicarbonyl derivatives have been investigated as ligands, and a range of  $[\text{ZnL}_2]$  ( $\text{HL} = \text{RCSCH}_2\text{COR}'$ ) complexes have been described [193-196]. The thioketone (44) has been used in the extraction of zinc as a synergistic complexone in the presence of other ligands such as pyridine, 4-methylpyridine quinoline, trioctylphosphine oxide, tributyl phosphate, 2,2'-bipyridine or 1,10-phenanthroline) [197].

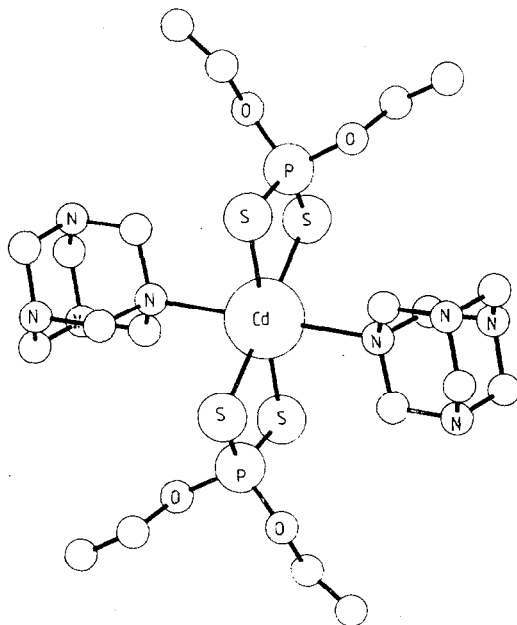


(44)

### 1.1.3.3 Phosphine sulphides and selenides

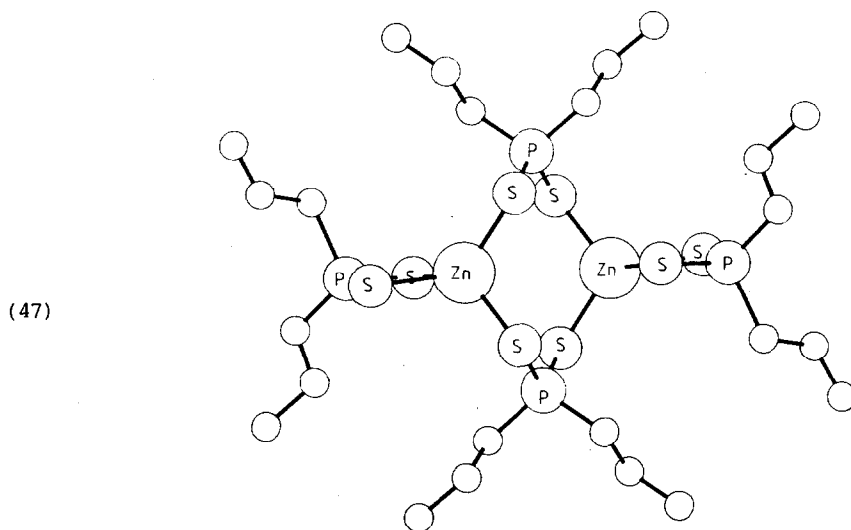
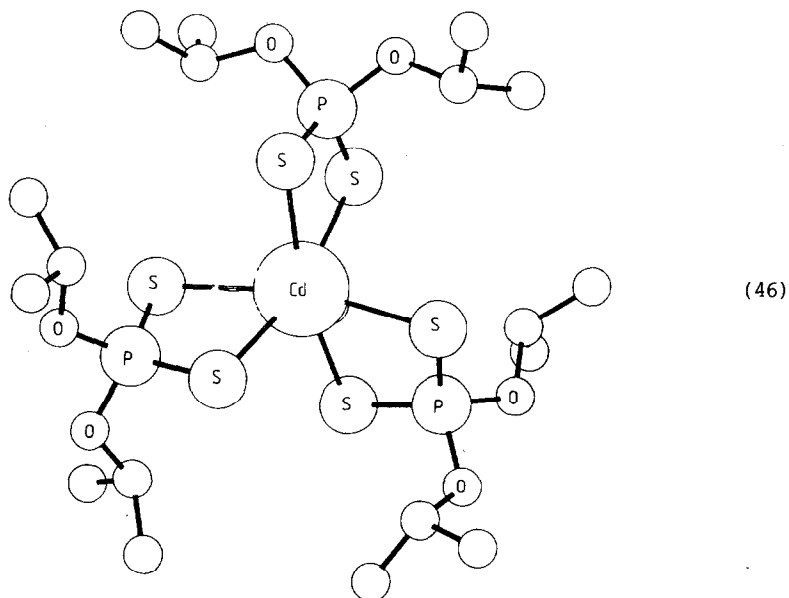
A cadmium complex of the potentially terdentate ligand  $(\text{Ph}_2\text{P}(\text{S}))_3\text{CH}$  has been reported, although the structure is not known in any detail [198].  $^{113}\text{Cd}$  NMR studies on a range of  $^{113}\text{Cd}$  enriched phosphine sulphide and selenide compounds have been reported [111].

Complexes of dithiophosphate ligands continue to attract attention, and a number of structural studies have appeared this year. In  $[\text{CdL}_2(\text{L}')_2]$  ( $\text{HL} = (\text{EtO})_2\text{PS}_2\text{H}$ ;  $\text{L}' = \text{hexamethylenetetramine}$ ) (45) the metal is in a distorted octahedral  $S_4N_2$  environment [199], whereas in  $[\text{NMe}_4][\text{CdL}_3]$  ( $\text{HL} = (\text{i-PrO})_2\text{PS}_2\text{H}$ ) the metal is in a geometry intermediate between octahedral and trigonal prismatic (46) [173]. The crystal structure of bis(di-*n*-propyldithiophosphinato)



(45)

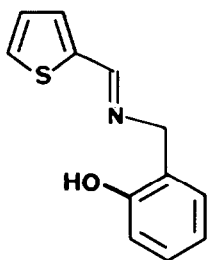
zinc(II) has also been reported, and the compound shown to exist as discrete dimers in the solid state (47) [200].



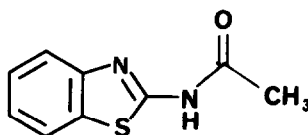
The complexes  $[ML_4][ClO_4]_2$  ( $M = Cd$  or  $Zn$ ;  $L = (EtO)_3PS$ ) have been reported; the ligands are exclusively *S*-bonded to the metal (*c.f.* Mercury in this volume) [201]. A multinuclear NMR investigation ( $^{31}P$  and  $^{113}Cd$ ) of cadmium dithiophosphate complexes has been described [202].

#### 1.1.3.4 Sulphur and selenium heterocycles

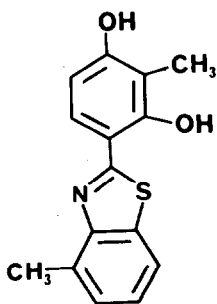
The complex  $[ZnL_2]$  (HL = 48) has been shown to exist with the ligand in the illustrated tautomer, rather than as its double bond isomer, with the imine bond towards the benzene ring [203]. Other complexes which have been described include  $[ML_2]$  (M = Zn or Cd; HL = 2-(2-hydroxyphenyl)benzothiazole) [204] and  $[ML_2Cl_2]$  (M = Zn or Cd; L = 49) [205], the latter ligand acting as a bidentate *NO* donor. Compounds with thiamine orthophosphate and thiamine pyrophosphate [206], 4-(4'-methyl-2'-thiazolylazo)-2-methylresorcinol (50) [207] and 2-alkylamino-1,3,4-thiadiazoles [208] have also been reported. The use of the benzothiazole derivative (51) as an extractant for Group IIB metals has been described [209].



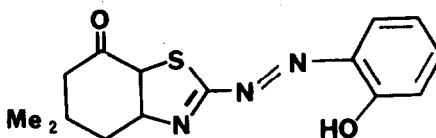
(48)



(49)



(50)



(51)

#### 1.1.4 Complexes with nitrogen donor ligands

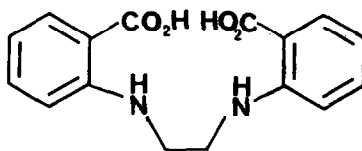
##### 1.1.4.1 Amines

A crystal structural analysis of  $[\text{Zn}(\text{NH}_3)_4]\text{I}_2$  has been reported; the near-tetrahedral cation closely resembles that found in the corresponding triiodide salt reported last year [1], with Zn-N distances in the range 1.997 - 2.030 Å [211]. The complexes  $[\text{M}(\text{NH}_3)_4][\text{ReO}_4]_2$  (M = Zn or Cd) have been described [212,213] and investigated spectroscopically and thermogravimetrically. Thermal decomposition of these salts leads to the novel species  $[\text{M}(\text{NH}_3)_2(\text{ReO}_4)_2]$ , which contain monodentate oxygen-donor perhenate ions. The crystal structure of  $[\text{Zn}(\text{NH}_3)_2\text{Cl}_2]$  shows the metal to be in a near-tetrahedral  $N_2Cl_2$  environment (Zn-N, 2.024 Å, Zn-Cl, 2.273 Å) [214]. A number of aniline derivatives, including  $[\text{MeNH}_3][\text{ZnCl}_3(\text{PhNH}_2)_2]$  [215],  $[\text{Zn}(\text{PhNH}_2)_2\text{X}_2]$  (X = Cl or Br) [33],  $[\text{Cd}(\text{ArNH}_2)_4][\text{ZnX}_4]$  (X = Cl, Br or I) [49] and  $\text{HCdX}_2\text{Br} \cdot 3\text{PhNH}_2$  (X = Cl or I) [216] have been described. Halogen NQR spectra of  $[\text{Zn}(\text{NH}_3)_2\text{X}_2]$  (X = Cl or Br) and a series of related complexes have been reported [33]. Crystal structural analyses of the complexes  $[\text{Zn}(\text{en})_2(\text{NO}_2)]$  and  $[\text{Zn}(\text{tmen})_2(\text{NO}_2)_2]$  have been described, and are discussed earlier in this review (Section 1.1.2) [95]. The reaction of  $[\text{MeNH}_3]_2[\text{ZnCl}_4]$  with ethylenediamine in ethanol gives  $[\text{MeNH}_3]_2[\text{Zn}(\text{en})\text{Cl}_4]$  as a product [215]. Zinc complexes of methacrylate polymer-bound ethylenediamine have also been reported [217], as have complexes with the tetramines  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}(\text{CH}_2)_n\text{NHCH}_2\text{CH}_2\text{NH}_2$  (n = 2, 3 or 4) [218]. Hexamethylene-tetramine is a potentially tetradentate ligand, and a number of groups have investigated the coordination behaviour of this compound [219-222]. A range of complexes with zinc and cadmium have been characterised, including  $[\text{ML}_2\text{X}_2]$  (X = OAc [219] or SCN [220]),  $[\text{ML}(\text{SO}_4)]$  [220] (M = Zn or Cd) and  $3\text{CdI}_2 \cdot 2\text{L} \cdot 4\text{H}_2\text{O}$  [222], in which the amine acts as a terminal monodentate or bridging bidentate ligand. A structural analysis of  $3\text{CdI}_2 \cdot 2\text{L} \cdot 4\text{H}_2\text{O}$  has shown the compound to consist of  $\text{Cd}_3\text{I}_x$  clusters bridged by the ligand [222]. Zinc complexes with a range of ligands  $\text{RCH}_2\text{NH}(\text{CH}_2)_n\text{NH}(\text{CH}_2)_n\text{NHCH}_2\text{R}$  (R = heteroaryl; n = 2 or 3) have been described [223], as have the compounds  $[\text{ML}_2\text{X}_2]$  and  $[\text{ZnLCI}_2]$  (M = Zn or Cd; X = halide or pseudohalide; L = MeNH<sub>2</sub>OH or MeONH<sub>2</sub>) [224] and  $[\text{M}(\text{N}_2\text{H}_4)_3(\text{NO}_3)_2]$  (M = Zn or Cd),  $[\text{Cd}(\text{N}_2\text{H}_4)_2(\text{NO}_3)_2]$  and  $[\text{Zn}(\text{N}_2\text{H}_4)_2(\text{N}_3)_2]$  [225], which are of interest as primary explosives.

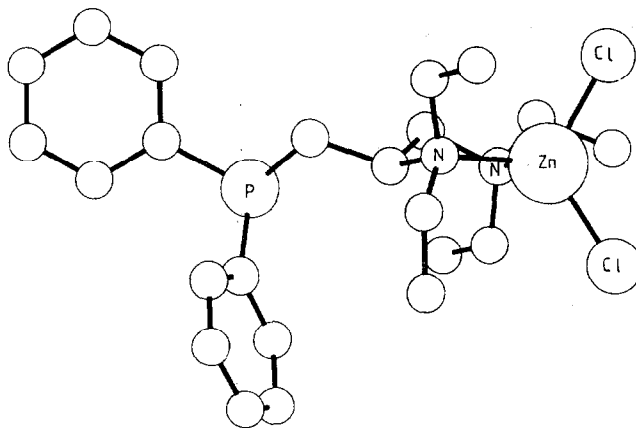
Clathrate complexes of the type  $\{[\text{CdL}_n][\text{Ni}(\text{CN})_4] \cdot \text{G}\}$  (L =  $\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$ ; n = 1 or 2; G = benzene, thiophen or pyrrole) have been prepared [226] and structurally characterised [227]. The use of amino alcohols as ligands has been investigated, and complexes with  $(\text{H}_2\text{NCH}_2)_2\text{CHOH}$  [228],  $(\text{HOCH}_2)_3\text{CHNH}_2$  [229],  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{OH}$  [230] and  $(\text{HOCH}_2\text{CH}_2)_3\text{N}$  [231] with zinc and cadmium have



been reported. The zinc complex of  $(\text{HOCH}_2)_3\text{CNH}_2$  (Tris) is a most effective catalyst for the hydrolysis and aminolysis of benzylpenicillin [229], and it is suggested that this observation may be of some relevance to the mode of action of zinc-dependent  $\beta$ -lactamases. Zinc complexes of amino substituted ethers and thioethers [154] and the aminocarboxyboranes  $\text{R}_3\text{N} \cdot \text{BH}_2\text{CO}_2\text{H}$  [232] have also been described. The tetrahedral complexes  $[\text{ML}]$  ( $\text{H}_2\text{L} = 52$ ) have been investigated [233,234]. A structural analysis of  $[\text{ZnLCl}_2]$  (53) ( $\text{L} = \text{Et}_2\text{NCH}_2\text{CH}_2(\text{NEt}_2)\text{CH}_2\text{PPh}_2$ ) has shown the metal to be in a distorted  $\text{N}_2\text{Cl}_2$  environment, with a pendant non-coordinated phosphine [235].



(52)

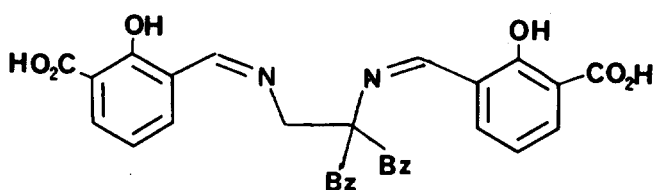


(53)

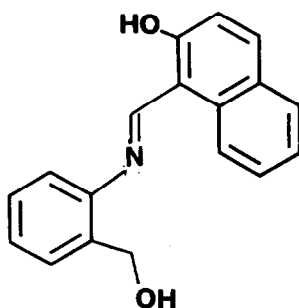
#### 1.1.4.2 Schiff bases, hydrazones and oximes

The Schiff bases formed in the condensation of amines with salicylaldehyde form a widely investigated group of anionic  $\text{N},\text{O}$ -donors, and a number of Group IIB complexes of these ligands have been described. Zinc complexes with the imines derived from the condensation of salicylaldehyde with amino acids [236] sulfa drugs (sulfofurazole, sulfaphenazole or sulfamethoxypyridazine) [237]

or aminoarenes [238] have been investigated. Related ligands have been prepared by the condensation of 2-hydroxyacetophenone with sulfa drugs [237], 3-carboxysalicylaldehyde with 1,1-dibenzylethylenediamine (54) [239] or 2-hydroxynaphthaldehyde with 2-aminobenzylalcohol (55) [240], and all have been shown to form zinc complexes. The imines derived from the condensation



(54)

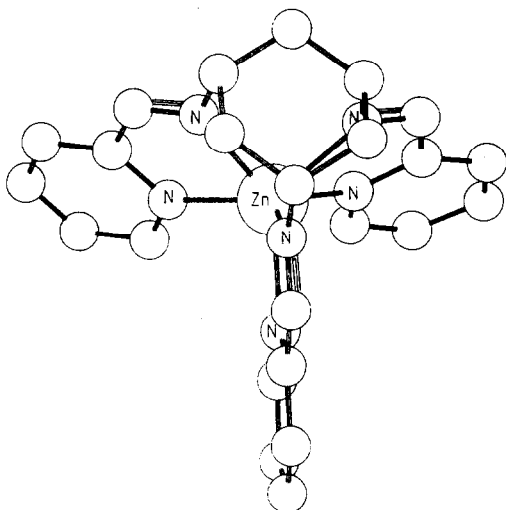


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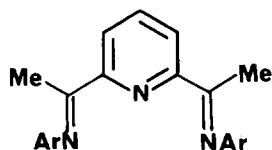
of pyruvic acid with amino acids act as *O,N,O'* donors, and form zinc complexes in which the imine nitrogen and two carboxylate oxygen atoms are coordinated to the metal. The interconversion of the isomers of cadmium complexes of the imines  $RC(S)CHR'CH=NR(i-Pr)$  has been followed by  $^1H$  NMR over the temperature range  $-50 - +60^\circ C$  [241]. A crystal structural analysis of the zinc complex of the imine derived from 2-pyridinealdehyde and *cis,cis,cis* -1,3,5-triamino-cyclohexane shows the metal to be in a trigonal prismatic environment ( $Zn-N(\text{pyridine})$ , 2.211-2.282 Å;  $Zn-N(\text{imine})$ , 2.142-2.167 Å) (56) [242].

Zinc and cadmium nitrate complexes of the 2,6-diacetylpyridine derivatives (57) have been prepared, and reveal a variety of nitrate bonding modes [243]. The template condensation of ethylenediamine or phenylenediamine with 2,6-diformylpyridine might be expected to give 2+2  $N_6$  - donor macrocycles, but with a range of metals, only open-chain complexes were obtained; a crystal structure of the product obtained from the reaction with phenylenediamine in

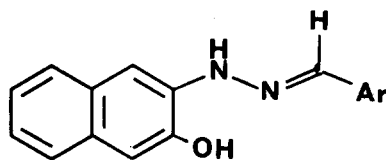
the presence of a cadmium template reveals that a 2 + 1 bisimino ligand is formed, which acts as the basal  $N_5$ -donor set in a pentagonal bipyramidal complex in which a monodentate phenylenediamine group occupies the axial position (58) [244].



(56)



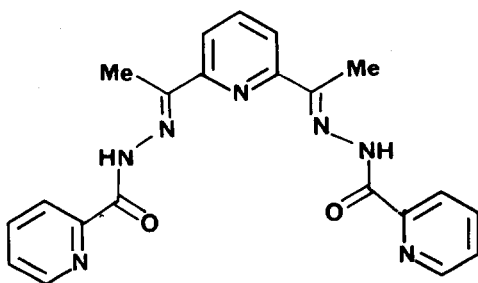
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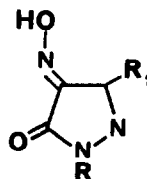
(59)

A number of complexes of  $\alpha, \alpha'$ -diimines (1,4-diaza-1,3-butadienes) with zinc and cadmium have been reported [245,246].

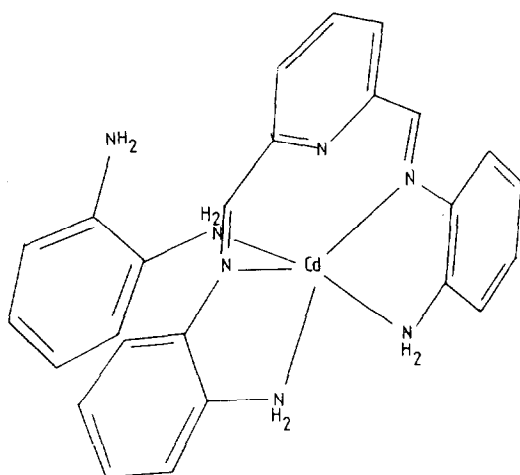
The complexes  $[ZnL_2]$  (HL = 59) [247] and  $[ZnLCl_2]$  (L = 60) [248] are thought to possess tetrahedral  $N_2O_4$  and pentagonal bipyramidal  $N_3O_2X_2$  coordination geometries respectively. Zinc complexes of a series of Schiff bases formed



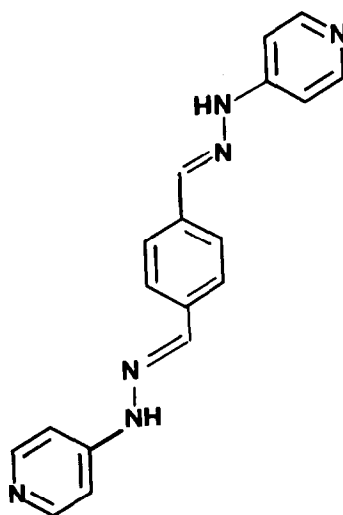
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(62)



(58)



(61)

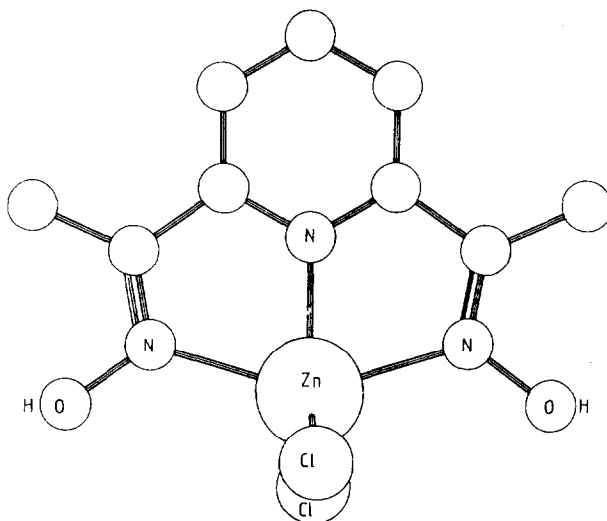
from the condensation of 3-hydroxy-2-naphthoic acid hydrazide with 1,3-dicarbonyls have been prepared [249].

The hydrazones of 1,2-dicarbonyl compounds have recently been investigated, and zinc or cadmium complexes of  $\text{PhCOC(Ph)=NNHPh}$  [250] and  $\text{MeC(=NNMe}_2\text{)C(Me)=NNMe}_2$  [251,252] have been described. The complexes  $\text{MLX}_2 \cdot x\text{H}_2\text{O}$  ( $\text{L} = 61$ ;  $\text{M} = \text{Zn}$  or  $\text{Cd}$ ) are polymeric [253].

A series of octahedral complexes  $[\text{ZnL}_2(\text{L}'_2)]$  ( $\text{HL} = 1,3$ -disubstituted 4-oximino-2-pyrazolin-5-one (62);  $\text{L}' = \text{pyridine}$  or 3-methylpyridine) have been prepared [254,255], as have the tetrahedral complex  $[\text{ZnL}(\text{Cl})(\text{H}_2\text{O})]$  ( $\text{HL} = 2$ -hydroxy-3-methoxybenzaldehyde) [256]. Benzil monoxime,  $\text{PhCOC(=NOH)Ph}$ , forms zinc and cadmium complexes [257], as does *N*-2'-diphenylacetohydroxamic acid [258]. A crystal structure of the complex  $[\text{ZnLCl}_2] \cdot \text{H}_2\text{O}$  ( $\text{L} = 2,6$ -diacetylpyridine dioxime) has shown the metal to be in a distorted trigonal bipyramidal  $\text{N}_3\text{Cl}_2$  environment ( $\text{Zn-Cl}$ , 2.233, 2.244 Å;  $\text{Zn-N(pyridine)}$ , 2.063 Å;  $\text{Zn-N(oxime)}$ , 2.238, 2.246 Å) [259]. The extraction of zinc by salicylaldehyde oximes has been studied [260].

#### 1.1.4.3 Amides, imides and hydrazides

A number of 'simple' amide complexes have been reported, including the compounds  $[\text{CdL}(\text{OAc})_2]$  ( $\text{L} = \text{EtCONH}_2$ ) [261] and  $[\text{ZnL}_2]$  ( $\text{HL} = \text{salicylamide}$ ) [262]. 12-Laurolactam forms *O*-donor complexes  $[\text{ZnL}_6][\text{BF}_4]_2$ , which decompose to  $\text{MF}_2$ ,  $\text{BF}_3$  and 12-laurolactam upon thermolysis [263]. Complexes with urea [264]



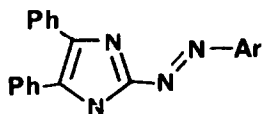
and its derivatives continue to be of interest, and the interaction of zinc perchlorate with urea [264] and dimethylurea [265] has been investigated. Complexes with biuret,  $\text{H}_2\text{NCONHCONH}_2$  [266], cyclic urethanes [267], cyclic amidines [268] and azodicarbonamide [269] have been described. The reaction of  $[\text{Ph}_4\text{P}]_2[\text{ZnBr}_4]$  with  $[\text{Ph}_4\text{As}][\text{NSOF}_2]$  or  $\text{Ag}[\text{NSOF}_2]$  results in the formation of  $[\text{Ph}_4\text{P}]_2[\text{Zn}(\text{NSOF}_2)_4]$  [270]. The polymeric cyanamide complex  $[\text{Cd}(\text{CN}_2)]$  is formed in the reaction of cadmium chloride with aqueous ammonia and diazomethane [271].

A large number of hydrazide complexes are known, and the interaction of a range of ligands of the type  $\text{RCONHNH}_2$  with zinc and cadmium has been investigated. The hydrazide ligands are thought to act as bidentate *N,O*-donors in the complexes  $[\text{CdL}_2(\text{SCN})_2]$  and  $[\text{CdL}_2][\text{NO}_3]_2$  ( $\text{L} = \text{RCONHNH}_2$ ;  $\text{R} = \text{Et}$ , *n*-Pr, *n*-C<sub>5</sub>H<sub>11</sub> or *n*-C<sub>7</sub>H<sub>15</sub>) [272], but as monodentate *N*-donors in  $[\text{ML}_n\text{Cl}_2]$  ( $\text{M} = \text{i-PrCH}_2\text{CONHNH}_2$ ;  $\text{M} = \text{Zn}$  or  $\text{Cd}$ ;  $n = 1$  or  $2$ ) [273]. The latter ligand is thought to coordinate to the metal in the iminol form  $\text{i-PrCH}_2\text{C}(\text{OH})=\text{NNH}_2$  [273]. Other complexes which have been described include  $\text{CdL}_3(\text{SO}_4)$ ,  $\text{CdL}_3\text{Cl}_2 \cdot \text{H}_2\text{O}$  ( $\text{L} = \text{C}_6\text{H}_{13}\text{CONHNH}_2$ ) [274] and  $\text{ZnL}_3(\text{S}_2\text{O}_6)$  ( $\text{L} = \text{PhCONHNH}_2$ ) [275]. The crystal structure of  $[\text{CdL}_2(\text{NCS})(\text{SCN})]$  ( $\text{L} = \text{PhCONHNH}_2$ ) shows the metal to be in a distorted octahedral environment, with the hydrazide acting as a bidentate *N,O*-donor, and one *N*-bonded and one *S*-bonded thiocyanate ligand [276]. 2:1 complexes of zinc and cadmium with cyanoacetyl hydrazide,  $\text{NCCH}_2\text{CONHNH}_2$ , in both its neutral and deprotonated forms have been described [277].

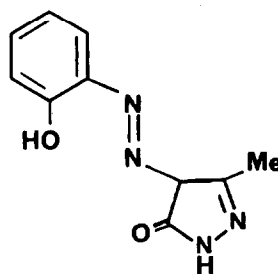
The thermal stability of the complexes  $(HL)_2ZnCl_4$  and  $(HL)_3Zn_4Cl_{11}$  ( $L$  = semicarbazide,  $H_2NCONHNH_2$ ) has been investigated [278]. The related ligand, carbohydrazide,  $H_2NNHCONHNH_2$ , forms 2:1 and 3:1 complexes with group IIB metals [279,280]. The formation of zinc and cadmium complexes of a series of dihydrazides  $(H_2NNHCO)_2(CH_2)_n$  has been investigated [281]. A number of complexes incorporating saccharin have been described, including  $[ZnL_2(H_2O)_4]$  ( $HL$  = saccharin) [374,376], in which the ligand is thought to act as a monodentate  $N$ -donor.

#### 1.1.4.4 Azo compounds

The 2-azoimidazoles (64) form complexes  $[CdL_2(NO_3)] [NO_3]$ ,  $[ZnLCl]Cl$  and  $[ZnL_2Cl]Cl$  ( $L$  = 64) [282]. Zinc complexes of the pyrazole derivative (65) [283]



(64)

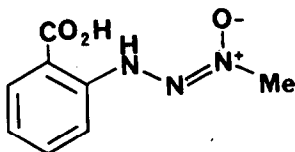


(65)

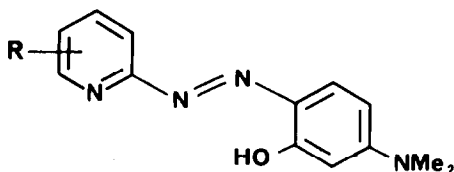
and the polymeric Schiff base from phenylenediamine and 2-formyl-4-hydroxyphenyl-azobiphenyl(sulphone),  $(ArN=NC_6H_4)_2SO_2$  [284] have been reported. The complexes  $[ \{ ML \} ]_n$  and  $[ \{ ML(phen) \} ]_n$  ( $M$  = Zn or Cd;  $L$  = 66) are all polymeric, with the triazene 1-oxide acting as a bridging bidentate  $O_2$ -donor [285]. The extraction of zinc by chloroform solutions of the azocompounds (67) has been studied [286].

#### 1.1.4.5 Amino acids

The interaction of zinc and cadmium with naturally occurring amino acids is intensively studied, and provides a model for the metal ion-peptide interactions which may occur in metalloenzymes. Complexes of zinc with histidine [287-289, 291], threonine [288], tyrosine [290], glutamic acid [292], DL-nor-leucine [293], aspartic acid [294] and tryptophan [295] have been described.



(66)



(67)

Circular dichroism studies of the  $[\text{ZnL}_n(\text{phen})_2]^{(2-n)+}$  (HL = chiral amino acid) systems have been reported [296].

Cadmium complexes with glycine [297,300], histidine [297], alanine [298,301], DL-nor-leucine [293], valine [299] and numerous other amino acids [302,303] have been reported. A study of the interaction of dipeptides with cadmium ions has also been described [304].

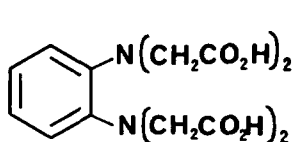
Zinc and cadmium complexes with the synthetic amino acid DL- $(\text{HO}_2\text{C})_2\text{CHNHCH}_2\text{-CH}(\text{CO}_2\text{H})\text{NHCH}(\text{CO}_2\text{H})_2$  have been prepared [305]. A crystal structure of the complex  $[\text{CdL}_2(\text{H}_2\text{O})_3]$  (HL = 4-aminobenzoic acid) has been reported; the metal is in a seven-coordinate  $N_2O_5$  environment, with the ligand acting as a bridge to form a polymeric one-dimensional structure [306].

#### 1.1.4.6 Iminodiacetic acid complexes

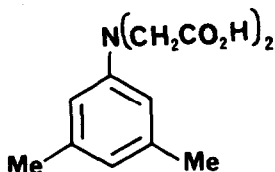
Iminodiacetic acids or complexones continue to be the study of numerous complexation studies, and new examples of this class of ligand are described each year. An ultrasonic study of the zinc and cadmium complexes of  $\text{H}_4\text{edta}$  has demonstrated a dynamic equilibrium in solution interconverting the pentadentate and hexadentate forms in solution [307]. A number of ternary zinc with  $\text{H}_4\text{edta}$  and glutamic acid have been reported [308], as has a kinetic study of the ligand substitution reaction:



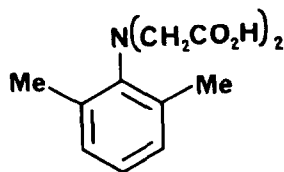
(L =  $(\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2)_2\text{NH}$ ) [309]. The phosphorus analogue of  $\text{H}_4\text{edta}$ ,  $(\text{HO}_2\text{CCH}_2)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_2\text{CO}_2\text{H})_2$ , has been shown to form zinc and cadmium complexes resembling those of  $\text{H}_4\text{edta}$  itself [310]. Related ligands which have been investigated include (68) [311],  $(\text{HO}_2\text{CCH}_2)\text{NCH}_2\text{CH}(\text{CO}_2\text{H})\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$  [312],



(68)

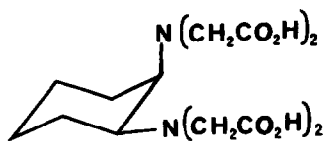


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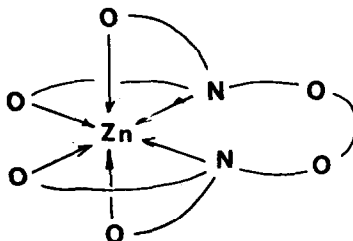


(70)

(69) [313], (70) [313], ethylenediaminedisuccinic acid [314],  $((\text{HO}_2\text{CCH}_2)_2\text{NCH}_2\text{CH}_2)_2\text{NCH}_2\text{CO}_2\text{H}$  [315],  $((\text{HO}_2\text{CCH}_2)_2\text{NCH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{OCH}=\text{CH}_2$  [316] and  $(\text{HO}_2\text{CCH}_2)_3\text{N}$  [317]. The cadmium complex of *cis*-1,2-cyclohexanediaminetetracetic acid (71) has been investigated by NMR methods; the complex is octahedral, and there is no evidence for the penetration of water into the inner coordination sphere of the metal [318]. An NMR study of the zinc complex of the ligand  $((\text{HO}_2\text{CCH}_2)_2\text{NHCH}_2\text{CH}_2\text{OCH}_2)_2$  has shown that the ether oxygen atoms are not coordinated to the metal, *i.e.* the configuration (72) is adopted [319].



(71)

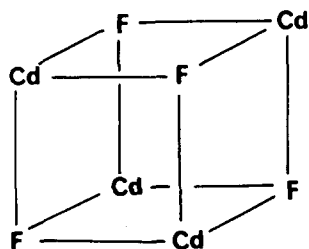


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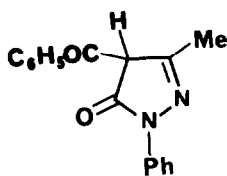
#### 1.1.4.7 Nitrogen heterocycles

The reaction of 5-methylpyrazole with cadmium tetrafluoroborate gives a complex which is formulated as the tetrameric species  $[\text{Cd}_4\text{F}_4\text{L}_{12}][\text{BF}_4]_4$  [320]. It is thought that the fluoride ion is generated by the (metal-assisted ?) hydrolysis of tetrafluoroborate, and that a heterocubane cluster core is formed (73). The use of pyrazolones in the extraction of Group IIB metal ions has been studied [321]. In particular, the pyrazolone (74) has been used for the extraction of zinc from aqueous solution [322]. The *N*-acylpyrazoline (75) forms a 1:1 complex with zinc, which is thought to be dimeric, but which is readily cleaved to the mononuclear complex  $[\text{ZnL}(\text{NH}_3)]$  on treatment with

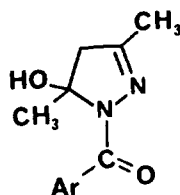




(73)



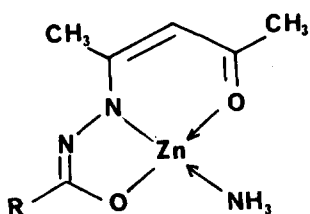
(74)



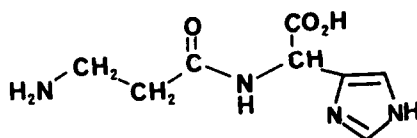
(75)

ammonia [323]. It is proposed that  $[\text{ZnL}(\text{NH}_3)]$  has the structure indicated in (76) [323].

Imidazole complexes are widely studied as models for zinc containing enzymes, and the complexes  $[\text{ZnL}_n]$  ( $n = 1-4$ ) have been characterised in aqueous solution [289]. A number of ternary complexes with imidazole and carboxylate ligands have been studied [324-329], and, in particular, the  $\text{Cd}^{2+}$ -Himid-malonate [328] and  $\text{Cd}^{2+}$ -Himid-succinate [329] systems have been well-characterised. Crystal structural analyses of the complexes  $[\text{Zn}(\text{O}_2\text{CCH}_3)_2(\text{Himid})_2]$  and  $[\text{Zn}(\text{O}_2\text{CCH}_2\text{CH}_3)_2(\text{Himid})_2]$  have been reported; in each case the metal is in a near-tetrahedral  $N_2O_2$  environment with monodentate carboxylate groups bonded to the metal (Zn-N, 1.987-2.010 Å; Zn-O, 1.947-1.987 Å; Zn-O(non-bonded), > 2.645 Å) [235]. These results are comparable to those obtained from the

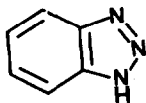


(76)

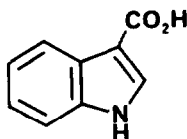


(77)

structural analysis of  $[\text{Zn}(\text{OAc})_2\text{L}_2]$  ( $\text{L} = N$ -ethylimidazole) which has also been reported this year (Zn-N, 2.031, 2.010 Å; Zn-O, 1.944, 1.976 Å; Zn-O(non-bonded) 2.850, 2.862 Å) [326]. The formation of zinc complexes of L-carnosine (77) has been reported [327]. The  $N$ -vinylimidazole complexes  $[\text{ZnL}_4]\text{X}_2$  ( $\text{X} = \text{NO}_3$ ,  $\text{BF}_4$  or  $\text{ClO}_4$ ) are tetrahedral, whereas  $[\text{CdL}_6]\text{X}_2$  are octahedral; the complex  $[\text{CdL}_3(\text{NO}_3)_2]$  has also been described [330]. A series of zinc and cadmium

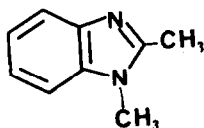


(78)



(79)

complexes of *N*-ethyl and *N*-propylimidazole have been described; the 1:1 complexes  $[ML_2X_2]$  ( $M = \text{Zn or Cd}$ ;  $L = N\text{-alkylimidazole}$ ;  $X = \text{halide}$ ) are monomeric tetrahedral species, whereas  $[MLX_2]_2$  ( $M = \text{Zn or Cd}$ ;  $L = N\text{-alkylimidazole}$ ;  $X = \text{halide}$ ) are halide-bridged dimers [321]. Crystal structures of the benzotriazole complexes  $[Zn(HL)Cl_2]$  and  $[Zn_2L_4]$  ( $HL = \text{benzotriazole (78)}$ ) have been reported; the former compound has the metal in a tetrahedral  $N_2Cl_2$  environment ( $Zn-N$ , 2.014, 2.034 Å;  $Zn-Cl$ , 2.241, 2.235 Å) and the latter is a polymeric species [332]. The complex  $[H_2L]_2[ZnCl_4]$  ( $HL = 78$ ) has also been described; it is isostructural with the tetrachlorocobaltate(II) analogue, which has previously been structurally characterised [332]. The synthesis and powder diffraction pattern for  $[ZnL_2Cl_2]$  ( $L = 78$ ) has also been reported [333]. Complexes of 3-indoleacetic acid (79) and 1,2-dimethylbenzimidazole (80) have been described [334,335].



(80)

The tetrahedral complexes  $[MX_2L_2]$  ( $M = \text{Zn or Cd}$ ;  $L = \text{pyridine or substituted pyridine}$ ;  $X = \text{halide}$ ) have been studied by halogen NQR and  $^{13}\text{C}$  NMR methods [336].

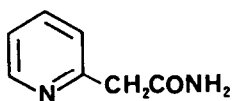
The perrhenate complexes  $[M(\text{py})_4][\text{ReO}_4]_2$  and  $[M(\text{py})_2(\text{ReO}_4)_2]$  ( $M = \text{Zn or Cd}$ ) closely resemble the corresponding ammine complexes discussed earlier [212]. Group IIB complexes of pyridine, 4-methylpyridine, 3,4-dimethylpyridine and 3,5-dimethylpyridine have been described [337,338]; the two latter ligands have been investigated as potential extractants for zinc and cadmium.

The complexes  $[ML(\text{SCN})_2]$  ( $M = \text{Zn or Cd}$ ;  $L = \text{bipy or phen}$ ) [339],  $[ML(\text{OAc})_2]$

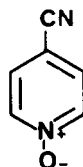
and  $[M(\text{bipy})_2(\text{OAc})_2]$  ( $M = \text{Zn}$  or  $\text{Cd}$ ;  $L = 4,4'$ -bipyridine) have been reported [340]. A combined crystallographic and  $^{113}\text{Cd}$  NMR study of the complex

$\text{Cd}(\text{bipy})_2(\text{NO}_3)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$  in the solid state and in solution has been described; the crystal structure reveals two crystallographically and chemically distinct octahedral environments for the metal. In one case, the metal has two monodentate  $O$ -donor nitrate ions coordinated ( $\text{Cd}-\text{N}$ , 2.33–2.43 Å;  $\text{Cd}-\text{O}$ , 2.41–2.435 Å), and in the other it is coordinated to one monodentate nitrate ion and to one water molecule ( $\text{Cd}-\text{N}$ , 2.34–2.39 Å;  $\text{Cd}-\text{ONO}_2$ , 2.43 Å;  $\text{Cd}-\text{OH}_2$ , 2.246 Å). The solid state  $^{113}\text{Cd}$  NMR investigations also indicated the presence of two metal sites [341].

The involvement of zinc in nicotinamide based hydride transfer reactions has led to numerous studies of Group IIB complexes of pyridine carboxylic acid derivatives. Cadmium complexes of 2-pyridinecarboxylic acid [342], 3-pyridinecarboxylic acid [343] and 3-pyridinecarboxamide [344] have been reported. The crystal structure of  $[\text{Cd}(\text{HCO}_2)_2\text{L}_2(\text{H}_2\text{O})_2]$  ( $L = 3$ -pyridinecarboxamide) has been described; the metal is in an octahedral environment, in which the amide acts as a monodentate  $N$ -donor [344]. Mixed ligand complexes  $[\text{Zn}(\text{acac})_2\text{L}]$  ( $L = 2$ -, 3- or 4-pyridinecarboxamide) [345], and a series of complexes with 3-substituted pyridines have been prepared [346]. The crystal structure of  $[\text{ZnL}_2(\text{H}_2\text{O})_2][\text{NO}_3]_2$  ( $L = 81$ ) shows the metal to be in an octahedral environment, with bidentate 2-pyridylacetamide ligands bonded through the ring nitrogen and amide oxygen atoms, and the water molecules occupying the axial sites [347]. The complex  $[\text{ZnL}_2(\text{NCS})_2]$  ( $L = 82$ ) is a monomeric tetrahedral  $O_2N_2$  complex, whereas the cadmium analogue is a dimer with bridging thiocyanate ligands [348].



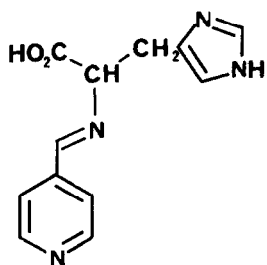
(81)



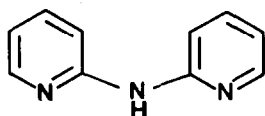
(82)

The Schiff base formed in the condensation of histidine with pyridoxal has the structure (83) and has been shown to form a range of zinc complexes [291]. The complex  $[\text{ZnL}_3]\text{Cl}_2 \cdot \text{EtOH}$  ( $L = 84$ ) forms a two-dimensional network, held together by  $-\text{NH} \dots \text{Cl}$  hydrogen bonding, and with bidentate  $N_2$ -donor ligands ( $\text{Zn}-\text{N}(\text{average})$ , 2.179 Å) [349].

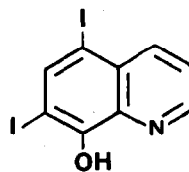
Complexes of 8-hydroxyquinoline have attracted considerable attention in the past, and methods for the determination of 8-hydroxyquinolinolate stability



(83)

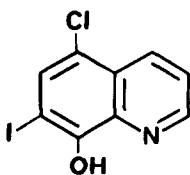


(84)



(85)

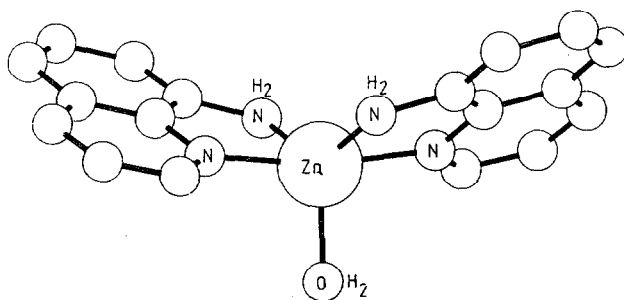
constants have been discussed [350]. The complex  $[\text{Zn}(\text{acac})_2 \cdot \text{L}] \cdot 2\text{H}_2\text{O}$  (HL = 8-hydroxyquinoline) has been reported [351]. Complexes with diodoquin (85) [352], chinoform (86) [353] and the sulphonamides (87) [354] have been described, and evidence presented for a metal-iodine interaction in the 7-iodo substituted compounds in hmpa or dioxane. The crystal structure of  $[\text{ZnL}_2(\text{H}_2\text{O})][\text{ZnCl}_4]$  (L = 8-aminoquinoline) has revealed the metal to be in a trigonal bipyramidal environment (88) [47]. The formation of zinc complexes with 5-amino and 5-nitro substituted 8-quinolinecarboxylic acids has been studied [355]. Zinc forms a 1:2 complex with orotic acid (89) [356,357]. Other complexes which have



(86)

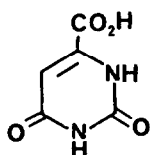


(87)

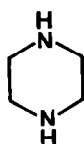


(88)

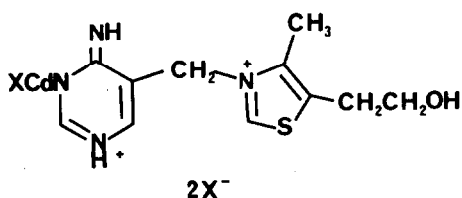
reported include  $[\text{ZnL}_2\text{X}_2]$  ( $\text{L} = 2\text{-aminopyrimidine}$ ;  $\text{X} = \text{Cl}$  or  $\text{Br}$ ) [358],  $[\text{CdLX}_2]$  ( $\text{L} = \text{piperazine}$  (90));  $\text{X} = \text{halide, carboxylate or pseudohalide}$ ) [359],  $[\text{ZnLX}_2]$  and  $[\text{ZnL}(\text{H}_2\text{O})_2]\text{X}_2$  ( $\text{L} = 90$ ) [360] and  $[\text{Cd}(\text{H}_2\text{L})\text{X}]\text{X}_2$  ( $\text{L} = 91$ ;  $\text{X} = \text{Br}$  or  $\text{I}$ ) [361]. A number of complexes with 2,3-pyrazinedicarboxylic acid have been



(89)



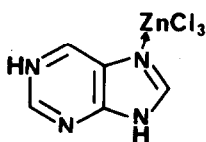
(90)

 $2\text{X}^-$ 

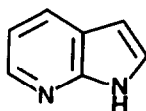
(91)

prepared [362].

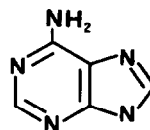
Complexes with nucleotide, nucleoside and related ligands are of interest as models for the *in vivo* interactions with metal ions, and a number of such compounds have been reported. The complex  $[(\text{HL})\text{ZnCl}_3]$  ( $\text{L} = \text{purine}$ ) has been shown to possess the tetrahedral structure (92) ( $\text{Zn-Cl}$ , 2.226–2.254 Å;  $\text{Zn-N}$ , 2.054 Å) [363]. The interaction of 7-azaindole (93) with zinc chloride has



(92)

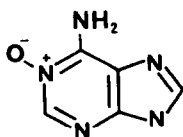


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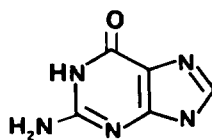


(94)

been investigated, and the products  $[\text{ZnL}_2\text{Cl}_2]$  ( $\text{Zn-Cl}$ , 2.231, 2.212 Å;  $\text{Zn-N}$ , 2.063, 2.038 Å) and  $[\text{LH}]_2[\text{ZnCl}_4]$  have been structurally characterised [363]. A number of zinc and cadmium complexes of adenine (94) [364,365], adenine N-oxide (95) [366], guanine (96) [367], inosine [368], cytidine [369] and other nucleosides [370] have been studied. A structural study of  $[\text{CdCl}_2(\text{dmsO})\text{L}]$



(95)

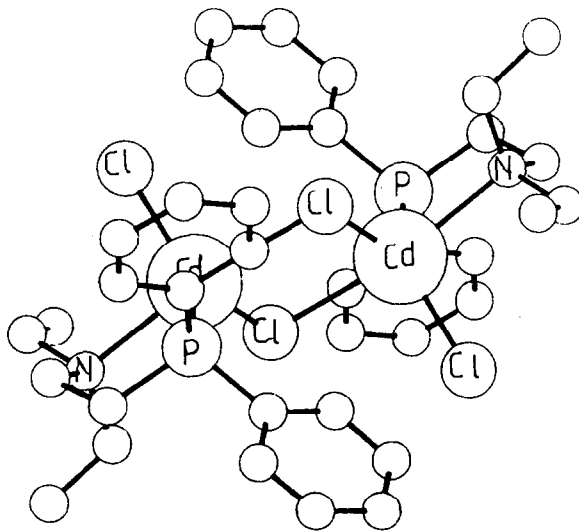


(96)

(L = 9-methyladenine) has shown the complex to form a one-dimensional polymeric network [371].

#### 1.1.5 Complexes with phosphorus donor ligands

The 'simple' complexes formed from the interaction of zinc and cadmium halides with tertiary phosphines continue to prove controversial, and a number of relevant studies have appeared this year. The complexes  $[M_2L_2X_4]$  (M = Zn or Cd; L = P(cych)<sub>3</sub>; X = Cl, Br or I) are readily prepared, and form halo-bridged dimers of  $C_{2h}$  symmetry [377]. In contrast, the previously reported compounds  $[ZnX_2(PR_3)_2]$  have been shown to be  $[ZnX_2(PR_3)OPR_3]$  (R = cych; X = Cl, Br or I) [377]. An intensive  $^{31}P$  and  $^{113}Cd$  NMR study of cadmium tri-n-butyl phosphine and tricyclohexylphosphine complexes has been reported [378]. Cadmium-triphenylphosphine complexes have also been studied in solution by NMR methods [379]. Complexes with  $(HO)_2P(O)CH_2CH_2P(O)(OH)_2$  [380],  $MePhP(O)OH$  [381],  $(HOCH_2CH_2)_2NCH_2P(O)(OH)_2$  [382],  $Et_2NCH_2CH_2PPh_2$  [383] and *hmpa* [384] have been described. The complex  $[CdL_2Cl_2]$  (L = *hmpa*) is tetrahedral (Cd-Cl, 2.399 Å; Cd-O, 2.179 Å) with monodentate O-donor ligands [384];  $[(Cl)Cd(\mu-Cl)]_2$  (L =  $Et_2NCH_2CH_2PPh_2$ ) is a chloro-bridged dimer (97) [383], whilst  $[(Zn(PhMePO_2)(dioxane))_n]$  is polymeric, with a repeat distance (Zn-Zn) of 4.614 Å [381]. A range of cadmium complexes with l-arylsolananes have been reported [385].



(97)

### 1.1.6 Macrocyclic complexes

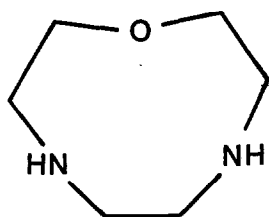
The kinetics of incorporation of zinc ions into the substituted tetraaza macrocycles 1,4,8,11-(CH<sub>2</sub>CO<sub>2</sub>H)<sub>4</sub>-[14]-ane-1,4,8,11-N<sub>4</sub> and 1,4,7,10-(CH<sub>2</sub>CO<sub>2</sub>H)<sub>4</sub>-[12]-ane-1,4,7,11-N<sub>4</sub> has been studied [386]. The formation of zinc complexes with a series of other [14]-ane-N<sub>4</sub> macrocycles has also been investigated [387]. The macrocycle [9]-ane-1-O-4,7-N<sub>2</sub> (98) forms a zinc complex [388], and the crown ether complex [ZnL][SbCl<sub>6</sub>]<sub>2</sub> (L = 18-crown-6) has also been characterised [389]. Zinc complexes of a range of encrypting ligands have been studied [390,391]. The template synthesis of phthalocyanine complexes [ZnL] by the condensation of dicyano compounds with urea in the presence of zinc chloride and ammonium molybdate has been described [392,393]. A number of studies related to the spectroscopic properties of zinc and cadmium phthalocyanines in the context of the photocatalytic decomposition of water, have been published [394-397].

Zinc porphyrin complexes are also of interest in such photochemical systems, and photochemical studies of a series of porphyrin, porphine and related complexes have been reported [398-403]. The formation of axially substituted complexes [MLL'] (M = Zn or Cd; H<sub>2</sub>L = porphyrin; L' = another ligand) has been investigated by a number of groups [404-407]. An EXAFS study has shown that there is no short axial Zn-S interaction in peptide substituted zinc porphyrins, in which the side-chain bears a cysteine residue [155].

The kinetics of metal insertion into a range of H<sub>2</sub>L species has been studied by a range of techniques [408-410]. The template condensation of phthalimide (or its potassium salt) with malonic acid or arylacetic acids in the presence of zinc or cadmium acetate has been shown to result in the formation of [ML] (H<sub>2</sub>L = tetrabenzoporphine or *meso*-tetraaryl-tetrabenzoporphine) [411,412]. A number of studies concerning zinc complexes of porphyrins or related ligands have also been reported [413-416].

## 1.2 MULTINUCLEAR NMR STUDIES

<sup>67</sup>Zn NMR studies of imidazole and carboxylate complexes [324] and the thermolysin-zinc complex [417] have been described. <sup>113</sup>Cd NMR studies of a wide range of complexes have been reported [111,141-143,202,300,318,341,378,418,419].



(98)

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