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12. ZINC AND CADMIUM

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CONTENTS

INTRODUCTION

The bulk of the work published on the chemistry of zinc and cadmium in the period under review has been concerned with the study in solution and in the solid state of coordination complexes of these cations. Much of this material is routine in character and will not be discussed in detail. While compounds are classified in terms of the nature of the ligand bound to the metal, it has not been possible to maintain this classification absolutely, and in some cases it is not clear which donor group is utilised from those available on the ligand.

The complexing of Zn^{2+} and Cd^{2+} by halides in aqueous and non-aqueous media has been much studied. The dissociation constants of $[H_2ZnCl_4]$ and $[H_2CdCl_4]$ in tributyl phosphate have been measured over a range of temperatures [1] Values of the overall formation constants β_n for the complexes $[ZnCl_n]^{(n-2)-}$ (n = 1—6) in mixed water—dimethylformamide systems (0—30 mol dm^{-3} in H_2O) decrease with increase in H_2O concentration [2]. Interaction with halide ions has also been studied [3] in dmf for Zn^{2+} and Cd^{2+}. For Zn^{2+}, β_n values have been determined for n = 1—6 (Cl^- and Br^-), n = 1—5 (NCS^-) and n = 1—4 (I^-), whilst for Cd^{2+}, overall formation constants have been determined for n = 1—5 with all these anions. In all cases higher coordination numbers and formation constants were obtained in dmf than in water, reflecting the weaker solvation by the former solvent, as evidenced in [2]. The careful study of Zn—Cl stretching frequencies by Raman spectroscopy in aqueous solutions of zinc chloride in hydrochloric acid solutions has allowed the quantitative study of $[ZnCl_4]^{2-}$ formation [4]. The formation of the species $HZn_2Cl_5 \cdot 3\ Et_2O$ in $ZnCl_2$—Et_2O—HCl systems has been established [5]. Heats of formation [6] in aqueous solutions of the iodo complexes of both metals ($[MI]^+$, $[MI_2]$, $[MI_3]^-$ and $[MI_4]^{2-}$) have been measured by microcalorimetry techniques.

Some useful information has been published on the nature of cadmium—halide complexes in solution. Large-angle X-ray scattering measurements [7] on solutions of CdI_2 and NaI in dimethylsulphoxide show the $[CdI_4]^{2-}$ species to be regularly tetrahedral $\{r(Cd—I) = 2.790\ Å\}$, the $[CdI_3]^-$ group to be pyramidal $\{r(Cd—I) = 2.773\ Å\}$, while in $[CdI]^+$, r(Cd—I) was found to be 2.75 Å. These results suggest that CdI_2 does not occur as a dominant species. (For formation constant data, see [8].)

Raman measurements on concentrated aqueous solutions of cadmium halides show the presence of chloro complexes of tetrahedral and octahedral symmetry, but the formation of only tetrahedral bromo complexes [9]. A combination of solution and solid state ^{113}Cd NMR spectroscopic results have allowed the compilation [10] of ^{113}Cd chemical shifts for the complexes $[CdX]^+$, $[CdX_2]$, $[CdX_3]^-$ and $[CdX_4]^{2-}$, for X = Cl, Br or I. Cadmium NMR studies on cadmium fluoride have also been reported [11].

Cadmium fluoride shows five polymorphic forms, with transitions at 550, 860 and 990°C [12]. The structure of the dimethylammonium pentachlorodicadmate(II), $[(CH_3)_2NH_2][Cd_2Cl_5] \cdot 2\ H_2O$, involves [13] polymeric chains of $\{CdCl_6\}$ and $\{CdCl_5(H_2O)\}$ octahedra, the dimethylammonium cations being located in the space between the chains. The compounds $[NH_4][CdCl_3]$ and $[(CH_3)_3NH][CdCl_3]$ also contain [14,15] infinite chains of $\{CdCl_6\}$ octahedra. The reaction of cadmium halides with cadmium metal and phosphorus is reported to give complexes of stoicheiometry $Cd_4P_2X_3$ (X = Cl, Br or I) [16].

There is continuing interest in bimetallic complexes of the type $MM'(NCS)_4 \cdot xL$

and $MM'(NCSe)_4 \cdot xL$; recent examples include $[Cd(thiourea)_4][Cd(SCN)_4]$ [17], $ZnM'(SCN)_4 \cdot xL$ ($M' = Cd(II)$ or $Hg(II)$; L = thiazolidinethione, thiohydantoin or ethylenethiourea, $x = 2$, 4 or 6) [18], $MM'(NCSe)_4 \cdot x$ L ($M = Co(II)$ or $Ni(II)$; $M' = Cd(II)$ or $Hg(II)$; L = isothiazole, 4-methylisothiazole or 4-benzylisothiazole; $x = 2$ or 4 [19], and $[ZnL_4][Zn(NCS)_4]$ (L = 2-, 3-, 4-toluidine or anisidine) [20]. The complexes above with unspecified stoicheiometries fall into two structural types; those with discrete ions e.g. $[ML_x][Cd(SCN)_4]$ and those with bridging thiocyanate, e.g. $[L_2Zn(NCS)_2Hg(SCN)_2]$. The donor atoms of the thiocyanate and selenocyanate groups (and of the ligands L) were determined by IR spectroscopy and confirmed by the calculation of softness parameters [18,19].

12 2 COMPLEXES WITH OXYGEN DONOR LIGANDS

12 2 1 Complexes with inorganic oxoanions

The heat of formation of zinc phosphate has been determined [21]. The formation of the mononitrato complex of Cd(II) has been reported [22], whilst vibrational spectroscopy has been used to characterise the $Zn(NO_3)_2$—water—ethanenitrile system [23]. Solubility isotherms for $Zn(NO_3)_2$—ethyl ethanoate—N_2O_4 show the formation [24] of the species $Zn(NO_3)_2 \cdot N_2O_4$, $Zn(NO_3)_2 \cdot 2\ N_2O_4$, $Zn(NO_3)_2 \cdot EtO_2CMe$ and $Zn(NO_3)_2 \cdot 1.5\ EtO_2CMe$.

Amongst the structures determined are potassium zincate, $K_2Zn_6O_7$ [25], which involves three-coordinate zinc, and the mineral bayldonite [26]. Bayldonite, $(Cu, Zn)_3Pb(AsO_4)_2(OH)_2$, involves partial substitution of copper by zinc. Its structure consists of two different interconnected sheets, a lead arsenate and a copper octahedral sheet. The latter sheet is formed from three crystallographically distinct $\{CuO_4(OH)_2\}$ octahedra. One of these, the Cu(2) octahedron, is subject to less distortion than the other two, and appears to be the likely site for zinc substitution. Indeed, this Cu(2) site in bayldonite is very similar to the octahedral $\{ZnO_4(OH)_2\}$ group in adamite, $Zn_2AsO_4(OH)$ [27].

The species Cd^+ and $[Cd_2]^{2+}$ are known, for example, in solutions of cadmium metal in molten cadmium halides, but are not well-characterised. However, crystallographic data are now available [28] on these species in Zeolite A, which have been prepared by exposing fully Cd^{2+}-exchanged Zeolite A to cadmium vapour. The crystal structure of the partially dehydrated, fully Cd^{2+}-exchanged Zeolite A, $[Cd(H_2O)^{2+}]_3[Cd^{2+}]_3$-A, shows that all six Cd^{2+} ions are associated with 6-oxygen rings of the aluminosilicate framework. Three of these Cd^{2+} extend into the large cavity and are three-coordinated by three framework oxides. The other three Cd^{2+} ions are recessed into the Sodalite unit, where each is coordinated to three framework oxides and to a fourth group (OH^-) to give a near-tetrahedral structure. Upon exposure to cadmium vapour, the three three-coordinate Cd^{2+} ions react to give Cd^+ and Cd_2^{2+} species. Two different coordination environments are present for the $[Cd_2]^{2+}$ ion, but the Cd—Cd distance is the same in both cases, at 2.35 Å. Each unit cell contains 3 Cd^{2+}, 3 Cd^{+} and 1.5 Cd_2^{2+} ions.

12 2 2 Complexes with carboxylic and related acid ligands

12.2.2 1 Mono and dicarboxylates. The enthalpy and entropy of complex formation between Zn(II) and picolinate and dipicolinate anions in aqueous solution have been determined [29] by calorimetry, and from formation constant data. The greater stability of the dipicolinate complex compared to the picolinate complex reflects an entropy effect, and ΔH^0 is actually less favourable. These anions are well-known to have a low basicity to H^+ compared to their complexing ability to metals. In the present case, this probably reflects the coplanarity of the carboxylate anions and the pyridine ring, so that the oxygen atoms are in a favourable position to coordinate.

Formation constant data have been reported for complexes with benzoate [30] and aminoethanoate [31] (for Zn^{2+}); with 3-(2-pyrrolylmethyleneamino)-propionate, 2-(2-pyrrolylmethyleneamino)benzoate [32], phenylethanoate [33], and phosphineethanoate [34] (for Zn^{2+} and Cd^{2+}); and with gluconate [35], 2-, 3- and 4-hydroxybutyrate [36], 5(3)-methylpyrazole-3(5)-carboxylic acid [37] and a range of monocarboxylates [38] (for Cd^{2+}).

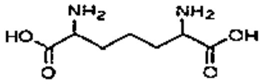
Some detailed solution studies have been published for dicarboxylates, including complexation of Cd^{2+} by adipate [39], bis(2-aminoethylether)-*N,N'*-dimalonate [40] and by mixed ligands to give [Cd(en)(adip)], $[Cd(en)(adip)_2]^{2-}$, $[Cd(en)_2(adip)]$, [41], $[Cd(maleate)(SCN)]^-$, $[Cd(itaconate)_2(SCN)]^{3-}$, $[Cd(adip)(SCN)_2]^{2-}$ [42] and $[CdL(S_2O_3)]^{2-}$ (L = malonate, oxalate or succinate) [43], and by succinate/1,2-diaminopropane [43a]. Reports on the complexation of Zn^{2+} involve malonate [44], fumarate [45], maleic acid copolymers [46], and phenylenediamine-tartrate mixed ligands [47].

The formation of 1 : 1 complexes between ethylenediamine-*N,N'*-diacetic acid (edda) and Zn(II) or Cd(II) have been studied by calorimetric (ΔH) and potentiometric techniques [48]. Earlier studies had omitted to allow for protonation reactions of the ethanoato groups in the ligand. Thermodynamic parameters for edda lie between those of nitrilotriacetate and triethylenetetramine. Edda appears to undergo a slow metal-ion catalysed hydrolysis in aqueous acid solution.

Aquabis(4-aminobenzoato)cadmium(II) involves seven-coordinate cadmium, with two chelating carboxylate groups, a water molecule, and axial positions filled by amino groups from ligands bound to neighbouring metal centres [49]. Spectroscopic data have been given for 3-(alkylthio)propionate (L) complexes of Zn(II) and Cd(II), $[ML_2]$ [50].

The oxalato complexes $[M(C_2O_4)L_2]$ (M = Zn or Cd; L = substituted pyridines or 4-toluidine) are polymeric with bridging oxalato groups [51]. The crystal structure of bis(2-methylimidazole)-μ-oxalatozinc(II) · 0.5 H_2O involves tetradentate oxalate bridges between the zinc atoms, with the two imidazoles *cis*-coordinated [52]. Zn(II) cyanoethanoate involves [53] a polymeric, octahedrahedral structure with bridging or chelating carboxylate groups and an *N*-bonded cyano group. On reaction with 2,2'-bipyridine or pyridine, the octahedral complexes [$Zn(O_2CCH_2CN)_2(bipy)$] or [$Zn(O_2CCH_2CN)_2(py)_2$] are formed, respectively. These contain bidentate carboxylate groups, but no metal—cyano interactions. The zinc complexes $ZnLQ_2$ (Q = quinoline or diethylamine; H_2L = phthalic or succinic acid) have been prepared [54], as has the coordination polymer of 3,3'-benzidine dicarboxylic acid (H_2L), [$Zn_4(HL)_2L_3$]$_n$ [55]. Humic acid, an ill-defined polyphenolic carboxylic acid extracted from sub-bituminous coal, forms 1 : 1, 2 : 1 and 3 : 1 complexes with Cd(II) [55a].

The thermal properties of chelate polymers of 2,6-diaminopimelic acid (dap; 1) and 4,4'-diamino-3,3'-dicarboxybiphenyl (bbdc; 2) with Zn(II) have been compared [56] with those of non-polymeric divalent metal chelates with amino acids. This confirms the expected enhancement of thermal stability when coordination polymerisation occurs, these results possibly being relevant to the thermal stability of certain bacterial spores which contain dap. Zn(II) complexes of dap are more thermally stable than those of bbdc, possibly because the latter chelate cannot pack as well, due to the intermolecular repulsions of the biphenyl groups.



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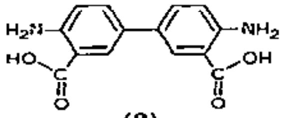

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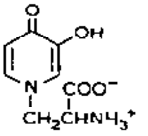
In the complex $ZnL_2 \cdot 2\ H_2O$ (HL = 2,2,5,5-tetramethyl-3-imidazoline-3-oxo-1-oxyl-4-carboxylic acid), L^- acts as a bidentate ligand via carboxylate and oxo oxygen donors. When the 3-oxo group is not present, the ligand is bidentate through the carboxylate and imino groups [57]. The IR spectra of Zn(II) monoiodoethanoate show a chelating carboxylate group rather than a bridging group, as found in a range of divalent metal iodoethanoates [58]. Other studies relate to the diaquaoxalato [59] and diaquabis(salicylato) [60] complexes of zinc(II). The chelating ligand derived from the Schiff base *N,N'*-bis(2-hydroxy-3-carboxybenzilidine)-1,2-diaminoethane offers two sites for metals with $—N_2O_2$ and $—O_2O_2$ donors. The vanadyl/zinc binuclear complex has been prepared [61].

12.2.2.2 Polydentate carboxylates. Formation constants have been measured for Cd(II) and the three unsubstituted benzene tricarboxylic acids, and for the 1,2,4,5-benzene tetracarboxylic acid [62]. In the case of the 1,2,3-benzene tricarboxylate ligand, there was evidence for a dinuclear complex. Complexing of Cd(II) and Zn(II) by nitriloacetate (nta) and edta has been studied further [63], while mixed ligand systems of nta with heterocyclic bases [64] and a range of diamines [65] have been characterised. Ternary complexes of Cd(II) with citrate and 2,2′-bipyridine are reported [66].

A number of tetraacetate ligands have been compared with edta, and formation constants discussed in terms of structural features in the ligands. Thus, constants for the formation of the 1 : 1 complexes of ethylenebis(*N*,*N*′-(2,6-dicarboxy)piperidine) with Zn(II) and Cd(II) are lower than those with edta due to the steric effects of the piperidine ring [67]. The influence of the $CH_2C{=}CCH_2$ structure on the chelating properties of 1,4-aminobutyne-2-tetraacetate has also been assessed [68]. Another development in the study of edta has involved the preparation of simple derivatives, such as the tetra-amide. This ligand is probably *O*-bonded *via* the amide function, but on deprotonation the donor atom changes to the amidate nitrogen [69]. Equilibria in acidic solutions of edta complexes of Zn(II) and Cd(II) involve the formation of mono- and polyprotonated complexes [70].

12 2 2.3 Amino acids and related compounds Solution studies include Zn(II) complexes with L-hydroxyproline [71], glutamate [72], glycine [73], glycine/histamine, glycine/L-histidine [74], L-histidine/histamine [75] and *N*,*N*′-dimethylglycine(HA)/2,2′-bipyridine [76] mixed ligands. In the last case, complexes $[Zn(bipy)A]^+$, $[Zn(bipy)_2A]^+$ and $[Zn(bipy)A_2]$ have been characterised. Mixed ligand complexes of *O*-phospho-DL-serine, Zn(II) and L (L = histamine, 1,10-phenanthroline or 2,2′-bipyridine) have been studied to model substrate, enzyme and metal ternary complex formation in the phosphoserine phosphohydrolyase catalysed hydrolysis of *O*-phosphoserine in the biosynthesis of serine [77]. A binuclear complex of Zn(II) and Cu(II) with histidine has also been reported [78]. Complexes of Cd(II) include those of L-hydroxyproline [79], DL-serine [80], glycine [81], aspartic acid (as the protonated complexes) [82] and citrulline [82a]. Several complexes with amino acids are covered in recent general reviews on ligands of biological importance [83].

The chelating properties of the amino acid mimosine ((3); α-amino-β(3-hydroxy-4-oxo-1,4-dihydro-pyridin-1-yl)propanoic acid) have been implicated in its inhibition of various metalloenzymes, and hence in its biological activities such as the defleecing of sheep. In this context, formation constants have been measured [84] for Zn(II) and Cd(II) with mimosine (3) and related compounds (4—6). These derivatives formed monomeric complexes, in which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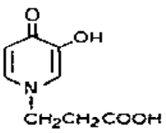
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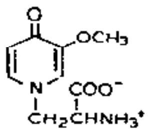
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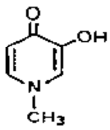
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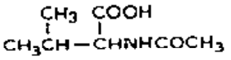
metal binding by the hydroxypyridine group was favoured relative to the amino acid group. With mimosine, dimeric complexes were major species. Consideration of a blood plasma model indicates that mimosine binds zinc (and copper) more strongly than do simpler amino acids, in accordance with the suggestion that mimosine exerts its biological action by depleting copper and zinc levels in blood plasma.

Complexes studied in the solid state include [Zn(*N*-acetyl-DL-leucinate)$_2$L$_2$] (L = H_2O, pyridine, 3-methylpyridine or 4-methylpyridine) which involves bidentate coordination of the amino acid via the carboxylate group [85], $ZnL_2 \cdot 2\ H_2O$ (HL = glutamine, histidine [86] or *N*-acetyl-DL-tryptophan [87]), and [Cd(L-Phe)$_2$] · *n* H_2O [88]. The L-phenylalanine ligand in the complex of Cd(II) is bidentate via NH_2 and CO_2^- groups for the complex dihydrate, and terdentate in the anhydrous complex, the second oxygen of the carboxylate being linked to another Cd(II). Although the use of *N*-acetyl-DL-valine (AcValH) [89] introduces the possibility of coordination via the peptide group (7), the complexes [Zn(AcVal)$_2$] and [Zn(AcVal)$_2$L$_2$] (L =



$\overset{CH_3}{CH_3CH}-\overset{COOH}{CH}NHCOCH_3$

(7)

pyridine, 3- and 4-methylpyridine, or 1,10-phenanthroline) probably only involve coordination via the carboxylate group. The IR spectrum of [Zn(glycineglycinate)X] · H_2O has been assigned [90]. Cycloserine forms complexes ZnL_3X_2, $CdLX_2$ and CdL_2X_2 (X = Cl or Br) [91].

12.2.2.4 Hydroxamates, sulphonates, phosphates and related ligands. The following substituted hydroxamic acids have been used to complex Zn(II) and/or Cd(II): 2,2-diphenylacetohydroxamic acid [92], *N*-3-tolyl-4-methoxybenzohydroxamic acid [93], and *N*-2-tolyl-4-X-benzohydroxamic acid (X = Me, MeO, F, Cl, Br or NO_2) [94]. Formation constants have also been measured for several sulphonic acids [95], while the solid products [ML(H_2O)] have been characterised (M = Cd or Zn and L is the Schiff base derived from benzoin and 1-amino-2-naphthol-4-sulphonic acid) [96].

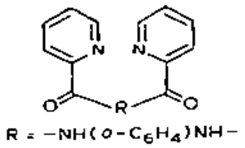
The compounds $Na_2ZnL \cdot 2\ H_2O$ and $Na_2Cd_3L_2 \cdot 6\ H_2O$ (where L = ATP) have been prepared [97], and coordination via the nitrogen base and phosphate group established. Formation constants have been determined for the ternary complex of Zn(II), ATP and 1,10-phenanthroline [98]. Ternary complexes usually involve metal-bridged ligands, but in some cases a ternary complex results from an aromatic ring-stacking between two suitable ligands, with a metal bound to only one of them. However, a particularly enhanced stability of the ternary complex results when stacking and bridging occur. In this context, it is important that ligand—ligand interactions were observed, (e.g. by electronic or ^1H NMR spectroscopy). This has allowed the intramolecular equilibrium constant for the equilibrium between triphosphate,

Zn^{2+}, L-tryptophanate, 2,2′-bipyridine or 1,10-phenanthroline to be determined by ^1H NMR. The percentages of the stacked isomers decrease in the order $[Zn(phen)(ATP)]^{2-}$, $[Zn(bipy)(ATP)]^{2-}$, $[Zn(bipy)(IPT)]^{4-}$, $[Zn(bipy)(UTP)]^{2-}$ (IPT = inosine 5′-triphosphate, UTP = uridine 5′-phosphate). This series is the same as the sequence of stabilities for the metal-free adducts $[(phen)(ATP)]^{4-} > [(bipy)(ATP)]^{4-} \simeq [(bipy)(IPP)]^{4-}$. These series reflect the decreasing size of the aromatic-ring systems forming the stacks [99].

The metal complexes of riboflavin-5′-phosphate (flavin mononucleotide, FMN) have been studied. $Zn(FMN) \cdot 2\ H_2O$ shows some perturbation of the IR bands of the phosphate group, suggesting metal binding occurs at the phosphate group [100]. $Zn(ClO_4)_2$ forms the complex $[ZnL_3][ClO_4]_2$ (L = diethyl acetylphosphonate) in which the ligand is bidentate through phosphoryl and acetyl oxygen atoms [101], and the complex $[ZnL_4(ClO_4)][ClO_4]$ (L = methyl methylphenylphosphinate) [102]. Complexes of tri-4-tolylphosphate (ttp) include $[Zn(ttp)_2Cl_2]$ (monomeric) and $[(ttp)_3M(ttp)_2M(ttp)_3][ClO_4]_2$ (M = Cd or Zn) [103]. Studies on IR data (and electronic spectra for transition metal species) indicate that ttp is a ligand almost as strong as the triorganophosphine oxides, and is significantly stronger than trimethylphosphate. The increased donor strength of ttp probably reflects inductive and steric effects. The complexing of Cd(II) by diethylenetriamine-*N*,*N*,*N*′,*N*″,*N*″-pentamethylphosphonic acid [104] and Zn(II) and Cd(II) by methyl diphenyl phosphate [105] have also been reported.

12.2.3 Complexes with amides and related species

The interest in amides as ligands has centred around the factors that control the alternative binding modes adopted by these compounds. Binding of Zn(II) enhances amide deprotonation of *N*,*N*-bis-(2′-pyridinecarboxamide)-1,2-benzene (8; LH_2) to give planar $[ZnL \cdot H_2O]$, having maximum electronic delocalisation. Coordination of the amide oxygens is hindered by the resulting decrease in the chelating ability of the ligand [106]. Zn(II) and Cd(II) complexes with 2,6-dipicolinic acid hydrazide involve a tridentate ligand, with two deprotonated amide nitrogens and a pyridine nitrogen acting as a donor. The amide oxygen atoms are sterically unable to coordinate (9). The resulting complex may be cyclised by treating with β-diketones [107]. The ligand *N*-(2-pyridyl)acetamide forms octahedral complexes $[ML_2X_2]$ (X = Cl, Br or I; M = Zn or Cd), that involve the carbonyl oxygen and heterocyclic nitrogen donors [108], while thermochemical measurements have been carried out on



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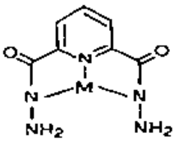


(9)

these compounds [109]. IR and Raman studies on the complex $[CdLX_2]$ (X = Cl or Br; L = *N,N'*-dimethyl-1-ethylimidazole-4,5-dicarboxamide) show the ligand to be oxygen bonded [110].

Diacetylhydrazine (LH_2) gives a cadmium complex $[Cd(H_2L)Cl_2] \cdot H_2O$, in which the ligand is bidentate via the carbonyl oxygen atoms. On heating, HCl is eliminated giving [CdL] [111]. The oxalyldihydrazide ($L'H_2$) complex of Zn(II) involves the ligand in the keto form, $[Zn(H_2L')Cl_2] \cdot 2\ H_2O$ [112], while ligands $CH_3(CH_2)_nCONHNH_2$ (L″) are bidentate in complexes $[CdL''_2]X_2$ and utilise the carbonyl oxygen atom [113]. The structure of diisothiocyanatobis(3-nitrobenzoylhydrazine)zinc(II) involves *N*-bonded thiocyanate and an *N,O* bidentate ligand (via the carbonyl oxygen) [114]. Other amides studied include the aminobenzamides (with Cd^{2+}) [115], while complexes $[Zn(RCONHCOR')Cl_2]$ have also been reported [116].

12.2.4 Complexes with ketones and other carbonyl ligands

Enthalpies of formation of metal pentane-2,4-dionates (including Zn(II)) have been measured directly [117]. The adducts $[Zn(acac)_2L]$ and $[Zn(benzac)_2L]$ have been prepared (L = piperazine, Et_2NH, Et_3N, Ph_3N, urea or thiourea) [118]. Powder EPR spectra for Mn(II)-doped compounds $[M(acac)_2(bipy)]$ (M = Zn or Cd), $[Zn(acac)_2(phen)]$ and $[Cd(acac)_2(phen)(H_2O)]$ [119] indicate that distortions from octahedral symmetry were greater for the bipyridine adduct than for the phenanthroline adduct, and greater for Cd than for Zn. IR measurements confirm all the compounds to be tris-bidentate, except for $[Cd(acac)_2(phen)(H_2O)]$) which probably has coordinated water and a free carbonyl group. The Schiff base ligand formed from β-diketones and isopropylamine forms a 1 : 2 complex with ZnI_2 [119a].

Work published on monothio-β-diketones includes formation constants for Zn(II) and Cd(II) [120], dipole moments for the Zn(II) complex with $RC(SH){=}CHCOCF_3$ [121], and ^{113}Cd NMR data for pyridine adducts of Cd(II) β-diketonates and thio-β-diketonates, which shows the influence of the sulphur and nitrogen donors on the chemical shift [122].

Zinc—oxygen and zinc—nitrogen stretching frequencies have been assigned in the IR spectra of $[ZnL_nCl_2]$ (L = 2-pyrrolidone; n = 2 or 3) [123] and $[Zn(R\text{-}sal)_2L_2]$ (R-sal = substituted salicylaldehyde; L = H_2O or pyridine) [124].

Formation constants have been measured for Zn(II) and the α-keto-enol ligands, 3-hydroxy-2-methyl-4-pyrone and 3-hydroxy-6-hydroxymethyl-4-pyrone (kojic acid) [125], and for Zn(II) and Cd(II) with ligands derived from 2-hydroxy-5-methyl-acetophenone and -benzophenone [126].

12.2.5 Complexes with alcohols and phenols

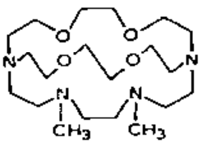
A particularly well-studied ligand is L-3,4-dihydroxyphenylalanine (L-DOPA): this may coordinate like alaninate or a pyrocatechol [127]. Zn(II) appears to favour binding to L-DOPA, as to pyrocatechols [128]. Formation constants have been measured for ternary complexes Zn(II): dopamine : alanine/pyrocatechol [129]; Zn(II): L-DOPA : L (L = penicillamine, L-alanine, glycine, 2,2′-bipyridine, citric acid, tartaric acid or sulphosalicylic acid) [130]; and Zn(II) and Cd(II) with naphthols [131] and chalkones [132]. The oxinate ligand is monodentate to Zn(II) through its phenolate group [133].

Formation constants have been obtained for the mixed ligand complexes $[Cd(L)_n(tris)_2]^{2+}$ ($n = 1$ or 2; L = piperidine; tris=tris(hydroxymethyl)methylamine) [134]. Polynuclear complexes of the type $M[CoL_2] \cdot 2\ H_2O$ have been reported (M = Zn(II) or Cd(II); H_2L = 1-amino-2,3-propanediol) [135]. The Schiff bases from tris and vanillin [136] and from salicylaldehyde and anisidines [137] have been used to complex Cd(II) and Zn(II), respectively.

The complex of vitamin B_6 (pyridoxine) with $CdCl_2$, $[CdLCl_2]$, involves infinite chains of chloro-bridged Cd(II). The ligand is bidentate through two oxygen donors and bridges via the third, so that each Cd atom is bound in a $\{CdCl_3O_3\}$ environment [137a].

12.2.6 Complexes with ethers

Complexing of Cd(II) by cryptands has been discussed in an endeavour to find ligands that will bind Cd(II) selectively with respect to Zn(II) and Ca(II), and so ultimately provide a suitable ligand for chelation therapy. The cryptand (**10**) shows a remarkable selectivity, of [Cd] over [Zn], of 10^6 and of [Cd] over [Ca] of 5×10^7. Lehn has reviewed these aspects of the cryptands [138]. Interaction of diazapolyoxa macrocycles (**11**) with Zn(II) have been reported [139]. The solvate $[Zn(thf)_6][SbCl_6]_2$ has been prepared [140], and heats of formation and lattice energies have been obtained for complexes of dioxane and morpholine with zinc fluoroborates [141].



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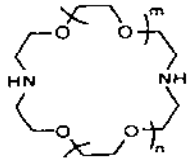

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12.2.7 Complexes with heterocyclic N-oxides

The complex with isonicotinate *N*-oxide $[Zn(N\text{-isonicO})_2(OH_2)_2] \cdot 4H_2O$ is polymeric, the ligand bridging adjacent zinc ions and coordinating via the *N*-oxide group and a carboxylate oxygen, whilst the species $[(N\text{-isonicO})_2Zn(OH_2)Zn(N\text{-isonicO})_2]_n$ involves bridging aqua groups in addition, the zinc being five-coordinate [142]. The analogous cadmium complex has a polynuclear structure [143]. The dioxide ligands [144] phenazine-5,10-dioxide-(N,N-phzO$_2$) and quinoxaline-1,4-dioxide(N,N-quoxO_2) give monomeric complexes $[Zn(N,N\text{-}phzO_2)_3(OH_2)_2(ClO_4)][ClO_4]$ and $[Zn(N,N\text{-}phzO_2)_2(OH_2)_2]$-$[ClO_4]_2 \cdot 2\ H_2O$, and polynuclear $Zn(N,N\text{-}quoxO_2)_3(ClO_4)_2 \cdot 6\ H_2O$. Other studies include picolinic acid *N*-oxide (with $Zn(ClO_4)_2$) [145], substituted pyridine *N*-oxides (with CdI_2) [146], the sterically hindered 3-methyliso quinoline *N*-oxide (with $Zn(ClO_4)_2$) [147], 2-pyridylcarbinol *N*-oxide (with $Zn(NO_3)_2$) [148] and 3,4,5-trimethyl-1-hydroxypyrazole *N*-oxide (with Zn(II)) [149].

12 2.8 *Complexes with phosphine oxides*

The vibrational spectra of zinc halide complexes (X = Cl, Br or I) with Me_3PO confirm the presence of the C_{2v} $\{ZnX_2O_2\}$ skeletal structure [150]. Complexes $[Zn(R_3PO)_4][BF_4]_2$ have been prepared [151] for R = Me, $HOCH_2$, Et, Pr, CMe_2H or Bu, whilst complexes with trimorpholinophosphine oxide (morpo) and chlorodimorpholinophosphine oxide (cdmpo) include $[Zn(morpo)_3][ClO_4]_2 \cdot H_2O$, $[Zn(morpo)_2][PF_6]_2 \cdot 2\ H_2O$ and $[Zn(cdmpo)_2X_2]$ (X = NO_3 or ClO_4) where the ligand probably coordinates by the oxide group and a morpholine N atom [152].

12.3 COMPLEXES WITH SULPHUR OR SELENIUM DONOR LIGANDS

12.3.1 *Inorganic sulphides*

Ab initio molecular orbital calculations [153] on the binding of H_2S and $[HS]^-$ to Zn(II) suggest that sulphur-binding is less favoured than the binding of H_2O, OH^- and NH_3, and also allow an assessment of the effect of coordination on the acidity of H_2S.

12.3.2 *Complexes with thiourea and related ligands*

Work on complexes of thiourea and its derivatives has been concerned mainly with the measurement of formation constants for interaction with Zn(II) [154] and Cd(II) [154,155]. Enthalpies of formation for cadmium complexes with thiosemicarbazide(L) and its 4-methyl derivative [156] have been determined, and entropy changes calculated for successive complexation (using literature values for formation constants). The variations in these functions have been interpreted in a model postulating coordination number changes from six in $[Cd(H_2O)_6]^{2+}$ to four in $[CdL(H_2O)_2]^{2+}$ and $[CdL_2]^{2+}$ and back to six in $[CdL_3]^{2+}$. In all cases, the ligand is bidentate. New complexes with thiosemicarbazides and related ligands include the $[Zn(O_2CMe)_2]$-thiosemicarbazide complex [157], octahedral $[ZnL_2X_2]$ (L = ethylmethylketone thiosemicarbazone; X = Cl, Br, I or NO_3) with bridging X and bidentate *N,S* bonded ligand, and tetrahedral $[ZnL_2][ClO_4]_2$ [158], and $[ZnL'Cl_2] \cdot H_2O$ (L′ = ethylacetoacetate semicarbazone) [159].

The 1 : 1 complex of Cd(II) with the ethylenebis(dithiocarbamate) ligand is polymeric [160]. Solution studies on the compounds $[Bu_4N][M(R_2NCS_2)_3]$ (M = Zn or Cd; R = Me or Et) show [161] the zinc complex (unlike the cadmium complex) to be some 90% dissociated into the neutral bis complex and the free ligand anion. This is in accord with the structure of the solid complex [162], which shows that only one dithiocarbamato group is bidentate, the other two being formally unidentate. Cyclic voltammograms on $[M(Et_2NCS_2)_3]^-$ show waves characteristic of the irreversible oxidation of the free $[Et_2NCS_2]^-$ ligand, the resulting radical rapidly dimerising to the thiuram disulphide. Mixed ligand complexes of Cd(II) dithiocarbamates with nitrogen donor ligands [163] have the stoicheiometries $[Cd(Et_2NCS_2)_2L]$, $[Cd(Et_2NCS_2)_2L_2]$, $[Cd(R_2NCS_2)_2L]$ and $[Cd(R'_2NCS_2)_2L_3]$ (R_2N = *N*-morpholine, R'_2N = *N*-piperidine; L = quinoline, isoquinoline, 2,4- or 3,5-dimethylpyridine). These involve coordination numbers five, six and seven. α-Benzoyl-β-phenylthiocarbamide forms octahedral complexes $[ML \cdot x\ H_2O]$ with Zn(II) and Cd(II) in which the ligand coordinates via *S*, *N* and *O* atoms [164]. Formation constants have been determined for the terdentate ligand *N*,*N'*-bis(mercaptoacetyl)1,2-diaminoethane with Zn(II) and Cd(II) [165].

12.3 3 Complexes with thioether ligands

Studies on ligands containing this group have received fresh impetus from the recent demonstration that one of the ligands to copper in plastocyanin is a thioether group. Naturally occurring species are L-methionine and *S*-methyl-L-cysteine, while biotin contains a thiophene group. Formation constants for metal . thioether interactions have been measured by observing the decrease in the intensity of the visible spectrum of a Cu-thioether complex resulting from the addition of a competing metal ion. In this way, constants have been determined [166] for Zn(II) and Cd(II) with 2,2'-thiodiethanol ($HOCH_2CH_2SCH_2CH_2OH$), tetrahydrothiophene and diethyl sulphide Data have also been reported for biotin [167], with enthalpies and entropies of complex formation for the thiophen-2-carboxylate ion [168]. A comparison of data for the last named ligand with those for ethylthioacetate and phenylthioacetate suggests that aromatic sulphur donors have a greater tendency to form bonds with these metals than do aliphatic sulphur donors. Some solid complexes of thiophene derivatives have been studied [169].

Other measurements on Zn(II) and Cd(II) complexes include formation constants for aliphatic thioethers [170], and calorimetry with dithiodiacetate, 3,3'-thiodipropionate, [171] and phenylthioacetate [172].

12 3.4 Complexes with sulphur-containing amino acids and other acids

The coordination chemistry of L-cysteine and D-penicillamine [173] and glutathione [174] has been reviewed. Complexes of Zn(II) and Cd(II) with *N*-benzoylcysteine involve $M(HL)_2$ stoicheiometry, with coordination occurring via a deprotonated mercapto group and carboxyl oxygen, as shown by the use of IR spectroscopy [175]. Formation constants have been reported for Zn(II) complexes with L-cysteine and D-penicillamine and with the mixed ligands [176], and for Zn(II) with cysteic acid [177]. The complexes [ML] (M = Zn or Cd; L = thiomalate) involve *S*, *O* binding groups and are probably polymeric [178].

12.3.5 Complexes with thione and mercapto ligands

These may be interrelated as tautomeric alternatives in certain heterocyclic ligands. The following complexes with 1,4,6-trimethylpyrimidine-2-thione(L) and 1-methylpyrimidine-2-thione(L′) have been characterised [179,180]: $[ZnL_3]X_2$ (X = I, ClO_4 or BF_4); $[ML_2X_2]$ (M = Zn or Cd; X = Cl or Br); $[ZnL_2'X_2]$ (X = Cl, Br or I); $[CdL_2'X_2]$ (X = Br or I) and $[CdL'Cl_2]$. The 1 : 3 complexes involve bidentate ligands (with four-membered chelate rings), while 1 : 2 complexes result from the presence of anions of greater coordinating power. The 1-methyl derivative, while a weaker ligand, shows greater variety in its coordination pattern. The IR spectra of the 1 : 2 complexes show metal—halogen stretching frequencies in between those usually observed for tetrahedral and octahedral halogen-bridged compounds. This is interpreted in terms of M—N, M—X and long M—S bonds. However, the crystal structure of tetrakis(1-methylpyrimidine-2-thione)zinc(II) perchlorate shows that the zinc is tetrahedrally coordinated by nitrogen atoms of four ligands. So in this case the sulphur atoms are not coordinated to zinc, the *r*(Zn—S) distances being 3.206 and 3.255 Å [181]. The complexes $[ML_2Cl_2]$ (M = Zn or Cd; L = 2-thiouracil) are probably pseudo-tetrahedral, with ν(Zn—Cl) at (319 or 337) and 287 cm^{-1} and ν(Zn—S) at 215 cm^{-1} [182].

Some interesting polynuclear complexes of zinc(II) have been characterised: 2-pyridinethiolate (pySH) reacts with $ZnCl_2$ in the presence of sodium hydroxide to give $[Zn(pyS)_2]$ [183]. A large excess of base leads, however, to the formation of oxohexakis-μ-[2(1*H*)pyridinethionato]tetrazinc(II) $[L_6Zn_4O]$, involving *N*, *S* coordination of the ligand. Similar complexes were prepared for L = 2-thiazolidinethiolate, 5-methyl-2-thiazolidinethiolate and 1-methyl-4-imidazolethiolate. The following chlorozinc complexes have also been prepared: $[(pyS)_3Zn_2Cl]$, $[(pyS)_4Zn_3Cl_2]$ and $[(pyS)ZnCl]$. The last compound is probably polymeric [184].

Other studies involve as ligands: various methyl substituted 8-mercaptoquinolines (with Zn(II)) [185]; 1-methyl-2-chloro-3-formyl-4-(phenylaminomethylene)-5X-pyrrolones (with Zn(II); X = O, S or Se; the ligand bidentate through X and the azomethine N atom) [186]; 1,2-bis(4-phenyl-1,2,4-triazoline-5-thione-3-yl)ethylene glycol (to form $ZnL(O_2CMe)_2 \cdot H_2O$, which is polymeric via C=S groups) [187]; 3-methyl and 3-ethyl derivatives of 4-amino-5-mercapto-1,2,4-triazole (with Zn(II) or Cd(II)) [188]; and 2-hydroxy-5-methylthiobenzophenone (with Zn(II) or Cd(II)) [189].

The crystal structure of *catena*-bis[μ-(*N*-methylpiperidinium-4-thiolato)]-cadmium(II) perchlorate dihydrate [190] involves infinite chains of cadmium atoms, each of them tetrahedrally coordinated to four sulphur atoms of four different N-methyl-piperidinium-4-thiolato groups. Each sulphur atom bridges two consecutive cadmium atoms {r(Cd—S) = 2.548 Å}.

12.3 6 Complexes with selenium ligands

In addition to the examples discussed above [186], work with selenium donors involves complexes with triphenylphosphine selenide, 2 $MX_2 \cdot Ph_3PSe$ and $MX_2 \cdot 2\ Ph_3PSe$ (M = Zn or Cd; X = halide) [191].

12.4 COMPLEXES WITH NITROGEN DONOR LIGANDS

12 4 1 Complexes with azide, ammines and various aliphatic nitrogen ligands

Formation constants for $[Cd(N_3)_n]^{(n-2)+}$ have been measured (n = 1—5) [3]. For Zn(II) or Hg(II), only four or two complexes may be formed, respectively. A number of structures in solution, of ammine and related complexes, have been determined by X-ray diffraction techniques, supported by the use of Raman spectroscopy. A study on aqueous solutions containing zinc(II) or cadmium(II) chlorides and ammonia at various mole ratios revealed the tetrahedral species $[Zn(NH_3)_4]^{2+}$ and $[Zn(NH_3)_3Cl]^+$, which were characterised [192] with r(Zn—N) = 2.03 Å, and r(Zn—N) = 2.00 Å and r(Zn—Cl) = 2.30 Å, respectively. No higher-coordination species could be observed. For $CdCl_2$, (with $[NH_3]/[Cd]$ = 9.9) the octahedral hexammine complex was present {r(Cd—N) = 2.37 Å} [193]. The same approach has been used to study [194] $[Zn(en)_2]^{2+}$ and $[Zn(en)_3]^{2+}$, which have tetrahedral and octahedral stereochemistries with r(Zn—N) at 2.131 and 2.276 Å, respectively. It is noteworthy that Zn—N for the tetrammine complex is shorter than that for $[Zn(en)_2]^{2+}$.

Thermochemical studies have been carried out on the halides of Zn(II) and Cd(II) solvated by propylamine, isopropylamine, butylamine or isobutylamine [195], and heats of formation determined. Formation constants are now available for these metals with 2,3-diamino-2,3-dimethylbutane [196], *N,N'*-dimethyl-1,2-diaminoethane [197], triethylenetetramine [198], and for the mixed complexes of Cd(II) with 1,2-diaminopropane and trimethylenediamine (1 : 1 : 1 and 1 : 1 : 2) [199]. $[ZnLCl_2]$ {L = *N*-(2-aminoethyl)-1,3-diaminopropane} has been characterised [200], whilst ^{14}N NQR data on the $Zn(ClO_4)_2$ complex with hexamethylenetetramine has been reported [201].

A normal-coordinate analysis of diformylhydrazine and its zinc complex with deprotonated ligand has been reported [202]. The following complexes with hydrazine derivatives have also been prepared: [Zn(malonic dihydrazide)-X_2] $\cdot$ n H_2O (X = Cl or 0.5 SO_4); [Cd(succinic dihydrazide)$(NCS)_2$], where the ligands are tetradentate and bridging [203]; $[Zn(H_2L)Cl_2]$ and $[ZnL(H_2O)]$ {H_2L = succinyl di(acetone hydrazone)} [204]; $[Cd(HL)Cl_2] \cdot H_2O$ and $[Cd(HL)_2Br_2] \cdot 5\ H_2O$ (HL = 6-formyl-7-hydroxy-5-methoxy-2-methylchromone-Girard T-hydrazone) [205]; and $[ZnL_2(H_2O)_2]$ (L is the hydrazone derived from 2,4-dinitrophenylhydrazine and salicylaldehyde) in which the ligand coordinates via the deprotonated hydroxyl group and the azomethine nitrogen atom [206].

The in-situ alcoholysis of the easily-prepared compound $Ph_3P{=}NSiMe_3$ in the presence of anhydrous halides of zinc and cadmium leads to the formation of a range of complexes of triphenylphosphinimine $Ph_3P{=}NH$ (L) [207], including $[ZnX_2L]_2$ (X = Cl, Br or I), $[CdCl_2L]_2$, $[CdI_2L_2]_2 \cdot (CHCl_3)_2$ and $[Cd_2Br_4L_3]$. The presence of an intense P=N absorption in the region 1106—1118 cm^{-1} of the IR spectrum confirms the ligand to be a two-electron nitrogen donor ($Ph_3{=}\ddot{N}H$). The dimeric complexes are all *trans* halogen-bridged structures. The 2 : 1 complex with CdI_2 involves two types of phosphinimine ligands (as evidenced by two different N—H stretching frequencies). This is shown in its structure [208], which involves two $\{CdI_2L_2\}$ units linked by N—H ··· I hydrogen bonds. The 3 : 2 complex with $CdBr_2$ is believed to have a polymeric structure in which $\{CdBr_2L_2\}$ and $\{CdBr_2L\}$ units are linked via halogen bridges

Oximes and dioximes have continued to attract attention as ligands. Attempts have been made to quantify the contributions of oxime deprotonation and oxime—oximato hydrogen bonding to the stability of metal oxime complexes. Thus a range of complexes, including zinc(II), of the diamine dioxime ligand 4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione dioxime (H_2dddo) and its *O*-methyl ester (Hddmo) have been studied potentiometrically [209]. H_2dddo coordinates in the oxime—oximato form $[Zn(Hdddo)]^+$, and the hydrogen bonding has been studied for $[Zn(Hdddo)]ClO_4$. Hddmo gives the complexes $[Zn(Hddmo)_2]^{2+}$ and $[Zn(Hddmo)(ddmo)]^+$.

Formation constants have been measured for the complexes with zinc(II) and cadmium(II) of 2,4-dihydroxyvalerophenone oxime [210] and with zinc(II) of peonoloxime [211]. The species $[Zn(HL)_2]$ and $[ZnL] \cdot 0.5\ H_2O$ (H_2L = 4-quinonedioxime) [212], and $[ZnL(HL)Cl] \cdot H_2O$, $[CdHLCl_2]$, $[CdH_2L'X_2]$ (X = Cl or Br; L = phenanthraquinone monooxime; L′ = phenanthraquinone dioxime) [213] have been isolated.

12.4.2 Complexes with aromatic compounds with nitrogen-containing substituents

Aniline complexes of $ZnCl_2$ and $ZnSO_4$ have been examined by X-ray powder diffraction techniques [214]. Comparison with the analogous complexes of 4-toluidine (of known structure) suggest they have similar structures. Calculations have been carried out on a number of aniline complexes, including hose of zinc(II) [215]. The IR spectra (3500—150 cm^{-1}) of $[Zn(aniline)_2X_2]$ X = Cl, Br or I) have been assigned with the help of ^{15}N labelling: ν(Zn—N) tretching frequencies occur in the range 450—350 cm^{-1} [216]. The double alts $[CdL_4][ZnX_4]$ (L = aniline, 2-, 3-, 4-toluidine or -anisidine) [217] and he complexes $[ZnL_2]$ (L = various *N,N′*-diaryl-β-iminoamines) [218] have been prepared. The platinum(II) complex *trans*-$[Pt(Cl)(PEt_3)_2(CH{=}NC_6H_4$-

$4\text{-}CH_3)]$ acts as a monodentate ligand to $CdCl_2$ [219].

Formation constants are available for zinc(II) with some heterocyclic azo dyes [220] and 2-hydroxy-1-naphthalidine-β-chloroaniline, and for Zn(II) and Cd(II) with 2-hydroxy-1-naphthalidine-α-naphthylamine [221].

The ligand 1,4-bis{bis(2-aminoethyl)aminomethyl}benzene hexahydrochloride [222] (L; 12) provides two terdentate moieties separated by a rigid

(12)

bridge, and so offers the possibility of synthesising binuclear complexes. Formation constants have been measured for interaction with several cations, including zinc(II), and indicate that $[Zn_2L]$ formation occurs.

A number of sterically hindered N_2O_2 and N_4 ligands have been prepared in which a quadridentate Schiff base is capped by condensation of salicylaldehyde or pyrrole-2-carbaldehyde with a series of bis(8-aminonaphthyl)-alkyl ethers. These ligands combine the versatility of the Schiff base with the protective features well-known for certain model porphyrin systems, and appear to be of some interest. The zinc(II) complex and other transition metal complexes have been prepared [222a].

12.4.3 Complexes with heterocyclic ligands

12.4.3.1 Pyridines. Complexes with pyridine and its derivatives have been reviewed [223]. The structure of deca-μ-ethanoatodioxobis(pyridine)heptazinc(II) involves seven zinc atoms, bridged by ethanoate groups, in a heptameric centrosymmetrical unit. In each of the two half-units, a central oxygen is surrounded tetrahedrally by four zinc atoms (one of which is common to both). Five of the six edges of this tetrahedron of zinc atoms are bridged by ethanoate groups, the remaining one being open. The structure thus contains three types of zinc; Zn(1) lies on the centre of symmetry in an octahedral environment, Zn(3) is coordinated to three oxygen atoms from ethanoate and the pyridine nitrogen, whilst Zn(2) and Zn(4) are tetrahedrally coordinated by oxygen atoms. The EPR spectrum of the copper-doped crystal has been measured [224].

ν(Cd—N) and ν(Cd—X) stretching frequencies have been assigned in the far IR ($\geqslant 30\ cm^{-1}$) and low-frequency Raman spectra of $[CdX_2(py)]$ (X = Cl or Br) [225]. The results support a structure for this common stoicheiometry comprising double-strand halogen-bridged polymeric chains, in which the Cd(II) is bound by one pyridine ligand, two bicoordinate halogens and three tricoordinate halogens. Complexes [226] and formation constant data [227] for a number of substituted pyridines and quinolines have been reported. Zinc complexes of nicotinamides have attracted particular attention [228] and the crystal structures of dichloro- and diiodobis(*N*,*N*-diethylnicotinamide)zinc(II) have been published [229].

12.4.3.2 Pyrimidines

Much coordination chemistry has been carried out with simple pyrimidines and the nucleic acid bases. The crystal structure [177] of tetrakis(1-methylpyrimidine-2-thione)zinc(II) perchlorate bis(propanone) demonstrates unidentate coordination by the non-methylated(N3) nitrogen atom, with $r(\mathrm{Zn{-}N})$ at 2.058 and 2.060 Å. The structure of dichlorobis(1-methylcytosine)cadmium(II) [230] involves two Cd—Cl bonds (2.497 and 2.485 Å) and two Cd—N(3) bonds (2.281 and 2.296 Å) with approximately tetrahedral stereochemistry. The zinc(II) complex with methyl-5-nitrosobarbituric acid has been reported [231], as have formation constants for mixed ligand complexes of Zn(II) and Cd(II) involving cytosine [232] and 2-aminopyrimidine [233], respectively.

Complexes with adenine and 9-methyladenine (to block the nitrogen atom utilised in binding ribose or deoxyribose groups in nucleic acids) continue to attract attention. $[\mathrm{Zn(9\text{-}Mead)X_2}]$ is tetrahedral, but $[\mathrm{Cd(9\text{-}Mead)X_2}]$ (X = Cl or Br) is octahedral with halide bridges. The zinc complex is isomorphous with the corresponding chloride, of known structure, and probably involves Zn—N interactions with N1 and N7 atoms in the purine ring [234]. Adenine complexes $[\mathrm{M(Had)_2X_2}]$ (X = Cl, Br, NO_3 or ClO_4), and those with deprotonated ligand, have also been reported [235,236].

12.4.3.3 Azoles

The complexing of zinc(II) and/or cadmium(II) has been investigated for the following azoles: 1-ethyl- and 1-propylimidazoles [237]; 1-vinyl-2-hydroxymethylimidazole and -benzimidazole [238]; methylpyrazoles, which act as bidentate ligands [239]; 1,2,4-triazole and 3-bromo-1,2,4-triazole, which are bi- or tridentate ligands [240]; 3-nitro-1,2,4-triazole, which is either monodentate or bidentate via the ring nitrogen and the nitro group [241]; 2,5-dimethyl-1,3,4-thiadiazole [242]; 2-amino-5-phenyl-1,3,4-oxadiazole [243]; and 5-aminoalkyltetrazoles [244].

Azoles with two different heteroatoms, used as ligands for zinc(II) and cadmium(II), include diphenyloxazole (L), which is *N*-coordinated in $[\mathrm{M(L)}_n\mathrm{X_2}]$ (M = Zn or Cd; X = Cl, Br, I, NO_3 or NCS; n = 1, 2 or 4) [245], 3-(*o*-hydroxyphenyl)-5-phenylisoxazole [246], and 2,2′-*o*-phenylenebisbenzothiazole [247].

12.4.3.4 Bipyridines and phenanthrolines

The factors that control the stability of ternary complexes involving bipy or phen continue to be studied. The methyl resonances of $[\mathrm{Me_3Si(CH_2)}_n\mathrm{SO_3}]^-$ (n = 2 or 3) are shifted upfield by $[\mathrm{Zn(bipy)}]^{2+}$ or by $[\mathrm{Zn(phen)}]^{2+}$, while Zn^{2+} caused no shift at all. This has been attributed [248] to a hydrophobic interaction between the trimethylsilyl group and the heterocyclic aromatic ring system. The effect of varying the π-acceptor properties of the bipyridine ligand on the ternary complex with pyrocatecholate (pyro) and zinc(II) has also been studied [249]. For the equilibrium

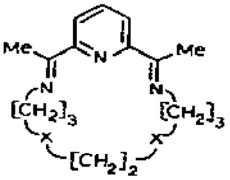
$$[M(pyro)_2]^{2-} + [M(dpx)_2]^{2+} \rightleftharpoons 2[M(dpx)(pyro)]$$

{dpx = 2,2′-dipyridylamine (dpa), 2,2′-dipyridylmethane(dpm) or 2,2′-dipyridylketone(dpk)}, the formation constants decrease in the series dpk > dpm > dpa. Thus, the enhanced stability of ternary complexes containing an *O*-donor and a heteroaromatic *N*-base is dependent on the π-acceptor properties of the latter ligand. Zinc and cadmium complexes with 4,4′-bipyridine have been prepared [250].

1,10-phenanthroline has been used to separate quantitatively cadmium(II) from zinc(II) by extraction from an aqueous solution into chloroform, and thus in conjunction with the use of dithizone offers a selective method for the determination of trace amounts of Cd in Zn [251].

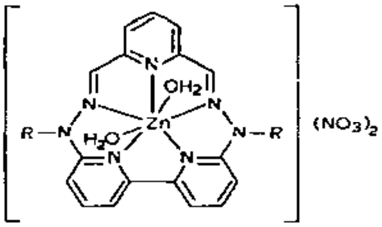
12.4.4 Complexes with macrocyclic ligands

The Zn(II) complex of a 14-membered hexaaza macrocycle has been prepared by the template condensation of 2,6-diacetylpyridine with hydrazine [252]. Reaction of this diacetylpyridine with 4,7-diazadecane-1,10-diamine [253] in the presence of Cd(II) gives the complexed 17-membered pentaaza ligand (13). This [CdLBr]Br · 0.5 H_2O species involves a pentagonal pyramidal structure with axial bromide ligands.

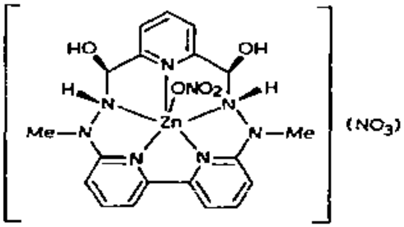


(13)

The condensations of primary amines with carbonyl groups to give macrocyclic imines in which the template ion is coordinated to the imine groups are thought to procede via carbinolamine intermediates, which then undergo elimination of water. Of considerable interest, therefore, is the isolation of a zinc complex (14) of a dicarbinolamine, which appears to be such an intermediate in the formation of the N_5-macrocycle. The carbinolamine complex (15) has the carbinolamine C—O and N—H bonds displaced to the same side



(14)

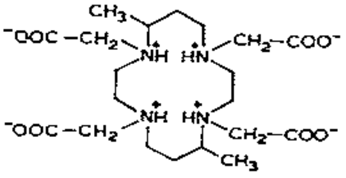


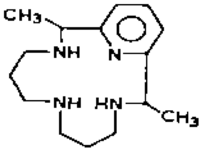
(15)

of the macrocycle [254].

The tetraazamacrocycle (16; LH_4), with four ethanoate groups, is readily prepared by treatment of the cyclic tetraamine with bromoethanoic acid [255]. Its complex $[ZnLH_2]$ utilises two amino *N*-atoms and two carboxylates as ligands. The fully deprotonated complex may be prepared in solution by treatment with NaOH.

The complex $[ZnL(H_2O)_2]^{2+}$ (L = 2,2,4-trimethyl-1,5,9-triazacyclododecane) loses a proton from an aqua group with a pK_a of 9.56 [256]. Macrocycles such as (17), with a pyridine group incorporated into the structure, react slowly with Zn^{2+} compared to other 14-membered cyclic aliphatic tetraaza systems [257], probably as a result of the rigidity introduced into their structure by the pyridine ring. Work on zinc(II) and cadmium(II) with porphyrins has not been covered in this review.


(16)


(17)

12.5 COMPLEXES WITH OTHER GROUP(V) LIGANDS AND MISCELLANEOUS SPECIES

Tetrahedral species $[ZnX_2L_2]$ (X = Cl, Br or I; L = Et_3P or Et_2PhP) have been included in a general study on compounds with these ligands, involving IR, and ^1H, ^{13}C and ^{31}P NMR spectroscopic measurements [258]. The structure of Cd_2As_3I involves As atoms in a helical structure, while the Cd atoms are five-coordinate to three As and two I atoms, with r(Cd—As) at 2.62—2.74 Å and r(Cd—I) at 2.98—3.43 Å [259].

The adduct $[(Cp)_2Nb(CO)H \cdot Zn(BH_4)_2]$ [260] involves hydrogen-bridged Nb and Zn ($Nb—\hat{H}—Zn$ = 107°) and direct Nb—Zn bonding {r(Nb—Zn) = 2.829 Å}. Each $[BH_4]^-$ fragment is bidentate with respect to the zinc. Several syntheses have been described for $MgZnH_4$ [261].

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