Coordination Chemistry Reviews, 78 (1987) 125—146
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

3 ZINC AND CADMIUM

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CONTENTS

INTRODUCTION

This review of the inorganic and coordination chemistry of zinc and cadmium covers material which appeared in volumes 100 and 101 of Chemical Abstracts. This year zinc and cadmium are again treated together. As last year [1] much of the reported chemistry is routine and has not been reported in detail. Consequently classification of donor ligands is sometimes difficult for compounds containing several different potential donor atoms and the reader may need to refer to more than one section.

3.1 HALIDE AND PSEUDOHALIDE COMPLEXES

Compounds $ZnH_2.nEt_2O$ ($n = 0.1-0.3$) were obtained from reaction of ZnI_2 with $LiAlH_4$ in Et_2O-toluene and characterised by X-ray diffraction and infrared studies [2]. The ions Zn^+ and ZnH^+ were produced using ICR [3]. High yield syntheses of ZnF_4^{2-} from reaction of $Zn(acac)_2$ and 40% HF have been described [4]. Electron diffraction and Raman spectroscopy of $ZnBr_2$-LiBr-dmf solutions indicate the presence of $ZnBr_3^-$ [5]. The crystal structure of anhydrous $ZnBr_2$ has been reported [6]. *Ab initio* finite SCF calculations were used in a study of NMR shielding constants of MCl_2, MCl_4^{2-}, $M(CN)_4^{2-}$ [7] and suggest that the p mechanism is more important than the d mechanism so that the chemical shifts increase with increasing electron-donating ability of the ligand. Ultrasonic

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absorption measurements on $ZnCl_2$ in aqueous dmf and MeOH show than an octahedral to tetrahedral geometry change occurs above a water mole fraction of 0.5 in both systems [8]. The Zn reduction product of VCl_3.3thf contains the $Zn_2Cl_6^{2-}$ anion [9]. The crystal structure determination of $[CdCl_3(H_2O)]_n^{n-}$ shows a linear chain with octahedrally coordinated Cd from four equatorial chlorines, forming the chain, and an axial chlorine and axial water molecule [10]. Both $KCdCl_3.H_2O$ and $KCdCl_3$ contain $CdCl_6$ octahedra [11]. Zinc has an approximate tetrahedral environment in $[ZnCl_3(thf)]^-$ [12, 13]. Chloride ion negative chemical ionisation mass spectra of ZnL_2 (where L = β-keto-enolates show radical addition and ligand displacement resulting in $[ZnCl_3]^-$, $[ZnLCl]^-$ and $[ZnLCl_2]^-$ [14].

3.2 COMPLEXES WITH OXYGEN DONOR LIGANDS

3.2.1 Inorganic molecules and ions

X-ray scattering and Raman spectra of aqueous $Cd(NO_3)_2$ solutions suggest the presence of an anionic hydration shell and an inner-sphere complex [15]. Data are consistent with the presence of $[Cd(OH_2)_5ONO_2]^+$ [15]. Zinc occupies both tetrahedral and octahedral positions in solid $ZnPO_3F(2.5H_2O)$ [16]. Zinc oxide and cadmium oxide both react with $P_2O_3F_4$ to give quantitative yields of $M(PO_2F_2)_2$ (M = Zn, Cd) [17]; the latter undergo thermal decomposition to give MPO_3F. The X-ray structure determination of $Na_3CdP_3O_{10}.12H_2O$ shows each triphosphate is bonded to cadmium by three oxygen atoms; the octahedral coordination is completed by coordination of three water molecules [18].

The compound $[Zn(S(NSO)_2)_2](AsF_6)_2.2SO_2$, prepared by reaction of $[Zn(SO_2)_2](AsF_6)_2$ and $S(NSO)_2$ in liquid SO_2, has a polymeric structure in which the Zn has an octahedral coordination by four oxygen atoms from different $S(NSO)_2$ groups and by two fluorine atoms from AsF_6 [19]. Oxidation of zinc in a mixture of bis(fluorosulphuryl)peroxide and fluorosulphuric acid gives $Zn(SO_3F)_2$ [20]. The thermal decomposition of hydrated $Cd(OAc)_2$ has been described [21].

3.2.2 Carboxylic acids and related ligands

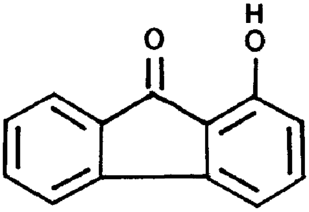
The crystal structure of $[Zn_2(OAc)_3][Mo_3O_2(OAc)_6(OMe)_3].2H_2O$ shows a cation which consists of two zinc atoms bridged by three acetate groups [22]. The compound $[ZnVO(O_2CC_6H_5)_3(thf)_4]$.2thf has been synthesised and its crystal structure determined; the zinc atom is in a trigonal bipyramidal O_5 environment [23]. Cadmium-113 shielding tensors have been derived from single crystal studies of a series of cadmium carboxylate compounds [24]. The cadmium atom in

$[Cd(OAc)_2(tu)]$ is six coordinated from one bidentate and two bridging bidentate acetate groups and two bridging sulphur atoms from two tu groups [25]. Potentiometric studies of complex formation between Cd^{2+} and citrate ion indicate species $[CdcitH_2]^+$, $[CdcitH]$, $[Cdcit]^-$ and $[Cdcit_2]^{4-}$ [26]. The crystal structure of $ZnL_2(H_2O)_2$ (LH = thiazolidine-4-carboxylic acid) shows octahedral O_4N_2 coordination from two thiazolidine chelates and two water molecules [27]. The compound $Zn(HL)_2$ (LH_2 = 6-(3-carboxy-4-hydroxyphenyl)-6-oxohexanoic acid) is thought to contain HL^- as a bidentate ligand with coordination via the aromatic carboxyl and phenolic oxygen atoms [28]. The compound $[ZnL_2(H_2O)_2]$ (LH = (phenylthio)acetic acid) contains zinc in a distorted octahedral O_6 environment whereas the compound $[CdL_2(H_2O)]_n$ is polymeric with cadmium in an octahedral O_5S environment [29]. The structures of $Cd(salH)_2py_3$ and $[Cd(salH)_2(H_2O)_2]_2$ show seven coordinate pentagonal bipyramidal O_4N_3 and O_7 environments, respectively, about cadmium [30]. Solid and solution cadmium-113 NMR data of these compounds were correlated with the number of lone pairs directed towards the cadmium atom [30]. The ligands in $\{[Zn(dicamba)_2(H_2O)_3].2H_2O\}_n$ (dicambaH = 3,6-dichloro-2-methoxybenzoic acid) are unidentate with the zinc being in an octahedral O_6 environment completed by coordination of three water molecules, one of them acting as a bridging ligand [31]. A variety of salicylic acid complexes with zinc and cadmium have been reported [32-35]. Mixed ligand complexes of cadmium with some carboxylic and dicarboxylic acids and amine bases have been described [36, 37]. Zinc and cadmium complexes with a number of substituted benzoic acids have been prepared [38-40]. Complexation equilibria between zinc and substituted glycine ligands continue to receive considerable attention [41-44] as do mixed ligand species involving glycine [45-47].

3.2.3 Diketone and other ligands

The compound $Zn(acac)_2$ is an effective catalyst for the addition of cyanogen to acacH to give 3-(cyanoiminomethyl)pentane-2,4-dione [48]. EXAFS has been used to determine the molecular species obtained in the synergistic extraction of zinc by a benzene solution of thenoyltrifluoroacetone and tributylphosphate [49]. Apparently the zinc in the extracted species is pentacoordinated by oxygen atoms [49]. The synergistic effect of a number of Lewis bases on the extraction of cadmium by thenoyltrifluoroacetone into benzene relates directly to the strength of the Lewis base [50]. The mixed ligand complex $Zn(acac)L.nH_2O$ (L = 1-nitroso-2-naphthol) is thought to be octahedral [51]. The crystal structure of $ZnL(H_2O)_2$ (L = 4-oxoheptandioate) shows the zinc to be in a grossly distorted octahedral environment formed by two water molecules and four carboxylate oxygen atoms from two different carboxylate groups [52]. In $ZnL_2.2H_2O$ (HL = 1,2-dihydroxy-9,10-anthracenedione) the ligand coordinates to zinc by one hydroxy and one carbonyl oxygen to form a six membered chelate ring [53]. The crystal structure of $ZnL_2(EtOH)_2$ (L = 1,3-bis(2-hydroxyphenyl)-1,3-propandionate) shows a distorted octahedral O_6 environment about zinc formed from two bidentate ligands and two coordinated ethanol molecules [54].

It was suggested that ML(OAc) complexes (M = Zn, Cd; L = 2-methyl-3-aminoquinazoline-4-one) are tetrahedral with the ligand coordinating through the oxygen of the amido carbonyl and nitrogen from the amino nitrogen [55, 56]. The complex $ZnL_2(H_2O)_2$ (where LH is (1)) has been reported [57]. Several cyclic hydroxamic acid complexes with zinc have been prepared [58]. Several complexes of 3-amino-2-acetylbenzofuran have been prepared and described [59, 60] as have complexes of 1,2-bis(phenylsulphinyl)ethane [61]. The crystal structure of $CdL_3(NO_3)_2$ (where L is (2)) shows a slightly distorted pentagonal bipyramidal environment about cadmium formed by two bidentate nitrate groups and the exocyclic oxygens of these ligands [62]. The related zinc complex $ZnL_2(NO_3)_2$ is tetrahedral with monodentate nitrate groups [63].



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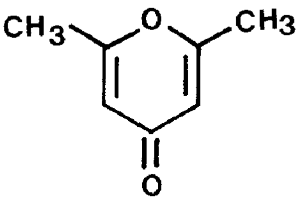

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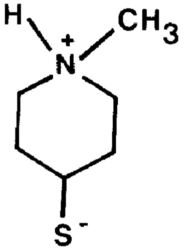
Zinc(II) triflate reacts with a number of phosphineoxide derivatives to give adducts, some of which contain coordinated triflate [64]. A number of dimethylphosphineoxide adducts of cadmium halides have been described [65]. The structure of $Cd[(EtO)_2PO_2]_2$ is polymeric with the cadmium atom in a highly distorted octahedral environment [66]. There are two further, long, interactions to oxygen atoms. A detailed study of the equilibria in aqueous medium of the system zinc(II)-pyridoxal 5'-phosphate-2-amino-3-phosphonopropionic acid has been reported [67]. Isomeric equilibria in aqueous solution have been proposed for zinc and cadmium complexes with adenosine-5-triphosphate [68]. In contrast, the analogous cytidine-5-triphosphate complexes appear to exist only in the phosphate coordinated form [68]. Crystal structures of cadmium complexes with uridine-5'-monophosphate and with 2'-deoxyuridine-5'-monophosphate show coordination of only phosphate to the metal [69]. The structure of $[CdL_2(H_2O)_2]_n$ (L = isonicotinate N-oxide) is polymeric with an octahedral O_6

environment about cadmium [70]. A polymeric structure has been proposed for zinc(II)bis(2-ethylhexyl)phosphate [71].

3.3 COMPLEXES WITH SULPHUR DONOR LIGANDS

Observation of $^{2}J(^{113}\mathrm{Cd}\text{-}\mathrm{S}\text{-}^{111}\mathrm{Cd})$ nuclear spin-spin coupling in $[\mathrm{Cd}_4(\mathrm{SPh})_{10}]^{2-}$ shows that the $[\mathrm{Cd}_4]$ core remains intact on the NMR time scale under conditions where rapid exchange of bridging and terminal thiolate groups is known to occur [72]. The crystal structures of $[\mathrm{E}_4\mathrm{M}_{10}(\mathrm{SPh})_{16}]^{4-}$ (E = S, Se; M = Zn, Cd) show molecular super tetrahedral fragments of the cubic metal chalcogenide lattice [73]. The crystal structure of $[\mathrm{Cd}_{10}(\mathrm{SCH_2CH_2OH})_{16}]^{4+}$, as the perchlorate salt, has appeared and solid state cadmium-113 resonances assigned to $[\mathrm{CdS_3O_3}]$, $[\mathrm{CdS_4O}]$ and $[\mathrm{CdS_4}]$ sites within the molecule [74]. In dmf solution at temperatures above -40 °C a single exchange average cadmium-113 resonance is seen for the $[\mathrm{CdS_4O}]$ and $[\mathrm{CdS_4}]$ sites [74]. Solution studies of polynuclear complexes of the Zwitterionic ligand 1-methyl-4-mercaptopiperidine with cadmium continue with the existence of two "core and link" series $\mathrm{Cd}[\mathrm{Cd(HA)_3}]_n^{(2n+2)+}$ and $(\mathrm{HA})_2[\mathrm{Cd(HA)_2}]_n^{2+}$ (HA is (3)) having been established [75]. Dimeric structures have been proposed for zinc and cadmium complexes 1-methyl-4,4-dimercaptopiperidine (4) [76]. A polarographic study of mixed ligand complexes of cadmium with glutamate and thiourea has been reported [77]. Complexes $\mathrm{ML_2Cl_2}$ (M = Zn, Cd; L = pyridyl-2-thiourea) are monomeric with coordination of L through the pyridine nitrogen and thione sulphur atoms [78]. The fungitoxicity of $\mathrm{M(HL)Cl_2}$ (M = Zn, Cd; LH = 1-phenyl-3-thiobenzoylthiourea) complexes has been assessed [79].



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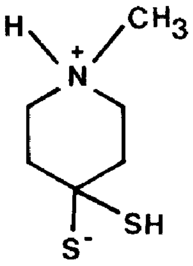
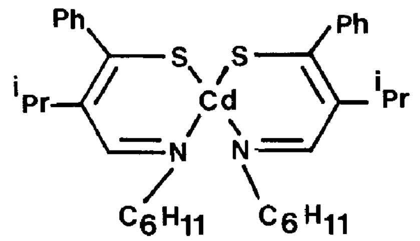


(4)

Energies of the zinc *3d* electrons in $\mathrm{Zn[S_2CNEt_2]_2}$ have been determined from XPS spectra [80]. The ligand ethyl N-phenyldithiocarbamate reportedly behaves as a monodentate through thiocarbonyl sulphur in its zinc and cadmium complexes [81]. The synthesis and characterisation of $\mathrm{ML_2}$ (M = Zn, Cd; HL = N-(chlorophenyl)dithiocarbamic acid) have been described [82]. A number of 1:1

Lewis base adducts of ZnL_2 (HL = bis(2-hydroxyethyl)dithiocarbamic acid) are thought to be five coordinate [83]. Zinc and cadmium complexes of morpholine-4-carbodithioic acid are polymeric [84]. A zinc complex of tetrathiooxalate contains bridging $C_2S_4^{2-}$ ligands [85].

Some tetrahedral complexes of 1,1-dicyanoethylene-2,2-dithiol have been described [86]. Zinc and cadmium complexes of a variety of substituted thioacetamides have been reported [87, 88] and these are probably bonded through nitrogen and sulphur as are complexes with ethoxythiocarbonyl hydrazide [89]. Cadmium-113 NMR studies of (5) and (6) show intermolecular ligand exchange via a mechanism which involves a five coordinated cadmium in a dimer intermediate [90].



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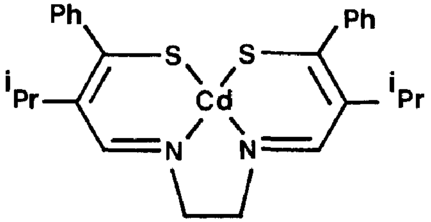


(6)

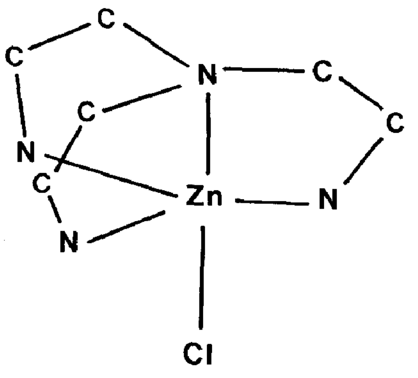
Zinc is tetrahedrally coordinated by two sulphur atoms and two nitrogen atoms in its complex with 2-propyl-8-mercaptoquinolinate [91]. The ligand benzimidazole-2-thiocarboxyarylamide is thought to coordinate to zinc by imadazole nitrogen and sulphur atoms [92]. The ligand pyrimidine-2-thione coordinates to zinc and cadmium solely through sulphur [93].

3.4 COMPLEXES WITH NITROGEN DONOR LIGANDS

3.4.1 Amines

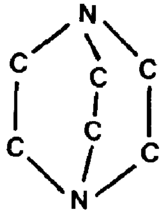
The X-ray structue of 4-chloropyridineaminecadmiumtetracyanonickelate shows a polymer in which $[Ni(CN)_4]^{2-}$ ions are coordinated to cadmium and chloropyridine and ammonia molecules are in *trans* positions [94]. Zinc is in a distorted octahedral environment in $[Zn(en)_3]^{2+}$ [95]. Complexes $K_2[ZnL_2]$ and $K_2[CdL_2(H_2O)_2]$ (LH = bis(*o*-aminobenzenesulphonyl)ethylenediamine) have been reported [96]. A polarographic study of mixed ligand complexes of cadmium with N-(2-hydroxyethyl)ethylenediamine and some amino acids has been described [97]. Some triethanolamine adducts with zinc salts contain nitrogen and oxygen bonded ligand [98]. The Cd(II)-diethylenetriaminepentaacetic acid-tartaric acid system has been examined by polarography [99]. An X-ray diffraction study of aqueous

$[Zn(tren)Cl]^+$ indicates a trigonal bipyramidal environment, similar to that found in the solid state, about zinc (7) [100].



(7)

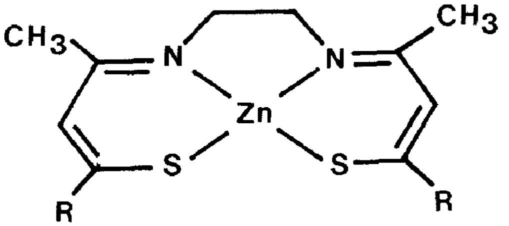
A potentiometric study of the formation of cadmium complexes with en and 1,2-pn shows the formation of 1:1 and 1:2 complexes but not 1:3 complexes [101]. Stability constants for the interactions of Cd^{2+} with N-(2-hydroxy-1-naphthalidene)-4-carbomethoxyaniline have been determined potentiometrically [102]. The crystal structure of $[Zn(en)_3]^{2+}$ shows the zinc to be in an approximate octahedral N_6 environment [103]. Complexes $[Zn(dmpd)Cl_2]$, $[Zn(dmpd)Br_2]$ (dmpd = 2,2-dimethylpropane-1,3-diamine) are isostructural with the zinc tetrahedrally coordinated by two halogen and two nitrogen atoms whereas $[Cd(dmpd)Br_2]$ is octahedrally coordinated by two nitrogen atoms, two terminal and two bridging bromine atoms [104]. Formation constants of mixed ligand complexes of cadmium with en and amino acids determined and discussed in relation to the sp^3 orbitals of cadmium [105]. The structure of $[ZnL_2(NH_3)_2]$ (L = 2-sulphanilidamidopyrimidinate) shows the zinc to be in a distorted tetrahedral N_4 environment [106]. The structure of $[CdL(H_2O)(NO_3)_3]$ where L is (8) shows a hexagonal bipyramidal O_7N environment about cadmium [107]. Complex formation between Cd^{2+} and mercaptoethylamine has been studied potentiometrically [108].



(8)

3.4.2 Schiff bases, hydrazones and oximes

Formation constants of zinc and cadmium complexes with the tridentate Schiff base 2-[(1H-benzimidazol-2-ylmethylene)amino]-4-chlorophenol have been determined [109]. Schiff bases derived from 2-benzoylpyridine and benzoylhydrazine or salicyloylhydrazine act as *NNO* donors towards zinc and cadmium [110]. A large number of tridentate and tetradentate Schiff base complexes have been synthesised and characterised [111-121]. Kinetics of metal exchange of the complex (9) (R = CH_3, CF_3, Ph, 4-Cl-Ph, 4-Br-Ph, 4-Me-Ph) have been studied [122].



(9)

The crystal structure determination of ZnL_2 (LH = pyridine-2-carbaldehyde salicyloylhydrazone) shows L to behave as a tridentate with coordination through carbonyl oxygen and azomethine nitrogen atoms resulting in a distorted octahedral environment about zinc [123]. Zinc(II) ions promote the formation of Schiff base between 2-formylpyridine and amino acids in neutral aqueous solution [124]. Tetrahedral complexes have been reported with the Schiff bases derived from benzoin and *m*-phenylenediamine or *o*-aminophenyl [125]. A series of complexes with chromone-3-aldehyde and acetylhydrazone have been prepared in which the ligand acts as a bidentate [126]. A variety of hydrazone derivatives have been used as ligands, with coordination usually through azomethine nitrogen atoms [127-131]. Hydrazones with pyridine or substituted pyridine residues coordinate to zinc through the pyridine ring nitrogen [132].

Zinc and cadmium complexes with vanillin thiosemicarbazone have been synthesised and characterised [133]. Benzalacetone thiosemicarbazone complexes of zinc and cadmium contain the ligand as a bidentate with coordination through azomethine nitrogen and thiocarbonyl sulphur [134]. The compound ZnL_2 (LH = 1,2-benzoquinone dioxime) contains bidentate ligands coordinating through nitrogen atoms [135]. A series of complexes of substituted hydroxamic acid are thought to be polymeric [136]. The crystal structure of tris(ethylenediamine)cadmium(II)dibenzohydroxamate shows an octahedral N_6 environment about cadmium from en and anionic benzohydroxamate [137].

Mononuclear complexes $M(LH_2)$ (M = Zn, Cd; LH_4 = benzene-1,2-bis(aminoglyoxime) have been synthesised [138].

3.4.3 Hydrazides and related compounds

Vibrational spectra of $Zn(ox)N_2H_4.xH_2O$ show only the presence of free and weakly bound NH_2 groups indicating that only a part of the hydrazine molecule is of a bridging type and that the rest is monodentate bound by weak hydrogen bonds to oxalate [139]. The complexes $[M(N_2H_4)_2(NCS)_2]$ (M = Zn, Cd) have a distorted octahedral environment about the metal with the hydrazine bridging to two metal centres [140]. Mixed ligand complexes with hydrazine and ox have been prepared [141]. The thiocyanate in $Cd(HL)_2(NCS)_2$ (HL = phenoxyacetylhydrazine) is *N*-bonded whereas the chloride in $Cd(HL)_2Cl_2$ is outer-sphere; in both cases the ligand, LH, is thought to be bidentate through the amino nitrogen and carbonyl oxygen atoms [142]. Complexes $ML_3(S_2O_6)$ (M = Zn, Cd; L = cyanoacetylhydrazine) are octahedral with bidentate L and outer-sphere $[S_2O_6]^{2-}$ [143]. Similar observations are reported for the complexes $ML_3(S_2O_6)$ (L = enanthic acid hydrazide) [144]. The synthesis of some zinc and cadmium complexes with furan-2-carboxylic acid salicylidenehydrazide have been described [145]. Some zinc complexes of *l*-tyrosine hydrazide have been prepared and screened for antifungal activity [146]. The compound ZnL, where H_2L is (10) is polymeric with tetradentate and bridging L [147]. The complex CdL_2 (HL = 1-benzoyl-4-phenyl-3-thiocarbazide) probably contains cadmium in a tetrahedral O_2N_2 environment [148].

(10)

$$\mathrm{EtO{-}\underset{\underset{S}{\|}}{C}{-}NHNH{-}\underset{\underset{E}{\|}}{C}{-}OEt}$$

E = O,S

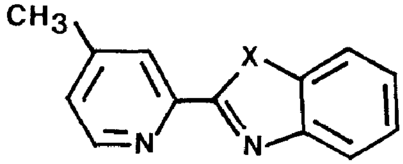
3.4.4 Amino acids

A nitrogen-15 NMR study of zinc cysteine complexes suggests that deprotonation of the cysteine amine does result in coordination to zinc [149]. Stability constants for a variety of zinc and cadmium complexes with 5'-biphosphates of adenosine and cytidine have been determined and compared [150]. The thermodynamics of mixed complexes of zinc with adenosine 5'-triphosphate, (ATP), *l*-histidine or histamine (hm), have been investigated and show the presence of ligand-ligand interactions in the complex $[Zn(ATP)(hm)]^{2-}$ [151]. Complex formation between zinc and asparagine and aspartic acid in aqueous solution has been studied potentiometrically [152] as has complexation with cyclo-*l*-histidyl-*l*-methionine [153]. Formation constants for mixed ligand complexes of zinc with aspartic acid and uracil or thyamine show stronger interactions with thyamine [154]. The stereochemistry and tautomeric equilibria of zinc complexes of the condensation products between (IR)-3-hydroxymethylenebornan-2-one and a series of *l*-amino acids have been studied [155]. Potentiometric studies of zinc and cadmium complexes with glycyl-*l*-histidine have been reported [156]. Equilibria studies of complex formation between zinc and cadmium with a variety of amino acids have been described [157-160].

3.4.5 Heterocycles

The 1:1 adducts between ZnL_2 (HL = chloroacetoanilide) and py or substituted pyridines are thought to be square pyramidal [161]. Five coordination is also proposed for py and substituted pyridine adducts of ZnL (LH_2 = $H_2NC(S)NH_2$) [162]. Mixed coordination complexes of zinc and cadmium acetates with aminopyridines have been prepared [163]. Pyridine adducts of $(NCS)_2Zn(NCSHgR)_2$ (R = pentyl, neopentyl) [164]. Three coordination has been proposed for py, 4-Mepy and 4-^{t}Bupy adducts of $Cd[N(SiMe_3)_2]$ [165]. The saccharinate complexes $[M(C_7H_4NO_3S)_2(H_2O)_4]$ (M = Zn, Cd) are isostructural with the metal in octahedral O_4N_2 environments [166-168].

The structure of $ZnCl_2L_2$ (L = 1-methylcytosine) shows a tetrahedral Cl_2N_2 environment about zinc [169]. The zinc complexes $ZnCl_2L$, where L is **(11)** , are tetrahedral with terminal chloride whereas the corresponding cadmium complexes are polymeric and octahedral with bridging halide; the ligands all act as bidentates through the nitrogen atoms [170].

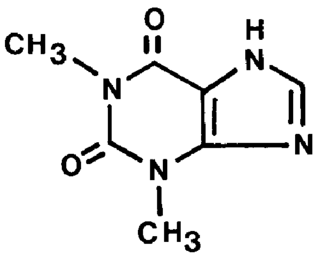
(11) 

X = NH_2, S, O

A variety of studies involving adduct formation with bipy and phen have appeared [171-176] including the crystal structure of $ZnCl_2$bipy [177]. Solid state and solution cadmium-113 NMR data for a series of complexes $CdX_2(bipy)_2$ (X = Cl, Br, NCS, NO_3) have been reported [178]. The structure of $Cd(NO_3)_2(bipy)_2.H_2O$ consists of two crystallographically and chemically different cadmium species separated by van der Waals distances. Although both cadmiums are in an approximate octahedral N_4O_2 environment, the coordinated oxygen atoms are from one nitrate oxygen and a water of hydration in one case whilst both oxygens are from nitrates in the other case [178]. The structure of $Cd(NCS)_2(bipy)_2$ contains the metal in an octahedral N_6 environment [178]. The compound $Zn(NCSe)_2$terpy is believed to be five coordinate with the selenocyanate bonded through nitrogen [179].

An imidazolate bridged zinc(II)-copper(II) complex has been synthesised and a polarographic study shows that the presence of zinc(II) increases the electron accepting ability of the copper(II) [180]. Zn^{2+} catalyses the decomposition of a tris(imidazol-2-yl)phine which involves oxidation of the phosphine and replacement of an imidazole by a hydroxide [181]. The crystal structure of [bis(4,5-diisopropylimidazol-2-yl)phosphinic acid]dichlorozinc hydrate shows a highly distorted tetrahedral $NOCl_2$ environment about zinc [181]. Zinc complexes with some bidentate ligands involving pseudo imidazole functional groups have been described [182]. NMR data for the formation of 1:1 adducts of 5-(1,2,5-dithiazepan-5-ylmethylene)-4-methyl-2-ethylimidazole have been reported; the structure of the adduct with $CdBr_2$ shows the ligand to act as a bidentate donor through the nitrogen atoms [183]. The crystal structure of $ZnCl_2L_2$ (L = 3,5-dimethylpyrazole) shows a tetrahedral N_2Cl_2 environment about zinc [184]. The structure of $CdCl_2L_2$ (L = benzotriazole) shows bridging N_2Cl_4 chlorine atoms resulting in polymer formation in which cadmium is in a environment [185]. The synthesis of a number of substituted imidazole complexes of zinc and cadmium have been described [186-189].

The complex $ZnCl_2L_2$ (L = 6-hydroxy-2,4-bis(isopropylamino)-1,3,5-triazine) is thought to be tetrahedral with the ligand L acting as a monodentate donor [190]. The ligand 3-amino-1,2,4-triazole behaves as a bridging bidentate donor in its 1:1 adduct with $CdCl_2$ [191]. Monoquarternised diaza-heterocyclic cations have been reacted with $ZnCl_2$ and $ZnBr_2$ [192]. The complex $CdL_2(OH_2)_4$ (HL = theophylline (**12**)) is octahedral with the cadmium in a N_2O_4 environment about zinc [193].



(12)

Creatinine forms 1:2 adducts with a series of zinc and cadmium halides in which cyclic nitrogen donor ligands are coordinated [194]. Thermodynamic parameters for complexation of inosine with zinc have been reported [195]. The crystal structure of $ZnL_2(OH_2)_4$ (L = nicotinate) at -120 °C shows an octahedral

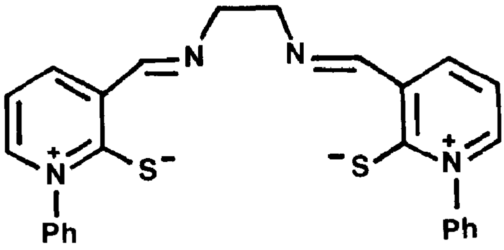
N_2O_4 environment about zinc [196]. Transmetallation reactions involving a substituted nicotinamide ligand proceed via a five coordinated intermediate [197].

3.5 COMPLEXES WITH PHOSPHORUS, ARSENIC AND CARBON DONOR LIGANDS

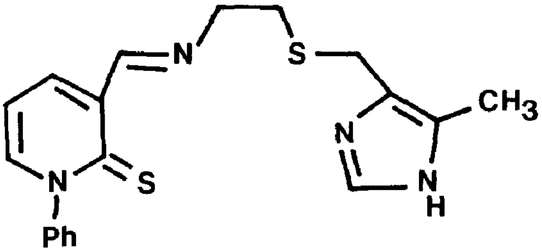
The crystal structure of $CdI_4Hg(PPr_3)_2$ shows a planar [CdI_2Hg] ring with both phosphines coordinated to mercury [198]. Phosphorus-31 and cadmium-113 NMR spectroscopy were used to study adduct formation of cadmium halides with dicyclohexylphosphine [199]. Reactions of the ligand dicyclohexylphosphino-*N*-phenyl(thioformamide) were investigated and suggest this ligand usually behaves as a simple phosphorus donor [199]. The crystal structure of $[Cd(CF_3COO)_2PPh_3]_2$ shows dimeric molecules in which two cadmium atoms are bridged by the four carboxylate ligands [200]. Some zinc and cadmium complexes with tertiary arsines have been described [201]. NMR studies suggest that complexes ML_2 and MLX (M = Zn, Cd; L = 2-[(dimethylamino)methyl]phenyl), which may be prepared from reaction of MCl_2 with LiL or by direct electrochemical oxidation, contain the ligand coordinated essentially through carbon [202]. The synthesis and structure of a zinc-alkyl caged cobalt(III) derivative in which the zinc-carbon bond appears extraordinarily stable, have been reported [203]. Some new cp complexes of cadmium have been described [204]. Reaction of cp_2NbH_3 with $Zncp_2$ gives the three compounds $Zn(cp_2NbH_2)_2$, $cp_2NbH(Zncp)_2$ and cp_2NbH_2Zncp with the crystal structure of the last having been determined [205]. Analogous reactions between $Zncp_2$ and $(Me\text{-}cp)_2TaH_3$ lead to isolation of the series $[(Me\text{-}cp)_2TaH_2]_2Zn$, $(Me\text{-}cp)_2TaH_2Zncp$ and $(Me\text{-}cp)_2TaH(Zncp)_2$, the last of which exists as two isomers [206]. A series of ylide-metal complexes derived from $(Me_3N)_3P{:}CH_2$ have been described [207].

3.6 MACROCYCLIC COMPLEXES

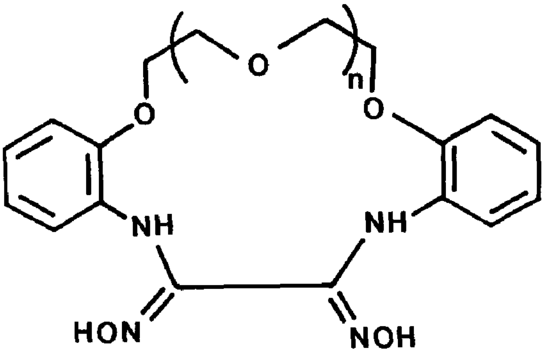
Complexes of **(13)** and **(14)** containing *N_2SS'* ligand donor sets have been synthesised and studied as models for "blue" copper proteins [208]. The ligand **(15)** in $M(OH)_2L$ (M = Zn, Cd) coordinates through the two oxine nitrogen atoms [209]. The crystal structure of a hexamethylenetetramine complex of $CdCl_2$ has been described [210]. Carbon-13 NMR shows that $[ZnL^1][NO_3]_2$ (L^1 is R = $CH_2CH_2NMe_2$ in **(16)**) is asymmetric, $[ZnL^2][NO_3]_2$ (L^2 is **(17)**) is symmetric whereas $[ZnL^3][NO_3]_2$ (L^3 is R = Me in **(16)**) exists as a 1:2 mixture of symmetric and asymmetric species [211]. The crystal structure of $[Cd[16]aneN_4(NO_3)(H_2O)]NO_3.H_2O$ shows cadmium to be in an approximately octahedral *N_4O_2* environment [212] whereas in $[CdL(NO_3)_2][Cd(NO_3)_4]$ (L is **(18)**) the cation contains cadmium in a trigonal bipyramidal environment whilst the



(13)

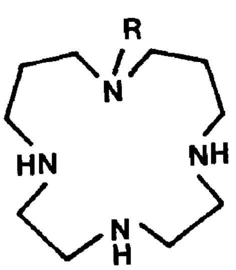


(14)

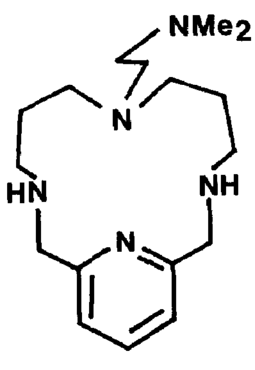


(15)

n = 1, 2, 3

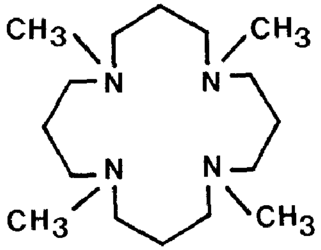


(16)



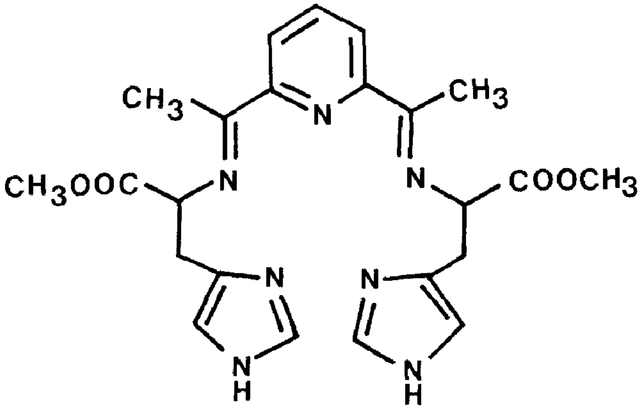
(17)

anion contains the metal in a dodecahedral geometry [213].



(18)

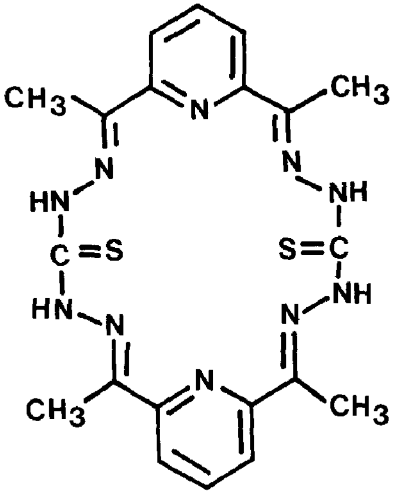
The cadmium in $CdCl_2$[18-crown-6] is in a hexagonal bipyramidal O_6Cl_2 environment [214]. Adducts of dibenzo-18-crown-6 with CdX_2 (X = Cl, Br, I, CN, SCN) have been prepared [215]. The crystal structure of $[Zn(\mathit{l}\text{-bisp})][ClO_4]_2$ (*l*-bisp is (**19**)) shows the zinc in an environment intermediate between trigonal bipyramidal and square pyramidal [216].



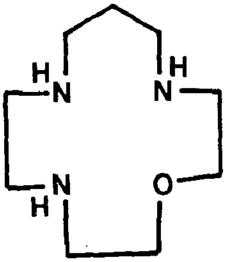
(19)

A five coordinated zinc complex of iminobisbenzaldehyde amine has been described [217]. A series of macrocyclic complexes of (20) have been synthesised [218]. The stability constant for formation of a zinc complex with (21) has been compared with those of related macrocycles [219]. Zinc complexes with the *ONNO* tetradentate ligand N,N'-bis(acetoacetanilide)-1,3-diaminopropane have been prepared and characterised [220] as has a zinc complex with 2,9-dimethyl-3,10-diphenyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene [221]. Solution studies of a substituted phthalocyanine zinc complex have been described [222].

A variety of porphyrin and substituted porphyrin complexes have been synthesised and investigated [223-229]. Some interesting applications of the zinc complex with $TPPH_2$ as a diamagnetic shift reagent have been described [230].



(20)



(21)

An NMR study of zinc complexes of some capped porphyrins has been reported [231]. Intramolecular coordination between the nitrogen of the cap and the central metal ion in 4,4'-bipy capped zinc porphyrins forces the porphyrin and 4,4'-bipy groups to be perpendicular [232]. The crystal structure of chloro(*N*-phenyl-5,10,15,20-tetraphenylphorphinato)zinc(II) shows the zinc to be displaced out of the N_4 plane and towards the chlorine [233].

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