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4. 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 102 and 103 of Chemical Abstracts. Zinc and cadmium are treated together and, as was the case last year [1], much of the reported chemistry is routine and has not been reported in detail. Rigorous classification of ligands continues to be a difficulty for compounds containing several different potential donor atoms and the reader may need to refer to more than one section. Although the scope of this review does not encompass bio-inorganic in general, some more interesting aspects of applications of ^{113}Cd probes for biological systems have been included this year.

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4.1 HALIDE AND PSEUDOHALIDE COMPLEXES

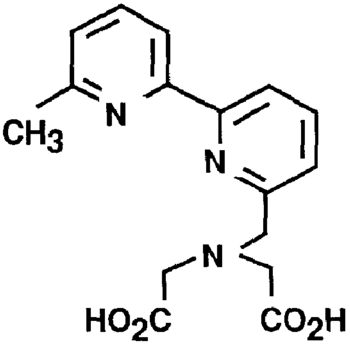
X-ray scattering measurements, Raman and infrared spectroscopy were used to investigate zinc bromide complexes in aqueous solution [2]. The highest bromide complex is $ZnBr_4^{2-}$ which is tetrahedral. $ZnBr_3^-$ is pyramidal and there is no evidence for the presence of Zn-Br-Zn bridging in the solutions studied. Potentiometric titrations were used to study formation of halide complexes of Cd in dmf and polycarbonate solutions [3]. The differences in the order of stability among the halide ions in non-aqueous solvents and water depend mainly on enthalpy changes. Cadmium-113 NMR chemical shifts of cadmium iodide complexes in supercooled aqueous solutions were measured [4] and resonances assigned to the following species in order of decreased shielding $CdI_3^- < CdI_4^{2-} < CdI_2 < CdI^+ < Cd^{2+}$. The Cd atom in solid $BaCdCl_4.4H_2O$ is octahedrally coordinated to six Cl atoms in edge-sharing $CdCl_6$ octahedra [5]. The complex *catena* -poly[(1,3 -thiazolidine-2-thionecadmium)-μ-chloro-μ_3-chloro], $[CdCl_2(C_3H_5NS_2)]_n$, is polymeric in the solid state with octahedrally coordinated Cd linked into infinite chains by double chloride bridges to give a Cl_5S environment about each Cd atom [6]. The complex $CdZn(NCS)_4$ is isomorphous to $CdHg(NCS)_4$ but with exchanged metal positions, consisting of tetrahedral $Cd(SCN)_4$ and $Zn(NCS)_4$ groups [7].

4.2 COMPLEXES WITH OXYGEN DONOR LIGANDS

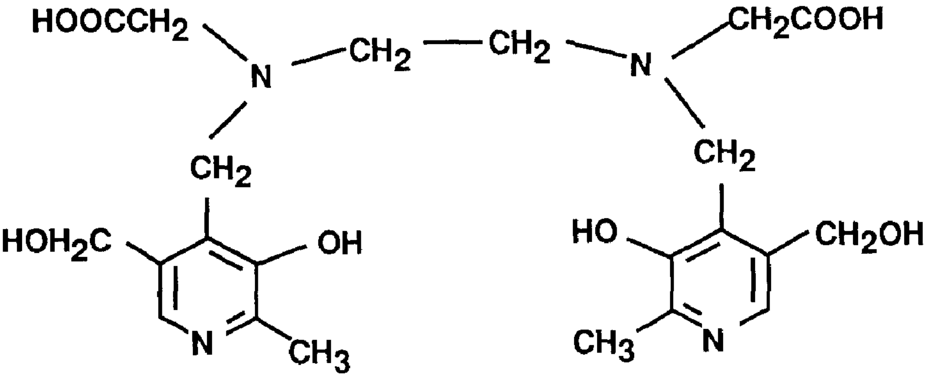
4.2.1 *Carboxylic acids and other related ligands*

A review of the sterochemistry of metal double-formates, including those of Cd, has appeared [8]. The crystal structure of Zn(II) 2-formylphenoxyacetate shows Zn in an octahedral O_6 environment formed by four water molecules, and two *trans* monodentate acetates from the ligand [9]. The structure of the zinc-tartrate complex $[Zn_2(C_4H_4O_6)_2(H_2O)_2].3H_2O$ consists of cyclic double chelates which are linked by additional coordination of each Zn to a carboxyl O of an adjacent group [10]. The stability of heterobinuclear complexes of Cd-citrate with some bivalent metal ions were determined and the existence of mixed-metal complexes discussed in connection with transport and absorption of metal ions in biological systems [11]. The complex $Zn(H_2L)_2$ (where H_3L is γ- (3-carboxy-4-hydroxybenzoyl)butanoic acid) is reportedly tetrahedral with coordination from both aromatic carboxylic and phenolic oxygen atoms [12]. Stability constants for $Zn(phen)L^+$ (where L^- = a variety of carboxylates) have been determined [13, 14]. Solution and solid state ^{113}Cd NMR data have been measured for the complexes diaquobis(p-chlorobenzoato)cadmium(II), diaquobis(*p* -nitrobenzoato)cadmium(II), and aquabis(*p* -chlorobenzoata)bis(pyridine)cadmium(II) [15]. The first two complexes have structures intermediate between octahedral and trigonal prismatric geometries whereas the last complex has a seven coordinate pentagonal bipyramidal geometry. The compounds $ZnL_2(H_2O)_4$ (where HL = 2, 4-hydroxybenzoic or 2, 5-dihydroxybenzoic acid) are octahedral with *trans* monodentate carboxylates [16, 17]. Zinc phenoxyisobutyrate is a one dimensional polymer based on a pentameric $[Zn_5L_{10}(H_2O)_2]$ unit [18]. The ligand (**1**) forms remarkably stable complexes with both Zn^{2+} and Cd^{2+} [19].

(1)



A complex $ZnL(H_2O)_2$ has been synthesised and described (where L^{2-} is pyridine-2,6-dicarboxylate N-oxide) [20]. A number of mixed-ligand complexes which are Lewis-base adducts of of zinc carboxylates have been described [21, 22]. The complex $[Zn(2\text{-}NPA)_2(H_2O)_2]$ (where 2-NPA is 2-nitrophenoxyethanoic acid) is polymeric in the solid state with the Zn atom in an octahedral O_6 environment [23]. The crystal structure of $CdL(H_2O)_2.2H_2O$ (where H_2L = thiosemicarbazidediacetic acid) shows a dimer in which the Cd atoms are seven coordinated [24]. In ZnH_2L (where H_4L is (2)) the pyridine nitrogen atoms are not coordinated to the metal but remain protonated to moderately high pH and the complex is thought to have a O_4N_2 coordination about the Zn atom [25].



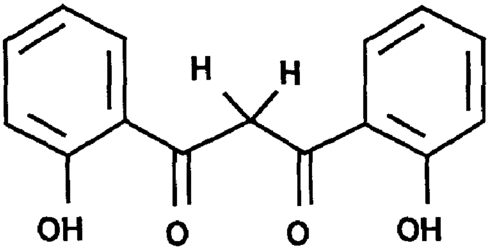
(2)

The crystal structure of *catena* -2, 2, 2-tetraaquo-μ-ethylenediaminetetraacetato-cadmium manganese dihydrate, $[Cd(C_{10}H_{12}N_2O_8)Mn(H_2O)_4]_n.2H_2O$, consists of finite chains of Mn and Cd coordination polyhedra in which the Cd atom is seven coordinate by coordination to four O and two N atoms of one EDTA and to an O atom of a second ligand [26]. Complexation with *o*-phenylenediamminetetraacetic acid has been studied both potentiometrically and spectrophotometrically [27]. A spectrophotometrical investigation of the Cd-EDTA-NH_3-H_2O system has also been described [28]. The crystal structure of hexaaquozincdisalicylatoborate tetrahydrate, $[Zn(H_2O)_6][(C_6H_4OCOO)_2B]_2.4H_2O$, shows the Zn to be in an octahedral environment from coordination to six water molecules [29]. A high yield synthesis of $Zn(HL)_2.4H_2O$ (where H_2L is *L*-ascorbic acid) has been described [30]. Formation constants for some mixed-ligand complexes of Zn with picolinic acid have been reported [31] and various substituted quinoline-2-carboxylic acids have been assessed for extraction of Zn^{2+} ions [32].

Phosphorus-31 and ^{13}C NMR spectroscopy indicate that the 2-(6-methylpyridyl)phosphonic acid complexes with Zn and Cd are similar in the solid state and in solution, with the ligand coordinating through the pyridyl nitrogen and the oxygen atom of the phosphonic group [33]. Cadmium forms three 1:1 complexes with ATP, each showing different degrees of ligand protonation [34]. The ^{113}Cd chemical shift tensor of Cd in $Cd[(EtO)_2PO_2]_2$ has been partially determined [35]. A series of tetradentate diammine-substituted phosphonic acid complexes of Zn and Cd are polymeric with coordination through phosphoryl O and amino N atoms [36].

4.2.2 Diketone and other ligands

The complex $Zn(H_2L)_2.2solv$ (where H_2L is **(3)**) has been used as intermediate for the synthesis of transition metal complexes of the same ligand [37].



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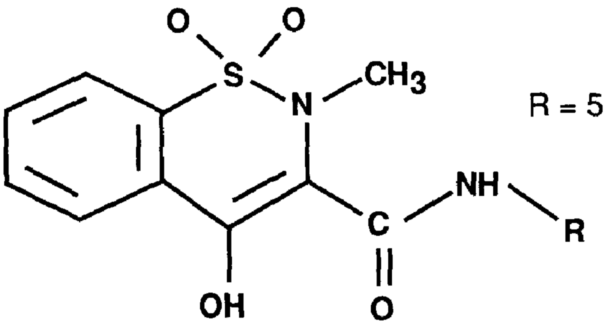
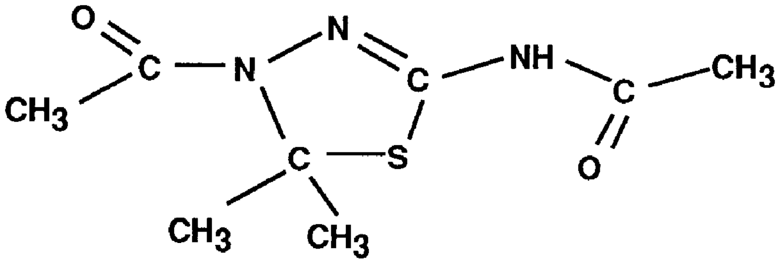


R = 5 - methyl -3 - isoxazolyl

(4)

The synthesis of $Zn(acac)_2L$ (where L is 2-, 3-, 4-pyridine- carboxylicacid hydrazide has been described [38] as has been synthesis of a Zn complex with the ligand isoxicam (4) [39]. The structures of the malonamide complexes $Zn(NCS)_2L_2$ and $Zn(NO_3)_2L_2$ are both *trans* octahedral with coordination from both carbonyl oxygen atoms and from N-bonded NCS and monodentate NO_3 respectively [40]. Zinc and Cd complexes with (5) are coordinated from the S and one carbonyl O atom [41] and have been tested on pathogenic fungi.



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4.3 COMPLEXES WITH SULPHUR DONOR LIGANDS

Coupling $^2J(^{113}Cd\text{-}S\text{-}^{111}Cd)$ is observed in the adamantoid cage complex $[Cd_4(SPh)_{10}]^{2-}$ even though there is rapid exchange of thiolate ligands [42]. This confirms that the exchange process is an intramolecular exchange of bridging and terminal thiolate ligands. A similar mechanism is proposed for the tetra-adamantanoid aggregate $[S_4Cd_{10}(SPh)_{16}]^{4-}$ [43]. The new and novel aggregate $[ClZn_8(SPh)_{16}]^-$ has a structure which contains a tetracapped tetrahedron of Zn atoms centred by the chloride ligand and bridged on the twelve edges by thiolate ligands, and with four terminal thiolate ligands [44]. Stepwise oxidative substitution reactions of $[Cd_4(EPh)_{10}]^{2-}$ (where E = S, Se) with I_2 and Br_2 lead to formation of $[Cd_4(EPh)_6X_4]^{2-}$ in high yield [45]. The series $[(\mu\text{-}SPh)_n(\mu\text{-}SePh)_{6-n}(CdX)_4]^{2-}$ (where X = Br, I) have been characterised by ^{113}Cd NMR spectroscopy [45]. The metal thiolate anions $[M_2(\mu\text{-}SEt)_2(SEt)_4]^{2-}$ (where M = Zn, Cd) consist of edge-shared tetrahedra in the solid state [46]. Use has been made of the easy oxidation of PhS^- ligands by S_x^0 in

$$[M(SPh)_4]^{2-} + 2S_x^0 \rightarrow [M(S_x)_2]^{2-} + 2PhSSPh$$

to synthesise $[Zn(S_4)_2]^{2-}$ which was subsequently characterised by its X-ray structure determination [47]. The crystal structure of the isotrithionedithiolate complex $[Zn(S_5C_3)_2]^{2-}$ shows the Zn atom in a distorted tetrahedral environment [48]. Some Zn and Cd complexes of isomaleonitriledithiolate have been described [49]. In the complex $[Cd(BCTA)_2I_2]$ (where BCTA is benzenecarbothioamide) coordination is from the two S atoms and two I atoms [50].

The synthesis of some mercaptopropylamine and mercaptopiperidine complexes of Zn and Cd have been described [51-53]. Mechanisms of the antioxidant action of zinc dialkyldithiocarbamate and zinc xanthate complexes have been investigated [54]. An electrochemical investigation of Cd(RR'dtc)$_2$ and Cd(RR'dsc)$_2$ (where dtc = dithiocarbamate and dsc = diselenocarbamate) show a series of reversible processes based on ligand exchange reactions [54]. The nature of these exchange reactions is also supported by ^{113}Cd NMR and mass spectroscopic studies [55]. The tris(diphenylthiophospinoyl)methanide complexes {[$R_2P(S)]_3C$}CdX (where R = Ph; X = Br, I) have been synthesised [56]. Ligand exchange in [M(TDSP)$_4$](ClO$_4$)$_2$ (where TDPS is tris(dimethylamino)phosphine sulphide; M = Zn, Cd) was examined by ^{31}P and ^{35}Cl NMR spectroscopy and the mechanism described as the interchange type [57]. The crystal structures of $Zn(NH_2C(O)C(S)O)_2.(H_2O)$ and $Zn(NH_2C(S)CO_2)_2.H_2O$ show the ligands coordinated by the O and S atoms to give five coordinated trigonal bipyramidal geometries about the Zn atom [58]. NMR spectroscopy was used to study some Zn and Cd halide complexes with 2-pyridinethione and 4-pyridinethione [59].

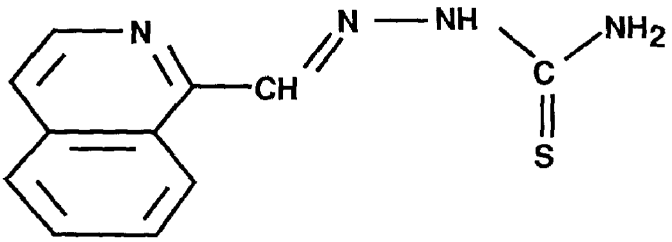
4.4 COMPLEXES WITH NITROGEN DONOR LIGANDS

4.4.1 Amines

Stability constants for Cd complexes with amines and pyridine were determined potentiometrically in dmso solution [60]. Stability constants for complex formation between Zn and 1, 2-ethanediammine were also reported [61]. Some Zn-ethylenendiammine complexes with iron carbonyl have been synthesised and their structures described [62]. The crystal structure of ZnI$_2$(*o*-Me$_2$N.C$_6$H$_4$.NMe$_2$) shows a tetrahedral environment about the Zn atom [63]. The crystal structure of the 1:2 ammonia adduct [Zn(N'-(2-pyrimidinyl)sulphanilamide)].2NH$_3$ shows coordination of one N from each ligand as well as from the two ammonia molecules to give a tetrahedral environment about the Zn atom [64].

4.4.2 Schiff bases, hydrazones, hydrazides and related compounds

The synthesis of Schiff base complexes of Zn and Cd continues unabated with most complexes thought to contain the metal in a tetrahedral environment [65-71]. In some instances the stability constants for new Schiff base complexes were reported [72]. Many new hydrazine and hydrazone complexes involving mainly routine synthesis were reported [73-84]. The crystal structure of the dimeric semicarbazide complex, $[ZnCl_2(NH_2NHCONH_2)]_2$, shows the semicarbazide ligand to act as a tridentate and the Zn atom to be in a distorted trigonal bipyramidal Cl_2O_2N environment [85]. Complexes ZnL(OH).H$_2$O and CdL$_2$ (where HL is thiosemicarbazide) contain the ligand as the imido-thiol tautomer [86]; in sulphatobis(thiosemicarbazide)Zn(II) the Zn atom is in a distorted square pyramidal environment [87]. The complex $Cd(NH_2CSNHNH_2)Cl_2.H_2O$ is polymeric in the solid state with the semicarbazide ligand bridging two Cd atoms and a bidentate S and Cl atom also forming bidentate bridges, the Cd atom is in a tetragonal pyramidal environment [88]. A Zn complex of the thiosemicarbazone derivative (6) has been synthesised and screened for anti-tumor activity [89].



(6)

The complexes Cd_2L (where L is 4-amino-1,6-dihydro-1-methyl-2-methylthio-5-nitroso-1,6-oxopyrimidine) and ZnX_2L' (where L' is bis(2-benzothiazolyl)disulphide) are thought to be tetrahedral [90, 91].

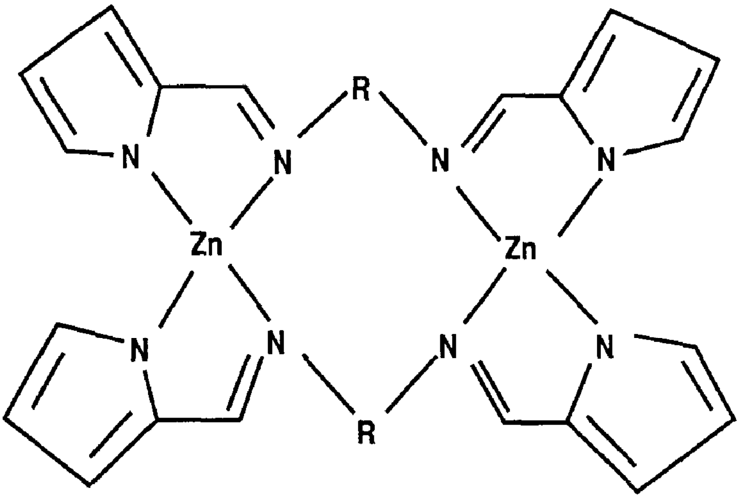
4.4.3 Amino acids and metalloproteins

An EXAFS study of Zn-glycinato complexes in aqueous solution show that the complex $Zn(gly)_2(H_2O)_2$ is octahedral [92]. X-ray diffraction studies on similar systems in aqueous solution show that the complexes $[Zn(gly)(H_2O)_4]^+$ and $[Zn(gly)_3]^-$ have regular octahedral structures [93]. Zn complexes with various glycine derivatives and mixed-ligand complexes with uracil have been reported [94, 95]. The crystal structure of $[ZnL_2(H_2O)_4]$ (where L is *N*-tosyl-β-alaninate) shows the Zn atom coordinated by two amino acid molecules, each through a carboxylic oxygen, and by four water molecules to give an approximate octahedral environment about the central metal atom [96]. Formation constants for Zn and Cd complexes with *N*-(2-mercaptopropionyl)glycine have been determined potentiometrically [97]. Proton NMR was used to study complexation of Zn by glycyl-L-histidyl-lysine and it was found that the ligand is tridentate with coordination by the deprotonated glycyl amino nitrogen, the deprotonated amide nitrogen atom of the glycyl-histidyl peptide bond, and the imidazole N atoms [98]. Binding sites for Zn by glycyl-*L*-histidine and *L*-alanyl-*L*-histidine were also investigated and it is suggested that complexes are N-bonded [99]. The use of 2D heteronuclear ^1H - ^{113}Cd and homonuclear ^{113}Cd - ^{113}Cd NMR spectroscopy continue to be powerful probes for the study of metalloproteins [100, 101]. Two metal clusters, one containing three Cd atoms and the other four Cd atoms, have been identified for a Cd-metallothionein from rabbit liver [102]. Solid Cd-metalloproteins have also been investigated by ^{113}Cd CPMAS spectra [103]. An ^{31}P spectroscopic investigation of Cd complexes of phosphorothiolates of guanosine nucleotides has been described [104].

4.4.4 Heterocycles

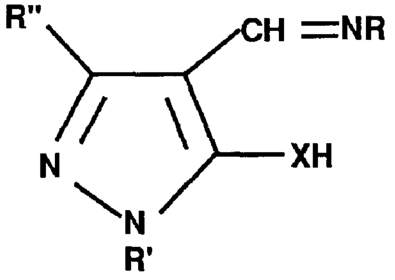
A crystal structure determination of $[CdI_2py_4].2py$ shows an octahedral environment about Cd provided by coordination from four py molecules and two *trans* iodine atoms; the remaining two py molecules are enclathrated [105]. The structure of $ZnL_2.2py$ (where L is monothiobenzoate) comprises a Zn atom in a distorted tetrahedral environment from two S and two N atoms [106]. A number of mixed-ligand complexes involving py, substituted pyridines, and acetoacetanilide or succinate have been described [107, 108]. A ^{113}Cd NMR spectroscopic study of py, bipy and *o*-phen adducts with $CdCl_2$ has appeared [109]. The crystal structure of bis(2-aminopyridine)zinc diiodide shows tetrahedral coordination from two iodine atoms and two ring N atoms [110]. Extraction rates of Zn and Cd into 1, 2 dichloroethane with 4, 7-diphenyl-1, 10-phen were studied [111]. Complexes ZnLL' (where HL is dipicolinic acid and L' is bipy, o-phen, or 2, 9-Me_2phen) were synthesised and are believed to be dimeric [112]. Stability constants for complex formation in the Cd-bipy-MeCN-MeOH system were determined conductiometrically [113]. A number of new quinoline and substituted quinolines complexes have been synthesised [114, 115]. The crystal structure of zinc 8-quinolinate is tetrameric with bridging O atoms of the ligands [116]. ZnL_2 (where L is 7-(methylthio)-8-mercaptoquinolinate) contains Zn in a tetrahedral environment of two mercapto S atoms and two quinoline N atoms [117]. A similar N_2S_2 environment about Zn is observed in the crystal structure of $ZnL_2.3H_2O$ (where L is 5-sulpho-8-mercaptoquinolinate) [118]. The complexes Cu_2ZnL_6, Cu_2CdL_6 and $[CuZnL_4]_2$ (where HL is 8-mercaptoquinoline) have been synthesised and are believed to contain bridging ligands [119]. A variety of new Zn and Cd complexes with the ligands *N*-(2-aminophenyl)pyridine-2'-carboxamide and *N*-(3-aminophenyl)pyridine-2'-carboxamide have been prepared and characterised by physiochemical techniques [120]. The complexes $ZnL_2(NH_3)_2$ and $CdL_2(NH_3).3H_2O$ (where HL is theophylline) contain the ligand coordinated through the N_7 atom [121]. The crystal structure of hexa(antipyrine)cadmium(II)perchlorate shows a regular octahedral structure [122]. The complex CdL_2Cl_2 (where L is tetrazole) has been synthesised and is monomeric [123].

The synthesis of some xanthine and adenine complexes with Zn have been described [124, 125]. The guanine complex $Zn(guH)Cl_2$ has been prepared and is thought to be polymeric with a single-bridged -(ZnguH)- backbone and two terminal chloro ligands per metal ion [126]. A vibrational spectroscopic study of $Zn(pyz)_2X_2$ and $Zn(pyz)X_2$ (where pyz is pyrazine and X is Cl or Br) has appeared [127]. Dimeric complexes (7) have been synthesised in which the Zn atom is tetrahedrally coordinated [128]. The ligand (2-pyridyl)phenylcarbinol (LH) forms complexes $ZnLH(L)ClO_4$ in which the Zn atom is thought to be octahedrally coordinated, one ligand remaining protonated [129].



(7)

Complexes ML_2 (M = Zn, Cd; HL is (**8**)) were prepared and a kinetic study using NMR spectroscopy undertaken to determine the activation and kinetic parameters for the inversion of configuration of the tetrahedral diastereomeric forms [130, 131].



X = O, Se
R = alkyl, aryl
R' = Ph, R" = ^{i}Pr

(8)

A series of five coordinated complexes derived from the ligand tris((3, 5-dimethylpyrazol-1-yl)methyl)amine have been synthesised in which the ligand acts as a tetradentate tripod [132]. The ligand *N*, *N*, *N′*-tris((3,5-dimethylpyrazol-1-yl)methyl)-1,3-diaminopropane acts as a pentadentate donor towards zinc [133]. The synthesis of $ZnL_2(ClO_4)_2.H_2O$, $ZnLCl_2$, and $ZnLSO_4.xH_2O$ (where L is 4-methoxy-2-(5-methoxy-3-methylpyrazol-1-yl)-6-methylpyrimidine have been described [134]. The crystal structure of $ZnL(NCS)_2$ (where L is 2-[bis-(2-benzimidazolylmethyl)amino]ethane) shows the Zn atom in a highly distorted trigonal bipyramidal environment where the alcoholic oxygen atom does not coordinate [135]. Formation constants for a series of Zn and Cd complexes with a series of substituted benzimidazoles have been reported [136]. The crystal structure of

$Cd(NO_3)_2L_2.H_2O$ (where L is 2-methylmercaptoaniline) shows that the Cd is in a trigonal bipyramidal SN_2O_2 environment formed by two oxygen atoms from different nitrate groups and from one of the ligands which contributes a N and a S atom whilst the other contributes only an aniline N atom [137].

4.5 COMPLEXES WITH PHOSPHORUS, CARBON AND OTHER METAL COMPLEXES AS DONOR LIGANDS

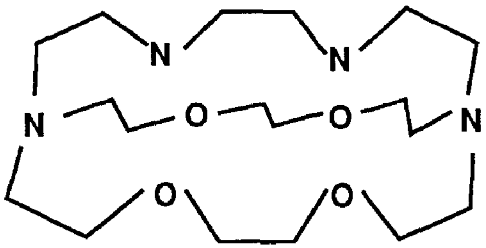
The synthesis and crystal structure of a rare example of a zinc complex containing a phosphorus ligand has been described [138]. High yield preparations of CF_3MX from the metal and CF_2X_2 (M = Zn, Cd; X = Cl, Br) have been detailed [139].

A number of reactions involving perfluoroorganocadmium compounds have been described [140, 141]. A series of new sulphonium ylide complexes of Cd were synthesised in which coordination occurs from the methine C atom, the sulphonium group apparently is not coordinated [142, 143]. Some new, thermally stable, complexes with methylenetriphenylarsorane have been synthesised [144]. Gas phase electron diffraction was used to determine the structure of some cyclic bis(methoxyalkyl)zinc compounds [145].

The X-ray structural analysis of the cluster compound $[(CO)_4CoZn]_2Co_2(CO)_7$ shows the molecule to consist of two $Co(CO)_3$ units, bridged by one CO ligand, and two $ZnCo(CO)_4$ groups; the Zn atom is in a trigonal planar Co_3 environment [146]. The compound $Zn[(CF_3)_3Ge]_2$ can be prepared in good yield from reaction between Ph_2Zn and $(CF_3)_3GeH$ in an appropriate solvent [147].

4.6 MACROCYCLIC COMPLEXES

The synthesis and characterisation of Zn complexes with tetraazacycloalkanes such as [14]-ane N_4 and [15]-ane N_4 have been described [148, 149]. These complexes, in alcoholic solution, readily and reversibly take up CO_2 to form monoalkyl carbonates. This process is apparently facilitated by addition of bases such as NaOR or Et_3N [148]. The crystal structures of $Zn(O_2COCH_3)([14]\text{-ane } N_4)(ClO_4)$, $\{[Zn(O_2COCH_3)([15]\text{-ane } N_4)]_3(O_2COCH_3)_2\}(ClO_4)$ and $[Zn(O_2COCH_3)(Me_4[14]\text{-ane } N_4)](ClO_4)$ have been determined [150]. The crystal structures of $Zn(NCS)_2([14]\text{-ane } N_4)$ and $Zn(NCS)_2([15]\text{-ane } N_4)$ are monomeric [151]. Stability constants for formation of Cd complexes with a series of tetraazamacrocycles were determined and discussed in terms of the macrocycle ring size [152]. Some new Zn complxes of N macrocycles were synthesised [153, 154]. Cadmium complexes with [18]-crown-6, and the ligands (9) were synthesised and studied using ^{113}Cd and ^{13}C NMR spectroscopy which show that the complexes are dynamically stable [155].



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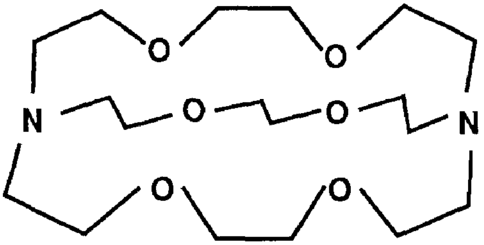

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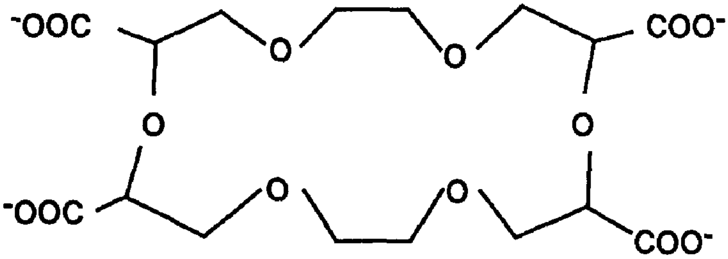

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The complexes Zn([15]-crown-5)$(ClO_4)_2$ contains one coordinated perchlorate group in inert solvents such as $MeNO_3$ [156]. The crystal structure of the phthalocyanine complex Zn(Pc)Cl has been determined [157]. Electrochemical reduction of Zn(Pc)$(CN)_8$ at a variety of electrodes indicates that only the ligand is electroactive [158]. The kinetics of tetraazophorphine complex formation with Zn and Cd in pyridine suggest a bimolecular mechanism for these reactions [159]. Base binding to a Zn complex of a gable porphyrin has been studied by NMR and electron spectroscopies [160]. Fluorescence spectroscopy was used to study the kinetics of Zn^{2+} and Cd^{2+} incorporation reactions into *meso* -tetraphenylporphyrin [161]. The crystal structure of bis(tetrahydrofuran)(5, 10, 15, 20, -tetraphenylporphinato)zinc(II) contains thf molecules which are weakly coordinated to the Zn atom [162]. The crystal structure of a piperidine adduct of (5, 10, 15, 20, -tetraphenylporphinato)cadmium(II) as its *o*-xylene solvate shows a five-coordinated Cd atom, with the *o*-xylene filling cavities between the molecules [163]. An electrochemical investigation of the Zn complex of tetrakis(3, 5-di-tert-butyl-4-hydroxyphenyl)porphine shows that this complex catalyses the two-electron reduction of dioxygen [164].

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