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Solid State Structures of Cadmium Complexes with Relevance for Biological Systems

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Contents

Abstract

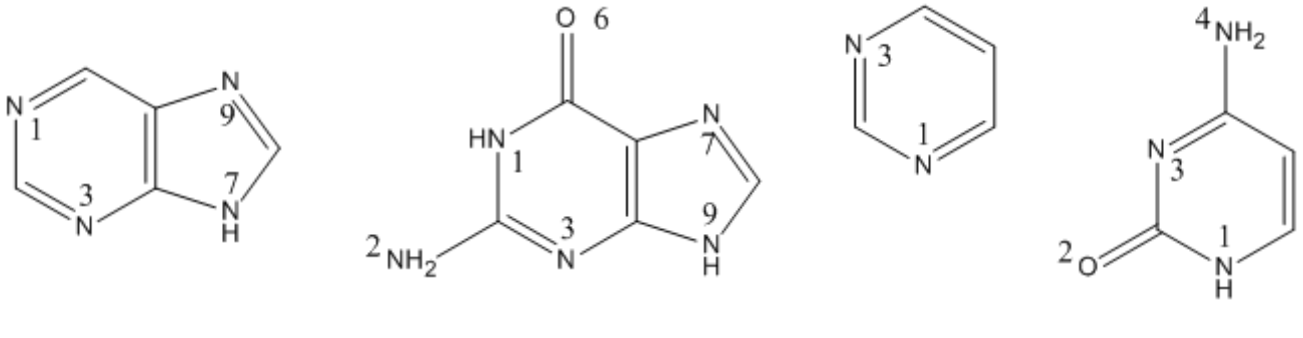
This chapter reviews the literature on structural information from crystal structures determined by X-ray diffractometry of cadmium(II) complexes containing ligands of potential biological interest. These ligands fall into three broad classes, (i) those containing N-donors such as purine or pyrimidine bases and derivatives of adenine, guanine or cytosine, (ii) those containing carboxylate groups such as α-amino acids, in particular the twenty essential ones, the water soluble vitamins (B-complex) or the polycarboxylates of EDTA-like ligands, (iii) and those S-donors such as thiols/thiolates or dithiocarbamates. For some representative complexes of these ligands, a crystal and molecular structural analysis has been made, specifically addressing the coordination mode of ligands, the coordination environment of cadmium and, in some significant cases, the intermolecular interactions.

Keywords: amino acids · cadmium complexes · crystal structures · nucleobases · thiolates· vitamins

1 Introduction

The biological interest of cadmium is based on the fact that its presence in a living being can seriously alter its metabolism, giving rise to episodes of acute or chronic intoxication, and therefore it has been classified among the toxic elements [1]. Although the molecular mechanism of the metal's toxicity is not known in detail, cadmium can be found in living beings as part of complexes with biochemical ligands and its toxic nature is due to coordination disrupting the biological functions of these ligands. With this in mind, the therapeutic strategies developed to favour detoxification processes – for both chronic intoxication as well as for acute diseases– are all based on the administration of external ligands which are able to successfully compete for the metal against the biological ligands, mobilising the cadmium and favouring elimination via one of the available excretion channels [2].

The stability of cadmium complexes varies depending on the types of ligands, and as the Cd^{2+} ion is considered a *soft* Lewis acid, it prefers easily oxidisable *soft ligands* [3], not dismissing its affinity for other ligands, above all when the *chelate effect* comes into play.



SCHEME I

When it comes to select which ligands of biological interest should be considered, for the purposes of carrying out a solid phase structural study of the cadmium complexes which are relevant to biological systems, we have taken into account their application as potential antidotes in the treatment of cadmium toxicity, considering several chelating agents such as ADTP (adenosine triphosphate), amino acids, nitrogenated bases, dithiocarbamates, thiolates and vitamins.

In what follows, we describe the crystal structures determined by single crystal X-ray diffraction of the cadmium compounds that may be important with regard to understanding the metal-ligand interactions in a biological detoxification context of the aforementioned metal, highlighting those compounds that illustrate the chemically (structurally) important species that may be formed by cadmium and those which are of biological relevance.

2 Cadmium complexes with nucleobases and related ligands

Given the stability of the oxidation state +2 of Cadmium, it exist a wide and varied structural information regarding complexes of purine or pyrimidine bases and some related ligands (Scheme I). In particular, attention should be addressed to N-derivatives of adenine or guanine and cytosine. Likewise, certain number of structures has been reported for cadmium complexes with nucleotides. These structures are not referred in detail herein. However, the main characteristic of such kind of compounds is that monophosphate nucleotides bind cadmium by the appropriate donor atom of the nucleobases (Figure 1a) whereas triphosphate nucleotides chelate cadmium through negatively charged O-phosphate donor atoms (Figure 1b).

2.1 Adenine

A relevant number of structures of cadmium complexes has been described for purine-like bases such as adenine (Hade) and 2,6-diaminopurine (Hdap), either in neutral, cationic or anionic forms. Neutral adenine has been reported in two polymeric compounds. The compound [4] $\{[Cd(\mu_2\text{-}ox)(H(N7)ade)(H_2O)]\cdot H_2O\}_n$ consists of 1D zig-zag chains where $Cd(H(N7)ade)(H_2O)^{2+}$ units are linked by μ_2-ox bridges with tetradentate oxalate ligands. Curiously, Hade coordinates by the less basic heterocyclic donor atom, giving rise to the bond Cd-N3 (2.282 Å) that is assisted with a H-bond (aqua)O-H···N9 (2.766 Å, 147.7º). Thus, the tautomer H(N7)ade seems to be favoured due to the implication of the bond N7-H in the crystal packing. The compound $[Cd(\mu_3\text{-}SO_4)(\mu_2\text{-}N7,N9\text{-}H(N1)ade)]_n$ [5] exhibits the tautomer H(N1)ade, according to the bidentate role of adenine and its basicity order (N9>N1>N7>N3>N6). The bond Cd-N9 (2.239 Å) does not cooperate with an interligand H-bonding interaction, whereas the bond Cd-N7 (2.204 Å) is reinforced by an N6-

H···O(sulphate) interaction (2.940 Å, 164.7º). In these polymers, the cadmium ion adopts a six-coordination.

The adeninium(1+) cation is reported in the binuclear compound $[Cd_2(\mu_2\text{-}N3,N9\text{-}H_2(N1,N7)ade)_2(\mu_2\text{-}H_2O)_2(O,O'\text{-}NO_3)_4](NO_3)_2$ [6] (Figure 2). In this compound, the coordination number of cadmium ion is eight. Both metal centres are separated 3.6 Å and the Cd-N3 (2.467 Å) and Cd-N9 (2.414 Å) bonds are rather longer than the usually observed. The adeninate(1-) anion is known in two mixed-ligand metal complexes. In $[Cd(tren)(N9\text{-}ade)]ClO_4$ [7], coordinates the pentacoordinated metal ion via its most basic donor atom giving rise to the Cd-N9 bond (2.193 Å) assisted by a very weak (electrostatic nature) interaction (tren)N-H···N3 (3.206 Å, 117.6º). The polymeric chain of $\{[Cd_3(\mu_3\text{-}ap)_2(\mu_3\text{-}N3,N7,N9\text{-}ade)_2(H_2O)_2]\cdot 1.5H_2O\}_n$ [8] is based on the catenation of trinuclear motifs in which the central metal ion is six-coordinated, involving two Cd-N9 (2.195Å) bonds. Alternatively, the other two metal centres have coordination number seven and show one Cd-N3 (2.326 Å) and Cd-N7 (2.282 Å) bond.

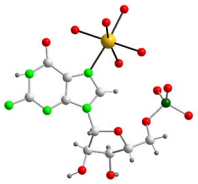


Figure 1a*

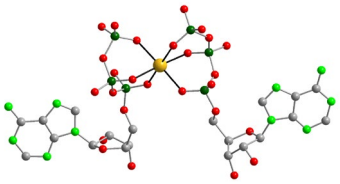


Figure 1b*

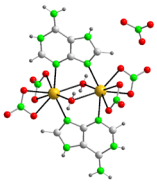


Figure 2*. $[Cd_2(\mu_2\text{-}N3,N9\text{-}H_2(N1,N7)ade)_2(\mu_2\text{-}H_2O)_2(O,O'\text{-}NO_3)_4](NO_3)_2$

*[Ref. 18]

There are known examples where the non-natural nucleobase 2,6-diaminopurine coordinates in cationic or anionic forms. In the compound $\{[Cd(H_2dap)(H_2O)_2(tp)]_2(tp)\cdot 2H_2O\}_n$ [9], the diaminopurinium(1+) cation binds cadmium through the bond Cd-N7 (2.342 Å) in cooperation with the intra-molecular interligand N6-H···O(coord., tp) interaction (2.923 Å, 146.6º). The anionic form dap^- builds the polymer $\{[Cd_3(\mu_3\text{-}adp)_2(\mu_3\text{-}N3,N7,N9\text{-}dap)_2(H_2O)_2]\cdot H_2O\}_n$ [9]. Note that this polymer is closely related with the adeninate above described (Cd-N3 2.586 Å, Cd-N7 2.298 Å, Cd-N9 2.387 Å).

2.2. N-Substituted purines with non-coordinating pendant arms

The N-substitution of a heterocyclic N-donor of purines represents a serious restriction on the tautomeric possibilities that are tied to the H atom usually linked to N9(purines). Thus, the alkylation in N9 of adenine or guanine increases the metal binding possibilities of the N7 donor atom. These general considerations can be applied to the following compounds: $[Cd(9Meade)(O\text{-}dmso)(\mu_2\text{-}Cl)_2]_n$ [10], $[Cd(9Megua)_2(H_2O)_4](NO_3)_2$ and $[Cd(9Etgua)_2(H_2O)_4](NO_3)_2$ [11]. These latter compounds have in common the Cd-N7 bond in cooperation with the intra-molecular interligand N6-H···O(dmso) (2.877 Å) or (aqua)O-H···O6 (2.905 or 2.752 Å) interactions, respectively. The coordination number of cadmium in these compounds is six and the Cd-N7 bond distance is 2.358 Å (9Meade) or 2.283 Å (9Megua or 9Etgua).

A certain number of N6-substituted adenines display kinetin activity. In this context, there has been reported cadmium derivatives with the N6-benzyl-adeninium(1+) (BAD^+) and N6-furfuryl-adeninium(1+) (FAD^+) cations yielding the compounds $[Cd(\mu_2\text{-}Cl)_2Cl(H_2(N3,N7)BAD)]_n$ and $[Cd(\mu_2\text{-}Cl)_2Cl(H_2(N3,N7)FAD)]_n$ [12]. In these polymers, the coordination number of cadmium is six. Both N6-adenine derivatives bind the metal via the Cd-N9 bond (2.348 or 2.361 Å, respectively) reinforced by an intra-molecular interligand N3-H···(μ-Cl) interaction (3.188 Å, 159.3º and 3.154 Å, 165.1º). The protonation sites (N3, N7) of these N6-substituted adenines should be related to the above mentioned intra-molecular N3-H···(μ-Cl) bond and the crystal packing. Indeed the N7-H bond is involved in a bifurcated H-bonding with two different chlorido ligands.

2.3. N-Substituted purines with potential chelating pendant arms

The most relevant N-substituted purine-like ligand with potential chelating pendant arm is the antiviral acyclovir (2-amine-9-(2-hydroxyethoxymethyl)-3*H*-purin-6-one). A recent paper [13] shows that this drug is able to bind metal ions forming a M-N7 bond, which can cooperate with an appropriate intra-molecular interligand H-bond involving the O6 atom as H-acceptor. However, the available structural information indicates that the N9-pendant arm of acyclovir does not usually participate in metal binding. In fact, the unique exception to this rule is found in the compound $\{[Cd(\mu_2\text{-}Cl)_2(\mu_2\text{-}O,N7\text{-}acv)]\cdot H_2O\}_n$ [14] where the O-acv donor is the OH-alcoholic group in the pendant arm. In this

compound, the metal ion is six-coordinated and the bridging role of acv represents the Cd-N7 (2.402 Å) and the referred Cd-O (2.305 Å) bonds.

There are known cadmium complexes with adenine, 2,6-diaminopurine and guanine derivatives with the 2-(ethylenediamine)ethyl N9-pendant arm (ede). In the compound $[Cd_3(Cl)_2(\mu_2\text{-}Cl)_4(\mu_2\text{-}N3,N7\text{-}[ede\text{-}ade])_2]_n$ [15], ede-ade acts both as tridentate chelate and bridging ligand. The chelating role involves the N3-ade donor atom (Cd-N3 2.418 Å) and two N atoms of the ethylenediamine moiety. Note that this chelating role represents the formation of one seven-membered and one five-membered chelate ring. Likewise, the bridging role also involves the Cd-N7 bond (2.389 Å). More recently, it has been described the structure of the compound $[Cd_3(Br)_2(\mu_2\text{-}Br)_4(\mu_2\text{-}N3,N7\text{-}[ede\text{-}ade])_2]_n$ [16]. The above referred polymers are isotypic crystals. Furthermore, two cadmium derivatives have been lately reported with derivatives of such ligand. In the mononuclear compound $[Cd(ede\text{-}dap)_2(NO_3)_3]$ [17], the metal exhibits a trans-octahedral coordination involving two ethylenediamine moieties and two unidentate nitrate ligands. In contrast, the crystal of the polymer $[Cd_2(\mu_2\text{-}[edp\text{-}dap])(H_2O)(Cl)_2(NO_3)_2]_n$ [17] exhibits two non-equivalent cadmium coordination polyhedra and the edp-dap ligand in a chelating and bridging role. The penta-coordinated cadmium centre has two N7-donor atoms (Cd-N7 2.407 Å) of two edp-dap ligands plus two chlorido and one aqua ligand. Each Cd-N7 bond is reinforced by one N6-H···Cl interaction (3.260 Å, 174.4º). The other cadmium centre has a trans-octahedral surrounding built by two ethylenediamine moieties from the edp ligand and two nitrate ligands. The ligand ede-gua is found in the polymer $\{[Cd(ede\text{-}gua)(SO_4)(H_2O)]_4\cdot 7H_2O\}_n$ [15] (Figure 3 plays chelating and bridging roles using the ethylenediamine moiety and the N7 donor atom giving rise to tetranuclear square-shaped motifs. The bond Cd-N7 (2.309 Å) is in cooperation with the N-H···O6 interaction (2.823 Å, 141.7º) which links the terminal primary amino group from the ethylenediamine moiety of one ede-gua ligand and the O6 exocyclic atom of another one. In the crystal, four sulphate anions bridge metal centres in adjacent squares to build cylindrical polymers that inter-connect to each other through π,π-stacking interactions between the six-membered ring of the guanine moieties.

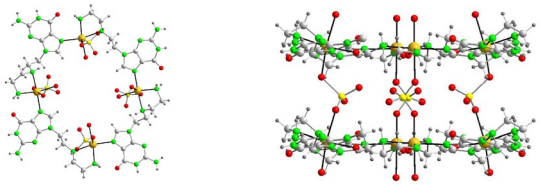


Figure 3. {[Cd(ede-gua)(SO_4)(H_2O)]$_4$·7H_2O}$_n$

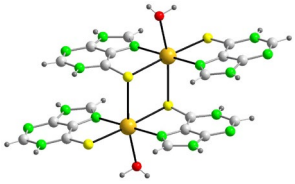


Figure 4. [Cd(μ_2-H6MP)(H6MP)(H_2O)]$_2$(NO_3)$_4$·2H_2O

A certain number of bis-adenine ligands with N,N'-spacers are also known. This is the case of the outer-sphere complexes with the diprotonated ligands tm-N^9,$N^{9'}$-diade and tem-N^9,$N^{9'}$-diade. In the compound (H_2tm-N^9,$N^{9'}$-diade)$_2$[Cd(μ_2-Cl)Cl_3(H_2O)]$_2$·4H_2O [19], the adenine moieties of the cation are protonated in N1 whereas in the related compound {(H_2tem-N^9,$N^{9'}$-diade)$_2$[Cd_4(μ_3-Cl)$_2$(μ_2-Cl)$_6Cl_4$(H_2O)$_2$]·4H_2O}$_n$ [20] there are two non-equivalent tautomeric cations in which the adenine moieties are protonated in N1 or N3. Regarding the asymmetric ligand tem-N^3,$N^{9'}$-diade, it has been reported a mixed-ligand 1D polymer {[Cd_2(H_2tem-N^3,$N^{9'}$-diade)$_2$(μ_2-Cl)$_4Cl_4$(H_2O)$_2$]·2H_2O}$_n$ [20] with two non-equivalent cadmium centres. One is surrounded by five chlorido ligands whilst the other is trans-six coordinated by four chlorido ligands and two (H_2tem-N^3,$N^{9'}$-diade)$^{2+}$ cations linked to the cadmium by the N7 donor atom of the N9-alkyl-substituted adenine moiety. Interestingly, the bonds Cd-N7 (2.375 Å) are reinforced by rather linear N6-H···Cl interaction (3.267 Å, 178.3º).

2.4 6-Mercaptopurine

Because of the soft character and the oxidation state stability of the cadmium(II) ion, we can expect a good affinity to soft S donor atoms without the interference of redox chemistry. On this basis, an interesting structural chemistry is documented for cadmium complexes with the non-natural nucleobase 6-mercaptopurine (H6MP). Five structures refer to compounds having the neutral H6MP. In [Cd(H6MP)$_2$(Cl_2)]·2H6MP [21], the metal is six-coordinated and H6MP acts as bidentate chelating ligand using the S6 and N7 donor atoms (Cd-S6 2.622 Å, Cd-N7 2.366 Å). The same chelating role of H6MP has been described in the binuclear complex molecule [Cd(H6MP)(μ_2-Cl)Cl(H_2O)]$_2$ [22] (Cd-S6 2.790 Å, Cd-N7 2.324 Å). H6MP plays both chelating and bridging roles in the compounds [Cd(μ_2-H6MP)(H6MP)(H_2O)]$_2$(NO_3)$_4$·2H_2O (Figure 4) and [Cd(μ_2-H6MP)(H6MP)(NO_3)]$_2$(NO_3)$_2$ [23]. As shown in Figure 4, the binuclear compound has one chelating-S6,N7 ligand (Cd-S6 2.653 Å, Cd-N7 2.339 Å) and one chelating-S6,N7 (Cd-S6 2.763 Å, Cd-N7 2.287 Å) plus bridging-S6 (Cd-S6 2.914 Å)

ligand per cadmium centre. Within the cation of this compound, pairs of purine ligands are π,π-stacked involving the five-membered ring of the chelating H6MP ligand and the six-membered ring of the chelating+bridging H6MP ligand. The Cg-Cg distance for the stacked ring is 3.418 Å. The complex plotted in Figure 4 exhibits six coordination polyhedra whereas in the binuclear complex cation $[Cd(\mu_2\text{-}H6MP)(H6MP)(NO_3)]_2^{2+}$ the bidentate role of nitrate ligands increase the coordination number of the metal ion to seven. Within this latter cation, there is not π,π-stacking interactions.

From a structural point of view, the compound $[Cd(\mu_2\text{-}Cl)Cl(H6MP)]_{2n}\cdot n[Cd(H6MP)_2(Cl)_2]$ consists of a 1D polymeric chain and discrete complex molecules, both with six-coordinated cadmium(II) centres. In the molecules $[Cd(H6MP)_2(Cl)_2]$, the H6MP ligand acts as bidentate chelator (Cd-S6 2.632 Å, Cd-N7 2.392 Å). In the polymer, the H6MP ligands play a unique chelating-S6,N7 plus bridging-N3 role (Cd-S6 2.743 Å, Cd-N7 2.300 Å, Cd-N3 2.409 Å) [24].

The univalent anion 6MP plays a chelating-S6,N7 (Cd-S6 2.689 Å, Cd-N7 2.283 Å) plus the bridging-S6 role (Cd-S6 2.868 Å) in the polymer $\{[Cd(6MP)_2]\cdot 2H_2O\}_n$ [21]. The same chelating plus bridging role has been reported for the polymeric compound $\{[Ca(\mu_2\text{-}H_2O)_2(H_2O)_4][Cd(\mu_2\text{-}6MP\text{-}H)_2]\}_n$ [23] where 6MP-H is the divalent anion of H6MP (Cd-S6 2.741 Å, Cd-N7 2.266 Å, Cd-S6 2.888 Å).

2.5 Oxopurines

Only a few structural evidences are available for cadmium(II) complexes with neutral oxopurines. Nevertheless, the basicity of the N-donors in this kind of oxo-purine ligands, as well as their softness, increase after the dissociation of at least one of theirs protons. Consequently, most of the available crystal data concerning complexes of such ligands refer to the univalent anions of hypoxanthine (Hhyp), xanthine (Hxan) or theophiline (Htheo). Neutral hypoxanthine yields the compound $[Cd_2(\mu_2\text{-}N3,N9\text{-}H(N7)hyp)_2(\mu_2\text{-}H_2O)_2(SO_4)_2(H_2O)_2]$ [25] in which the metal exhibits a six-coordination and the bridging μ_2-N3,N9-H(N7)hyp and μ_2-H_2O ligands yield a binuclear complex molecule with a Cd···Cd separation of 3.452 Å. This bridging μ_2-N3,N9 coordination mode (Cd-N3 2.367 Å, Cd-N9 2.274 Å) is reported for cationic, neutral and anionic forms of adenine [26]. The hypoxanthinate(1-) anion yields the compound $[Cd_2(tren)_2(\mu_2\text{-}N7,N9\text{-}hyp)](ClO_4)_3\cdot 0.5H_2O$ [7] where the Cd-N7 (2.204 Å) and the Cd-N9 (2.197 Å) bonds are weakly assisted by H-bonding interactions [(tren)N-H···O6 3.061 Å, 128.9º or

(tren)N-H···N3 3.171 Å, 135.3º, respectively]. Both metallic centres in this complex are five coordinated.

The cadmium(II) chelate with the tripodal tetradentate ligand 'tren' also yields the mixed-ligand complex cation of the salt $[Cd(tren)(xan)]ClO_4 \cdot H_2O$, where the metal ion is only five-coordinated, and the anionic xan^- ligand builds the Cd-N7 bond (2.224 Å) reinforced by the intra-molecular interligand H-bond (tren)N-H···O6 (2.889 Å, 117.6º).

In the compound *trans*-$[Cd(theo)_2(H_2O)_4] \cdot 2DMF$ [27], each theophilinate(1-) anion binds the cadmium(II) centre by the Cd-N7 bond (2.300 Å) cooperating with an intra-molecular H-bond (aqua)O-H···O6 (2.689 Å, 158.5º).

2.6. Pyrimidines

The structural information concerning to cadmium(II) complexes with pyrimidine nucleobases and closely related ligands is rather limited. However, their diversity is a good source of information. Most structures in this field concern to cytosine and 1-substituted cytosine ligands. The compound $\{[Cd(\mu_2\text{-}Cl)_2(H_2O)_2] \cdot 2Hcyt\}_n$ [28] is a cytosine solvate of a polymeric complex where the metal is six-coordinated. In the crystal of this compound, there is a H-bonded chain of Hcyt molecules built by two pairs of H-bonding interactions (N1-H···O2(exocyclic) and (exocyclic)N4-H···N3 with their symmetry related interactions). A cytosinium(1+) salt of formula $(H_2cyt)[CdBr_4]$ [29] has been reported. Herein, two different cytosinium(1+) cations are present. In this outer-sphere complex, the cadmium(II) ion is tetrahedrally surrounded by the rather bulky bromide ligands and the cytosinium cations involved in an extensive H-bonding network. Closely related to the latter compounds is the complex $[Cd(Hcyt)_2(Br)_2]$ [30] where the metal exhibits a rather distorted six-coordination due to the size of bromide ligands and the chelating-O2,N3 role of Hcyt bases. Because of the crystal packing (mainly the H-bonded network), both bromide and cytosine ligands are not strictly equivalent. The Hcyt ligands build strained four-membered chelate ring (Cd-N3 2.243 or 2.281 Å, Cd-O2 2.825 or 2.780 Å, respectively). In the binuclear complex $[Cd(\mu_2\text{-hip})(hip)(Hcyt)(H_2O)]_2$ [31], the cadmium(II) is seven-coordinated. In this centro-symmetric complex, the Hcyt ligand plays the bidentate- O2,N3 role (Cd-N3 2.240 Å, Cd-O2 2.2687 Å). All hippurate(1-) ligands play bidentate roles for one metal centre or bridging between two

cadmium(II) atoms. An interesting salt with mixed-ligand cation and anion has been reported. $[Cd(Hcyt)_3Cl][Cd(Hcyt)Cl_3]$ [28] is a nice example to show how the crystallographic work is the best evidence for the mixed-ligand nature of the compounds. The five-coordinated anion is bonded by one chelating-O2,N3-Hcyt ligand (Cd-N3 2.253 Å, Cd-O2 2.751 Å) whereas the seven-coordinated cation have three non-equivalent chelating-O2,N3-Hcyt ligands (Cd-N3 2.266, 2.285 or 2.289 Å, Cd-O2 2.797, 2.680 or 2.982 Å, respectively).

Only one mixed-ligand cadmium(II) complex has been reported for the Hcyt isomer isocytosine (Hicyt). $[CdCl_2(Hicyt)_2]$ [32] exhibit a six-coordination for the metal with two non-equivalent chlorido and chelating-N3,O4-Hicyt ligands (Cd-N3 2.261 or 2.286 Å, Cd-O4 2.682 or 2.624 Å, respectively). Regarding uracile (Hura), in the structure of the molecular complex $[Cd(ura)_2(H_2O)_3]$ [33], the cadmium(II)···O4(ura) distance is 3.203 Å so that it can not be considered as a coordination bond (the sum of Van der Walls radii of cadmium(II) (1.60 Å) and oxygen (1.50) is 3.10 Å). Therefore, this complex has five-coordinated cadmium(II) atoms in a bipyramidal-trigonal topology with two *trans*-apical aqua ligands (Cd-O 2.439 Å) and the remaining aqua ligand (Cd-O 2.269 Å) with the two uracilate(1-) ligands (Cd-N3 2.211 Å) in the equatorial plane.

In the molecular complex *cis*-$[Cd(1Mecyt)_2Cl_2]$ [34] the chloro ligands fall in *cis*-coordination sites but are not equivalent for crystal packing reasons. Besides, both 1Mecyt ligands are not equivalent and play the chelating-O2,N3 role (Cd-N3 2.282 or 2.297 Å, Cd-O2 2.780 or 2.676 Å). A closely related compound to the just referred complex is *cis*-$[Cd(1Toscyt)_2Cl_2]$ [35] where again, the chloride and 1Toscyt ligands are non-equivalents and the 1Toscyt bases play a chelating-O2,N3 role (Cd-N3 2.260 or 2.278 Å, Cd-O2 2.839 or 2.846 Å, respectively).

3 Cadmium(II) complexes with α-amino acids

Structural studies about cadmium(II) complexes with amino acids include a vast number of compounds. Therefore, hereafter, we will focus exclusively on those complexes that contain one or more of the twenty essential α-amino acids.

Upon reviewing the CCDC database, we observe that, to date, only cadmium(II) complexes with 11 essential α-amino acids have been structurally studied in solid state. Among them, there is only one

known structure for methionine (Hmet), phenylalanine (Hphe), tryptophan (Htrp), asparagine (Hasn), aspartic acid (H_2asp) or histidine (H_2his). However, the number of structures containing glycine (Hgly), alanine (Hala), proline (Hpro) cysteine (H_2cys) and glutamic acid (H_2glu) is relatively varied and includes up to a total of 28.

3.1 Complexes of α-amino acids as sole ligand

In those complexes where only the α-amino acid is coordinated to the cadmium, the complex may be a monomer, such as $[Cd(L\text{-}Hhis)_2]\cdot 2H_2O$, in which the cadmium is octahedrally coordinated by two histidinate ligands via the amine [2.287(9) Å] and imidazole [2.290(8) Å] nitrogen atoms and via two carboxyl oxygen atoms [2.480(9) Å], adopting each histidinate ligand a closed conformation with the imidazole ring folded back on top of the carboxylate group [36] (Figure 5). Nevertheless, the carboxylate group usually acts as an *anti-syn* bridging bidentate ligand, giving rise to chain structures such as $\{[Cd(gly)_2]\cdot H_2O\}_n$. In the referred compound, cadmium ions display a distorted octahedral coordination where two glycinate(1-) ligands bind the metal through the nitrogen and oxygen atoms in a *trans* square planar configuration, whilst the axial positions are occupied by oxygen atoms of carboxylate groups from neighbouring amino acids [37] (Figure 6). A similar behaviour can be observed in complexes with methionine or asparagine [38], or in $[Cd(L\text{-}trp)(D\text{-}trp)]_n$ [39]. The novelty of the latter complex lies in the fact that, having used only L-tpr as the starting material in the synthesis, the cadmium ion is coordinated by two nitrogen atoms and two oxygen atoms from an L-tpr and a D-tpr, respectively, and by two oxygen atoms from another two carboxylate groups in adjacent positions, L-tpr and D-tpr.

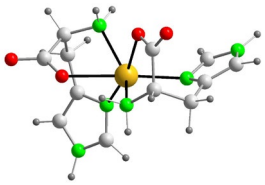


Figure 5. $[Cd(L\text{-}Hhis)_2]$

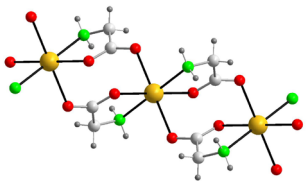


Figure 6. $\{[Cd(gly)_2]\}_n$

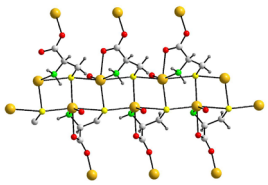


Figure 7. $[Cd(L\text{-}cys^{2-})]_n$

$[Cd(L\text{-}cys)]_n$ is a different polymer based on a 1D ladder arrangement of Cd and S produced by thiolate bridges of the cysteine. These 1D units are linked in a regular manner by the carboxylate groups of the amino acid, which bind the metal centres from two neighbouring ladders via their two oxygen atoms. The coordination sphere of each cadmium atom is octahedrally distorted, with a L-cysteinate dianion acting as tridentate chelating ligand in an imposed *fac* manner via its amine, carboxylate and thiolate groups. The aforementioned coordination sphere is completed by two new sulphur atoms from two cysteinate ligands which chelate two neighbouring cadmium ions in the chain itself and a carboxylate oxygen atom from a cysteinate from a neighbouring chain (Figure 7). As a result, the three sulphur atoms bonded to the same cadmium are in a *mer* arrangement and the two oxygen atoms are *cis* [40]. Interestingly, the L-cys^{2-} ligand plays an important role, the S-thiolate atom bind three cadmium centres whilst the α-carboxylate groups bridge two Cd(II) in an *anti-syn* manner.

3.2. α-Amino acid complexes with water as co-ligand

There are also some known polymeric as well monomeric cadmium complexes with α-amino acids, which contain coordinated water. An example of monomer is $[Cd(L\text{-}ala)_2(H_2O)]\cdot H_2O$ where the metal is octahedrally coordinated by two molecules of alaninate that act as *cis*-O,O-*trans*-N,N chelating bidentate ligands (Cd-O, 2.326(5) Å, Cd-N, 2.334(5) Å] and by two water molecules that occupy *cis* positions [Cd-O, 2.296(4) Å] [41]. An example of a polymer is $\{[Cd(L\text{-}glu)(H_2O)]\cdot H_2O\}_n$ with the cadmium octahedrally coordinated to a L-glutamate molecule, by the oxygen carboxylate and nitrogen amine atoms; along with the metal, this forms a five-membered chelate ring with the two oxygen atoms from the second carboxylate group of a neighbouring amino acid molecule, with the oxygen atom of the carboxylate group from another neighbouring glutamate molecule and with the oxygen atom from a water molecule. As a result, each glutamate molecule bind the cadmium ion using its five donor atoms, with the carboxylate group as an *anti-syn* type bidentate bridge, and the second carboxylate as bidentate chelate [42]. Furthermore, there is reported another coordination polymer with glutamate and water, of formula $\{[Cd(L\text{-}glu)(H_2O)Cd(L\text{-}glu)(H_2O)_2]\cdot H_2O\}_n$ in which there are two crystallographically independent and hepta-coordinated cadmium atoms. One of them has a “distorted square-based

trigonal-capped" coordination polyhedron whereas the coordination geometry of the second is distorted trigonal bipyramidal [38].

3.3. α-Amino acid complexes with a halogen as co-ligand

There are several structures of cadmium chlorido complexes with α-amino acids, all are coordination polymers with the amino acid in its zwitterionic form. In $[CdCl_2(Hgly)_2]_n$, each cadmium atom has an octahedral Cl_3O_3 environment with a terminal chlorido ligand and the other two bridging to a neighbouring cadmium atom, to one oxygen atom from the carboxylate group of a glycine molecule and to two oxygen atoms from two glycines which act as *anti-syn* type bidentate bridging ligands to neighbouring cadmiums [43]. This structure contrasts with that of the complex $[Cd_3Cl_6(Hgly)_4]_n$ that contains two symmetrically independent cadmium atoms with different coordination environments; one is surrounded by four chlorido ligands and two oxygen atoms in *trans* positions, from two glycine zwitterions which act as O-monodentate ligands, and the other is also bonded to four chlorido ligands and to two oxygen atoms from an asymmetric chelating bidentate glycine zwitterions [Cd-O, 2.318(5) and 2.534(5) Å]. The bridging chlorido ligands join the metal centres to form chains with the glycine zwitterions that are connected to them in a hanging decorative fashion [44] (Figure 8). In $\{[CdCl_2(Hala)]\cdot xH_2O\}_n$ (x = 0 o 1) [45, 46] and in $\{[CdCl_2(Hpro)]\cdot H_2O\}$n [47], each cadmium ion is coordinated by four chlorido ligands and two carboxylate oxygen atoms, forming a distorted octahedron. The four chlorido ligands, that are coordinated to the metal centre, form square planes which are linked to each other by means of *syn-syn* type bidentate carboxylate bridges, giving rise to 1D polymers in which the fragments of amino acid are hanging at the sides of the chain.

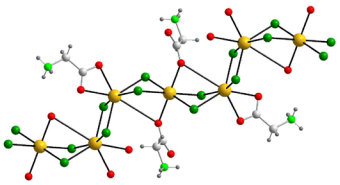


Figure 8. $[Cd_3Cl_6(Hgly)_4]_n$

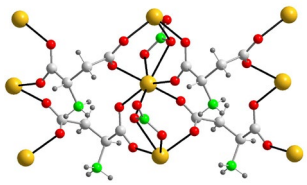


Figure 9. $[Cd(Hasp^-)(NO_3)]_n$

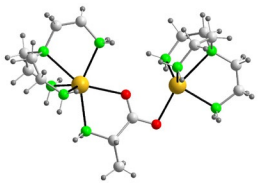


Figure 10. $[Cd_2(D,L\text{-ala})(tren)]^{3+}$

3.4. Complexes with α-amino acids and other co-ligands

There are reported some structures of cadmium complexes that besides containing an α-amino acid and a halogen, contain an additional neutral ligand, such as $[CdCl(gly)(DABT)]_n$ (DABT = 2,2'-diamine-4,4'-bi-1,3-thiazole) in which each cadmium(II) is coordinated by a chlorido ion, a molecule from the diamine-bithiazole ligand and by two glycinate ions (one O-monodentate and the other N,O-bidentate). Consequently, the glycinate anions act as bridges between neighbouring cadmiums and form zig-zag chains [48].

In other structures an oxoanion is present instead of a halide. For example, in $[Cd(Hasp)(NO_3)]_n$ the aspartate anion is in its zwitterionic form and the Cd^{2+} ion is heptacoordinated, with an distorted environment, where the sixth position is doubly occupied by two oxygen atoms from the NO_3^-, which acts as a chelating bidentate. The remaining coordination positions are occupied by an oxygen atom from a crystallographically equivalent nitrate ion, *trans* to the other nitrate, and by four oxygen atoms from four equivalent aspartate ligands which are in *cis* postions to the nitrates. As a result, the nitrate and aspartate act as bridges between neighbouring metal centres, leading to a 2D structure [49] (Figure 9). This structure is in contrast to that found in $[Cd(L\text{-}pro)(NO_3)(4,4'\text{-}bipy)]_n$ (4,4'-bipy = 4,4'-bipyridyl) where a deprotonated proline molecule chelates a cadmium centre in a N,O coordination mode. The structure extends in one dimension through the non-chelating carboxylate oxygen atom, which is bonded to an adjacent cadmium atom which is *trans* to the chelating oxygen. Furthermore, the bipy ligand coordinates orthogonally linking the cadmium-proline chains into 2D sheets. The coordination environment is completed with a monodentate NO_3^- anion bound in a *trans* position to the amine nitrogen of the proline [50].

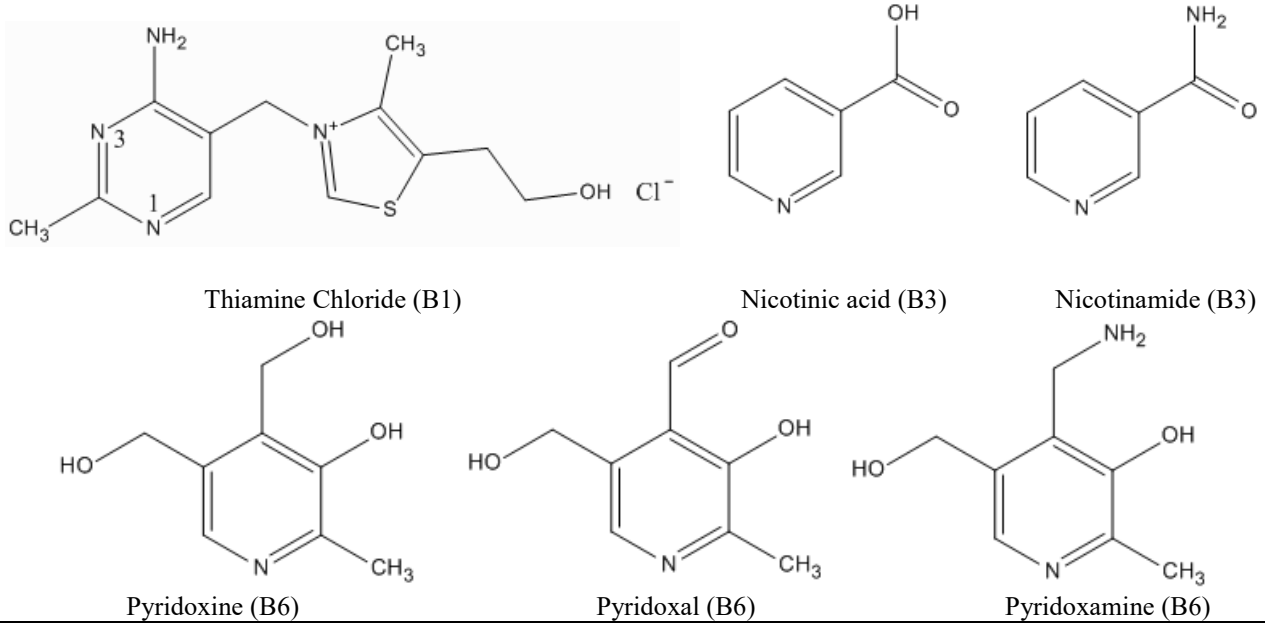
There are also some cationic cadmium complexes with α-amino acids. In $[Cd_2(D,L\text{-}ala)(tren)](ClO_4)_3$ [tren = tris-(2-aminoethyl)amine], the structural analysis indicates an ionic character, including two Cd^{2+} ions with different coordination environments in the cation $[Cd_2(D,L\text{-}ala)(tren)]^{3+}$ (Figure 10). One is hexacoordinated with a distorted octahedral geometry, whereas the other is pentacoordinated with a trigonal bipyramidal geometry. The alaninate anion acts as a bridging ligand between both metal centres coordinating to a cadmium in a bidentate N,O-chelate fashion, and to the other in a monodentate fashion via the second oxygen atom from the carboxylate group [51].

4 Complexes of Cadmium with Vitamins and derivatives

Although they have different structures, sources, requirements and mechanisms of action, vitamins are classified according to their solubility in water or in fats. Vitamins A, D, E and K are liposoluble, whereas B-complex (B_1, B_2, B_6, B_{12}, niacin, pantothenic acid, biotin and folic acid) and C vitamins are hydrosoluble. Moreover, there are some organic compounds related to vitamins, which are usually classified with B vitamins and are also hydrosoluble; p-Aminobenzoic acid is included among these substances similar to vitamins.

To date, only some hydrosoluble vitamins are known to interact as ligands with several metal ions and, with some exceptions, very few solid phase structures of these complexes have been obtained (Scheme II). Indeed the number of cadmium complex structures is even less.

In what follows, we will describe the most significant aspects of the known structures of cadmium complexes with vitamins, obtained by means of X-ray diffraction structural analyses.



SCHEME II

4.1 Thiamine (Vitamin B_1)

Thiamine is a monovalent cation which structure corresponds to a substituted pyrimidine bonded to a substituted thiazole. This fact is related to the presence of a quaternary N atom tied to the former thiazole ring. Thus, thiamine, so-called vitamin B1, exists as salts of the physiological chloride anion or

a large variety of counter anions. For solubility reasons, thiamine is commercially available as its hydrochloride, namely thiaminium(2+) dihydrochloride. The structures of its metal complexes correspond to two groups: those containing the divalent thiaminium cation and a cadmium complex as counter ion, and those where there is a direct cadmium-thiamine interaction.

There are two known structures with a thiaminium cation, one with the tetrahedrally coordinated cadmium ion in the anion $[CdCl_4]^{2-}$ [52], and the other with a 1D polymeric anion $[Cd_3Br_{4.4}Cl_{3.6}]^{2-}$,in which two out of the three cadmium atoms are octahedrally coordinated and the third has a tetrahedral coordination [52]. In both cases, as expected, the nitrogen atom in the pyrimidine ring *trans* to the exocyclic amine group is the protonation site for the thiamine cation, hereafter N1. Thus, such N-heterocyclic atom is considered the preferred protonation site of thiamine cation and the selective metal binding donor atom in their metal complexes. In the crystal, the cations are linked to the anions by means of hydrogen bonds in which the O-H and N-H are donors and the halogen atoms of the anions are acceptors.

To date, there are only four reported cadmium complexes with thiamine and another three with derivatives in which there is a direct metal-ligand bond. The compound $[Cd(thiamine)Cl_3]\cdot 0.6H_2O$ (Figure 11) contains a tetracoordinated cadmium ion by three chlorides and the nitrogen atom from the pyrimidine *trans* to the amine group (Cd-N distance of 2.239(2) Å). The thiamine molecule adopts the *S* conformation (ϕ_T = 113º, ϕ_P = 130º) [53]. A second compound of formula $[Cd(thiamine)(SCN)_3]_n$ has a polymeric structure with each cadmium octahedrally coordinated to a thiamine molecule through the oxygen atom from the hydroxyethyl side chain [Cd-O = 2.351(6) Å] and by five thiocyanate ligands, one of which is terminal and the remaining four are bridging, leading to the coordination $CdON_3S_2$. In this compound, the thiamine ligand adopts the *F* conformation (ϕ_T = 0º, ϕ_P = -80º) [54]. A third structure consists of centrosymmetric dimmers $[Cd(thiamine)Cl_3]_2$, where two thiamine molecules act as N,O bridges to two $CdCl_2$ units [Cd-N = 2.264(5) Å, Cd-O = 2.697(5) Å showing a $CdCl_3NO$ trigonal bipyramidal coordination environment (Figure 12). The vitamin adopts a *F* conformation (ϕ_T = 11º, ϕ_P = 98º) [55]. The fourth known cadmium complex with vitamin B_1 is the octahedral $[Cd(thiamine)_2Cl_4]$ with a $CdCl_4N_2$ environment in which the metal is coordinated by two thiamine

molecules in *trans* positions [Cd-N = 2.446(6) Å], and where the vitamin adopts a *S* conformation (ϕ_T = -92º, ϕ_P = 176º) [56].

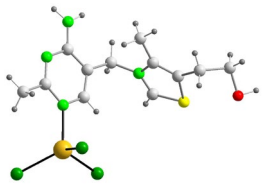


Figure 11. [Cd(thiamine)Cl_3]

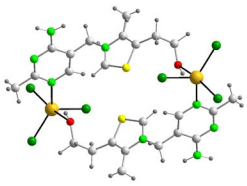


Figure 12. [Cd(thiamine)Cl_3]$_2$

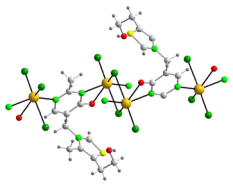


Figure 13. [Cd(Oxithiamine)Cl_2]$_n$

There are also two known structures of cadmium complexes with 2-(α-hydroxybenzyl)thiamine (HBthiamine), an intermediate of thiamine catalysis, with the α-hydroxybenzyl substituent in the C(2) position of the thiazolium ring. The complexes [Cd(HBthiamine)X_3] (X = Cl or Br) are isotypic, with a structure similar to that of [Cd(thiamine)Cl_3] (Cd-N = 2.251(3) Å and 2.257(9) Å]. In these structures the conformation of the thiamine skeleton is *S* (ϕ_T = 97 and -97º, ϕ_P = 173º) [57]. Furthermore, another structure of a cadmium complex with a thiamine derivative has been studied by Casas *et al*. [58], namely [Cd(oxithiamine)Cl_2]$_n$, where oxithiamine is an antagonist of thiamine, which differs from it in that the exocyclic amine group within the pyrimidine ring is replaced by a hydroxyl group. The structure is polymeric and each cadmium is coordinated by three chloride ligands, two of which act as bridges between neighbouring cadmium atoms, by the zwitterionic oxithiamine, via the nitrogen and oxygen *cis* from the pyrimidine ring [Cd-N, 2.317(4) Å; Cd-O, 2.561(4) Å; ∠N-C-O, 1170(5)º; ∠N-Cd-O, 54.5(1)º] and by the nitrogen atom from the pyrimidine ring *trans* to the carbonyl of one oxithiamine molecule [Cd-N, 2.301(4) Å]. Consequently, the cadmium has a distorted octahedral coordination $CdCl_3N_2O$ (Figure 13). The conformation of the ligand seems to be closer to *V* rather than to the traditional *F* or *S* (ϕ_T = -115º, ϕ_P = 61º). In this structure it is worth noting the altered order of basicity within the nitrogen atoms of the pyrimidine ring when passing from thiamine to oxithiamine.

4.2 Nicotinic acid (Vitamin B_3)

Niacin and niacinamide (also known as nicotinic acid and nicotinamide, respectively) or vitamin B_3, chemically 3-pyridinecarboxylic acid and 3-pyridinecarboxamide, are able to form various cadmium

complexes with known crystal and molecular structures. In order to rationalise the analysis, hereafter the complexes have been differentiated according to the ligand and, within each case, we have only considered the most relevant structures.

In niacin, the existence of the pyridinic nitrogen atom and the variety of coordination possibilities of its carboxylic group, lead to the formation of 1D, 2D and 3D networks, albeit with some exceptions. One of these exceptions is the $[Cd(NA)_2(H_2O)_4]$ (Figure 14), in which each metal atom is coordinated by two nitrogen atoms from the nicotinate groups and by four oxygen atoms from four water molecules, in a slightly distorted octahedral geometry. Both nicotinate groups occupy *trans* positions with Cd-N distances of 2.309(5) Å. The Cd-O distance is 2.321(4) Å [59].

There is also reported a dinuclear complex which, besides water, contains ethylenediamine (en) as co-ligand (Figure 15). In $[Cd_2(NA)_4(en)_2(H_2O)_2]\cdot H_2O$ (NA = nicotinate), both Cd^{2+} ions display distorted octahedral coordination geometry that includes two nitrogen atoms from two nicotinate anions, the nitrogen atoms from an ethylenediamine molecule which forms a five-membered chelate ring, an oxygen atom from one of the nicotinate ions (which acts as N,O bridge between the two cadmium ions) and an oxygen atom from a water molecule [60].

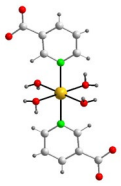


Figure 14. $[Cd(NA)_2(H_2O)_4]$

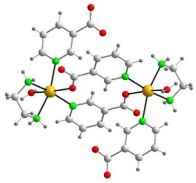


Figure 15. $[Cd_2(NA)_4(en)_2(H_2O)_2]$

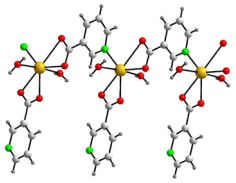


Figure 16. $[Cd(NA)_2(H_2O)_2]_n$

Two different groups of polymeric structures with nicotinate ions can be defined. Those containing additional neutral ligands, such as H_2O, aromatic diamines, etc., and those with anionic ligands such as halides, thiocyanate, azide or nitrate.

$[Cd(NA)_2]_n$ is an example of the former, with the cadmium ions coordinated by two nitrogen pyridyl atoms from two nicotinate molecules and by four carboxylate oxygen atoms from another two nicotinates, in an asymmetric chelating manner. As a result, two Cd-O bonds, one from each chelate, [2.397(3) Å and 2.247(3) Å] are much longer than the other two [2.271(3) Å and 2.317 (3) Å]. Each

tridentate nicotinate ligand bridges two adjacent cadmium atoms and gives rise to a 2D network [61]. Likewise, there is another structure with the same stoichiometry, based on distorted square pyramidal cadmium centres coordinated by two independent nicotinate ligands. One of them acts as N,O_2-tridentate and the other as bidentate N,O. Every two cadmium atoms are bridged by two carboxylate groups from the tridentate nicotinate ligands in an *anti-syn* bridging bidentate manner, to form a binuclear unit $Cd_2(NA)_4$. One of those oxygen atoms occupies the axial site of the pyramid whilst the other occupies one of the basal positions, along with two nitrogen pyridyl atoms and an oxygen from three nicotinate ligands, two of which are bidentate, thus resulting in a 3D network [62].

Among the structures of polymeric complexes containing coordinated H_2O, $[Cd(NA)_2(H_2O)_2]_n$ (Figure 16) is a zig-zag chain with heptacoordinated Cd^{2+} ions in a distorted pentagonal bipyramidal geometry, involving one nitrogen donor atom and four oxygen donor atoms from two nicotinate ligands arranged in the equatorial plane, as well as the oxygen atoms from two coordinated water molecules at the axial sites. Therefore, one of the nicotinate ligands acts as tridentate bridge whereas the other acts as bidentate terminal via the carboxylate group. In this structure, the Cd-O distance lies between the 2.255(4) and 2.724(5) Å and the Cd-N distance is 2.278(4) Å [63].

There are also some 1D structures of complexes including an anion besides the nicotinate, such as the luminescent complexes $\{(Cd(NA)(phen)(NO_3)]\cdot 1/2H_2O\}_n$ and $\{[Cd(NA)(ptola)(H_2O)_2]\cdot(Hptola)\}_n$ (phen = 1,10 phenanthroline, ptola = p-toluic acid) [64]. In both complexes, the nicotinate acts as N,O_2 tridentate bridging ligand, but in the first case the Cd^{2+} ion is hexacoordinated, with the nitrate as a monodentate ligand and, in the second case it is heptacoordinated with the toluate as chelating bidentate ligand.

In other complexes, the characteristic polymeric coordination is achieved by a neutral auxiliary ligand which acts as bridge besides the nicotinate, or by an anionic ligand, such as halides [65, 66] or thiocyanate [67]. In the latter complex, $\{[Cd(SCN)_2(HNA)_2]\cdot HNA\}_n$, the Cd^{2+} ion is coordinated by two nitrogen pyridyl atoms from two molecules of nicotinic acid, by two nitrogen atoms from two thiocyanate and by two sulphur atoms from another two thiocyanate in a *trans* octahedral geometry, so that each pair of adjacent cadmium atoms are bridged by two μ-SCN-S,N ligands giving rise to a 1D structure (Figure 17).

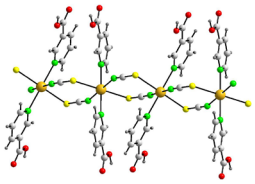


Figure 17. $[Cd(SCN)_2(HNA)_2]_n$

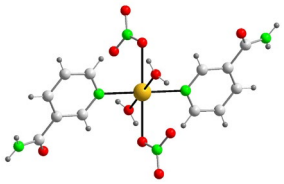


Figure 18. $[Cd(H_2O)_2(NADA)_2(NO_3)_2]$

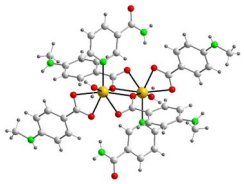


Figure 19. $[Cd(PMAB)(NADA)(H_2O)]_2$

In the few known structures of cadmium with nicotinamide (NADA), this ligand acts as monodentate via its pyridyl nitrogen atom, and in every case the coordination environment of the metal is octahedral. Depending on the behaviour of the anion, two types of mononuclear complexes can be distinguished: neutral, if the anion is coordinated as in $[Cd(H_2O)_2(NADA)_2(NO_3)_2]\cdot 2NADA$ [68] (Figure 18) or $[Cd(H_2O)_2(NADA)_2(NBZ)_2]\cdot 2H_2O$ (NBZ = 2-nitrobenzoate) [69]. Nevertheless, if the anion is not coordinated, the complex is cationic with two molecules of nicotinamide in the axial positions and four coordinated water molecules at the equatorial sites, as in $[Cd(NADA)_2(H_2O)_4]X_2$ (X = 4-formilbenzoate) [70, 71].

In some complexes, a carboxylate anion acts as bidentate bridge yielding structures based on dinuclear complexes, as observed in $[Cd(PMAB)(NADA)(H_2O)]_2$ (Figure 19) and $[Cd(DMAB)(NADA)(H_2O)]_2$ [PMAB = 4-(methylamino)benzoate, DMAB = 4-(dimethylamino)benzoate], with the metal ion is chelated by two carboxylate groups of aminobenzoate anions and coordinated by a nicotinamide molecule and a water molecule. An oxygen atom from a carboxylate group of an adjacent anion which bridges the cadmium atom completing an irregular heptacoordinated geometry [72, 73].

To date, only has been reported one 2D cadmium coordination polymer constructed with thiocyanate and nicotinamide. Herein, each Cd^{2+} ion, located in a centrosymmetric octahedral environment, is coordinated by two nicotinamide molecules in *trans* positions and four thiocyanate ions, which act as N,S bridging ligands, linking to four neighbouring cadmium ions [67].

4.3 Vitamin B_6

There are known two crystal structures determined by X-ray diffraction of a cadmium complex with vitamin *B_6*. In both compounds the pyridoxine is found as a zwitterion, by migration of the phenolic hydrogen atom to the heterocyclic nitrogen atom. That enables the chelating role of pyridoxine by the O-phenolate and the adjacent O-methanolic donor to build six-membered chelate rings. The coordination of Cd(II) atom is octahedral, but the ligand:metal ratio is different in both compounds. The 1:1 compound [Cd(μ-O-pyridoxine)(μ-Cl)Cl]$_n$ [74] is a 1D-polymer, where a chlorido ligand and the O-phenolate donor of pyridoxine act as bridging atoms between two adjacent Cd(II) centres (Figure 20). The salt trans-[Cd(pyridoxine)$_2$(H$_2$O)$_2$]SO$_4$·6H$_2$O [75] display the Cd(II) atom in the centro-symmetric environment of the cationic complex (Figura 21). As expected, the bonds involved in bridging atoms are longer than those similar in unidentate roles. Hence, in [Cd(μ-O-pyridoxine)(μ-Cl)Cl]$_n$, the Cd-(μ-Cl) bonds (2.666 and 2.655 Å) are longer than the Cd-Cl bond (2.530 Å). Moreover, in this polymeric compound, the Cd-μ-O(phenolate) bonds (Cd-O, 2.316 and 2.307 Å) are longer than the single Cd-O(phenolate) bond (2.221 Å) in the complex cation *trans*-[Cd(pyridoxine)$_2$(H$_2$O)$_2$]$^{2+}$.

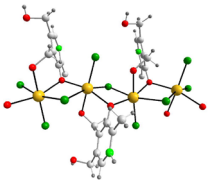


Figure 20. [Cd(pyridoxine)Cl$_2$]$_n$

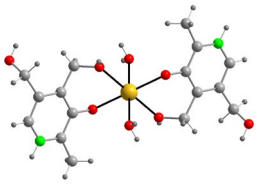


Figure 21. [Cd(pyridoxine)$_2$(H$_2$O)$_2$]SO$_4$·6H$_2$O

5 Other Cadmium Complexes

From the d^{10} state of the Cd^{2+} ion, the coordination chemistry of this metal ion would be expected to be dominated by examples of coordination to four donors of two electrons. In this sense, the ligands containing thiolate or carboxylate groups are interesting to mimic zinc-thiolate or zinc-carboxylate active sites which play a relevant role in bioinorganic chemistry and in the field of cadmium detoxification by chelation.

5.1 Cadmium-Thiolate complexes

At the molecular level, cadmium ions (Cd^{+2}) bind to the thiolate (-S) groups of proteins, cysteine, and glutathione and inhibit the function of these biomolecules. Nevertheless, the CSD database only refers three crystal structures with thiols S-bonded to cadmium centres. Furthermore, cadmium ions are able to block the function of a number of cellular enzymes as well as mimic calcium (Ca^{+2}) and zinc (Zn^{2+}). For example, Cd^{+2} can deposit in bone and binds Ca^{+2} binding proteins. Not surprisingly, biological systems have responded to this toxicity with different strategies that share the same basic chemical principle: the strong affinity of Cd^{+2} for thiol ligands. The strategy adopted by mammals mainly consists of Cd^{+2} complexation and sequestration by metallothioneins, ubiquitous low-molecular-weight, cysteine-rich metalloproteins. [76].

5.1.1 Monothiolate ligands

Cadmium thiolates here considered include those mononuclear compounds which, involve only ligation by organothiolate anions (RS^-) and, if polynuclear, only contain as skeletal bridging ligands these groups. A nice report about the structural chemistry of metal thiolate complexes has been published in 1986 by Dance [77].

5.1.1.1 Mononuclear and dinuclear complexes

The C_{3h} and Y-shaped isomers of $[Cd(S\text{-}2,4,6\text{-}iPr_3C_6H_2)_3]^-$ are examples of monomeric, three-coordinate complexes of cadmium with monothiolate ligands.. The $[CdS_3]$ units in both isomers are planar and the sum of the three S-Cd-S angles in each compound is close to 360º. The C_{3h} isomer is characterized by S-Cd-S angles close to 120º and nearly equal Cd-S bond distances (between 2.417 and 2.427 Å) (Figure 22) [78]. The Y-shaped isomer is characterized by a wider range of S-Cd-S angles (between 100.71 and 135.33º) and Cd-S distances (between 2.422-2.453 Å) [79]. The distortions observed in the Y-shaped isomer can be thought of as an intermediate structure along the pathway toward the formation of a linear two-coordinate complex by the dissociation of the third thiolate ligand. The dinuclear $[Cd_2(S\text{-}2,4,6,^t\text{butyl } C_6H_2)_4]$, which in solution dissociates to monomers, has also trigonal–planar coordinate cadmium ions bridged by two thiolate ligands, with Cd-S_b distances close to

2.5 Å and a shorter Cd-S_t distance of 2.376 Å and angles in the Cd_2S_2 core of 83.24 (S-Cd-S) and 96.7º (Cd-S-Cd) (Figure 23) [80].

The structural principles for $[M^{II}(SPh)_4]^{2-}$ complexes were described in detail by Coucouvanis *et al.* [81]. The distortion of the tetrahedral MS_4 core can be caused by intermolecular interaction between sulfur thiolate atom and an ortho proton of the RS^- group. There are two possible conformations for the $[M^{II}(SPh)_4]$ unit: the D_{2d} and S_4 conformational isomers. The reduction in symmetry of the $[MS_4]$ core from T_d to D_{2d} symmetry converts the S-Cd-S tetrahedral angles (of 109.5º) into two sets of equivalent angles: the two S-Cd-S angles bisected by the S_4 axis are greater than 109.5º and the four remaining S-Cd-S angles which are less than the tetrahedral angle. The D_{2d} isomer is predicted to have a tetragonally elongated $[MS_4]$ core as has been observed in $[Et_4N]_2[Cd(S\text{-}2\text{-}Ph\text{-}C_6H_4)_4]$. [82]. The S_4 conformation is more difficult to discern but all the S_4 structures have $[MS_4]$ cores which are tetragonally compressed as in $[Me_4N]_2[Cd(SPh)_4]$ [83].

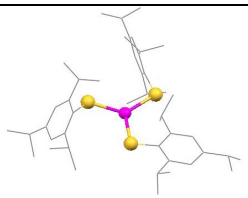


Figure 22*. $[Cd(S\text{-}2,4,6\text{-}iPr_3C_6H_2)_3]^-$

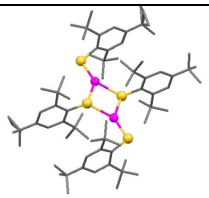


Figure 23. $[Cd_2(S\text{-}2,4,6,^t\text{butyl } C_6H_2)_4]$

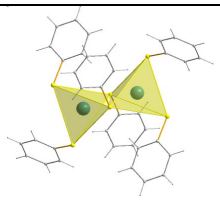


Figure 24. $[Cd_2(SC_6H_5)_6]$

*[Ref. 84]

The dinuclear compound $(Ph_4P)_2[Cd_2(SPh)_6]$ crystallizes in two possible dimorphic forms, the monoclinic [85] (Figure 24) and the triclinic [86]. Both dimorphs contain the centrosymmetric $[(PhS)_2Cd(\mu\text{-}SPh)_2Cd(SPh)_2]^{2-}$ anion, with approximately tetrahedral coordination stereochemistry at cadmium ion. The Cd-S_t distances are similar in the two dimorphs, but there are differences in the bridging region. The $[Cd_2S_2]$ core of the monoclinic dimorph is almost square and has equal Cd-S_b distances, but in the triclinic the two independent Cd-S_b bond distances are different (2.583 and 2.651 Å) and the Cd···Cd distance is shorter (3.549 vs 3.692 Å). The overall crystal packing of the ions in the dimorphs is similar. The study by density functional methods shows that the intermolecular crystal packing energies are dominant, being greater than the energies involved in the intramolecular

conformational differences, while the energy differences associated with bond length variation of ± 0.04 Å are the smallest, only ca. 1 kcal mol^{-1} [86].

5.1.1.2 Complexes with higher nuclearities

The core of the trinuclear cluster anion $[Cd_3(S\text{-}2,4,6\text{-}iPr_3C_6H_2)_7]^-$ is formed by a defect cubane Cd_3S_4 cluster with three cadmium ions and four sulphur atoms at its vertices. The cluster closely approaches the C_{3v} symmetry. Each cadmium atom exhibits tetrahedral coordination and there are three types of coordination modes in the seven thiolate ligands: three terminal, three doubly bridging and one triply bridging thiolates [87] (Figure 25). In the uncharged trinuclear cadmium complex $[Cd_3(S\text{-}2,4,6\text{-}iPr_3C_6H_2)_6(HS\text{-}2,4,6\text{-}iPr_3C_6H_2)]$ the three cadmium atoms are coordinated by six thiolate (RS^-) and one thiol (RSH) ligands. Two of three cadmium atoms have tetrahedral coordination and the third is trigonal planar [88].

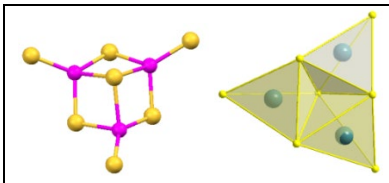


Figure 25. $[Cd_3(S\text{-}2,4,6\text{-}iPr_3C_6H_2)_7]^-$

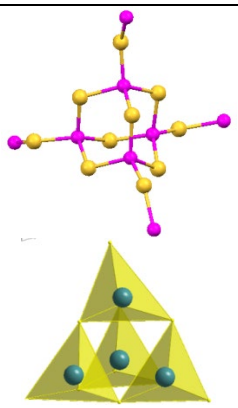


Figure 26. $[Cd_4S_6]$ core

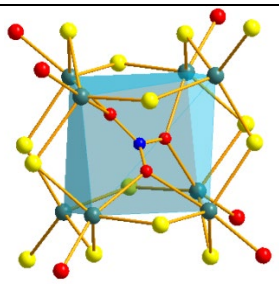


Figure 27. $[Cd_8(SPhF\text{-}3)_{14}(dmf)_6(NO_3)]^+$

A revision of the structural chemistry of $[M_x(SR)_y]^{2-}$ complexes with $x \geq 4$ reveals the existence of molecular cages in which bridging thiolate sulfur atoms and metal atoms each form recognizable polyhedra [89]. A frequently encountered structural unit is the adamantane-type tetranuclear cluster with a $[M_4(\mu\text{-}SR_6)]$ core containing a tetrahedrally disposed set of metal atoms and an octahedron of bridging thiolate atoms with overall (idealized) *Td* symmetry. This structural type has been established for the inorganic polymer $Cd(SPh)_2$ which consists of $Cd_4(SPh)_6$ cages, each of which is linked with

four surrounding cages by four SPh bridges in the same helical conformation as the SiO_4 tetrahedra in cristobalite [90] (Figure 26). This [Cd_4S_6] adamantane-like cage is also present in the tetranuclear anionic complexes $[Cd_4(SPh)_{10}]^{2-}$ [91] and $[Cd_4(ScHex)_{10}]^{2-}$ [92] with each Cd(II) ion bonded to one terminal (the outside of adamantane-like cage) and three bridging thiolate ligands.

The terminal positions on the adamantane-like cage can be substituted by other ligands such as halogenide ions leading complexes such as $[Cd_4(SC_6H_4Bu^t\text{-}4)_7Cl_3]^{2-}$ [93] and $[Cd_4(SPh)_6I_4]^{2-}$ [94].

Some crystal structures of cadmiun-thiolates complexes with nuclearity higher than 4 can be found in the literature. For example, the octanuclear molecule $[Cd_8(SPhF\text{-}3)_{14}(DMF)_6(NO_3)](NO_3)$ [95] (Figure 27) consist of a cubic cluster $[Cd_8(SPhF\text{-}3)_{14}(DMF)_6]^{2+}$ with eight cadmium ions arranged at the corners of a cube while 12 -SPhF-3 groups are distributed off the center of each cubic edge as bridging ligands. Six pentacoordinated cadmium sites are bonded to solvent DMF molecules and NO_3^- within the cage while the remaining two corners (tetrahedral cadmium sites) are occupied by -SPhF-3 groups.

5.1.2. Dithiolate ligands of BAL type

The toxicity of cadmium is determined by chelation reactions: in vivo, Cd^{2+} exists exclusively in coordination complexes with biological ligands, or with administered chelating agents. Generally, the stability of complexes increases with the number of coordination groups contributed by the ligand. Consequently, complexes of Cd^{2+} with polydentate ligands containing SH groups are very stable. In chelation terapy, the requirement for induction of efficient detoxification of Cd^{2+} seems to be a relatively lipophilic chelating agent with two adjacent SH groups favouring tedrahedral coordination as in the Cd-MT complex [96]. Dithiolate ligands such as 2,3-dimercaptopropanol (dimercaprol, BAL = British Anti-Lewisite), dimercaptosuccinic acid (DMSA, Succimer) and 2,3-dimercapto-1-propanesulfonic acid (DMPS, Unithiol) have proven to be good chelating agents towards several toxic divalent metallic cations.

The coordination geometry in the ethanedithiolate compound $(Et_4N)_2[Cd(edt)_2]$ [97] approximates to tetrahedral (D_{2d}) symmetry (Figure 28) and the bond distances are comparable with those of other tetrahedral $M(SR)_4$ units and other mononuclear tetrahedral cadmium dithiolate complexes [98]. In the mononuclear tetrahedral benzenedithiolate compound $(PPh_4)_2[Cd\{bpvbd\}_2]$ [99] (Figure 29) the presence of intramolecular NH···S hydrogen bonds was established by X-ray crystal structures, IR, and NMR spectra. The contribution of the NH···S hydrogen bond was analyzed using the NBO (Natural Bond Orbital) program, which suggests the stabilization of the complex by hydrogen bonding. The role of hydrogen bonds in metallothioneins has been previously discussed using model complexes [100] or a modified metallothionein [101]. In this way the X-ray crystal structure analysis of rat metallothionein-2 suggested that the coordinating sulfur atoms formed NH···S hydrogen bonds with the amide protons in the polypeptide backbone and with the ammonium protons in the lysine residues [102]. All the experimental and theoretical results suggested that the N···S hydrogen bond influences the efficient capture of toxic cadmium ions by metallothioneins.

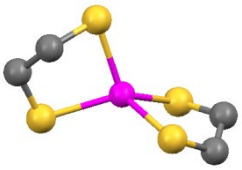


Figure 28. $[Cd(edt)_2]^{2-}$

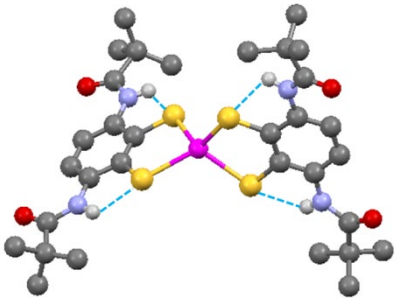


Figure 29. $[Cd\{bpvbd\}_2]^{2-}$

5.2 Dithiocarbamate Cadmium Complexes

The importance of $[S_2CNR_2]^-$ dithiocarbamates in biological systems has emerged as result of the discovery by Gale *et al*. in 1981 of sodium diethyldithiocarbamate as an antidote for acute cadmium(II) chloride poisoning [103]. Since the publication of the aforementioned article, the coordination chemistry of cadmium(II) with dithiocarbamates has been steadily developed. Although studies have been carried out mainly in solution; it has not been until recently that this research has been focused on

the solid state, due to the fact that dithio-/diselenocarbamates of cadmium are excellent precursors for the synthesis of CdS or CdSe nanoparticles, which have unique electronic and optical properties, suitable for optoelectronic applications [104-106].

In spite of this development, the number of cadmium complex structures with dithiocarbamates known to date is not very high and they fit within the motifs recently described for 1,1-dithiolates of group 13 metals [107]. These structures can be grouped into anionic and neutral categories. The former are monomeric with hexacoordinated cadmium, in a distorted trigonal prismatic geometry, with three diethyldithiocarbamate ligands acting as chelating bidentate S,S' ligands in an anisobidentate manner, that is, one Cd-S bond is somewhat shorter in comparison to the other, but the C-S distances are the same, if the cation is tetra-n-butylammonium [108] (Figure 30), but if the cation is $[M(en)_3]^{2+}$ (M = Ni, Zn or Cd) or PPh_4^+, both distances are different to a greater or lesser degree [109-111]. Nevertheless, there are two structures with a pentacoordinated cadmium, one including isothiocyanate as an additional ligand [112] and the other with a coordinated molecule of tri-t-butoxysilanethiolate and one iodide [113]. A third structure contains cadmium tetracoordinated by one molecule of dithiocarbamate and two tri-t-butoxysilanethiolate [114].

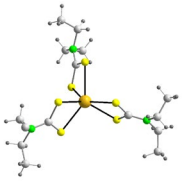


Figure 30. $[Cd(S_2CNEt_2)_3]^-$

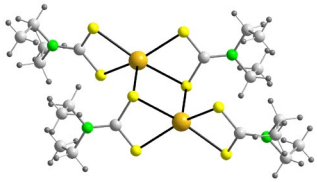


Figure 31. $[Cd(S_2CNEt_2)_2]_2$

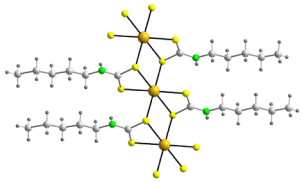


Figure 32. $[Cd\{S_2CNH(n\text{-}C_5H_{11})\}_2]_n$

There are two types of neutral complexes: homoleptic and heteroleptic. The former are generally dimers, with two cadmium atoms pentacoordinated by two molecules of dithiocarbamate acting as anisobidentate ligand (Figure 31). One sulphur atoms from one of the molecules coordinated to cadmium ion acts as a bridge to the other cadmium atom, bringing about distorted square pyramidal coordination geometry, with the axial position occupied by the bridging sulphur atom [115].

Some neutral homoleptic complexes with dithiocarbamates containing long alkyl substituents on the nitrogen atom, such as N-phenyldithiocarbamate or N-dodecyldithiocarbamate, are 1D chains based

on flat rectangular molecular units $[Cd(S_2CNHR)_2]$ connected by means of Cd···S intermolecular interactions (average 2.937 Å), giving rise to a hexacoordinated S_6 (4+2) environment around cadmium ion in a rectangular bipyramidal geometry [116] (Figure 32). There is also a 1D methylcadmium polymer showing coordination number 4 (CNS_2) [117].

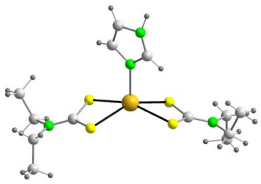


Figure 33. $[Cd(S_2CNEt_2)_2(HIm)]$

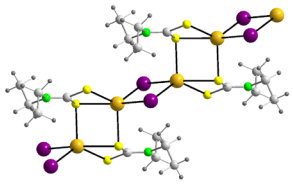


Figure 34. $[Cd(S_2CNEt_2)I]_n$

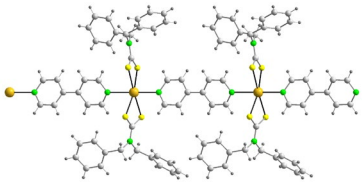


Figure 35. $[Cd(S_2CNBz_2)(4,4'\text{-bipy})]_n$

In the heteroleptic complexes, the auxiliary ligands are usually nitrogen donor ligands, although there are also some complexes with phosphine. The structure of these complexes and the coordination number of the cadmium ion depend on the type of co-ligand. If the ligand is monodentate, such as imidazole [118] (Figure 33) or pyridine [119, 120] the coordination number is 5 (NS_4) and the complex is mononuclear, but if it is an aromatic α,α'-diamine such as 2,2'-bipy or 1,10-phen or derivatives, the metal ion coordination number is 6 (N_2S_4) [121-124]. However, some complexes are dinuclear because the auxiliary ligand acts like a bridge, as in $(\mu\text{-dppf})\{Cd(S_2CNEt_2)_2\}_2$ [125], or in $[Cd_2(\mu\text{-paa})(S_2CNPr_2)_4]$ [126]. In the first case, the cadmium coordination number is 5 and in the second 6. In $[Cd\{SSi(OBu^t)_3\}(S_2CNEt_2)]_2$ the coordination number of each metal centre is four and the coordination geometry is tetrahedral [114]. There are also some pentacoordinated cadmium(II) dimers of S_2CNEt_2 with 1,4-diazabicyclo[2.2.2]octane as a bridging ligand and fullerene C_{60} of crystallisation [127]. To date, there are only four known coordination polymers based on heteroleptic cadmium complexes with dithiocarbamates in which the auxiliary ligand acts as a bridge. The structure of $[Cd(S_2CNEt_2)I]_n$ consists of dimeric units $[Cd_2(\mu\text{-}S_2CNEt_2)_2]^{2+}$ linked by two iodine bridges which link neighbouring *cis* cadmium ions, bringing about 1D chains where each cadmium ion is pentacoordinated by an I_2S_3 group with an intermediate geometry between tetragonal pyramidal and trigonal pyramidal [128] (Figure 34). The structure of $[Cd(S_2CNEt_2)_2(dpe)]_n$ (dpe = 1,2-di(pyridin-4-yl)ethane) is based on flat $Cd(S_2CNEt_2)_2$ units linked by *trans* dpe molecules, which give rise to a 1D chain in which each

cadmium ion presents a distorted octahedral coordination geometry with a *trans*-N_2S_4 donor group [129]. Identical structures contain 4,4'-bipyridine or 1,2-bis(4-pyridyl)ethylene as spacers between rectangular $[Cd(S_2CNR_2)_2]$ units [130, 131] (Figure 35).

An analysis of the most significant bonding parameters involved in the coordination of dithiocarbamates to the cadmium ion in the 59 different structures reported to date reveals that the Cd-S distances in each CdS_2C chelate, in general, differ less than 0.1 Å, with average values of 2.610 and 2.716 Å. Nevertheless, in the dinuclear complexes, with one of the sulphur atoms acting as bridge, the difference between both Cd-S distances has an average value of 0.320 Å, with inferior and superior limits of 2.768 and 2.975 Å, respectively, which contrasts with the average value of 2.604 Å for the distance from this sulphur atom to the second cadmium atom.

Also, the value of the S-Cd-S angle (*bite angle*) depends on the type of coordination and the geometry. Therefore, in anionic complexes with S_6 coordination, the average value is 65.62º, whereas in neutral complexes with N_2S_4 coordination it is 67.32º. In monomers with NS_4 coordination the average value is 68.97º and in the S_5 dimers the values are 66.71 and 70.07º for the two molecules of the ligand. Furthermore, the average value of the S-Cd-S angle in complexes with coordination number 4 is 69.11º.

Moreover, the coordination of the dithiocarbamates to the cadmium atom leads to a redistribution of the charge on the S_2CN group of the ligand, resulting in a partial positive charge located over the nitrogen atom whilst another negative charge is delocalised over the CdS_2C chelate ring; this is manifested in the values of the average C-S distances for each ligand of 1.712 and 1.728 Å, and also in the C-N bond, which is 1.329 Å.

5.3 Polycarboxylate ligands of EDTA Type

Aminopolycarboxylate ligands such as the potentially hexadentate ethylenediaminetetraacetate, (EDTA) and related tetraacetate compounds, the potentially tetradentate nitrilotriacetate, (NTA) and the potentially tridentate iminodiacetate, (IDA) are useful chelating agents for metal chelation therapy.

The degree of ionization of these polycarboxylates can be controlled by the pH value giving rise to anionic [132] or neutral Cd(II) complexes.

In the neutral mononuclear $[Cd(H_2EDTA)(H_2O)]\cdot 2H_2O$ [133] (Figure 36), the diprotonated H_2EDTA acts as hexadentate (2N + 4O) ligand, and one water molecule increases the coordination number of the metal atom to seven. The tetraanion ethylenediaminetetraacetate (EDTA) is found in the 2D polymer $\{[Cd_2(EDTA)(H_2O)]\cdot H_2O\}_n$, [134] which presents two crystallographically independent Cd^{II} cations. One of the Cd(II) ions, Cd1, is coordinated by five O atoms and two N atoms from two tetraanionic EDTA ligands in a distorted pentagonal-bipyramidal coordination geometry. The other Cd(II) ion, Cd2, is six-coordinated by five carboxylate O atoms from five EDTA ligands and one water molecule in a distorted octahedral geometry. Two neighbouring Cd1 ions are bridged by a pair of carboxylate oxygen atoms to form a centrosymmetric $[Cd_2(EDTA)_2]^{4-}$ unit which is further extended into a two-dimensional structure through Cd2-O bonds.

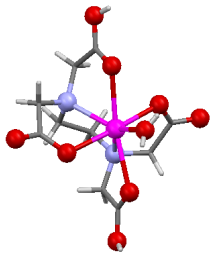


Figure 36. $[Cd(H_2\ EDTA)(H_2O)]\cdot 2H_2O$,

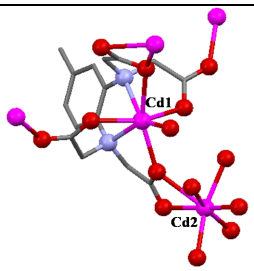


Figure 37. $[(H_2O)Cd(\mu\text{-}3,4\text{-}TDTA)Cd(H_2O)]$,

The substitution of the ethylenic group of EDTA for rigid aromatic rings such as phenylene (*o*-PhDTA) or toluene (3,4-TDTA) leads to ligands which are good complexing agents for Cd(II) in a wide pH range. Also they behave as complexing groups towards several metal ions, inducing the formation of extended interlocked high dimensional structures. The 3D polymer $[(H_2O)Cd(\mu\text{-}3,4\text{-}TDTA)Cd(H_2O)]$ presents two types of cadmium environments [135]. The chelated Cd1 is coordinated to two N atoms and four carboxylate oxygen atoms from the ligand and a water molecule with a roughly capped trigonal prismatic environment forming a $[Cd1(3,4\text{-}\ TDTA)]^{2-}$ unit which is joined to four Cd2 atoms (Figure 37) in such a way that all the carboxylate oxygen atoms of the ligand are bound to Cd(II) ions, which makes the ligand behave as decadentate. The Cd2 center is seven-coordinated

with six oxygen atoms from four different $[Cd1(3,4\text{-}TDTA)]^{2-}$ units and a water molecule in a very distorted capped trigonal prismatic coordination geometry.

In the 2D polymer $\{[Cd_3(IDA)_3(H_2O)]\cdot 3H_2O\}n$, [136] the iminodiacetate dianions behaves as tridentate chelating ligand showing both facial and meridional chelating configurations. One Cd(II) ion is surrounded by three IDA ligands: one N-monodentate, one O,O-bidentate and one N,O,O-tridentate in the *mer*- configuration. A second Cd(II) ion is coordinated by three IDA ligands (two O-monodentate and one N,O,O-tridentate in a *fac*- configuration) and one water molecule. The iminodiacetate dianion bridges neighbouring Cd(II) ions to form polymeric sheets.

6 General conclusions

The electronic configuration ($4d^{10}$) and size of cadmium(II) clearly favour its affinity for soft donor atoms as well as certain variability of coordination numbers and polyhedra. The structures here referred reveal the ability of Cd(II) to exhibit coordination numbers from three to eight being the six-coordination (octahedral or trigonal prism) polyhedra the most usual. Examples are reported where Cd(II) shows two different coordination numbers in the same crystal. Moreover, high coordination numbers favour the formation of polymers with various dimensionalities, whereas the tridentate ability of soft S-tiolate atoms build nice clusters.

Purine ligands bind Cd(II) in monodentate (N3) or bridging modes (μ_2-N7,N9, μ_2-N3,N9, μ_3-N3,N7,N9). Purine derivatives with N9-non-coordinating groups coordinate to Cd(II) by N7, usually assisted by an H-bonding interaction. Likewise, related purines with N-donor atoms in the N9-pendant arm are able to bind Cd(II) by N7, by N-donors from the pendant arm or as a combined mode of these two alternatives. N6-substituted purines bind Cd(II) by N9 whilst 6-mercaptopurine promotes the S6,N7-bidentate mode in Cd(II) complexes due to the softness of the S atom and the chelate effect related to the five-membered chelating ring. Anionic forms of 6-mercaptopurine also play a μ_2-bridging role. In contrast, 6-oxopurines can bind Cd(II) by its N-heterocyclic donors but do not build O6,N7-chelate rings, according to the hardness of O6 atom. Nevertheless, some pyrimidine nucleobases can build constrained four-membered N(heterocyclic),O(exocyclic)-Cd(II) chelate rings. Cd(II) complexes

with various vitamins of B group also reveal a remarkable structural diversity. In particular, thiamine binds Cd(II) by its less hindered N heterocyclic donor or the O-alcoholic donor from its pendant arm or as a combined N,O-bidentate bridging mode. Interestingly, a closely related N,O- bridging role has been observed in the Cd(II)-acyclovir complex. Cd(II) complexes with amino acids are rich in examples where zwitterionic forms of these ligands acts via the carboxylate groups. Suitable side chains with donor atoms increases the denticity and the chelating ability of amino acidate ligands. Hence, L-histidinate(1-) acts as chelating tridentate in the bis-chelate $[Cd(L\text{-}Hhis)_2]\cdot 2H_2O$ but the dianion L-cysteinate(2-) acts as hexadentate in the polymer $[Cd(L\text{-}cys)]_n$ (N,O,S-chelating tridentate as well as S_3(thiolate)- and O,O'(carboxylate)-bridging roles). The affinity between soft Cd(II) ions and S donor atoms yield a rich structural pathway. Thiolate atoms act as mono-, bi- or tri-dentate donor groups. Dithiocarbamate ligands tend to build rather stable four-membered chelate rings, where the S-Cd-S bite angle seems to depend on the coordination geometry. Curiously, structures of Cd(II) complexes with those dithiolate ligands proposed for Cd(II) detoxification have not yet reported. Chelate ring constraints in EDTA-type Cd(II) complexes favour seven-coordination polyhedra.

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Abbreviations and Definitions

1Mecyt	1-methylcytosine
1Toscyt	1-(*p*-toluenesulfonyl)cytosine
9Etgua	9-Ethylguanine

9Meade	9-methyladenine
9Megua	9-methylguanine
2,2'-bipy	2,2'-bipyridine
3,4-TDTA	3,4-toluenediamine-*N*,*N*,*N*',*N*'-tetraacetate(4-)
4,4'-bipy	4,4'-bipyridine
acv	acyclovir (2-amine-9-(2-hydroxyethoxymethyl)-3*H*-purin-6-one)
BAD^+	N^6-benzyladeninium cation
BAL	British Anti-Lewisite (2,3-dimercaptopropanol)
bpvbd	3,6-bis(pivaloylamino)benzene-1,2-dithiolato-S,S' (2-)
DABT	2,2'-diamine-4,4'-bis-1,3-thiazole
DMAB	4-(dimethylamino)benzoate(1-)
DMF	*N*,*N*- Dimethylformamide
DMPS	2,3-Dimercapto-1-propanesulfonate (1-)
DMSA	dimercaptosuccinate(2-)
dmso	dimethylsulfoxide
dpe	1,2-di(pyridin-4-yl)ethane
dppf	(diphenylphosphino)ferrocen
ede-ade	2-(ethylenediamine)ethyl-N9-adenine
ede-dap	2-(ethylenediamine)ethyl-N9-2,6-diaminopurine
ede-gua	2-(ethylenediamine)ethyl-N9-guanine
edp-dap	2-(ethylenediamine)propyl-N9-2,6-diaminopurine
edt	ethane-1,2-dithiolato
EDTA	ethylenediaminetetraacetate(4-)
en	1,2-ethylenediamine
FAD^+	N^6-furfuryladeninium cation

H6MP	6-mercaptopurine
Hade	adenine
Hala	alanine
Hasn	asparagine
Hcyt	cytosine
Hdap	2,6-diaminopurine
Hgly	glycine
Hhip	hippuric acid
Hhyp	hypoxanthine
Hhis	histidine hypoxanthine
Hicyt	isocytosine
HIm	1*H*-Imidazole
Hmet	methionine
Hphe	phenylalanine
Hpro	proline
Htheo	theophiline
Htrp	tryptophan
Hura	uracile
Hxan	xanthine
H_2ap	adipic acid
H_2asp	aspartic acid glycine
H_2glu	glutamic acid
H_2tp	terephthalic acid
IDA	iminodiacetate(2-)
NA	nicotinate(1-)

NADA	nicotinamide
NBO	natural bond orbital program
NBZ	2-nitrobenzoate(1-)
niacin	3-pyridinecarboxylic acid
niacinamide	3-pyridinecarboxamide
NTA	nitrilotriacetate(3-)
ox	oxalate(2-)
o-PhDTA	*ortho*-phenylenediamine-*N*,*N*,*N*',*N*'-tetraacetate(4-)
paa	2-pyridinealdazine
phen	1,10-phenanthroline
PMAB	4-(methylamino)benzoate(1-)
ptola	p-toluic acid
S-2,4,6-$iPr_3C_6H_2$	(2,4,6-tri-isopropyl)benzenethiolato(1-)
S-2,4,6,^{t}butyl C_6H_2	(2,4,6-tri-tertbutyl)benzenothiolato(1-)
$SC_6H_4Bu^t$-4	4-tertbutylbenzenothiolato(1-)
SC_6H_5	benzenothiolato(1-)
ScHex	cyclohexanethiolato(1-)
SPhF-3	3-fluorobenzenethiolato(1-)
tem-N^9,$N^{9'}$-diade	N^9,N^9 tetramethylene-bis(adenine)
tm-N^9,$N^{9'}$-diade	N^9,$N^{9'}$-trimethylene–bis(adenine)
tren	tris(2-aminoethyl)amine

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