Adsorption of Zn^{2+} and Cd^{2+} from Aqueous Solution onto a Carbon Sorbent Containing a Pyrimidine–Polyamine Conjugate as Ion Receptor

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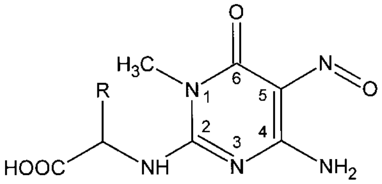
The compound *N*-(4-amino-1-methyl-5-nitroso-6-oxo-1,6-dihydropyrimidin-2-yl)-*N'*-[bis(2-aminoethyl)]ethylenediamine (HL) was synthesised and structurally characterised by analytical methods and ^{1}H, ^{13}C and ^{15}N NMR spectroscopy. The protonation of HL and its coordinating ability towards Zn^{2+} and Cd^{2+} ions in water solution were also studied by potentiometric methods and UV/Visible and ^{1}H-^{13}C NMR spectroscopy. The molecular structures of $[H_3L]^{2+}[CdI_4]^{2-}\cdot 2H_2O$ and $[(Cl_3Zn)(\mu\text{-}Cl)\{Zn(\mu_2\text{-}HL)\}]_2\cdot 2.5H_2O$ were solved by single-crystal X-ray diffraction methods. On the basis of these data, the performance of HL anchored to activated carbon (AC) was evaluated as a molecular receptor for Zn^{2+} and Cd^{2+} metal ions in aqueous solution. This was done by a comparative study of the adsorption capacity of the adsorbents AC alone and HL anchored on the AC (AC-HL) for these metal ions and by a structural study of the AC-HL, AC-HL-Zn^{2+} and AC-HL-Cd^{2+} solid phases by XPS and IR spectroscopy.

Introduction

Substitution reactions at the C(2) atom of the 4-amino-1-methyl-5-nitroso-6-oxo-1,6-dihydropyrimidin-2-yl moiety with an α-amino acid residue result in molecular compounds containing a rigid, flat pyrimidine moiety and a pendant amino-acidic residue[1] (Scheme 1).



Scheme 1.

These compounds have two Lewis base-type environments that control their coordinating behaviour: one is constituted by the neighbouring C(5)–NO and C(6)=O substituents in the pyrimidine ring, and the other by the characteristic basic functions existing at the amino acid residue linked to the C(2) position of the pyrimidine nucleus. Steric factors prevent co-operative binding of both pyrimidine and amino acid functions, to a single metal centre, and this favours the formation of 1D, 2D and 3D polynuclear solid complexes. In fact, the structures of some of the crystalline polynuclear complexes of these ligands with alkali and alkaline-earth metal ions have been solved[2] and show interesting features similar to those of metal–organic compounds with non-linear optical properties.[3]

The molecules depicted in Scheme 1 are characterised by a strong electronic polarisation at the pyrimidine nucleus as a result of the co-operative effect of the marked electron-withdrawing character of the C(5) nitroso function and the electron-donating character of the amino function at C(2). This fact is consistent with the non-basic character of the N(3) atom which, in our studies, has never been found to be a metal-binding centre of these ligands.[2] The strong polarisation of the pyrimidine π-electron cloud[1b] suggests the existence of low-energy LUMO orbitals that are able to interact with high-energy HOMO orbitals provided by electron-rich aromatic centres. Accordingly, in a recent work[4] we have explained the observed irreversible adsorption of two of these nitrosopyrimidine-amino acid conjugates onto an activated carbon (AC) as being due to π–π donor–acceptor interactions between the pyrimidine moiety of the ligands (acting as acceptor) and the arene centres of the AC[5] (acting as donor). These results suggest that, after adsorption of these molecules on the AC, their pyrimidine moieties remain attached to the carbon surface, coplanar with the graphene sheets, thus losing their ability to bind to metal ions. On the other hand, the amino acid residue linked to C(2) of the pyrimidine ring is projected outside of the carbon surface and becomes the only potential reactive centre for metal ions in the ligand–AC adducts. Hence, although the interactions between metal ions and free ligands

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are rather non-specific in aqueous solution, it is expected that the carbon-anchored ligands would behave as monofunctional ligands to metal ions by using only the basic function linked to C(2) of the pyrimidine ring as binding site.

Activated carbons have been extensively used to remove metals from industrial and municipal wastewater as they are cheap and accessible materials. Nevertheless, their efficiencies are strongly limited due to the non-specific nature of the basic functions which are usually added by the activation processes.[6] Moreover, the functionalisation by activation is limited to the edges of the graphene layers and to the entrance of the pores. For these reasons, although advantageous textural (e.g. adequate surface area and specific pore size distribution) and functional properties (both easily achievable by adequate activation processes) are important, the development of specific chemical properties at the carbon surface[7] to improve its metal-capturing properties, which is more difficult to attain, is also vital.

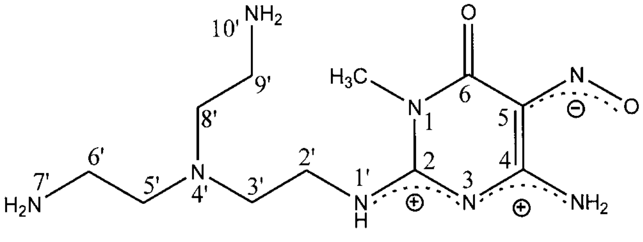
The adducts resulting from the irreversible adsorption of a monolayer of the C(2)-functionalised nitrosopyrimidines on the AC graphitic surface can be regarded as new selectively functionalised activated carbons whose mechanical and textural properties are provided by the carbon skeleton while the chemical functionalisation is provided by the functionality introduced as the C(2)-substituent at the nitrosopyrimidine derivative. Moreover, whenever the basic functions existing at the C(2) substituent of the pyrimidine moiety can be tailored, the adsorption of these compounds becomes an easy and suitable method to develop the desired functionality at the carbon surface. Of course, the efficacy of the proposed method is conditioned to maintaining the heteroaromatic moiety unaltered on changing the substituents at the C(2) position of the pyrimidine moiety.

As already commented, in a recent paper[4] we studied the adsorption of a new molecular receptor of this class, *N*-(4-amino-1-methyl-5-nitroso-6-oxo-1,6-dihydropyrimidin-2-yl)-*N′*-(bis-2-aminoethyl)ethylenediamine (HL), at several pHs, on a basic AC. We found that HL is irreversibly anchored at the arene centres of the carbon surface through the pyrimidine moiety, by strong π–π interactions,[4] thus providing functionalisation of the AC with a triamine grouping. The aim of this work was to gain insight into the performance of the proposed model by comparison of the capacity of an activated carbon and the above ligand previously adsorbed on it (AC-HL) to capture metal ions. For this, the adsorption data of $ZnCl_2$ and $CdCl_2$ in aqueous solution on an AC and AC-HL adsorbent were analysed in the light of the structural data of HL, which was characterised by X-ray diffraction methods, and also the coordination chemistry behaviour of Zn^{II}/HL and Cd^{II}/HL systems in aqueous solution.

Results and Discussion

Characterisation of the Ligand

HL was prepared by a procedure consisting of the nucleophilic attack of one of the amino primary groups of tris(2-aminoethyl)amine to the C(2) position of the pyrimidine precursor 4-amino-2-methoxy-1-methyl-5-nitroso-6-oxo-1,6-dihydropyrimidine (Scheme 2). For this, the pH of the reaction mixture was adjusted such that one of the three amino primary groups remained unprotonated.[8]



Scheme 2.

N projections in the ^1H-^{15}N HMBC spectrum of HL·2HCl exhibit the same signals as the pyrimidine precursor (see Experimental Section) along with another two signals attributable to the secondary and tertiary N atoms of the polyamine residue, with the former at lower field than the latter. The lack of signals for two of the primary amino groups means that they have been protonated and thus confirms the monosubstitution of the polyamine. The carbon atoms were assigned in the ^1H-^{13}C HSQC spectrum after the methylene protons of the polyamine moiety had been assigned in the ^1H-^{15}N HMBC spectrum.

The structure of compound $[H_3L]^{2+}[CdI_4]^{2-}\cdot 2H_2O$ was solved by single-crystal X-ray diffraction analysis. The molecular structure consists of protonated cations $[H_3L]^{2+}$, tetraiodocadmiate(II) anions and water solvent molecules (Figure 1). This allowed an analysis of the $[H_3L]^{2+}$ unit in which, as expected, the two protons attached to HL are at the primary amino groups of the polyamine.

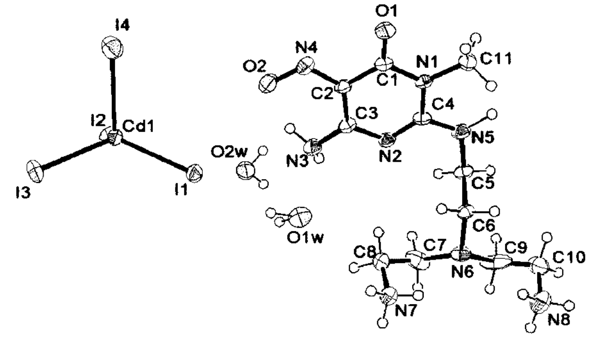


Figure 1. ORTEP drawing of $[H_3L]^{2+}[CdI_4]^{2-}\cdot 2H_2O$.

The structure of $[H_3L]^{2+}$ exhibits a planar conformation of the heterocyclic moiety [including the pyrimidine substituents labelled in Scheme 2 as C(6)O, C(5)NO, C(4)NH_2 and C(2)NH], whereas the C(2) substituent deviates from the aromatic plane. This suggests π electronic delocalisation in the pyrimidine and precludes the C(2)NH and C(4)NH_2 exocyclic substituents from acting as metal ion acceptors. The C(5)-nitroso group is oriented *trans* to C(6), which allows the formation of an intramolecular N–H···O hydrogen bond in an S(6) motif. An intramolecular hydrogen bond also exists between the N(7′) atom of a primary amino group as donor and the N(4′) atom as acceptor. This description resembles the structure of analogous α-amino acid derivatives.[1,9]

The similarity between the C(5)–NO and N–O bond lengths, (1.320 Å and 1.302 Å, respectively), which are in the range of those observed in oximate anions [RR′C–N–O]$^-$, suggests the existence of a delocalised double bond in the C(5)NO grouping.[10,11] All of the C–N bonds lengths in the HN^2–C(2)–N(3)–C(4)–N^{4}H$_2$ fragment are rather similar [C(2)–N^{2}H = 1.33 Å; C(2)–N(3) = 1.30 Å; N(3)–C(4) = 1.353 Å and C(4)–N^{4}H$_2$ = 1.314 Å] and it is not possible to distinguish between single and double bonds. All of these parameters taken together suggest that the representation of Scheme 2 is the most appropriate for HL.

Ligand Protonation

The protonation constants of HL obtained by potentiometric methods in aqueous medium are reported in Table 1. The monoanion L$^-$, which exists at high pH values, binds four protons in the pH range investigated (2.5–10.5). The first three protonations are markedly grouped, and their log *K* values indicate a strongly basic character of the corresponding protonation positions, i.e. they take place at strongly basic atoms. On the contrary, the fourth protonation constant (log *K* = 2.12) indicates a far lower basicity for this position.

Table 1. Protonation constants (log *K*) of HL (0.1 M KCl, 298.1 K).

Reaction	log *K*
$L^- + H^+ \leftrightharpoons HL$	10.94
$HL + H^+ \leftrightharpoons [H_2L]^+$	9.70
$[H_2L]^+ + H^+ \leftrightharpoons [H_3L]^{2+}$	8.75
$[H_3L]^{2+} + H^+ \leftrightharpoons [H_4L]^{3+}$	2.12

The UV/Visible adsorption spectra of HL at various pH values is given in Figure 2. The spectrum at pH 5 is similar to that of the pyrimidine chromophore[2f] and consists of two UV bands due to π–π* transitions at λ_1 = 328 nm (ε_1 = 2.23×10^4 cm^{-1}mol^{-1}L) and λ_2 = 230 nm (ε_2 = 8.85×10^3 cm^{-1}mol^{-1}L). The visible band with a maximum at λ_3 = 524 nm (ε_3 = 76.50 cm^{-1}mol^{-1}L), is assigned to a forbidden n→π* transition of the non-bonding O electron pair of the C(5)NO group.[2f]

The spectra are unchanged in the pH range 4.1 to 10.0, thus indicating that the second and third protonations do not affect the pyrimidine chromophore, i.e. they take place on the primary amino groups of the polyamine. On the contrary, the small red-shift of the 328 nm band as the pH increases above about 10 indicates that the first protonation step takes place either at the -N$^-$-C(2) or NH$^-$-C(4) anions. To gain further insight into this protonation step we studied the ^{1}H and ^{13}C NMR spectroscopic data obtained from HL in D$_2$O at different pH values; the results are summarised in Figure 3. The significant upfield shifts of the methylene protons at pH values up to 10 suggest that the process

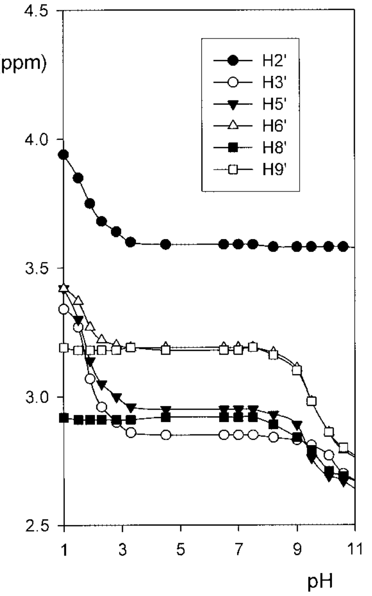


Figure 3. ^{1}H NMR chemical shifts of the HL signals as a function of pH.

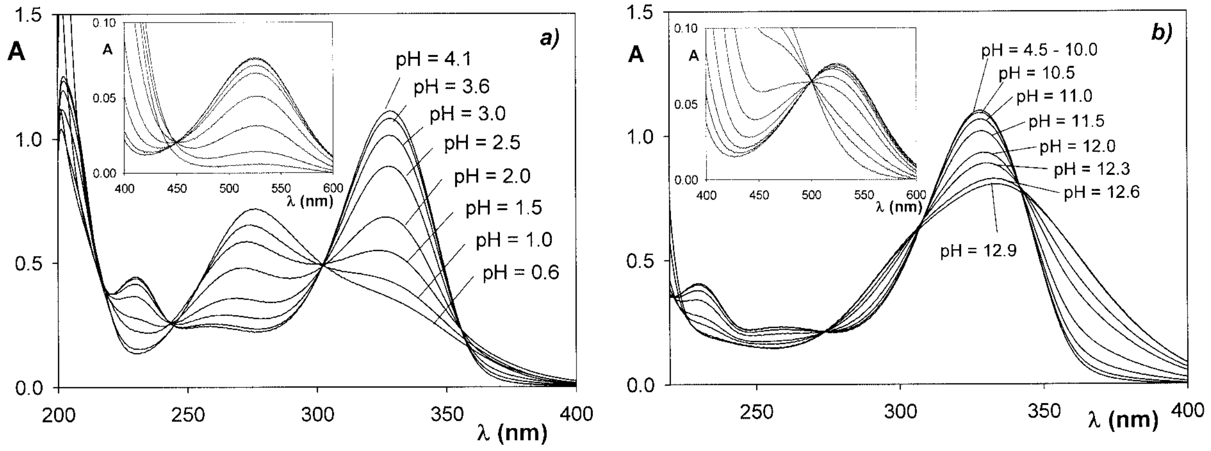
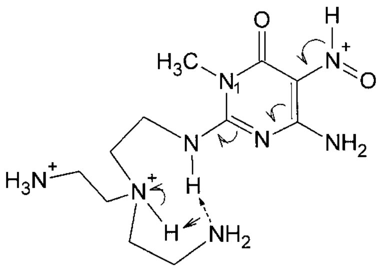


Figure 2. pH-Dependence of the absorption spectra of HL in the UV ([HL] = 5×10^{-5} M, 0.1 M KCl), and visible (inset, [HL] = 10^{-3} M, 0.1 M KCl) regions, a) in acidic media and b) in basic media.

studied occurs at $-N^{-}$-C(2). Moreover, the deshielding of such protons in the pH range 10–7 indicates the protonation of the two primary amino groups in this pH range.

In the pH range 1–4, where the fourth protonation step occurs (see Figure 2), a blue-shift of the 328 nm band and quenching of the absorption at 524 nm are observed with decreasing pH values. The latter indicates that the σ nonbonding pair on C(5)NO is used in binding this proton, thus hindering the $n \rightarrow \pi$ transition (band at 524 nm, see above). Protonation of the NO group instead of the $N(3)_{ring}$ atom is consistent with the above-described polar character of HL, according to which the electron density is higher at NO than at $N(3)_{ring}$.

In addition, in a ^1H NMR titration experiment of HL during this protonation (pH range 1–4) a deshielding of the protons at the 2′, 3′, 5′ and 6′ carbon atoms of the polyamine was observed (Figure 3). The non-chemical equivalence of the H5′ and H8′ and H6′ and H9′ signals in the polyamine residue indicates a conformational change accompanying this process, which is probably induced by the formation of an intramolecular hydrogen bond of the $H_2N\cdots HN{-}C(2)$ type (Scheme 3).



Scheme 3.

Complex Formation in Aqueous Solution

Complex formation in the HL/Zn^II and HL/Cd^II systems in an aqueous medium was studied by a potentiometric method at [ligand]/[metal] = 1. The complex species formed, together with their stability constants, are listed in Table 2, and the species distribution plots are given in Figure 4.

Table 2. Stability constants of Zn^{II} and Cd^{II} complexes (log *K*) with HL (0.1 M KCl, 298.1 K).

Reaction	log *K* Zn^{II}	Cd^{II}
$M^{2+} + H_3L^{2+} \leftrightharpoons [MH_3L]^{4+}$	3.96	2.80
$M^{2+} + [MH_3L]^{4+} \leftrightharpoons [M_2H_2L]^{5+} + H^+$	6.33	
$M^{2+} + H_2L^+ \leftrightharpoons [MH_2L]^{3+}$		4.85
$M^{2+} + HL \leftrightharpoons [MHL]^{2+}$	9.56	7.45
$M^{2+} + 2HL \leftrightharpoons [M(HL)_2]^{2+}$	17.33	13.88
$M^{2+} + [MHL]^{2+} \leftrightharpoons [M_2HL]^{4+}$	3.84	2.94
$M^{2+} + L^- \leftrightharpoons [ML]^+$		9.82
$[ML]^+ + L^- \leftrightharpoons ML_2$		7.59
$M^{2+} + L^- + OH^- \leftrightharpoons MLOH$	3.00	
$M^{2+} + OH^- \leftrightharpoons [MOH]^+$		–8.35
$M^{2+} + 2OH^- \leftrightharpoons M(OH)_2$	–14.60	

Zn^{II} forms mono- and dinuclear complexes with HL in aqueous solution. At low pH values only the complex $[Zn(H_3L)]^{4+}$, with the metal bonded through the pyrimidine moiety, exists. The stability constant (log *K* = 3.96) is similar to the five-membered metal chelates formed by Zn^{II} with N,O donor ligands, such as the single amino acids glycine (log *K* = 5.16), methionine (log *K* = 4.38), ornithine (log *K* = 4.10) and valine (log *K* = 5.00) and the nucleoside guanosine (log *K* = 4.6).[8] This suggests that in the $[Zn(H_3L)]^{4+}$ complex the coordination to the metal ion takes place through the nitrogen atom of the C(5)NO group and the oxygen of C(6)O. This coordinating behaviour of the pyrimidine residue is the only one observed in the tetranuclear complex $[Zn_2(HL)_2][ZnCl_4]_2$ (see below) and also in the polynuclear complexes formed by Zn^{II} with pyrimidine analogues derived from L-valine and L-methionine.[12]

Figure 4 (a) shows that mono-deprotonation of $[Zn(H_3L)]^{4+}$ starts at a pH of around 3.5. The resulting $[Zn(H_2L)]^{3+}$ species is able to bind a second Zn^{II} through the two unprotonated amino groups of the polyamine residue to form the binuclear complex $[Zn_2(H_2L)]^{5+}$. The log *K* value calculated for the association of a Zn^{2+} ion to the

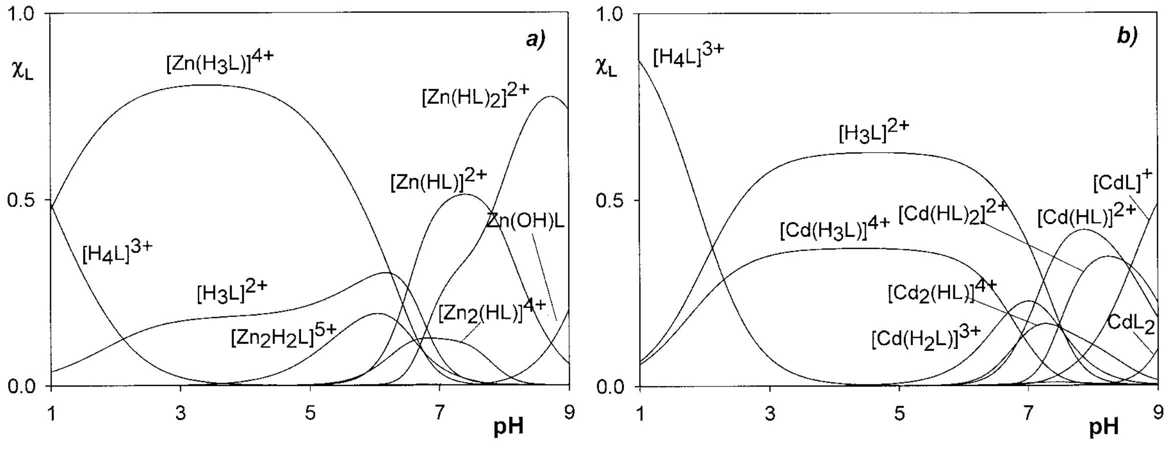


Figure 4. Species distribution plot for a) the HL/Zn^{II} system and b) the HL/Cd^{II} system in aqueous solution (1:1 molar ratio) as a function of pH ([HL] = [Zn^{II}] or [Cd^{II}] = 10^{-3} M, 0.1 M KCl, 298.1 K).

polyamine moiety, $Zn^{2+} + [ZnH_3L]^{4+} \leftrightharpoons [Zn_2H_2L]^{5+} + H^+$, is 6.33. This suggests the coordination of Zn^{2+} by two of the nitrogen atoms of this moiety. The amount of $[Zn_2(H_2L)]^{5+}$ decreases sharply at slightly alkaline pH due to the formation of $Zn(OH)_2$ (not included in Figure 4 (a) for simplicity), but an additional increase of pH produces the complete deprotonation of the polyamine, and this favours the formation of $[Zn(HL)_2]^{2+}$ rather than the hydroxide species. The stability constant for $[Zn(HL)_2]^{2+}$ ($\log K = 17.33$) is consistent with that found for the 1:1 complex $[Zn(TrenH)]^{3+}$ ($\log K = 7.95$), where $TrenH^+$ is the N-tridentate ligand analogous to HL.[8,13] Finally, at a pH of about 8 deprotonation of the C(2)NH group is promoted by Zn^{II}, resulting in the formation of the complex [ZnL(OH)]. The calculated stability constant for the addition of a hydroxy plus an L anion to a Zn^{II} metal ion is $\log K = 16.70$. This value is similar to the Zn^{II} complex with the analogous *N,N,N,N* tetradentate ligand tris(2-aminoethyl)amine (Tren)[13] and suggests a similar coordinating behaviour.

With the aim of getting further information about the structures of the complexes formed in solution, the ^1H and ^{13}C NMR spectra were recorded of a 1:1 HL/Zn^{II} mixture and HL in aqueous solution at various pH values. Figure 5 displays the differences between the chemical shift values ($\Delta\delta$) of proton and carbon atoms vs. pH obtained from these experiments.

In the pH range 1–5, the $\Delta\delta$ values are significant for the C(5) and C(6) atoms of the pyrimidine and negligible for the remainder (see Figure 5, a1). This indicates that in the main species existing in this pH range, $[Zn(H_3L)]^{5+}$, the ligand is coordinated through the C(5)NO and C(6)O groups. This is also supported by the negligible $\Delta\delta$ values found for all of the methylene protons, which indicates that the polyamine unit is not involved in metal coordination.

In the pH range 4–6, non-zero $\Delta\delta$ values for the 5′, 6′, 8′ and 9′ methylene protons indicate that the formation of $[Zn_2(H_2L)]^{5+}$ by addition of a Zn^{II} ion to $[Zn(H_3L)]^{4+}$, which occurs at this pH, takes place at the monoprotonated

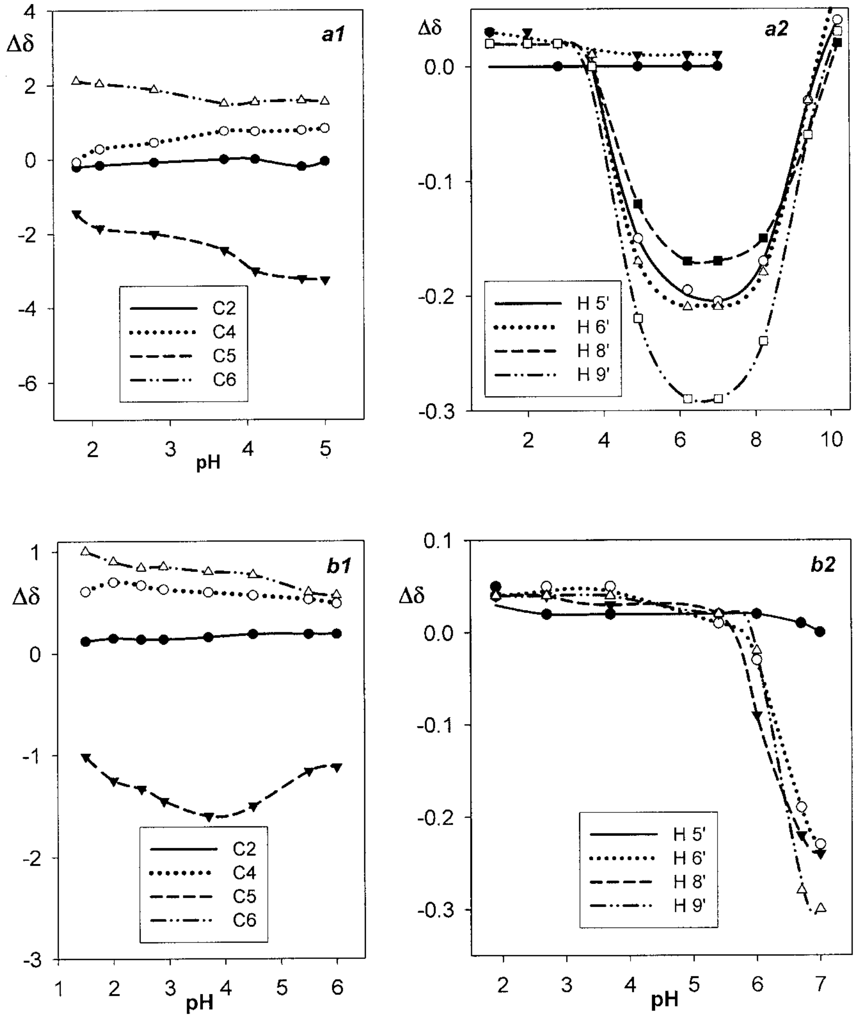


Figure 5. a1: Chemical shift differences between HL/Zn^{II} mixtures (1:1 molar ratio) and HL, at different pHs, for the ring-carbon signals. a2: Chemical shift differences for the polyamine methylenic protons. b1 and b2: Chemical shift differences for Cd^{II}.

polyamine. Figure 5 (a2) also shows the non-equivalence of the analogous methylene groups of each of the two terminal arms of the polyamine residue. This clearly indicates the involvement of only one of the two primary amine groups in the coordination.

The formation of [ZnLOH] species above pH 8 is accompanied by an increasing deshielding of all of the methylene protons (see Figure 5a2) except that of 2′ (not included in this figure for simplicity), which suffers a small opposite effect. This accounts for the involvement of the deprotonated C(2)-NH group of the polyamine in metal coordination and confirms that L acts as a tetradentate *N*,*N*,*N*,*N* ligand.

The complexation equilibria for HL/Cd^{II} system are given in Table 2, with the speciation plots in Figure 4 (b). These highlight that the coordination chemistry of Cd^{II} is similar to that of Zn^{II} as regards the stoichiometries of most of the complex species formed. The structures of the Cd^{II} complexes are also similar to the analogous Zn^{II} complexes described above. This was proved by an analysis of the data obtained from a NMR pH titration experiment of a 1:1 [Cd^{II}]/[HL] mixture (Figures 5, b1 and b2), which shows similar features to those discussed above for the Zn^{II}/HL system.

The stability constants of $[CdH_2L]^{3+}$ and $[CdHL]^{2+}$ complexes are similar to those of the analogous *N*,*N* bidentate 3-phenylpropane-1,2-diamine ($\log K = 4.1$), pentane-1,2-diamine ($\log K = 5.5$) and hexane-1,2-diamine ($\log K = 5.4$)[14] and *N*,*N*,*N* tridentate, 1,4,7-triazaheptanediene ($\log K = 8.3$)[15] ligands, respectively, thus indicating that the polyamine moiety acts either as a bidentate or tridentate chelating ligand, depending on the pH of the medium.

The main difference between the Zn^{II} and Cd^{II} complexes is that the Zn^{II} complexes are more stable than their Cd^{II} analogues. Hence, the speciation diagrams (Figures 4a and 4b) show that each of the Zn^{II} complexes is formed at significantly lower pHs than the analogous Cd^{II} ones. The higher affinity of Zn^{II} for nitrogen donors[15] than the softer acid Cd^{II} accounts for the lower stability constants of mononuclear complexes of Cd^{II} with the polyamine moiety compared to the analogous Zn^{II} complexes. This agrees with the structural differences observed between $[Zn_2(HL)_2]^{4+}$ and $[H_3L]^{2+}[CdI_4]^{2-}\cdot 2H_2O$ (see below), even when both of them are obtained at the same pH of 6 (Figures 1 and 6): whereas Zn^{II} is bonded to the polyamine in the former, in the latter the Cd^{II} is coordinated to the soft basic iodide ions and the tri-amine remains doubly protonated.

Crystal Structures of $[H_3L]^{2+}[CdI_4]^{2-}\cdot 2H_2O$ and $[(Cl_3Zn)(\mu\text{-}Cl)\{Zn(\mu_2\text{-}HL)\}]_2\cdot 2.5H_2O$

The crystal structures of $[H_3L]^{2+}[CdI_4]^{2-}\cdot 2H_2O$ and $[(Cl_3Zn)(\mu\text{-}Cl)\{Zn(\mu_2\text{-}HL)\}]_2\cdot 2.5H_2O$ were solved by single-crystal X-ray diffraction methods. The crystal and structure refinement data are summarised in Table 3. The molecular structure of $[H_3L]^{2+}[CdI_4]^{2-}\cdot 2H_2O$ consists of $[H_3L]^{2+}$ (whose structure was discussed above), tetraiodocadmiate(II) anions and water molecules (Figure 1). It is interesting to note that the Cd^{II} ion is not coordinated either to the pyrimidine or to the polyamine, but is bonded to four iodide ions. The structure of the CdI_4^{2-} anion corresponds to a deformed tetrahedron due to the involvement of two of the iodide anions in hydrogen bonding as hydrogen acceptors, with two amine primary groups of adjacent $[H_3L]^{2+}$ units acting as hydrogen donors.

The molecular structure of $[(Cl_3Zn)(\mu\text{-}Cl)\{Zn(\mu_2\text{-}HL)\}]_2\cdot 2.5H_2O$ consists of a neutral $[(Cl_3Zn)(\mu\text{-}Cl)\{Zn(\mu_2\text{-}HL)\}]_2$ complex and 2.5 water molecules. Figure 6 shows an ORTEP[16] drawing of the tetranuclear Zn^{II} complex, which contains two HL molecules and eight chloride ions as ligands. Each of the two HL molecules binds to the same

Table 3. Crystal data and structure refinement for $[H_3L]^{2+}[CdI_4]^{2-}\cdot 2H_2O$ and $[(Cl_3Zn)(\mu\text{-}Cl)\{Zn(\mu_2\text{-}HL)\}]_2\cdot 2.5H_2O$.

	$[H_3L]^{2+}[CdI_4]^{2-}\cdot 2H_2O$	$[(Cl_3Zn)(\mu\text{-}Cl)\{Zn(\mu_2\text{-}HL)\}]_2\cdot 2.5H_2O$
Empirical formula	$C_{11}H_{28}CdI_4N_8O_4$	$C_{22}H_{49}Cl_8N_{16}O_{6.50}Zn_4$
Formula mass	956.41	1186.85
Temperature [K]	153(2)	153(2)
Wavelength [Å]	0.71073	0.71073
Space group	$P\bar{1}$	$P2_1/c$
a [Å]	8.1007(8)	16.2932(7)
b [Å]	8.9842(9)	20.6708(7)
c [Å]	17.6145(17)	13.8365(6)
α [°]	86.726(8)	90
β, [°]	83.389(8)	111.885(3)
γ [°]	83,432(8)	90
V [Å^3]	1263.8(2)	4324.2(3)
Z	2	4
Calcd. density [Mg m^{-3}]	2.513	1.823
Absorption coeff. [mm^{-1}]	5.781	2.745
Crystal size [mm]	0.39 × 0.33 × 0.05	0.50 × 0.12 × 0.11
Final *R* indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0616$	$R_1 = 0.0321$
	$wR_2 = 0.1855$	$wR_2 = 0.0800$
R indices (all data)[a]	$R_1 = 0.0635$	$R_1 = 0.0413$
	$wR_2 = 0.1876$	$wR_2 = 0.0842$

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

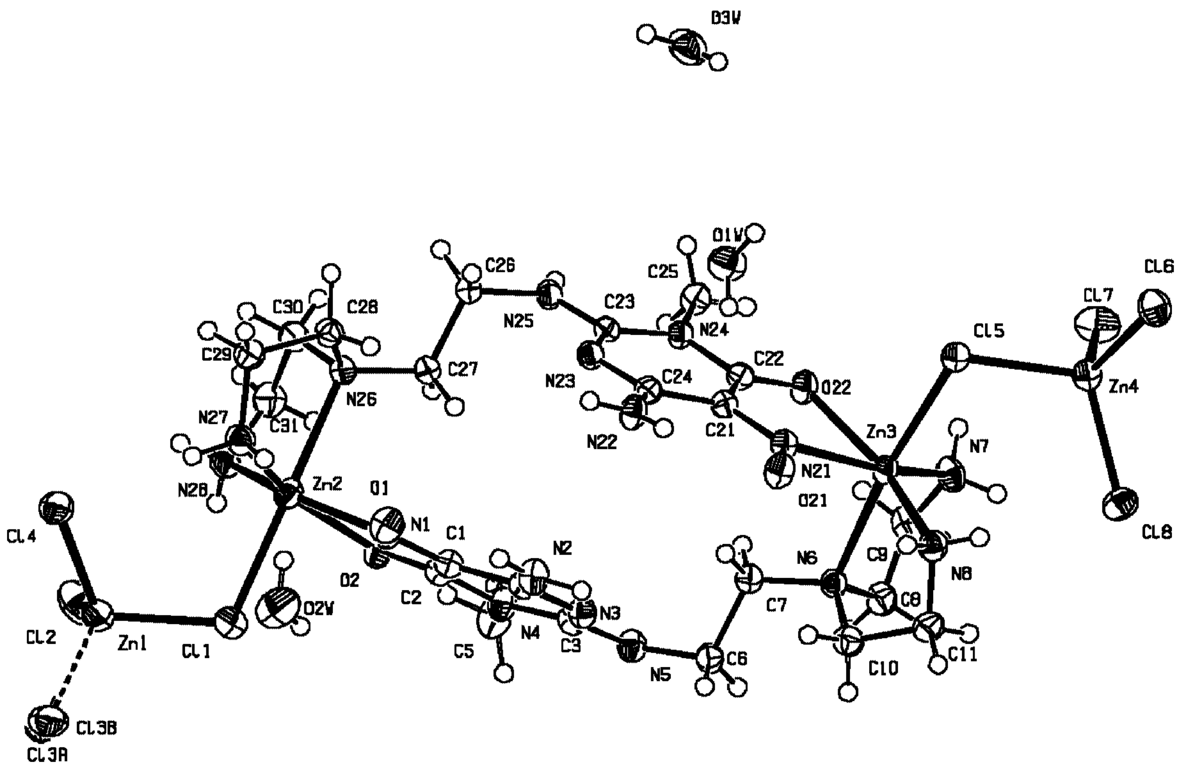


Figure 6. ORTEP drawing of $[(Cl_3Zn)(\mu\text{-}Cl)\{Zn(\mu_2\text{-}HL)\}]_2\cdot 2.5H_2O$.

two Zn^{II} centres as a bridging ligand. The polyamine moiety acts as an *N*,*N*,*N* tridentate chelating ligand binding to a single Zn^{II} ion, whereas the pyrimidine acts as a didentate chelating ligand to a second Zn^{II} centre through the nitrogen of the NO group and the oxygen of C(6)O. Each of these Zn^{II} centres does is bound to a tetrachlorozincate(II) unit through a bridging chloride ligand. Therefore, the two zinc centres linked to HL have similar hexacoordinate environments consisting of the three nitrogen atoms of the polyamine from one HL molecule, the NO and C(6)O pyrimidine substituents from another HL unit and a chloride anion. The resulting coordination geometry can be described as tetragonal bipyramidal due to the fact that the bond lengths in the equatorial plane are notably shorter than those between the metal centre and the atoms in the apical positions.

The two remaining zinc atoms of the tetranuclear unit are placed in similar tetrahedral environments, with the Zn–μ-chloride bond significantly longer than the three terminal ones. It is noteworthy that none of the N_{cyclic} atoms of the HL units take part either in coordination to zinc or in hydrogen bonding, which points out the poor basicity character of this atom.

The main structural features highlighted for the pyrimidine moiety in $[H_3L]^{2+}$ $[CdI_4]^{2-}\cdot 2H_2O$ above are also exhibited by the HL molecules of the Zn^{II} complex. With this in mind, the opposed orientation of the pyrimidine planes of the two HL molecules in the $[(Cl_3Zn)(\mu\text{-}Cl)\{Zn(\mu_2\text{-}HL)\}]_2$ unit (Figure 6) is probably induced by the attractive dipole–dipole interactions between planes, which would stabilize the formed tetranuclear cyclic unit. This trend to the inverse orientation of the pyrimidine planes in the stacking of analogous pyrimidine compounds has been widely observed.[17]

Adsorption of $Zn^{2+}$and Cd^{2+}

As was mentioned above, a pH study of the adsorption/desorption of water-solved HL on a granular activated carbon (AC) showed the existence of π–π donor–acceptor interactions between the arene centres of the AC and the pyrimidine moiety of HL as the cause of the irreversible character of the adsorption process.[4] Further insight on this is obtained by comparison of the N_{1s} signals of the XPS spectra of the HL and AC-HL systems (Figure 7). This was done by assuming that the low nitrogen content of the AC (0.75%) implies negligible contribution (less than 1/10) to these signals compared to the HL nitrogen. Each of the N_{1s} signals is composed of two overlapping peaks corresponding to the five heterocyclic nitrogen atoms, i.e. the nuclear heterocyclic nitrogen atoms plus those directly bonded to the pyrimidine ring (at 400.02 eV for HL and 400.91 eV for AC-HL), and the three sp^3-type nitrogens of the tetraamine residue (at 398.40 eV for HL and 399.60 eV for AC-HL).

Both of these peaks are significantly shifted in the AC-HL spectrum relative to the HL spectrum. However, this fact is not relevant in the case of the peaks of the nitrogen atoms of the triamine due to the full involvement of these in the supramolecular assembling of solid HL by hydrogen bonds. On the contrary, the shifting of the peak of the heterocyclic nitrogens in AC-HL to higher energies relative to

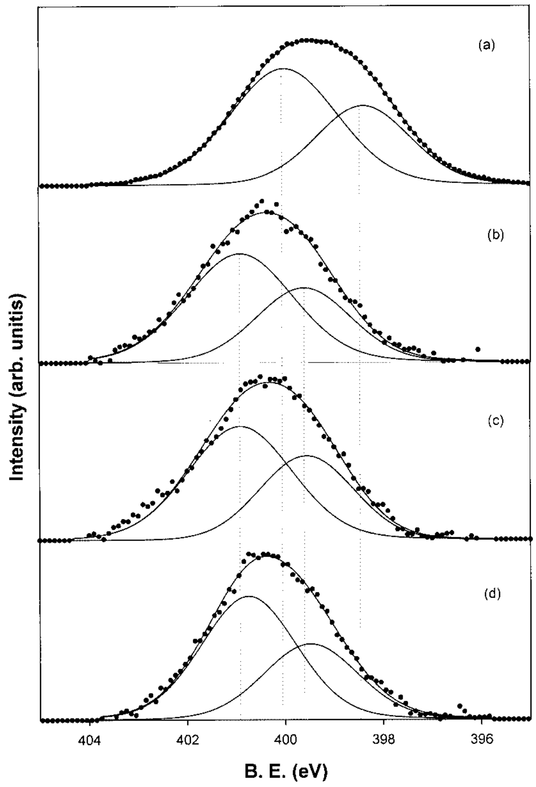


Figure 7. N_{1s} XPS spectra of (a) HL, (b) AC-HL, (c) AC-HL-Zn and (d) AC-HL-Cd.

HL is consistent with electron donation from the arene centres of the AC to the HL aromatic residue, which accompanies the adsorption process.

The anchorage of HL to the arene centres provides functionalisation of the AC with a potential tridentate *N*,*N*,*N* ligand that should enhance its capacity for the capture of metal ions. The shapes of the adsorption isotherms of $ZnCl_2$ and $CdCl_2$ on AC and AC-HL in aqueous solution, obtained at pH 5, show a significant improvement of the adsorption capacity relative to unfunctionalised AC, as shown in Figure 8. A pH of 5 was chosen as a compromise value to avoid the precipitation of metal hydroxides whilst ensuring the existence of a non-negligible amount of the partially or totally unprotonated polyamine function, which is available for metal ion–polyamine interaction, as deduced from the solution studies (see Figure 4).

Each of the final solutions obtained in the study of the adsorption of the metals on AC-HL was analysed by UV/visible spectroscopy to prove that no HL was desorbed. The XPS spectra of AC-HL-Zn^{II} and AC-HL-Cd samples, including the N_{1s} peaks, are similar to that of the non-metallated adsorbent, except for a new peak in the former due to the metals ($Zn_{2p3/2}$ at 1022 eV and $Cd_{3d5/2}$ at 406 eV). This indicates that the improvement in the adsorptivity on AC-HL relative to AC alone is due to the presence of HL on the carbon surface. Moreover, further evidence of interactions between the metal ions and HL was obtained by comparison of the IR spectra of the AC-HL adsorbent and AC-HL-metal solid phases, which show the appearance of new bands in the second cases at 488 cm^{-1} and 482 cm^{-1} for Zn^{II} and Cd^{II}, respectively, which are assignable to ν(M–N). In these spectra relatively strong bands assignable to ν(M–O) (at around 420 cm^{-1} in both cases) due to metal atoms bonded to the oxygen functional groups of the AC also appear.[18] These bands were assigned previously by comparing the IR spectrum of an AC sample with those of the AC-Zn and AC-Cd solid phases obtained from the adsorption experiments carried out to obtain the corresponding isotherms.

Both isotherms in Figure 8 fit the Langmuir equation. This allowed us to calculate the maximum adsorption capacity values of 0.042 and 0.097 $mmol\,g^{-1}$ for AC and AC-HL adsorbents, respectively, in the case of Zn^{II}, and 0.040 and 0.143 $mmol\,g^{-1}$ for AC and AC-HL in the case of Cd^{II}. These values show that binding of HL to AC enhances the adsorption capacity of AC by a factor of 2.5 in the case of Zn^{II} and 3.5 for Cd^{II}. Nevertheless, these results disagree with the relative values found for the association constants of HL with Zn^{II} and Cd^{II} (see above), which suggest a

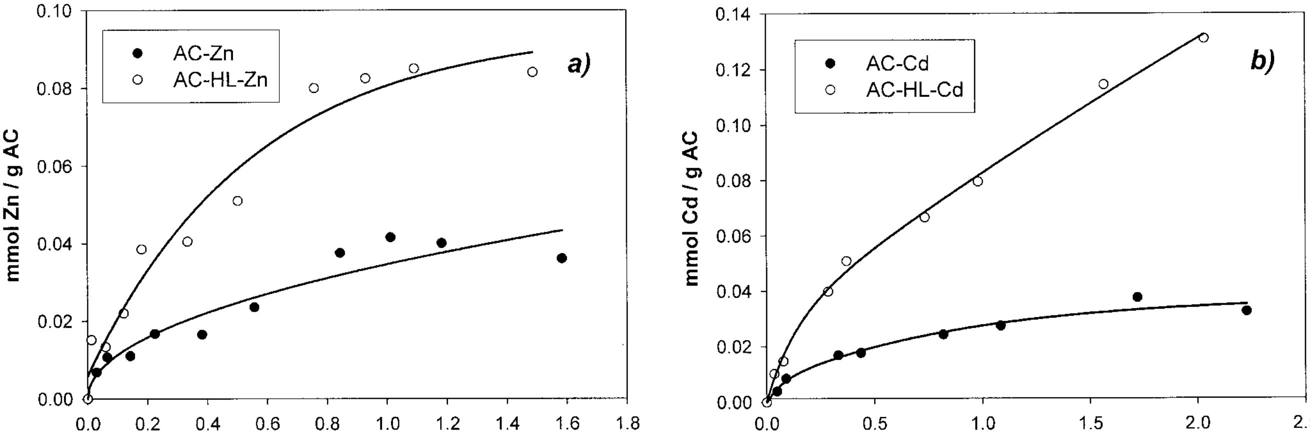


Figure 8. Adsorption isotherms of (a) Zn^{II} and (b) Cd^{II}.

higher affinity of the triamine function for Zn^{II} than for Cd^{II}. This finding can be explained by assuming that the metals can be adsorbed either as single metal ions, when the triamine is unprotonated, or as MCl_4^{2-} when the triamine group is doubly protonated.

Considering these aspects, the two adsorption mechanisms in the case of Cd^{II} are plausible due to a non-negligible co-existence of $CdCl_4^{2-}$ and Cd^{2+} species in the medium, (log $K = 6.63$ for $CdCl_4^{2-}$) at the Cl^- concentrations used in the adsorption experiments. On the contrary, in the case of Zn^{2+} only the adsorption of the single metal ion on the unprotonated triamine is expected due to the lack of the more labile $ZnCl_4^{2-}$ species (log $K = -0.18$).[19] These findings agree with the isolation of the tetraiodocadmiate salt of the doubly protonated ligand from HL/Cd^{II} mixtures at pH 6, and the binuclear Zn^{II} complex of neutral HL from HL/Zn^{II} mixtures at the same pH. These are in accordance with the softer Lewis acid character of Cd^{II} than Zn^{II}.

Some of the chemical pollutants existing in the environment, such as arsenate, phosphate, sulfate, pertechnate, chromate, etc., are water-soluble tetrahedral anionic species. Thus, the above results suggest a possible interest in wastewater detoxification for this class of anions. In fact, the assembling of tetrahedral anions with polyamine receptors has been described in some recent monographs.[20] With this in mind, the observed affinity of the AC-HL adsorbent containing a triamine as available functional group to $CdCl_4^{2-}$ anion is not surprising and suggests the usefulness of the model compound described in this work as a host for tetrahedral anions. It has been suggested[21a] that the specificity of a polyamine receptor to a tetrahedral anion would be determined by the binding affinity, i.e. the nature of the ion-pair interaction. In the case of some macrocyclic polyamines, the strong binding of polyphosphates was found to be due to the existence of both electrostatic and hydrogen-bonding interactions.

The adsorption of a CrO_4^{2-} solution at pH 7 by the AC-HL receptor has been studied by us previously.[4] In that study, the IR spectra of a $[CrO_4]^{2-}[H_3L]^{2+}$ solid compound isolated from aqueous solution prove the existence of strong hydrogen-bonding interactions in the formation of the ion pair. These hydrogen-bonding interactions are likely responsible for the high maximum adsorption capacity of the adsorbent found (up to 0.14 mmol of CrO_4^{2-} per gram of carbon).

These results, together with other previous ones, highlight the versatile behaviour of HL-type receptors anchored on activated carbons, which makes them useful for the capture of both single metal ions and tetrahedral anions. They also encourage further studies with other single and tetrahedral ions for a better comprehension of the factors (topological, chemical, ...) that control the chemical affinity between the model receptor developed and the ions.

Conclusions

HL is characterised by a polarized aromatic moiety and a polyamine function linked by a soft bis-methylene spacer. The compound behaves as bifunctional ligand for Zn^{2+} and Cd^{2+} metal ions in aqueous solution. At low pH values it forms mononuclear complexes with these ions, which are coordinated through the C(5)NO-C(6)O grouping, and acts as a bidentate chelating ligand. The availability of the polyamine function for complex formation with metal ions occurs at slightly acidic pH values and depends on the polarizing character of the metal ion. This is reflected in the fact that the formation of bi- and mononuclear complexes with a metal ion linked through the polyamine moiety takes place at lower pH values with Zn^{2+} than with Cd^{2+} ion. In these complexes, the *N,N,N* coordinated triamine gives rise to stable metal–amine bonds.

HL is anchored on AC with the pyrimidine ring flat to the arene centres. This process, which is irreversible in water, seems to be due to π–π donor–acceptor interactions between the two aromatic moieties. Moreover, it is favoured by the electron-withdrawing character of the C(5)NO substituent of the pyrimidine moiety of HL. HL adsorption provides functionalisation of the arene centres with $NH_2–(CH_2)_2–NH–(CH_2)_2$ functions and this explains the improvement of the capacity of the AC for the adsorption of Zn^{2+} and Cd^{2+} metal ions. Moreover, in the case of Cd^{II}, the amphoteric character of the polyamine function allows it to adsorb Cd^{2+} and $[CdCl_4]^{2-}$ ions. All these results suggest the feasibility of the model proposed for specific functionalisation of the AC based on the topological and electronic properties of HL-type ligands. All these results have been discussed in the light of the coordination chemistry of the polyamine groups existing at the AC modified surface, which highlights the relevance of the solution and crystallographic data obtained in the coordination chemistry study of the ligand.

Experimental Section

Synthesis of 4-Amino-2-methoxy-1-methyl-5-nitroso-6-oxo-1,6-dihydropyrimidine (1): Compound **1**, which is a precursor of the ligand HL, was obtained by a previously reported method.[21]

***N*-(4-Amino-1-methyl-5-nitroso-6-oxo-1,6-dihydropyrimidin-2-yl)-*N*′-[bis(2-aminoethyl)]ethylenediamine Dihydrochloride (HL·2HCl; 2):** A solution of monohydrated **1** (5.5 g, 27.2 mmol) in CH_3CN (100 mL) was added slowly to a refluxing and stirred solution of tris(2-aminoethyl)amine dihydrochloride (6.5 g, 29.7 mmol). After the addition, the solution was refluxed for an additional 2 h, after which time a pink powdery solid appeared. The suspension was then filtered. The solid was washed with ethanol and diethyl ether and used without further purification. Yield: 9.5 g (90%). $C_{11}H_{24}Cl_2N_8O_2·1/2H_2O$ (380.01): calcd. C 34.73, H 6.58, N 29.47; found C 34.68, H 6.46, N 29.43. ^1H-^{15}N HMBC ([D$_6$]DMSO): δ = 25, 68, 103, 137 ppm. ^1H NMR ([D$_6$]DMSO): δ = 2.67 (t, 2 H), 2.71 (t, 4 H), 2.91 (t, 4 H), 3.39 (s, 3 H), 3.53 (t, 2 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 27.8, 36.8, 40.2, 51.1, 52.5, 142.0, 149.8, 154.5, 161.6 ppm.

$[ZnCl_4]_2[Zn_2(HL)_2]·2.5H_2O$ (3): A water solution (10 mL) of $ZnCl_2$ (90 mg, 0.66 mmol) was added, whilst stirring, to a solution of **2** (190 mg, 0.5 mmol) in water (10 mL). The pH of the resulting mixture was adjusted to 6 by adding 2 N KOH. Orange crystals of **3** suitable for X-ray analysis were obtained by slow evaporation of this solution. $C_{11}H_{24.5}Cl_4N_8O_{3.25}Zn_2$ (593.08): calcd. C 22.25, H 4.13, N 18.88; found C 21.76, H 4.67, N 18.42.

$[H_3L][CdI_4]\cdot 2H_2O$ (4): An aqueous solution (10 mL) of $CdCl_2\cdot 2.5H_2O$ (0.15 g, 0.66 mmol) was added to a solution of **2** (0.19 g, 0.5 mmol) and NaI (0.15 g, 1 mmol) in water (30 mL). The pH was then adjusted at 6 by adding 2 N KOH. Orange crystals of **4** were obtained by slow evaporation of the solution. $C_{11}H_{28}CdI_4N_8O_4$ (956.01): calcd. C 13.81, H 2.93, N 11.72; found C 14.60, H 2.99, N 12.35.

Potentiometric Measurements: The potentiometric titrations were carried out at 298.1 ± 0.1 K in 0.1 M KCl with a 713 Metrohm pH-mV meter, equipped with a combined glass electrode and connected to a Metrohm 765 Dosimat autoburette (1 ± 0.001 mL). The experimental procedure used was the same as that described elsewhere.[22] The system was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with CO_2-free KOH solutions and determining the equivalent point by Gran's method,[23] which allows the determination of the standard potential, E^0, and the ionic product of water ($pK_w = 13.76$ in 0.1 M KCl at 298.1 ± 0.1 K). Ligand concentrations of $1–1.5\times 10^{-3}$ M and 1:1 ligand-to-metal molar ratios were employed in the potentiometric measurements. At least four titration experiments (about 150 data points for each one) were performed in the pH ranges 2.5–10. The computer program HYPERQUAD[24] was used to calculate equilibrium constants from emf data.

Spectrophotometric Measurements: Absorption spectra of HL solutions were recorded with a Perkin–Elmer Lambda 19 spectrophotometer. HCl and KOH were used to adjust the pH values, which were measured with a Crison 2002 micropH meter.

X-ray Crystallography: Suitable crystals of **3** and **4** were obtained as orange plates and orange rods, respectively. The intensity data were collected at 153 K (–120 °C) on a Stoe Mark II-Image Plate Diffraction System[25] equipped with a two-circle goniometer and using graphite-monochromated Mo-K_α radiation. The structures were solved by direct methods using the programme SHELXS-97.[26] The refinement and all further calculations were carried out using SHELXL-97.[27] In the case of compound **4** the H-atoms were either located from Fourier difference maps and refined isotropically or included in calculated positions and treated as riding atoms using the SHELXL default parameters. For compound **3**, the majority of the H-atoms were located from Fourier difference maps and refined isotropically. The water H-atoms were located from difference maps but then either refined isotropically or constrained to be 0.83(1) Å and $U_{iso} = 1.5\cdot U_{eq}$(O-atom) Å^2. The non-H atoms were refined anisotropically by weighted full-matrix least-squares procedures on F^2.

CCDC-259715 (for **3**) and -259716 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

NMR Spectroscopy: ^{1}H (300.13 MHz), ^{13}C (75.48 MHz) and two dimensional spectra in [D$_6$]DMSO and in D_2O solutions at different pH values were recorded at 300 K with a Bruker DPX300 spectrometer. The pD values of HL and HL–metal ion solutions were adjusted by adding small amounts of NaOD and DCl solutions. The pH was calculated from the measured pD values using the relationship pH = pD – 0.40.[28]

XPS and IR Data: XPS measurements were performed with an Escalab 200R system (VG Scientific Co.) equipped with an Mg-K_α X-ray source ($h\nu$ = 1253.6 eV) and hemispherical electron analyzer. Prior to the analysis, the samples were pretreated in situ at 623 K for 6 h in He, dry air, or wet air. The IR spectra of AC, AC-metal, AC-HL and AC-HL-metal solid samples, were obtained from KBr pellets of the samples in the 650–400 cm^{-1} range with a Bruker Tensor 27 TGA-IR spectrometer

Adsorption of Zn^{2+} and Cd^{2+}: Adsorption experiments of Zn^{2+} and Cd^{2+} ions on an activated carbon (Merck K24504014; AC) and AC-HL as adsorbent materials, respectively, at pH 5, were carried out. Typically, amounts of 0.0500 g of the adsorbent were added to a 100-mL plastic flask containing 50 mL of the appropriate aqueous solution of the adsorbate ($ZnCl_2$ or $CdCl_2$ salts). For the adsorption experiments of the metals on AC-HL, the adsorbent was obtained from a previous experiment consisting of the adsorption of an HL solution on the AC, at pH 5, by fixing conditions at which the overall HL was irreversibly adsorbed (100 ppm of HL in 100 mL of water and 0.500 g AC[4]). The pH was adjusted in each of the experiments with KOH or HCl. The suspensions were shaken at 25 ± 0.1 °C for two days until equilibrium was reached. After the adsorption experiments, the adsorbents were carefully filtered and the residual metal concentration in the solutions was measured by ICP mass spectroscopy with an AGILENT 7500 Series (Shield Torch System).

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[1] a) J. N. Low, M. L. Godino, R. López, A. Pérez-Cadenas, M. Melguizo, J. Cobo, *Acta Crystallogr., Sect. C* **1999**, *55*, 1727–1730; b) J. N. Low, M. López, P. Arranz, J. Cobo, M. L. Godino, R. López, M. D. Gutierrez, M. Melguizo, G. Ferguson, C. Glidewell, *Acta Crystallogr., Sect. B* **2000**, *56*, 882–892; c) J. N. Low, A. Quesada, C. Glidewell, M. A. Fontecha, P. Arranz, M. L. Godino, R. López, *Acta Crystallogr., Sect. E* **2002**, *58*, 942–945.

[2] a) J. M. Moreno, P. Arranz, R. López, M. D. Gutierrez, M. L. Godino, J. Cobo, *Polyhedron* **1999**, *18*, 1635–1640; b) R. López, P. Arranz, M. L. Godino, M. D. Gutierrez, A. Pérez, J. Cobo, J. M. Moreno, *Inorg. Chim. Acta* **2000**, *308*, 59–64; c) P. Arranz, R. López, M. D. Gutierrez, M. L. Godino, J. M. Moreno, *Inorg. Chim. Acta* **2000**, *304*, 137–143; d) J. N. Low, J. M. Moreno, P. Arranz, M. L. Godino, R. López, J. Cobo, C. Glidewell, *Acta Crystallogr., Sect. B* **2001**, *57*, 317–328; e) J. N. Low, P. Arranz, J. Cobo, M. A. Fontecha, M. L. Godino, R. López, C. Glidewell, *Acta Crystallogr., Sect. C* **2001**, *57*, 534–537; f) R. López, P. Arranz, M. L. Godino, M. D. Gutierrez, R. Cuesta, J. M. Moreno, *Inorg. Chim. Acta* **2003**, *355*, 41–48; g) R. Cuesta, C. Glidewell, R. López, J. N. Low, *Acta Crystallogr., Sect. C* **2003**, *59*, 315–318.

[3] a) H. Minemoto, Y. Ozaki, N. Sonoda, *Appl. Phys. Lett.* **1993**, *63*, 3565–3567; b) H. Minemoto, Y. Ozaki, N. Sonoda, *J. Appl. Phys.* **1994**, *76*, 3975–3980; c) R. P. Sharma, S. Kumar, K. K. Bashin, E. R. T. Tiekink, *Z. Kristallogr.* **1997**, *212*, 742–744; d) S. Brahadeeswaran, V. Venkataramanan, J. N. Shewood, H. L. Bhat, *J. Mater. Chem.* **1998**, *8*, 613–618; e) M. Muthuraman, M. Bagieu-Beucher, R. Masse, J. F. Nicoud, R. J. Desiraju, *J. Mater. Chem.* **1999**, *9*, 1471–1474, references cited therein.

[4] J. García-Martín, R. López-Garzón, M. L. Godino-Salido, M. D. Gutiérrez-Valero, P. Arranz-Mascarós, R. Cuesta, F. Carrasco-Marín, *Langmuir*, in press.

[5] a) J. S. Mattson, H. B. Mark, *Activated Carbon Surface Chemistry and Adsorption from Solution*, Marcel Dekker, New York,

1971; b) R. W. Coughlin, F. S. Ezra, R. N. Tan, *J. Colloid Interface Sci.* **1968**, *28*, 386–396; c) C. A. Leon y Leon, J. M. Solar, V. Calemma, L. R. Radovic, *Carbon* **1992**, *30*, 797–811; d) H. Tamon, M. Okazaki, *J. Colloid Interface Sci.* **1996**, *179*, 181–187.

[6] a) L. Radovic, C. Moreno-Castilla, J. Rivera-Utrilla, in *Chemistry and Physics of Carbon* (Ed.: L. Radovic), Marcel Dekker, New York, **2000**, vol. 27, p. 241–283; b) S. D. Faust, O. M. Aly, *Chemistry of Water Treatment*, Ann Arbor Press, Chelsea, **1998**; c) S. D. Faust, O. M. Aly, A*dsorption Processes for Water Treatment*, Butterworths, Boston, **1987.**

[7] L. R. Radovic, I. F. Silva, J. I. Ume, J. A. Menéndez, C. A. Leon y Leon, A. W. Scaroni, *Carbon* **1997**, *35*, 1339–1348.

[8] A. E. Martell, R. M. Smith, R. J. Motekaitis, *NIST Critical Stability Constants of Metal Complexes Database*, Version 7, Texas A & M University, College Station, TX, **2003**.

[9] M. L. Godino, P. Arranz, R. López, M. D. Gutiérrez, J. N. Low, J. F. Gallagher, C. Glidewell, *Acta Crystallogr., Sect. B* **2004**, *60*, 46–64.

[10] a) H. J. Talberg, *Acta Chem. Scand., Ser. A* **1977**, *31*, 485–491; b) E. O. Schlemper, R. K. Murmann, M. S. Hussain, *Acta Crystallogr., Sect. C* **1986**, *42*, 1739–1743.

[11] a) M. J. Davis, J. E. Boggs, D. Coffey, H. P. Hanson, *J. Phys. Chem.* **1965**, *69*, 3727–3730; b) S. H. Bauer, A. L. Andreassen, *J. Phys. Chem.* **1972**, *76*, 3099–3108 (see also ref.[10]).

[12] a) R. López-Garzón, P. Arranz-Mascarós, M. L. Godino-Salido, M. Gutierrez-Valero, A. Perez-Cadenas, J. M. Moreno, *Inorg. Chim. Acta* **2000**, *308*, 59–64; b) R. López-Garzón, M. L. Godino-Salido, P. Arranz-Mascarós, M. A. Fontecha-Cámara, M. D. Gutiérrez-Valero, R. Cuesta, J. M. Moreno, H. Stoeckli-Evans, *Inorg. Chim. Acta* **2004**, *357*, 2007–2014.

[13] M. M. Ibrahim, N. Shimomura, K. Ichikawa, M. Shiro, *Inorg. Chim. Acta* **2001**, *313*, 125–136.

[14] M. J. Robertson, G. N. De Iuliis, M. Maeder, G. A. Lawrence, *Inorg. Chim. Acta* **2004**, *357*, 557–570.

[15] P. Jiang, Z. Guo, *Coord. Chem. Rev.* **2004**, *248*, 205–229.

[16] PLATON/PLUTON version Jan. **1999**: A. L. Spek, *Acta Crystallogr., Sect. A* **1999**, *46*, C-34.

[17] a) A. Quesada, A. Marchal, M. Melguizo, M. Nogueras, A. Sánchez, J. N. Low, D. Cannon, D. M. M. Farell, C. Glidewell, *Acta Crystallogr., Sect. B* **2002**, *58*, 300–315; b) E. J. MacLean, J. N. Low, A. Quesada, M. Melguizo, M. Nogueras, C. Glidewell, *Acta Crystallogr., Sect. C* **2002**, *58*, o442–o444; c) M. Melguizo, A. Quesada, J. N. Low, C. Glidewell, *Acta Crystallogr., Sect. B* **2003**, *59*, 263–276; d) A. Quesada, A. Marchal, M. Melguizo, J. N. Low, C. Glidewel, *Acta Crystallogr., Sect. B* **2004**, *60*, 76–89.

[18] a) J. R. Ferraro, *Low Frequency Vibrations of Inorganic and Coordination Compounds*, Plenum Press, New York, **1971**, pp. 220, 65–75; b) G. Sócrates, *Infrared Characteristic Group Frequencies*, John Wiley & Sons, Chichester, **1994**, p. 233.

[19] *Comprehensive Inorganic Chemistry* (Ed.: J. C. Bailar), vol. 3, Pergamon Press, New York, **1973**.

[20] a) *Supramolecular Chemistry of Anions* (Eds.: A. Bianchi, K. Bowman-James, E. García-España), Wiley, New York, **1997**, chapter 2; b) M. W. Hosseini, J. M. Lehn, *Helv. Chim. Acta* **1987**, *70*, 1312–1319; c) C. Seel, J. de Mendoza, in *Comprehensive Supramolecular Chemistry*, Pergamon, New York, **1996**, vol. 2, chapter 17..

[21] a) M. Engelman, *Ber. Dtsch. Chem. Ges.* **1909**, *42*, 177; b) J. Lifschitz, *Ber. Dtsch. Chem. Ges.* **1922**, *55*, 1619.

[22] M. L. Godino, M. D. Gutiérrez, R. López, J. M. Moreno, *Inorg. Chim. Acta* **1994**, *221*, 127–181.

[23] a) G. Gran, *Analyst* **1952**, *77*, 661–671; b) A. Liberti, T. S. Light, *J. Chem. Educ.* **1962**, *39*, 236–239.

[24] P. Gans, A. Sabatini, A. Vacca, *Talanta* **1996**, *43*, 1739–1753.

[25] Stoe & Cie. *X-Area V1.17 & X-RED32 V1.04 Software*, Stoe & Cie GmbH, Darmstadt, Germany, **2002**.

[26] SHELXS-97, Program for Crystal Structure Determination: G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.

[27] G. Sheldrick, "SHELXL-97", University of Göttingen, Göttingen, Germany, **1999**.

[28] A. K. Covington, M. Paabo, R. A. Robinson, R. G. Bates, *Anal. Chem.* **1968**, *40*, 700–706.

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