Polymeric Thiolate Complexes in Solution. Stability Constants of the Cadmium(II) Complexes of 3-Aminopropane-1-thiol

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Complex formation between Cd^{II} and 3-aminopropane-1-thiol has been studied by means of nearly 425 e.m.f. measurements with a glass electrode in 10 separate titrations at 25 °C in 3 mol dm^{-3} (sodium) perchlorate medium [+10%(v/v) CH_3OH]. Conclusions drawn from graphical methods based on the 'core + links' hypothesis and on the 'extended variation' technique are in accord with results obtained from the numerical treatment. Experimental data for $3 < -\log [H^+] < 11$ can be explained by assuming that the following complexes predominate over a wide pH range: $[Cd(HA)_3]^{2+}$, $[Cd_3(HA)_8]^{6+}$, $[Cd_4(HA)_8]^{8+}$, and $[Cd_5(HA)_{12}]^{10+}$, HA being the uncharged ligand. The deprotonation of these species gives rise to several mono- and poly-nuclear ternary complexes $Cd_pA_qH_r$, $r < q$, A denoting the deprotonated form of the ligand. Chelate formation seems very likely. Comparisons with other cadmium(II)–mercaptoamine systems are made.

The renewed interest in the chemistry of metal thiolate complexes is mainly due to the important role of the thiol group of the cysteinyl residues in metalloproteins[1] in co-ordinating metal atoms. Recent reviews[2,3] show that the amount of experimental data related to the structural features of those complexes has increased very much in the past years. While topological relationships have been proposed for several metal thiolate complexes[4] and also new synthetic strategies have been developed,[5] it is still difficult to predict the stoicheiometry and the geometry of a complex with a given metal:thiol molar ratio.

Solution equilibria studies of metal–thiol systems should help to make accurate predictions but they are practically impossible in aqueous solutions unless the problem of the low solubility of metal thiolates is overcome. The introduction of a non-co-ordinating solubilizing group in the thiol molecule led us in the past to choose γ-mercaptoamines as models for the behaviour of simple thiol ligands. The stability constants of the complexes formed between 4-mercapto-1-methylpiperidine and Zn^{II}[6] and Cd^{II}[7] as well as the crystal and molecular structures of several solid complexes of Zn^{II},[8] Cd^{II},[9] and Hg^{II}[10] with different γ-mercaptoamine ligands have been reported.

In this paper we report the stability constants of the soluble complexes found potentiometrically while in the system cadmium(II)–3-aminopropane-1-thiol in water–methanol (9:1 v/v). The results obtained are compared with those with 4-mercapto-1-methylpiperidine[7] and with 2-aminoethane-1-thiol.[11]

Experimental

Reagents.—An acidified stock solution of 3-aminopropane-1-thiol, synthesized according to known procedures[12] and purified by sublimation, was prepared. The ligand content of the potentiometric solutions was tested by means of iodometric determination of the SH group. Acidified solutions of the ligand were kept for several weeks without evidence of oxidation. The acidified stock solution of cadmium perchlorate and the remaining stock solutions were prepared and analyzed as indicated elsewhere.[7] Methanol (Merck, p.a.) was used without further treatment.

Apparatus and Procedures.—The titrations were performed in 10% v/v aqueous methanolic solutions at constant temperature (25.0 ± 0.1 °C) and ionic strength ($NaClO_4$, 3 mol dm^{-3}), under a nitrogen atmosphere. The computerized titrator used (four Hamilton, Microlab M, microburettes and a Crison, Digilab, potentiometer), the standardization of the glass (Ingold HA 201) and Ag–AgCl reference electrodes, as well as the rest of the potentiometric system have been described.[7] The titration procedures followed in order to determine the acidity constants of the ligand[13] and the formation constants of the soluble complexes[6] have also been given.

Calculations and Results

Acid Dissociation Constants of the Cation 3-*Ammoniopropane*-1-*thiol from E.M.F. Data.*—Three potentiometric titrations were carried out. It was assumed that the species present in solution were of the type H_jA (charges are omitted throughout for clarity), where j is an integer, $0 \leqslant j \leqslant 2$, and A denotes the completely deprotonated ligand. Values for log $[H^+]$ and $\bar{j}$, the average number of protons bound, were calculated by means of known equations[13] from the primary data and the calculated value for K_w ($pK_w = 14.16$) in the medium used. Numerical treatment of 104 experimental points with the program SUPERQUAD[14] in conjunction with a VAX/VMS computer gave the following acid dissociation constants (standard deviations in parentheses): $H_2A^+ \rightleftharpoons HA + H^+$, $pK_1 = 9.94(2)$; $HA \rightleftharpoons A^- + H^+$, $pK_2 = 11.19(2)$.

Cadmium Complex-formation Constants from E.M.F. Data.—Ten potentiometric titrations divided into two sets, one at constant L_t, the analytical ligand concentration, and the other at constant M_t, the analytical metal-ion concentration, were carried out. In each titration L_t and M_t were held constant; M_t was varied in the range 0.4—9.0 mmol dm^{-3} and L_t according to the ratio $2 < L_t/M_t < 8$.

Assuming complexes of general formula $Cd_pA_qH_r$, values for $\log[H^+]$ and $\bar{j}$ were calculated from the primary data according to equations (1) and (2), where E_0 denotes a calibration constant[13] and H_t the total concentration of hydrogen ion.

$$\log[H^+] = (E - E_0)/59.16 \qquad (1)$$

$$\bar{j} = (H_t - [H^+] + K_w[H^+]^{-1})/L_t \qquad (2)$$

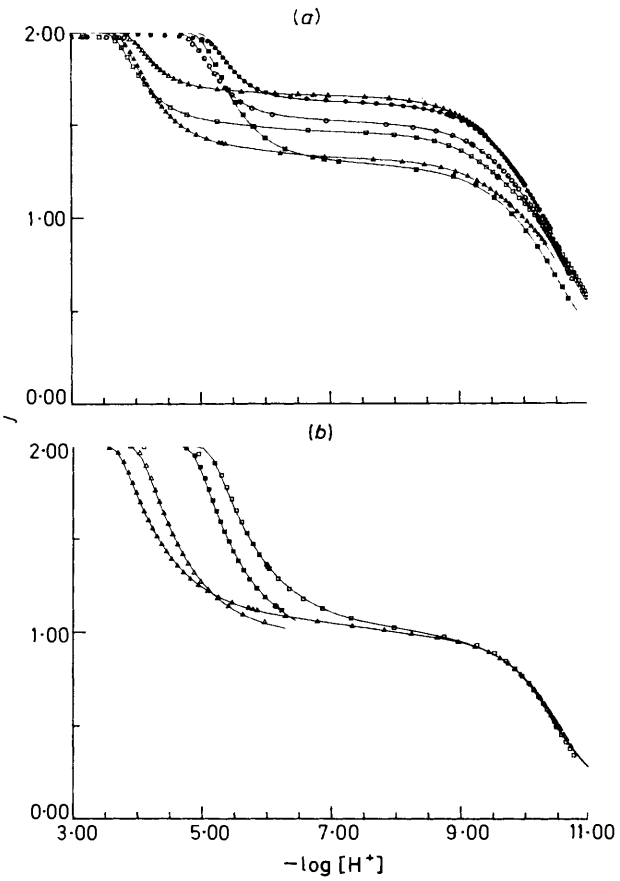

Figure 1. Average number of protons bound to the ligand, $\bar{j}$, as a function of $-\log[H^+]$ at different ligand-to-metal ratios. The lines drawn were calculated from the constants in Table 3. L_t/M_t (*a*) > 4, (*b*) < 4. Conditions (M_t, L_t/mmol dm^{-3}): (*a*) (▲) 6.01, 24.02; (□) 6.01, 30.38; (△) 2.99, 24.02; (■) 0.760, 2.99; (○) 0.763, 4.43; (●) 0.397, 2.99; (*b*) (▲) 8.89, 24.02; (△) 6.01, 12.56; (■) 1.53, 2.99; (□) 0.763, 2.21

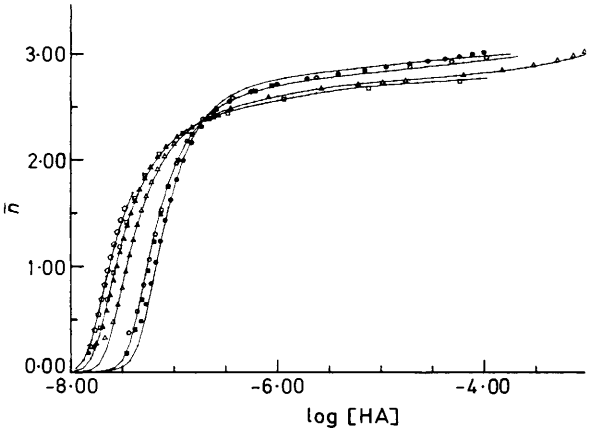

Figure 2. Formation curve for $Cd_p(HA)_q$ species at different ligand-to-metal ratios. The lines drawn were calculated from the constants in Table 3. Conditions (M_t, L_t/mmol dm^{-3}): (⬡) 8.89, 24.02; (▲) 6.01, 24.02; (□) 6.01, 30.38; (△) 2.99, 24.02; (■) 0.760, 2.99; (○) 0.763, 4.43; (●) 0.397, 2.99

Table 1. Set of possible p,q values, for $Cd_p(HA)_q$ species, that meet the requirements $p_{max.} = 6$, $\bar{n}_{max.} = 2.5$, and $2.15 < t < 4.25$

p	2	2	3	3	3	4	4	4	5	5	5	5	6	6	6	6
q	3	4	5	6	7	7	8	9	9	10	11	12	11	12	13	14

While plots of $\bar{j}$ against $-\log[H^+]$ for $L_t/M_t \geqslant 4$ [Figure 1(*a*)] show a plateau for values $1 < \bar{j} < 2$, those corresponding to $L_t/M_t < 4$, Figure 1(*b*), have a plateau at $\bar{j} \leqslant 1$. This suggests that in the first case the ligand is in a monoprotonated form up to pH ≈ 8.5 or that the species present in solution can be represented as $Cd_pA_qH_q$,[7] while $\bar{j} \leqslant 1$, in any of the two cases, the complexes must be considered of the type $Cd_pA_qH_r$, where $r \leqslant q$.

Species of Formula $Cd_p(HA)_q$.—*Graphical treatment and 'core + links' hypothesis.* First, only experimental data corresponding to $\bar{j} \geqslant 1.35$ were treated while considering the system as a two-component one, $Cd_p(HA)_q$. For this value of $\bar{j}$ the fraction of unprotonated ligand, $[A]/L_t$, is at most 5%, [A] denoting the concentration of the free completely deprotonated ligand. The graphical methods used,[7] based on the 'core + links' hypothesis,[15] led us to conclude that for the range $0.4 < \bar{n} < 1.9$, Figure 2, where $\bar{n}$ denotes the average number of monoprotonated ligands bound per metal, t or the numerical ratio of ligand to metal in the links of core + links complexes, $Cd[Cd(HA)_t]_x$, and its standard deviation, σ, have the values 3.2 and 0.35. In a two-component system the experimental function $\bar{n}$ can be calculated using equation (3) and thus the

$$\bar{n} = \frac{L_t(\bar{j} - X)}{M_t(1 - X)}, \quad X = \frac{2[H^+]^2 + K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2} \qquad (3)$$

concentration of free monoprotonated ligand, [HA], can also be determined by means of equation (4). However, the variation

$$[HA] = \frac{(L_t - \bar{n}M_t)K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2} \qquad (4)$$

of the total concentration of Cd^{II} with that of the free monoprotonated ligand for several $\bar{n}$ values showed a strong dependence of t on $\bar{n}$, suggesting that several 'core + links' families coexist, the corresponding t values being included in the range $t \pm 3\sigma$.

Numerical methods. In order to determine the different series of 'core + links' complexes existing in solutions where $\bar{n} < \bar{n}_{max.}$ a simple numerical method was used. By comparing the formulae $Cd_p(HA)_q$ and $Cd[Cd(HA)_t]_x$ the following relations hold: $p = x + 1$, $q = tx$ and thus an infinite number of p, q pairs can be obtained by varying x in integer numbers for t values (which were increased by 0.005 units) within the given range. The following restrictions gave the first set of possible species: (*a*) p and q must be very close to integer numbers; (*b*) $q/p < \bar{n}_{max.}$, which limits the nuclearity of the complex for each value of t, as $\bar{n}_{max.} = t - t/x_{max.}$; together with the conditions $p_{max.} = 6$, $\bar{n}_{max.} = 2.5$, $2.15 < t < 4.25$. To establish the complex of highest nuclearity, $p_{max.}$, additional information about the stoicheiometries of soluble cadmium–mercaptoamine complexes was taken into account without finding evidence for $p > 6$. The set of possible p, q values for species with formula $Cd_p(HA)_q$ is given in Table 1.

In order to find the set of complexes existing up to $\bar{n} = 3$ it was necessary to add the 'core + links' family $(HA)_2[Cd(HA)_2]_x$ to the species given in Table 1, which correspond to $\bar{n} \leqslant 2.5$. The resemblance of the curves $\bar{n}$ *vs.* log [HA] for $\bar{n} > 2.5$ obtained in this work with those for the system cadmium(II)–4-mercapto-1-methylpiperidine[7] was the basis for choosing the $(HA)_2[Cd(HA)_2]_x$ series. The absence of these

Table 2. Cadmium complex-formation constants for the reaction $p\text{Cd} + q\text{HA} \rightleftharpoons \text{Cd}_p(\text{HA})_q$

p	q	$\log \Psi_{p,q}$*
4	8	67.4
5	12	99.0
3	8	63.2
1	3	20.6
1	4	22.6

* $\Psi_{p,q}$ is related to the stoicheiometric overall stability constant by the relationship $\beta_{p,q,q} = \Psi_{p,q}K_2^{-q}$; K_2 has been calculated in this work (see text).

data would have compelled us to employ a graphical treatment corresponding to the case $[\text{M}] \ll M_t$,[15a] where [M] denotes the concentration of the free metal. Moreover, mononuclear complexes of formula Cd(HA)_q, q = 2—4, were also introduced as the experimental curves $\log M_t$ *vs.* $\log [\text{HA}]$ suggested their presence in solution.

The formation constant of each complex was defined and its corresponding value estimated as indicated elsewhere.[7] In the particular case where the stoicheiometry was the same as the one found in the system 4-mercapto-1-methylpiperidine–cadmium(II) this formation constant was chosen as the estimated value in the present study.[7] The set of species and constants that gave the lowest values for σ are given in Table 2.

Species of Formula $\text{Cd}_p\text{A}_q\text{H}_r$*.—Graphical treatment.* Finally, all the experimental data were considered and thus complex species of the type $\text{B}_p\text{A}_q\text{H}_r$, probably formed by deprotonation of $\text{B}_p(\text{HA})_q$ species, were expected. The first information about the system came from curves of $\bar{n}_{\text{calc.}}$ against $\log l$, where $\bar{n}_{\text{calc.}}$ denotes the average number of completely deprotonated ligands bound per metal, equation (5), and l the calculated concentration of free completely deprotonated ligand, equation (6). The mass-balance equations underlying equations (5) and (6) neglect bound HA. This approximation is a mathematical requirement in order to be able to calculate the Bjerrum formation function, $\bar{n}_{\text{calc.}}$, in a ternary system. Consequently, $\bar{n}_{\text{calc.}}$ and l are only theoretical values and can be taken only as indicative of the real values for $\bar{n}$ and [A] in the system.

$$\bar{n}_{\text{calc.}} = \frac{L_t(1 - Y\bar{j})}{M_t}, \quad Y = \frac{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2}{2[\text{H}^+]^2 + K_1[\text{H}^+]} \qquad (5)$$

$$l = \frac{(L_t - \bar{n}_{\text{calc.}}M_t)K_1K_2}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2} \qquad (6)$$

Plots of $\bar{n}_{\text{calc.}}$ vs. $\log l$ for different series of titrations with either M_t or L_t constant demonstrated the presence of dependences on the total metal and total ligand concentrations in the whole range studied. Consequently, polynuclear and/or ternary complexes of formula $\text{Cd}_p\text{A}_q\text{H}_r$, $r \leqslant q$, predominate under such conditions. This, together with the unusual shape of the curves with increasing free ligand concentration, although previously found in similar systems,[11] showed the difficulty of obtaining information from these curves.

Average Composition of Species in Solution Analysis.—More valuable information about the system was obtained by means of the extended variation method[16] which allows calculation of the average stoicheiometric coefficients of the species present in solution, $\bar{p}$, $\bar{q}$, and $\bar{r}$, from only pH-electrode data and without any assumption about the identity of the species. However, the complexity of the mathematical treatment involved together with the risk of propagation of experimental errors in the calculation of the Sillén complexity sum[17] may cause important errors in the values of $\bar{p}$, $\bar{q}$, and $\bar{r}$. These errors can be partially avoided if one calculates only the ratios $\bar{q}/\bar{p}$ and $\bar{r}/\bar{p}$ which are easily deduced from equations (7)—(9) where $S' = S - [\text{A}][\text{H}^+]K_2^{-1} - [\text{A}][\text{H}^+]^2(K_1K_2)^{-1}$.

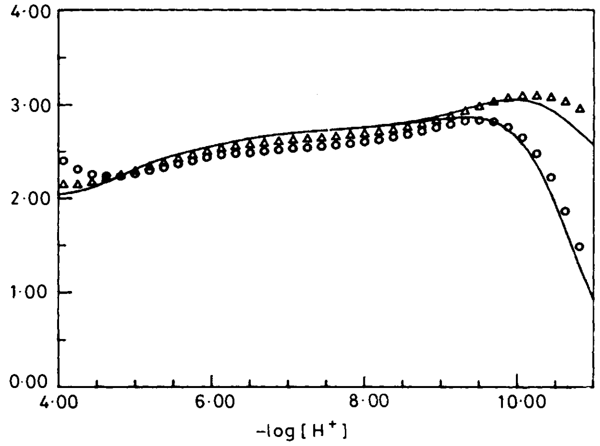

Figure 3. Number of bound ligands and hydrogens per metal ion, $\bar{q}/\bar{p}$ and $\bar{r}/\bar{p}$ respectively, as a function of pH, for the 'common point' titration (ref. 16). The lines drawn were calculated from the constants in Table 3. M_t = 6.01, L_t = 24.02 mmol dm^{-3}

$$\bar{p} = (M_t - [\text{M}])/S' \qquad (7)$$

$$\bar{q} = \{L_t - [\text{A}] - [\text{A}][\text{H}^+]K_2^{-1} - [\text{A}][\text{H}^+]^2(K_1K_2)^{-1}\}/S' \qquad (8)$$

$$\bar{r} = (H_t - [\text{A}][\text{H}^+]K_2^{-1} - 2[\text{A}][\text{H}^+]^2(K_1K_2)^{-1} - [\text{H}^+] + K_w[\text{H}^+]^{-1})/S' \qquad (9)$$

The normalized curves of $\bar{q}/\bar{p}$ and $\bar{r}/\bar{p}$ *versus* pH corresponding to the solution referred to as the 'common point'[16] are given in Figure 3. The variation of the number of bound ligands and hydrogens per metal ion, $\bar{q}/\bar{p}$ and $\bar{r}/\bar{p}$ respectively, for $L_t/M_t \approx 4$, indicates that up to pH $\approx$ 9.0 the soluble complexes can be formulated as $\text{Cd}_p\text{A}_q\text{H}_q$ in good accord with other experimental data already given. From this pH value the number of protons bound as well as that of the ligands decreases, suggesting that chelation occurs.

Refinement of the Equilibrium Model.—The mathematical treatment of all experimental data with a modified version[18] of the computer program SUPERQUAD (Florence version)[14] was carried out in several phases. First, only titrations corresponding to the highest L_t/M_t ratios were considered, as in this case complexes of the type $\text{Cd}_p(\text{HA})_q$, already found when considering the system as a two-component one (see Table 2), must predominate, and also it is likely that the species $\text{Cd}_p\text{A}_q\text{H}_r$ formed arise from the deprotonation of major species existing at pH $\approx$ 8.5, that is $[\text{Cd(HA)}_3]$ and $[\text{Cd(HA)}_4]$. In the second phase the rest of the curves were treated while the stoicheiometry of the species and corresponding formation constants already found were kept constant. At this stage all possible partially or completely deprotonated species arising from those found in the first phase of the treatment were introduced. Finally, all the species and corresponding constants were refined in order to get the best model.

The set of species and constants that gave the lowest value for σ[14] are given in Table 3. The low value for σ together with the theoretical curves, drawn as solid lines in the different figures, show that there is good agreement between the model found

Table 3. Cadmium complex-formation constants for $p\mathrm{Cd} + q\mathrm{A} + r\mathrm{H} \rightleftharpoons \mathrm{Cd}_p\mathrm{A}_q\mathrm{H}_r$ at 25 °C and $I = 3.0$ mol dm^{-3} (NaClO$_4$) from SUPERQUAD

Species	p	q	r	$\log \beta_{p,q,r}$
a	4	8	8	156.86 ± 0.03
b	5	12	12	233.27 ± 0.03
c	3	8	8	152.65 ± 0.03
d	1	3	3	54.15 ± 0.03
e	1	4	4	67.39 ± 0.05
f	3	6	4	102.9 ± 0.3
g	3	6	3	94.99 ± 0.08
h	3	6	1	73.9 ± 0.3
i	3	6	0	63.76 ± 0.09
j	1	2	0	18.97 ± 0.07
k	1	3	2	43.95 ± 0.03
l	1	3	1	33.02 ± 0.06

Number of points: 424, from 10 separate titrations. Estimated variances of the electrode and volume readings are, respectively, $\sigma_E = 0.1$ and $\sigma_V = 0.01$ cm^3. Sample standard deviation: $\sigma = 5.64$. σ_E, σ_V, and σ are defined as in ref. 14.

and the experimental data. The removal from this model of species f and h, Table 3, which under our experimental conditions have less than 10% abundance, Figure 4, and show relatively large standard deviations, increased the value of the sample standard deviation, σ, to 0.2. When species e, because of the small amount present, was also discarded, σ increased to 0.4.

Discussion

The calculated species distribution curves as a function of pH for two different ligand-to-metal ratios, $L_t/M_t < 4$ and > 4 [Figure 4(*a*) and (*b*) respectively], indicate that under the experimental condition of our study there is a predominance of protonated complexes, $[\mathrm{Cd_4(HA)_8}]^{8+}$, $[\mathrm{Cd_5(HA)_{12}}]^{10+}$, $[\mathrm{Cd_3(HA)_8}]^{6+}$, and $[\mathrm{Cd(HA)_3}]^{2+}$, over a wide pH range and also that in the presence of an excess of ligand the formation of polynuclear complexes is severely suppressed, favouring the mononuclear species $[\mathrm{Cd(HA)_3}]^{2+}$. Both major features were also apparent in other solution equilibria studies of cadmium(II)–mercaptoamine systems.[7,11,19]

The behaviour of aliphatic γ-mercaptoamines as unidentate neutral ligands co-ordinating only through their sulphur atom has been demonstrated in several *X*-ray crystallographically determined structures. Those referring to Group 12 metals have been given above. All these data allow us to propose that the monoprotonated form of the ligand, denoted as HA throughout this work, corresponds to the zwitterion 3-ammoniopropane-1-thiolate, $\mathrm{H_3\overset{+}{N}(CH_2)_3S^-}$.

The stoicheiometry of the polynuclear protonated complexes explains well the results obtained in the graphical treatment of the experimental data corresponding to the system when behaving as two components. Despite the fact that $[\mathrm{Cd_4(HA)_8}]^{8+}$, $[\mathrm{Cd_5(HA)_{12}}]^{10+}$, and $[\mathrm{Cd_3(HA)_8}]^{6+}$ belong to different 'core + links' series of complexes (Table 4), if they are written as $\mathrm{Cd[Cd(HA)_t]_x}$ they give rise to t values of 2.66, 3, and 4 respectively. Thus, the theoretical average value for t agrees well with the one found experimentally, 3.2, and also the wide range $2.66 < t < 4.00$ justifies the high value found for σ. The predominance of the mononuclear species $[\mathrm{Cd(HA)_3}]^{2+}$ in solutions where the total metal-ion concentration is low, and possibly close to that of the 'mononuclear wall,'[20] explains the deviation of the experimental points from the calculated straight lines for log M_t *vs.* log[HA] curves.

The stoicheiometry of $[\mathrm{Cd_5(HA)_{12}}]^{10+}$ and $[\mathrm{Cd_3(HA)_8}]^{6+}$, already found in similar systems,[6,7] suggests that they can be considered as short fragments of an infinite polymeric chain, analogous to the one found in the complex $[\mathrm{Cd(HRS)_2}][\mathrm{ClO_4}]_2\cdot2\mathrm{H_2O}$,[9a] where HRS denotes 4-mercapto-1-methylpiperidine in its zwitterionic form. In $[\mathrm{Cd_4(HA)_8}]^{8+}$, which under our experimental conditions is always the first complex formed, possibly two terminal co-ordination sites of cadmium cannot be occupied by sulphur atoms owing to the lack of

Table 4. Possible ways of representing complexes of formula $\mathrm{M}_p\mathrm{L}_q$[a] according to the 'core + links' hypothesis

	$\mathrm{M(ML}_t)_x$[a]		$\mathrm{L_2(ML}_t)_x$[a]	
$\mathrm{M}_p\mathrm{L}_q$	t	x	t	x
$\mathrm{Cd_4(HA)_8}$[b]	2.66	3		
$\mathrm{Cd_5(HA)_{12}}$	3	4	2	5
$\mathrm{Cd_3(HA)_8}$	4	2	2	3
$\mathrm{Cd_3(HRS)_6}$	3	2		
$\mathrm{Cd_4(HRS)_9}$	3	3		
$\mathrm{Cd_4(HRS)_{10}}$	3.33	3	2	4
$\mathrm{Cd_3(HRS)_8}$	4	2	2	3

[a] Sillén's symbols *B*, *A*, and *n* have been replaced by M, L and *x*, respectively. [b] HA = uncharged form of the ligand 3-aminopropane-1-thiol. [c] HRS = uncharged form of the ligand 4-mercapto-1-methylpiperidine.

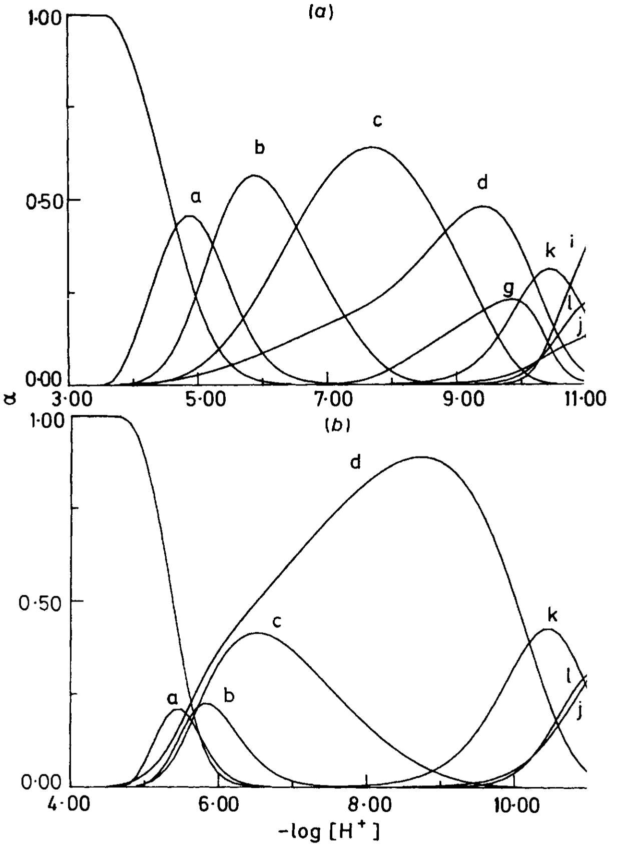

Figure 4. Distribution of species as a function of pH. Species whose concentration is lower than 10% have been omitted. For key to symbols see Table 3. L_t/M_t (*a*) < 4, (*b*) > 4. Conditions (M_t, L_t/mmol dm^{-3}): (*a*) 8.89, 24.02; (*b*) 0.763, 4.43

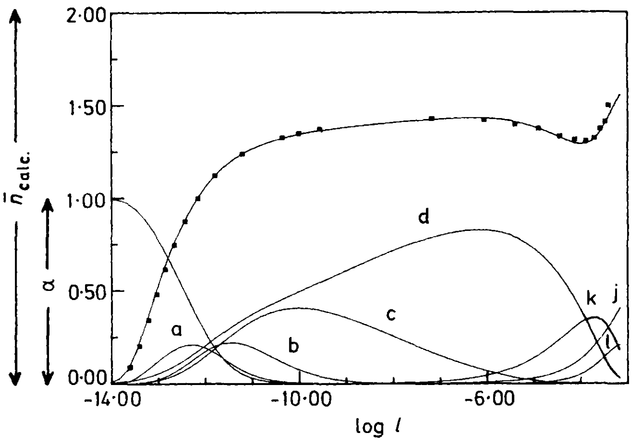

Figure 5. Species distribution curves and variation of the average number of completely deprotonated ligands bound per Cd^{II}, $\bar{n}_{calc.}$, as a function of the calculated concentration of free completely deprotonated ligand, l. For key to symbols see Table 3. $M_t = 0.760$, $L_t = 2.99$ mmol dm^{-3}

monoprotonated ligand at relatively low pH values [Figure 4(*a*) and (*b*)].

By comparing the systems cadmium(II)–3-aminopropane-1-thiol and –4-mercapto-1-methylpiperidine[7] it can be concluded that in both cases several 'core + links' families coexist. One possible interpretation of the experimental data is that in the first case the soluble species are members of two series of complexes, $Cd[Cd(HA)_{2.66}]_x$ ($x = 3$) and $(HA)_2[Cd(HA)_2]_x$ ($x = 3$ or 5), while in the second, the complexes also belong to two 'core + links' families, $Cd[Cd(HRS)_3]_x$ ($x = 2$ or 3) and $(HRS)_2[Cd(HRS)_2]_x$ ($x = 3$ or 4), but only the latter is common to both systems (Table 4). It is worth noting that the highest nuclearity in the soluble species is found in $Cd_5(HA)_{12}$ and $Cd_4(HRS)_{10}$ respectively. The stoicheiometry of the former has also been found in the system zinc(II)–4-mercapto-1-methylpiperidine.[6] The fact that the solubility of the polymeric cation $[M(H\overset{+}{N}RS^-)_2]_n{}^{2n+}$, where $M = Zn^{II}$ or Cd^{II} and $H\overset{+}{N}RS^-$ represents any of the two γ-mercaptoamines previously mentioned, decreases in going from Zn^{II} to Cd^{II} and also from 3-aminopropane-1-thiol to 4-mercapto-1-methylpiperidine explains well the maximum nuclearity achieved by the soluble species.

The deprotonation of $Cd(HA)_q$ in solutions where $L_t/M_t > 4$, Figure 4(*b*), starts at pH ≈ 8, giving rise to several CdA_qH_r species in which $r < q$. This, together with the fact that, instead of forming $[Cd(HA)_4]^{2+}$, the complex $[Cd(HA)_3]^{2+}$ is deprotonated and gives rise to $[CdA_3H_2]^+$, indicates that the acidity of the amine group of the complexed ligands has been enhanced and that chelation, by means of NS binding, occurs. The normalized curves, $\bar{q}/\bar{p}$ and $\bar{r}/\bar{p}$ *vs.* pH, Figure 3, are in accord with this interpretation. It is obvious that chelate formation is favoured only for low ligand-to-metal ratios and thus in the presence of a deficit of ligand, Figure 4(*a*), it has to start at lower pH values. This is the case with species $Cd_3A_6H_3$ [denoted by g in Figure 4(*a*)] where, if related structurally to $Cd_3(HA)_8$, two ligands behave as chelates by means of S-bridging and N-terminal co-ordination. The different co-ordinating behaviour of the ligands in the same complex is confirmed by i.r. data. By comparing the i.r. spectrum of a solid complex which separates out from potentiometric solutions (see below) with that of 3-aminopropane-1-thiol in CCl_4 solution, and those of $[Cd(HA)_2][ClO_4]_2$ and $[Co(HA)_3][ClO_4]_3$,[21] where there is only *S*-co-ordination, and that of $[Cd_3A_4][ClO_4]_2$,[22] where there is only NS-binding, it can be concluded that some of the deprotonated ligands in the complex mentioned behave as chelating agents.

The chelating ability of 3-aminopropane-1-thiol[23] and specially that of 2-aminoethane-1-thiol[24] is well known. Chelate structures have been proposed for solid cadmium complexes of both ligands[22,24] as well as for soluble complex species of the latter compound.[11] However the equilibrium constant, log $K = -10.2$, for reaction (10) compared to that (-8.03) reported[11]

$$[Cd(HA)_3]^{2+} \rightleftharpoons [Cd(HA)_2A]^+ + H^+ \qquad (10)$$

for 2-aminoethane-1-thiol clearly indicates that under these conditions the chelating ability of 3-aminopropane-1-thiol is low. Probably, chelate formation is competing with deprotonation of complexed ligands. The existence of mono- and completely deprotonated γ-mercaptoamine ligands in polynuclear metal complexes has been demonstrated crystallographically very recently.[25]

The fact that in solutions where $L_t/M_t < 2$ a solid complex of formula $[Cd_5(HA)_2A_6][ClO_4]_4$ appears inevitably makes very difficult the detection of any species $Cd_pA_qH_r$ in which q/p is lower than two. This could explain the absence of a species with stoicheiometry $[Cd_3A_4]^{2+}$ that is expected on the basis of previous results either for solid complexes[22–24] or in solution equilibria studies.[11] It is very likely that the presence of chloride ions in the latter case does not allow the formation of species with high nuclearity, thus facilitating the existence of the mentioned complex species.

The species distribution curve together with the corresponding plot of $\bar{n}_{calc.}$ *vs.* log l is given in Figure 5. The relationship between the two representations becomes apparent as the maximum of the latter corresponds to the predominance of $Cd_pA_qH_r$ species with the highest r/p ratio, $[CdA_3H_3]$. Also, when $\bar{n}_{calc.}$ decreases, deprotonation commences and finally when $\bar{n}_{calc.}$ goes up again species with $r = 0$ or low values are formed. The information obtained from plots of $\bar{n}_{calc.}$ *vs.* log l can thus be extended and also be used in similar systems to provide indications about the stoicheiometry of ternary complex species despite the inevitable approximations made when calculating $\bar{n}_{calc.}$

A comparison of the behaviour of Cd^{II} with aliphatic γ-mercaptoamine ligands in solution including the results obtained with 3-dimethylaminopropane-1-thiol[19] will be published in the near future.

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