Polymeric Thiolate Complexes in Solution. Stability Constants of the Zinc(II) Complexes of 1-Methyl-4-mercaptopiperidine

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The equilibrium reaction between Zn^{II} and 1-methyl-4-mercaptopiperidine has been studied by e.m.f. measurements with a glass electrode at 25 °C in a 3 mol dm^{-3} (sodium) perchlorate medium [+10% (v/v) CH_3OH]. Conclusions drawn from graphical methods based on the ' core + links ' hypothesis are in agreement with the results obtained from the numerical treatment. The e.m.f. data obtained in the range $4 < -\log[H^+] < 9$ can be explained by assuming the existence of the following species: $[Zn_3(HA)_6]^{6+}$ ($\log \psi_{3,6} = 39.71 \pm 0.01$), $[Zn_5(HA)_{12}]^{10+}$ ($\log \psi_{5,12} = 79.87 \pm 0.01$), and $[Zn_2(HA)_6]^{4+}$ ($\log \psi_{2,6} = 35.26 \pm 0.02$) where HA is the uncharged ligand. A mechanism for the formation of these species and their possible geometries are suggested.

THE present investigation of complex formation between zinc ion and the ligand 1-methyl-4-mercaptopiperidine in aqueous methanolic solution (9 : 1 v/v) is part of a more extensive study of complex formation between metal ions and γ-mercaptoamine ligands. Although much information has been obtained concerning metal complexes of β-mercaptoamine ligands and sulphur-containing amino-acids, both in the solid state and in solution, very little is known about the behaviour of γ-mercaptoamines.

From the data we already have [1-3] on solid metal complexes of 1-methyl-4-mercaptopiperidine, we conclude that this compound behaves as a unidentate neutral ligand, in the zwitterionic form $^{-}S{-}C_5H_9\overset{+}{N}(CH_3)H$. Therefore, equilibrium studies in solution should provide a model for the behaviour of simple thiol ligands whose metal complexes have not been extensively investigated. Difficulties in studying the thiol ligands arise mainly from the very slight solubility of these ligands and their complexes in aqueous medium. For this reason, Schwarzenbach *et al.*[4-6] studied the interaction of several metal cations with thioglycol, which is a water-soluble mercaptan, but *X*-ray crystallographic determination of the structure of solid complexes showed that in some cases the oxygen of the thioglycolate anion also acted as a donor atom.[4,7,8]

1-Methyl-4-mercaptopiperidine is not very soluble in water. Thus, the potentiometric determination of the acidity constants of 1-methyl-4-mercaptopiperidinium ion in 3 mol dm^{-3} (sodium) perchlorate medium at 25 °C was carried out in a water-methanol (9 : 1 v/v) mixture and so the same medium has been used here. Spectrophotometric determination of the acidity constants [9] of this cation has shown that K_1 is practically the dissociation constant of the mercapto-group.[10]

The pronounced tendency of mercaptide sulphur atoms to form bridges between metal cations is well known and thus the formation of polynuclear species should be expected. In this work the equilibrium constants for the complex species formed have been determined by potentiometric titrations. The structures of the soluble complexes and their mechanism of formation are postulated.

EXPERIMENTAL

Zinc perchlorate stock solution was prepared from Alfa-Ventron p.a. $Zn[ClO_4]_2 \cdot 6H_2O$ and acidified by means of $HClO_4$. The zinc content was determined gravimetrically as $Zn[NH_4][PO_4]$ and volumetrically with ethylenediaminetetra-acetate (edta). The two methods gave the same result within 0.2%. Potentiometric solutions were prepared by adding a weighed volume of the stock solution to a volumetric flask that contained an adequate weight and volume of sodium perchlorate stock solution and methanol respectively. The sodium perchlorate stock solution was prepared and analysed according to the method of Biedermann.[11] Sodium hydroxide solution was prepared from freshly filtered 50% Na[OH] solution and CO_2-free water. Methanol and $Na[ClO_4]$ stock solution were boiled separately under a N_2 atmosphere before addition of concentrated Na[OH] solution to a suitable mixture of the two. The stock solution of perchloric acid was prepared from 70% $HClO_4$. 1-Methyl-4-mercaptopiperidine was synthesized according to Barrera and Lyle [12] and purified by distillation under reduced pressure (68 °C at 14 mmHg) † until its purity was greater than 99.5%. Determinations of the SH and amine groups were performed iodometrically and acidimetrically respectively. Both methods gave results within 0.1% which indicated that the impurities in the ligand solution came from the solvent, essentially isopropyl alcohol, used in its synthesis. Potentiometric solutions of the ligand with a free hydrogen-ion concentration, *h*, of *ca.* 20—50 mmol dm^{-3} were kept for 2 weeks without evidence of oxidation. Methanol (p.a.) was used without further purification.

The silver electrode was prepared according to Brown.[13] It was coated with a thin layer of AgCl (prepared by anodic oxidation in a 10 mmol dm^{-3} HCl solution). An Ingold glass electrode, type HA 201, was used in combination with a Crison Digilab 517 potentiometer (±0.1 mV). A ' Wilhelm ' glass apparatus was used for the salt bridge and reference half-cell.[14] The potentiometric vessel was submerged, like the ' Wilhelm ', in an oil thermostat at 25.0 ± 0.1 °C. Stirring was effected by a stream of oxygen-free nitrogen, the last wash bottle containing the ionic medium being submerged in the thermostatted bath. All e.m.f. readings reached a constant value within 20 min and remained almost constant for at least 24 h.

Titration Procedure.—A series of potentiometric titrations of solutions of differing concentrations containing zinc

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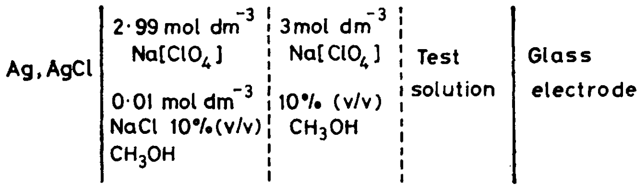
† Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

perchlorate and 1-methyl-4-mercaptopiperidinium perchlorate in an excess of perchloric acid was carried out. In each titration the total concentration of metal, B, and that of the ligand, L, were held constant; B was varied in the range 0.8—27.0 mmol dm^{-3} and L according to the molar ratio $2 < L/B < 8$.

The test solution in the titration vessel was composed of $L + B + H + 3.0\ ClO_4^- + 10\%$ (v/v) CH_3OH. The hydrogen-ion concentration in the test solution, H, was varied by adding equal volumes of the burette solutions S_1, S_2, S_i ($i = 3$ or 4) with the following compositions: $S_1 = 3L + H_1 + [3.0 - 3L - (H_1 - 6L)]Na^+ + 3.0\ ClO_4^- + 10\%$ (v/v) CH_3OH; $S_2 = 3B + H_2 + [(3.0 - 6B - H_2)]Na^+ + 3.0\ ClO_4^- + 10\%$ (v/v) CH_3OH; $S_3 = H_3 + (3.0 - H_3)Na^+ + 3.0\ ClO_4^- + 10\%$ (v/v) CH_3OH; and $S_4 = H_4 + 3.0\ Na^+ + (3.0 + H_4)ClO_4^- + 10\%$ (v/v) CH_3OH (all values in mol dm^{-3}). Solution S_4 was a sodium hydroxide solution containing the medium salt. In basic solutions, H denotes hydroxide-ion concentration with a minus sign.

The reversibility of the system was checked by back titrations. The initial value for h in test solution was determined potentiometrically.[15] The cell for the e.m.f. measurements was as shown below. The free hydrogen-ion concentration can be calculated from the e.m.f. of the cell using equation (1), where E_0 is a constant determined before



$$E = E_0 + 59.16 \log h + E_j \qquad (1)$$

each titration [15] and the found value checked at the end, and E_j is the liquid-junction potential. The linearity of plots of $E - 59.16 \log h$ against h allows us to express E_j as $E_j = wh$, according to Biedermann and Sillén.[16] The value of w was found to be -9.3 ± 0.3, where E_j is given in mV and h in mol dm^{-3}, thus E_j was negligible under our experimental conditions.

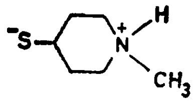
CALCULATIONS AND RESULTS

E.M.F. Data.—Six potentiometric titrations were carried out. Assuming that the complex species present in solution were of the type $Zn_pA_qH_r$ where $p \geqslant 1$, $q \geqslant 1$, r is an integer, and A denotes the completely deprotonated ligand, values for $\log h$ and $\bar{r}$ were calculated using equations (2) and (3) from the primary data and the calculated value

$$E = E_0 \pm 59.16 \log h \qquad (2)$$

$$\bar{r} = (H - h + K_w h^{-1})/L \qquad (3)$$

for K_w ($-\log K_w = 14.16$) in the medium salt. Plots of $\bar{r}$ against ($-\log h$), corresponding to the six titrations, are given in Figure 1. By comparing these curves with the one obtained in the absence of metal it can be concluded that complexation occurs for $h \leqslant 10^{-4}$. It also appears that in the range $4 \leqslant -\log h \leqslant 8$ the ligand behaves as a ' monoprotonated ' ligand. Based on the known structures of crystalline solid complexes of the same ligand, on the pronounced tendency of the co-ordinated mercapto-group to form bridges, and also on data from this work, which suggested that polynuclear complexes were formed, we assume that the ' monoprotonated ' form of the ligand (HA) has the structure (I). Thus, the formation constant of the complex



(I)

$[Zn_p(HA)_q]^{2p+}$ can be defined by equation (4) where $\psi_{p,q}$ is related to the stoicheiometric overall stability constant by the relationship (5) and K_2 is the second acid-dissociation constant.

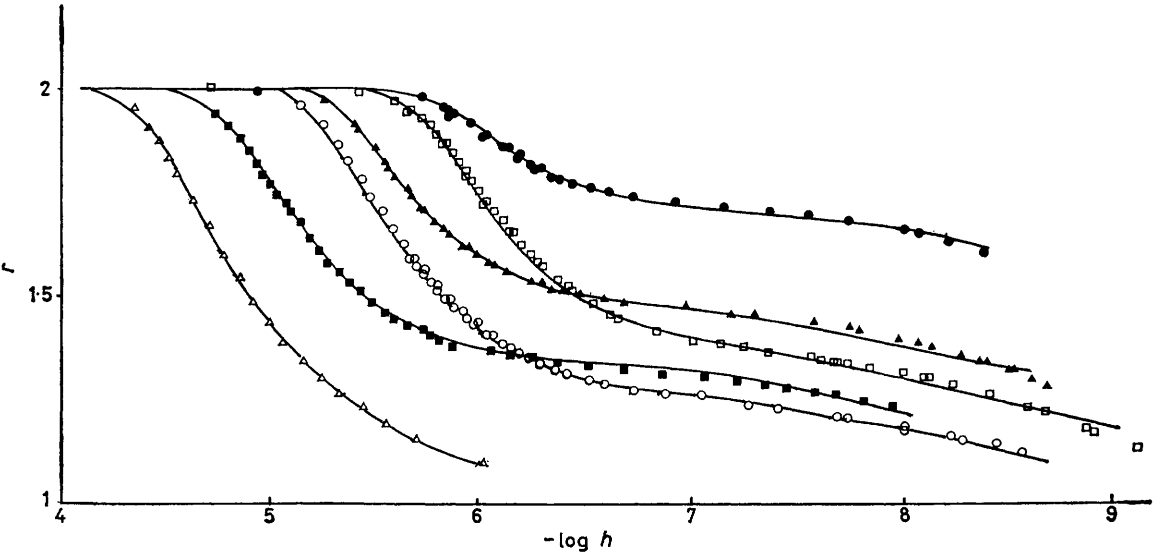


FIGURE 1 Average number of protons bound to the ligand, $\bar{r}$, as a function of $\log h$ at different ligand : metal ratios: $B = 0.863$, $L = 7.97$ (●); $B = 1.996$, $L = 7.97$ (□); $B = 3.21$, $L = 15.37$ (▲); $B = 5.28$, $L = 17.50$ (○); $B = 10.84$, $L = 40.1$ (■); $B = 27.62$, $L = 66.1$ mol dm^{-3} (△). The lines drawn were calculated from the constants in the Table (end of Results section)

$$\psi_{p,q} = [Zn_p(HA)_q{}^{2p+}][Zn^{2+}]^{-p}[HA]^{-q} \qquad (4)$$

$$\beta_{p,q,q} = \psi_{p,q}K_2{}^{-q} \qquad (5)$$

In a two-component system, the experimental function, Z, which represents the average number of ligands bound to one metal atom, can be calculated, as can the free ligand concentration, using equations (6) and (7) respectively.

$$Z = L(1 - \bar{r}X)/B(1 - X),$$
$$X = (h^2 + K_1h + K_1K_2)/(2h^2 + K_1h) \qquad (6)$$

$$[HA] = (L - ZB)/(h^2 + K_1h + K_1K_2) \qquad (7)$$

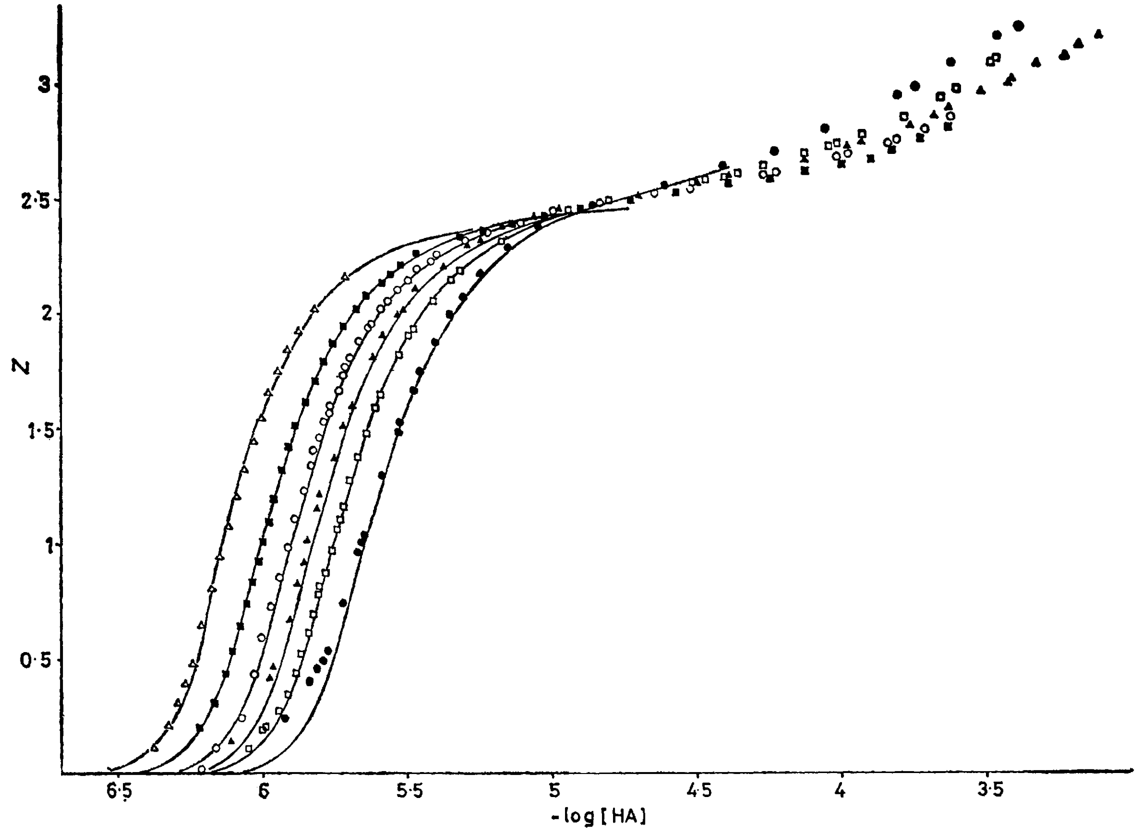


FIGURE 2 Formation curve for $[Zn_p(HA)_q]^{2p+}$ species at different ligand : metal ratios; for key to symbols see Figure 1. The lines drawn were calculated from the constants in the Table

A survey of the plots of Z against log [HA], Figure 2, indicates that on adding Na[OH] there is an initial range, between $Z = 0$ and 2.0, in which the curves for various L and B values are almost parallel. For $B = 0.863$ and $Z < 0.5$, there is a small deviation from parallelism. From $Z = 2.0$ upwards, the curves start to converge until they appear to coincide at Z *ca.* 2.5. For $Z > 2.5$ there is a divergence of the curves.

Zinc Complex Stability Constants.—Methods based on the ' core + links ' hypothesis. For Z values up to *ca.* 2.2, the ' core + links ' hypothesis was used.[17,18] The value of t in $Zn[Zn(HA)_t]_n{}^{2(n+1)+}$ was determined by plotting log B against log [HA] for several Z values, Figure 3. The slope of each line is $-t$. The average value found, $\bar{t}$, was 3.10, $s = 0.055$ being the standard deviation. Accepting that the true value for t should be in the range $\bar{t} \pm 3s$, possible values were $2.94 \leqslant t \leqslant 3.26$. Within this range, $t = 3.00$ allows the existence of several ' core ± links ' complexes while the values $t = 3.25$ ($n = 4$), 3.20 (5), 3.17 (6), *etc.* imply the existence of species for which $Z_{max.} > 2.5$ and these were only considered in the numerical treatment.

The experimental results for $t = 3$ fell satisfactorily on a normalised curve [17] y *vs.* x, Figure 4, where $x = \log B + t \log [HA]$ and $y = Zt^{-1}$ for $y < 0.8$. Experimental points for which $Z < 1$, corresponding to the titration in which $B = 0.863$ mmol dm^{-3}, were disregarded, since it is likely that this metal concentration is close to that of the ' mononuclear wall '.[19] Neither were these points considered in the graphical nor in the numerical treatments.

Curve-fitting methods. According to Sillén,[18] the hypotheses most widely used were tested. First, assuming that only one ' core + links ' species was present, a set of theoretical curves, y against x, was plotted for different n values. Secondly, considering that species for all values of n were present in solution and that the corresponding formation constants were of the form $\psi_n = K_0K^n$, theoretical curves y against x were plotted for several K_0 values. None of these theoretical curves fitted the experimental curve completely.

Linear regression methods. In order to obtain more information about the existing species and corresponding formation constants, two auxiliary variables, u and g defined by equations (8) and (9) respectively, were employed

$$u = [Zn^{2+}][HA]^t \qquad (8)$$

$$g = \sum_{n=1} \psi_n u^n \qquad (9)$$

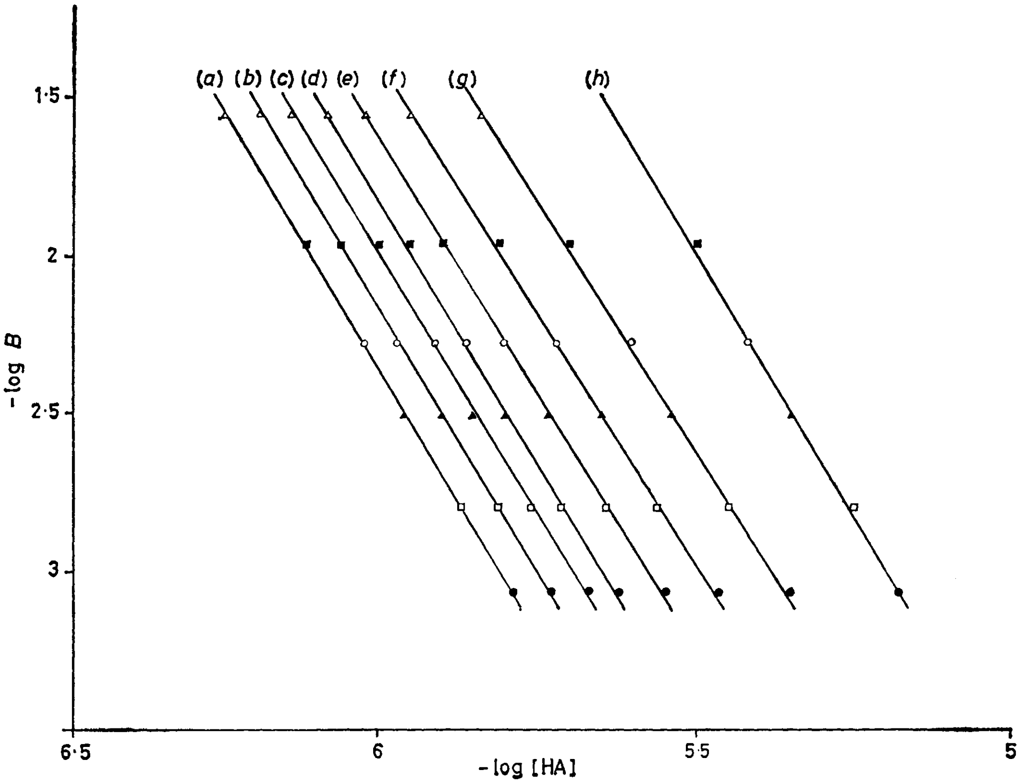


FIGURE 3 Variation of total concentration of Zn^{II} with that of the free monoprotonated ligand for several Z values: $Z = 0.5$ (*a*); 0.75 (*b*); 1 (*c*); 1.25 (*d*); 1.5 (*e*); 1.75 (*f*); 2 (*g*); 2.25 (*h*). The straight lines were calculated by linear regression (for key to symbols see Figure 1)

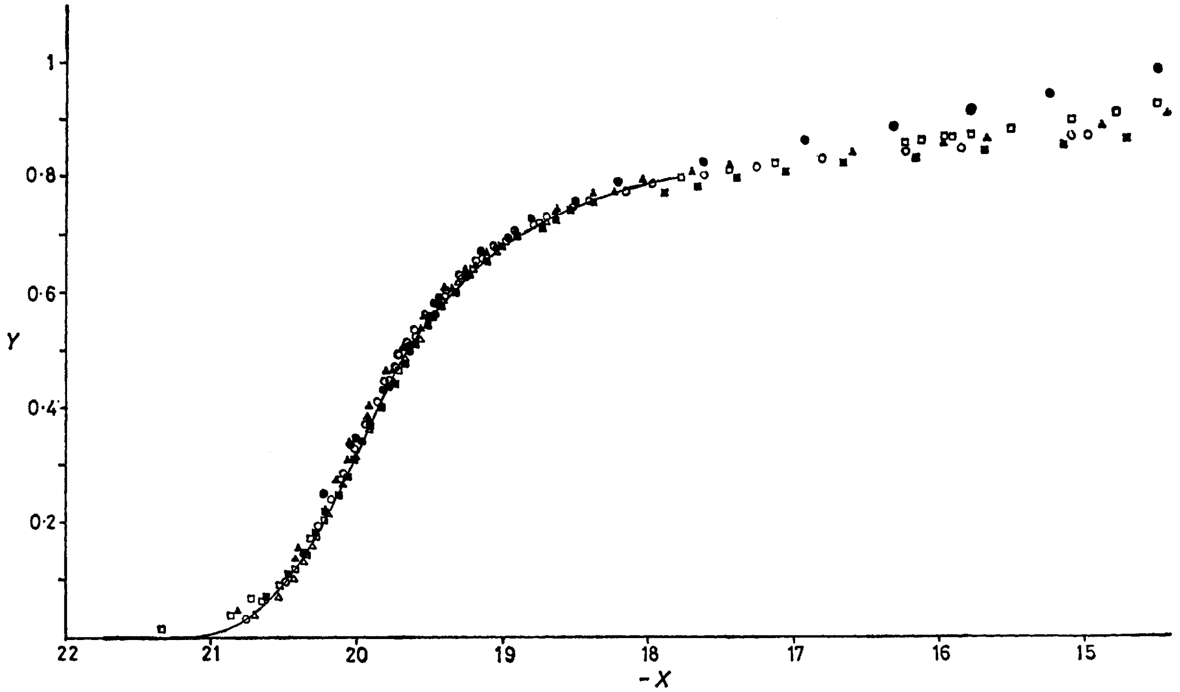


FIGURE 4 Normalised curve of y against x for $Zn[Zn(HA)_t]_n^{2(n+1)+}$ complexes at different ligand : Zn^{II} ratios, taking $t = 3$, from experimental data. The line drawn was calculated from the constants in the Table (for key to symbols see Figure 1)

where ψ_n is the formation constant of $Zn[Zn(HA)_t]_n$ and variables u and g are related to the previous x and y variables as indicated elsewhere.[17] Values for log g and log u were calculated using Hietanen's procedure.[20] The slope of the curve of log g against log u, which is equal to the average number of links bound to the core, $\bar{n}$, confirmed that more than one polynuclear species was present.

For $1 \leqslant Z \leqslant 2.4$, curves gu^{-2} against u^2 gave a straight line of slope ψ_4 ($=1.1 \times 10^{80}$) and of intercept ψ_2 ($\psi_2 = 6 \times 10^{39}$). The observed deviation for $Z \leqslant 1$ is probably due to the lack of accuracy in the graphical integration. Therefore, according to this treatment only 'core + links' species with odd n values were present in solution.

Numerical method. In order to determine the set of $[Zn_p(HA)_q]^{2p+}$ species and equilibrium constants for reaction (10) that best fit the experimental data, the program

$$p\,Zn^{2+} + q\,HA \rightleftharpoons [Zn_p(HA)_q]^{2p+} \qquad (10)$$
$$\psi_{p,q} = [Zn_p(HA)_q{}^{2p+}][Zn^{2+}]^{-p}[HA]^{-q}$$

MINIQUAD 75 [21] was used in conjunction with a UNIVAC 1108 computer.

Assuming that the species $[Zn(HA)_3]^{2+}$, $[Zn(HA)_4]^{2+}$, and $[Zn_2(HA)_6]^{4+}$ could exist in solutions in which $Z \geqslant 2.5$, *ca.* 40 different sets of species and corresponding estimated constants were introduced into the program. The species $[Zn_2(HA)_6]^{4+}$ was taken into account since experimental data gave us only odd n values for $t = 3$, which suggested that this species could be the ' link ' in complexes of the type $Zn[Zn_2(HA)_6]_n{}^{(4n+2)+}$, where n is any integer. Furthermore, the existence of the binuclear solid complex $[\{Zn[SC_5H_9NH(CH_3)]Cl_2\}_2]\cdot H_2O$ [3] gave support to this assumption. The set of species and constants that gave the lowest values for U and σ are given in the Table.

Zinc complex stability constants from MINIQUAD 75

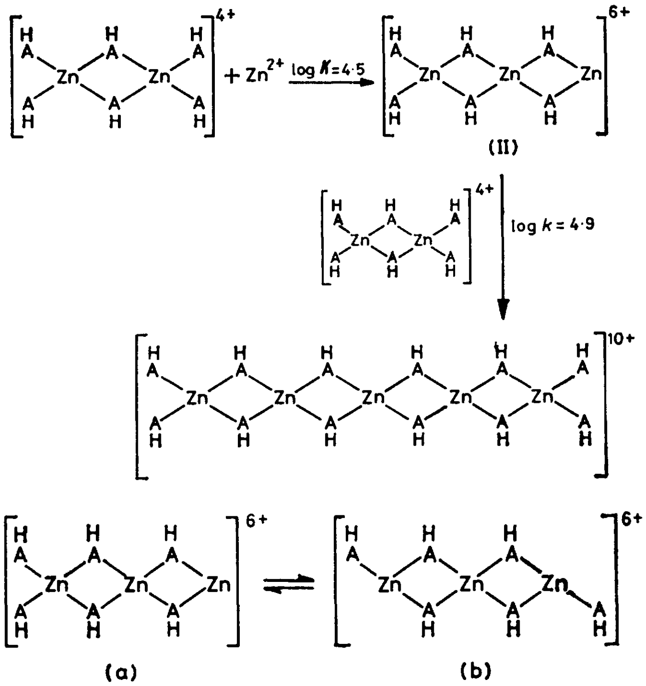
$[Zn_3(HA)_6]^{6+}$	$\log \psi_{3,6}$	$= 39.71 \pm 0.01$	$U = 1.18 \times 10^{-6}$ (138 points) $\sigma = 5.3 \times 10^{-5}$
$[Zn_5(HA)_{12}]^{10+}$	$\log \psi_{5,12}$	$= 79.87 \pm 0.01$	
$[Zn_2(HA)_6]^{4+}$	$\log \psi_{2,6}$	$= 35.26 \pm 0.02$	

DISCUSSION

In view of the final results, it is clear that neither of the curve-fitting hypotheses could fit the experimental data adequately. However, assumptions made in the linear-regression method were consistent, as is shown by comparing ψ values obtained by this method with those from the numerical treatment.

The assumption that the complex $[Zn_2(HA)_6]^{4+}$ could be a possible link becomes perfectly valid after the numerical treatment, since the three species predominating in solution can be written as $[Zn_2(HA)_6]^{4+}$, $Zn[Zn_2(HA)_6]^{6+}$, and $Zn[Zn_2(HA)_6]_2{}^{10+}$. The solubility of these species must be due to the protonated amine groups that spread out around the metal atoms making them behave similarly to protonated polyamines.

Taking into account information already given here, and based on the stoicheiometry of the complex species, the mechanisms of formation and geometry of the species may be as suggested in the Scheme. Evidently species (II) could be in any of the possible forms between structures (a) and (b), and hence, it could be a fragment of the polymeric chain suggested for several zinc mercaptides [22] and found in the complex $[Cd\{SC_5H_9NH(CH_3)\}_2][ClO_4]_2\cdot 2H_2O$.[1]



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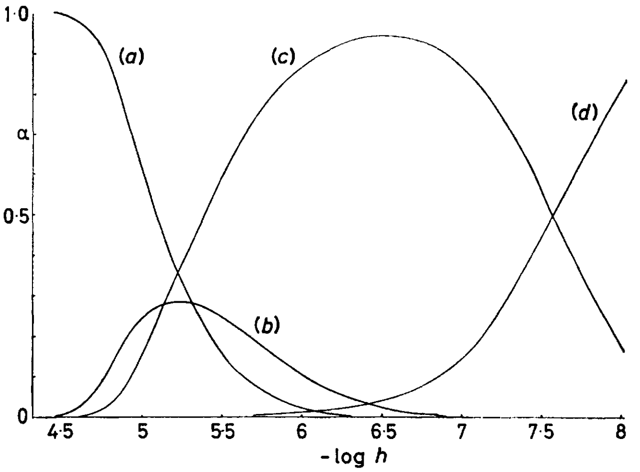

FIGURE 5 Concentration distribution of the complexes $[Zn_p(HA)_q]^{2p+}$ formed in the zinc(II)–1-methyl-4-mercaptopiperidine system. $B = 10$ mmol dm^{-3}, $L = 40$ mmol dm^{-3}: $p = 1, q = 0$ (*a*); $p = 3, q = 6$ (*b*); $p = 5, q = 12$ (*c*); $p = 2, q = 6$ (*d*)

The fraction of Zn^{II} complexed in the various species $[Zn_p(HA)_q]^{2p+}$, $\alpha_{p,q}$, for $B = 10$ mmol dm^{-3} and $L = 40$ mmol dm^{-3}, is shown as a function of log h in Figure 5.

A comparison of the zinc(II) complexes with those of cadmium(II) and mercury(II) with the same ligand is now being investigated.

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