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A CALORIMETRICAL STUDY OF THE POLYNUCLEAR Zn(II) AND Pb(II) AND THE POLYMERIC Ni(II) AND Cd(II) COMPLEXES OF 2-MERCAPTOETHANOL AND 3-MERCAPTO-1,2-PROPANEDIOL

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ABSTRACT

The ΔG, ΔH and ΔS values for the dissociation of 2-mercaptoethanol (MEL) and 3-mercapto-1,2-propanediol and for the formation of complexes between these ligands and the metal ions Ni^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} have been determined calorimetrically in 0.5 M KNO_3 and at 25 °C.

INTRODUCTION

The complex formation between Ni^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} and 2-mercaptoethanol and 3-mercapto-1,2-propanediol was reported in a series of earlier papers[1–4]. In all cases polynuclear complexes B_qA_p are formed, B meaning the metal ion and A the ligand. With Ni^{2+} polymeric complexes are formed represented by the formula $B(A_2B)_n$ with n great. There is also strong evidence that the Cd^{2+} complexes are polymeric. They can be represented by the formula $B(A_5B_3)_n$ with a large value for n. In the case of Zn^{2+} a series $B(A_3B)_n$ was found with a maximum number of five for n. With Pb^{2+} the predominant species in solution are B_3A_5, B_2A and B_3A_4.

In order to obtain more information about the complex formation, in this paper the enthalpy and entropy changes accompanying formation of the complexes are reported from thermometric titration. The $\Delta H_{q,p}$ values of the polynuclear complexes were calculated with a number of adapted computer programs. A new method is worked out in order to represent and calculate enthalpy changes accompanying the formation of polymeric complexes.

EXPERIMENTAL

Reagents

Stock solutions of nickel-, zinc-, cadmium- and leadnitrate (Baker) were standardized gravimetrically as, respectively, bis-(dimethylglyoximato)nickel, $ZnNH_4$

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PO_4, $CdNH_4PO_4 \cdot H_2O$ and $PbCrO_4$[5]. Both thiols (Fluka p.a.) were redistilled before use. Solutions of both ligands were prepared directly before use. All solutions were made up to an ionic strength of 0.5 M KNO_3.

Calorimetrical titration procedure

Calorimetric measurements were carried out with an LKB 8700-2 titration calorimeter. The reagent was added with a piston buret "Tacussel electroburap", equipped with a preselection unity. Four thermometric titrations were performed for each system. In each titration the volume in the reaction vessel was 80 ml and was composed as indicated in Table 1. The solutions were titrated with 1 M KOH in 0.25 ml fractions.

TABLE 1
COMPOSITION OF THE MIXTURE IN THE REACTION VESSEL

No. of titration	*0.032 M Metal nitrate (ml)*	*0.128 M Ligand (ml)*	*0.5 M KNO_3 (ml)*
1	0	40	40
2	40	40	0
3	30	30	20
4	20	20	40

Calculations

The calculations were performed with a number of computer programs written in Fortran IV. The programs were executed on a Siemens 4004/150 computer.

RESULTS AND DISCUSSION

List of symbols

The symbols used are those recommended by the IUPAC commission[6] and are listed below.

B = (1) symbol for a metal ion; (2) total metal ion concentration
A = (1) symbol for the ligand; (2) total ligand concentration
b = free metal ion concentration
a = concentration of free ligand
$h_i a$ = concentration of protonated ligand H_iA
h = activity of the hydrogen ion
K_{Hi} = mixed protonation constant of H_iA defined as:
$K_{Hi} = h_i a / h \cdot h_{(i-1)} a$
N = maximum number of hydrogen ions that the ligand can take up
$\beta_{q,p}$ = overall stability constant of a complex B_qA_p defined as:
$\beta_{q,p} = (B_qA_p)/b^q \cdot a^p$
$B(A_tB)_n$ = "core+links" representation of a series complexes
k, k_0 = constants defining a polymeric "core+links" series

v = $ka^i b$

Q = heat liberated during a titration

Q_{dil} = heat of dilution of the titrant

V = total volume in the titration cell

ΔG_{Hi}, ΔH_{Hi}, ΔS_{Hi} = free enthalpy, enthalpy and entropy change of protonation of the ligand H_iA

$\Delta G_{q,p}$, $\Delta H_{q,p}$, $\Delta S_{q,p}$ = free enthalpy, enthalpy and entropy change of formation of a complex B_qA_p

Δg_0 and Δg, Δh_0 and Δh, Δs_0 and Δs = free enthalpy, enthalpy and entropy representations for a polymeric series $B(A_tB)_n$

Determination of the enthalpy of protonation of the ligands

The enthalpy and entropy of protonation of the mercaptogroup in the ligands MEL and MPD were calculated from titration 1 (Table 1) with the aid of eqns (1) and (2)

$$-\frac{Q-Q_{dil}}{V} = (\Delta H_{H_2O} - \Delta H_{Hi})\,[OH^-] \tag{1}$$

where $[OH^-]$ means the concentration of base added.

$$\Delta G_{Hi} = -RT \ln K_{Hi} = \Delta H_{Hi} - T\,\Delta S_{Hi} \tag{2}$$

ΔH_{H_2O} was taken to be -13.34 kcal mol^{-1} according to Vanderzee and Swanson[7], Izatt[8] and our experiments. The results are given in Table 2.

TABLE 2

ENTHALPY AND ENTROPY OF PROTONATION OF THE LIGANDS

Ligand	*log* K_{Hi}	ΔG_{Hi} (*kcal mol*$^{-1}$)	ΔH_{Hi} (*kcal mol*$^{-1}$)	ΔS_{Hi} (*cal mol*$^{-1}$ *K*$^{-1}$)
MEL	9.49	−12.93	−6.15	+22.77
MPD	9.43	−13.85	−6.73	+20.55

Determination of the enthalpy of formation of the polynuclear complexes formed between Pb^{2+}, Zn^{2+} *and MEL, MPD*

The enthalpy and entropy of formation of these complexes were determined from titrations 1–3 (Table 1). A computer-program THER was written for solving the $\Delta H_{q,p}$ values from eqn (3).

$$-\frac{Q-Q_{dil}}{V} = \sum_p \sum_q \beta_{q,p}\, b^q a^p \left[\Delta H_{q,p} + p \sum_{i=1}^{N} (\Delta H_{H_2O} - \Delta H_{Hi})\right] + \sum_{i=0}^{N-1} K_{Hi} \cdot h^i \cdot a \sum_{i'=1}^{N-i} (\Delta H_{H_2O} - \Delta H_{Hi'}) \tag{3}$$

TABLE 3

CALORIMETRIC RESULTS FOR MEL/Zn^{2+}

Complex	*log* $\beta_{q,p}$	$\Delta G_{q,p}$ (*kcal mol*$^{-1}$)	$\Delta H_{q,p}$ (*kcal mol*$^{-1}$)	$\Delta S_{q,p}$ (*cal mol*$^{-1}$ *K*$^{-1}$)
B_2A_3	18.320	−24.970	—	—
B_3A_6	38.615	−52.631	(−13)	(+133)
B_4A_9	57.813	−78.798	(−53)	(+86)
B_5A_{12}	77.179	−105.193	−40	+220
B_6A_{15}	95.924	−130.742	−67	+214

TABLE 4

CALORIMETRIC RESULTS FOR MPD/Zn^{2+}

Complex	*log* $\beta_{q,p}$	$\Delta G_{q,p}$ (*kcal mol*$^{-1}$)	$\Delta H_{q,p}$ (*kcal mol*$^{-1}$)	$\Delta S_{q,p}$ (*cal mol*$^{-1}$ *K*$^{-1}$)
B_2A_3	18.089	−24.655	—	—
B_3A_6	37.805	−51.527	(−37)	(+47)
B_4A_9	56.537	−77.059	−32	+151
B_5A_{12}	74.741	−101.870	(−30)	(+238)
B_6A_{15}	93.873	−127.947	−73	+184

TABLE 5

CALORIMETRIC RESULTS FOR MEL/Pb^{2+}

Complex	*log* $\beta_{q,p}$	$\Delta G_{q,p}$ (*kcal mol*$^{-1}$)	$\Delta H_{q,p}$ (*kcal mol*$^{-1}$)	$\Delta S_{q,p}$ (*cal mol*$^{-1}$ *K*$^{-1}$)
B_3A_5	38.484	−52.453	−39.0	+44.0
B_2A	9.066	−12.347	(−4.0)	(+27.0)
B_3A_4	32.780	−44.678	−30.0	+49.0

TABLE 6

CALORIMETRIC RESULTS FOR MPD/Pb^{2+}

Complex	*log* $\beta_{q,p}$	$\Delta G_{q,p}$ (*kcal mol*$^{-1}$)	$\Delta H_{q,p}$ (*kcal mol*$^{-1}$)	$\Delta S_{q,p}$ (*cal mol*$^{-1}$ *K*$^{-1}$)
B_3A_5	38.088	−51.913	−39	+43.0
B_2A_1	7.870	−10.727	(−12.0)	(−6.0)
B_3A_4	32.415	−44.181	−32.0	+41.0
BA	6.634	−9.042	−3	+21.0
BA_2	12.495	−17.030	−14.0	+10.0
BA_3	15.901	−21.673	−14.0	+25.0

The values of b, a and h were calculated from the $\beta_{q,p}$ and K_{Hi} values, the total metal-ion concentration B and total ligand concentration A with a program BDTV[9].

The resulting $\Delta H_{q,p}$ values are given in Tables 3–6. Not all $\Delta H_{q,p}$ values could be calculated. It can be understood that if the coefficients of a certain parameter $\Delta H_{q,p}$ are small, the term containing this parameter can be negligible in all eqns (3). In that case no reasonable solution can be found for that $\Delta H_{q,p}$ value.

It would be ideal if all parameters should dominate some of the right hand-side terms of the eqns (3). When only mononuclear complexes are formed this condition is mostly fulfilled: the complex BA dominates at the beginning, the complex BA_N at the end of the titration. As can be seen in Fig. 1 this condition is not always fulfilled when polynuclear complexes are formed. In this figure the distribution curves of

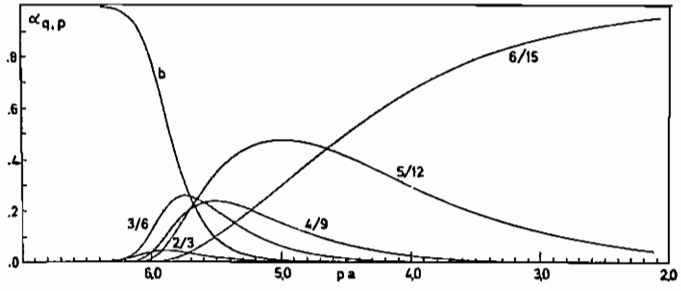

Fig. 1. Distribution curves of the system Zn^{2+}/MEL. B = 0.016.

the system Zn^{2+}/MEL for B = 0.016 are shown. In these distribution curves the fraction of the total metal-ion concentration $\alpha_{q,p}$ present as free metal ions or bound to a certain complex B_qA_p is plotted against the free ligand concentration. $\alpha_{q,p}$ was calculated by means of eqn (4). The curves are calculated and plotted with a program VERD

$$\alpha_{q,p} = \frac{q\beta_{q,p} b^q a^p}{B} \tag{4}$$

As can be seen in Fig. 1, $\alpha_{2,3}$ does not exceed a maximum value of 5%. Taking into account that $\Delta H_{2,3}$ will be smaller than $\Delta H_{5,12}$ and that the complex is formed in a narrow *pa* range, the value of $\Delta H_{2,3}$ cannot be obtained with a reasonable accuracy. The same reasoning holds in a lesser degree for the complexes $\Delta H_{3,6}$ en $\Delta H_{4,9}$. These values are placed between brackets.

Determination of the enthalpy of formation of the polymeric complexes formed between Ni^{2+}, Cd^{2+} and MEL, MDP

When a series of complexes $B(A_iB)_n$ with n great is formed in solution, eqn (3) cannot be used. It is indeed senseless to calculate an infinite number of ΔH_n values. Sillén[10] defined a polymeric "core+links" series with two constants only: k and k_0.

All stability constants β_n can be calculated from eqn (5)

$$\log \beta_n = \log k_0 + n \log k \tag{5}$$

Using eqns (5) and (6) also the free enthalpy of formation can be calculated in that way (eqn 7).

$$\Delta G = -RT \ln \beta \tag{6}$$

$$\Delta G = \Delta g_0 + n \log \Delta g \tag{7}$$

Analogously we propose to calculate all changes of enthalpy and entropy with eqns (8)–(10)

$$\Delta H_n = \Delta h_0 + n\ \Delta h \tag{8}$$

$$\Delta S_n = \Delta s_0 + n\ \Delta s \tag{9}$$

$$v = k a^t b \tag{10}$$

Substitution of eqns (5), (8) and (10) in eqn (3) gives eqn (11)

$$\frac{Q - Q_{dil}}{V} = \left(k_0 b \frac{1}{1-v}\right) \Delta h_0 + \frac{k_0 b v}{(1-v)^2} \Delta h + \Delta H_{N1} \left(a + \frac{t k_0 b v}{(1-v)^2}\right) \tag{11}$$

ΔH_{N1} is the neutralisation enthalpy of the mercapto group. Δh and Δh_0 were calculated from the results of titrations 2, 3 and 4 using eqn (11) with a program POKA. The values of v and b are calculated from k, k_0 and the initial concentrations in the titration cell with a program POLY. The results are given in Table 7. For the system Ni^{2+}/MPD no results are given because the reaction velocity is too slow for direct titration[2].

TABLE 7
CALORIMETRIC RESULTS FOR POLYMERIC COMPLEXES

	MEL/Ni^{2+}	*MEL*/Cd^{2+}	*MPD*/Cd^{2+}
$\log k_0$	−2.126	−1.625	−1.665
$\log k$	13.023	15.205	14.769
Δg_0	2.898	2.216	2.270
Δg	−17.25	−20.724	−20.130
Δh_0	(+8)	(+10)	(+10)
Δh	−8	−15	−15
Δs_0	(+17)	(+30)	(+30)
Δs	+32	+20	+19

DISCUSSION

From the results, given in Tables 3–7, it can be derived that the enthalpy change is the most important factor in the change of free enthalpy ΔG during complex formation of thiols with the metal ions Ni^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}. In comparison with the complexes of organic amines the formation reaction is more exothermic.

The enthalpy change of the formation of a Ni–S–Ni bound is about -4 kcal mol^{-1}. The same value is found for the Zn–S–Zn bound. In an earlier paper[11] a value of about -5 kcal mol^{-1} was found for the formation of a Ni–S–Ni bound between Ni^{2+} and thioglycolic acid. These two values are in good agreement with each other. An enthalpy change of ± 1.5 kcal mol^{-1} was found for the formation of a single Ni–S and Zn–S bound[11,12]. When the mercaptide ion forms a bound with a second metal ion, more heat is liberated than for the formation of the first one.

The enthalpy change of formation of a Cd–S–Cd bound is about -8 kcal mol^{-1} or twice the value found for Ni^{2+} and Zn^{2+}. This corresponds, at least for polynuclear complexes, with less favorable entropy changes, indicating that the structure of the Cd^{2+} complexes is more rigid than that of Ni^{2+} and Zn^{2+} complexes.

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