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Mixed Complexes of Bivalent Cations Containing Methyliminodiacetate and Glycinates

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The formation constants of the mixed complexes containing a bivalent cation, methyliminodiacetate, and glycine in the proportion 1:1:1, were calculated for several temperatures, from the pH metric titration curves. The reaction of formation of the mixed complexes is exothermic and is characterized also by a positive formation entropy.

The stability of the mixed complexes is greatly influenced by steric effects, and the stability constants of the complexes containing sustituted glycines decrease in the following order glycine>sarcosine> dimethylglycine.

glycine > sarcosine > dimethylglycine

Introduction

The formation of mixed complexes by the reaction of monodentate and bidentate ligands with aminopolycarboxylates was studied recently in several laboratories.[1-13]

A discussion on the chemistry of these mixed complexes is found also in the monography of Beck.[14]

As a continuation of our work in this field, we studied in this paper the mixed complexes formed by the reaction of metal(II) methyliminodiacetates with glycine and substituted glycines.

Experimental Section

All the titrations were performed in a 150 ml jacketed cell connected to a Colora circulating thermostat and the temperature was maintained constant within 0.1°C.

The pH of the solutions was measured with a Radiometer 26 pH meter calibrated with standard buffers.

In all the experiment the ionic strngth was adjusted to 0.1 with potasium nitrate and the activity coefficient of the protons was calculated by the formula of Davies.[15]

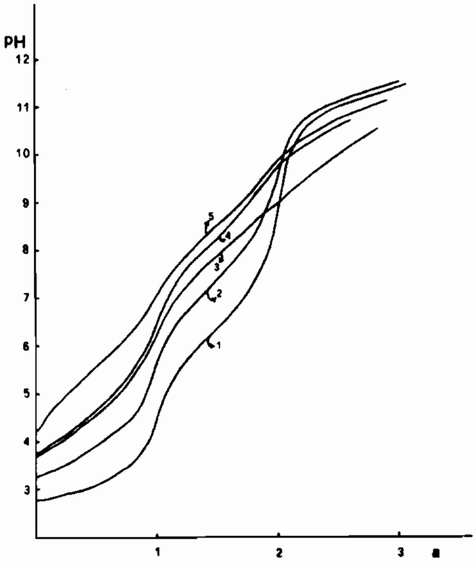

Figure 1. Titration of a mixture containing equimolar amounts of metallic nitrate ($Me(NO_3)_2$), sodium methyliminodiacetate (XH^-) and glycine (LH) all at a concentration of 0.005*M*.

1) $Me=Cu^{II}$ 2) $Me=Ni^{II}$ 3) $Me=Zn^{II}$
4) $Me=Co^{II}$ 5) $Me=Cd^{II}$ $I=0.1M(KNO_3)$

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Table I. The formation constants of the mixed complexes $MeXL^{1-}$ at different temperatures and $I = 0.1\,M$ (KNO_3).

LH	Glycine						Sarcosine	DMG*
	log $K_f \pm 0.05$				$-\Delta H^\circ$	ΔS°	log $K_f \pm 0.05$	
Me	15°C	25°C	50°C	70°C	(Kcal/mole)	(e u/mole)	25°C	25°C
Cu^{II}	6.14	5.92	5.66	5.13	8.1±0.4	0.3±0.2	5.73	5.57
Ni^{II}	5.06	4.91	4.68	4.43	2.6±0.3	5.4±0.2	4.63	4.45
Zn^{II}	4.53	4.41	4.13		4.6±0.2	6.5±0.1		
Co^{II}	4.14	4.03	3.74	3.63	5.0±0.3	1.8±0.2	3.72	3.40
Cd^{II}	3.92	3.82	3.53	3.36	4.4±0.2	2.8±0.2	3.40	3.37
$pK_a \pm 0.01$	9.84	9.55	8.92	8.56			9.95	9.75

* DMG = dymethylglycine.

Results

Figure 1 shows the titration by NaOH of equimolar amounts of metallic nitrate ($Me(NO_3)_2$), sodium methyliminodiacetate (XH^-) and glycine (LH).

Two inflexion points are observed: one at a = 1 and the other at a = 2, « a » representing the number of moles of base added per one mole of metal ion.

As the formation constants of metallic(II) methyliminodiacetates (MeX) are about a thousand times larger than the formation constants of metallic glycinates (MeX^{1+}), only simple metallic methyliminodiacetates are formed until a = 1.

Between a = 1 and a = 2, the mixed complexes are formed by the reaction:

$$MeX + LH \rightleftharpoons MeXL^{1-} + H^+ \qquad (1)$$

The experimental points of this region were used to calculate the formation constants of the mixed complexes by a graphical method based on the papers of Schwarzenbach,[16] Martell,[17] and Thompson.[6] This method was described in detail in a previous paper.[9] The following formulas are relevant for the calculations:

$$(L) = \frac{(2\text{-}a)C_{Me} - (H^+) + (OH^-)}{(H^+)/Ka} \qquad (2)$$

$$K_f(L) + 1 = \frac{C_{Me}}{(L)[1 + (H^+)/Ka]} \qquad (3)$$

$$K_f = \frac{(MeXL^-)}{(MeX)\,.\,(L^-)} \qquad (4)$$

From eq(3) it is seen that a plot of y *versus* (L) gives a straight line with an intercept equal to 1 and with a slope equal to K_f.

The experiments were performed at several concentrations with $C_{Me} = C_{XH} = C_{LH}$ varying between 0.005M and 0.001 *M* and eq (3) was always obeyed. The values of K_f calculated in this way were found to be independent of the initial concentration of the substances.

The values of log K_f and the thermodynamic functions, ΔH° and ΔS°, are given in Table I.

The titration with NaOH of a mixture of metallic nitrate, sodium methyliminodiacetate and glycine, in the proportion 1 : 1 : 2, shows two inflexion point situated respectively at a = 1 and a = 2 and no perceptible inflexion point is observed at a = 3.

In these experiments, in the region between a = 2 and a = 3, beside the possible formation of mixed complexes of the type $MeXL_2^{2-}$, the following equilibria can also occur:

$$2MeXL^- + L^- \rightleftharpoons MeX_2^{2} + MeL_2 \qquad (5)$$

The equilibrium constant for the reaction (5) can be easily calculated with the aid of the published stability constants.[18]

For the reasons mentioned above, it was not possible to investigate the complexes of the type $MoXL_2^{2-}$.

We calculated also the formation constants at 25°C of mixed complexes containing methylglycine (sarcosine) or dimethylglycine instead of glycine. The formation constants of these mixed complexes is also given in Table I.

Discussion

The formation constants of the mixed complexes follow the Irving-Williams sequence and they decrase in the following order:

$$Cu > Ni > Zn > Co > Cd.$$

The formation constants of the metallic (II)-methyliminodiacetates-glycinates is larger than the formation constants of the metallic (II)-nitrilotriacetates-glycinates studied by us in a previous paper.[13]

The reaction leading to the formation of the mixed complexes is exothermic, and the entropy of this reaction is always positive, only in the case of copper the entropy being nearly negligible.

In order to explain the positive entropy for the formation reaction of the mixed complexes, we suppose that the glycine is displacing two water molecules from the simple complex MeX, by the following scheme:

$$MeX3H_2O + L \rightleftharpoons MeXLH_2O + 2H_2O \qquad (6)$$

In the case of copper (II), this positive entropy is

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counterbalanced by the Jahn-Teller effect in virture of which, in the mixed complex a carboxylate group of methyliminodiacetate is not bond to the metal and is solvated by the solvent, the net result of these effects being the nearly negligible entropy observed.

The stability constants of the mixed complexes is very much influenced by steric effects, which are more important than the basicity of the ligand, and we can arrange them in the following order: glycine > sarcosine > dimethylglycine.

glycine > sarcosine > dimethylglycine

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