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Mixed Complexes Containing Imidazole

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By the reaction of imidazole perchlorate (LH^+) with metallic nitrolotriacetates (MeX^-) mixed complexes ($MeXL^-$) are formed. The nickel(II) and copper(II) can also form mixed complexes with the composition $MeXL_2^-$. The metallic ethylenediamine tetraacetates (MeY^{2-}) also form mixed complexes with the composition $MeYL^{2-}$. The formation constants of these mixed complexes were calculated using the pHmetric titrations performed at 25°C and at $\mu = 0.1$ M ($NaClO_4$).

Introduction

In a previous publication,[1] the interaction of histamine with metallic nitrilotriacetates was studied and it was shown that at low pH mixed complexes are formed in which the metallic nitrilotriacetates are bound only to the tertiary imidazolic nitrogen.

In this work, the interaction of imidazole with metallic nitrilotriacetates and with metallic ethylenediamine tetraacetates was studied by pHmetry.

Experimental Section

The stock solutions of metallic perchlorates used in this work were standardised by complexometric methods.[2,3]

The potentiometric titrations were performed in a 100 ml jacketed titration cell connected to a Haake circulating thermostat.

The concentration of protons was measured with a Radiometer 26 pHmeter, with the calomel electrode connected, to the solution to be titrated, by a Fischer bridge 13-639-65 filled with $NaNO_3$ 0.5 *M*. The pH meter was calibrated to give directly $-\log[H^+]$.[4] All potentiometric titrations and calibrations were made at 25°±0.1°C and at an ionic strength adjusted to 0.1 *M* with sodium perchlorate.

Results and Discussion

In Figure 1 it is shown the pHmetric titration with NaOH of a mixture containing equimolar amounts of metallic perchlorate ($Me(ClO_4)_2$), disodium nitrilotriacetate (XH^{2-}) and imidazole perchlorate (LH^+). The titration curves show two inflexion points situated respectively at a = 1 and at a = 2, where " a " is the number of moles of base added per mole of metal ion.

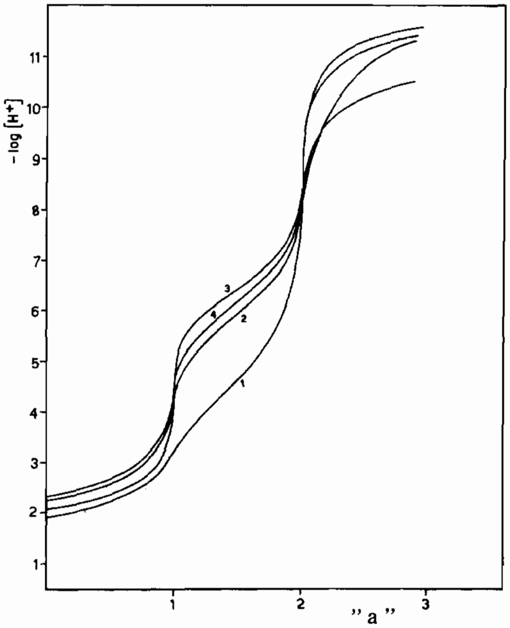

Figure 1. Titration of a mixture containing equimolar amounts of metal perclhorate ($Me(ClO_4)_2$), disodium nitrilotriacetate (XH^{2-}) and imidazole perchlorate (LH^+) all at a concentration of 0.02. M. 1) Me = Cu^{II}; 2) Me = Ni^{II}; 3) Me = Co^{II}; 4) Me = Zn^{II}. « a » is the number of moles of base added per mole of metal ion. μ = 0.1M ($NaClO_4$) and t = 25°C.

Until a = 1, the proton of disodium nitrilotriacetate is titrated and the metallic nitrilotriacetate complex (MeX^-) is formed.

Between a = 1 and a = 2, the proton of imidazole perchlorate is titrated and the mixed complex ($MeXL^-$) is formed by the reaction:

$$MeX^- + LH^+ \rightleftarrows MeXL^- + H^+ \qquad (1)$$

The formation constants K_{f1}^{MeXL} of the mixed complexes was calculated by the method of Schwarzenbach[5] and Martell[6] using the experimental points on the titration curves between a = 1 and a = 2. In this

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(1) A. L. Beauchamp, J. Israeli, and H. Saulnier, *Can. J. Chem.*, in press.
(2) F. J. Welcher, «The Analytical Use of EDTA», Van Nostrand, Toronto (1958).
(3) H. Flaschka, «EDTA Titrations», Pergamon Press, London (1959).
(4) A. Beauchamp and R. L. Benoit, *Can. J. Chem.*, *42*, 2161 (1964).

region the following equations are valid:

$$C_{Me}=C_X=C_L \tag{2}$$

$$C_{Me}=[MeX]+[MeXL] \tag{3}$$

$$C_L=[LH]+[L]+[MeXL] \tag{4}$$

$$(2-a)C_{Me}=[LH]+[H]-[OH] \tag{5}$$

$$K_{f1}^{MeXL}=\frac{[MeXL]}{[MeX][L]} \tag{6}$$

From these equations the following formulas are obtained:

$$[L]=\frac{(2-a)C_{Me}-[H]+[OH]}{[H]/K_a} \tag{7}$$

$$K_{f1}^{MeXL}\,.\,[L]+1=\frac{C_{Me}}{[L](1+[H]/K_a)}=y \tag{8}$$

The acid dissociation constant of imidazole perchlorate was redetermined in this work and it was found that $pK_a=7.00\pm0.01$ at 25°C and at $\mu=0.1$.

Equations (8) shows that a plot of y against [L] is a straight line whose intercept is 1. This relationship was verified in all the experiments performed and in which $C_{Me}=C_X=C_L$ varied between 0.004 *M* and 0.020 *M*.

In Table I are presented the formation constants K_{f1}^{MeXL} of the mixed complexes $MeXL^-$ together with the formation constants K_1^{MeL} of the 1:1 complexes of the metal with imidazole.[7]

Table I. The formation constants K_{f1}^{MeXL} of the mixed complexes $MeXL^-$ compared with the formation constants K_1^{MeL} of the complexes MeL^{2+}

Me	log K_{f1}^{MeXL}	log K_1^{MeL}
Cu^{II}	4.35±0.03	4.20
Ni^{II}	3.01±0.05	2.94
Zn^{II}	2.73±0.03	2.60
Co^{II}	2.35±0.03	2.43

Table I shows that the formation constants of the mixed complexes $MeXL^-$ is very close to the formation constants of the complexes MeL^{2+}. Therefore in this case the metallic nitrilotriacetate behaves as a free metallic ion.

It is to be mentioned that in the case of $NiXL^-$, the curve y=f(L) shows deviations from a straight line when " a " was greater than 1.7. To explain these deviations, pHmetric titrations were performed in which the concentration of imidazole perchlorate was four times greater than the concentration of the metallic perchlorate. In these experiments, between a=1 and a=5, the following equations are valid:

$$C_L=4C_{Me}=4C_X \tag{9}$$

$$C_{Me}=[MeX]+[MeXL]+[MeXL_2] \tag{10}$$

$$(5-a)C_{Me}=[LH]+[H]-[OH] \tag{11}$$

$$K_{f2}^{MeXL_2}=\frac{[MeXL_2]}{[MeXL][L]} \tag{12}$$

From these equations it is easy to obtain the following formulas:

$$[L]=\frac{(5-a)C_{Me}-[H]+[OH]}{[H]/K_a} \tag{13}$$

$$\bar{n}=\frac{[MeXL]+[MeXL_2]}{C_{Me}}=\frac{4C_{Me}-[L]\{1+[H]/K_a\}}{C_{Me}} \tag{14}$$

Using these values of $\bar{n}$ and L, K_{f1}^{MeXL} was recalculated by the method of Rossotti[8] as the intercept of

$$F_1=\frac{\bar{n}}{(1-\bar{n})[L]} \quad \text{against} \quad \frac{(2-\bar{n})[L]}{(1-\bar{n})}$$

By the same method $K_{f1}^{MeXL}\,.\,K_{f2}^{MeXL_2}$ was calculated as the intercept of

$$F_2=\frac{\bar{n}-(1-\bar{n})K_{f1}^{MeXL}\,[L]}{(2-\bar{n})[L]^2} \quad \text{against} \quad \frac{(3-\bar{n})[L]}{(2-\bar{n})}$$

This method has given the same value of K_{f1}^{MeXL} as that obtained by the method of Schwarzenbach-Martell. In Table II are presented $K_{f2}^{MeXL_2}$ for copper(II) and nickel(II). For zinc(II) and cobalt(II), $\bar{n}$ was always less than 1 and so it was not possible to calculate $K_{f2}^{MeXL_2}$ for these metals.

Table II. The formation constants $K_{f2}^{MeXL_2}$ of the complexes $MeXL_2^{2-}$

Me	log $K_{f2}^{MeXL_2}$
Ni^{II}	1.57±0.05
Cu^{II}	−0.65±0.05

It is interesting to note that $K_{f2}^{MeXL_2}$ is bigger than $K_{f2}^{CuXL_2}$. Such a reversal in the formation constants has been observed previously in the literature[9,10] for the cases in which the coordination number of copper is higher than four. On the other hand, as Table I shows, the K_{f1}^{MeXL} follow te Irving-Williams sequence.[11]

In Figure 2 is shown the titration by NaOH of a mixture containing equimolar amounts of metal per-

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(5) G. Schwarzenbach, A. Welli, and O. R. Bach, *Helv. Chim. Acta*, 30, 1303 (1947).

(6) A. E. Martell adn S. Chaberek, *J. Am. Chem. Soc.*, 24, 5053 (1952.)

(7) «Stability Constants of Metal in Complexes», Chemical Society, London (1964).

(8) F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, 9, 1166 (1955).

(9) J. Bjerrum and C. K. Jørgensen, *Rec. Trav. Chim. Pays Bas*, 76, 116 (1956).

(10) K. B. Yatsimirskii, *Zhur. Neorg. Khim.*, 1, 2451 (1956).

(11) H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 3192 (1953).

(12) J. Israeli and M. Cecchetti, *Talanta*, in press.

chlorate ($Me(ClO_4)_2$), disodium ethylenediamine tetraacetate (YH_2^{2-}) and imidazole perchlorate (LH^+). It is seen clearly that two inflexion points are occuring, the first at a = 2 and the second at a = 3.

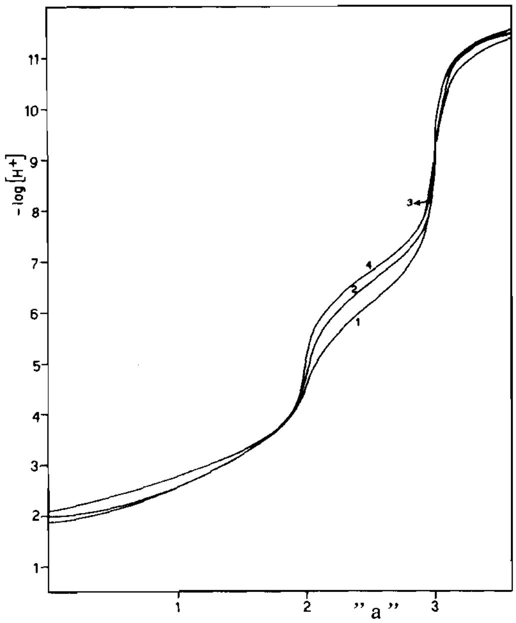

Figure 2. Titration of a mixture containing equimolar amounts of metal perchlorate ($Me(ClO_4)_2$), disodium ethylenediamine tetraacetate (YH_2^{2-}) and imidazole perchlorate (LH^+) all at a concentration of 0.018 *M*. (1), Me = Cu^{II}; (2), Me = Ni^{II}; (3), Me = Co^{II}; (4), Me = Zn^{II}. "a" is the number of moles of base added permole of ligand. $\mu = 0.1\,M$ ($NaClO_4$) and t = 25°C.

Until a = 2, the two protons of disodium ethylenediamine tetraacetate are titrated and at the same time the metallic ethylenediamine tetraacetate (MeY^{2-}) is formed.

Between a = 2 and a = 3, the proton of imidazole perchlorate is titrated and in this region the mixed complex ($MeYL^{2-}$) is formed. Using the experimented points of this region, the formation constants K_{f1}^{MeYL} were calculated using the following formulas:

$$[L] = \frac{(3-a)C_{Me} - [H] + [OH]}{[H]/K_a} \qquad (15)$$

$$K_{f1}^{MeYL} \,.\, [L] + 1 = \frac{C_{Me}}{[L]\{1 + [H]/K_a\}} = y \qquad (16)$$

These formulas were derived from equations analogous to (2) and (6). In Table III are presented the formation constants of the mixed complexes $MeYL^{2-}$. These constants were calculated from experiments in which $C_{Me} = C_Y = C_L$ varied between 0.004 *M* and 0.018 *M*.

Table III. Formation constants of the complexes $MeYL^{2-}$

Me	$\log K_{f1}^{MeXL}$
Cu^{II}	2.79 ± 0.03
Ni^{II}	2.23 ± 0.02
Zn^{II}	1.79 ± 0.09
Co^{II}	1.66 ± 0.05

The formation constants of the complexes $MeYL^{2-}$, follow the Irving-Williams sequence.

The experimental results in this work do not permit us to speculate about the coordination number of the central metal ion in the complexes $MeYL^{2-}$. However the following linear relationship exist between the K_{f1}^{MeXL} and K_{f1}^{MeYL}:

$$\log K_{f1}^{MeXL} = 1.45 \log K_{f1}^{MeYL} + 0.1 \qquad (17)$$

If K^{MeX} and K^{MeY} denote respectively the formation constants of the complexes MeX^- and MeY^{2-}, the overall stability constants of the mixed complexes are:

$$K_s^{MeXL} = K^{MeX} \,.\, K_{f1}^{MeXL} \qquad (18)$$

$$K_s^{MeYL} = K^{MeY} \,.\, K_{f1}^{MeYL} \qquad (19)$$

The following empirical relationships exist between the overall stability constants of the mixed complexes and the formation constants of the simple complexes:

$$\log K_s^{MeXL} = 1.05 \log K^{MeX} \,.\, K_f^{MeL} + 7.8 \qquad (20)$$

$$\log K_s^{MeYL} = 0.80 \log K^{MeY} \,.\, K_f^{MeL} + 8.8 \qquad (21)$$

It is to note also the existence of the following empirical relations:

$$\log K_{f1}^{MeXL} = 0.98 \log K_f^{MeL} + 0.1 \qquad (22)$$

$$\log K_{f1}^{MeYL} = 0.580 \log K_f^{MeL} + 0.375 \qquad (23)$$

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