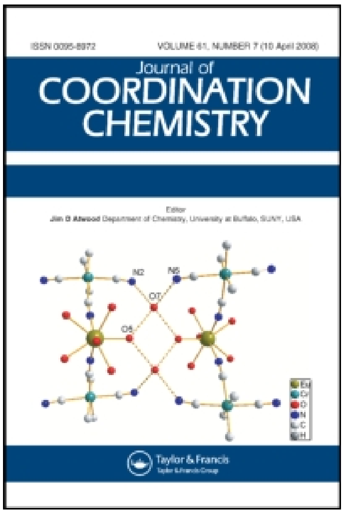

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Aldo Napoli[a]
[a] Department of Chemistry, University of Rome, Rome, Italy

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LEAD(II) COMPLEXES WITH SOME *N*-SUBSTITUTED IMINODIACETIC ACIDS

ALDO NAPOLI
Department of Chemistry, University of Rome, 00185 Rome, Italy

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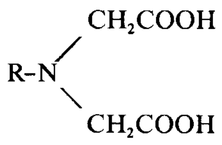
Complex formation between lead(II) ions and some *N*-substituted iminodiacetic acids has been studied at 25° in aqueous sodium perchlorate with ionic strength 0.50 M. Measurements have been carried out with glass and lead amalgam electrodes. For all the ligands 1:1 mononuclear complexes form, one of which monoprotonated. The stability constants have been evaluated.

Keywords: stability constants; lead(II); iminodiacetic acids; potential measurements; complexes

INTRODUCTION

In a previous paper[1] the complexes formed in aqueous solution by lead(II) ions and iminodiacetic acid, (I), (R = H),



(I)

studied by potentiometry, were reported.

In acid medium and over the investigated concentration range, experimental data can be explained by assuming the presence of 1:1 mononuclear complexes, PbL, $PbHL^+$, and PbH_2L^{2+}, whose stability constants have been calculated at 25° in $NaClO_4$ (0.50 M). Measurements have been carried out with glass and lead amalgam electrodes in order to obtain both hydrogen ion and free lead(II) concentrations. This simplifies the interpretation of experimental data, especially for testing the presence of mixed complexes in more acidic solutions where the measurement of hydrogen ion concentration alone does not give useful information.

In this paper the previous study was extended to some *N*-substituted iminodiacetic acids in order to compare the formation constants under the same experimental conditions, as the presence of substituents can effect the stability of the complexes. The presence of mixed complexes with hydrogen ion was tested by using both glass and amalgam electrodes.

The ligands examined were methyliminodiacetic acid (MIDA, (I), R = CH_3), hydroxyethyliminodiacetic acid (HIMA, (I), R = CH_2CH_2OH), and nitrilotriacetic acid (NTA, (I), R = CH_2COOH). The complexes were studied as a function of $-\log[H^+]$ in order to determine the nature of the possible interactions which take place in aqueous solutions. Investigations were carried out at 25° in 0.50 M aqueous sodium perchlorate.

EXPERIMENTAL

Methyliminodiacetic (Aldrich), hydroxyethyliminodiacetic (Sigma), and nitrilotriacetic (Merck) acids were used without further purification. Potentiometric titrations carried out with sodium hydroxide on the dried acids corresponded with theoretical molecular weights. Solutions of bisodium salts were prepared, when required, by adding to weighted amounts of the acids, the calculated quantity of carbonate-free sodium hydroxide and sodium perchlorate to obtain the right ionic strength.

Lead(II) perchlorate was prepared from PbO (Merck), dissolved in dilute perchloric acid. The analytical excess of hydrogen ions was estimated by a Gran plot.[2] The metal concentration was determined by complexometry. Other chemicals were of analytical purity.

The emf measurements were carried out at 25.0 ± 0.1° with a Radiometer pHM4 potentiometer to within 0.1 mV, using a Wilhelm cell as described by Forsling *et al.*,[3]:

R.E.|test solution|G.E. (A)

Pb(Hg)|test solution|R.E. (B)

The reference half-cell (R.E.) was Ag, AgCl|0.01 M NaCl, 0.49 M $NaClO_4$|0.50 M $NaClO_4$. In a constant ionic medium the activity coefficients remain constant[4] and the activities can be substituted by concentrations, so that the emf of the cells (A) and (B) can be expressed, in mV, as: $E = E_A + 59.16 \log[H^+] + E_J$, and $E = E^\circ - 29.58 \log[Pb^{2+}] - E_J$ where E_J ($J[H^+]$, ($J = -100$ mV/M)) is the junction potential between the test solution and $NaClO_4$(0.50M). E_A and E_B were determined before and after each series of measurements in the absence of the ligand so that $[H^+]$ and $[Pb^{2+}]$ can be calculated from measurements of E.

Lead amalgam was prepared by dissolving freshly cut metal (Merck silberfrei) in twice distilled mercury (1% w/w) and was stored under 0.02M $HClO_4$. It was prepared fresh each week and during the measurements a strong stream of purified nitrogen was passed through the test solution. The glass electrode was a G202B Radiometer unit calibrated in concentration units and the Ag, AgCl electrode was prepared according to Brown.[5]

RESULTS AND DISCUSSION

Potentiometric titrations with sodium hydroxide of the ligands in the presence and absence of lead ions were performed. As an example, titrations of metyliminodiacetic acid are reported in Figure 1. The curves obtained in the presence of lead(II) exhibit a sharp inflexion when one mole of sodium hydroxide is added per mole of metal ion, besides the neutralization of the first proton of the acid, according to the following reactions.

$$H_2L + OH^- \rightleftharpoons HL^- + H_2O$$

$$Pb^{2+} + HL^- + OH^- \rightleftharpoons PbL + H_2O$$

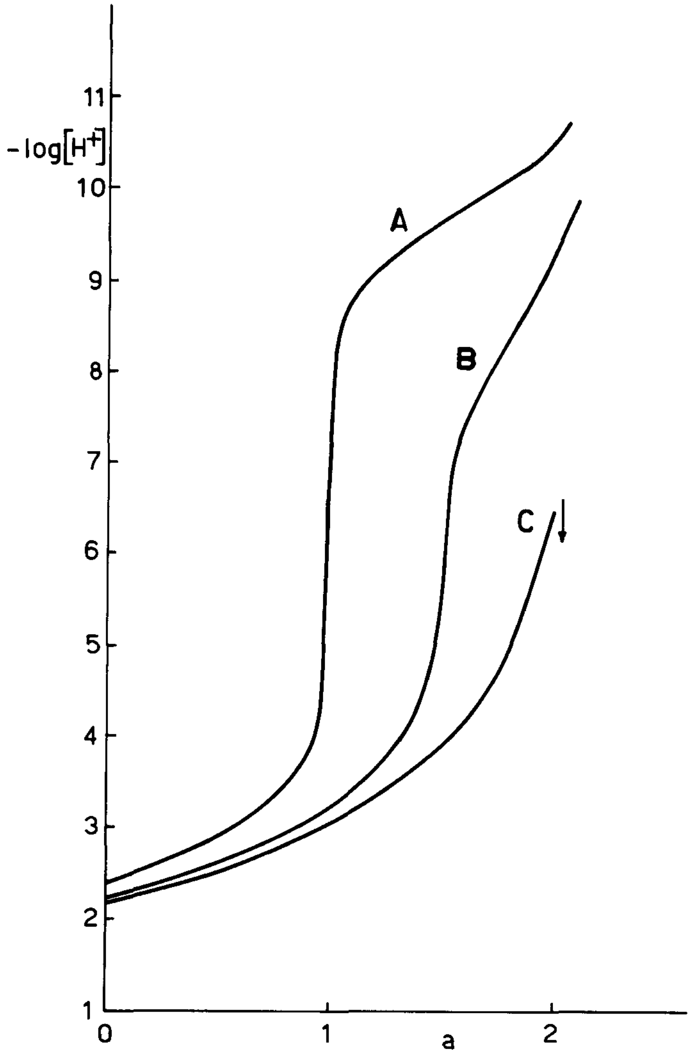


FIGURE 1 Titration curves for methyliminodiacetic acid; a = moles of NaOH per mole of ligand. Curve A: acid alone; curve B: acid plus lead(II), $C_L/C_M = 2$; curve C: acid plus lead(II), $C_L/C_M = 1$; (↓) precipitate formation.

This is true also in the presence of excess ligand (2:1 mole ratio with respect to the metal ion), meaning that only 1:1 complexes are formed in acidic medium.

Several determinations of free ion concentrations were carried out using the amalgam electrode in solutions in which $C_L > C_M$ (the analytical concentrations of the ligand and metal ion respectively) at different values of $-\log[H^+]$. The metal concentration was varied from 2.50 to 7.50 mM and the ligand concentration from 7.50 to 20.0 mM. The acidity of the medium was maintained sufficiently low that hydrolytic products of the lead ion were always negligible.[6]

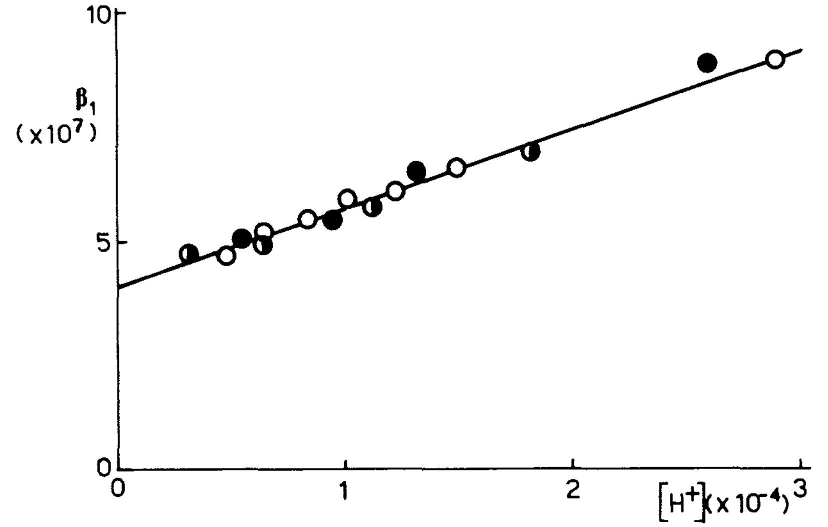


FIGURE 2 Conditional formation constant (β_1') as a function of [H$^+$]: ○ $C_M = 2.50$ mM, $C_L = 7.50$ mM; ● $C_M = 5.00$ mM, $C_L = 15.0$ mM; ◑ $C_M = 7.50$ mM, $C_L = 20.0$ mM.

The conditional formation constants for the 1:1 complexes were calculated for each value of $-\log[H^+]$ by the following equations.[+]

$[PbL'] = C_M - [Pb^{2+}]$

$[L^{2-}] = (C_L - [PbL'])/\alpha$

$\beta_1' = [PbL']/([Pb^{2+}][L^{2-}])$ where

$[PbL'] = \Sigma_p\Sigma_q[Pb_pH_qL_p]$ with $q \geqslant 0$, and $\alpha = \Sigma_i\ \beta_{0i1}[H^+]^i$.

The protonation constants of the ligands, utilised in the calculation, refer to the experimental conditions of temperature and ionic medium.[7]

Some of the experimental data for the lead-methyliminodiacetic acid system are plotted in Figure 2. The value of β_1' was found to be independent of C_M, meaning that polynuclear complexes are negligible in our solutions. The plot of β_1' *vs* [H$^+$] gives a straight line with positive slope and intercept, meaning that two complex species are predominant in solution, PbL and PbHL$^+$, the formation constants of which are related to β_1' by the expression

$$\beta_1' = \beta_{101} + \beta_{111}\,[H^+]\,.$$

For the other ligands examined similar complexes are formed. The values of the stability constants, deduced from the slope and the intercept using least-squares treatment, are listed in Table I, together with the values of the protonation constants of the acids.

In acid medium and in the concentration range examined only 1:1 complexes are formed with the ligands investigated. A monoprotonated species was also found for all the ligands. The value for the NTA mixed complex species is in agreement with that obtained by Karadakov *et al.*[8] if the different experimental conditions are considered. The stability order for the normal complexes, compared by taking into account the values of ligand basicity[9] represented by protonation constants, increases in the order IMDA, MIDA, HIDA, NTA. Protonated forms are present to a detectable amount over

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[+] β_{pqr} represents the stability constant of the $Pb_pH_qL_r$ species.

TABLE I
Stability constants for iminodiacetic acid derivatives, at T = 25°, 0.50 M $NaClO_4$.

	IMDA[1]	MIDA	HIDA	NTA
$\log \beta_{011}$	9.17	9.42	8.52	8.98
$\log \beta_{021}$	11.73	11.78	10.80	11.31
$\log \beta_{031}$	13.49			13.01
$\log \beta_{101}$	7.31	7.60 ± 0.04	8.75 ± 0.04	10.02 ± 0.05
$\log \beta_{111}$	10.36	11.23 ± 0.10	11.51 ± 0.13	12.30 ± 0.10

almost all the acidity range examined (up to $-\log[H^+] = 4$) for the ligands. In Figure 3, for example, the distributions are reported for the Pb-MIDA system (equimolar solutions). In this case, $PbHL^+$ represents the prevailing complex species down to $-\log[H^+] = 3.5$.

For the protonated complexes the same order of stability can be found, if the equilibrium $M + HL \rightleftharpoons MHL$ is considered. This means that probably also in these cases a chelate is formed, as the HL^- species are potentially terdentate in the case of nitrilotriacetic acid and bidentate otherwise.

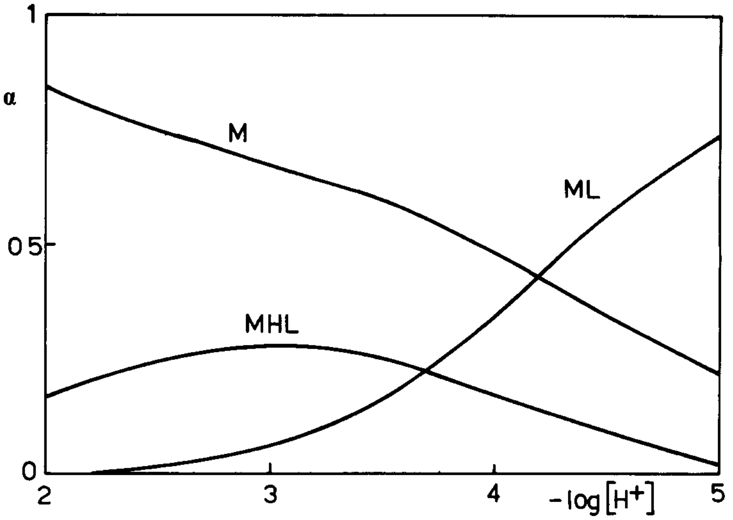

FIGURE 3 Distribution diagram for Pb-MIDA complexes under equimolar conditions.

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