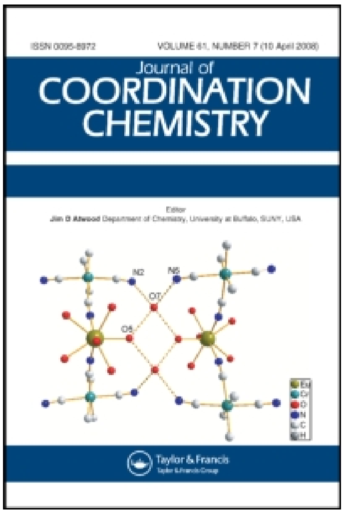

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Polarographic and Potentiometric Study of Ternary Complexes of Cadmium with Penicillamine and Histidine

Jadwiga Urbańska[a]; Henryk Kozlowski[a]; Barbara Kurzak[b]
[a] Institute of Chemistry, University of Wroclaw, Wroclaw, Poland [b] Institute of Chemistry, Pedagogical University, Siedlce, Poland

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POLAROGRAPHIC AND POTENTIOMETRIC STUDY OF TERNARY COMPLEXES OF CADMIUM WITH PENICILLAMINE AND HISTIDINE

JADWIGA URBAŃSKA, HENRYK KOZLOWSKI*
Institute of Chemistry, University of Wroclaw, F. Joliot-Curie 14, 50-383 Wroclaw, Poland

and BARBARA KURZAK
Institute of Chemistry, Pedagogical University, Siedlce, Poland

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Polarographic and potentiometric studies have shown the formation of ternary complexes in the Cd(II)-*D*-penicillamine–*L*-histidine system. Both ligands also form ternary species with oxalate anion. Stabilities of the ternary complexes with penicillamine are much higher than predicted by statistical models.

Keywords: Cd^{2+} complexes, penicillamine, histidine, ternary complexes, stability constants

INTRODUCTION

The presence of thiol groups in a ligand significantly influences its binding ability, particularly towards such metal ions as Cd(II).[1,2] The high affinity of thiol donors for heavy metal ions is exploited by natural systems which use cysteine-rich peptides to remove metals from living organisms.[3–6]

Histidine is also a very effective ligand and its imidazole side-chain is often a coordination site for metal ions in natural systems. Thus, both thiol and imidazole donors may be critical functions for binding cadmium ions in naturally occuring complexes. The most likely complex formed with several competing effective ligands is a ternary species (strongly favoured at equilibrium in natural liquids). The mixed ligand systems may be stabilized by geometrical and entropic factors as well as by various interligand interactions.

The Cd(II)–histidine–penicillamine system, among others, may mimic the ternary complex formed between cadmium ion bound to a biomolecule (peptide or protein) and chelating agents involved in removing the heavy metal ion from natural system. It is of interest to follow the competitive binding of thiol and imidazole side-chains and to evaluate the possibility of mixed ligand complex formation in living systems. The early work of Sugiura[7] has shown that, according to potentiometric data, the formation of such ternary systems is rather unlikely. Solution with 1 : 1 : 1 metal : his : penicillamine mol ratio solutions with Cd(II) concentration 0.002 mol dm^{-3} were studied. Titration curves of ternary system were the same as those of Cd(II)–penicillamine solutions. Thus, no formation of ternary system was assumed.

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* Author for correspondence.

EXPERIMENTAL

L-histidine (His) and *D*-penicillamine (Pen) were used, as obtained from Sigma. $3CdSO_4.8H_2O$ (analytical grade) was used as the metal ion source.

Polarographic measurements

Electrode processes were studied by differential puls polarography (DPP) on a Telpod Puls Polarograph (PP-04 A) using a dropping mercury electrode as working electrode and a saturated calomel electrode as reference electrode. Measurements were made at 25°C with a constant ionic strength of 1 mol dm^{-3} ($NaClO_4$). The high ionic strength used in the polarographic measurements eliminated effects of high ligand concentrations needed to evaluate the stability constants by DPP. The cadmium ion concentration was adjusted to 10^{-4} mol dm^{-3}. Argon was bubbled through the solutions to remove oxygen and pH values were adjusted with NaOH and $HClO_4$. In the solutions containing His 0.004% gelatin was added to suppress reduction wave maxima.

Potentiometric measurements

The protonation constants of the ligands and the stability constants of the parent and mixed complexes were determined. In the Cd(II)–His (ligand B) system, 1:1, 1:2 and 1:4 metal : ligand ratios were employed. The concentration of the ligand in the experimental solution was 5×10^{-3} mol dm^{-3}. For the determination of the stability constants of the mixed complexes, the Cd(II) concentration in all samples was 2×10^{-3} mol dm^{-3} and the concentration ratios metal : ligand A : ligand B were 1 : 1 : 1, 1 : 2 : 1, 1 : 1 : 2 and 1 : 2 : 2. Titrations were carried out at 25°C and at 0.1 mol dm^{-3} ionic strength (KCl). Measurements were performed with a Radelkis OP-208/1 instrument, using OP 7183 glass and OP 830 calomel electrodes. The electrode system was calibrated by periodic titrations of $HClO_4$ solution (0.1 mol dm^{-3} in $NaClO_4$) with standard NaOH solution. The resulting titration data were used to calculate the standard electrode potential, E°, and the dissociation constant for H_2O. These values were then used in the calculation of hydrogen ion concentration $[H^+]$ from potential readings.[8] Calculations on the pH-metric data were performed with the aid of the SUPERQUAD computer program.[9]

RESULTS AND DISCUSSION

Polarographic measurements of the ternary or binary solutions containing 2×10^{-3} mol dm^{-3} of each ligand (His and/or Pen) and 10^{-4} mol dm^{-3} cadmium ion (pH 7.6–8.4) indicate that the reduction potential of the metal ion is more negative in the presence of both ligands than in the presence of each ligand separately. These variations are not very large (4–6.5 mV), but are outside the range of experimental error (0.5–1 mV). Increase in pH causes an increase of the concentration of deprotonated forms (pK's are given in Table IV) of both ligands (*i.e.*, the forms which bind metal ion). This leads to a limiting current decrease and a potential shift towards more negative values (formation of the complexes, Table I). Using the data collected in Table I (shifts of metal ion reduction potential and the limiting currents) and the Schaap and McMasters approach to the ternary systems,[10] a stability constant for the ternary species [Cd(His)(Pen)], MAB, could be evaluated (Table IV, Fig. 1). The average value of $\log\beta_{MAB}$, 17.10, indicates the formation of, relatively, a very stable ternary complex. The stability constants for the binary complexes (Table IV) were also evaluated under the same experimental conditions as those for the ternary systems. The values obtained are relatively close to those calculated from potentiometric data[1] (*vide infra*).

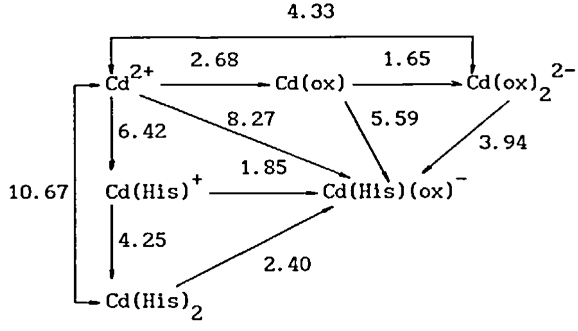

FIGURE 1 Equilibria and log K values established by polarographic measurements for the Cd–Pen–His system.

TABLE I
Values of potentials and limiting currents for metal ion reduction at different pH values for the Cd(II)–Pen–His solutions; $Cd(II) = 1 \times 10^{-4}\,mol\,dm^{-3}$, $c_{His} = 0.002\,mol\,dm^{-3}$, $c_{Pen} = 0.002\,mol\,dm^{-3}$, 0.004% gelatin; $t_1 = 2\,s$, $\Delta E = 20\,mV$, $I = 1\,mol\,dm^{-3}$ ($NaClO_4$).

pH	$-E_p$(mV)	i_p(μA)	$\log\beta_{MAB}$
	589	1.285	
7.62	820	0.964	16.17
7.67	824	0.940	16.59
7.72	829	0.937	16.87
7.82	837	0.913	16.96
7.86	840	0.906	17.00
7.92	845	0.890	17.09
8.00	852	0.875	17.18
8.16	864	0.851	17.20
8.39	879	0.813	17.19

In order to verify the method described above to evaluate the stability of the ternary complexes, we have carried out polarographic studies of two other ternary systems, Cd(II)–His–oxalate and Cd(II)–Pen–oxalate. Oxalate ion, ox, was chosen as an ion which at pH above 5.5 is completely deprotonated, $[ox]^{2-}$; its concentration over the pH range studied can be assumed to be constant. The concentrations of the other two ligands, His and Pen, in their deprotonated (binding) forms are pH-dependent and they were chosen to give $[ox]^{2-}/[His]^-$ and $[ox]^{2-}/[Pen]^{2-}$ ratios favouring the formation of the ternary systems (Tables II and III). The results collected in these Tables indicate that the addition of $[ox]^{2-}$ ions to solutions of binary systems causes more negative shifts of reduction potentials of metal ions than

TABLE II

Values of potentials and limiting currents for metal ion reduction at different pH values for the Cd(II)–ox–His solutions; Cd(II) = 1×10^{-4} mol dm^{-3}, c_{ox} = 0.1 mol dm^{-3}, c_{His} = 0.04 mol dm^{-3}, 0.004% gelatin; t_1 = 2 s, ΔE = 20 mV, I = 1 mol dm^{-3} ($NaClO_4$).

pH	$-E_p$(mV)	i_p(μA)	$\log\beta_{MAB}$
	575	1.335	
6.12	668	1.107	8.361
6.21	671	1.107	8.380
6.29	673	1.157	8.322
6.39	676	1.161	8.292
6.44	678	1.184	8.276
6.51	680	1.173	8.262
6.58	683	1.204	8.249
6.66	686	1.215	8.233
6.73	689	1.227	8.198
6.82	691	1.238	8.121

TABLE III

Values of potentials and limiting currents for metal ion reduction at different pH values for the Cd(II)–ox–Pen solutions; Cd(II) = 1×10^{-4} mol dm^{-3}, c_{ox} = 0.1 mol dm^{-3}, c_{Pen} = 0.001 mol dm^{-3}, t_1 = 2 s, ΔE = 20 mV, I = 1 mol dm^{-3} ($NaClO_4$).

pH	$-E_p$(mV)	i_p(μA)	$\log\beta_{MAB}$
	561	1.339	
6.30	723	0.998	14.621
6.42	730	1.068	14.538
6.56	738	1.115	14.465
6.73	748	1.107	14.403
6.84	755	1.068	14.420
6.99	762	1.049	14.303
7.16	771	0.987	14.254
7.31	780	0.937	14.279
7.52	791	0.897	14.204

is found in binary systems (13 mV for Cd–His–ox and 14 mV for Cd–Pen–ox). The stability constants calculated from the polarographic data are given in Table IV (Figs 2 and 3).

Comparison of the stability constants obtained using the Schaap and McMasters approach and those calculated according to the method of Watters–De Witt[11] for the statistical β value ($\log \beta^{stat} = 1/2(\log \beta_{MA_2} + \log \beta_{MB_2} + 0.6)$, Table IV) indicates that both ternary complexes with Pen, [Cd(His)(Pen)] and [Cd(ox)(Pen)], are much more stable than predicted statistically (see also value of $\log X = 2\log\beta_{MAB} - (\log\beta_{MA_2} + \log\beta_{MB_2})$,[12] Table IV). The third complex studied, [Cd(His)(ox)], has a stability close to that predicted by the statistical model.

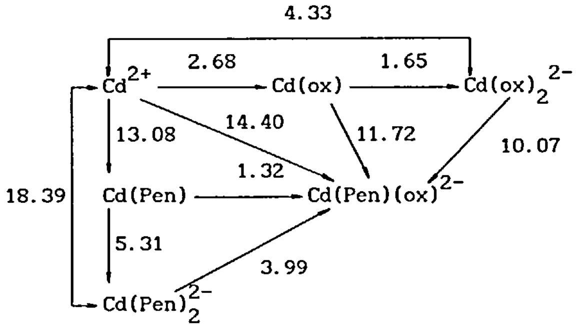

FIGURE 2 Equilibria and log K values established by polarographic measurements for the Cd–His–ox system.

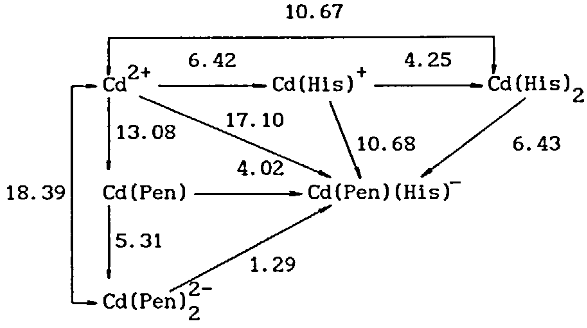

FIGURE 3 Equilibria and log K values established by polarographic measurements for the Cd–Pen–ox system.

TABLE IV

Stability constants (log β) for binary and ternary Cd(II) complexes with *D*-penicillamine, *L*-histidine and oxalate ligands at 25°C; pK's for His were 9.13 (NH_3), 6.06 (N_{im}) and 1.68 (COOH), and for Pen, 10.59 (SH), 7.88 (NH_3) and 1.90 (COOH).

	logβ					
Ligand	CdL	CdL_2	Cd_2L_3	CdLH	$CdLH_{-1}$	$logK_1/K_2$
Pen	13.08[a]	18.39[a]				7.77
	11.50[b]	19.26[b]	49.77[b]			3.74
His	6.42[a]	10.67[a]				2.17
	5.44[b]	9.39[b]		11.56[b]	−4.04[b]	1.49
ox^{2-}	2.68[a]	4.33[a]				1.03

Species	logβ	$log\beta^{stat.}$	logX
[Cd(Pen)(His)]	17.10;[a] 16.84[b]	14.83[a]	5.14;[a] 5.03[b]
[Cd(His)(ox)]	8.27[a]	7.80[a]	1.54[a]
[Cd(Pen)(ox)]	14.40[a]	11.66[a]	6.08[a]

[a] Polarographic method in 1 M $NaClO_4$, [b] pH-metric method in 0.2 M KCl.

In order to obtain support for the formation of the ternary species in the Cd(II)–Pen–His system, the potentiometric titrations were performed with the use of modern potentiometric facilities and a recently developed computing program with respect to the conditions obtaining in earlier work.[7] The results obtained indicate the formation of ternary species with stability constants close to those evaluated by the polarographic method. The only major differences were found for the [Cd(Pen)] complex, for which the value of the stability constant obtained from the polarographic method is distinctly higher than that obtained from the potentiometric data (Table IV and ref. 1). This difference may be caused by the different experimental conditions and the fact that the metal reduction waves obtained in this study are not completely reversible. In addition, the ionic strengths used in both techniques are distinctly different, and the ligand to metal mol ratio used in the polarographic study was considerably higher than that used in the potentiometric titrations. All these differences derive from the various experimental conditions necessary for both techniques.

The log K_1/K_2 ratio calculated for the binary systems studied in this work clearly indicate that the formation of the $[Cd(Pen)_2]$ complex is sterically least favoured.[1] Both ligands are bound as tridentates and are bulky, due to the large thiol donor and the two methyl groups lying close to the sulfur binding site. This causes strong interligand steric interactions which effectively destabilize the formation of ML_2 species. Much lower values of $\log K_1/K_2$ obtained for His and ox ligands indicate that, in these two cases, inter-ligand steric factors are much less critical for the stability of ML_2 species. Thus, the favourable formation of the ternary systems with Pen observed for both His and ox may derive from lower steric hindrance introduced by coordination of His or ox to the [Cd(Pen)] binary complex as compared to the binding of a second Pen molecule.

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