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Mixed Metal Complexes in Solution. Part II. Potentiometric Study of Heterobinuclear Metal(II)–Citrate Complexes in Aqueous Solution

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Though the formation of mixed ligand ternary complexes is well known in the literature, the study in solution of mixed metal complexes having one ligand and two different metal ions has been developed very little. The formation of this type of ternary species might explain a number of apparently anomalous data and some interferences in analytical procedures. Moreover, the structural properties of these compounds or the stoichiometry of the species present in the systems where such a complexation occurs are little known. The aim of our investigation was to study a selected series of biofunctional ligands in order to obtain quantitative data on the factors influencing the stability of this type of complex and to assess their relevance in biological processes.

We have previously reported the stability constants of heterobinuclear copper(II)–L-histidinate complexes with nickel(II), zinc(II) or cadmium(II) in aqueous solution [1]. Such mixed metal complexes are formed by another imidazole derivative too [2]. Now we are extending our investigation to another set of ligands namely hydroxypolycarboxylic acids, widely used as buffers, which are of relevant importance in the analytical field and also in biofluids.

In this paper we report the stability constants of heterobinuclear complexes of citrate (cit^{3-}) with Cu(II)–Ni(II), Ni(II)–Zn(II) and Cu(II)–Zn(II), determined in aqueous solution at $t = 25$ °C and $I = 0.1$ mol dm^{-3} (KNO_3). The values of stability constants for the parent binary systems have been determined previously under the same experimental conditions [3, 4]. The measurements were carried out as described elsewhere [5, 6]. The stock solutions of metal nitrates were prepared and standardized as reported in the literature [7]. Citric acid (Merck) was used without further purification.

The type of the species present in solution was determined by graphical methods [8, 9]. The approximate values of the stability constants so obtained were then refined by two different least-squares computer programs [9–11]. Computations relative to the purity of the ligand, to the E^0 determination and to the standardization of the stock solutions were performed by means of the least-squares computer program ACBA [12]. In the alkalimetric titrations the reagent ratios were $C_M:C_{M'}:C_L = 1:1:2$ or $1:1:3$ (C_M, $C_{M'}$ = total concentrations of different metal ions, C_L total concentration of the ligand) with C_M and $C_{M'}$ ranging from 2 to 5 mmol dm^{-3}.

Mixed metal complexes of hydroxypolycarboxylic acids with a variety of metal ions have been reported in the literature. These data do not include the stability constants of these complexes, dealing with almost exclusively their identification [13, 14]. The formula $[M\,M'(L)_2]$ has been generally proposed, but other formulas have been suggested [15–18].

The alkalimetric titration curves of solutions containing citric acid and two different metal ions exhibit two buffer regions, one in the acidic and the other in the neutral–alkaline range. By comparing the experimental titration curves of ternary systems with those calculated neglecting any ternary complex (see Fig. 1), it can be seen that, in a suitable range of pH values, the experimental and calculated curves differ significantly to each other (with $pH_{exp} < pH_{calcd}$ for each C_{OH} values). This means that species

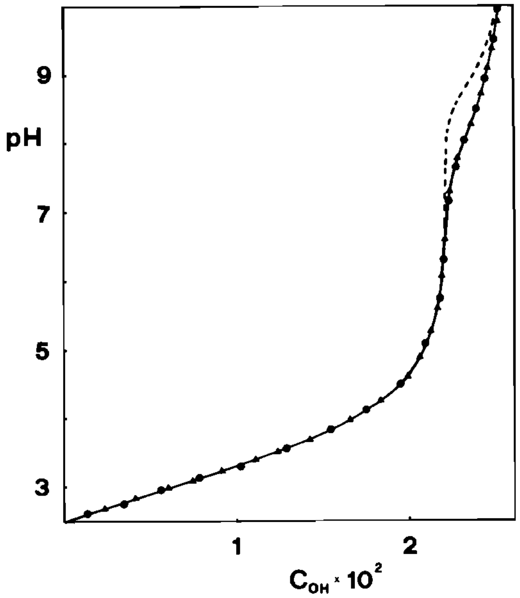

Fig. 1. Alkalimetric titration curve for Cu(II)–Ni(II)–citric acid system. $C_{Cu} = C_{Ni} = 3.00$; $C_{cit} = 6.36$ mmol·dm^{-3}. ●, ▲ experimental points. Dotted line: calculated neglecting any formation of ternary complexes. Full line: calculated by the set of the stability constants that we have determined.

TABLE I. Formation Constants of the Species Formed in Cu(II)–Ni(II)–Zn(II)–Citrate Binary and Ternary Systems and Formation Percentages at Some pH Values, at 25 °C and I = 0.1 mol dm^{-3} (KNO_3)[a].

M	$\log\beta_{110}$[b]	$\log\beta_{111}$	$\log\beta_{220}$	$\log\beta_{22\text{-}1}$	$\log\beta_{22\text{-}2}$
Cu(II)	–	9.47	14.60	10.75	6.00
Ni(II)	5.30	8.84	–	–	–4.71
Zn(II)	4.83	8.43	–	–	–2.94
	$pK_1^H = 2.87$,	$pK_2^H = 4.30$,	$pK_3^H = 5.61$,	$pK_w = 13.75$	

M	M′	$\log\beta_{112\text{-}2}$[c]	pH	$(\%)_{0110}$[d]	$(\%)_{1010}$	$(\%)_{202\text{-}2}$	$(\%)_{022\text{-}2}$	$(\%)_{112\text{-}2}$	$(\%)_{\text{other species}}$
Cu(II)	Ni(II)	1.55(5)[e]	7	45		47		6	2
			8	30		31	1	35	3
			9	10		15	5	69	1
Cu(II)	Zn(II)	1.51(11)	7	37		43	4	12	4
			8	9		35	25	28	3
			9	1		34	32	32	1
Ni(II)	Zn(II)	–2.92(8)	7	48	41		5	2	4
			8	31	8	1	25	32	3
			9	9	1	5	15	69	1

[a] Binary complexes, refs. 3, 4; ternary complexes, this work. [b] The indexes refer to the reaction $pM + q\,cit + rH \rightleftharpoons [M_p(cit)_qH_r]$. [c] The indexes refer to the reaction $pM + qM' + r\,cit + sH \rightleftharpoons [M_pM'_q(cit)_rH_s]$. [d] Percentages refer to citrate concentration; $C_{cit} = 2C_M = 2C_{M'} = 3.10^{-3}$ mol dm^{-3}. [e] 3σ in parenthesis.

other than binary complexes are formed in solution. On these bases the existence of heterobinuclear complexes in the acidic region was excluded, whilst it was strongly evident in the neutral–alkaline region. The species present in the latter pH range, when considering the binary systems, are of the type $[M_2(cit)_2H_{-2}]^{4-}$, [M = Cu(II), Ni(II) or Zn(II) [3, 4]; graphical analysis and computer calculation showed the presence of the $[M\,M'(cit)_2H_{-2}]^{4-}$ complex for each couple of metals considered. The stability constants are reported in Table I together with the values for the binary complexes. The mixed metal compounds are generally the main species when the citrate is present as tetraionized anion (Table 1 and Fig. 2).

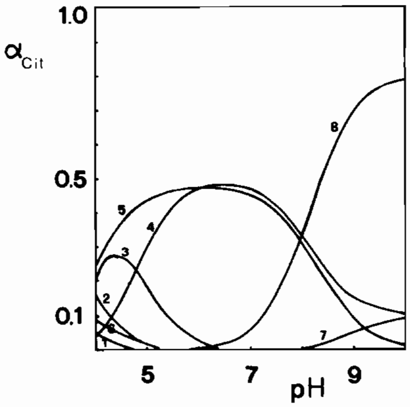

Fig. 2. Distribution of the species as α_{cit} *vs* pH for the ternary Cu(II)–Ni(II)–citric acid system. $C_{Cu} = C_{Ni} = 3.00$; $C_{cit} = 6.36$ mmol·dm^{-3}. 1: $[Cu(cit)]^-$; 2: $[Cu_2(cit)_2]^{2-}$; 3: $[Cu_2(cit)_2H_{-1}]^{3-}$; 4: $[Cu_2(cit)_2H_{-2}]^{4-}$; 5: $[Ni(cit)]^-$; 6: $[Ni(cit)H]$; 7: $[Ni_2(cit)_2H_{-2}]^{4-}$; 8: $[CuNi(cit)_2H_{-2}]^{4-}$.

On the basis of e.s.r. measurements in solution on copper(II)–citrate system [19, 20], it has been proposed that the dimer involves the ionization of the α-hydroxyl group with an axis of symmetry joining the two copper(II) ions. It is tempting to assume that the mixed metal complexes of copper(II)–citrate has a structure analogous to that of copper(II) dimer by simply replacing one Cu^{2+} by Ni^{2+} or Zn^{2+}. Although changes in the coordination number of metal ions cannot be excluded, it is possible to suppose that the formation and the great stability of heterobinuclear complexes involves stereochemical and size considerations, which can result in less strained arrangements of the donor atoms around the two different metal ions.

In any case, the formation of these complexes confirms our previous assertion [1] that the existence of this type of species in solution does not necessarily need a ligand with coordination sites having different donor properties (*e.g.* 'hard' and 'soft'). In fact we have demonstrated that the same kind of donor atoms (oxygen atoms) binds different metal ions. Further investigations are in progress in order to characterize other heterobinuclear complexes of this ligand. Up to now it is not possible to know in which way the electronic and the stereochemical properties of different metal ions can affect the stability of these complexes. Owing to the pH range in which they are formed and to the high degree of formation, these complexes may be relevant from the biological point of view. A larger amount of data will hopefully allow us to tackle on a wider basis the problem of the speciation of this ligand, present in biofluids [21] and in natural waters [22]

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