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Stabilities of Binary and Ternary Complexes of Divalent Metal Ions with Tiron and 2,2′-Bipyridyl

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The formation constants have been measured for the mixed complexes MBT and MBT(OH), where M = Mn(II), Co(II), Ni(II), Zn(II), Cd(II), B = 2,2′-bipyridyl and T = tiron, by computer-aided pH-potentiometry at 25 °C and 0.1 M potassium nitrate. The parent complexes with tiron have also been studied, giving species such as MT, MT_2, MT_3, MHT and $MT_2(OH)$. The stability constants of the parent and mixed complexes follow the Irving–Williams sequence. For all mixed complexes an increase in stability compared to the statistical case was found and characterized by the re-proportionation constant X. The high stability of mixed complexes is attributed to π back-bonds between the 3d-metal ions and the π systems of the ligands.

Introduction

At present increasing attention is paid to the reactivity of ternary complexes. In natural systems biological reactions occur with participation of ternary complexes. Likewise ternary complexes are formed in many reactions used in the chemical laboratory. Thus, in metal ion catalyzed reactions ternary complexes are of great importance, *e.g.* in the so-called template reactions [1] or in analytically used reactions [2].

Most often these complexes are of considerable stability, and therefore their equilibria with other ligands and metal ions in solution have to be regarded. In order to evaluate the competing behaviour of different ligands and metals on a given ternary complex the stabilities of all species present in solution must be known.

In this work the stabilities of complexes of Mn(II), Co(II), Ni(II), Zn(II) and Cd(II) with tiron (1,2-dihydroxybenzene-3,5-disulphonic acid, disodium salt) and 2,2′-bipyridyl are reported. This study became necessary to describe in more detail the catalytic behaviour of metal traces in the analytically-used reaction between tiron, bipyridyl and hydrogen peroxide [3].

Up to now, ternary complexes with tiron and bipyridyl have only been reported for Cu(II) [4] and V(IV) [5]. In addition, only few data exist for the stabilities of binary tiron complexes at an ionic strength of 0.1 *M* [6–8]. For these reasons a thorough computer-aided pH-metric study of the equilibria of metal complexes with tiron and mixed complexes with bipyridyl as the second ligand was undertaken, at an ionic strength of 0.1 *M* (KNO_3) and a temperature of 25 °C.

Experimental

Reagents

Stock solutions of Mn(II), Ni(II), Co(II), Zn(II) and Cd(II) were prepared from their reagent grade nitrates, whose titer was determined by chelatometric titration [9]. Reagent grade tiron (Riedel de Haën) and 2,2′-bipyridyl (Schönert KG, Leipzig) were used as received, their purity being checked by elemental analysis and by potentiometric titration.

Carbonate-free solution of potassium hydroxide (0.2 *M*) was prepared by passing diluted KOH (Suprapur, MERCK) through an OH-form strong basic anion-exchange column (Wofatit-SBW, VEB Chemiekombinat Bitterfeld, G.D.R.) and stored under O_2- and CO_2-free argon. The solution was standardized against potassium hydrogen phthalate. Double-distilled water was applied throughout the work.

Instruments

Potentiometric titrations were carried out at 0.1 *M* KNO_3 under an argon atmosphere in 50 ml of a stirred solution placed in a thermostatted vessel (25 °C). The potentiometric measurements were made with a digital pH-meter MV 87 (VEB Präcitronic Dresden, G.D.R.) equipped with a B- or C-glass electrode and a silver reference electrode (Forschungsinstitut Meinsberg, G.D.R.) separated from the measured solution by a glass frit filled with agar gel. The meter was calibrated with Meinsberg standard buffer solutions.

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Measurements and Calculations

The proton associated ligands and the binary and ternary complexes can be characterized by the general equilibrium process:

$$pM + qT + rB + sH \rightleftharpoons M_pT_qB_rH_s \qquad (1)$$

where M, T, B and H refer to divalent metal ion, tiron (fully deprotonated), bipyridyl and hydrogen ion concentration respectively.

The stability constants of the species are expressed as follows:

$$\beta_{pqrs} = \frac{M_pT_qB_rH_s}{[M]^p[T]^q[B]^r[H]^s} \qquad (2)$$

In agreement with our investigations the following protonation constants have been used at 25 °C and 0.1 M KNO_3: $\log \beta_{HB} = 4.41$ [10]; $\log \beta_{HT} = 12.48$ [14, 15]; $\log \beta_{H_2T} = 20.08$ [14]. For determination of the stability constants of binary and ternary complexes the metal concentrations varied between 1.5×10^{-3} and 2.5×10^{-3} M and those of the ligands ranged from 3×10^{-3} up to 1.2×10^{-2} M. Diluted nitric acid was added to adjust initial pH-values to about 3. In the case of binary systems with tiron, as a first approximation Bjerrums formation functions [11] were plotted *versus* pT values indicating the presence of other than simple MT_n complexes for Mn(II), Co(II) and Zn(II). For that reason in the computer treatment sets for different complexes have been tried. The models were further checked by simulating the titration curves with the computer program HALTAFALL [12] in a FORTRAN translation. The constants were refined by the method of non-linear least squares with the aid of the program SCOGS in its corrected version [13]. In order to get analytical concentrations of hydrogen and hydroxide ions, diluted nitric acid was titrated with standard hydroxide solution at 0.1 M KNO_3. The actual pK_w value was calculated to be 13.998 and the hydrogen ion concentration was given by $10^{-pH}/0.78$. Deviations from the activity coefficient of 0.78 at the pH extremes were corrected to make the data compatible with the program SCOGS [13]. Reproducibility of titration experiments was checked by replicate runs at different metal to ligand ratios.

Results and Discussion

Binary Systems

The stability constants for the binary systems had only to be determined for metal tiron complexes, as for complexes with bipyridyl the constants at I = 0.1 M are known [10]. Typical titration curves of tiron solutions in the absence and presence of metal ions are shown in Fig. 1. Computer simulated curves (including the species MT, MT_2, MHT and in the case of Mn(II) also MT_3) fit the experimental points up to pH values of about 10. From this it was concluded that at higher pH values it will be necessary to reckon with the existence of hydrolyzed complexes, as found by Gergely *et al.* [16] for the Ni(II) tiron complex. Taking into account the species MT(OH) and MT_2(OH) the calculations revealed the complex MT_2(OH) as being the only hydrolyzed species present to a considerable extent. This is well illustrated by the species distribution curves shown for a typical case in Fig. 2a. By use of the mentioned model the titration plots coincide with the theoretical curves in a wide pH range, as is seen from comparison of computer simulated curves with the experimental titrations in Fig. 1. The final stability constants for the tiron complexes are summarized in Table I. The constants obtained are in agreement with the few data available from the literature. The lack of hydrolyzed Mn(II)–tiron complexes seems to be caused by stabilization of manganese in its tris-chelate complex at high pH values (Fig. 2b). The stability constants for both of the complexes MT and MT_2 follow the Irving–Williams sequence: Mn(II) < Co(II) < Ni(II) < Cu(II) > Zn(II), Cd(II).

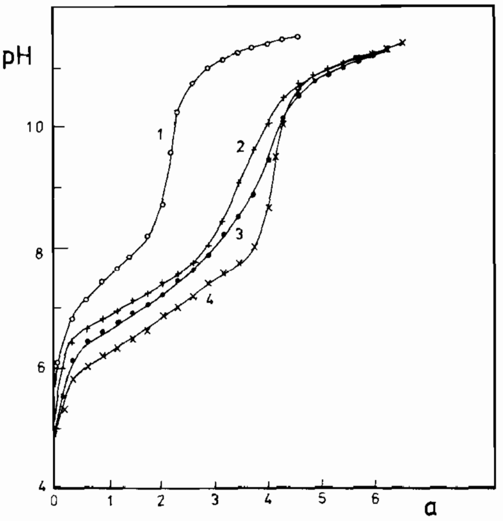

Fig. 1. Titration curves for metal tiron solutions calculated by the HALTAFALL program in comparison with experimental points (a = mol of base added per mol of tiron (1) or of metal ion (2–4)): 3.27×10^{-3} M tiron alone (1) and in the presence of 1.5×10^{-3} M solutions of Cd(II) (2), Co(II) (3) and Zn(II) (4).

Ternary Systems

Representative titration curves of metal solutions in the presence of tiron and bipyridyl (B) are presented in Fig. 3. For computing the ternary complex stability constants all complex species evaluated for metal tiron complexes, as well as the bipyridyl containing species HB, MB, MB_2 and MB_3, have been taken into account. The used

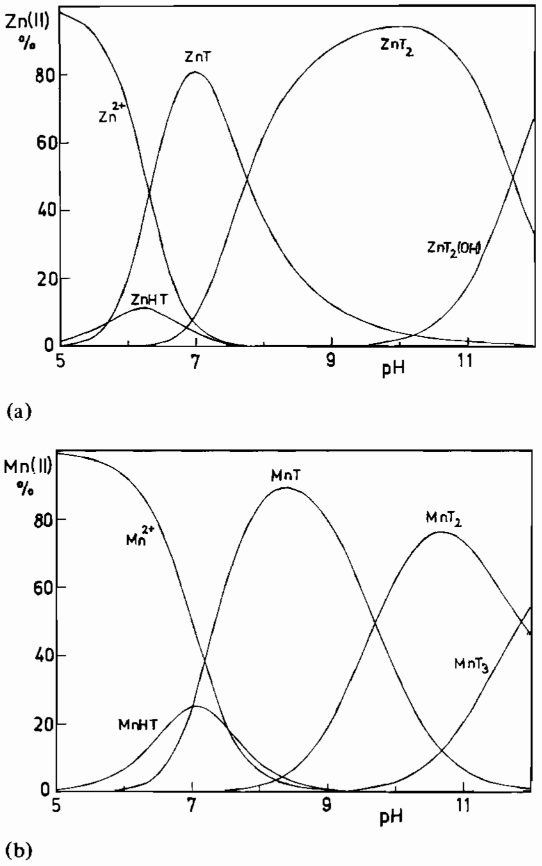

Fig. 2. Species distribution curves as a function of pH for complexes formed in the Zn(II)–tiron (a) and Mn(II)–tiron (b) system at metal ion to ligand ratios of 1:2 and 1:3, respectively.

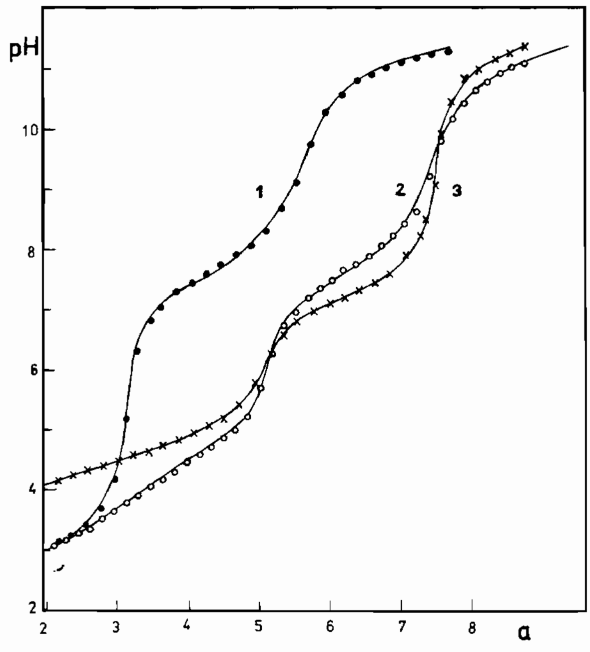

Fig. 3. Titration curves for ternary systems (a = mol of base added per mol of metal ion): (1) 2×10^{-3} *M* Co(II), 3.32×10^{-3} *M* tiron, 6.36×10^{-3} *M* bipyridyl, 5×10^{-3} *M* HNO_3; (2) 2.48×10^{-3} *M* Zn(II), 3.32×10^{-3} *M* tiron, 1.27×10^{-2} *M* bipyridyl, 1×10^{-2} *M* HNO_3; (3) 2.48×10^{-3} *M* Mn(II), 3.32×10^{-3} *M* tiron, 1.27×10^{-2} *M* bipyridyl, 1×10^{-2} *M* HNO_3.

stability constants for bipyridyl complexes at an ionic strength of 0.1 *M* have the values recommended by McBryde [10].

TABLE I. Stability Constants of Metal Complexes with Tiron; t = 25 °C, I = 0.1 *M* (KNO_3).

Metal ion	log β ± s[a]				
	MT	MT_2	MT_3	MHT	MT_2H_{-1}
Mn(II)	8.30 ± 0.02 (8.6)[b]	13.74 ± 0.05	17.57 ± 0.06	15.30 ± 0.05	–
Co(II)	9.37 ± 0.04 (9.49)[c]	16.08 ± 0.07	–	15.74 ± 0.12 (15.8)[c]	4.88 ± 0.08
Ni(II)	9.76 ± 0.02 (9.96)[d]	16.73 ± 0.06	–	–	5.23 ± 0.06
Cu(II)	(14.23)[f]	(25.49)[f]	–	–	–
Zn(II)	10.14 ± 0.02 (10.14)[d] (11.07)[e]	18.22 ± 0.03	–	15.84 ± 0.10 (16.0)[d]	6.56 ± 0.04
Cd(II)	8.76 ± 0.03	14.74 ± 0.08	–	–	3.35 ± 0.07

[a] Estimates of standard deviations.
[b,e,f] Constants at 25 °C and 0.1 *M* KNO_3 from ref. [6], [14], [15].
[c,d] Values at 0.1 *M* KCl and 20 °C from ref. [7] and [14], resp.

Different models have been tested for the existence of mixed species including complexes at fractions of metal ion–bipyridyl–tiron of 1:1:1, 1:2:1, 1:1:2 and hydrolyzed species as well. From the computational analysis best agreement of the experimental and calculated data was always obtained by taking the complexes MBT and MBT(OH) into consideration. The evaluated constants for these complexes are given in Table II.

Particularities were observed for Mn(II) and Cd(II) complexes. In the case of Mn(II) no convergence in the computations could be reached by the assumption of hydrolyzed mixed complexes. Again, this may be rationalized by complexation of manganese in a tris-tiron chelate complex at high pH values (Fig. 4a). For Cd(II) the solubility of the mixed ligand complex is too low for studying its behaviour at pH values higher than 8.

The equilibrium constants for mixed bipyridyl tiron complexes follow the Irving–Williams sequence (cf. Table II). For further characterization of the trend in their stabilities the so-called re-proportionation constants X [17] were calculated. As it may be stated from the data in Table II the formation of mixed complexes of the type MBT is favoured with respect to all metal ions studied as the statistical value for log X is 0.6 [17]. The main contribution to this high stability is due to the π systems of bipyridyl and tiron that enable π back-bonds to be formed with Mn(II), Co(II), Cu(II), Ni(II), and to a lesser extent also with Zn(II) [18].

Compared to the value given for the mixed complex of Cu(II) (Table II) [17], very high extra-stabilizations are calculated for the complexes of Co(II) and Ni(II). This may be explained by the fact that in [17] the tris-chelate of bipyridyl was not included in the calculations. For the same reason the stability constants of the mixed Ni(II), Co(II) and Zn(II) complexes differ significantly from those found for similar mixed complexes with bipyridyl and pyrocatechol (PC) as the ligands [18]. The constants evaluated for the complexes NiB(PC) and CoB(PC) are lower by about 2 orders of magnitude in comparison to mixed tiron complexes (values for log $\beta^{M}_{MB(PC)}$ are 16.38 and 15.43, respectively [18]). Only in the case of ternary Mn(II) complexes are the stability constants with pyrocatechol (log $\beta^{Mn}_{MnB(PC)}$ = 11.01 [8]) and tiron (*cf.* Table II) nearly the same.

By neglecting the tris-bipyridyl complexes of Co(II), Ni(II) and Zn(II) in our computations, similar low stability constants result as reported for mixed bipyridyl pyrocatechol complexes [18]. However, under our experimental conditions, where excess of bipyridyl is present, tris-chelates cannot be disregarded, as is seen from the species distribution curves in Fig. 4b. In addition, computations without MB_3 complexes lead to a much worse fit of the experimental data than in its presence.

TABLE II. Equilibrium Constants of Mixed Complexes with Tiron and 2,2′-Bipyridyl; t = 25 °C, I = 0.1 *M* (KNO_3).

Metal ion	log β ± s		log X[a]
	MBT	$MBTH_{-1}$	
Mn(II)	11.24 ± 0.09	–	4.12
Co(II)	17.33 ± 0.07	5.99 ± 0.08	7.33
Ni(II)	18.89 ± 0.11	7.08 ± 0.10	7.25
Cu(II)	(22.39)[b]	–	(5.69)[b]
Zn(II)	16.41 ± 0.08	5.59 ± 0.12	4.90
Cd(II)	13.49 ± 0.10	–	4.44

[a] Log X = 2 log β_{MBT} – (log β_{MB_2} + log β_{MT_2}). [b] Value at 0.1 *M* $NaClO_4$ from ref. [17].

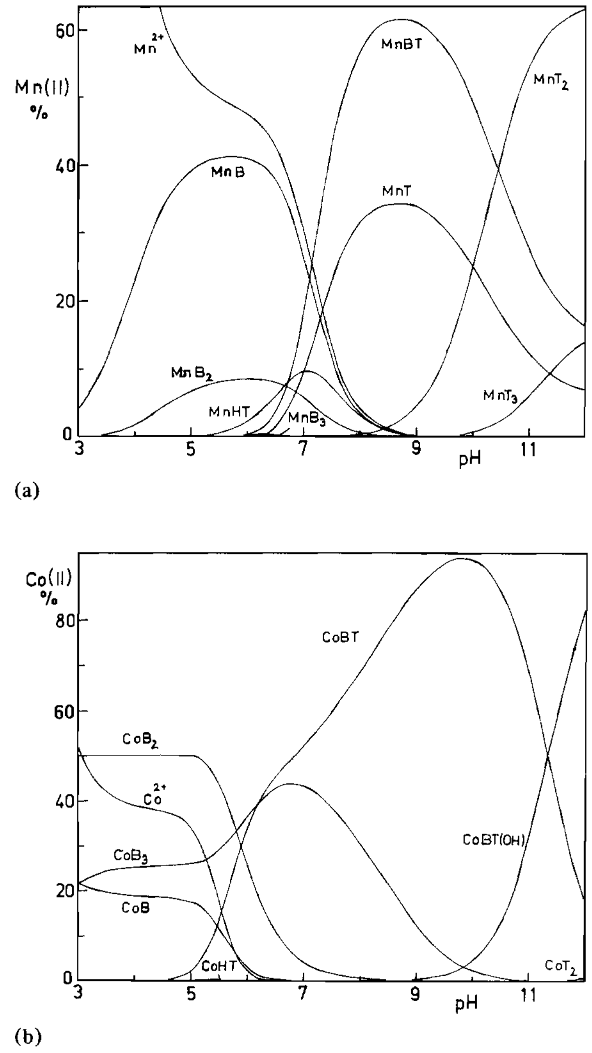

Fig. 4. pH-dependence of distribution curves in ternary systems with Mn(II)–tiron–bipyridyl (a) and Co(II)–tiron–bipyridyl (b) at a metal ion–ligand–ligand ratio of 1:2:2.

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