Potentiometric Study of the Complex-formation Equilibria of Manganese(II), Cobalt(II), Nickel(II), Copper(II), and Zinc(II) with Ethylenediamine-*N*-acetic Acid

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The complex-formation equilibria between Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} and ethylenediamine-*N*-acetic acid (Hedma) were investigated by potentiometric titrations in 0.5 mol dm^{-3} KCl solution at 25 °C. It was found that no protonated or hydrolysed complexes were formed in the pH range 2.0—11.5. The following overall formation constants $\beta_{pqr} = [M_pH_qL_r]/[M]^p[H]^q[L]^r$ were obtained: edma, $\log \beta_{011} = 9.888(2)$, $\log \beta_{021} = 16.860(3)$, $\log \beta_{031} = 18.350(4)$; edma–$Mn^{II}$, $\log \beta_{101} = 3.629(18)$; edma–$Co^{II}$, $\log \beta_{101} = 8.123(3)$, $\log \beta_{102} = 13.050(9)$; edma–$Ni^{II}$, $\log \beta_{101} = 10.106(5)$, $\log \beta_{102} = 16.629(10)$; edma–$Cu^{II}$, $\log \beta_{101} = 12.854(11)$, $\log \beta_{102} = 20.373(19)$; edma–$Zn^{II}$, $\log \beta_{101} = 8.064(4)$, $\log \beta_{102} = 13.655(7)$. The probable structures of the chelated compounds formed in aqueous solution were deduced and their stability constants compared with those of analogous chelated compounds. The equilibrium constants follow the Irving–Williams series.

Ethylenediamine-*N*-acetic acid, Hedma, is a simple and basic amino acid formed during the carboxymethylation of ethylenediamine.[1] Only a few papers have appeared on the complex formation equilibria between metal ions and the $edma^-$ anion, in contrast to those of analogous ligands such as ethylenediaminetetra-acetate (edta). Fujii and co-workers[2–6] have prepared this ligand by using a new, simple method and examined the complex-formation equilibria with Pb^{II}, Cd^{II}, and Cu^{II} by a d.c. polarographic technique and with Ni^{II} by spectrophotometric methods. Oyama *et al.*[7] have studied in detail the Cd^{II}–edma system by means of potentiometry as well as the d.c. polarographic method. However, no data on the complex-formation equilibria between Mn^{II} and $edma^-$ seems to have been reported. Besides, those equilibrium data reported in the literature have been obtained by various experimental techniques, and cannot therefore always be compared. In this paper, the potentiometric determination of the solution equilibria between metal ions and $edma^-$ will be described.

Experimental

Reagents.—Ethylenediamine-*N*-acetic acid–hydrogen chloride (1/2) dihydrate ($Hedma\cdot 2HCl\cdot 2H_2O$) was prepared and purified by the method described by Fujii.[5] Its purity was checked by means of elemental analysis (Found: C, 20.6; H, 7.20; N, 12.45. Calc. for $C_4H_{16}Cl_2N_2O_4$: C, 21.15; H, 7.10; N, 12.35%), and the concentration of edma or hydrogen chloride solutions was evaluated from the potentiometric titrations by using the interpolation of Fortuin.[8] Concentrations of stock solutions of bivalent metal chlorides (AnalaR products) were determined by conventional analytical methods. The starting solutions for each potentiometric titration were prepared by adding successively to the titration vessel a known volume of edma solution, and an exact volume of metal chloride; then the required quantities of potassium chloride (AnalaR) and a sufficient amount of doubly distilled water were added to make up the total volume V_0, which was 25.00 ± 0.002 cm^3. The ionic medium was 0.5 mol dm^{-3} KCl at the beginning of each potentiometric titration.

Potentiometry.—The titration vessel was maintained at 25.0 ± 0.1 °C by the circulation of thermostatted water. A slow nitrogen stream, presaturated by bubbling it through an appropriate KCl solution (0.5 mol dm^{-3}), was maintained in the cell. The potentiometric measurements were made by using a Metrohm Titroprocessor E 636, equipped with an H 268 glass electrode (Schott-Jena) and a B 343 Talamid reference electrode (Schott-Jena). The standard electrode potential, E° and the concentration of the potassium hydroxide solution were determined before and after each experiment by dynamic titration [density of the measuring points with a step of variable volume is equal at each point of the titration curve, the amount of added KOH (Δv) being inversely proportional to the last difference (ΔE) in the electromotive force] of a known amount of HCl in 0.5 mol dm^{-3} KCl with KOH solution, according to Gran's method[9] using the computer program NBAR.[10,11] The ionic product K_w was obtained from the alkaline region of the same calibration curve by using NBAR and varying its values until the average E° in alkaline media equalled that in acidic solution. Starting from the same experimental data (about 20 unequally spaced points both for acidic and alkaline media), it was moreover possible to evaluate the liquid-contact potential whether in acid (A_j) or basic (B_j) solution by using the NBAR program. For each experimental point of the titration curve, $E^{\circ\prime}$ was calculated from the Nernst equation $E^{\circ\prime} = E - (RT/F) \ln [H^+]$ (acidic solution) or $E^{\circ\prime} = E + (RT/F) \ln [OH^-] - (RT/F) \ln K_w$ (basic solution), where $[H^+]$ is the hydrogen-ion concentration and E is the electromotive force (mV) measured. The standard electrode potential, E°, and the coefficients of the correction terms for the effect of liquid-junction potentials in acidic and basic solution were then obtained from equations (1) and (2) by a least-squares method.

$$E^{\circ\prime} = E^{\circ} + A_j[H^+] \qquad (1)$$

$$E^{\circ\prime} = E^{\circ} + B_j(K_w/[H^+]) \qquad (2)$$

In the present calculations all terms ($E^{\circ\prime}$, $[H^+]$) are considered from $k = 1$ to $k = S$, where S is the kth value of $E^{\circ\prime}$ after which two successive points lie more than 0.1 mV from a straight line of slope (A_j or B_j) and intercept (E°) derived from all the previous points. From the results reported in Table 1 it is possible to see the excellent agreement between the parameters (E°, N) calculated for acidic solution and those calculated for

Table 1. Evaluation of $E^{\ominus}$ (standard potential), A_j and B_j (junction potentials/mV mol^{-1}), concentration of KOH, and K_w (ionic product) from potentiometric titrations of HCl with KOH both in acidic and alkaline solutions, using the NBAR program

	$E^{\ominus}$/mV				[KOH]/mol dm^{-3}		
Titration	Acidic	Basic	Acidic	Basic	Acidic	Basic	$10^{14}K_w$/mol^2 dm^{-6}
1	1 161.7	1 162.2	38.02	−94.42	0.368 22	0.368 17	1.9443
2	1 166.0	1 166.7	−15.75	−78.44	0.368 22	0.368 85	1.9238
3	1 167.5	1 167.3	−80.55	−133.65	0.387 31	0.387 42	1.9844
4	1 165.4	1 165.5	1.96	−144.79	0.387 22	0.387 10	2.1338
5	1 165.7	1 166.0	−6.64	−176.17	0.387 00	0.387 06	2.1598
6	1 157.4	1 157.6	−3.71	−121.06	0.272 34	0.272 71	2.2413
7	1 156.9	1 156.9	0.45	−85.33	0.272 47	0.272 64	2.2397
8	1 154.3	1 153.8	198.0	245.78	0.272 39	0.272 36	2.2232
9	1 157.7	1 157.6	24.11	−76.41	0.272 48	0.272 77	2.2397
10	1 155.2	1 155.4	20.29	−170.18	0.213 84	0.213 93	2.2413
11	1 154.8	1 155.1	10.41	−151.58	0.213 87	0.214 12	2.2423
12	1 155.6	1.156.2	20.93	−160.15	0.213 87	0.213 94	2.2486
13	1 156.5	1 157.1	14.41	−270.81	0.213 92	0.213 85	2.2486

Table 2. Protonation and complex-formation constant determinations. Initial amounts (T_M, T_H, T_L in mmol) of the reagents for the alkalimetric titrations of ethylenediamine-*N*-acetic acid with bivalent metal ions at 25 °C and I = 0.5 mol dm^{-3} KCl

Run	Ion	T_M	T_H	T_L
1	H^+		1.538 424	0.505 218
2			1.470 546	0.483 252
3			1.678 948	0.552 285
4			1.343 894	0.441 828
5			1.305 500	0.512 100
6			1.306 257	0.512 100
7			1.499 646	0.588 915
8	Mn^{2+}	0.093 994	1.104 903	0.431 231
9		0.046 997	1.104 903	0.431 231
10		0.037 598	1.104 903	0.431 231
11		0.187 988	1.104 903	0.431 231
12		0.093 994	0.883 922	0.344 985
13		0.093 994	0.736 602	0.287 488
14	Co^{2+}	0.191 228	0.104 903	0.431 231
15		0.382 457	1.104 903	0.431 231
16		0.111 550	1.104 903	0.431 231
17		0.175 293	1.473 204	0.574 975
18		0.318 714	1.473 204	0.574 975
19		0.478 071	1.473 204	0.574 975
20	Ni^{2+}	0.108 069	0.695 683	0.225 660
21		0.231 576	1.043 524	0.338 490
22		0.077 192	0.695 683	0.225 660
23		0.308 768	1.043 524	0.338 490
24		0.162 103	0.834 819	0.270 792
25	Cu^{2+}	0.053 686	0.668 923	0.219 865
26		0.053 686	0.468 246	0.153 910
27		0.026 843	1.337 846	0.439 730
28		0.042 948	1.337 846	0.439 730
29		0.032 211	1.337 846	0.439 730
30		0.021 474	1.003 385	0.329 798
31		0.053 686	1.404 739	0.461 717
32		0.010 737	2.006 769	0.659 596
33	Zn^{2+}	0.093 331	1.104 903	0.431 231
34		0.046 666	1.104 903	0.431 231
35		0.139 997	1.104 903	0.431 231
36		0.093 331	1.325 884	0.517 478
37		0.046 666	1.325 884	0.517 478
38		0.233 328	1.104 903	0.431 231

alkaline solution. In the refinement procedure (see below) the calculated electromotive force, $E_{\text{calc.}}$ is obtained from equation (3). Since the liquid-contact potential, relative to the cell

$$E_{\text{calc.}} = E^{\ominus} = \frac{RT}{F}\cdot\ln[H^+] + A_j[H^+] + B_j\cdot\frac{K_w}{[H^+]} \qquad (3)$$

engaged in the measurements, is fairly small and not prominent in the calculations of the equilibria (pH interval used 2.6—11.0), it has been neglected. All the calculations were made on the CDC CYBER computer 70/76 of the Consorzio per la Gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord Orientale, Casalecchio, Bologna, with financial support from the University of Parma. The compositions of the starting solutions for each potentiometric titration are quoted in Table 2.

Results and Refinement

The protonation constants (Table 3) were determined by the usual graphical methods and then refined by the computer program BETAREF.[12] The latter computes the values of the overall protonation or formation constants which minimize the sum of the squares of the residual between the observed and calculated e.m.f. values [equation (4)], where Z is the number of

$$U = \sum_{i=1}^{Z} w_i(E_i^{\text{obs.}} - E_i^{\text{calc.}})^2 \qquad (4)$$

the potentiometric readings and w_i is a weighting factor. The present program uses the method of 'rigorous least squares' in which the instrumental uncertainties in the e.m.f. measurements, σ_E, and in the added titrant volume, σ_V, are taken into account as sources of experimental error. The data are weighted by a statistically sound scheme [equation (5)] using the cubic spline

$$w_i = 1/\sigma_i^2 = 1/[\sigma_E^2 + (\partial E_i/\partial V_i)^2\sigma_v^2] \qquad (5)$$

interpolation procedure, as modified by Stanton and Hoskins.[13] The minimization is based on the measured e.m.f. values E_i and all requisite derivatives ($\partial E_i/\partial p_i$) for each experimental data point, with respect to the parameters (p_i) to be refined, are obtained analytically.

BETAREF can be used to refine other parameters in addition to formation constants. Such parameters are quantities characteristic of a single titration curve, *e.g.* the initial amounts of reagents, their concentrations in the titration vessel, the standard cell potentials, the liquid-junction potentials, and the initial volume of the solution. For other important features of BETAREF the previous programs MINIQUAD[14] and MIQUV[15,16] should be examined. In the final stage of calculations, in addition to the protonation constants, the initial amounts of reagents (T_L, T_H/mmol) were minimized for each titration. The standard deviations of the refined quantities were

Table 3. Cumulative and stepwise protonation complex-formation constants[a] of ethylenediamine-*N*-acetic acid at 25 °C and $I = 0.5$ mol dm^{-3} (KCl). Standard deviations (σ values) are given in parentheses

	H^+	Mn^{II}	Co^{II}	Ni^{II}	Cu^{II}	Zn^{II}
$\log \beta_{011}$[a]	9.888(2)					
$\log \beta_{021}$	16.860(3)					
$\log \beta_{031}$	18.350(4)					
$\log K_2^{H}$[b]	6.972(3)[c]					
$\log K_3^{H}$	1.490(4)					
$\log \beta_{101}$		3.629(18)	8.123(3)	10.106(5)	12.854(11)	8.064(4)
$\log \beta_{102}$			13.050(9)	16.629(10)	20.373(19)	13.655(7)
$\log K_2$			4.927(7)	6.532(8)	7.519(16)	5.591(6)
Z[d]	590	223	343	216	337	311
U[e]	$0.591\,082 \times 10^5$	$0.130\,364 \times 10^4$	$0.743\,189 \times 10^5$	$0.453\,262 \times 10^5$	$0.127\,400 \times 10^5$	$0.977\,494 \times 10^5$
χ^2[f]	6.69	8.71	16.58	10.07	10.99	23.28

[a] $\beta_{pqr} = [M_pH_qL_r]/[M]^p[H]^q[L]^r$. [b] $\log K_n = \log \beta_{0n1} - \log \beta_{0\,n-1\,1}$. [c] $\sigma(\log K_n) = \{[\sigma^2(\log \beta_{0n1}) + \sigma^2(\log \beta_{0n-11})]/2\}^{\frac{1}{2}}$. [d] Total number of data points used in the refinement. [e] See equation (4). [f] Observed chi square, while calculated value (6 degrees of freedom, 95% confidence level in the χ^2 distribution) should be 12.6.

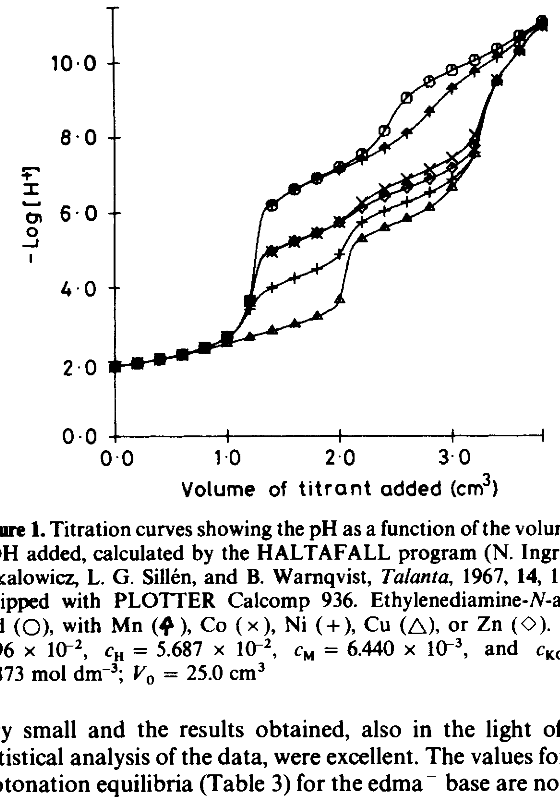


Figure 1. Titration curves showing the pH as a function of the volume of KOH added, calculated by the HALTAFALL program (N. Ingri, W. Kakalowicz, L. G. Sillén, and B. Warnqvist, *Talanta*, 1967, **14**, 1261), equipped with PLOTTER Calcomp 936. Ethylenediamine-*N*-acetic acid (○), with Mn (⍏), Co (×), Ni (+), Cu (△), or Zn (◇). $c_L = 1.896 \times 10^{-2}$, $c_H = 5.687 \times 10^{-2}$, $c_M = 6.440 \times 10^{-3}$, and $c_{KOH} = 0.3873$ mol dm^{-3}; $V_0 = 25.0$ cm^3

very small and the results obtained, also in the light of the statistical analysis of the data, were excellent. The values for the protonation equilibria (Table 3) for the edma$^-$ base are not the same as obtained previously. In fact Fujii and Kodama[4] reported values of $\log \beta_{011} = 10.15$, $\log \beta_{021} = 16.80$, and $\log \beta_{031} = 18.95$ at an ionic strength of 0.2 mol dm^{-3} at 25 °C, while Ohsaka *et al.*[17] obtained the values $\log \beta_{011} = 9.97(2)$, $\log \beta_{021} = 16.71(2)$, and $\log \beta_{031} = 18.76(2)$ at $I = 1.0$ mol dm^{-3} ($NaClO_4$) at 25 °C.

In particular, the greatest differences, as regards the data reported in the literature, occur for $\log K_3^H$. This might be caused by the influence of the ionic strength on the protonation constant which changes in a manner similar to that of acetic acid[18] or glycine[19] and of other analogous compounds.[20-22] The titration diagrams of the protonated ligand, H_3L^{2+}, in the presence or in the absence of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}, are shown in Figure 1. The curve for edma with potassium hydroxide exhibited three sharp inflections corresponding to the successive stages of neutralization. The $\log \beta_{011}$ value corresponding to the protonation of the primary amine group was estimated to be 9.888(2). On the basis of the results and by analogy with known values for analogous functional groups, $\log K_2 = 6.972(3)$ and $\log K_3^H = 1.490(4)$ can be assigned to the protonation of the secondary amine (H_2L^+) and carboxylate (H_3L^{2+}) group, respectively. In the presence of metal ions the titration curves did not reveal an appreciable complexing capacity in the strongly acidic media, but showed, after neutralization of the carboxylate group, one or two distinct buffer zones, at pH *ca.* 2.6—6.2 and 5.4—8.9, respectively. The formation functions, $\bar{n}$ (concentration of ligand bound to metal divided by total concentration of metal), calculated on the assumption that the protonated complexes do not exist, suggest the existence of mononuclear complexes with metal to ligand ratios of 1:1 (ML) and 1:2 (ML_2). In the final refinement, T_M was kept constant and T_L and T_H together with the formation constants were varied. The analysis and refinement of the formation constants of the complexes of edma with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} show that the following complexes are formed: $[Mn(edma)]^+$, $[Co(edma)]^+$, $[Co(edma)_2]$, $[Ni(edma)]^+$, $[Ni(edma)_2]$, $[Cu(edma)]^+$, $[Cu(edma)_2]$, $[Zn(edma)]^+$, and $[Zn(edma)_2]$. The refined constants for the complex-formation equilibria, obtained by using the program BETAREF, are reported in Table 3. A complete list of the experimental data and of the final computations is available from the author.

Discussion

Using the stability constants given in Table 3 and the protonation constants of the ligand under the same conditions, the percentage of each complex involving H^+, metal ions, and ligand has been calculated. A representative distribution diagram for Cu^{2+} is reported in Figure 2. Some general observations about the behaviour of the various systems are: (*a*) for the edma–Mn^{2+} system (M:L *ca.* 1:4) the only complex $[MnL]^+$ reaches a maximum concentration of 94.7% total metal at pH 11.0; (*b*) for the edma–Co^{2+} system (M:L *ca.* 1:4), $[CoL]^+$ reaches a maximum of 94.8% at pH 6.5 and $[CoL_2]$ reaches a peak of 99.3% at pH 10.0; (*c*) for the edma–Ni^{2+} system (M:L *ca.* 1:4), $[NiL]^+$ reaches 96.8% total metal at pH 5.5 and $[NiL_2]$ reaches a peak of 99.12% at pH 8.0; (*d*) for the edma–Cu^{2+} system (M:L *ca.* 1:4), $[CuL]^+$ has a maximum of 99.57% total metal at pH 4.5 and $[CuL_2]$ a maximum of 99.30% at pH 7.25; (*e*) for the edma–Zn^{2+} system (M:L *ca.* 1:4), $[ZnL]^+$ reaches a peak of 89.6% at pH 6.25 and $[ZnL_2]$ reaches a maximum of 99.2% at pH 9.0. The complexes of Co^{2+}, Ni^{2+}, and Zn^{2+} exhibit similar behaviour to those of Cu^{2+}, but have lower stability as expected. The maximum concentrations of the various complex species of the different systems shift to lower

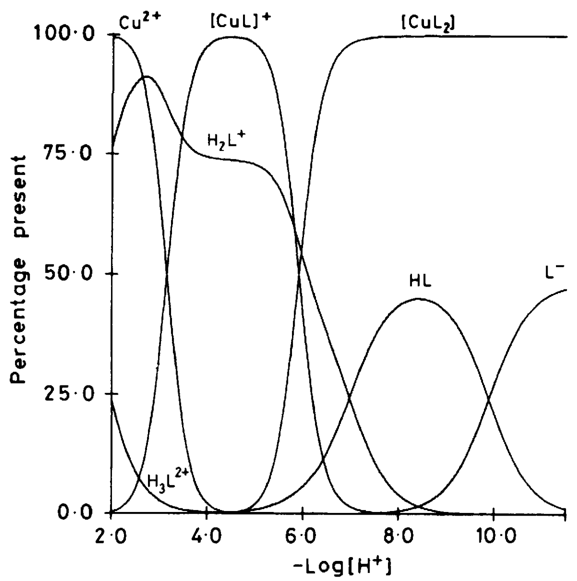
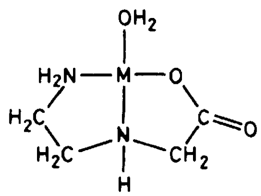
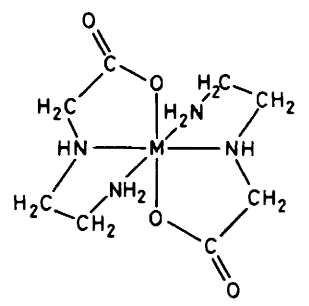


Figure 2. Typical distribution diagram for the system edma–Cu^{2+}. The percentage of each species has been calculated from the data of a hypothetical solution of copper ions (0.001 543 mol dm^{-3}) and edma (0.005 955 mol dm^{-3}) using the HALTAFALL program, equipped with PLOTTER Calcomp 936. The concentrations of the species not containing metal were calculated as percentages of the total ligand, those containing metal as percentages of the total metal



(1)



(2)

pH values with regard to [MnL]$^+$ (pH 11.0), due to an increase in stability.

Since an edma anion has two nitrogen atoms and one acetate group it may act as a tridentate ligand forming five-membered chelate rings. Therefore, the metal(II) ions may be expected to form complexes with 1:1 and 1:2 compositions. The probable bonding in the metal chelates of edma is given by structures **(1)** and **(2)**, the square-planar and octahedral geometries corresponding to the ML and ML$_2$ complex types, respectively. The orders of the cumulative (log β_{101} and log β_{102}) and stepwise (log K_2) formation constants are in accordance with the Irving–Williams series. The absence of complexes higher than 1:1 for Mn^{2+} may be due to the radius of this ion, which is large in comparison with the N···N bite of the entering ligand. A glycine-type chelate with only N,O as donor atoms is excluded by a comparison of the constants in Table 3 with corresponding values for various metal–α-amino acid systems.[23–25] The much higher stability of the 1:1 and 1:2 complexes of the present ligand with various metal ions compared with the corresponding complexes of analogous N,N donor compounds[26] such as ethylenediamine, propane-1,2-diamine, and α,γ-diaminobutyric acid can be attributed to co-ordination of the carboxylato-group, *i.e.* the present ligand is tridentate. The participation of the carboxylate group in complex formation was also demonstrated by Fujii and Kodama[4] for the Cu^{2+}–edma system from the i.r. spectra and by ion-exchange chromatography. The large difference in log K_1/K_2 for the various metals suggest that the complexes do not possess the same structure. The higher value for Cu^{2+}, log $K_1/K_2 = 5.335$, could be explained either by a different arrangement of the ligand or even by the Jahn–Teller effect. The data reported in the literature (log $\beta_{101} = 7.51$, log $\beta_{102} = 14.05$ for Co^{2+},[17] $I = 1.0$ mol dm^{-3} NaClO$_4$, potentiometric method; log $\beta_{101} = 10.44$, log $\beta_{102} = 16.78$ for Ni^{2+},[6] $I = 0.3$ mol dm^{-3}, spectrophotometric method; log $\beta_{101} = 13.40$, log $\beta_{102} = 21.44$ for Cu^{2+},[4] $I = 0.2$ mol dm^{-3}, polarographic method) are not in a good agreement with the equilibrium constants obtained in this work, perhaps because of the different experimental conditions and the various calculation procedures. For cobalt, the behaviour of log K_2 does not follow the Irving–Williams series.

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