190. Potentiometric and Spectrophotometric Titration of Cu^{2+} Complexes with *N*-Isopropyl-2-methyl-1,2-propanediamine

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The complexation of Cu^{2+} by *N*-isopropyl-2-methyl-1,2-propanediamine (L) has been studied by potentiometric and spectrophotometric titration. The dominant complexes formed in this system are $[CuL]^{2+}$, $[CuL_2]^{2+}$, $[Cu_2L_2(OH)_2]^{2+}$, and $[CuL(OH)_2]$. The data were thoroughly tested for different models with $[CuL(OH)]^+$, $[CuL_2(OH)]^+$, $[Cu(OH)]^+$, and $[Cu_2(OH)_2]^{2+}$ as additional species. The importance of steric factors is indicated by the d-d* spectra: for $[CuL_2]^{2+}$ ($\lambda_{max} = 499$ nm) the absorption maximum is shifted by 50 nm to high energies relative to $[Cu(en)_2]^{2+}$ ($\lambda_{max} = 549$ nm), whereas the opposite is true for the 1:1 complexes ($[CuL]^{2+}$: $\lambda_{max} = 712$ nm, $[Cu(en)]^{2+}$: $\lambda_{max} = 660$ nm).

Introduction. – In the course of studies on the crystal structures of Cu^{2+} complexes with *N*-isopropyl-2-methyl-1,2-propanediamine (L) and various anions, mainly carboxylates [1] [2], we have become interested in the solution equilibria of ternary diamine dicarboxylate equilibria [3].

It was felt, however, that a thorough study of the binary Cu^{2+}/amine system was in order before expanding on this problem. Ligand protonation constants [4] and equilibrium constants for the Cu^{2+} complexes $[CuL]^{2+}$ and $[CuL_2]^{2+}$ [5] have been determined previously from potentiometric titrations using data obtained in a rather limited pH range, precluding any knowledge of species formed above pH 6.5. For related chelating diamines, the following species have been reported in addition to $[CuL]^{2+}$ and $[CuL_2]^{2+}$: $[CuL(OH)]^+$ and $[Cu_2L_2(OH)_2]^{2+}$ [6] [7], $[CuL(OH)_2]$ [8], $[CuL_2(OH)]^+$ [9]. Here, we describe a combined potentiometric and spectrophotometric study with the aim of determining the stability constants of all major species, checking the formation of additional minor complexes and obtaining some clues about solution structures from the d-d* absorption spectra.

Experimental. – *Materials and Instrumentation.* N-*Isopropyl-2-methyl-1,2-propanediamine (Aldrich)* was converted to the dihydrochloride (m.p. 546–548 K) with conc. HCl in abs. EtOH, and the crude product was twice recrystallized from abs. EtOH. Other reagents were 2-amino-2-(hydroxymethyl)-1,3-propanediol (tris), $CuSO_4 \cdot 5H_2O$, KCl, and NaOH (*Titrisol*, all *Merck, p.a.*) and used as obtained. Twice dist. H_2O was used throughout.

Potentiometric titration curves were obtained on a *Metrohm-E600* ionmeter equipped with a combined glass electrode, a *Metrohm-655* digital burette, and the microprocessor-controlled data acquisition system described previously [10].

Spectrophotometric titration curves were obtained on a *Philips-PU-8800* spectrophotometer and instrumentation analogous to the one described in [11]. A *Twix 286-AT* was used for complete computer control of data acquisition.

All calculations were done on a *HP-300* desk-computer using the programs TITFIT [12] and SPECFIT [13] [14] for potentiometric and spectrophotometric data, respectively. All experiments were done at 298 ± 0.1 K with $I = 0.5$ (KCl).

Potentiometric titrations were performed under N_2 with 0.4M NaOH. Exact calibration of the electrode was achieved by titrating 25 ml of a stock soln. of tris as described in [15]. Protonation constants K^{H}_{LH} and $K^{H}_{LH_2}$ were obtained by titrating 3 × 50 ml of 3.2 mM ligand dihydrochloride. Stability constants of the metal complexes were calculated from three independent batches made up of 4 or 5 titration curves defined by concentration of ligand, concentration of metal ion, and initial volume (c_L, c_M, v_0). *Batch A: A1* (3.2 mM, 1.44 mM, 50 ml); *A2* (2.667 mM, 2.133 mM, 48 ml); *A3* (1.306 mM, 1.045 mM, 98 ml); *A4* (6.40 mM, 2.56 mM, 25 ml). *Batch B: B1* (3.20 mM, 1.44 mM, 50 ml); *B2* (5.565 mM, 4.452 mM, 23 ml); *B3* (2.56 mM, 1.536 mM, 50 ml); *B4* (1.306 mM, 1.045 mM, 98 ml). *Batch C: C1* (7.347 mM, 5.863 mM, 15 ml); *C2* (5.51 mM, 4.397 mM, 20 ml); *C3* (4.384 mM, 3.498 mM, 25 ml); *C4* (2.204 mM, 1.759 mM, 50 ml); *C5* (1.102 mM, 0.8794 mM, 100 ml).

Spectrophotometric titrations were done on eight carefully filtered samples (2.3 ml) which were combined into 4 batches of two individual experiments, run as duplicates: *Batch D, E:* $c_L = 6.53$ mM, $c_M = 5.21$ mM, and $c_L = 13.07$ mM, $c_M = 5.21$ mM; NaOH = 0.4M (0.1M KCl). *Batch F, G:* $c_L = 3.27$ mM, $c_M = 2.61$ mM, and $c_L = 6.53$ mM, $c_M = 2.61$ mM; NaOH = 0.2M (0.3M KCl). 36 to 46 spectra per experiment were obtained by adding NaOH in appropriate steps of 0.003 to 0.02 ml. All spectra were digitally recorded between 450 and 750 nm at 10 nm intervals.

Equilibrium constants were calculated as concentration constants using the activity coefficient $\alpha = 0.918$ for H^+ and $pK_W = 13.885$ as determined previously for our experimental conditions [15]. Final values are the means of all batches, and all results are given with twice their standard errors as the estimated uncertainties.

Results and Discussion. – *Major Species.* Even by superficial inspection of the potentiometric titration curves, it was obvious that the simple model [5] with $[CuL]^{2+}$ and $[CuL_2]^{2+}$ as the only complexes was not appropriate to describe the data. Also, factor analysis of the spectrophotometric data invariably indicated five absorbing species, irrespective of the ligand to metal ratio. With five factors, residual noise reduces to less

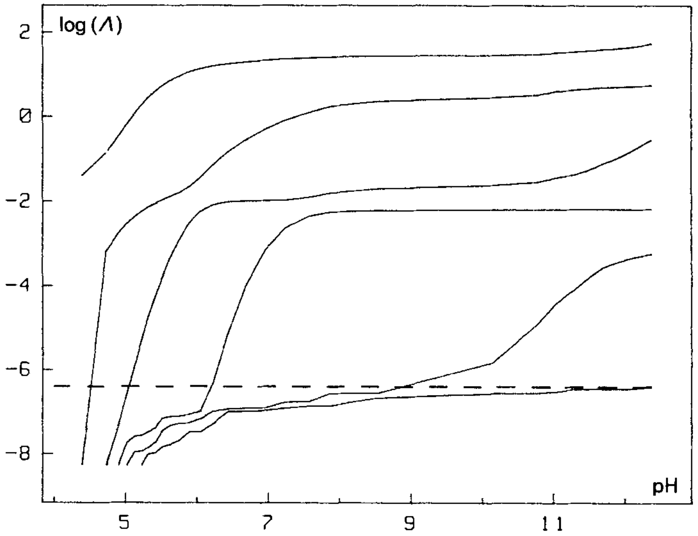

Fig. 1. *Evolving factor analysis of spectrophotometric titration.*
$c_L = 6.53$ mM, $c_M = 5.21$ mM. ———: Logarithms of evolving *eigenvalues* Λ. – – – –: Level of significance (value of first Λ corresponding to noise level).

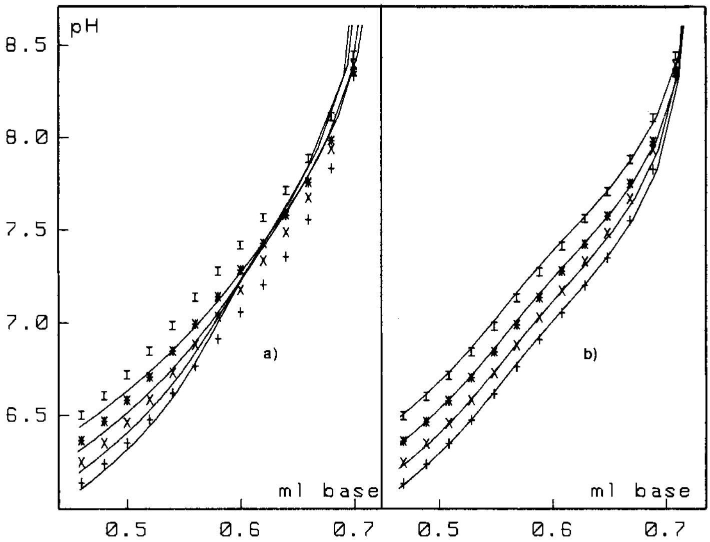

Fig. 2. *Potentiometric titrations* (*Batch C*, section).
+ : *C1*; ×: *C3*; *: *C4*; I: *C5* (experimental points). ——— : Calculated based on complete *Batch C*. *a*) Model with $[CuL]^{2+}$, $[CuL_2]^{2+}$, $[CuL(OH)]^+$, and $[CuL(OH)_2]$; $\sigma = 7.9$ µl. *b*) Standard model; $\sigma = 2.4$ µl.

Table 1. *Logarithms of Ligand-Protonation Constants and Equilibrium Constants from Potentiometric and Spectrophotometric Titrations*

a) *Ligand Protonation Constants*

Curve No.	K^{H}_{LH}	$K^{H}_{LH_2}$	σ[a]
1	10.29	6.95	0.54
2	10.29	6.94	0.67
3	10.29	6.95	0.55
Mean	10.29	6.95	
2σ	< 0.01	< 0.01	

b) *Equilibrium Constants*

Batch	K^{Cu}_{CuL}	$K^{CuL}_{CuL_2}$	K[b]	$\beta_{[CuL(OH)_2]}$	σ	σ^*[c]	$F = (\sigma/\sigma^*)^2$
A	9.00	7.10	15.67	18.03	2.03[a]	1.75[a]	1.35
B	8.99	7.10	15.66	17.95	2.09[a]	1.91[a]	1.20
C	8.99	7.11	15.64	17.91	2.40[a]	2.36[a]	1.03
D	9.05	7.13	15.70	17.89	1.50[d]	1.10[d]	1.86
E	9.05	7.13	15.70	17.85	1.67[d]	1.36[d]	1.51
F	9.04	7.12	15.66	17.81	0.74[d]	0.48[d]	2.38
G	9.06	7.13	15.72	17.84	0.94[d]	0.57[d]	2.72
Mean	9.03	7.12	15.68	17.91			
2σ	0.02	0.01	0.02	0.06			

[a] Standard deviation in µl of added base.

[b] $K = [[Cu_2L_2(OH)_2]^{2+}]/([[CuL^{2+}]^2][OH^-]^2)$.

[c] Values for a model including $[CuL(OH)]^+$.

[d] Standard deviation in absorbance units, $\times 10^3$.

than 10^{-4} absorbance units (a.u.), normally $5–6 \cdot 10^{-5}$ a.u. were obtained. Evolving factor analysis [16] [17] fully corroborated this conclusion. As indicated in *Fig. 1*, four species are formed in neutral and slightly acidic solution, a fifth one appearing above pH 10. In titrations with at least two mol of ligand per metal ion the formation of one species is strongly suppressed, only three factors appearing below pH 7 and 2 above pH 10.

Based on these results, a model consisting of Cu^{2+}_{aq}, $[LH_2]^{2+}$, LH^+, L, $[CuL]^{2+}$, $[CuL_2]^{2+}$, $[Cu_2L_2(OH)_2]^{2+}$, and $[CuL(OH)_2]$ was selected to explain the data. As shown in *Fig. 2*, the logical alternative, *i.e.* replacing $[Cu_2L_2(OH)_2]^{2+}$ by the corresponding monomer, $[CuL(OH)]^+$ is completely out of question. Ligand protonation constants as well as the equilibrium constants from potentiometric and spectrophotometric titrations are compiled in *Table 1*, along with the estimated uncertainties, as indicated by twice their standard errors. The quality of fit is indicated as $\sigma_{\mu l}$ (added base) for potentiometric or σ_a (a.u.) for spectrophotometric data. Overall averages of the equilibrium constants as obtained from all experiments are also included in *Table 1*. As may be seen, the fit is quite satisfactory considering the variety of analytical concentration and the differences in experimental approach. The results of the spectrophotometric titrations should be specifically commented upon, since each set of equilibrium constants was obtained from data combined of two completely independent experiments, and since it is by no means trivial to avoid errors of 10^{-3} a.u. simply by reposition of the cuvette between the two titrations.

Minor Species. As mentioned above, additional species, $[CuL_2(OH)]^+$ [9] and $[CuL(OH)]^+$ [6] [7] have been suggested for the complexation of Cu^{2+} to related diamines. Also, hydrolysis of Cu^{2+}_{aq} to $[Cu(OH)]^+$ and/or $[Cu_2(OH)_2]^{2+}$ [18] [19] would seem a reasonable possibility, since complexation with L does not start below pH 5 and substantial amounts of Cu^{2+}_{aq} remain even at pH 6.5. Potentiometric and spectrophotometric data thus were carefully checked for the significance of any of the above species. The results are: $[CuL_2(OH)]^+$ is completely rejected based on either type of data. We assume that the corresponding species postulated with en [9] is an artefact or, more likely, unrecognized formation of $[CuL(OH)_2]$ *(Eqn. 1)* under the influence of a strong base. This latter assumption is supported by the practically identical absorption spectra (λ_{max} = 599 nm reported for $[CuL_2(OH)]^+$ [9]; λ_{max} = 589 nm for $[CuL(OH)_2]$, this work, see below).

$$[CuL_2]^{2+} + 2OH^- \rightleftarrows [CuL(OH)_2] + L \qquad (1)$$

Either $[Cu(OH)]^+$ or $[Cu_2(OH)_2]^{2+}$ can be calculated based on the potentiometric or the spectrophotometric data. The equilibrium constants based on potentiometry are quite close to those obtained previously: $\log K(Cu^{2+}_{aq} \rightleftarrows [Cu(OH)]^+ + H^+) = -7.86$ ([18]: -7.97; $\log K(2\,Cu^{2+}_{aq} \rightleftarrows [Cu_2(OH)_2]^{2+} + 2\,H^+) = -11.07$ ([18]: -10.89, [19]: -10.95). The values obtained by spectrophotometry are, however, roughly one order of magnitude less negative. The corresponding spectra are erratic and in general not compatible with a Cu^{2+} complex. Calculated levels of significance are low, normally less than 90% based on the *F* test [20]. These species must, of course, be formed, and maximum concentrations in the order of 1% can be calculated based on literature values. Obviously, this seems to be below the detection limit even for potentiometric and for very high accuracy spectrophotometric data. The most significant *F* values are obtained for $[CuL(OH)]^+$, results for which are also included into *Table 1*. For this species *F* values corresponding to levels of significance around 90 to more than 99% were obtained for all but one batch, and from some but not all batches even reasonable spectra could be calculated. Putting all evidence together, the dimerization constant K_D of $[CuL(OH)]^+$ can be calculated *(Eq. 2)*.

$$2\,[CuL(OH)]^+ \rightleftarrows [Cu_2L_2(OH)_2]^{2+}:\ \log K_D = 4.4 \pm 0.2 \qquad (2)$$

This value may be compared to results obtained earlier for related diamines: *N,N*-diethylethylenediamine: $\log K_D = 3.18$ [7]; *N,N'*-diethylethylenediamine: $\log K_D = 3.58$ [7]; *N,N'*-dimethylethylenediamine: $\log K_D = 3.69$ [8]. We feel, however, that this result should be viewed with due caution and considered as an upper limit for the stability of $[CuL(OH)]^+$, *i.e.* a *lower* limit for the dimerization constant defined by *Eqn. 2*; the dimeric species $[Cu_2L_2(OH)_2]^{2+}$ is strongly dominant over $[CuL(OH)]^+$ under all experimental conditions.

Absorption Spectra and Solution Structures. Absorption spectra (λ_{max}, ε_{max}) based on the model with Cu^{2+} and four complexes are compiled in *Table 2*. Reasonable agreement is obtained from the different batches. The results are, however, somewhat unexpected and need some comment: *a*) $[CuL]^{2+}$, $[Cu_2L_2(OH)_2]^{2+}$, and $[Cu_2L(OH)_2]$ all must contain a two N-donor set and based on the position of amines, H_2O and OH^- in the spectrochemical series should have roughly the same absorption maximum [21] [22]. This is not the case, a shift of 120 nm is observed for the deprotonation of $[CuL]^{2+}$ to $[Cu_2L_2(OH)_2]^{2+}$ or $[CuL(OH)_2]$. *b*) For $[CuL]^{2+}$, λ_{max} of 712 nm is at very low energy compared to 660 nm for $[Cu(en)]^{2+}$ [21], more in line with the predicted absorption for 1:1 chelates with only one N-donor such as $[Cu(gly)]^+$ ($\lambda_{max} = 715$ nm [23]). *c*) The effect observed under *b* may not be ascribed to electronic factors, since an equally remarkable shift in the opposite direction is observed for the 1:2 complexes, where $\lambda_{max} = 498$ nm with our ligand compares with $\lambda_{max} = 550$ nm for $[Cu(en)_2]^{2+}$ [24]. Steric factors must be largely responsible. In fact, the absorbance of $[CuL_2]^{2+}$ is at unusually short wavelengths, approaching those found in solid state spectra of complexes with no axial coordination as in $[CuL_2]^{2+}$ with L = *N,N*-diethylethylenediamine, $\lambda_{max} = 463$ nm [25]. Thus, the *N*-(i-Pr) group in our ligand has profound influence on the solution structure of both $[CuL]^{2+}$ and $[CuL_2]^{2+}$, relative to the complexes with en, and this observation should be borne in mind in complexes with substituted ethylenediamines.

Table 2. *Absorption Maxima λ_{max} and Molar Absorptivities ε_{max} of the Cu^{2+} Complexes*

Batch	[CuL]		[CuL$_2$]		[Cu$_2$L$_2$(OH)$_2$]		[CuL(OH)$_2$]	
	λ_{max} [nm]	ε_{max} [$M^{-1}\cdot cm^{-1}$]	λ_{max} [nm]	ε_{max} [$M^{-1}\cdot cm^{-1}$]	λ_{max} [nm]	ε_{max} [$M^{-1}\cdot cm^{-1}$]	λ_{max} [nm]	ε_{max} [$M^{-1}\cdot cm^{-1}$]
D	711	96	499	127	593	64	590	74
E	708	96	498	129	594	64	590	75
F	714	98	499	127	594	67	590	76
G	715	97	499	127	592	64	592	76
Mean	712	97	499	128	593	65	591	75
2σ	3	1	1	1	1	2	1	1

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