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Spectrophotometric Study of Solution Equilibria between Ammonia and Copper(II) and Nickel(II) Chelates of Aminopolycarboxylic Acids

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The addition of ammonia produces a remarkable change in the visible absorption spectra of copper(II)- and nickel(II)-aminopolycarboxylate chelates. This can be ascribed to the formation of a mixed ligand chelate involving ammonia and the aminopolycarboxylate anion. On the basis of the change in the absorbance of copper(II)- and nickel(II)-aminopolycarboxylate chelates, the solution equilibria between ammonia and these aminopolycarboxylate chelates were investigated. Copper(II) and nickel(II) chelates of ethylenediaminetetraacetic acid (EDTA), *N*-(2-hydroxyethyl)-ethylenediamine-*N,N',N'*-triacetic acid (EDTA-OH), ethylenediaminetetrapropionic acid (EDTP), cyclohexanediaminetetraacetic acid (CyDTA), and diethylenetriaminepentaacetic acid (DTPA) were found to form mixed ligand chelates with a composition of $M(NH_3)Z^{2-n}$. From the intercept of the linear relation between $\log (A_Y-A)/(A-A_M)$ and $\log [NH_3]_f$, the equilibrium constant, K^{NH_3}, defined as $K^{NH_3}=[M(NH_3)Z^{2-n}]/[MZ^{2-n}]\cdot[NH_3]_f$, was determined.

In a previous paper,[1] we studied the effects of ammonia and the thiocyanate ion on the substitution reaction of the nickel(II)-EDTA chelate with Eriochrom Black T (BT). The addition of ammonia or the thiocyanate ion brought about a considerable change in the absorption spectrum of the nickel(II)-EDTA chelate in the visible-light region, and made the substitution reaction of nickel(II)-EDTA chelate more sluggish. This was ascribed to the formation of a mixed ligand chelate involving ammonia or the thiocyanate ion, which is non-reactive in the substitution reaction between the nickel(II)-EDTA chelate and BT.

Ammonia was also found to exert a strong effect on the visible absorption spectra of copper(II) and nickel(II) chelates of EDTA and its related compounds. This also can be attributed to the formation of a mixed ligand chelate involving ammonia. In this paper, a spectrophotometric study of the solution equilibria between ammonia and copper(II) and nickel(II) chelates of aminopolycarboxylic acids will be presented.

Experimental

Reagents. The purification of ethylenediaminetetraacetic acid (EDTA), *N*-(2-hydroxyethyl)-ethylenediamine-*N,N',N'*-triacetic acid (EDTA-OH), ethylenediaminetetrapropionic acid (EDTP), cyclohexanediaminetetraacetic acid (CyDTA), and diethylenetriaminepentaacetic acid (DTPA) and the preparation of their solutions have been described previously.[2-5] The methods of preparing and standardizing metal(II) perchlorate solutions have also been given in previous papers.[2,4] The concentration of the ammonia solution was standardized against a standard hydrochloric acid solution, using Methyl Organge as an indicator. All the other chemicals were of an analytical reagent grade and were used without further purification. The ionic strength of the sample solution was adjusted to 0.30 by adding an appropriate volume of a 1.0 M sodium perchlorate solution.

Apparatus and Experimental Procedures. All the absorption measurements were conducted at 25°C using a Hitachi EPS-3 pen-recording spectrophotometer. The experimental procedures employed were the same as before.[2]

Results and Discussion

The visible spectra of copper(II) and nickel(II) chelates of EDTA, EDTA-OH, EDTP, CyDTA, and DTPA in solutions ($\mu=0.30$) containing an excess amount of un-complexed aminopolycarboxylate are reproduced in Figs. 1 and 2. Copper(II)- and nickel(II)-aminopolycarboxylate chelates showed absorption maxima at about 700 and 370 mμ respectively. When ammonia was added to the metal(II)-aminopolycarboxylate chelate solution, as has previously been observed in the absorption curve of the nickel(II)-EDTA chelate,[1] a remarkable change in the absorbance of these metal(II)-aminopolycarboxylate chelates was also observed. However, the shape of the absorption

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[1] M. Kodama and K. Miyamoto, This Bulletin, **42**, 833 (1969).

[2] M. Kodama and H. Ebine, *ibid.*, **40**, 1857 (1967).

[3] M. Kodama and A. Kimura, *ibid.*, **40**, 1639 (1967).

[4] M. Kodama, *ibid.*, **40**, 2575 (1967).

[5] M. Kodama and C. Sasaki, *ibid.*, **41**, 127 (1968).

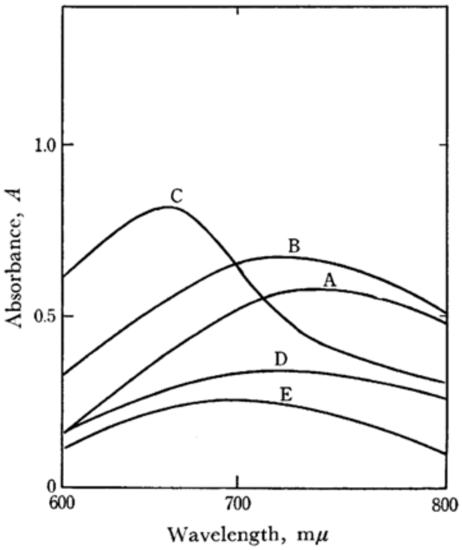


Fig. 1. Absorption spectra of copper(II)-aminopolycarboxylate chelates.
$\mu=0.30$, pH=9.30
Concentration of un-complexed aminopolycarboxylate=10.0 mM
Concentration of copper(II)-aminopolycarboxylate chelate=5.0 mM
A: EDTA, B: EDTA-OH, C: EDTP,
D: CyDTA, E: DTPA

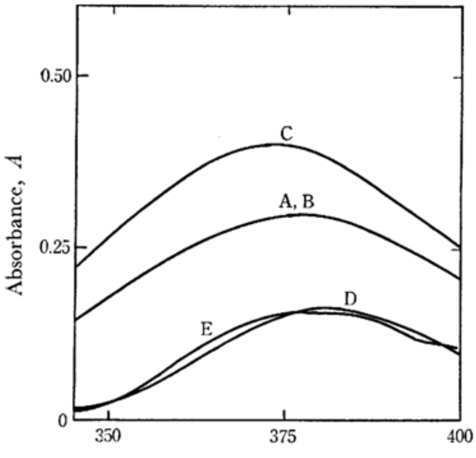


Fig. 2. Absorption spectra of nickel(II)-aminopolycarboxylate chelates.
$\mu=0.30$, pH=9.30
Concentration of un-complexed aminopolycarboxylate=10.0 mM
Concentration of nickel(II)-aminopolycarboxylate chelate=10.0 mM
A: EDTA, B: EDTA-OH, C: EDTP,
D: CyDTA, E: DTPA

spectra was little affected by the addition of ammonia. Typical results obtained in an EDTA-OH system are shown in Figs. 3 and 4. Although the results are not shown here, similar results were also obtained in other systems. In the copper(II)-EDTA-OH system, as is illustrated by the absorption curves in Fig. 3, the absorbance decreased with an increase in the concentration of ammonia until

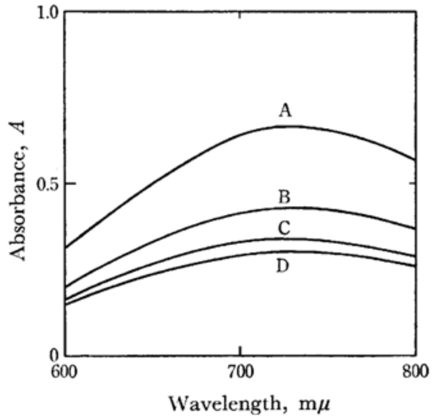


Fig. 3. Effect of ammonia on the absorption spectra of copper(II)-EDTA-OH chelate.
$\mu=0.30$, pH=9.30
Concentration of un-complexed EDTA-OH=10.0 mM
Concentration of copper(II)-EDTA-OH chelate=5.0 mM
Concentration of ammonia
A: no ammonia, B: 15.0 mM, C: 50.0 mM,
D: 100.0 mM

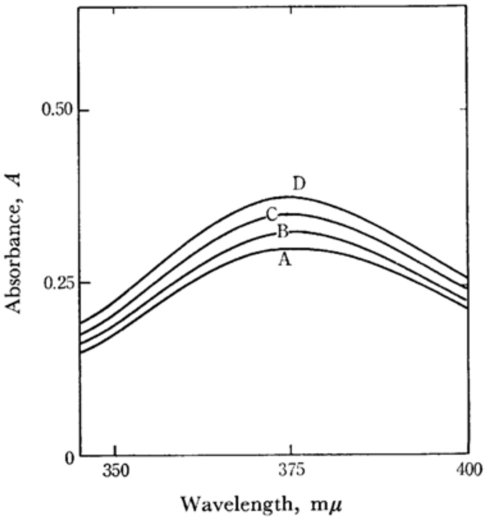


Fig. 4. Effect of ammonia on the absorption spectra of nickel(II)-EDTA-OH chelate.
$\mu=0.30$, pH=9.30
Concentration of un-complexed EDTA-OH=10.0 mM
Concentration of nickel(II)-EDTA-OH chelate=10.0 mM
Concentration of ammonia
A: no ammonia, B: 16.0 mM, C: 30.6 mM,
D: 52.8 mM

it reached its minimum value. On the other hand, in the nickel(II) system, the absorbance in the region from 300 to 450 mμ was found to increase with an increase in the concentration of ammonia until it reached its maximum value (Fig. 4). The above change in the absorbance of metal(II)-aminopolycarboxylate chelates upon the addition of ammonia may be attributed to the formation of a mixed ligand chelate involving ammonia.

As has been discussed previously,[1,2] if the mixed ligand chelate $M(NH_3)Z^{2-n}$ is formed, the following relation can be expected thermodynamically:

$$\log \frac{A_Y - A}{A - A_M} = \log K^{NH_3} + \log [NH_3]_f \qquad (1)$$

where A_Y, A, A_M, K^{NH_3}, and $[NH_3]_f$ have the same meanings as before.[1] Here, $(A_Y-A)/(A-A_M)$ can be equated with $[M(NH_3)Z^{2-n}]/[MZ^{2-n}]$.

When $M(NH_3)_2Z^{2-n}$ and $M(NH_3)Z^{2-n}$ are both formed, the following relation can be derived in place of Eq. (1), provided that the molar extinction coefficients of $M(NH_3)Z^{2-n}$ and $M(NH_3)_2Z^{2-n}$ are the same:

$$K^{NH_3}(1+K^{2NH_3}[NH_3]_f) = \frac{A_Y - A}{A - A_M} \times \frac{1}{[NH_3]_f} \qquad (2)$$

where $K^{2NH_3} = [M(NH_3)_2Z^{2-n}]/[M(NH_3)Z^{2-n}]\cdot[NH_3]_f$ and $(A_Y-A)/(A-A_M)$ can be equated with $[M(NH_3)_iZ^{2-n}]_t/[MZ^{2-n}]$. Here, $[M(NH_3)_iZ^{2-n}]_t$ means the total concentration of mixed ligand chelates.

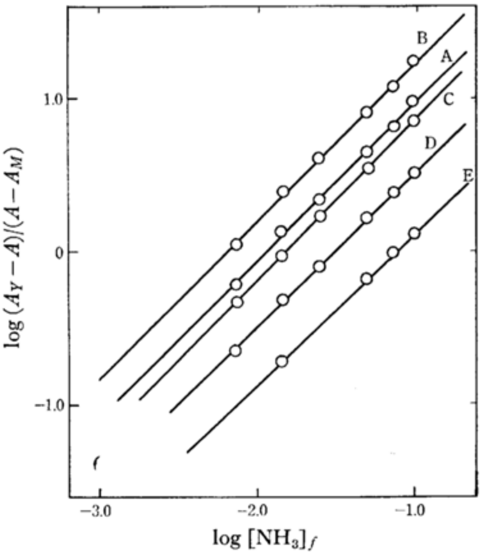


Fig. 5. The plot of $\log (A_Y - A)/(A - A_M)$ against $\log [NH_3]_f$.
$\mu = 0.30$, pH = 9.30
Concentration of copper(II)-aminopolycarboxylate chelate = 5.0 mM
Concentration of un-complexed aminopolycarboxylate = 10.0 mM
A: EDTA, B: EDTA-OH, C: EDTP,
D: CyDTA, E: DTPA

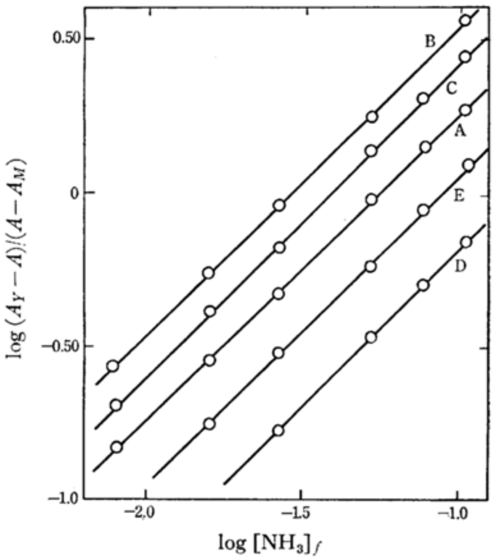


Fig. 6. The plot of $\log (A_Y - A)/(A - A_M)$ against $\log [NH_3]_f$.
$\mu = 0.30$, pH = 9.30
Concentration of nickel(II)-aminopolycarboxylate chelate = 10.0 mM
Concentration of un-complexed aminopolycarboxylate = 10.0 mM
A: EDTA, B: EDTA-OH, C: EDTP,
D: CyDTA, E: DTPA

The effect of ammonia on the absorption curves of copper(II)- and nickel(II)-aminopolycarboxylate chelates was studied in the ammonia concentration range from 15 to 200 mM. The experimental data were then analyzed with the aid of Eqs. (1) and (2). In both cases, only the plot of $\log (A_Y-A)/(A-A_M)$ against $\log [NH_3]_f$ gave a straight line with a slope of unity. The results are shown in Figs. 5 and 6. This clearly indicates that, under the present experimental conditions, only the mixed ligand chelate $M(NH_3)Z^{2-n}$ is formed.

$\log K^{NH_3}$ values were evaluated from the $\log (A_Y-A)/(A-A_M)$ values at $\log [NH_3]_f = 0$; they are listed in Table 1. At lower ammonia concentrations, the decrease in the concentration of un-complexed ammonia due to the formation of the mixed ligand chelate should be taken into consideration. Hence, the correct concentration of un-complexed ammonia at lower ammonia concentrations was calculated by using successive approximations with the aid of the following relations:

$$\frac{[NH_3]_i - X}{(\alpha)_{HNH_3}} = [NH_3]_f \qquad (3a)$$

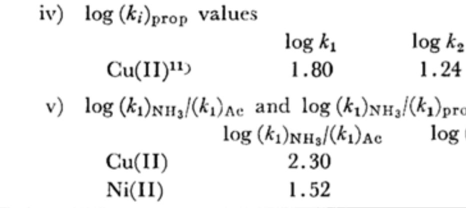
$$\frac{K^{NH_3}}{(\alpha_H)_{NH_3}}\cdot X^2 - \left[\frac{K^{NH_3}}{(\alpha_H)_{NH_3}}([NH_3]_i + MZ^{2-n}]) - 1\right]\cdot X + \frac{K^{NH_3}}{(\alpha_H)_{NH_3}}([NH_3]_i \times [MZ^{2-n}]) = 0 \qquad (3b)$$

TABLE 1. EQUILIBRIUM CONSTANTS AND $(k)_{NH_3}/(k)_{Ac}$ OR $(k)_{NH_3}/(k)_{prop}$

i) $\log K^{NH_3}$ values						
	EDTA	EDTA-OH	EDTP	CyDTA	DTPA	
Cu(II)	1.96	2.23	1.85	1.55	1.10	
Ni(II)	1.25	1.53	1.41	0.82	1.05	
ii) $\log (k_i)_{NH_3}$ values						
	$\log k_1$	$\log k_2$	$\log k_3$	$\log k_4$	$\log k_5$	$\log k_6$
Cu(II)6)	3.97	3.32	2.71	1.95	−0.61 7)	−2.66 8)
Ni(II)6)	2.59	2.04	1.53	0.99	0.55	−0.26
iii) $\log (k_i)_{Ac}$ values						
	$\log k_1$	$\log k_2$				
Cu(II)9)	1.67	0.23				
Ni(II)10)	1.07	0.67				
iv) $\log (k_i)_{prop}$ values						
	$\log k_1$	$\log k_2$				
Cu(II)11)	1.80	1.24				
v) $\log (k_1)_{NH_3}/(k_1)_{Ac}$ and $\log (k_1)_{NH_3}/(k_1)_{prop}$						
	$\log (k_1)_{NH_3}/(k_1)_{Ac}$	$\log (k_1)_{NH_3}/(k_1)_{prop}$				
Cu(II)	2.30	2.11				
Ni(II)	1.52	—				

where $(\alpha_H)_{NH_3}$ is the (α_H) value of ammonia; $[NH_3]_i$, the initial concentration of ammonia, and $[MZ^{2-n}]$, the concentration of the metal(II)-aminopolycarboxylate chelate.

In EDTA, EDTP, and CyDTA system, if these aminopolycarboxylates act as hexadentate ligands and if metal(II)-aminopolycarboxylate chelates have octahedral configurations, the formation of the mixed ligand chelate with ammonia will always involve the breakage of one metal(II)-oxygen (carboxylate) bond and the subsequent formation of one metal(II)-nitrogen (ammonia) bond. Therefore, the mixed ligand chelate would have one of the two structures shown in Fig. 7.



I II

Fig. 7. The structure of a mixed ligand chelate.

As is illustrated by the successive formation constants of copper(II)-ammine complexes,6) if the structure I is assumed for the copper(II) chelate, the equilibrium constant, K^{NH}, must be very small because of the expected Jahn-Teller distortion of the copper(II) chelate. On the other hand, if the structure II fits, the equilibrium constant is expected to have a value nearly identical with $(k_1)_{NH_3}/(k_1)_{Ac}$. Here, $(k_1)_{NH_3}=[Cu(NH_3)^{2+}]/[Cu^{2+}]\cdot[NH_3]_f$, $(k_1)_{Ac}=[Cu(Ac)^{+}]/[Cu^{2+}]\cdot[Ac^-]_f$ and $[Ac^-]_f$ denotes the concentration of un-complexed acetate ions. From the thermodynamic point of view, $(k_1)_{NH_3}/(k_1)_{Ac}$ corresponds to the following chemical equilibrium, where an acetate ion replaced by ammonia gains its complete translational, rotational, and conformational freedom:

$$CuZ(Ac)^{1-n} + NH_3 = Cu(NH_3)Z^{2-n} + Ac^- \qquad (4)$$

In the formation of the mixed ligand chelate between metal(II)-aminopolycarboxylate chelate and ammonia, however, the $-CH_2-COO^-$ group of the aminopolycarboxylate anion replaced by ammonia obtains in part its freedom of translation, rotation, and conformation. Therefore, in the above discussion, the instability due to the fact that the $-CH_2-COO^-$ group gains less translational, rotational and conformational freedom should be taken into consideration. Because of the lack of knowledge on the entropy effect described above, we can not estimate the instability due to the entropy loss quantiatively or even semi-quantitatively. At least, however, from the thermodynamic point of view, K^{NH_3} can safely be expected to be smaller than the $(k_1)_{NH_3}/(k_1)_{Ac}$ value. In spite of the rather rough approximation, however, the agree-

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6) A. Ringbom, "Complexation in Analytical Chemistry," Insterscience Publishers, New York (1963), p. 301.

7) J. Bjerrum, *Kgl. danske Vindenskab Selskab, mat-fys. Medd.*, **12**, No. 15 (1934).

8) J. Bjerrum, C. J. Ballhausen and C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 1276 (1954).

9) N. Tanaka and K. Kato, This Bulletin, **33**, 417, 1412 (1960).

10) S. K. Siddhanta and S. N. Baberjee, *J. Indian Chem. Soc.*, **35**, 423, 427 (1958).

11) D. L. Marten and F. J. C. Rossotti, unpublished results.

ment between the observed K^{NH_3} value and the calculated $(k_1)_{NH_3}/(k_1)_{Ac}$ value was satisfactory (Table 1). This agreement may confirm the latter structure, II, for the copper(II) chelate. In the EDTP system, $(k_1)_{prop}$, defined as $[Cu(prop)^+]/[Cu^{2+}]\cdot[prop^-]_f$, was used in place of $(k_1)_{Ac}$. Here, the smaller K^{NH_3} values for the CyDTA and DTPA systems can be ascribed to the steric effect due to the cyclohexane ring of CyDTA and the $-CH_2-CH_2-N(CH_2-COO^-)-CH_2-CH_2-N(CH_2-COO^-)_2$ group of DTPA. It is also interesting to note that the K^{NH_3} value of the EDTA-OH chelate is approximately twice that of the EDTA chelate. This may be attributed to the fact that, statistically, ammonia is expected to form a mixed ligand chelate more easily with the EDTA-OH chelate than the EDTA chelate.

In the nickel(II) system, as nickel(II)-aminopolycarboxylate and ammine complexes are essentially octahedral, no definite conclusion about the location of coordinated ammonia in the mixed ligand chelate can be drawn on the basis of a comparison of the observed K^{NH_3} value with the $(k_1)_{NH_3}/(k_1)_{Ac}$ value.