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The Near-ultraviolet Absorption of Aqueous Solution of Copper(II) Ammine Complex with an Excess of Ammonia

Masatomi SAKAMOTO* and Sigeo KIDA
Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Fukuoka 812

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In 1941 Kubota[1] observed absorption spectra of copper(II) ammine complex in aqueous solutions with various concentration of ammonia, and found that an absorption appears in the near-ultraviolet region (~31 kK) at the presence of some excess ammonia. Kubota attributed the origin of this absorption to the formation of *trans*-$[Cu(NH_3)_4(OH)_2]$. However, his conclusion appears to be based on an old-fashioned theory, and therefore, it was attempted in this study to clarify the origin of the band in the light of the modern ligand field theory.

Recently, Kida *et al.*[2,3] studied some binuclear copper(II) complexes bridged with two alkoxo or hydroxo groups, and concluded that a band at the near-ultraviolet region (28—31 kK) is attributable to the charge transfer transition from nonbonding π-orbitals of bridged oxygen atoms to copper ions. Thus, it is expected that the origin of the near-ultraviolet band observed for copper(II)-ammonia solution should reasonably be explained by a similar basis to that of the above cases.[2,3]

Results and Discussion

Figure 1 shows the near-ultraviolet absorption spectra of copper sulfate with various concentration of ammonia. The result qualitatively agrees with that reported by Kubota. As seen in Fig. 1 the solution of $Cu/NH_3 = 1/10$ showed the maximum absorption at 31.5 kK.

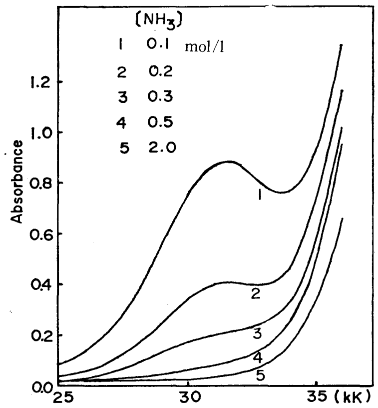

Fig. 1. UV spectra of 0.01 M $CuSO_4$ in aqueous ammonia solutions.

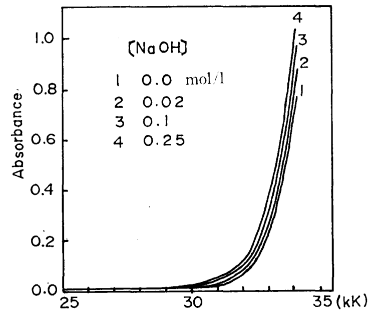

Fig. 2. UV spectra of aqueous solutions containing 0.01 M $CuSO_4$ and 0.1 M ethylenediamine at various OH^- concentrations.

However, in the copper(II)-ethylenediamine solution, as indicated in Fig. 2, no specific band was observed in the ultraviolet region (28—31 kK) even at the addition of sodium hydroxide. If the near-ultraviolet absorption were due to the formation of $[Cu(NH_3)_4(OH)_2]$ as Kubota concluded,[1] a similar absorption should have been observed for the solutions of Fig. 2 where $[Cu\ en_2(OH)_2]$ should exist in some extent. Therefore, it is obvious that the band is not due to the *trans*-coordination of two hydroxide ions.

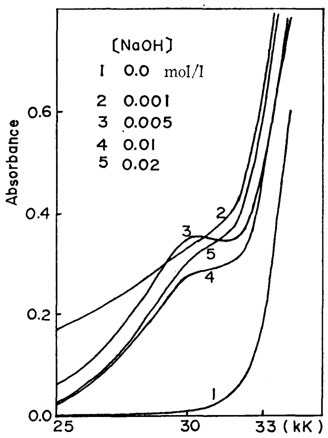

Fig. 3. UV spectra of aqueous solutions containing 0.01 M $CuSO_4$ and 0.018 M ethylenediamine at various OH^- concentrations.

As shown in Fig. 3, however, in the copper(II)-ethylenediamine solution with the mole ratio of 1 : 1.8, a remarkable absorption was observed at 30.8 kK when sodium hydroxide was added. From this fact and the results of our previous studies,[2,3] we assume that the band is due to partially formed di-μ-hydroxo-bis(ethylenediamine)dicopper(II) ion. Considering from

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* Present address: Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Bunkyo-cho, Matsuyama 790.

[1] M. Kubota, *Nippon Kagaku Kaishi*, **62**, 509 (1941).

[2] Y. Ishimura, Y. Nonaka, and S. Kida, This Bulletin, in press.

[3] S. Kida, Y. Nishida, and M., Sakamoto, This Bulletin, **46**, 2428 (1973).

the stepwise stability constants[4] an appreciable amount of $[\mathrm{Cu\ en\ aq}]^{2+}$ is present in the solution of Cu/en $=1/1.8$ (where aq denotes "aquated"). Accordingly, addition of sodium hydroxide to this solution will lead to formation of the dihydroxo-bridged binuclear complex. Further addition of sodium hydroxide may cause destruction of the binuclear structure, accompanying the decrease of the near-ultraviolet band, as observed in Fig. 3. Recently, the formation of the dihydroxo-bridged binuclear complex under a similar condition was proved by the potentiometric study of Barbucci *et al.*[5]

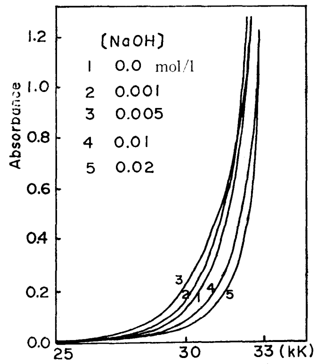

Fig. 4. UV spectra of aqueous solution containing 0.01 M $CuSO_4$ and 0.01 M diethylenetriamine at various OH^- concentrations.

In a solution of copper(II)-diethylenetriamine solution with the 1:1 ratio the dihydroxo-bridged binuclear complex is not liable to be formed even at a high pH region, but only mononuclear complexes, such as $[\mathrm{Cu\ dien\ aq}]^{2+}$ and $[\mathrm{Cu\ OH\ dien\ aq}]^{+}$, are formed. In fact, as shown in Fig. 4, no appreciable near-ultraviolet band was observed in the spectra of the copper(II)-diethylenetriamine solutions of various OH^- concentrations. This is supporting our view for the origin of the near-ultraviolet band, and eliminating the possibility that a mononuclear complex with hydroxide ion at an in-plane coordinating position, such as $[\mathrm{Cu(OH)_2\ en\ aq}]$, $[\mathrm{Cu\ OH\ en\ aq}]^{+}$ or $[\mathrm{Cu\ OH\ dien\ aq}]^{+}$, is the origin of the near-ultraviolet band.

From the above discussion we may conclude that the absorption band at the near-ultraviolet region observed for the aqueous copper(II)-ammonia solution is attributable to the partially formed binuclear complex $[(NH_3)_2Cu(OH)_2Cu(NH_3)_2]^{2+}$. The decrease of intensity of the absorption at the very high concentration of ammonia can be well elucidated in terms of the conversion of the binuclear species into the mononuclear tetraammine complex.

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[4] "Stability Constants of Metal-ion Complexes," Sec. II, compiled by A. E. Martell, Special Publication of the Chem. Soc., London (1964), p. 371.

[5] R. Barbucci, L. Fabbrizzi, and P. Paoletti, *J. Chem. Soc.*, Dalton, **1972**, 740.