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Infrared Spectra and the Structure of Copper Biuret Complexes

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Cupric ion reacts with biuret in an alkaline solution, giving two chelate compounds, *i.e.*, red crystals, $Na_2[Cu(C_2H_3N_3O_2)_2] \cdot 4H_2O$, and violet crystals, $Na[Cu(C_2H_3N_3O_2)(OH)(OH_2)] \cdot H_2O$. The infrared and the visible absorption spectra of these complexes have been observed. From these measurements, it is concluded that ligand biuret molecules in the red complex act as bidentate groups coordinated with the metal ion through nitrogen atoms of the end NH groups. In the violet complex, the rest of the positions in the coordination square are occupied by OH and OH_2 groups.

Introduction

Biuret was first obtained by Wiedemann[1] in 1848 and since then the characteristic color reaction in basic solutions with Cu^{2+} ion has been well known (biuret reaction). Spectroscopic studies on this reaction have been so far mainly concentrated in the visible or ultraviolet regions[2] and no infrared absorption study has yet been reported.

We have isolated two complexes by changing the conditions of the biuret reaction. The purpose of this study is to obtain evidence relating to the structure of these complexes from their infrared and visible absorption spectra.

Experimental

Complexes used were prepared according to the usual manner.[3] Depending upon the conditions, the following two complexes were obtained. Aqueous solution which contains $CuCl_2$, biuret, and NaOH in mole ratios of 1:2:4 displays a red color and from this solution the red crystals were obtained. The aqueous solution having the mole ratios of 1:1:4 shows a violet color and gave violet crystals. The effect of the amount of alkali on the biuret reaction has been discussed by Sone, *et al.*[2] In the present study, the alkali was added in excess with respect to the metal ion.

Red crystals. *Anal.* Calcd. for $Na_2[Cu(C_2H_3N_3O_2)_2] \cdot 4H_2O$: C, 12.53; H, 3.68; N, 21.90. Found: C, 13.33; H, 3.78; N, 21.85. Violet crystals. *Anal.* Calcd. for $Na[Cu(C_2H_3N_3O_2)(OH)(OH_2)] \cdot H_2O$: C, 9.98; H, 3.35; N, 17.46. Found: C, 10.67; H, 3.33; N, 17.64.

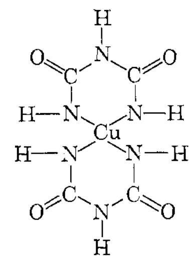
Infrared absorption spectra were measured in Nujol and in hexachlorobutadiene mulls over their proper regions by means of a Perkin-Elmer Model 21 spectrophotometer with a sodium chloride prism. Visible absorption spectra were measured on aqueous solutions of these complexes by means of a Hitachi EPS-2U spectrophotometer.

Results and Discussion

The infrared absorption spectrum of the red complex is shown in Fig. 1 and the observed frequencies are listed in Table I.

Kuroda, *et al.*,[4] have reported the infrared absorption spectra of Cu– and Ni–oxamide complexes. According to their results, ligand oxamide molecules in those complexes act as bidentate groups coordinated with central metal ions through nitrogen atoms, and the coordinated NH stretching frequencies are observed at 3310 and 3320 cm.$^{-1}$ in Cu– and Ni–oxamide complexes, respectively. Thus, the observed band at 3320 cm.$^{-1}$ in the red Cu–biuret complex most likely is NH stretching vibrations. Consequently, in the case of the Cu–biuret complex, it would appear that nitrogen atoms of the end NH groups and the ligands act as bidentate groups as in the case of the oxamide complexes.

This conclusion is consistent with the result of the X-ray analysis on the biuret complex carried out by Freeman, *et al.*[5] Consequently, the red complex can be represented as follows, in which the biuret molecules have a *cis-cis* configuration.



As is seen from this figure, the vibration of the central imide type NH group must be analogous to that of cyclic imides. The frequency of this cyclic imide type NH stretching vibration is generally lower than that of amide type NH stretching vibration and has been assigned at about 3200 cm.$^{-1}$ in the condensed phase.[6,7] Therefore, the band at 3220 cm.$^{-1}$ in the Cu–biuret complex can be assigned to this vibration.

Tentative assignments for the vibrations below 2000 cm.$^{-1}$ have been made by analogy to related compounds such as urea,[8] succinimide,[7] maleimide,[7] *cis*-N-methylformamide,[9] and the Cu–oxamide complex[4] and are summarized in Table I.

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(1) G. Wiedemann, *Ann.*, **68**, 324 (1848).

(2) K. Kato, Y. Komuro, and K. Sone, *Chem. Soc. Japan, Pure Chem. Sect.*, **75**, 1134 (1954); **76**, 1034 (1955); **78**, 896 (1957).

(3) For instance, L. F. Fieser and M. Fieser, "Textbook of Organic Chemistry," Asian Edition, Maruzen Co. Ltd., 1952, p. 376.

(4) Y. Kuroda, M. Kato, and K. Sone, *Bull. Chem. Soc. Japan*, **34**, 877 (1961).

(5) H. C. Freeman, J. Smith, and J. Taylor, *Nature*, **184**, 707 (1959).

(6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 208.

(7) T. Uno and K. Machida, *Bull. Chem. Soc. Japan*, **35**, 276 (1962).

(8) A. Yamaguchi, T. Miyazawa, T. Shimanouchi, and S. Mizushima, *Spectrochim. Acta*, **10**, 170 (1957).

(9) I. Suzuki, *Bull. Chem. Soc. Japan*, **35**, 540 (1962).

TABLE I

OBSERVED INFRARED ABSORPTION FREQUENCIES AND THEIR TENTATIVE ASSIGNMENTS FOR THE RED COMPLEX[a]

Frequency, cm.$^{-1}$	Tentative assignments
3370 w	ν_{OH} (water of crystallization)
3320 s	ν_{NH} (coordinated)
3220 s	ν_{NH} (imide type)
3050 w	1590 + 1460 or 1655 + 1460
2890 w	1460 × 2
2560 w	1375 + 1235
1700 bd	δ_{OH} (water of crystallization)
1655 s	$\nu_{C=O}$ (out-of-phase)
1590 s	$\nu_{C=O}$ (in-phase)
1460 s	ν_{CN} (in-phase)
1375 s	ν_{CN} (out-of-phase) + δ_{NH} (imide type)
1253 s	ν_{CN} (out-of-phase) + δ_{NH} (imide type)
1235 s	ν_{CN} (out-of-phase) + δ_{NH} (imide type)
1150 w	δ_{NH} (coordinated)
975 w	ν_{CN} (in-phase)
775 m	π_{NH} (coordinated)
763 m	π_{NH} (imide type)
745 m	$\delta_{C=O}$

[a] s, strong; m, medium; w, weak; bd, broad; ν, stretching; δ, in-plane deformation; π, out-of-plane deformation.

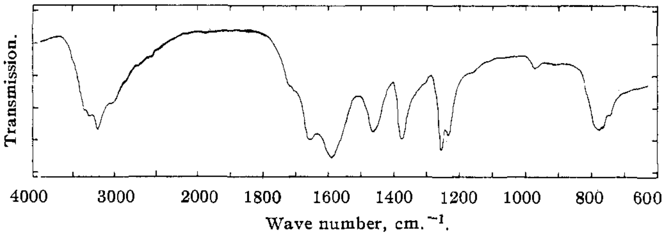


Fig. 1.—Infrared absorption spectrum of the red complex.

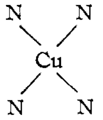
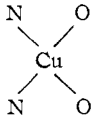
The infrared absorption spectrum of the violet complex is similar to that of the red complex and is not shown. Minor differences are naturally expected because of the different compositions between the red and violet complexes, but the general similarity can be interpreted as indicating the configuration of the ligand molecules in these complexes is essentially the same. In other words, the ligand biuret molecule acts as a bidentate group coordinated with the metal ion through nitrogen atoms of the end NH groups in the violet complex as in the red complex.

Visible absorption spectra were measured on the aqueous solutions of these complexes and the band maxima are given in Table II.

According to the results of Sone, *et al.*,[2] λ_{max} is 505 mμ when four nitrogen atoms are coordinated with Cu^{2+} ion, while it is 570 mμ in the case of two nitrogen and two oxygen atoms. Although the absorption curves are very broad, it can be said that the present results agree with those of Sone, *et al.*[2] The evidence thus indicates that two positions in the coordination square of the violet complex are occupied by oxygen atoms. The study of the effect of alkali on the biuret reaction carried out by Sone, *et al.*,[2] the study of Ley, *et al.*,[10] and the analytical results in this study suggest that the most probable structure is the one in which each of the OH and OH_2 groups is coordinated through the oxygen atom in this violet complex.

TABLE II

OBSERVED λ_{max} OF COPPER COMPLEXES IN AQUEOUS SOLUTIONS

	Red	Violet
Observed, mμ	515	560
Sone, *et al.*,[2] mμ	505	570
Type		

Conclusion

The infrared absorption spectra of two copper complexes formed by the biuret reaction have been recorded in the region from 4000 to 650 cm.$^{-1}$.

The red complex has the composition of Cu:biuret in a ratio of 1:2. Comparing the spectrum with those of the related compounds, it is concluded that the coordination has occurred through nitrogen atoms of the end NH groups.

The violet complex has the composition of Cu:biuret in a ratio of 1:1 and gives almost identical infrared absorptions with those of the red one. From this result, together with the measurements in the visible region, it is concluded that the configuration of the ligand molecule is the same as in the red complex and the other two positions in the coordination square are occupied by OH and OH_2 groups.

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(10) H. Ley and F. Werner, *Ber.*, **46**, 4040 (1913).