of the whole molecule for a given normal mode of vibration ($Q\lambda$), may be expressed as[13]

$$T = \frac{1}{2}\dot{Q}_\lambda^2\Sigma'(G^{-1})_{kl}kL_{k\lambda}L_{l\lambda}$$

$$V = \frac{1}{2}Q_\lambda^2\Sigma F_{kl}L_{k\lambda}L_{l\lambda}$$

where $(G^{-1})_{ii}L_{i\lambda}^2$ and $F_{ii}L_{i\lambda}^2$ are the distribution of energies in the coördinate, S_i, in a normal mode of vibration (Q_λ). The results of the calculation of the potential energy distribution, $F_{ii}L_{i\lambda}^2$, for each normal mode of vibration, are shown in Table VI, where figures in italics refer to the largest terms. In this way we determined the nature of each vibration more reasonably.

TABLE VI

THE POTENTIAL ENERGY DISTRIBUTION $F_{ii}L_i^2$ FOR EACH NORMAL MODE OF VIBRATION[a]

(A_{1g})	ν_1	ν_2		
S_1	0.174	*0.119*		
S_2	*2.594*	.008		
(A_{2g})	ν_3			
S_3	*0.036*			
(B_{1g})	ν_4	ν_5		
S_4	*0.033*	*0.0024*		
S_5	*.034*	*.0024*		
(B_{2g})	ν_6	ν_7		
S_6	0.168	*0.116*		
S_7	*2.594*	.008		
(E_u)	ν_8	ν_9	ν_{10}	ν_{11}
S_8	0.176	*0.149*	0.000	0.000
S_9	*2.592*	.010	.000	.000
S_{10}	0.000	.000	.017	*.0025*
S_{11}	.000	.000	*.035*	.0012

[a] The values of force constants are given in the unit of 10^5 dynes/cm.

Assignment.—The absorption bands observed at 3600–3400 cm.$^{-1}$ and at 1630–1600 cm.$^{-1}$ are assigned, respectively, to the stretching and deformation vibrations of the water molecules present in the crystal.[14] There is no doubt as to the assignment of the bands in the 2100 cm.$^{-1}$ region to the various C≡N stretching vibrations.

According to our calculation made for the planar $Pt(CN)_4^=$ ion, we should observe in the absorption spectra no other in-plane fundamental vibration down to the region of 500 cm.$^{-1}$ where the E_u vibration (one of the metal to ligand vibrations) is expected to appear at 519 cm.$^{-1}$. This is nicely shown by our experiment, the difference between the computed value, 519 cm.$^{-1}$, and the observed value, 505 cm.$^{-1}$, being only 3%. One of the in-plane deformation vibrations is expected to appear at 299 cm.$^{-1}$ and this is in complete agreement with our observation of an absorption band at 300 cm.$^{-1}$. The other in-plane deformation vibration with the calculated frequency of 80 cm.$^{-1}$ lies outside the observable region. Therefore, the absorption peak observed at 411 cm.$^{-1}$ is not an in-plane deformation vibration, but one of the out-of-plane vibrations (ν_{12}, ν_{13}).

The determination of the metal to ligand frequencies has been a subject in which inorganic chemists as well as molecular spectroscopists have been interested. As our results described above are based on the experimental data of infrared absorption and the Raman effect as well as the normal vibration calculation with a suitable force field, we can consider that our assignment of the metal to ligand frequency is very reasonable. Furthermore, from the value of the force constant K_1, we can conclude that the metal to ligand bond should be fairly covalent in this cyanide complex.

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(13) I. Nakagawa, *J. Chem. Soc. Japan*, **74**, 243 (1953); Y. Morino and K. Kutchitsu, *J. Chem. Phys.*, **20**, 1809 (1952).

(14) The weak bands at 1630 and 1600 cm.$^{-1}$ of KCN are also due to the trace of water present in the crystal.

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

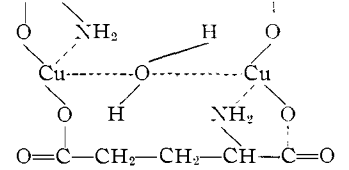
The Structure of Copper Monoglutamate

BY BASUDEB DAS SARMA

RECEIVED AUGUST 4, 1955

The properties of copper monoglutamate are somewhat different from those of the normal α-amino acid complexes of copper in its low solubility, incomplete dehydration, infrared spectra, optical rotation and high electrical resistance in aqueous solution. A structure, explaining all its behavior, shows it to be a dimer,[1] the two copper ions being joined together through two glutamate ions and a water bridge. Water bridges are rather uncommon, but the infrared spectrum shows a definite band at 2880 cm.$^{-1}$, indicating the presence of a strongly coördinated water molecule. This is further verified by the spectrum of the compound where H_2O is replaced by D_2O, the OD band appearing at 2400 cm.$^{-1}$ as compared to 2787 cm.$^{-1}$ in D_2O. This band is absent in the sodium, barium, cobalt and nickel compounds of copper bis-glutamate. Reaction with anhydrous ammonia gas replaces the water molecule by two molecules of ammonia, which cannot function as a bridging group. The barium compound $Ba[CuG_2]$, prepared from the copper monoglutamate, has been employed to isolate the cobalt and nickel compounds. The solubility and electrical resistance of their aqueous solutions shows the sodium, barium, cobalt and nickel compounds to be similar, having the normal structure $M[CuG_2]$, while the copper monoglutamate $\begin{bmatrix} CuG_2Cu \\ H_2O \end{bmatrix}$ and diamino-bis-glutamato-copper $[Cu(NH_3)G_2(NH_3)Cu]$ belong to the bridge type.

(1)



Metal complexes with glutamic acid have been described by various workers. The compounds with Cu(II) were studied by Cheronis,[2] Abderhalden,[3] Pfeiffer,[4] Horrigan[5a] and Rebertus.[5b]

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(2) N. D. Cheronis, U. S. Patent 1,985,977 (Jan. 1, 1934).

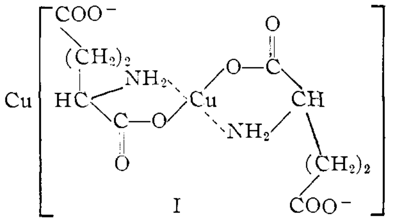
(3) E. Abderhalden and K. Kautzsch, *Z. physiol. Chem.*, **64**, 447 (1910); **68**, 487 (1910); **78**, 333 (1912).

(4) P. Pfeiffer and H. Werner, *ibid.*, **246**, 212 (1937).

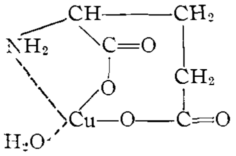
(5) (a) P. A. Horrigan, Thesis, University of Illinois, 1953, (b) R. L. Rebertus, Thesis, University of Illinois, 1954.

Glutamic acid, $HOOCCH_2CH_2CH(NH_2)COOH$, here abbreviated as GH_2, is especially interesting as a complexing agent, since it may behave as either a tri- or bidentate ligand. With copper it gives two different types of compounds, in which the $Cu:GH_2$ ratios are 1:1 and 1:2, respectively. The latter was obtained as the sodium and the barium salts by Pfeiffer and Werner. Copper monoglutamate is the easier compound to obtain, since it forms over a wide range of Cu:glutamate ratios in the *p*H range 5–7.5. From potentiometric, polarographic, absorption, conductivity and magnetic data, Rebertus found that glutamic acid behaves as a tridentate ligand toward nickel(II) and cadmium(II) in their monoglutamato compounds. These complexes are ionic and supposedly tetrahedral.

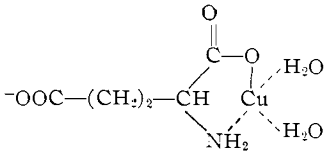
On the assumption that copper(II) has a coördination number of 4, copper monoglutamate may be supposed to have one of the following structures.



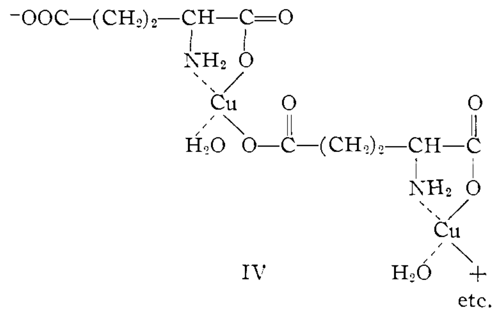
I



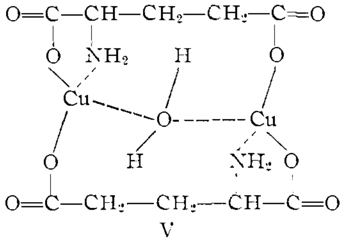
II



III



IV



V

Of these, the first was advanced by Pfeiffer and Werner on the basis of their observation that half of the total copper present is precipitated as hydroxide when excess sodium hydroxide is added. They wrote the reaction $Cu[CuG_2] + NaOH = Cu(OH)_2 + Na_2[CuG_2]$ although they regarded the evidence as inconclusive. In all probability a drastic reaction with excess of strong alkali decomposes the complex, and half of the copper is held in solution as the highly soluble sodium salt of copper bisglutamate which is stable under the circumstances. Rebertus found no evidence from polarographic data for the presence of two types of copper, one coördinated and the other ionic. Polarographic and spectroscopic data for copper monoglutamate and other α-amino acid complexes of copper show that in all probability the ligand is not tridentate to a single copper ion.

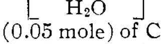
Structure II requires a tetrahedral configuration around the copper, which is uncommon, and is improbable in view of the strong absorption in the region 7000 Å. where other, planar compounds of Cu-monoaminoacid complexes absorb most.[6]

Structures III and IV are proposed by Rebertus as alternatives.

Copper monoglutamate, obtained as blue crystalline $[CuG]\cdot 2H_2O$, (sometimes as $2.5H_2O$), loses 1.5 molecules of water at 90–95° but the remaining half molecule cannot be removed without partial decomposition of the complex. This copper monoglutamate, on reaction with requisite amounts of barium hydroxide and glutamic acid, gives a barium salt that analyzes as $Ba[CuG_2]$. The sodium salt, made in a similar way with sodium hydroxide and GH_2, analyzes as the anhydrous compound. The sodium and barium salts are extremely soluble in water, while $[CuG]\cdot 0.5H_2O$, formulated as $Cu[CuG_2]\cdot H_2O$ by Pfeiffer, is very slightly soluble (0.0006 mole/l.). The following scheme shows a number of derivatives made from the copper monoglutamate complex.

According to Pfeiffer and Werner, copper monoglutamate (A) is to be formulated as $Cu[CuG_2]$, and so should show similarities to the barium, sodium, nickel and cobalt salts (B, C and D). Instead, however, there are some striking differences. Compounds B, C and D are highly soluble in water and are easily dehydrated at 90°, whereas compound A is very sparingly soluble and retains one molecule of water per two copper ions at 95°, even under vacuum. The dimeric formula V, with a water-bridge between two copper ions, explains the retention of water and the reaction with ammonia to take up two molecules of ammonia in place of the one molecule of water. The low solubility would also be expected on the basis of this structure. The conductivity of a dilute solution (0.0005 *M*) of $[CuG]\cdot 0.5H_2O$ is very low compared to the conductivities of B, C and D. Infrared spectra of these compounds show a definite OH band for $[CuG]\cdot 0.5H_2O$ at about 2880 cm.$^{-1}$, which indicates a strong bonding for the coördinated water. Absence of such a band in the spectra of the dehydrated B, C and D as well as in the spectrum of $[CuG\cdot NH_3]$ obtained from $[CuG]\cdot 0.5H_2O$ supports the view.

Experimental



$\left[\underset{H_2O}{CuG_2Cu}\right]\cdot 3H_2O$ **(Compound A).**—A solution of 8.5 g. (0.05 mole) of $CuCl_2\cdot 2H_2O$ in 100 cc. of cold water was added slowly to a solution of 4 g. of sodium hydroxide and 7.5 g. of *l*-glutamic acid. The solution was filtered immediately

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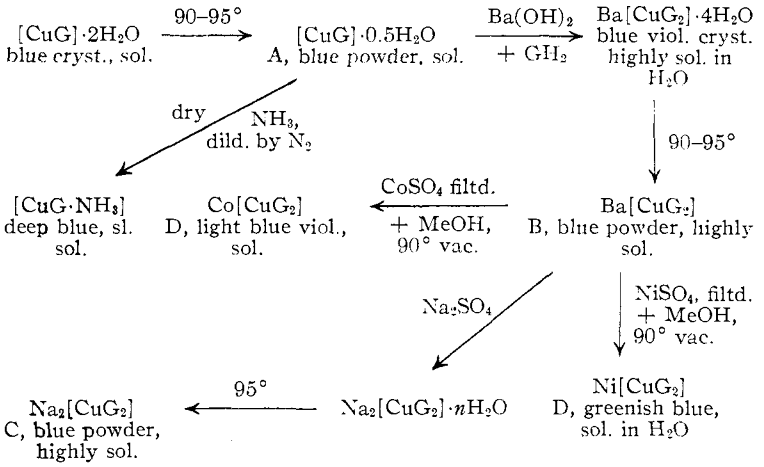
[6] W. C. Waggener, Am. Chem. Soc., 122nd meeting, Atlantic City, N. J., September, 1952.



and allowed to stand overnight at room temperature. Blue rectangular prismatic crystals separated, were filtered by suction, washed with water and finally with absolute alcohol and dried in a vacuum desiccator.

Anal. Calcd. for $\begin{bmatrix}\mathrm{CuG_2Cu}\\ \mathrm{H_2O}\end{bmatrix}\cdot 3H_2O$: C, 24.54; H, 4.49; N, 5.72; Cu, 25.97. Found: C, 24.68; H, 4.55; N, 5.65; Cu, 26.05.

This product, prepared in a different way, was described by Lifschitz and Schoutender,[7] who obtained the compositions $[CuG_2]\cdot 2H_2O$ and $\cdot 2.5H_2O$. The product was found to be soluble to the extent of 0.0005 mole/l. at 25°. When dried at 90–95°, it lost three molecules of water and then the weight remained constant for 8–12 hours at the same temperature or at 90° *in vacuo*.

Anal. Calcd. for $\begin{bmatrix}\mathrm{CuG_2Cu}\\ \mathrm{H_2O}\end{bmatrix}$: C, 27.59; H, 3.7; N, 6.45. Found: C, 27.49; H, 4.01; N, 6.54.

This product was described previously by Pfeiffer and Werner (dried at 100°).

$[Cu(NH_3)G_2(NH_3)Cu]$.—A stream of carefully dried ammonia gas, diluted with nitrogen, was passed over a sample of $\begin{bmatrix}\mathrm{CuG_2Cu}\\ \mathrm{H_2O}\end{bmatrix}$ in a porcelain boat. In about half an hour, the whole mass turned deep blue. The system was freed from excess ammonia by a stream of nitrogen and heated to 85–90° for 1–2 hours while vacuum was applied. The boat was then cooled in a vacuum desiccator over sulfuric acid. The gain in weight was 3.8% compared to the 3.91% calculated for the replacement of one molecule of water by two molecules of ammonia.

Anal. Calcd. for $[Cu(NH_3)G_2(NH_3)Cu]$: C, 26.66; H, 4.44; N, 12.41. Found: C, 27.03; H, 4.60; N, 12.36.

$Ba[CuG_2]\cdot 4H_2O$.—8.7 grams of $\begin{bmatrix}\mathrm{CuG_2Cu}\\ \mathrm{H_2O}\end{bmatrix}$ was ground with 3.3 g. of $Ba(OH)_2\cdot 8H_2O$ and 1.47 g. of *l*-glutamic acid in a mortar and transferred into about 200 cc. of water. The mixture was stirred for 4–8 hours and filtered. To the deep blue solution, cooled in ice, was added 200 cc. of methanol in small portions, stirring it continuously. The deep blue product which separated was washed with methanol by decantation, dried at 90°, powdered, dissolved in a minimum quantity of water and precipitated with methanol. These operations were repeated two or three times. The blue powder was then dissolved in water and the solution was concentrated at room temperature. The solid which separated was filtered with suction, washed with a little cold water, and was dried by suction for 5–6 days on the filter. The dry mass consisted of a mixture of a blue-violet crystalline product and a blue product, which were separated mechanically. It was found that the violet product became blue on drying at 90–95°.

Anal. Calcd. for $Ba[CuG_2]\cdot 4H_2O$: C, 21.31; H, 3.91; N, 4.97. Found: C, 21.77; H, 4.37; N, 5.00. *Anal.* of the dehydrated product. Calcd. for $Ba[CuG_2]$: Cu, 12.89; C, 24.46; H, 2.85; N, 5.7. Found: Cu, 13.03; C, 24.37; H, 3.04; N, 5.64.

The anhydrous product was described by Pfeiffer.

Preparation of CoG_2Cu **(Compound D).**—A concentrated solution of $Ba[CuG_2]$ was mixed with an equivalent quantity of cobalt sulfate dissolved in water. To the filtrate was added an equal volume of methanol, and the solution was cooled and filtered. The light blue-violet product was washed with methanol and then with acetone, and was dried at 85° *in vacuo*. It was readily soluble in water.

Anal. Calcd. for $[CoG_2Cu]$: C, 28.09; H, 3.33; N, 6.65; Cu, 15.35. Found: C, 28.47; H, 3.50; N, 6.42; Cu, 15.11.

Preparation of $NiCuG_2$ **(Compound D).**—This was made in exactly the same way as the cobalt compound. A light greenish-blue powder was obtained, fairly soluble in water.

Anal. Calcd. for NiG_2Cu: C, 28.10; H, 3.33; N, 6.66; Cu, 15.36. Found: C, 28.15; H, 3.97; N, 6.66; Cu, 15.52.

A portion of the green nickel monoglutamate was treated in a solution of copper nitrate in water for 24 hours, during which time the upper part of it turned blue—the color of the copper monoglutamate.

Infrared spectra were recorded with a Perkin-Elmer spectrophotometer, Model 21, using a sodium chloride crystal grating. Samples I–IV were run in perfluoro-lube oil by du Pont, as Nujol blocked the region where O–H (str.) bands are present in these compounds. A broad band at 2880 cm.$^{-1}$ in I indicates strongly coördinated water in the molecule. In order to clarify the point, compound I was prepared in the following way, where H_2O was replaced by D_2O.

Barium copper bis-glutamate, $Ba[CuG_2]$ (0.049 g.), was dissolved in 1 cc. of heavy water (99.8%) and mixed with a solution of 0.016 g. of anhydrous copper sulfate in 1 cc. of heavy water. The mixture was stirred for 10 minutes and the precipitated barium sulfate filtered off. In about an hour, blue crystals of copper monoglutamate separated. They were filtered off and dried *in vacuo* at 80° for an hour. The infrared spectrum of this compound in nujol showed a strong band at 2400 cm.$^{-1}$ compared to 2666–2784 cm.$^{-1}$ reported in the literature for normal O–D (str.) vibration. There is another band at 2455 cm.$^{-1}$ and two small shoulders to the 2400 cm.$^{-1}$ band at 2320 and 2350 cm.$^{-1}$. The band at 2455 probably is the N–D band due to some exchange of the hydrogen on coördinated NH_2. Further investigation of the role of the water molecule in the complex will be communicated later.

A portion of copper monoglutamate, treated with nickel nitrate in the same way, showed no change of color, indicating the copper compound to be much more stable than the nickel compound. Since the change occurred bodily in the solid state, the slightly lower solubility of the copper compound is expected to have no great effect.

Electrical resistance of copper glutamates (0.0005 *M* solutions, 25°).

	Compound	Resistance
1	$\begin{bmatrix}\mathrm{CuG_2Cu}\\ \mathrm{H_2O}\end{bmatrix}$	4.46×10^4
2	$[Cu(NH_3)G_2(NH_3)Cu]$	1.60×10^4
3	$Co[CuG_2]$	0.33×10^4
4	$Ba[CuG_2]$	0.85×10^4
5	$Na_2[CuG_2]$	0.60×10^4

The author expresses his deep gratitude to Dr. John C. Bailar, Jr., for his keen interest in this work, and valuable suggestions. He is indebted to the University of Illinois and the National Science Foundation for financial help and to Mr. J. J. Brader for the infrared spectra.

URBANA, ILLINOIS

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[7] I. Lifschitz and F. L. M. Schoutender, *Rec. trav. chim.*, **58**, 411 (1939).