ing and finally disappears completely. The assignment of this band to one of the nitrito stretching frequencies seems reasonable. The band at 1430 cm.$^{-1}$, however, grows in intensity on aging the sample. As described above, this band is identified with the unsymmetrical stretching vibration of the nitro ligand.

In the spectrum of [Co(NH$_3$)$_5$NO$_2$]Cl$_2$, the broad shouldered absorption band with a peak at 1315 cm.$^{-1}$ results from an overlapping of the two peaks previously assigned to the symmetric nitro and the symmetric ammonia vibrations. A comparison of the spectrum of [Co(NH$_3$)$_5$NO$_2$]Cl$_2$ with

the superposition of the spectra of Na$_3$[CO(NO$_2$)$_6$] and [Co(NH$_3$)$_6$]Cl$_3$ which show absorption bands at 1338 and 1333 cm.$^{-1}$, respectively, makes this evident. Only a single relatively sharp band, however, appears in this region for the freshly prepared nitrito complex. It has been shown that the nitrito isomer on standing several days at room temperature gives rise to an absorption spectrum almost identical with the spectrum of the pure nitro compound. This experimental result can be explained as a change in the coördinating group from (Co–ONO) to (Co–NO$_2$).

NOTRE DAME, INDIANA

Infrared Absorption Spectra of Inorganic Coördination Complexes. VIII. Normal Vibrations of Tetracyanoplatinate(II) Ion[1]

By D. M. Sweeny,[2a] Ichiro Nakagawa, San-ichiro Mizushima[2b] and J. V. Quagliano

RECEIVED APRIL 6, 1955

The infrared absorption spectra of potassium tetracyanoplatinate(II) have been recorded over the range from 2 to 40 μ. In addition to the characteristic peak observed at about 2100 cm.$^{-1}$, there were observed several peaks in the low frequency region. The frequency values of these peaks, together with those of the known Raman lines in the same region, can be brought into good agreement with the values of the calculated normal frequencies of the complex cyanide ion. The calculation was made as a nine-body problem on the basis of the Urey–Bradley field.

Introduction

An understanding of the nature of the metal–ligand bonds in complexes is of fundamental significance in the study of coördination compounds. Investigations of the infrared absorption of metal cyanide complexes offer an interesting problem in this field, since these compounds are expected to show relatively simple spectra. Specifically, cyanide frequencies are present at about 2100 cm.$^{-1}$, but no other fundamentals would be expected to appear until the KBr region, where the metal to ligand bond frequencies appear in the vibrational spectra. That such is actually the case may be expected from the Raman studies of Mathieu[3] who calculated only the A$_{1g}$ vibration of the skeleton. Later, this calculation of skeletal motions was improved by Maccoll,[4] using the modified valence-force field but still regarding C≡N as a dynamical unit. However, the nine-body calculation is not very difficult and, as has been shown in previous papers,[5] the Urey–Bradley field is much more suitable to explain the vibrational spectra of such a molecule. Therefore, the normal frequencies were calculated as a nine-body problem using this field, and the computed frequencies have been compared with those obtained in the present investigation, in the region from 5000 to 250 cm.$^{-1}$ (2 to 40 μ).

(1) For paper VII in this series see THIS JOURNAL, 78, 887 (1956).

(2) (a) Presented in part before the 126th meeting of the American Chemical Society, September, 1954. Supported in part under AEC Contract AT(11-1)-38, Radiation Project of the University of Notre Dame. Abstracted in part from the Ph.D. Thesis of D. M. Sweeny, Notre Dame, 1955. (b) Visiting Professor, from the Faculty of Science, University of Tokyo.

(3) J. Mathieu, J. chim. phys., 36, 308 (1939).

(4) A. Maccoll, Proc. Roy. Soc. N.S.W., 77, 130 (1943).

(5) T. Shimanouchi, J. Chem. Phys., 17, 245, 734, 848 (1949); see also reference 12.

Experimental

Preparation of Compounds.—Potassium tetracyanoplatinate (II) trihydrate, K$_2$Pt(CN)$_4$·3H$_2$O, was prepared (a) according to the method of Meillet.[6]

The analysis was carried out on sample dried in an Abderhalden drier at 110° for 3 days. Anal. Calcd. for K$_2$Pt-(CN)$_4$·^{3}/$_5$H$_2$O: C, 12.51; N, 14.56. Found: C, 12.46; N, 14.56.

(b) The compound was also prepared according to the method of Claus.[7] This preparation gave a product spectroscopically identical with that of the analyzed sample (a). In the region of the OH stretching frequency some slight differences exist which probably are attributable to different degrees of hydration in the two samples investigated.

Absorption Measurements.—Spectra were obtained by means of a Perkin-Elmer, model 21, infrared spectrophotometer, using CaF$_2$, NaCl, KBr and CsBr prisms. Preparation of potassium bromide disks was carried out according to the direction of Stimson and O'Donnell.[8] The disks were used for observation in the region of 2 to 24 μ, and the resulting spectra were checked using Nujol mulls of these compounds. In the spectrum of K$_2$Pt(CN)$_4$·3H$_2$O obtained by the potassium bromide disk technique a few absorption peaks were observed in the region between 1500 and 600 cm.$^{-1}$ which should not appear according to our calculations. The positions and intensities of these peaks depend upon the previous history of the sample. It has been possible to demonstrate that these absorption peaks are due to the water of crystallization and can be avoided by dehydrating the material at 197° in vacuo. Unusual optical behavior of hydrated planar Pt(CN)$_4$$^-$ complex compounds has been reported.[9,10] Tetrahedral metal cyanide complexes examined in this Laboratory do not show these additional absorption peaks.

Beyond 24 μ the Nujol mull technique was employed; however, KBr disks can be used conveniently up to about 32 μ.

(6) A. Meillet, J. Pharm. Chim., [3] 3, 444 (1843).

(7) C. Claus, Ann., 107, 132 (1855).

(8) M. M. Stimson and M. J. O'Donnell, THIS JOURNAL, 74, 1805 (1952); see also J. P. Faust and J. V. Quagliano, ibid., 76, 5346 (1954).

(9) L. A. Levy, J. Chem. Soc., 93, 1446 (1908).

(10) S. Yamada, Bull. Chem. Soc. Japan, 24, 125 (1951).

Results

The spectrum of the $Pt(CN)_4^=$ ion is shown in Fig. 1 and Table I shows the frequency values in cm.$^{-1}$ recorded for potassium tetracyanoplatinate(II) trihydrate together with those for potassium cyanide. This table represents a composite of
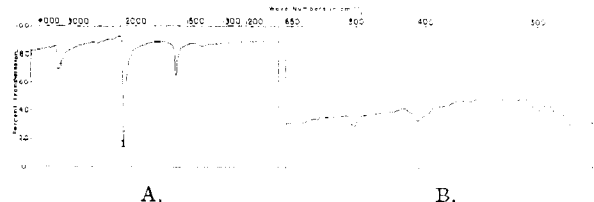

Fig. 1.—Infrared absorption spectra of $K_2Pt(CN)_4 \cdot H_2O$: A, in KBr disk; B, in nujol mull.

the spectra of each of these substances obtained with the four prisms employed.

TABLE I

INFRARED ABSORPTION SPECTRA OF $K_2Pt(CN)_4 \cdot 3H_2O^a$

KCN	$K_2Pt(CN)_4 \cdot 3H_2O^?$	$K_2Pt(CN)_4 \cdot 3H_2O^b$
..	3610 s	3600 s
..	3430 s	3400 s
..	2150 vs	2150 vs
2080 m	2090 sh	2090 sh
1630 w	1630 m	1630 m
1600 w	1610 w	1610 w
..	505 s	505 s
..	411 m	411 m
..	300 m	300 m

^{a} Abbreviations: w = weak; m = medium; s = strong; sh = shoulder; v = very.

Calculation of Normal Vibrations.—The point group of the planar complex ion $(M(CN)_4)^=$ is D_{4h}. Therefore, the twenty-one normal vibrations are grouped into nine classes as shown in Table II, in which the vibrational modes and activities are also shown. The normal modes of the eleven in-

TABLE II

NORMAL VIBRATIONS OF $Pt(CN)_4^=$ ION BELONGING TO EACH CLASS OF SYMMETRY

Class	No. of vibrations	Activity Raman	Activity Infra-red		Vibrational mode^a
A_{1g}	2	+	−	ν_1	$\nu(C≡N)$
				ν_2	$\nu(Pt-C)$
A_{2g}	1	−	−	ν_3	$\delta(Pt-C≡N)$
B_{1g}	2	+	−	ν_4	δ_1
				ν_5	δ_2
B_{2g}	2	+	−	ν_6	$\nu(C≡N)$
				ν_7	$\nu(Pt-C)$
E_u	4	−	+	ν_8	$\nu(C≡N)$
	(degenerate)			ν_9	$\nu(Pt-C)$
				ν_{10}	δ_1
				ν_{11}	δ_2
A_{2u}	2	−	+	ν_{12}	π
				ν_{13}	π
B_{1u}	1	−	−	ν_{14}	π
B_{2u}	1	−	−	ν_{15}	π
E_g	1	+	−	ν_{16}	π
	(degenerate)				

^{a} See Fig. 3 and Tables V and VI. The symbols ν, δ and π are, respectively, stretching, in-plane deformation and out-of-plane deformation vibrations.

plane vibrations $(\nu_1-\nu_{11})$ will be calculated in this paper. The remaining five vibrations $(\nu_{12}-\nu_{16})$ corresponding to out-of-plane motions will be treated elsewhere.

The symmetry coördinates for the in-plane vibrations have been taken as

$$S_1(A_{1g}) = (^1/_2)\Delta(r_{01} + r_{02} + r_{03} + r_{04})$$
$$S_2(A_{1g}) = (^1/_2)\Delta(r_{11}' + r_{22}' + r_{33}' + r_{44}')$$
$$S_3(A_{2g}) = (^1/_2)\Delta(\alpha_{011}' + \alpha_{022}' + \alpha_{033}' + \alpha_{044}')$$
$$S_4(B_{1g}) = (^1/_2)\Delta(\alpha_{102} - \alpha_{203} + \alpha_{304} - \alpha_{401})$$
$$S_5(B_{1g}) = (^1/_2)\Delta(\alpha_{011}' - \alpha_{022}' + \alpha_{033}' - \alpha_{044}')$$
$$S_6(B_{2g}) = (^1/_2)\Delta(r_{01} - r_{02} + r_{03} - r_{04})$$
$$S_7(B_{2g}) = (^1/_2)\Delta(r_{11}' - r_{22}' + r_{33}' - r_{44}')$$
$$S_{8a}(E_u) = (1/\sqrt{2})\Delta(-r_{01} + r_{03}).$$
$$S_{8b} = (1/\sqrt{2})\Delta(-r_{02} + r_{04})$$
$$S_{9a}(E_u) = (1/\sqrt{2})\Delta(-r_{11}' + r_{33}')$$
$$S_{9b} = (1/\sqrt{2})\Delta(-r_{22}' + r_{44}')$$
$$S_{10a} = (^1/_2)\Delta(\alpha_{102} - \alpha_{203} - \alpha_{304} + \alpha_{401})$$
$$S_{10b} = (^1/_2)\Delta(\alpha_{102} + \alpha_{203} - \alpha_{304} - \alpha_{401})$$
$$S_{11a}(E_u) = (1/\sqrt{2})\Delta(-\alpha_{022}' + \alpha_{044}')$$
$$S_{11b} = (1/\sqrt{2})\Delta(\alpha_{011}' - \alpha_{033}')$$

The r's are the changes in bond lengths and the α's the changes in bond angles (see Fig. 2).
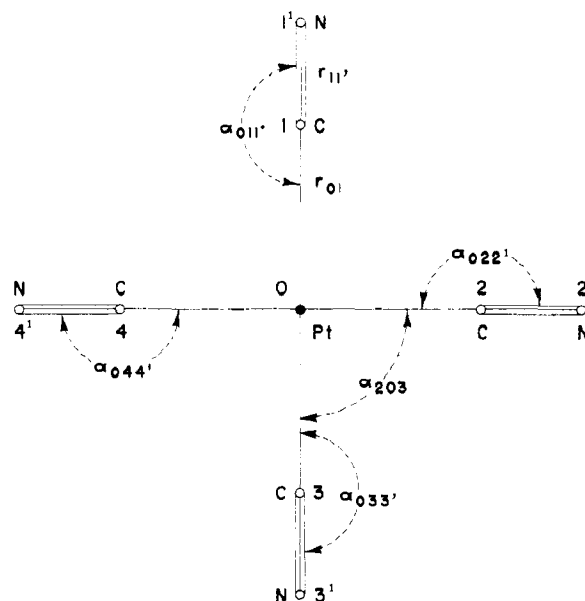

Fig. 2.—Internal coördinates of $[Pt(CN)_4]^=$ ion.

Using these symmetry coördinates, the secular equation is set up according to Wilson's procedure.[11] The G and F matrices of this equation are calculated as:

$$G_{A_{1g}} = \begin{pmatrix} \mu & -\mu \\ -\mu & \mu + \mu' \end{pmatrix}$$
$$F_{A_{1g}} = \begin{pmatrix} k_1 + 2F_q & 0 \\ 0 & k_2 \end{pmatrix}$$
$$G_{A_{2g}} = [\mu'\tau'^2 + \mu(\tau^2 + 2\tau\tau' + \tau'^2)]$$
$$F_{A_{2g}} = (H_2 r r')$$
$$G_{B_{1g}} = \begin{pmatrix} 4\mu\tau^2 & 2\mu(\tau^2 + \tau\tau') \\ 2\mu(\tau^2 + \tau\tau') & \mu'\tau'^2 + \mu(\tau^2 + 2\tau\tau' + \tau'^2) \end{pmatrix}$$
$$F_{B_{1g}} = \begin{pmatrix} (H_1 + 11/20F_q)r^2 & 0 \\ 0 & H_2 r r' \end{pmatrix}$$

(11) E. B. Wilson, J. Chem. Phys., 7, 1047 (1939); 9, 76 (1941).

$$G_{B_{2g}} = \begin{pmatrix} \mu & -\mu \\ -\mu & \mu + \mu' \end{pmatrix}$$

$$F_{B_{2g}} = \begin{pmatrix} k_1 - 1/5\ F_q & 0 \\ 0 & k_2 \end{pmatrix}$$

$$G_{E_u} = \begin{pmatrix} 2\mu_0 + \mu & -\mu & 2\sqrt{2}\mu_0\ \tau & 2\mu_0\tau \\ -\mu & \mu + \mu' & 0 & 0 \\ 2\sqrt{2}\mu_0\ \tau & 0 & 2(2\mu_0 + \mu)\tau^2 & \sqrt{2}[2\mu_0\tau^2 + \mu(\tau^2 + \tau\tau')] \\ 2\mu_0\ \tau & 0 & \sqrt{2}[2\mu_0\tau^2 + \mu(\tau^2 + \tau\tau')] & 2\mu_0\tau^2 + \mu'\tau'^2 \\ & & & + \mu(\tau^2 + 2\tau\tau' + \tau'^2) \end{pmatrix}$$

$$F_{E_u} = \begin{pmatrix} k_1 + 9/10\ F_q & 0 & -9\sqrt{2}/20\ rF_q & 0 \\ 0 & K_2 & 0 & 0 \\ -9\sqrt{2}/20\ rF_q & 0 & (H_1 + 11/20\ F_q)r^2 & 0 \\ 0 & 0 & 0 & H_2rr' \end{pmatrix}$$

Here r and r' are the bond lengths of Pt–C and C≡N, τ and τ' the reciprocals of r and r', μ, μ' and μ_0 the reciprocals of the masses of C, N and Pt, K_1 and K_2 the Pt–C and C≡N bond stretching force constants, H_1 and H_2 the force constants for the deformation of the C–Pt–C and Pt–C≡N bond angles, and F_q the force constant for the non-bonded C . . . C distances. (F_q' is assumed to be equal to $-^1/_{10}\ F_q$.[5,12]) The values of force constants are shown in Table III. These values have

<div align="center">

TABLE III

FORCE CONSTANTS OF Pt(CN)$_4^-$ IN 10^5 DYNES/CM.

K_1 = 3.425 H_1 = 0.080 F_q = 0.050
K_2 = 16.823 H_2 = 0.077

</div>

been selected to give the best fit with the observed Raman frequencies[3] shown in Table IV.

With these values of the force constants, the calculation has been made according to the usual procedure[12] and the results are shown in Table IV.

<div align="center">

TABLE IV

CALCULATED AND OBSERVED FREQUENCIES OF THE Pt(CN)$_4^-$ ION IN CM.$^{-1}$

</div>

	Calcd.	Raman	Infrared
$\nu_1(A_{1g})$	2168	2168	Inactive
$\nu_2(A_{1g})$	465	465	Inactive
$\nu_3(A_{2g})$	249	Inactive	Inactive
$\nu_4(B_{1g})$	338	318	Inactive
$\nu_5(B_{1g})$	91	95	Inactive
$\nu_6(B_{2g})$	2166	2149	Inactive
$\nu_7(B_{2g})$	458	455	Inactive
$\nu_8(E_u)$	2168	Inactive	2150
$\nu_9(E_u)$	519	Inactive	505
$\nu_{10}(E_u)$	299	Inactive	300
$\nu_{11}(E_u)$	80	Inactive	Outside the region of observation

In order to determine the nature of the vibrations, we have calculated the relative amplitude for each of the internal symmetry coördinates in a given normal mode of vibration. The internal symmetry coördinates, S, are related linearly to the normal coördinates, Q, through the matrix expression[12]

$$S = LQ$$

If, therefore, we calculate the elements of the L-matrix for a given normal vibration, we can at once determine the relative amplitude for each symme-

(12) S. Mizushima, "The Structure of Molecules and Internal Rotation," Academic Press, Inc., New York, N. Y., 1954.

try coördinate. Such calculations have been made for all the in-plane vibrations and the results are shown in Table V, where the figures in *italics* refer to the larger amplitudes (see also Fig. 3).

In some of these vibrations the amplitude of a symmetry coördinate is nearly the same as that for another and therefore, the assignment of the vibrational mode such as made in Table II becomes ambiguous. In order to make a more reasonable assignment in such a case, as well as to distinguish between stretching and deformation vibrations, we
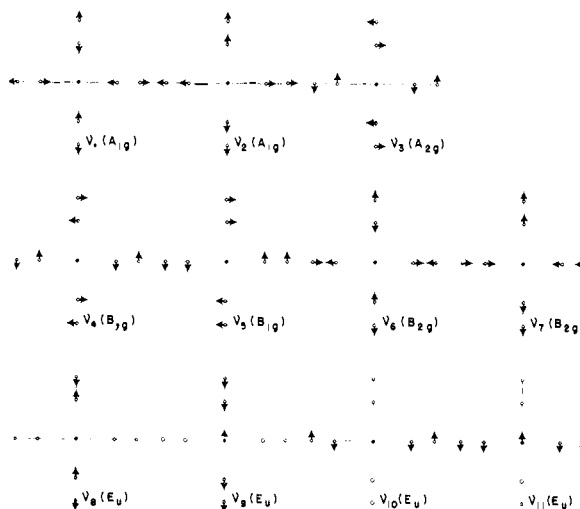

Fig. 3.—In-plane normal vibrations of [Pt(CN)$_4$]$^-$ ion.

have calculated the distribution of energy in the internal symmetry coördinates for each normal vibration.

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TABLE V

THE L-MATRICES OF IN-PLANE NORMAL VIBRATIONS OF Pt(CN)$_4^-$ ION[a]

</div>

(A$_{1g}$)	Q_1	Q_2		
S_1	-0.222	0.184		
S_2	$.393$	$.022$		
(A$_{2g}$)	Q_3			
S_3	0.191			
(B$_{1g}$)	Q_4	Q_5		
S_4	0.289	-0.078		
S_5	$.447$	$.119$		
(B$_{2g}$)	Q_6	Q_7		
S_6	-0.222	0.184		
S_7	$.393$	$.021$		
(E$_u$)	Q_8	Q_9	Q_{10}	Q_{11}
S_8	-0.225	0.207	-0.004	-0.001
S_9	$.392$	$.024$	$-.001$	$.000$
S_{10}	$-.002$	$.038$	$.206$	$-.080$
S_{11}	$-.001$	$.033$	$.457$	$.085$

[a] Calculations have been made with bond lengths in Å., bond angles in radians and masses in atomic weight units. It should be noted that the dimension of L for the stretching coördinates is different from that for the deformation coördinates. However, the deformation displacement of each atom can be obtained by multiplying by the equilibrium bond length in ångström units.

The kinetic energy (T) and potential energy (V)

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

$$T = \frac{1}{2} \dot{Q}_\lambda^2 \Sigma'(G^{-1})_{k_1} k L_{k\lambda} L_{1\lambda}$$

$$V = \frac{1}{2} Q_\lambda^2 \Sigma F_{k_1} L_{k\lambda} L_{1\lambda}$$

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.

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

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$\equiv$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.

(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

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)
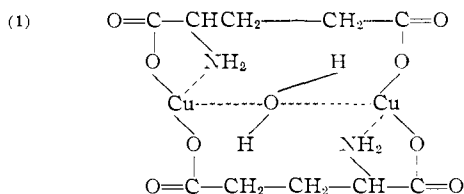
Metal complexes with glutamic acid have been

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

(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.