Contribution from the Department of Chemistry, Illinois Institute of Technology, Technology Center, Chicago, Illinois 60616, U.S.A.

The Normal Coordinate Analysis and Infrared Spectrum of Bis(glycinamido)copper(II)monohydrate *

J. A. Kieft and K. Nakamoto**

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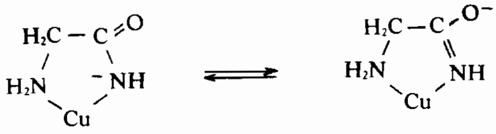
The infrared spectra of bis(glycinamido)copper(II) monohydrate and its N-deuterated analog have been measured from 4000 to 200 cm^{-1}. In order to compare the strength of the Cu–N(amido) and the Cu–N (amino) bonds, a normal coordinate analysis has been carried out on the 1:1 (metal-ring) model. The results indicate that the stretching force constants of the Cu–N(amido) and Cu–N(amino) bonds are 1.02 and 0.88 mdyn/Å, respectively. It has been shown in general that the Cu–N bond becomes stronger as the net negative charge on the nitrogen atom increases.

Introduction

A copper(II) complex of glycinamide ($NH_2CH_2CONH_2$) was isolated by Rising and Yang[1] in 1932. Their analysis revealed that two amide molecules combined with one Cu^{II} ion plus a water molecule to form a neutral complex. Isolation of other metal-amide complexes lacking a water molecule led to the assumption that neutrality was achieved by dissociation of a proton from the amide nitrogen. Potentiometric measurements by Datta and Rabin[2] later confirmed this assumption.

Rosenberg,[3] noting that these changes in the amide molecule should be accompanied by changes in the infrared absorption due to NH stretching vibrations in the amino and amide groups and also by changes in the C=O stretching vibration, investigated bis(glycinamido)copper(II)monohydrate in the 3 and 6 micron regions. He found that chelate formation resulted in a shift of the NH stretching band to a lower frequency. He tentatively assigned two bands at 3329 and 3218 cm^{-1} to the NH stretching vibrations of the amino group and the band at 3106 cm^{-1} to the NH stretching vibration of the amido group. He stressed, however, that the 6 micron (~ 1600 cm^{-1}) region is more suitable for investigation of metal ion influence on the peptide linkage as the bands in this region are not as broad as those in the 3 micron region. This region contains the amide I and II bands,[4] and their normal modes are difficult to assess without normal coordinate analysis. Rosenberg concluded that upon chelation with copper(II), the carbonyl band shifted 90 to 100 cm^{-1} lower, and that this shift was due to a shift of the resonance equilibrium shown below to the right.



Because of the reason mentioned above, it is desirable to confirm such a conclusion through normal coordinate analysis.

Thus far, no previous investigators have discussed the nature of the Cu–N(amido) and Cu–N(amino) bonds in glycinamido complexes. The main purpose of this work is to obtain the force constants for the C=O, C–N, and Cu–N bonds thorugh normal coordinate analysis of bis(glycinamido) copper complex and to compare the strength of two types of bonds as well as to confirm the validity of Rosenberg's conclusion in terms of force constants.

Experimental Section

Preparation of Compounds. 1.0 grams of glycinamide hydrochloride and 0.608 grams of anhydrous cupric chloride were added to 50 ml. of dimethyl formamide (DMF). These reactants do not readily dissolve in DMF, but the reaction was allowed to proceed with the reactants in suspension. 0.761 grams of KOH was dissolved in 10 ml. H_2O and added dropwise to the DMF mixture with constant stirring. A purple precipitate was collected by filtration and washed with cold H_2O, acetone, and ether. It was then dried over P_2O_5 under vacuum for forty-eight hours.

Anal. Calcd. for $[Cu(NH_2CH_2CONH)_2 . H_2O]$: N, 24.61; C, 21.10; H, 5.31. Found: N, 24.41; C, 21.03; H, 5.16.

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(**) Present address, Shell Chemical Company, P.O. Box 305, Union, N. J. 07083.

(1) M. M. Rising and P. S. Yang, *J. Biol. Chem.*, 99, 755 (1932).

(2) S. P. Datta and B. R. Rabin, *Trans. Faraday Soc.*, 52, 1117 (1956).

(3) A. Rosenberg, *Acta Chem. Scand.*, *11*, 1390 (1957).

(4) T. Miyazawa, T. Shimanouchi, and S. Mizushima, *J. Chem. Phys.*, *24*, 408 (1956).

The deutero analog was prepared by recrystallization from 99.84 mole% D_2O.

Determination of Infrade Spectra. A Beckman IR-12 double beam infrared spectrophotometer was used to obtain the spectra in the 4000-200 cm^{-1} region. Calibrations were performed using polystyrene film, water vapor, and carbon dioxide. Sampling techniques employed were both the conventional KBr disc method using 13 mm. diameter discs at various concentrations and the Nujol mull technique using cesium iodide plates.

The following symbols have been utilized in describing the various vibrations: ν, stretching; δ, bending; ρ_r, rocking; ρ_w, wagging; ρ_t, twisting; π, out-of-plane bending; s, symmetric; as, asymmetric; deg., degenerate; and def., deformation. Intensities of absorption bands are symbolized: v, very; b, broad; s, strong; m, medium; and w, weak.

Results and Discussion

Microanalysis has shown that the ratio of glycinamido ligands to metal is two to one. In order to simplify the calculation, the 1:1 (metal/ligand) model shown in Figure 1 has been adopted although the spectra observed are of 1:2 complexes. This approximation is not expected to cause serious errors for most of the vibrations since vibrational coupling between the two chelate rings is negligible for most of the high-frequency vibrations. Previous work[5] has revealed that this type of approximation overestimates the metal-ligand stretching force constant by not more than six per cent.

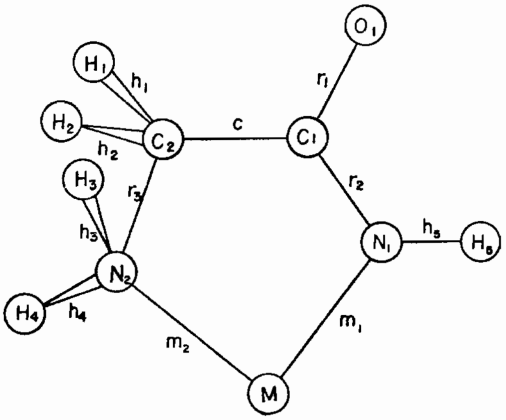

Figure 1. The structure and stretching coordinates of the metal glycinamido chelate ring.

The 11-atom model shown in Figure 1 will have 27 normal vibrations which are classified into two species, 17A′+10A″, under C_s symmetry. This calculation includes all of the in-plane modes and six of the A″ modes (those concerning the angles around the C_2 and N_2 atoms). The out-of-plane vibrations to be expected from N_1–H_5 and $C_1=O_1$ bendings are identifiable from deuteration studies and by comparison with observed frequencies for these modes in bis(oxamido)copper(II)[6] and bis(glycino)-copper(II) complexes,[7] respectively. Other A″ vibrations were eliminated from the calculation since they are out-of-plane skeletal modes which absorb at relatively low frequencies. Figure 1 also shows the 30 internal coordinates used for the calculation of 23 normal vibrations. A simple Urcy-Bradley[8] force field consisting of stretching (K), bending (H), and repulsive (F) force constants was employed to express the F-matrix elements. In addition, two internal tension constants were included for the angles around the C_2 and N_2 atoms. Construction of the G and F matrices,[9] using these 30 internal coordinates and subsequent reduction of redundant coordinates through coordinate transformations (concerning the sum of the angles around N_1, C_1, C_2, N_2, and the sum of the five angles in the ring) left a 19th order A′ and a 6th order A″ matrices. The two remaining redundancies are included as they are complicated functions of bond distances and angles and are not easily removed from the calculation. The symmetry coordinates resulting from these matrix transformations are listed in Table I.

Table I. Symmetry Coordinatem for the Copper(II) Glycinamido Chelate Ring

Species	Symmetry Coordinates	Vibrational Mode
A′	$S_1 = 1/\sqrt{2}(\Delta h_3 + \Delta h_4)$	$\nu(N_2-H)$
	$S_2 = \Delta h_5$	$\nu(N_1-H)$
	$S_3 = 1/\sqrt{2}(\Delta h_1 + \Delta h_2)$	$\nu(C-H)$
	$S_4 = \Delta r_1$	$\nu(C=O)$
	$S_5 = \Delta(HN_2H)$	$\delta(NH_2)$
	$S_6 = \Delta(HC_2H)$	$\delta(CH_2)$
	$^*S_7 = \Delta(MN_1H_5) - \Delta(H_5N_1C_1)$	$\delta(N_1-H)$
	$S_8 = \Delta r_2$	$\nu(C_1-N_1)$
	$S_9 = \Delta r_3$	$\nu(C_2-N_2)$
	$S_{10} = \Delta c$	$\nu(C-C)$
	$^*S_{11} = \Delta(N_1C_1O_1) - \Delta(O_1C_1C_2)$	$\delta(C=O)$
	$^*S_{12} = \Delta(H_3N_2C_2) + \Delta(H_4N_2C_2) - \Delta(H_3N_2M) - (H_4N_2M)$	$\rho_w(NH_2)$
	$^*S_{13} = \Delta(H_1C_2C_1) + \Delta(H_2C_2C_1) - \Delta(H_1C_2N_2) - \Delta(H_2C_2N_2)$	$\rho_w(CH_2)$
	$S_{14} = (1/\sqrt{20})[4\Delta(N_2MN_1) - \Delta(MN_1C_1) - \Delta(N_1C_1C_2) - \Delta(C_1C_2N_2) - \Delta(C_2N_2M)]$	Ring def.
	$S_{15} = 1/2[\Delta(MN_1C_1) + \Delta(N_1C_1C_2) - \Delta(C_1C_2N_2) - \Delta(C_2N_2M)]$	Ring def.
	$S_{16} = 1/2[\Delta(MN_1C_1) - (N_1C_1C_2) + \Delta(C_1C_2N_2) - \Delta(C_2N_2M)]$	Ring def.
	$S_{17} = 1/2[\Delta(MN_1C_1) - \Delta(N_1C_1C_2) - \Delta(C_1C_2N_2) + \Delta(C_2N_2M)]$	Ring def.
	$S_{18} = \Delta m_2$	$\nu(M-N_2)$
	$S_{19} = \Delta m_1$	$\nu(M-N_1)$
A″	$S_{20} = 1/\sqrt{2}(\Delta h_3 - \Delta h_4)$	$\nu(N-H)$
	$S_{21} = 1/\sqrt{2}(\Delta h_1 - \Delta h_2)$	$\nu(C-H)$
A″	$^*S_{22} = \Delta(H_1C_2C_1) - \Delta(H_2C_2C_1) + \Delta(H_1C_2N_2) - \Delta(H_2C_2N_2)$	$\rho_r(CH_2)$
	$^*S_{23} = \Delta(H_3C_2N_2) - \Delta(H_4N_2C_2) + \Delta(H_3N_2M) - \Delta(H_4N_2M)$	$\rho_r(NH_2)$
	$^*S_{24} = \Delta(H_1C_2C_1) - \Delta(H_2C_2C_1) - \Delta(H_1C_2N_2) + \Delta(H_2C_2N_2)$	$\rho_t(CH_2)$
	$^*S_{25} = \Delta(H_3N_2C_2) - \Delta(H_4N_2C_2) - \Delta(H_3N_2M) + \Delta(H_4N_2M)$	$\rho_t(NH_2)$

* These coordinates are not normalized (see refs. 5, 6).

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[5] J. Fujita, A. E. Martell, and K. Nakamoto, *J. Chem. Phys.*, 36, 331 (1962).

[6] P. X. Armendarez and K. Nakamoto, *Inorg. Chem.*, 5, 796 (1966).

[7] R. A. Condrate and K. Nakamoto, *J. Chem. Phys.*, 42, 2590 (1965).

[8] T. Shimanouchi, *J. Chem. Phys.*, 17, 245, 734, and 848 (1949).

[9] E. B. Wilson, J. C. Decius, and P. C. Cross, «Molecular Vibrations», McGraw-Hill, New York (1955).

Table II lists the molecular parameters used to construct the G-matrix elements. Since there is no X-ray data available for this particular complex, these values were selected from similar complexes such as bis(glycino)copper(II)monohydrate[10] and glycylglycino copper(II) trihydrate[11] for which X-ray data are available. The glycylglycino complex also revealed two different C–N distances. The C–N distance in the peptide portion is 0.21 Å less than that of the C–N distance in the amino portion. This lends support to the Rosenberg's conclusion that delocalization occurs upon deprotonation of the amide group and results in a partial double bond character of the C–N bond.

Table II. Molecular Parametsers Used to Evaluate G-Matrix Elements

Bond Distance (Angstroms)	Bond Angle (Degrees)
m$_1$ = 1.87	(N$_2$MN$_1$) = 85.5
m$_2$ = 1.98	(MN$_1$C$_1$) = 115.5
r$_1$ = 1.28	(N$_1$C$_1$C$_1$) = 120.0
r$_2$ = 1.26	(N$_1$C$_1$O$_1$) = 120.0
r$_3$ = 1.47	(C$_2$C$_1$O$_1$) = 120.0
c = 1.47	(C$_1$C$_2$N$_2$) = 109.47
h$_1$ = 1.10	(H$_1$C$_2$C$_1$) = 109.47
h$_2$ = 1.10	(H$_2$C$_2$C$_1$) = 109.47
h$_3$ = 1.00	(H$_1$C$_2$H$_2$) = 109.47
h$_4$ = 1.00	(H$_1$C$_2$N$_2$) = 109.47
h$_5$ = 1.02	(H$_2$C$_2$N$_2$) = 109.47
	(C$_2$N$_2$M) = 109.47
	(H$_3$N$_2$C$_2$) = 109.47
	(H$_4$N$_2$C$_2$) = 109.47
	(H$_3$N$_2$H$_4$) = 109.47
	(H$_3$N$_2$M) = 109.47
	(H$_4$N$_2$M) = 109.47
	(MN$_1$H$_5$) = 122.25
	(C$_1$N$_1$H$_5$) = 122.25

The 19th order A′ and 6th order A″ secular equations of the form $|GF-E\lambda|=0$ were solved by the Householder method[12] using an IBM 7094 computer. The fact that two «zero frequencies» were obtained in the A′ species provides a good check of the calculation. Table III lists the set of force constants which gives the best fit to the observed frequencies of the two isotopic species. Table IV compares the observed frequencies with those calculated by using the set of force constants shown in Table III. Agreement is quite satisfactory; the average error is 1.41 per cent for the 46 observed frequencies with a maximum error of 5.36 percent for the N–D bending mode. The theoretical band assignments given in the last column of Table IV were obtained from the calculation of the potential energy distribution[13] for the non-deuterated species. The results of a similar calculation for the deuterated species show that the pattern of vibrational coupling is different in each species.

Band Assignments. Figure 2 and 3 illustrate the spectra of bis(glycinamido)copper(II)monohydrate and

Table III. Force Constants for Bis(glycinamido)copper(II) Monohydrate (millidynes/angstrom)

Stretching	Bending
K(Cu—N$_2$) = 0.88	H(N$_2$CuN$_1$) = 0.05
K(Cu—N$_1$) = 1.02	H(CuN$_1$C$_1$) = 0.05
K(C$_1$—N$_1$) = 5.30	H(N$_1$C$_1$C$_2$) = 0.30
K(C$_1$—C$_2$) = 2.75	H(N$_1$C$_1$O$_1$) = 0.40
K(C$_2$—N$_2$) = 3.00	H(C$_2$C$_1$O$_1$) = 0.50
K(C=O) = 7.50	H(C$_1$C$_2$N$_2$) = 0.55
K(C—H) = 4.21	H(H$_1$C$_2$C$_1$) = 0.25
K(N$_2$—H$_3$) = 5.80	H(H$_1$C$_2$H$_2$) = 0.39
K(N$_1$—H$_5$) = 5.80	H(H$_1$C$_2$N$_2$) = 0.17
	H(C$_2$N$_2$Cu) = 0.05
Repulsive	H(H$_3$N$_2$C$_2$) = 0.22
F(N...N) = 0.05	H(H$_3$N$_2$H$_4$) = 0.60
F(Cu...C$_1$) = 0.05	H(H$_3$N$_2$Cu) = 0.13
F(N$_1$...C$_2$) = 0.70	H(CuN$_1$H$_5$) = 0.23
F(N$_1$...O$_1$) = 2.00	H(C$_1$N$_1$H$_5$) = 0.11
F(C$_2$...O$_1$) = 0.80	
F(C$_1$...N$_2$) = 0.20	Molecular tension[a]
F(H$_1$...C$_1$) = 0.40	$\varkappa$(N) = −0.05
F(H$_1$...H$_2$) = 0.09	$\varkappa$(C) = +0.05
F(H$_1$...N$_2$) = 0.60	
F(C$_2$...Cu) = 0.05	
F(H$_3$...C$_2$) = 0.32	
F(H$_3$...H$_4$) = 0.04	
F(H$_3$...Cu) = 0.12	
F(Cu...H$_5$) = 0.08	
F(C$_1$...H$_5$) = 0.50	

[a] The units are millidynes-angstroms (see reference 8).

Table IV. A comparison of the Observed and Calculated Frequencies of Bis(glycinamido)copper(II) Monohydrate and its N-Deuterated Analog

	Non-deuterated		Deuterated		Band Assignment[a]
A′	Species				
	Obs.	Calc.	Obs.	Calc.	
ν_1	3338 (s)	3336	2400 (s)	2437	$\nu(_1-H_5)$
ν_2	3225 (s)	3267	2360 (m)	2366	$\nu_s(NH_2)$
ν_3	2930 (w)	2929	2960 (w)	2929	$\nu_s(C-H)$
ν_4	1605 (s)	1604	1180 (m)	1183	$\delta(NH_2)$
ν_5	1570 (s)	1585	1590 (s)	1586	$\nu(C=O)$
ν_6	1440 (m)	1444	1435 (w)	1443	$\delta(CH_2)$
ν_7	1400 (m)	1392	1400 (s)	1388	$\nu(C_1-N_1)$
ν_8	1340 (m) 1310 (m)	1343	1325 (s)	1339	$\rho_w(CH_2)$
ν_9	1280 (s)	1249	1030 (s)	1079	$\delta(N_1-H_5)$
ν_{10}	1105 (m)	1123	1090 (w)	1088	$\nu(C_2-N_2)$
ν_{11}	1030 (s)	1013	770 (m)	752[b]	$\rho_w(NH_2)+\nu(C_2-N_2)$
ν_{12}	950 (w)	924	820 (w)	856[b]	$\nu(C-C)$
ν_{13}	740 (w)	742	715 (m)	694	$\delta(C=O)+$Ring def.
ν_{14}	530 (m)	536	540 (m)	521	$\delta(C=O)+$Ring def. $+\nu(Cu-N_2)$
ν_{15}	470 (m)	470	450 (m, b)	438	$\nu(Cu-N_1)$
ν_{16}	330 (m)	329	330 (m)	324	Ring def.$+\nu(Cu-N_2)$
ν_{17}	220 (m)	228	230 (m)	226	Ring def.
A″	Species				
	Obs.	Calc.	Obs.	Calc.	
ν_{18}	3338 (s)	3323	2500 (s)	2450	$\nu_{as}(NH_2)$
ν_{19}	2960 (w)	2954	2985 (w)	2954	$\nu_{as}(CH_2)$
ν_{20}	1180 (w)	1178	1180 (m)	1175	$\rho_t(CH_2)$
ν_{21}	1080 (m)	1098	770 (m)	747	$\rho_t(NH_2)$
ν_{22}	910 (s) 890 (s)	889	900 (m)	933	$\rho_r(CH_2)$
ν_{23}	613 (m)	611	460 (sh)	477	$\rho_r(NH_2)$
	Bands not calculated				
	800 (w)		680 (m)		$\pi(N_1-H_5)$
	560 (m)		560 (sh)		$\pi(C=O)$
	405 (m)		390 (m)		$\nu(Cu-N_2)+$Ring def.

[a] Band assignments are given for the non-deuterated compound. [b] Extensive coupling observed in the potential energy distribution.

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(10) K. Tomita, *Bull. Chem. Soc., Japan*, *34*, 286 (1961).

(11) B. Strandberg, I. Lindquist, and R. Rosenstein, *Z. Krist.*, *116*, 266 (1961).

(12) J. H. Wilkinson, *Numerische Mathematik*, *4*, 354 (1962); A. S. Householder and F. L. Bauer, *ibid.*, *1*, 29 (1959); J. H. Wilkinson, *Computer*, J., 3, 23 (1960).

(13) Y. Morino and K. Kuchitsu, *J. Chem. Phys.*, *20*, 1809 (1952).

its N-deuterated analog from 4000 to 500 and from 600 to 200 cm^{-1}, respectively. The band at 3338 cm^{-1} is assigned as an overlapping of the NH_2 asymmetric stretching (ν_{18}) with the NH(amido) stretching vibration (ν_1). Rosenberg[3] had previously assigned a band at 3106 cm^{-1} to the N–H(amido) stretching of this complex. However, bis(glycino)copper(II) monohydrate[7] exhibits a band at around 3100 cm^{-1} and hence this band is not exclusive to the amido group.

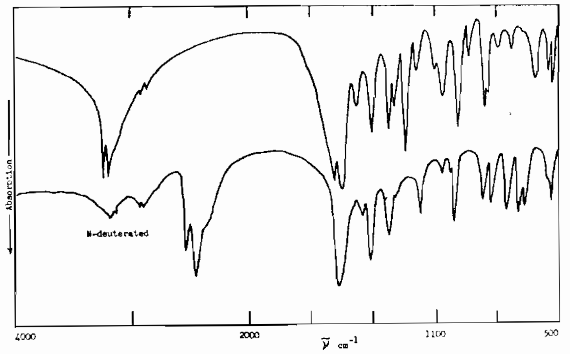

Figure 2. The infrared spectra of bis(glycinamido)copper(II) monohydrate and its N-deuterated analog (4000-500 cm^{-1}).

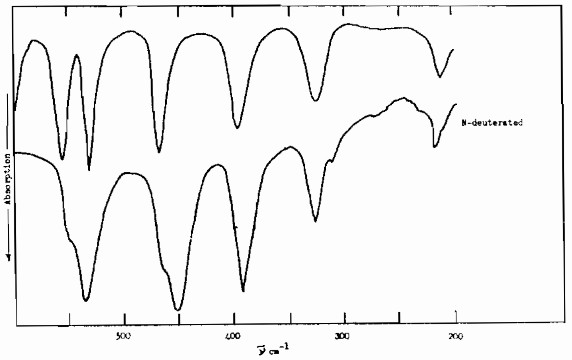

Figure 3. The infrared spectra of bis(glycinamido)copper(II) monohydrate and its N-deuterated analog (600-200 cm^{-1}).

In addition, it would seem unlikely that the proton remaining after ionization would be held less strongly than prior to ionization even if some of the electron density were shifted upon coordination to a metal. Furthermore, complexes of copper(II) with oxamide[6] and biuret[14] also exhibit their N–H(amido) stretching at around 3310 cm^{-1}. Thus, the assignment given in this investigation seems to be more reasonable for this vibration. The inplane bending mode of this group appears at 1280 cm^{-1} (ν_9) and shifts to 1030 cm^{-1} upon deuteration. These values are approximately the same as those found for this mode in the oxamido and biureto complexes.

According to the calculation of the potential energy distribution, the non-deuterated species exhibits the asymmetric stretching (ν_{18}), symmetric stretching (ν_2), scissoring (ν_4), wagging (ν_{11}), twisting (ν_{21}), and rocking (ν_{23}) vibrations of the NH_2 group at 3323, 3267, 1604, 1013, 1098, and 611 cm^{-1}, respectively. These modes are shifted to 2500, 2360, 1180, 770, 770, and 460 cm^{-1}, respectively, upon deuteration. It should be noted that the NH_2 wagging mode couples with the C_2–N_2 stretching in the non-deuterated complex to give the band at 1030 cm^{-1}. This coupling alters upon deuterium substitution to include a contribution from the C–C stretching.

The calculated and observed frequencies for all the CH_2 vibrations are in very good agreement. It does appear, however, that the wagging (ν_8) and rocking (ν_{22}) bands split in the non-deuterated species. Since this splitting is not apparent in the N-deuterated species, it may be due to Fermi resonance involving some NH_2 or NH group vibrations. The values for the various modes found in this study are colse to those found in the bis(glycino)copper(II) complex.[7] The C=O stretching vibration (ν_5) exhibits a band at 1570 cm^{-1} in the non-deuterated species which shifts to 1590 cm^{-1} in the deuterated complex. This small shift may be due to changes in the nature of the intermolecular hydrogen bonding, $C{=}O\ldots H{-}N\!<$, which is weakened by D substitution. Coupling is observed for the in-plane bending mode of the C=O group as it combines with ring deformations and Cu–N_2 stretching to give two bands at 740 (ν_{13}) and 530 (ν_{14}) cm^{-1} in the non-deuterated complex.

Of particular interest are the stretching vibrations of the two C–N groups in this complex. The C_1–N_1 stretching of the amido portion exhibits a band at 1400 cm^{-1} (ν_7) which is markedly higher than C_2–N_2 stretching of the amino portion at 1105 cm^{-1} (ν_{10}). Although the C–C stretching frequency of the glycinamido Cu^{II} complex is almost same as that of the glycino copper(II) complex, the potential energy distribution for the deuterated glycinamido complex shows that this mode couples extensively with the N–D in-plane bending and ND_2 wagging to give rise to two bands at 820 and 770 cm^{-1}, respectively.

The Cu–N(amido) stretching vibration is assigned to the band at 470 cm^{-1} (ν_{15}) in the non-deuterated complex. The potential energy distribution shows that this mode does not include any serious coupling with other vibrations. The Cu–N(amino) stretching vibration, on the other hand, couples with ring deformation and C=O in-plane bending modes to give two bands at 530 (ν_{14}) and 330 cm^{-1} (ν_{16}) in the non-deuterated complex. This was quite unexpected in view of the fact that this mode does not show extensive coupling in the bis (glycino)copper(II) complex.[7] The values calculated and observed for copper-nitrogen stretching in this study are in the same region as those observed for the bis(oxamido)copper(II) complexes (473, 365 cm^{-1}),[6] bis(glycino)copper(II) complexes (460 cm^{-1}),[7] bis(biureto)copper(II) complexes (485, 349 cm^{-1}),[14] and $[Cu(N_2H_4)_2]Cl_2$ (440 cm^{-1}).[15]

Bands not calculated in this study are easily assigned in an empirical manner. The weak band at 800 cm^{-1} in the non-deuterated complex is assigned to the N–H out-of-plane bending. This band shifts to 680 cm^{-1} upon deuteration. A similar band and shift is observed in the biureto and oxamido complexes at 800 cm^{-1} in the non-deuterated and 660

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(14) B. B. Kedzia, P. X. Armendarez, and K. Nakamoto, *J. Inorg. Nucl. Chem.*, *30*, 849 (1968).

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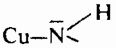
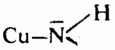
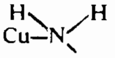
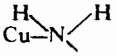
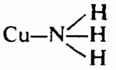
cm^{-1} in the deuterated complex. The medium intensity band at 560 cm^{-1} is assigned to the C=O aut-of-plane bending mode. The glycino[7] and oxamido[6] complexes also exhibit a band near 560 cm^{-1} which has been assigned to this mode in both cases. This band appears as a shoulder on the 540 cm^{-1} band in the deuterated complex. Finally, a band at 405 cm^{-1} has been assigned to one of the out-of-plane ring deformations which are not calculated in this study. A similar assignment is made for a band at 380 cm^{-1} in the bis(glycino)copper(II) complexes.[7] The higher frequency and observed shift of this band to 390 cm^{-1} upon deuteration indicates the possibility that there may be coupling with the copper-nitrogen stretching mode of the amino nitrogen.

Force Constants. The force constants listed in Table III have been transferred from normal coordinate analyses of similar molecules such as bis(oxamido)nickel(II)[6] and bis(glycino)copper(II)[7] complexes. It has been found that the nitrogen-hydrogen stretching force constants take the same value for the amino and amido group, although they are expected to be different; the difference in their force constants is probably too small to be determined by the present approximate calculation. Table III also indicates that the C_1–N_1 stretching force constant (5.30 mdyn/Å) is greater than the C_2–N_2 stretching force constant (3.00 mdyn/Å). Since the Urey-Bradley stretching force constant for a pure C–N single bond is about 3.7 mdyn/Å,[16] the present result supports the Rosenberg's conclusion that the C_1–N_1 bond has a partial double bond character. It should be mentioned that the larger value of $F(N_1...O_1)$ in the Urey-Bradley force field is common to this type of compound; 1.50 and 0.75 to 1.50 mdyn/Å in N-methylacetamide and formamide,[4] respectively.

Perhaps the most interesting force constants are those related to copper-nitrogen stretching. Table III reveals that there is a difference in the force constants pertaining to copper-nitrogen stretchings of the amido and the amino groups. The latter (0.88 mdyn/Å) is close to the value used for copper-nitrogen stretching in the bis(glycino)copper(II) complexes[7] (0.90 mdyn/Å). The former (1.02 mdyn/Å) is larger by 0.14 mdyn/Å than $K(Cu–N_2)$. It is also larger than the copper-nitrogen(amido) stretching force constant (0.91 mdyn/Å) of bis(biureto) copper(II).[14] The latter increase may be due to the greater stability of a five membered ring over that of a six-membered ring. It is interesting to note that Watt and Knifton[17] have observed increases in the frequency of the nickel(II)-nitrogen stretching vibration (from 435 to around 480 cm^{-1}) upon deprotonation of the amino group in complexes of nickel(II) with glycine and alanine. This increase in frequency would be accompanied by a corresponding increase in the stretching force constant related to this bond as has been observed in this study. The larger value of $K(Cu–N_1)$ relative to $K(Cu–N_2)$ also agrees with the conclusion of Strandberg *et al.*[11] for similar bonding in (glycylglycino)copper(II) monohydrate. They concluded that the differences in bond length (1.87 Å for the copper-nitrogen bond to the amido nitrogen with a dissociated proton versus 1.98 Å for the copper-nitrogen bond to the amino group) are due to differences in bond strength. Several other investigators[18,19,20] have suggested that the strength of donor-acceptor bonds for similar donor molecules increases with the net negative charge on the donor atom. Brändén and Lindqvist[21] have observed large differences in bond length due to this effect. Table V gives a comparison of the bond distances and force constants for several copper complexes containing copper-nitrogen bonds of varying length and strength. It is seen that the Cu–N stretching constant increases and the Cu–N distance decreases progressively as the net negative charge on the nitrogen atom increases. However, the Cu–N stretching frequency does show irregularity because vibrational coupling persists in certain compounds.

Table V. Trends in Force Constant *vs.* Bond Distance for Various Copper-Nitrogen Bonds

Complex	Bond Schematic	Copper-Nitrogen Bond Distance (Å)	Force Constant (mdyns/Å)	Observed Frequency (cm^{-1})
Bis(glycinamido)Cu^{II}		1.87	1.02	470
Bis(biureto)Cu^{II}		1.93	0.908 [13]	458 [a] 358
Bis(glycino)Cu^{II}		1.98	0.90 [7]	460
Bis(glycinamido)Cu^{II}		1.98	0.88	530 [a] 330
$[Cu(NH_3)_4]SO_4$		2.05 [b]	0.84 [c]	420

[a] Extensive coupling observed in the potential energy distribution. [b] Q. F. Mazzi, *Acta Cryst.*, *8*, 137 (1955). [c] I. Nakagawa and T. Shimonouchi, *Spectrochim. Acta*, *22*, 759 (1966).

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