

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

## Infrared Absorption Spectra of Inorganic Coördination Complexes.

### I. The Nature of Chelation Bonding in Bis-(glycino)-copper(II) Monohydrate and Bis-(glycino)-nickel(II) Dihydrate<sup>1</sup>

BY D. N. SEN, SAN-ICHIRO MIZUSHIMA,<sup>2a</sup> COLUMBA CURRAN<sup>2b</sup> AND J. V. QUAGLIANO<sup>2c</sup>

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Infrared spectra of bis-(glycino)-copper(II) monohydrate and bis-(glycino)-nickel(II) dihydrate have been measured and compared with the spectra of potassium glycinate, ethyl glycinate and glycine hydrochloride. A number of vibrational frequencies have been assigned. It was concluded that the resonance structure of the carboxylate ion is essentially maintained and the bond between the central metal ion of the complex and the carboxylate group is essentially ionic. Previous results for complexes containing ions within and without the coördination sphere are in agreement with this conclusion.

Preliminary work on the infrared absorption spectra of inorganic coördination complexes was undertaken in this Laboratory by Faust,<sup>3</sup> using the potassium bromide disk method devised by Stimson and O'Donnell.<sup>4</sup> Studies of the directive influences, stabilities, *cis-trans* and optical isomers, and the general structural properties of coördination complexes have been carried out for a number of compounds, and this report deals with the nature of the chelation bonding in the complexes of bis-(glycino)-copper(II) monohydrate and bis-(glycino)-nickel(II) dihydrate.

X-Ray diffraction studies by Stosick<sup>5</sup> have revealed a *trans* coplanar square arrangement of the chelating groups around the metal atom in both bis-(glycino)-nickel(II) dihydrate and copper *dl*- $\alpha$ -aminobutyrate. Magnetic susceptibility studies by Ray and Sen<sup>6</sup> led these authors to conclude that bis-(glycino)-copper(II) monohydrate is an outer orbital type copper complex. They obtained a moment of 1.93 Bohr magnetons for this compound as compared to a range of 1.90–2.20 Bohr magnetons for compounds in which they considered the unpaired copper electron is in a shielded inner d orbital (outer orbital complexes) and a range of 1.72–1.82 Bohr magnetons for a series of compounds in which they assigned the unpaired electron to an outer p orbital where its orbital moment is quenched by the fields of neighboring molecules. Infrared spectra of powdered glycinate of copper and nickel have been determined by Duval and Lecomte,<sup>7</sup> but they reported only a few absorption maxima and did not discuss the structure of these complexes in detail.

#### Experimental

**Bis-(glycino)-copper(II) Monohydrate, Cu(NH<sub>2</sub>CH<sub>2</sub>-COO)<sub>2</sub>·H<sub>2</sub>O.**—This salt was previously reported by Abderhalden and Schnitzler.<sup>8</sup> To 4.98 g. of CuSO<sub>4</sub>·5H<sub>2</sub>O (0.05 mole) dissolved in 200 cc. of cold water was added 20 cc. of

an aqueous solution of 1.7 g. of NaOH (0.41 mole). The precipitated cupric hydroxide was filtered, washed thoroughly with cold water until free from alkali, and then dissolved in a warm solution containing 3 g. of glycine (0.04 mole) in 150 cc. of water. This resulting solution was warmed on the water-bath at 60° for 30 minutes and then filtered. On concentration and cooling, blue crystalline flakes of bis-(glycino)-copper(II) monohydrate deposited. These crystals were filtered, washed with a small quantity of ice-cold water, twice recrystallized from water, and finally dried in a vacuum desiccator over concentrated sulfuric acid for several days. A yield of 50% of purified material was obtained.

*Anal.* Calcd. for Cu(NH<sub>2</sub>CH<sub>2</sub>COO)<sub>2</sub>·H<sub>2</sub>O: C, 20.91; H, 4.39. Found: C, 21.06; H, 4.39.

**Bis-(glycino)-nickel(II) Dihydrate, Ni(NH<sub>2</sub>CH<sub>2</sub>COO)<sub>2</sub>·2H<sub>2</sub>O.**—The procedure used by Stosick<sup>5</sup> was followed with some modifications in the preparation of this compound. A solution of 7.5 g. of glycine (0.1 mole) in 50 cc. of water was digested on the water-bath at 70° with 7 g. of nickel carbonate (0.06 mole). After the reaction was complete, the solution was filtered, evaporated to 20 cc. and cooled in an ice-bath; the blue crystals formed were filtered under suction, washed with a little ice-cold water and then redissolved in the minimum quantity of hot water. On air evaporation of the almost saturated solution, shining light-blue crystals of the complex were obtained. The crystals were dried in air. A yield of 6 g. (50%) of pure compound was obtained.

*Anal.* Calcd. for Ni(NH<sub>2</sub>CH<sub>2</sub>COO)<sub>2</sub>·2H<sub>2</sub>O: C, 19.78; H, 4.98; Ni, 24.17; N, 11.54. Found: C, 20.42; H, 5.01; Ni, 24.53; N, 11.48.

**Absorption Measurements.**—The infrared spectra were obtained by means of a Perkin-Elmer Infrared Spectrophotometer Model 21 using a sodium chloride prism. Preparation of the disks and infrared measurements were made according to the procedure of Stimson and O'Donnell.<sup>4</sup>

#### Results

The spectra of bis-(glycino)-copper(II) monohydrate and bis-(glycino)-nickel(II) dihydrate are given in Fig. 1. In the 3  $\mu$  region peaks are observed for the copper complex at 3300, 3250 and 3150 cm.<sup>-1</sup>, and for the nickel complex at 3300, 3250 and 3170 cm.<sup>-1</sup>. These compare with the peak at 3330 cm.<sup>-1</sup> of potassium glycinate and can be assigned to N-H stretching vibrations. In the 6  $\mu$  region the spectra of glycine hydrochloride and ethyl glycinate in potassium bromide disks show a strong band at about 1750 cm.<sup>-1</sup> (5.7  $\mu$ ), assigned to the carbonyl stretching vibration. The spectra of potassium glycinate and sodium acetate show a peak at about 1600 cm.<sup>-1</sup> (6.3  $\mu$ ), which arises from the antisymmetric carbon-oxygen stretching vibration in the carboxylate ion. The spectra of the metal glycinate show bands in the 1600 cm.<sup>-1</sup> region indicating the presence of the carboxylate ion. Absorption due to the NH<sub>2</sub> bending vibration also occurs in this region and is probably responsible for the broadness of these bands. The NH<sub>2</sub> de-

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(2) (a) Visiting Professor. Present address: Faculty of Science, Tokyo University. (b) Brother Columba Curran, C.S.C. (c) To whom correspondence concerning this article should be addressed.

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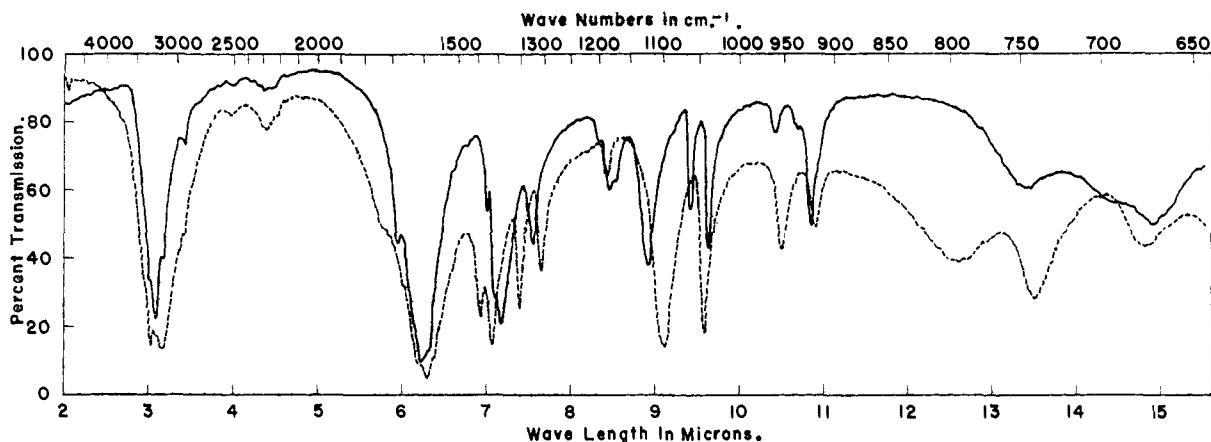


Fig. 1.—Infrared absorption spectra in KBr disks: —, bis-(glycino)-copper(II) monohydrate  $[\text{Cu}(\text{NH}_2\text{CH}_2\text{COO})_2] \cdot \text{H}_2\text{O}$ ; ---, bis-(glycino)-nickel(II) dihydrate  $[\text{Ni}(\text{NH}_2\text{CH}_2\text{COO})_2] \cdot 2\text{H}_2\text{O}$ .

formation vibrations other than that at  $1600 \text{ cm.}^{-1}$  are expected to appear in a lower frequency region.

One of the two peaks in the  $1400 \text{ cm.}^{-1}$  ( $7 \mu$ ) range is assigned to the  $\text{CH}_2$  bending vibration. This is expected to occur in this frequency range from the calculations,<sup>9</sup> and the corresponding absorptions have been observed in the spectra of glycine and potassium glycinate.

The glycine band observed at  $1035 \text{ cm.}^{-1}$  arises possibly from the C-N stretching vibrations. The corresponding bands have been observed for potassium glycinate and metal glycine complexes at almost the same frequency. The remaining bands in the  $1400\text{--}700 \text{ cm.}^{-1}$  ( $7\text{--}14 \mu$ ) range can be assigned to other  $\text{CH}_2$  and  $\text{NH}_2$  deformation vibrations and to the C-C stretching and carboxylate ion symmetric vibrations. Of these  $\text{CH}_2$  deformation vibrations, the wagging vibration can be assigned to a band having a frequency higher than that of C-N vibration whereas the rocking vibration appears at a frequency lower than the C-N vibration.

#### Discussion

The peaks in the  $3 \mu$  region reveal that the N-H stretching vibration frequency is considerably changed on formation of the N-M bond, which is to be expected, if the bond is essentially covalent. The absorption in the  $1600 \text{ cm.}^{-1}$  region indicates that the resonance in the carboxylate ion (resulting in equivalent carbon to oxygen bonds) is preserved in the complexes. *The oxygen-to-metal bonds in these complexes must, therefore, be essentially electrostatic.* The bonds are more adequately represented by dashed lines,  $\text{COO}^- \cdots \text{M}$ , than by the full lines previously used in diagramming the structural formulas.

The paramagnetism of the hydrated salts of the transitional metals shows that these bonds are usually electrostatic. Of the bonds formed by nickel and copper in these coordination complexes, therefore, only the metal-to-nitrogen bonds appear to be covalent. From the X-ray evidence for a *trans* coplanar arrangement of the two chelate rings in both bis-(glycino)-nickel(II) dihydrate and copper *dl*- $\alpha$ -aminobutyrate,<sup>5</sup> it appears likely that bis-(glycino)-copper(II) monohydrate has the same coplanar configuration. The magnetic data indicate

that the unpaired electron in the latter compound is in an inner d orbital. The blue color of bis-(glycino)-nickel(II) dihydrate suggests that this compound is paramagnetic and that the inner d orbitals are not used in bond formation. *In both the nickel and copper complexes, therefore, it appears that the metal atoms use sp orbitals in forming linear bonds with the nitrogen atoms of the ligand molecules.* If this electrostatic character of the oxygen-to-metal bonds in the metal complexes of the amino acids is a general phenomenon, it follows that whenever inner d orbitals are not available for bond formation complexes of the type  $\text{M}(\text{glycino})_2$  are planar rather than tetrahedral. From this point of view, the structures of some metal glycinate which could not be explained by the supposition of covalent oxygen-to-metal bonds can be made clear.

Another possible electronic configuration for the copper complex in accord with the experimental evidence cited above is dp hybridization, the lone electron being in the 4s level. If the nickel complex is diamagnetic, possible electronic configurations are dp hybridization for electrostatic copper-to-oxygen bonds and  $\text{dsp}^2$  and  $\text{dsp}^3$  if the oxygen-to-nickel bonds have partial covalent character.

The similarity of the carboxylate frequencies in the glycine complexes and in sodium glycinate is in contrast to the complete change in the absorption characteristics of ions on coordination with a metal ion.<sup>10</sup> In the complex  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ , for example, the normal frequencies of the tetrahedral sulfate ion outside the coordination sphere are not changed very much, whereas in the complex  $[\text{Co}(\text{NH}_3)_6]\text{SO}_4 \cdot \text{Cl}$  the strongest absorption band at  $1100 \text{ cm.}^{-1}$  characteristic of the free sulfate ion disappears, and other significant spectral changes also occur. These changes reveal that the sulfur-to-oxygen bonds in the sulfate ion are no longer equivalent in the latter complex, implying appreciable covalent character to the oxygen-to-cobalt bond. Investigation of the spectra of these compounds is being extended to the potassium bromide and cesium bromide regions to determine the nitrogen-to-metal stretching vibration frequencies.

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