

TABLE I

THE LOWERING OF THE FREEZING POINT OF SODIUM HYDROXIDES BY VARIOUS SOLUTES

| Solute Na ₂ CO ₃ | | | | | |
|--|---------|---------|---------|--------|--------|
| <i>N</i> | 0.00460 | 0.00912 | 0.0136 | 0.0199 | 0.0261 |
| ΔT , °C. | 1.8 | 4.6 | 7.1 | 10.0 | 12.8 |
| <i>i</i> | 0.85 | 1.10 | 1.13 | 1.09 | 1.07 |
| Solute NaBr | | | | | |
| <i>N</i> | 0.00765 | 0.0147 | 0.02520 | 0.0370 | |
| ΔT , °C. | 3.2 | 6.5 | 12.1 | 17.0 | |
| <i>i</i> | 0.93 | 0.96 | 1.00 | 1.00 | |
| Solute KBr | | | | | |
| <i>N</i> | 0.00282 | 0.00566 | 0.00924 | 0.0132 | 0.0178 |
| ΔT , °C. | 2.5 | 5.0 | 7.8 | 11.4 | 15.7 |
| <i>i</i> | 1.92 | 1.92 | 1.83 | 1.84 | 1.92 |
| Solute K ₂ CO ₃ | | | | | |
| <i>N</i> | 0.00515 | 0.00818 | 0.0110 | 0.0137 | |
| ΔT , °C. | 7.0 | 11.9 | 15.5 | 18.9 | |
| <i>i</i> | 2.95 | 3.17 | 3.07 | 3.00 | |

"*i*" factors come as close to whole numbers as they do.

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Infrared Absorption Spectra of Inorganic Coordination Complexes. IV. The Infrared Spectrum of Bis-(glycino)-zinc(II) Monohydrate^{1a,b}

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In the course of the investigation of metal amino acid complexes in progress in this Laboratory, the infrared spectrum of solid bis-(glycino)-zinc(II) monohydrate has been obtained. The spatial arrangement of ligands about the zinc ion has usually been considered to be tetrahedral,² corresponding to sp³ hybridization of the bond orbitals. However, the X-ray investigations of Low³ show conclusively that the glycine ligands are arranged in a planar fashion about the central zinc ion.

In a previous communication⁴ it was postulated that the *trans* planar configuration of bis-(glycino)-copper(II) monohydrate complex is the result of an sp linear hybridization of copper bond orbitals. This explanation was based upon the observed infrared absorption spectrum of the copper(II) complex in

(1) (a) Paper III in series, *J. Chem. Phys.*, in press. (b) Supported in part under AEC Contract AT(11-1)-38, Radiation Project of the University of Notre Dame.

(2) R. G. Dickinson, *THIS JOURNAL*, **44**, 774 (1922); C. H. MacGillavry and J. M. Bijvoet, *Z. Krist.*, **94**, 249 (1936).

(3) Private communication from Dr. Barbara Low, University Laboratory of Physical Chemistry Related to Medicine and Public Health, Harvard University.

(4) D. N. Sen, S. Mizushima, C. Curran and J. V. Quagliano, *THIS JOURNAL*, **77**, 211 (1955).

the solid state. The spectrum was interpreted as indicating essentially covalent N → Cu⁺⁺ bonds

and essentially ionic $\left. \begin{array}{c} \text{O} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{O} \end{array} \right\} \text{---Cu}^{++}$ bonds in which

the carboxylate ion resonance is preserved.

Experimental

Bis-(glycino)-zinc (II) monohydrate, Zn(NH₂CH₂COO)₂·H₂O was prepared according to the method of Dubsky and Rabas.⁵ The compound prepared in our laboratory was spectroscopically identical with a sample kindly supplied by Dr. Low.

Spectra were obtained from samples prepared in accordance with the KBr disk technique described previously.⁶ The zinc complex gave very well-defined spectra similar to those reported for the Cu(II) and Ni(II) salts.⁴ The frequencies in cm.⁻¹ observed for bis-(glycino)-zinc(II) monohydrate are as follows: 3450 (m), 3270 (m), 1603 (vs), 1447 (m), 1419 (m), 1404 (m), 1350 (w), 1314 (w), 1190 (w), 1146 (m), 1100 (m), 1060 (s), 954 (w), 907 (w), 719 (w). Abbreviations: m = medium, s = strong, w = weak, v = very.

Discussion

It is to be noted that absorption bands are observed at 3450 cm.⁻¹ (2.9 μ), 3270 cm.⁻¹ (3.06 μ) and 1603 cm.⁻¹ (6.24 μ) and no absorption band was observed in the region of 1720 cm.⁻¹ (5.8 μ). These regions are critical for the determination of the type of metal-ligand bonding present in amino acid-metal complexes.⁴ The appearance of the NH stretching absorption maximum at 3270 cm.⁻¹, compared to the 3330 maximum in the spectrum of sodium glycinate, indicates the presence of N → Zn⁺⁺ coordination. The absence of an absorption band near 1720 cm.⁻¹ (5.8 μ) and the presence of a very strong band at 1603 cm.⁻¹ (6.24 μ) indicate that the carboxyl to zinc bond has a high degree of ionic character.

These observations regarding the spectrum of bis-(glycino)-zinc(II) monohydrate are in accord with the evidence from X-ray diffraction of a square planar configuration for the zinc(II) complex. They indicate that linear sp metal bond orbitals are involved in the nitrogen-to-metal bonds in this complex as well as in the copper(II) and nickel(II) complexes previously reported. It is to be expected that all complexes of the type ZnX₂ in which X is a bidentate ligand having as one coordinating center a COO⁻ group forming essentially electrostatic COO⁻ --- Zn⁺⁺ bonds, should have a *trans* square planar configuration if the other metal-to-ligand bonds are covalent. Further spectral studies on complexes of this type are being pursued in this Laboratory.

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(5) J. V. Dubsky and A. Rabas, *Spisy vydávané privodovědeckou fakultou Masarykovy Univ. No. 123*, 3 (1930); *C. A.*, **25**, 2655 (1931).

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