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INFRARED BAND ASSIGNMENTS OF COPPER AMINO ACID COMPLEXES

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The IR spectra of four copper amino acid complexes have been investigated from 4000 to 250 cm^{-1} and detailed assignments for the observed bands have been made. Further, on the basis of symmetric and antisymmetric COO stretching vibrations, the relative covalency of different Cu-O bonds has been discussed.

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1. *Introduction*

The infrared studies are of much importance in the sense that they provide information about the modes of coordination as well as about the spatial configuration of the atoms within the molecule [1] and therefore have drawn the attention of several workers [2–4]. The infrared spectra of crystalline amino acids have been studied by Klotz and Gruen [5] and Thompson et al. [6]. Krishnan and Balsubramanian [7] have also studied the Raman spectra of amino acids in the crystalline state. The spectra of some amino acid complexes in the solid state have also been thoroughly studied [8–10]. It has been concluded from these studies that coordination of amino groups with metal ion decreases the frequencies of the N-H stretching vibrations as compared to the potassium salt of the ligand and that the magnitude of the frequency shift increases with increasing covalent character of the metal-nitrogen bond. Nakagawa et al. [11] have also demonstrated that the NH_2 rocking frequencies follow the same order as the M-N bond stretching force constants for several DL-valine complexes. The above conclusion was later confirmed by Jackovitz and Walter [12] for a number of DL-Leucine complexes.

In this investigation, the infrared spectra of four copper amino acid complexes, namely Cu/DL-alanine, Cu/DL-proline, Cu/L-phenylalanine and Cu/L-leucine, have been studied. The assignments for all the observed frequencies have been made and the relative covalency

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of the copper-ligand bonds has been discussed. Although the spectra of these complexes have been studied earlier employing normal coordinate treatments [13, 14], recently Percy and coworkers [15] and Pinchas et al. [16] have shown, by means of isotopic labelling of the chelate ring, that many of the assignments which resulted from normal coordinate treatments required substantial revision. Therefore it was thought desirable to revise the assignments of various frequencies in the infrared spectra of these complexes in the light of the assignments proposed [15] by Percy et al.

2. *Experimental*

2.1. Sample preparation

Cu(II)-DL-alanine complex was prepared by the modification of the method of Abderhalden and Schnitzler [17]. Copper (II) hydroxide was prepared by adding a solution of 1.1 gm (0.0276 mole) of sodium hydroxide in 17 ml of water to a solution of 3.34 gm (0.0134 mole) of copper sulphate pentahydrate in 134 ml of water. The precipitate was collected, washed and filtered. It was heated for one hour on a steam bath with 2.37 gm of DL-alanine in 70 ml of water; the hot solution was filtered and dark-violet crystals formed on cooling. These crystals were powdered and washed with boiling alcohol, filtered and then dried over sulphuric acid [18]. The complex crystallised as monohydrate.

Crystals of Cu/DL-proline were prepared [19] by the action of a solution of amino acid on an excess of freshly precipitated copper carbonate employing sodium carbonate and copper sulphate pentahydrate. The resultant filtered solution was allowed to evaporate slowly. The deep-blue plate type crystals were stored after drying properly.

For the preparation [20] of copper complex with L-phenylalanine, the solution of the required amount of amino acid was neutralized with the equivalent amount of NaOH and then the solution of copper sulphate (0.5 equimolar) was slowly added. After 10–20 minutes stirring the mixture was filtered and the solid washed with water, alcohol, ether and finally dried over P_4O_{10}. This method over the temperature range 0–70°C gave a blue needle like product.

Copper (II) complex with L-leucine amino acid was prepared by the method of Graddon and Munday [21]. Aqueous solution of the sodium salt of the amino acid was prepared from exactly equivalent quantities of the free acid and sodium bicarbonate and added to the aqueous solution of the equivalent quantity of copper sulfate. The precipitated Cu(II) complex was collected, washed and dried in the air. The complex was light blue in colour.

2.2. Spectral measurements

The infrared spectra were recorded in the region 4000–250 cm^{-1} using a Perkin–Elmer (Model 521) automatic recording grating infrared spectrophotometer. The spectrophotometer was calibrated using polystyrene film and frequencies are accurate to 1 cm^{-1}. The complexes were ground and thin pellets were prepared of the mixture. These pellets were subjected to spectral analysis using pure KBr pellet as a blank.

3. *Results and discussion*

The assignments of all the frequencies appearing in the spectra from 4000–250 cm^{-1} have been made by comparison with the study [15] of Percy et al. out of which a few have been given in Table I along with their intensity category. The vast remaining data are available on request from the authors.

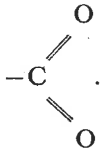
TABLE I

Band frequencies (cm^{-1}) and assignments along with the intensity category in the i.r. spectra of copper complexes

Cu/DL-alanine ν	Cu/DL-proline ν	Cu/L-phenylalanine ν	Cu/L-leucine ν	Assignments
3412 S	3462 S	—	—	—O—H stretch (water)
3282 S	—	3337 S 3317 S(Sh)	3332 S	N—H asym. stretch
3172 S	3232 S (broad)	3247 S 3237 S(Sh)	3252 S	N—H symm. stretch
1590 S	1625 S	1617 S	1615 S	COO^- asym. stretch
1398 S	1385 S (broad)	1425 M	1395 S	COO^- symm. stretch
1390 S				
365 S	380 S 370 S(Sh)	365 M	375 M	Cu—O stretch
345 M(Sh)	355 M	348 S	350 S	
330 S	345 M	335 M	338 M	Cu-ligand bend
	330 S	320 M	328 S	
		295 M	298 M	Cu...O stretch
		270 M	290 M	

Abbreviations: S — strong, M — medium, Sh — shoulder.

All the complexes show strong absorption bands in the region 3337–2872 cm^{-1}. These bands have been assigned to NH and CH stretching vibrations. The appearance of NH stretching absorption in our complexes in the region 3337-3172 cm^{-1} indicates the presence of $N \rightarrow Cu^{++}$ coordination [10, 22]. The frequency order of NH stretching vibrations in the complexes can be used as a measure of the covalent character of the copper-nitrogen bonds. Since the NH_2 rocking frequencies follow the same order as the Cu-N bond stretching force constants [11, 12], the covalent character of the Cu-N bonds varies in the order Cu/DL-alanine > Cu/DL-proline > Cu/L-phenylalanine > Cu/L-leucine. It is known from previous studies [1, 22] that the carboxylate ion group absorbs strongly near 1600–1590 cm^{-1} and more weakly near 1400 cm^{-1}. These bands result, respectively, from asymmetrical and symmetrical COO stretchings. In our case it varies from 1625 to 1590 cm^{-1} for asymmetric and from 1425 to 1385 cm^{-1} for symmetric stretching. The difference of asymmetric and symmetric stretching frequencies of COO, $\nu_{as} - \nu_s$ in each complex has been calculated and this is proposed [9, 23] to be proportional to the covalent character of copper-oxygen bond in the complex. The results of $\nu_{as} - \nu_s$ for Cu/DL-alanine, Cu/DL-proline, Cu/L-phenylalanine and Cu/L-leucine are 192, 240, 192 and 220 cm^{-1} respectively. The frequency separation of the carboxylate stretching vibrations for the complexes decrease in the order Cu/DL-proline > Cu/L-leucine > Cu/DL-alanine, Cu/L-phenylalanine which indicates a corresponding variation in the strength of the copper-oxygen bond. The absence of absorption band near 1724 cm^{-1} and the presence of a strong band in the region 1626–1600 cm^{-1} indicate that the carboxyl to Cu bond has a high degree of ionic character [1, 22]. This also demonstrates that the resonance in carboxylate ions is preserved so that the two carbon to oxygen bonds are equivalent and can be represented as



$-C\overset{\displaystyle O}{\underset{\displaystyle O}{\diagup\!\!\diagdown}}$.

The above observations of copper amino acid complexes are in conformity with the X-ray crystal structure data [19, 24, 25] of a square planar configuration. They show that linear *sp* metal bond orbitals are involved in the Cu—N bonds in these complexes. The blue colour of the complexes also shows that the inner *d*-orbitals are not used for bond formation. If this type of electrostatic bonding between copper and oxygen in copper amino acid complexes is a general phenomenon and the bonds are formed only with the outer-*d*-orbitals, then the complexes of the type Cu(ligand)$_2$ are always expected to be planar rather than tetrahedral. This has been found in the complexes studied here.

5. *Conclusion*

The information drawn from infrared studies regarding the metal-ligand bonding indicate that the copper to nitrogen coordination is present in all the complexes. Copper to oxygen bonding is ionic and the complexes are planar in nature.

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