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THE PREPARATION, SEPARATION AND KINETIC STUDIES OF THE OPENING OF THE CHELATE RINGS OF THE ISOMERS OF *BIS*(-ASPARTATO) AND *TRIS*(-GLYCINATO) COPPER(II) COMPLEXES

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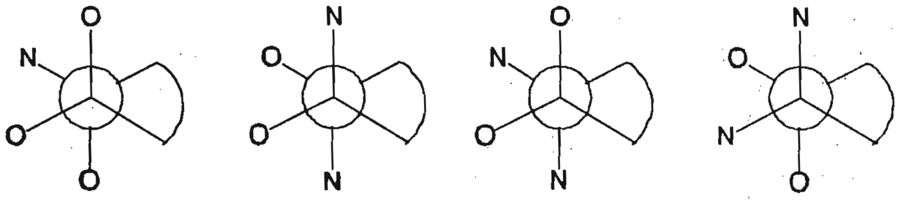
ABSTRACT. The preparation of *cis*-amine/*trans*-carboxylate and *trans*-amine/*cis*-carboxylate isomers of complexes of copper(II); $Cu[NH_2CH(COO)CH_2COO]_2^{2+}$ and $Cu[NH_2CH_2COO]_3^{2+}$ is described. The mechanism of the chelate ring-opening of these isomers is investigated by spectrophotometric measurements in nitric acid solutions. The products of the ring-opening reactions were identified by chemical tests and infrared spectroscopy. Results indicate that hydroxyacids may be prepared *via* the ring-opening processes as an alternative route.

INTRODUCTION

There have been numerous reports on transition metal complexes of amino acids in the last two decades [1-15]. Most of these reports were centred on the synthesis, characterisation, structures and stereochemistries of these complexes. The amino acid ligands were shown to coordinate with the central metal atom in either a *bis*- or a *tris*-fashion, with nitrogen and oxygen as the donor atoms and in two geometrical forms (Figure 1) [16-17].

We have recently reported some amino acid complexes with chromium(III), cobalt(III) and nickel(II), [18-20]. In the present paper, we have extended this investigation to copper(II) in an attempt to verify the influence of the Jahn Teller effect usually experienced in copper(II) complexes. The methods of preparation, the kinetics and mechanism of the opening of the chelate rings of the isomers of the title complexes are dealt with in this paper.



(*trans* carboxylate) (*trans* amine) (*cis* carboxylate) (*cis* amine)

Figure 1

EXPERIMENTAL

Physical Measurements. The infrared spectra were recorded on a Perkin-Elmer 257 grating spectrophotometer on KBr discs. The elemental analyses were carried out with a Perkin-Elmer, C, H, N micro analyzer. The mechanism of the ring-opening process was monitored using a Perkin-Elmer 420 spectrophotometer.

All the chemicals used were BDH chemicals and were used without further purification. The solvents used were of analytical grade.

Preparation of the Complexes. Bis(-aspartato) Copper(II) Complexes. To a solution of copper(II) chloride (0.01 mole) in 30 ml butanol, a solution of aspartic acid (0.03 mole) in 30 ml butanol:water (3:1, V/V) was added dropwise at *ca.* 60°. The mixture was then refluxed with constant stirring for about 2 hrs. Upon cooling, a blue solid product separated from the solution and was filtered off, washed with butanol and dried in an oven at 60°.

Tris(-glycinato) Copper(II) Complexes. A solution of copper(II) chloride (0.01 mole n 20 ml butanol) was allowed to react with a solution of glycine (0.04 mole in 20 ml butanol) at *ca.* 60° for 2 hrs. Upon cooling the reaction mixture, a pale-blue solid separated which was filtered off, washed with butanol and dried in an oven at *ca.* 60°.

Table 1. The elemental analysis and infrared spectral data for the *bis*(-aspartato) and *tris*(-glycinato) copper(II) complexes.

Complex	Elemental analysis			I.R. (cm^{-1})		
	C	H	N	C-H	NH_2	C=O
$Cu[NH_2CH(COO)CH_2COO]_2^{2+}$	29.60	3.11	8.65	2950	3135	1735
	(29.52)	(3.07)	(8.60)	2990	3160	1750
$Cu(NH_2CH_2COO)_3^{2+}$	25.35	4.25	14.80	2950	3140	1740
	(25.21)	(4.20)	(14.71)	2980	3145	1750

Elemental Analyses and Infrared Spectra. The *bis*(-aspartato) and *tris*(-glycinato) copper(II) complexes were characterized by elemental analyses and infrared spectroscopy as shown in Table 1. The IR spectra indicate the characteristic absorption bands for alkenes (2950 - 2990 cm^{-1}), carbonyl groups (1735 - 1750 cm^{-1} and amino groups (3135 - 3160 cm^{-1}). These absorption bands are in agreement with those reported for compounds with similar structures (21-23).

Separation of the Isomers of the Complexes. The isomers of these complexes were separated by cation exchange chromatography using CM sephadex cation exchange resin. The latter was swollen up in sodium chlorate solution (0.02M) to about 8 times its original size at *ca.* 60° in 1 hr. It was then packed into a chromatographic column. $Cu[NH_2CH(COO)CH_2COO]_2^{2+}$ (5.0 g), dissolved in ethanol (10 ml), was applied to the column and was eluted using the sodium chlorate solution. The eluting process was continued until two light-blue and blue-green solutions separated from the deep-blue coloured complex solution. Removal of the solvent *in vacuo* gave crystals of the isomers.

Similarly, cation exchange chromatography of the isomers of $Cu[NH_2CH_2COO]_3^{2+}$ resulted in the isolation of a pale-green and an ashy-coloured solids.

Table 2. Infrared spectral data for the isomers of *bis*(-aspartato) and *tris*(-glycinato) copper(II) chelates.

Isomer Complex	C-H	NH_2	C=O (cm^{-1})
$Cu[NH_2CH(COO)CH_2COO]_2^{2+}$	---	3130,3150	1730,1740
Light-blue isomer	3300-3450	3125,3140	1730,1740
Blue-green isomer	3410-3455	3130,3150	1730,1740
$Cu[NH_2CH_2COO]_3^{2+}$	----	3140	1735,1750
Pale-green isomer	3450-3500	3145	1735,1750
Ashy-coloured isomer	3450-3500	3140	1735,1750

Table 3. Kinetic measurements of acid-catalyzed ring-opening of the isomers of *bis*(-aspartato) copper(II) chelates.

Complex	Temperature (°C)	[H^+] x10^3 M	Kobs.x 10^3 (S^{-1})	
			Light-blue Isomer	Blue-green Isomer
$Cu[NH_2CH(COO)CH_2COO]_2^{2+}$	25	1.0	4.50	5.20
		2.0	6.20	7.10
		3.0	8.50	8.80
		4.0	10.50	10.80
		5.0	13.55	14.20
		6.0	15.80	16.00
		7.0	17.50	18.00
		8.0	21.30	22.30
	45	1.0	6.30	6.50
		2.0	7.50	8.50
		3.0	11.00	10.50
		4.0	14.55	15.85
		5.0	16.05	17.95
		6.0	20.50	23.30
		7.0	24.75	25.00
		8.0	26.50	28.00

Kinetic Measurements. Solutions of the isomers of *bis*(-aspartato) copper(II) complex were prepared in 0.1M nitric acid and thermostated in the cell holder of Perkin Elmer 420 spectrophotometer for 3 hrs. In each case, measurements were taken at 630 nm where maximum absorbance was noticed. The complexes were taken in large excess in order to give first order kinetics. Values of the observed first-order rate constants ($k_{observed}$) were evaluated from a plot of log (A_∞ - A_t) *versus* time and the value of each rate constant is an average of duplicate readings. Kinetic measurements of the isomers of *tris*(-glycinato) copper(II) in nitric acid solutions were carried out in a similar way. The results of these measurements are summarized in Tables 3 and 4.

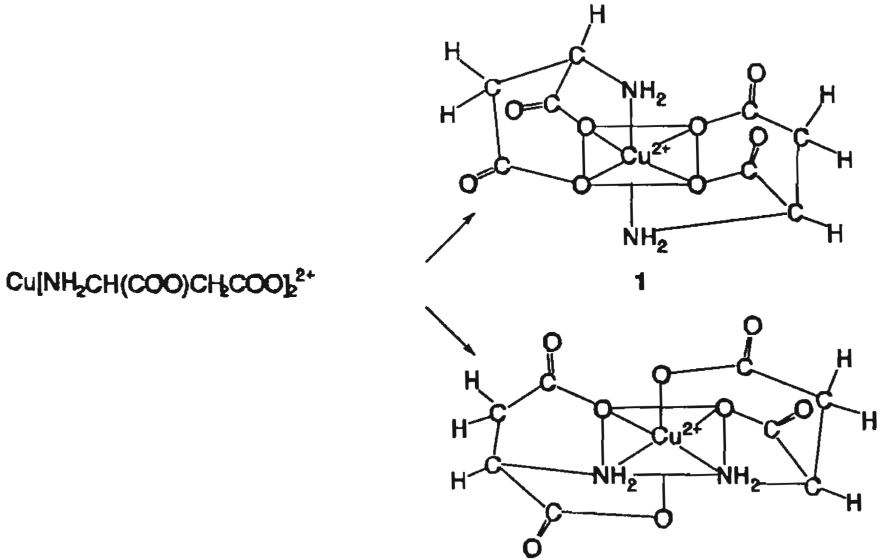
Table 4. Kinetic measurements of the acid-catalyzed ring-opening of *tris*(-glycinato) copper(II) chelates.

Complex	Temperature (°C)	$[H^+]$ x10^3 M	Kobs. x 10^3 (S^{-1})	
			Pale-green Isomer	Ashy-Coloured Isomer
$Cu[NH_2CH_2COO]_3^{2+}$	25	1.0	6.50	6.00
		2.0	8.00	8.50
		3.0	10.00	11.80
		4.0	12.00	13.30
		5.0	15.50	15.85
		6.0	19.30	20.00
		7.0	22.10	23.85
		8.0	25.35	28.00
	45	1.0	7.00	7.25
		2.0	8.50	8.85
		3.0	13.85	14.00
		4.0	16.50	16.95
		5.0	19.00	18.70
		6.0	20.50	24.90
		7.0	23.65	24.70
		8.0	28.10	31.00

RESULTS AND DISCUSSION

Isolation of the bis(-asparato) copper(II) was attempted by following the procedures given in the literature [2-4] but with no success. However, the glycinato copper(II) complex was successfully isolated by the above procedure. Characterization of the complex showed unambiguously that the compound isolated was $Cu[NH_2CH_2COO]_2^{2+}$ instead of $Cu[NH_2CH_2COO]_3^{2+}$. This is not totally unexpected since the axial bonds of copper(II) are of higher energies than the equatorial bonds and so bonding on the axial position has to be done under more severe conditions. This behaviour of Cu(II) is attributed to the Jahn Teller effect. The title complexes were therefore prepared by using the ligands in large excess of the copper(II) salt. These gave the complexes in satisfactory yields and analysis showed that they correspond to $Cu[NH_2CH(COO)CH_2COO]_2^{2+}$ and $Cu[NH_2CH_2COO]_3^{2+}$, respectively.

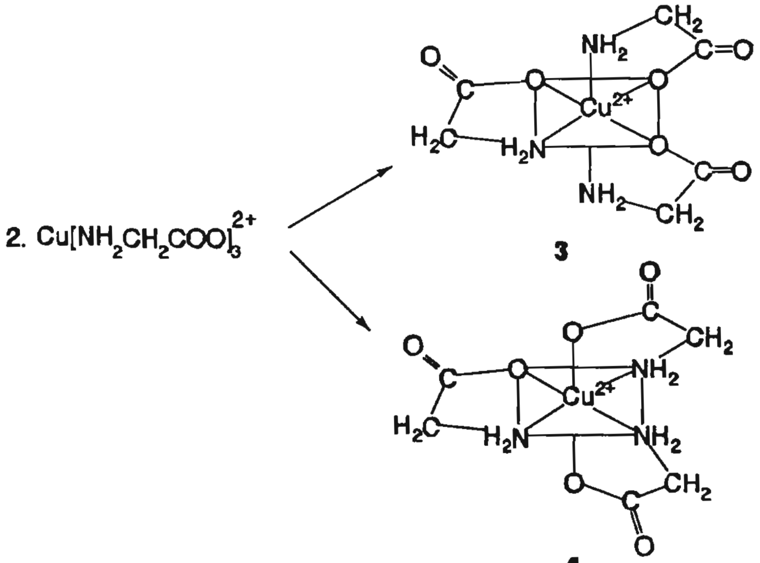
In our previous reports [18-20] the isomer having the amino group at the axial position (*trans*) separated as the upper layer while the isomer with oxygen at the axial position separated as the lower layer of the liquid in the cation exchange chromatography of the complexes. A comparison of our present results with the previous results shows that the *bis*(aspartato) copper(II) complex gave the *trans*-amine/*cis*-carboxylate, (**1**), as the light-blue isomer and the *trans*-carboxylate/*cis*-amine, (**3**), as the blue-green isomer. Similarly the *tris*(-glycinato) copper(II) complex gave the *trans*-carboxylate/*cis*-amine, (**4**), in the ashy-coloured isomer.



$Cu[NH_2CH(COO)CH_2COO]_2^{2+}$

1

2



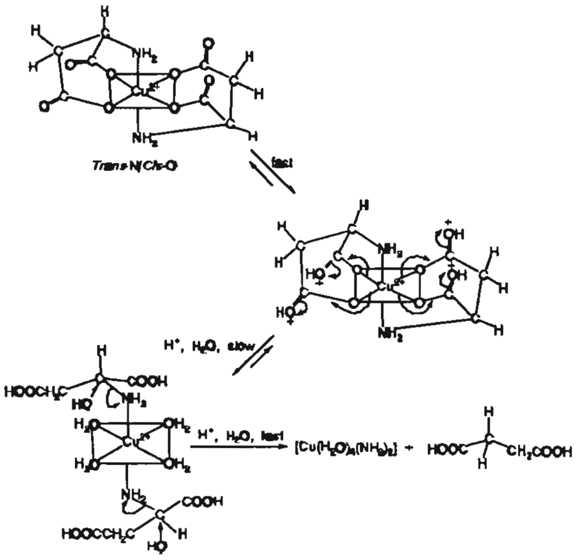
2. $Cu[NH_2CH_2COO]_3^{2+}$

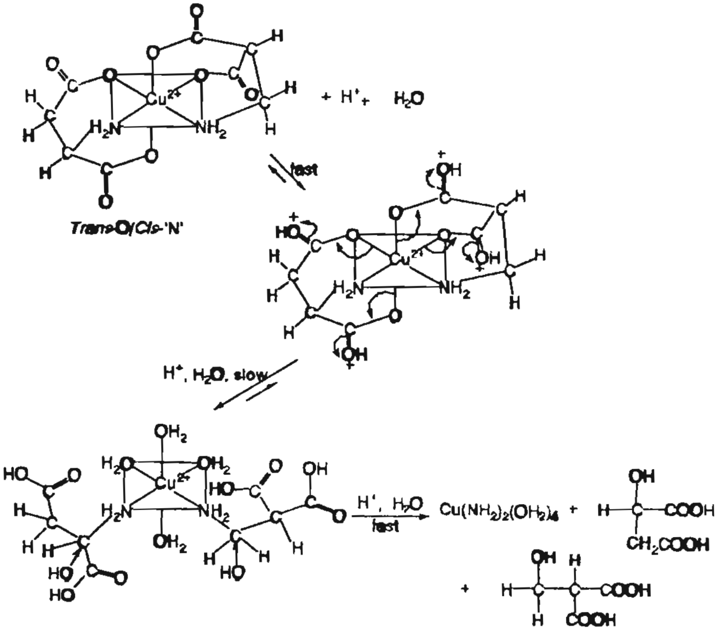
3

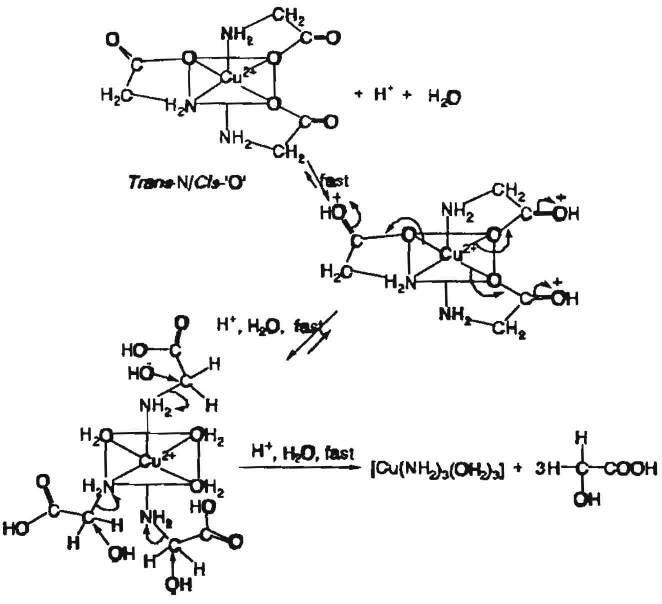
4

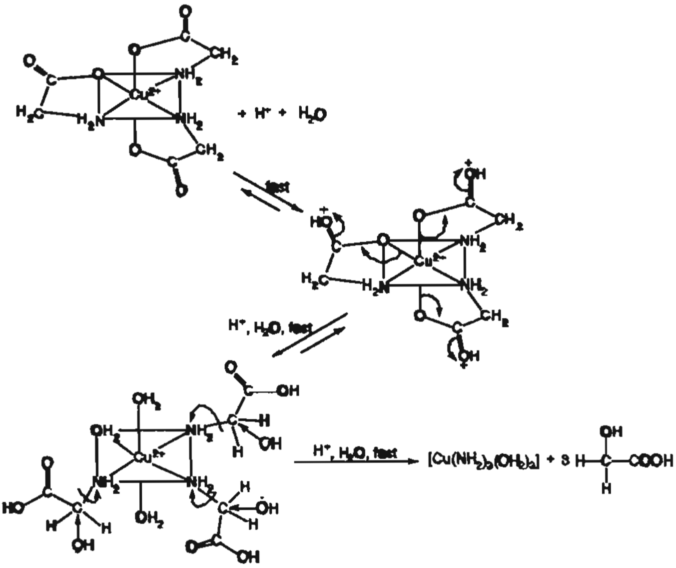
Infrared Spectral Evidence for the Isomers. The infrared spectral data shown in Table 2 indicates no absorptions in the 3300 cm^{-1} region attributed to hydrogen bonding in the *bis*(-aspartato) and *tris*(-glycinato) copper(II) complexes. However, broad bands in the 3400 - 3500 cm^{-1} region in the IR spectra of the isomers of these complexes indicate hydrogen bonding. The $\nu_{(C=0)}$ stretching absorptions remain unaltered at the expected position in the 1730 - 1750 cm^{-1} region in all the complexes prepared. This observation is in agreement with the report that the ionized carbonyl frequencies usually appear at the same positions both in the free ligands and in the metal complexes [22]. This fact has been interpreted as indicative of a fully ionic bond between oxygen and metal atoms, although this implies a degree of equivalence between the two oxygen atoms of the carbonyl group which is difficult to reconcile with the square planar configurations assigned to many of the metal chelates such as copper [23]. The ν_{NH_2} absorptions appear at the 3130 - 3150 cm^{-1} region. These are higher than the corresponding hydrochloride frequencies which is consistent with the concept of lone-pair donation by nitrogen atoms. Low-temperature studies on metal chelates of glycine and leucine indicate that in the unhydrated leucine series, the ν_{NH2} stretching frequencies which usually feature within the above region rise to about 3350 cm^{-1} [24]. It has been possible to differentiate between such compounds as these *cis*- and *trans*- forms of platinum-glycine complexes by taking advantage of the minor differences which occur in the NH_2 absorption in the two cases [25]. In the present report, such minor differences in the infrared absorption frequencies have been used to differentiate between the *trans*-amine/*cis*-carboxylate and *cis*-amine/*trans*-carboxylate isomers.

Kinetic Results. Solutions of *cis*/*trans* isomers of $Cu[NH_2CH(COO)CH_2COO]_2^{2+}$ and $Cu[NH_2CH_2COO]_3^{2+}$ in dil. nitric acid were thermostated in the cell holder of Perkin-Elmer 420 Spectrophotometer. Results indicate decrease in the wavelength of absorption in the UV spectra of these complexes. Based on our previous analogous reactions [18-20], the decrease in the wavelength of absorption is assumed to occur as a result of direct acid catalysis of the chelate ring-opening reactions of these isomers. The following mechanisms are therefore proposed:-




+ H⁺ + H₂O
fast
Trans-O/Cis-'N'
H⁺, H₂O, slow
H⁺, H₂O
fast
Cu(NH₂)₂(OH₂)₄ +
+


+ H⁺ + H₂O
Trans-N/Cis-'O'
fast
H⁺, H₂O, fast
H⁺, H₂O, fast
[Cu(NH₂)₃(OH₂)₃] + 3



The products of the ring-opening reactions were characterised by chemical tests and infrared spectroscopy as was the case in our previous reports [18-20]. Positive tests were recorded for copper(II) salt in the lower layer of the liquid product, in all the isomers reported. The upper layer of the liquid product was identified as hydroxylated in each case.

The rate of the chelated ring-opening process is given by:-

$$\textbf{Rate} = k_H\,[\textbf{Isomeric complex}]\,[H^+].$$

The rate is therefore linearly related to $[H^+]$ as shown in Figures 2 and 3. The relatively high rate constants observed in the ring-opening reactions of the title isomers can be attributed to Jahn Teller distortion. This fact is in agreement with the previously reported fact that in copper(II) complexes the axial bonds are difficult to form and when formed, they become unstable as a result of Jahn Teller distortion [26,27]. Our results also show that the Jahn Teller distortion affects only the rate of the ring-opening process but does not affect the mechanism and products of the reaction.

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