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Syntheses & Characterisation of Complexes of Copper (II) Glycinates†

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Copper (II) glycinate complexes with chloro, bromo and oxyanions like sulphate, perchlorate and nitrate as anionic ligands and potassium as cation, have been synthesised. The complexes are characterised by thermogravimetric analysis, magnetic susceptibility, electronic, infrared and E P R spectral measurements. The effect of introduction of these anions into the coordination polyhedra of Cu(II) and the nature of bonding in the resultant complexes have been discussed.

A part of our research interest involves the study of metal complexes with physiologically important ligands. As copper (II) is one of the biologically important metal ions, studies on its complexes with amino acids are important. Investigations have been earlier made on the Cu(II)-glycine systems[1,2]. The crystal structure determination of *cis*-$[Cu(gly)_2H_2O]$ revealed that it contains six coordinated Cu(II) moiety with two long Cu-O bonds, one each formed with water and carbonyl oxygen, in a tetragonally distorted octahedron[3]. Our aim was to replace these loosely bonded axial ligands with various anionic ligands so that monomeric mixed ligand complexes of copper (II) featuring glycinate and anions could be isolated. The effect of introduction of the anions into the corrdination sphere of copper (II) glycinate, and the resultant synthesis of several new complexes are reported in this paper.

Materials and Methods

Glycine and metal salts used were of AR grade.

Preparation of complexes

1 *Chloroglycinatoaquocopper (II),* $[Cugly(Cl)H_2O]$—It was prepared by the interaction of an ethanolic solution of $CuCl_2$ (20 mmol) with glycine (20 mmol). The solution was stirred for sometime and the blue precipitate thus obtained was filtered, washed with acetone and dried. This method was used to prepare bromoglycinatoaquocopper (II), $[Cugly(Br)H_2O]$, also taking $CuBr_2$ instead of $CuCl_2$.

2 *Potassium dichloroglycinatoaquocuprate (II),* $K[CuglyCl_2H_2O]$—It was prepared by mixing 40 ml of methanolic solution of $CuCl_2$ (20mmol) with 20ml of an aqueous solution containing 20 mmol each of KOH and glycine. The precipitate that separated out on stirring was filtered, washed with ethanol and acetone and dried. Potassium dibromoglycinatoaquocuprate (II), $K[CuglyBr_2H_2O]$, and potassium glycinatosulphatoaquocuprate (II) were also prepared by this method, taking $CuBr_2$ and $CuSO_4$ respectively instead of $CuCl_2$.

3 *Chloroglycinatoaquoglycinecopper (II),* $[CuglyCl(glyH)H_2O]$—It was obtained from the interaction of 40 ml of an ethanolic solution of $CuCl_2$ (20 mmol) with glycine solution (40 mmol) in 30 ml of 0.05 *N* HCl. The resultant solution was concentrated on a water-bath and the green solid that precipitated was filtered, washed with acetone and dried. The green crystalline solid, bromoglycinatoaquoglycinecopper (II), $[CuglyBr(glyH)H_2O]$, was also isolated by adopting the above procedure taking $CuBr_2$ and dil. HBr in place of $CuCl_2$ and dil. HCl respectively.

4 *Potassium tris(glycinato)cuprate (II),* $K[Cu(gly)_3]$—It was obtained by the interaction of glycine solution (60 mmol) with 20 mmol each of $CuSO_4.5H_2O$ and KOH. To a copper sulphate solution (20 mmol) was added a solution containing barium hydroxide (20 mmol) and glycine (60 mmol). $BaSO_4$ obtained was filtered and the filtrate was concentrated over a water-bath. On cooling a blue complex separated out which was filtered, washed with acetone and dried.

5 *Glycinatoperchloratoaquocopper (II),* $[Cugly(ClO_4)H_2O]$—It was prepared from an ethanolic solution of $Cu(ClO_4)_2$ (10 mmol) and an aqueous solution of glycine (10 mmol). The contents were stirred and a blue product that separated out immediately was filtered, washed with ethanol and dried over $CaCl_2$ in a desiccator. Glycinatonitratoaquocopper (II), $[Cu(NO_3)glyH_2O]$ was prepared by following this procedure taking $Cu(NO_3)_2$ instead of $Cu(ClO_4)_2$.

6. *Potassium glycinatobis(perchlorato)cuprate (II),* $K[Cugly(ClO_4)_2]$—It was obtained by the reaction of an aqueous solution containing 10 mmol each of KOH

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and glycine with 10 mmol of $Cu(ClO_4)_2$ in ethanol. The resultant solution was stirred and after sometime a blue crystalline solid separated out which was filtered, washed with acetone and dried. Potassium glycinatobis(nitrato)cuprate (II), $K[Cu(gly)(NO_3)_2]$, was prepared by the same method taking $Cu(NO_3)_2$ instead of $Cu(ClO_4)_2$.

The copper content of the complexes was estimated iodometrically and nitrogen was determined by Kjeldahl's method. Sulphate was determined gravimetrically as $BaSO_4$, and the halides were estimated gravimetrically as silver halides. The analytical data are given in Table 1.

The thermogravimetric analysis of the complexes was carried out on a Stanton recording thermobalance at a linear heating rate of 6° per min. The magnetic susceptibility measurements were made at room temperature using Gouy balance and the $\mu_{eff.}$ values were calculated after applying diamagnetic corrections[4]. The E P R measurements were carried out on a Varian E4 spectrometer at the X-band using DPPH as a g marker. The visible spectra of solid complexes were taken on a Carl Zeiss DMR 21 spectrophotometer in nujol emulsion.

The infrared spectra were recorded in KBr and nujol on Perkin-Elmer 257 and Beckman IR-12 spectrophotometers.

Table 1—Characterisation Data of Copper (II) Glycinates

Sl. No.	Complexes (Colour)	Found (Calc.), %		Halide/ sulphate
		Cu	N	
1	$[CuglyClH_2O]$	33.4	7.5	18.4
	Blue	(33.26)	(7.32)	(18.56)
2	$K[CuglyCl_2H_2O]$	23.8	5.4	26.6
	Blue	(23.92)	(5.27)	(26.70)
3	$[Cugly(glyH)ClH_2O]$	24.0	10.5	13.1
	Green	(23.88)	(10.52)	(13.33)
4	$[CuglyBrH_2O]$	27.0	5.8	33.8
	Blue	(26.98)	(5.94)	(33.94)
5	$K[CuglyBr_2H_2O]$	17.8	3.8	45.0
	Blue	(17.92)	(3.94)	(45.09)
6	$[Cugly(glyH)BrH_2O]$	20.3	8.9	25.6
	Green	(20.46)	(9.01)	(25.74)
7	$K[Cu(gly)_3]$	19.4	12.8	—
	Blue	(19.57)	(12.93)	
8	$K[CuglySO_4H_2O]$	21.7	4.6	33.0
	Blue	(21.86)	(4.81)	(33.03)
9	$[Cugly(ClO_4)H_2O]$	24.9	5.4	—
	Blue	(24.91)	(5.49)	
10	$K[Cugly(ClO_4)_2]$	16.8	3.6	—
	Blue	(16.91)	(3.72)	
11	$[Cugly(ClO_4)_2]$	16.8	3.6	—
	Blue	(16.91)	(3.72)	
12	$K[Cugly(NO_3)_2]$	21.0	13.8	—
	Blue	(21.13)	(13.97)	

Results and Discussion

The isolated complexes are insoluble in common organic solvents and their insolubility precluded conductance studies, solution spectral measurements and molecular weight determination. The complexes dissociate in water to give $Cu(gly)_2$ as one of the products.

The X-ray powder patterns taken with a Debye-Scherrer camera using CuK_α radiation suggest that they are crystalline compounds.

The thermogravimetric data of the complexes along with the end products of decomposition obtained around 700°C, which are based on mass loss curves and chemical analyses, are given in Table 2.

The complexes having perchlorate and nitrate decompose with mild explosion. The aquo complexes dehydrate in the temperature range 120-180°C suggesting the coordination of water in these complexes to copper. The glycine moiety starts decomposing in all the complexes above 200°C.

Magnetic and visible spectral studies

The effective magnetic moments of the complexes measured at room temperature are in the range 1.9-2.1 B.M. suggesting that they are magnetically normal with an unpaired electron[5] as expected for Cu(II).

It is fairly well established that the electronic transitions in the region 13-16 kK are characteristic of hexa- and penta-coordinated Cu(II)[2,3,6]. In majority of the hydrated Cu(II) amino acid complexes the energy maxima appear at 16 kK[3,7]. The present mixed ligand complexes exhibit a broad band in the region 13.0-14.3 kK; this decrease in energy maxima may be due to the change in chromophore from CuN_2O_4 to $CuNXO_4$ ($X = Cl$ or Br). As the halide donors are considered to cause lesser splitting than nitrogen donors, the halo complexes in the present investigation have electronic transition bands in the lower energy regions[8].

The absorption maxima for chloro complexes appear in the higher energy region than those for the corresponding bromo complexes in accordance with their positions in the spectrochemical series. The complex, $K[Cu(gly)_3]$ with CuN_3O_3 chromophore unusually exhibits a broad band at higher regions.

EPR spectral studies

The EPR spectra of $K[CuglyBr_2H_2O]$ and $K[Cugly(ClO_4)_2]$ exhibit a single isotropic line similar[9] to that of $Cu(en)_3SO_4$. However, the latter compound is trigonally distorted and the orbital degeneracy of the ground state of Cu^{2+} (^2E) cannot be removed. The observed isotropic EPR signal can be explained in terms of the dynamic Jahn-Teller mechanism. In the present two compounds, as the

Table 2—TG Data of Copper (II) Glycinates

Complex Sl. No.	Temp. range (°C)	Loss of H_2O Found (Calc.), %	Temp. range (°C)	Loss of glycinate Found (Calc.), %	Final product
1	120-160	9.2 (9.4)	220-560	39.0 (39.26)	CuO
2	120-160	6.4 (6.8)	230-520	28.0 (28.25)	KCl + CuO
3	120-160	6.5 (6.8)	220-550	56.4 (56.40)	CuO
4	120-180	7.5 (7.7)	230-530	31.8 (31.85)	CuO
5	120-160	5.0 (5.0)	220-550	21.0 (21.15)	KBr + CuO
6	120-180	5.6 (5.8)	230-520	48.3 (48.30)	CuO
7	—	—	220-550	68.4 (68.38)	K_2CO_3 +CuO
8	130-180	8.1 (8.3)	220-400	34.0 (34.15)	K_2SO_4 +CuO
9	120-180	6.9 (7.0)	220-550	29.0 (29.01)	—
10	—	—	230-520	19.5 (19.70)	—
11	120-180	8.1 (8.3)	220-550	33.8 (34.01)	—
12	—	—	220-560	24.5 (24.60)	—

For Sl. Nos. see Table 1

point group symmetry is less than O_h or D_3, and as the chemical reasoning suggests a tetragonal or lower distortion, the single EPR line could be simply due to the exchange narrowing.

Proctor, Hathaway and Nicholls[10] have postulated that the magnitude of the ratio, $G=(g_\parallel-2)/(g_\perp-2)$ indicates the possibility of exchange interaction in Cu(II) complexes. Thus, when $G<4$, there is significant exchange coupling in the complexes. In the present complexes, though the G values are less than 4, the interaction may be weak as the magnetic moments of these complexes are normal at room temperature[10-12]. However, low temperature magnetic measurements should throw more light on this aspect.

In Cu(II) complexes the visible absorption maxima shift to shorter wavelength region and the g parameters become smaller as the copper-ligand bondings in the molecular plane become more covalent[13]. Yokai *et al.*[14] have calculated the degree of covalency, k_0^2, ($k_0^2 = \frac{\Delta E_0}{4\lambda}(g_0-2)$ where ΔE_0 is the approximate energy of the *d-d* transition, λ is the spin-orbit coupling constant for Cu(II) taken as $-825\,\text{cm}^{-1}$ and g_0 is the average g value) for a series of Cu(II)-amino acid complexes. It was found to be in the range 0.55-0.65. As seen from Table 3, the degree of covalency for the present complexes falls in the range 0.56-0.68.

Infrared spectral studies

The complex, *cis*-[$Cu(gly)_2H_2O$] exhibits a broad band around $3400\,\text{cm}^{-1}$ which is assigned to νOH of coordinated water molecules[15]. The appearance of similar bands in the hydrated complexes indicates the coordination of water. The exact location of other modes of vibrations of water molecules in the lower regions is rather difficult due to overlapping with other bands[16].

Significant spectral changes are observed in the region $3400\text{-}3000\,\text{cm}^{-1}$ of the complexes as compared with the spectra of amino acid and its sodium salt. A band at $3050\,\text{cm}^{-1}$ observed for glycine is assigned to NH_3^+ absorption as it is present in the zwitter ion form. This band is shifted to $3360\,\text{cm}^{-1}$ in sodium glycinate due to the deprotonation of NH_3^+. The formation of Cu-N bond in the complexes is considered to be essentially covalent and considerable changes in the νNH are to be expected. In fact, in the present complexes νNH_2 absorption appears in the region $3200\text{-}3310\,\text{cm}^{-1}$ and this shift to the lower frequency compared with the position of the band in sodium glycinate indicates the presence of Cu-N coordination[17].

ν_{as}COO is shifted from $1580\,\text{cm}^{-1}$ in the free ligand spectrum to around $1600\,\text{cm}^{-1}$ in the spectra of complexes suggesting the chelation of the ligand. The

Table 3—Magnetic, Electronic and EPR Data of Copper (II) Glycinates

Complex Sl. No.	Magnetic moment (B.M.)	Electronic spectra (kK)	$g_{\parallel}$	$g_{\perp}$	g_{av}	$G=\frac{(g_{\parallel}-2)}{(g_{\perp}-2)}$	k_0^2
1	2.1	14.0	2.23	2.12	2.16	1.92	0.678
2	2.0	14.3	2.20	2.10	2.13	2.00	0.560
3	1.9	14.1	2.24	2.09	2.14	2.66	0.597
4	1.9	13.7	2.22	2.12	2.15	1.83	0.623
5	2.1	14.0	—	—	2.14	—	0.606
6	1.9	13.2	2.22	2.12	2.15	1.83	0.598
7	2.1	16.0	2.23	2.08	2.13	2.88	0.630
8	2.0	13.7	2.38	2.09	2.19	4.22	0.788
9	1.9	13.9	2.20	2.12	2.15	1.66	0.637
10	1.9	14.3	—	—	2.15	—	0.649
11	1.9	14.3	2.26	2.08	2.14	3.25	0.606
12	1.9	13.9	2.16	2.07	2.10	2.28	0.421

For Sl. No. see Table 1.

separation between asymmetric and symmetric COO vibrations ($\Delta\nu$COO) is an indicator of the nature of the bonding of carboxylate to the metal in metal carboxylates. The covalent character of M – O bond increases[18-20] with an increase in $\Delta\nu$COO values; however, when carboxylate group acts as a bridge the strength of M – O bond increases with decreases in the $\Delta\nu$COO values. If the interaction is mainly ionic, the $\Delta\nu$COO values will be minimum.

Both glycine and Nagly exhibit ν_{as}COO and ν_sCOO vibrations at 1580 and 1420 cm^{-1} respectively with the ΔCOO values of 160 cm^{-1}. The $\Delta\nu$COO value is around 200 cm^{-1} for complexes 2,5,7,10 and 12 whereas it is around 190 cm^{-1} for other complexes. On the basis of these values and the positions of individual peaks, it is tentatively inferred that the glycinate group acts as a bidentate chelating ligand in the former complexes and as a terdentate ligand in other complexes (by bonding through the carbonyl oxygen to the adjacent copper in addition to chelating). In the complexes [Cugly(glH)(H)H$_2$O], X = Cl, Br, apart from a band around 1600 cm^{-1}, there appears a band around 1700 cm^{-1} corresponding to νC = O of the free – COOH[21]. The bands appearing in the regions 325-380 cm^{-1} and 420-460 cm^{-1} in the complexes are assigned to Cu-O and Cu-N stretching frequencies respectively[22].

K[CuglyCl$_2$.H$_2$O] exhibits a band in the far infrared region at 300 cm^{-1} which is characteristic of terminal stretching mode of Cu-Cl whereas a band appearing around 240 cm^{-1} in the spectra of [CuglyClH$_2$O] and [Cugly(glyH)ClH$_2$O] is assigned to the bridging νCu-Cl mode. The ratio $\nu_{bri.}/\nu_{ter.}$ is found to be 0.80 which is the normal expected value[23]. Similarly, a band at 240 cm^{-1} appearing in the spectrum of K[CuglyBr$_2$H$_2$O] is assigned to the terminal νCu-Br and the bands appearing around 220 cm^{-1} in the spectra of [CuglyBrH$_2$O] and [Cugly(glyH)BrH$_2$O] are characteristic of bridging[24] νCu-Br mode.

The sulphato complex, K[Cugly(SO$_4$)H$_2$O] shows absorptions at 1170, 1110, 1040, 970, 610, 585 and 455 cm^{-1} due to the anion and these bands are characteristic of bidentate sulphate group of C_{2v} symmetry. The absence of a band around 1220 cm^{-1} suggests that the sulphate group is bridging rather than chelating[25].

The perchlorato complexes, [Cugly(ClO$_4$)H$_2$O] and K[Cugly(ClO$_4$)$_2$], exhibit four bands around 1140, 1100, 1050 and 940 cm^{-1}, which are attributed to bidentate perchlorate group of C_{2v} symmetry[26].

The bands appearing around 1460, 1300, 1050, 820, 750 and 710 cm^{-1} in [Cu(gly)(NO$_3$)H$_2$O] and K[Cugly(NO$_3$)$_2$] and the $\Delta(\nu_1+\nu_4)$ value of around 40 cm^{-1} clearly indicate the presence of bidentate nitrate group in the complexes[27]. Further, in these complexes the ν_5 and ν_1 bands of nitrate are observed around 1460 and 1300 cm^{-1} respectively, and the difference, $\Delta\nu(\sim 160$ cm$^{-1})$ is indicative of bidentate nitrate coordination[28]. Moreover, the absence of 1380 cm^{-1} band in the complexes rules out the possibility of monodentate nitrate coordination[27-29].

Thus, in all the present complexes, Cu(II) satisfies the maximum coordination number of six with the glycinate moiety in the equatorial positions resulting in the formation of a highly distorted structure. Glycine also acts as a monodentate ligand through N-coordination without the deprotonation of the carboxyl group in a few cases. These complexes dissociate in aqueous solution to give more stable Cu(II) glycinate as one of the species.

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