Synthesis & Characterisation of Ternary Complexes of Copper(II) with 2-Hydroxy-1-naphthaldehyde & α-Amino Acids

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The ternary complexes of Cu(II) with 2-hydroxy-1-naph-thaldehyde (A¹) and some α-amino acids have been synthesized and characterized by analytical, conductivity, thermal, magnetic, infrared, electronic and ESR spectral data. Based on analytical and thermal data, the stoichiometry of the complexes is found to be 1:1:1. The infrared spectral data of the ternary complexes (1) [Cu A¹ gly]; (2) [Cu A¹ α-ala]; (3) [Cu A¹ β-ala]; (4) [Cu A¹ val]; (5) [Cu A¹ leu]; (6) [Cu A¹ φ-ala]; (7) [Cu A¹ ser] and (8) [Cu A¹ threo] indicate that the ligands act as bidentate ones while in the complexes (9) [Cu A¹ his H₂O]; (10) H[Cu A¹ asp.H₂O] and (11) [Cu A¹.glut.H₂O], the amino acids act as tridentate ligands. The electronic spectra of the Cu(II) complexes suggest that complexes 1-8 are square-planar while complexes 9-11 are tetragonal. Various parameters like $g_\parallel$, $g_\perp$, α^2 and λ have been calculated from ESR spectral data.

In continuation of our earlier work on mixed ligand complexes of copper(II) and dioxouranium(VI)[1,2], we report here the preparation and characterisation of ternary complexes of Cu(II) with O⁻, O⁻ donor ligand 2-hydroxy-1-naphthaldehyde (A¹) and O⁻, N-donors glycine (gly), DL-α-alanine (α-ala), DL-β-alanine (β-ala), L-valine (val), L-leucine (leu), DL-phenylalanine (ala), DL-serine (ser), DL-threonine (threo), L-histidine (hist), L-aspartic acid (asp) and L-glutamic acid (glut).

The ligand 2-hydroxy-1-naphthaldehyde was obtained from Sigma Chemical Company (USA) while α-amino acids were obtained from Loba Chemical Company and were recrystallized before use. Their purities were checked by TLC and melting point determination.

The following general procedure was adopted for the synthesis of ternary complexes of Cu(II) with 2-hydroxy-1-naphthaldehyde (A¹) and the α-amino acids:

The solutions of 2-hydroxy-1-naphthaldehyde (0.02 mol) in methanol and of amino acid (0.02 mol) in water were simultaneously added to a methanolic solution of copper acetate (0.01 mol) with constant stirring. The pH of the resulting solution was adjusted (6-7) by adding sodium acetate. The reaction mixture was refluxed on a water bath for about 30 min. On cooling the reaction mixture, the solid complex separated out, which was filtered and washed with hot water and methanol to remove the excess ligand and the metal ion. The complexes so obtained were dried *in vacuo* over fused anhydrous calcium chloride.

The analytical data (C, H and N) for the solid complexes were obtained from the Micro-analytical Laboratory, Calcutta University, Calcutta. The metal contents in the complexes were determined by standard procedures[3]. The conductivity measurements were made in DMF using a Digital Conductivity bridge model-304. The magnetic susceptibility measurements were made at room temperature by Gouy method using Hg[Co(NCS)₄] as the calibrant. Diamagnetic corrections were made using Pascal's constants. The thermal data of the complexes were obtained using a Stanton thermobalance. The infrared spectra of the ligands and complexes (4000-200 cm⁻¹) were recorded on a Perkin-Elmer infrared spectrophotometer model-283. The electronic spectra of the complexes were recorded in DMF on a Shimadzu Multipurpose spectrophotometer model MPS-5000. The ESR spectra of the complexes were recorded in solid state at room temperature on a varian V₃ Q spectrometer.

All the complexes are non-hygroscopic, stable at room temperature, insoluble in water and common organic solvents, but soluble in DMF and DMSO. The molar conductances of 1×10^{-3} *M* solutions of the complexes of 1-9 (see Table 1) were low (10-15 ohm⁻¹ cm² mol⁻¹) indicating them to be non-electrolytes. The values for the complexes (10) and (11) were in the range 40-60 ohm⁻¹ cm² mol⁻¹ indicating that they were 1:1 electrolytes[4]. The elemental analysis and conductivity data of the complexes support the formulation of complexes shown in Table 1.

All the complexes except (9) to (11) were thermally stable upto 225°C indicating that they were not hydrated. This was confirmed by the absence of endothermic peak in the DTA curves of these complexes in the temperature range 150-200°C. The complexes (9) to (11) showed an endothermic peak in the temperature range 160-190°C indicating the presence of coordinated water[5]. The amount of water present in these complexes was confirmed by the thermogravimetric curves. These curves showed a mass loss in the temperature range 150-200°C which corresponded to one water molecule. All the complexes decomposed in a

Table 1—Elemental Analyses, Electronic Spectral and Magnetic Moments of Copper(II) Complexes

| S. No. | Complex | m.p. (°C) | Found (Calc.), % | | | | ν_{max} (cm^{-1}) | Magnetic moment (B.M.) |
			Metal	C	H	N		
1	[Cu A^l gly]	280	19.88 (20.66)	50.96 (50.56)	3.88 (3.57)	4.36 (4.52)	15625 20533	1.88 (1.85)
2	[Cu A^l α-ala]	265	19.04 (19.71)	51.03 (52.08)	4.13 (4.03)	3.95 (4.34)	15625 24570	1.87 (1.83)
3	[Cu A^l β-ala]	275	19.18 (19.71)	51.37 (52.08)	3.86 (4.03)	4.21 (4.34)	15504 24570	1.88 (1.85)
4	[Cu A^l val]	270	17.64 (18.13)	53.77 (54.76)	4.36 (4.85)	4.27 (4.99)	15337 20618	1.90 (1.86)
5	[Cu A^l leu]	265	16.85 (17.44)	55.18 (55.96)	5.16 (5.21)	4.02 (3.84)	15455 20471	1.87 (1.85)
6	[Cu A^l O-ala]	255	15.03 (15.48)	61.04 (61.46)	3.97 (4.17)	3.28 (3.41)	15503 20672	1.82 (1.85)
7	[Cu A^l ser]	275	18.54 (18.54)	49.27 (49.62)	3.59 (3.84)	3.94 (4.14)	15552 24390	1.84 (1.86)
8	[Cu A^l threo]	250	17.62 (18.03)	50.56 (51.05)	4.33 (4.25)	3.68 (3.97)	15576 24570	1.86 (1.85)
9	[Cu A^l hist.H$_2$O]	255	15.67 (16.15)	49.04 (48.78)	3.74 (4.07)	10.44 (10.67)	16000*	1.90 (1.81)
10	H[Cu A^l asp.H$_2$O]	275	16.15 (16.57)	46.16 (46.93)	4.03 (3.65)	3.38 (3.65)	15625*	1.82 (1.82)
11	H[Cu A^l glut.H$_2$O]	265	15.36 (15.95)	48.35 (48.17)	4.13 (4.27)	3.22 (3.1)	15576*	1.89 (1.83)

*Broad band indicates the overlapping of different transitions.

single step in the temperature range 250-500°C corresponding to the loss of ligand moiety. The final products of decomposition as computed from the pyrolysis corresponded in each case to metallic oxide.

The presence of characteristic bands of the two ligands in the IR spectra of the complexes indicate the formation of ternary complexes. The bands observed at 3360(b) and 1725 cm^{-1} in the infrared spectrum of 2-hydroxy-1-naphthaldehyde are assigned to stretching vibrations of phenolic hydroxyl and ν(C=O) of aldehyde group, respectively. The disappearance of the former band and a shift in latter towards lower frequency region (35-50 cm^{-1}) in all the ternary complexes confirms the involvement of phenolic oxygen, with deprotonation, and carbonyl oxygen in the coordination. The bands around 3265 and 3120 cm^{-1} observed in the IR spectra of free amino acids are assigned to ν_{as} (NH$_2$) and ν_s (NH$_2$) respectively[6-8]. In the ternary complexes, a shift of the NH$_2$ stretching vibrations to lower frequency side ($\Delta\nu = 50$-80 cm^{-1}) shows the complex formation through amino nitrogen. Further, the free ligands display a band at 1515 cm^{-1} due to the bending vibration of NH$_2$ group. In the complexes this band undergoes a negative shift to an extent of 40-50 cm^{-1}, confirming the involvement of amino group in co-

ordination. The ν_{as}COO and ν_sCOO modes of the carboxylate anion in the IR spectra of free amino acids occur in the regions 1630-1600 and 1420-1400 cm^{-1}, respectively. These bands are shifted towards the lower frequency region by 25-30 and 30-40 cm^{-1}, respectively in the ternary complexes indicating the participation of carboxylic oxygen in coordination. Further, the disappearance of the ν(O−H) of the carboxylic group, appearing at 2600 cm^{-1} in the IR spectra of free amino acids, confirms its involvement in coordination[9].

The amino acids containing hydroxyl group, like serine and threonine, show an additional broad band centred at 2800 cm^{-1} due to the ν(O−H). The lower position of this band indicates the involvement of this group in hydrogen bonding with the nitrogen of the amino group. The non-disappearance of this band in their ternary complexes confirms the non-involvement of hydroxyl oxygen in coordination with the central metal ion.

In the IR spectrum of free histidine, broad bands observed at 3230 and 3160 cm^{-1} may be assigned to the asymmetric and symmetric stretching of the amino and imino grops. A shift of these bands towards the lower region to an extent of 30-20 cm^{-1} in the ternary complex is observed;

Table 2—ESR Spectral Data of Copper(II) Complexes

S. No.	Complex	$g_{\parallel}$	$g_{\perp}$	$|g|$	α^2	$-\lambda\,(cm^{-1})$
1	[Cu A^1 gly]	2.25	2.08	2.13	0.603	249
2	[Cu A^1 α-ala]	2.23	2.07	2.12	0.556	230
3	[Cu A^1 β-ala]	2.25	2.08	2.14	0.645	267
4	[Cu A^1 val]	2.22	2.11	2.15	0.684	283
5	[Cu A^1 leu]	2.22	2.10	2.14	0.642	266
6	[Cu A^1 O-ala]	2.23	2.07	2.12	0.551	228
7	[Cu A^1 ser]	2.23	2.10	2.14	0.647	268
8	[Cu A^1 threo]	2.22	2.10	2.14	0.648	268
9	[Cu A^1 hist.H$_2$O]	2.14	2.08	2.10	0.472	195
10	H[Cu A^1 asp.H$_2$O]	2.18	2.06	2.10	0.461	191
11	H[Cu A^1 glut.H$_2$O]	2.23	2.07	2.12	0.554	229

this indicates the involvement of amino and imino nitrogens in coordination with the metal ion.

In the complexes (9), (10) and (11) additional bands are observed around 3600-3200, 1630-1600 and 800-700 cm^{-1}, due to the presence of coordinated water and these are assigned to ν(OH), δ(HOH) and ρ(HOH), respectively[10]. Further, in the far infrared spectra all the complexes show vibrations of ν(Cu$-$N) and ν(Cu$-$O) around 500 and 400 cm^{-1} respectively[11-14].

The electronic spectra of the copper(II) complexes (1)-(8) show strong bands around 15500 and 25000 cm^{-1} which may be assigned to $^2B_{2g}\leftarrow{}^2B_{1g}$ and $^2E_g\leftarrow{}^2B_{1g}$ transitions respectively (characteristic of square planar geometry)[15], while the remaining complexes, (9)-(11), each show a broad absorption band around 16000 cm^{-1}. Tetragonal copper(II) complexes are expected to show the transitions $^2A_{1g}\leftarrow{}^2B_{1g}$, $^2B_{2g}\leftarrow{}^2B_{1g}$ and $^2E_g\leftarrow{}^2B_{1g}$, but bands due to these transitions usually overlap to give one broad absorption band[16]. The broad band observed in the present complexes around 16000 cm^{-1} suggests that it has tetragonal configuration around copper(II) ion. Further, all the complexes show bands above 26000 cm^{-1} which are attributed to charge transfer[17].

All the complexes are found to be paramagnetic (Table 1) showing the presence of one unpaired electron. The small excess over the spin-only value (1.73 B.M.) observed in the present complexes may be due to spin-orbit coupling. The μ_{eff} for these complexes have also been calculated and the experimental values are in good agreement with the calculated ones.

The ESR spectra of Cu(II) complexes in solid state at room temperature exhibit two peaks, one intense absorption at high field and the other with lower intensity at low field. From these peaks the values of $g_{\parallel}$ and $g_{\perp}$ have been calculated using Kneubuhl's method[18]. All the complexes show an isotropic ESR spectra with $g_{\parallel}>g_{\perp}$ (Table 2), characteristic of $d_{x^2-y^2}$ ground state[19]. The $g_{\parallel}$ obtained for these Cu(II) complexes is less than 2.3 indicating that the metal-ligand bond is of covalent character[20]. The α^2 values for all the complexes fall in the range 0.4-0.6 indicating the presence of appreciable in-plane covalency[21].

The spin-orbit coupling constant (λ) for all the complexes is found to be less than that of the free metal ion ($\lambda_0=-828$ cm^{-1}) suggesting considerable mixing of ground and excited terms. The $|g|$ values are also useful for calculating the magnetic moments (μ) of the complexes and the calculated values are in agreement with the experimental ones[22].

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