

Copper(II) Complexes of 3,5-Dimethylsalicylal-4-aminoantipyrine

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Copper(II) perchlorate, nitrate, acetate, chloride and bromide complexes of 3,5-dimethylsalicylal-4-aminoantipyrine (DMSAAPH) having the composition CuLX where $\text{L} = \text{DMSAAPH}$ and $\text{X} = \text{ClO}_4$, NO_3 , OAc , Cl or Br have been isolated. The IR spectra of the complexes reveal that DMSAAPH behaves as a monovalent tridentate ligand coordinating through the hydroxyl, carbonyl and azomethine groups. Molar conductances of the complexes in nitrobenzene show 1:1 electrolytic behaviour of the perchlorate complex and the non-electrolytic nature of the other complexes. All the complexes dissociate in acetonitrile and methanol. The magnetic measurements show the presence of weak metal-metal interaction in the perchlorate complex.

Studies carried out in our laboratory on copper(II) complexes of salicylal-4-aminoantipyrine¹, 2-hydroxynaphthal-4-aminoantipyrine² and structurally similar ligands² showed that these ligands act as univalent tridentate and the perchlorate complexes have a dimeric structure showing low magnetic moments. Presently complexes of copper(II) perchlorate, nitrate, acetate, chloride and bromide with 3,5-dimethylsalicylal-4-aminoantipyrine have been prepared and characterised. It appears that the presence of two methyl groups in the aromatic moiety, though adjacent to two of the three donor sites, has no marked effect on the coordination characteristics of the ligand in comparison to the parent salicylal-4-aminoantipyrine.

Preparation of complexes and their characterization

An equimolar mixture of 4-aminoantipyrine and 2,5-dimethylsalicylaldehyde in ethanol was heated on a water-bath (75°C) for about 1 hr. On cooling bright yellow crystals were formed, which were filtered, washed with ethanol and recrystallised from hot ethanol to give 3,5-dimethylsalicylal-4-aminoantipyrine (DMSAAPH), m.p. 230° (Found: C, 71.69; H, 6.24; N, 12.47; $\text{C}_{20}\text{H}_{21}\text{N}_3\text{O}_2$ requires C, 71.62; H, 6.30; N, 12.52); PMR: δ 3.28 (3H, CH_3), 7.37-7.67 (m, 7H, ArH), 10.20 (1H, azomethine H), 12.76 (1H, OH, exchangeable with D_2O).

Copper(II) perchlorate and acetate complexes were prepared as follows: $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.01 mol) (or $\text{CuOAc}_2 \cdot \text{H}_2\text{O}$ in the case of acetate complex) dissolved in hot 1:1 acetone-ethyl alcohol was slowly added to a solution of DMSAAPH (0.01 mol) in the same solvent. The green solution was warmed, allowed to cool, the green precipitate filtered off, washed with acetone and benzene successively and finally dried over CaCl_2 .

Copper(II) chloride and bromide complexes were prepared by the following general method. A solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.01 mol) or anhydrous CuBr_2 (0.01 mol) in hot ethanol (95%) was added to a solution of DMSAAPH (0.01 mol) in hot ethanol. The solution was warmed, allowed to cool, the green complexes which separated were filtered, washed with acetone and hot benzene and dried over CaCl_2 .

Copper(II) nitrate complex was obtained by treating a hot solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.01 mol) in hot acetone with a solution of DMSAAPH (0.01 mol) in hot acetone. The green complex which separated out was filtered, washed successively with acetone and hot benzene, and finally dried over CaCl_2 .

The analytical data of the green coloured complexes are given in Table 1.

The molar conductances of nitrate, acetate, chloride and bromide complexes show them to behave as non-electrolytes in nitrobenzene³⁻⁵. All the complexes show considerable dissociation in methanol. Only the nitrate complex shows dissociation in acetonitrile. The perchlorate complex behaves as a 1:1 electrolyte in nitrobenzene, methanol and acetonitrile.

The salient features of the IR spectra of the complexes are: (i) νOH (hydrogen-bonded) of the ligand around 3300 cm^{-1} disappears in the spectra of all the complexes; (ii) The $\nu\text{C}=\text{O}$ of the free ligand around 1640 cm^{-1} is shifted to lower wavenumber in all the complexes; and (iii) $\nu\text{C}=\text{N}$ of the free ligand at 1585 cm^{-1} is shifted to lower wavenumbers. These observations support the coordination of the ligand through the $-\text{OH}$ group, carbonyl group and azomethine nitrogen. The IR spectrum of the nitrate complex also showed coordination of the nitrate group (1025 cm^{-1} band) to the central metal ion. The nitrate group is monodentate as the separation of the two new bands (1290 and 1450 cm^{-1}) of the coordinated nitrate group is 160 cm^{-1} (see ref. 6). The perchlorate complex shows a band around 1080 cm^{-1} which is not very sharp. This can only be due to solid state interaction as the conductance data show the ionic nature of the perchlorate group. The nature of the acetate group

Table 1—Characterisation Data of Cu(II) Complexes

Complex	Found (Calc.), %				μ_{eff}	Λ_M (ohm ⁻¹ cm ² mol ⁻¹)		
	M	C	N	Anion		Nitro-benzene	Methanol	Aceto-nitrile
Cu(DMSAAP)ClO ₄	12.63 (12.75)	48.42 (48.42)	8.32 (8.43)	20.1 (19.95)	1.71	28.0	113.0	168.0
Cu(DMSAAP)NO ₃	13.91 (13.78)	51.85 (52.11)	12.01 (12.16)	—	1.92	7.3	71.7	68.7
Cu(DMSAAP)OAc	13.69 (13.88)	58.20 (57.70)	9.13 (9.138)	—	2.10	6.0	75.1	16.6
Cu(DMSAAP)Cl	14.75 (13.63)	55.05 (55.30)	9.63 (9.67)	8.05 (8.16)	2.02	8.4	70.3	13.4
Cu(DMSAAP)Br	13.51 (13.27)	50.25 (50.16)	8.81 (8.78)	16.55 (16.55)	1.92	5.9	79.7	13.2

cannot be predicted from the IR spectra because there are ligand vibrations in the region where carboxyl group vibrations are expected. However, a weak broad band at 1565 cm⁻¹ and a medium intensity, sharp band at 1335 cm⁻¹ can be attributed to the $\nu\text{C}=\text{O}$ and $\nu\text{C}-\text{O}$ respectively. The positions of these vibrations and their separation (230 cm⁻¹) correspond to the unidentate coordination of the acetate group⁶.

The effective magnetic moments of all the complexes (Table 1) except that of the perchlorate complex are in the range expected for copper(II) complexes containing one unpaired electron. The perchlorate complex shows a value slightly lower than the normal value indicating the presence of a weak interaction between copper atoms in this complex.

The electronic spectra of all the complexes show broad absorption band around 700 nm indicating a distorted octahedral configuration for these complexes. An intense band around 450 nm in all complexes is attributed to charge transfer process.

The perchlorate complex of DMSAAPH may have a dimeric structure similar to the one reported earlier¹. But the magnetic moment data indicate that the

interaction between the two copper atoms is very weak. Attempts to isolate pure monomeric perchlorate complex were unsuccessful. Strong σ -donors like pyridine and dimethyl sulphoxide were found to disrupt the complex completely while comparatively weaker donors like dioxan and acetonitrile did not have any effect on the complex. The two CH₃ groups adjacent to the coordinating hydroxyl and azomethine groups probably cause greater magnetic dilution in the present case.

The nitrate, acetate, chloride and bromide complexes can be assigned a structure having three donor atoms from a ligand molecule and the fourth position being occupied by an anion. Six coordination of the copper can be achieved by interaction with two electron rich sites in the nearby molecules.

References

- 1 Radhakrishnan T, Joseph P T & Prabhakaran C P, *J inorg nucl Chem*, **38** (1976) 2217.
- 2 Gopalakrishnan Nair M R & Prabhakaran C P, *J inorg nucl Chem*, **43** (1981) 3390.
- 3 Walmsley J A & Tyree S V, *Inorg Chem*, **2** (1963) 312.
- 4 Sathyanarayana D N & Patel C C, *Indian J Chem*, **5** (1967) 360.
- 5 Deacon G B, Green J H S & Nyholm R S, *J chem Soc*, (1965) 3411.
- 6 Preti C & Tosi G, *Can J Chem*, **53** (1975) 117.