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SYNTHESIS AND X-BAND EPR SPECTRA OF BINARY AND TERNARY COMPLEXES OF COPPER(II) WITH SALICYLIDENEANTHRANILIC ACID AND IMIDAZOLES

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ABSTRACT

The synthesis and EPR spectra of some binary and ternary complexes of copper(II) with a terdentate ligand, salicylideneanthranilic acid (H_2SAA) and some monodentate imidazoles viz. imidazole (im) and 2-ethylimidazole (e-im), are described. The binary complex with copper(II) and salicylideneanthranilic acid shows a subnormal magnetic moment and EPR spectra for spin-spin interaction. The zero-field splitting parameter D has been evaluated as 190 G and the copper-copper distance as 5.227 Å. The ternary complexes show magnetic moments and EPR spectra which suggest a distorted tetrahedral geometry around copper(II).

INTRODUCTION

This communication describes the synthesis and EPR spectra of binary and ternary complexes of copper(II) with a terdentate ligand, salicylideneanthranilic acid (Fig. 1, H_2SAA). We have only recently

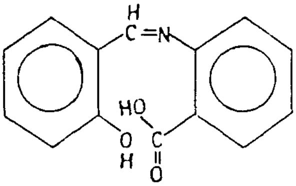

Fig. 1. The Tridentate Ligand H_2SAA.

reported[1-3] polarographic and X-band EPR studies on ternary complexes of copper(II) with glycylglycine and imidazoles. Ternary complexes of copper(II) are important biologically as copper transport species in living systems[4].

RESULTS AND DISCUSSION

Salicylideneanthranilic acid crystallizes out from an equimolar mixture of salicylaldehyde and anthranilic acid in ethanol[5].

Cu(II)-SAA Complex

$$Cu^{2+} + H_2SAA \rightarrow [Cu(SAA)] + 2H^+$$

H_2SAA forms a crystalline yellowish-green 1:1 complex with copper(II) as shown by the analyses in Table I. Salicylideneanthranilic acid is a potential terdentate ligand, $O\frown N\frown O$, coordinating through the imino nitrogen, phenolic oxygen and the carboxylic group. Such terdentate ligands are known to form binuclear copper(II) complexes, which have been the subject of extensive magnetochemical studies[6] for exploring the nature of the spin-spin interaction. The copper(II) complex of salicylideneanthranilic acid under investigation also shows a subnormal magnetic moment value (1.67 B.M.) at room termperature, indicating the presence of spin-exchange

Table I
Analytical and Physical Data

Sl. No.	Complex (Empirical Formula	Color	M.p. (°C)	Yield (%)	% Found (Calc)		μ_{eff} (B.M.)	λ_{max} (nm)
					Cu	N		
1	H_2SAA ($C_{14}H_{11}NO_3$) [F.W., 241]	Light Red	195	78	-	5.81 (5.81)	-	-
2	$[Cu(SAA)]_2$ ($C_{28}H_{20}N_2O_6Cu_2$) [F.W., 607.1]	Yellowish green	280[a]	65	20.45 (20.93)	4.68 (4.61)	1.67	691
3.	[Cu(SAA)(im)] ($C_{17}H_{12}N_3O_3Cu$) [F.W., 369.5]	Green	260[a]	75	16.95 (17.19)	11.13 (11.37)	2.19	662
4.	[Cu(SAA)(e-im)] ($C_{19}H_{16}N_3O_3Cu$) [F.W., 397.5]	Light Green	240[a]	70	15.82 (15.98)	10.59 (10.56)	2.13	687

[a] Decompostion temperature.

interaction. X-band EPR spectra of the complex, discussed below, are also characterisitic of a triplet state resulting from interaction between the unpaired spins of two copper(II) ions. The following tentative structure (Fig. 2), therefore, is proposed for this complex.

X-band EPR spectra of the complex have been recorded at room temperature as well as at liquid nitrogen temperature. The spectrum at room temperature is shown in Fig. 3 (a). The spectrum is unlike that of a tetragonal copper(II) complex and indicates the pressence of spin-spin interaction. The value[7-9] of G (= g_1-2/g_2-2) comes out to be 3, which again suggests spin-spin interaction supporting the results obtained from the magnetic moment measurements. The EPR spectrum of the copper(II)

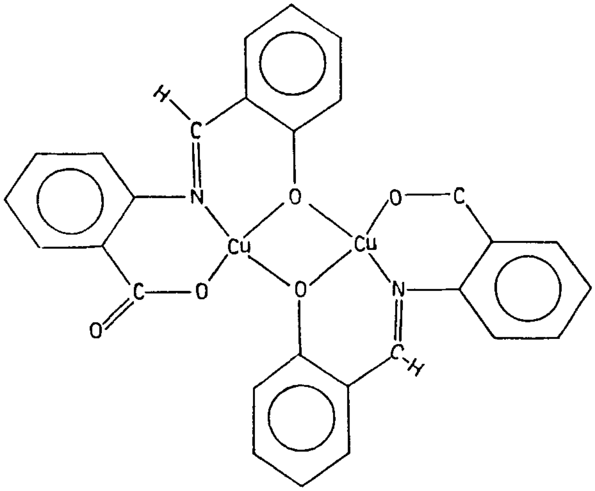

Fig. 2. Copper(II) Complex of H_2SAA.

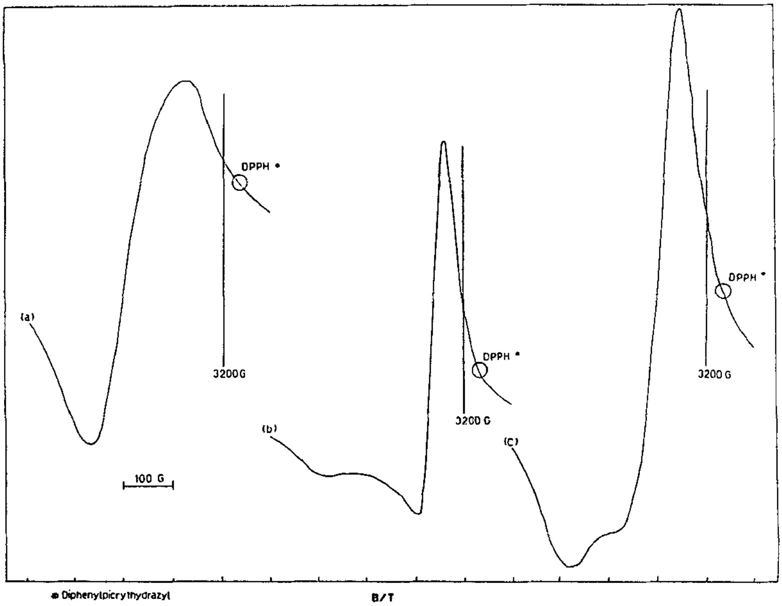

Fig. 3. X-band EPR Spectra (room temperature); (a) $[Cu(SAA)]_2$ (b) [Cu(SAA)(im)] and (c) [Cu(SAA)(e-im)].

complex involving spin-spin interaction may be interpreted by following the energy level diagram shown in Fig. 4. When two copper(II) centres with S = ½ interact, the EPR results from the state with S = 1 yield states for M_S = 0, ±1. The two expected spin-allowed EPR transitions occur at 2925 G and 3125 G, respectively, yielding the two g-values as $g_1 = 2.214$ and $g_2 = 2.073$. From these values, the zero field spliting parameter has been obtained as 190 G. Following Chasteen et al[10]. the copper-copper distance has been evaluated as 5.227 Å.

Cu-SAA-im/e-im Complexes

$$Cu^{2+} + H_2SAA + im/e\text{-}im \rightarrow [Cu(SAA)(im/e\text{-}im)] + 2H^+$$

In the presence of imidazole/2-ethylimidazole a green species with a ratio 1:1:1 of Cu:SAA:im/e-im is isolated. In view of the terdentate nature of SAA, the following tentative structure (Fig. 5) is suggested for the ternary complexes.

The Cu(II)-SAA-im/e-im complexes show magnetic moments of 2.19 and 2.16 B.M., respectively. The tetra-coordinate structure, as suggested above, may provide a planar or a tetrahedral geometry around copper(II). The observed room termperature magnetic moment values favour a tetrahedral structure.

The X-band EPR spectra of the two complexes have been recorded at room temperature as well as at liquid nitrogen temperature. No temperature variation either in shape or intensity is observed in either case. The spectra at room temperature are shown in Fig. 3 (b) and (c). The EPR parameters evaluated from the spectra are presented in Table II.

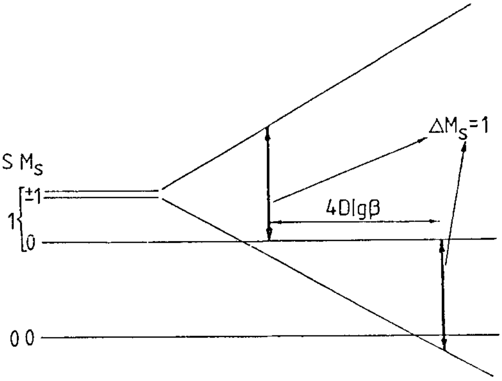

Fig. 4. Energy Level Diagram Showing EPR Transitions in a Dinuclear Copper(II) System.

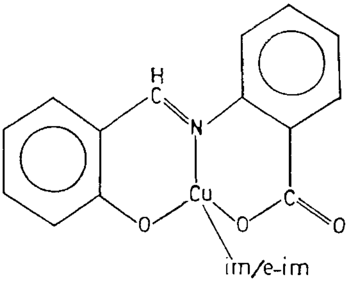

Fig. 5. Suggested Structure of Ternary Complex.

Electronic Spectra

Electronic spectra for all the complexes have been recorded in ethanol. The binary complex $[Cu(SAA)]_2$ and the ternary complexes [Cu(SAA)(im/e-im)] show similar spectra. The λ_{max} values are presented in Table I. It appears that the dimeric complex $[Cu(SAA)]_2$ breaks down to a monomer, $[Cu(SAA)(solvent)_n]$, in solution. The ternary complexes also undergo solvation in solution to form $[Cu(SAA)(im/eim)(solvent)_n]$ to

Table II
EPR Parameters of Copper(II) Complexes

Sl. No.	Complex	Temp.	g_1	g_2	g_{av}
1	$[Cu(SAA)]_2$	RT	2.214	2.073	2.144
		LNT	2.213	2.071	2.142
			$g_{\parallel}$	$g_{\perp}$	g_{av}
2.	[Cu(SAA)(im)]	RT	2.218	2.053	2.108
		LNT	2.227	2.057	2.114
3.	[Cu(SAA)(e-im)]	RT	2.213	2.061	2.112
		LNT	2.208	2.061	2.110

acquire an octahedral environment around copper(II). This conclusion is based on the positions of the absorption bands, at 15100 cm^{-1} for [Cu(SAA)(im)] and 14550 cm^{-1} for [Cu(SAA)(e-im)], which fall in the range for octahedral copper(II). Also, the positions of the absorption bands in the three complexes suggest the following sequence of the ligand field strength: ethanol (or water) < ethyl imidazole < imidazole.

EXPERIMENTAL

Materials

Salicylaldehyde (E. Merck), anthranilic acid (S. D. Fine Chem. Ltd.), copper sulphate pentahydrate (E. Merck) and the imidazoles (Aldrich) were used as purchased from the companies. All other chemicals used were of reagent grade.

Salicylideneanthranilic Acid (H_2SAA) Equimolar ethanolic solutions (50 mL each) of salicylaldehyde (120 mg, 1 mmol) and anthranilic acid (137 mg, 1 mmol) were mixed together and stirred. The resulting

Schiff base crystallized out, which was filtered, washed with small amounts of ethanol and dried in an electric oven at 60°C, yield 0.188 g (78%); mp. 195°C.

Preparation of the complexes

Copper(II)-SAA (Binary Complex) An ethanolic solution (50 mL) of the ligand (241 mg, 1 mmol) and an aqueous solution (50 mL) of copper(II) sulphate pentahydrate (250 mg, 1 mmol, 50 mL) were mixed together and refluxed for half an hour. A yellowish-green complex separated out. It was filtered, washed with water/ethanol (1:1) and dried in an electric oven at 60°C, yield 0.395 g.

Copper(II)-SAA-im/eim (Ternary Complexes). An ethanolic solution (50 mL) of Cu(SAA) (607 mg, 1 mmol) and an aqueous solution (50 mL) of imidazole/2-ethylimidazole (68 mg/83 mg, 1 mmol) were mixed together and refluxed for nearly half an hour. The resulting product crystallized out on cooling. It was filtered, washed with ethanol and dried in an electric oven at 60°C, yield 0.277 g for the imidazole and 0.278 g for the 2-ethylimidazole containing ternary complexes.

EPR Spectra

X-band EPR spectra were recorded with a Varian E-line Century Series EPR spectrometer equipped with a dual cavity and operating at X-band with 100 KHz modulation. Solid diphenylpicrylhydrazyl (DPPH) was used as field marker.

Magnetic Moments

Magnetic susceptibility measurements were made on a Gouy Balance using mercury(II) tetrathiocynatocobaltate(II) as calibrating agent ($\chi_g = 16.44 \times 10^{-6}$ c.g.s. units).

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