

## ESR and Magnetic Properties of Copper(II)–Hydroxycarboxylic Acid Complexes

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Received January 2, 1979

*Hydroxycarboxylatocopper(II) complexes of the type  $\text{Cu}(\text{o-ca})_2$ ,  $\text{Cu}(\text{m-ca})_2$  and  $\text{Cu}(\text{hna})_2$  [o-ca = o-cresotic acid, m-ca = m-cresotic acid, hna = 2-hydroxy-3-naphthoic acid] synthesized in aqueous and alcoholic medium were studied by ESR and magnetic susceptibility measurements. The ESR spectra of o-ca complexes show three lines and anomalous low magnetic moment values are observed at varying temperature (295–85 K). The results indicate a binuclear bridged structure with exchange interaction between  $\text{Cu}^{2+}$  pairs. m-ca Complexes are magnetically dilute and  $\mu_{\text{eff}}$  values are nearly temperature independent including those of hna complexes. ESR parameters  $g_{\parallel}$ ,  $g_{\perp}$ ,  $g_{\text{av}}$ , and  $D$  have also been calculated.*

### Introduction

Hydroxycarboxylic acids are widely employed for various analytical studies such as metallochromic

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indicator, chromogenic reagent for the spectrophotometric, fluorescent and excellent gravimetric reagent for the determination of metal ions [1–3]. Thermodynamic values of stepwise stability constants involving mononuclear and mixed ligand complexes have also been reported [4–8]. In the present paper, ESR and magnetic studies at varying temperature of copper complexes formed by o-cresotic acid (o-ca), m-cresotic acid (m-ca) and 2-hydroxy/3-naphthoic acid (hna) isolated in aqueous, methanol and ethanol media have been described.

### Experimental

Samples analysed by elemental, infrared and thermal studies were available from earlier work and given in Table I [9].

Derivatives of the ESR spectra were recorded on a Varian V-4500-10 ESR Spectrophotometer with a 100-kc/sec Modulation unit (V-4560), together with a 12-in magnet and a Varian Fieldial V-FR 2501 power supply. The magnetic field was earlier calibrated. DPPH was used as g marker.

TABLE I. Analytical Data for Complexes.

Complex	%C		%H	
	Calcd.	Found	Calcd.	Found
$\text{Cu}(\text{o-ca})_2 \cdot \text{H}_2\text{O}$	50.04	50.00	4.17	4.40
$\text{Cu}(\text{o-ca})_2 \text{EtOH} \cdot \text{H}_2\text{O}$	50.27	49.90	5.12	4.90
$\text{Cu}(\text{o-ca})_2 \text{MeOH} \cdot \text{H}_2\text{O}$	49.08	49.25	4.81	4.40
$\text{Cu}(\text{m-ca})_2 \cdot \text{H}_2\text{O}$	50.04	50.10	4.17	3.95
$\text{Cu}(\text{m-ca})_2 \text{EtOH}$	52.47	51.85	4.85	4.80
$\text{Cu}(\text{m-ca})_2 \text{MeOH} \cdot \text{H}_2\text{O}$	49.08	49.60	4.81	4.30
$\text{Cu}(\text{hna})_2 \text{EtOH} \cdot 2\text{H}_2\text{O}$	55.45	55.40	4.62	4.26
$\text{Cu}(\text{hna})_2 \cdot 2.5\text{H}_2\text{O}$	54.73	55.00	3.94	4.09
$\text{Cu}(\text{hna})_2 \text{MeOH} \cdot 1.5\text{H}_2\text{O}$	55.60	55.20	4.23	4.27

TABLE II. Detailed Magnetic Data for Cu(II)-Hydroxy-carboxylic Acid Complexes.<sup>a</sup>

Complex	Temp. K	$\chi'_M \times 10^6$ cgs/mol	$\mu_{\text{eff}}$	
Cu(o-ca) <sub>2</sub> ·H <sub>2</sub> O	86	218	0.36	
	97	242	0.40	
	112	385	0.56	
	137.5	535	0.74	
	215	600	0.99	
	293	828	1.37	
Cu(o-ca) <sub>2</sub> EtOH·H <sub>2</sub> O	87.5	668	0.66	
	97	645	0.68	
	111.5	566	0.69	
	135.5	553	0.75	
	190	651	0.98	
	293	908	1.43	
Cu(o-ca) <sub>2</sub> MeOH·H <sub>2</sub> O	85	557	0.60	
	97	706	0.72	
	111.5	619	0.72	
	137.5	542	0.75	
	194	519	0.87	
	292	946	1.46	
Cu(m-ca) <sub>2</sub> EtOH	86	362	0.50	
	96.5	493	0.62	
	136	393	0.65	
	187.5	406	0.78	
	292	1002	1.53	
	Cu(m-ca) <sub>2</sub> ·H <sub>2</sub> O	86.5	4436	1.66
97		4179	1.71	
$\theta = -8$ K		112	3907	1.79
137		3541	1.90	
202		2311	1.88	
292		1690	1.94	
Cu(m-ca) <sub>2</sub> MeOH·H <sub>2</sub> O	86.5	3610	1.53	
	97	3305	1.55	
	$\theta = -5$ K	112	3013	1.59
	136	2370	1.57	
	191	1760	1.60	
	293	1582	1.88	
Cu(hna) <sub>2</sub> EtOH·2H <sub>2</sub> O	88	5244	1.85	
	97	4791	1.86	
	$\theta = -6$ K	112	4274	1.89
	136.5	3566	1.92	
	155	3173	1.93	
	293	1761	1.99	
Cu(hna) <sub>2</sub> ·2.5H <sub>2</sub> O	84.5	6239	1.95	
	97	5589	1.99	
	$\theta = -8$ K	111	4170	1.85
	137.5	3494	1.89	
	167	2764	1.86	
	293	1815	2.01	
Cu(hna) <sub>2</sub> MeOH·1.5H <sub>2</sub> O	86.5	5144	1.88	
	97	5073	1.97	
	$\theta = 0$ K	111.5	4322	1.95
	137	3370	1.91	
	192.5	1868	1.68	
	292	1638	1.94	

<sup>a</sup> Abbreviations: o-ca = o-cresotic acid; m-ca = m-cresotic acid; hna = 2-hydroxy-3-naphthoic acid.

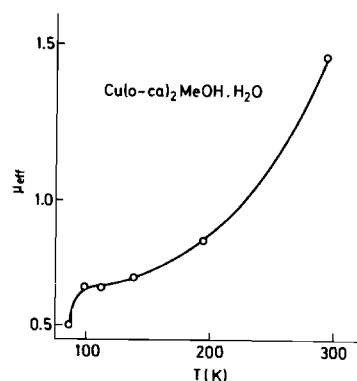


Fig. 1. Temperature dependence of the magnetic moment of Cu(o-ca)<sub>2</sub>MeOH·H<sub>2</sub>O complex.

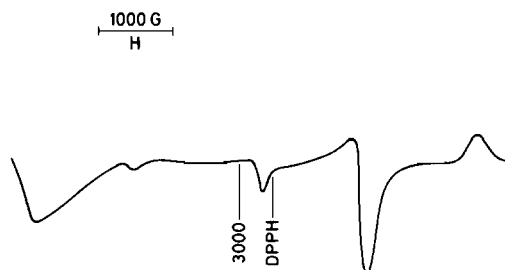


Fig. 2. ESR spectra of Cu(o-ca)<sub>2</sub>·H<sub>2</sub>O.

Magnetic susceptibility measurements were done in the temperature range 85–295 K by Faraday's method [10] consisting of a Mettler BE 22 single pan balance, an electromagnet with a power supply, a liquid nitrogen cryostat together with a temperature variation and control unit and EMCO Digital Micro-voltmeter EE 214.

## Results and Discussion

### Binuclear Species

The temperature independent paramagnetism  $N\alpha$  was taken into account and was subtracted from the corrected molar susceptibility  $\chi'_M$  using Pascal's Constant. The correction is particularly necessary for those complexes where  $\chi'_M$  values are relatively low. The effective magnetic moment,  $\mu_{\text{eff}}$ , was calculated using the equation,

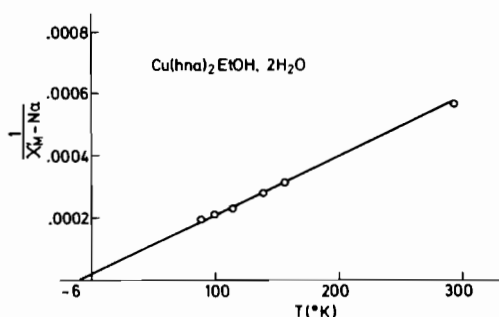
$$\mu_{\text{eff}} = 2.83 [(\chi'_M - N\alpha)T]^{1/2}$$

Values of  $\mu_{\text{eff}}$  are given in the Table II.

Copper(II) complexes formed by o-cresotic acid show a low magnetic moment in the range 1.37–1.46 B.M. at room temperature which is strongly temperature dependent and is characteristic of anti-ferromagnetism. These values are anomalously low as compared with the theoretical spin-only moment

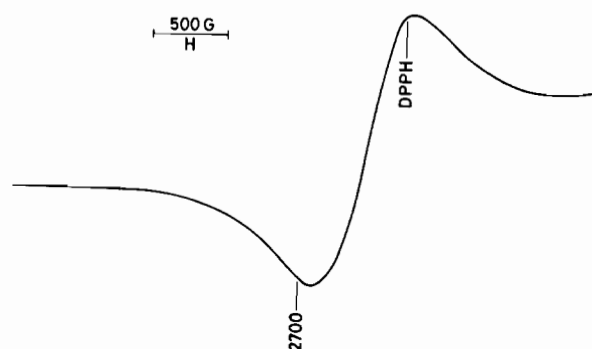
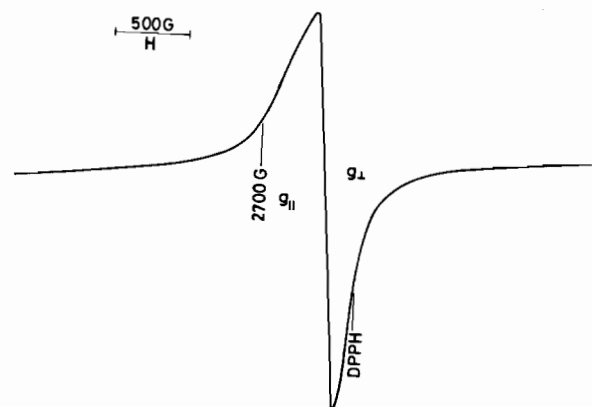
TABLE III. ESR Parameters for Cu(II)–Hydroxycarboxylic Acid Complexes Obtained from Powder Spectra.

Complex	$g_{\parallel}$	$g_{\perp}$	$g_{av}$	D (cm <sup>-1</sup> )
Cu(o-ca) <sub>2</sub> ·H <sub>2</sub> O	2.25	2.17	2.19	0.316
Cu(o-ca) <sub>2</sub> EtOH·H <sub>2</sub> O	2.30	2.12	2.18	0.307
Cu(o-ca) <sub>2</sub> MeOH·H <sub>2</sub> O	2.20	2.19	2.19	0.318
Cu(m-ca) <sub>2</sub> EtOH	2.34	2.15	2.21	0.297
Cu(m-ca) <sub>2</sub> ·H <sub>2</sub> O	–	–	2.17	–
Cu(m-ca) <sub>2</sub> MeOH·H <sub>2</sub> O	–	–	2.18	–
Cu(hna) <sub>2</sub> EtOH·2H <sub>2</sub> O	2.25	2.05	2.12	–
Cu(hna) <sub>2</sub> ·2.5H <sub>2</sub> O	2.20	2.08	2.12	–
Cu(hna) <sub>2</sub> MeOH·1.5H <sub>2</sub> O	2.24	2.07	2.13	–

Fig. 3. Weiss constant  $\theta$  for Cu(hna)<sub>2</sub>EtOH·2H<sub>2</sub>O.

of an unpaired electron of Cu(II) ion (1.73). The value further falls on lowering the temperature (Fig. 1) which seems to indicate a binuclear structure. It is further supported by the values of the energy separation between lowest singlet and higher triplet,  $|2J|$  calculated from the average values of  $g$ -factor obtained from ESR measurements and experimental values for  $\chi'_M$ . All those values lie in the same range (314, 279, 267 cm<sup>-1</sup>) as those observed by J. Krätšmar-Šmogrovič *et al.* [11, 15] for similar copper(II) complex, copper(II) acetate monohydrate and by other investigators [12–14].

The ESR spectra of *o*-cresotatocopper(II) complexes (Fig. 2) show together three lines in the range of magnetic field  $H_1 = 100$ –260 Oe,  $H_{11} = 3480$ –4730 Oe,  $H_{111} = 5930$ –6310 Oe. The lines  $H_1$  and  $H_{111}$  arise out of the transition of triplet state ( $S = 1$ ) and evidently the spectra indicate the presence of Cu<sup>2+</sup> pairs. This fact is supported by the anomalous low magnetic moment value as stated above. The ESR parameters  $g_{\parallel}$ ,  $g_{\perp}$ , and the zerofield splitting parameter  $D$ , have been calculated and given in Table III. The average  $g$  values obtained from the above principal  $g$  values range between 2.18–2.19. In the binuclear *o*-cresotatocopper(II) complexes, the influence of water and alcohol molecules are approximately equal which is indicated by the closely related  $D$  values (0.307–0.318 cm<sup>-1</sup>). The calculated

Fig. 4a. ESR spectra of Cu(m-ca)<sub>2</sub>MeOH·H<sub>2</sub>O.Fig. 4b. ESR spectra of Cu(hna)<sub>2</sub>EtOH·2H<sub>2</sub>O.

values of  $g_{\parallel}$ ,  $g_{\perp}$ ,  $g_{av}$ , and  $D$  agree very well with the characteristic values for carboxylatocopper(II) complex [16]. This is a known 2-centre carboxyl copper complex in which the antiferromagnetic exchange interaction is present. Both ESR and magnetic data evidently confirm a binuclear structure having linked Cu–Cu atoms in this series of complexes.

#### Mononuclear Species

In the case of *m*-cresotic acid and hydroxycarboxylic acid complexes Weiss constant  $\theta$  was found by

plotting  $1/(\chi'_M - N\alpha)$  against T (Fig. 3).  $\mu_{\text{eff}}$  was calculated by using the expression

$$\mu_{\text{eff}} = 2.83[\chi'_M - N\alpha(T + \theta)]^{1/2}$$

Values of  $\mu_{\text{eff}}$  are given in the Table II.

The complexes formed by m-cresotic acids are magnetically dilute and the magnetic moment was found to be nearly temperature independent, except for those isolated in ethanolic medium. This is in good agreement with the theoretical predictions for monomeric copper(II) complexes. Similar observations were made for hydroxynaphthoic acid complexes where changes in  $\mu_{\text{eff}}$  values with changes in temperature were not significant enough.

The ESR spectrum of m-cresotatocopper(II) complex is different from the above spectra (Fig. 4a), except for those isolated in ethanolic medium. It consists of a single comparatively broad line at g values varying from 2.17–2.21. It is found that  $g_{\parallel} > g_{\perp}$ . This is in agreement with the similar ESR spectra observed by Lancaster and Coworkers [17] for a copper(II) complex and interpreted as pseudoisotropic arising from the exchange interaction between crystallographically non-equivalent  $\text{Cu}^{2+}$  ions and the weak hyperfine splitting.

$\mu_{\text{eff}}$  values were also determined by substituting g,  $g_{\parallel}$  and  $g_{\perp}$  values for monomeric copper(II) complexes in the following equation,

$$\mu_{\text{eff}}^2 = \frac{g_{\parallel}^2}{4} + \frac{g_{\perp}^2}{2} + \frac{3kT}{\lambda_0}(g - 2)$$

The values obtained are consistent with those observed by magnetic susceptibility measurements. In hydroxynaphthoic acid complexes, one sharp absorption band was observed (Fig. 4b). Monomeric Cu(II) complexes formed by m-ca and hna have tentative structures involving two carboxylic groups and the other two positions occupied by O atom of  $\text{H}_2\text{O}$  or alcohol. The  $-\text{OH}$  group does not take part in complexation which has also been observed by other investigators [11, 12].

## Acknowledgements

The author is grateful to Prof. G. Govil, Tata Institute of Fundamental Research, Bombay, for providing facilities and helpful suggestions, to Prof. A. Chakravorty, Calcutta, for reviewing the manuscript and to the University Grants Commission, New Delhi, for awarding a National Associateship.

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