# SPECTRAL AND ESR FEATURES OF SOME COPPER(II) CHELATES WITH 2-HYDROXYARYLOXIMES

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Abstract—Copper(II) complexes of 2-hydroxyaryloximes were synthesized and characterized on the basis of elemental analyses, molecular weight determinations, conductivity and magnetic moment measurements, and ESR, IR and electronic absorption (in solutions and in solid state) spectroscopy. Implications of the magnetic and spectral data in relation to the structures of the complexes are discussed. Solvent effects are also considered.

Considerable interest has been shown in the coordination chemistry of bivalent transition metals with hydroxyoximes during the last decades because of their applications as analytical reagents in solvent extraction systems<sup>1–3</sup> and in hydrometallurgy.<sup>4–6</sup> However, most of the studies have been concerned with kinetic and equilibrium extraction properties and relatively little work has been reported on the isolation and characterization of the extracted species.<sup>7</sup>

It was, therefore, thought worthwhile to undertake a systematic study of the isolated bivalent metal chelates with some 2-hydroxyoximes. Moreover, the new application of copper(II) chelates of salicylaldoxime and related ligands as anti-proliferative and anti-neoplastic agents<sup>8a,8b</sup> has focused our interest in the preparation and chemical characterization of some copper(II) chelates with the following 2-hydroxyaryloximes: 2-OH,C<sub>6</sub> H<sub>4</sub>CR=NOH [R = H (Hsaox), CH<sub>3</sub> (Hapox), C<sub>2</sub>H<sub>5</sub> (Hppox), C<sub>6</sub>H<sub>5</sub> (Hbpox)] or 2-OH,5-Me,C<sub>6</sub> H<sub>3</sub>C(CH<sub>3</sub>)=NOH (Hmpox), 2-OH,4-MeO,C<sub>6</sub>H<sub>3</sub>C (C<sub>6</sub>H<sub>5</sub>)=NOH (Hopox).

The compounds prepared characterized by elemental analysis, conductivity and magnetic susceptibility measurements, spectral (IR, electronic in solution and in solid state, reflectance) and ESR studies. Based on these, tentative structures for some copper(II) chelates are proposed.

## EXPERIMENTAL

## Preparation of the compounds

The synthesis of the ligands was achieved employing literature methods.<sup>9,10</sup> The chelates were prepared by established methods,<sup>11,12</sup> that is by adding to an ethanolic solution of the oxime (10 mmol) the appropriate amount of the metal chloride (5 mmol) dissolved in water slightly acidified with hydrochloric acid  $(1 \text{ cm}^3 \text{ of } 1 \text{ M solution})$ . The dropwise addition of CuCl<sub>2</sub> took ca 10 min while the oxime solution was stirred magnetically. The mixture was then filtered and the precipitate was purified with repeated recrystallization from chloroform-ether solution. The chelates prepared are olive-green and are stable in air, both in the solid state and in solution, and rather soluble in most common organic solvents. The compounds prepared, their melting points, molecular weights, magnetic moments and elemental analyses are listed in Table 1.

## Physical measurements

IR spectra were recorded in the range 4000-250 cm<sup>-1</sup> on a Perkin–Elmer 1430 spectrophotometer using KBr pellets. Electronic spectra in chloroform solutions were obtained on a Perkin–Elmer Hitachi 200 spectrophotometer employing 10 mm teflon stoppered quartz cells. Reflectance spectra of undiluted compounds were measured on a Beckman DK2 spectrophotometer in both the UV-vis and

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	Complex	M.p. (°C)	Mol. wt	Yield (%)	μ <sub>eff</sub> ( <b>B</b> . <b>M</b> .)	N (%)	C (%)	H (%)	Cu (%)
1	Cu(saox) <sub>2</sub> <sup>a</sup>	222-223	335	74	1.82	8.3	49.5	4.1	18.9
2	Cu(apox) <sub>2</sub>	240-241	363	69	1.82	$(8.3)^{\circ}$ 7.4 (7.7)	(49.8) 52.4 (52.5)	(4.1) 4.6 (4.9)	(18.9) 17.6 (17.5)
3	Cu(mpox) <sub>2</sub>	278–279	391	84	1.84	6.9 (7.1)	53.7 (54.9)	5.0	16.1 (16.2)
4	Cu(ppox) <sub>2</sub>	226-228	391	71	1.83	7.1	54.5 (54.9)	5.1 (5.6)	16.1 (16.2)
5	Cu(bpox) <sub>2</sub>	290-291	487	66	1.88	5.3 (5.7)	63.7 (63.7)	4.1 (4.5)	13.0 (13.0)
6	Cu(opox) <sub>2</sub>	255–257	547	80	1.82	5.0 (5.1)	61.1 (61.1)	4.7 (4.7)	11.5 (11.6)

Table 1. Analytical, physical and magnetic data for the copper(II) chelates

<sup>a</sup> Given for comparison.

<sup>b</sup> Calculated values in parentheses.

near-IR regions. Mobile solutions in dichloromethane and solid-state ESR spectra were recorded on a Bruker X-band spectrometer calibrated against DPPH.

Carbon, hydrogen and nitrogen were determined by microanalysis using a Perkin–Elmer 240B elemental analyser. Melting points were determined on a Reichert heated plate apparatus and are uncorrected. Molar conductivities were measured on a WTW conductivity bridge employing a calibrated dip-type cell in nitrobenzene. Magnetic susceptibility measurements on powdered samples were performed at 25°C employing the Faraday method on a home-build balance calibrated against Hg[Co(SCN)<sub>4</sub>]. Diamagnetic corrections were estimated from Pascal's constants.

## **RESULTS AND DISCUSSION**

The reaction of the copper(II) ion with 2-hydroxyaryloximes proceeds smoothly. The presence of additional substituents in the phenyl ring does not affect the progress of the reaction and neither do the groups attached to the carbon bearing the oxime group. The elemental analyses are consistent with a metal-to-ligand ratio of 1:2.

The solubility of these chelates in a wide variety of organic solvents precludes polymeric and multinuclear structures and these indications are augmented by the molecular mass determinations. The molar conductivity of their solutions indicates that these chelates are non-electrolytes.

#### Magnetic measurements

The mononuclear copper(II) complexes with a  $d^9$  electronic configuration usually give magnetic

moments close to the spin-only value 1.73 B.M. at room temperature. Actually, the corrected values found ( $\mu_{eff} = 1.82-1.88$  B.M., Table 1) suggest a monomeric structure with strong covalent bonds.<sup>13,14</sup> These values are also in agreement with those normally found for copper(II) complexes having an orbitally non-degenerate ground state.<sup>15</sup>

#### IR spectra

The IR bands of the ligands that are of interest in the present work and their assignment are given in Table 2. The IR spectra of the ligands disclose the influence of the substituents. Upon coordina-



Fig. 1. (a) X-band ESR spectrum of a powdered sample of the Cu(mpox)<sub>2</sub> complex, recorded at room temperature. (b) X-band ESR spectrum of the Cu(box)<sub>2</sub> complex in mobile solution.

	Complex	=N—OH	—C—N	PhOH v	PhOH $\delta$	С—О	Cu—N
1	Cu(saox) <sub>2</sub>	3020	1600			1190st	490
		(3380) <sup>a</sup>	(1615)	(1410)	(1255)	(1190w)	
2	Cu(apox) <sub>2</sub>	3080	1600		_	1145st	450
		(3330)	(1610)	(1405)	(1285)	(1125w)	
3	Cu(mpox) <sub>2</sub>	2960	1615			1145st	520
		(3330)	(1615)	(1360st)	(-)	(1130w)	
4	Cu(ppox) <sub>2</sub>	2970	1595		_	1135m	540
		(3350)	(1610)	(1410)	(1285)	(1120w)	
5	Cu(bpox) <sub>2</sub>	2940	1600		` <u> </u>	1150st	560
		(3360)	(1600)	(1410)	(1285)	(1150w)	
6	Cu(opox) <sub>2</sub>	3060	1600			1180	
		(3390)	(1600)	(1370)	(—)	(—)	

Table 2. Wavenumber  $(\bar{\nu}/cm^{-1})$  of selected absorption bands in the IR spectra of the chelates and the corresponding free ligands

<sup>a</sup> Values in parentheses refer to the free ligand.

w = weak; m = medium; st = strong.

tion the intense bands stemming from the stretching and bending vibrational modes of the phenolic OH disappear indicating the removal of a hydrogen atom, while the sharp band at  $3360 \pm 30$  $cm^{-1}$  that is attributed to the stretching vibration of the O-H bond in the N-O-H group is shifted to significantly lower frequencies (Table 2), indicative of the coordination of a nitrogen atom and strong hydrogen bonding.<sup>16,17</sup> Evidence for this coordination also arises from the small shift towards lower frequencies of the band at 1600 cm<sup>-1</sup> assigned to the C=N bond.<sup>18,19</sup> The bands originating from the C-O stretching vibrations exhibit very small shifts while their intensity is enhanced appreciably (Table 2). These bands are not split nor are those due to the Cu-N bonds, which is indicative of the trans configuration of these chelates.<sup>12,20</sup> In the region 400-600 cm<sup>-1</sup> the chelates exhibited the medium intensity bands attributable to M-N bonds, while the M-O ones are not so distinguishable.

## ESR spectra

The room temperature ESR spectra of powdered samples of the complexes exhibit absorptions typical for the mononuclear species with axial symmetry. A representative spectrum of the Cu  $(mpox)_2$  complex is shown in Fig. 1(a). In the case of Cu(ppox)<sub>2</sub> and Cu(opox)<sub>2</sub> complexes, however, there is a strong exchange interaction with  $g_{\perp}$  being averaged at 2.058 and 2.052, respectively.

The ESR spectrum in mobile  $CH_2Cl_2$  solution of the  $Cu(bpox)_2$  complex [Fig. 1(b)] consists of four groups splitting to five lines each, although the first two are not so well resolved. This hyperfine interaction observed for all the complexes [with the exception of  $Cu(saox)_2$ ] is attributable to interactions with the two nitrogen nuclei adjacent to the copper ion.

The  $g_{\perp}$ ,  $g_{\parallel}$  and  $g_{iso}$  parameters and the copper coupling constant  $A_{iso}$ , as well as the nitrogen coupling constant  $a_{iso}$  calculated from the spectra, are

	Complex	$g_{\perp}$	${oldsymbol{g}}_{{\scriptscriptstyle \parallel}}$	$g_{\parallel}$ calc.	$g_{ m iso}$	A <sub>iso</sub> (G)	a <sub>iso</sub> (G)
1	Cu(saox) <sub>2</sub>	2.060	2.179	2.174	2.098	92	
2	Cu(apox) <sub>2</sub>	2.045	2.185	2.204	2.098	92	17
3	Cu(mpox) <sub>2</sub>	2.042	2.189	2.207	2.097	90	17.5
4	Cu(ppox) <sub>2</sub>	2.058	_	2.181	2.099	91	16.5
5	Cu(bpox) <sub>2</sub>	2.045	2.190	2.204	2.098	90	16
6	Cu(opox) <sub>2</sub>	2.052		2.187	2.097	90	16

Table 3. ESR data for the chealtes

summarized in Table 3. It has been shown that the relative magnitudes of the q values for copper(II) complexes can be used to distinguish certain types of coordination environments. The g values calculated for the complexes under investigation are not influenced by the ligands in a noticeable way and are closely comparable to those found in other mononuclear copper(II) tetra-coordinated complexes of square planar arrangement with  $D_{2h}$  or  $D_{4h}$  symmetry.<sup>21,22</sup> Especially from the  $g_{\parallel}$  and  $g_{iso}$ magnitudes we can predict the planar (2.22 and 2.11, respectively) or tetrahedral (2.23-2.53 and 2.13, respectively) symmetry for the  $CuN_2O_2$  chromophore.<sup>23,24</sup> So, our values found  $g_{\parallel} = 2.18-2.20$ ,  $g_{\parallel} > g_{\perp} \simeq 2.0$  and  $g_{\rm iso} = 2.098$  are in good agreement with a co-planar structure, which is correlated with the  $d_{x^2-y^2}$  ground state electron configuration.<sup>25</sup> In addition, the values found for  $A_{iso}$  and  $a_{iso}$  parameters (90 and 16 G, respectively) are a little higher but comparable with those found for the related copper(II) bis(salicylaldehyde) imines.26,27

### Electronic absorption spectra

From X-ray diffraction studies<sup>28,29</sup> it is known that the bis(salicylaldoximato)copper(II) as well as the 5-chloro complexes have a trans-planar configuration which deviates slightly from complete planarity. The copper(II) ion has a distorted octahedral coordination with Cu-N = 1.94 Å, Cu - O = 1.92 Å and N - Cu - O angle = 91°. Based on these data and those found from IR, magnetic moments and ESR for the copper complexes under investigation, we can assume a  $D_{2h}$  microsymmetry in which the x, y Cartesian coordinates bisect the bidentate ligands. The upper orbital is xy and the four lower orbitals are close together in energy.<sup>30</sup> In chloroform solutions a single absorption band is observed in the visible region for all the complexes centred at 646 nm (15,500 cm<sup>-1</sup>). The electronic spectra were obtained in CHCl<sub>3</sub> solutions and in Nujol mulls. The spectrum of a representative complex such as Cu(opox), in Nujol is given in Fig. 2(a) together with the spectrum of the free ligand Hopox [Fig. 2(b)]. Comparison of the two spectra suggests that the two intense bands (log  $\varepsilon = 4.7$ ) at 240 and 300 nm are due to the ligand and should be assigned to  $\pi - \pi^*$  transitions. The band at 360 nm (27,800  $\text{cm}^{-1}$ ) is assigned to metalto-ligand charge-transfer because of its intensity and position. Besides the major ligand field band at 646 nm (Band I) there are two shoulders at 450  $(22,200 \text{ cm}^{-1})$  and 540 nm  $(18,500 \text{ cm}^{-1})$  (Bands II and III) due to the metal as well, which steal intensity from the arising MLCT transition. These two



Fig. 2. (a) Electronic absorption spectra of Cu(opox)<sub>2</sub> in Nujol mull. (b) Electronic absorption spectra of the ligand Hopox in Nujol mull. (c) Reflectance spectrum for the complex Cu(ppox)<sub>2</sub>.

shoulders are apparent in the reflectance spectra of the complexes, a representative one is given in Fig. 2(c) for the complex Cu(ppox)<sub>2</sub>.

The assignments of the electronic spectra in Nujol and in  $CHCl_3$  as well as those of the reflectance are given in Table 4. The position of the bands is not influenced by the ligands in a noticeable way and



Fig. 3. Electronic absorption spectra of Cu(ppox)<sub>2</sub> in several solutions. (a) CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub>; (b) DMF; and (c) pyridine.

	Complex	а	$\frac{\mathbf{MLCT}}{(\bar{\boldsymbol{\nu}}/\mathbf{cm}^{-1})}$		Band III $(\bar{\nu}/\mathrm{cm}^{-1})$	Band II $(\bar{\nu}/cm^{-1})$	Band I $(\bar{\nu}/\mathrm{cm}^{-1})$	
		R	27,000		22,000	18,500sh	15,500	
1	$Cu(saox)_2$	Ν	28,000		22,200	18,000sh	15,000	
		С	29,200	(3.95) <sup>b</sup>			15,000	(1.96)
		R	23,800		20,500	19,000	15,700	
2	$Cu(apox)_2$	Ν	28,700		22,500	18,500	15,000	
		С	30,100	(3.93)			15,600	(1.91)
		R	26,300		21,600	18,200	15,100	
3	$Cu(mpox)_2$	Ν	27,300		22,200	18,300	15,000	
	/-	С	29,200	(3.94)			15,300	(2.11)
		R	27,400		21,900	18,200	15,500	
4	$Cu(ppox)_2$	Ν	28,000		21,700	18,400	15,200	
		С	29,800	(3.90)			15,700	(2.02)
		R	26,600		22,700	19,200	15,300	
5	Cu(bpox) <sub>2</sub>	Ν	28,000			18,900	15,300	
		С	29,200	(3.98)			15,300	(2.07)
		R	27,800		22,200	18,500	15,400	
6	Cu(opox) <sub>2</sub>	Ν	27,800		22,200	18,500	15,500	
		С	30,200	(4.36)			15,300	(2.09)

Table 4. Band maxima in the electronic excitation spectra  $(\bar{\nu}/cm^{-1})$ 

 ${}^{a}R = Data$  from reflectance spectra; N = data from Nujol mull spectra; C = data from chloroform solution spectra.

<sup>b</sup> Log  $\varepsilon$  in parentheses. Band maximum was taken as the highest absorbance of the band.

is related with those found in the literature for the  $Cu(saox)_2$  and  $Cu(bpox)_2$  complexes.<sup>31,32</sup>

In order to study the behaviour of the complexes under investigation in solution, the UV–vis spectra were obtained in  $CH_2Cl_2$ , DMF and in pyridine. It is noticed (Fig. 3) that in  $CH_2Cl_2$  the spectrum profile is the same as in  $CHCl_3$  and in the solid state, while in DMF (solvent with a great donor number) there is a shift to higher frequencies. In the case of pyridine, the spectrum reveals that a coordination of one pyridine molecule takes place leading to a five-coordinate square pyramid geometry.<sup>33,34</sup>

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