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ESR Spectra of Halogeno–Copper(II) Complexes with Tripod-like Ligands

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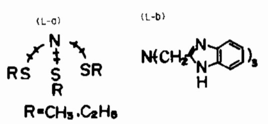
In the course of the study on the catalytic activity of copper(II) complexes for the oxidation of diphenols [1], we found that some halogeno–copper(II) complexes with tripod-like ligands, such as (L-a) and (L-b) (illustrated below) show unusual solution ESR spectra at room temperature.



The copper(II) complexes of [Cu(L-a)X]Y have already been prepared by Ciampolini *et al.* [2] (X = Y = Br), and Suzuki *et al.* [3] (X = Cl⁻, Br⁻, I⁻, Y = ClO_4^-). The ligand, (L-b) has been prepared by Thompson *et al.* [4], and its copper(II) complexes were prepared in this study. The preparative method for [Cu(L-b)I] ClO_4 is as follows. To a cold methanol solution (15 ml) of $[Cu(H_2O)_6](ClO_4)_2$ (0.001 mol) and (L-b) (0.001 mol), was added dropwise a cold methanol solution (10 ml) of NaI (0.002 mol). Brilliant brownish-red crystals were yielded. *Anal.* Found: C, 41.2%; H, 3.0%; N; 14.0%. Calcd. for $[Cu(C_{24}H_{21}N_7)I]ClO_3$: C, 40.8%; H, 3.4%; N; 13.7%. ESR spectra were measured with a JEOL ESR apparatus model JES-3X-ME by use of an X-band.

Figure 1 shows the ESR spectra of [Cu(L-a)X]·ClO_4 (X = Cl⁻, Br⁻, I⁻) in nitromethane solution at room temperature. In the case of X = Cl⁻, a four-lined hyperfine structure due to the copper nuclear spin (I = 3/2) was observed, as is generally observed for usual copper(II) complexes. However, in the ESR spectra of [Cu(L-a)Br]ClO_4 and [Cu(L-a)I]ClO_4, seven and nine peaks were observed, respectively. Similar spectrum was also observed for [Cu(L-b)I]·ClO_4. The ESR parameters obtained at room temperature are listed in Table I.

The ESR spectra of these complexes in frozen solutions (77 K) and in corresponding Zn(II) complexes are very similar to those reported by Barbucci *et al.* [5], thus indicating that one unpaired electron of these halogeno–copper(II) complexes with (L-a) and (L-b) lies in the d_{z^2}-orbital [6]. Since this orbital combines with p- and s-orbitals of halogens to form the Cu–X bond, the unpaired electron is delocalized over the copper d_{z^2} and halogen p and s orbitals. This may be the main origin for unusual ESR spectra observed for $[Cu(L\text{-}a)Br]^+$ and $[Cu(L\text{-}a)I]^+$ complexes.

TABLE I. ESR Parameters of Copper(II) Complexes.*

Complex	R	X	g_{ave}	$\lvert A_{ave}\rvert$(gauss)
[Cu(L-a)X] ClO_4	CH_3	Cl	2.085	66
		Br	2.074	65
		I	2.071	85
	C_2H_5	Cl	2.085	65
		Br	2.070	65
		I	2.073	88
[Cu(L-b)X] ClO_4		I	2.108	59

*295 K, in nitromethane.

TABLE II. A_{iso} Values of Chlorine, Bromine and Iodine Atoms.

Atom	Natural Abundance (%)	A_{iso}(gauss)	Nuclear Spin (I)
^{35}Cl	75.4	1672	3/2
^{37}Cl	25.6	1391	3/2
^{79}Br	50.57	7764	3/2
^{81}Br	49.43	8370	3/2
^{127}I	100	7320	5/2

The isotropic coupling, A_{iso} is related to the electron spin density at the interacting nucleus, and is also related to the magnetic moments of the nucleus. The full expression is [7]

$$A_{iso} = 8\pi/3 \cdot g_N \beta_N \cdot \lvert\psi_o\rvert \text{ (gauss)}$$

where $\lvert\psi_o\rvert$ is the probability of finding the electron in a unit volume at the nucleus [7]. In the case of solution spectra, the A_{iso} value is determined by the contribution from s-orbital only, and the values are given in Table II. It is noteworthy that the value of A_{iso} of chlorine atom is much smaller than those of bromine and iodine atoms. Thus, the hyperfine splitting due to the chlorine atom should be much smaller than those of bromine, iodine and also copper atoms.

It is well known that Br⁻ and I⁻ are softer ligands than Cl⁻, suggesting that more covalent Cu–X σ-bonding is formed for X = Br⁻ and I⁻ than that for X =

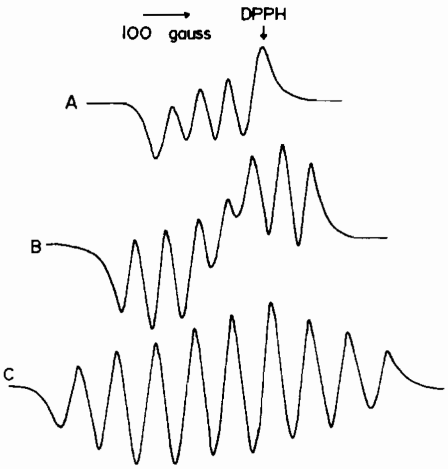


Fig. 1. ESR spectra of copper(II) complexes in nitromethane at 295 K. A, $[Cu(L\text{-}a)Cl]ClO_4$; B, $[Cu(L\text{-}b)Br]ClO_4$; C, $[Cu(L\text{-}a)I]ClO_4$.

Cl^-. From this point of view, larger hyperfine splitting is also expected for Br^- and I^- analogues compared with the Cl^- analogue.

Similar ESR spectra were also found for the halogeno–copper(II) complexes with tripod-like ligands of the N_2S_2 donor-set, $R_2NCH_2CH_2N(CH_2CH_2SCH_3)_2$ [8]. More detailed investigations by use of computer simulation are now in progress.

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