Cu(II) Complexes of the Oximes of 2-Hydroxy-5-methyl-acetophenone, -propiophenone & -butyrophenone

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Received 30 *May* 1975; *accepted* 11 *August* 1975

Cu(II) complexes of 2-hydroxy-5-methyl-acetophenone, -propiophenone and -butyrophenone oximes have been prepared and assigned square-planar structures on the basis of magnetic moment, visible and ESR spectral studies.

THE present note describes the preparation and characterization of Cu(II) complexes of 2-hydroxy-5-methylacetophenone oxime (HMAO), 2-hydroxy-5-methylpropiophenone oxime (HMPO) and 2-hydroxy-5-methylbutyrophenone oxime (HMBO). Magnetic moments and electronic and ESR spectra of the complexes have been studied.

Preparation of complexes — Ethanolic solution of the ligand and aqueous solution of Cu(II) sulphate were mixed in 1:2 (metal-ligand) ratio. *p*H was raised to 7·0 by adding ammonia solution and the contents refluxed for 30 min when dirty-white complex separated out. It was filtered, washed with water, 50% ethanol and dried at ~80°. The complexes are insoluble in water and ethanol but soluble in other common organic solvents.

The complexes have 1:2 stoichiometry as revealed by analytical data (Table 1) and behave as non-electrolytes in nitrobenzene. Magnetic susceptibility measurements on solid complexes were carried out at room temperature by Gouy method using $Hg[Co(NCS)_4]$ as the calibrant. $Cu(HMAO)_2$, $Cu(HMPO)_2$ and $Cu(HMBO)_2$ show $\mu_{eff.}$ values of 1·898, 1·901 and 1·900 BM respectively.

Irrespective of the stereochemistry involved, Cu(II) complexes should show magnetic moments corresponding to one unpaired spin[1]. Although, theory suggests that there should be some correlation between the magnitude of the orbital contribution and the coordination geometry, in practice this is not observed, because of distortions in geometry and other factors like covalence. The observed magnetic moments of Cu(II) complexes fall in the range 1·9-2·1 BM unless there is some interaction between the unpaired electrons on different Cu atoms[2]. The present complexes show values close to 1·9 BM indicating absence of any interaction between different Cu atoms.

The visible spectra of the complexes (recorded in chloroform on Perkin-Elmer 37 UV-visible spectrophotometer) resemble those of square-planar complexes of Cu(II) and show bands at 15400 and 19600 cm^{-1} (as a shoulder to the charge-transfer absorption). Following Figgis[3], the band at 15400 cm^{-1} is assigned to the transition $^2A_{1g} \rightarrow {}^2B_{1g}$ and that at 19600 cm^{-1} to the transition $^2E_g \rightarrow {}^2B_{1g}$.

The *g* values in the ESR spectra of the complexes (for powdered solid samples recorded on a Varian V-4502-12 EPR spectrometer) have been calculated by standard procedure[4] and are presented in Table 1. As against three different *g* values expected in principle, only two different *g* values are observed as usual. The results are in good agreement with the magnetic data of the complexes.

Kivelson and Neiman[5] have shown that $g_\parallel$ is a moderately sensitive function for indicating covalency. For ionic environments $g_\parallel$ is normally 2·3 or larger, and for more covalent environments it is less than 2·3. In view of this the covalency of the metal-ligand bond in the present complexes may be taken to follow the order: HMAO>HMPO>HMBO. This is reverse to the order of the metal-ligand stability constants as determined by *p*H-metric titrations (log β_2; HMAO = 23·7, HMPO = 24·0 and HMBO = 24·2).

The authors thank Dr G. D. Sootha of the National Physical Laboratory, New Delhi for ESR measurements.

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TABLE 1 — ANALYTICAL, MELTING POINT AND ESR DATA OF THE COMPLEXES

Complexes	m.p. (°C)	Analytical data, Found (calc.)				$g_\perp$	$g_\parallel$	$g_{av.}$*
		Metal (%)	C (%)	H (%)	N (%)			
$Cu(C_9H_{10}O_2N)_2$	254	16·2 (16·2)	55·8 (55·4)	5·30 (5·10)	7·03 (7·15)	2·086	2·151	2·108
$Cu(C_{10}H_{12}O_2N)_2$	244	15·01 (15·1)	57·0 (57·2)	6·12 (5·72)	6·52 (6·67)	2·117	2·158	2·131
$Cu(C_{11}H_{14}O_2N)_2$	213	14·4 (14·2)	59·2 (59·0)	6·35 (6·25)	6·10 (6·25)	2·129	2·173	2·147

*$g_{av.} = \frac{1}{3}(g_\parallel + 2g_\perp)$. (Ref. 6).