On the Hyperfine Structure of the ESR Spectra of Copper(II) Complexes

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(Received May 17, 1966)

The solvent effects on the ESR spectra of several copper(II) complexes have been investigated in order to examine the theoretical basis of the ESR of copper(II) complexes. When planar 4-coordinated copper(II) complexes are dissolved in basic solvent, one or two of the basic solvent molecules are known to coordinate to the complexes along the axis normal to the molecular plane; spectroscopical studies of these phenomena have been carried out by several authors.(1) For this work the ESR spectra of cupric bis-acetylacetone chelate (I) and cupric bis-acetylacetone-ethylenediimine chelate (II) were measured in various solvents; the ESR spectra of II in all the solvents used show a clearly-resolved extra hyperfine structure due to the two nitrogen nuclei of ligand. The magnetic parameters determined are listed in Table I.

It is shown in Table I that the g values increase and the absolute A values decrease remarkably when the basicity of the solvent used is increased. The odd electron is placed in the antibonding B_{1g} molecular orbital, in which the coefficient of $d_{x^2-y^2}$ is taken as α. The values of α^2 were evaluated from copper hyperfine interaction by the usual procedures;(2) they are listed in the last column of Table I, from which it may be seen that α^2 decreases as the solvent basicity increases. However, it is reasonable to consider that α^2 should increase in basic solvents for the following reasons: First, the covalency of the metal-ligand bonding should decrease upon the coordination of basic solvent molecules because of the repulsion between the 3d electrons and the electrons which come from the solvent molecules, and the increase of α^2 is theoretically consistent with the tendency for $g_{\parallel}$ to increase. Second, the extra hyperfine interaction energy of the ligand nitrogen nuclei in II decreases in basic solvent; this fact definitely indicates that α^2 increases in basic solvents. It may be concluded from the above discussion that there is some uncertainty as to the theoretical basis of the ESR of copper(II) complexes.

The Fermi contact term, k_0, arises from the spin polarization of s-electrons and has been assumed to be constant.(3) In the case of planar copper(II) complexes in basic solvents, the 4s-orbital of the copper atom interacts with the σ-orbitals of solvent molecules; the degree of their mixing depends on the basicity of the solvents. Therefore, the spin polarization of the 4s-electrons contributes to the value of k_0 to a varying extent, and k_0 is not exactly constant. It seems that the above mentioned uncertainty can be ascribed to this property of k_0. Recently, Kivelson and Lee reported k_0 to vary in vanadyl complexes.(4) Some other copper(II) complexes show the same solvent effects as the complexes under discussion. Details will be published elsewhere.

TABLE I. MAGNETIC(a) AND BONDING PARAMETERS

Copper complex	Solvent(b)	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}\times 10^4$ (cm^{-1})	$A_{\perp}\times 10^4$ (cm^{-1})	$A_N\times 10^4$ (cm^{-1})	α^2
I	A(c)	2.256	2.056	197	22		0.86
	B	2.309	2.070	167	14		0.84
	C	2.322	2.071	158	14		0.83
II	A	2.191	2.05	207		12.9	0.83
	B	2.218	2.06	195		12.2	0.82
	C	2.230	2.06	186		12.2	0.81

a) All ESR spectra were measured in ca. 0.01 M solution at 77°K.

b) Solvent A: toluene. Solvent B: 10% pyridine, 90% toluene. Solvent C: 10% piperidine, 90% toluene. Magnetic parameters did not depend on the mixing ratio of two solvents in solvents B and C.

c) Although the solubility of I in toluene is very small, the magnetic parameters of I in toluene could be determired from the ESR spectrum measured in toluene-chloroform solvent. Details will be published elsewhere.

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