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Electron Paramagnetic Resonance (EPR) Investigation of Dynamic-Static Jahn-Teller Effect in Cu(II) Doped Ba(5-amino-3,4-dimethylisoxazole)$_6$(SCN)$_2$

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Electron paramagnetic resonance(EPR) studies have been carried out on Cu(II) doped hexakis(5-amino-3,4-dimethylisoxazole)Ba(SCN)$_2$ in the temperature range $300 > T/\mathrm{K} > 90$. Spectra are characteristic of cupric ion substituting Ba(II) ion with O_h point symmetry at room temperature and subsequently distorting to a lower symmetry at 90 K. This observation is made for the first time of Cu(II) ion substituting Ba(II) ion sites.

Cupric ion has been the subject of large number of EPR studies in single crystals, polycrystalline and frozen solution forms.[1] In all these studies the coordination around the cupric ion is found to vary usually from 4 to 6 (though a few cases are reported for the seven and eight coordinated) the point symmetry changing from square planar or tetrahedral to octahedral. Within the six coordination, large variations have been observed. However, the undistorted octahedral or trigonally distorted octahedral are again less common due to the restrictions imposed by the Jahn-Teller theorem. It states, " if a non-linear molecule has an orbital degeneracy when the nuclei are in a symmetrical configuration, then the molecule is unstable with respect to at least one asymmetric distortion of the nuclei. The molecule will distort to lower its energy and remove the orbital degeneracy". In majority of cases the distortion has been a tetragonal distortion of the octahedron.

CuN_6 chromophore has been investigated previously[2-6] when it has been incorporated into its diamagnetic isomorphous lattices involving Zn(II) cation as well as in its undiluted form.[7,8] These studies have involved Cu(ligand)$_6^{2+}$, Cu(ligand)$_3^{2+}$ (bidentate ligand) and Cu(ligand)$_2^{2+}$ (tridentate ligand). We report here for the first time a study involving Ba(II) ion for which cupric ion has been substituted.

Hexakis(5-amino-3,4-dimethylisoxazole)Ba(SCN)$_2$, incorporating less than 0.1% of Cu(II) impurity, is prepared by the method described in the literature.[9] The compound, in brief Ba(5-ADI)$_6$(SCN)$_2$, 1:2 electrolyte in the near and medium IR spectrum shows bands at 2030, 735 and 445 cm^{-1}, respectively, attributed to ν(CN), ν(CS) and ν(NCS). The band positions strongly suggests the thiocyanate groups are ionic. An octahedral structure with an O_h symmetry can be suggested for the thiocyanate compound. EPR spectra were recorded on a Varian E-4 X-band spectrometer with 100 kHz magnetic field modulation. Variable temperature measurements are made with Varian accessories.

In a field of octahedral symmetry, the Cu(II) ion would have a ^2E_g ground state, which, however, is not stable.10) To lift the degeneracy of this ground state, the symmetry of Cu(II) ion must be lowered. This can be affected by superimposing on the octahedron, along one of its axes, tetragonal distortion involving either an elongation or a compression. As a consequence to this, coinciding with the three principal axes of the "copper - octahedron" minima in potential energy are introduced. When the ion is located permanently at one of these minima, the Jahn-Teller distortion is static. The EPR spectra of such compounds will be anisotropic. At higher temperature, higher vibrational modes become occupied, which may carry the ion over the potential energy barriers and thus through the various possible distortions.11) In this case one speaks of dynamic Jahn-Teller distortion. When the measurement time is long compared to the re-orientation time (relaxation time) it would appear as if the Cu(II) ion is in a tetragonally distorted octahedral environment. EPR measurement time is generally longer. In this case of dynamic distortion one obtains isotropic EPR spectrum.

The EPR measurements of Cu(II) doped $Ba(5\text{-}ADI)_6(SCN)_2$ at room temperature gave a symmetric signal with a peak-to-peak linewidth of 9.5 mT and $g_{iso}=2.149\pm0.005$. This suggests that the Cu(II) ion has entered the lattice substitutionally without altering the stereochemistry around Ba(II) ion. The isotropic line is consistent with the expectation for Cu(II) ion entering high symmetry (O_h) site. No other spectral features are observed which would indicate the simultaneous presence of other low symmetry sites as reported for some other lattices.12) At 120 K the isotropic structureless line gives way to hyperfine structure in the low field region. At 90 K, complete anisotropic spectrum is recorded and it is possible to analyze the spectrum using an axial spin-Hamiltonian:

$$H=\beta[g_{||}H_ZS_Z + g_{\perp}(H_XS_X+H_YS_Y)] + A_{||}S_ZI_Z + A_{\perp}(S_XI_X+S_YI_Y),$$

where the terms have the usual meaning. The evaluated parameters are given in Table 1 along with those for other CuN_6 studies. The hyperfine lines are somewhat broad. This is not unusual since Cu(II) ion (ionic radius-0.80Å) replaces Ba(II) ion (ionic radius-1.35 Å).

The range 120> T/K > 90 over which complete anisotropy is reached is an indication of this being a pure dynamic-static Jahn-Teller transition rather a Jahn-Teller transition accompanied by a structural phase transition. The absence of any low symmetry sites also suggests that the arrangement of six monodentate nitrogen donating 5-ADI ligand around Ba(II) ion prevents any weak interaction that may come into play between the cupric ions (helped also by low concentration) when they replace the diamagnetic rather large sized barium cation. In the absence of any structural information on this compound it is not possible to extract more useful information regarding the Jahn-Teller effect.

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Table 1. Spin-Hamiltonian parameters for Cu(II) ion in CuN_6 chromophore in different lattices

Compound[a]	Ligand	g_{iso}[b]	$g_{\parallel}$[c]	$g_{\perp}$[c]	$A_{\parallel}$[c] $/10^{-4}cm^{-1}$	$A_{\perp}$[c] $/10^{-4}cm^{-1}$	Ref.
$Ba(5\text{-}ADI)_6(SCN)_2$	mono-dentate	2.149 ±0.005	2.276 ±0.005	2.077 ±0.005	167.0 ±3	19.0 ±5	This work
$Zn(Im)_6Cl_6$	mono-dentate	2.1702	2.3137	2.1043	171.3	43.0	3)
			2.323	2.085(x) 2.052(y)	169.4	22.0	2)
$Zn(Im)_6(NO_3)_2$	mono-dentate	2.166	2.287	2.097	167.1	24.0	4)
$Zn(N\text{-}MeIm)_6\text{-}(ClO_4)_2$	mono-dentate	2.150	2.307	2.065	165.0	13.0	11)
$Cu(Im)_6(NO_3)_2$	mono-dentate	-	2.275[d]	2.068[d]	-	-	8)
				2.039[d]	-	-	
			2.273[e]	2.059[e]	-	-	8)
				2.039[e]	-	-	
$Zn(en)_3(NO_3)_2$	bi-dentate	2.139	2.248	2.082	167.0	-	5)
$Zn(tach)_2(ClO_4)_2$	tri-dentate	2.121 2.190 2.106 2.080	2.250[f]	2.05[f]	176[f]	15[f]	6)

a) Im, N-MeIm, en, and tach stand for imidazole, N-methylimidazole, ethylenediamine, and *cis,cis*-1,3,5-triaminocyclohexane, respectively.

b) 300 K. c) 90 K. d) 290 K. e) 160 K. f) 80 K.

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