

# EPR SPECTROSCOPY OF COPPER(II) COMPLEXES WITH N-DONOR LIGANDS AND CHLOROSALICYLIC ACID IN FROZEN SOLUTIONS

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The chemical environments of copper(II) ions in the copper(II) complexes containing chlorosalicylic acid (ClSalH) and Cu(II) salts ( $\text{Cu}(\text{ac})_2$  or  $\text{CuSO}_4$ ) and *N*-donor ligands (3-pyridylmethanol (ronicol) or *N,N'*-diethylnicotinamide (denia), with varying ligand-to-metal ratio,  $x$ , [ $\text{Cu}(\text{ac})_2(\text{aq})$  or  $\text{CuSO}_4(\text{aq}) + 2 (\text{ClSalH}(\text{solv})) + x(\text{ronicol}$  or  $\text{denia}(\text{solv}))$ ], where  $x = 0, 1, 2, 4, 6, 8, 12, 16$ , were studied by X-band EPR spectroscopy in the frozen solutions at low temperature of 100 K. The effects of two copper(II) salts (containing anions of different basicity), chlorosalicylic acid and two *N*-donor ligands with varying ligand-to-metal ratio on the formation of resulting complexes in the water/methanol (1:3 v/v) solutions are herein precisely discussed. Well-resolved  $^{14}\text{N}$  superhyperfine splitting lines in the parallel and perpendicular part of the second- and third- derivative axially symmetric Cu(II) EPR spectra indicate that nitrogen atoms could be coordinated to the central Cu(II) ion in the equatorial plane. When *N*-donor ligand concentration was increased, the line resolution and signal intensity of the  $^{14}\text{N}$  superhyperfine splitting patterns increased (for ronicol more progressively) becoming saturated at higher ligand concentrations ( $x > 4$ ). The trend in  $g$ -values ( $g_{\parallel} > g_{\perp} > 2.0023$ ) indicates that the unpaired electron is localized on the  $d_{x^2-y^2}$  orbital on central copper(II) ion. Such rich data cannot be obtained by X-band EPR spectroscopy of powder samples of the given copper(II) complexes.

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