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ORIGINAL PAPER

Investigation of 3,5-dichlorosalicylate-copper(II)-(3-pyridylmethanol or N,N'-diethylnicotinamide) complex systems by EPR spectroscopy

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Copper(II) complex systems, containing 3,5-dichlorosalicylic acid (3,5-Cl_2salH) and different copper salts ($Cu(ac)_2$ or $CuSO_4$), with varying concentrations of 3-pyridylmethanol (ronicol, ron) or N,N'-diethylnicotinamide (denia) as ligands, were prepared. The effects of Cu(II) salts containing anions of different basicity and two different N-donor ligands with varying ligand-to-metal ratio (x) on the formation of the resultant complexes in the water/methanol solutions were studied by EPR spectroscopy at low temperature of 98 K. When ligand concentration was increased, the resolution and signal intensity of the ^{14}N perpendicular super-hyperfine splitting patterns increased (for ron more progressively), becoming saturated at higher ligand concentrations. In comparing the ronicol- and denia-containing systems, both g-factors ($g_\perp$, $g_\parallel$) are systematically higher and the parallel hyperfine splitting ($A_\parallel$) systematically lower in denia-containing systems for both Cu(II) salts.

Keywords: 3,5-dichlorosalicylic acid, 3-pyridylmethanol, N,N'-diehylnicotinamide, copper(II) complexes, EPR spectroscopy

Introduction

Spectroscopic studies of benzoic acid and its derivatives are performed due to their biological and pharmaceutical importance. Salicylic acid and its derivatives find extensive usages in medicine, e.g. as anti-rheumatics, intestinal antiseptics, antipyretics, and analgesics (Krishnakumar & Mathammal, 2009). In particular, the 5-chlorosalcylic and 3,5-dichlorosalicylic acids are important derivatives, which are widely used in medical and pharmaceutical research and industry (Grimes, 1999; Roberts, 2004). In addition, salicylic acid and a number of its derivatives, such as 3,5- and 3,6-dichlorosalicylic acids, are currently finding applications in the cosmetic industry (Paul et al., 2010a).

The use of 3,5-dichlorosalicylic acid has been studied extensively over the last five years. For example, in a series of papers, Dhagat et al. (2008), Carbone et al. (2008), and El-Kabbani et al. (2010, 2011) studied 3,5-dichlorosalicylic acid as a potent inhibitor of human 20α-hydroxysteorid dehydrogenase. Paul et al. (2010a, 2010b, 2011) explored an influence of the chlorine substitution of salicylic acid on the benzene ring (in the sequence of 5-chlorosalicylic, 3,5-dichlorosalicylic and 3,5,6-trichlorosalicylic acids) on the intra-molecular hydrogen bond energy and excited state proton transfer barrier through steady-state absorption, emission, and time-resolved fluorescence spectroscopy.

The structure and properties of Cu(II) complexes with chlorine-substituted derivatives of salicylic acid have been extensively studied by selected spectroscopic techniques in our laboratories (Mojumdar et al., 2003, 2005; Maroszová et al., 2006; Korabik et al., 2011; Martiška et al., 2010, 2011). One of the most useful spectroscopic techniques, which can provide valu-

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