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Imidazolate-bridged Binuclear Copper(II) Complexes with Tripodal Ligands containing Sulfur Donor Atoms

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Imidazolate(Im)-bridged binuclear metal complexes are of interest in connection with some metalloproteins such as bovine superoxide dismutase (Cu(II)–Im–Zn(II)) [1] and cytochrome c oxidase (high-spin Fe(III)–Im–Cu(II)) [2]. Recently, the syntheses and characterization of the Im-bridged binuclear copper(II) complexes have been reported [3, 4]. All the complexes exhibited antiferromagnetic spin-exchange interaction. The energy separation between the spin-singlet ground state and the spin-triplet excited state, –2J, were in the range 40–80 cm^{-1}. Those complexes, however, are composed of nitrogen donor atoms and no Im-bridged binuclear copper(II) complexes containing sulfur donor atoms have been synthesized. Therefore, it is of interest to investigate the physical properties of the Im-bridged binuclear copper(II) complexes containing sulfur donor atoms which play an important role in biological systems. In this work, we report the syntheses and magnetic properties of the Im-bridged binuclear copper(II) complexes with tripodal ligands having NS_3 and N_2S_2 donor sets, $[Cu_2(NS_3\text{-}Me)_2Im](ClO_4)_3$ (1), $[Cu_2(NS_3\text{-}Et)_2Im](ClO_4)_3$ (2), $[Cu_2(N_2S_2)_2Im](ClO_4)_3 \cdot H_2O$(3), and $[Cu_2(N_2S_2\text{-}py)_2Im](ClO_4)_2$ (4), where NS_3-Me, NS_3-Et, N_2S_2, and N_2S_2-py are tris(2-methylthioethyl)amine, tris(2-ethylthioethyl)amine, N,N-bis(2-methylthioethyl)ethylenediamine and 2-[N,N-bis(2-methylthioethyl)amino-methyl]pyridine, respectively.

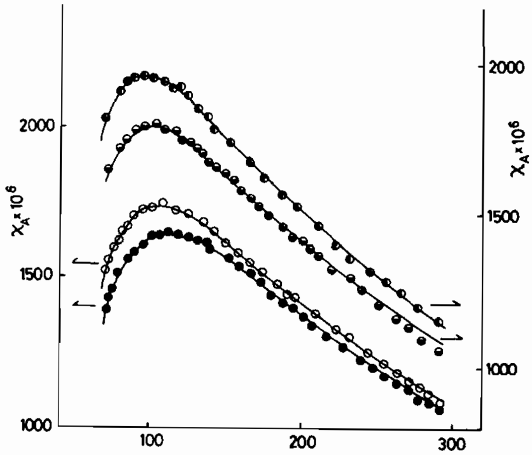

Fig. 1. Temperature dependence of magnetic susceptibilities of $[Cu_2(NS_3\text{-}Me)_2Im](ClO_4)_3$ (○), $[Cu_2(NS_3\text{-}Et)_2Im](ClO_4)_3$ (●), $[Cu_2(N_2S_2)_2Im](ClO_4)_3 \cdot H_2O$ (◐), and $[Cu_2(N_2S_2\text{-}py)_2Im](ClO_4)_2$ (◐).

NS_3-Me and NS_3-Et were prepared according to the method of Sacconi and Morassi [5]. The synthetic methods of the complexes are nearly the same. A typical procedure is as follows. An acetonitrile solution (20 ml) of imidazole (1 mmol) was added to an acetonitrile solution (30 ml) containing $Cu(ClO_4)_2 \cdot 6H_2O$ (2 mmol) and NS_3-Me (2 mmol), and to this mixture was added 10 ml of 0.1 *M* KOH methanol solution. A small amount of insoluble materials was removed by filtration. To this filtrate was added 30 ml of ethanol and the resulting blue-green solution was allowed to stand at room temperature overnight. Deep blue-green crystals which separated were collected and recrystallized from acetonitrile–ethanol (1:1) mixture.

Elemental analyses of the complexes are given in Table I. The results are in good agreement with the calculated values for the Im-bridged binuclear complexes.

Magnetic susceptibilities were measured over a temperature range 78–300 K by the Faraday method.

TABLE I. Elemental Analyses of Complexes.

Complex	Found (Calcd), %		
	C	H	N
$[Cu_2(NS_3\text{-}Me)_2Im](ClO_4)_3$	25.62(25.97)	4.58(4.67)	5.77(5.77)
$[Cu_2(NS_3\text{-}Et)_2Im](ClO_4)_3$	30.46(30.72)	5.36(5.44)	5.36(5.31)
$[Cu_2(N_2S_2)_2Im](ClO_4)_3 \cdot H_2O$	24.67(24.61)	4.83(4.89)	8.99(9.06)
$[Cu_2(N_2S_2\text{-}py)_2Im](ClO_4)_3$	32.11(32.27)	4.51(4.31)	8.54(8.36)

TABLE II. Magnetic Data and Estimated Paramagnetic Impurity.

Complex	$-2J$ (cm^{-1})	g	N × 10^6 (c.g.s./mol)	Paramagnetic Impurity (%)
$[Cu_2(NS_3\text{-}Me)_2Im](ClO_4)_3$	125	2.02	30	
$[Cu_2(NS_3\text{-}Et)_2Im](ClO_4)_3$	132	2.02	30	
$[Cu_2(N_2S_2)_2Im](ClO_4)_3 \cdot H_2O$	118	2.06	30	2
$[Cu_2(N_2S_2\text{-}py)_2Im](ClO_4)_3$	125	2.02	30	2

The susceptibility *vs.* T plots displayed a maximum, indicating an antiferromagnetic spin-exchange interaction between metal ions.

The magnetisms of the complexes are well interpreted on the basis of the Bleany-Bowers equation [6],

$$\chi_A = N\beta^2 g^2/3\kappa T[1 + 1/3\exp(-2J/\kappa T)]^{-1} + \\ + N\alpha + PAR \qquad (i)$$

where each symbol has the general meaning. The third term, PAR, in equation (i) was added to account for the presence of paramagnetic (monomeric) impurity which was found in the complexes (3) and (4), the magnetic moment of a paramagnetic impurity being estimated at 1.90 B.M.

The magnetic parameters obtained by best-fit technique are given in Table II. The $-2J$ values of these complexes are in the range 118–132 cm^{-1}. Antiferromagnetic spin-exchange interactions of these complexes are considerably stronger than those of the complexes previously reported [3, 4], the $-2J$ values of the complexes with N_4 tripodal ligand, tris(2-aminoethyl)amine, being *ca.* 80 cm^{-1} [4]. It is worth noting that the replacement of nitrogen donor atoms by sulfur atoms causes an increase in antiferromagnetic spin-exchange interaction. This is in line with Mikuriya *et al.'s* finding that the binuclear copper(II) complexes with SNO donor sets exhibit a stronger antiferromagnetic spin-exchange interaction compared with the complexes with NNO donor sets [7]. It is also noted that the present complexes show rather lower g-values and temperature-independent paramagnetism. This fact might be attributed to the 'soft' sulfur donor atom. However, in order to discuss such problems more fully, precise structural data are necessary.

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