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Synthesis and Structure of Tris(N-methyl-1-benzimidazol-2-yl) Amine Copper(II) Nitrate with Two-Dimethylsulfoxide Solvate

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Superoxide dismutase (SOD) is a kind of enzyme defending organism from injuxics of superoxygen anionic free radical [1–2]. Its biological active center is the multinuclear transition metal complex, in which the metal ions are bridged by imidazole. Recently, it is known that histidine (imidazole) ligands play a key role in functioning and stabilizing the active sites of numerous copper-protein, such as haemocyanine [3–5], azurin [6–7], whose active sites both contain histidine ligands. Mimicking of those copper proteins through the synthesis of small molecule active site analogues can provide useful data [8–9] and improve the understanding of the relationship between their structures, electronic properties and functions. Therefore, these copper complexes with imidazole ligands are of interest as models. But only a few structures of copper complexes containing imidazole moiety ligands have been reported [10–12]. And it is difficult to synthesize the constructing model of copper proteins [13–15].

The ligand of tris(2-benzimidazolemethyl) amine (NTB) was prepared by the method [16]. 0.01 mol of $Cu(NO_3)_2$ and 0.01 mol of NTB (L) were mixed in the heated methanol solution, keeping the temperature at 50°C, stirring 10 min, cooled to room temperature and then the crude products were obtained. The products were washed with the cooled methanol and dried in air. Blue-green single crystals suitable for X-ray analysis were obtained from slow cooling of warmed DMSO solution. IR spectra were determined with a KBr disk on a PE 1730 infrared spectrophotometer (U.S.A). The strong band at 1460 cm^{-1} assignable to the stretching mode for –C=N of benzimidazole rings of the ligand is shifted to lower frequency by 10 cm^{-1} in the Cu-complex, which indicates SP^2 N atom of benzimidazole rings in the ligand coordi-

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Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC – 150589. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail:deposit@ccdc.cam.ac.uk).

nated to the Cu atom. The broad absorption band at 3200 cm^{-1} suggests that hydrogen bond from NH···O is formed and the bands around 440 cm^{-1} are for the Cu–N stretching modes.

A single crystal with dimensions of 0.25 x 0.30 x 0.35 mm was mounted on a CAD4 diffractometer for data collection with graphite monochromatic MoKα (λ = 0.71073 Å) radiation [17] (Enraf-Nonius, 1992). A total of 4902 independent reflections were collected using $\omega/2\theta$ scan mode in the range of $4 < 2\theta < 46°$, of which 3012 reflections with $I > 2\sigma(I)$ were used for refinements. The intensities were corrected for LP factor and no empirical absorption was corrected. The crystal data are as follows: a = 9.8654(3), b = 12.6656(4), c = 14.8894(3) , α = 94.93(2), β =100.81(2), γ =107.31(2)°, triclinic, space group P-1, Z = 2, F(000) = 778, Dc = 1.44 g cm^{-3}, μ = 0.807 mm^{-1}. The structure was solved by direct method with SHELXS program [18] and refined by full-matrix least-square method with SHELXL program [19]. All non-H atoms were refined anisotropically and all H atoms were fixed geometrically at calculated distances. The final refinement converges to R = 0.0766 on F^2, the goodness-of-fit on F^2 is 1.061. The highest and lowest electron densities on the final difference Fourier map were 0.955 and –0.632 e·Å^{-3}. All work was performed on PC computer with WINGX package [20]. The crystal structure of the title compound consists of separate $[\mathrm{Cu(NTB)NO_3}]^+$ cation, one un-coordinated $\mathrm{NO_3^-}$ anion and 2 DMSO solvent molecules. View of the compound showing the labeling of the non-H atoms (50% probability displacement ellipsoids) is shown in Fig 1. A shape-determining angle $e_3 = 0°$ for square pyramid (SP) coordination configuration and e_3 = 53° for triangle bi-pyramid (TBP) coordination configuration were introduced by Muetterties and Guggenberger [21]. The shape-determining angle e_3 = 0.45° (nearly 0.0°) is found in the title compound, which indicates the copper coordination geometry is a square pyramid (SP). This case is closed to $\mathrm{CuL^{Bu^n}(NO_3)_2}$ amine ($\mathrm{L^H}$ =

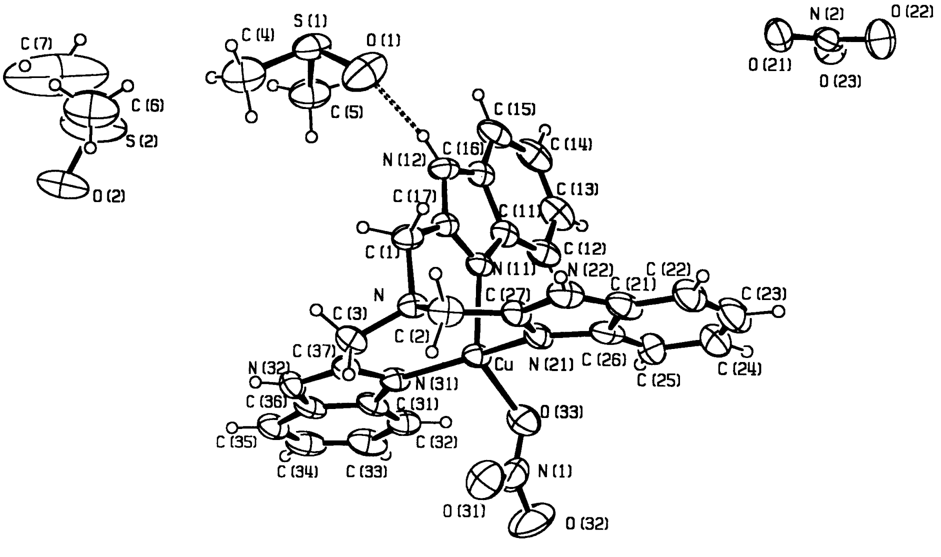

Figure 1. The ORTEP drawing of [Cu(NTB)No$_3$]NO$_3$·2DMSO.

N,N-bis(benzimidazole-2-yl-methyl) (SP configuration) [22], but different from $[Cu_2(tmbma)_2(bztz)(NO_3)]^+$ (TBP configuration) [23]. The Cu(II) atom is five coordinated by N(11), N(21), N(31) and N atoms from the NTB and O(33) atom from one NO_3^-. The N(21), N(31), N and O(33) atoms form an equatorial plane and N(11) atom occupies the apical position. Cu atom is 0.280(2) Å below the equatorial plane. The coordination bonds of Cu(1)–N(11), Cu(1)–N(21), Cu(1)–N(31), Cu(1)–N and Cu(1)–O(33) are 2.094(5), 1.940(5), 1.960(5), 2.252(5) and 2.007(6) Å, respectively. The 1.981 Å of mean Cu–benzimidazole bond distance in the title compound is shorter than 2.049 Å of Cu–imidazole bond distances in the literature [24]. The Cu–benzimidazole bond distances are significantly shorter than the Cu–amine bond distance, which due in part to the greater π bonding ability of benzimidazole pendants compared to alkylamines and exclusively σ-donors [25]. A similar case was also observed in tris(N-methylbenzimidazole-2-yl) amine copper(II) perchlorate hemihydrate [26]. The angles and distances in the benzimidazole parts are quite normal and the phenyl and imidazole rings are planar. The 2.756 Å intra-hydrogen bond distance of N(12)–H(12)- - -O(1) (from DMSO) was found in the structure, which indicates that there are van der Waals contacts and hydrogen bond interactions in the crystal.

Table 1. Selected bond lengths (Å) with estimated standard deviations.

Cu(1)–N(11)	2.094(5)	N(11)–C(11)	1.410(8)	N(31)–C(31)	1.410(8)
Cu(1)–N(21)	1.940(5)	N(11)–C(17)	1.283(8)	N(31)–C(37)	1.290(8)
Cu(1)–N(31)	1.960(5)	N(12)–C(16)	1.355(8)	N(32)–C(36)	1.381(9)
Cu(1)–O(33)	2.007(6)	N(12)–C(17)	1.344(8)	N(32)–C(37)	1.346(8)
Cu(1)–N	2.252(5)	N(21)–C(26)	1.418(10)	C(1)–C(17)	1.509(9)
N–C(1)	1.481(8)	N(21)–C(27)	1.289(8)	C(2)–C(27)	1.490(10)
N–C(2)	1.495(8)	N(22)–C(21)	1.361(10)	C(3)–C(37)	1.496(9)
N–C(3)	1.460(8)	N(22)–C(27)	1.355(8)		

Table 2. Selected bond angles (°) with estimated standard deviations.

N(21)–Cu–N(31)	155.2(2)	C(1)–N–Cu	108.2(4)
N(21)–Cu–O(33)	99.9(2)	C(2)–N–Cu	104.8(4)
N(31)–Cu–O(33)	95.7(2)	C(17)–N(11)–C(11)	106.7(5)
N(21)–Cu–N(11)	93.7(2)	C(17)–N(11)–Cu	113.2(4)
N(31)–Cu–N(11)	97.1(2)	C(11)–N(11)–Cu	139.9(4)
O(33)–Cu–N(11)	114.7(2)	C(17)–N(12)–C(16)	108.1(5)
N(21)–Cu–N	80.1(2)	C(27)–N(21)–C(26)	107.6(6)
N(31)–Cu–N	79.6(2)	C(27)–N(21)–Cu	116.6(5)
O(33)–Cu–N	164.1(2)	C(26)–N(21)–Cu	135.4(5)
N(21)–Cu–N	80.1(2)	C(27)–N(22)–C(21)	107.6(6)
C(3)–N–C(1)	112.2(5)	C(37)–N(31)–C(31)	106.2(6)
C(3)–N–C(2)	114.0(5)	C(37)–N(31)–Cu	117.0(4)
C(1)–N–C(2)	111.6(5)	C(31)–N(31)–Cu	136.7(5)

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