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A new heterospin complex from oxamide-bridged Cu(II) binuclear units and carboxy-phenyl-substituted nitronyl nitroxide

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Abstract

A new heterospin complex **1**, $[Cu_2(oxpn)(NITPBA)_2]$, derived from *trans*-oxamido-bridged copper(II) binuclear units $[Cu_2(oxpn), oxpn = N,N'-bis(2-aminopropyl)oxamide]$ and carboxyl-substituted nitronyl nitroxide, (NITPBAH = 2-(4-carboxy-phenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl-3-oxide), has been synthesized and characterized structurally and magnetically. The complex **1** is a four-spin system. The magnetic susceptibility of **1** was measured over the range 2–300 K, which shows that there are unusually moderate antiferromagnetic-interactions between two copper(II) ions bridged by the oxamato bridge. © 2005 Published by Elsevier B.V.

Keywords: Copper(II) complex; Heterospin; Trans-oxamido-bridged; Crystal structure; Antiferromagnetism

The synthesis and magnetic characterization of polynuclear heterospin complexes derived from paramagnetic metal ions and organic radical molecules have attracted much attention in recent years [1–4]. One of the best strategies to design and synthesize polynuclear species is the 'complex as ligand' approach. For the mononuclear Cu(II) complexes of N,N'-bis(coordinating-group)-substituted oxamides [5], such as [Cu(oxpn)] (Scheme 1), one of the most outstanding characters is the easy transformation of *cis–trans* conformations upon coordination to metal ions (Scheme 2), which makes it practical to design tunable molecular materials with extended structures and desired properties [6,7].

Meanwhile, stable organic radicals, especially, introduction of potential donor atoms into the substituent group of the nitronyl nitroxide, have been found widespread used as ligands in the metal-radical approach to molecular magnetic materials [8–10]. Investigation on the magnetic behavior of the salts of cationic nitronyl nitroxides have been performed and fascinating results have been obtained [11,12]. The use of anionic derivatives will probably offer more possibilities to synthesize extended systems.

Thus, it would be interesting to obtain oxamidobridged dimetallic complex with carboxyl-substituted nitronyl nitroxide radical. Herein, we reported the synthesis, crystal structure and magnetic properties of a novel heterospin complex from *trans*-oxamido-bridged copper(II) binuclear units and carboxyl-substituted nitronyl nitroxide radical ligands.

The carboxyl-substituted nitronyl nitroxide radical ligands HL (*p*-NITPBAH) (Scheme 3) was prepared by the literature method [13]. Cu(oxpn) was synthesized according to the reported procedure [5].

The title complex 1 was prepared by the following method: To a green aqueous methanol solution (20 mL in 1:1 ratio) containing $Cu(ClO_4)_2 \cdot 6H_2O$ (2 mmol) and Cu(oxpn) (2 mmol) was added *p*-NITP-BAH, dissolved in 10 mL of methanol. The mixture

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solution was further stirred for 1 h at room temperature, and filtered off. The filtrate was kept at room temperature within a couple of days to grow well-formed dark-blue crystals of the complex 1 [Cu₂(oxpn)(p-NIT-PBA⁻)₂], suitable for an X-ray structure determination. Yield: 34%. Anal. Calcd. for Elem. C, 49.10; H, 5.50; N, 12.73. Found: C, 48.78; H, 5.35; N, 12.69%.

The IR spectra of the complex 1 show the N–O stretching vibration of the NITPBA⁻ at ca. 1360 cm⁻¹ as well as the antisymmetric v(C-O) and the symmetric v(C-O) stretching mode of the carboxyl group at 1605 and 1428 cm⁻¹, respectively, in accordance with a bidentate-bridging mode [14,15].

The crystal structure was determined by single crystal X-ray analysis [16,17] (Fig. 1). Complex 1 is a binuclear centro-symmetric unit. Only one oxygen atom from one p-NITPBA⁻ anion is coordinated to each Cu(II) of the *trans*-oxamido-bridged copper(II) binuclear unit, respectively, to form a new four-spin complex. The coordination geometry around each Cu(II) ion is the slightly distorted square plane, composed of one carboxylic oxygen from p-NITPBA⁻ radical, one carbonyl oxygen, and two nitrogen atoms from the amide and amine of the oxamide ligand. The Cu–O bonds are 1.983(3) (Cu1–O1), 1.995(3) Å (Cu1–O5), respectively. The bond lengths of the Cu–N are in the range of 1.946(3)–



1.980(4) Å. Both copper atoms are displaced towards the apices, which are hypothetically perpendicular the mean plane (N3, N3A, O5, O5A), by 0.0634 and -0.0634 Å, respectively. The N3A–Cu1–N4A angle is 96.30(15)°, and the N3A–Cu1–O1 is 169.36(14)°. The angle of O1–Cu1–O5 is 88.52(13)°. Dihedral angle between the planes of the nitronyl (O3, N1, C8, N2, O4) and the phenyl ring is 35.3°, while the plane (O5, O1, N3A, N4A) shows an angle of 47.4° with the phenyl ring. The mean plane (N3, N3A, O5, O5A) shows an angle of 26.6° with the nitronyl nitroxide moiety (O1, N2, C6, N3). The separation between the neighboring Cu(II) ions through the oxamide bridge is 5.226 Å.

The molecular units are interconnected to form a 1-D chain along the *a*-axis via O (2 - x, 2 - y, -z)–Cu1 (+x, +y, +z) weak coordinated bond, as illustrated in Fig. 2. The separation of the nearest Cu(II) ions through the oxygen bridge is 3.267 Å. The shortest distant of O–O of carboxyl-substituted nitronyl nitroxide radical from two different molecular units is 3.621 Å.

The magnetic susceptibilities, χ_M , of **1** were measured between 2 and 300 K at 2000 Oe, and Fig. 3 shows the plots of χ_M and $\chi_M T$ versus *T*. The $\chi_M T$ value at room temperature is 1.58 cm³ K mol⁻¹, close to the value expected for non-coupling two $S_{Cu} = 1/2$ spin and two $S_{Rad} = 1/2$ spins (1.50 cm³ K mol⁻¹). When the temperature is lowered, the value of $\chi_M T$ decreases, indicating that the spins are antiferromagnetically coupled in the complex **1**.

In complex 1, there are four kinds of magnetic interactions, namely: (i) Cu(II) interacting with the coordinated radical ligand, (ii) Cu(II)–Cu(II) interaction via the oxamato bridge, (iii) a magnetic coupling between



Scheme 2.



Fig. 1. ORTEP drawing of the complex 1; thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and bond angles (°): Cu(1)-N(3)#1 1.946(3), Cu(1)-N(4)#1 1.980(4), Cu(1)-O(1) 1.983(3), Cu(1)-O(5) 1.995(3), O(1)-C(1) 1.281(6), O(2)-C(1) 1.226(6), O(3)-N(1) 1.282(5), O(4)-N(2) 1.269(5), O(5)-C(15) 1.278(5) and N(3)#1-Cu(1)-N(4)#1 96.30(15), N(3)#1-Cu(1)-O(1) 169.36(14), N(4)#1-Cu(1)-O(1) 91.47(15), N(3)#1-Cu(1)-O(5) 84.81(14), N(4)#1-Cu(1)-O(5) 171.88(16), O(1)-Cu(1)-O(5) 88.52(13), O(2)-C(1)-O(1) 124.4(5), N(3)#1-Cu(1)-O(1)-C(1) 25.9(9), O(5)-Cu(1)-O(1)-C(1) 77.1(3), N(3)#1-Cu(1)-O(5)-C(15) 2.0(3).



Fig. 2. Showing 1-D chain parallel to a-axis and the O···Cu interactions in the crystal packing. (The distance of O···Cu is 2.592 Å.)



Fig. 3. The plots of χ_M (\Box) and $\chi_M T$ (\bigcirc) versus *T* for the complex, the solid line showing the best fit to the value.

neighboring NO groups of two NITPBA⁻ (3.621 Å), (iv) a interaction between neighboring Cu \cdots Cu (3.267 Å) through the oxygen bridge space.

$Cu1(II) \xleftarrow{J} Cu2(II) \xleftarrow{j} Cu3(II) \xleftarrow{J} Cu4(II)$

Scheme 4. Simplified illustration of the spin-spin interaction in the unit of the complex 1.

Due to the shortest intermolecular $O \cdots O$ (from NIT-PBA⁻) distance of more than 3.5Å, the intrachain radical spin–spin interaction from two adjacent units can be neglected in order to avoid the complicated analysis. Density functional calculation of the spin density in L⁻ shows the unpaired electron to be localized on the NO-groups with little contributions from the phenyl ring due to spin polarization, and the spin density on the carboxylate group to be negligible [18]. The spin density on the carboxylate group is vanishing small in this case, which explains the lack of exchange interaction between the NIT-carboxylate and coordinated copper(II) ion. The intramolecular exchange interaction between the radical ligand and Cu(II) ion is negligible. So, the spin–spin interaction of the complex **1** can be simplified as shown as Scheme 4.

The Hamiltonian for the complex 1 can be written as $\hat{H} = -J(\hat{S}_{Cu1}\hat{S}_{Cu2} + \hat{S}_{Cu3}\hat{S}_{Cu4}) - j\hat{S}_{Cu2}\hat{S}_{Cu3}$. To simplify the question, when $g_{Cu} = g_R = g$ is assumed, based on the above isotropic Hamiltonian, the temperature dependence of the magnetic susceptibility can be expressed as:

$$\chi = \frac{Ng^2\beta^2}{kT}\frac{A}{B},$$

$$A = 10 \exp(-E_1/kT) + 2 \exp(-E_2/kT) + 2 \exp(-E_3/kT) + 2 \exp(-E_4/kT),$$

$$B = 5 \exp(-E_1/kT) + 3[\exp(-E_2/kT) + \exp(-E_3/kT) + \exp(-E_4/kT)] + \exp(-E_5/kT) + \exp(-E_6/kT),$$

$$E_1 = -J/2 - j/4, \quad E_2 = J/2 - j/4,$$

$$E_3 = j/4 + (J^2 + j^2)^{1/2}/2, \quad E_4 = j/4 - (J^2 + j^2)^{1/2}/2,$$

$$E_5 = J/2 + j/4 + (4J^2 - 2jJ + j^2)^{1/2}/2,$$

$$E_6 = J/2 + j/4 - (4J^2 - 2jJ + j^2)^{1/2}/2.$$

The least-squares analysis of magnetic susceptibility data lead to $J = -50.25 \text{ cm}^{-1}$, $j = -11.9 \text{ cm}^{-1}$, g = 2.1 and the agreement factor $R = 9.78 \times 10^{-3}$. The agreement factor is defined as

$$R = \sum \left[(\chi_{\rm M})_{\rm obs} - (\chi_{\rm M})_{\rm calc} \right]^2 / \sum (\chi_{\rm M})_{\rm obs}^2$$

As expected, the magnetic interaction between two Cu(II) ions through the *trans*-oxamide bridge is strong antiferromagnetic [19–21]. However, the antiferromagnetic interaction has been weaked [22] due to the oxygen bridge space intervention [23].

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 260168 for structure of the complex. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc. cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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