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A novel two-dimensional copper(II)–radical complex $[Cu(NITmPy)_2(N_3)_2]_n$: structure and magnetic properties†

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A two-dimensional copper(II)–radical complex $[Cu(NITmPy)_2(N_3)_2]_n$ (NITmPy = 2-(3′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) has been prepared and characterized by X-ray crystallography. The crystal structure consists of neutral polymeric sheets in which each copper atom is bridged by the oxygen and nitrogen atoms of the NITmPy radical ligands. The variable-temperature magnetic susceptibility data show that the complex exhibits ferromagnetic interactions. The magnetic behavior is discussed in connection with the crystal structure.

Introduction

The design and synthesis of multidimensional molecular-based magnetic materials with ferromagnetic ordering is one of the major challenges in molecular materials research.[1] For a magnetic system, the macroscopic magnetic properties are strongly dependent on the dimensionality of the structure and on the magnitude of the exchange interactions between the spin carriers. Therefore, the simplest strategy in designing molecular-based magnetic materials is to enhance the dimensionality of the magnetic coupling system.

In the field of molecular-based magnetic materials, the combination of metal ions and nitronyl nitroxides (metal–radical approach) has attracted much more attention in the last few years[2,3] and has been successfully used to design one of the first one-dimensional ferrimagnetic chains that show magnetic order at low temperature.[4] However, the weakly basic character of nitronyl nitroxides limits strongly their coordination ability. This has led to the development of functionalized nitronyl nitroxide radicals in which a strong coligand is incorporated. Using this strategy, some discrete molecules,[5–8] high-spin clusters[9] and linear chains[10] have been synthesized. Very recently, a two-dimensional system was reported[11] with imidazole-subsituted nitronyl nitroxide ligands. Therefore it is possible to build up high-dimensionality magnetic systems by choosing appropriate coligands. Among functionalized nitronyl nitroxide radical ligands, the pyridyl-substituted nitroxide radicals are extensively used to assemble extended coordination geometries with changing magnetic coupling due to their donor atoms. NITmPy ligand (NITmPy = 2-(3′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) was used as a bridging ligand between metals in order to obtain high-nuclearity magnetic materials,[12,13] such as $[Cu_2(Me_3CCO_2)_4(NITmPy)]_n$[12] in which the NITmPy radical ligand links dimer units of the paddle-wheel copper(II) complex *via* the nitrogen atom of the pyridyl ring and the oxygen atom of the NO group to form a chain structure. However, reports on high-dimensionality transition metal complexes with the NITmPy radical ligand are scarce. Hence we report herein the synthesis, X-ray structure, and magnetic properties of a novel two-dimensional metal–radical complex $[Cu(NITmPy)_2(N_3)_2]_n$ which exhibits ferromagnetic interactions.

Experimental

Materials

All reagents and chemicals were purchased from commercial sources and used as received. 2-(3′-Pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (NITmPy) was prepared by the literature method.[14]

Synthesis of $[Cu(NITmPy)_2(N_3)_2]_n$

A 10 ml methanol solution of copper nitrate trihydrate (0.120 g, 0.5 mmol) was mixed with a methanol solution (20 ml) of NITmPy (0.234 g, 1 mmol) followed by the addition of an aqueous solution of sodium azide (0.065 g, 1 mmol). The resulting dark solution was allowed to stand at room temperature for one week and dark green crystals were obtained. (Found: C, 46.70; H, 4.95; N, 26.80. Calc. for $C_{24}H_{32}CuN_{12}O_4$: C, 46.78; H, 5.23; N, 27.27%.) The IR spectrum displays a strong broad band at 2075 cm^{-1}, which is characteristic of $\nu(N_3^-)$. The strong band observed at 1365 cm^{-1} is due to $\nu_{N–O}$.

Physical measurements

Elemental analysis for carbon, hydrogen and nitrogen was carried out on a Perkin-Elmer elemental analyzer, model 240. The infrared spectrum was recorded on a Shimadzu IR spectrophotometer, model 408, using KBr pellets. Variable temperature magnetic susceptibilities were measured on a MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms, and the magnetic moments were calculated by the equation $\mu_{eff} = 2.828\ (\chi_M T)^{1/2}$. Experimental susceptibilities were also corrected for temperature-independent paramagnetism (60×10^{-6} $cm^3\ mol^{-1}$ per copper(II)).

Crystallography

The X-ray crystal data were collected at room temperature on a Bruker Smart 1000 CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). A total of 5575 reflections were collected in the $2.03 < \theta < 25.03°$ range including 2417 independent reflections ($R_{int} = 0.0577$). The structure was solved by direct methods using the SHELXS-97 program.[15] The H atoms were assigned with common isotropic displacement factors and included in the final refinement by the

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† Dedicated to the memory of Professor Olivier Kahn.

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use of geometrical restraints. A full matrix least-squares refinement on F^2 was carried out using SHELXL-97[16] and the goodness-of-fit on F^2 was 0.909. The final agreement factor values are $R_1 = 0.0422$ $wR_2 = 0.0796$ ($I > 2\sigma(I)$). $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $wR_2 = (\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^2)^2$, $w = 1/[\sigma^2(F_o^2) + (0.0382P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$. Maximum and minimum peaks in the final difference Fourier synthesis were 0.272 and −0.462 e Å^{-3}. $C_{24}H_{32}CuN_{12}O_4$, $M = 616.16$, monoclinic, space group $P2_1/c$, $a = 10.239(3)$, $b = 11.040(4)$, $c = 12.383(4)$ Å, $\beta = 101.761(6)°$, $U = 1370.3(7)$ Å^3, $Z = 2$, $F(000) = 642$, $\mu = 8.53$ cm^{-1}.

CCDC reference number 171153.

See http://www.rsc.org/suppdata/dt/b1/b108476n/ for crystallographic data in CIF or other electronic format.

Results and discussion

Crystal structure

An ORTEP drawing of the molecular structure of the title complex is shown in Fig. 1 with selected bond lengths and angles in Table 1. The crystal structure of $[Cu(NITmPy)_2(N_3)_2]_n$ shows it to be a neutral sheetlike molecule in which each copper atom is six-coordinate in a distorted octahedral CuN_4O_2 environment, which is centrosymmetric. The equatorial plane is formed by two nitrogen atoms from two azido groups (N(4), N(4A)) and two nitrogen atoms from the pyridyl rings of the NITmPy ligands (N(1), N(1A)). The Cu–N bond lengths in the basal plane are 1.939(3) and 2.049(3) Å for Cu–N_{azide} and Cu–$N_{pyridine}$, respectively. The axial positions are occupied by oxygen atoms from the NO groups of two other NITmPy radical ligands, which belong to related units. The Cu–O bond length is 2.775(4) Å, which is somewhat longer than the equatorial Cu–N distances. Each copper atom is coordinated by four NITmPy radical ligands through the nitrogen or oxygen atom; each NITmPy radical links two copper atoms *via* the oxygen atom of the NO group and the nitrogen atom of the pyridyl ring, leading to a two-dimensional network (Fig. 2). The two NO groups of each NITmPy ligand have bond lengths of 1.277(3) and 1.266(3) Å for coordinated and uncoordinated NO groups, respectively, as is generally observed.[2] The fragment O(1)–N(2)–C(6)–N(3)–O(2) is nearly planar but forms a dihedral angle of 31.6° with the plane of the pyridyl ring. The shortest contact (O(2)–O′(1)) between nitroxide groups is 3.983 Å. It should be noted that closest contact is observed between the oxygen atom (O(1)) of the nitroxide group and the carbon atom (C′(3)) belonging to the adjacent NITmPy ligand ((O(1)–C′(3) = 3.170 Å) (Fig. 3). The azido ligands, which are linear (N(4)–N(5)–N(6): 177.6(4)°), coordinate to the copper atom as terminal ligands.

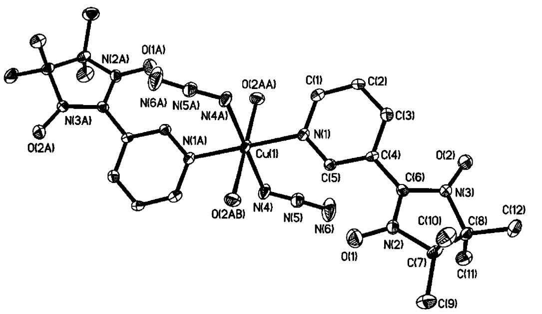

Fig. 1 An ORTEP[31] drawing, with 30% probability thermal ellipsoids, showing the atom labeling of $[Cu(NITmPy)_2(N_3)_2]_n$.

Table 1 Selected bond lengths (Å) and angles (°) for $[Cu(NITmPy)_2(N_3)_2]_n$

Cu(1)–N(4)	1.939(3)	Cu(1)–N(1)	2.049(3)
O(2)–N(3)	1.277(3)	N(2)–O(1)	1.266(3)
Cu(1)–O(2AA)	2.775(4)	N(1)–C(5)	1.341(4)
N(1)–C(1)	1.347(4)	N(3)–C(6)	1.354(4)
N(2)–C(6)	1.344(4)		
N(4)–Cu(1)–N(4A)	180.000(1)	N(4)–Cu(1)–N(1A)	87.28(11)
N(4)–Cu(1)–N(1)	92.72(11)	N(1A)–Cu(1)–N(1)	180.00(9)
O(1)–N(2)–C(6)	125.7(3)	O(1)–N(2)–C(7)	121.4(3)
O(2)–N(3)–C(6)	126.1(3)	O(2)–N(3)–C(8)	121.7(3)
N(6)–N(5)–N(4)	177.6(4)	N(5)–N(4)–Cu(1)	126.9(3)

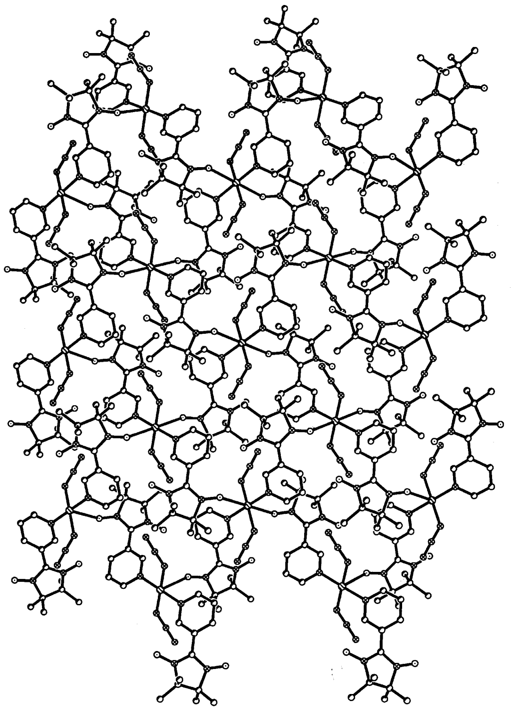

Fig. 2 The two-dimensional structure of $[Cu(NITmPy)_2(N_3)_2]_n$.

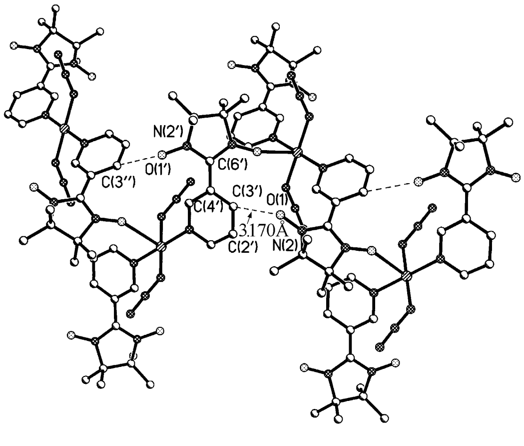

Fig. 3 The closest contact in $[Cu(NITmPy)_2(N_3)_2]_n$ showing exchange coupling through an NO–C pathway.

Magnetic properties

The magnetic susceptibility data are shown in Fig. 4 in the form of χ_M and μ_{eff} *vs.* T plots. The μ_{eff} value at room temperature is 2.99 μ_B, which is close to the value expected for three uncoupled $S = 1/2$ spin systems. As the temperature is lowered, the μ_{eff} value continuously increases and reaches a value of 4.04 μ_B at 5.01 K. This behavior is characteristic of a system with ferromagnetic interactions.

There are four kinds of magnetic interaction for the present system, namely: (i) interaction between copper(II) and the nitroxide group of the axial NITmPy radical (J); (ii) magnetic

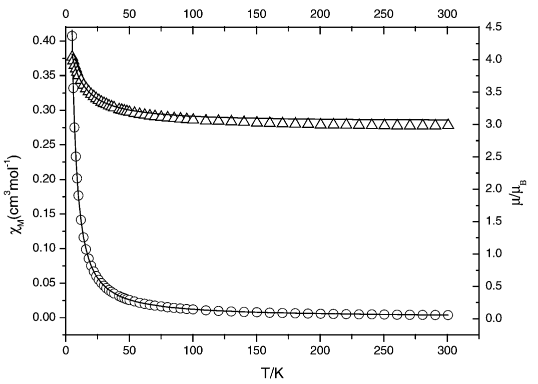

Fig. 4 Plots of χ_M (○) and μ_{eff} (Δ) *versus* T for [Cu(NITmPy)$_2$(N$_3$)$_2$]$_n$. The solid line corresponds to the best theoretical fits.

coupling between neighboring NITmPy radicals through an NO–C pathway; (iii) interaction between copper(II) and nitroxide radical through the pyridine ring; (iv) interaction between neighboring NO groups of NITmPy radicals through space (3.983 Å). According to the structural results, the ferromagnetic behavior of this complex is caused by direct exchange coupling between copper(II) and the nitroxide group of the axial NITmPy radical, and magnetic coupling between neighboring NITmPy radicals through an NO–C pathway. The magnetic interaction between copper(II) ion and nitroxide radical through the pyridine ring of NITmPy ligand should be weakly antiferromagnetic[12,17] due to the small spin density on the nitrogen atom of the NITmPy pyridine ring.[18] The extent of magnetic coupling of the two adjacent NO groups depends on their distance and the relative orientation of the π* orbitals.[19] In the present complex, the shortest O–O separation between nitroxide groups is rather large (3.983 Å) and the planes of the π systems of two adjacent NO groups tilt toward each other with an angle of 49.3°. These geometrical parameters are not disposed favorably for strong overlap and lead to very weakly antiferromagnetic interactions.[19–21] In order to fit quantitatively the magnetic data in such a complicated magnetic system, we tried to simplify it by treating it as a trinuclear interaction[1] (Scheme 1) with the exchange coupling (J') transferred by NITmPy radical ligands and space as an inter-trinuclear molecular field[22] (eqn. (1)). In this case, J is the direct exchange coupling constant between copper(II) and the axial nitroxide group; J' represents the sum of the magnetic interactions of the Cu(II)–nitroxide group through the pyridine ring, the neighboring nitroxide groups and the adjacent NITmPy radicals through an NO–C pathway.

$$\text{Rad}\overset{J}{—}\text{Cu(II)}\overset{J}{—}\text{Rad}$$

Scheme 1 (Rad represents the axial NITmPy radical ligand).

$$\chi_{tri} = \frac{N\beta^2}{4kT}\frac{g_{1/2,1}^2 + g_{1/2,0}^2\exp(J/kT) + 10g_{3/2,1}^2\exp(3J/2kT)}{1+\exp(J/kT)+2\exp(3J/2kT)} \quad (1a)$$

$$\chi_M = \chi_{tri}/[1 - \chi_{tri}(2zJ'/Ng^2\beta^2)] \quad (1b)$$

With

$$g_{1/2,1} = (4g_{rad} - g)/3 \quad (3)$$

$$g_{3/2,1} = (2g_{rad} + g)/3 \quad (4)$$

$$g_{1/2,0} = g \quad (5)$$

The best fit for magnetic data led to $g = 2.02$, $g_{rad} = 2.0$ (fixed), $J = 14.90$ cm^{-1}, $zJ' = 0.39$ cm^{-1} and $R = 2.54 \times 10^{-5}$; R is defined as $\Sigma[(\chi_M)_{obs} - (\chi_M)_{calc}]^2/\Sigma[(\chi_M)_{obs}]^2$.

The ferromagnetic interaction between copper(II) and a nitroxide radical in an axial position is well established[23–26] and appears to be determined by accidental orthogonality of the magnetic orbital of the copper ion ($d_{x^2-y^2}$) and the radical π* magnetic orbital. The amplitude of the ferromagnetic interaction in axial ligation is not usually strong because the apical axis is elongated by Jahn–Teller distortion. The same situation can also be found in the present complex; the magnetic orbital of the copper(II) ion has $d_{x^2-y^2}$ symmetry located in the basal plane which keeps the orthogonality of the axial radical π* orbital and this results in the occurrence of the ferromagntic interaction. The relatively low J value observed arises from the fact that the Cu–O distance is fairly long (2.775(4) Å). The small positive zJ' value confirms that the exchange coupling between neighboring NITmPy radicals through an NO–C pathway is ferromagnetic. This can be explained by McConnell's mechanism.[27] The spin density distributions in some nitronyl nitroxides have been determined by polarized neutron diffraction studies and MO calculations.[28–30] The large positive spin density is located on the NO groups, while the large negative spin density is located on the sp^2 carbon atom bridging two NO groups, and there is weak alternative delocalization over the pyridyl ring. The crystal structure shows that the closest contact involves the oxygen atom (O(1)) of the uncoordinated NO group carrying a large positive spin density and the carbon atom (C′(3)) of the adjacent NITmPy radical that carries a small negative spin density (O(1)–C′(3) = 3.170 Å). These two atoms carrying opposite signs of spin density alternate in the title complex, thus we have ↑N(2)–O(1)↑---↓C′(3)–↑C′(4)–↓C′(6)–↑N′(2)–↑O′(1)---↓C″(3), and this matches McConnell's criteria. Ferromagnetic coupling should be observed and dominate at low temperature. However, we can not determine the magnitude of this ferromagnetic coupling. The ferromagnetic coupling of the title complex is sufficient to overcome all antiferromagnetic interactions, as observed.

Conclusion

A novel two-dimensional copper(II)–nitronyl nitroxide complex [Cu(NITmPy)$_2$(N$_3$)$_2$]$_n$ has been synthesized and characterized structurally and magnetically. The NITmPy radical as bridging ligand links two copper(II) ions *via* the nitrogen atom of the pyridine and the oxygen atom of the nitroxide group. As a result, a two-dimensional network is achieved. Ferromagnetic interaction is observed in this complex. It is possible to build high dimensionality magnetic materials by using paramagnetic metal ions with the NITmPy radical as a bridging ligand.

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