The first one-dimensional copper(II)-radical system with alternating double end-on and end-to-end azido bridges

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A novel one-dimensional copper(II)-radical complex $[Cu(NITmPy)(N_3)_2(CH_3OH)]$ [NITmPy = 2-(3′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide] has been synthesized and structurally characterized. The structure consists of neutral chains of copper(II) ions alternatively bridged by double symmetric end-on and asymmetric end-to-end azide groups. The NITmPy radical ligand coordinates to the copper(II) ions through the nitrogen atom of the pyridyl ring. The magnetic properties were investigated in the temperature range 5–300 K. The complex exhibits ferromagnetic interactions between the copper(II) ions through the end-on and end-to-end azido bridging ligands, and between the copper(II) ion and NITmPy radical. The magnetic behavior is discussed with reference to the crystal structure.

Introduction

The investigation of transition metal complexes of nitronyl nitroxide radicals has become a fascinating subject in the field of molecule-based magnetic materials.[1–7] Considerable efforts have been directed towards preparing and characterizing metal-radical multidimensional systems that can exhibit ferromagnetic properties.[8–12] One synthetic strategy relies on transition metal ions surrounded by paramagnetic nitronyl nitroxide radicals linked by inorganic or organic bridging ligands to produce polymeric structures.[13–17] In particular, the azide ligand is a versatile bridging ligand, able to participate in new materials with different magnetic properties, which led to an intensive study of magnetostructural correlations in discrete complexes[18–20] as well as in polymeric 1D,[21–28] 2D[29–32] and 3D[33] molecular systems. However, the majority of polynuclear azido systems reported so far are pyridine-like or bipyridine adducts. To the best of our knowledge, there has been no report on metal-radical multi-dimensional systems with azido bridging ligands. With a view to obtaining materials with unusual magnetic properties, derived from nitroxide radicals and the azide ligand, we succeeded in synthesizing the first copper(II)-radical complex, $[Cu(NITmPy)(N_3)_2(CH_3OH)]$ [NITmPy = 2-(3′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide], with alternating double end-on and end-to-end azido bridges. In this paper, we report the synthesis, crystal structure and magnetic properties of this one-dimensional complex.

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.[34]

Preparation of $[Cu(NITmPy)_2(N_3)_2(CH_3OH)]$. A 10 mL methanol solution of copper nitrate trihydrate (0.120 g, 0.5 mmol) was added dropwise to a methanol solution (25 mL) of NITmPy (0.117 g, 0.5 mmol), then the sodium azide solid (0.065 g, 1 mmol) was added. The mixture was stirred for 3 h at room temperature. The solution was allowed to stand at room temperature for 5 days and dark green needle crystals were obtained. Anal. found: C, 37.61; H, 4.83; N, 31.24; calcd. for $C_{13}H_{20}CuN_9O_3$: C, 37.75; H, 4.87; N, 30.44%. The I.R. spectrum has a strong band at 2100 cm^{-1}, characteristic of the $\nu_{N_3^-}$ vibration and a strong band at 1365 cm^{-1} ($\nu_{N–O}$).

Physical measurements

Elemental analysis for C, H and N was carried out on a Perkin–Elmer elemental analyzer model 240. The infrared spectrum was taken on a Shimadzu IR spectrophotometer model 408, using KBr pellets. Variable temperature magnetic susceptibilities on polycrystalline samples in a gelatin capsule were measured on a Quantum Design MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constitute atoms. Experimental susceptibilities were also corrected for the temperature-independent paramagnetism [$60 \times 10^{-6} cm^3 mol^{-1}$ 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 7150 reflections were collected in the $1.80 < \theta < 25.01°$ range including 3166 independent reflections ($R_{int} = 0.1026$). The structure was solved by direct methods using the SHELXS-97 program[35] and refined with SHELXL 97[36] by full-matrix least-squares methods on F^2. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were located geometrically and refined isotropically. The goodness-of-fit on F^2 was 0.974. The final agreement factor values

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are $R_1 = 0.0501$ $wR_2 = 0.0836$ $[I > 2\sigma(I)]$, with $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$, $wR_2 = (\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^2)^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0340P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$. Maximum and minimum peaks in the final difference Fourier synthesis were 0.375 and −0.502 e Å^{-3}.

Crystal data. $C_{13}H_{20}CuN_9O_3$, $M =$ 413.92, monoclinic, space group $P2_1/n$, $a = 10.358(8)$, $b = 7.680(5)$, $c = 23.191(17)$ Å, $\beta = 102.903(10)°$, $T = 293(2)$ K, $U = 1798(2)$ Å^3, $Z = 4$, $\mu = 1.249$ mm^{-1}. CCDC reference number 194670. See http://www.rsc.org/suppdata/nj/b2/b209397a/ for crystallographic files in CIF or other electronic format.

Result and discussion

Crystal structure

An ORTEP[37] drawing and a view of the unit cell of the copper chains are displayed in Figs. 1 and 2, respectively. Selected bond distances and angles are listed in Table 1. The structure of the complex consists of chains of copper(II) ions alternatively bridged by symmetric double end-on (EO) and asymmetric double end-to-end (EE) azide ligands. The NITmPy radical ligand coordinates to the copper(II) ion *via* the nitrogen atom of the pyridyl ring. The coordination geometry around each copper(II) ion is distorted octahedron. The equatorial positions are occupied by four nitrogen atoms: two from two EO azide groups [Cu(1)–N(7), –N(7A), 1.986(5), 2.007(5) Å], one from the EE azido bridging ligand [Cu(1)–N(4), 1.954(5) Å] and one from the pyridyl ring of the NITmPy radical [Cu(1)–N(1), 1.994(5) Å]. The apical sites are occupied by one oxygen atom from solvent molecule CH_3OH [Cu(1)–O(3), 2.368(4) Å] and one nitrogen atom from the remaining EE azido bridging ligand [Cu(1)–N(6B), 2.875(6) Å], which is longer than the equatorial Cu–N(azide) bond. Thus the copper(II) ions are alternatively linked by the symmetric double EO azide ligands and the asymmetic double EE azide ligands. The double EO and EE azide bridges are arranged in a *cis* position. The Cu(1)–N(7)–Cu(1A) angle in the EO mode is 102.3(2)°, which lies within the typical range for this kind of bridge. For the EE bridges, the Cu(1)–N(4)–N(5) and Cu(1)–N(6B)–N(5B) angles are 127.6(4)° and 135.5°, respectively. The intrachain Cu–Cu separation through the EO azide is 3.109 Å and that through the EE azide is 5.808 Å. For the NITmPy radical ligand, the fragment O(1)–N(2)–C(6)–N(3)–O(2) is nearly planar but forms a dihedral angle of 39.6° with the plane of the pyridyl ring. The shortest contact between nitroxide groups is 4.705 Å.

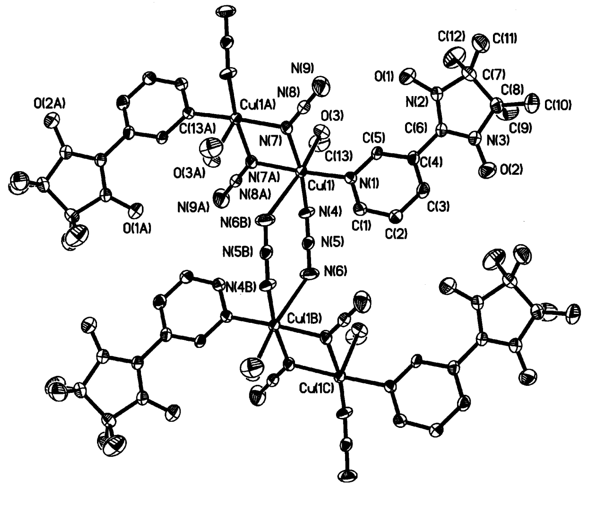

Fig. 1 ORTEP drawing with 30% thermal ellipsoid probability showing atom labeling of $[Cu(NITmPy)(N_3)_2(CH_3OH)]$.

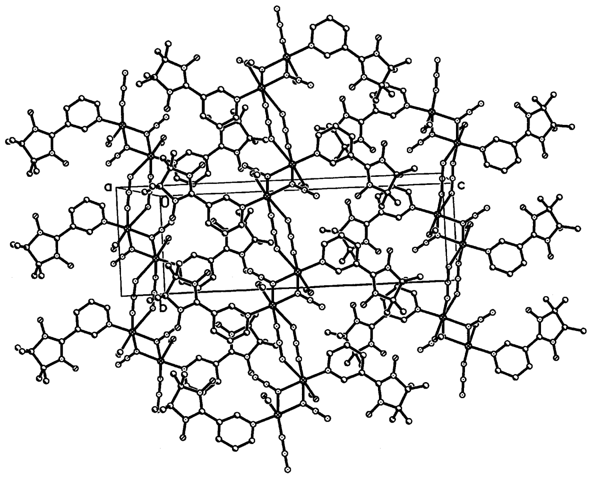

Fig. 2 View of the chains of $[Cu(NITmPy)(N_3)_2(CH_3OH)]$ in the unit cell.

Magnetic properties

Variable-temperature magnetic susceptibility measurements were performed on a polycrysalline sample in the range of 5–300 K at 1000 G, and the results are shown in Fig. 3 in the form of a $\chi_M T$ *vs.* T plot. At room temperature, the value of $\chi_M T$ per molecule is 0.856 cm^3 K mol^{-1}, which is slightly higher than the spin-only value of 0.75 cm^3 K mol^{-1} expected for a two uncoupled $S = 1/2$ spin system. As the temperature is lowered, the $\chi_M T$ value continuously increases and reaches 1.124 cm^3 K mol^{-1} at 25.02 K, then it increases sharply to 1.768 cm^3 K mol^{-1} at 5.0 K. The magnetic susceptibility behavior of the complex indicates bulk ferromagnetic coupling. According to the crystal structure of the complex, the uncoordinated nitroxide groups are well-isolated (4.705 Å), thus the magnetic interaction between the NO groups can be neglected. Since the EE bridges are asymmetric and link the copper(II) ions through short equatorial Cu–N bonds and long axial Cu–N bonds, the magnetic coupling between the copper(II) ions *via* these kinds of EE bridges should be very weak.[38] Therefore, the present magnetic system can be simplified as a tetra-spin interaction (see below) with the spin Hamiltonian: $\hat{H} = -2J_1\hat{S}_1\hat{S}_2 - 2J_2\hat{S}_2\hat{S}_3 - 2J_1\hat{S}_3\hat{S}_4$ where J_1 is the magnetic coupling constant between the copper(II) and NITmPy radical, and J_2 that between the copper(II) ions *via* the symmetric EO bridges, as shown here:

$$\mathrm{Rad}\overset{J_1}{\overline{\qquad\quad}}\mathrm{Cu}\overset{J_2}{\overline{\qquad\quad}}\mathrm{Cu}\overset{J_1}{\overline{\qquad\quad}}\mathrm{Rad}$$

Table 1 Selected bond lengths (Å) and angles (deg) for $[Cu(NITmPy)(N_3)_2(CH_3OH)]$

Cu(1)–N(4)	1.954(5)	Cu(1)–N(7)	1.986(5)
Cu(1)–N(1)	1.994(5)	Cu(1)–N(7A)	2.007(5)
Cu(1)–O(3)	2.368(4)	Cu(1)–N(6B)	2.875(6)
N(2)–O(1)	1.282(6)	N(3)–O(2)	1.270(6)
N(4)–Cu(1)–N(7)	170.5(2)	N(4)–Cu(1)–N(1)	93.9(2)
N(7)–Cu(1)–N(1)	95.3(2)	N(4)–Cu(1)–N(7A)	92.9(2)
N(7)–Cu(1)–N(7A)	77.7(2)	N(1)–Cu(1)–N(7A)	172.5(2)
N(4)–Cu(1)–O(3)	93.7(2)	N(7)–Cu(1)–O(3)	87.70(19)
N(1)–Cu(1)–O(3)	94.15(18)	Cu(1)–N(7)–Cu(1A)	102.3(2)
N(4)–N(5)–N(6)	176.7(6)	N(7)–N(8)–N(9)	178.8(7)

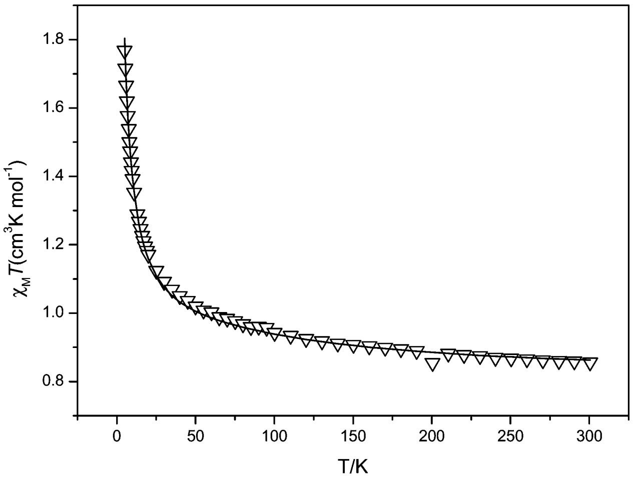

Fig. 3 Plot of $\chi_M T$ *versus* T for [Cu(NITmPy)(N$_3$)$_2$(CH$_3$OH)] (▽). The solid line corresponds to the best theoretical fit.

The expression of the magnetic susceptibility was derived[39] as:

$$\chi_M = \frac{Ng^2\beta^2}{kT}\left[\frac{A}{B}\right]$$

where

$$A = 10\exp(-E_1/kT) + 2\exp(-E_2/kT) + 2\exp(-E_3/kT) + 2\exp(-E_4/kT)$$
$$B = 5\exp(-E_1/kT) + 3[\exp(-E_2/kT) + \exp(-E_3/kT) + \exp(-E_4/kT)] + \exp(-E_5/kT) + \exp(-E_6/kT)$$

and

$$E_1 = -J_1 - J_2/2$$
$$E_2 = J_1 - J_2/2$$
$$E_3 = J_2/2 + \sqrt{J_2^2 + J_1^2}$$
$$E_4 = J_2/2 - \sqrt{J_2^2 + J_1^2}$$
$$E_5 = J_1 + J_2/2 + \sqrt{4J_1^2 - 2J_1J_2 + J_2^2}$$
$$E_6 = J_1 + J_2/2 - \sqrt{4J_1^2 - 2J_1J_2 + J_2^2}$$

Considering the weak magnetic interactions between the copper(II) ions through the EE azide bridges, the mean field approximation,[40] zJ', was introduced. The total magnetic susceptibility is:

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

The best-fit parameters were $g = 2.03$, $J_1 = 6.37$ cm^{-1}, $J_2 = 75.73$ cm^{-1}, $zJ' = 0.19$ cm^{-1} and $R = 9.88 \times 10^{-5}$ {R is the agreement factor, defined as $R = \sum[(\chi_M T)_{\text{obsd}} - (\chi_M T)_{\text{calcd}}]^2/\sum[(\chi_M T)_{\text{obsd}}]^2$}. The fitting results show that the magnetic interaction between the copper(II) ions through the EO and EE bridges, and between the copper(II) ion and NITmPy radical, are ferromagnetic. The molar magnetization measurement at 5.0 K confirms the ferromagnetic behavior of the complex: the plot of M *vs.* applied magnetic field reaches a value of 1.83 $N\beta$ at 70 kG and tends to $S = 1$ (Fig. 4).

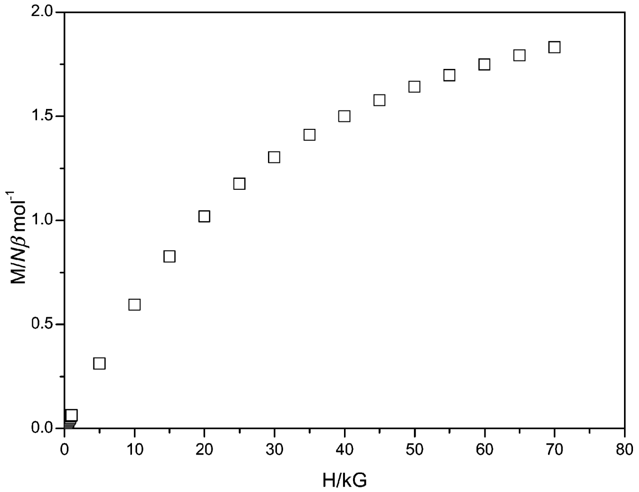

Fig. 4 Magnetization *versus* field up to $H = 70$ kG at 5.0 K for [Cu(NITmPy)(N$_3$)$_2$(CH$_3$OH)].

As is well-known, the azido ligand stabilizes either end-on or end-to-end coordination modes when it links two copper(II) ions, giving ferro- and antiferromagnetic interactions, respectively, subject to certain restrictions on bond angles and Cu–N bond distances. In order to compare the results for the present complex with others found in the literature, the relevant magneto-structural data concerning symmetric double end-on azido bridges in copper(II) complexes are listed in Table 2. It can be seen that the magnetic coupling between copper(II) ions through end-on azido bridge is strongly dependent on the value of the angle (θ) at the bridging nitrogen atom of the Cu–N–Cu unit: the larger the value of θ, the weaker is the ferromagnetic coupling, and the strongest ferromagnetic coupling is observed for the smaller θ values. In the present complex, the ferromagnetic coupling between copper(II) ions through the EO bridges ($J_2 = 75.73$ cm^{-1}) is also in accordance with the density functional calculations of Ruiz *et al.*,[44] which show a clear correlation between the magnetic constant J and the Cu–N–Cu angle θ; the J value decreases from a maximum at about $\theta = 85°$ with increasing θ, eventually reaching an antiferromagnetic regime for $\theta \geqslant 104°$.The small positive zJ' value indicates the magnetic coupling between the copper(II) ions through the asymmetric EE bridges is very weakly ferromagnetic. This is mainly due to the quasi-orthogonality of the magnetic orbitals of two copper(II) centers linked by the asymmetric EE bridges.[45,46] The weakly ferromagnetic coupling is attributed to ineffective transfer by asymmetric end-to-end azido bridges with short Cu–N bonds [1.954(5) Å] and long axial Cu–N bonds [2.875(6) Å] at copper(II) ions.

The weak ferromagnetic coupling between copper(II) ion and the NITmPy radical is consistent with reported relevant copper(II)-NITmPy complexes. Table 3 summarizes the magnetic coupling constant J found in the literature for other related copper(II)-NITmPy complexes. The ferromagnetic

Table 2 Selected magneto-structural data for symmetric double end-on azido-bridged copper(II) complexes

Complex[a]	θ/°	Cu–N/Å	J/cm^{-1}	Ref.
[Cu$_2$(μ-N$_3$)$_2$(*t*-Bupy)$_4$](ClO$_4$)$_2$	100.5	1.979	105 ± 20	38
[Cu$_2$(μ-N$_3$)$_2$(N$_3$)$_2$ ([24]ane-N$_2$O$_6$)]·H$_2$O	101.7 105.4	2.012	70 ± 20	18
[Cu$_2$(μ-N$_3$)$_2$(N$_3$)$_2$(ptdz)]	104.0 98.5	1.988	170 ± 2	41
[Cu$_2$(μ-N$_3$)$_2$(N$_3$)$_2$(bzm)$_2$]	104.6	2.048	23	42
[Cu$_2$(μ-N$_3$)$_2$(4-Etpy)$_4$(μ-NO$_3$)$_2$]	98.3	1.996	230.1	43
[Cu$_2$(μ-N$_3$)$_2$(3-ampy)$_4$(μ-NO$_3$)$_2$]·C$_2$H$_5$OH	97.5	2.000	223.2	43
[Cu(NITmPy)(N$_3$)$_2$(CH$_3$OH)]	102.3	1.996	75.73	This work

[a] *t*-Bupy = 4-*tert*-butylpyridine; ptdz = 2,5-bis[(pyridylmethyl)thio]-thiadiazole; bzm = bis(2-benzimidazolyl)propane; 4-Etpy = 4-ethylpyridine; 3-ampy = 3-aminopyridine.

Table 3 Selected magneto-structural data reported for relevant copper(II)–NITmpy complexes

Complex	J/cm^{-1}	Coordination sites	$\beta/°$	Ref.
$[Cu(Cl_2CHCO_2)_2(NITmPy)_2(H_2O)_2]$	12.0	Equatorial	24.91 25.26	47
$[Cu(tta)_2(NITmPy)_2]\cdot C_7H_8$	6.1	Equatorial		48
$[Cu(NITmPy)(N_3)_2(CH_3OH)]$	6.37	Equatorial	39.6	This work

[a] β is defined as the dihedral angle between pyridyl ring and nitroxide group for NITmPy radical; tta = thenoyltrifluoroacetonate.

coupling between copper(II) ion and the NITmPy radical can be understood by the symmetry of the orbitals. The magnetic orbital of the NITmPy radical is a π^* orbital and the spin density can delocalize on the pyridyl ring by spin polarization.[47,49] The magnetic orbital of the copper(II) ion is $d_{x^2-y^2}$ with σ symmetry, which is orthogonal to the magnetic orbital of nitroxide, leading to a ferromagnetic interaction as observed. For the present complex, since the nitroxide moiety forms a large dihedral angle of 39.6° with the plane of the radical's pyridyl ring, this results in minimal delocalization of the spin density of the NO group in the radical and the exchange coupling between copper(II) ion and NITmPy is weak.

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