

Synthesis, Crystal Structure and Magnetic Properties of a 1-D Polymer, $[\text{Cu}(\text{NITpPy})_2(\text{H}_2\text{TCB})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$

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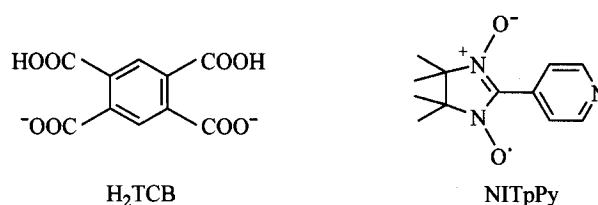
A novel complex $[\text{Cu}(\text{NITpPy})_2(\text{H}_2\text{TCB})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ (NITpPy = 2-(pyrid-4'-yl)-4,4,5,5-tetramethyl-1,3-dioxoimidazoline; H_2TCB = 1,5-dicarboxybenzene carboxylic-2,4-diacid) has been synthesized and characterized by X-ray crystallography analysis. The crystal structure consists of infinite chains of $\text{Cu}(\text{NITpPy})_2(\text{H}_2\text{O})$ units linked by H_2TCB ligands. The complex crystallizes in triclinic system with space group $P\bar{1}$. Crystal data: $a = 1.0594(2)$ nm, $b = 1.3830(3)$ nm, $c = 1.5551(3)$ nm, $\alpha = 67.75(3)^\circ$, $\beta = 89.83(3)^\circ$, $\gamma = 70.54(3)^\circ$. The variable magnetic susceptibility studies lead to magnetic coupling constant values of $J_1 = -11.18 \text{ cm}^{-1}$ (Cu—Rad) and $J_2 = -4.06 \text{ cm}^{-1}$ (Cu—Cu).

Keywords 1,3-dioxoimidazoline, copper, 1,2,4,5-benzenetetracarboxylic acid, crystal structure, magnetic property

Introduction

Nitronyl nitroxides acting as useful paramagnetic building blocks have been extensively used to assemble molecular magnetic materials in the past few years.¹⁻⁴ However, their weakly basic character strongly limits their coordination ability. This has led to the development of functionalized nitronyl nitroxide radicals in which a strong coligand is incorporated. 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. Meanwhile, it has also documented that the tetracarboxybenzene can be regarded as an ideal ligand to construct polynuclear compounds because of its good binding ability.^{5,6} Therefore, to combine the two synthetic approaches, namely, realizing networks and metallic centers coordinated by spin-carrying ligands, the tetracarboxybenzene and nitronyl nitroxide ligands (Scheme 1) were chosen to synthesize a one-dimensional complex, $[\text{Cu}(\text{NITpPy})_2(\text{H}_2\text{TCB})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ (NITpPy = 2-(pyrid-4'-yl)-4,4,5,5-tetramethyl-1,3-dioxoimidazoline; H_2TCB = 1,5-dicarboxybenzenecarboxylic-2,4-diacid).

Scheme 1



Experimental

Physical measurements

Elemental analyses for C, H and N were carried out with a Perkin-Elmer-240 elemental analyzer. The infrared spectrum of a KBr pellet was recorded in the range of 4000—600 cm^{-1} on a SHIMADZU-408 IR spectrometer. Variable-temperature magnetic susceptibilities were measured on a MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's Constants for all the constituent atoms.

Synthesis of the title complex

2-(Pyrid-4'-yl)-4,4,5,5-tetramethyl-1,3-dioxoimidazoline (NITpPy) was prepared according to the reported method.^{7,8} The title complex was prepared as follows: 0.064 g (0.25 mmol) of benzenetetracarboxylic acid was added to a stirred solution of 0.234 g (1 mmol) NITpPy and 0.093 g (0.25 mmol) $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in 20 mL of ethanol-water ($V/V = 1:1$). The solution was further stirred at room temperature for 5 h, a small amount of blue precipitates were formed and were removed by filtration. The filtrate was slowly evaporated at room temperature in the dark for a month. The blue single crystal suitable for X-ray analysis was obtained. Elemental analysis calcd (%) for $\text{C}_{34}\text{H}_{42}\text{CuN}_6\text{O}_{15}$: C 48.72,

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H 5.05, N 10.03; found C 48.41, H 5.08, N 10.10. The IR spectrum displays a strong broad band at 1645 cm^{-1} , which is the characteristic ν_{COO} band. The strong broad band at 1380 cm^{-1} is the $\nu_{\text{N-O}}$ band.

Crystal structure determination and refinement

A blue single crystal of the title complex with approximate dimensions of $0.25\text{ mm} \times 0.20\text{ mm} \times 0.18\text{ mm}$ was selected and mounted on a glass fiber. All measurements were made on R-Axis-IV diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.071073\text{ nm}$). Data were collection at $291(2)\text{ K}$ to a θ_{max} of 27.53° with a total of

5933 independent reflections ($R_{\text{int}} = 0.0000$). A summary of the crystallographic data is given in Table 1. The structure was solved by the direct methods using the SHELXS 97⁹ program. The hydrogen atoms were included in the final refinement model in calculated and fixed positions with isotropic thermal parameters. A full-matrix least-squares refinement on F^2 was carried out using SHELXL 97,¹⁰ and the goodness-of-fit on F^2 was 1.032. The final agreement factor values are $R_1 = 0.0766$ and $wR_2 = 0.1386$ [$I > 2\sigma(I)$]. Maximum and minimum peaks in the final difference Fourier synthesis were 680 and $-525\text{ e} \cdot \text{nm}^{-3}$, respectively. Selected bond lengths and angles are given in Table 2.

Table 1 Crystal data and structural refinements of the complex

Compound	$[\text{Cu}(\text{NITpPy})_2(\text{H}_2\text{TCB})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$
Empirical formula	$\text{C}_{34}\text{H}_{42}\text{CuN}_6\text{O}_{15}$
Formula weight	838.28
Crystal size	$0.25\text{ mm} \times 0.20\text{ mm} \times 0.18\text{ mm}$
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit-cell dimensions	$a = 1.0594(2)\text{ nm}$, $\alpha = 67.75(3)^\circ$ $b = 1.3830(3)\text{ nm}$, $\beta = 89.83(3)^\circ$ $c = 1.5551(3)\text{ nm}$, $\gamma = 70.54(3)^\circ$
Volume	$1.9685(7)\text{ nm}^3$
Z	2
Density (calc.)	$1.414\text{ g} \cdot \text{cm}^{-3}$
Absorption coefficient	0.630 mm^{-1}
$F(000)$	874
Temperature	$291(2)\text{ K}$
θ Range	1.43° to 27.53°
Index ranges	$-13 \leq h \leq 12$, $-17 \leq k \leq 0$, $-19 \leq l \leq 18$
Reflections collected	5933
Reflections used in refinement	3532
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.032
Final R [$I > 2\sigma(I)$]	$R_1 = 0.0766$, $wR_2 = 0.1386$
R indices (all data)	$R_1 = 0.1493$, $wR_2 = 0.1631$
Largest diff. peak and hole	680 and $-525\text{ e} \cdot \text{nm}^{-3}$

Table 2 Selected bond lengths (nm) and bond angles ($^\circ$) of the complex

Cu(1)—O(6)	0.1994(3)	Cu(1)—N(4)	0.2008(3)
Cu(1)—N(1)	0.2008(3)	Cu(1)—O(13)	0.2078(3)
Cu(1)—O(12A)	0.2112(3)	O(1)—N(2)	0.1292(5)
O(2)—N(3)	0.1290(6)	O(3)—N(5)	0.1241(8)
O(4)—N(6)	0.1265(6)	O(5)—C(25)	0.1248(4)
O(6)—C(25)	0.1262(5)	O(7)—C(32)	0.1212(5)
O(8)—C(32)	0.1323(5)	O(9)—C(34)	0.1214(5)
O(10)—C(34)	0.1322(5)	O(11)—C(33)	0.1229(4)
O(12)—C(33)	0.1257(5)	O(12)—Cu(1C)	0.2112(3)
N(1)—C(1)	0.1330(5)	N(1)—C(5)	0.1350(5)
N(2)—C(6)	0.1324(6)	N(2)—C(8)	0.1513(6)
N(3)—C(6)	0.1337(6)	N(3)—C(7)	0.1487(6)
N(3)—C(7)	0.1438(6)	N(4)—C(17)	0.1330(5)
N(4)—C(13)	0.1348(5)	N(5)—C(18)	0.1314(6)
N(5)—C(19)	0.1492(7)	N(6)—C(18)	0.1323(7)

Continued

O(6)-Cu(1)-N(4)	87.55(12)	O(6)-Cu(1)-N(1)	87.56(12)
N(4)-Cu(1)-N(1)	173.56(12)	O(6)-Cu(1)-O(13)	147.85(12)
N(4)-Cu(1)-O(13)	90.17(12)	N(1)-Cu(1)-O(13)	96.19(12)
O(6)-Cu(1)-O(12A)	115.56(10)	N(4)-Cu(1)-O(12A)	88.56(13)
N(1)-Cu(1)-O(12A)	89.77(13)	O(13)-Cu(1)-O(12A)	96.42(11)
C(25)-O(6)-Cu(1)	107.8(2)	C(33)-O(12)-Cu(1C)	123.1(3)
C(1)-N(1)-C(5)	117.7(3)	C(1)-N(1)-Cu(1)	118.4(3)
C(5)-N(1)-Cu(1)	123.8(3)	O(1)-N(2)-C(6)	126.1(4)
O(1)-N(2)-C(8)	123.0(4)	C(6)-N(2)-C(8)	110.9(4)
O(2)-N(3)-C(6)	126.5(4)	O(2)-N(3)-C(7)	122.4(4)
C(6)-N(3)-C(7)	110.8(4)	C(17)-N(4)-C(13)	117.4(3)
C(17)-N(4)-Cu(1)	116.2(2)	C(13)-N(4)-Cu(1)	126.3(3)

Results and discussion

Description of the crystal structure

An ORTEP drawing of the title complex is shown in Fig. 1 and the noncoordination solvent molecule H₂O is omitted for clarity. Each Cu(II) ion is pentacoordinate and has a distorted trigonal bipyramid coordination environment with two carboxylic oxygen atoms [O(12A), O(6)] from two H₂TCB, and a oxygen atom [O(13)] from water molecule comprise the equatorial plane, whereas the axial positions are filled by two nitrogen atoms [N(1), N(4)] from NITpPy ligands. The bond lengths of two Cu—N [Cu(1)—N(1) and Cu(1)—N(4)] are equal to 0.2008 (3) nm. The bond distances of Cu—O (carboxylate) are 0.1994 (3) and 0.2112 (3) nm for Cu(1)—O(6) and Cu(1)—O(12A), respectively, which are in agreement with those reported for other carboxylato-containing Cu(II) complexes.¹¹ The Cu—O

(water) bond length is 0.2078(3) nm. Each H₂TCB dianion binds two Cu(II) ions in a bis-monodentate mode, which results in the linear coordination chain. With the linear chain, the distance between successive Cu atoms is 1.0594 nm, which corresponds to *a*-axis length (*a*). The shortest Cu...Cu distance of two chains is 0.5803 nm. The phenyl ring of H₂TCB makes angles of 2.6° with the equatorial plane of the copper(II) ion and 0.9° with the coordinated carboxylate. For NITpPy ligand, O(1)-N(2)-C(6)-N(3)-O(2) is as expected coplanar, but form dihedral angles 34.7° with the plane of the pyridyl ring. The shortest contact between nitroxide groups is 0.4253 nm. Three different types of hydrogen bond interaction exist between 1-D chains. The first type is formed by the coordinated water molecules and the uncoordinated carboxyl oxygen atoms [0.2762 nm and 163.03° for O(5) (-*x* + 4, -*y*, -*z* + 3) ... O(13); 0.2619 nm and 156.84° for O(11) (*x* + 1, *y*, *z*) ... O(13)], the second one is formed by uncoordinated

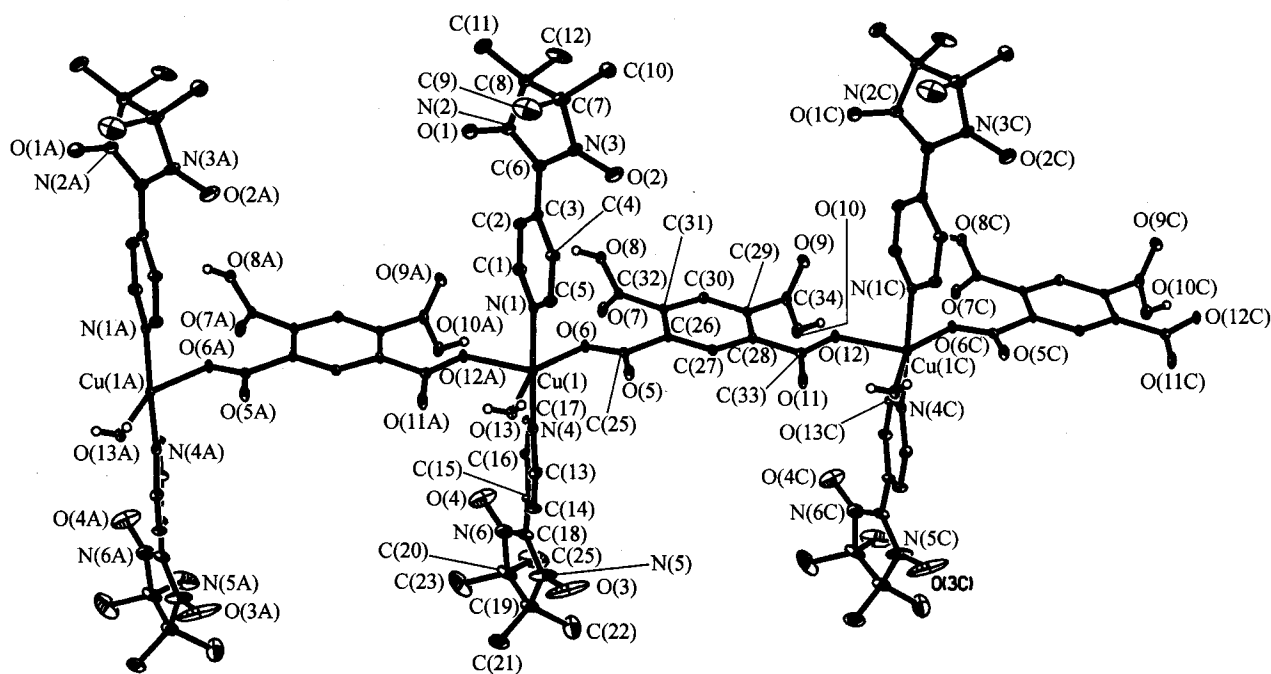


Fig. 1 ORTEP drawing of the complex (thermal ellipsoids are drawn at the 30% probability level).

water molecules and the uncoordinated carboxyl oxygen atoms [0.2778 nm and 168.41° for O(7) ($-x+3, -y, -z+2$) \cdots O(15); 0.2832 nm and 164.29° for O(7) ($x-1, y, z$) \cdots O(15); 0.2605 nm and 169.47° for O(8) \cdots O(14) ($-x+4, -y+1, -z+2$)] and the third one is formed by uncoordinated water molecules and the oxygen atoms of the NO groups of NITpPy radicals [0.2814 nm and 138.86° for O(14) \cdots O(1)]. Thus the whole molecular structure becomes a 3-D network (Fig. 2).

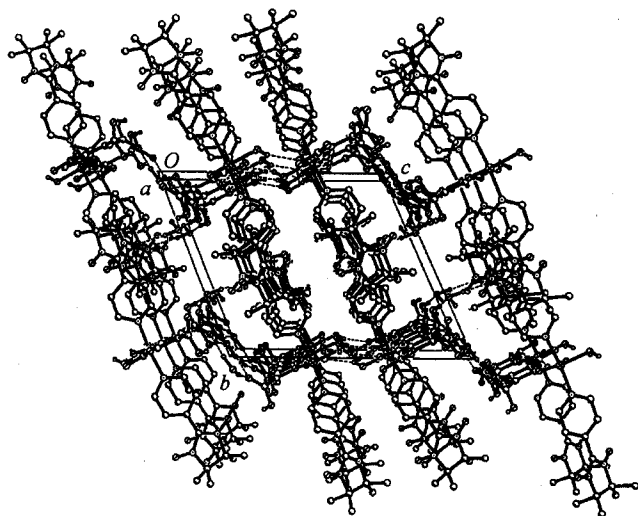


Fig. 2 3-D network structure of the complex.

Magnetic behavior

The magnetic susceptibility data are shown in Fig. 3 in the form of χ_M and μ_{eff} vs. T plots. The μ_{eff} value at room temperature is 2.95 μ_B , which is close to the value expected for three uncoupling $S = 1/2$ spin systems. As the temperature is lowered, the μ_{eff} value continuously decreases and reaches a value of 1.21 μ_B at 4.96 K. This behavior is characteristic of system with antiferromagnetic interactions.

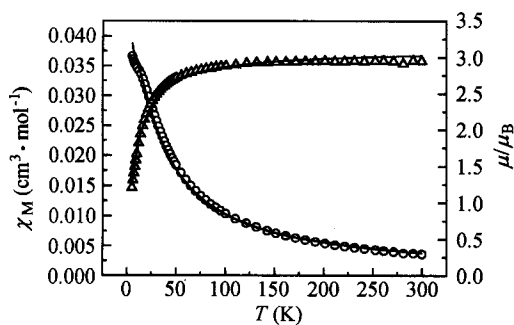
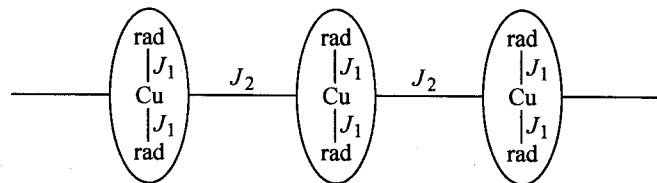


Fig. 3 Plots of χ_M (○) and μ_{eff} (△) vs. T for the complex, the solid line shows the fitting values.

There are three kinds of magnetic interactions for the present system, namely, (I) Cu(II)-coordinated NITpPy radical (J_1), (II) Cu(II)-Cu(II) through the H_2TCB bridge ligand (J_2), (III) neighboring NITpPy radicals

through space (0.4253 nm). The first two kinds of exchange coupling exist in the 1-D chain. The last one of a exchange coupling should be weak.^{12,13} In order to evaluate the exchange coupling constants in such a magnetic system, it was treated as a 1-D chain of a radical-Cu(II)-radical species (Scheme 2) with the parameter θ representing the magnetic interactions of radical-radical through space.

Scheme 2



The modified Fisher's model for the classic spin chain system¹⁴ was applied for the 1-D chain. Thus the magnetic susceptibility for the present system can be expressed as

$$\chi_M = \frac{Ng^2\beta^2}{3k(T-\theta)} [S_T(S_T+1)]^{\frac{1+u}{1-u}} \quad (1)$$

Where S_T represents temperature-dependent spin of the radical-Cu(II)-radical species.

$$u = \coth[J_2 S_T(S_T+1)/kT] - kT/[J_2 S_T(S_T+1)]$$

$$S_T(S_T+1) = 3k\chi_T T / Ng^2\beta^2$$

$$\chi_T = \frac{Ng^2\beta^2}{4kT} \times \frac{1 + \exp(J_1/kT) + 10 \exp(3J_1/2kT)}{1 + \exp(J_1/kT) + 2 \exp(3J_1/2kT)}$$

The least squares analysis of magnetic susceptibility data led to $J_1 = -11.18 \text{ cm}^{-1}$, $J_2 = -4.06 \text{ cm}^{-1}$, $g = 2.06$, $\theta = -0.9 \text{ K}$ and the agreement factor, define as $R = \sum [(\chi_M)_{\text{obs}} - (\chi_M)_{\text{calcd}}]^2 / [(\chi_M)_{\text{obs}}]^2$, was 1.27×10^{-3} , for all of the 56 observations. The weak antiferromagnetic interaction between the Cu(II) ion and NITpPy radical is in agreement with those found previously for related compounds.^{15,16} The relatively strong antiferromagnetic coupling between Cu(II) ions through H_2TCB bridging ligand is due to the coplanarity of the basal plane of Cu(II) ion and H_2TCB bridge (2.6°).⁵

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