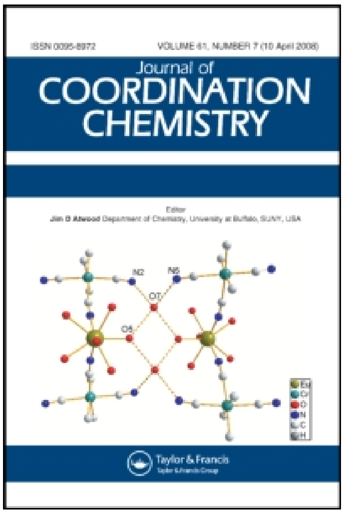

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Binuclear terephthalato-bridged copper(II) complex with N_2O_2 coordinating tripodal ligand: synthesis, structure, magnetic properties, and DFT study

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Binuclear terephthalato-bridged copper(II) complex with N_2O_2 coordinating tripodal ligand: synthesis, structure, magnetic properties, and DFT study

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The bluish green binuclear dicarboxylato bridged copper(II) complex $[Cu_2(HL)_2(\mu\text{-tp})]$, **1** has been synthesized, where (HL^-) is the monodeprotonated form of *N*,*N*-bis(2-hydroxybenzyl)-*N*′,*N*′-dimethylethylenediamine and tp = terephthalate dianion. Herein, we report the synthesis, spectral and structural characterization, and magnetic behavior of **1**. The coordination geometry of Cu(II) has a distorted square pyramidal geometry ($\tau = 0.117$). The variable temperature magnetic moment reveals that the complex exhibits very weak antiferromagnetic interaction ($J_{\text{Exp}} = -0.30\,\text{cm}^{-1}$) and the calculated J value ($J_{\text{Calcd}} = -1.05\,\text{cm}^{-1}$) using broken symmetry DFT method is in agreement with the experimentally observed value.

Keywords: Copper(II); Structure; Magnetic properties; DFT study

1. Introduction

The richness of coordination chemistry of copper(II) complexes has attracted considerable interest to establish the superexchange interaction between metal ions through extended bridging dicarboxylate ligands [1–14]. Much attention has been paid to the architecture of the polymeric magnetic system having cavities inside the multidimensional frameworks [15–17]. The formation of polynuclear chelates largely depends on the nature of bridging ligands as well as hydrogen bonding [18–20]. Terephthalate (tp) has been used due to its different bonding modes (scheme 1) [6, 20–25].

Terephthalato dianion has proved to be an appropriate bridging unit with a separation of 11–12 Å between the two magnetic centers [26–30]. In most of the cases not only weak antiferromagnetic interactions were observed with bridged dicarboxylato compounds [2, 19, 30–33], but ferromagnetically coupled complexes were also reported [2, 7, 34].

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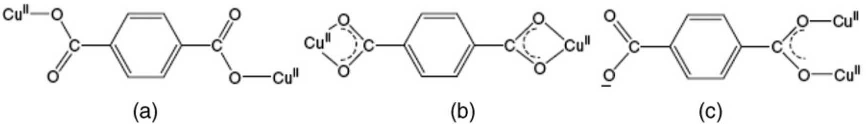


Scheme 1. Different binding modes of terephthalate.

Herein, we describe the synthesis of a μ-terephthalato bridged binuclear copper(II) complex incorporating an O,O,N,N-coordinated tripodal ligand. The X-ray structure of the complex has been determined, which allows the hydrogen bonding in the solid state to be investigated. The complex was also characterized by IR, UV-Vis, EPR spectra, and elemental analysis. Variable temperature magnetic susceptibility measurement indicates weak antiferromagnetic behavior which was also established by DFT calculation.

2. Experimental

2.1. *Materials*

All starting chemicals were analytically pure and used without purification.

2.2. *Physical measurements*

UV-Vis and IR spectra were recorded on a Perkin Elmer LAMBDA EZ-301 spectrophotometer and Perkin Elmer L-0100 spectrometer, respectively. Elemental analysis (C, H, and N) was performed on a Perkin Elmer 2400 Series II elemental analyzer. EPR was performed on a Varian E-109C (X band, 9.1 GHz) spectrometer at a microwave power of 30 dB and modulation amplitude of 12.5 gauss; spectra were collected using a quartz dewar. Diphenylpicrylhydrazyl (dpph, $g = 2.0037$) was used to calibrate the spectra. Magnetic measurements were carried out on polycrystalline samples with a Quantum Design MPMS XL SQUID susceptometer operating at a magnetic field of 0.1 T between 2 and 300 K. The diamagnetic corrections were evaluated from Pascal's constants.

2.3. *DFT study and computational details*

DFT calculations were performed on **1** using the crystallographic coordinates. The magnetic exchange interactions between the transition metal ions were studied on the basis of DFT coupled with the broken symmetry approach [35–37] for weakly interacting magnetic ions. The exchange coupling constant J for two center magnetic ion can be evaluated according to the following equation:

$$E_{\mathrm{HS}} - E_{\mathrm{BS}} = -(2S_1S_2 + S_2)J$$

where S_1 and S_2 stand for the total spin for the paramagnetic centers, in case of $S_1 = S_2 = 1/2$, $E_{HS} - E_{BS} = -J$, using the Heisenberg Hamiltonian, $\hat{H} = -J\hat{S}_1\hat{S}_2$.

The term E_{HS} corresponds to the energy of the triplet state and that of E_{BS} to the broken-symmetry state. The positive and the negative value of the coupling constant (J) indicates the ferromagnetic and antiferromagnetic ground states of the system.

The value of exchange coupling constant is often overestimated in DFT–BS calculation [38–42]. In spite of these, BS calculation is very useful to understand the exchange pathways for the polynuclear transition metal complexes [43–45] where the molecule is treated as two weakly coupled monomers.

Ground state electronic structure calculation of the complex has been carried out using DFT [46] methods with Gaussian 03 program [47]. The Becke's hybrid function [48] with Lee–Yang–Parr (LYP) correlation function [49, 50] was used throughout the study. We used 6-31G basis set for H atoms, a double-ζ all-electron basis set [51] for C, N, and O atoms and a triple-ζ quality all-electron basis set (TZP) [52] for copper. All the energy calculations were performed using the SCF = Tight option of the Gaussian to ensure sufficiently well converged values for the state energies.

2.4. *Crystallographic studies*

Single crystals of suitable quality for single crystal X-ray diffraction on [Cu_2(HL)(μ-tp)] (**1**) were grown by slow evaporation of methanolic solution. X-ray intensity data were measured at 293 K on a Bruker AXS SMART APEX CCD diffractometer (Mo-Kα, $\lambda = 0.71073$ Å). The detector was placed at a distance 6.03 cm from the crystal. Total 606 frames were collected with a scan width of 0.3° in different settings of φ. The data were reduced in SAINTPLUS [53] and empirical absorption correction was applied using the SADABS package [53]. Copper was located by direct methods and the rest of the non-hydrogen atoms emerged from successive Fourier synthesis. The structures were refined by full matrix least-square procedure on F^2. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were included in calculated positions. Calculations were performed using the SHELXTL v.6.14 [54] program package. Molecular structure plots were drawn using ORTEP [55]. Relevant crystal data are given in table 1.

2.5. *Synthesis of the complex*

[$Cu_2(HL)_2$(μ-tp)] (**1**). To a methanolic solution (30 mL) of $Cu(NO_3)_2 \cdot 3H_2O$ (0.5 mmol, 120.8 mg) was added the aqueous solution of disodium terephthalate (0.25 mmol, 52.5 mg, in 5 mL H_2O), immediately a light blue colloidal solution appeared and was stirred for 30 min, then H_2L (0.5 mmol, 150 mg) was added to this solution. The resulting green solution was stirred for another hour at ambient temperature. Slow evaporation of the solution yielded the bluish green crystalline product. Yield: (72%). $C_{44}H_{50}N_4O_8Cu_2$ (889.98); found C 59.42, H 5.63, N 6.25; Calcd C 59.38, H 5.66, N 6.29. UV-Vis (MeOH): λ_{max} (ε/(mol $L^{-1})^{-1}$ cm^{-1}) = 710 nm (303), 430 nm (2570), 290 nm (21230). IR (KBr, cm^{-1}): $\nu_s(COO^-)$ 1603, $\nu_{as}(COO^-)$ 1363, ν(O–H_{phenol}) 1380, ν(C–$O_{phenoxo}$) 1247. EPR: $g_{(298\,K)} = 2.104$, $g_{(77\,K)} = 2.119$.

Table 1. Crystal data and structure refinement parameters for **1**.

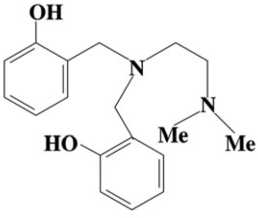
Complex	$[Cu_2(HL)_2(\mu\text{-tp})]$
Empirical formula	$C_{44}H_{50}N_4O_8Cu_2$
Formula weight	889.96
Temperature (K)	293(2)
Crystal system	Monoclinic
Space group	*p21/c*
Unit cell dimensions (Å, °)	
a	10.442(2)
b	17.834(3)
c	11.749(2)
α	90.00
β	113.244(3)
γ	90.00
Volume (Å^3), Z	2010.4(7), 2
Calculated density (mg m^{-3})	1.470
Absorption coefficient, μ (mm^{-1})	1.118
θ range for data collection (°)	2.12−26.38
Goodness-of-fit on F^2	1.047
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0388$, $wR_2 = 0.0881$

$R_1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$, $wR_2 = [w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

3. Results and discussion

3.1. *Synthesis*

The tetradentate tripodal ligand of the general formula H_2L has been synthesized by the reported procedure [56].



H_2L

The stoichiometric reaction of $Cu(NO_3)_2 \cdot 3H_2O$ with H_2L in the presence of disodium terephthalate(Na_2tp) furnished the bluish green complex of formula $[Cu_2(HL)_2(\mu\text{-tp})]$, **1** in good yield.

3.2. *IR spectra*

The IR difference in the stretching frequencies in the bounded bridging dicarboxylato complexes $\Delta\nu(COO^-)$ between the observed asymmetric, $\nu_{as}(COO^-)$ and the symmetric $\nu_s(COO^-)$ bands provide information about the binding of bridged dicarboxylato ligands [20, 30, 31, 57]. The absorption band due to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ are at 1603 and 1363 cm^{-1}, respectively, with $\Delta = 240$ cm^{-1} characteristic of monodentate

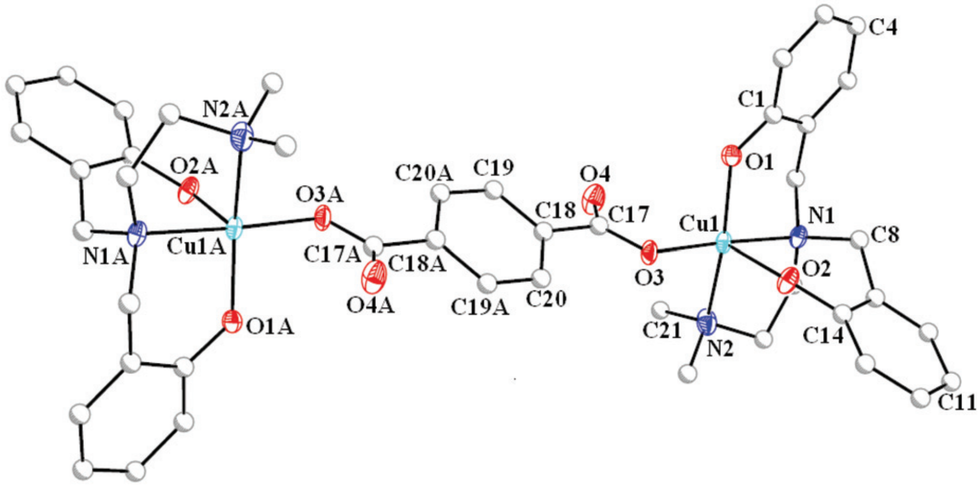


Figure 1. Molecular view of **1**. Hydrogens have been omitted for clarity and all coordinating atoms are represented by their 25% thermal probability ellipsoids.

coordination of the terephthalic dianion [32, 58, 59]. Vibration of O–H_{phenol} and ν(C–$O_{phenoxo}$) at 1380 and 1247 cm^{-1} indicate binding of phenolic–OH group in protonated and deprotonated form in the complex.

3.3. *UV-Vis spectra*

The UV-Vis spectrum of **1** recorded in methanol shows a broad band centered at 710 nm at room temperature, from a d–d transition in distorted square pyramidal Cu(II). The band is tentatively attributed to the electronic transition $^2B_1 \rightarrow {}^2E$ and $^2B_1 \rightarrow {}^2B_2$. The absorption near 430 nm is probably due to Cu(II) → phenolate(axial) metal to ligand charge transfer (MLCT) or phenoxo and/or carboxylato → Cu(II) ligand to metal charge transfer (LMCT) transition. The peak at 290 nm is assigned as an intraligand π–π* transition.

3.4. *EPR spectra*

The X-band EPR of **1** did not exhibit any sign of exchange interaction either at room temperature or at 77 K. The calculated *g* values were 2.104 and 2.119 at room temperature and 77 K, consistent with other distorted square pyramidal Cu(II) complexes [60].

3.5. *Molecular structure*

Bluish green crystals of **1** were obtained by slow evaporation of their methanolic solution. The molecular view of **1** is shown in figure 1 and selected bond distances and

Table 2. Selected bond distances and angles for **1**.

Distances (Å)		Angles (°)	
Cu1–O1	1.960(2)	O1–Cu1–O2	93.88(7)
Cu1–O2	2.293(2)	O1–Cu1–O3	91.03(7)
Cu1–O3	1.922(2)	O1–Cu1–N1	92.30(8)
Cu1–N1	2.036(2)	O1–Cu1–N2	166.46(9)
Cu1–N2	2.064(2)	O2–Cu1–O3	92.13(7)
Cu1 ··· Cu1A	11.053(3)	O2–Cu1–N1	88.06(7)
		O2–Cu1–N2	99.36(9)
		O3–Cu1–N1	176.64(8)
		O3–Cu1–N2	91.29(9)
		N1–Cu1–N2	85.38(9)

angles are presented in table 2. Complex **1** crystallizes in *p21/c* space group with two formula units present per unit cell.

The two copper(II) centers in the complex are bridged by terephthalate dianion where Cu ··· Cu separation is 11.053(3) Å. Each copper is five coordinate N_2O_3. The CuN_2O_3 polyhedron can be described as a distorted square pyramid [61] ($\tau = 0.117$) in which the two tripodal nitrogens, one phenoxo oxygen and one carboxylato oxygen of the bridges form the basal plane and one phenolic–OH of L occupies the apical position ($Cu–O_{phenol} = 2.293(2)$ Å). The $Cu–O_{carboxylato/phenoxo}$ and Cu–N bond distances span the range (1.92–1.96) and (2.04–2.06) Å, respectively. The copper is displaced toward the apical phenolic oxygen by 0.117 Å.

3.6. *Hydrogen bonding*

The solid state structure of **1** is remarkably different from the normal primary crystal structure due to involvement of secondary interactions. In the extended solid state structure a self assembled 1-D chain is formed by hydrogen bonding.

Axially coordinated phenolic–OH and equatorially bonded phenoxo group of one copper is attached through hydrogen bonding with the phenoxo and phenolic–OH of the other molecule with O ··· O distances being 2.553(5) Å. The intermolecular interactions are shown in figures 2 and 3.

3.7. *Magnetic study*

The variable temperature magnetic susceptibility measurement was carried out on a polycrystalline sample of **1** in the temperature range 2–300 K. The $\chi_M T$ *versus* T plot is given in figure 4. The room temperature (300 K) $\chi_M T$ value is 0.76 $cm^3 mol^{-1}$ K, similar to that expected for two uncoupled $S = 1/2$ spins with $g = 2.0$. In this case, the value of $\chi_M T$ (0.76 $cm^3 mol^{-1}$ K) for **1** remains almost unaltered upon cooling to 20 K and then decreases rapidly to 0.71 $cm^3 mol^{-1}$ K at 2 K. This behavior is a signature of weak antiferromagnetic interaction. The $\chi_M T$ *versus* T plot for the compound does not show any maximum over the temperature range studied.

The experimental data have been fitted using the Hamiltonian $\hat{H} = -J\hat{S}_A\hat{S}_B$, where $\hat{S}_A = \hat{S}_B = 1/2$. Least squares fitting of all experimental data leads to $J = -0.30\,cm^{-1}$, $g = 2.008$. The weak antiferromagnetic interaction found in **1** is in accordance with the

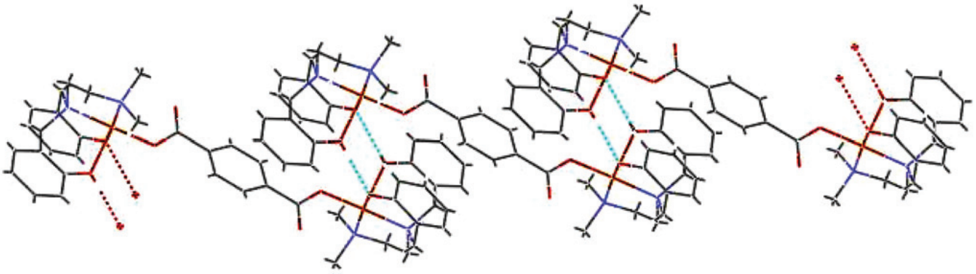


Figure 2. Extended 1-D supramolecular network in the lattice of **1**. Dotted lines represent intermolecular hydrogen bonding.

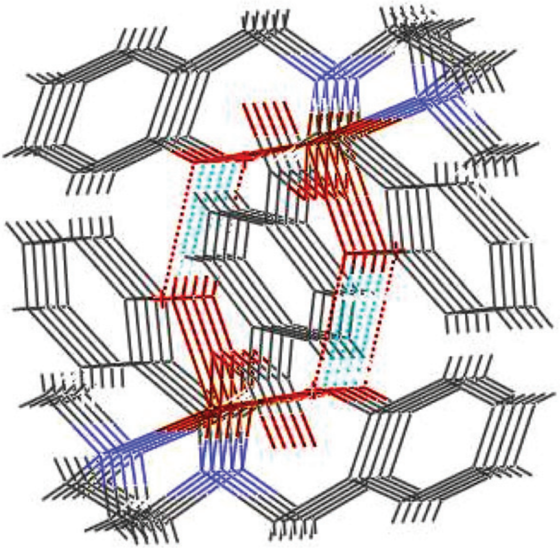


Figure 3. View of 3-D hydrogen bond network in **1**.

literature as terephthalate is not a good bridging ligand to mediate significant exchange coupling. Such weak antiferromagnetic behavior is consistent with the other reported terephthalato and other bridged binuclear copper(II) complexes [1, 2, 19, 62–65].

3.8. *Theoretical interpretation*

Density functional calculations on **1** predict an antiferromagnetic ground state with singlet-triplet splitting ($J_{\text{Calcd}} = -1.05\,\text{cm}^{-1}$), which is slightly higher than the experimental value ($J_{\text{Exp}} = -0.30\,\text{cm}^{-1}$). Since the calculation correctly predicts the sign and magnitude of the coupling constant, it reinforces the fact that its relatively small magnitude is not simply an artifact of the fitting procedure or sample impurity. We have calculated the spin density of the triplet state of **1** to understand the behavior

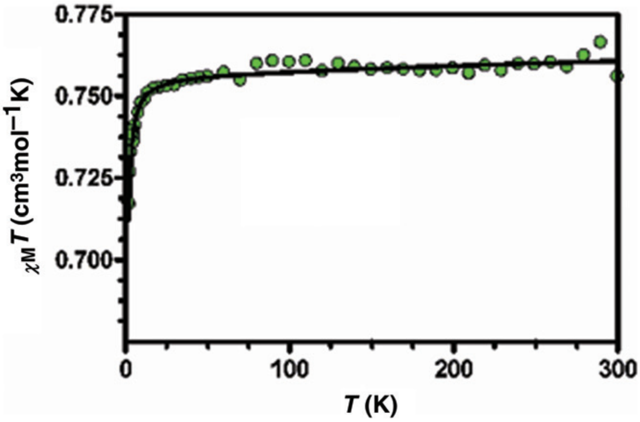


Figure 4. $\chi_M T$ *vs.* T for **1**. Circular points are the experimental data and solid line represents the best fit obtained.

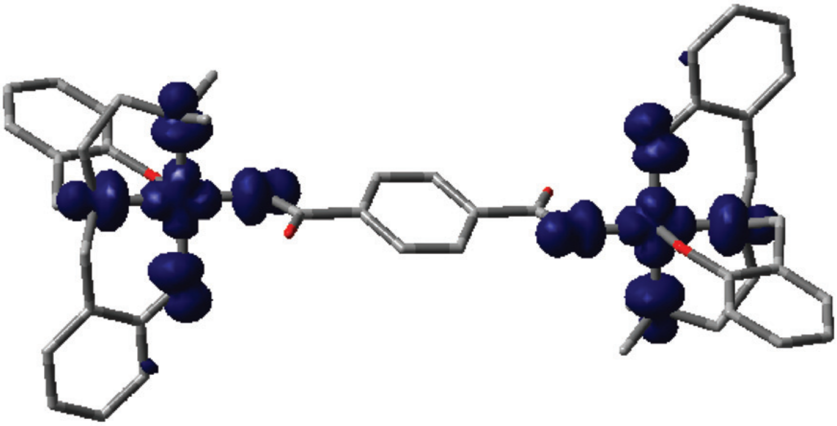


Figure 5. Spin density plot of the triplet state for **1** (isosurface cut-off value = 0.002).

of the unpaired electron and hence the exchange interaction between the two copper centers.

The calculated spin density for the triplet state from a DFT study provides insights for understanding the behavior of the unpaired electron and hence the exchange coupling between the two metal centers [66–71]. It is well documented in the literature that the antiferromagnetic interaction depends on the delocalization of the unpaired electron through the suitable orbital of the bridging ligand [66, 67]. It is clear from the spin density plot (figure 5) that the spin density is mainly in the copper $d_{x^2-y^2}$ magnetic orbital and the equatorially coordinated donors (table 3). The weak antiferromagnetic coupling may be explained as a result of: (1) large separation of the magnetic centers ($\mathrm{Cu}\cdots\mathrm{Cu} = 11.053$ Å), and (2) poor delocalization of the spin density between the copper $d_{x^2-y^2}$ orbital and the hybrid orbitals of the bridging terephthalate ligand. There is a short range spin delocalization of spin density of copper toward the

Table 3. Calculated Mulliken spin densities for **1**.

O(phenoxo)	0.1093
O(coordinated carboxylato)	0.1027
O(phenolic OH)	0.0031
O(non-coordinated carboxylato)	0.0018
N_{av}	0.0958
C_{av}(terephthalato)	0.0051
Cu	0.5751

equatorial phenoxo oxygen of the N_2O_2 ligand, which serves to draw spin density away from the bridging group.

Energies of the singly occupied molecular orbitals (SOMOs) in the triplet state are also very useful to give a qualitative idea about the exchange coupling constant, proposed by Hay *et al.* [72]. According to this model, antiferromagnetic exchange coupling constant for the binuclear metal complexes (each bearing one unpaired electron) is linearly proportional to the square of the energy difference between the two SOMOs. In our case, the marginal energy difference (0.0008 eV) between the two SOMOs in the triplet state is also a signature of the very weak antiferromagnetic interaction.

4. Conclusion

We have synthesized and characterized a terephthalato bridged binuclear Cu(II) complex of formula $[Cu_2(HL)_2(\mu\text{-tp})]$ using a N_2O_2 tetradentate tripodal ligand. In the solid state structure a self assembled extended 1-D chain is formed by simultaneous hydrogen bonding. The solid IR spectral data for the stretching frequencies of the tp-carboxylato $\nu(COO^-)$ reveals the existence of bis(monodentate) coordination mode for the bridged terephthalate ligand. Variable temperature magnetic moment confirms very weak antiferromagnetic interaction in the complex. We have performed the DFT calculation to understand the exchange pathway and observed that large separation of the two Cu(II) centers and negligible delocalization of the spin density through the bridged terephthalate ligand are responsible for the very weak antiferromagnetization.

Supplementary material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Center, CCDC reference no. 754542. Copies of these information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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