



A Novel Three-Dimensional Copper(II) Complex Linked by Covalent and Hydrogen Bonds: $[\text{Cu}_2(\text{L})(\text{PDC})_2(\text{H}_2\text{O})_2] \cdot 12\text{H}_2\text{O}$ (L = 3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0^{1.18},0^{7.12}]docosane, PDC = 2,3-pyrazinedicarboxylate) *

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Abstract

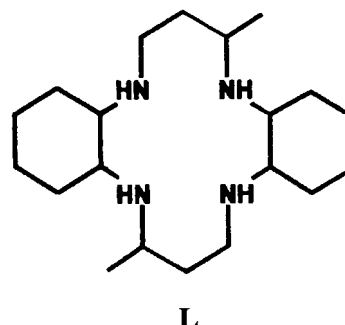
A new compound $[\text{Cu}_2(\text{L})(\text{PDC})_2(\text{H}_2\text{O})_2] \cdot 12\text{H}_2\text{O}$ (**1**) (L = 3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0^{1.18},0^{7.12}]docosane, PDC = 2,3-pyrazinedicarboxylate) was prepared and its structure was determined by X-ray diffraction method. Complex **1** crystallizes in the monoclinic space group $P2_1/c$ with $a = 15.653(2)$ Å, $b = 9.879(2)$ Å, $c = 15.202(2)$ Å, $\beta = 98.98(1)^\circ$, $V = 2321.9(6)$ Å³, and $Z = 2$. Each copper atom in complex **1** reveals an axially elongated octahedral geometry with an inversion center. Magnetic susceptibility measurement shows a weak ferromagnetic interaction between two Cu(I) and Cu(2) centers with a J value of $+0.12 \text{ cm}^{-1}$. The intermolecular hydrogen-bonding interaction gives rise to a three-dimensional network.

Introduction

Recently, there is a well-recognized and rapidly growing class of materials based on the supramolecular assembly of inorganic metal species, organic ligands, and anion systems [1, 2]. Self-assembled coordination polymers with specific network topologies can provide highly ordered networks with different dimensionalities, particularly as one- or two-dimensional solids [3, 4]. Generally, some control over the type and topology of functional materials can be achieved by the choice of the metal and organic ligand species, solvent system, inorganic counterion, and metal-to-ligand ratio [5–9]. The benzoic acid-based ligands have led to a variety of structures as these ligands can form short bridges via one carboxylate end, or longer bridges through the benzene ring [10, 11]. The terephthalate-bridged copper(II) centers have included the ligand as being coordinated to the metal in either a chelating bis-bidentate [12, 13] or bis-monodentate [14–16] or bridging bis monodentate [11] fashion. For example, an intermolecular one-dimensional chain compound $[\text{Cu}(\text{L})(\text{terephthalato})_n] \cdot 2n\text{H}_2\text{O}$ (L = 3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0^{1.18},0^{7.12}]docosane) shows that each bridging terephthalate anion coordinates to two copper(II) ions in a bis-monodentate mode, where each

chain is further extended by the interchain hydrogen bonding interactions mediated through water molecules [14]. On the other hand, the long terephthalate-bridges typically produce $\text{M} \cdots \text{M}$ separations of ~ 11 Å, which generally leads to weak antiferromagnetic interactions between metal centers [10, 11]. However, the one-dimensional water-bridged chain compound $\text{bis}(\text{aqua})[\mu\text{-terephthalato-}\kappa\text{O}]$ copper(II) reveals a weak ferromagnetic behavior [17].

Here we present the synthesis, structure, and properties of a chain compound $[\text{Cu}_2(\text{L})(\text{PDC})_2(\text{H}_2\text{O})_2] \cdot 12\text{H}_2\text{O}$ (**1**) (PDC = 2,3-pyrazinedicarboxylate).



* **Supplementary data.** Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 173313 for compound **1**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>.

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

Compound	[Cu ₂ (L)(PDC) ₂ (H ₂ O) ₂] \cdot 12H ₂ O
Color/shape	Violet/block
Chemical formula	C ₃₂ H ₇₂ Cu ₂ N ₈ O ₂₂
Formula weight	1048.06
Temperature	289 K
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 15.653(2) Å <i>b</i> = 9.879(2) Å, β = 98.98(1) $^\circ$ <i>c</i> = 15.202(2) Å
Volume	2321.9(6) Å ³
Z	2
Density (calculated)	1.499 mg/m ³
Absorption coefficient	1.003 mm ⁻¹
Diffractometer/scan	Enraf-Nonius CAD4/ ω -2 θ
Radiation/wavelength	Mo-K α (graphite monochrom.)/0.71069 Å
<i>F</i> (000)	1108
Crystal size	0.23 \times 0.20 \times 0.10 mm
θ range for data collection	2.45 to 24.97 $^\circ$
Index ranges	0 $\leq h \leq$ 18, 0 $\leq k \leq$ 11, -18 $\leq l \leq$ 17
Reflections collected/unique	4228/4069 [R(int) = 0.0395]
Absorption correction	ψ -scan
Max. and min. transmission	0.928 and 0.873
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	4069/0/292
Goodness of fit on <i>F</i> ²	1.022
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0675P)^2 + 0.8024P]$ with $P = (F_o^2 + 2F_c^2)/3$
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ ^a = 0.0560, <i>wR</i> ₂ ^b = 0.1297
<i>R</i> indices (all data)	<i>R</i> ₁ ^a = 0.1185, <i>wR</i> ₂ ^b = 0.1551
Largest diff. peak and hole	0.372 and -0.379 eÅ ⁻³

$$^a R_1 = \frac{\sum |F_o| - \sum |F_c|}{\sum |F_o|}$$

$$^b wR_2 = \left[\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right]^{1/2}$$

Experimental

Materials and physical measurements

All the reagents used for the preparation of the complex were of reagent grade and were used without further purification. The macrocyclic ligand **L** was prepared as described previously [18]. IR spectra were recorded as KBr pellets on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer. Uv/vis diffuse reflectance spectra were obtained on a Shimadzu UV2401 PC/DRS spectrophotometer. Magnetic susceptibility data were collected in the temperature range 5.0–300 K in an applied field of 1 T with the use of a Quantum Design MPMS7 SQUID magnetometer. The diamagnetic corrections were estimated from Pascal tables. Elemental analyses were carried out by the Korea Research Institute of Chemical Technology, Taejon, Korea.

Preparation of [Cu₂(L)(PDC)₂(H₂O)₂] \cdot 12H₂O (**1**)

To a solution of CuCl₂ \cdot 2H₂O (170 mg, 1 mM) in methanol (20 mL) was added **L** (337 mg, 1 mM) and Na₂PDC (212 mg, 1 mM). The mixture was refluxed for 1 h and then cooled to room temperature. The solution was filtered to remove the sodium chloride. The filtrate was then taken to dryness and the crude product dissolved in acetonitrile/water (1:1, 10 mL). After the solution was allowed to stand at room temperature over a period of several days, a quantity of violet crystals formed. These were filtered

off, washed with diethyl ether and dried in air. Yield: 68%. Calcd. for C₃₂H₇₂Cu₂N₈O₂₂: C, 36.67; H, 6.92; N, 10.69%. Found: C, 36.75; H, 6.83; N, 10.54%. IR (ν_{\max} , cm⁻¹): 3352(s), 3117(s), 2940(s), 1641(s), 1470(s), 1430(m), 1390(s), 1309(m), 1262(m), 1218(w), 1176(m), 1125(w), 1099(s), 1058(m), 1011(m), 993(m), 968(m), 954(w), 905(m), 876(w), 799(m), 712(w), 668(m), 548(w) (KBr). UV/VIS (diffuse reflectance spectrum, λ_{\max}): 576 nm.

X-ray crystallography

A violet crystal was mounted on an Enraf-Nonius CAD4 diffractometer. X-ray data were collected using graphite-monochromated Mo-K α radiation ($\lambda = 0.71069$ Å). Accurate cell parameters and an orientation matrix were determined by least-squares fit of 25 reflections. An asymmetric unit of intensity data was collected in the ω -2 θ scan mode. The intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction based on ψ -scan was applied. The crystallographic data, conditions used for the intensity collection, and some features of the structure refinement are listed in Table 1. The structure was solved by direct methods [19] and refined [20] on *F*² by full-matrix least-squares with anisotropic displacement parameters for the non-hydrogen atoms. All hydrogen atoms except for the water hydrogen atoms were placed in calculated positions with isotropic displacement parameters. Final

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	$U(\text{eq})$
Cu(1)	5000	0	5000	28(1)
Cu(2)	0	0	5000	44(1)
O(1)	3573(2)	2597(4)	5737(3)	49(1)
O(2)	3694(2)	331(4)	5793(3)	47(1)
O(3)	2200(2)	849(4)	4182(2)	44(1)
O(4)	842(2)	244(4)	4210(2)	51(1)
N(1)	5128(2)	2014(4)	4897(2)	24(1)
N(2)	5980(2)	177(4)	6051(2)	25(1)
N(3)	2404(3)	1581(5)	6988(3)	35(1)
N(4)	951(3)	632(4)	5912(3)	33(1)
C(1)	5968(3)	2419(5)	5419(3)	31(1)
C(2)	6060(3)	3936(5)	5583(4)	44(2)
C(3)	6933(4)	4251(6)	6149(4)	54(2)
C(4)	7048(4)	3494(6)	7030(4)	50(2)
C(5)	6949(3)	1977(6)	6860(4)	43(1)
C(6)	6083(3)	1638(5)	6279(3)	29(1)
C(7)	6027(3)	-760(5)	6837(3)	32(1)
C(8)	5408(4)	-357(6)	7457(4)	48(2)
C(9)	5907(3)	-2206(5)	6518(3)	37(1)
C(10)	5017(3)	-2562(5)	6015(3)	37(1)
C(11)	3309(3)	1426(7)	5851(3)	38(1)
C(12)	2419(3)	1291(5)	6125(3)	31(1)
C(13)	1659(3)	1379(6)	7287(3)	35(1)
C(14)	948(3)	880(6)	6773(3)	37(1)
C(15)	1684(3)	857(5)	5583(3)	28(1)
C(16)	1589(3)	625(6)	4577(3)	35(1)
Ow(1)	-410(4)	2471(6)	4866(4)	102(2)
Ow(2)	-1365(3)	-334(4)	7716(3)	60(1)
Ow(3)	-2291(5)	2444(7)	4195(4)	134(3)
Ow(4)	-303(3)	3742(5)	6548(3)	85(2)
Ow(5)	-790(4)	2346(6)	7941(4)	119(2)
Ow(6)	2389(3)	4617(5)	5908(3)	69(1)
Ow(7)	1026(4)	4004(6)	4456(4)	100(2)

atomic coordinates and equivalent isotropic displacement parameters are given in Table 2.

Results and discussion

Description of the structure

An ORTEP diagram of $[\text{Cu}_2(\text{L})(\text{PDC})_2(\text{H}_2\text{O})_2] \cdot 12\text{H}_2\text{O}$ (**1**) with the atomic numbering scheme is shown in Figure 1. The selected bond distances and angles are listed in Table 3. The crystallographically independent copper(II) cations are located on centers of inversion. The macrocyclic ligand in the present compound adopts the most stable *trans*-III(*R,R,S,S*) conformation and contains a derivative of *trans*-cyclohexane-1,2-diamine with two enantiomeric forms. Each copper(II) ion is connected by PDC ligands to give a chain structure in the lattice. The coordination geometry of the Cu(1) ion reveals an axially elongated octahedron with secondary amines of the macrocycle in which two *trans* carboxylate oxygens of PDC ligand have assembled around each metal center. The equatorial Cu(1)–N (2.008(4) and 2.042(4) Å) and axial Cu(1)–O(2) (2.552(4) Å) bond distances are typical of tetraaza macrocyclic copper(II) complexes with tetragonally elongated six-coordinated geomet-

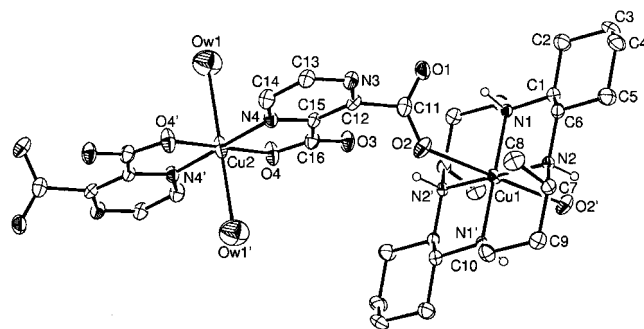


Figure 1. An ORTEP drawing of **1** with the atomic numbering scheme. The water molecules are omitted for clarity.

ries [21–23]. The axial Cu(1)–O(2) bonds are bent slightly off the perpendicular to the CuN_4 plane by 0.4–10.3°. The coordination environment of Cu(2) is described as an axially elongated octahedron with carboxylate oxygen atoms (O(4) and O(4')) and nitrogen atoms (N(4) and N(4')) of two PDC ligands that comprise the equatorial plane, whereas the axial positions are filled by two water molecules (Ow(1) and Ow(1')). The axial Cu(2)–Ow(1) distance of 2.524(6) Å is much longer than the Cu(2)–O(4) distance (1.932(3) Å) in the $\text{Cu(2)N}_2\text{O}_2$ plane. Furthermore, the axial Cu(2)–Ow(1) linkage is not perpendicular to the $\text{Cu(2)N}_2\text{O}_2$ plane with Ow(1)–Cu(2)–N(4) and Ow(1)–Cu(2)–O(4) angles of 84.55(15) and 91.1(2)°, respectively. The O(4)–Cu(2)–N(4) bite angle of 83.35(15)° is smaller than the O(4)ⁱⁱ–Cu(2)–N(4) angle (96.65(15)°, symmetry code: (ii) $-x, -y, -z + 1$). The intramolecular Cu(1)···Cu(2) separation along the one-dimensional PDC-bridged chain is 7.827 Å; the Cu(1) atom is bridged by the carboxylate oxygen atom of PDC ligand, while the Cu(2) atom is connected by the carboxylate oxygen and nitrogen atom of the PDC ligand. The coordination of the carboxylate oxygen and nitrogen atom of the PDC bridge is slightly asymmetrical (Cu(1)–O(2)–C(11) = 125.1(3), Cu(2)–O(4)–C(16) = 115.7(3)° and Cu(2)–N(4)–C(14) = 129.1(3), Cu(2)–N(4)–C(15) = 112.8(3)°). The dihedral angles between the pyridine plane and the carboxylate end groups O(1)–C(11)–O(2) and O(3)–C(16)–O(4) planes are 76.5(3) and 6.6(4)°, respectively. There are a number of hydrogen-bonded contacts in the crystal structure. The secondary amines of the macrocycle form hydrogen bonds with carboxylate oxygen atoms of the PDC ligand. Furthermore, the water molecules form hydrogen bonds with carboxylate oxygen atoms and with the other water inclusions. This intermolecular hydrogen-bonding interaction gives rise to a three-dimensional network (Table 4 and Figure 2).

Chemical properties

The infrared spectrum for the complex **1** shows $\nu(\text{NH})$ of the coordinated secondary amines and $\nu(\text{COO})$ of the PDC ligand at 3117 and 1641 cm^{-1} . The bands at 3352 and 1099 cm^{-1} are also assigned to the $\nu(\text{OH})$ and $\nu(\text{CN})$ stretching modes, respectively. The diffuse reflectance absorption spectrum of **1** shows maximum absorption at 576 nm, which

Table 3. Selected bond distances (Å) and angles (°) for **1***

Cu(1)–N(1)	2.008(4)	Cu(1)–N(2)	2.042(4)
Cu(1)–O(2)	2.552(4)	Cu(2)–N(4)	1.970(4)
Cu(2)–O(4)	1.932(3)	Cu(2)–Ow(1)	2.524(6)
C(11)–O(1)	1.249(7)	C(11)–O(2)	1.248(6)
C(16)–O(3)	1.226(6)	C(16)–O(4)	1.272(6)
C(12)–N(3)	1.346(6)	C(13)–N(3)	1.331(6)
C(14)–N(4)	1.333(6)	C(15)–N(4)	1.339(6)
Cu(1)··Cu(2)	7.827		
N(1)–Cu(1)–N(2)	84.5(2)	N(1)–Cu(1)–N(2) ⁱ	95.5(2)
O(2)–Cu(1)–N(1)	90.4(1)	O(2)–Cu(1)–N(2)	100.3(1)
O(2)–Cu(1)–N(1) ⁱ	89.6(1)	O(2)–Cu(1)–N(2) ⁱ	79.7(1)
O(4)–Cu(2)–N(4)	83.35(15)	O(4) ⁱⁱ –Cu(2)–N(4)	96.65(15)
Ow(1)–Cu(2)–N(4)	84.55(15)	Ow(1)–Cu(2)–O(4)	91.1(2)
Ow(1)–Cu(2)–N(4) ⁱⁱ	95.45(18)	Ow(1)–Cu(2)–O(4) ⁱⁱ	88.9(3)
Cu(1)–O(2)–C(11)	125.1(3)	O(1)–C(11)–O(2)	128.2(5)
O(1)–C(11)–C(12)	117.2(5)	O(2)–C(11)–C(12)	114.6(5)
Cu(2)–O(4)–C(16)	115.7(3)	O(3)–C(16)–O(4)	124.9(5)
O(3)–C(16)–C(15)	120.1(5)	O(4)–C(16)–C(15)	114.9(4)
Cu(2)–N(4)–C(14)	129.1(3)	Cu(2)–N(4)–C(15)	112.8(3)
C(12)–N(3)–C(13)	116.8(4)	C(14)–N(4)–C(15)	118.1(4)

*Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $-x, -y, -z + 1$.

Table 4. Hydrogen bonding parameters (Å, °) for **1**

D-H...A	D.H (Å)	H.A (Å)	D.A (Å)	D-H...A (°)
N(1)–HN(1),O(1)	0.91	2.10	2.976(5)	160.6
N(2)–HN(2),O(2) ⁱ	0.91	2.43	2.969(5)	117.8
Ow(1)··Ow(3)			2.962(9)	
Ow(1)··O(4) ⁱⁱ			3.150(7)	
Ow(2)··O(3) ⁱⁱ			3.018(5)	
Ow(2)··Ow(5)			2.800(7)	
Ow(3)··Ow(5) ⁱⁱⁱ			3.256(9)	
Ow(3)··Ow(6) ^{iv}			2.910(8)	
Ow(4)··Ow(1)			2.829(7)	
Ow(4)··Ow(2) ^v			2.827(6)	
Ow(5)··Ow(1) ^{vi}			2.900(8)	
Ow(5)··Ow(4)			2.733(8)	
Ow(6)··Ow(2) ^v			2.827(6)	
Ow(6)··O(1)			2.764(6)	
Ow(7)··Ow(6)			2.885(7)	
Ow(7)··Ow(1)			2.859(8)	
Ow(7)··Ow(4) ^{vii}			2.834(8)	

Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $-x, -y, -z + 1$; (iii) $x, -y - 1/2, z - 3/2$; (iv) $-x, -y + 1, -z + 1$; (v) $-x, y + 1/2, -z + 3/2$; (vi) $x, -y - 1/2, z - 1/2$; (vii) $-x, y + 3/2, -z + 3/2$.

can be assigned to d–d transition of the copper(II) ion in an octahedral environment [22, 23].

The temperature dependency of the magnetic susceptibilities (χ_m) and the effective magnetic moments (μ_{eff}) for **1** is shown in Figure 3. The room temperature μ_{eff} is $1.82\mu_B$, in good agreement with the spin-only value for copper(II). The magnetic moments (μ_{eff}) gradually increase with decreasing temperature, suggesting the presence of a ferromagnetic interaction between the copper(II) ions. The variation of magnetic susceptibility with temperature for chain compound **1** could satisfactorily be fitted following the Baker et al. equation [24]

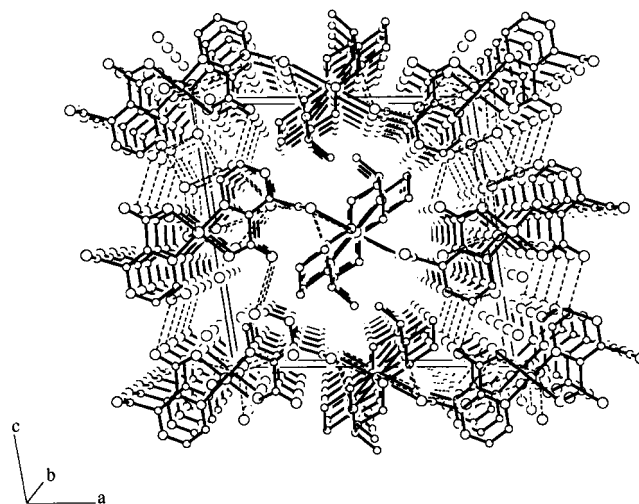


Figure 2. Crystal packing of **1**, showing the intermolecular hydrogen bonds as dotted lines. The hydrogen atoms are omitted for clarity.

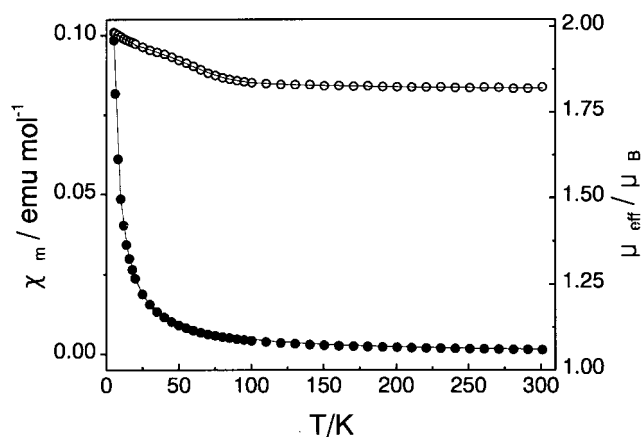


Figure 3. Plots of χ_m vs T (●) and μ_{eff} vs T (○) for **1**. The solid line represents the best fit of the experimental data to Equation (1).

$$\chi_m = \frac{Ng^2\beta^2}{4kT} \left[\frac{N}{D} \right]^{2/3}, \quad (1)$$

where $N = 1.0 + 5.7979916x + 16.902653x^2 + 29.376885x^3 + 29.832959x^4 + 14.036918x^5$, $D = 1.0 + 2.7979916x + 7.0086780x^2 + 8.653644x^3 + 4.5743114x^4$, and $x = |2J|/kT$. The best fit to the ferromagnetic $S = 1/2$ Heisenberg regular chain model was obtained for $J = +0.12 \text{ cm}^{-1}$ with $g = 2.228$. This result indicates that there exists a very weak intramolecular ferromagnetic interaction between the Cu(II) centers along the chain via the bridging PDC ligand. Compound **1** compares with that reported for the weak ferromagnetic compound bis(aqua)[μ -(terephthalato- κ O)]copper(II), which may be attributed to the favorable orbital orientations at the water oxygen atom [17]. In contrast to **1**, the terephthalato-bridged binuclear compound [$\text{Cu}_2(\text{bipy})_4(\mu\text{-ta})(\text{ClO}_4)_2$ (bipy = 2,2'-bipyridine, ta = terephthalate) exhibits a weak antiferromagnetic interaction ($J = -2.2 \text{ cm}^{-1}$) [12]. This fact may be due to the long terephthalato-bridge (11.0 Å) and dihedral angle (10.2°) compared to compound **1** (Cu··Cu = 7.827 Å, dihedral angle = 76.5(3) and 6.6(4)°).

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