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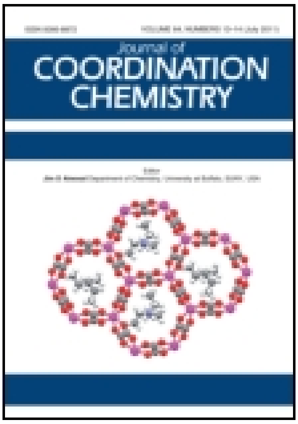

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A 2-D CdI_2 coordination network with 7-oxabicyclo[2.2.1]-5-heptene-2,3-dicarboxylate: synthesis, crystal structure, and luminescent properties

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A 2-D CdI_2 coordination network with 7-oxabicyclo[2.2.1]-5-heptene-2,3-dicarboxylate: synthesis, crystal structure, and luminescent properties

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The *in situ* reaction of $Cd(ClO_4)_2 \cdot 6H_2O$ with 7-oxabicyclo[2.2.1]-5-heptene-2,3-dicarboxylic anhydride in the presence of lithium hydroxide affords a 2-D Cd^{II} coordination polymer, $[Cd(\mathbf{L})(H_2O)]_\infty$ (**1**) (**L** = 7-oxabicyclo[2.2.1]-5-heptene-2,3-dicarboxylate), which exhibits an unusual (3,6)-connected $(4^6.6^6.8^3)(4^3)_2$ CdI_2-type topology. The luminescent and thermal properties of **1** were investigated.

Keywords: Cd^{II} complex; 7-Oxabicyclo[2.2.1]-5-heptene-2,3-dicarboxylic anhydride; Crystal structure; Topology; Luminescence

1. Introduction

Although various metal-organic frameworks (MOFs) with intriguing topologies and interesting fluorescent, magnetic, and catalytic properties have been prepared [1–3], design of coordination networks still remains a challenge in crystal engineering [4]. In this regard, the appropriate choice of well-designed organic ligands as building blocks with metal ions or metal clusters as nodes is an effective synthetic approach for such systems [5, 6]. Organic ligands with carboxyl groups have been used for assembling coordination architectures. Aromatic multicarboxyl ligands have been widely employed [7]. Far less common has been investigation of heterocyclic carboxylic acid ligands [8]. In this research, we chose 7-oxabicyclo[2.2.1]-5-heptene-2,3-dicarboxylic anhydride to fabricate MOFs (scheme 1). As a versatile tecton, it contains two carboxylic groups which can be partially or completely deprotonated to exhibit various coordination modes. It can serve as a trigonal-shaped connector by incorporating

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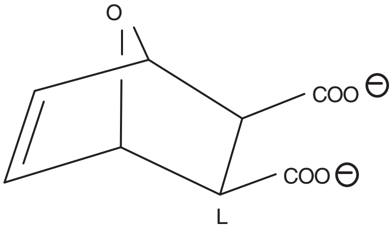

Scheme 1. 7-oxabicyclo[2.2.1]-5-heptene-2,3-dicarboxylate (L) ligand used in this work.

bridging oxygen in the backbone with the two carboxylic groups. Cd^{II}-containing coordination polymers have attracted interest because of their structural diversities, interesting topologies, and potential applications in catalysis, luminescent, and nonlinear optic materials, as well as phase transformation and host–guest chemistry [5c, 9, 10].

Network topology is an important and essential aspect of the design and analysis of MOFs and also of inherent interest in understanding supramolecular assembly. New or unusual network topologies are a focus, particularly those deliberately constructed from nodes with connectivity commonly displayed by typical metal ions and organic tectons used in MOFs synthesis [11]. Generally, nodes of three-, four-, and six-connectivity are of most relevance, and a variety of such uninodal network topologies have been realized. However, there is a lack of systematic investigation on higher dimensional networks with mixed connectivity [12], such as (3,6)-, (4,6)-, and (4,8)-connected frameworks, which are considered to be difficult to achieve [13].

In this research, we focus on the *in situ* reaction of Cd^{II} with 7-oxabicyclo[2.2.1]-5-heptene-2,3-dicarboxylic anhydride in the presence of lithium hydroxide. Herein, we report a photoluminescent 2-D Cd^{II} coordination polymer, $[Cd(\mathbf{L})(H_2O)]_\infty$ (**1**), which exhibits an unusual (3,6)-connected $(4^6.6^6.8^3)(4^3)_2$ CdI_2-type topology.

2. Experimental

2.1. *General methods*

All starting reagents and solvents were commercially available and used as received. IR spectra were measured on a TENSOR 27 (Bruker) FT-IR spectrometer with KBr pellets from 4000 to 400 cm^{-1}. Elemental analyses of C and H were performed on a Vario EL III elemental analyzer. The powder X-ray diffraction (PXRD) was recorded on a Bruker D8 Advance diffractometer at 40 kV and 30 mA using a Cu-target tube and a graphite monochromator. The intensity data were recorded by continuous scan in a $2\theta/\theta$ mode from 3° to 80° with a step size of 0.02° and a scan speed of $2^\circ\,min^{-1}$. Simulation of the PXRD spectra was carried out by the single-crystal data and diffraction-crystal module of the commercially available Cerius2 program [14]. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer Diamond SII thermal analyzer from room temperature to 800°C under nitrogen at a heating rate of $10^\circ C\,min^{-1}$. The emission/excitation spectra were recorded on an F-7000 (HITACHI) spectrophotometer at room temperature.

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

Empirical formula	$C_8H_8CdO_6$
Formula weight	312.54
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	
a	12.106(5)
b	6.373(3)
c	10.355(4)
α	90
β	101.489(5)
γ	90
Volume (Å^3), Z	782.8(6), 4
Calculated density (g cm^{-3})	2.652
$F(000)$	608
θ range for data collection (°)	3.43–24.99
Reflections collected	5147
Independent reflection	1363 [$R(\text{int}) = 0.0400$]
Goodness-of-fit on F^2	1.074
R_1[a], wR_1[b] [$I > 2\sigma(I)$]	0.0843, 0.2293
R_2,[a] wR_2[b] (all data)	0.0873, 0.2316

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

2.2. *Synthesis of 1*

A mixed solution of 7-oxabicyclo[2.2.1]-5-heptene-2,3-dicarboxylic anhydride (0.05 mmol) and lithium hydroxide (0.1 mmol) in water was stirred for *ca* 5 min upon heating to 60°C. After cooling to room temperature, the resultant solution was filtered and deposited in a test tube. With that, a mixed solution (10 mL) of methanol and water (v/v = 1 : 1) was carefully layered as a buffer layer, finally a solution of $Cd(ClO_4)_2{\cdot}6H_2O$ (0.1 mmol) in CH_3OH (5 mL) was carefully layered on top. Colorless cubic single crystals suitable for X-ray analysis appeared at the tube wall after *ca* 3 weeks at room temperature. Yield: *ca* 30% based on 7-oxabicyclo[2.2.1]-5-heptene-2,3-dicarboxylic anhydride. Anal. Calcd for $C_8H_8CdO_6$: C, 30.74; H, 2.58. Found (%): C, 30.61; H, 2.66. IR (KBr pellet, cm^{-1}): 3449(m, br), 1582(vs), 1390(s), 1329(w), 1301(m), 1272(m), 1228(w), 1207(w), 1176(m), 1097(w), 1040(m), 1015(w), 987(m), 942(m), 898(m), 876(w), 828(m), 812(m), 741(m), 696(m), 596(w), 497(w), 472(w), 424(w).

2.3. *Crystal structure determination*

A crystal of 0.21 × 0.16 × 0.15 mm^3 was examined on a Bruker Smart 1000 CCD area-detector diffractometer at 294(2) K with Mo-Kα radiation ($\lambda = 0.71073$ Å) by ω scan mode. The program SAINT [15] was used for integration of the diffraction profiles. Semi-empirical absorption corrections were applied using SADABS. All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares with SHELXL [16]. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were added according to theoretical models. A summary of crystallographic data and refinement parameters is provided in table 1. Selected bond lengths and angles are listed in table 2.

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Cd1–O1W	2.160(17)	Cd1–O2$^{\#1}$	2.202(14)
Cd1–O3$^{\#2}$	2.229(12)	Cd1–O4$^{\#3}$	2.306(12)
Cd1–O1	2.378(13)	Cd1–O5	2.411(13)
Cd1–O3	2.414(12)		
O2$^{\#1}$–Cd1–O3$^{\#2}$	123.3(5)	O1W–Cd1–O4$^{\#3}$	126.9(6)
O2$^{\#1}$–Cd1–O4$^{\#3}$	106.6(5)	O3$^{\#2}$–Cd1–O4$^{\#3}$	96.5(5)
O1W–Cd1–O1	73.4(6)	O2$^{\#1}$–Cd1–O1	84.9(5)
O3$^{\#2}$–Cd1–O1	91.0(5)	O4$^{\#3}$–Cd1–O1	159.3(5)
O1W–Cd1–O5	123.2(5)	O2$^{\#1}$–Cd1–O5	84.5(5)
O3$^{\#2}$–Cd1–O5	149.3(4)	O4$^{\#3}$–Cd1–O5	86.2(4)
O1–Cd1–O5	77.8(4)	O1W–Cd1–O3	138.0(6)
O2$^{\#1}$–Cd1–O3	156.2(5)	O3$^{\#2}$–Cd1–O3	72.5(5)
O4$^{\#3}$–Cd1–O3	87.2(4)	O1–Cd1–O3	76.6(5)
O5–Cd1–O3	77.1(4)		

Symmetry codes for **1**: $^{\#1} = x, -y+5/2, z-1/2$; $^{\#2} = -x+1, -y+2, -z$; $^{\#3} = x, -y+3/2, z-1/2$.

3. Results and discussion

3.1. *Synthesis and general characterization*

Lowering the reaction speed may result in the formation of crystalline products, facilitating the slow growth of well-shaped larger single crystals suitable for X-ray diffraction. Considering this, complex **1** was synthesized by using slow diffusion in a test tube under ambient temperature and pressure. In addition, the use of lithium hydroxide is a key point for formation of **1**, which will not only adjust the pH of the reaction system to basic but also facilitate the *in situ* hydrolyzation from 7-oxabicyclo [2.2.1]-5-heptene-2,3-dicarboxylic anhydride to 7-oxabicyclo[2.2.1]-5-heptene-2,3-dicarboxylate (**L**).

IR spectra of **1** show features attributable to each component of **1** [17]. Strong broad bands centered at 3449 cm^{-1} indicate O–H stretching of coordinated water in **1**. IR absorptions of carboxylate groups are very complicated owing to its coordination diversity with metal ions. For **1**, characteristic bands of carboxylates at 1582 and 1390 cm^{-1} are ascribed to antisymmetric and symmetric stretching vibrations, respectively [18]. Furthermore, the $\Delta\nu$ value [$\Delta\nu = \nu_{asym}(COO^-) - \nu_{sym}(COO^-)$] is 192 cm^{-1}, consistent with structural features as observed in the crystal structure.

3.2. *Crystal structure of 1*

Single-crystal X-ray diffraction analysis reveals that **1** is a neutral 2-D layered coordination network (figure 1). The asymmetric unit contains one Cd^{II}, one **L**, and one coordinated water molecule (figure 1a). The Cd1 center is distorted pentagonal-bipyramidal occupied by six oxygen atoms from four different **L** [five from the carboxylate groups and one bridging in the backbone] and one coordinated water molecule. All the Cd–O bond distances [2.160(17) – 2.414(12) Å] and angles [45.5(6) – 159.3(5)°] around each Cd^{II} are typical and comparable to those of similar complexes in the literature [18, 19] (table 2). Each **L** uses its five oxygen atoms [four from carboxylate and one bridging oxygen in the backbone] to coordinate to four Cd^{II}'s and adopts two different coordination modes, μ_3-η^1:η^2-bridging for O3–C8–O4

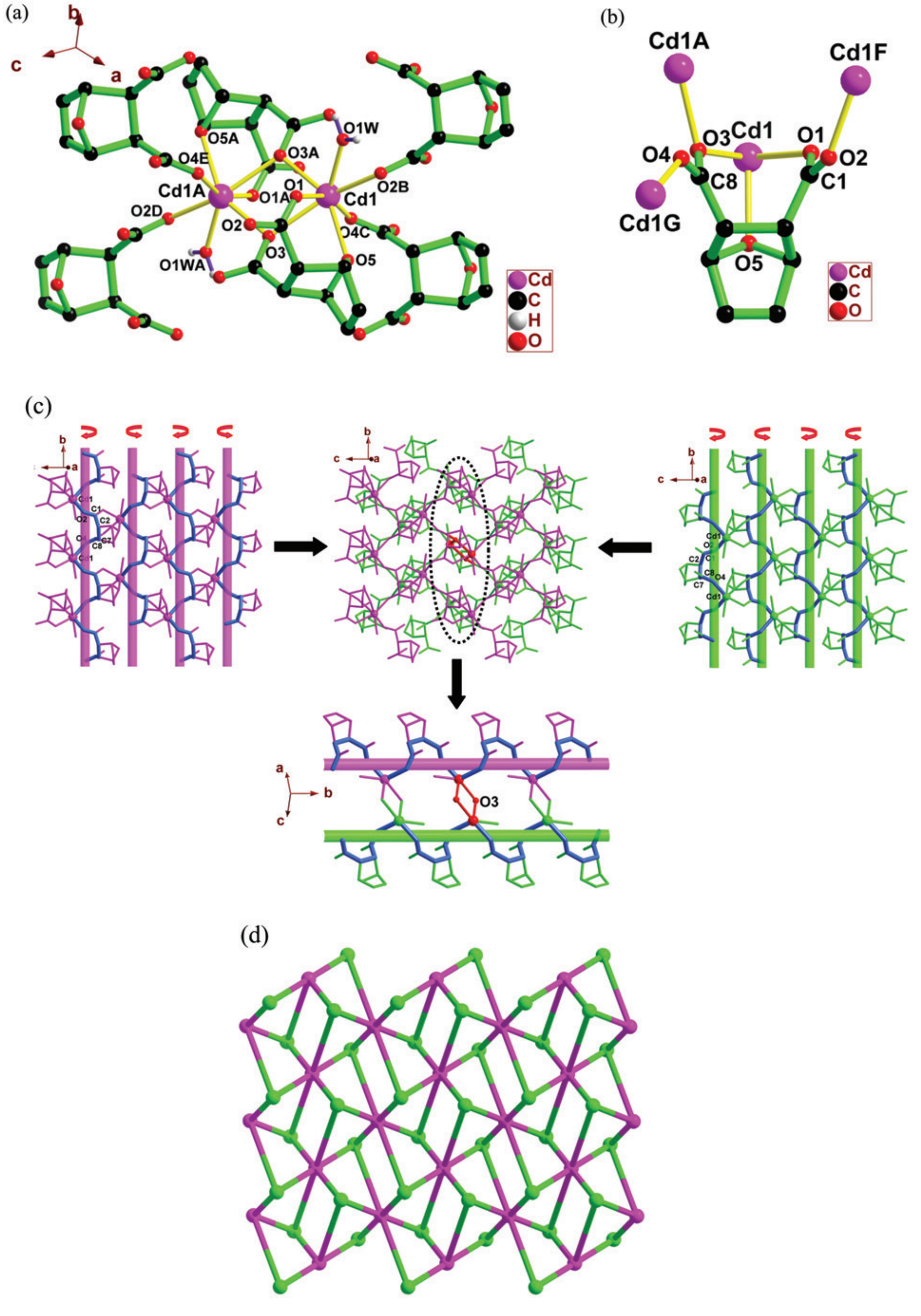

Figure 1. View of (a) the coordination environment of Cd^{II}, (b) the coordination modes of **L** ligand: μ_2-η^1:η^1-*syn-anti* bridging mode for O1–C1–O2 carboxylate group and μ_3-η^1:η^2-bridging mode for O3–C8–O4 carboxylate group, (c) the 2-D layer running parallel to the (100) plane, and (d) the schematic representation of the binodal (3,6)-connected 2-D $(4^6.6^6.8^3)(4^3)_2$ CdI_2-type topology. The symmetry-related atoms labeled with the suffixes A, B, C, D, E, F, and G are generated by the symmetry operation $(-x+1, -y+2, -z)$, $(x, -y+5/2, z-1/2)$, $(x, -y+3/2, z-1/2)$, $(-x+1, y-1/2, -z+1/2)$, $(-x+1, y+1/2, -z+1/2)$, $(x, -y+5/2, z+1/2)$, and $(x, -y+3/2, z+1/2)$, respectively. For clarity, only hydrogen atoms involved in coordinated water are shown.

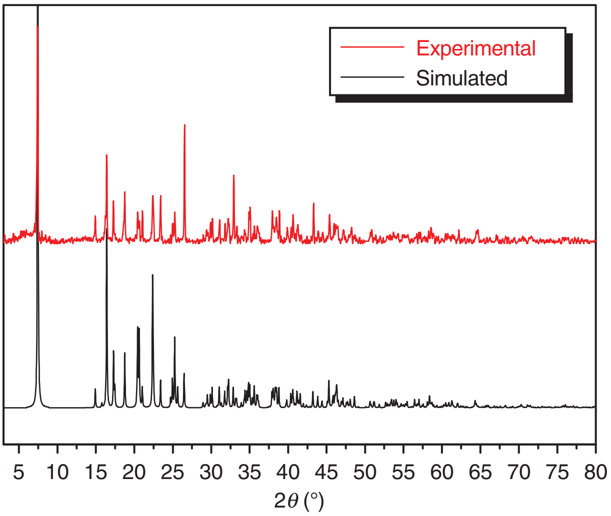

Figure 2. PXRD pattern of **1**.

carboxylate and μ_2-η^1:η^1-*syn-anti* bridging for O1–C1–O2 carboxylate (figure 1b). The O3–C8–O4 carboxylates connect adjacent Cd^{II}'s through O3 to form a dinuclear unit with a non-bonding Cd···Cd separation of 3.745(2) Å, which are further interlinked through carboxyl O2 and O4 to generate a 2-D layer running parallel to the (100) plane (figure 1c). To better understand the connectivity between components of the 2-D structure, **1** can be separated into two uniform 2-D fragments, sharing the $[Cd(1)_2O(3)_2]$ dinuclear unit (figure 1c bottom). In each 2-D fragment, there are two–Cd1–O2–C1–C2–C7–C8–O4–Cd1– helical chains alternately arranged in a right- and left-handed sequence with a pitch of 6.373 Å (figure 1c left and right).

Topological analysis of **1** revealed that it has a CdI_2-type net as shown in figure 1(d). If **L** is regarded as a 3-connecting node, the 6-connecting nodes are $[Cd(1)_2O(3)_2]$ dimeric units and a 2-D binodal net is obtained. There are twice as many 3-connecting nodes (vertex symbol of 4^3) than 6-connecting nodes (vertex symbol $4^6.6^6.8^3$). Therefore, the short Schläfli vertex notation of the net can be represented as $(4^6.6^6.8^3)(4^3)_2$ (figure 1d), which is characteristic of CdI_2-type networks [11a, 20, 21]. CdI_2-type network is common for binary inorganic compounds, but quite rare for metal-organic coordination polymers, although it has been reported recently for some cyano-bridged ones [11a].

3.3. *PXRD result*

To confirm whether the crystal structure is truly representative of the bulk material, PXRD has been carried out for **1**. The PXRD experimental and computer-simulated patterns of the complex are shown in figure 2. Although the experimental pattern has a few unindexed diffraction lines and some are slightly broadened in comparison with those simulated from the single crystal, it can still be considered that the bulk synthesized materials and the as-grown crystals are homogeneous for **1**.

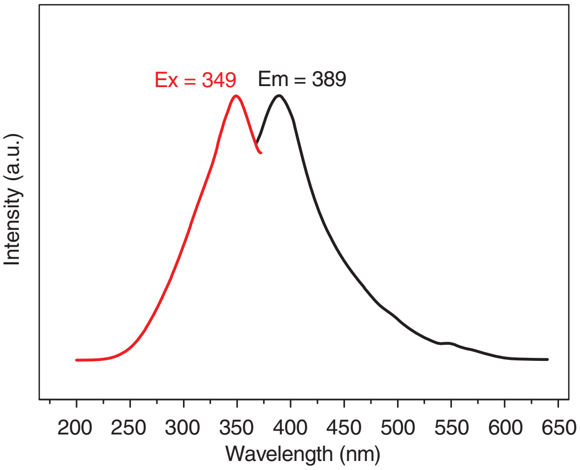

Figure 3. Solid-state excitation/emission spectra of **1** at room temperature.

3.4. *Luminescent property*

Luminescent properties of compounds which contain d^{10} metal centers have attracted interest because of their potential applications in chemical sensors, photochemistry, and electroluminescent displays [22]. The solid-state emission spectrum of **1** has been investigated at room temperature (figure 3). Excitation of the microcrystalline sample of **1** at 349 nm produces intense luminescence with the peak maximum at 389 nm. We presume that the emissions are neither metal-to-ligand charge transfer nor ligand-to-metal charge transfer in nature, because Cd^{II} with d^{10} configuration is difficult to oxidize or to reduce [5c, 10b, 22], and tentatively assign them to intraligand fluorescent emission [23]. The present finding indicates that the polymeric material may be an excellent candidate for thermally stable and solvent-resistant photoluminescent material because they are almost insoluble in most common solvents.

3.5. *Thermogravimetric analysis*

To examine the stability of **1**, TGA was performed from room temperature to 800°C with a heating rate of 10°C min^{-1} under nitrogen, as shown in figure 4. The TGA curve for the complex shows no weight loss between 30°C and 220°C, indicating that **1** remains stable to 220°C. Decomposition of the polymer begins from 220°C with four-step weight loss. From 220°C to 240°C (peaking at 225°C), first weight loss of 5.93% of the total weight occurs, assigned to removal of coordination water (calcd: 5.77%). Pyrolysis of the residue is followed by three steps of sharp weight decreases (peaking at 312°C, 367°C, and 470°C) from 260°C to 510°C, and further heating above 700°C results in complete weight loss, presumably due to the sublimation of volatile cadmium species formed in N_2 [24], indicating the 2-D network has completely collapsed. The final residues ($<5\%$) cannot be identified.

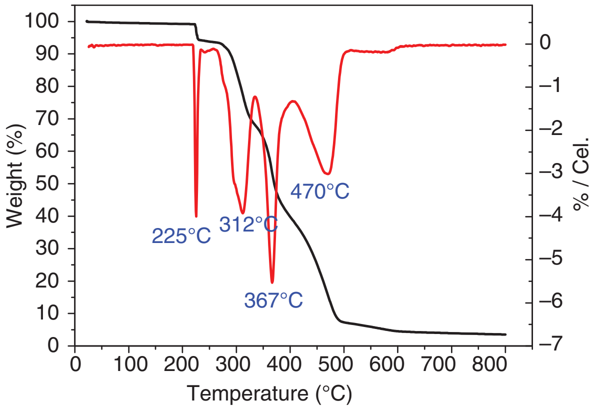

Figure 4. TGA plot of **1**.

4. Conclusion

We have constructed a 2-D Cd^{II} coordination polymer with an unusual (3,6)-connected $(4^3)_2(4^6.6^6.8^3)$ CdI_2-type topology by the *in situ* reaction of $Cd(ClO_4)_2{\cdot}6H_2O$ and 7-oxabicyclo[2.2.1]-5-heptene-2,3-dicarboxylic anhydride in the presence of lithium hydroxide. Isolation of **1** is proof of the coordination versatility of dicarboxylates with heterocyclic ring skeleton, which might be generally used to react with different transition metal ions, such as Cu^{II}, Co^{II}, and Mn^{II} for constructing other coordination complexes with fascinating structures and potential magnetic properties.

Supplementary material

Crystallographic data (excluding structure factors) for the crystal structure reported in this article have been deposited with the Cambridge Crystallographic Data Center and allocated the deposition number: CCDC-790282. This material can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

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