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Constructing Two Mn^{II} Coordination Polymers with 1,4-Bis(1-imidazol-yl)-2,5-dimethyl Benzene and Different Dicarboxylate Ligands: Syntheses, Crystal Structures, and Luminescent Properties

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Abstract. Two new coordination polymers, $[Mn(tda)(bimb)_{0.5}]_n$ (**1**) and $[Mn(obb)(bimb)]_n$ (**2**) [H_2tda = 2,5-thiophenedicarboxylic acid, H_2obb = 4,4′-oxybis(benzoic acid) and bimb = 1,4-bis(1-imidazol-yl)-2,5-dimethyl benzene], were hydrothermally synthesized by reactions of Mn^{II} salt with a rigid ligand 1,4-bis(1-imidazol-yl)-2,5-dimethyl benzene and dicarboxylate ligands. Complex **1** exhibits an unusual binodal (3,7)-connected three-dimensional (3D) architecture with point symbol $(4^4.6^{17}).(6^3)$. Complex **2** is a three-dimensional structure with pcu topology. Furthermore, the luminescent properties of complexes **1** and **2** are investigated.

Introduction

The construction of new coordination polymers (CPs) has aroused intense interests in the last decade not only for their intriguing structures and variety of topological net, but also for their potential applications as functional materials in the areas of magnetism, gad adsorption, catalysis, luminescence and so on.[1–12] In order to construct new CPs, much effort has been devoted on the design and modification of the organic ligands to control the architectures of CPs because the geometries of organic ligands have a great effect on the structural frameworks of CPs.[13,14] For the self-assembly processes of CPs, the mixed-ligand strategy of multicarboxylate and N-donor ligands has been certified an effective method for construction of the new frameworks, which can result in greater tenability of structural frameworks than single ligands.[15–21] Among N-donor bridging ligands, imidazole-containing ligands have been widely employed to construct CPs due to their flexible and diverse coordination modes, which can lead to form versatile topologies. Up to now, a large number of CPs are constructed by flexible imidazole-containing ligands.[22–25] The CPs constructed by rigid bidentate 1,4-bis(1-imidazol-yl)-2,5-dimethyl benzene are scarcely reported.[26,27] In the bimb ligand, the two imidazole rings can rotate around the central phenyl ring with the result that a variety of intriguing structures would be obtained.

Considering the above mentioned, we employed the mixed-ligand strategy of the rigid imidazole-containing ligand (bimb) and different carboxylate ligands to synthesize two Mn^{II} coordination polymers $[Mn(tda)(bimb)_{0.5}]_n$ (**1**) and $[Mn (obb)(bimb)]_n$ (**2**). Furthermore, the luminescent properties of complexes **1** and **2** are investigated at room temperature.

Results and Discussion

Structural Description

$[Mn(tda) (bimb)_{0.5}]_n$ (1)

Single crystal X-ray analysis reveals that complex **1** crystallized in the monoclinic space group $P2_1$. Crystal structure analysis reveals that the asymmetric unit of **1** consists of two central Mn^{II} atoms. As shown in Figure 1, the Mn1 ion adopts a distorted octahedral arrangement, which is ligated by three carboxylate oxygen atoms and one nitrogen atoms composing the equatorial plane, and one oxygen atom and one nitrogen

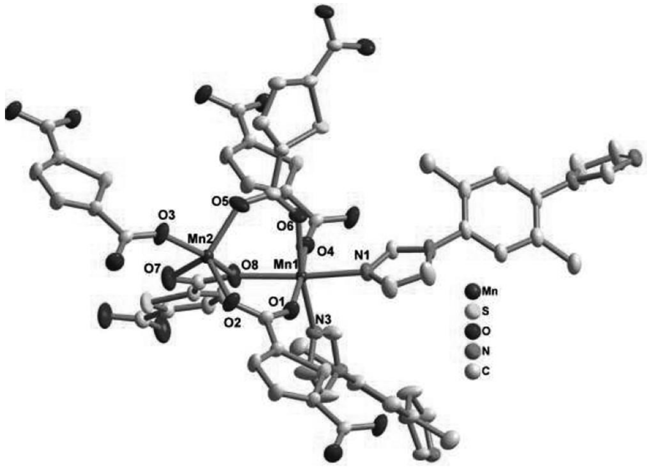

Figure 1. Coordination environment of the Mn^{II} ion in complex **1**. Hydrogen atoms are omitted for clarity.

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atom at the apical positions with the O8–Mn1–N1 angle of 172.60(8)°. The central Mn2 atom is five-coordinated by five carboxylate atoms with a distorted square-pyramidal arrangement.

The Mn–O bond lengths vary from 2.024(2) Å and 2.265(2) Å. Mn–N bond lengths are 2.214(2) Å and 2.244(2) Å. In **1**, the carboxylate ligands adopt chelating/bridging and bis(bridging-bidentate) coordination modes. Two independent central Mn^{II} atoms are bridged together by three carboxylate groups to form a dinuclear unit with the Mn–Mn distance of 3.586 Å. The manganese(II) cations are bridged by the carboxylate groups to form a rod-like chain. These chains as infinite rod-shaped secondary building units are further interlinked by the carboxylate ligands to produce a three-dimensional network with a large widow (approximate 11.440 × 18.946 Å based on the Mn1···Mn1 distance) (Figure 2). The bimb ligands lie in the large widows and connect the Mn2 ions (Figure 3). From the view point of topology, the final 3D structure can be represented as a (3,7)-connected net with $(4^4.6^{17}).(6^3)$ by reducing the dinuclear Mn^{II} unit and BDC^{2-} ligand as 7-connected and 3-connected nodes (Figure 4).

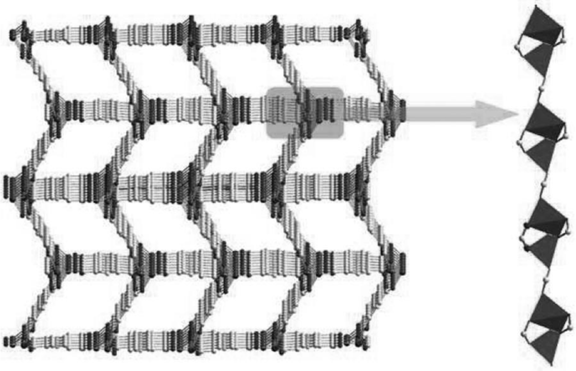

Figure 2. Left: 3D Mn^{II}-carboxylate framework; right: the chain formed from the SBUs with two corner-sharing Mn polyhedra.

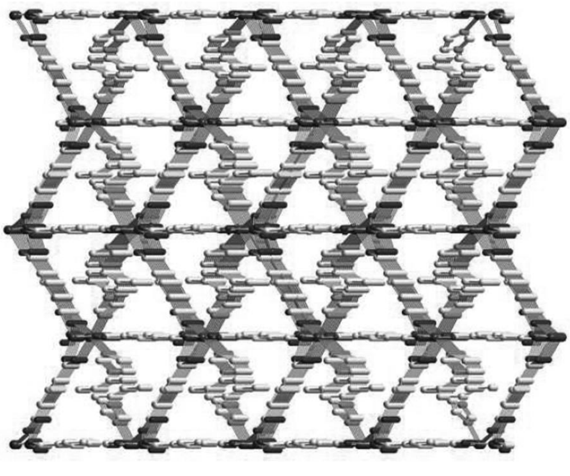

Figure 3. Final 3D framework constructed by Mn-carboxylate-bimb system.

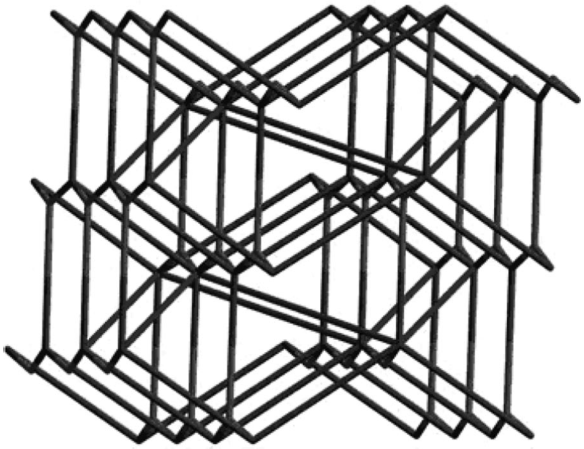

Figure 4. (3,7)-connected topology for complex **1**.

*[Mn(obb) (bimb)]$_n$ (**2**)*

When H_2tda was replaced by H_2obb, a structurally different complex **2** was obtained. Single crystal X-ray analysis reveals that complex **2** belongs to the triclinic system with space group $P\bar{1}$ and with a pcu topological net. Each Mn^{II} ion is six-coordinate with an octahedral arrangement completed by four carboxylate oxygen atoms [Mn–O, ranging from 2.1072(16) Å to 2.3200(17) Å] and two nitrogen atoms [Mn(1)–N(1) = 2.264 Å and Mn(1)–N(3) = 2.223(2) Å] (Figure 5). The four carboxylate oxygen atoms comprise the equatorial plane and two nitrogen atoms occupy the axial positions. In **2**, the carboxylate groups adopt the μ_2-η^1:η^1 and μ_1-η^1:η^1 coordination modes. The μ_2-η^1:η^1 carboxylate ligands connect the Mn^{II} ions to a one-dimensional chain based on the dinuclear Mn^{II} unit with Mn–Mn distances of 4.849 Å along the *a* axis (Figure 6). Furthermore, the 1D chains are connected by bimb ligands to form a 3D structure. If the dinuclear Mn^{II} ion and the organic ligands can be viewed as nodes and linkers, the 3D structure can be simplified as a pcu topological net (Figure 7).

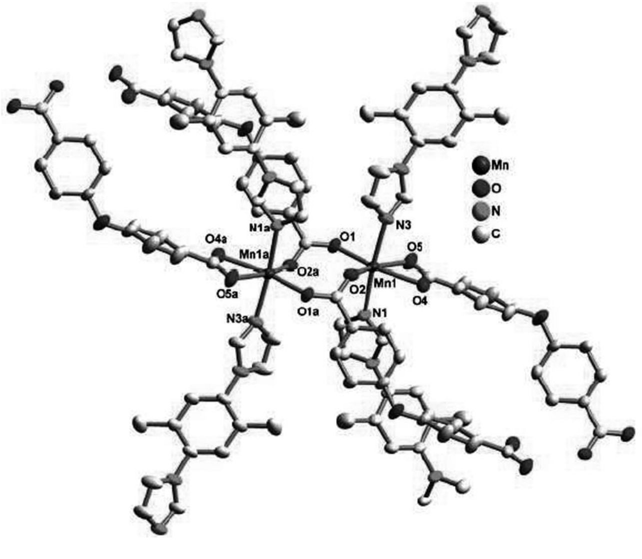

Figure 5. Coordination environment of the Mn^{II} ion in complex **1**. Hydrogen atoms are omitted for clarity.

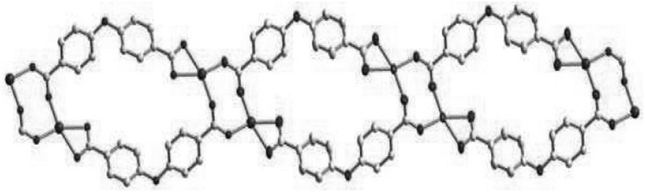

Figure 6. 1D chain constructed by carboxylate ligands and Mn^{II} ions.

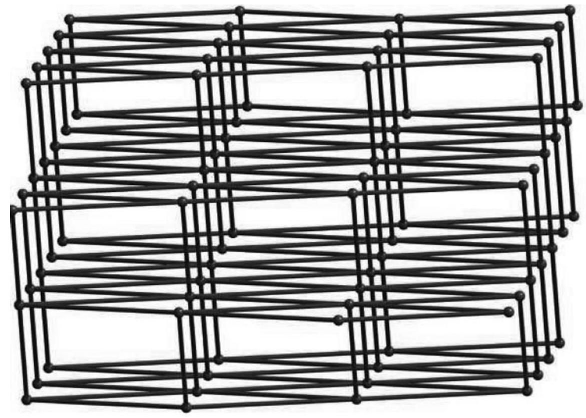

Figure 7. 3D pcu topological net for complex **2**.

Luminescent Properties

The simulated and experimental X-ray powder pattern is shown in Figure S1 (Supporting Information). All the peaks presented in the measured curves approximately match the simulated curves generated from single-crystal diffraction data, which confirms the phase purity of the as-synthesized product.

In the solid state, the complexes **1** and **2** show photoluminescence at room temperature. Complexes **1** and **2** exhibit emission at ca. 395 nm (λ_{ex} = 334 nm) and 409 nm (λ_{ex} = 338 nm) at room temperature (Figure 8). To understand the nature of the emission bands, we analyzed the photoluminescence properties of carboxylate and bimb ligands. The carboxylate ligands have not obvious emission bands and the bimb ligand shows emission at 421 nm.[28] As well known, Mn^{II} ion is not an excellent metal source for photoluminescence, whereas complexes **1** and **2** exhibit obvious emission spectra, which indicates that the photoluminescence properties are closely related with the ligand structure. The emissions of complexes **1** and **2** are different from those of the free organic ligands, which might be assigned to the intraligand emission excited state.[29,30] Several factors might serve for the emissions, such as a change in the highest occupied and lowest unoccupied molecular orbital energy levels of deprotonated dicarboxylate anions and neutral ligands coordinating to central metal atoms, a charge-transfer transition between ligands and metal atoms, and a joint contribution of the intraligands or charge-transfer transitions between the coordinated ligands and central metal atoms.[31,32]

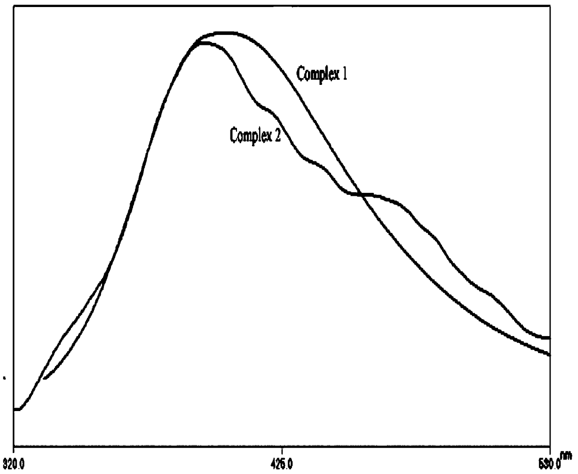

Figure 8. Luminescent emission spectra for complexes **1** and **2** in the solid state at room temperature.

Conclusions

We obtained two new Mn^{II} coordination polymers based on dicarboxylate and imidazole-containing ligands. Complex **1** shows a (3,7)-connected topological net, whereas complex **2** features a pcu topological net. The complexes **1** and **2** show emissions at room temperature.

Experimental Section

General Materials and Methods: All reagents and solvents employed were commercially available and used as received. C, H, and N analyses were carried out with a Perkin-Elmer 240C elemental analyzer. FT-IR spectra were recorded with a Bruker Equinox 55 FT-IR spectrometer as a dry KBr pellet in the 400–4000 cm^{-1} range. Solid-state fluorescence spectra were recorded with a Hitachi F-4600 equipped with a xenon lamp and a quartz carrier at room temperature. Topological analysis were performed and confirmed by the Topos program.[33,34]

Synthesis of $[Mn(tda)(bimb)_{0.5}]_n$(1): A mixture of $MnCl_2 \cdot 4H_2O$ (0.099 g, 0.5 mmol), H_2tda (0.086 g, 0.5 mmol), bimb (0.105 g, 0.5 mmol), NaOH (0.04 g, 1 mmol) and deionized water (15 mL) was heated at 140 °C for 72 h, and afterwards cooled to room temperature. The brown block crystals were obtained and washed with alcohol for several times (Yield: 41 % based on Mn). $C_{13}H_9MnN_2O_4$: calcd. C 45.36; H 2.64; N 8.14; S 9.32 %; found: C 45.38; H 2.63; N 8.15 %. **IR** (KBr): $\tilde{\nu}$ = 1622 (m), 1537 (m), 1423 (s), 1347 (m), 1230 (s), 1017 (m), 914 (m), 876 (m), 778 (m), 647 (m) cm^{-1}.

Synthesis of $[Mn(obb)(bimb)]_n$ (2): Complex **2** was obtained by a similar method as described for **1** by using of H_2obb (0.129 g, 0.5 mmol) instead of H_2tda. The yellow crystals of **2** (54 % based on Mn) were obtained in pure phase, washed with water and ethanol, and dried at room temperature. $C_{28}H_{22}MnN_4O_5$: calcd. C 61.21; H 4.04; N 10.20 %; found: C 61.23; H 4.05; N 10.22 %. **IR** (KBr): $\tilde{\nu}$ = 1604 (m), 1517 (m), 1447 (m), 1330 (m), 1241 (m), 1131 (m), 907 (m), 833 (m), 771 (m), 630 (m) cm^{-1}.

X-ray Crystallography: Single crystal X-ray diffraction analyses of complexes **1** and **2** were carried out with a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) by using a ω-scan mode. Empirical absorp-

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Table 1. Crystallographic data and structure refinement summary for complexes **1** and **2**.

	1	**2**
Empirical formula	$C_{13}H_9MnN_2O_4S$	$C_{28}H_{22}MnN_4O_5$
Formula weight	344.22	549.44
Crystal system	monoclinic	triclinic
Space group	$P2_1$	$P\bar{1}$
Unit cell dimensions		
a /Å	8.762(4)	8.536(5)
b /Å	17.118(3)	11.402(7)
c /Å	9.854(7)	15.099(9)
α /°	90	91.470(8)
β /°	108.920(5)	101.496(7)
γ /°	90	111.362(7)
Volume /Å^3	1398.1(11)	1333.3(11)
Z	2	2
Calculated density /mg·m^{-3}	1.635	1.369
Independent reflections [$I > 2\sigma(I)$]	4222	4642
F(000)	696	566
θ range for data collection	2.380–27.551	1.38–27.51
Limiting indices	$-11 \leq h \leq 11$	$-10 \leq h \leq 11$
	$-22 \leq k \leq 11$	$-12 \leq k \leq 14$
	$-12 \leq l \leq 12$	$-19 \leq l \leq 19$
Goodness-of-fit on F^2	1.086	1.032
R_1 $^{a)}$,wR_2 $^{b)}$ [$I > 2\sigma(I)$]	$R_1 = 0.0238$	$R_1 = 0.0412$
	$wR_2 = 0.0645$	$wR_2 = 0.1061$
R_1 $^{a)}$,wR_2 $^{b)}$ (all data)	$R_1 = 0.0252$	$R_1 = 0.0599$
	$wR_2 = 0.0656$	$wR_2 = 0.1158$

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

tion correction was applied using the SADABS programs.[35] All the structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 using the program SHELXTL 97.[36] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by geometrically calculations, and their positions and thermal parameters were fixed during the structure refinement. The crystallographic data and experimental details of structural analyses for coordination polymers are summarized in Table 1. Selected bond lengths and bond angles are listed in Table S1 (Supporting Information).

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-975329 and CCDC-975330 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): Additional plots of the structures of **1** and **2**; XRPD patterns of **1** and **2**.

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