DOI: 10.1002/ejic.201000832

Three New Polycatenation Networks Based on 4,4′-Oxybis(benzoate) and Bis(imidazole) Ligands: Synthesis, Structure and Photoluminescence

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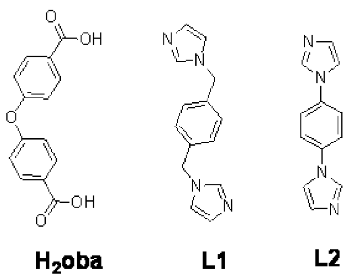
Keywords: Metal-organic frameworks / Structure elucidation / Luminescence / Polycatenation

In this paper we report three new metal–organic frameworks (MOFs), [Zn(oba)(**L1**)$_{0.5}$(H$_2$O)]$_n$ (**1**), [Zn$_2$(oba)$_2$(**L2**)$_2$](H$_2$O)$_3$ (**2**) and [Co(oba)(**L1**)]$_n$ (**3**) [oba = 4,4′-oxybis(benzoate), **L1** = 1,4-bis(imidazol-1-ylmethyl)benzene, **L2** = 1,4-bis(imidazol-1-yl)benzene] that have been obtained under hydrothermal conditions and characterized by single-crystal X-ray diffraction, powder X-ray diffraction (PXRD), infrared spectroscopy (IR), thermogravimetric analysis (TGA) and elemental analysis (EA). A structural investigation revealed that all three coordination compounds present polycatenation features. Interestingly, **1** shows a rare 1D→2D structure formed by the catenation of 1D ladders. Both **2** and **3**, however, are unusual cases that have 3D frameworks constructed from 2D 4^4-**sql** layers by parallel polycatenation. The photoluminescence properties of **1** and **2** have also been investigated.

Introduction

Metal–organic frameworks have attracted much attention largely due to their possible applications in catalysis, sorption, magnetism and non-linear optics.[1–5] Their intriguing structures and topological studies are still of great interest.[6] What is particularly important, in addition to the associated preparative strategy, is to be able to correlate functionalities with molecular structures. By doing so, researchers will be able to access the optimized synthetic strategy for the desired compound.[7] Currently, an interesting area of research is the construction of entangled networks as a new class of potential materials,[8–12] for example, penetration, (poly)catenation and (poly)knotting networks. Of these entanglements, the phenomenon of interpenetration, which happens when two or more identical independent networks pass through each other so that they cannot be untangled without breaking some covalent bonds, has been extensively investigated.[13] Most of these networks are confined to those with the same dimensionality as their constituent motifs.[14] In comparison with the widely studied interpenetrating networks, polycatenation networks, which lead to an increase in dimensionality (1D+1D→2D, 2D+2D→3D, 1D+2D→3D, 1D+1D→3D), have been less explored.[14c,15]

In recognition of the close relationship between the chemical topology of the target supramolecular compound and the structural particularity of the organic ligand, we can selectively design ligands with special features for the preparation of desired compounds. Typically, the polycatenation system is generated from the presence of a large free space within the single net.[13,14a,14b] It is recognized that the formation of a polycatenation system is favourable when a flexible long ligand is applied.[16] Taking into account these considerations, we employed 4,4′-oxybis(benzoate), which has proven to be an ideal ligand for forming interpenetrating networks due to the flexible nature of the –O– spacer between the two phenyl groups and its variability in coordination modes.[17,18] To pursue the possibility of increasing the dimensionality, two neutral N-donor ligands (**L1** and **L2**) were chosen for our synthetic strategy because they have different chain lengths and potential bendability in terms of their molecular structures (Scheme 1). As a continuation of our work on entangled networks,[16d,19] we herein report three new polycatenation networks, [Zn(oba)(**L1**)$_{0.5}$(H$_2$O)]$_n$ (**1**), [Zn$_2$(oba)$_2$(**L2**)$_2$](H$_2$O)$_3$ (**2**) and [Co(oba)(**L1**)]$_n$ (**3**). Compound **1** exhibits 1D→2D polycatenation and is quite distinct from **2** and **3**, which are two rare examples of parallel polycatenation (2D→3D).



Scheme 1. Molecular structures of the ligands used in this study.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201000832.

Results and Discussion

Crystal Structure of 1: Single-crystal X-ray diffraction analysis revealed that compound **1** crystallizes in the monoclinic space group *C*2/*c*. The asymmetry unit of **1** consists of one Zn^{II} ion, one $oba^{2–}$ anion, half of a **L1** ligand and one coordinated water molecule. As shown in Figure 1, the Zn1 atom is pentacoordinated by three carboxylic oxygen atoms from two different $oba^{2–}$ anions [Zn1–O 1.990(2)–2.461(2) Å], one O_{water} atom [Zn1–O6 1.997(2) Å] and one N**L1** atom [Zn1–N1 1.993(3) Å] to give a distorted square pyramidal geometry. Each Zn atom is connected to three others through one **L1** and two $oba^{2–}$ ligands, thus leading to the generation of a single flat ladder with the Zn···Zn separation in the range of 13.679–14.391 Å (Figure 2). As depicted in Figure 3, two flat ladders run in parallel directions and are laterally catenated by two other parallel ladders on each side to form 2D entangled layers. A better insight into the nature of this intricate framework can be achieved by the application of a topological approach. As shown in Figure 3 (b), the angle between two catenation ladders is 76.840°. Until now, to the best of our knowledge, there is only one example of 1D → 2D polycatenation based on this type of ladder.[20]

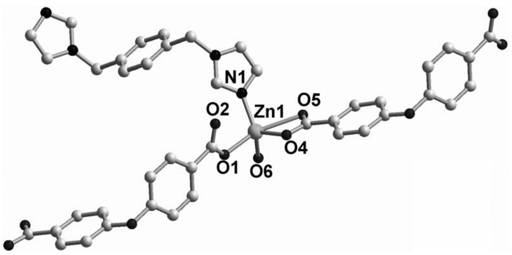

Figure 1. View of the local coordination environment of the Zn atom in **1**. Hydrogen atoms have been omitted for clarity.

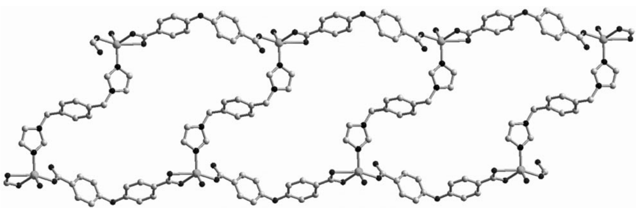

Figure 2. A single flat ladder of **1**.

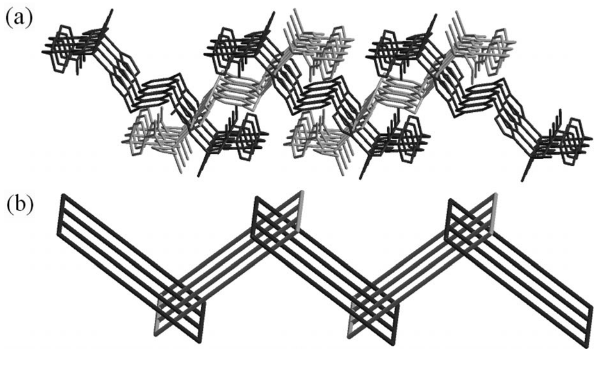

Figure 3. (a) View of the 1D → 2D polycatenation of compound **1**. (b) Schematic representation of the 1D → 2D catenation of **1**.

Crystal Structure of 2: When the **L2** ligand was used instead of the **L1** ligand in **1**, an unusual 2D → 3D parallel polycatenation framework, **2**, was obtained. The structure of **2** is composed of one Zn atom, one $oba^{2–}$ anion, one **L2** ligand and one and a half molecules of water. As illustrated in Figure 4, the tetracoordinated Zn atom in the tetrahedral coordination environment is ligated to two **L2** [Zn–N 2.005(3)–2.035(3) Å] and two bi-monodendate $oba^{2–}$ ligands [Zn–O 1.950(3)–1.973(3) Å]. Four Zn atoms are interlinked through $oba^{2–}$ and **L2** to form a 4-connected 2D corrugated layered structure with a 4^4-**sql** topology.[21] Within each layer, two square windows with dimensions of 14.359 × 13.514 and 14.359 × 13.464 Å based on the metal–metal distance are observed. Further inspection indicates that the $oba^{2–}$ ligands adopt a V-shaped conformation due to the rotation of the two phenyl groups around the –O– spacer in between. More importantly, the V-shaped bridges protrude away from the 4^4-**sql** sheet on both sides and thus they can readily catenate with two others (one above and one below). As a result, an infinite 3D framework is achieved by polycatenation of the 4^4-**sql** sheet (Figure 5). As shown in Figure 6, each 4^4-**sql** sheet is penetrated in parallel by two others ("above" and "below") leading to a 2D → 3D polycatenation network. The total volume for potential solvent intercalation was evaluated to be 111.5 $Å^3$, equal to 8.9% of the volume of the unit cell (1250.5 $Å^3$).[22]

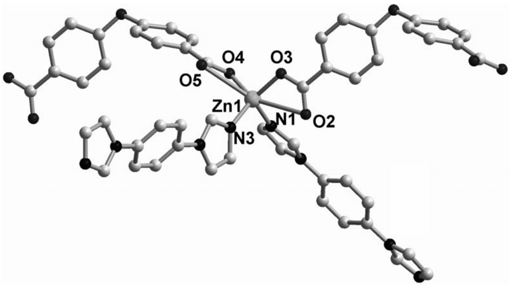

Figure 4. The local coordination environment of the Zn atom in **2**. Hydrogen atoms and lattice water have been omitted for clarity.

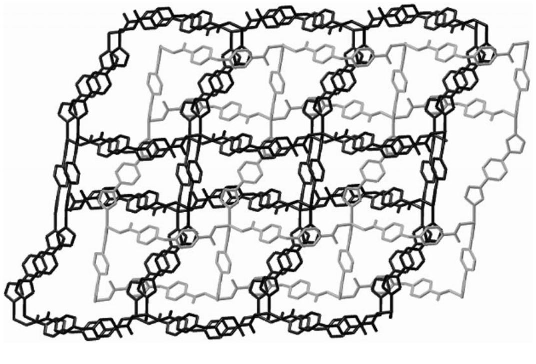

Figure 5. View of the catenation of three adjacent layers for compound **2**.

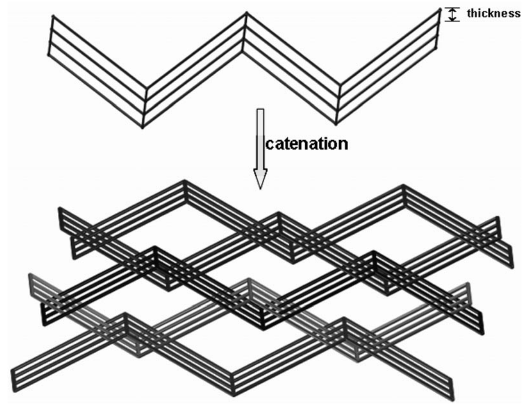

Figure 6. View of the undulating 4^4-**sql** sheet of **2** and, following catenation, schematic representation of the 3D parallel polycatenation of **sql** observed for **2** with a degree of catenation, doc = 2.

We were aware that a small number of polycatenation structures have previously been reported. For example, Ciani and coworkers studied the 2D→3D [Ag(sebn)$_2$]X (X = SbF$_6$, CF$_3$SO$_3$) network that is simultaneously catenated by two others due to the thickness of the 2D diamond-6^6 sheets.[23] Another interesting example of a 2D→3D network is the copper compound [Cu$_4$(p-BDC)$_3$(bipy)$_2$] of Williams and coworkers.[24] The component motif of this framework exhibits a thick double-layered 2D structure with 5-connected 4^86^2 topology and two others are catenated with the top and bottom layers of the same species. Very recently, Ma and coworkers described a Cd-containing polymer showing 2D→3D parallel polycatenation architecture based on oba^{2-} and **L1** ligands.[18b] And here, compound **2** demonstrates that the use of ligand **L2** is also advisable to generate 2D→3D parallel polycatenation networks.

Crystal Structure of 3: When a Co^{II} ion was used instead of the Zn^{II} ion in **1**, 2D→3D parallel polycatenation framework **3** was obtained. The structure of **3** contains one Co atom, one oba^{2-} anion and one **L1** ligand. As illustrated in Figure 7, the Co atom is coordinated by three carboxylic oxygen atoms from two different oba^{2-} anions [Co–O 1.985(3)–2.264(3) Å] and two nitrogen atoms from two **L1** ligands with a Co–N distance ranging from 2.044(3) to 2.045(3) Å to give a considerably distorted square pyramidal geometry. Four Co atoms are interlinked through oba^{2-} and **L1** to form a 4-connected 2D corrugated layered structure with 4^4-**sql** topology. In this case, the oba^{2-} anions adopt the μ_1:η^1,η^0 and μ_1:η^1,η^1 coordination modes. Further studies suggested that the overall structure of **3** is very similar to **2**, that is, compound **3** also forms a 2D→3D polycatenation net constructed from a 4^4-**sql** undulating sheet with a "thickness" of 14.483 Å (Figure 8, Figure S1 in the Supporting Information).

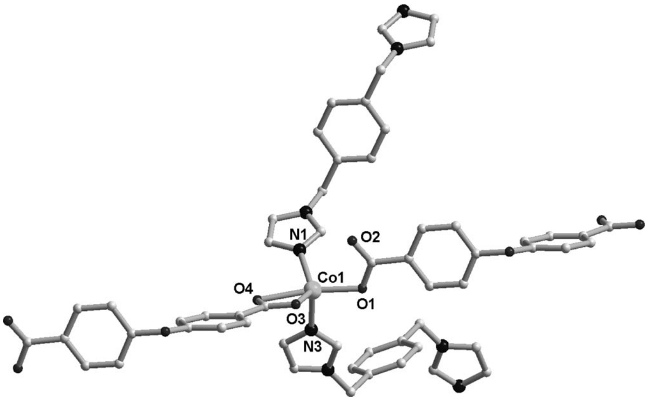

Figure 7. The local coordination environment for the Co atom in **3**. Hydrogen atoms have been omitted for clarity.

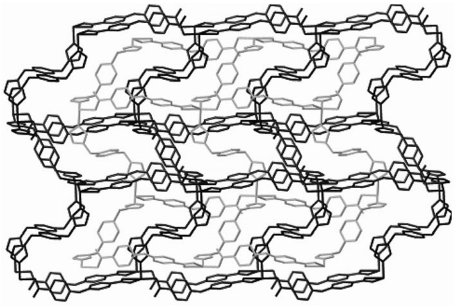

Figure 8. View of the catenation of three adjacent layers for compound **3**.

Comparison of the Structures 1–3: The three coordination compounds **1**–**3** were successfully synthesized by using V-shaped H$_2$oba ligand and long-chain bis(imidazole)-based ligands and structurally characterized. The pure phases of compounds **1**–**3** were confirmed by powder X-ray diffraction measurements (Figure S2). All the structures present polycatenation networks: **1** displays a rare 1D→2D polycatenation, whereas **2** and **3** are examples of 2D→3D parallel polycatenation networks. What are the differences between these structures that are of significance? Compounds **1** (**L1**) and **2** (**L2**) differ in their organic ligands and **1** (Zn) and **3** (Co) differ in their metal atoms. Therefore, the V-shaped oba^{2-} anion and the neutral bis(imidazole) ligands have an effect on the desired structures as well as the metal sources used.

Photoluminescence of 1 and 2: Photoluminescence experiments on the Zn-containing compounds **1** and **2**, with typical d^{10} transition-metal configurations, were performed at room temperature in the solid state.[25] As shown in Figure 9, an intense luminescence peak at around 388 nm was detected in the emission spectrum of **1** when it was excited at 332 nm. However, the luminescence peak of compound **2** is clearly blue-shifted to 316 nm (λ_{ex} = 298 nm) relative to that of compound **1**. The emission bands for free **L1** and **L2** occur at 451 (λ_{ex} = 379 nm) and 335 nm (λ_{ex} = 299 nm), respectively. In addition, the free H$_2$oba ligand shows an emission peak at about 318 nm (λ_{ex} = 303 nm). Accordingly, each of the two emission bands in **1** and **2** can be attributed to ligand-to-metal charge-transfer (LMCT) transitions (Figure 9).

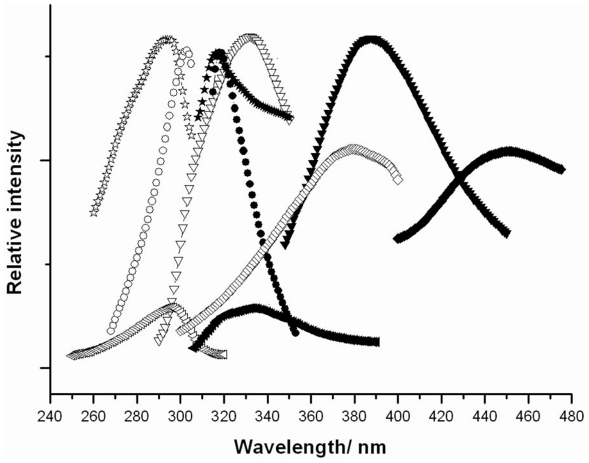

Figure 9. Excitation and emission spectra of **1**, **2** and the three ligands [symbols: the down triangle depict the excitation and emission spectra of **1**; the stars depict the excitation and emission spectra of **2**; the circles depict the excitation and emission spectra of the H_2oba ligand; the diamonds depict the excitation and emission spectra of the **L1** ligand; the left triangles depict the excitation and emission spectra of **L2**, solid symbol (EM) and point symbol (EX)].

TG Analysis of 1–3: Thermogravimetric analyses were performed on to assess the thermal stability of 3D compounds **1**–**3**. Their TG curves are presented in Figure S3. At about 138 °C, compound **1** shows a weight loss corresponding to coordinated water (calcd. 3.92%; found 3.98%). Rapid weight loss was detected from 281 to 620 °C, which has been attributed to the decomposition of the **L1** and $oba^{2–}$ ligands. The remaining residue was presumed to be ZnO (calcd. 17.66%; found 17.61%). At about 43 °C, compound **2** showed a weight loss corresponding to lattice water (calcd. 4.83%; found 4.87%). The host framework was stable up to 370 °C at which temperature it starts to decompose until above 670 °C. In contrast, the decomposition of compound **3** occurs in a lower temperature range (342–646 °C). The remaining residue was presumed to be a 1:1 $CoO/CoCO_3$ mixture (calcd. 17.54%; found 17.62%).

Conclusions

Three new polycatenation compounds based on the $oba^{2–}$ and bis(imidazole) ligands have been synthesized under hydrothermal conditions and structurally characterized. Compound **1** is a rare 1D→2D parallel polycatenation based on a flat ladder whereas **2** and **3** are novel 2D→3D parallel polycatenation networks based on the undulating 4^4-**sql** sheet. This investigation has demonstrated an effective synthetic strategy for the synthesis of polycatenation systems by controlling the rigidity of the N-donor ligands incorporated with flexible V-shaped *exo*-bidentate molecules, which play a crucial role in the formation of 2D (4,4) layers with arc-shaped bridges. Both the organic ligands and metal atoms are crucial for the construction of the desired frameworks. The application of this methodology to other functional materials is ongoing.

Experimental Section

Materials and General Procedures: Solvents and starting materials were purchased commercially and used as received without further purification. Ligand **L2** was synthesized as reported previously.[26] The IR spectra were recorded as KBr pellets with a Nicolet Magna-FT-IR 560 spectrometer in the range 4000–400 cm^{-1}. Elemental analysis was performed with a Perkin–Elmer 240 analyser. The photoluminescence measurements were carried out on crystalline samples at room temperature and the spectra were collected with a Hitachi F-2500FL spectrophotometer. Thermogravimetric analyses (TGA) were performed with a standard TG-DTA analyser under a flow of nitrogen at a heating rate of 5 °C/min for all measurements. Powder diffraction data were collected with a Rigaku D/max-RC diffractometer using a Cu target (λ = 1.54060 Å) operated at 50 kV and 180 mA.

Synthesis of $[Zn(oba)(L1)_{0.5}(H_2O)]_n$ (1): A mixture of $Zn(NO_3)_2\cdot 6H_2O$ (0.15 g, 0.5 mmol), H_2oba (0.13 g, 0.5 mmol) and **L1** (0.12 g, 0.5 mmol) was dissolved in distilled water (8 mL). The pH value was then adjusted to 5.5 with a 1 M NaOH solution and the resulting mixture was transferred and sealed in a 25 mL Teflon®-lined stainless-steel vessel. This was then heated at 160 °C for 3 d. Afterwards the reactor was slowly cooled to room temperature and white rod-shaped crystals were filtered off and dried in air; yield 96.3 mg, 42% (based on Zn). IR (KBr): $\tilde{\nu}$ = 3393 (m), 3127 (m), 1626 (s), 1592 (m), 1343 (s), 1236 (s), 1095 (m), 884 (m), 777 (m) cm^{-1}. $C_{21}H_{17}N_2O_6Zn$ (458.76): calcd. C 54.98, H 3.74, N 6.11; found C 54.95, H 3.70, N 6.13.

Synthesis of $[Zn_2(oba)_2(L2)_2](H_2O)_3$ (2): A mixture of $Zn(NO_3)_2\cdot 6H_2O$ (0.15 g, 0.5 mmol), H_2oba (0.13 g, 0.5 mmol) and **L2** (0.11 g, 0.5 mmol) was dissolved in distilled water (8 mL). The pH value was then adjusted to 6.5 with a 1 M NaOH solution and the resulting mixture was transferred and sealed in a 25 mL Teflon®-lined stainless-steel vessel. This was then heated at 160 °C for 3 d. Afterwards the reactor was slowly cooled to room temperature and light-yellow block-shaped crystals were filtered off and dried in air; yield 142.5 mg, 51% (based on Zn). IR (KBr): $\tilde{\nu}$ = 3437 (s), 3136 (m), 1609 (s), 1532 (m), 1389 (s), 1217 (m), 1164 (m), 1134 (m), 1067 (m), 961 (m), 839 (m), 773 (m), 645 (m) cm^{-1}. $C_{52}H_{42}N_8O_{13}Zn_2$ (1117.68): calcd. C 55.88, H 3.79, N 10.03; found C 55.83, H 3.75, N 9.98.

Synthesis of $[Co(oba)(L1)]_n$ (3): A mixture of $CoCl_2\cdot 6H_2O$ (0.12 g, 0.5 mmol), H_2oba (0.13 g, 0.5 mmol) and **L1** (0.12 g, 0.5 mmol) was dissolved in distilled water (8 mL). The pH value was then adjusted to 6.5 with a 1 M NaOH solution and the resulting mixture was transferred and sealed in a 25 mL Teflon®-lined stainless-steel vessel. This was then heated at 160 °C for 3 d. Afterwards the reactor was slowly cooled to room temperature and purple block-shaped crystals were filtered off and dried in air; yield 149.4 mg, 54% (based on Co). IR (KBr): $\tilde{\nu}$ = 3424 (m), 3111 (m), 1599 (s), 1565 (m), 1384 (m), 1231 (m), 1162 (m), 1110 (m), 879 (m), 832 (m), 715 (m), 659 (m) cm^{-1}. $C_{28}H_{22}CoO_5N_4$ (553.43): calcd. C 60.77, H 4.00, N 10.12; found C 60.72, H 4.03, N 10.11.

X-ray Crystallographic Determinations: Single-crystal analyses were performed with the RAXIS-RAPID AUTO CCD diffractometer systems (Mo-K_α radiation, λ = 0.71073 Å) for **1**, **2** and **3**. All data were corrected for absorption effects by semiempirical methods using the SADABS program.[27] The program SAINT was applied to the integration of the diffraction profiles.[27] Data analyses were carried out with the program XPREP.[28] Structures were solved by direct methods using SHELXS-97 following structure refinement on F^2 with the program SHELXL-97.[28] All non-hydrogen atoms were refined anisotropically. Aromatic hydrogen atoms were assigned to calculated positions with isotropic thermal parameters. Crystal data and experimental details are summarized in Table 1. Selected bonds and angles are listed in Table S1.

Table 1. Crystal data and structure refinements for **1**, **2** and **3**.

Compound	**1**	**2**	**3**
Empirical formula	$C_{21}H_{17}N_2O_6Zn$	$C_{52}H_{42}N_8O_{13}Zn_2$	$C_{28}H_{22}CoN_4O_5$
M_r	458.76	1117.68	553.43
Temperature [K]	293(2)	298(2)	298(2)
Crystal system	monoclinic	triclinic	monoclinic
Space group	$C2/c$	$P\bar{1}$	$P2_1/c$
a [Å]	22.880(5)	8.8207(18)	9.2422(18)
b [Å]	12.496(3)	11.273(2)	14.546(3)
c [Å]	22.617(8)	14.120(3)	18.867(4)
α [°]		112.20(3)	
β [°]	143.126(12)	98.62(3)	102.24(3)
γ [°]		98.91(3)	
V [Å^3]	3880.2(19)	1250.5(4)	2478.8(9)
Z	8	1	4
$d_{calcd.}$ [g cm^{-3}]	1.571	1.484	1.483
μ [mm^{-1}]	1.308	1.033	0.740
θ range [°]	1.88–27.86	3.00–29.80	3.01–27.48
Completeness [%]	99.2	99.8	99.9
Goodness-of-fit on F^2	1.100	1.048	0.943
Final R indices $[I>2\sigma(I)]$[a]	$R_1 = 0.0574$, $wR_2 = 0.1280$	$R_1 = 0.0517$, $wR_2 = 0.1248$	$R_1 = 0.0694$, $wR_2 = 0.1140$

[a] $R_1 = \Sigma(||F_o - F_c||)/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{½}$.

CCDC-784326 (for **1**), -722327 (for **2**) and -722328 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Additional plots of the structures, tables of bond lengths and angles for all the compounds and the experimental PXRD of the three complexes.

Acknowledgments

The authors thank the National Natural Science Foundation of China (50872057) for the financial support of this work.

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Received: August 2, 2010