Three new 3D metal-organic frameworks based on the Tetrakis(imidazol-1-ylmethyl)methane and 1,4-Benzenedicarboxylic acid ligands with transition metal (Zn/Cd/Co) and properties research

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Three novel 3D metal-organic frameworks, $\{[\text{Zn}_2(\text{L})(\text{BDC})_2] \cdot \text{H}_2\text{O}\}_n$ (**1**), $\{[\text{Cd}_2(\text{L})_2(\text{BDC})] \cdot (\text{BDC}) \cdot 7.7(\text{H}_2\text{O})\}_n$ (**2**), and $\{[\text{Co}(\text{L})(\text{H}_2\text{O})_2] \cdot (\text{BDC}) \cdot 5(\text{H}_2\text{O})\}_n$ (**3**) (L = tetrakis(imidazol-1-ylmethyl)methane, H₂BDC = 1,4-benzenedicarboxylic acid), have been successfully synthesized by self-assembly of transition-metal salts with a flexible N-containing ligand and 1,4-dicarboxybenzene ligand. Complexes **1-3** have 3D structures with various topologies. In complex **1**, the L connects Zn(II) atoms to form 2D layers, which are linked by two kinds of 1D $[\text{Zn}(\text{BDC})]_n$ chains to generate a 4-connected three-dimensional structure with $(6 \cdot 8^5)(6^4 \cdot 8^2)(8^6)$ topology. In complex **2**, Cd(II) atoms are coordinated by L to furnish a 2D layer, and the adjacent layers are linked by BDC ligands as bridging ligands to general a new (4,5)-connected three-dimensional network with a point symbol of $(4^4 \cdot 6^2)(4^4 \cdot 6^6)$. In Complex **3**, the L ligands act as 4-connected linkers connecting Co(II) ions to display a 4-connected three-dimensional structure with $4 \cdot 6^5$ topological net directly. In addition, the solid-state fluorescence, infrared spectra, magnetic property and thermal stability of these complexes have also been investigated.

Keywords: MOFs; Crystal structure; Fluorescent property; Magnetic property

1. Introduction

In recent years, metal-organic frameworks (MOFs) have received much attention not only due to structural diversity, but also their great potential application value in many fields, such as, ion exchange [1, 2], catalysis [3-5], gas adsorption and separation [6-8], luminescence [9-11], magnetism [12, 13] etc. To date, though lots of MOFs have been reported and studied within the past decades, the establishment of novel structures remain a big challenge in the long term [14]. Generally, the

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self-assembly of MOFs is dominated by various factors such as organic ligand, metal ions, anions, reaction solvent, temperature, pH value, and so on. Then it is so important to select the organic ligand in the construction of MOFs [15-17]. For the past few years, using flexible ligands to create MOFs is a common tactics, especially the study of tetrakis(imidazol-1-ylmethyl)methane ligand has been a lot. In the previous studies, Ma and co-workers systematically reported several 2D or 3D coordination complexes containing tetrakis(imidazol-1-ylmethyl)methane (L) ligand and other anions with different transition metals(Co/Zn/Cd/Ni) ions [18-21]. The L ligand is a good candidate for the construction of coordination polymers with interesting topologies. And the proper subsidiary bridging linkers are also critical in constructing coordination polymers. 1,4-benzenedicarboxylic acid (H₂BDC), may act as bridging ligands and has been extensively used [22-24].

In this work, we report the synthesis and structures of three metal-organic frameworks with the formulas $\{[\text{Zn}_2(\text{L})(\text{BDC})_2] \cdot \text{H}_2\text{O}\}_n$ (**1**), $\{[\text{Cd}_2(\text{L})_2(\text{BDC})] \cdot (\text{BDC}) \cdot 7.7(\text{H}_2\text{O})\}_n$ (**2**), $\{[\text{Co}(\text{L})(\text{H}_2\text{O})_2] \cdot (\text{BDC}) \cdot 5(\text{H}_2\text{O})\}_n$ (**3**) using tetrakis(imidazol-1-ylmethyl)methane (L, as shown in Scheme 1) ligand as organic linker, 1,4-benzenedicarboxylic acid (H₂BDC, as shown in Scheme 1) as bridging linker, divalent transitional-metal ions Zn(II), Cd(II), Co(II) as connectors respectively. And the three coordination modes between H₂BDC and metal ions are shown in Scheme 2. All Complexes are characterized by elemental analysis, X-ray crystallography, and thermal stability. The luminescent properties of Complexes **1** and **2** have been investigated. The magnetism of complex **3** also has been studied.

Scheme 1. The L ligand and H₂BDC.

Scheme 2. Three coordinated modes of H₂BDC in the text.

2. Experimental section

2.1. General

All the reagents were used as received from commercially purchased without any further purification. The ligand tetrakis(imidazol-1-ylmethyl)methane (L) was synthesized and purified as reported previously [18]. Elemental analysis was carried out with an Elementar vario ELIII analyzer. Infrared spectra were recorded with a Bruker Tensor 27 FT-IR spectrometer using KBr pellets in the

400–4000 cm^{-1} region. PXRD patterns of the samples were collected on a Bruker D8-Advance diffractometer equipped with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at a scan speed of $10^\circ/\text{min}$. Thermogravimetric (TG) analysis datas were collected on a simultaneous SDT thermal analyzer at a heating rate of $10^\circ\text{C}/\text{min}$ under a N_2 atmosphere (N_2 flow rate = $0.06 \text{ L}/\text{min}$). The emission spectrum and luminescent decay of Complexes **1** and **2** were measured on a Hitachi FL-7000 Fluorescence Spectrometer. Magnetic data of complex **3** was collected using a Quantum Design vibrating sample magnetometer in Physical Property Measurement System.

2.2. Syntheses of $\{[\text{Zn}_2(\text{L})(\text{BDC})_2]\cdot\text{H}_2\text{O}\}_n$ (**1**).

A mixture of **L** (0.1 mmol, 0.0336 g), $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.2 mmol, 0.0595 g), H_2BDC (0.2 mmol, 0.0332 g), 5 mL H_2O and a drop of DMF was stirred for 0.5 h, then transferred to a 20 mL Teflon-lined stainless steel container, heated at 120°C for 2 days, and then cooled to room temperature slowly. Colorless crystals of **1** can be obtained. Yield: 28% based on Zn^{II} . Elemental analysis (%) for $\text{C}_{33}\text{H}_{30}\text{Zn}_2\text{N}_8\text{O}_9$ (813.39). Calcd: C, 48.73; H, 3.72; N, 13.78. Found: C, 48.57; H, 3.79; N, 13.68. IR (KBr, cm^{-1}): 3459(s), 3118(s), 1599(s), 1338(s), 1103(s), 1024(w), 948(m), 881(m), 826(m), 740(s), 658(m), 630(w), 569(w), 514(w).

2.3. Syntheses of $\{[\text{Cd}_2(\text{L})_2(\text{BDC})]\cdot(\text{BDC})\cdot 7.7(\text{H}_2\text{O})\}_n$ (**2**).

A mixture of **L** (0.2 mmol, 0.0673 mg), $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ (0.4 mmol, 0.1234 g), H_2BDC (0.4 mmol, 0.0664 g), 8 mL H_2O , 3 mL DMF and 10 % sodium hydroxide solution (0.1 mL) was stirred for 0.5 h, then transferred to a 20 mL Teflon-lined stainless steel container, heated at 130°C for 3 days, and then cooled to room temperature slowly. Colorless crystals of **2** can be obtained. Yield: 47% based on Cd^{II} . Elemental analysis (%) for $\text{C}_{50}\text{H}_{63.4}\text{Cd}_2\text{N}_{16}\text{O}_{15.7}$ (1364.59). Calcd: C, 44.01; H, 4.68; N, 16.42. Found: C, 44.71; H, 4.98; N, 16.09. IR (KBr, cm^{-1}): 3423(s), 3127(w), 2922(w), 1558(s), 1382(s), 1242(m), 1093(s), 1024(m), 932(m), 830(m), 751(m), 657(m), 624(w), 515(w).

2.4. Syntheses of $\{[\text{Co}(\text{L})(\text{H}_2\text{O})_2]\cdot(\text{BDC})\cdot 5(\text{H}_2\text{O})\}_n$ (**3**).

The similar synthetic method for **1** was used except that $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ was replaced by $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.4 mmol, 0.1164 g). Colorless crystals of **3** can be obtained. Yield: 46% based on Co^{II} . Elemental analysis (%) for $\text{C}_{25}\text{H}_{38}\text{CoN}_8\text{O}_{11}$ (685.56). Calcd: C, 43.80; H, 5.59; N, 16.35; Found:

C, 43.52; H, 5.51; N, 16.37. IR (KBr, cm^{-1}): 3385(s), 3133(w), 1565(s), 1455(m), 1384(s), 1292(m), 1241(s), 1089(s), 1026(m), 938(m), 824(m), 752(s), 663(s), 623(w), 508(w).

2.5. Crystallographic data collection and refinement

Single-crystal X-ray diffraction measurements for Complexes 1-3 were carried out on a Bruker Smart APEX II CCD at 298 K with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Empirical absorption corrections were carried out using the SADABS program. The structures were solved by direct methods and refined on F² by the full-matrix least-squares technique by using the SHELXL-97 program [25, 26]. The hydrogen atoms on the water molecule were generated geometrically. The details on crystallographic data collection refinement parameters are shown in Table 1.

Table 1

Crystal data and structure refinement details for Complexes **1-3**.

3. Results and discussion

3.1. Crystal structure of complex **1**

Complex **1** crystallizes in the $Pca2_1$ space group and in a triclinic system. As shown in Fig. 1a, there are two unique Zn(II) atoms (Zn1 and Zn2), one L ligand, two BDC ligands, and one lattice water molecule in the asymmetric unit of **1**. Both Zn1 and Zn2 have the same coordinated environment, while each Zn(II) atom is four-coordinated by two N atoms from two individual L ligands [Zn1–N4 = 2.013(6) $\text{\AA}$ and Zn1–N7 = 2.058(7) $\text{\AA}$; Zn2–N2 = 2.016(5) $\text{\AA}$ and Zn2–N5 = 2.027(6) $\text{\AA}$], two O atoms from two BDC ligands [Zn1–O1 = 1.961(5) $\text{\AA}$ and Zn1–O3^{#1} = 1.970(5) $\text{\AA}$; Zn2–O5 = 1.959(6) $\text{\AA}$ and Zn2–O7^{#2} = 1.953(6) $\text{\AA}$] to form two distorted tetrahedron coordination geometry respectively.

Along a axis and c axis, every BDC ligand connects two adjacent Zn atoms to form a 1D flat $[\text{Zn}(\text{BDC})]_n$ chains with the neighbouring Zn distances being 10.952 $\text{\AA}$ and 10.910 $\text{\AA}$, respectively (Fig. 1b). There are $\pi \cdots \pi$ interactions between the phenyls of BDC anions with centroid distance of 3.8960 $\text{\AA}$ and 3.9120 $\text{\AA}$ in Fig. S1. In this Complex, the BDC ligands adopt mode 1 connecting Zn1 atoms and mode 2 bridging Zn2 atoms severally to form 1D chains. And each L ligand coordinated

four Zn atoms through its four imidazole groups to form a 2D layer structure (Fig. 1c). Adjacent layers are linked by the 1D chains to form one 3D framework structure (Fig. 1d). From a topological view point, the Zn atoms and the L ligands can be all considered as a four-connected node, so the 3D structure of Complex **1** is simplified to a 4-connected net with the point symbol $(6 \cdot 8^5)(6^4 \cdot 8^2)(8^6)$ (Fig. 1e).

Fig. 1. (a) Coordination environment of the Zn(II) ion in **1** with hydrogen atoms and other solvent molecules omitted for clarity (symmetry codes: #1 $-0.5+x, 3-y, z$; #2 $-x, -y, -0.5+z$; #3 $0.5+x, 3-y, z$; #4 $-x, -y, 0.5+z$). (b) The 1D chains constructed from BDC ligands and Zn (Zn1 and Zn2) ions along *a* axis and *c* axis respectively. (c) The 2D layer constructed from L ligands and Zn(II) ions. (d) The 3D structure of complex **1**. (e) Schematic representation of the 4-connected net of complex **1** with the point symbol $(6 \cdot 8^5)(6^4 \cdot 8^2)(8^6)$.

3.2. Crystal structure of complex **2**

The result of XRD showed that the Complex **2** is in the $P2_1/c$ space group, a triclinic system. As shown in part of Fig. 2a, the asymmetric unit of **2** contains one crystallographic independent Cd(II) ion, one L ligand, one half of BDC ligand, one dissociative half of BDC molecule and five lattice water molecules. The Cd(II) center is six-coordinate, and is bound to four nitrogen atoms from different L ligands [$\text{Cd1-N1} = 2.327(3) \text{ \AA}$, $\text{Cd1-N6}^{\#1} = 2.276(3) \text{ \AA}$, $\text{Cd1-N7}^{\#2} = 2.324(3) \text{ \AA}$ and $\text{Cd1-N8}^{\#3} = 2.332(3) \text{ \AA}$] and two oxygen atoms from one BDC ligand [$\text{Cd1-O1} = 2.437(3) \text{ \AA}$ and $\text{Cd1-O2} = 2.387(3) \text{ \AA}$] in a distorted octahedral arrangement.

The L ligand lines the Cd centers tetradentate mode to form a 2D layer (Fig. 2b), which is further linked by the BDC ligands to form a 3D framework (Fig. 2c). In this complex, the carboxylic groups of BDC ligands adopt mode 3 chelating adjacent Cd atoms. If each Cd(II) center is considered as a 5-connected node, the L ligand is reduced to 4-connected node, the 3D structure of **2** can be described as 2-nodal net with the point symbol $(4^4 \cdot 6^2)(4^4 \cdot 6^6)$ (Fig. 2d).

Fig. 2. (a) Coordination environment of the Cd(II) ion in **2** with hydrogen atoms and other solvent molecules omitted for clarity (symmetry codes: #1 $1-x, 1-y, 1-z$; #2 $-x, 2-y, 1-z$; #3 $x, y, 1+z$). (b) The 2D layer constructed from L ligands and Cd(II) ions. (c) The 3D framework of complex **2**. (d)

Schematic representation of the 2-nodal net of **2** with the point symbol $(4^4 \cdot 6^2)(4^4 \cdot 6^6)$.

3.3. Crystal structure of complex **3**

The XRD study showed that Complex **3** is in the $P2_1/c$ space group, a triclinic system. As shown in Fig. 3a, the asymmetric unit of **3** contains one crystallographic independent Co(II) ion, one L ligand, two coordinated water molecules, two dissociative half of BDC ligands and five lattice water molecules. Every Co(II) is coordinated by four imidazole N atoms from different four L ligands [Co1–N1 = 2.122(3) Å, Co1–N4^{#1} = 2.134(3) Å, Co1–N8^{#2} = 2.152(3) Å and Co1–N6^{#3} = 2.159(3) Å], and two O atoms from two coordinated water molecules [Co1–O1 = 2.177(3) Å and Co1–O2 = 2.121(3) Å], which generates a distorted octahedral CoO₂N₄ coordination sphere.

Each L ligand is a tetradentate ligand and connects four Co atoms through its four imidazole groups to form a 3D framework structure as shown in Fig. 3b, and there are two kinds of 1D channels (Fig. S2). Topologically, the Co(II) ions and L ligands can be reduced to same 4-connected nodes, so the 3D structure of **3** can be described as a 4-connected net with the point symbol $4 \cdot 6^5$ (Fig. 3c), and it is the same with that reported for complex [Zn(L)](NO₃)₂·3H₂O of L [20], but the metals ions are different. In addition, the carboxylate groups of BDC ligand and lattice water molecules form hydrogen bonds (Table S4). In these hydrogen bonds, the water molecules donate hydrogen atoms to carboxylate oxygen atoms of BDC ligands (Fig. S3).

Fig. 3. (a) Coordination environment of the Co(II) ion in **3** with hydrogen atoms and other solvent molecules omitted for clarity (symmetry codes: #1 -1+x, y, z; #2 1-x, 0.5+y, 0.5-y; #3 x, 0.5-y, 0.5+z). (b) The 3D structure of compound **3** viewed along *c* axis. (c) The 4-connected net of **3** with the point symbol $(4 \cdot 6^5)$.

3.4. Thermal and PXRD analyses

In order to study the thermal stability of 1-3, thermal analyses were performed using TGA techniques from 50 to 700 °C (Fig. S4). For complex 1, the weight loss corresponding to the free water molecules before 140 °C (expt. 1.79%, calcd. 2.21%). The framework structure began to decompose at 370 °C corresponding to the ligand L and BDC. For 2, the first weight losses

corresponding to the release of water molecules are observed before 146 °C (expt. 3.52%, calcd. 10.16%). The framework structure began to decompose from 207 °C corresponding to the ligand L and BDC. Based on the mass losses curve, two-step decomposition is proposed for **3** with the first stage of decomposition at 55 °C and finished at 137 °C. The mass loss in this region accounts for the elimination of lattice water (expt. 8.97%, calcd. 13.1%). The second mass loss was observed after 190°C, which may be attributed to the departure of organic components. To identify the phase purity of these complexes, power X-ray diffraction (PXRD) patterns were measured at 298 K. As shown in Fig. S5, the peak positions of the simulated and experimental PXRD patterns are in good agreement with each other, indicating the good purity of these complexes.

3.5. Photoluminescence of complexes **1** and **2**

The metal complexes containing Zn(II) and Cd(II), as the result of the existence of d^{10} electronics, have exhibited some potential applications in chemical sensors, photochemistry and electroluminescent [27-29]. The solid-state photoluminescence properties of L ligand, H₂BDC, complexes **1** and **2** have been investigated at room temperature. The peak of main emission of L is at 435 nm (λ_{ex} = 365 nm), probably due to the $\pi^* \rightarrow \pi$ transitions [30, 31]. The emission peak of H₂BDC is at 380 nm (λ_{ex} = 330 nm), which can be presumed that the peak originate from the $\pi^* \rightarrow n$ transition (Fig. S6). The emission peaks of complexes **1** and **2** are at 407 nm (λ_{ex} = 350 nm), 425 nm (λ_{ex} = 340 nm) respectively (Fig. 4.). Comparing to the H₂BDC ligand and the free L ligand, the emission peak of complex **1** is red-shift about 27 nm and blue-shift about 28 nm respectively. The emission peak of complex **2** is blue-shift about 10 nm compared to the free L ligand. It is possible that the coordinated mode effects of the H₂BDC ligand to the metal center. Since the Zn(II) and Cd(II) ions with d^{10} configurations are difficult to oxidize or to reduce, the emissions of complexes **1** and **2** are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) [32, 33]. The solid state luminescence of complexes **1** and **2** can be deemed to intraligand charge transfer. In summary, the fluorescent emission peak of complex **1** may come from the L ligand and the H₂BDC, while the emission peak of complex **2** may come from the L ligand mainly. It is important for the fluorescence emission-shift of complexes **1** and **2** that the coordination modes of H₂BDC. As the various coordination environments, the difference of emission peaks is observed [34].

Fig. 4. Photoluminescence emission spectra for Complexes **1**, **2** at room temperature.

3.6. Magnetic Property of complex **3**

The temperature dependence of the magnetic susceptibility of complex **3** has been measured under 1000 Oe in the temperature range of 2-300 K. The χ_M and $\chi_M T$ versus T plots of **3** are shown in Fig. 5a. The $\chi_M T$ value at room temperature is $4.00 \text{ cm}^3 \text{ K mol}^{-1}$, much larger than the expected value for one isolated spin-only Co(II) ions with $S = 3/2$ ($1.88 \text{ cm}^3 \text{ K mol}^{-1}$, $g = 2.0$), which can be attributed to the orbital contribution to the magnetic moment of Co(II). Upon lowering temperature, $\chi_M T$ value decreases until a minimum value ($2.32 \text{ cm}^3 \text{ K mol}^{-1}$) at 16 K, which can be indicative of dominant antiferromagnetic interaction. The $\chi_M T$ value abruptly increases to a maximum ($2.46 \text{ cm}^3 \text{ K mol}^{-1}$), upon lowering of the temperature to 4 K. Then it drops rapidly to the minimum value $1.88 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. The final rapid drop in $\chi_M T$ below 12 K may arise from the magnetic field saturation effect. And the susceptibility data of χ_M^{-1} versus T is above 58 K fitted by Curie-Weiss law [$\chi_M = C/(T - \theta)$], giving the Curie constant values $C = 4.51 \text{ cm}^3 \text{ K mol}^{-1}$ and the Weiss constant values $\theta = -39.26 \text{ K}$ (Fig. 5b). Actually, the mutual competition between ferromagnetic and antiferromagnetic coupling results in a minimum in the $\chi_M T$ versus T curve. In conclusion, the molecular magnetic behavior of complex **3** can be attributed to spin canting magnetic behavior[35].

Fig. 5. (a) χ_M and $\chi_M T$ vs T curves for complex **3**. (b) χ_M^{-1} vs T plot. The solid line represents the best-fit curve

4. Conclusions

Three new complexes based on L ligands and H_2BDC with Zn/Cd/Co metal salts have been synthesized and characterized. All the complexes show three-dimensional framework structure and different topologies, the point symbol $(6 \cdot 8^5)(6^4 \cdot 8^2)(8^6)$ for **1**, the point symbol $(4^4 \cdot 6^2)(4^4 \cdot 6^6)$ for **2**, the point symbol $4 \cdot 6^5$ for **3**, respectively. Their structural difference mainly is due to discrepancy of the metals and effect of BDC ligand. The luminescent emissions of complexes **1** and **2** show that they may be good candidates for luminescent materials. The magnetic data of complex **3** indicates that there is antiferromagnetic exchange between Co(II) ions.

Supplementary material

Selected bond lengths and angles for the complexes **1-3** are listed in Tables S1-S3 (see Supporting Information). PXRD graphics are available as supplementary material. CCDC 1470940, 1470942 and 1470941 contain the supplementary crystallographic data for **1**, **2**, and **3** in this paper.

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Scheme 1. The L ligand and H₂BDC.

Scheme 2. Three coordinated modes of H₂BDC in the text.

Table 1Crystal data and structure refinement details for Complexes **1-3**.

Compound	1	2	3
Empirical formula	C ₃₃ H ₃₀ Zn ₂ N ₈ O ₉	C ₅₀ H _{63.4} Cd ₂ N ₁₆ O _{15.7}	C ₂₅ H ₃₈ CoN ₈ O ₁₁
F_w	813.39	1364.59	685.56
Crystal system	orthorhombic	triclinic	monoclinic
Space Group	$Pca2_1$	$P\bar{1}$	$P2_1/c$
$a / \text{\AA}$	21.098(3)	11.1345(8)	10.7228(9)
$b / \text{\AA}$	7.7762(10)	11.1659(8)	16.7740(14)
$c / \text{\AA}$	19.979(3)	12.6916(9)	19.6191(13)
$\alpha (^\circ)$	90	88.0670(10)	90
$\beta (^\circ)$	90	88.9070(10)	120.924(3)
$\gamma (^\circ)$	90	65.2260(10)	90
$V / \text{\AA}^3$	3277.8(7)	1431.85(18)	3027.2(4)
Z	4	2	4
$D_x / \text{g cm}^{-3}$	1.648	1.624	1.515
μ / mm^{-1}	1.534	0.827	0.639
Reflections collected	21443	11331	20425
Unique reflections	7193	5089	7087
$F(000)$	1664	718	1456
R_{int}	0.0830	0.0235	0.0396
GOF on F^2	1.007	1.015	1.011
$R_1^{[a]}, wR_2^{[b]} [I > 2\sigma(I)]$	0.0630, 0.1445	0.0373, 0.1041	0.0643, 0.1683
$R_1^{[a]}, wR_2^{[b]} [\text{all data}]$	0.1030, 0.1727	0.0430, 0.1162	0.0920, 0.1899
Residuals/ $e \text{\AA}^{-3}$	0.853, -0.477	1.159, -0.755	1.079, -0.966

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

Figure(s)

(a)

(b)

(c)

(d)