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Substitution, Addition, and Recombination Reactions of Precursor Complexes with Ferrocenyl Carboxylate Units

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With the use of sodium β-ferrocenylacrylate and sodium *p*-ferrocenylbenzoate as functional ligands, we synthesized mononuclear precursor complexes containing facile leaving groups or coordinatively unsaturated metal ions: $[Cd(\eta^2\text{-}OOCCH{=}CHFc)_2(C_2H_5OH)_2]$ (**1**), $\{[Cd(\eta^2\text{-}OOCC_6H_4Fc)_2(dmf)_2(H_2O)]\}$ (**2**), $\{[Cd(\eta^2\text{-}OOCC_6H_4Fc)_2(phen)(H_2O)](CH_3OH)\}$ (**3**), and $\{[Zn(OOCC_6H_4Fc)_2(phen)](H_2O)\}$ (**4**) (phen = 1,10-phenanthroline). Investigation of the four precursor ferrocenyl carboxylate complexes as building blocks resulted in ten complexes. The complexes $\{[Cd(\eta^2\text{-}OOCCH{=}CHFc)_2(bbbm)](H_2O)\}_n$ (**1a**), $\{[Cd_2(\eta^2\text{-}OOCCH{=}CHFc)_4(pbbm)_2](CH_3OH)_6(H_2O)_4\}$ (**1b**), $\{[Cd(\eta^2\text{-}OOCC_6H_4Fc)_2(py)_3](CH_3OH)_4\}$ (**2a**), $\{[Cd_2(\eta^2\text{-}OOCC_6H_4Fc)_4(btx)_2](thf)_3(CH_3OH)_2\}$ (**2b**), $\{[Cd_2(\eta^2\text{-}OOCC_6H_4Fc)_2(OOCC_6H_4Fc)_2(phen)_2(bbbm)](CH_3OH)_4(thf)_2\}$ (**3a**), and $[Zn(OOCC_6H_4Fc)_2(phen)(H_2O)]$ (**4a**) were obtained by the substitution or addition reactions of the precursor complexes under moderate conditions. As anticipated, the structural integrity of the precursor complexes can be maintained from the precursors to these complexes. We designed the structures of the complexes by controlling the number of leaving groups in the precursor complexes. In addition, a recombination may have taken place in the reactions of the precursor complexes with organic ligands under severe conditions. The "recombinant" complexes $\{[Cd_2(\eta^2\text{-}OOCCH{=}CHFc)_2(\mu_2\text{-}\eta^2\text{-}OOCCH{=}CHFc)_2(L)_2](CH_3OH)_4\}_n$ [L = 1,4-bis(imidazol-1-ylmethyl)benzene (bix), **1c**; L = btx, **1d**], $\{[Cd(\eta^2\text{-}OOCC_6H_4Fc)_2(pbbm)(H_2O)](H_2O)\}_n$ (**3b**) and $\{[Zn(OOCC_6H_4Fc)_2(bbbm)](CH_3OH)_3\}_n$ (**4b**) were also obtained under reflux conditions.
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Introduction

The rational design and synthesis of novel metal–organic frameworks (MOFs) have been of great research interest, not only because of their versatile intriguing architectures and topologies, but also because of their potential applications in smart optoelectronic, magnetic, microporous, and biomimetic materials.[1–13] Considerable progress has been made on the theoretical forecast and practical approaches aimed at controlling the topology structure and geometry of the network. Some structures of MOFs can, to a certain extent, be predicted by exploiting organic ligands as building blocks and elaborately by choosing metal salts to control the coordination geometry.[14–19] However, in many cases it is quite difficult to synthesize a desired MOF in a truly deliberate manner[20–22] owing to the influence of many factors, such as the coordination geometry of the central metal ion and the structural characteristics of the ligand,[23–24] solvent, and temperature.[25–27]

An approach that utilizes precursor complexes as building blocks was presented in recent years.[28–43] Precursor complexes possess specific rigid geometries and potentially extend to a multi-dimensional framework, so this kind of building block is helpful to direct the construction of a given structure.[44–51] Rather than relying on the self-assembly of fundamental building units, an alternative synthetic strategy for the construction of MOFs is to assemble precursor complexes as building blocks into predetermined structures by decoration and expansion of the basic net topologies.[52] We believe that these complexes possess the same framework of precursor complexes. Accordingly, the complexes should be easily constructed with the goal of obtaining predictable structure types from precursor complexes without framework distortion. In addition, sometimes framework distortion will occur from precursor complexes to produced complexes when the reaction conditions are relatively severe.

Nevertheless, the study of the synthesis of complexes by using precursor complexes as building units is still a challenge to chemists. With this background and as an extension of studies on the crystal engineering of coordination polymers, our group recently started a program that aims to explore the production of complexes by using the reactions of precursor complexes containing facile leaving groups or coordinatively unsaturated metal ions. Obviously, if the facile leaving groups could be replaced by appropriate ligands, complexes with the destination topology structures should be obtained by controlling the number of leaving groups in the precursor complexes under moderate reaction conditions. At the same time, complexes could also be syn-

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thesized by the addition reaction of coordinatively unsaturated metal ions in the precursor complexes. If there were only one facile leaving group in the precursor complex, a dimer could be obtained by replacing the leaving group with a bidentate bridging ligand. If there were two leaving groups that could easily be removed in the precursor complex, the conformation of a one-dimensional polymer or a dimer could be gained by a substitution reaction with bidentate-bridging ligands. By substituting these leaving groups with monodentate ligands, we could design complexes whose structures were similar to those of the precursor complexes.[53,54] However, under severe reaction conditions, the strengths of coordination bonds become weak, and then "recombinant" complexes may be obtained. This results in the occurrence of framework distortion from precursor complexes to produced complexes. In the present work, we synthesized four mononuclear precursor complexes, from which six complexes without framework distortion were gained under moderate reaction conditions, and four complexes with framework distortion were obtained under severe conditions. Therefore, our findings demonstrate that the number of facile leaving groups in precursor complexes can control the topology structures of the desired complexes under moderate reaction conditions. Additionally, under severe conditions, the reactions of precursor complexes with ligands can lead to the formation of "recombinant" complexes.

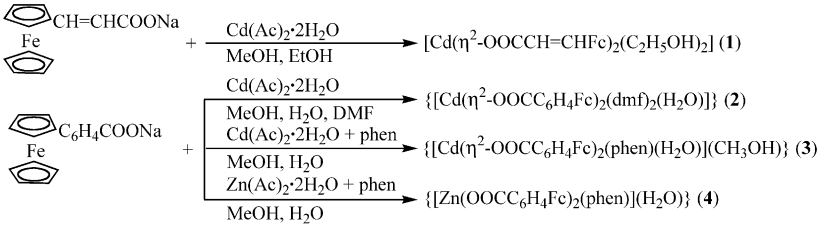
Results and Discussion

The Syntheses of Precursor Complexes $[Cd(\eta^2\text{-}OOCCH{=}CHFc)_2(C_2H_5OH)_2]$ (1), $\{[Cd(\eta^2\text{-}OOCC_6H_4Fc)_2(dmf)_2(H_2O)]\}$ (2), $\{[Cd(\eta^2\text{-}OOCC_6H_4Fc)_2(phen)(H_2O)](CH_3OH)\}$ (3), and $\{[Zn(OOCC_6H_4Fc)_2(phen)](H_2O)\}$ (4)

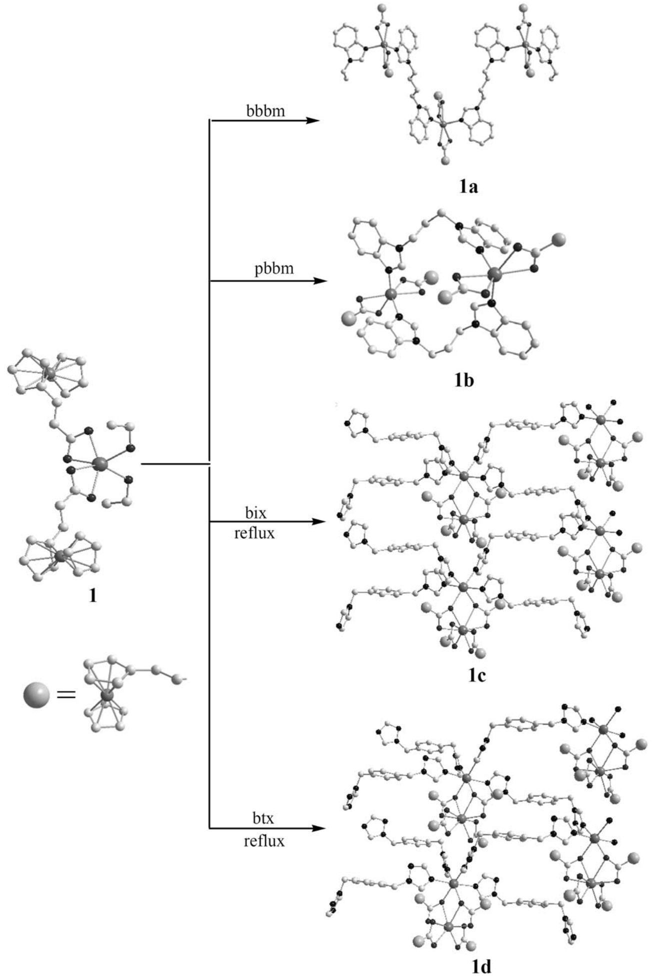
As is well known, the coordinating capability of ferrocenyl carboxylate groups to metal ions is strong, and the coordination modes are also versatile, such as terminal monodentate, bidentate, and O,O′-bridging coordination modes. It makes the self-assembly of crystal engineering easily available.[55–59] Therefore, we selected sodium β-ferrocenylacrylate and sodium *p*-ferrocenylbenzoate as functional ligands to synthesize the precursor complexes. It is reported that the reaction of the two ferrocenyl carboxylate compounds with some metal salts usually produced coordination polymers.[60] As far as coordination polymers are concerned, they do not dissolve easily in common solvents, and sometimes they contain relatively few facile leaving groups or coordinatively unsaturated metal ions. Hence, coordination polymers are not the best precursor complexes. Mononuclear complexes are dissolved easily, and these complexes may contain facile leaving groups or coordinatively unsaturated metal ions, which allows complexes to be designed by substitution or addition reactions. Moreover, we believe that some coordinated solvent molecules can serve as facile leaving groups in complexes. Some N-donor chelating ligands and solvent molecules were added to the reactions of ferrocenyl carboxylate compounds with metal salts to obtain our desired precursor complexes. Accordingly, mononuclear precursor complexes **1**–**4** were obtained by treatment of FcCH=CHCOONa or FcC_6H_4COONa with the appropriate metal salts and subsidiary ligands in different solvents (Scheme 1). By using these precursor complexes as building blocks, the corresponding complexes were designed and synthesized.

The Syntheses and Crystal Structures of $\{[Cd(\eta^2\text{-}OOCCH{=}CHFc)_2(bbbm)](H_2O)\}_n$ (1a), $\{[Cd_2(\eta^2\text{-}OOCCH{=}CHFc)_4(pbbm)_2](CH_3OH)_6(H_2O)_4\}$ (1b), $\{[Cd_2(\mu_2\text{-}\eta^2\text{-}OOCCH{=}CHFc)_2(\eta^2\text{-}OOCCH{=}CHFc)_2(bix)_2](CH_3OH)_4\}_n$ (1c), and $\{[Cd_2(\mu_2\text{-}\eta^2\text{-}OOCCH{=}CHFc)_2(\eta^2\text{-}OOCCH{=}CHFc)_2(btx)_2]\ (CH_3OH)_4\}_n$ (1d)

X-ray diffraction analysis reveals that, in precursor complex **1**, the Cd^{II} ion is six-coordinate with two oxygen atoms from two ethanol molecules and four oxygen atoms from two $FcCH{=}CHCOO^-$ units. The two ethanol molecules are facile leaving groups. So a one-dimensional polymer or a dimer can be designed by a substitution reaction of **1** with a bidentate bridging ligand under moderate reaction conditions. As anticipated, one-dimensional polymer **1a** was obtained through the reaction of **1** with bbbm [1,1-(1,4-butanediyl)bis-1*H*-benzimidazole] at room temperature. Under the same conditions, dimer **1b** was also obtained by using pbbm [1,1-(1,3-propylene)bis-1*H*-benzimidazole] instead of bbbm (Scheme 2). However, it is reported that two-dimensional ferrocenecarboxylate-containing polymer $\{[Cd(\eta^2\text{-}OOCCH{=}CHFc)(bbbm)_{1.5}Cl]\cdot 1.5H_2O\}_n$ was obtained from the one-pot reaction of FcCH=CHCOONa, $CdCl_2\cdot 2.5H_2O$, and bidentate bridging ligand bbbm.[61]



Scheme 1. The syntheses of precursor complexes **1**–**4**.



Scheme 2. The synthesis and conversion of precursor complex **1** into complexes **1a**, **1b**, **1c**, and **1d**.

Although the structures of bridging ligands bbbm and pbbm are similar, the structures of **1a** and **1b** have a distinct difference. Two benzimidazole units are connected by –CH_2–CH_2–CH_2–CH_2– and –CH_2–CH_2–CH_2– in ligands bbbm and pbbm, respectively. The torsion angle of C43–C44–C44A–C43A is 180.0° in **1a**, and the angle of C34–C35–C36 is 112.1° in **1b**. So, by using bbbm as a bridging ligand, one-dimensional polymers are easily formed, but dimers are easily obtained by using pbbm as a replacement to bbbm.

Polymer **1a** exhibits one-dimensional zigzag chains (as shown in Figure 1a), each Cd^{II} ion is six-coordinate in a distorted octahedral environment with four oxygen atoms from two terminal chelating η^2-OOCCH=CHFc$^-$ units and two nitrogen donors from two bridging bbbm ligands. The bbbm ligands connect the Cd^{II} ions by replacing the ethanol molecules, which leads to an infinite one-dimensional chain. In **1b**, two Cd^{II} ions are bridged by two bridging pbbm ligands to form a dimer (Figure 1b). Each Cd^{II} ion is also six-coordinate, and the coordination environment around the Cd^{II} ion is similar to that of **1a**. In addition, the Cd···Cd distance in **1b** (9.603 Å) is distinctly shorter than that of **1a** (14.463 Å).

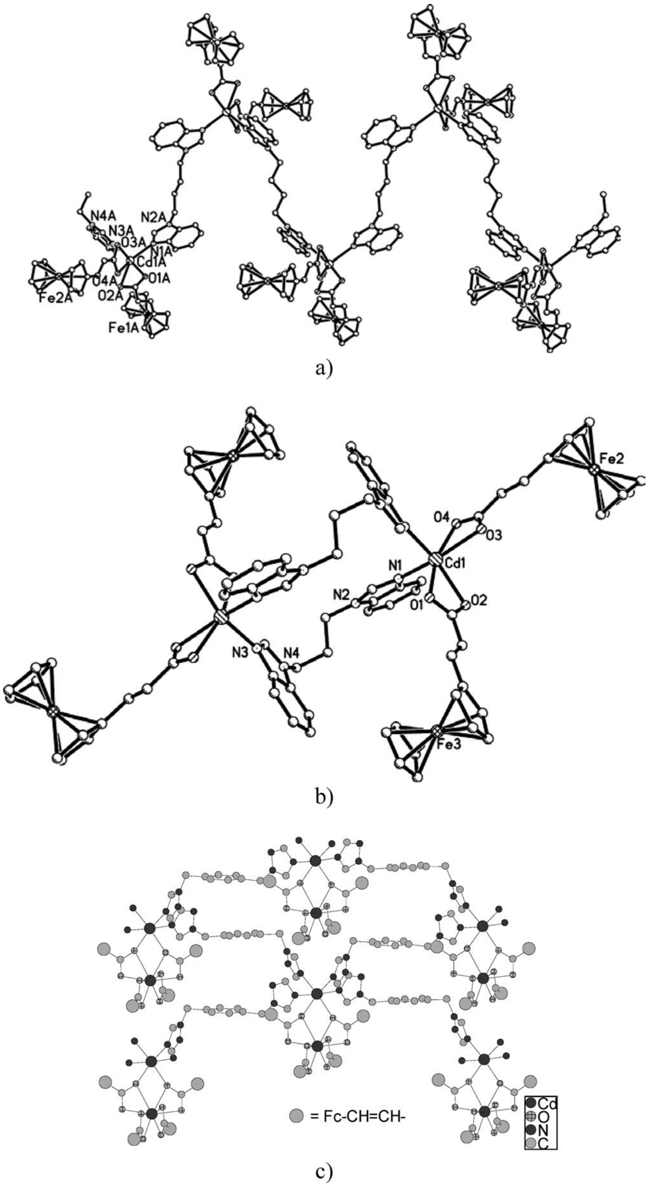


Figure 1. (a) The structure of {[$Cd_2(\eta^2$-OOCCH=CHFc$)_4$(pbbm$)_2$]($CH_3OH)_6(H_2O)_4$} (**1a**) with heteroatom numbering; (b) the structure of {[$Cd_2(\eta^2$-OOCCH=CHFc$)_4$(pbbm$)_2$]($CH_3OH)_6(H_2O)_4$} (**1b**) with heteroatom numbering; (c) two-dimensional network structure of {[$Cd_2(\mu_2$-η^2-OOCCH=CHFc$)_2(\eta^2$-OOCCH=CHFc$)_2$(btx$)_2$]($CH_3OH)_4$}$_n$ (**1d**) (hydrogen atoms and solvent molecules are omitted for clarity).

Coordination bonds in our precursor complexes are relatively stable except for those formed by the solvent molecules with metal ions under moderate reaction conditions. So the structural integrity of the precursor complexes can be maintained when the precursor complexes react with the ligands, and complexes with destination structures could be designed by using the framework of the precursor complexes, such as the formation of **1a** and **1b**. Nevertheless, the strengths of the coordination bonds become weak under severe reaction conditions (such as reflux). Some coordination bonds were easily broken. Hence, framework distortion will occur from precursor complexes to produced complexes. As a result, "recombinant" complexes may take place under the influence of the ligands.

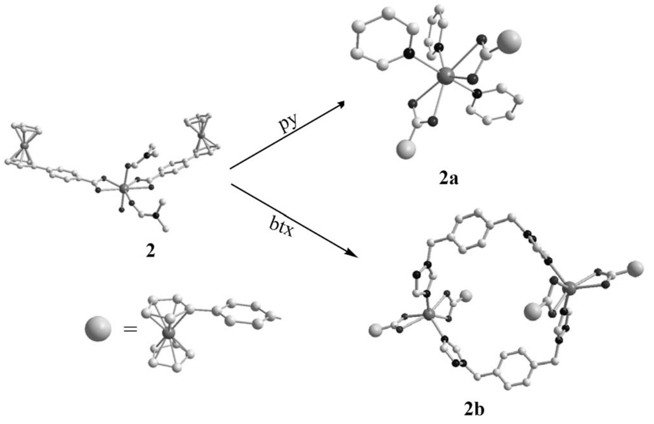
What will happen when precursor complex **1** is treated with bidentate bridging ligands under severe conditions? Herein, two-dimensional network polymers **1c** and **1d** were produced by the reaction of **1** with the organic bix [1,4-bis(imidazol-1-ylmethyl)benzene] or btx [1,4-bis(triazol-1-ylmethyl)benzene] ligands under reflux conditions (Scheme 2). Complexes **1c** and **1d** are produced from framework distortion of precursor complex **1**. From the structures of **1c** and **1d**, it is concluded that the phenomenon of recombination took place in the reaction of **1** with bridging ligands under severe reaction conditions.

Single-crystal X-ray analysis revealed that **1c** and **1d** are isostructural (Figure 1c), and the structures of **1c** and **1d** are distinctly different from those of **1a** and **1b**. It is interesting that the FcCH=CHCOO⁻ units in **1c** or **1d** display two kinds of coordination modes: one coordinates with one Cd^{II} ion as a chelating bidentate ligand, whereas the other bridges two adjacent Cd^{II} ions as a bridging bidentate ligand. Cd^{II} ions have two kinds of coordination environments in **1c** or **1d**. The coordination sphere of Cd1 is eight-coordinate and binds to four oxygen atoms from two η^2-OOCCH=CHFc units and four oxygen atoms from two μ_2-η^2-OOCCH=CHFc units. However, Cd2 is six-coordinate and binds two oxygen atoms from different μ_2-η^2-OOCCH=CHFc units and four nitrogen atoms from four btx or bix molecules. The neighboring two Cd^{II} ions are connected by μ_2-η^2-OOCCH=CHFc groups to form a binuclear unit, and all of the binuclear units are joined together by the bix or btx ligands, which leads to an infinite two-dimensional network. The Cd···Cd distances in the binuclear units of **1c** and **1d** are 3.964 and 3.983 Å, respectively, which are longer than those in reported dimeric cadmium–tetracarboxylate complexes (3.278–3.452 Å).[62–64] The Cd–N distances [from 2.290(2) to 2.352(4) Å] associated with the bridging btx and bix ligands are comparable to those found in the literature.[65–68]

The Syntheses and Crystal Structures of {[Cd(η^2-$OOCC_6H_4Fc)_2(py)_3](CH_3OH)_4$} (2a) and {[$Cd_2$($\eta^2$-$OOCC_6H_4Fc)_4(btx)_2](thf)_3(CH_3OH)_2$} (2b)

Treatment of FcC_6H_4COONa with $Cd(OAc)_2{\cdot}2H_2O$ in DMF/H_2O yielded precursor complex **2**. The Cd^{II} ion is seven-coordinate with four oxygen atoms from two chelating $FcC_6H_4COO^-$ units, one oxygen atom from one H_2O molecule, and two oxygen atoms from two DMF molecules. The H_2O and DMF molecules are three leaving groups that can easily be displaced. Interestingly, the structure of complex **2** resembles a butterfly and the two coordinated $FcC_6H_4COO^-$ units are the wings. Accordingly, we thought that the syntheses of mononuclear complexes should be completed by substitution reactions of **2** with monodentate ligands. In fact, mononuclear complex **2a** with the framework of **2** was obtained through the addition of pyridine into **2** at room temperature.

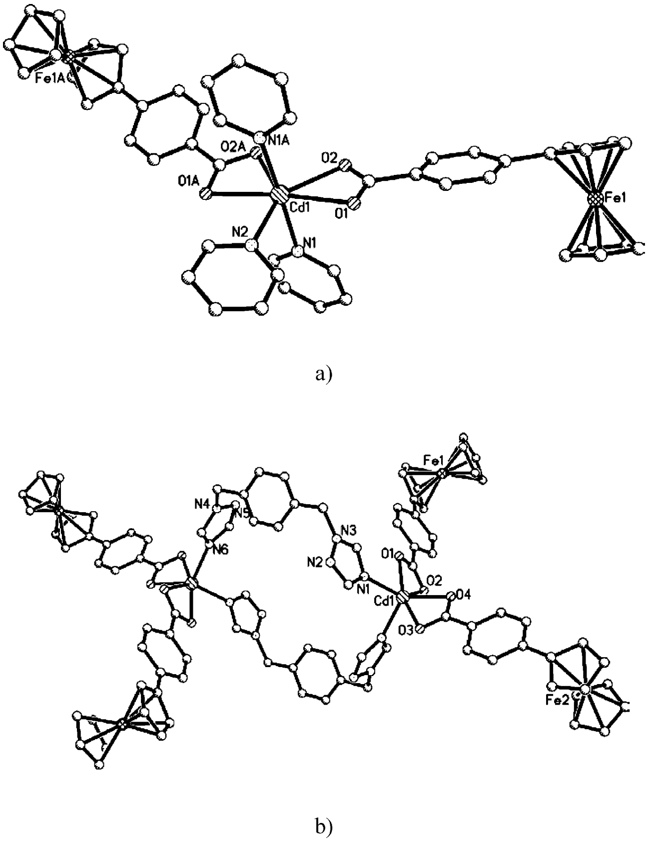
It is well known that six or seven-coordinate Cd^{II} is common in ferrocenyl carboxylate complexes. The Cd^{II} is seven-coordinate in precursor complex **2**. So, six- or seven-coordinate Cd^{II} complexes may be obtained by a substitution reaction of **2**. If the coordination number of Cd^{II} in complexes is seven, the structures may form a two-dimensional network by a substitution reaction of **2** with bidentate bridging ligands under moderate reaction conditions. If the Cd^{II} is six-coordinate in the obtained complexes, the structures may be binuclear or form a one-dimensional chain under the same conditions. As a matter of fact, complex **2b** was obtained by a substitution reaction of **2** with the bidentate bridging btx ligand at room temperature (Scheme 3). Because of the spatial configuration and the steric effect of btx, it is difficult to obtain a two-dimensional polymer through the reaction of **2** with btx. Relatively, a dimer or a one-dimensional polymer may be synthesized easily. Just as we thought, **2b** is a dimer, and the coordination number of the Cd^{II} ion is six.



Scheme 3. The synthesis and conversion of precursor complex **2** into complexes **2a** and **2b**.

Mononuclear complex **2a** is depicted in Figure 2a, from which we can see that the Cd^{II} ion is seven-coordinate, and the coordination mode of the central Cd^{II} of **2a** is consistent with that of **2**. The equatorial positions are occupied by O1, O2, O1A, O2A, and N2 (the mean deviation is 0.0811 Å), and the coordination environment around the Cd^{II} ion is a distorted penta bipyramid.

X-ray diffraction analysis revealed that, in **2b**, two Cd^{II} ions are bridged by two bridging btx ligands to form a dimer (Figure 2b). Each Cd^{II} ion coordinates with four oxygen atoms from two chelating $FcC_6H_4COO^-$ units and two nitrogen donors from two btx molecules. The Cd–O bond lengths are in the range of 2.253(5)–2.506(5) Å. In accordance with **2a**, one Cd1–$O_{carboxyl}$ distance in the bidentate mode is longer than those of **2** [from 2.360(5) to 2.454(5) Å], whereas the other distance is shorter than that of **2**. Nevertheless, treatment of FcC_6H_4COONa and $Cd(OAc)_2{\cdot}2H_2O$ with bridging ligand bbp (bbp = 4,4′-trimethylene-dipyridine) generated an infinite one-dimensional ladder-like polymer {[Cd(μ_2-$OOCH_4C_6Fc$)(η^2-



a)

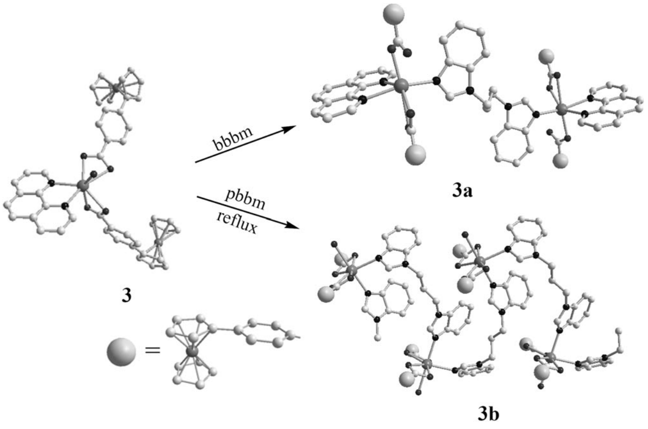
b)

Figure 2. (a) The structure of $\{[Cd(\eta^2\text{-}OOCC_6H_4Fc)_2(py)_3]\text{-}(CH_3OH)_4\}$ (**2a**) with heteroatom numbering; (b) the structure of $\{[Cd_2(\eta^2\text{-}OOCC_6H_4Fc)_4(btx)_2](thf)_3(CH_3OH)_2\}$ (**2b**) with heteroatom numbering (hydrogen atoms and solvent molecules are omitted for clarity).

$OOCH_4C_6Fc)(bbp)](CH_3OH)\}_n$ in which the neighboring Cd^{II} ions are linked by the coaction of the $FcC_6H_4COO^-$ ions and the bbp ligand.[60]

The Syntheses and Crystal Structures of $\{[Cd_2(\eta^2\text{-}OOCC_6H_4Fc)_2(OOCC_6H_4Fc)_2(phen)_2(bbbm)](CH_3OH)_4\text{-}(thf)_2\}$ (3a) and $\{[Cd(\eta^2\text{-}OOCC_6H_4Fc)_2(pbbm)(H_2O)]\text{-}(H_2O)\}_n$ (3b)

Precursor complex **3** was obtained successfully by using FcC_6H_4COONa as a functional ligand and by introducing the chelate phen ligand and solvent molecule H_2O. There is one facile leaving group (H_2O molecule) in **3**. In view of the structural features of **3**, we expected that a dimer could be obtained by using **3** as a building block and by replacing the water molecule with a bidentate bridging ligand under moderate reaction conditions. As anticipated, the reaction of **3** with bbbm resulted in dimer **3a** at room temperature. Because of the framework distortion of **3** that occurs under severe reaction conditions, one-dimensional polymer **3b** was synthesized by a recombination reaction of **3** with pbbm ligands under reflux conditions (Scheme 4).



Scheme 4. The synthesis and conversion of precursor complex **3** into complexes **3a** and **3b**.

The structure of **3a** is shown in Figure 3a, and it features a six-coordinate Cd^{II} ion in a distorted octahedral geometry defined by three oxygen atoms from two coordinated $FcC_6H_4COO^-$ units, two nitrogen donors from one chelating phen, and one nitrogen donor from a bridging bbbm ligand. A bbbm ligand links two Cd^{II} ions to form a dimer.

By comparison with **3**, the $[Cd(\eta^2\text{-}OOCC_6H_4Fc)_2(H_2O)]$ units are bridged by pbbm to form one-dimensional quadrate-wave-like chain polymer **3b** under reflux conditions (Figure 3b). The intrachain Cd···Cd distance (9.841 Å) of **3b** is considerably shorter than that of **3a** (13.640 Å). The $Cd1–N_{phen}$ distances in dimer **3a** [2.387(7), 2.395(7) Å] are consistent with those in **3** [2.366(7), 2.390(8) Å]. Therefore, the substitution reaction of the bbbm replacing H_2O in **3** has little influence on the phen group. Because of the spatial configuration and the steric effect of the ferrocene group and the pbbm ligand, the length of the $Cd1–O_{water}$ bond in polymer **3b** [2.512(8) Å] is longer than that in precursor complex **3** [2.347(7) Å].

The Syntheses and Crystal Structures of $[Zn(OOCC_6H_4Fc)_2\text{-}(phen)(H_2O)]$ (4a) and $\{[Zn(OOCC_6H_4Fc)_2(bbbm)]\text{-}(CH_3OH)_3\}_n$ (4b)

The structure of precursor complex **4** is shown in Scheme 5. Among three $Zn\cdots O_{\eta^2\text{-}OOCC_6H_4Fc}$ distances, two of them [Zn–O1 = 1.992(4) and Zn–O4 = 1.975(4) Å] compare well with the distances found in the reported zinc carboxylate complexes[69] and another [Zn···O2 = 2.448(4) Å] is longer than the common $Zn–O_{carboxyl}$ bond length; in other words, the O2 atom coordinates to the Zn^{II} ion weakly. We think the Zn···O2 bond is an uncoordinated bond.

The Zn^{II} ion is usually four, five, or six-coordinate in complexes.[70] In precursor complex **4**, the Zn^{II} ion is four-coordinate, thus we can obtain complexes by the addition reaction of **4** with some ligands. As a result, the addition reaction of **4** with H_2O yielded complex **4a** at room temperature. Further, as the emergence of **3b**, one-dimensional

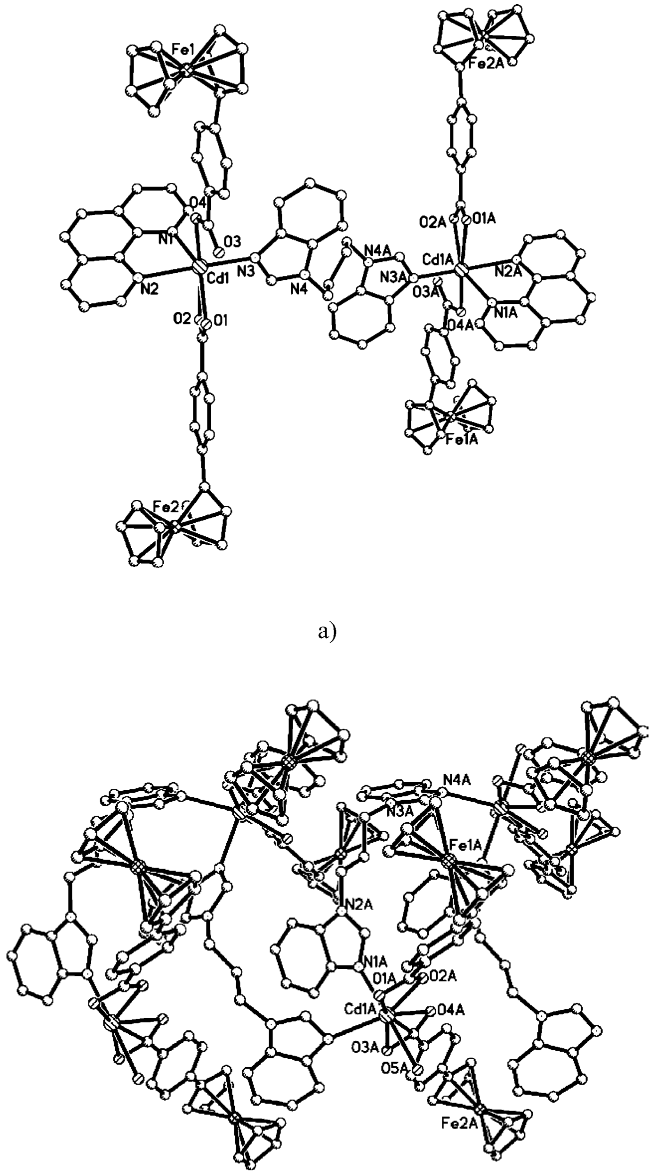
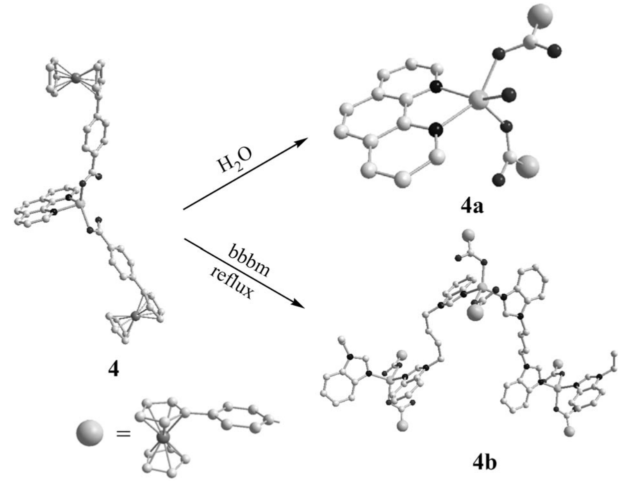


Figure 3. (a) The structure of $\{[Cd_2(\eta^2\text{-}OOCC_6H_4Fc)_2(OOCC_6H_4Fc)_2(phen)_2(bbbm)](CH_3OH)_4(thf)_2\}$ (**3a**); (b) perspective view of the one-dimensional chain structure of $\{[Cd(\eta^2\text{-}OOCC_6H_4Fc)_2(pbbm)(H_2O)](H_2O)\}_n$ (**3b**) (hydrogen atoms and solvent molecules are omitted for clarity).

polymer **4b** was also synthesized by the reaction of **4** with bbbm under reflux conditions (Scheme 5).

The structure of mononuclear complex **4a** is shown in Figure 4a; the Zn^{II} ion is five-coordinate in a distorted square pyramid geometry, and the O1, O5, N1, and N2 atoms are nearly located on the same plane (the mean deviation is 0.0221 Å). Because of the introduction of the H_2O molecule, the distance of Zn1–$O5_{water}$ (2.088 Å) in **4a** is shorter than Zn···O2 [2.448(4) Å] in **4**. The length of Zn–$O_{carboxyl}$ in **4a** (1.953 and 2.009 Å) is in conformity with those in **4** (1.975 and 1.992 Å). Therefore, **4a** results from the addition reaction of **4** with H_2O. However, the recombi-



Scheme 5. The synthesis and conversion of precursor complex **4 in**to complexes **4a** and **4b**.

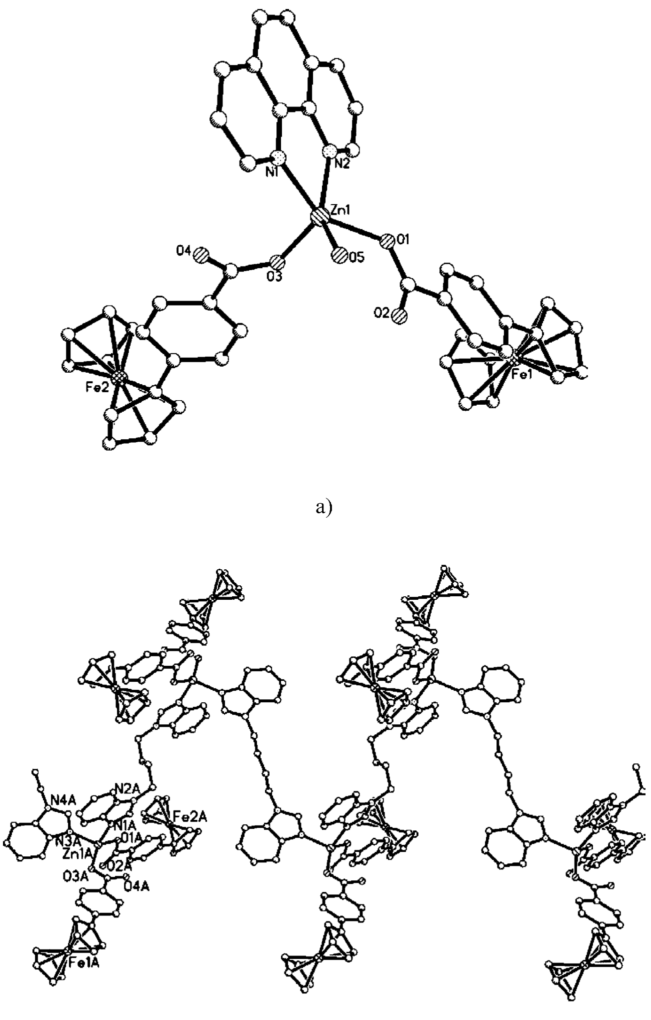


Figure 4. (a) The structure of $[Zn(OOCC_6H_4Fc)_2(phen)(H_2O)]$ (**4a**) with heteroatom numbering; (b) one-dimensional chain structure of $\{[Zn(OOCC_6H_4Fc)_2(bbbm)](CH_3OH)_3\}_n$ (**4b**) (hydrogen atoms and solvent molecules are omitted for clarity).

nant reaction of **4** with bbbm yielded one-dimensional chain polymer **4b** (Figure 4b). Each Zn^{II} ion is four-coordinate with two oxygen atoms from two monodentate coordinated $FcC_6H_4COO^-$ units and two nitrogen donors from two bbbm molecules. The torsion angle of C42–C43–C43A–C42A is 180.0°. The Zn^{II} ions are connected by bbbm ligands, and the Zn···Zn distance is 12.310 Å in **4b**.

Conclusions

The syntheses of precursor complexes **1**–**4** are necessary to obtain the desired complexes. The structural integrity of the precursor complexes can be maintained in substitution or addition reactions of the precursor complexes with ligands under moderate reaction conditions. Noteworthy is the idea that under moderate reaction conditions "the structures of the complexes are dominated by the number of facile leaving groups in the precursor complexes". Because the self-assembly of complexes lies on a delicate thermodynamic balance between enthalpy and entropy effects,[71] and the strengths of the coordination bonds become weak under severe reaction conditions, "recombinant" complexes could be obtained by the reaction of ligands and metal ions. The obtained complexes result from framework distortion of the precursor complexes. In addition, crystals of these complexes that originated from the precursor complexes could not be obtained from one-pot reactions of ferrocenyl carboxylate, metal salts, and organic ligands.

Experimental Section

β-Ferrocenylacrylic and *p*-ferrocenylbenzoic acid and their corresponding sodium salts were prepared according to literature methods.[72,73] 1,1-(1,4-Butanediyl)bis-1*H*-benzimidazole (bbbm), 1,1-(1,3-propylene)bis-1*H*-benzimidazole (pbbm), 1,4-bis(triazol-1-ylmethyl)benzene (btx), and 1,4-bis(imidazol-1-ylmethyl)benzene (bix) were prepared according to literature methods.[74,63,75] All other staring materials were of reagent-grade quality and were obtained from commercial sources and used without further purification. Elemental analyses (C, H, and N) were carried out with a FLASH EA 1112 elemental analyzer. Infrared spectra data were recorded with a Bruker TENSOR 27 spectrophotometer with KBr pellets in the 400–4000 cm^{-1} region.

$[\mathrm{Cd}(\eta^2\text{-}\mathrm{OOCCH{=}CHFc})_2(\mathrm{C_2H_5OH})_2]$ (1): FcCH=CHCOONa (55.6 mg, 0.20 mmol) in methanol (8 mL) was added dropwise to a solution of $Cd(OAc)_2 \cdot 2H_2O$ (26.8 mg, 0.1 mmol) in methanol (5 mL) and ethanol (2 mL). The resulting red solution was allowed to stand at room temperature in the dark. Good quality red crystals were obtained several days later. Yield: 48.6 mg (68%). IR (KBr): $\tilde{\nu}$ = 3439 (s), 3126 (s), 2361 (m), 1634 (s), 1519 (s), 1402 (s), 1253 (m), 1102 (m), 1039 (m), 816 (m), 486 (m) cm^{-1}. $C_{30}H_{34}CdFe_2O_6$ (714.67): calcd. C 50.42, H 4.80; found C 50.32, H 4.86.

$\{[\mathrm{Cd}(\eta^2\text{-}\mathrm{OOCC_6H_4Fc})_2(\mathrm{dmf})_2(\mathrm{H_2O})]\}$ (2): FcC_6H_4COONa (65.6 mg, 0.2 mmol) in methanol (6 mL) was added to a solution of $Cd(OAc)_2 \cdot 2H_2O$ (26.8 mg, 0.1 mmol) in methanol (4 mL) and H_2O (3 mL). A red precipitate formed immediately, and DMF (3 mL) was then added to the mixture to dissolve the precipitate. Several days later, good quality red crystals were obtained from the red solution at room temperature in the dark Yield: 53.2 mg (60%). IR (KBr): $\tilde{\nu}$ = 3422 (s), 2367 (m),1633 (s), 1539 (m), 1476 (m), 1400 (s), 1308 (m), 1108 (m), 1053 (m), 813 (m), 710 (m), 519 (m) cm^{-1}. $C_{40}H_{42}CdFe_2N_2O_7$ (886.86): calcd. C 54.04, H 4.89, N 3.20; found C 53.77, H 4.82, N 3.15.

$\{[\mathrm{Cd}(\eta^2\text{-}\mathrm{OOCC_6H_4Fc})_2(\mathrm{phen})(\mathrm{H_2O})](\mathrm{CH_3OH})\}$ (3): A methanol (6 mL) solution of the subsidiary phen ligand (19.8 mg, 0.1 mmol) was added to an aqueous solution (2 mL) of $Cd(OAc)_2 \cdot 2H_2O$ (26.8 mg, 0.1 mmol). A methanol solution (8 mL) of FcC_6H_4COONa (65.6 mg, 0.2 mmol) was then added to the above mixture. The resulting orange solution was allowed to stand at room temperature in the dark. After 1 week, good quality red crystals of **3** were obtained. Yield: 50.5 mg (53%). IR (KBr): $\tilde{\nu}$ = 3420 (m), 1584 (s), 1537 (s), 1395 (s), 1103 (m), 851 (m), 789 (m), 727 (m), 473 (m) cm^{-1}. $C_{47}H_{42}CdFe_2N_2O_6$ (952.91): calcd. C 58.01, H 4.05, N 2.68; found C 57.74, H 3.96, N 2.56.

$\{[\mathrm{Zn}(\mathrm{OOCC_6H_4Fc})_2(\mathrm{phen})](\mathrm{H_2O})\}$ (4) The preparation was similar to that for **3**, except $Zn(OAc)_2 \cdot 2H_2O$ (21.9 mg, 0.1 mmol) was used instead of $Cd(OAc)_2 \cdot 2H_2O$. The resulting orange solution was allowed to stand at room temperature in the dark. After two weeks, good quality red crystals of **4** were obtained. Yield: 43.2 mg (50%). IR (KBr): $\tilde{\nu}$ = 3424 (m), 3080 (m), 1605 (s), 1547 (m), 1387 (s), 1179 (m), 1104 (m), 850 (m), 788 (m), 727 (m), 478 (m) cm^{-1}. $C_{46}H_{42}Fe_2N_2O_4Zn$ (863.89): calcd. C 63.94, H 4.92, N 3.20; found C 63.90, H 4.86, N 3.24.

$\{[\mathrm{Cd}(\eta^2\text{-}\mathrm{OOCCH{=}CHFc})_2(\mathrm{bbbm})](\mathrm{H_2O})\}_n$ (1a): The crystals of complex **1** (17.9 mg, 0.025 mmol) were dissolved in THF (3 mL). A solution of bbbm (7.3 mg, 0.025 mmol) in methanol (6 mL) was added dropwise to the above solution. The resulting red solution was allowed to stand at room temperature in the dark. Good quality red crystals were obtained after several days. Yield: 14.4 mg (62%). IR (KBr): $\tilde{\nu}$ = 3421 (m), 3099 (m), 2932 (m), 1636 (s), 1541 (m), 1508 (m), 1463 (m), 1404 (s), 1291 (m), 1255 (m), 1200 (m), 1105 (m), 1043 (m), 975 (m), 748 (m), 496 (m) cm^{-1}. $C_{44}H_{42}CdFe_2N_4O_5$ (930.92): calcd. C 56.72, H 4.51, N 6.02; found C 56.04, H 4.51, N 5.88.

$\{[\mathrm{Cd_2}(\eta^2\text{-}\mathrm{OOCCH{=}CHFc})_4(\mathrm{pbbm})_2](\mathrm{CH_3OH})_6(\mathrm{H_2O})_4\}$ (1b): The conversion of **1** to **1b** was similar to the procedures mentioned above, except pbbm (6.9 mg, 0.025 mmol) was used instead of bbbm. Three weeks later good quality red crystals were obtained from the red solution at room temperature in the dark. Yield: 17.5 mg (68%). IR (KBr): $\tilde{\nu}$ = 3423 (m), 3103 (m), 1636 (s), 1542 (m), 1510 (m), 1463 (m), 1404 (s), 1290 (m), 1254 (m), 1199 (m), 976 (m), 748 (m), 685 (m), 495 (m) cm^{-1}. $C_{92}H_{107}Cd_2Fe_4N_8O_{18}$ (2061.06): calcd. C 53.57, H 5.19, N 5.43; found C 53.02, H 5.08, N 5.50.

$\{[\mathrm{Cd_2}(\mu_2\text{-}\eta^2\text{-}\mathrm{OOCCH{=}CHFc})_2(\eta^2\text{-}\mathrm{OOCCH{=}CHFc})_2(\mathrm{bix})_2]\text{-}(\mathrm{CH_3OH})_4\}_n$ (1c): A methanol solution (10 mL) of bix (6.8 mg, 0.025 mmol) was added to a THF (4 mL) solution of **1** (17.9 mg, 0.025 mmol) at room temperature. The reaction mixture was heated at refluxed for 10 min. The mixture was then allowed to set at room temperature in the dark for two weeks to afford the product as red crystals. Yield: 14.7 mg (65%). IR (KBr): $\tilde{\nu}$ = 3428 (m), 3120 (m), 1635 (s), 1545 (s), 1402 (s), 1250 (m), 1108 (m), 1027 (m), 936 (m), 824 (m), 657 (m), 496 (m) cm^{-1}. $C_{84}H_{88}Cd_2Fe_4N_8O_{12}$ (1809.76): calcd. C 54.49, H 4.76, N 6.05; found C 53.68, H 4.69, N 6.11.

$\{[\mathrm{Cd_2}(\mu_2\text{-}\eta^2\text{-}\mathrm{OOCCH{=}CHFc})_2(\eta^2\text{-}\mathrm{OOCCH{=}CHFc})_2(\mathrm{btx})_2]\text{-}(\mathrm{CH_3OH})_4\}_n$ (1d): The synthesis was the same as that for **1c**, except with the use of btx (7.8 mg, 0.025 mmol) and **1** (17.9 mg, 0.025 mmol). Yield: 15.3 mg (66%). IR (KBr): $\tilde{\nu}$ = 3423 (m), 3114 (m), 1636 (s), 1547 (s), 1463 (m), 1403 (s), 1280 (m), 1255 (m), 1136 (s), 1010 (m), 983 (m), 872 (m), 825 (m), 675 (m), 497 (m) cm^{-1}. $C_{80}H_{84}Cd_2Fe_4N_{12}O_{12}$ (1853.79): calcd. C 51.78, H 4.53, N 9.06; found C 51.68, H 4.47, N 8.98.

$\{[Cd(\eta^2\text{-}OOCC_6H_4Fc)_2(py)_3](CH_3OH)_4\}$ (2a): Methanol (9 mL) was added to a solution of complex **2** (22.2 mg, 0.025 mmol) in pyridine (2 mL). The mixture was kept at room temperature in the dark. About one month later good quality red crystals were obtained. Yield: 13.6 mg (50%). IR (KBr): $\tilde{\nu}$ = 3428 (m), 1604 (m), 1585 (m), 1537 (m), 1398 (s), 1183 (m), 1105 (m), 1034 (m), 1007 (m), 856 (m), 818 (m), 790 (m), 707 (m), 475 (m) cm^{-1}. $C_{53}H_{57}CdFe_2N_3O_8$ (1088.12): calcd. C 58.46, H 5.24, N 3.86; found C 57.80, H 5.16, N 3.83.

$\{[Cd_2(\eta^2\text{-}OOCC_6H_4Fc)_4(btx)_2](thf)_3(CH_3OH)_2\}$ (2b): A solution of btx (7.8 mg, 0.025 mmol) in methanol (6 mL) was added to a solution of **2** (22.2 mg, 0.025 mmol) in THF (3 mL) to give a clear solution. The solution was kept at room temperature in the dark. A few days later, red crystals of **2b** were obtained. Yield: 17.0 mg (62%). IR (KBr): $\tilde{\nu}$ = 3423 (m), 3114 (m), 1588 (s), 1543 (s), 1398 (s), 1279 (s), 1135 (m), 1105 (m), 1011 (m), 731 (m), 710 (m), 674 (m), 474 (m) cm^{-1}. $C_{106}H_{96}Cd_2Fe_4N_{12}O_{13}$ (2194.15): calcd. C 57.97, H 4.38, N 7.66; found C 57.12, H 4.28, N 7.62.

$\{[Cd_2(\eta^2\text{-}OOCC_6H_4Fc)_2(OOCC_6H_4Fc)_2(phen)_2(bbbm)](CH_3OH)_4(thf)_2\}$ (3a): A solution of bbbm (7.3 mg, 0.025 mmol) in methanol (6 mL) was added slowly with stirring to a solution of **3** (23.8 mg, 0.025 mmol) in THF (3 mL). One week later, good quality red crystals were obtained from the red solution at room temperature in the dark. Yield: 20.6 mg (70%). IR (KBr): $\tilde{\nu}$ = 3423 (m), 3096 (m), 1589 (s), 1543 (s), 1395 (s), 1104 (m), 849 (m), 790 (m), 747 (m), 728 (m), 710 (m), 474 (m) cm^{-1}. $C_{122}H_{110}Cd_2Fe_4N_8O_{14}$ (2360.38): calcd. C 62.02, H 4.66, N 4.74; found C 61.57, H 4.60, N 4.79.

$\{[Cd(\eta^2\text{-}OOCC_6H_4Fc)_2(pbbm)(H_2O)](H_2O)\}_n$ (3b): A solution of pbbm (6.9 mg, 0.025 mmol) in methanol (6 mL) was added dropwise to a solution of **3** (23.8 mg, 0.025 mmol) in THF (3 mL). This reaction mixture was heated at reflux for 10 min to give a clear

Table 1. Selected bond lengths [Å] and angles [°] for complexes **1**, **1a**–**c**, **2**–**4**.

Complex **1**[a]							
Cd1–O3	2.228(4)	Cd1–O1	2.297(3)	Cd1–O2	2.362(4)	O3–Cd1–O3#1	87.2(3)
O1–Cd1–O2	55.77(13)	O3–Cd1–O1#1	89.36(15)	O1#1–Cd1–O1	152.6(2)	O2–Cd1–O2#1	89.8(2)
O2–Cd1–O2#1	89.8(2)	O3#1–Cd1–O2	145.03(15)	O1#1–Cd1–O2	103.15(14)	O3–Cd1–O1	110.72(17)
Complex **2**							
Cd1–O6	2.293(5)	Cd1–O5	2.307(5)	Cd1–O7	2.312(4)	Cd1–O4	2.360(5)
Cd1–O2	2.454(5)	Cd1–O3	2.402(4)	Cd1–O1	2.408(5)	O5–Cd1–O4	143.63(17)
O5–Cd1–O2	78.22(16)	O3–Cd1–O2	165.17(17)	O7–Cd1–O4	90.99(17)	O1–Cd1–O2	53.69(16)
O4–Cd1–O1	85.31(14)	O7–Cd1–O2	96.12(18)	O5–Cd1–O1	131.04(16)	O6–Cd1–O3	91.6(2)
O4–Cd1–O3	54.42(15)	O3–Cd1–O1	139.69(15)	O6–Cd1–O2	80.7(2)	O6–Cd1–O1	90.6(2)
Complex **3**							
Cd1–O2	2.327(7)	Cd1–O5	2.347(7)	Cd1–O4	2.354(7)	Cd1–O1	2.505(7)
Cd1–N2	2.390(8)	Cd1–O3	2.524(7)	Cd1–N1	2.366(7)	O2–Cd1–O5	143.0(3)
N1–Cd1–O3	156.1(3)	N1–Cd1–N2	70.0(3)	O2–Cd1–O1	54.1(2)	O2–Cd1–N1	93.0(3)
N2–Cd1–O1	136.3(3)	O4–Cd1–N1	142.2(3)	O5–Cd1–O1	88.9(3)		
Complex **4**							
Zn1–O4	1.975(4)	Zn1–O1	1.992(4)	Zn1–N1	2.097(6)	Zn1–N2	2.098(5)
N1–Zn1–N2	78.7(3)	O4–Zn1–O1	129.01(17)	O4–Zn1–N1	116.13(18)	O1–Zn1–N1	98.7(2)
O4–Zn1–N2	101.28(19)	O1–Zn1–N2	122.11(17)				
Complex **1a**[b]							
Cd1–N3	2.264(3)	Cd1–O4	2.276(3)	Cd1–O2	2.462(4)	Cd1–O3	2.530(3)
N1–Zn1–N2	78.7(3)	Cd1–O1	2.299(4)	N3–Cd1–O4	115.12(12)	N3–Cd1–N1	103.14(11)
O1–Cd1–O2	53.21(15)	N1–Cd1–O1	91.71(14)	O4–Cd1–N1	116.91(12)	N3–Cd1–O1	107.16(15)
N1–Cd1–O2	144.37(13)	O4–Cd1–O2	81.61(12)	N3–Cd1–O3	84.82(11)		
Complex **1b**[c]							
Cd1–N1	2.257(5)	Cd1–N3#1	2.278(5)	Cd1–O2	2.328(5)	Cd1–O3	2.335(5)
Cd1–O4	2.400(5)	Cd1–O1	2.407(5)	N1–Cd1–N3#1	98.86(19)	N1–Cd1–O2	98.1(2)
N3#1–Cd1–O2	138.05(19)	N1–Cd1–O3	151.1(2)	O3–Cd1–O4	55.14(19)	O2–Cd1–O3	89.70(18)
O3–Cd1–O1	109.9(2)	O4–Cd1–O1	163.65(19)	N1–Cd1–O1	97.2(2)		
Complex **1c**[d]							
Cd1–O2	2.5728(19)	Cd1–O3	2.301(2)	Cd1–O4	2.599(3)	Cd1–O1	2.370(2)
Cd2–N4#2	2.348(3)	Cd2–N1	2.290(2)	Cd2–O4	2.321(2)	O3#1–Cd1–O3	164.81(10)
O1#1–Cd1–O1	88.98(10)	O1–Cd1–O2#1	139.20(8)	O3–Cd1–O1	101.50(7)	O1–Cd1–O4	121.30(8)
O1–Cd1–O2	50.58(7)	O3–Cd1–O4	51.17(7)	O3#1–Cd1–O4	114.02(7)	O2–Cd1–O4	77.28(7)
N1#1–Cd2–O4	84.14(8)	N1#1–Cd2–N1	176.90(12)	N1–Cd2–O4	98.31(8)	O4–Cd2–N4#2	161.68(9)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x$, y, $-z + 1/2$. [b] Symmetry transformations used to generate equivalent atoms: #1 $- x$, $y + 2$, $-z + 1$, #2 $-x$, $y + 2$, $-z$. [c] Symmetry transformations used to generate equivalent atoms: #1 $- x$, $-y$, $-z$, #2 $-x + 1$, $-y + 1$, $-z$. [d] Symmetry transformations used to generate equivalent atoms: #1 $-x + 2$, y, $-z + 1/2$, #2 $x + 1/2$, $y + 1/2$, z, #3 $-x + 3/2$, $y + 1/2$, $-z + 1/2$, #4 $x - 1$, $y - 1/2$, z, #5 $-x + 3/2$, $-y + 1/2$, $-z$.

solution. The resulting red solution was allowed to stand at room temperature in the dark. Good quality red crystals were obtained after two weeks. Yield: 14.5 mg (56%). IR (KBr): ṽ = 3421 (m), 3099 (m), 1601 (s), 1534 (s), 1461 (m), 1398 (s), 1180 (m), 1104 (m), 817 (m), 789 (m), 746 (m), 710 (m), 473 (m) cm^{-1}. $C_{51}H_{46}CdFe_2N_4O_6$ (1035.02): calcd. C 59.13, H 4.44, N 5.41; found C 59.08, H 4.41, N 5.36.

[Zn(OOCC$_6$H$_4$Fc)$_2$(phen)(H$_2$O)] (4a): Complex **4** (21.6 mg, 0.025 mmol) was dissolved in THF (3 mL) whilst stirring. Methanol (6 mL) and H_2O (3 mL) was added to the above solution. A few days later good quality red crystals were obtained from the red solution at room temperature in the dark. Yield: 10.0 mg (46%). IR (KBr): ṽ = 3423 (m), 3088 (m), 1606 (s), 1543 (m), 1389 (m), 1178 (m), 1104 (m), 843 (m), 790 (m), 726 (m), 520 (m), 478 (m) cm^{-1}. $C_{46}H_{36}Fe_2N_2O_5Zn$ (873.84): calcd. C 63.17, H 4.12, N 3.20; found C 62.86, H 4.08, N 3.22.

{[Zn(OOCC$_6$H$_4$Fc)$_2$(bbbm)](CH$_3$OH)$_3$}$_n$ (4b): Compound **4** (21.6 mg, 0.025 mmol) was dissolved in THF (3 mL) whilst stirring. A methanol solution (6 mL) of bbbm (7.3 mg, 0.025 mmol) was added to the above solution. The reaction mixture was heated at reflux for 15 min. Two weeks later good quality red crystals were obtained at room temperature in the dark. Yield: 16.5 mg (62%). IR (KBr): ṽ = 3423 (m), 3100 (m), 2362 (m), 1607 (s), 1555 (m), 1516 (m), 1464 (m), 1383 (s), 1297 (m), 1180 (m), 1104 (m), 823 (m), 789 (m), 745 (m), 709 (m), 518 (m), 477 (m) cm^{-1}. $C_{55}H_{56}Fe_2N_4O_7Zn$ (1062.11): calcd. C 62.14, H 5.27, N 5.27; found C 61.67, H 5.22, N 5.32.

Crystal Structure Determination: Measurements of **1**, **2**, **3**, **2b**, and **3a** were made with a Rigaku RAXIS-IV image plate area detector for study by using graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation at 291(2) K with the ω-2θ scan technique. The data were corrected for Lorentz and polarization factors and for

Table 2. Selected bond lengths [Å] and angles [°] for complexes **1d**, **2a**,**b**, **3a**,**b**, **4a**,**b**.

Complex **1d**[a]							
Cd1–O2	2.399(4)	Cd1–O4	2.321(4)	Cd1–O1	2.501(4)	Cd1–O3	2.637(5)
Cd2–N1	2.352(4)	Cd2–O3	2.266(4)	Cd2–N6#2	2.340(4)	O4–Cd1–O2	101.81(12)
O3–Cd1–O3#1	66.0(2)	O4–Cd1–O1	92.32(13)	O2–Cd1–O1	52.88(12)	O1–Cd1–O1#1	168.18(17)
O2#1–Cd1–O1	138.88(12)	O4–Cd1–O3	51.58(12)	O2–Cd1–O3	122.75(14)	O3–Cd2–O3#1	78.7(3)
O1–Cd1–O3	76.07(13)	N6#2–Cd2–N1	86.17(14)	O3–Cd2–N1#1	163.48(17)	O3–Cd2–N1	88.70(17)
Complex **2a**[b]							
Cd1–N1	2.353(2)	Cd1–O2	2.339(2)	Cd1–N2	2.356(4)	Cd1–O1	2.593(2)
O2#1–Cd1–O2	82.94(11)	O2#1–Cd1–N1	95.67(9)	O2–Cd1–N1	87.10(9)	N1–Cd1–N1#1	176.32(12)
N1–Cd1–N2	88.16(6)	O2–Cd1–N2	138.53(6)	O2#1–Cd1–O1	135.04(8)	O2–Cd1–O1	52.73(7)
N1–Cd1–O1	89.78(9)	N2–Cd1–O1	86.10(5)	O1–Cd1–O1#1	172.20(10)		
Complex **2b**[c]							
Cd1–O1	2.253(5)	Cd1–N6#1	2.280(5)	Cd1–O4	2.294(4)	Cd1–N1	2.303(6)
Cd1–O3	2.411(5)	Cd1–O2	2.506(5)	O1–Cd1–N6#1	114.03(19)	N6#1–Cd1–O3	88.62(19)
N6#1–Cd1–O4	123.7(2)	N1–Cd1–O3	91.70(19)	O1–Cd1–O2	54.52(16)	N6#1–Cd1–O2	83.64(19)
O4–Cd1–O3	55.46(16)	O1–Cd1–N1	86.05(19)	O4–Cd1–N1	117.89(18)		
Complex **3a**[d]							
Cd1–O4	2.248(6)	Cd1–O1	2.304(6)	Cd1–N3	2.312(7)	Cd1–N1	2.387(7)
Cd1–O2	2.583(6)	Cd1–N2	2.395(7)	O4–Cd1–O1	127.3(3)	N1–Cd1–O2	92.7(2)
O4–Cd1–O2	176.0(2)	O1–Cd1–O2	53.6(2)	O1–Cd1–N1	142.1(2)	N3–Cd1–N1	94.6(2)
N2–Cd1–O2	81.1(2)	O1–Cd1–N2	86.2(2)	N1–Cd1–N2	70.0(3)		
Complex **3b**[e]							
Cd1–O2	2.315(5)	Cd1–N1	2.354(2)	Cd1–O3	2.375(10)	Cd1–N4#1	2.397(4)
Cd1–O5	2.512(8)	Cd1–O4	2.474(8)	Cd1–O1	2.546(7)	N1–Cd1–O1	98.37(11)
O2–Cd1–N1	92.97(12)	O2–Cd1–N4#1	131.57(16)	N1–Cd1–O3	95.53(15)	O2–Cd1–O1	49.15(16)
N1–Cd1–N4#1	85.97(5)	N1–Cd1–O4	86.79(12)	N1–Cd1–O5	177.0(2)	O3–Cd1–O4	55.2(2)
O2–Cd1–O5	89.73(19)	O5–Cd1–O1	84.5(2)	O3–Cd1–O5	81.4(2)		
Complex **4a**							
Zn1–O3	1.9526(14)	Zn1–O1	2.0095(13)	Zn1–O5	2.0887(16)	Zn1–N1	2.1102(15)
Zn1–N2	2.1593(16)	O1–Zn1–N1	147.87(6)	O3–Zn1–N2	105.76(7)	N1–Zn1–N2	77.41(6)
O5–Zn1–N1	90.37(6)	O3–Zn1–N1	113.84(6)	O3–Zn1–O1	97.43(6)	O3–Zn1–O5	107.34(8)
O1–Zn1–O5	87.03(6)						
Complex **4b**[f]							
Zn1–O3	1.927(5)	Zn1–O1	1.934(6)	O3–Zn1–O1	132.4(3)	O3–Zn1–N1	103.9(2)
N1–Zn1–N3	103.2(3)	Zn1–N1	2.028(6)	Zn1–N3	2.033(6)	O1–Zn1–N1	96.8(3)
O3–Zn1–N3	104.9(2)	O1–Zn1–N3	111.5(3)				

[a] Symmetry transformations used to generate equivalent atoms: #1 –*x*, *y*, –*z* + 1/2, #2 *x* – 1/2, *y* – 1/2, *z*, #3 –*x* + 1/2, *y* – 1/2, –*z* + 1/2, #4 *x* + 1/2, *y* + 1/2, *z*. [b] Symmetry transformations used to generate equivalent atoms: #1 –*x*, *y*, –*z* + 1/2. [c] Symmetry transformations used to generate equivalent atoms: #1 –*x* + 1, –*y* + 2, –*z*. [d] Symmetry transformations used to generate equivalent atoms: #1 –*x* + 1/2, –*y* – 1/2, –*z* + 1. [e] Symmetry transformations used to generate equivalent atoms: #1 *x* – 1/2, –*y* + 1, *z*, #2 *x* + 1/2, –*y* + 1, *z*. [f] Symmetry transformations used to generate equivalent atoms: #1 –*x*, –*y* + 2, –*z* + 2, #2 –*x* + 1, –*y* + 2, *z*.

absorption by using empirical scan data. The structure was solved with the *SHELX* program, and refined by full-matrix least-squares methods based on F^2,[76] with anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were located theoretically and not refined.

For **4**, **1a**, **1b**, **1c**, **1d**, **2a**, **3b**, **4a**, and **4b**, single-crystal X-ray diffraction was performed by using a Bruker SMART APEX CCD diffractometer equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 nm) at room temperature. The data were integrated by using the Siemens SAINT program.[77] Absorption corrections were applied. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares with SHELXTL.[78] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located at geometrically calculated positions and refined with isotropic thermal parameters.

Selected bond lengths and bond angles are listed in Tables 1 and 2. Crystal data and experimental details for all complexes are contained in Tables 3, 4, and 5. CCDC-627164 to -627177 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.

Table 3. Crystal data and structure refinement for complexes **1**–**4**.

Complex	**1**	**2**	**3**	**4**
Formula	$C_{30}H_{34}Fe_2O_6$ Cd	$C_{40}H_{42}Fe_2N_2$ O_7Cd	$C_{47}H_{40}Fe_2N_2$ O_6Cd	$C_{46}H_{42}Fe_2N_2$ O_4Zn
Fw	714.67	886.86	952.91	863.89
T [K]	291(2)	291(2)	291(2)	273(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	orthorhombic	orthorhombic	triclinic	monoclinic
Space group	*Pbcn*	*P*2(1)2(1)2(1)	$P\bar{1}$	$P2_1/n$
a [Å]	7.6097(15)	9.3707(19)	13.145(3)	20.534(8)
b [Å]	10.596(2)	9.5073(19)	13.145(3)	10.010(4)
c [Å]	35.320(7)	43.188(9)	9.0832(18)	21.134(8)
α [°]	90	90	99.75(3)	90
β [°]	90	90	104.02(3)	90.778(7)
γ [°]	90	90	83.18(3)	90
V [Å^3]	2847.9(10)	3847.6(13)	1962.9(7)	4344(3)
Z	4	4	2	4
$D_{calcd.}$ [g cm^{-3}]	1.667	1.531	1.612	1.321
F(000)	1448	1808	968	1784
θ range for data collection [°]	1.15–27.55	1.89–27.51	1.20–25.00	2.45–25.03
Reflections collected/unique	6774/2576	12845/485	5646/5646	7617/4037
Data/restraints/parameters	2576/0/177	7485/0/471	5646/2/534	7617/48/551
Goodness-of-fit on F^2	0.992	0.990	1.130	1.002
Final R_1,[a] wR_2[b]	0.0434, 0.0872	0.0469, 0.1090	0.0937, 0.2527	0.0574, 0.1223

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$. $w = 1/[\sigma^2(F_o)^2 + 0.0297P^2 + 27.5680P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 4. Crystal data and structure refinement for complexes **1a**–**d**.

Complex	**1a**	**1b**	**1c**	**1d**
Formula	$C_{44}H_{42}Fe_2N_4O_5Cd$	$C_{92}H_{107}Fe_4N_8O_{18}$ Cd_2	$C_{82}H_{86}Fe_4N_8$ $O_{11}Cd_2$	$C_{80}H_{84}Fe_4N_{12}$ $O_{12}Cd_2$
Fw	930.92	2061.06	1809.76	1853.79
T [K]	291(2)	291(2)	291(2)	273(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	*C*2/*c*	*C*2/*c*
a [Å]	10.0300(7)	11.7382(19)	24.9352(17)	25.027(6)
b [Å]	14.6378(10)	12.2097(19)	10.2209(7)	10.104(2)
c [Å]	16.3998(16)	17.531(3)	33.244(2)	33.428(8)
α [°]	112.2210(10)	87.466(2)	90	90
β [°]	94.2100(10)	88.095(3)	106.4920(10)	107.542(4)
γ [°]	108.3400(10)	83.145(3)	90	90
V [Å^3]	2064.4(3)	2491.2(7)	8124.0(10)	8060(3)
Z	2	1	4	4
$D_{calcd.}$ [g cm^{-3}]	1.498	1.374	1.475	1.528
F(000)	948	1059	3672	3776
θ range for data collection [°]	2.69–27.50	2.28–25.50	2.33–25.50	2.35–25.50
Reflections collected/unique	12995/9119	13348/9096	17502/7472	20556/7441
Data/restraints/parameters	9119/9/513	9096/75/562	7472/16/439	7441/321/455
Goodness-of-fit on F^2	1.045	1.042	1.054	1.047
Final R_1,[a] wR_2[b]	0.0451, 0.1364	0.0620, 0.1700	0.0570, 0.1486	0.0638, 0.1519

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$. $w = 1/[\sigma^2(F_o)^2 + 0.0297P^2 + 27.5680P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 5. Crystal data and structure refinement for complexes **2a**,**b**, **3a**,**b**, and **4a**,**b**.

Complex	**2a**	**2b**	**3a**	**3b**	**4a**	**4b**
Formula	$C_{53}H_{57}CdFe_2N_3O_8$	$C_{106}H_{96}Cd_2Fe_4N_{12}O_{13}$	$C_{122}H_{110}Cd_2Fe_4N_8O_{14}$	$C_{51}H_{46}CdFe_2N_4O_6$	$C_{46}H_{36}ZnFe_2N_2O_5$	$C_{55}H_{56}ZnFe_2N_4O_7$
Fw	1088.12	2194.15	2360.38	1035.02	873.84	1062.11
T [K]	291(2)	291(2)	291(2)	291(2)	291(2)	291(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	orthorhombic	triclinic	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	*Pbcn*	$P\bar{1}$	*C*2/*c*	*Pca*2(1)	$P2_1/n$	$P2_1/n$
a [Å]	14.8564(16)	10.589(2)	34.278(7)	10.2482(6)	11.0675(5)	15.2198(14)
b [Å]	14.2892(16)	12.554(3)	9.1203(18)	15.5570(9)	12.5784(6)	10.4325(10)
c [Å]	23.187(3)	20.524(4)	36.266(7)	34.1530(19)	26.9840(12)	34.029(3)
α [°]	90	106.90(3)	90	90	90	90
β [°]	90	95.01(3)	106.25(3)	90	90.1610(10)	95.4730(10)
γ [°]	90	96.63(3)	90	90	90	90
V [Å^3]	4922.3(9)	2572.0(9)	10885(4)	5445.1(5)	3756.5(3)	5378.4(9)
Z	4	1	4	4	4	4
$D_{\text{calcd.}}$ [g cm^{-3}]	1.468	1.417	1.440	1.263	1.545	1.312
$F(000)$	2240	1120	4840	2112	1792	2208
θ range for data collection [°]	2.65–27.49	1.71–25.00	1.17–25.00	2.38–27.50	2.45–27.50	2.29–25.50
Reflections collected/unique	29129/5658	7650/7650	13620/8330	32462/10925	22665/8425	40093/10010
Data/restraints/ parameters	5658/0/308	7650/2/617	8330/3/635	10925/339/593	8425/3/513	10010/117/613
Goodness-of-fit on F^2	1.028	1.062	1.101	1.036	1.027	1.031
Final R_1,[a] wR_2[b]	0.0367, 0.0913	0.0662, 0.1535	0.0899, 0.1941	0.1341, 0.3481	0.0292, 0.0704	0.0804, 0.2341

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$. $w = 1/[\sigma^2(F_o)^2 + 0.0297P^2 + 27.5680P]$, where $P = (F_o^2 + 2F_c^2)/3$.

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