

## Novel ferrocene-based mixed-metal coordination polymers

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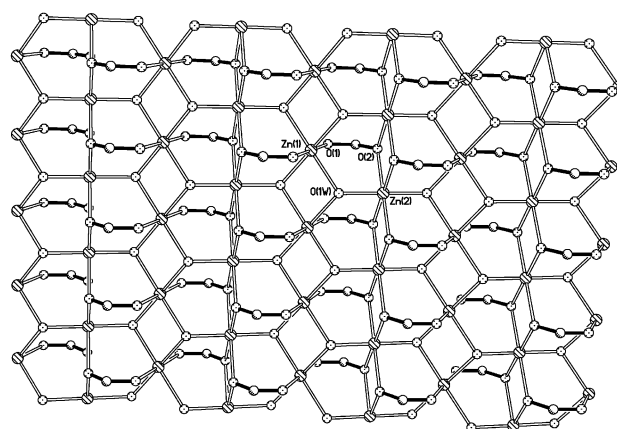
A novel 2D ferrocene-containing sandwich sheet coordination polymer, consisting of NaZnO inorganic inner and ferrocene-packing outer layers, has been achieved by simply diffusing a solution of  $\text{Zn}(\text{BF}_4)_2$  into a solution of 1,1'-ferrocenedicarboxylic acid in the presence of NaOH.

Crystal engineering and the design of solid-state architectures of coordination polymers have been very attractive fields in recent years.<sup>1,2</sup> Assembly of such extended supramolecular architectures by selecting the chemical structure of the organic ligands and the coordination geometry of the metal ions may yield a large number of new networks exhibiting interesting topologies and potential properties as new materials.<sup>3,4</sup> During the past decade unimetallic coordination polymers, which contain only one kind of metal center, have been the predominant synthetic target in this rapidly expanding area of research.<sup>2</sup> Though mixed-metal extended structures based on inorganic counterions such as cyanide and oxalate have been reported,<sup>5</sup> the chemistry of mixed-metal coordination polymers has received considerably less attention.<sup>6,7</sup> These mixed-metal coordination polymers have the potential to exhibit interesting physical properties such as electrical conductivity or magnetic ordering and propagation of the structural preferences of the different metal centers in mixed-metal systems should lead to a broader palette of polymer structural motifs than is achievable in unimetallic systems, in turn leading to a better understanding of the relationships between composition and structure.

In this communication, we use 1,1'-ferrocenedicarboxylic acid as the building block to assemble mixed-metal coordination polymers, namely,  $\text{NaZn}_3\text{L}_2(\text{OH})_3(\text{H}_2\text{O})$  **1** and  $\text{CdL}(\text{DMF})_2(\text{H}_2\text{O})$  **2** ( $\text{H}_2\text{L} = 1,1'$ -ferrocenedicarboxylic acid). The ferrocene moiety provides potential for developing new optically active materials and electronics devices due to its inherent optical and redox properties and the conformational freedom of ferrocene (especially, the characteristic 1,1'-spatial arrangement), affords opportunities for generating novel topologies. To the best of our knowledge, no coordination polymers derived from 1,1'-ferrocenedicarboxylic acid have been reported in the literature.

Complex **1**<sup>†</sup> was obtained by slowly diffusing a methanol solution of  $\text{H}_2\text{L}$  into an aqueous solution of  $\text{Zn}(\text{BF}_4)_2$  in a molar ratio of 1 : 1 in the presence of NaOH. Elemental analysis and the IR spectrum of complex **1** are in agreement with the formula. A single-crystal X-ray structural determination<sup>‡</sup> reveals that complex **1** crystallizes in the monoclinic system, space group  $C2/m$ . It should be noted that the  $b$  axial dimension is only 3.33 Å, which is extremely unusual for common coordination compounds since the van der Waals radius for an atom is always longer than 1.5 Å. Consequently, all the atoms of complex **1** occupy crystallographic special positions.

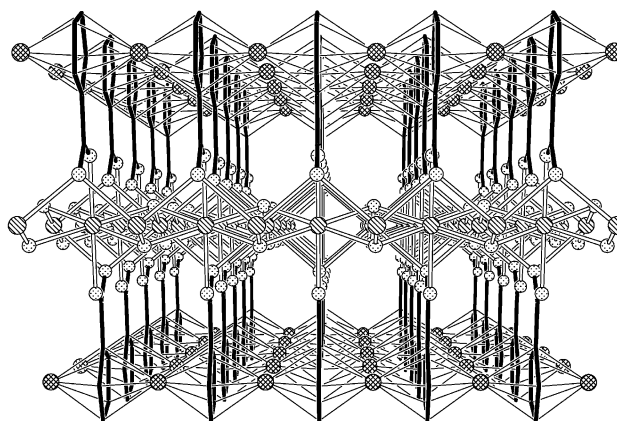
Fig. 1 shows two kinds of different zinc(II) atoms in **1** with the  $\text{Zn} \cdots \text{Zn}$  distance being *ca.* 3.4 Å on average. While the Zn(1) atom is in a distorted octahedral geometry coordinated by two oxygen atoms from the coordinated carboxylates in axial sites and four oxygen atoms from two aqua ligands in equatorial sites, the Zn(2) atom is octahedrally ligated by two oxygen atoms from the aqua ligands in axial sites and four oxygen atoms from the coordinated carboxylates in equatorial sites. The conformation of the cyclopentadienyl rings in **1** is com-



**Fig. 1** The two-dimensional NaZnO layer of complex **1** with ferrocene groups omitted for clarity. Selected bond lengths (Å): Zn(1)–O(1) 2.128(5), Zn(1)–O(1W) 2.174(3), Zn(2)–O(1W) 1.952(5), Zn(2)–O(2) 2.215(4).

pletely 1,1'-disubstituted and this special conformation plays an important role in determining the unusual topological motif of **1**. It should be pointed out that the sites of the Zn(2) atoms are practically occupied by zinc or sodium atoms. It seems that such polymeric aggregates featuring sheets of metal ions may have potential as ionic conductors, charge-storage devices, and as biomimetic models.<sup>8</sup>

As shown in Fig. 2, the zinc, sodium and oxygen atoms

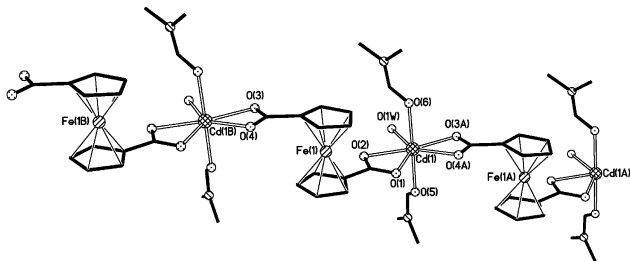


**Fig. 2** Perspective view of the sandwich sheet in **1** showing the NaZnO inorganic inner layer and the ferrocene-packing outer layers.

compose the two-dimensional inner layers of the slightly wavy sandwich sheets in stoichiometry  $\text{NaZn}_3\text{O}_{12}$  with the ferrocene moieties slanting up and down the layers. It is noteworthy that the distance between parallel cyclopentadienyl rings is crystallographically equal to the length of the  $b$  axis, 3.33 Å, and the Fe(II) atoms are so disordered that only half of the positions between the adjacent parallel cyclopentadienyl rings are occupied by Fe(II) atoms with the neighboring ones being empty. In the empty site, each pair of Cp rings is packed through such

strong  $\pi$ - $\pi$  stacking interactions that the ring...ring separation is 3.33 Å; equal to the separation of Cp rings connected by the covalent interactions of the Fe-C bonds! To the best of our knowledge, such a strong  $\pi$ - $\pi$  stacking interaction and closed stacking arrangement of the Cp rings is unprecedented in ferrocene-containing systems.<sup>9</sup>

Complex **2**§ was obtained by slowly diffusing a weak base, triethylamine, into a DMF solution of H<sub>2</sub>L and Cd(II) salt in 1 : 1 molar ratio. Complex **2** consists of infinite zigzag [CdL(DMF)<sub>2</sub>(H<sub>2</sub>O)]<sub>n</sub> chains (Fig. 3) in which the ligand L adopts a



**Fig. 3** Drawing of the zigzag chain in complex **2** with hydrogen atoms omitted for clarity. Selected bond lengths (Å): Cd(1)-O(1W) 2.304(4), Cd(1)-O(5) 2.330(4), Cd(1)-O(2) 2.344(4), Cd(1)-O(6) 2.343(4), Cd(1)-O(3A) 2.368(4), Cd(1)-O(1) 2.420(5). Symmetry code: A  $x, y - 1, z$ .

1,3'-disubstituted bridging mode and these chains are linked *via* hydrogen bonds between the aqua ligands and coordinated carboxylate oxygen atoms into two-dimensional networks.

Herein, we present a method for the preparation of mixed-metal coordination polymers by using ferrocene derivatives as metal-containing building block ligands. The incorporation of the ferrocene moiety into the metal-organic frameworks gives opportunities for creating novel topological structures that are of importance not only for their aesthetic appeal, but also for their potential use in the design of functional solids.

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## Notes and references

† Synthesis of NaZn<sub>3</sub>L<sub>2</sub>(OH)<sub>3</sub>(H<sub>2</sub>O) **1**: A solution of H<sub>2</sub>L (0.082 g, 0.30 mmol) and NaOH (0.024 g, 0.60 mmol) in methanol (10 mL) was layered onto a solution of Zn(BF<sub>4</sub>)<sub>2</sub> (0.072 g, 0.30 mmol) in water (10 mL). The solutions were left for 3 days at room temperature in darkness to afford red block crystals (0.07 g, 0.08 mmol, 84%) suitable for X-ray work. Calc. for C<sub>24</sub>H<sub>21</sub>Fe<sub>2</sub>NaZn<sub>3</sub>O<sub>12</sub>: C, 34.6; H, 2.5; Fe, 13.4. Found: C, 35.1; H, 3.0; Fe, 13.2%. IR (KBr, cm<sup>-1</sup>): 3608.8m, 3418.8m, 3083.4w, 1583.9s, 1486.6s, 1392.7s, 1367.3s, 1355.1s, 1191.0m, 1034.7m, 818.3s, 804.1s, 788.8s, 657.0m, 577.4m, 525.8s, 495.3m, 444.1w.

‡ Crystal data for **1**: C<sub>24</sub>H<sub>21</sub>Fe<sub>2</sub>NaZn<sub>3</sub>O<sub>12</sub>,  $M_r = 832.21$ , monoclinic, space group  $C2/m$ ,  $a = 28.719(8)$ ,  $b = 3.329(1)$ ,  $c = 6.272(2)$  Å,  $\beta = 97.517(4)^\circ$ ,  $V = 594.5(3)$  Å<sup>3</sup>,  $T = 293$  K,  $Z = 2$ ,  $\mu(\text{Mo-K}\alpha) = 4.265$  mm<sup>-1</sup>, 1867 reflections measured, 801 independent reflections ( $R_{\text{int}} = 0.0438$ ),  $R1 = 0.056$ ,  $wR2 = 0.181$  for 600 observed reflections [ $I > 2\sigma(I)$ ].

For **2**: C<sub>18</sub>H<sub>24</sub>N<sub>2</sub>FeCdO<sub>7</sub>,  $M_r = 548.65$ , triclinic, space group  $P\bar{1}$ ,  $a = 5.915(1)$ ,  $b = 10.285(2)$ ,  $c = 17.189(3)$  Å,  $\alpha = 88.915(3)$ ,  $\beta = 89.652(3)$ ,  $\gamma = 85.133(4)^\circ$ ,  $V = 1041.8(3)$  Å<sup>3</sup>,  $T = 293$  K,  $Z = 2$ ,  $\mu(\text{Mo-K}\alpha) = 1.758$  mm<sup>-1</sup>, 6580 reflections measured, 4679 independent reflections ( $R_{\text{int}} = 0.0507$ ),  $R1 = 0.061$ ,  $wR2 = 0.133$  for 3336 observed reflections [ $I > 2\sigma(I)$ ].

In order to ensure that the space group and unit cell of compound **1** were correct, new crystals were grown and a further unit cell was collected which gave similar cell dimensions to the first collection [ $a = 28.75(2)$ ,  $b = 3.311(2)$ ,  $c = 6.255(5)$  Å,  $\beta = 97.67(8)^\circ$ ,  $V = 590.0(1)$  Å<sup>3</sup>]. In addition, refinements in  $C2$  and  $Cm$  space groups were attempted, the results proved that the  $C2/m$  space group was correct. CCDC reference numbers 179761 and 179762. See <http://www.rsc.org/suppdata/dt/b2/b201604b/> for crystallographic data in CIF or other electronic format.

§ Synthesis of CdL(DMF)<sub>2</sub>(H<sub>2</sub>O) **2**: A DMF mixture (5 mL) of Cd(BF<sub>4</sub>)<sub>2</sub> (0.086 g, 0.30 mmol) and H<sub>2</sub>L (0.082 g, 0.30 mmol) was added into a small tube, which was placed in a larger vial containing triethylamine (10 mL). The larger vial was sealed and left undisturbed in darkness at room temperature for 7 days. The yellow block crystals which formed on the bottom of the vial were isolated and then washed with 3 × 10 mL of ethanol to give 0.12 g (70%) of product. Calc. for C<sub>18</sub>H<sub>24</sub>N<sub>2</sub>FeCdO<sub>7</sub>: C, 39.4; H, 4.4; N, 5.1. Found: C, 39.5; H, 4.9; N, 5.1%. IR (KBr, cm<sup>-1</sup>): 3395.7m, 3089.5w, 2931.5w, 1669.4s, 1648.9s, 1542.9s, 1475.9s, 1386.8s, 1351.6m, 1255.8w, 1185.4w, 1108.2m, 1033.0w, 811.1m, 797.4m, 674.2w, 518w, 431.7w.

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