LETTER

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Synthesis and structure of a novel two-dimensional bilayer framework of a [M(C_5O_5)(dpe)] coordination polymer

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The novel coordination polymers [M(μ_3-C_5O_5)$_{0.5}$(μ_4-C_5O_5)$_{0.5}$(*anti*-dpe)$_{0.5}$(*gauche*-dpe)$_{0.5}$] [M = Mn 1a, Fe 1b, Cd 1c; dpe = 1,2-bis(4-pyridyl)ethane] consist of a two-dimensional bilayered framework, each being constructed from the cross-linkage of two infinite 2D [M(μ_3-C_5O_5)$_{0.5}$(μ_4-C_5O_5)$_{0.5}$(*anti*-dpe)$_{0.5}$] brick-wall layers by *gauche*-dpe ligands.

Metal coordination frameworks [1] have attracted much attention not only because of the wide variety of structural topologies that they exhibit but also for their potential applications as zeolite-like solids, in molecular selection, ion exchange and catalysis.[2] The design and synthesis of metal-organic networks *via* self-assembly of metal ions and multifunctional ligands depends both on the selection of the coordination geometry of the metal centres and on the coordination behaviour of the organic ligands. Many of these frameworks, including honeycomb, brick wall, grid, T-shape, ladder, diamondoid and octahedral geometries, have been generated using simple N,N′-donor spacers with rod-like characteristics, such as 4,4′-bipyridine (4,4′-bpy), pyrazine and related species.[3] Among the N,N′-donor spacers, 1,2-bis(4-pyridyl)ethane (bpe) represents an excellent alternative for structural research as it exhibits two different conformations, *gauche* and *anti*.[4–11] Several supramolecular motifs, including ladder (1D), brick wall (2D), molecular bilayer (2D) and frame (3D), based on the T-shape coordination configuration of metal centres with dpe have been created.[4–11] Amongst these motifs, the molecular bilayer is a novel motif that has not been reported until recent years.[5,11] However, simple octahedral polymers containing 2D bilayer motifs are rare and remain largely unexplored. In this contribution, we report on the preparation, crystal structure and thermal properties of [M(μ_3-C_5O_5)$_{0.5}$(μ_4-C_5O_5)$_{0.5}$(*anti*-dpe)$_{0.5}$(*gauche*-dpe)$_{0.5}$], **1** (M = Mn **1a**, Fe **1b**, Cd **1c**), which represents a remarkable new three-dimensional architecture sustained by a bilayered motif from the cross-linkage of two infinite 2D [M(μ_3-C_5O_5)$_{0.5}$(μ_4-C_5O_5)$_{0.5}$(*anti*-dpe)$_{0.5}$] brick-wall layers by *gauche*-dpe ligands.

Compounds **1a** (Mn) and **1b** (Fe) were synthesized by the reactions of $MnCl_2 \cdot 4H_2O$ or anhydrous $FeBr_2$ with 1,2-bis(4-pyridyl)ethane and disodium croconate ($Na_2C_5O_5$) in a 1:1:1 molar ratio in aqueous solution. After slow evaporation for several days, yellow-green crystals of **1a** and brown crystals of **1b** were obtained. Compound **1c** (Cd) was synthesized by stoichiometric mixing of $Cd(NO_3)_2 \cdot 4H_2O$ and disodium croconate with dpe in a 1:1:1 molar ratio in an aqueous solution (6 mL) at 180 °C (3 days) under hydrothermal conditions. The crystal structure of **1** is illustrated in Fig. 1 using **1a** as an example. X-Ray single-crystal analyses revealed that **1a**–**1c** are isostructural and contain two-dimensional brick-wall bilayers cross-linked by *gauche*-dpe, in which each metal centre has a slightly distorted {MN_2O_4} octahedral coordination sphere, with two nitrogen atoms from two dpe ligands (one *anti* and one *gauche*) located in *cis* positions and with four oxygen atoms from two croconate ligands (Fig. 1). The croconate and dpe both act as bridging ligands with two bridging modes, bis-bidentate through three adjacent (μ_3-) or four (μ_4-) oxygen atoms for C_5O_5 and two bridging conformations, *anti*, *gauche* for dpe, to connect the metal centres. The brick-like layer is formed with a rectangular grid as the basic building unit (Fig. 2), which consists of six metal atoms bridged by two μ_3-croconates, two μ_4-croconates and two bis-monodentate *anti*-dpe, giving rise to a 12-membered rectangular aperture [Fig. 3(a)] with approximate sizes of 18.12 × 7.26, 18.00 × 7.17 and 18.31 × 7.40 Å^2 for **1a**, **1b** and **1c**, respectively. Two layers inter-cross at an angle of *ca.* 55° and cross-linkage by an out-of-plane *gauche*-dpe in a bis-monodentate fashion gives a two-dimensional bilayer framework, as illustrated in Fig. 3(b). The interlayer distance is approximately 8 Å. A remarkable feature of **1** is that it is the first coordination polymer with a rectangular grid framework whose 2D bilayer motif is constructed by hybrid ligands, croconate and dpe, in which C_5O_5 adopts hybrid bridging modes (μ_3-, μ_4-croconates) and dpe adopts hybrid bridging conformations (*anti*-, *gauche*-dpe). It is also interesting to note that a new coordination polymer structural topology is formed, having a one-dimensional chain alternating trapezoid, inverse-trapezoid units in the

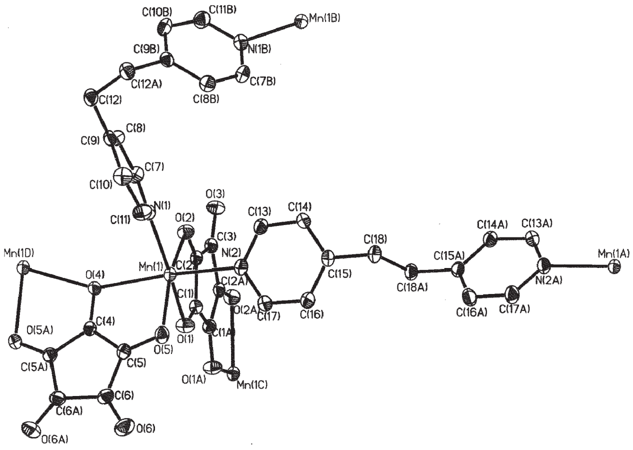


Fig. 1 ORTEP drawing of **1a** around the Mn centre (ellipsoids at 30% probability); the hydrogen atoms are omitted for clarity.

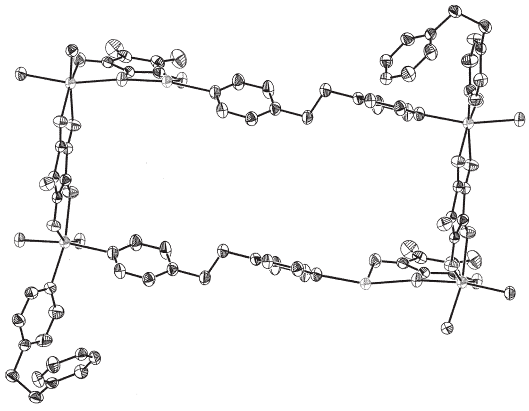
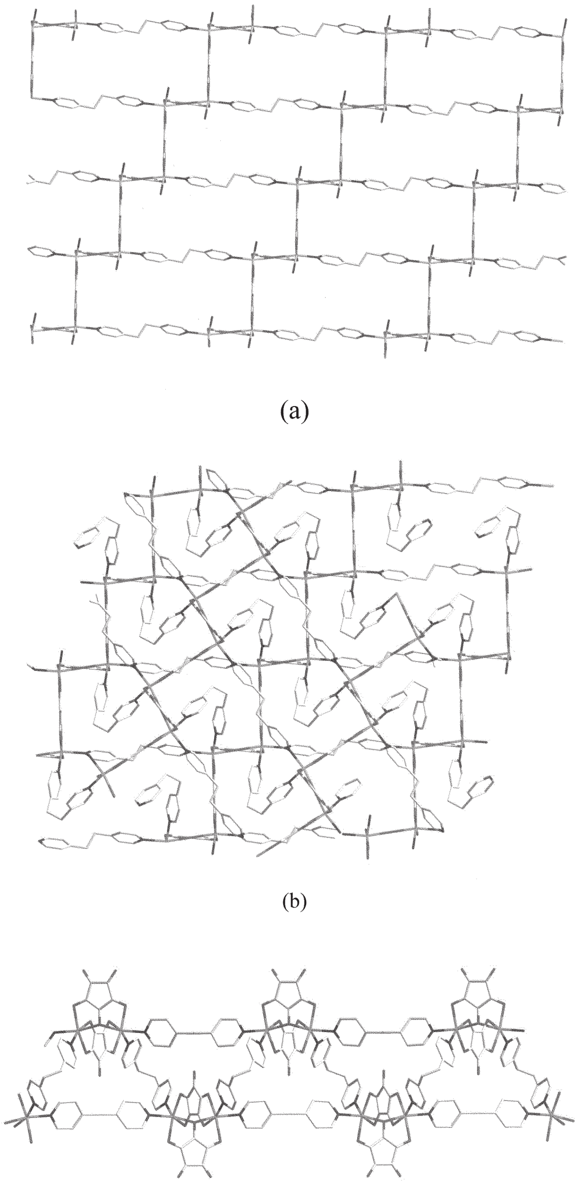


Fig. 2 Rectangular grid building unit of **1**, consisting of six metal atoms bridged by two μ3-croconates, two μ4-croconates and two *anti*-dpe.



(a)

(b)

(c)

Fig. 3 (a) One brick-like layer of **1** showing the rectangular grid as the basic building unit; (b) two-dimensional bilayer motif of **1** viewed along the *c* axis; (c) one-dimensional chain alternating trapezoid, inverse-trapezoid units in the bilayer of **1**, viewed along the *a* axis.

bilayer motif when viewed along the direction of the *a* axis [Fig. 3(c)].

To study the thermal stability of these materials, thermogravimetric analysis (TGA) was performed on polycrystalline samples of **1** heated with a ramp rate of 2 °C min^{-1} from room temperature to 800 °C under nitrogen flux. During the heating process, the TGA analyses show that all three compounds are stable and the 2D bilayer framework started decomposing at temperatures of 241, 250 and 310 °C for **1a**, **1b** and **1c**, respectively. The temperature-dependent magnetic moments of **1a** and **1b** both show an antiferromagnetic interaction among the metal centres through the croconate bridges. The detailed analysis of the magnetic phenomena exhibited by **1a** and **1b** is beyond the scope of this communication and will form the basis of a future contribution.

In conclusion, a novel coordination polymer containing an unusual two-dimensional bilayer motif has been synthesized under conventional aqueous conditions [**1a** (Mn), **1b** (Fe)] and hydrothermal conditions [**1c** (Cd)]. These compounds may be considered as the first examples of an octahedral structure containing a 2D bilayer motif formed by using hybrid ligands with hybrid bridging modes. Further work on this subject is in progress.

Experimental

Syntheses

1a. A solution (2 mL) of sodium croconate ($Na_2C_5O_5$, 18.9 mg, 0.1 mmol) was added to a solution (4 mL) of $MnCl_2\cdot 4H_2O$ (19.8 mg, 0.1 mmol) and 1,2-bis(4-pyridyl)ethane (18.7 mg, 0.1 mmol) at room temperature to give a clear solution. Yellow-green crystals were obtained after several days in *ca.* 68% yield. Anal. calcd for $C_{17}H_{12}MnN_2O_5$: C 53.84, N 7.39, H3.19; found: C 54.22, N 7.20, H 3.13.

1b. A solution (2 mL) of sodium croconate ($Na_2C_5O_5$, 18.9 mg, 0.1 mmol) was added to a solution (4 mL) of $FeBr_2$ (21.8 mg, 0.1 mmol) and 1,2-bis(4-pyridyl)ethane (18.7 mg, 0.1 mmol) at room temperature to give a clear solution. Brown crystals were obtained after several days in *ca.* 70% yield. Anal. calcd for $C_{17}H_{12}FeN_2O_5$: C 53.72, N 7.37, H 3.18; found: C 53.28, N 7.12, H 3.34.

1c. The reaction of $Cd(NO_3)_2\cdot 4H_2O$ (32.6 mg, 0.1 mmol), $Na_2C_5O_5$ (19.8 mg, 0.1 mmole), 4,4′-bpy (17.1 mg, 0.1 mmole) and deionized water (6 mL) was allowed to proceed at 180 °C for 3 days, then the reactant mixture was cooled at a rate of *ca.* 6 °C h^{-1} to give 36% yield (based on Cd) of **1c** as bright yellow sheet-like crystals, which were collected by mechanical isolation and washed with water. Anal. calcd for $C_{17}H_{12}CdN_2O_5$: C 46.76, N 6.41, H 2.77; found: C 45.91, N 6.81, H 2.51.

X-Ray crystallography

Crystallographic data for **1a**–**c** were collected on a Brucker SMART-CCD diffractometer using Mo(Kα) radiation ($\lambda = 0.7107$ Å). The data were corrected for Lorentz and polarization effects and for absorption using the SADABS program. Structures were solved using direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in geometrically calculated positions.†

Crystal data for 1a. Orthorhombic, *Pcca*, $a = 15.7601(2)$, $b = 8.9331(1)$, $c = 22.1109(3)$ Å, $U = 3112.92(3)$ Å^3, $Z = 8$,

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† CCDC reference numbers 228300–228302. See http://www.rsc.org/suppdata/nj/b3/b308379a/ for crystallographic data in .cif or other electronic format.

$D_c = 1.618$ g cm^{-3}, $T = 295(2)$ K, $\mu(\text{MoK}\alpha) = 0.880$ mm^{-1}, $F(000) = 1544$, $2\theta_{\max} = 27.5°$. Final residuals (for 229 parameters) were $R_1 = 0.0393$ and $wR_2 = 0.0921$ for 2665 reflections with $I > 2\sigma(I)$ and $R_1 = 0.0686$ and $wR_2 = 0.1114$ for all 3585 data.

Crystal data for 1b. Orthorhombic, *Pcca*, $a = 15.6685(11)$, $b = 8.8628(5)$, $c = 21.9418(13)$ Å, $U = 3047.0(3)$ Å^3, $Z = 8$, $D_c = 1.657$ g cm^{-3}, $T = 295(2)$ K, $\mu(\text{MoK}\alpha) = 1.023$ mm^{-1}, $F(000) = 1552$, $2\theta_{\max} = 27.5°$. Final residuals (for 228 parameters) were $R_1 = 0.0481$ and $wR_2 = 0.1115$ for 2791 reflections with $I > 2\sigma(I)$ and $R_1 = 0.0664$ and $wR_2 = 0.1202$ for all 3512 data.

Crystal data for 1c. Orthorhombic, *Pcca*, $a = 15.9401(8)$, $b = 9.0137(4)$, $c = 22.0831(11)$ Å, $U = 3172.9(3)$ Å^3, $Z = 8$, $D_c = 1.828$ g cm^{-3}, $T = 295(2)$ K, $\mu(\text{MoK}\alpha) = 1.408$ mm^{-1}, $F(000) = 1728$, $2\theta_{\max} = 27.5°$. Final residuals (for 228 parameters) were $R_1 = 0.0272$ and $wR_2 = 0.0636$ for 3139 reflections with $I > 2\sigma(I)$ and $R_1 = 0.0341$ and $wR_2 = 0.0668$ for all 3661 data.

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