

Charge-assisted Hydrogen-bonded Linear Second-sphere Assemblies $[M^{\text{II}}(\text{DABP})_3]_3[\text{Cr}(\text{C}_2\text{O}_4)_3]_2 \cdot 14\text{H}_2\text{O}$ ($M = \text{Cu}, \text{Ni}, \text{Fe}, \text{Zn}, \text{and Mn}$) with a Discrete $(\text{H}_2\text{O})_{14}$ Cluster of S_6 Symmetry

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A series of isomorphous second-sphere coordination compounds $[M^{\text{II}}(\text{DABP})_3]_3[\text{Cr}(\text{C}_2\text{O}_4)_3]_2 \cdot 14\text{H}_2\text{O}$ (DABP = 5,5'-diamino-2,2'-bipyridine; $M = \text{Cu}$ (1), Ni (2), Fe (3), Zn (4), and Mn (5)) have been constructed through multiple charge-assisted N–H⁺–O hydrogen-bonding interactions between the oxalate ligands in $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ (unit B) and the NH_2 groups in the $[M(\text{DABP})_3]^{2+}$ complex (unit A). The chiral $[M(\text{DABP})_3]^{2+}$ cations and $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ anions with the same Λ (or Δ) configuration interdigitate alternately, affording linear A_3B_2 secondary building units. Two adjacent A_3B_2 units adopting opposite configurations are linked by a six-cornered star-shaped 14-water cluster of S_6 symmetry (unit C) to form a racemic 1D linear chain $-A_3B_2(\Lambda)-C-A_3B_2(\Delta)-C-$. The microstructure of compound 1 shows a 3D flower-like morphology.

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Introduction

Crystal design of novel supramolecular architectures has attracted much interest in recent years.^[1] Hydrogen bonding has been an important aspect in supramolecular assembly owing to its combination of strength and directionality.^[2,3] The enhancement of hydrogen bond strength – which may be linked to robustness – by ionic charge has long been recognized and some of the strongest hydrogen bonds are ‘charge-assisted’, wherein the hydrogen bond donor and acceptor carry positive and negative ionic charges respectively.^[4,5] The tris(oxalate) chromate(III) anion, $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$, as a highly versatile chiral and paramagnetic building block, is an excellent partner in the formation of hydrogen-bonded functional solid-state assemblies.^[6] The $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ anion combines with its homologous chiral counter-cation $[\text{Cr}(\text{en})_3]^{3+}$ (en = ethylenediamine) or $[\text{Co}(\text{H}_2\text{oxado})_3]^{3+}$ (H_2oxado = oxamide dioxime) to yield the compounds $\Delta[\text{Cr}(\text{en})_3]-\Delta[\text{Cr}(\text{C}_2\text{O}_4)_3]$ ^[7a] and $[\text{Co}(\text{H}_2\text{oxado})_3][\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 5\text{H}_2\text{O}$,^[7b] respectively, in which chiral cations and anions are arranged alternately, forming 1D hydrogen-bonded chains or pillars. Moreover, metallic molecular salts $\beta'-(\text{BEDT-TTF})_4\text{A}[\text{M}(\text{C}_2\text{O}_4)_3]$, where BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene, A represents a monovalent cation such as NH_4^+ or K^+ , and M is a metal ion like Fe^{3+} , Cr^{3+} , Co^{3+} ,

Al^{3+} , or Ge^{4+} , have been reported to integrate the metallic conductivity and electron paramagnetism.^[8,9] Thus, the increasing interest in this chemistry is mainly justified by the search for new advanced materials possessing promising magnetic or other physical (such as electronic and optical) properties.^[10]

With the aim of synthesizing oxalate-based functional materials, we used the complexes $[M(\text{DABP})_3]^{2+}$ ($M^{\text{II}} = \text{Cu}$ (1), Ni (2), Fe (3), Zn (4), and Mn (5); DABP = 5,5'-diamino-2,2'-bipyridine) to assemble with the $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ anion. The $[M(\text{DABP})_3]^{2+}$ complexes^[11] have been previously reported in second-sphere coordination with nitrophenolate, crown ethers, carboxylate anions, and a tripodal tris(3-pyridylurea) ligand that led to a series of supramolecular assemblies through the hydrogen-bonding abilities of the amino groups in the DABP ligand.^[5a,12] Recently, we also reported a second-sphere linear chain compound, $[\text{Co}(\text{DABP})_3][\text{Fe}(\text{CN})_6]$, which showed a uniform and perfect hexagonal microrod morphology.^[13] Here, we continue the approach of second-sphere coordination of $[M(\text{DABP})_3]^{2+}$ with oxalate, and five hydrogen-bonded compounds $[M(\text{DABP})_3]_3[\text{Cr}(\text{C}_2\text{O}_4)_3]_2 \cdot 14\text{H}_2\text{O}$ (1–5) are described. The microstructures and surface morphology of compound 1 ($M = \text{Cu}$) are also studied.

Results and Discussion

Bulk single crystals of compounds **1–5** suitable for X-ray diffraction analysis were obtained at room temperature by diffusion of an aqueous solution of $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$ with a water/methanol (v/v, 1:4) solution of $[M(DABP)_3]X$ ($X = SO_4, Cl_2$ or $(NO_3)_2$).^[11] To slow down the diffusion process, a layer of water/methanol (v/v, 1:1) was introduced in between the two phases. The compounds have melting points above 300°C and are only soluble in DMF and DMSO and insoluble in other common organic solvents.

IR spectra (Fig. S1 in the accessory publication) of the five compounds show absorption bands in the range 1678–1679 cm^{-1} (ν_{CO}) and 807–809 cm^{-1} (δ_{CO}), which are typical of the oxalate ligand. The bands at 3336–3342 and 3217–3222 cm^{-1} are assigned to the symmetric and asymmetric NH stretch, and are obviously red-shifted relative to those of free $[Fe(DABP)_3]SO_4 \cdot 9H_2O$ (3420 and 3340 cm^{-1}),^[11] indicating the formation of hydrogen bonds from amino groups to the oxalate oxygen atoms (see below).^[14]

Single-crystal X-ray diffraction analyses reveal that the five compounds are isomorphous, crystallizing in the space group $R\bar{3}c$. Thus only the compound $[Cu(DABP)_3][Cr(C_2O_4)_3] \cdot 2 \cdot 14H_2O$ (**1**) is described in detail as a representative. The structure of **1** is built of $[Cu(DABP)_3]^{2+}$ cations (unit A), $[Cr(C_2O_4)_3]^{3-}$ anions (unit B), and 14-water clusters (H_2O)₁₄ (unit C) (Fig. 1). The first-sphere complex $[Cu(DABP)_3]^{2+}$ exhibits a pseudo-octahedral tris(chelate)-metal environment that is similar to the previously published $[M(DABP)_3]^{2+}$.^[11] The Cr atom is chelated by three oxalate ligands in a slightly distorted octahedron. The carboxylate groups of the oxalate ligands are not coplanar and the two $-CO_2$ entities are twisted by 8.1° with respect to each other around the C–C bond.

The $[Cu(DABP)_3]^{2+}$ cations and $[Cr(C_2O_4)_3]^{3-}$ anions are connected by multiple charge-assisted N–H...O hydrogen-bonding interactions between the NH_2 groups of DABP and negatively charged oxygen atoms of oxalate ligands (Fig. 1a),

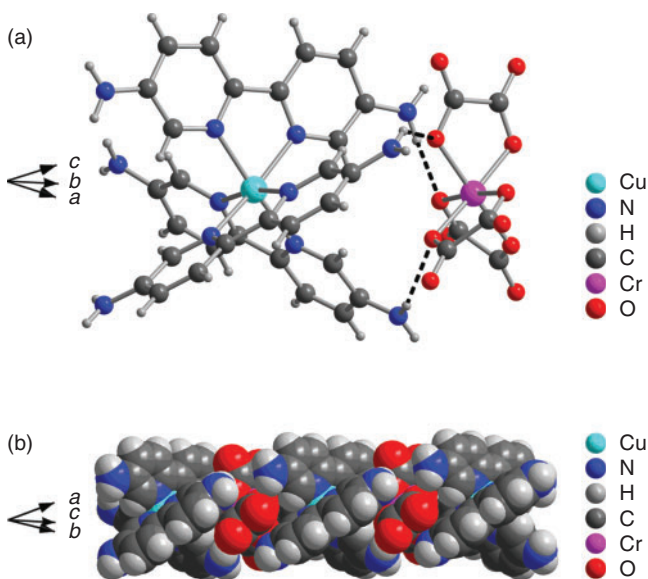


Fig. 1. (a) Molecular structure of the $[Cu(DABP)_3]^{2+}$ cation (unit A) and $[Cr(C_2O_4)_3]^{3-}$ anion (unit B) with the charge-assisted N–H...O hydrogen bonding. (b) Space-filling representation of an A_3B_2 secondary building unit with the interdigitation along the clefs of the C_3 -symmetric tris-chelate complexes.

forming $[Cu(DABP)_3]_3[Cr(C_2O_4)_3]_2$ (A_3B_2) aggregates or secondary building units (SBU) (Fig. 1b). Within the A_3B_2 SBU, an effective Coulomb attraction of the highly charged metal complexes ($2+/3-$) provides a close fit or interdigitation along the clefs of the $[Cu(DABP)_3]^{2+}$ and $[Cr(C_2O_4)_3]^{3-}$ building units. The nearest cation–anion approach (Cu–Cr ~ 6.2 Å) coincides with the orientation of the $[Cu(DABP)_3]^{2+}$ cation and $[Cr(C_2O_4)_3]^{3-}$ anion along their C_3 axes (parallel to the abc diagonal) (Fig. 1b). The A_3B_2 aggregates are capped by and separated along the abc diagonal by the 14-water clusters via N–H...O(water) hydrogen-bonding interactions. As a result, an infinite 1D linear chain is formed along the C_3 axis, with a repeating pattern of ...[ABABA]C[ABABA]C... (Fig. 2).

In the hydrogen-bonded five-metal $[Cu(DABP)_3]_3[Cr(C_2O_4)_3]_2$ (A_3B_2) SBU (Fig. 1b), each $[Cr(C_2O_4)_3]^{3-}$ anion accepts six N–H...O hydrogen bonds from two neighbouring $[Cu(DABP)_3]^{2+}$ cations (three N2–H2A–O2 bonds from Cu1 unit and three N4–H4C–O1 bonds from Cu2 unit; see Table 1). Meanwhile, each $[Cu(DABP)_3]^{2+}$ cation donates six N–H...O hydrogen bonds to two neighbouring $[Cr(C_2O_4)_3]^{3-}$ anions (cf. Fig. 1a). The $(H_2O)_{14}$ cluster, associated by O–H...O hydrogen bonds, links two terminal $[Cu(DABP)_3]^{2+}$ cations belonging to two $[Cu(DABP)_3]_3[Cr(C_2O_4)_3]_2$ units via six N–H...O_w contacts (Fig. 2b). The $(H_2O)_{14}$ cluster forms a six-cornered star with S_6 symmetry when the hydrogen-bonded O–O contacts from 2.69 to 3.1 Å (typical for embedded water clusters)^[15] between the 14 O atoms are taken into account (Fig. 3). The star-shaped $(H_2O)_{14}$ cluster is constructed from six corrugated six-membered rings (in the book conformation) that are mutually fused through two adjacent edges each (Fig. 3). Although such a discrete water cluster cannot be given an exact motif according to Infantes' classification for $(H_2O)_n$ clusters,^[16] its structure is very similar to another $(H_2O)_{14}$ aggregate reported recently that also features the fused, book-conformation cyclic hexamers.^[17]

Both tris-chelated $[Cu(DABP)_3]^{2+}$ and $[Cr(C_2O_4)_3]^{3-}$ units have metal-centered Λ or Δ -chirality. In each A_3B_2 SBU, all five interdigitating ionic metal complexes (three $[Cu(DABP)_3]^{2+}$ cations and two $[Cr(C_2O_4)_3]^{3-}$ anions) adopt the same Λ (or Δ) configuration (Λ in Fig. 1b),^[12b] as required by the interdigitation for close fit, which could not be achieved otherwise. However, this chirality is interrupted by the $(H_2O)_{14}$ cluster, so that two adjacent A_3B_2 SBUs separated by the $(H_2O)_{14}$ cluster have opposite configurations (Fig. 2b). Hence, each hydrogen-bonded infinite 1D chain is formed by a repeating configuration $-A_3B_2(\Lambda)-C-A_3B_2(\Delta)-C-$ and the compound is racemic.

Hydrogen-bonding interactions also exist between the adjacent chains (Fig. 2b and Fig. 4). Six non-coordinating oxygen atoms (O_3, O_4) of one anionic $[Cr(C_2O_4)_3]^{3-}$ complex accept N–H...O hydrogen bonds from the amino groups of $[Cu(DABP)_3]^{2+}$ in the six surrounding chains (Table 1, Fig. 4a). Meanwhile, each $(H_2O)_{14}$ cluster donates six O–H...O bonds to six non-coordinating O atoms of oxalate ligands from six surrounding chains (O03–O03, 2.968(6) Å, Fig. 4b). Compared with the short cation–anion approach along the C_3 axes (6.2 Å), the next closest Cu–Cr contacts are ~ 11.1 Å. The packing diagram (Fig. 4c) shows that each $-A_3B_2-C-A_3B_2-C-$ chain is surrounded by six neighbouring chains.

Morphology of the Aggregates of Compound **1**

The morphology of materials may have great effects on their physical, chemical and biological properties. At present, morphological control focusses mainly on classical inorganic structures such as metals, oxides, sulfides, and ceramic materials,

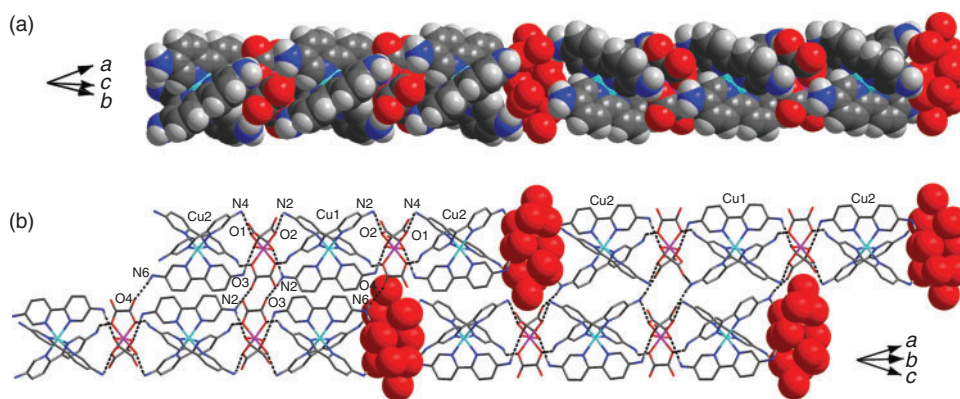


Fig. 2. (a) Space-filling representation of two A_3B_2 SBUs separated and capped by 14-water clusters. (b) Two parallel 1D chains (note the shift by one A + B-unit along abc -diagonal axis) linked by charge-assisted N-H...O and O-H...O interactions (the 14-water clusters are drawn in the space-filling mode; see also Fig. 3).

Table 1. N-H...O hydrogen-bonding interactions in compound **1**

N-H...O	Symmetry code	H-O	N-O	N-H	\angle N-H-O
Intra- A_3B_2C chain					
N4-H4C-O1	y, z, x	2.41	3.081(5)	0.86	135.3
N2-H2A-O2	y, z, x	2.24	2.938(4)	0.86	138.3
Interchain					
N2-H2B-O3	$-x + 1, -y + 1, -z$	1.99	2.819(5)	0.86	162.1
N6-H6B-O4	$y - 1/2, x + 1/2, z + 1/2$	2.03	2.876(5)	0.86	165.7
N6-H6C-O02		2.14	2.974(7)	0.86	162.5

whereas micro- and nanoscale materials based on supramolecular structures have been less studied. Very recently, there have been some investigations of nanoscale metal-organic frameworks (NMOFs),^[18] but morphological studies of hydrogen-bonded frameworks remain unexplored.^[13]

The microstructure and surface morphologies of the molecular aggregates of the compound $[Cu(DABP)_3]_3[Cr(C_2O_4)_3]_2 \cdot 14H_2O$ (**1**) were studied by field-emission scanning electron microscope (FE-SEM). The samples for microstructure analysis were prepared using a precipitation method in the presence of an equivalent amount of hexadecyltrimethylammonium bromide (CTAB) as a surfactant. As shown in Figs 5, 3d, flowerlike products were obtained by this method. The powders consist of 2D nanosheets (Fig. 5a, b), which are free of aggregation and assemble as 'petals' into flowerlike structures. The high-magnification images (Fig. 5c, d) indicate that the diameter of the flowers is $\sim 7.5 \mu m$ and the thickness of the nanosheets is ~ 100 – 150 nm. Powder X-ray diffraction (PXRD) reveals that the flowerlike materials have the same structure as the bulk crystals of **1** (Fig. S2). In addition to PXRD spectra, the IR spectra and analytical data also confirmed that the flowerlike products have identical inner structures but different outer shapes to the bulk crystalline solids (see Experimental Section and Fig. S3).

Conclusions

In summary, we obtained five isomorphous hydrogen-bonded compounds $[M^I(DABP)_3]_3[Cr(C_2O_4)_3]_2 \cdot 14H_2O$ through second-sphere coordination. The chiral $[M(DABP)_3]^{2+}$ cations (A) and $[Cr(C_2O_4)_3]^{3-}$ anions (B) of the same Λ (or Δ) configuration interdigitate alternately into linear A_3B_2 secondary building units, which are further linked by a star-shaped $(H_2O)_{14}$ cluster

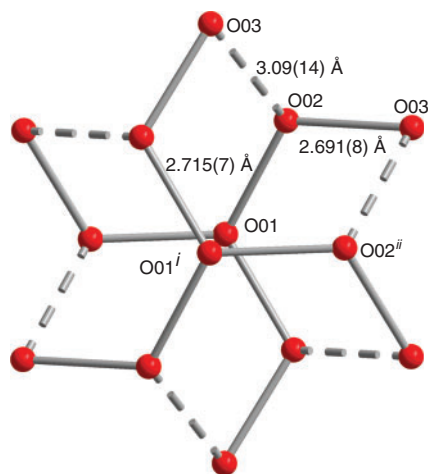


Fig. 3. Topology of the $(H_2O)_{14}$ cluster in **1** with S_6 symmetry. The S_6 axis passes through O01 and O01ⁱ. The three unique O-O contacts are labelled with their distances. Symmetry codes: $i = 1 - x, 1 - y, 1 - z$; $ii = 1 - z, 1 - x, 1 - y$.

of S_6 symmetry (unit C) to form a racemic 1D linear chain $-A_3B_2(\Lambda)-C-A_3B_2(\Delta)-C-$. In addition, a 3D flowerlike morphology of **1** was obtained via a precipitation method in the presence of CTAB surfactant.

Experimental

General

The ligand DABP and its complexes, $[Cu(DABP)_3]Cl_2$, $[Ni(DABP)_3]Cl_2$, $[Fe(DABP)_3]SO_4$, $[Zn(DABP)_3](NO_3)_2$, and

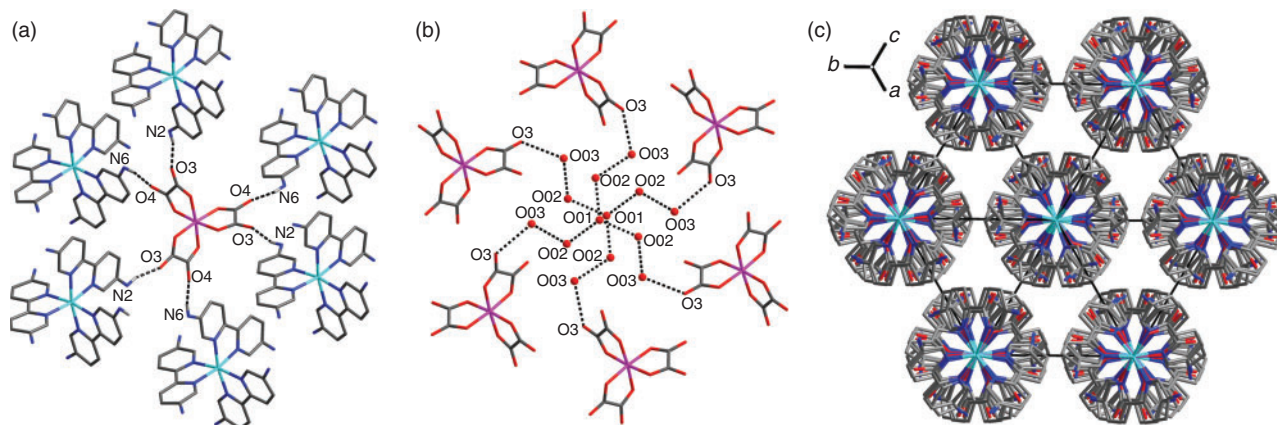


Fig. 4. (a) Each $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ anion links six neighbouring $[\text{Cu}(\text{DABP})_3]^{2+}$ cations through charge-assisted $\text{N}-\text{H}\cdots\text{O}$ interactions. (b) Each $(\text{H}_2\text{O})_{14}$ cluster links six neighbouring $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ anions through charge-assisted $\text{O}-\text{H}\cdots\text{O}$ interactions. (c) Packing diagram of **1** showing the arrangement of seven neighbouring chains.

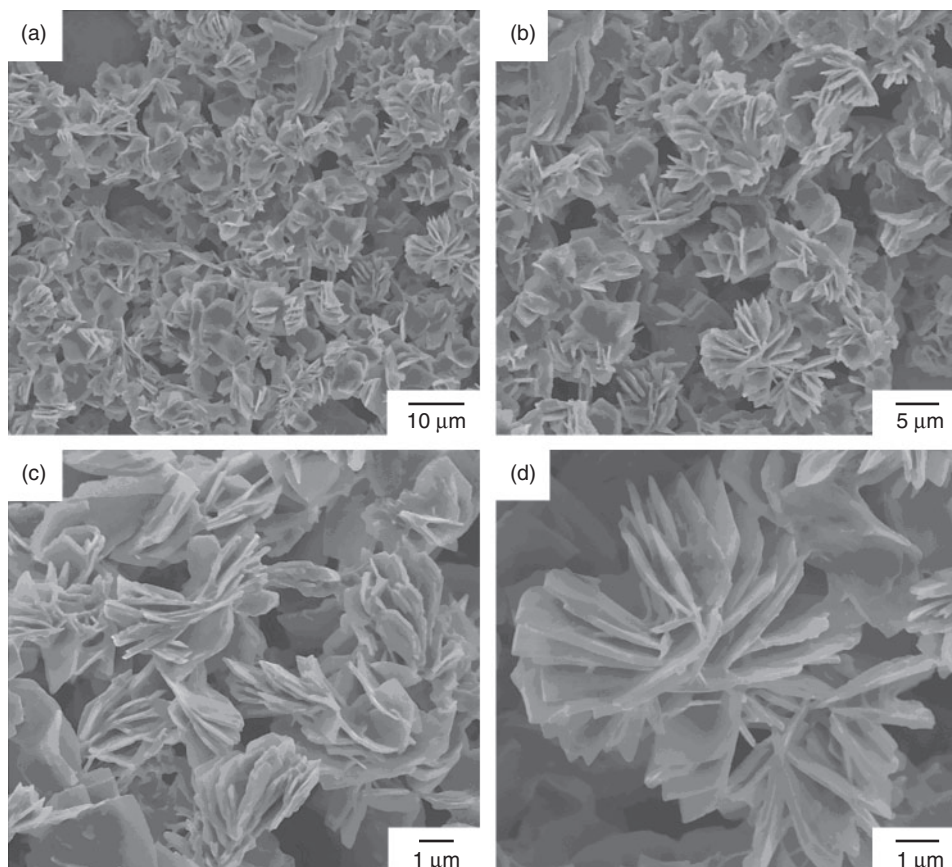


Fig. 5. Field-emission scanning electron microscope (FE-SEM) images of **1**, (a, b) low magnification; (c, d) high magnification.

$[\text{Mn}(\text{DABP})_3]\text{Cl}_2$, were prepared following previously published procedures.^[11] The oxalate that serves as the second-sphere ligand, $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$, was prepared as described in the literature^[19] and purified by recrystallization from water.

Elemental analyses for C, H, and N were performed on a VarioEL instrument from Elementar Analysensysteme GmbH. IR spectra were recorded on a Nicolet AVATAR 360 Fourier-transform (FT)-IR spectrometer as KBr disks. Powder X-ray diffraction patterns were obtained with a D/max RB diffractometer using $\text{Cu K}\alpha$ radiation. The FE-SEM images were taken

using a field-emission scanning electron microscope (JEOLJSM-6701F) operated at an accelerating voltage of 5 kV.

Synthesis of $[\text{Cu}(\text{DABP})_3]_3[\text{Cr}(\text{C}_2\text{O}_4)_3]_2\cdot 14\text{H}_2\text{O}$ (**1**)

An aqueous solution (1 mL) of $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$ (2.0 mg, 0.005 mmol) in a test tube was layered first with water/methanol (5 mL, 1:1 v/v) and then with a water/methanol solution (2 mL, 1:4 v/v) of in situ-prepared $[\text{Cu}(\text{DABP})_3]\text{Cl}_2$ (5.0 mg, 0.0075 mmol). After several days, deep-green crystals were formed at the boundary layer. Yield: 3 mg (44%). M.p. $> 300^\circ\text{C}$. Anal. calc. for

$C_{102}H_{118}Cr_2Cu_3N_3O_{38}$ (2750.94): C 44.53, H 4.32, N 18.33. Found: C 44.52, H 3.95, N 18.72%. ν_{\max} (KBr/cm⁻¹): 3411 (m, br), 3336 (s, br), 3218 (m, br), 1703 (s), 1679 (s, br), 1604 (s), 1581 (m), 1490 (w), 1434 (m), 1386 (m), 1323 (m), 1273 (m), 1255 (m), 1159 (w), 1117 (w), 1060 (w), 1034 (w), 895 (w), 835 (w), 808 (m), 723 (w), 658 (w).

Synthesis of [Ni(DABP)₃][Cr(C₂O₄)₃]₂·14H₂O (2)

Compound **2** was prepared by a similar method to that for **1**, except that [Cu(DABP)₃]Cl₂ was replaced by equivalent in situ-prepared [Ni(DABP)₃]Cl₂. Deep-orange crystals were isolated. Yield: 2 mg (30%). M.p. > 300°C. Anal. calc. for $C_{102}H_{118}Cr_2Ni_3N_3O_{38}$ (2736.45): C 44.77, H 4.35, N 18.43. Found: C 44.41, H 4.05, N 18.63%. ν_{\max} (KBr/cm⁻¹): 3419 (m, br), 3338 (s, br), 3219 (m, br), 1699 (s), 1679 (s, br), 1601 (s), 1581 (m), 1487 (w), 1433 (m), 1386 (m), 1321 (m), 1300 (m), 1255 (m), 1159 (w), 1117 (w), 1059 (w), 1034 (w), 969 (w), 902 (w), 831 (w), 808 (m), 727 (w), 658 (w), 610 (w).

Synthesis of [Fe(DABP)₃][Cr(C₂O₄)₃]₂·14H₂O (3)

Compound **3** was prepared by a similar method to that for **1**, except that [Cu(DABP)₃]Cl₂ was replaced by equivalent in situ-prepared [Fe(DABP)₃]SO₄. Red crystals were isolated. Yield: 4 mg (59%). M.p. > 300°C. Anal. calc. for $C_{102}H_{118}Cr_2Fe_3N_3O_{38}$ (2727.87): C 44.91, H 4.36, N 18.49. Found: C 45.26, H 4.50, N 18.79%. ν_{\max} (KBr/cm⁻¹): 3412 (m, br), 3340 (s, br), 3221 (s, br), 1700 (m), 1679 (s, br), 1600 (s), 1577 (s), 1486 (s), 1432 (m), 1386 (s), 1321 (m), 1298 (m), 1255 (m), 1150 (w), 1117 (w), 1054 (w), 1027 (w), 884 (w), 825 (w), 807 (m), 724 (w).

Synthesis of [Zn(DABP)₃][Cr(C₂O₄)₃]₂·14H₂O (4)

Compound **4** was prepared by a similar method to that for **1**, except that [Cu(DABP)₃]Cl₂ was replaced by equivalent in situ-prepared [Zn(DABP)₃](NO₃)₂. Brown crystals were isolated. Yield: 3 mg (44%). M.p. > 300°C. Anal. calc. for $C_{102}H_{118}Cr_2Zn_3N_3O_{38}$ (2756.43): C 44.45, H 4.31, N 18.29. Found: C 44.44, H 3.98, N 18.73%. ν_{\max} (KBr/cm⁻¹): 3419 (m, br), 3342 (s, br), 3222 (m, br), 1698 (s), 1678 (s, br), 1601 (s), 1582 (s), 1489 (s), 1432 (m), 1385 (s), 1320 (m), 1274 (m), 1255 (m), 1161 (w), 1105 (w), 1060 (w), 1032 (w), 904 (w), 832 (w), 808 (m), 728 (w), 703 (w), 656 (w), 596 (w).

Synthesis of [Mn(DABP)₃][Cr(C₂O₄)₃]₂·14H₂O (5)

Compound **5** was prepared by a similar method to that for **1**, except that [Cu(DABP)₃]Cl₂ was replaced by equivalent in situ-prepared [Mn(DABP)₃]Cl₂. Deep-orange crystals were isolated. Yield: 2 mg (30%). M.p. > 300°C. Anal. calc. for $C_{102}H_{118}Cr_2Mn_3N_3O_{38}$ (2725.14): C 44.96, H 4.36, N 18.50. Found: C 45.10, H 4.05, N 18.87%. ν_{\max} (KBr/cm⁻¹): 3417 (m, br), 3339 (m, br), 3217 (m, br), 1697 (m), 1678 (s, br), 1601 (s), 1580 (m), 1488 (s), 1430 (m), 1386 (s), 1318 (m), 1297 (m), 1256 (m), 1162 (w), 1099 (w), 1056 (w), 1031 (w), 899 (w), 831 (w), 808 (m), 727 (w), 699 (m), 657 (w), 597 (w).

Synthesis of the Samples of **1** for Microstructural Studies

Samples for the microstructure and morphology studies of compound **1** were fabricated by a precipitation method at room temperature. In situ-prepared [Cu(DABP)₃]Cl₂ (0.015 mmol) was added to a methanol solution of 1 equivalent of surfactant CTAB (10 mL, 5.0 mg, 0.015 mmol), to which was added an aqueous solution of K₃[Cr(C₂O₄)₃]·3H₂O (10 mL, 5.0 mg, 0.01 mmol) drop by drop under vigorous stirring. The precipitated product

was washed with water and acetone via centrifugation to remove excess CTAB, and finally dissolved in ethanol. Yield: 7 mg (51%). M.p. > 300°C. Anal. calc. for $C_{102}H_{118}Cr_2Cu_3N_3O_{38}$ (2750.94): C 44.53, H 4.32, N 18.33. Found: C 44.75, H 3.75, N 18.37%. ν_{\max} (KBr/cm⁻¹): 3412 (m, br), 3336 (m, br), 3219 (m, br), 1702 (s), 1679 (s, br), 1603 (s), 1581 (m), 1490 (w), 1434 (m), 1386 (m), 1323 (m), 1273 (m), 1255 (m), 1159 (w), 1060 (w), 1035 (w), 896 (w), 835 (w), 808 (m), 723 (w), 658 (w).

X-Ray Crystallography

Diffraction data for the compounds **1–5** were collected on a Bruker SMART APEX II diffractometer at room temperature (293 K) with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). An empirical absorption correction using *SADABS* was applied for all data.^[20] The structures were solved by direct methods using the *SHELXS* program. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 by the use of the program *SHELXL*.^[21] Hydrogen atoms bonded to carbon and nitrogen were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Hydrogen atoms of the crystal water molecules were not included.

Accessory Publication

Cambridge Crystallographic Data Centre (CCDC) Nos. 781614–781618 contain the supplementary crystallographic data for this paper. Crystal data and IR and PXRD spectra of the compounds are available on the Journal's website.

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