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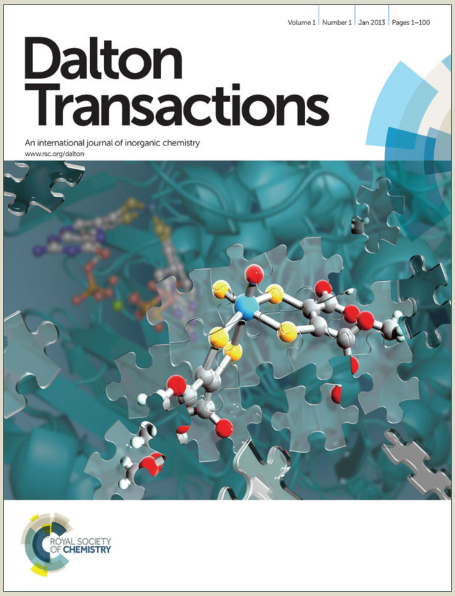

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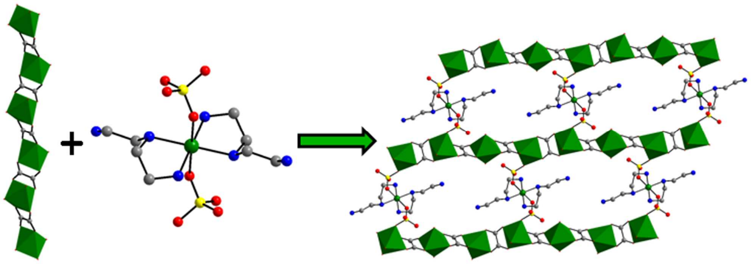

Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

New open-framework cobalt sulfate-oxalates based on molecular and chain-like building blocks†

Kangcai Wang,[a] Daibing Luo,[b] Dingguo Xu,*[a] Furong Guo,[a] Lin Liu[a] and Zhien Lin*[a]

Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X

DOI: 10.1039/b000000x

Presented here are two novel open-framework cobalt sulfate-oxalates constructed from molecular and chain-like building blocks. The two compounds have different structures: a hcb-type layer with 20-ring windows and a mog-type framework with 12-ring channels. Amine molecules play dual roles in the two structures: chelating ligand and charge-balancing agent.

The synthesis of new crystalline open-framework materials has advanced extensively due to their potential applications in gas storage, separation, catalysis, and sensing.[1] Zeolites are the most well-known such materials constructed from corner-sharing TO_4 tetrahedra (T = Si, Al). Since the discovery of aluminophosphate molecular sieves in 1982, great efforts have been devoted to the synthesis of new open-framework inorganic solids containing different oxoanions, such as metal phosphates, germanates, phosphites, borates, sulfates.[2] The variation of oxoanins in zeotype material synthesis not only diversifies their chemical compositions and framework topologies, but also pushes the existing maximum channel size from 14-member ring (14 MR) in zeolites forward up to 72 MR in metal phosphites.[3] Another class of crystalline porous materials are known as metal-organic frameworks.[4] These materials consist of metal ions or metal clusters as the nodes, and organic ligands as the linkers. By choosing suitable organic linkers with different lengths, the isoreticular expansion of the pore apertures of metal-organic frameworks may be achieved.[5]

Open-framework hybrid solids are of current interest because they combine both advantages of zeolitic inorganic solids (e.g., good thermal stability, active sites for catalysis) and metal-organic frameworks (e.g., low density, high surface area).[6] The flexibility of organic ligands indicates that the rational design of hybrid frameworks may be realized through judicious choice of organic linkers. As a simple multidentate organic ligand, oxalate has been extensively studied due to its strong ability to bind metal ions in various coordination modes.[7] During the past years, a large number of metal phosphate-oxalate hybrid solids have been prepared and structurally characterized.[8] A notable example is the gallium phosphate-oxalate NTHU-6, which is an unprecedented intrinsic yellow luminescent phosphor.[9] In comparison, open-framework metal sulfate-oxalates, especially those containing transition metals, have been rarely reported.[10]

Hydrothermal crystallization is a common method for the synthesis of zeolitic materials. The development of new synthetic methods is highly desired since the formation of open-framework strucures is sensive to the synthetic conditions.[11] Recently, we develop a solvent-free approach for the synthesis of new metal phosphites, metal oxalates, and related inorganic-organic hybrid solids.[12] As part of our continuous work in this system, here we report the facile synthesis of two new open-framework cobalt sulfate-oxalates, namely, $Co_2(Hdeta)(H_2O)_2(SO_4)(C_2O_4)_{1.5}$ (**1**), and $Co_{1.5}(Haep)(SO_4)(C_2O_4)$ (**2**), where deta = diethylenetriamine (melting point: -35 °C), and aep = 1-(2-aminoethyl)piperazine (melting point: -19 °C). Structural analysis reveals that compound **1** has a hcb-type layered structure with 20-ring windows, while compound **2** has a mog-type framework with 12-ring channels.‡ Their framework structures are constructed from molecular and chain-like building blocks, which can be isolated as good quality single crystals.

Red crystals of compound **1** were obtained by heating a mixture of $CoSO_4·7H_2O$, $H_2C_2O_4·2H_2O$, and deta in a molar ratio of 1:1:1 at 150 °C for 8 days (43.6 % yield based on cobalt). The increasement of the amounts of $CoSO_4·7H_2O$ and/or

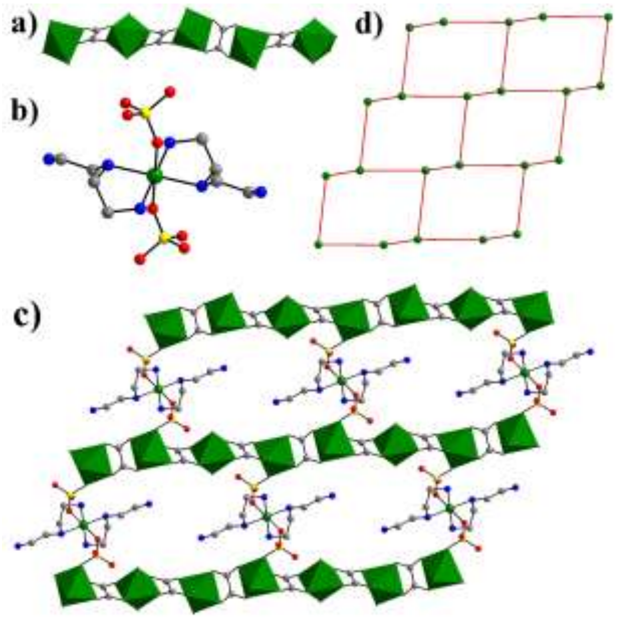

Fig.1. (a) The cobalt oxalate chain. (b) The linear $Co(Hdeta)_2(SO_4)_2$ trimer. (c) A view of the layered structure of **1** with 20-ring window. (e) The structure of **1** has a hcb topology. Color code: cobalt/CoO_6 octahedra, green; sulfur, yellow; oxygen, red; carbon, gray, nitrogen, blue.

$H_2C_2O_4\cdot 2H_2O$ in the reaction (e.g., $CoSO_4\cdot 7H_2O$:$H_2C_2O_4\cdot 2H_2O$: deta = 2:1.5:1, an ideal molar ratio of reagents for **1**) only produced unindentified powders. CHN elemental analysis gave C 17.37%, H 3.65% and N 8.42%, consistent with the calculated values of C 17.29%, H 3.73% and N 8.64 %. The powder X-ray diffraction pattern of as-synthesized compound is in good agreement with the simulated one on the basis of single crystal data, indicating the phase purity of as-synthesized compound (Fig. S1, ESI†). The IR spectrum indicates the presence of oxalate and sulfate units in the structure (Fig. S2, ESI†). The strong bands at 1620 and 1320 cm^{-1} correspond to the C=O and C–O stretching vibrations in the oxalate groups, respectively. The band at 1100 cm^{-1} is due to the asymmetric stretch of SO_4 tetrahedra.

Compound **1** crystallizes in the triclinic space group *P*-1 (no. 2). The asymmetric unit contains three cobalt atoms, one and a half of oxalate ligands, one SO_4 tetrahedron, two water molecules, and one monoprotonated deta cation. Co(1) atom locates in a general position, while Co(2) and Co(3) atoms locates in special positions with two fold symmetry. All the cobalt atoms are octahedrally coordinated with the Co–O(N) bond lengths ranging from 2.0676(18) Å to 2.2685(19) Å. Each oxalate ligands adopts a typical bisbidentate chelating coordination mode to connect two cobalt atoms to form a chain-like structure, as shown in Fig. 1a. It is noteworthy that four nitrogen atoms from two Hdeta cations locate in the equatorial sites of Co(3) atom, leaving two axial sites occupied by two sulfate oxygen atoms. As a result, a linear $Co(Hdeta)_2(SO_4)_2$ trimer was formed (Fig. 1b), which acts as a bridge between two cobalt oxalate chains.

The linkages between $Co(Hdeta)_2(SO_4)_2$ trimers and cobalt oxalate chains create a layered structure with extra-large 20-ring windows (delimited by 2 CoO_2N_4 octahedra, 4 SO_4 tetrahedra, 6 oxalate ligands, and 8 CoO_6 octahedra), as shown in Fig. 1c. By regarding the Co(1) atoms as 3-connected nodes, the structure has a hcb topology (Fig. 1d). It should be pointed out that layered metal oxalates, such as $[H_3N(CH_2)_3NH_3]^{2+}[Zn_2(C_2O_4)_3]^{2-}\cdot 3H_2O$, often adopt hcb structures with 12-ring apertures.[13] The insertion of $Co(Hdeta)_2(SO_4)_2$ trimers between metal oxalate chains in the structure of **1** could expand the pore aperture from 12-ring to 20-ring.

Red crystals of compound **2** were obtained by heating a mixture of $CoSO_4\cdot 7H_2O$, $H_2C_2O_4\cdot 2H_2O$, and aep in a molar ratio of 1.5:1:1 (an ideal molar ratio of reagents for **2**) at 170 °C for 8 days (44.3 % yield based on cobalt). Elemental analysis calcd for **2**: C, 23.86%; H, 4.00%; N, 10.43 %; Anal. Found: C 23.25%; H 3.83%; N 10.19%. The phase purity of this compound is confirmed by powder X-ray diffraction (Fig. S3, ESI†). The IR spectrum indicates the existence of both oxalate and sulfate units (Fig. S4, ESI†). The bands at 1620 cm^{-1} and 1320 cm^{-1} are characteristic of the stretching vibrations of C=O and C–O in oxalate ligands, while the band for SO_4 units appear at 1080 cm^{-1}.

Compound **2** crystallizes in the triclinic space group *P*-1 (no. 2). The asymmetric unit contains two crystallographically independent cobalt atoms, both of which have octahedral coordination environments. Co(1) atom locates in a general position, bonded by four oxalate oxygen atoms and two sulfate oxygen atoms. Co(2) atom lies on an inversion center, coordinated by two sulfate oxygen atoms and four nitrogen atoms from two monoprotonated aep cations. The Co–O(N) bond lengths are between 2.072(2) Å to 2.384(3) Å.

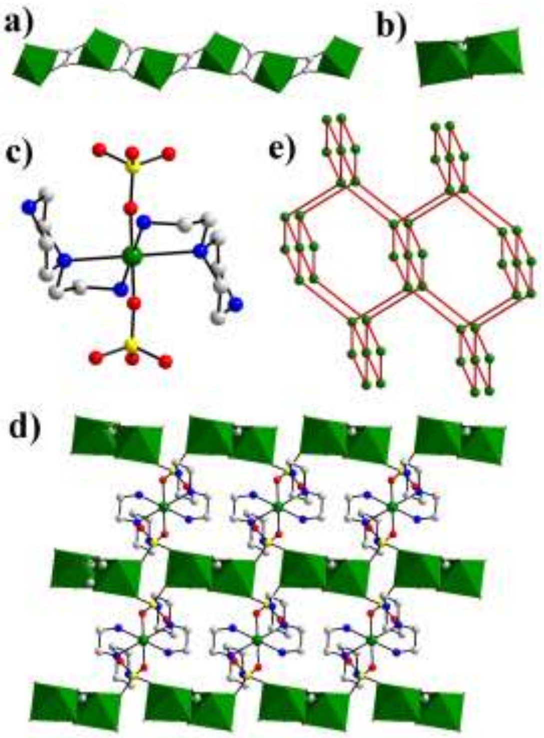

Fig.2. (a) A side and (b) perspective view of the cobalt oxalate chain. (c) The linear $Co(Hape)_2(SO_4)_2$ trimer. (d) A view of the three-dimensional structure of **2** with 12-ring channels. (e) The structure of **2** has a rare mog topology. Color code: cobalt/CoO_6 octahedra, green; sulfur, yellow; oxygen, red; carbon, gray, nitrogen, blue.

Similar as compound **1**, there are two types of building blocks in compound **2**: cobalat oxalate chain and $Co(Haep)_2(SO_4)_2$ trimer (Fig. 2a-2c). The cobalt oxalate chains run along the [001] direction and bridged by $Co(Haep)_2(SO_4)_2$ trimers to form a three-dimensional structure, as shown in Fig. 2d. Each $Co(Haep)_2(SO_4)_2$ trimer in the structure make four S–O–Co connections to four adjacent cobalt oxalate chains. Viewed along the [100] and [001] direction, the compound exhibit different 12-ring channels. By regarding the Co(1) atoms and $Co(Haep)_2(SO_4)_2$ trimers as 4-connectd nodes, the framework structure of **2** has a mog topology (Fig. 2e). Such 4-connected topology is of particular interest since it combine both left- and right-handed features of quartz-type framework.

The framework structure of **2** can be alternatively understood as a pillared layered structure. As seen in Fig. S5 (ESI†), the linkages between Co(1) atoms, oxalate ligands, and SO_4 tetrahedra result in the formation of layered structures parallel to the *ac* plane. The $Co(Haep)_2$ complexes reside within the interlayer region and act as pillars to connect adjacent layers into a three-dimensional structure. In metal sulfate-oxalate chemistry, amine molecules were usually found to be located in the free voids of the host frameworks. They interact with the host frameworks through hydrogen bonding and electrostatic interactions. In this work, amine molecules attach to the walls of host frameworks and play dual roles in the formation of the two structures: chelating ligand and charge-balancing agent.

According to the *aufbau* principle,[14] the structures of **1** and **2** can be viewed as the assemblies of the molecular and chain-like building blocks: $Co(HL)_2(SO_4)_2$ (L = deta or aep) trimer and $Co(H_2O)_2(ox)$ chain. It is noteworthy that the chain-like cobalt oxalate can be successfully isolated under similar synthetic condition to prepare compound **2**. The reaction of $CoSO_4{\cdot}7H_2O$, $H_2C_2O_4{\cdot}2H_2O$, and aep in a molar ratio of 2:3:2 at 170 °C for 7 days gave rise to $H_3aep{\cdot}Co_{1.5}(H_2O)_3(ox)_{1.5}{\cdot}2H_2O{\cdot}1.5SO_4$ (**3**), which consists of $Co(H_2O)_2(ox)$ chains, triply protonated aep cations, sulfate anions and water molecules (Fig. S6, ESI†). However, the molecular cobalt sulfates cannot be obtained in our experiments. By replacing $CoSO_4{\cdot}7H_2O$ with $NiSO_4{\cdot}7H_2O$, its nickel analogue, $Ni(Hdeta)_2(SO_4)_2$ (**4**) can be obtained as good quality single crystals (Fig. S7, ESI†). When the coordinated water molecules in the chain-like structure are removed, the sulfate oxygen atoms of $Co(HL)_2(SO_4)_2$ trimers will occupy the open coordination sites and complete the octahedral coordination of cobalt centers. In the case of compound **1**, only one third of the coordinated water molecules are replaced by sulfate oxygen atoms and each $Co(HL)_2(SO_4)_2$ trimer only make two S–O–Co linkages to two cobalt oxalate chains. In the case of compound **2**, all the coordinated water molecules are replaced by sulfate oxygen atoms and each $Co(HL)_2(SO_4)_2$ trimer connect four cobalt oxalate chains.

Thermogravimetric analysis showed that compound **1** remained stable up to 200 °C (Fig. S8, ESI†). On further heating, the framework started to decompose. The weight loss of 64.16% between 200-800 °C is attributed to the departure of coordinated water molecules, the decomposition of deta molecules, oxalate ligands, and partial sulfate units. In comparison, compound **2** exhibits much better thermal stability than compound **1** since no water molecules are present in its framework structure. It started to decompose upon 350 °C (Fig. S9, ESI†).

The temperature dependence of the magnetic susceptibility of the two compounds was measured in the temperature range 2-300 K (Fig. 3). The thermal evolution of χ_m follows the Curie-Weiss law at temperature above 50 K (for **1**) and 20 K (for **2**), with C_m = 4.58 cm^3 K mol^{-1} and θ = -88.7 K (for **1**), and C_m = 3.40 cm^3 K mol^{-1} and θ = -45.1 K (for **2**). The negative θ values indicate the existence of antiferromagnetic interactions between the cobalt centers. The magnetic moment (μ_{eff}) at 300 K per mole of cobalt atom is 5.38 μ_B for **1** and 4.87 μ_B for **2**, agrees with those reported for other Co(II) compounds.[15]

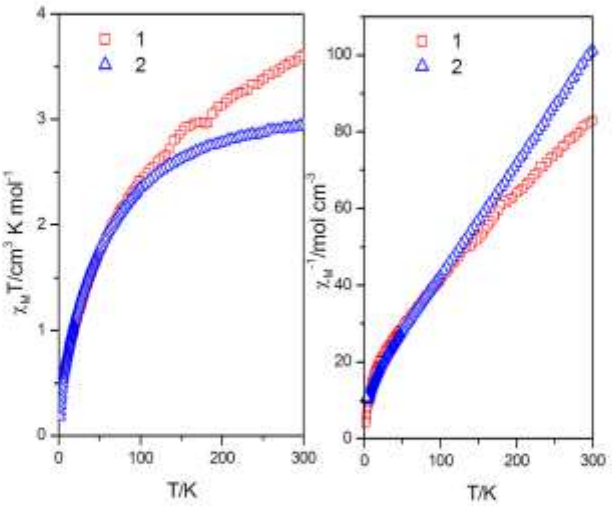

Fig.3. Temperature dependence of χ_MT (left) and χ_M^{-1} (right) for compounds **1** and **2**.

In summary, two open-framework metal sulfate-oxalates have been synthesized without the addition of water in the reaction systems. The two compounds have layered and framework structures with hcb and mog topologies, respectively. Their molecular and chain-like building blocks can be successfully isolated as good-quality single crystals, demonstrating a possible pathway for the formation of the two compounds. Besides metal sulfate-oxalates, this synthetic approach may be readily extended to prepare other inorganic-organic hybrid frameworks, such as metal sulfite-oxalates, and metal borate-oxalates. Further work on this project is in progress.

This work was supported by the NNSF of China (no. 21171121), and the Program for New Century Excellent Talents in Univerity (nos. NCET-10-0606 and NCET-12-0375).

Notes and references

[a] *College of Chemistry, Sichuan University, Chengdu 610064, P. R. China. E-mail: dgxu@scu.edu.cn, zhienlin@scu.edu.cn*
[b] *Analytical & Testing Center, Sichuan University, Chengdu 610064, P. R. China.*

† Electronic Supplementary Information (ESI) available: X-ray data, experimental details, additional crystallographic figures, IR spectra, powder XRD patterns, TGA curves. CCDC 1003128-1003129. See DOI: 10.1039/b000000x/

‡ Crystal data for compound **1**, $C_7H_{18}Co_2N_3O_{12}S$, *M* = 486.16, triclinic, space group *P*-1 (no. 2), *a* = 8.6065(3), *b* = 9.5595(5), *c* = 9.5987(5) Å, α = 77.884(4)º, β = 82.774(4)º, γ = 87.356(4)º, *V* = 765.79(6) Å^3, *Z* = 2, *D*c = 2.108 g cm^{-3}, μ = 2.375 mm^{-1}, 5782 reflections measured, 2696 unique (R_{int} = 0.0218). Final wR_2 (all data) = 0.0638, final R_1 = 0.0266. Crystal data for compound **2**, $C_8H_{16}Co_{1.5}N_3O_8S$, *M* = 402.69, triclinic, space group *P*-1 (no. 2), *a* = 8.4331(6), *b* = 9.4691(5), *c* = 9.5144(5) Å, α = 71.522(5)º, β = 64.356(6)º, γ = 89.622(5)º, *V* = 642.00(7) Å^3, *Z* = 2, *D*c = 2.083 g cm^{-3}, μ = 2.171 mm^{-1}, 4709 reflections measured, 2256 unique (R_{int} = 0.0253). Final wR_2 (all data) = 0.0704, final R_1 = 0.0311.

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