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Synthesis and structure of the first open-framework cadmium oxalate possessing channels

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A three-dimensional open-framework cadmium oxalate, $K[C_3N_2H_5][Cd(C_2O_4)_2]$, in which both the amine and the K^+ ion participate in the formation of the structure, has been synthesized and characterized for the first time.

Amongst the variety of open-framework inorganic materials, those of the metal carboxylates constitute a new family.[1–3] While the literature abounds in reports of the synthesis and characterization of aluminosilicates and metal phosphates with open architectures,[4] recent studies of metal carboxylates have also brought out certain novel structural features.[1,2] For example, OZn_4 clusters have been observed in zinc benzenedicarboxylates[2a] and Co–O–Co layers in a cobalt succinate.[1c] Metal oxalates synthesized hydrothermally in the presence of organic amines exhibit two- and three-dimensional architectures.[5,6] In the latter type of metal oxalates, the oxalate units lie in the plane of honeycomb-type layers and also provide the out-of-plane bridges to form the three-dimensional structure. The oxalate unit also plays a dual role in metal oxalate–phosphates where it forms an integral part of the layer structure predominantly constituted by the phosphate network and also acts as the link to create the third dimension.[7] Up to now open-framework metal oxalates synthesized in the presence of structure-directing amines have been restricted to those of Sn(II) and Zn. We have been exploring ways of preparing open-framework cadmium oxalates for some time. Here, we report the first successful synthesis and characterization of a Cd oxalate of the formula $K[C_3N_2H_5][Cd(C_2O_4)_2]$ **I**, with open architecture and possessing channels.

The cadmium oxalate **I** was synthesized by employing hydrothermal methods. Typically, 0.5 g of cadmium oxalate was dispersed in a mixture of 4.3 ml of butan-2-ol (BuOH) and 1.1 ml of water. To this, 0.328 ml of glacial acetic acid and 0.24 g of imidazole were added, followed by a small quantity of KCl (0.04 g). The approximate molar ratio of the reaction mixture was $5CdC_2O_4 : KCl : 5.5C_3N_2H_4 : 9MeCO_2H : 75BuOH : 100H_2O$. The mixture was homogenized for 30 min at room temperature (298 K), sealed in a 23 ml Teflon-lined acid digestion bomb and heated at 110 °C for 46 h. The product, a crop of tiny colorless diamond-shaped crystals, was recovered by suction filtration, washed with deionized water and dried at ambient temperature and conditions. Powder X-ray diffraction (XRD) indicated that the product was a new material, the pattern being entirely consistent with the structure determined by single crystal X-ray diffraction. Thermogravimetric analysis (TGA) under a nitrogen atmosphere (50 ml min^{-1}) from room temperature to 700 °C (heating rate = 10 °C min^{-1}) shows only one mass loss in the region 280–380 °C. The mass loss of 53.2% corresponds well with the loss of the oxalate and amine (calc. 55.6%). The powder X-ray diffraction pattern of the decomposed sample indicated that it was amorphous.

A suitable single crystal was carefully selected and subjected to X-ray diffraction using a Siemens SMART diffractometer with a CCD detector† and the structure was solved by direct methods. The asymmetric unit contains 20 independent non-hydrogen atoms. The structure of **I** consists of a network of cadmium and oxalate units forming an anionic framework with formula $[Cd(C_2O_4)_2]^{2-}$. Charge neutrality is achieved by the monoprotonated amine and potassium ions. Two K^+ ions occupy special positions with a site occupancy factor (SOF) of 0.5 per framework formula unit. The framework is built-up of four oxalate units, linked *via* the oxygens to the cadmium atoms with Cd–O distances in the range 2.327(3)–2.528(3) Å [$(Cd–O)_{av}$ = 2.422 Å] and O–Cd–O angles in the range 67.5(1)–151.3(1)° [$(O–Cd–O)_{av}$ = 88.6°]. The cadmium atoms are eight-coordinated with respect to oxygens forming a dodecahedral arrangement as shown in Fig. 1(a). The dodecahedral arrangement of oxygen atoms around the cadmium is of note since Cd atoms are generally octahedrally coordinated.

The complex framework structure of **I** can be understood in terms of simpler building units. Thus, the *in-plane* connectivity between the oxalate units [$C(2)–C(3)O_4$ and $C(4)–C(4)O_4$] and Cd results in the formation of honeycomb-like layers with twelve-membered apertures (six Cd and six oxalate units) along the [011] direction, as shown in Fig. 1(b). The remaining oxalate unit [$C(1)–C(1)O_4$] bridges (out-of-plane connection) these layers giving rise to one-dimensional elliptical channels (10.4 ×

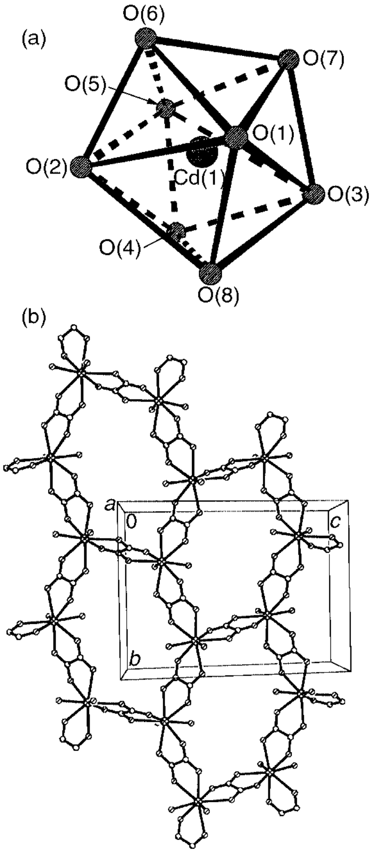

Fig. 1 (a) The environment of cadmium atoms in **I**. Note that the oxygen atoms form a dodecahedral arrangement around Cd. (b) In-plane connectivity between the oxalates and cadmium in **I**, along the *bc* plane, showing honeycomb-like layers.

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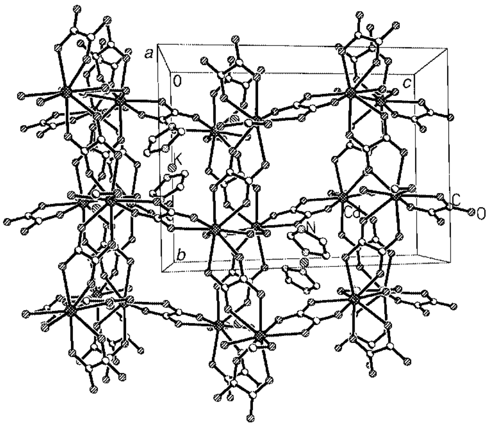

Fig. 2 Structure of K[$C_3N_2H_5$][Cd(C_2O_4)$_2$] **I** along the *a* axis, showing one-dimensional channels. Note that both K^+ and imidazolium cations occupy the same channels.

7.2 Å, shortest atom–atom contact distances not including the van der Waals radii), along the *a* axis. The imidazolium and K^+ ions reside in these channels (Fig. 2). The linkages between C(2)–C(3)O_4 and C(1)–C(1)O_4 oxalates and Cd (in-plane) result in a layer with twelve-membered rectangular apertures, along the *ab* plane. These layers are pillared by the C(4)–C(4)O_4 oxalate units (out-of-plane) forming another one-dimensional channel of width (4.1 × 11.3 Å) along the *c* axis. To our knowledge, **I** is the first example of an open-framework cadmium oxalate possessing channels.

The structure of **I** shows close similarity to that of [NH_4][Ti(C_2O_4)$_2$]·2H_2O.[8] In the latter, the Ti atom is surrounded by eight oxygens forming a square antiprism. Connectivity between the Ti and oxalate units results in a three-dimensional structure with channels containing [NH_4]$^+$. Connectivity between Cd and the two oxalates in **I** leads to layers, which are then connected by another oxalate leading to three-dimensional connectivity.

In summary, the synthesis and structure of a novel open-framework cadmium oxalate **I** has been accomplished. It is likely that the formation of such an architecture is facilitated by the presence of two types of structure-directing species, the protonated organic amine and the alkali metal cation. The formation of channels in the presence of alkali metal cations is reminiscent of aluminosilicate zeolites,[9] and paves the way for possible ion-exchange and related studies. Since **I** is the first example of an open-framework cadmium oxalate it would be profitable to explore the formation of similar or related compounds by employing structure-directing agents. Work in this direction is in progress.

Notes and references

† *Crystal data* for **I**: K[$C_3N_2H_5$][Cd(C_2O_4)$_2$], M = 396.6, crystal dimensions 0.2 × 0.2 × 0.16 mm, monoclinic, space group $C2/c$, a = 13.016(1), b = 11.291(1), c = 15.754(1) Å, β = 105.04(1)°, V = 2236.01(9) Å^3, Z = 8, D_c = 2.356 g cm^{-3}, μ(Mo-Kα) = 2.37 mm^{-1}, λ = 0.71073 Å. Structure solved by direct methods (SHELXTL-PLUS). A total of 4641 reflections were collected at 298 K in the θ range 2.42–23.25° and merged to give 1617 unique data (R_{int} = 0.033) of which 1463 with $I > 2\sigma(I)$ were considered to be observed. The structure was solved by direct methods with SHELXS-86[10] and difference Fourier synthesis. Final R_1 = 0.02 and wR_2 = 0.049 and S = 1.07 were obtained for 174 parameters. All the hydrogen atoms were located initially in the difference Fourier maps and for the final refinements, hydrogen atoms for the amine molecule were placed geometrically and held in the riding mode. Final Fourier map minimum and maximum: −0.664/0.359 e Å^{-3}. Full-matrix least-squares structure refinement against $|F^2|$ were carried out with SHELXTL-PLUS program package.[11]

CCDC 182/1668. See http://www.rsc.org/suppdata/cc/b0/b002684k/ for crystallographic files in .cif format.

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