

# Unusual aquation of Ba<sup>2+</sup> ions in the solid state: synthesis and X-ray structural and spectroscopic characterization of the novel polymeric complex salt of empirical formula {Ba<sub>6</sub>(H<sub>2</sub>O)<sub>17</sub>[Cr(ox)<sub>3</sub>]<sub>4</sub>}·7H<sub>2</sub>O (ox = oxalate dianion) †

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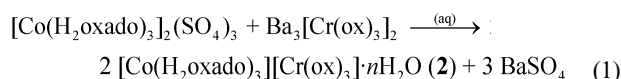
Received 4th March 2003, Accepted 9th April 2003

First published as an Advance Article on the web 17th April 2003

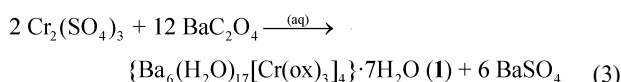
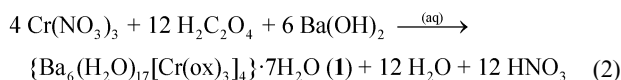
Reaction of Ba<sup>II</sup> and Cr<sup>III,VI</sup> compounds with oxalates in water affords a salt of empirical formula {Ba<sub>6</sub>(H<sub>2</sub>O)<sub>17</sub>[Cr(ox)<sub>3</sub>]<sub>4</sub>}·7H<sub>2</sub>O (**1**), consistent with the expected 3Ba<sup>II</sup>/2Cr<sup>III</sup> ratio; the triclinic structure is held together by unusual water and oxalate bridges, and compound **1** proved to be suitable for the synthesis of new salts with chiral cations and anions.

The well-documented tris(oxalato)chromate ion [Cr(ox)<sub>3</sub>]<sup>3-</sup> has moved into the focus of a worldwide research activity looking for new advanced materials for emerging technologies in which this paramagnetic and chiral complex ion plays a key role.<sup>1</sup> Materials of interest in this context include optically active systems,<sup>2,3</sup> polymeric microporous open frameworks<sup>4</sup> and, most importantly, molecular magnets.<sup>2,3,5</sup>

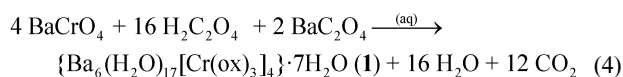
Results obtained from our on-going research on transition metal complexes of oxamide dioxime<sup>6</sup> inspired us to design a new broadly-based family of highly versatile complex salts with the unprecedented potential of accumulating within a single system a whole set of relevant functionalities, such as nanoscale structural features, extended hydrogen bonding, strong magnetic interactions, chiroptical phenomena, *etc.* The target salts can be generally formulated as [M(H<sub>2</sub>oxado)<sub>3</sub>]<sub>m</sub>[M'(ox)<sub>3</sub>]<sub>n</sub>·xH<sub>2</sub>O, where M = metal(II) or metal(III), M' = metal(III), m = 1 or 3, n = 1 or 2, 0 ≤ x < 15, H<sub>2</sub>oxado = oxamide dioxime. An obvious efficient method for their preparation appears to be by metathesis involving two precursors, *e.g.*, as idealized in reaction (1) yielding salt **2**:



By three distinct reaction paths (2), (3) and (4) in aqueous solution, we invariably isolated the well-crystallized precursor **1**, which we describe in this paper. ‡



† Electronic supplementary information (ESI) available: coordination patterns of 6 × Ba and 4 × Cr; molecular packing in the unit cell. See <http://www.rsc.org/suppdata/dt/b3/b302489j/>



The structure of **1**§ has a number of noteworthy aspects. First, to the best of our knowledge, no example of the same type featuring solely the ionic couple Ba<sup>2+</sup>/[Cr(ox)<sub>3</sub>]<sup>3-</sup> in the exact ratio 3 : 2 has been reported hitherto. Furthermore, even some of the most closely related systems described previously, such as NaMg[Cr(ox)<sub>3</sub>]·10H<sub>2</sub>O<sup>7</sup> and KCa[Cr(ox)<sub>3</sub>]·5H<sub>2</sub>O<sup>8</sup> are rather “double salts” in essence, and the compound [BaCr<sub>2</sub>(bipy)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>4</sub>(H<sub>2</sub>O)]<sub>n</sub>·nH<sub>2</sub>O,<sup>9</sup> in which the coordination sphere of the Ba sites is comparable to the present case, does not contain distinct [Cr(ox)<sub>3</sub>]<sup>3-</sup> fragments. Fig. 1 depicts the asymmetric unit of the pseudo-dimer **1** (the 7 H<sub>2</sub>O molecules of hydration are omitted for clarity). It is clear that this dimer with its ten metal sites can be visualized adequately as the association of two non-identical, asymmetric monomers, a reason why it is dubbed “pseudo-dimeric”. The four independent Cr<sup>III</sup> sites are exclusively coordinated by oxalates to produce the well-established helical coordination geometry of [Cr(ox)<sub>3</sub>]<sup>3-</sup> ions (Fig. 2). The six independent Ba<sup>II</sup> sites, by contrast, are differently coordinated both by H<sub>2</sub>O and oxalate ligands. The [Cr(ox)<sub>3</sub>]<sup>3-</sup> ions act as complex ligands and, together with some of the coordinating H<sub>2</sub>O molecules, efficiently bridge neighboring Ba<sup>2+</sup> ions to produce a tight 3-D network. As a result, the bulk structure is an extended, stable solid which does not melt below 380 °C. The unit cell contains two asymmetric pseudo-dimers. Due to its P1̄ symmetry, however, it is achiral. Fragments of four quasi-rectilinear Ba sites, including Ba(1)–Ba(6) and their

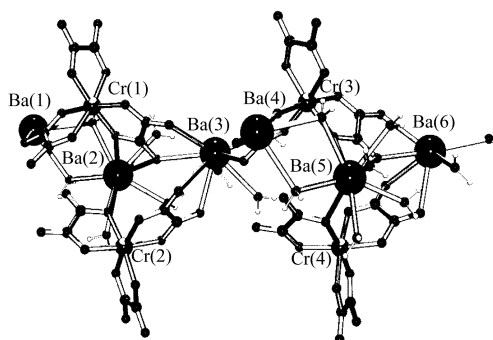
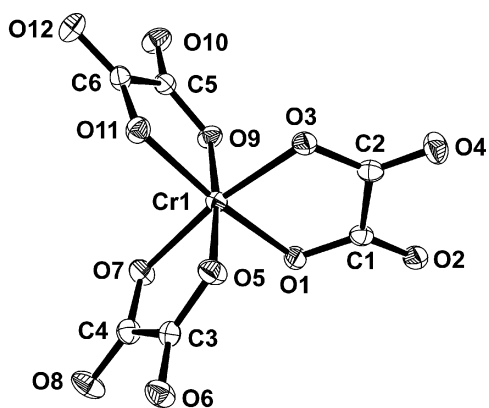
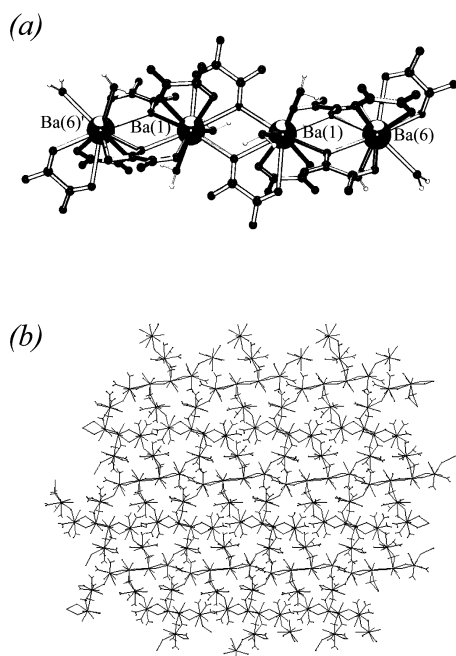


Fig. 1 Asymmetric unit of the pseudo-dimer **1** emphasizing the coordination of Ba and Cr sites; H<sub>2</sub>O molecules of hydration are omitted for clarity.



**Fig. 2** ORTEP<sup>13</sup> plot of one  $[\text{Cr}(\text{ox})_3]^{3-}$  ion in **1**, showing the familiar helical connectivity between the central  $\text{Cr}^{\text{III}}$  atom and the three oxalate ( $\text{ox}^{2-}$ ) units.

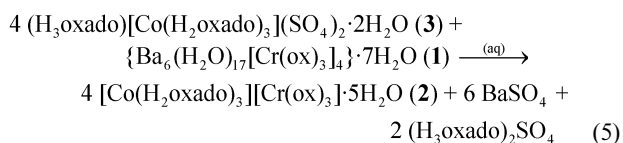


**Fig. 3** Nearly rectilinear  $\text{Ba}(6)'\text{-Ba}(1)'\text{-Ba}(1)\text{-Ba}(6)$  fragment (a) and projection of the structure of **1** along the  $a$  axis, showing the ordering of these fragments in zigzag chains parallel to the (110) direction (b). Symmetry transformation used to generate equivalent atoms in (a):  $-x + 1, -y + 1, -z + 1$  (centre of inversion).

inverted counterparts  $\text{Ba}(1)'\text{-Ba}(6)'$ , are observed within each cell. These fragments line up head-to-tail in the structure to form zigzag chains that run parallel to the (110) direction (Fig. 3).

There are no significant metal-metal interactions in this structure; the shortest intermetallic separation of 4.711 Å between  $\text{Ba}(3)$  and  $\text{Ba}(4)'$  is still too large to be thus considered. This fact of matter clearly obviates any urgent need for looking into the temperature dependent magnetic behavior of this system. Nonetheless, the effective magnetic moment measured at 296 K is  $3.89 \mu_{\text{B}}$ , consistent with  $\text{Cr}^{\text{III}}$ . All coordinating atoms are oxygen atoms, either from water or from oxalate ligands. The overall O-Ba distances range from 2.757 to 3.273 Å. The structural parameters within the  $[\text{Cr}(\text{ox})_3]^{3-}$  ions with respect to their geometry, bond lengths and bond angles, are very similar to those reported previously.<sup>1b,c</sup> The bulk structure is an extended solid in nature.

The relevance of the present compound to current research is not just related to its interesting new structure. In fact, we have already used it successfully in the metathetic synthesis (eqn. (5))<sup>10</sup> of **2**, the first member of a wide range of *multiple-functionality materials* which are a series of novel salts based on



paramagnetic chiral complex cations and anions, with extended intermolecular hydrogen bonding.

## Notes and references

‡ **1** was obtained in highest yield by reaction (4). Freshly prepared  $\text{BaC}_2\text{O}_4$  (1.10 g, 5 mmol) and commercial  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  (5 g, 40 mmol, Merck) were dissolved in  $\text{H}_2\text{O}$  (200 ml) at 60 °C. The filtered solution was stirred at this temperature, and a fine powder of  $\text{BaCrO}_4$  (2.5 g, 10 mmol, PROLABO pur) was added in successive small portions. Stirring was maintained for 45 min. The bluish-violet reaction solution was then filtered and left to evaporate slowly over a few weeks. The resulting elongated violet-brown crystals were washed twice with  $\text{H}_2\text{O}$  (5 ml), dried in air, then in an oven (120 °C). Yield: 4.00 g (89.3%). Single crystals suitable for X-ray diffraction were grown over several months by repeated slow concentration of saturated aqueous solutions. Found: C, 11.42; H, 1.84. Calc. for  $\text{C}_{24}\text{H}_{48}\text{Ba}_6\text{Cr}_4\text{O}_{72}$ : C, 11.43; H, 1.92%. IR ( $\text{KBr}, \text{cm}^{-1}$ ): 3450 (s), 1706 (s), 1672 (s), 1413 (s), 1274 (m), 906 (w), 822 (m), 548 (m), 482 (m). UV-Vis ( $\text{H}_2\text{O}$  solution, nm): 419, 569.

§ Crystal data for **1**:  $\text{C}_{24}\text{H}_{48}\text{Ba}_6\text{Cr}_4\text{O}_{72}$ ,  $M = 2520.66$ , triclinic, space group  $P\bar{1}$ ,  $a = 1094.1(1)$ ,  $b = 1759.5(1)$ ,  $c = 1857.7(1)$  pm,  $a = 88.850(1)$ ,  $\beta = 85.813(1)$ ,  $\gamma = 76.546(1)^\circ$ ,  $Z = 2$ ,  $V = 3.4690(3) \text{ nm}^3$ ;  $D_{\text{calc}} = 2.413 \text{ Mg m}^{-3}$ ,  $T = 208(2) \text{ K}$ ,  $\lambda = 71.073 \text{ pm}$ ,  $\mu = 4.086 \text{ mm}^{-1}$ ,  $F(000) = 2400$ ,  $2\theta$  range =  $2.20\text{-}57.72^\circ$ , reflections collected = 22074, indep. reflections = 15491 [ $R(\text{int}) = 0.0135$ ], Smart area CCD diffractometer (Siemens), structure solved by Patterson methods (SHELXS<sup>11</sup>), non hydrogen atoms refined anisotropically, H-atoms located and refined isotropically (SHELXL<sup>11</sup>), empirical absorption correction (SADABS<sup>12</sup>), refinement: full matrix least-squares on  $F^2$ ,  $\text{GOF}/F^2 = 1.021$ ,  $R_{\text{I}} >_{2\sigma(I)}$ ;  $R1 = 0.0228$ ,  $wR2 = 0.0523$ ;  $R_{\text{calc}}$ :  $R1 = 0.0303$ ,  $wR2 = 0.0549$ , residual electron density: 0.76 and  $-0.814 \text{ e } \text{Å}^{-3}$ . CCDC reference number 206134. See <http://www.rsc.org/suppdata/dt/b3/b302489j/> for crystallographic data in CIF or other electronic format.

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