

## Tricaesium tris(oxalato- $\kappa^2O^1,O^2$ )-chromate(III) dihydrate

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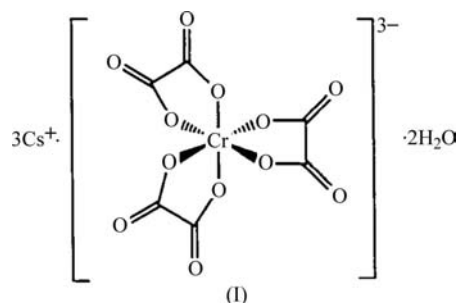
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The title compound,  $Cs_3[Cr(C_2O_4)_3] \cdot 2H_2O$ , has been synthesized for the first time and the spatial arrangement of the cations and anions is compared with those of the other members of the alkali metal series. The structure is built up of alternating layers of either the *D* or *L* enantiomers of  $[Cr(\text{oxalate})_3]^{3-}$ . Of note is that the distribution of the  $[Cr(\text{oxalate})_3]^{3-}$  enantiomers in the  $Li^+$ ,  $K^+$  and  $Rb^+$  tris(oxalato)chromates differs from those of the  $Na^+$  and  $Cs^+$  tris(oxalato)chromates, and also differs within the corresponding BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene] conducting salts. The use of tris(oxalato)chromate anions in the crystal engineering of BEDT-TTF salts is discussed, wherein the salts can be paramagnetic superconductors, semiconductors or metallic proton conductors, depending on whether the counter-cation is  $NH_4^+$ ,  $H_3O^+$ ,  $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Rb^+$  or  $Cs^+$ . These materials can also be superconducting or semiconducting, depending on the spatial distribution of the *D* and *L* enantiomers of  $[Cr(\text{oxalate})_3]^{3-}$ .

### Comment

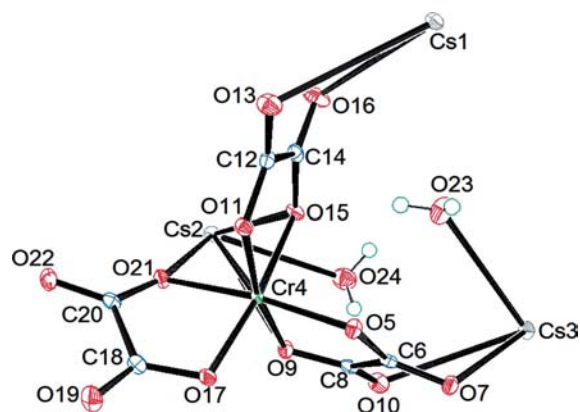
The title compound,  $Cs_3[Cr(C_2O_4)_3] \cdot 2H_2O$ , (I), represents a new salt of the tris(oxalato)chromate(III) anion, as this is the first study of the caesium analogue and the first report of any tris(oxalato)metallate with  $Cs^+$  cations. The first examples of  $[Cr(\text{oxalate})_3]^{3-}$  were studied by Werner (1912). The  $[Cr(\text{oxalate})_3]^{3-}$  anion has more recently been used as a component in molecular radical cation salts of BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene] (Martin *et al.*, 1997), which have been widely studied because of the opportunities they afford for making new combinations of physical properties through crystal engineering. The series of BEDT-TTF salts containing tris(oxalato)chromate anions can be paramagnetic superconductors, semiconductors or metallic proton conductors, depending on whether the counter-cation is  $NH_4^+$ ,  $H_3O^+$ ,  $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Rb^+$  or  $Cs^+$  (Martin *et al.*, 2007). These materials can also be superconducting or semiconducting, depending on the spatial distribution of the *D* and *L* enantiomers of  $[Cr(\text{oxalate})_3]^{3-}$ .

(ate) $_3]^{3-}$  (Martin *et al.*, 1999). It is the opportunities for crystal engineering afforded by  $[Cr(\text{oxalate})_3]^{3-}$  that have led us to synthesize the title caesium analogue, (I), which completes the series of alkali metal tris(oxalato)chromates.

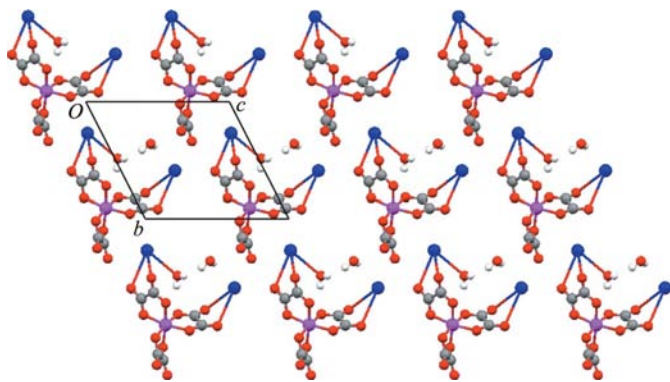


In (I), the  $Cr^{III}$  cation is coordinated by three bidentate oxalate groups in an approximate octahedral geometry (Fig. 1). The  $Cr-O$  distances are in the range 1.967 (3)–1.966 (3) Å and the internal  $O-Cr-O$  angles of the chelate rings are 82.68 (13), 82.29 (13) and 82.29 (13)°, similar to those observed in the alkali metal tris(oxalato)chromate salts of lithium (Sekine *et al.*, 1994), sodium (Bulc *et al.*, 1982), rubidium (van Niekerk & Schoening, 1952) and potassium (Taylor, 1978). The  $Cs^+$  compound crystallizes in the triclinic space group  $P\bar{1}$  and has two formula units in the asymmetric unit. The lithium analogue also crystallizes in the space group  $P\bar{1}$ , the sodium analogue in the monoclinic space group  $C2/c$ , and the potassium and rubidium analogues in the monoclinic space group  $P2_1/c$ .

All three of the  $Cs^+$  cations form close contacts with both the oxalate and water O atoms. The numerous  $Cs \cdots O$  close contacts to oxalate O atoms are in the range 3.021 (3)–3.512 (4) Å, with each of the three  $Cs^+$  cations forming seven such  $Cs \cdots O$  contacts, including a single short contact to a water O atom [3.109 (4), 3.112 (4) and 3.270 (4) Å]. There is hydrogen bonding between the oxalate O atoms and three of the H atoms on the two water molecules, while the fourth H atom forms a hydrogen bond with the O atom of a neighbouring water molecule (Table 1). By comparison, the lithium



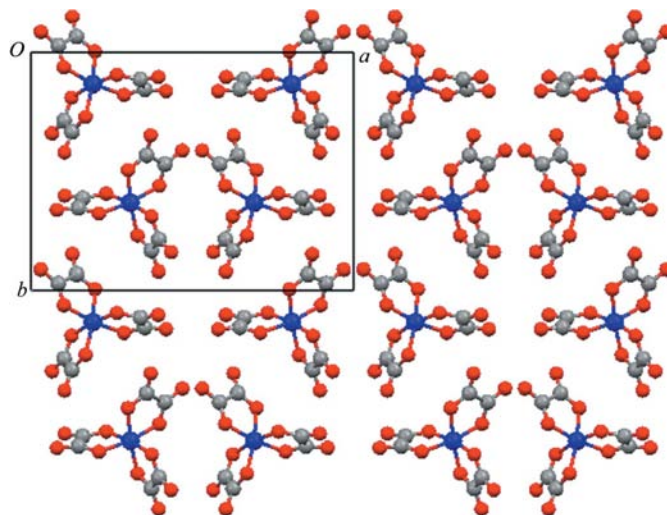
**Figure 1**  
The asymmetric unit of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.


**Figure 2**

The structure of (I), viewed down the  $a$  axis, showing the packing of the  $[\text{Cr}(\text{oxalate})_3]^{3-}$  anions, water molecules and  $\text{Cs}^+$  cations. In the electronic version of the journal, the colour scheme is: O red, C grey, Cr pink, Cs blue and H white.

$[\text{Cr}(\text{oxalate})_3]^{3-}$  analogue has six water molecules in the asymmetric unit, four of which are coordinated to  $\text{Li}^+$  cations and two tetrahedrally hydrogen bonded to other water molecules or oxalate ligands. The three  $\text{Li}^+$  cations have octahedral, square-pyramidal and tetrahedral coordination geometries. The sodium salt contains five water molecules in the asymmetric unit. Four of these form a separate layer containing polymeric chains of  $\text{H}_2\text{O}$  molecules and  $\text{Na}^+$  cations between the  $[\text{Cr}(\text{oxalate})_3]^{3-}$  layers, whilst a fifth resides in cavities between these layers. The four water molecules in the layers with  $\text{Na}^+$  cations form two interlayer hydrogen bonds, while the fifth  $\text{H}_2\text{O}$  molecule forms hydrogen bonds with both the  $\text{H}_2\text{O}/\text{Na}^+$  layer and the  $[\text{Cr}(\text{oxalate})_3]^{3-}$  layer. The  $\text{Na}^+$  cations in the  $\text{H}_2\text{O}/\text{Na}^+$  layers form close contacts with water O atoms within the layer and also with oxalate O atoms in the  $[\text{Cr}(\text{oxalate})_3]^{3-}$  layer, whilst the other  $\text{Na}^+$  cations form only close contacts with oxalate O atoms in the anion layer. The potassium salt contains 2.7 water molecules in the asymmetric unit, all of which form hydrogen bonds to two  $\text{K}^+$  cations and two oxalate O atoms. Two  $\text{K}^+$  cations are coordinated to six oxalate O atoms and two  $\text{H}_2\text{O}$  molecules, whilst the third  $\text{K}^+$  cation is coordinated to four oxalate O atoms and two  $\text{H}_2\text{O}$  molecules. The rubidium salt contains three water molecules in the asymmetric unit which are hydrogen bonded to a single oxalate O atom each. Two  $\text{H}_2\text{O}$  molecules are also hydrogen bonded to each other, whilst the third is coordinated to two  $\text{Rb}^+$  cations. Two  $\text{Rb}^+$  cations are coordinated to six oxalate O atoms and two  $\text{H}_2\text{O}$  molecules, whilst the third is coordinated to five oxalate O atoms and two  $\text{H}_2\text{O}$  molecules.

The structure of  $\text{Cs}_3\text{Cr}(\text{C}_2\text{O}_4)_3 \cdot 2\text{H}_2\text{O}$  is built up of layers of  $[\text{Cr}(\text{oxalate})_3]^{3-}$  anions in the  $bc$  plane that stack in the  $a$  direction, with each layer consisting exclusively of only a single enantiomer (Fig. 2) of either D- or L- $[\text{Cr}(\text{oxalate})_3]^{3-}$  anions and adjacent layers consisting exclusively of the opposing enantiomer.  $\text{Na}_3\text{Cr}(\text{oxalate})_3 \cdot 5\text{H}_2\text{O}$  is also built up of layers of opposing D- or L- $[\text{Cr}(\text{oxalate})_3]^{3-}$  anions in the  $c$  direction, with adjacent layers having opposing enantiomers (Fig. 3). These  $[\text{Cr}(\text{oxalate})_3]^{3-}$  layers are segregated by layers


**Figure 3**

The packing of a layer containing a single enantiomer of  $[\text{Cr}(\text{oxalate})_3]^{3-}$  in  $\text{Na}_3[\text{Cr}(\text{oxalate})_3] \cdot 5\text{H}_2\text{O}$  (Bulc *et al.*, 1982). In the electronic version of the journal, the colour scheme is: O red, C grey and Cr blue.

built up of polymeric chains of  $\text{H}_2\text{O}$  molecules and  $\text{Na}^+$  cations. The anion packing in  $\text{Li}_3\text{Cr}(\text{oxalate})_3 \cdot 6\text{H}_2\text{O}$  does not consist of layers of a single enantiomer. Instead, pairs of D- and L- $[\text{Cr}(\text{oxalate})_3]^{3-}$  anions form columns in the  $a$  direction segregated by the  $\text{H}_2\text{O}/\text{Li}^+$  layers. The packing of  $[\text{Cr}(\text{oxalate})_3]^{3-}$  anions in the potassium and rubidium salts is similar, with pairs of opposing enantiomers in the  $bc$  plane rather than enantiomers occupying discrete layers.

In summary, the  $[\text{Cr}(\text{oxalate})_3]^{3-}$  anion has now been studied with a series of counter-cations, including five alkali metal cations. It has been postulated that the structures of the  $\text{NH}_4^+$  and  $\text{K}^+$  salts differ due to the ability of the ammonium cation to form tetrahedral hydrogen bonds, and no conclusions could be drawn on the effects of changing the size of the cation (van Niekerk & Schoening, 1952). Whilst the alkali metal atomic radii increase in size in the order  $\text{Li} \rightarrow \text{Na} \rightarrow \text{K} \rightarrow \text{Rb} \rightarrow \text{Cs}$ , we have observed no direct correlation between cation size and packing of the  $[\text{Cr}(\text{oxalate})_3]^{3-}$  layer. As expected, the smaller members of the family contain more coordinated water than the larger members. There is also no relationship between cation size and the chirality of the layers, with the  $\text{Na}^+$  and  $\text{Cs}^+$  salts having segregated layers of each enantiomer whilst the  $\text{Li}^+$ ,  $\text{K}^+$  and  $\text{Rb}^+$  salt layers contain mixtures of both enantiomers. The structures of the segregated layers of enantiomers in the  $\text{Na}^+$  and  $\text{Cs}^+$  salts differ greatly, as can be seen by the packing of  $[\text{Cr}(\text{oxalate})_3]^{3-}$  anions in the  $\text{Na}^+$  salt in Fig. 3 compared with the  $\text{Cs}^+$  salt in Fig. 2.

The  $[\text{Cr}(\text{oxalate})_3]^{3-}$  anion has been used as a component in molecular radical cation salts of BEDT-TTF to study the effects of small structural changes upon the bulk physical properties. The  $\text{Li}^+$ ,  $\text{K}^+$  and  $\text{Rb}^+$  salts all give a hexagonal packing arrangement of  $[\text{Cr}(\text{oxalate})_3]^{3-}$  anions and cations, with a guest solvent molecule able to fit into the hexagonal cavity, which differs in size depending on which cation is present. This can lead to metallic, semiconducting or super-

conducting behaviour. Interestingly, it is the Na<sup>+</sup> and Cs<sup>+</sup> salts which have given nonhexagonal packing arrangements in semiconducting BEDT-TTF salts (Martin *et al.*, 2007, 2008), both salts having no layer segregation by enantiomer. The Na<sup>+</sup> salt contains separate layers of BEDT-TTF, [Cr(oxalate)<sub>3</sub>]<sup>3-</sup> or Na<sup>+</sup>/H<sub>2</sub>O, whilst the salt grown from Cs<sub>3</sub>[Cr(oxalate)<sub>3</sub>]-2H<sub>2</sub>O contains only layers of BEDT-TTF or H<sub>2</sub>O/[Cr(oxalate)<sub>3</sub>]<sup>3-</sup>, with no Cs<sup>+</sup> being included in the structure.

## Experimental

Dark-blue plate-shaped crystals of the title compound with well developed {010} faces were grown by slow evaporation from an aqueous solution of oxalic acid dihydrate, caesium oxalate monohydrate and caesium dichromate (7:2:1).

### Crystal data

Cs <sub>3</sub> [Cr(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ]-2H <sub>2</sub> O	$\gamma = 77.221 (5)^\circ$
$M_r = 750.80$	$V = 809.14 (9) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 8.2299 (5) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.2956 (6) \text{ \AA}$	$\mu = 7.43 \text{ mm}^{-1}$
$c = 10.9902 (5) \text{ \AA}$	$T = 120 \text{ K}$
$\alpha = 63.662 (5)^\circ$	$0.22 \times 0.15 \times 0.13 \text{ mm}$
$\beta = 89.775 (4)^\circ$	

### Data collection

Oxford Xcalibur Sapphire3 diffractometer	mented in SCALE3 ABSPACK scaling algorithm]
Absorption correction: multi-scan [CrysAlis Pro (Oxford Diffraction, 2009); empirical absorption correction using spherical harmonics, imple-	$T_{\min} = 0.743$ , $T_{\max} = 1.000$
	5562 measured reflections
	3631 independent reflections
	3326 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.018$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$	217 parameters
$wR(F^2) = 0.059$	H-atom parameters constrained
$S = 0.98$	$\Delta\rho_{\text{max}} = 0.91 \text{ e \AA}^{-3}$
3621 reflections	$\Delta\rho_{\text{min}} = -1.62 \text{ e \AA}^{-3}$

The H atoms were all located in a difference map. They were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (O–H = 0.82 Å) and  $U_{\text{iso}}(\text{H})$  values (in the range 1.2–1.5 times  $U_{\text{eq}}$  of the parent atom), after which the positions were refined with riding constraints.

Data collection: CrysAlis Pro (Oxford Diffraction, 2009); cell refinement: CrysAlis Pro; data reduction: CrysAlis Pro; program(s)

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O23–H232 <sup>i</sup> ··O15	0.83	2.25	2.963 (7)	145
O24–H242 <sup>i</sup> ··O10	0.83	2.15	2.974 (7)	173
O23–H231 <sup>i</sup> ··C6 <sup>i</sup>	0.82	2.58	3.333 (7)	154
O23–H231 <sup>i</sup> ··O7 <sup>i</sup>	0.82	1.99	2.809 (7)	178
O24–H241 <sup>i</sup> ··O23 <sup>ii</sup>	0.83	2.10	2.886 (7)	158

Symmetry codes: (i)  $-x, -y + 3, -z$ ; (ii)  $-x + 1, -y + 3, -z$ .

used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: CRYSTALS (Betteridge *et al.*, 2003); molecular graphics: CAMERON (Watkin *et al.*, 1996); software used to prepare material for publication: CRYSTALS.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3237). Services for accessing these data are described at the back of the journal.

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