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The tris(malonato)chromate(III) anion with an organic cation

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The structure of 1,2-bis(4-pyridyl)ethylenium tris(malonato-κ^2O,O')chromate(III) octahydrate, $(Hbpe)_3[Cr(mal)_3]\cdot 8H_2O$, where mal is the malonate dianion ($C_3HO_4^{2-}$) and bpe is 1,2-bis(4-pyridyl)ethylene ($C_{12}H_{12}N_2$), is presented. The crystal structure is made up of $[Cr(mal)_3]^{3-}$ anions, $Hbpe^+$ cations and water molecules of crystallization. The anions are connected through hydrogen bonding involving malonate O atoms and uncoordinated water molecules in distinct layers, with the cations stacked in separate layers. One of the Hbpe cations is located on a center of inversion, another one on a twofold rotation axis.

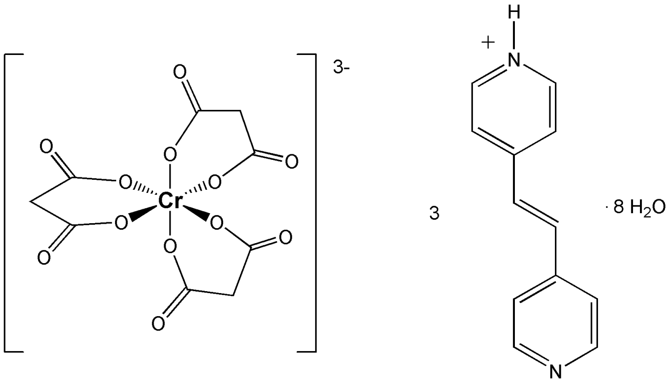
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.004 Å
Disorder in solvent or counterion
R factor = 0.067
wR factor = 0.179
Data-to-parameter ratio = 13.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Malonate (mal) and 1,2-bis(4-pyridyl)ethylene (bpe) are known to be useful connectors in the design of polynuclear transition metal assemblies (Delgado *et al.*, 2003). In addition, mono- and multinuclear chromium(III)–carboxylate complexes serve as models of the carboxylate-rich polypeptide low-molecular-weight chromium-binding substance, or 'chromodulin', which possesses four chromic ions (Yamamoto *et al.*, 1987; Jacquamet *et al.*, 2003). The Cr_4 assembly in holochromodulin comprises a single Cr atom and a trinuclear unit (Jacquamet *et al.*, 2003). However, polynuclear chromium(III)–carboxylate complexes, including those with peptidic ligands, have not been fully described in the literature. This report is a portion of our continuing work directed at understanding the biomimetic chemistry of Cr^{III} with carboxylate ligands. Also, the paramagnetic nature of octahedral Cr^{III} has potential importance as a source of molecule-based magnets and electronic materials.



(I)

A perspective view of the title compound, (I), is shown in Fig. 1 and selected geometric parameters are listed in Table 1. The structure contains a hexacoordinate octahedral Cr atom

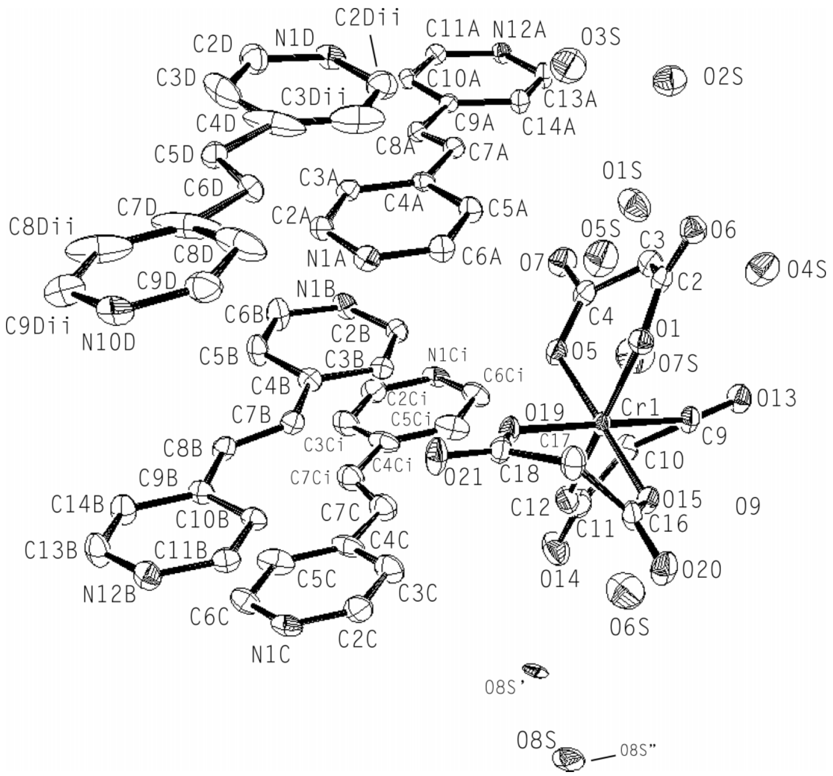


Figure 1

Perspective view of the asymmetric unit of (I) and connected symmetry-equivalent atoms, with the atom-numbering scheme. H atoms have been omitted for clarity. Atom O8*S*″ is covered by O8*S*. Cation *C* is disordered and sits on a center of symmetry [symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, -z$]; cation *D* is disordered and was found on a twofold crystallographic axis [symmetry code: (ii) $-x, y, \frac{1}{2} - z$].

surrounded by six O atoms from three malonate ions, forming the $[Cr(mal)_3]^{3-}$ anion. Three $Hbpe^+$ cations complete the structure, together with water molecules. One cation (*C*) sits on a center of symmetry. Another cation (*D*) is disordered over a twofold crystallographic axis. Both ordered and disordered water molecules are found in the structure (Fig. 2). The cations form hydrogen bonds among themselves (Table 2) and are stacked in a separate layer from the anions. The distances between the stacked units, about 3.5 Å, indicate π interactions between the cations (Fig. 2). Water atom O8*S* is disordered and was modeled in three orientations with refined occupancies of 0.325 (17), 0.338 (17), and 0.337 (17), for the unprimed, primed and double-primed atoms. Restraints on the displacement parameters of the disordered atoms were required. The anions are linked *via* hydrogen bonding that includes solvent water molecules and carboxylate O atoms (Table 2 and Fig. 2). The mean value of the Cr—O bond distances is 1.965 (6) Å, which is similar to that reported for $[Co(1,2\text{-diaminopropane})_3][Cr(mal)_3]\cdot 3H_2O$ [1.953 (7) Å; Butler & Snow, 1976]. The mean angle subtended at the Cr atom by the malonate ligand (O—Cr1—O) is 88.9 (6)°, somewhat smaller than that previously determined in the above complex [91.9 (7)°].

Experimental

Compound (I) was synthesized by combining a slurry of freshly prepared chromic hydroxide in water and a mixture of malonic acid and potassium hydroxide in water (molar ratio 1:2:1) on a steam bath. The resulting purple solution was mixed with an aqueous solution of malonic acid and an ethanolic solution of bpe in a 1:1 molar ratio. Purple crystals were found when the solution was allowed to evaporate slowly at room temperature.

Crystal data

$(C_{12}H_{12}N_2)_3[Cr(C_3HO_4)_3]\cdot 8H_2O$
$M_r = 1051.95$
Monoclinic, $C2/c$
$a = 21.319$ (4) Å
$b = 11.997$ (2) Å
$c = 38.300$ (6) Å
$\beta = 100.632$ (3)°
$V = 9628$ (3) Å^3
$Z = 8$

$D_x = 1.451$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 9927 reflections
$\theta = 2.2$–26.0°
$\mu = 0.32$ mm^{-1}
$T = 100$ (2) K
Prism, purple
0.50 × 0.19 × 0.12 mm

Data collection

Bruker SMART APEX area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
$T_{\min} = 0.855$, $T_{\max} = 0.962$
26 496 measured reflections

9450 independent reflections
8293 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$
$\theta_{\max} = 26.0°$
$h = -26 \rightarrow 26$
$k = -9 \rightarrow 14$
$l = -47 \rightarrow 47$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.179$
$S = 1.07$
9450 reflections
681 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.084P)^2 + 40P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 1.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.55$ e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

Cr1—O19	1.959 (2)	Cr1—O8	1.963 (2)
Cr1—O12	1.961 (2)	Cr1—O15	1.970 (2)
Cr1—O5	1.962 (2)	Cr1—O1	1.974 (2)
O12—Cr1—O8	88.50 (9)	O5—Cr1—O1	88.72 (9)
O19—Cr1—O15	89.47 (9)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1A—H1$A\cdots$N12$A^{\rm i}$	0.88	1.84	2.715 (3)	174
N1B—H1$B\cdots$N12$B^{\rm ii}$	0.88	1.82	2.702 (4)	175
N1C—H1$C\cdots$N1$C^{\rm iii}$	0.88	1.78	2.664 (5)	179
O1S—H1S1$\cdots$O6	0.90	1.94	2.802 (3)	161
O2S—H2S1$\cdots$O6	0.91	1.83	2.733 (3)	176
O4S—H4S2$\cdots$O20$^{\rm ii}$	0.93	1.93	2.853 (4)	172
O5S—H5S1$\cdots$O21$^{\rm ii}$	0.90	1.97	2.838 (4)	161
O6S—H6S1$\cdots$O14	0.89	1.84	2.722 (4)	174

Symmetry codes: (i) $x, 1+y, z$; (ii) $x, y-1, z$; (iii) $\frac{1}{2}-x, \frac{3}{2}-y, -z$.

The positions of H atoms bonded to C and N atoms were determined geometrically (C—H = 0.95 and 0.99 Å, and N—H = 0.88 Å) and refined using a riding model. H atoms bound to water O atoms were located in a difference map and their positions were kept fixed during refinement (O—H = 0.8598–0.9323 Å). The $U_{\rm iso}$(H) values were set at 1.2$U_{\rm eq}$ of the bonded atom.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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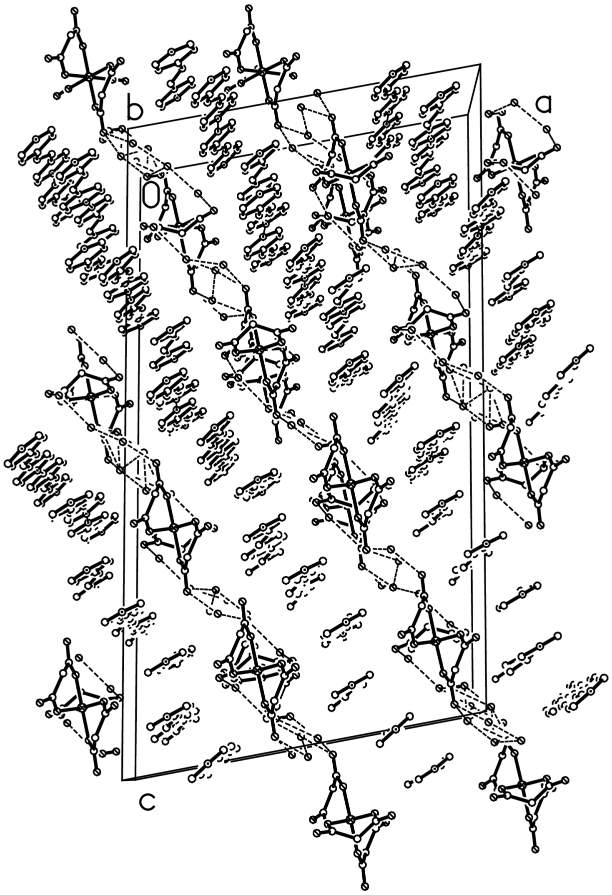

Figure 2
View of the unit-cell contents of (I), showing the stacked cations and layers of anions.

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