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Hexaaquachromium(III) triaquabis(benzene-1,3-dioxyacetato)sodate(I) pentahydrate

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The title complex, $[Cr(H_2O)_6][Na(C_{10}H_8O_6)_2(H_2O)_3]\cdot 5H_2O$ ($C_{10}H_8O_6$ = benzene-1,3-dioxyacetate), consists of $[Na(C_{10}H_8O_6)_2(H_2O)_3]^{3-}$ trianions, $[Cr(H_2O)_6]^{3+}$ trications and five uncoordinated water molecules. The Cr cation has six-coordinate slightly distorted octahedral geometry, whereas the Na-ion coordination is distorted trigonal prismatic. The cations, anions and water molecules are linked by O—H···O intermolecular hydrogen bonds into a three-dimensional network.

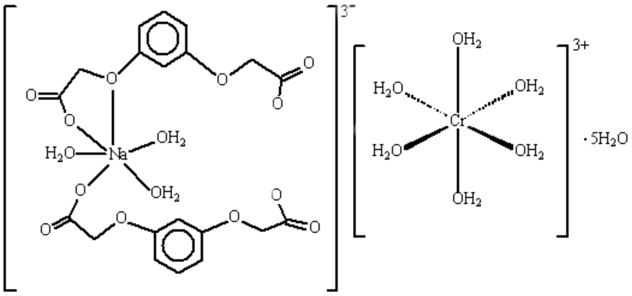
Key indicators

Single-crystal X-ray study
T = 293 K
Mean *σ*(C–C) = 0.003 Å
R factor = 0.041
wR factor = 0.107
Data-to-parameter ratio = 14.2

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

Comment

Phenylenedioxydiacetic acids, which have been known to show biological activities, are multidentate flexible ligands with versatile binding modes. To our knowledge, some structures of transition metal complexes with benzene-1,2-dioxyacetic acid and benzene-1,4-dioxyacetic acid ligands have been reported (Gao *et al.*, 2004; Liu *et al.*, 2004; McCann *et al.*, 1995, 1996; Kennard *et al.*, 1986), whereas the structures of the complex with benzene-1,3-dioxyacetic acid ligands are rare. Recently, we have reported the crystal structure of a one-dimensional chain Zn^{II} polymer, $\{[Zn(C_{10}H_8O_6)(H_2O)_2]\cdot(H_2O)_2\}_n$ (Gao *et al.*, 2004), in which benzene-1,3-dioxyacetate functions as a bridging ligand. Here, our study is extended to the structure of the title complex, $[Cr(H_2O)_6][Na(C_{10}H_8O_6)_2(H_2O)_3]\cdot 5H_2O$, (I), obtained from the reaction of $Cr(ClO_4)\cdot 6H_2O$ and sodium benzene-1,3-dioxyacetate under hydrothermal conditions.



(I)

As shown in Fig. 1, complex (I) consists of $[Na(C_{10}H_8O_6)_2(H_2O)_3]^{3-}$ trianions, $[Cr(H_2O)_6]^{3+}$ trications and five uncoordinated water molecules. In the $[Cr(H_2O)_6]^{3+}$ cation, the Cr^{3+} atom is coordinated by six water molecules with a slightly distorted octahedral geometry. The Cr—O bond lengths range from 1.959 (2) to 1.994 (2) Å. In the $[Na(C_{10}H_8O_6)_2(H_2O)_3]^{3-}$ anions, benzene-1,3-dioxyacetate ligands have both monodentate and bidentate chelating

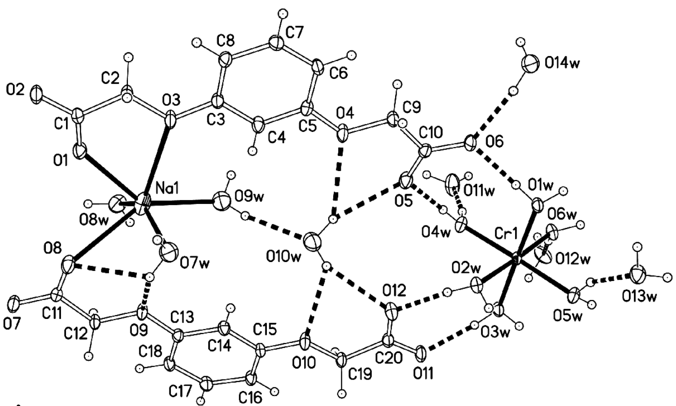


Figure 1
*ORTEP*II (Johnson, 1976) drawing of the title complex, showing 30% probability displacement ellipsoids. Hydrogen bonds are shown as dashed lines.

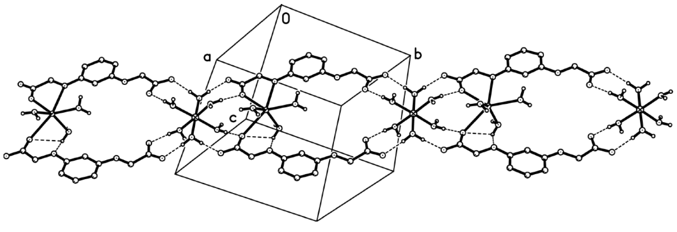


Figure 2
The chain structure of the title complex, constructed by the hydrogen bonds (dashed lines) between carboxyl O atoms and the coordinated water molecules. The other hydrogen bonds which complete the three-dimensional structure have been omitted.

modes. The Na^+ atom is also six-coordinate, involving two carboxyl O atoms and one ether O atom of different oxyacetate ligands and three water molecules, and displays a distorted trigonal prismatic configuration. The angles around the central Na ions vary from 58.68 (6) to 147.08 (9)°. The Na—O bond distances are in the range 2.365 (2)–2.966 (2) Å. Each benzene-1,3-dioxyacetate is almost plannar [r.m.s. deviations = 0.04 (5) and 0.08 (5) Å] and they are nearly parallel with a dihedral angle of 3.98 (5)°. The uncoordinated water O10*W* simultaneously forms five hydrogen bonds with carboxyl O atoms (O5 and O12), ether O atoms (O4 and O10) and the coordinated water molecule O9*W* (see Fig. 1. and Table 2). The cation and anion are linked by a number of O—H···O intermolecular hydrogen bonds through the carboxylate O atoms and coordinated water molecules, resulting in a one-dimensional chain (Fig. 2). In the chain, the Cr···Na distances are 5.421 (4) and 10.650 (4) Å. These chains are in turn linked by further O—H···O hydrogen bonds to form a three-dimensional supramolecular network (see Table 2 for a complete listing of the hydrogen-bonding geometry). The hydrogen bonding is probably the principal feature in the supramolecular assembly and stabilization of the crystal structure, in addition to normal ionic interactions.

Experimental

Benzene-1,3-dioxyacetic acid was prepared according to the method described for the synthesis of benzene-1,2-dioxyacetic acid by Mirci (1990). Chromium perchlorate (20 mmol) and benzene-1,3-dioxyacetic acid (40 mmol) were dissolved in water, and then the pH was adjusted to 7 with 0.1 *M* sodium hydroxide. The mixture was sealed in a Teflon-lined stainless steel bomb and held at 433 K for 5 d. The bomb was cooled naturally to room temperature. Purple crystals separated from the filtered solution after several days. Analysis calculated for $C_{20}H_{44}CrNaO_{26}$: C 30.98, H 5.72%; found: C 31.20, H 5.56%.

Crystal data

$[Cr(H_2O)_6][Na(C_{10}H_8O_6)_2(H_2O)_3]\cdot 5H_2O$
$M_r = 775.54$
Triclinic, $P\overline{1}$
$a = 9.334$ (2) Å
$b = 11.780$ (2) Å
$c = 16.303$ (3) Å
$\alpha = 103.54$ (3)°
$\beta = 104.82$ (3)°
$\gamma = 97.78$ (3)°
$V = 1648.1$ (7) Å^3

$Z = 2$
$D_x = 1.563$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7094 reflections
$\theta = 3.0$–27.4°
$\mu = 0.46$ mm^{-1}
$T = 293$ (2) K
Rhomboid, purple
0.32 × 0.23 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.866$, $T_{max} = 0.922$
15466 measured reflections

7345 independent reflections
5533 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 27.5°$
$h = -12 \rightarrow 12$
$k = -15 \rightarrow 15$
$l = -21 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.107$
$S = 1.01$
7345 reflections
517 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0568P)^2 + 0.6104P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cr1—O1*W*	1.966 (2)	Na1—O1	2.381 (2)
Cr1—O2*W*	1.994 (2)	Na1—O3	2.966 (2)
Cr1—O3*W*	1.962 (2)	Na1—O8	2.635 (2)
Cr1—O4*W*	1.959 (2)	Na1—O7*W*	2.365 (2)
Cr1—O5*W*	1.969 (2)	Na1—O8*W*	2.495 (2)
Cr1—O6*W*	1.967 (2)	Na1—O9*W*	2.426 (2)
O1*W*—Cr1—O2*W*	89.14 (7)	O7*W*—Na1—O9*W*	94.21 (8)
O1*W*—Cr1—O5*W*	88.70 (7)	O7*W*—Na1—O1	101.84 (8)
O3*W*—Cr1—O1*W*	178.83 (6)	O7*W*—Na1—O3	80.76 (8)
O3*W*—Cr1—O2*W*	91.06 (7)	O7*W*—Na1—O8	73.64 (7)
O3*W*—Cr1—O5*W*	90.14 (7)	O8*W*—Na1—O3	131.81 (8)
O3*W*—Cr1—O6*W*	89.26 (7)	O8*W*—Na1—O8	88.97 (8)
O4*W*—Cr1—O1*W*	92.50 (7)	O9*W*—Na1—O8*W*	82.57 (8)
O4*W*—Cr1—O2*W*	87.64 (7)	O9*W*—Na1—O3	90.36 (7)
O4*W*—Cr1—O3*W*	88.66 (7)	O9*W*—Na1—O8	142.29 (8)
O4*W*—Cr1—O5*W*	178.37 (7)	O1—Na1—O8*W*	100.74 (7)
O4*W*—Cr1—O6*W*	90.28 (7)	O1—Na1—O9*W*	141.47 (9)
O5*W*—Cr1—O2*W*	91.28 (7)	O1—Na1—O3	58.68 (6)
O6*W*—Cr1—O1*W*	90.58 (7)	O1—Na1—O8	76.20 (7)
O6*W*—Cr1—O2*W*	177.88 (7)	O8—Na1—O3	121.38 (6)
O6*W*—Cr1—O5*W*	90.82 (7)	C3—O3—C2	114.9 (2)
O7*W*—Na1—O8*W*	147.08 (9)	C13—O9—C12	114.8 (2)

Shan Gao *et al.* • $[Na(C_{10}H_8O_6)_2(H_2O)_3][Cr(H_2O)_6]\cdot 5H_2O$ **m623**

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*1···O6	0.85 (2)	1.76 (3)	2.606 (2)	177 (3)
O1*W*—H1*W*2···O2$^{\rm i}$	0.85 (2)	1.72 (3)	2.561 (2)	173 (3)
O2*W*—H2*W*1···O8*W*$^{\rm ii}$	0.84 (2)	2.06 (3)	2.828 (3)	152 (2)
O2*W*—H2*W*2···O12	0.86 (2)	1.70 (2)	2.550 (2)	174 (2)
O3*W*—H3*W*1···O11	0.85 (2)	1.78 (2)	2.618 (2)	172 (3)
O3*W*—H3*W*2···O7$^{\rm i}$	0.84 (2)	1.69 (2)	2.536 (2)	176 (2)
O4*W*—H4*W*1···O5	0.85 (2)	1.72 (2)	2.567 (2)	178 (2)
O4*W*—H4*W*2···O11*W*	0.84 (2)	1.89 (3)	2.715 (3)	169 (3)
O5*W*—H5*W*1···O13*W*	0.84 (2)	1.87 (3)	2.678 (2)	161 (3)
O5*W*—H5*W*2···O8$^{\rm i}$	0.85 (3)	1.77 (3)	2.617 (2)	174 (3)
O6*W*—H6*W*1···O1$^{\rm i}$	0.85 (2)	1.73 (2)	2.576 (2)	175 (3)
O6*W*—H6*W*2···O12*W*	0.85 (2)	1.84 (2)	2.680 (2)	175 (3)
O7*W*—H7*W*1···O14*W*$^{\rm iii}$	0.86 (2)	1.99 (3)	2.830 (3)	167 (3)
O7*W*—H7*W*2···O8	0.86 (2)	2.46 (3)	3.004 (3)	122 (3)
O7*W*—H7*W*2···O9	0.86 (2)	2.51 (2)	3.093 (2)	126 (2)
O8*W*—H8*W*1···O11$^{\rm iv}$	0.84 (3)	2.12 (3)	2.901 (3)	155 (3)
O8*W*—H8*W*2···O12*W*$^{\rm v}$	0.84 (3)	2.03 (3)	2.868 (3)	175 (4)
O9*W*—H9*W*1···O10*W*	0.84 (2)	2.21 (3)	3.049 (3)	169 (3)
O9*W*—H9*W*2···O13*W*$^{\rm vi}$	0.85 (3)	2.13 (3)	2.982 (3)	174 (3)
O10*W*—H20*A*···O4	0.85 (2)	2.43 (3)	3.152 (3)	143 (2)
O10*W*—H20*A*···O5	0.85 (2)	2.43 (3)	3.189 (3)	148 (3)
O10*W*—H20*B*···O12	0.85 (2)	2.27 (3)	3.052 (3)	154 (3)
O10*W*—H20*B*···O10	0.85 (2)	2.43 (3)	3.117 (3)	138 (2)
O11*W*—H21*A*···O10*W*$^{\rm vii}$	0.84 (2)	2.14 (3)	2.939 (3)	159 (3)
O11*W*—H21*B*···O7*W*$^{\rm vii}$	0.85 (2)	1.94 (3)	2.788 (3)	175 (4)
O12*W*—H22*A*···O12$^{\rm vii}$	0.84 (2)	2.12 (3)	2.883 (3)	151 (3)
O12*W*—H22*B*···O7$^{\rm iv}$	0.85 (2)	1.86 (3)	2.696 (2)	166 (3)
O13*W*—H23*A*···O2$^{\rm iii}$	0.86 (3)	1.98 (1)	2.818 (2)	168 (3)
O13*W*—H23*B*···O14*W*$^{\rm viii}$	0.86 (6)	1.95 (3)	2.795 (3)	171 (3)
O14*W*—H24*A*···O6	0.85 (3)	1.94 (3)	2.768 (3)	166 (3)
O14*W*—H24*B*···O5$^{\rm ix}$	0.84 (3)	2.09 (3)	2.880 (3)	157 (3)

Symmetry codes: (i) $1+x, y-1, z$; (ii) $x, y-1, z$; (iii) $-x, 1-y, 1-z$; (iv) $-x, 1-y, -z$; (v) $x-1, 1+y, z$; (vi) $x, 1+y, z$; (vii) $1+x, y, z$; (viii) $1-x, -y, 1-z$; (ix) $1-x, 1-y, 1-z$.

C-bound H atoms were placed in calculated positions [C—H = 0.93 (aromatic) or 0.97 Å (aliphatic)] and refined using the riding-model approximation, with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C). The H atoms of water molecules were located in a difference map and refined with O—H and H···H distance restraints of 0.85 (1) and 1.39 (1) Å, respectively, and $U_{\rm iso}$(H) = $1.5U_{\rm eq}$(O).

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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