N14—Mo12—O15	76.8 (6)	N26—Mo22—O25	87.3 (7)
N15—Mo12—O15	80.5 (6)	N24—Mo22—O25	79.7 (7)
N16—Mo12—O15	82.4 (6)	N23—Mo22—O25	78.6 (7)
Mo12—O13—Mo11	157.9 (7)	Mo22—O23—Mo21	156.7 (8)
N11—C11—S11	176 (2)	N21—C21—S21	177 (4)
N12—C12—S12	177 (2)	N22—C22—S22	174 (2)
N13—C13—S13	176 (3)	N23—C23—S23	176 (3)
N14—C14—S14	178 (2)	N24—C24—S24	175 (3)
N15—C15—S15	174 (3)	N25—C25—S25	174 (2)
N16—C16—S16	176 (2)	N26—C26—S26	175 (3)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
N32—H32···O16$^{\rm i}$	1.97	2.77 (2)	154
N41—H41···O27	2.07	2.83 (2)	148
N51—H51···O16$^{\rm i}$	1.91	2.76 (2)	170
N61—H61···O17	2.66	3.01 (3)	106
N71—H71···O27	2.08	2.86 (3)	150
N81—H81···O17$^{\rm i}$	1.79	2.62 (2)	162
N91—H91···O26	2.06	2.90 (3)	165
N104—H104···O26	1.85	2.67 (3)	159

Symmetry code: (i) $1 + x, y, z$.

Data collection and cell refinement: *DIF*4 (Stoe & Cie, 1992*a*). Data reduction: *REDU*4*S* (Stoe & Cie, 1992*b*). The structure was solved by Patterson and Fourier methods using *SHELXS*86 (Sheldrick, 1985) and refined by full-matrix least-squares on F using *SHELX*76 (Sheldrick, 1976) and on F^2 (in order to have a better ratio between the number of observations and the number of refined parameters) using *SHELXL*93 (Sheldrick, 1993). Residual indices obtained in the F^2 refinement were $R1 = 0.084$ for 3231 reflections with $F > 4\sigma(F)$ and 698 parameters (scale factor, positional and anisotropic displacement parameters for all atoms of the complex anions, positional and isotropic displacement parameters for C and N atoms of the pyridinium cations and an overall isotropic displacement parameter for H atoms), $wR2 = 0.348$ for 14 370 independent reflections and $wR2 = 0.389$ for all 14 446 reflections (76 reflections with $\Delta/\sigma > 5$ were omitted). The H atoms attached to the pyridinium cations were positioned geometrically (C—H 0.93 and N—H 0.86 Å) and included as riding atoms in the structure-factor calculations. All structural parameters discussed in the *Comment* are from the F^2 refinement. Software used to prepare molecular graphics and material for publication: *PLUTON* (Spek, 1982); *SHELXL*93; *CSU* (Vicković, 1988).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: NA1097). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Głowiak, T., Rudolf, M. F., Sabat, M. & Jezowska-Trzebiatowska, B. (1977). *J. Less-Common Met.* **54**, 35–50.

Kamenar, B., Kaitner, B. & Strukan, N. (1991). *Croat. Chem. Acta*, **64**, 329–341.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* Univ. of Cambridge, England.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL93. Program for Crystal Structure Refinement.* Univ. of Göttingen, Germany.

Shibahara, T., Kuroja, H., Matsumoto, K. & Ooi, S. (1983). *Bull. Chem. Soc. Jpn*, **56**, 2945–2948.

Spek, A. L. (1982). *The EUCLID Package. Computational Crystallography*, edited by D. Sayre, p. 528. Oxford: Clarendon Press.

Stoe & Cie (1992*a*). *DIF*4. *Diffractometer Control Program.* Revision 7.09.x/DOS. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1992*b*). *REDU4S. Data Reduction Program.* Revision 7.03/S. Stoe & Cie, Darmstadt, Germany.

Vicković, I. (1988). *J. Appl. Cryst.* **21**, 987–990.

Yang, R. & Yu, X. (1984). *Jiegou Huaxue*, **3**, 101–104.

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Lithium Tris(oxalato-*O*,*O*′)chromate(III) Hexahydrate

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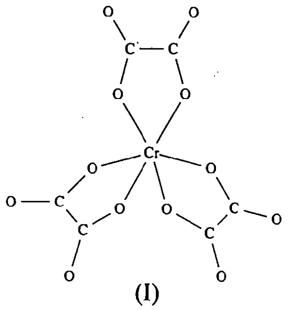
Abstract

In the title compound, $3\mathrm{Li[Cr(C_2O_4)_3].6H_2O}$, the Li cations are coordinated by O atoms of both the oxalato ligands and the solvent water molecules. Two of the six water molecules are not bonded to the Li cations but are instead hydrogen bonded to other water molecules or oxalato ligand molecules. The tris(oxalato)chromate(III) anion takes the form of a distorted octahedron. The average Cr—O distance and O—Cr—O angle of the chelate rings are 1.979 Å and 82.3°, respectively.

Comment

The effect of the environment around the $\mathrm{Cr^{3+}}$ ion on its luminescence and relaxation has been studied extensively using various ligands. The relationship between the complex distortion and the relative intensity of the 0–0 band and the vibronic band has been reported (Flint, 1974). We have examined the effect of the solvent water molecules in tris(oxalato)chromate(III) complex crystals on the luminescence intensity of relaxation from ^2E_g to $^4A_{2g}$. In order to elucidate the mechanism, the structure of the title complex has been determined.

The chromate ion (I) is octahedrally coordinated by three oxalato ligands. The averages of the six Cr—O bonds and the three O—Cr—O angles of the chelate rings are 1.979 Å and 82.3°, respectively, which are very similar to the corresponding values for the sodium (Bulc, Golič & Šiftar, 1982) and potassium salts (Taylor, 1978). The three oxalato ligands deviate slightly from a planar conformation, which is probably due to the intermolecular hydrogen bonding. The Li^+ ions are coordinated by the O atoms of both the water molecules and the oxalato ligands. The Li1, Li2 and Li3 atoms have octahedral, square-pyramidal and tetrahedral conformations, respectively, although they do deviate significantly from the ideal structures. The Li···O distances range from 2.024 (4) to 2.270 (3) Å for Li1, from 1.999 (4) to 2.131 (4) Å for Li2 and from 1.946 (5) to 2.000 (4) Å for Li3. The other Li···O distances are greater than 2.75 Å.



(I)

Four solvent water molecules (*O*W1, *O*W2, *O*W3 and *O*W6) are tightly bound to the Li cations, while the other two (*O*W4 and *O*W5) are tetrahedrally hydrogen bonded to water molecules and the O atoms of oxalato ligands. Dehydration by the loss of *O*W4 may bring a reduction of emission intensity, which has been discussed in detail in a previous paper (Otsuka, Sekine, Ohashi & Kaizu, 1992).

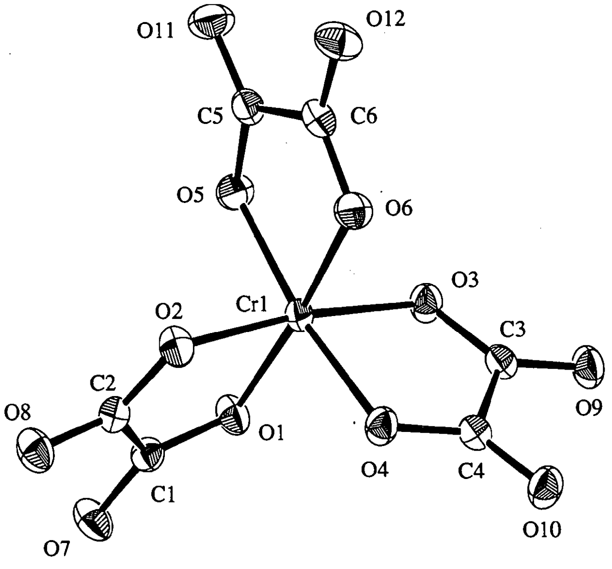


Fig. 1. Plot (*ORTEP*II; Johnson, 1976) of the molecular structure of the tris(oxalato)chromate(III) anion showing the labeling of the atoms. Displacement ellipsoids are shown at 50% probability.

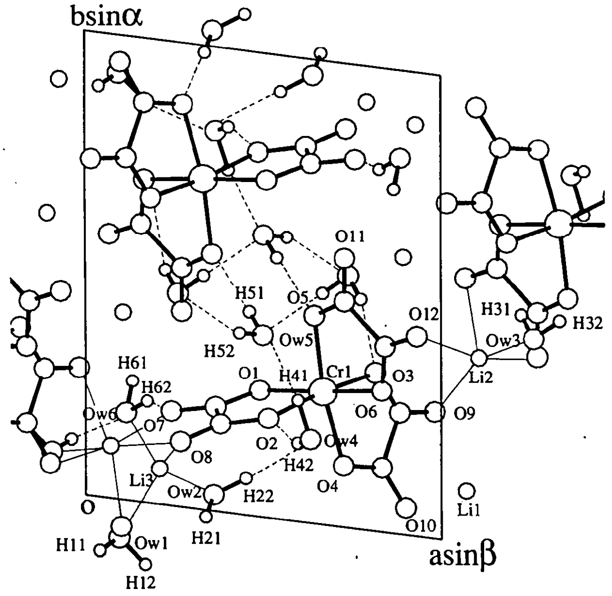


Fig. 2. The crystal structure viewed along the *c* axis. Fine and dashed lines indicate coordination and hydrogen bonds, respectively.

Experimental

Crystal data

$3Li[Cr(C_2O_4)_3].6H_2O$
$M_r = 444.969$
Triclinic
$P\bar{1}$
$a = 9.321$ (2) Å
$b = 11.947$ (2) Å
$c = 8.066$ (2) Å
$\alpha = 104.86$ (1)°
$\beta = 109.44$ (1)°
$\gamma = 91.79$ (1)°
$V = 811.9$ (3) Å^3
$Z = 2$
$D_x = 1.82$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 14.87$–$15.04°$
$\mu = 0.776$ mm^{-1}
$T = 296.15$ K
Plate
0.5 × 0.4 × 0.1 mm
Dark purple
Crystal source: grown from water

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: none
3969 measured reflections
3739 independent reflections
3399 observed reflections [$I > 3.0\sigma(I)$]

$\theta_{max} = 27.5°$
$h = 0 \rightarrow 12$
$k = -15 \rightarrow 15$
$l = -10 \rightarrow 9$
3 standard reflections monitored every 100 reflections
intensity variation: 0.8%

Refinement

Refinement on F
$R = 0.032$
$wR = 0.048$
$S = 2.3$
3399 reflections
253 parameters
H-atom parameters not refined

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.77$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Cr	0.66754 (3)	0.28763 (2)	0.29828 (4)	0.0175
O1	0.4895 (1)	0.2735 (1)	0.0732 (2)	0.0228
O2	0.5132 (1)	0.2146 (1)	0.3704 (2)	0.0233
O3	0.8149 (1)	0.3432 (1)	0.1985 (2)	0.0235
O4	0.7253 (1)	0.1328 (1)	0.1982 (2)	0.0232
O5	0.6434 (1)	0.4476 (1)	0.4198 (2)	0.0241
O6	0.8333 (1)	0.3051 (1)	0.5372 (2)	0.0260
O7	0.2402 (1)	0.2042 (1)	−0.0532 (2)	0.0280
O8	0.2656 (2)	0.1401 (1)	0.2568 (2)	0.0277
O9	0.9820 (1)	0.2742 (1)	0.0651 (2)	0.0263
O10	0.9001 (2)	0.0586 (1)	0.0808 (2)	0.0285
O11	0.7295 (2)	0.5788 (1)	0.6969 (2)	0.0326
O12	0.9318 (2)	0.4314 (1)	0.8170 (2)	0.0321
O*W*1	0.0947 (2)	−0.0831 (1)	0.2890 (2)	0.0376
O*W*2	0.3591 (2)	0.0348 (2)	0.6283 (3)	0.0501
O*W*3	1.2602 (2)	0.4579 (1)	−0.0621 (2)	0.0389
O*W*4	0.6322 (2)	0.1801 (2)	0.7288 (2)	0.0475
O*W*5	0.4983 (2)	0.3923 (2)	0.7759 (3)	0.0508
O*W*6	0.1135 (2)	0.1890 (2)	0.5735 (2)	0.0476
C1	0.3649 (2)	0.2252 (1)	0.0726 (2)	0.0191
C2	0.3784 (2)	0.1894 (1)	0.2477 (2)	0.0196
C3	0.8838 (2)	0.2628 (2)	0.1304 (2)	0.0197
C4	0.8334 (2)	0.1391 (1)	0.1351 (2)	0.0199
C5	0.7289 (2)	0.4858 (2)	0.5899 (2)	0.0216
C6	0.8424 (2)	0.4013 (2)	0.6580 (2)	0.0222
Li1	1.0705 (4)	0.1122 (3)	−0.0148 (5)	0.0298
Li2	1.1061 (4)	0.4032 (3)	0.0376 (5)	0.0322
Li3	0.2077 (5)	0.0767 (3)	0.4282 (5)	0.0375

Table 2. *Selected geometric parameters* (Å, °)

Cr—O1	1.975 (1)	O6—C6	1.282 (2)
Cr—O2	1.977 (2)	O7—C1	1.229 (2)
Cr—O3	1.982 (2)	O8—C2	1.222 (2)
Cr—O4	1.987 (1)	O9—C3	1.218 (3)
Cr—O5	1.969 (1)	O10—C4	1.227 (2)
Cr—O6	1.984 (1)	O11—C5	1.218 (2)
O1—C1	1.278 (2)	O12—C6	1.225 (2)
O2—C2	1.282 (2)	C1—C2	1.545 (3)
O3—C3	1.280 (2)	C3—C4	1.550 (3)
O4—C4	1.279 (3)	C5—C6	1.551 (3)
O5—C5	1.286 (2)		
O1—Cr—O2	82.68 (6)	O5—Cr—O6	82.77 (5)
O3—Cr—O4	82.74 (6)		

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989*a*). Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989*b*). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1109). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bulc, N., Golič, L. & Šiftar, L. (1982). *Vestn. Slov. Kem. Drus.* **29**, 211–225.

Flint, C. D. (1974). *Coord. Chem. Rev.* **14**, 47–66.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (1989*a*). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1989*b*). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Otsuka, T., Sekine, A., Ohashi, Y. & Kaizu, Y. (1992). *Bull. Chem. Soc. Jpn*, **65**, 3378–3385.

Taylor D. (1978). *Aust. J. Chem.* **31**, 1455–1462.

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Two Mononuclear Tetraphenylphosphonium Oxochromium Complexes: $(PPh_4)[Cr^{V}O_3(H_2O)]$ and $(PPh_4)[Cr^{VI}O_3(OH)]$

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Abstract

The crystal structures of two isostructural compounds, tetraphenylphosphonium aquatrioxochromium(V), (1), $[P(C_6H_5)_4][CrO_3(H_2O)]$, and tetraphenylphosphonium hydroxytrioxochromium(VI), (2), $[P(C_6H_5)_4][CrO_3(OH)]$, have been determined by single-crystal X-ray diffraction. (1) is paramagnetic and (2) is diamagnetic. The P atoms in the cations of both structures lie on the crystallographic $\bar{4}$ symmetry axis at the unit-cell origin. The anions are found near the $\bar{4}$ sites at 0, $\frac{1}{2}$, $\frac{1}{4}$ and are fourfold disordered. The Cr atoms in the anions have a deformed tetrahedral coordination geometry with three normal Cr═O bonds [average 1.56 (3) Å] and a fourth Cr—O(aqua) or Cr—O(hydroxy) bond [2.07 (3) and 2.02 (3) Å in compounds (1) and (2), respectively].

Comment

High-valent chromium complexes featuring oxo ligands are of use in catalytic oxidation reactions. The title chromium compounds were obtained during our studies of oxo- and sulfido-bridged metal complexes (Bhattacharya *et al.*, 1991). Preliminary spectroscopic data