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Spinel-type $HgCr_2O_4$ from single-crystal data

Matthias Weil* and Berthold Stöger

Institute for Chemical Technologies and Analytics, Division of Structural Chemistry, Vienna University of Technology, Getreidemarkt 9/164-SC, A-1060 Vienna, Austria

Correspondence e-mail: mweil@mail.zserv.tuwien.ac.at

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Cr–O) = 0.001 Å
R factor = 0.011
wR factor = 0.023
Data-to-parameter ratio = 15.3

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

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The crystal structure of mercury(II) chromium(III) tetroxide has been redetermined from a single crystal grown from an HgO–CrO_3 mixture at 743 K in an evacuated silica ampoule. The present investigation confirms the previous study, which was based on powder data [Wessels, Czekalla & Jeitschko (1998). *Mater. Res. Bull.* **33**, 95–191], but with higher precision and with all displacement parameters refined anisotropically. $HgCr_2O_4$ adopts the normal 2–3-spinel structure, with mercury in one-eighth of the tetrahedral and chromium in one-half of the octahedral voids of the cubic closed-packed O atoms.

Comment

Crystallographically well characterized mercury chromates include the double basic $HgCrO_4{\cdot}2HgO$ (Hansen *et al.*, 1995), the neutral α- and β-$HgCrO_4$ (Stålhandske, 1978; Stöger & Weil, 2006), the hemihydrate $HgCrO_4{\cdot}0.5H_2O$ (Aurivillius & Stålhandske, 1975), the monohydrate $HgCrO_4{\cdot}H_2O$ (Stöger & Weil, 2006), the dichromate $HgCr_2O_7$ (Weil *et al.*, 2006), the basic mercury(I) compound $2Hg_2CrO_4{\cdot}Hg_2O$ (Weil & Stöger, 2006), the mixed-valent mercury(I,II) compound $2Hg_2CrO_4{\cdot}2HgO$ (Weil & Stöger, 2006), the mineral watterssite, Hg_5CrO_6 [= $(Hg_2)_2CrO_4{\cdot}HgO_2$] that likewise comprises mixed-valent mercury in oxidation states +I and + II (Groat *et*

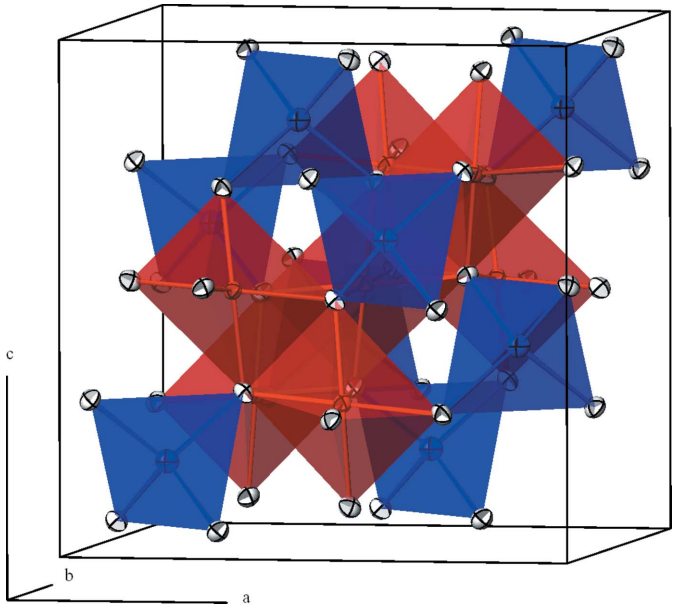

Figure 1
The crystal structure of 2–3 spinel type $HgCr_2O_4$ in polyhedral representation. The displacement ellipsoids are given at the 90% probability level. Colour key: O atoms white spheres, HgO_4 tetrahedra dark blue and CrO_6 octahedra red.

al., 1995), and the mercury(II) chromate(III) $HgCr_2O_4$ (Wessels *et al.*, 1998).

Experiments on the thermal behaviour of $HgCr_2O_7$ led to a yet unknown phase in the system Hg—Cr—O which was observed in the temperature range 573–743 K (Weil *et al.*, 2006). During systematic studies on phase formation of this unknown compound, single crystals of $HgCr_2O_4$ were obtained incidentally. The crystal structure of $HgCr_2O_4$ has been previously determined by Rietveld analysis from laboratory X-ray powder data to a profile residual of R_p = 0.092 (Wessels *et al.*, 1998). The present single crystal study confirms the basic structural features determined from the powder refinement, but with higher precision and with all displacement parameters refined anisotropically.

$HgCr_2O_4$ adopts the normal 2–3 spinel structure. The Hg atoms occupy one-eighth of the tetrahedral voids, and the Cr atoms occupy one-half of the octahedral voids of the cubic close-packed O atoms. As discussed previously (Wessels *et al.*, 1998), the O atoms deviate from a perfectly packed arrangement which would require a positional parameter x of exactly 0.25. The deviation resulting from x = 0.22968 (14) in the present case leads to larger tetrahedral voids for the Hg atoms and to a slight distortion of the corresponding CrO_6 octahedra. The Cr—O distances (Table 1) are in the usual range for octahedrally coordinated Cr^{3+}, whereas Hg^{2+} typically prefers a pronounced linear $[2 + x]$ coordination, where x may range from 2 to 8 (Wells, 1975), instead of a perfect tetrahedral coordination as observed here.

Experimental

A mixture of HgO (212.9 mg, 0.930 mmol) (Merck, p.A.) and CrO_3 (206.8 mg, 2.068 mmol) (Merck, p.A.) was placed in a silica ampoule which was evacuated, sealed and then heated in a conventional laboratory furnace at 743 K for 24 d. The product consisted of dark-green to black glistening crystals of $HgCr_2O_4$ with octahedral shape, besides very small amounts of liquid mercury.

Crystal data

$HgCr_2O_4$
M_r = 368.59
Cubic, $Fd\bar{3}m$
a = 8.6443 (3) Å
V = 645.94 (4) Å^3
Z = 8
D_x = 7.580 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 53.86 mm^{-1}
T = 293 (2) K
Octahedron, black
0.06 × 0.05 × 0.05 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: numerical (*HABITUS*; Herrendorf, 1997)
T_{min} = 0.093, T_{max} = 0.216
3703 measured reflections
122 independent reflections
114 reflections with $I > 2\sigma(I)$
R_{int} = 0.099
θ_{max} = 40.0°
3 standard reflections
frequency: 200 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.011
$wR(F^2)$ = 0.023
S = 1.15
122 reflections
8 parameters
$w = 1/[\sigma^2(F_o^2) + 1.36P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.18 e Å^{-3}
$\Delta\rho_{min}$ = −1.66 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00043 (12)

Table 1
Selected geometric parameters (Å, °).

Hg—O1	2.176 (2)	Cr—O1^{i}	2.0009 (10)
O1^{i}—Cr—O1^{ii}	100.48 (8)	Cr^{iv}—O1—Hg	118.13 (5)
O1^{i}—Cr—O1^{iii}	79.52 (8)		

Symmetry codes: (i) $-x, y-\frac{1}{4}, z-\frac{1}{4}$; (ii) $-x+\frac{1}{4}, -y+\frac{1}{4}, z$; (iii) $x-\frac{1}{4}, y-\frac{1}{4}, -z$; (iv) $x, -y+\frac{1}{4}, -z+\frac{1}{4}$.

The atomic coordinates were taken from the previous refinement (Wessels *et al.*, 1998) as starting parameters, with setting 2 of space group $Fd\bar{3}m$ [origin at centre $\bar{3}m$]. The highest peak in the final Fourier map is 0.59 Å from Hg and the deepest hole is 1.57 Å from O.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *HELENA* implemented in *PLATON* (Spek, 2003); method used to solve structure: coordinates taken from a previous refinement; program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *SHELXL97*.

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