

Crystal Structure and Characterisation of Mercury(II) Dichromate(VI)

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Summary. Dark-red single crystals of HgCr_2O_7 were grown by reacting HgO and CrO_3 in excess at 200°C for four days. The crystal structure (space group $P3_2$, $Z = 3$, $a = 7.2389(10)$, $c = 9.461(2)$ Å, 1363 structure factors, 57 parameters, $R[F^2 > 2\sigma(F^2)] = 0.0369$, $wR(F^2 \text{ all}) = 0.0693$) was determined from a crystal twinned by merohedry according to (110). It consists of nearly linear HgO_2 units ($\bar{d}(\text{Hg}-\text{O}) = 2.02$ Å) and dichromate units that are linked into infinite chains ‘ $\text{O}_3\text{Cr}-\text{O}-\text{CrO}_3-\text{Hg}-\text{O}_3\text{Cr}-\text{O}-\text{CrO}_3$ ’ running parallel to the c -axis. Six additional $\text{Hg}-\text{O}$ contacts between 2.73 and 2.96 Å stabilise the structural arrangement. The dichromate anion exhibits a staggered conformation with a bent $\text{Cr}-\text{O}-\text{Cr}$ bridging angle of $140.7(6)^\circ$. Upon heating above 300°C , HgCr_2O_7 decomposes in a two-step mechanism to Cr_2O_3 . The title compound was additionally characterised by vibrational spectroscopy.

Keywords. Crystal structure; Dichromates(VI); Mercury(II); Thermal behaviour; Vibrational spectroscopy.

Introduction

The *Gmelin* handbook on chromium and its compounds reports several phases within the system $\text{Hg}-\text{Cr}-\text{O}-(\text{H})$ [1]. The crystal structures for some of these compounds have in the meantime been solved and refined. Crystallographically well-characterised compounds include the mercury(II) chromates(VI) in the form of the double basic salt $\text{HgCrO}_4 \cdot 2\text{HgO}$ [2], which is isotypic with the mineral *schuetteite*, $\text{HgSO}_4 \cdot 2\text{HgO}$ [3], the neutral salt HgCrO_4 [4], and the hemihydrate $\text{HgCrO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ [5]. Besides the mineral *wattersite*, Hg_5CrO_6 [6], which contains chromate(VI) anions and mixed-valent mercury in oxidation states +I and +II, the spinel-type mercury(II) chromate(III) HgCr_2O_4 is also known [7]. In a very recent study on hydrothermal phase formation of mercury(II) chromates(VI), a second

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modification of HgCrO_4 and the monohydrate $\text{HgCrO}_4 \cdot \text{H}_2\text{O}$ were obtained and structurally elucidated [8].

Mercury(II) dichromate(VI), HgCr_2O_7 , was reported to exist under equilibrium conditions in the system $\text{CrO}_3\text{--HgO--H}_2\text{O}$ at 25°C and low pH [9]. However, no structural information on this compound has ever been given since. The present communication reports on crystal growth and the crystal structure of HgCr_2O_7 which was further characterised by thermal analysis and vibrational spectroscopy.

Results and Discussion

Formation and Thermal Decomposition

According to X-ray powder diffraction (XRPD), formation of single phase HgCr_2O_7 by solid state reaction is only achieved when a minimum excess of 7% by weight with respect to the stoichiometric amount of CrO_3 was applied. Below this value $\alpha\text{-HgCrO}_4$ was observed as a minor by-product in each batch. The previously conducted gravimetric determination of the water content of the employed CrO_3 yielded values of *ca.* 1.4% by weight. Hence an excess of about 4–5% by weight of CrO_3 was present in the reaction products (not detected by XRPD), which is in agreement with the results of the thermal behaviour of the as-synthesized HgCr_2O_7 . The differential scanning calorimetry (DSC) curve of this material clearly indicates the melting point of CrO_3 at 197°C [10] (see DSC curve of the employed CrO_3 for comparison, Fig. 1). The amount of excessive CrO_3 explains also the discrepancy

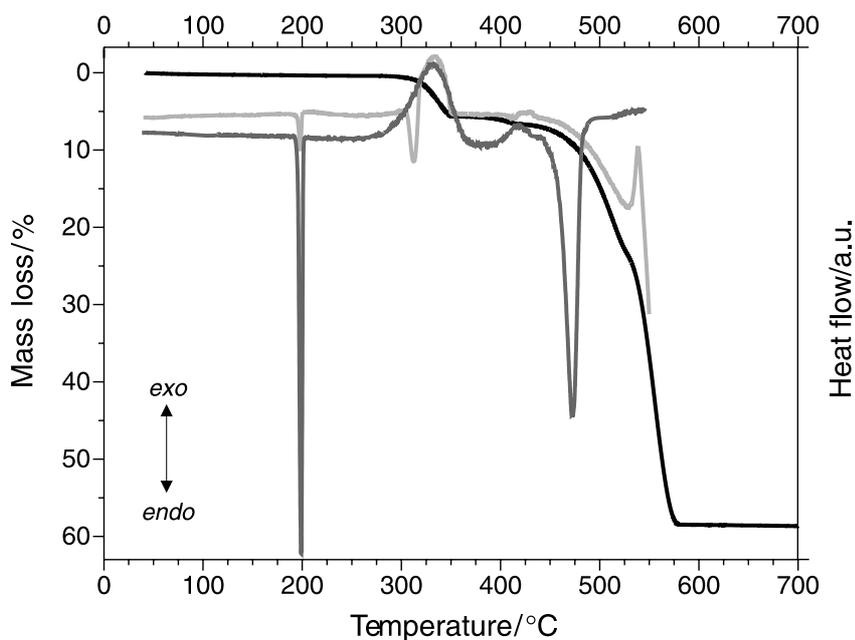
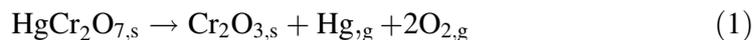


Fig. 1. TG and DSC curves of the thermal decomposition of HgCr_2O_7 and the employed CrO_3 ; the TG curve of HgCr_2O_7 is represented as a black line, the DSC curve of HgCr_2O_7 as a light-grey line, and the DSC curve of CrO_3 as a dark-grey line

between the theoretical mass loss of 63.5% and the mass loss of 58.1% observed during the thermal decomposition.

According to Eq. (1), the overall decomposition reaction of HgCr_2O_7 yields Cr_2O_3 in the form of a microcrystalline green powder which was detected by XRPD of the product heated up to 700°C.



However, there is a previous thermolysis reaction starting at about 300°C with a decomposition range up to *ca.* 450°C, which is accompanied by an endothermal effect at *ca.* 310°C and a mass loss of *ca.* 6.5%. XRPD of the almost black product obtained at 450°C did not indicate any known phase in the system Hg–Cr–O. Semi-quantitative energy-dispersive X-ray spectra of this solid revealed averaged Hg:Cr ratios of $\approx 1:3.5$, indicating a phase with lower Hg content than the educt. Even if the excess of chromium owing to the formation conditions of single phase HgCr_2O_7 is neglected, the loss of nearly 1.5 Hg atoms per formula unit is not in accordance with the observed mass loss. Thus the composition of this intermediate phase remains unclear, but for the future further TG experiments with coupled mass spectrometry are planned to get a deeper insight into the formed volatile decomposition product(s). X-Ray powder diffraction of a sample heated up to 530°C showed mainly the spinel-phase HgCr_2O_4 [7], and minor amounts of the yet unknown phase.

Experiments on phase formation and crystal growth of HgCr_2O_7 under hydro-thermal conditions (200°C, 4 d) were not successful. Even very high $\text{CrO}_3:\text{HgO}$ molar ratios ≥ 10 did not yield the desired product but led instead to crystal growth of α - and β - HgCrO_4 [8].

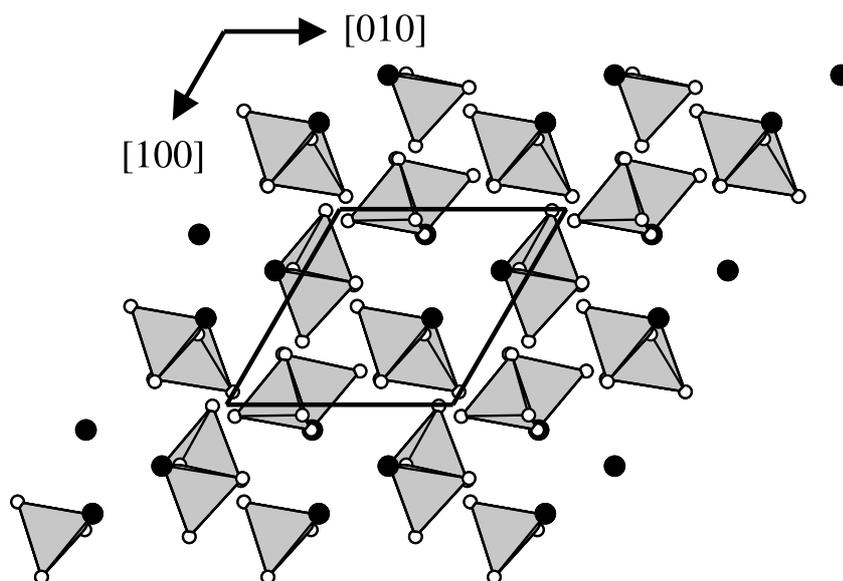


Fig. 2. The crystal structure of HgCr_2O_7 in projection along [001]; the unit cell is outlined and the dichromate anion is plotted in the polyhedral representation; Hg atoms are given as black spheres and O atoms as white spheres with black rims

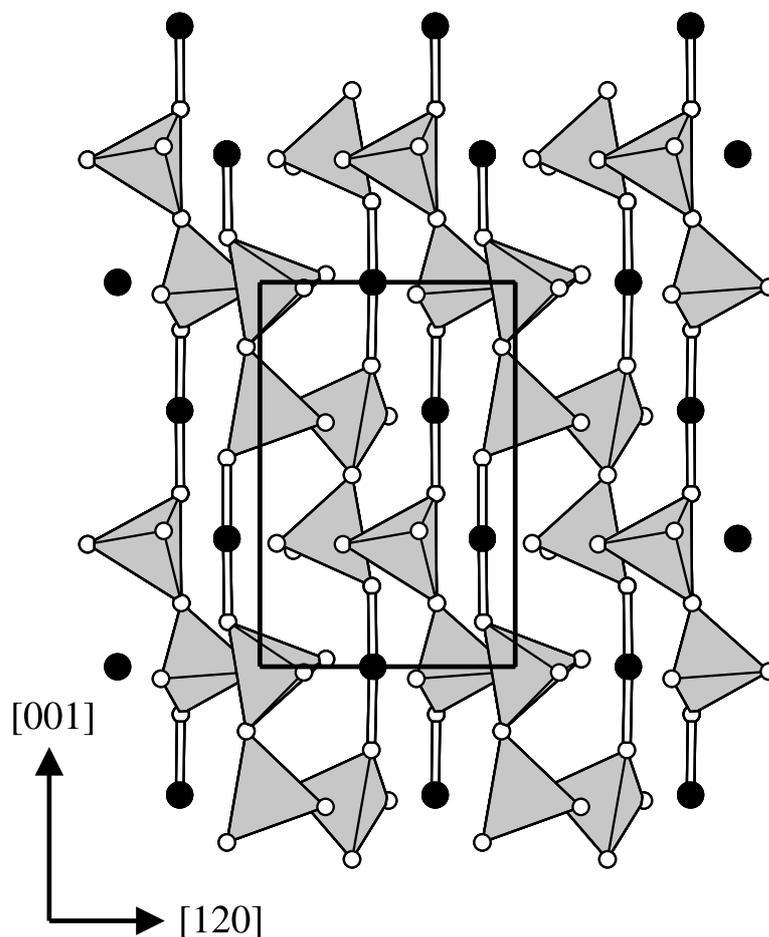


Fig. 3. The crystal structure of HgCr_2O_7 in projection along $[100]$; colour key as in Fig. 2; for clarity, only short Hg–O bonds are indicated by solid lines

Crystal Structure

The crystal structure comprises HgO_2 and Cr_2O_7 groups as the main building blocks that are linked into infinite chains ‘ $\text{O}_3\text{Cr}-\text{O}-\text{CrO}_3-\text{Hg}-\text{O}_3\text{Cr}-\text{O}-\text{CrO}_3$ ’ parallel to the c axis (Figs. 2 and 3). The Hg atom shows a nearly linear coordination ($\angle(\text{O}-\text{Hg}-\text{O}) = 178.0(5)^\circ$) to the two tightly bonded oxygen atoms O5 and O6 with an average Hg–O distance of 2.02 Å. The coordination sphere around Hg is augmented by six additional oxygen atoms with Hg–O distances between 2.73 and 2.96 Å, which leads to a cross-linking of the building units parallel to the ab plane. The resulting $[\text{HgO}_2\text{O}_6]$ polyhedron might be described as a distorted hexagonal bipyramid with two short bonds to the apices. The preference for a linear coordination under formation of $[\text{HgO}_2\text{O}_x]$ polyhedra, where the number x of the remote oxygen atoms may range from 2 to 8, is characteristic for Hg^{2+} and observed in many other mercuric oxocompounds [11–13].

The dichromate anion is composed of two corner-sharing CrO_4 tetrahedra and has a staggered conformation with a $\angle(\text{Cr}-\text{O}-\text{Cr})$ bridging angle of $140.7(6)^\circ$.

The average bond length in the two CrO₄ tetrahedra of 1.657 Å is very similar to that observed for most other dichromate(VI) groups. The differences in Cr–O distances to the terminal ($\bar{d}(\text{Cr–O})_{\text{terminal}} = 1.625 \text{ \AA}$) and to the bridging O atoms ($\bar{d}(\text{Cr–O})_{\text{bridging}} = 1.749 \text{ \AA}$) are also typical of Cr₂O₇ groups. Peculiarities of dichromate anions and similar condensed dianions of the type X₂O₇ⁿ⁻ containing four-coordinate X atoms (X = Si, Ge: *n* = 6; P, As, V: *n* = 4; S: *n* = 2) have been reviewed in detail in the past [14–16]. Besides the title compound, to our knowledge only two other dichromates(VI) of the formula type MCr₂O₇ have so far been structurally characterised. SrCr₂O₇ [17] and BaCr₂O₇ [18] contain two dichromate units each, all of which exhibit an eclipsed conformation and bridging angles of 132.8 and 140.5° for the Sr compound, and 129.2 and 137.7° for the Ba compound, respectively. For all three MCr₂O₇ compounds (*M* = Sr, Ba, Hg), the bridging oxygen atoms of the dichromate units do not belong to the coordination spheres of the corresponding cations. In contrast to this behaviour, the bridging oxygen atoms of the dichromate units in the compounds of formula type M₂Cr₂O₇ with monovalent counter cations are also involved in the coordination sphere of the respective cations (*M* = Na, Ag, K, Rb, NH₄).

The coordination numbers of the O atoms range from 2 to 3. The two-coordinate atoms O1, O2, O3, and O4 have one Hg atom and one Cr atom as coordination partners, whereas the bridging atom O7 of the dichromate group is exclusively bonded to both Cr atoms; the three-coordinate O atoms O5 and O6 are bonded to two Hg atoms and one Cr atom with one very short Hg–O bond, one very long Hg–O bond, and one comparatively long Cr–O bond. For all atoms in the structure, results of the bond-valence analysis [19], using the parameters provided by *Brese* and *O'Keefe* [20], are within the range of the expected values (Table 1).

Table 1. Selected distances [Å], angles [°] and bond valence sums (BVS) [v.u.]

| | | | | | | |
|-----|---------------------|-----------|--------------------|-----|---------------------|-----------|
| Hg | O6 | 1.98(3) | O2 ^(vi) | Cr1 | O4 | 106.3(8) |
| Hg | O5 | 2.05(4) | O2 ^(vi) | Cr1 | O5 ^(vi) | 114.7(10) |
| Hg | O2 ⁽ⁱ⁾ | 2.726(16) | O4 | Cr1 | O5 ^(vi) | 112.4(8) |
| Hg | O3 ⁽ⁱⁱ⁾ | 2.728(14) | O2 ^(vi) | Cr1 | O7 ⁽ⁱⁱⁱ⁾ | 108.7(8) |
| Hg | O1 ⁽ⁱⁱⁱ⁾ | 2.829(17) | O4 | Cr1 | O7 ⁽ⁱⁱⁱ⁾ | 108.3(9) |
| Hg | O4 | 2.868(16) | O5 ^(vi) | Cr1 | O7 ⁽ⁱⁱⁱ⁾ | 106.2(10) |
| Hg | O5 ^(iv) | 2.938(19) | O3 | Cr2 | O1 | 107.4(9) |
| Hg | O6 ^(v) | 2.963(15) | O3 | Cr2 | O6 | 109.9(8) |
| Cr1 | O2 ^(vi) | 1.574(16) | O1 | Cr2 | O6 | 109.2(8) |
| Cr1 | O4 | 1.612(16) | O3 | Cr2 | O7 ^(iv) | 111.6(8) |
| Cr1 | O5 ^(vi) | 1.67(3) | O1 | Cr2 | O7 ^(iv) | 110.6(8) |
| Cr1 | O7 ⁽ⁱⁱⁱ⁾ | 1.762(18) | O6 | Cr2 | O7 ^(iv) | 108.1(9) |
| Cr2 | O3 | 1.585(14) | Cr2 | O7 | Cr1 | 140.7(6) |
| Cr2 | O1 | 1.590(17) | O6 | Hg | O5 | 178.0(5) |
| Cr2 | O6 | 1.72(2) | | | | |
| Cr2 | O7 ^(iv) | 1.736(17) | | | | |

Symmetry codes: (i) $1 - x + y, 2 - x, 1/3 + z$; (ii) $1 - y, x - y, z - 1/3$; (iii) $2 - y, 1 + x - y, z - 1/3$; (iv) $-x + y, 1 - x, 1/3 + z$; (v) $1 - y, 1 + x - y, z - 1/3$; (vi) $1 - x + y, 1 - x, 1/3 + z$; BVS: Hg 2.23, Cr 5.89, O1 1.83, O2 1.94, O3 1.88, O4 1.72, O5 2.27, O6 2.28 O7 2.26

Table 2. Assignment of the infrared and *Raman* spectra of HgCr_2O_7 (band positions in cm^{-1})

| Infrared | <i>Raman</i> | Assignment |
|--------------|----------------------|---|
| 947 vs, br | 960 sh, 947 vs | $\nu_{\text{as}}(\text{CrO}_3)$ |
| 904 m, 885 m | 907 s, 871 sh, 844 s | $\nu_{\text{s}}(\text{CrO}_3)$ |
| 764 vs, br | | $\nu_{\text{as}}(\text{Cr-O-Cr})$ |
| 565 w, 530 w | 552 w, 527 s | $\nu_{\text{s}}(\text{Cr-O-Cr})$ |
| 459 m | 417 w, 383 s, 352 m | $\delta(\text{CrO}_3)$ |
| | 311 m | $\delta(\text{CrO}_3)\text{-sciss}/\rho(\text{CrO}_3)(?)$ |
| | 216 m | $\delta(\text{Cr-O-Cr}) (?)$ |
| | 176 m | torsion + lattice |

vs very strong; s strong; m medium; w weak; sh shoulder; br broad

Vibrational Spectroscopy

For the “free” dichromate anion of approximately C_{2v} symmetry, twenty-one fundamental vibrations belonging to non-degenerate species are expected [21]. In the present case, and as all the ions are located at general positions C_1 in the crystal lattice, under site-symmetry conditions [21, 22] all these are A species. Besides, as the unit cell contains three formula units, under factor group symmetry (C_3) [21, 22] a greater number of bands (21A + 42E), all showing IR- and *Raman*-activity, are expected. Notwithstanding, the obtained spectra are relatively simple showing a limited impact of correlation field effects.

Therefore, we have performed an approximate assignment of these spectra, on the basis of the solution *Raman* spectrum of $\text{K}_2\text{Cr}_2\text{O}_7$ discussed in the classical paper of *Stammreich et al.* [23], and on some other studies on different crystalline dichromates [23–28]. This assignment is presented in Table 2.

In the region of the stretching vibrations of the terminal CrO_3 -groups the IR spectrum shows only a strong and relatively broad band assignable to the antisymmetric mode, and two medium intensity components of the respective symmetric vibration. In the *Raman* spectrum the ν_{as} -vibration is seen as the strongest line with a weak shoulder at higher energies whereas the symmetric mode appears related to two strong peaks and a shoulder.

The bridge stretching vibrations show the usual behaviour: the antisymmetric mode presents a high IR intensity and is absent in the *Raman* spectrum, whereas the corresponding symmetric vibration presents the inverse behaviour (two weak IR components and a strong *Raman* line preceded by a weak satellite band at higher energies).

From the remaining bands only a group of CrO_3 -deformational modes can be assigned with certainty. Torsion and rocking modes are more difficult to assign. The Cr–O–Cr bending vibration is expected to occur at about 220 cm^{-1} [23]. Therefore, the 216 cm^{-1} line seen in our *Raman* spectrum may be assignable to this vibration, although it is possible that it lies at lower energies, as has been suggested for some other $\text{O}_3\text{X-O-XO}_3$ species [29–32].

Finally, another interesting aspect should be remarked. The IR spectrum of HgCr_2O_7 clearly shows the presence of water absorptions (a relatively strong doublet with components at 3583 and 3525 cm^{-1} , assignable to the O–H-stretching vibrations and a strong and well defined feature at 1612 cm^{-1} , assignable to the

$\delta(\text{HOH})$ deformational mode). The appearance of water bands can probably be related to the presence of small amounts of CrO₃ as an impurity (*cf.* the synthesis procedure) or to the observed slow decomposition of the compound, which also generates CrO₃. As it is known, chromium trioxide is highly hygroscopic and, therefore, can strongly absorb ambient humidity. The presence of a small amount of CrO₃ in the measured sample is also possibly responsible for the broadening of the 947 cm⁻¹ IR band, because the strongest IR band of the trioxide lies in this same region [24]. Besides, the unexpected intensity enhancement of the *Raman* line assigned to the $\nu_{\text{as}}(\text{CrO}_3)$ stretching may also have its origin in the presence of the trioxide, because the strongest line is expected for the symmetric and not for the antisymmetric CrO₃ components [23, 28].

Experimental

Preparation

All chemicals used were of analytical grade. HgCr₂O₇ was prepared by solid state reaction of thoroughly mixed HgO (freshly prepared from an aqueous HgCl₂ solution to which NaOH was added) and CrO₃ which were heated in a porcelain crucible at 200°C for several days. Since the reaction temperature was slightly above the melting temperature of CrO₃ (197°C [10]), it is assumed that at least partial formation of a liquid phase was achieved. The experiment for single crystal growth consisted of 108 mg HgO (0.5 mmol) and 190 mg CrO₃ (1.9 mmol) and a reaction time of 4 d. A nearly black powder was obtained from which small dark-red single crystals of HgCr₂O₇ with a rod-like shape were isolated. X-Ray powder diffraction of this batch revealed HgCr₂O₇ and CrO₃ as products. Microcrystalline HgCr₂O₇ was prepared from a mixture of 109 mg HgO (0.5 mmol) and 107 mg CrO₃ (1.07 mmol). According to XRPD, the as-obtained material was single phase. All batches with CrO₃:HgO ratios lower than 2.14 led to HgCr₂O₇ and partial formation of α -HgCrO₄ [8].

Single Crystal X-Ray Diffraction

Intensities of HgCr₂O₇ were collected in the ω -scan technique with 0.3° rotation width and 30 s exposure time per frame using a SMART APEX three-circle diffractometer (Bruker AXS; Mo K_{α} radiation, $\lambda = 0.71073 \text{ \AA}$) equipped with a CCD camera. Three independent sets of 600 frames were measured thus scanning the whole reciprocal sphere. The measured intensities were corrected for *Lorentz* and polarisation effects and an empirical absorption correction based upon the multi-scan approach was applied using the program SADABS [33]. The crystal structure was solved by direct methods and refined with the SHELXTL program package [34]. During the refinement procedure it turned out that the measured crystal was twinned by merohedry. Consideration of racemic twinning according to (110) reduced the *R*-indices significantly from $R[F^2 > 2\sigma(F^2)] = 0.086$ and $wR2(F^2 \text{ all}) = 0.182$ to 0.0369 and 0.0693, respectively. The ratio of the two twin components amounts to 1.44:1. In the last least-squares cycles the thermal parameters of Hg and Cr atoms were refined anisotropically while those of O atoms were refined isotropically. The final difference *Fourier* maps did not indicate any additional atomic sites, and the highest difference peaks were located close to the mercury positions. Analysis of the refined atomic coordinates with the program PLATON [35] did not reveal any higher symmetry. Further details of data collection and structure refinement are summarised in Table 3. Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 4. Selected interatomic distances and angles have been given in Table 1. Additional crystallographic information on the crystal structure is available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, e-mail: crysdata@fiz-karlsruhe.de, by quoting the literature citation, the name of the authors and the depository number listed at the end of Table 3. Drawings of structural details were produced using the program ATOMS [36].

Table 3. HgCr₂O₇; details of data collection and structure refinement

| | |
|---|--------------------------------------|
| Temperature/°C | 22(2) |
| Crystal dimensions/mm | 0.012·0.024·0.060 |
| Crystal color; shape | red; bar |
| Crystal system | trigonal |
| Space group, no. | <i>P</i> 3 ₂ , #145 |
| Formula units <i>Z</i> | 3 |
| <i>a</i> /Å | 7.2389(10) |
| <i>c</i> /Å | 9.461(2) |
| <i>V</i> /Å ³ | 429.36(13) |
| Formula weight/g·mol ⁻¹ | 416.59 |
| μ /mm ⁻¹ | 30.455 |
| X-Ray density/g·cm ⁻³ | 4.833 |
| Range θ_{\min} – θ_{\max} | 2.15–27.87 |
| Range <i>h</i> | –9 → 9 |
| <i>k</i> | –9 → 9 |
| <i>l</i> | –12 → 12 |
| Measured reflections | 4122 |
| Independent reflections | 1363 |
| Obs. reflections [<i>I</i> > 2σ(<i>I</i>)] | 1286 |
| <i>R</i> _i | 0.051 |
| Trans. coef. <i>T</i> _{min} ; <i>T</i> _{max} | 0.2623; 0.7114 |
| Number of parameters | 57 |
| Diff. elec. dens. max; min e ⁻ ·Å ⁻³ (dist./Å, atom) | 1.73 (0.07, Hg); –1.51 (0.53, O6) |
| <i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] | 0.0369 |
| <i>wR</i> 2(<i>F</i> ² all) | 0.0693 |
| Goof | 1.020 |
| Flack parameter [37] | 0.01(3) |
| CSD number | 416169 |

Table 4. Atomic coordinates and equivalent isotropic displacement parameters [Å]; all atoms are on *Wyckoff* position 3*a*

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> _{eq} ¹ |
|------|-------------|-------------|------------|-------------------------------------|
| Hg | 0.55722(11) | 0.68621(11) | 0.6665(6) | 0.02236(14) |
| Cr1 | 0.9320(8) | 0.3517(5) | 0.6623(2) | 0.0193(8) |
| Cr2 | 0.7568(9) | 0.7482(8) | 0.9996(2) | 0.0174(8) |
| O1 | 0.934(2) | 0.993(3) | 0.9876(17) | 0.038(5) |
| O2 | 0.882(3) | 0.623(2) | 0.353(2) | 0.034(4) |
| O3 | 0.869(2) | 0.613(2) | 0.969(2) | 0.029(4) |
| O4 | 0.828(3) | 0.503(2) | 0.6519(19) | 0.033(4) |
| O5 | 0.564(2) | 0.689(2) | 0.450(4) | 0.044(7) |
| O6 | 0.5616(18) | 0.6907(19) | 0.876(3) | 0.022(5) |
| O7 | 0.307(3) | 0.9467(18) | 0.8323(19) | 0.026(3) |

¹ *U*_{eq} is defined as one third of the trace of the orthogonalized *U*_{*ij*} tensor

Thermoanalytical Measurements

They were performed in an open system under a flowing N₂ atmosphere on a Mettler-Toledo TG50 (35–700°C, heating rate 5°C·min⁻¹, corundum crucibles) and a DSC 25 system (35–550°C, heating rate 5°C·min⁻¹, aluminum capsules).

Vibrational Spectroscopy

IR spectra in the range 4000–400 cm⁻¹ were recorded with a Bruker IF66 Fourier transform (FT) IR instrument using the KBr pellet technique. A total of 80 scans were accumulated. Raman spectra were measured on powdered samples using the FRA 106 Raman accessory of the same FTIR instrument. Radiation of 1064 nm from a Nd:YAG solid-state laser was used for excitation.

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