and has the typical 4 + 2 distorted coordination, as in $Cu(NH_4)_2(SO_4)_2.6H_2O$ (Brown & Chidambaram, 1969) and $CuK_2(SeO_4)_2.6H_2O$ (Whitnall *et al.*, 1975). However, the difference between the two bond distances in the equatorial plane of the CuO_6 octahedra, Cu–O(5) and Cu–O(6) [1·990 (5), 2·031 (5) Å], is less than in $CuK_2(SeO_4)_2.6H_2O$ (Whitnall *et al.*, 1975) and the S compounds.

The bond lengths and angles for the anion are as expected and similar to those in $CuK_2(SeO_4)_2.6H_2O$ (Whitnall *et al.*, 1975). All the water molecules form either inter- or intramolecular hydrogen bonds connecting the O atoms coordinated to Cu and Se. In the same way, all the H atoms of NH_4^+ are bonded to O atoms of the anion.

The geometry implied in these hydrogen bonds is given in Table 4.

All the hydrogen bonds, including O(5)–H···O(3) [O(8)–H···O(4) in Brown & Chidambaram's (1969) numbering] and the bifurcated $N-H(4)\underset{\cdots O(3)}{\overset{\cdots O(4)}{\cdots}}$, agree with those found by Brown & Chidambaram (1969).

Most of the calculations were carried out with XRAY 70 (Stewart, Kundell & Baldwin, 1970). Thanks are due to the staff of the Computing Center of JEN (Madrid) for the facilities provided on a Univac 1100/80 computer.

References

BROWN, G. M. & CHIDAMBARAM, R. (1969). *Acta Cryst.* B25, 676–687.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–98. Birmingham: Kynoch Press.
MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J. P. (1977). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
MARTÍNEZ-RIPOLL, M. & CANO, F. H. (1975). *PESOS* program. Instituto Rocasolano, CSIC, Madrid, Spain.
STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.
WHITNALL, V., KENNARD, C. H. L., NIMMO, J. K. & MOORE, F. H. (1975). *Cryst. Struct. Commun.* 4, 709–712.

Structure of Dimercury(II) Germanate(IV)

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Abstract. Synthetic Hg_2GeO_4, orthorhombic, *Fddd*, $a_o = 6·603$ (1), $b_o = 10·596$ (2), $c_o = 11·485$ (2) Å, $Z = 8$, $D_x = 8·89$ Mg m^{-3}. The *R* values obtained are $R = 0·076$, and $R_w = 0·061$ for 683 independent reflections. The compound is isostructural with thenardite, $Na_2SO_4(V)$. The structure consists of isolated $[GeO_4]$ tetrahedra (Ge–O distance 1·753 Å) and Hg atoms with an irregular sixfold coordination. Two Hg–O distances are very short (2·08 Å) and four rather long (2·66, 2·64 Å).

Introduction. Hg_2GeO_4 was synthesized hydrothermally by Röpke & Eysel (1978) at 673 K and 2 × 10^8 Pa in a welded gold capsule. Hg_2GeO_4 is the only known compound in the system $HgO-SiO_2-GeO_2$.

Single-crystal investigations established that it is isostructural with thenardite [$Na_2SO_4(V)$]. On the basis of geometrical considerations a rough structure proposal was given by Mehrotra, Hahn, Eysel, Röpke & Illguth (1978). The aim of the present paper is a structure refinement with particular emphasis on the O coordination of Hg.

A crystal 0·10 × 0·09 × 0·25 mm was used for data collection on an automatic Philips PW 1100 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0·7107$ Å) and a θ–2θ scan ($\theta_{max} = 50°$). The intensities of 4231 reflections were measured; of these, 693 independent reflections had $I \geq 3\sigma(I)$ and were used for the subsequent refinement. The standard deviations, $\sigma(I)$, were estimated using the formula of Stout & Jensen (1968).

Table 1. *Positional and thermal parameters* ($\times 10^4$) *with standard deviations*

Data proposed by Mehrotra *et al.* (1978) are in square brackets. The anisotropic temperature factors have the form

$$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg	1250	4472 (1) [4430]	1250	109 (4)	81 (3)	55 (3)	0	17 (6)	0
Ge	1250	1250	1250	88 (17)	1 (12)	58 (15)	0	0	0
O	−171 (27) [−280]	2320 (14) [2210]	420 (14) [370]	167 (79)	69 (58)	46 (58)	3 (43)	−23 (53)	10 (50)

Table 2. *Bond lengths* (Å) *and angles* (°)

Data proposed by Mehrotra *et al.* (1978) are in square brackets.

[GeO$_4$] tetrahedra

Ge–O	1·753 (15) ×4 [1·75]		
O(a)–O(b)	2·962 (31) ×2	O(a)–Ge–O(b)	115·3 (11) [109·5]
O(a)–O(c)	2·675 (33) ×2	O(a)–Ge–O(c)	99·4 (9) [109·5]
O(a)–O(d)	2·943 (31) ×2	O(a)–Ge–O(d)	114·1 (11) [109·5]
Mean	2·860	Mean	109·6 [109·5]

[HgO$_6$] polyhedra

Hg–O$_I$	2·656 (15) ×2 [2·67]
Hg–O$_{II}$	2·644 (15) ×2 [2·75]
Hg–O$_{III}$	2·079 (20) ×2 [1·99]
Mean	2·460 [2·47]

Fig. 1. Projection of Hg$_2$GeO$_4$ along [010].

Lorentz, polarization and absorption corrections (Busing & Levy, 1957) were applied [μ(Mo $K\alpha$) = 85·5 mm^{-1}]. The structure was solved using Fourier techniques and refined by full-matrix least-squares analysis with the program *SHELX* 76 (Sheldrick, 1976), starting with the atomic coordinates proposed by Mehrotra *et al.* (1978). The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Anisotropic refinement of the crystal structure converged at $R = 0·076$ and $R_w = 0·061$ $\{R_w = [\sum w(|F_o| - |F_c|)^2]^{1/2}/(\sum wF_o^2)^{1/2}, w = 1/\sigma^2\}$.*

A list of positional and thermal parameters (origin at $\bar{1}$), together with estimated standard deviations, is given in Table 1. Interatomic distances and angles are shown in Table 2.

Discussion. The original structure proposal for Hg$_2$GeO$_4$ by Mehrotra *et al.* (1978) was confirmed, in general, by the present structure determination. In particular, the preference of Hg^{2+} for twofold coordination (Grdenić, 1970) is clearly evident from the two very short and four rather long Hg–O distances (Table 2), resulting in the most 'distorted' structure of

the thenardite family (compare, for example, Fig. 1 of this paper and Fig. 1 of Mehrotra *et al.*, 1978).

The bonding properties of Hg^{2+} result in rather rare crystalline Hg^{2+} compounds, since the possibilities of building three-dimensional crystal structures on the basis of the coordination number two are limited. Thus it has not so far been possible to synthesize other Hg^{2+}-containing germanates or silicates in M^{2+}O–HgO–SiO$_2$–GeO$_2$ systems (W. Eysel, H. Röpke & D. Götz, 1978; unpublished results). The exception, Hg$_2$GeO$_4$, arises because in the thenardite structure the M^{2+}O$_6$ polyhedron (Fig. 1, strongly distorted trigonal prism) allows Hg to be placed only slightly above the base formed by the oxygens O$_I$, O$_I'$, O$_{III}$ and O$_{III}'$ and thus enables the approach of a nearly linear twofold coordination O$_{III}$–Hg–O$_{III}$, with an angle of 159·5°. This angle and the Hg–O bond lengths compare well with data of other compounds reported by Grdenić (1970).

There are some minor differences compared to the originally proposed structure of Hg$_2$GeO$_4$. Even though for the [GeO$_4$] tetrahedron the bond distance of 1·753 Å is in excellent agreement with other data (*cf.* Wittmann, 1969), the tetrahedron is rather distorted (angles in Table 2). This might be partially attributed to the difficulty of determining the O positions exactly in

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35722 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the presence of the heavy Hg atoms. The authors are convinced, however, that the distortion is at least to some extent real and due to the irregular coordination of the O atoms by one Ge and three Hg atoms. This effect, although less, is also visible in the ionic compounds Na_2SO_4 and Na_2SeO_4 (Mehrotra et al., 1978). In addition, the differences between the observed and geometrically derived Hg—O distances (Table 2) are a consequence of the distortion of the $[GeO_4]$ tetrahedron.

Finally, it should be stated that the present results justify the geometrical method applied by Mehrotra et al. (1978) for rather detailed structure predictions of compounds with thenardite-type structures.

References

BUSING, W. R. & LEVY, H. A. (1957). Acta Cryst. **10**, 180–182.
GRDENIĆ, D. (1970). Handbook of Geochemistry, Section 80-A, edited by K. H. WEDEPOHL. Berlin: Springer.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
MEHROTRA, B. N., HAHN, TH., EYSEL, W., RÖPKE, H. & ILLGUTH, A. (1978). Neues Jahrb. Mineral. Monatsh. pp. 408–421.
RÖPKE, H. & EYSEL, W. (1978). Neues Jahrb. Mineral. Monatsh. pp. 1–9.
SHELDRICK, G. M. (1976). SHELX 76. A program for crystal structure determination. Univ. of Cambridge, England.
STOUT, G. H. & JENSEN, L. H. (1968). X-ray Structure Determination. New York: Macmillan.
WITTMANN, A. (1969). Handbook of Geochemistry, Section 32-A, edited by K. H. WEDEPOHL. Berlin: Springer.

Sodium Chromate (II) at 296 K (Neutron)

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Abstract. Na_2CrO_4 (II), orthorhombic, $Cmcm$, $a = 5\cdot862$ (2), $b = 9\cdot251$ (5), $c = 7\cdot145$ (3) Å at 296 K, $Z = 4$, $D_c = 2\cdot78$ Mg m^{-3}, λ (neutron) $= 0\cdot9884$ Å; $R = 0\cdot03$; single crystal; source of material: BDH. The structure proposed by Niggli [Acta Cryst. (1954), **7**, 776] is confirmed.

Introduction. The present structure determination was made in the course of an investigation of thermal phase transitions in Na_2CrO_4 and Na_2SO_4 at atmospheric pressure. Whereas Na_2SO_4 undergoes a series of transitions, Na_2CrO_4 is only known to have one transition at 694 ± 4 K (Pistorius, 1965). However, Na_2CrO_4 (II) (<694 K) and Na_2SO_4 (III) (458–514 K and metastably at room temperature) are thought to be isostructural, as indeed are Na_2CrO_4 (I) (>694 K) and Na_2SO_4 (I) (>514 K) (Fischmeister, 1954; Eysel, 1973). Various orthorhombic and tetragonal space groups have been suggested for Na_2CrO_4 (II) and/or Na_2SO_4 (III):

Miller (1936):	Na_2CrO_4 (II), $Pbnn$, $Z = 4$
Frevel (1940):	Na_2SO_4 (III), $Pbnn$, $Z = 4$
Dasgupta (1953, 1954):	Na_2SO_4 (III), $I\bar{4}2d$, $Z = 16$
Niggli (1954):	Na_2CrO_4 (II), $Cmcm$, $Z = 4$
Fischmeister (1954):	Na_2SO_4 (III) and Na_2CrO_4 (II), $Cmcm$, $Z = 4$.

In view of this controversy and the fact that no accurate structure determination of either Na_2CrO_4 (II) or Na_2SO_4 (III) has been made, it was decided to investigate Na_2CrO_4 (II) with single-crystal neutron diffractometer data.

A crystal (42 mm³) was grown by evaporation of an aqueous solution at 349 K. Above 343 K Na_2CrO_4 (II) crystallizes and there is no water of crystallization (Hartford, 1949). Data were collected on the Australian Institute of Nuclear Science and Engineering (AINSE) four-circle computer-controlled diffractometer located on the 2 TAN A facility at HIFAR, the research reactor of the Australian Atomic Energy Commission (AAEC) at Lucas Heights. ω–2θ scans were made for all Bragg intensity measurements, with a step size of $0\cdot01°$ in 2θ. Background measurements were made for each Bragg reflexion. A standard reflexion was measured after every 25 reflexions to check stability of the specimen and the experimental system. Two equivalent sets of Bragg intensities ($2\theta <$ 75°) were collected. The neutron wavelength was $0\cdot9884$ Å.

From 443 relatively strong centered reflexions, the cell was determined by least squares to be orthorhombic. The conditions limiting possible reflexions were hkl: $h + k = 2n$, $h0l$: $l = 2n$, and the space group was deduced as $Cmcm$.