

numbers on the threefold axes leads to the deviation from stoichiometry of the compound. The chemical formula can be described as Mn<sub>5,11</sub>Ge<sub>2</sub> instead of Mn<sub>5</sub>Ge<sub>2</sub> according to the results of the refinement. This deviation sensitively affects the magnetic properties as shown by Yamada *et al.* (1986).

The structure is fairly complex with long periodicity along *c*. The structure is not directly related to Mn<sub>5</sub>Si<sub>2</sub> (Shoemaker & Shoemaker, 1976), contrary to the relation between Mn<sub>5</sub>Ge<sub>3</sub> and Mn<sub>5</sub>Si<sub>3</sub>.

The separation of a single crystal of  $\zeta_2$ -Mn<sub>5</sub>Ge<sub>2</sub> is now being attempted in order to perform a structure determination.

The present work has partly been supported by a Scientific Research Grant from the Ministry of Education, Science and Culture, to which the authors' thanks are due.

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*Acta Cryst.* (1987). **C43**, 10–12

## Refinement of the Structure of Copper(II) Chromate from Single-Crystal Data

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(Received 23 October 1985; accepted 18 July 1986)

**Abstract.** CuCrO<sub>4</sub>,  $M_r = 179.54$ , orthorhombic, *Cmcm*,  $a = 5.433$  (1),  $b = 8.968$  (3),  $c = 5.890$  (3) Å,  $V = 287.0$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_m$  (pycnometrically) = 4.04,  $D_x = 4.155$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 109.5$  cm<sup>-1</sup>,  $F(000) = 340$ ,  $T = 293$  K,  $R = 0.039$  with 556 unique observed reflections. The structure is built up by chains of edge-linked tetragonally distorted CuO<sub>6</sub> octahedra, which are connected by slightly irregular CrO<sub>4</sub> tetrahedra sharing their O atoms with the octahedra. Cu–O(equatorial) = 1.965 (2), Cu–O(axial) = 2.400 (3), mean Cr–O = 1.665 Å. These bond lengths are significantly different from those found previously from powder data.

**Introduction.** Compounds *ABO*<sub>4</sub> have been shown to exist in numerous structures, many of which are polymorphous at atmospheric pressure and also adopt different structures at higher pressure. These compounds range from those with silica-like structures, with tetrahedral coordination of *A* and *B*, to oxide salts

containing well defined anions *BO*<sub>4</sub> and exhibiting high coordination number of *A* (Wells, 1984).

CuCrO<sub>4</sub> is isomorphous with CrVO<sub>4</sub>, and its structure has been determined from powder data by Brandt (1943). Owing to the limited data – strong reflections at small  $2\theta$  angles such as 110, 020 are not mentioned – the previous work cannot be considered as very precise. Since mixed oxides containing chromium in various oxidation states and other transition metals are of importance in heterogeneous catalysis, a refinement of the crystal structure of CuCrO<sub>4</sub> using diffractometer data was undertaken.

**Experimental.** Dark red twinned preferentially needle-shaped crystals of CuCrO<sub>4</sub>, with a metallic lustre, were obtained by heating an aqueous solution of CrO<sub>3</sub> with an excess of Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> in a sealed glass tube at 470 K for ~20 h. Structure determination with an irregularly shaped tabular single crystal 0.30 × 0.06 × 0.02 mm, cut from a twin. Preliminary precession and

Weissenberg photographs established symmetry and systematic absences consistent with the orthorhombic space groups  $Cmcm$  or  $Cmc2_1$ . Data collection: Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized  $Mo K\alpha$  radiation; unit-cell parameters and crystal orientation from least-squares refinement of 25 automatically centered reflections in the range  $15 < 2\theta < 48^\circ$ ;  $\omega$ - $2\theta$  scan, 673 unique data,  $\sin\theta/\lambda \leq 0.99 \text{ \AA}^{-1}$ ,  $0 \leq h \leq 10$ ,  $0 \leq k \leq 17$ ,  $0 \leq l \leq 11$ . 6 standard reflections, no significant changes in the intensities. Intensities reduced to  $F_o$  by applying Lorentz and polarization corrections. No absorption correction. The published atomic coordinates were consistent with our Patterson function and served as initial values in the subsequent full-matrix LS refinements based on  $F$  [21 variables, 556 unique reflections with  $I \geq 1\sigma(I)$ ]. Weighting scheme  $0.6431/[\sigma^2(F) + 0.002F^2]$ . Refinement converged at  $R = 0.039$ ,  $wR = 0.050$ . In final cycle max. shift/e.s.d.  $< 0.001$ . Final difference synthesis max. and min. peaks 1.70 and  $-1.66 \text{ e \AA}^{-3}$ . Error analysis showed no systematic errors as function of  $\sin\theta/\lambda$  or  $F_o$ . Scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations were carried out using *SHELX76* (Sheldrick, 1976).

**Discussion.** The crystal structure of  $CuCrO_4$  as determined by Brandt (1943) is in principle confirmed, and the general description given in that paper is consistent with our results. Fig. 1 shows the atomic arrangement in the unit cell. Because of the availability of high-quality single-crystal data in our investigation, precise positional parameters (Table 1) and anisotropic thermal parameters\* could be obtained. Concerning the bond lengths, significant deviations from the previous

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43263 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

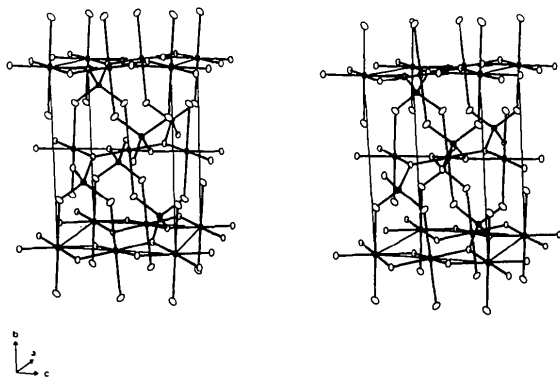


Fig. 1. Stereoview of the unit cell of  $CuCrO_4$ .

Table 1. *Positional and isotropic thermal parameters for  $CuCrO_4$*

	x	y	z	$U_{eq}(\text{\AA}^2)^*$
Cu	0.0000	0.0000	0.0000	0.0098 (3)
Cr	0.0000	0.3705 (1)	0.2500	0.0095 (4)
O(1)	0.0000	0.2669 (3)	0.0292 (5)	0.0161 (16)
O(2)	0.2371 (4)	-0.0205 (3)	0.2500	0.0115 (13)

\* Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter defined as  $U_{eq} = \frac{1}{3}\sum U_{ii}$ .

Table 2. *Selected bond distances (Å) and angles (°)*

Cu—O(1)	2.400 (3) 2x	O(1)—Cu—O(1')	180.0
Cu—O(2)	1.965 (2) 4x	O(1)—Cu—O(2)	92.3 (1)
		O(2)—Cu—O(2')	180.0
		O(2)—Cu—O(2'')	98.1 (1)
Cr—O(1)	1.599 (3) 2x	O(1)—Cr—O(1')	108.9 (2)
Cr—O(2)	1.731 (2) 2x	O(1)—Cr—O(2)	109.2 (1)
		O(2)—Cr—O(2')	111.3 (2)
Cu—Cu	2.945 (2)		
Cu—Cr	3.301 (1)		

data were found. The Cu atom shows the usual tetragonally distorted octahedral coordination with four shorter equatorial [Cu—O(2): 1.965 (2) Å] and two longer axial [Cu—O(1): 2.400 (3) Å] bonds. The  $CrO_4$  tetrahedra are slightly irregular with a mean Cr—O bond length of 1.665 Å. A summary of calculated bond distances and angles is given in Table 2.

More recent powder diffraction data in addition to absorption and EPR spectra of  $CuCrO_4$  have been communicated by Arsène, Lenglet, Erb & Granger (1978), and thermogravimetric studies by Gabelica, Derouane & Hubin (1980), Hanic, Horváth, Plesch & Gálíková (1985) and Horváth & Hanic (1985). High-resolution electron microscopy of  $CuCrO_4$  and its decomposition products is reported by Marks & Günter (1984). Structures of isomorphous chromates with cobalt and nickel have been determined by neutron diffraction by Pernet, Quezel, Coing-Boyat & Bertaut (1969). Intensity calculations from X-ray diffraction powder data have also been used to confirm the same structural type for Ni-, Mg- and  $CdCrO_4$  by Muller, White & Roy (1969).

We gratefully acknowledge the help of Dr W. Bensch in using the computer programs and the support of the Swiss National Science Foundation under Project No. 2.023-083.

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*Acta Cryst.* (1987). **C43**, 12–14

## Bis(1,3-diamino-2-propanol-*N,N'*)platinum(II) Chloride 1/3-Hydrate

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(Received 13 May 1986; accepted 13 July 1986)

**Abstract.** [Pt(C<sub>3</sub>H<sub>10</sub>N<sub>2</sub>O)<sub>2</sub>]Cl<sub>2</sub>·1/3H<sub>2</sub>O, *M<sub>r</sub>* = 452.25, trigonal, *R*3̄, hexagonal axes, *a* = 20.168 (6), *c* = 8.201 (2) Å, *V* = 2889 (1) Å<sup>3</sup>, *Z* = 9, *D<sub>m</sub>* = 2.31 (4), *D<sub>x</sub>* = 2.34 g cm<sup>-3</sup>, graphite-monochromated Mo *K*α radiation, λ = 0.71069 Å, *F*(000) = 1938, μ = 119.0 cm<sup>-1</sup>, *T* = 297 K, *R* = 0.0417 for 1492 unique reflections (*I* > 0) and 66 parameters. Platinum binds through the two N atoms of each diaminopropanol molecule to give a square-planar environment. The cation has Pt occupying the common vertex of two six-membered rings. The two chloride ions are involved in hydrogen bonding to the O and N atoms of the cation. The water molecule is disordered and at best only weakly hydrogen-bonded to the hydroxyl group. Bond lengths and angles are normal.

**Introduction.** Attempts to synthesize dichloro(1,3-diamino-2-propanol-*N,N'*)platinum(II) by the reaction of K<sub>2</sub>PtCl<sub>4</sub> and 1,3-diamino-2-propanol in water gave one minor product as pale orange crystals which were separated by hand picking. X-ray studies have now identified these crystals as the title compound.

**Experimental.** Crystals suitable for X-ray analysis were obtained by slow evaporation of an aqueous solution. Density measured by flotation in a CH<sub>2</sub>I<sub>2</sub>/CHCl<sub>3</sub> mixture. Crystal 0.3 × 0.3 × 0.5 mm. Space group *R*3̄ chosen over *R*3̄*m* because all atoms except Pt and O(H<sub>2</sub>) not in special positions. Justified by successful structure solution. Unit-cell parameters refined by least-squares fit of positional angles of 15 strong independent reflections measured on a Nicolet P3 diffractometer. 4869 reflections measured for 2.3 < 2θ < 55.1°, monochromated Mo *K*α radiation. Intensities of *h*, *k*, ±*l* measured by the ω–2θ scan technique.

Scan rate 6.0 to 29.3° min<sup>-1</sup> in 2θ. The ratio of total background time to scan time is 1:1. Two standard reflections monitored every 48 scans showed that no correction for instrument instability or crystal decay was required. Data averaged to give 1500 unique and 1492 observed reflections (*I* > 0). *R*<sub>int</sub> = 0.024. *Lp* and absorption corrections were made (absorption correction factors 16.0–48.9). Structure solved by heavy-atom method. Anisotropic least-squares refinement (isotropic for oxygen) minimizing ∑w(|*F<sub>o</sub>*| – |*F<sub>c</sub>*|)<sup>2</sup>, *w* = (σ<sub>*F*</sub><sup>2</sup> + 0.000684 *F<sub>o</sub>*<sup>2</sup>)<sup>-1</sup> excluding unobserved (*I* < 0) reflections. Some H atoms were located in a difference map but attempts to refine their positional parameters and temperature factors were unsuccessful. Their positions were fixed and temperature factors assigned to be 1.5 times *U*<sub>eq</sub> of the atom to which they were attached. Final *R* = 0.0417 and *wR* = 0.0485. Inspection of *F<sub>o</sub>* and *F<sub>c</sub>* values indicated no correction for secondary extinction was necessary. In final refinement cycle (Δ/σ)<sub>max</sub> = 0.17. Final difference map revealed no significant regions of electron density with max. 0.63 and min. –0.75 e Å<sup>-3</sup>. Scattering factors for non-hydrogen atoms from *International Tables for X-ray Crystallography* (Cromer & Waber, 1974). Corrections for anomalous dispersion were made for Pt and Cl (Cromer & Ibers, 1974). Calculations employed the *SHELX76* (Sheldrick, 1976) system of programs and *ORTEP* (Johnson, 1976).\*

\* Lists of structure factors, anisotropic thermal parameters, H-atom positions and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43239 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.