the effect of extending the range of the methods of electron-diffraction structure analysis beyond that admitted by earlier theoretical work, it must be born in mind that, as for montmorillonite, mentioned in the Introduction, excessive bending can render difficult or impossible a structure analysis in the conventional sense of the term. This provides an additional argument for the requirement that any quantitative electron-diffraction work should be accompanied by detailed and careful electron-microscope examination of the specimen.

References

BLACKMAN, M. (1939). *Proc. Roy. Soc.* A, **173**, 68.
BLACKMAN, M. (1951). *Proc. Phys. Soc.* B, **64**, 625.
BRINDLEY, G. W. & ROBINSON, K. (1948). *Min. Mag.* **28**, 393.
COWLEY, J. M. (1953*a*). *Acta Cryst.* **6**, 516.
COWLEY, J. M. (1953*b*). *Acta Cryst.* **6**, 522.
COWLEY, J. M. (1956). *Acta Cryst.* **9**, 391.
COWLEY, J. M. & GOSWAMI, A. (1961). (In press.)
COWLEY, J. M. & IBERS, J. A. (1956). *Acta Cryst.* **9**, 421.
COWLEY, J. M. & KUWABARA, S. (1961). (In press.)
COWLEY, J. M. & MOODIE, A. F. (1959*a*). *Acta Cryst.* **12**, 353.
COWLEY, J. M. & MOODIE, A. F. (1959*b*). *Acta Cryst.* **12**, 360.
FOCK, V. A. & KOLPINSKY, V. A. (1940). *J. Phys. USSR.* **3**, 125.
FUKUSHIMA, E. (1933). *J. Sci. Hiroshima Univ.* **3**, 177.
HONJO, G. & MIHAMA, K. (1954). *Acta Cryst.* **7**, 511.
KUNZE, G. (1956). *Acta Cryst.* **9**, 841.
NEWNHAM, R. E. & BRINDLEY, G. W. (1956). *Acta Cryst.* **9**, 759.
WARREN, B. E. (1941). *Phys. Rev.* **59**, 693.
WASER, J. (1955). *Acta Cryst.* **8**, 142.
WHITTAKER, E. J. W. (1955). *Acta Cryst.* **8**, 726.
WHITE, J. E. (1950). *J. Appl. Phys.* **21**, 855.
WILSON, A. J. C. (1949). *Acta Cryst.* **2**, 220.
UYEDA, R., ICHINOKAWA, T. & FUKANO, Y. (1954). *Acta Cryst.* **7**, 216.

Acta Cryst. (1961). **14**, 927

The Crystal Structure of Chromium(II) Chloride

BY JOSEPH W. TRACY,* N. W. GREGORY AND E. C. LINGAFELTER
Department of Chemistry, University of Washington, Seattle 5, U.S.A.

AND J. D. DUNITZ AND H.-C. MEZ
Laboratorium für Organische Chemie, Eidg. Technische Hochschule, Zürich, Switzerland

AND R. E. RUNDLE AND CHRISTIAN SCHERINGER
Department of Chemistry, Iowa State College, Ames, U.S.A.

AND H. L. YAKEL, JR. AND M. K. WILKINSON
Oak Ridge National Laboratory, Tennessee, U.S.A.

(*Received* 12 *October* 1960)

$CrCl_2$ is found to have an orthorhombic unit cell, *Pnnm*, with

$$a_0 = 6{\cdot}64 \pm 0{\cdot}01,\ b_0 = 5{\cdot}98 \pm 0{\cdot}01,\ c_0 = 3{\cdot}48 \pm 0{\cdot}01\ \text{Å}\ .$$

The cell contains the equivalent of two $CrCl_2$ groups in which chromium(II) is surrounded by an elongated octahedron of halogens. The structure consists of interacting planar chains in which chromium ions are bridged by two chloride ions.

Chromium(II) chloride is the only dichloride of the first row transition metals for which the crystal structure has not been reported. Handy & Gregory (1951) observed that X-ray powder diagrams could be indexed on the basis of an orthorhombic unit cell, $6{\cdot}65 \times 5{\cdot}99 \times 3{\cdot}48$ Å^3, and that the structure appeared to be of a deformed rutile type, similar to $CaCl_2$; however the atomic positions were not determined. It became known to the authors of the present paper that the structure had recently been determined independently and at practically the same time in four different laboratories; hence results will be reported under joint authorship.

---

* From the Ph.D. thesis of JWT, University of Washington, 1960; present address Northwest Nazarene College, Nampa, Idaho. Financial support for the work at Seattle was received from the Office of Ordnance Research, U.S. Army.

Experimental

$CrCl_2$ may be prepared by reaction of chromium metal at 900 °C. with dry hydrogen chloride gas or by reduction of $CrCl_3$ with hydrogen at 500 °C. (Schlaefer, 1957), and purified by fractional sublimation in an evacuated silica tube. Crystals suitable for X-ray examination may be grown in a silica tube in a pressure of ca. 25 cm. (Hg) of argon. After a sample was held near 835 °C. for twenty-four hr., small lath-shaped thin needles were found attached to the wall near the mouth of the furnace. The crystals are colorless, easily cleaved into fibers, extraordinarily deliquescent and when moist are quickly oxidized in air. They may be kept indefinitely in a dry atmosphere, however. Specimens to be X-rayed were selected and inserted into thin-walled Pyrex (or Lindemann) capillary tubes in a dry box; the crystal end was anchored in a wax and the capillary sealed.

At Seattle, diffraction lines from sodium chloride (a_0 taken as 5·640 Å) were superimposed on rotation and Weissenberg photographs used to determine cell dimensions; Cu $K\alpha$ radiation, $\lambda=1·5418$ Å, was used with a crystal ca. $0·08\times0·13$ mm. in cross-section. Systematic absences of $(h0l)$ for $h+l$ odd and of $(0kl)$ for $k+l$ odd indicated the space group to be *Pnnm* or *Pnn*2. After allowance for angular intensity factors, corresponding reflections on alternate layer lines for rotation about *c* were observed to have similar intensities. This indicates a symmetry plane perpendicular to *c* and hence the space group *Pnnm*, provided all atoms lie at $z=0$ or $z=\frac{1}{2}$. $hk0$ projections were used to fix the only two remaining parameters, namely x and y for the chloride ions. Unintegrated Weissenberg exposures were taken with Cu radiation on multiple films; intensities were estimated visually and independently with a scanning recording microphotometer (intensities taken as proportional to peak heights). Lorentz and polarization factors were applied and an overall anisotropic temperature factor (exp $-B(\sin\theta/\lambda)^2$ with final value of $B=0·8+3\cos^2(\chi-0·15)$; χ is the negative of the acute angle (cycles) between b^* and the normal to the plane) used in calculation of structure factors. Scattering factors for Cr^{++} and Cl^- (Berghuis *et al.*, 1955) were used. No correction for absorption was included. Calculations were performed on an IBM 650 computer.

At Zürich, 30° precession photographs of the $(0kl)$, $(2kl)$, $(h0l)$ and $(h1l)$ sections and Weissenberg photographs of the $(hk0)$ layer were taken with Mo $K\alpha$ radiation, $\lambda=0·7107$ Å. The cell dimensions were determined from the zero-level precession photographs. Intensities of $(hk0)$ and $(0kl)$ reflections were recorded with a double beam microdensitometer. The crystal cross-section was ca. 0·07 mm. Temperature factors of the form $(\exp(-0·0137h^2-0·0119k^2)$ were applied (anisotropic; $B_x=2·4$, $B_y=1·7$, $B_z=0$ Å^2).

Table 1. *Summary of results*

		TGL	*DM*	*RS*	*YW*
Cell parameters	a_0 Å	6·653 Å	6·631 Å	6·621 Å	6·638 Å
	b_0 Å	5·992 Å	5·980 Å	5·957 Å	5·984 Å
	c_0 Å	3·494 Å	3·487 Å	3·480 Å	3·476 Å
Density	Observed* 2·878	Calculated 2·930 g.cm.$^{-3}$ (2 $CrCl_2$ in unit cell)			
Space group		D_{2h}^{12}–*Pnnm*			
Atomic coordinates		Cr (0, 0, 0); $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ Cl $\pm(x, y, 0)$; $\pm(x+\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2})$			
	x	0·362	0·360	0·359	0·36
	y	0·274	0·275	0·270	0·28
Final reliability index		0·106	0·084	0·148	—
Bond lengths	Cr–Cl	2·40 Å	2·39 Å	2·40 Å	2·37 Å
	Cr–Cl	2·91 Å	2·90 Å	2·88 Å	2·92 Å

* Biltz & Birk (1924).

Table 2. *Observed and calculated structure factors*

h k l	F_o	F_c
2 0 0	12·7	13·4
4	2·4	2·6 −
6	10·5	11·6
8	8·2	7·5
1 1 0	24·3	22·7
2	22·1	23·5 −
3	11·7	11·7
4	5·4	5·3
5	9·1	8·0
6	7·5	7·7
7	5·8	5·9
8	3·7	3·6 −
0 2 0	5·7	5·9 −
1	5·7	5·6 −
2	18·0	18·8
3	< 2·3	2·4
4	18·2	22·1
5	3·8	3·2
6	< 3·1	1·6
7	< 3·5	0·2
8	< 3·8	0·2 −
1 3 0	8·2	8·6
2	14·6	14·3
3	15·9	16·2
4	2·8	3·9 −
5	7·4	8·2
6	5·7	5·9 −
7	< 3·6	1·3
8	< 3·9	2·8
0 4 0	22·9	23·1
1	6·8	6·5
2	8·8	7·8
3	3·4	3·4
4	< 3·1	0·5 −
5	4·6	4·8 −
6	6·5	7·6
7	< 3·8	0·4 −
8	5·0	5·1
1 5 0	12·8	15·1
2	7·3	7·5 −
3	< 3·2	0·7
4	< 3·3	2·2
5	4·3	3·2
6	4·6	3·5
7	6·3	6·2
0 6 0	< 3·2	0·9
1	5·7	5·8 −
2	6·7	6·8
3	< 3·5	3·1 −
4	8·8	8·4
5	6·0	4·5
6	< 4·0	1·6
1 7 0	< 3·6	0·6
2	3·6	3·1
3	8·4	9·0
4	< 3·9	0·9 −
5	4·1	4·4
0 8 0	5·6	5·5
1	4·0	4·1
2	4·0	3·1
0 1 1	15·9	14·5
3	21·4	21·0
5	< 5·6	0·1
7	12·6	11·4
0 0 2	28·5	33·9
2	< 4·9	3·2 −
4	20·7	19·4
0 1 3	11·0	8·5
3	16·2	14·3
0 0 4	21·2	22·4
2	< 4·9	3·7
4	12·8	14·8

$R=45·7/542·2=0·0843$

At Ames, data were collected with Mo radiation and a temperature factor of the form $\exp(-B\sin^2\theta/\lambda^2)$ was used with $B_{Cr}=3·75$, $B_{Cl}=4·97$. At Oak Ridge, the structure was determined by a combination of powder X-ray (Cr $K\alpha$ radiation, $\lambda=2·290$ Å) and neutron diffraction data. The results of the four independent determinations are summarized in Table 1. Table 2 lists the calculated and observed structure factors compiled at Zürich. Similar tables may be obtained from the other laboratories by direct inquiry, if desired.

Discussion

While results are in good general agreement, the values reported for the cell dimensions vary slightly more than the uncertainty estimated independently by the separate groups of authors. The structure is shown in Fig. 1 which also includes the bond lengths and angles calculated from the Seattle data (indicated uncertainty calculated from Cruickshank's criteria (1949)). Each chromium atom is in the center of a plane of four chlorine atoms at equal distances, 2·40 Å, with two others at a somewhat greater distance, 2·91 Å, in directions nearly perpendicular to this plane. The elongated and slightly distorted CrCl$_6$ octahedra share their shortest edges and form a densely packed linear 'ribbon' or chain (indicated by the dashed lines, Fig. 1) parallel to c. The long bonds, e.g. Cr(2)–Cl(2), Cr(1)–Cl(1), etc., link each ribbon to its four neighboring ribbons which are oriented approximately 90° to it. Ligand field theory (e.g. Jahn & Teller, 1937; Nyholm, 1956; Orgel & Dunitz, 1957) leads one to expect a distorted arrangement for octahedral coordination of halide ions around chromium(II) with four spin free d electrons. Jack & Maitland (1957) report a somewhat similar arrangement in monoclinic CrF$_2$ although in the fluoride the short bonds are of two slightly different lengths and the shared edges are not those that would give maximum density in the 'ribbon'. The strong interaction in the infinite chain or ribbon is undoubtedly associated with the observed acicular morphology. The smallest vibration amplitude (anisotropic temperature factors) is also observed in the direction parallel to the chains. c_0 gives the effective diameter of the chloride ion along the ribbon, 3·49 Å, appreciably less than found in more symmetrical ionic crystals, e.g. 3·62 Å (Pauling, 1960). This diameter gives an apparent radius of 0·64 Å for Cr^{++} in the plane of chloride ions. A larger radius is possible in the perpendicular direction.

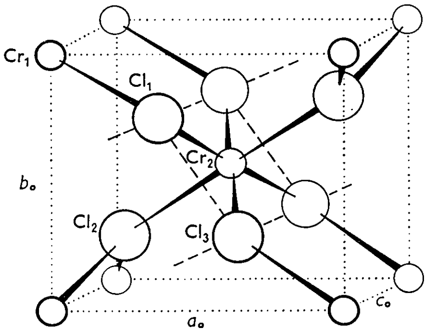

Fig. 1. Chromium(II) chloride.

Interatomic distances and bond angles

Cr(1)–Cr(2)	4·806 ± 0·010 Å
Cr(2)–Cl(1)	2·395 ± 0·012
Cr(2)–Cl(2)	2·915
Cl(1)–Cl(2)	3·775 ± 0·013
Cl(1)–Cl(3)	3·272
Cl(2)–Cl(3)	3·768
Cl(1)–Cr(2)–Cl(3)	86·2 ± 0·3°
Cl(1)–Cr(2)–Cl(2)	90·1

References

Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A.L. (1955). *Acta Cryst.* **8**, 478.

Biltz, W. & Birk, G. (1924). *Z. anorg. Chem.* **134**, 125.

Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 65.

Handy, L. L. & Gregory, N. W. (1951). *J. Chem. Phys.* **19**, 1314.

Jack, K. H. & Maitland, R. (1957). *Proc. Chem. Soc.* p. 232.

Jahn, H. A. & Teller, E. (1937). *Proc. Roy. Soc.* A, **161**, 220.

Nyholm, R. S. (1956). *Quelques Problemes de Chimie Minerale*, p. 268. (Report of the Tenth Solvay Conference, Brussels, 1956, R. Stoops, Editor, Brussels).

Orgel, L. E. & Dunitz, J. D. (1957). *Nature, Lond.* **179**, 462.

Pauling, L. (1960). *The Nature of the Chemical Bond*, p. 514, 3rd ed. Ithaca, New York: Cornell University Press.

Schlaefer, H. (1957). *Z. Phys. Chem., Neue Folge*, **11**, 277.