is not unusual in an H-bonded crystal. The H–H vector (water) makes an angle of 18° with the x axis indicating that the hydrogen atoms are not located exactly on the plane containing O(1), O(w) and $O_I(1)$ atoms. Listed in Table 2 are the dimensions of the oxalate and NH_4 groups.

The observed length of the N–H bond is good agreement with values from the compounds $NH_4H_2PO_4$ (N–H 1·00 ± 0·02 Å; Tenzer, Frazer & Pepinsky, 1958) and NH_3OHCl (N–H 1·04 ± 0·01 Å; Padmanabhan, Smith & Peterson, 1962). The H–N–H angles vary between 104 and 117°. Tenzer *et al.* have also reported distortion of the tetrahedral NH_4 group in $NH_4H_2PO_4$. The distortion observed may be due to hydrogen bonding resulting in a linear N–H ⋯ O bond. For further discussion on the distortion of the NH_4 tetrahedron, a more detailed study of thermal parameters of the hydrogen atoms with three-dimensional data is required.

We wish to thank Dr R. Ramanna for his interest and Dr R. Chidambaram for leaving the spectrometer at our disposal.

References

CHIDAMBARAM, R. (1962). *Acta Cryst.* **15**, 619.
CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
HENDRICKS, S. B. & JEFFERSON, M. E. (1936). *J. Chem. Phys.* **4**, 102.
JEFFREY, G. A. & PARRY, G. S. (1952). *J. Chem. Soc.* p. 4864.
JEFFREY, G. A. & PARRY, G. S. (1954). *J. Amer. Chem. Soc.* **76**, 5283.
PADMANABHAN, V. M., SMITH, H. G. & PETERSON, S. W. (1962). Unpublished.
SMITH, H. G. & LEVY, H. A. (1962). *Acta Cryst.* **15**, 1201.
TENZER, L., FRAZER, B. C. & PEPINSKY, R. (1958). *Acta Cryst.* **11**, 505.
WYCKOFF, R. W. G. (1960). *Crystal Structure*, Vol. IV, p. 64. New York: Inter Science Publishers.

Acta Cryst. (1965). **18**, 568

Interatomic distances in solid chlorine.

By JERRY DONOHUE and STEWART H. GOODMAN, *Department of Chemistry, University of Southern California, Los Angeles, California, U.S.A.*

(*Received* 5 *October* 1964)

Introduction

A tetragonal structure for solid chlorine was proposed by Keesom & Taconis (1936), based on powder data and limited single-crystal data; it was later shown to be incorrect by Collin (1952) on the basis of single-crystal data. The structure described by Collin is orthorhombic, and isotypic with those of solid bromine (Vonnegut & Warren, 1936) and iodine (Harris, Mack & Blake, 1928; Kitaigorodskii, Khotsyanova & Struchkov, 1953); the two positional parameters and one isotropic temperature factor were determined by trial and error. Because of our interest in interatomic distances and thermal vibrations in simple substances, we decided to carry out additional refinements on Collin's single-crystal data, including allowance for anisotropic thermal motion.

Table 1. *Comparison of single-crystal with powder data*

	Collin		Keesom & Taconis		
hkl	d_c†	$pF_o^2 \times 10^{-3}$	d_o	I_o	d_c‡
002	4·13	3	—	—	4·10
111	3·33	51	3·26	*w*	3·31
200	3·13	22	3·07	*m*	3·09
112	2·73	45	$2{\cdot}68_5$	*s*	2·72
202	2·49	4	$2{\cdot}45_5$	*w*	2·48
113	2·19	3	2·21	*w*	2·18
021	2·16	13	2·15	*s*	2·16
004	2·07	9	2·03	*s**	2·06
114	1·80	6	1·82	*m*	1·79
023	1·74	16	$1{\cdot}75_5$	*w*	1·74
204	1·73	16	1·70	*s*	1·71
400	1·56	8	$1{\cdot}54_5$	*w*	1·54
223	1·52	22	1·50	*w*	1·52
115	1·51	12	1·49	*s*	1·50

* Intensity enhanced by silver sample holder.
† Calculated with $a = 6{\cdot}24$, $b = 4{\cdot}48$, $c = 8{\cdot}26$ Å (Collin, 1956).
‡ Calculated with $a = 6{\cdot}17$, $b = 4{\cdot}49$, $c = 8{\cdot}22$ Å.

Refinement

The 44 observed values of F tabulated by Collin were used to refine the parameters by least squares, with the full-matrix program ACA No. 217 of Gantzel, Sparks & Trueblood with the weighting scheme of Hughes (1941) and the form factors of Dawson (1960). In the first series the variables were the y and z parameters for the chlorine atom, a single temperature factor, and the scale factor. In addition, the effect on the results of varying the value of $4\,F_{\min}$ in the weighting scheme was studied. It was found that when $4\,F_{\min}$ was varied from 17·6 to 85·8 (on the same scale the smallest F_o, F_{337}, is 5·2, and the largest, F_{200}, is 85·8) the following parameters were obtained: $y = 0{\cdot}1155 \pm 0{\cdot}0034$ to $0{\cdot}1161 \pm 0{\cdot}0035$, $z = 0{\cdot}1014 \pm 0{\cdot}0008$, and $B = 3{\cdot}70 \pm 0{\cdot}24$ to $3{\cdot}43 \pm 0{\cdot}22$. In the second series anisotropy was allowed, and the same range of $4\,F_{\min}$ was used. The results in this case were $y = 0{\cdot}1166 \pm 0{\cdot}0038$ to $0{\cdot}1173 \pm 0{\cdot}0041$, $z = 0{\cdot}1016 \pm 0{\cdot}0008$ to $0{\cdot}1014 \pm 0{\cdot}0010$, $B_{11} = 3{\cdot}42 \pm 0{\cdot}47$ to $3{\cdot}27 \pm 0{\cdot}31$, $B_{22} = 4{\cdot}09 \pm 0{\cdot}40$ to $3{\cdot}85 \pm 0{\cdot}40$, $B_{33} = 3{\cdot}55 \pm 0{\cdot}27$ and $B_{23} = -2{\cdot}1 \pm 1{\cdot}2$ to $-1{\cdot}2 \pm 1{\cdot}6$. In each of the above refinements the shifts in the last cycle were less than 1×10^{-6}. The absence of any significant changes in the results as $4\,F_{\min}$ is varied would tend to indicate that there are no serious systematic errors in Collin's data. The values for the parameters for $4\,F_{\min} = 20{\cdot}8$ are: isotropic, $y = 0{\cdot}1161 \pm 0{\cdot}0035$, $z = 0{\cdot}1014 \pm 0{\cdot}0008$, $B = 3{\cdot}67 \pm 0{\cdot}23$, $R = 10{\cdot}4\,\%$; anisotropic, $y = 0{\cdot}1173 \pm 0{\cdot}0038$, $z = 0{\cdot}1016 \pm 0{\cdot}0009$, $B_{11} = 3{\cdot}43 \pm 0{\cdot}31$, $B_{22} = 4{\cdot}09 \pm 0{\cdot}40$,

Table 2. *Interatomic distances in halogen crystals*

	Bond	Intralayer	Interlayer	Van der Waals*
Chlorine	1·98 Å	3·32, 3·82 Å	3·74, 3·84, 3·97 Å	3·60 Å
Bromine	2·27	3·31, 3·79	3·99, 4·02, 4·14	3·90
Iodine	2·67	3·57, 4·05	4·39, 4·35, 4·50	4·30

* Twice the van der Waals radius of Pauling (1960).

$B_{33} = 3·55 \pm 0·27$, $B_{23} = -2·5 \pm 1·9$, $R = 9·9\%$. These may be compared with Collin's values $y = 0·130$, $z = 0·100$, $B = 3·3$. and $R = 11·7\%$.

Discussion

The values for the positional parameters obtained for the case of $4\,F_{\text{min}} = 20·8$, together with the revised lattice constants (Collin, 1956), lead to the following interatomic distances per chorine atom: Cl–Cl bond distance, 1·980 ± 0·014 Å; Cl ... Cl intermolecular distances, within the *bc* layers, two at 3·32, and 3·82 Å, and between layers, two at 3·74, four at 3·84, and two at 3·97. The bond distance is slightly shorter than the value 2·02 ± 0·04 Å reported by Collin, and is in excellent agreement with the spectroscopic value of 1·988 Å (Herzberg, 1950) and the electron diffraction value of 1·986 Å (Shibata, 1963), both of which refer to gaseous chlorine.

In the three isotypic halogens, chlorine, bromine, and iodine, the shortest intermolecular distances within the layers do not increase regularly as the atomic number increases, as shown in Table 2. (The distances in the case of bromine were recalculated from the parameters and lattice constants given by Vonnegut & Warren (1936), and those for iodine were calculated from the parameters of Kitaigorodskii, *et al.* (1953) and the lattice constants of Swanson, Fuyat & Ugrinic (1954).) The shortest between-layer distances are uniformly 1·72 ± 0·04 Å longer than the intramolecular distance; these interlayer distances are all close to twice the van der Waals radii given by Pauling (1960). The relative decrease in the shortest intralayer distance from 1·34 Å larger than the covalent bond distance in the case of chlorine to 0·90 Å in iodine reflects an increasing tendency for the heavier atoms to form secondary bonds, such as are formed in the triiodide ion. In solid iodine the distances in the nearly linear I–I ... I feature of the structure are close to those found between the I_2 molecules and the I_5^- ion in tetramethylammonium enneaiodide (James, Hach, French & Rundle, 1955), and are not far from those predicted by Slater (1959) in her discussion of polyiodides, even though iodine, of course, contains no isolated I_3 groups. Similar information for polychlorides and polybromides is, at present, lacking.

It should be noted that the four values of B_{ij} obtained in the anisotropic refinement do not differ significantly from the value of the single isotropic B. It thus appears that, within the limits of error of this study, the thermal motion of the chlorine atoms is isotropic. The lack of significant anisotropy in this layer structure is rather surprising. The data are incapable of detecting the intramolecular bond stretching vibration of r.m.s. amplitude 0·021 Å (as calculated from the spectroscopic value of 565 cm^{-1} for w_e); this amplitude is negligible compared with the r.m.s. amplitude 0·22 Å implied by the B value of 3·67.

It is interesting that the powder data of Köhler (1934), which Keesom & Taconis (1936) indexed on the basis of a tetragonal unit cell with $a = 8·56$ and $c = 6·12$ Å, may also be indexed on the basis of the orthorhombic unit cell of Collin (1956) with slightly adjusted lattice constants; moreover, the intensity correlation is moderately good, as may be seen in Table 1, where data for the powder lines of Köhler and the fourteen innermost reflections of Collin are presented. The tetragonal lattice constants are closely approximated by the relations $c_{\text{tetr}} = a_{\text{orth}}$ and $a^2_{\text{tetr}} = \frac{1}{2}(2b^2_{\text{orth}} + c^2_{\text{orth}})$. This numerical coincidence enables good agreement to be obtained with the incorrect cell for a majority of the powder lines.

The thermal expansion data for solid chlorine of Hawes & Cheesman (1959) were based on the tetragonal indexing of powder photographs and are accordingly incorrect. These authors were apparently unaware of the papers by Collin (1952, 1956).

This work was supported by a grant from the National Science Foundation.

References

Collin, R. L. (1952). *Acta Cryst.* **5**, 431.

Collin, R. L. (1956). *Acta Cryst.* **9**, 539.

Dawson, B. (1960). *Acta Cryst.* **13**, 403.

Harris, P. M., Mack, E. & Blake, F. C. (1928). *J. Amer. Chem. Soc.* **50**, 1583.

Hawes, L. L. & Cheesman, G. H. (1959). *Acta Cryst.* **12**, 477.

Herzberg, G. (1950). *Molecular Spectra and Molecular Structure. Infrared Spectra of Diatomic Molecules.* 2nd edition. New York: Van Nostrand Co.

Hughes, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.

James, W. J., Hach, R. J., French, D. & Rundle, R. E. (1955). *Acta Cryst.* **8**, 814.

Keesom, W. H. & Taconis, K. W. (1936). *Physica*, **3**, 237.

Kitaigorodskii, I. I., Khotsyanova, V. & Struchkov, M. (1953). *Zh. fiz. Khim.* **27**, 780.

Köhler, J. W. L. (1934). Thesis, Leiden.

Pauling, L. (1960). *The Nature of the Chemical Bond.* 3rd edition, Ithaca: Cornell Univ. Press.

Shibata, S. (1963). *J. Phys. Chem.* **67**, 2256.

Slater, R. C. L. M. (1959). *Acta Cryst.* **12**, 187.

Swanson, H. E., Fuyat, R. K. & Ugrinic, G. M. (1954). *Nat. Bur. Stands. Circular* 539, **3**, 16.

Vonnegut, B. & Warren, B. E. (1936). *J. Amer. Chem. Soc.* **58**, 2459.