*Acta Cryst.* (1961). **14**, 202

# On the structure of $AgClO_2$.*

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(*Received* 2 *June* 1960)

Recently Curti, Riganti & Locchi (1957) (C.R.L.) have undertaken an X-ray diffraction investigation of the structure of silver chlorite, $AgClO_2$. They found the crystals to be orthorhombic and reported the space group to be $D_{2h}^{11}$–*Cmma*. Coordinates for the silver, chlorine, and oxygen atoms were assigned on the basis of zonal and partial three-dimensional data.

A number of surprising features in the reported structure have led us to undertake a reinvestigation. Among these features are: (1) a silver–chlorine distance of 2·20 Å, which is far shorter than the expected ionic separation and which was interpreted by C.R.L. as representing a covalent bond; (2) a separation between oxygen atoms of adjacent molecules of only 2·24 Å, which is far shorter than the normal van der Waals distance; (3) an irregular environment of the silver atom, which is surrounded by two oxygen atoms at distances of 2·22 Å and two others at 3·50 Å. Even taken separately, any one of these features would cast severe doubt on the correctness of the structure. Initial attempts to deduce an alternative structure based on the published data of C.R.L. were unsuccessful, and we have accordingly collected new data. We have interpreted these data in terms of a satisfactory structure which is quite different from that derived by C.R.L.

## Experimental

Reagent-grade $AgNO_3$ and $NaClO_2$ were dissolved in hot water (90–95°) in equimolar proportions, and the solutions were mixed. The mixture was cooled and the fine precipitate was filtered, washed sparingly with cold water, and immediately redissolved in hot water. Upon slow cooling of this solution, yellow, translucent laminae or occasionally needles of $AgClO_2$ were formed which, after being washed and dried, could be kept almost indefinitely. Equi-inclination Weissenberg photographs (copper radiation) were prepared for layer lines 0 through 5 about the needle axis; precession photographs (molybdenum radiation) were also prepared for the two zero-layer nets parallel to this axis. Intensities were estimated visually; no absorption correction was applied.

## Results

The unit cell was confirmed as being orthorhombic with the dimensions reported by C.R.L. (we have not redetermined the exact lattice constants). However, the presence of a relatively large number of weak reflections whose indices are not compatible with the *C*-centered cell of C.R.L. indicate the true space group to be $D_{2h}^{8}$–*Pcca*. (In order to conform with this space group setting, the *b* and *c* axes of C.R.L. have been interchanged; *a* remains the needle axis.) The magnitude and distribution of the intensities of these weak reflections indicated that only the oxygen atoms contribute to them and hence that the silver and chlorine atoms conform to the *C*-centered symmetry.

Table 1. *Final parameters and estimated probable errors*

Space group: *Pcca*.

$a = 6{\cdot}07$, $b = 6{\cdot}68$, $c = 6{\cdot}13$ Å.

| | | |
|---|---|---|
| 4 Ag in 4(*c*) 0, *y*, ¼ etc. | $y$ | $= 0{\cdot}112 \pm 0{\cdot}002$ |
| 4 Cl in 4(*c*) 0, *y*, ¼ etc. | $y$ | $= 0{\cdot}638 \pm 0{\cdot}007$ |
| 8 O in 8(*f*) *x*, *y*, *z* etc. | $x$ | $= 0{\cdot}36 \pm 0{\cdot}01$ |
| | $y$ | $= 0{\cdot}23 \pm 0{\cdot}01$ |
| | $z$ | $= 0{\cdot}095 \pm 0{\cdot}01$ |

Although there were many significant discrepancies between our observed structure factors and those reported by C.R.L. (see Table 2), the general pattern of agreement indicated that the coordinate $y = 0{\cdot}12$ assigned by them to the silver atom must be approximately correct. The position of the chlorine atom was deduced from an electron-density projection onto (100) (this projection was similar in general appearance but different in detail from Fig. 1(*a*) of C.R.L.) and was confirmed by a line synthesis along $(0, y, \frac{1}{4})$ calculated from the complete three-dimensional data. Adjusted *y* parameters for the silver and chlorine atoms and approximate *y* and *z* coordinates for the oxygen atom were derived from a difference projection onto (100); final *x*, *y*, and *z* coordinates for the oxygen atom were arrived at by trial and error adjustments based on the weak reflections having $(h+l) = 2n+1$. No attempt for accurate refinement was made. The final coordinates are listed in Table 1.

In Table 2 there are listed our observed and calculated structure factors for the zero and first layer lines; for comparison, the values of C.R.L. are also listed. Our calculated structure factors include a temperature factor with $B = 0{\cdot}95$.

The structure of $AgClO_2$ viewed along the *a* axis is shown in Fig. 1. Within the chlorite ion the Cl–O distance

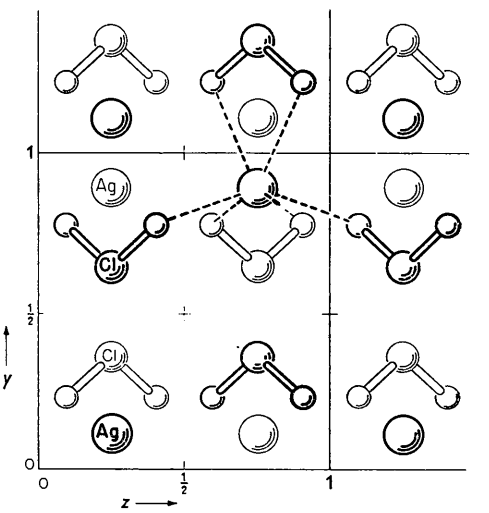


Fig. 1. The structure of $AgClO_2$, viewed along the *a* axis. Dashed lines are drawn from a silver atom to its six neighboring oxygen atoms, which form a distorted triangular prism.

* Contribution No. 2594 from the Gates and Crellin Laboratories.

Table 2. *Observed and calculated structure factors*

| | C.R.L. | | This work | |
|---|---|---|---|---|
| *hkl* | $F_o$ | $F_c$ | $F_o$ | $F_c$ |
| 000 | — | 320 | — | 320 |
| 1 | 100 | 112 | 46* | 100 |
| 2 | 46 | −55 | 24 | −29 |
| 3 | 79 | −80 | 42 | −48 |
| 4 | 130 | −124 | 120 | −115 |
| 5 | 65 | −65 | 76 | −64 |
| 6 | <20 | −2 | 44 | −43 |
| 7 | <20 | 10 | 17 | −20 |
| 8 | 69 | 69 | 67 | 69 |
| 002 | 227 | −251 | 116* | −190 |
| 1 | 86 | −100 | 76 | −80 |
| 2 | 30 | 45 | 30 | −29 |
| 3 | 56 | 76 | 39 | 27 |
| 4 | 113 | 114 | 171 | 138 |
| 5 | 69 | 63 | 91 | 79 |
| 6 | <20 | 3 | 31 | 20 |
| 7 | <20 | −10 | <10 | 1 |
| 8 | 54 | −67 | 68 | −58 |
| 004 | 168 | 184 | 113 | 120 |
| 1 | 76 | 79 | 54 | 58 |
| 2 | 31 | −34 | 41 | 30 |
| 3 | 54 | −67 | 23 | −17 |
| 4 | 93 | −98 | 132 | −119 |
| 5 | 56 | −55 | 74 | −70 |
| 6 | <20 | −3 | 20 | −12 |
| 006 | 115 | −142 | 85 | −118 |
| 1 | 51 | −67 | 36 | −44 |
| 2 | 22 | 26 | <10 | 8 |
| 3 | 37 | 60 | 22 | 24 |
| 4 | 65 | 83 | 74 | 67 |
| 5 | 49 | 47 | 42 | 40 |
| 111 | 57 | −51 | 52 | −45 |
| 2 | 134 | (−)134 | 135* | −186 |
| 3 | 124 | −134 | 96 | −102 |
| 4 | 60 | −41 | 32 | −29 |
| 5 | 64 | 70 | 14 | 15 |
| 6 | 140 | 129 | 92 | 98 |
| 7 | 87 | 85 | 49 | 60 |
| 8 | 27 | −5 | 16 | 20 |
| 102 | — | — | 47 | −31 |
| 1 | — | — | 5 | −4 |
| 2 | — | — | 32 | 26 |
| 3 | — | — | 11 | 8 |
| 4 | — | — | 17 | −18 |
| 5 | — | — | 8 | −10 |
| 113 | 52 | 47 | 75 | 72 |
| 2 | 106 | 113 | 145 | 152 |
| 3 | 106 | 115 | 61 | 59 |
| 4 | 33 | 37 | 15 | 14 |
| 5 | 50 | −65 | <14 | 4 |
| 6 | 134 | −121 | 79 | −75 |
| 7 | 78 | −80 | 39 | −63 |
| 104 | — | — | 15 | −15 |
| 115 | 43 | −38 | 38 | −36 |
| 2 | 90 | −90 | 94 | −108 |
| 3 | 74 | −97 | 44 | −58 |
| 4 | 33 | −33 | 15 | −17 |
| 5 | 37 | 58 | <12 | 9 |
| 6 | 100 | 109 | 55 | 70 |
| 106 | — | — | 11 | 6 |
| 117 | 32 | 31 | 15 | 16 |
| 2 | 79 | 75 | 58 | 80 |
| 3 | 52 | 82 | 32 | 49 |

* These observed values probably are affected by extinction.

is 1·55 Å, the O · · · O distance is 2·55 Å and the O–Cl–O angle is 111°, the probable errors being about 0·05 Å and 3°. Each $Ag^+$ ion is surrounded by six oxygen atoms which form a distorted triangular prism; the Ag–O distances range from 2·4 to 2·6 Å. There is no direct Ag–Cl contact. The shortest intermolecular O–O distance is 3·25 Å. The packing explains the major cleavage which we observe to be parallel to (010).

The structure confirms the expected ionic character of $AgClO_2$. It also suggests that the majority of the negative charge on the chlorite ion is borne by the oxygen atoms, as would be expected from a consideration of the relative electronegativities of chlorine and oxygen.

### Reference

CURTI, R., RIGANTI, V. & LOCCHI, S. (1957). *Acta Cryst.* **10**, 687.

*Acta Cryst.* (1961). **14**, 203

## The unit cell and space group of 2,2 dimethyl-1,3 propanediol.

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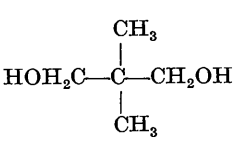
(*Received* 29 *August* 1960)

The compound:



grows from benzene as white-needle shaped crystals.

Several X-ray photographs have been taken using Cu $K\alpha$ radiation. Weissenberg and precession photographs have shown the unit cell to be monoclinic with dimensions:

$$a = 5{\cdot}98 \pm 0{\cdot}02,\ b = 11{\cdot}00 \pm 0{\cdot}03,\ c = 10{\cdot}81 \pm 0{\cdot}03\ \text{Å};$$
$$\beta = 112°\ 24' \pm 20',$$

where $a$ is parallel to the length of the needle.