radii of the 20 elements involved that differ by such a small amount as 0·025 Å (mean deviation) from the metallic radii for ligancy 12 that were formulated for the metals in 1947.

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Comments on the Preceding Paper by L. Pauling Entitled "The Use of Atomic Radii, etc."

By S. Geller

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(*Received* 27 *June* 1957)

The writer believes that his position regarding the various aspects of the *β*-W type structure has been made abundantly clear in his two papers (Geller, 1956, 1957) and therefore, that there is no point in his further discussing this most recent paper (Pauling, 1957).

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The Crystal Structure of $AgClO_2$

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The structure of $AgClO_2$ has been determined, using the Fourier difference method to locate the chlorine and oxygen atoms. The crystals of $AgClO_2$ are orthorhombic, with four molecules in a unit cell. The lattice constants are $a = 6{\cdot}07$, $b = 6{\cdot}13$, $c = 6{\cdot}68$ Å, all $\pm 0{\cdot}01$ Å, space group D_{2h}^{21}-*Cmma*. The structure is built up of $AgClO_2$ molecules, rather than of Ag^+ and ClO_2^- ions.

Introduction

The salts of chlorous acid represent a field which has been little studied from a structural point of view. Of preceding research, that of Levi & Scherillo (1931; see also Wyckoff, 1951) on NH_4ClO_2 is considered the most complete. This salt has high symmetry (tetragonal) but decomposes in a few hours and cannot tolerate long exposure to X-rays.

This paper describes the study of $AgClO_2$, which with $Pb(ClO_2)_2$ represents the only anhydrous chlorite which gives distinct crystals. $AgClO_2$ is also the most stable salt of chlorous acid. Of other chlorites, $NaClO_2.3\,H_2O$ is being studied.

Experimental

$AgClO_2$ crystallizes in flat, rectangular laminae, or rarely in rectangular parallelepipeds, with cleavages parallel to (001) and (010). The crystals, which are a shiny yellow upon preparation, become slightly black in time. Optical examination along the z axis reveals a strong birefringence, with $n_x > n_y$. The X-ray

Table 1. *Sign relationships*

From the Sayre equation

S 020 . S 024 = S 044
S 020 . S 003 = S 023
S 020 . S 021 = S 041
S 020 . S 025 = S 045
S 020 . S 043 = S 063
S 020 . S 023 = S 043
S 020 . S 041 = S 061
S 020 . S 045 = S 065
S 020 . S 001 = S 021
S 020 . S 005 = S 025
S 020 . S 004 = S 024
S 020 . S 008 = S 028
S 020 . S 040 = S 060
S 020 . S 044 = S 064
S 024 . S 02$\bar{4}$ = S 040
S 024 . S 02$\bar{8}$ = S 04$\bar{4}$
S 024 . S 00$\bar{3}$ = S 021
S 024 . S 021 = S 045
S 024 . S 02$\bar{1}$ = S 043
S 024 . S 02$\bar{5}$ = S 04$\bar{1}$
S 024 . S 04$\bar{3}$ = S 061
S 024 . S 02$\bar{3}$ = S 041
S 024 . S 041 = S 065
S 024 . S 04$\bar{1}$ = S 063
S 024 . S 04$\bar{5}$ = S 06$\bar{1}$
S 024 . S 001 = S 025
S 024 . S 00$\bar{1}$ = S 023
S 024 . S 00$\bar{5}$ = S 02$\bar{1}$
S 024 . S 004 = S 028
S 024 . S 00$\bar{4}$ = S 020
S 024 . S 00$\bar{8}$ = S 02$\bar{4}$
S 024 . S 040 = S 064

S 024 . S 04$\bar{4}$ = S 060
S 023 . S 041 = S 064
S 023 . S 001 = S 024
S 028 . S 00$\bar{3}$ = S 025
S 028 . S 02$\bar{5}$ = S 043
S 028 . S 04$\bar{3}$ = S 065
S 028 . S 02$\bar{3}$ = S 045
S 028 . S 04$\bar{5}$ = S 063
S 028 . S 00$\bar{5}$ = S 023
S 028 . S 00$\bar{4}$ = S 024
S 028 . S 00$\bar{8}$ = S 020
S 028 . S 04$\bar{4}$ = S 064
S 060 . S 003 = S 063
S 060 . S 001 = S 061
S 060 . S 004 = S 064
S 060 . S 005 = S 065
S 064 . S 00$\bar{3}$ = S 061
S 064 . S 001 = S 065
S 064 . S 00$\bar{1}$ = S 063
S 064 . S 00$\bar{5}$ = S 06$\bar{1}$
S 064 . S 00$\bar{4}$ = S 060
S 064 . S 00$\bar{8}$ = S 06$\bar{4}$
S 003 . S 021 = S 024
S 003 . S 025 = S 028
S 003 . S 04$\bar{3}$ = S 040
S 003 . S 061 = S 064
S 003 . S 02$\bar{3}$ = S 020
S 003 . S 041 = S 044
S 003 . S 06$\bar{3}$ = S 060
S 003 . S 001 = S 004
S 003 . S 005 = S 008
S 003 . S 00$\bar{4}$ = S 00$\bar{1}$

S 003 . S 00$\bar{8}$ = S 00$\bar{5}$
S 003 . S 040 = S 043
S 003 . S 04$\bar{4}$ = S 04$\bar{1}$
S 023 . S 005 = S 028
S 023 . S 00$\bar{4}$ = S 02$\bar{1}$
S 023 . S 00$\bar{8}$ = S 02$\bar{5}$
S 021 . S 02$\bar{5}$ = S 04$\bar{4}$
S 021 . S 043 = S 064
S 021 . S 023 = S 044
S 021 . S 04$\bar{1}$ = S 060
S 021 . S 04$\bar{5}$ = S 06$\bar{4}$
S 021 . S 00$\bar{1}$ = S 020
S 021 . S 00$\bar{5}$ = S 02$\bar{4}$
S 021 . S 004 = S 025
S 021 . S 00$\bar{4}$ = S 02$\bar{3}$
S 021 . S 040 = S 061
S 021 . S 044 = S 065
S 021 . S 04$\bar{4}$ = S 06$\bar{3}$
S 025 . S 04$\bar{1}$ = S 064
S 025 . S 04$\bar{5}$ = S 060
S 025 . S 00$\bar{1}$ = S 024
S 025 . S 00$\bar{5}$ = S 020
S 025 . S 00$\bar{4}$ = S 021
S 025 . S 00$\bar{8}$ = S 02$\bar{3}$
S 025 . S 040 = S 065
S 025 . S 04$\bar{4}$ = S 061
S 043 . S 02$\bar{3}$ = S 060
S 043 . S 001 = S 044
S 043 . S 00$\bar{4}$ = S 04$\bar{1}$
S 043 . S 00$\bar{8}$ = S 04$\bar{5}$
S 061 . S 00$\bar{1}$ = S 060
S 061 . S 004 = S 065

S 065 . S 00$\bar{1}$ = S 064
S 065 . S 00$\bar{4}$ = S 061
S 023 . S 040 = S 063
S 041 . S 00$\bar{1}$ = S 040
S 041 . S 00$\bar{5}$ = S 04$\bar{4}$
S 041 . S 004 = S 045
S 041 . S 00$\bar{4}$ = S 04$\bar{3}$
S 045 . S 00$\bar{1}$ = S 044
S 045 . S 00$\bar{5}$ = S 040
S 045 . S 00$\bar{4}$ = S 041
S 045 . S 00$\bar{8}$ = S 04$\bar{3}$
S 063 . S 001 = S 064
S 063 . S 00$\bar{4}$ = S 06$\bar{1}$
S 063 . S 00$\bar{8}$ = S 06$\bar{5}$
S 001 . S 00$\bar{5}$ = S 00$\bar{4}$
S 001 . S 004 = S 005
S 001 . S 00$\bar{4}$ = S 00$\bar{3}$
S 001 . S 040 = S 041
S 001 . S 044 = S 045
S 001 . S 04$\bar{4}$ = S 04$\bar{3}$
S 005 . S 00$\bar{4}$ = S 001
S 005 . S 00$\bar{8}$ = S 00$\bar{3}$
S 005 . S 040 = S 045
S 005 . S 04$\bar{4}$ = S 041
S 004 . S 00$\bar{8}$ = S 00$\bar{4}$
S 004 . S 040 = S 044
S 008 . S 04$\bar{4}$ = S 044
S 061 . S 00$\bar{5}$ = S 06$\bar{4}$
S 061 . S 00$\bar{4}$ = S 06$\bar{3}$
S 065 . S 00$\bar{5}$ = S 060
S 065 . S 00$\bar{8}$ = S 06$\bar{3}$
S 023 . S 04$\bar{4}$ = S 06$\bar{1}$

From the Harker–Kasper inequalities

S 040 = S 008 = +1
S 002 = S 042
S 020 = S 042 = S 028
S 004 = S 044
S 041 = S 001
S 045 = S 005 = S 043 = S 003
S 063 = S 023 = S 065 = S 025
S 061 = S 027 = S 021

photographs were made from crystals having a diameter of approximately 0·4 mm. perpendicular to the axis about which the Weissenberg and precession photographs were taken.

Lattice constants and space group

The lattice constants were measured on Weissenberg and oscillation photographs about the three axes. With λ(Cu $K\alpha$) = 1·5418 Å the following values for the lattice constants were obtained:

$$a = 6{\cdot}07 \pm 0{\cdot}01,\quad b = 6{\cdot}13 \pm 0{\cdot}01,\quad c = 6{\cdot}68 \pm 0{\cdot}01\ \text{Å}\,.$$

The limits of error listed are estimated standard deviations. With four molecules per unit cell the density was calculated to be 4·68 g.cm.$^{-3}$; the experimental value is 4·67 g.cm.$^{-3}$ at 20° C. In the equatorial patterns almost all independent reflexions within the Cu $K\alpha$ sphere were observed: 74 out of 76 independent reflexions allowed by the space group. On the precession photographs, with angle of precession $\mu = 25°$ and Mo $K\alpha$ radiation, we have measured the intensities of 58 of the equatorial reflexions. For the structural examination preference was given to precession photographs with Mo $K\alpha$, because they yield a greater number of measurable reflexions and also permit brief exposures, which are advisable because of the possible crystal alteration. The space group established by geometric means (Buerger, 1935) is derived from the diffraction symbol *mmmC–a* as *Cm*2*a* or *Cmma*. These results agree with the reflexions on the Weissenberg photographs: *hkl* present only when $h+k = 2m$; $hk0$ only when $h = 2n$. No measurable pyroelectricity could be detected. The statistical method (Howells, Phillips & Rogers, 1950), applied to the semi-absolute intensities, brings us to the centrosymmetrical space group, which was confirmed by the result of the structure determination.

Structure factors

The numerical values of the diffraction spots were obtained for the strongest reflexions by integration,

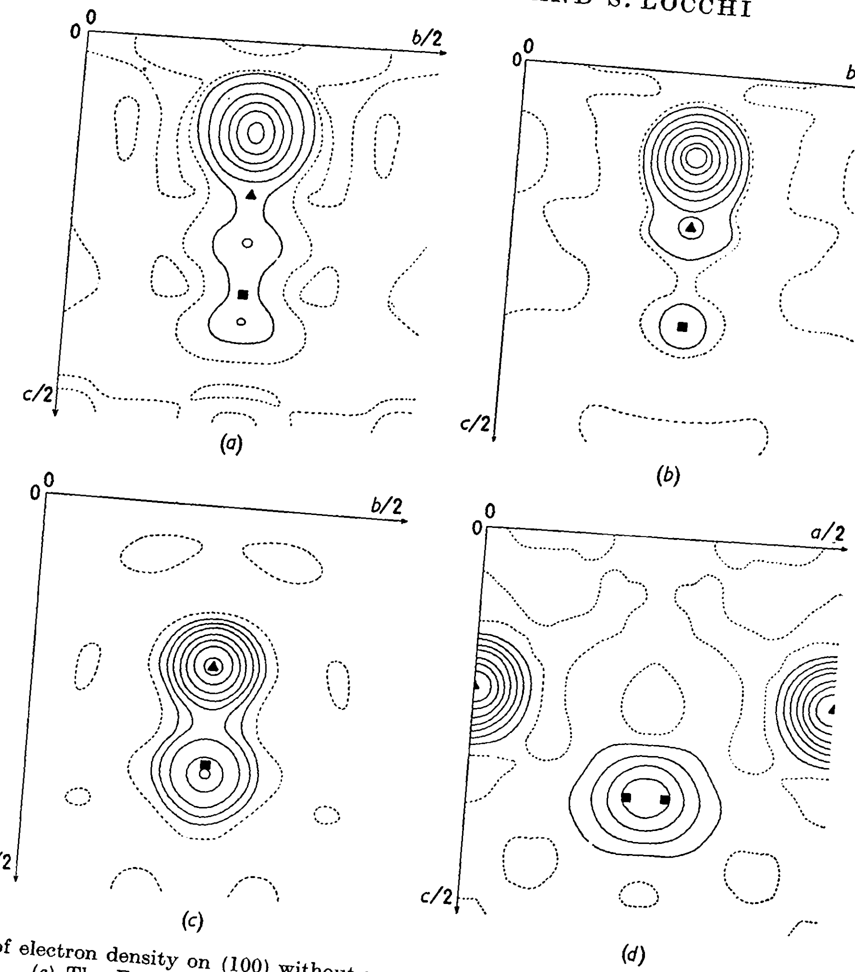

Fig. 1. (*a*) Projection of electron density on (100) without removal of series-termination error. (*b*) Final projection of electron density on (100). (*c*) The F_o-F_{Ag} synthesis on (100). (*d*) The F_o-F_{Ag} synthesis on (010). Contours are drawn at equal intervals on an arbitrary scale with the zero contour broken. Triangles show the final positions of the Cl atoms, and squares the final positions of the O atoms.

using a G.E.-XRD$_3$ Geiger-counter spectrometer with copper anticathode and correction of the white radiation by balanced filtration with nickel and iron filters. The less intense reflexions were estimated visually, and put on an absolute scale by comparison with strips calibrated by timed exposures of the spectrometrically measured reflexions. The calculated structure factors were based upon the Viervoll & Ögrim (1949) scattering curves for chlorine and oxygen, and the Thomas–Fermi (*International Tables*, 1935) curve for silver.

A correction for absorption and for thermal vibration was applied. The strong percentage of covalent bond found in Ag–ClO$_2$ causes asymmetry in the thermal vibration, but even by applying an isotropic temperature factor $B = 1{\cdot}52$ Å^{-2}, we remained under the standard deviation of the parameters.

Derivation of structure

We have the following preliminary evidence concerning the structure: cleavage parallel to (010), refractive index $n_x > n_y$. These two facts agree with a stratified structure, in which the optically active groups (ClO$_2$) are oriented in planes parallel to xz. Besides, close visual inspection of the $h0l$ and $h2l$ intensities revealed that they were virtually identical in distribution, suggesting that the reflecting units were situated on or very near the levels $y = \pm\frac{1}{4}$. The Patterson function $P(0, v, w)$ and $P(u, v, 0)$ gave only the parameters of the very strongly reflecting Ag. The determination of the other parameters by successive projections on $0kl$, and the refinement, were facilitated by means of extensive application of the relations between the phases of the structure factors. The Sayre and Harker–Kasper equations have permitted us to work on structure-factor groups instead of single factors. Limiting the application of the Harker–Kasper inequalities to the strongest factors, the inequality

$$u^2_{h,k,l} \leq \tfrac{1}{2}(1+u_{2h,2k,2l})$$

gives us the phase of two factors; the inequality

$$(u_{h,k,l} \pm u_{h'k'l'}) \leq (1 \pm u_{h+h',k+k',l+l'})(1 \pm u_{h-h',k-k',l-l'})$$

gives us 7 relations, which connect the phases of 20 structure factors out of 30 independent reflexions in the *xy* plane. On the 0*kl* reflexions, the Sayre equation

$$S_{h,k,l} = S_{h',k',l'} \cdot S_{h+h',k+k',l+l'}$$

gives us 129 relations, connecting the phases of almost all the structure factors. These relations are listed in Table 1.

The (100) Fourier projection was refined until there were no further changes of signs. The projection of the asymmetrical unit at this stage is given in Fig. 1(*a*). However, the error due to the series-termination effect is large, in our case, because of the relatively small number of terms, and made even larger by the presence of the heavy atom; for this reason, one should not put reliance on the position of the lighter peaks in Fig. 1(*a*). We have therefore prepared the one-dimensional F_o and F_{Ag} projections, using the 0*kl* terms, at $y = \frac{1}{4}$ (Fig. 2, curves *A* and *B*) and the $F_o - F_{Ag}$ (Fig. 2, curve *C*) and $F_o - F_{Ag,Cl}$ projections. The definite parameters give us the final projection (Fig. 1(*b*)). This procedure was repeated on the *h*0*l* plane. The $F_o - F_{Ag}$ projections, using 0*kl* and *h*0*l*, are given in Figs. 1(*c*) and 1(*d*). With the parameters found in the $F_o - F_c$ synthesis the discrepancy factor for all the structure factors in the final set was 0·13. The atomic parameters are given in Table 2, the list of observed and calculated structure factors in Table 3, and the interatomic distances in Table 4. The standard error for the interatomic distances is ±0·05 Å, and that of bond angles is ±5°.

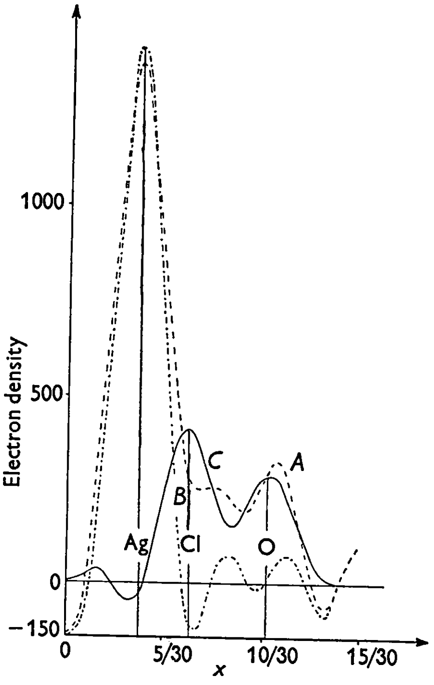

Fig. 2. Projection of electron density on (100), at $y = \frac{1}{4}$. Curve *A*: F_o projection; Curve *B*: F_{Ag} projection; Curve *C*: $F_o - F_{Ag}$ projection.

Table 2. *Final parameters for* $AgClO_2$

	x	*y*	*z*
Ag_1	0	$\frac{1}{4}$	0+0·12
Ag_2	$\frac{1}{2}$	$\frac{1}{4}$	0+0·88
Ag_3	0	$\frac{3}{4}$	0+0·88
Ag_4	$\frac{1}{2}$	$\frac{3}{4}$	0+0·12
Cl_1	0	$\frac{1}{4}$	0+0·79
Cl_2	$\frac{1}{2}$	$\frac{1}{4}$	0+0·21
Cl_3	0	$\frac{3}{4}$	0+0·21
Cl_4	$\frac{1}{2}$	$\frac{3}{4}$	0+0·79
O_1	0+0·22	$\frac{1}{4}$	0+0·66
O_2	0+0·78	$\frac{1}{4}$	0+0·66
O_3	0+0·28	$\frac{1}{4}$	0+0·34
O_4	0+0·72	$\frac{1}{4}$	0+0·34
O_5	0+0·78	$\frac{3}{4}$	0+0·34
O_6	0+0·22	$\frac{3}{4}$	0+0·34
O_7	0+0·72	$\frac{3}{4}$	0+0·66
O_8	0+0·28	$\frac{3}{4}$	0+0·66

Discussion of structure

Levi & Curti (1953) have demonstrated that chlorous acid is very weak: $K = 3 \times 10^{-6}$ at 18° C. This suggests that in the case of $AgClO_2$ the Ag–Cl bond possesses a notable percentage of covalent character. The crystal structure is well demonstrated in the projection along the *b* axis (Fig. 3). It is built up from $AgClO_2$ molecules rather than from Ag^+ and ClO_2^- ions. We have in effect a discrete group of atoms held together by obviously covalent bonds. The structure is made up

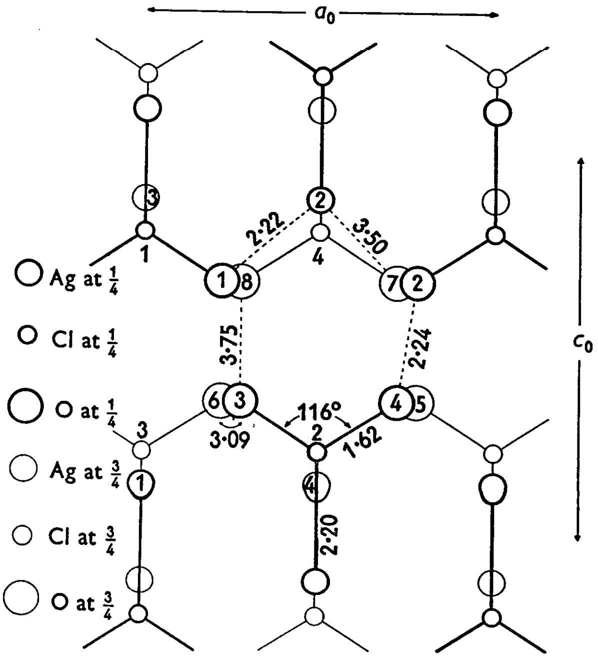

Fig. 3. Projection of the crystal structure along the *b* axis.

Table 3. *Observed and calculated structure factors*

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
001	100	+112	205	73	−49	241	89	+102	133	106	+115
002	46	−55	206	38	−37	261	65	−83	134	33	+37
003	79	−80	207	29	+32	311	73	−68	135	50	−65
004	130	−124	208	63	+72	331	40	+57	136	134	−121
005	65	−65	400	189	+176	351	45	−46	137	78	−80
006	< 20	−2	401	87	+83	371	38	+38	151	43	−38
007	< 20	+10	402	34	−30	401	90	+84	152	90	−90
008	69	+69	403	60	−74	421	76	−79	153	74	−97
020	227	−251	404	102	−95	441	68	+72	154	33	−33
021	86	−100	405	57	−53	461	45	−64	155	37	+58
022	30	+45	406	< 20	−7	511	37	−26	156	100	+109
023	56	+76	600	91	+117	531	29	+25	171	32	+31
024	113	+114	601	59	+81	551	25	−23	172	79	+75
025	69	+63	602	< 20	−16	601	66	+81	173	52	+82
026	< 20	+3	603	50	−84	621	57	−78			
027	< 20	−10	604	65	−69	641	57	+72	222	< 20	+12
028	54	−67	605	39	−41	711	45	−46	262	< 20	+12
040	168	+184				731	45	+43	312	110	−93
041	76	+79	020	227	−251	111	57	−51	332	95	+83
042	31	−34	040	168	+184	131	70	+47	352	71	−73
043	54	−67	060	115	−142	151	39	−38	462	< 20	+21
044	93	−98	220	142	−146	171	29	+31	512	99	−102
045	56	−55	420	145	−163	021	108	−100	532	93	−94
046	< 20	−3	620	120	−114	041	88	+80	552	68	−83
060	115	−142	240	120	+121	061	65	−67	622	< 20	+16
061	51	−67	440	138	+143				642	< 20	−15
062	22	+26	640	113	+106	112	134	+134	712	63	−60
063	37	+60	260	115	−106	113	124	−134	732	49	+58
064	65	+83	460	113	−123	114	60	−41	112	134	−134
065	49	+47	200	158	+160	115	64	+70	132	93	+113
			400	158	+176	116	140	+129	152	93	−90
200	180	+160	600	91	+117	117	87	+85	172	69	+75
201	119	+146				118	27	−5	242	< 20	−11
202	21	−13	201	146	+146	131	52	+47	422	20	+28
203	71	−140	221	114	−126	132	106	+113	442	< 20	−25
204	102	−81									

Table 4. *Interatomic distances between nearest neighbors in* $AgClO_2$

Ag–Cl	2·20 Å	Cl_1–O_1	1·62 Å
Ag–O	3·36	O_1–O_3	2·24
Ag_2–O_1	2·22	O_1–O_6	3·75
Ag_2–O_7	3·50	O_1–O_8	3·09

of a series of planes parallel to (010), composed of ClO_2 groups related to the silver atoms with Ag–Cl bond length = 2·20 Å. These planes are at a distance of 3·06 Å, while the observed atomic diameter of the oxygen is 2·24 Å. The Ag atoms have nearest to them four O atoms in a plane: two at distance of 2·22 Å, and two at distance of 3·36 Å. There is no other coordination of Ag. The O–Cl–O angle is 116±5°, which is comparable with the value determined by Levi & Scherillo in NH_4ClO_2 (110°); the same value was confirmed spectroscopically by Mathieu (1952) for $NaClO_2 . 3\,H_2O$. It is not possible to compare the valence angles obtained for the gaseous chlorine dioxide since these vary from 116° to 137° according to the method and authors. Deducing for oxygen a radius $r_O = 1{\cdot}12$ Å from the minimum distance observed between the O_1 and O_3 atoms, we propose for the chlorine $r_{Cl} = 0{\cdot}54$ Å.

The authors wish to thank Prof. G. R. Levi for helpful discussion, and Dr A. Pontoglio for his invaluable assistance in carrying out the research.

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