Acta Cryst. (1976). B**32**, 610

Anhydrous Sodium Chlorite

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(*Received* 30 *July* 1975; *accepted* 26 *September* 1975)

Abstract. $NaClO_2$, $I2/a$, monoclinic, $a=6{\cdot}456$ (2), $b=6{\cdot}442$ (2), $c=6{\cdot}813$ (2) Å, $\beta=120{\cdot}6$ (1)°, $Z=4$, $D_x=2{\cdot}468$ g cm^{-3}. The Cl–O bond length is 1·564 (3) Å and the OClO bond angle is 108·6 (1)°, which are values close to those found in $NaClO_2.3H_2O$. The ClO_2^- groups are oriented with antiparallel dipole moments along **b** and the O atoms form a sixfold coordination unit about the Na^+ ions in the form of a distorted triangular prism.

Introduction. In a previous paper (Tarimci, Schempp & Chang, 1975) we reported the crystal structure of sodium chlorite trihydrate, $NaClO_2.3H_2O$, where the water molecules appear to have a strong influence on the final structure. On the other hand, a phase transition occurs at 37·4°C (Cunningham & Oey, 1955) at which the waters of hydration are lost. Nuclear quadrupole resonance (n.q.r.) ^{35}Cl measurements show little difference between the hydrated and anhydrous material (Tarimci & Schempp, 1976). We have therefore studied the structure of anhydrous $NaClO_2$ in order to complete the crystallographic data on this system and to determine how the absence of the water molecules would change the structure and affect the electric field gradient (e.f.g.) at the chlorine site.

$NaClO_2$ is available commercially. The material obtained from the Matheson Chemical Co. was labelled $NaClO_2.xH_2O$ which, after recrystallization yields $NaClO_2.3H_2O$ (m.p. 37·4°C). Crystals of the anhydrous compound were obtained by heating the trihydrate in a glass vial and holding at 50°C for 24–48 h; crystallization seems to occur optimally at this temperature. The resulting crystals were mostly thin plates or needles without prominent cleavage, and they are apparently stable in air. Nonetheless, a 0·2 × 0·2 × 0·5 mm needle-shaped crystal was placed in a thin-walled capillary tube for data collection. With graphite-monochromated Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å), 585 reflections were collected at room temperature on a Nonius CAD-4 computer-controlled four-circle diffractometer. A correction factor of 0·02 was included in the estimated standard deviation of intensities [$\sigma^2(I)=\sigma^2(\text{scan})+\sigma^2(\text{background})+(0{\cdot}02\ \text{scan})^2$] owing to instrumental fluctuations. Lorentz and polarization factors (Shiono, 1971) were then applied to obtain the structure factors.

Weissenberg and precession photographs showed systematic absences $h0l$, l odd, and $0k0$, k odd, which indicate the centrosymmetric space group $P2_1/c$ if for a general reflection hkl there are no other conditions. However, there were only a few reflections with $h+k+l$ odd. A series of direct method programs (Dewar, 1970) followed by an E synthesis gave a solution for the structure; Cl and Na were located at nearly $\frac{1}{4},y,0$ and $\frac{3}{4},y,0$ respectively. With the scattering factors of Cromer & Waber (1965), the *ORFLS* anisotropic full-matrix least-squares program was used to refine the structure to $R=0{\cdot}08$ (where $R=\sum|\Delta|/\sum F_{\text{meas}}$). However, for the hkl reflections with $h+k+l$ odd, R was about 0·55, and hence these reflections were not properly accounted for by the trial structure. Azimuthal scans were made to check whether the intensities obtained for this class of reflections, along with a few other suspicious reflections, were enhanced by multiple reflection. In fact, most were clearly shown to be affected by double reflection (520, 620, 540, 011, 061, 421, $\bar{2}41$, $\bar{1}12$, $\bar{2}12$, 322, $\bar{2}32$, $\bar{2}52$, $\bar{2}04$, $\bar{4}14$) and their structure factors were accordingly adjusted, leading to an $R=0{\cdot}071$.

After removal of all reflections with $h+k+l$ odd and refinement in space group $I2/a$ with the Cl and Na atoms in special positions, the structure converged at $R=0{\cdot}056$, for a total of 222 reflections. However, the five reflections 104, 124, 221, $\bar{4}21$, $\bar{6}21$ are disallowed

Table 1. *Atomic parameters* (× 10⁴) *in anhydrous sodium chlorite*

Positional parameters are given as fractions of the lattice translations. Anisotropic temperature factors correspond to the expression $T=\exp\left[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)\right]$. Estimated standard deviations are given in parentheses.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O	4766 (4)	2923 (4)	1341 (5)	82 (10)	134 (8)	183 (10)	−29 (5)	28 (8)	−9 (6)
Na	7500	3662 (3)	0	119 (6)	111 (6)	161 (9)	0	61 (8)	0
Cl	2500	1507 (2)	0	89 (6)	64 (4)	217 (6)	0	41 (5)	0

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* This work was supported in part by a Cottrell Research Grant from the Research Corporation and by a University Science Development Award, No. GU-3184, from the National Science Foundation.

in $I2/a$ and these remain unexplained; although weak, their intensities are still substantially greater than 2σ. A similar situation was recently reported by Klewe & Pedersen (1974) for $\mathrm{NaCl.2H_2O}$. The final atomic parameters are listed in Table 1.*

Discussion. In sodium chlorite trihydrate (Tarimci, Schempp & Chang, 1975; Tazzoli, Riganti, Giuseppetti & Coda, 1975), the two chlorite O atoms have different environments; one is in contact with three H atoms and the Cl, while the other is involved with the $\mathrm{Na^+}$ coordination, the Cl, and only two H atoms. The two Cl–O bond lengths thus differ by 7σ. With the absence of the water molecules, the structure assumes a higher symmetry – a twofold axis passes through the Cl and Na atoms and thus both O atoms are in equivalent positions. The Cl–O bond length is 1·564 (3) Å and the OClO angle is 108·6 (1)°, which can be compared with 1·564, 1·557 Å and 108·23° in $\mathrm{NaClO_2.3H_2O}$ and 1·55 Å and 111° in silver chlorite (Cooper & Marsh, 1961).

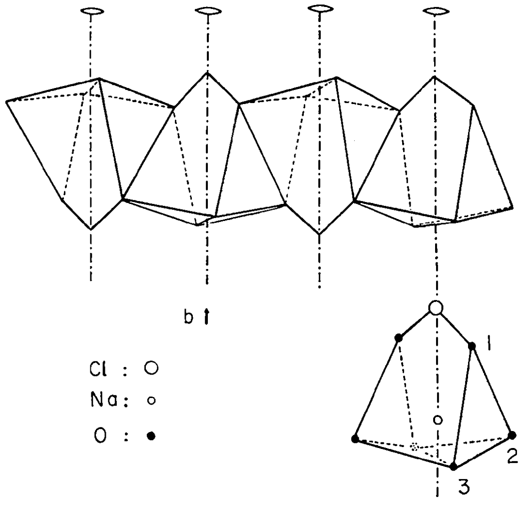

Fig. 1. $\mathrm{Na^+}$ coordination in anhydrous sodium chlorite.

Common to both the hydrated and anhydrous structures is the fact that each Na atom is coordinated to six O atoms in van der Waals contact. In the hydrate, the water O atoms and one of the chlorite O atoms are coordinated with the Na and form a distorted octahedron with an average Na–O distance of 2·409 Å. In the anhydrous structure, the coordination becomes a six-faced prism (Fig. 1) with an average Na–O distance of 2·460 Å, which is about 0·05 Å longer than that found in the hydrate. Table 2 shows the distances and angles for the $\mathrm{Na^+}$ coordination. By sharing edges, the $\mathrm{Na^+}$ coordination prisms form zigzag chains normal to the **b** axis (Fig. 1). The $\mathrm{ClO_2^-}$ groups are oriented so that the dipole moments, which lie along **b**, are antiparallel. The O atoms are in sheets parallel to the *bc* plane and form layers alternating with the sheets formed by Na and Cl (Fig. 2). This arrangement allows the chlorine a next nearest oxygen neighbor at 3·191 Å, just within the van der Waals contact distance 3·2 Å.

Table 2. *Distances* (Å) *and angles* (°) *of* $\mathrm{Na^+}$ *coordination in anhydrous sodium chlorite*

The labeling is defined in Fig. 1.

i	j	k	D_{ij}	D_{jk}	$\angle_{ijk}$
O(1)	Na	O(2)	2·540 (4)	2·412 (4)	84·8 (1)
O(1)	Na	O(3)	2·540 (4)	2·427 (4)	90·6 (1)
O(2)	Na	O(3)	2·412 (4)	2·427 (4)	90·9 (1)

In silver chlorite, $\mathrm{AgClO_2}$ (Cooper & Marsh, 1961), there is a somewhat similar arrangement of antiparallel $\mathrm{ClO_2^-}$ ions stacked along **b**, except that the $\mathrm{ClO_2^-}$ planes in neighboring chains are normal to each other, whereas in $\mathrm{NaClO_2}$ they are parallel. The $\mathrm{AgClO_2}$ structure contains zones parallel to the *ac* plane in which only Cl atoms are found; such zones are absent in $\mathrm{NaClO_2}$. The $\mathrm{Ag^+}$ coordination involves six neighboring oxygens forming a distorted triangular prism very similar to the one found in sodium chlorite (Fig. 1). There are also similarities to the structure of the ferroelectric phase of sodium nitrite, $\mathrm{NaNO_2}$ (Canut & Hosemann, 1964) where $\mathrm{NO_2^-}$ groups in parallel planes

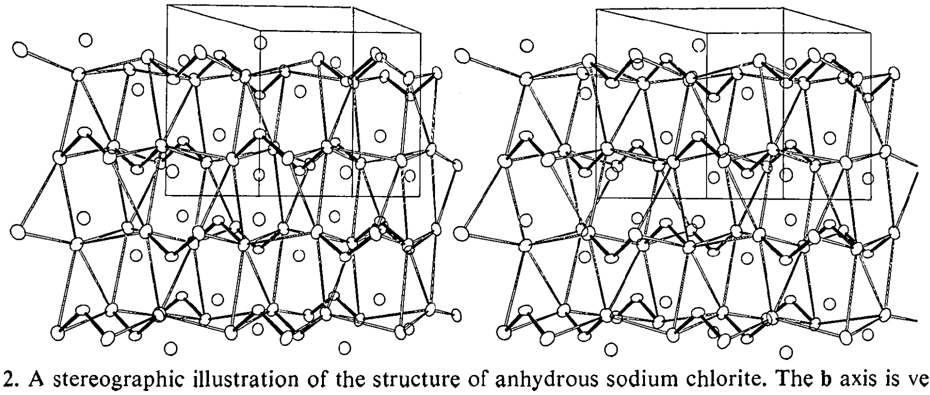

Fig. 2. A stereographic illustration of the structure of anhydrous sodium chlorite. The **b** axis is vertical.

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* A list of measured and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31414 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

are stacked along **b** and the Na^+ ion is six-coordinated to oxygen forming triangular prisms. In this case, of course, the NO_2^- groups are oriented with their dipole moments parallel.

$NaClO_2$ is close to orthorhombic since the cell can be transformed to an orthogonal cell by $\mathbf{T}=201/010/001$, where, approximately, $a'=11{\cdot}02$, $b'=6{\cdot}42$, $c'=6{\cdot}85$ Å. However, this cannot be considered truly orthorhombic because of the missing mirror symmetry in the intensities.

The sodium chlorite structure may be described in the equivalent space group $C2/c$ by applying the transformation matrix $\mathbf{T}=-101/010/100$; $\mathbf{TA}=\mathbf{B}$ converts the cell parameters **A** in $I2/a$ to those **B** in $C2/c$ and the inverse $\mathbf{XT}^{-1}=\mathbf{Y}$, where $\mathbf{T}^{-1}=00-1/010/10-1$, gives the new atom coordinates **Y** in $C2/c$.

We are grateful to Dr Mical K. Wood for numerous helpful discussions.

References

Canut, M. & Hosemann, R. (1964). *Acta Cryst.* **17**, 973–981.

Cooper, J. & Marsh, R. E. (1961). *Acta Cryst.* **14**, 202–203.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Cunningham, G. & Oey, T. S. (1955). *J. Amer. Chem. Soc.* **77**, 799–801.

Dewar, R. B. K. (1970). In *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, p. 63. Copenhagen: Munksgaard.

Klewe, B. & Pedersen, B. (1974). *Acta Cryst.* B**30**, 2363–2371.

Shiono, R. (1971). Technical Report No. 49, Department of Crystallography, Univ. of Pittsburgh, Pittsburgh, Pa.

Tarimci, Ç. & Schempp, E. (1976). To be published.

Tarimci, Ç., Schempp, E. & Chang, S. C. (1975). *Acta Cryst.* B**31**, 2146–2149.

Tazzoli, V., Riganti, V., Giuseppetti, G. & Coda, A. (1975). *Acta Cryst.* B**31**, 1032–1037.

Acta Cryst. (1976). B**32**, 612

Note on the Space Group Reported for the Dimeric 6-Mercaptopurine Copper(I) Chloride Complex

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(*Received* 27 *June* 1975; *accepted* 24 *September* 1975)

Abstract. The space group is $P\overline{1}$ and not $P1$; the asymmetric unit is $[C_5H_5N_4S.CuCl_2.H_2O]$. The structure has now been refined in $P\overline{1}$ to $R=0{\cdot}046$ for 1584 observed data and yields satisfactory bond lengths and angles.

Introduction. Caira & Nassimbeni (1975) reported the structure of the 6-mercaptopurine copper(I) chloride complex as having the space group $P1$ thus requiring the dimer not only to be the asymmetric unit but also to be chiral. However, if the fractional atomic coordinates as published are summed for each equivalent pair of atoms *A–B*, then it is evident that the sums are identical and that the two halves *A* and *B* are related by a pseudo-centre of inversion at 0·847, −0·153, −0·089. Although R was low (0·051), the standard deviations were high and some chemically equivalent bonds differed in length by over 0·1 Å, *e.g.* C(8)–N(9) *A* 1·39, *B* 1·27 Å; C(4)–C(5) *A* 1·32, *B* 1·41 Å; C(2)–N(3) *A* 1·39, *B* 1·24 Å; N(1)–C(6) *A* 1·44, *B* 1·33 Å (e.s.d. of 0·03 Å in each case, so these differences are as great as 5σ). The planes of the two mercaptopurine units have closely similar direction cosines (0·321, 0·314; 0·884, 0·878; −0·340, −0·360) and thus, within the quoted standard deviations, the planes of these two units are parallel and related by the same pseudo-centre. That a dimeric molecule should apparently retain a centre of inversion yet pack in a non-centrosymmetric space group is most unusual (Kitaigorodskii, 1961).

A statistical analysis of the intensities had originally shown strong indications that the space group was centrosymmetric (av. $|E^2-1|=0{\cdot}965$, av. $|E|=0{\cdot}803$, $|E|>1=31{\cdot}7\%$, $|E|>2=4{\cdot}7\%$, $|E|>3=0{\cdot}1\%$) but repeated attempts to solve the structure in $P\overline{1}$ by both vector and direct methods had failed. The refinement in $P1$ yielded very large correlation coefficients between atomic parameters for each pair of atoms *A–B*; for the Cl and S atoms the mean value of the correlation coefficients for corresponding positional parameters was 0·90.

The structure has been re-examined and successfully refined in $P\overline{1}$ to $R=0{\cdot}046$ and $R_w=0{\cdot}052$ for 1584 reflexions* with $I>2{\cdot}5\sigma I$. The weighting scheme was $w=1/\sigma^2F+gF^2$ with $g=0{\cdot}00196$ chosen to give the

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31398 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.