

3.10(1) Å for Rb(1) and 3.15(1) Å for Rb(2). The shortest Rb–C distances of rubidium ion Rb(1) to the COT rings of two other Rb<sub>2</sub>COT units are 3.37(1) Å and 3.43(1) Å for the distances Rb(1')–C(1) and Rb(1')–C(4) respectively. Bond distances and angles are summarized in Table 2. The numbering system is shown in Fig. 2. The cyclooctatetraene dianion is planar and has an average C–C bond length of  $1.40 \pm 0.02$  Å. A weighted least-squares plane through the C atoms of the COT ring ( $0.0169X + 0.0Y - 1.0Z + 8.20$  Å = 0) has all of the atoms of the ring within  $0.01 \pm 0.01$  Å of the plane.

In the paper on K<sub>2</sub>COT.diglyme (Noordik *et al.*, 1974), we mentioned that we were unable to create paramagnetic centres in the alkali COT single crystals by ultraviolet irradiation at low temperatures. However, with X-ray irradiation produced by a W-tube at

50 kV paramagnetic centres were created, which were identified as COT monoanions by e.p.r. From the e.p.r. spectra of the K<sub>2</sub>COT.diglyme single crystal (Mooij, Degens, Klaassen & de Boer, 1974) it could be concluded that the COT molecules rapidly rotate around an axis perpendicular to the aromatic plane. Results of these experiments will be published elsewhere.

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## Sodium Chlorite Trihydrate

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**Abstract.** NaClO<sub>2</sub>.3H<sub>2</sub>O, triclinic,  $P\bar{1}$ ,  $a = 5.492(1)$ ,  $b = 6.412(1)$ ,  $c = 8.832(1)$  Å,  $\alpha = 72.06(5)$ ,  $\beta = 87.73(5)$ ,  $\gamma = 70.88(5)^\circ$ , and  $Z = 2$ . The bond distances and angles of the ClO<sub>2</sub><sup>-</sup> group are Cl–O(1) = 1.564(1), Cl–O(2) = 1.557(1) Å, and O–Cl–O = 108.23(6)°. One of the oxygens belonging to the ClO<sub>2</sub><sup>-</sup> ion together with the oxygen atoms of the waters of hydration form a distorted octahedron around the sodium. These octahedra form zigzag columns by sharing edges along the  $a$  axis, and the columns are connected by hydrogen bonds. Nuclear quadrupole resonance studies have shown that the largest component of the diagonalized electric field gradient tensor is normal to the ClO<sub>2</sub><sup>-</sup> plane.

**Introduction.** The electronic structure of the chlorite ion, ClO<sub>2</sub><sup>-</sup>, is of interest for comparison with neutral chlorine dioxide and other oxychloride anions. Although the single nuclear quadrupole resonance (n.q.r.) frequency in NaClO<sub>2</sub>. $x$ H<sub>2</sub>O was observed by Ragle (1960), a complete interpretation of n.q.r. data requires knowledge of the orientation of the electric field gradient (e.f.g.) principal axes as well as the quadrupole coupling constant and asymmetry parameter. In order to determine the orientation of the e.f.g. tensor with respect to the chemical bonds

(Tarimci & Schempp, 1975), it was necessary to obtain the crystal structure. NaClO<sub>2</sub>.3H<sub>2</sub>O was chosen from among other chlorites because it was relatively easy to grow a large single crystal for the n.q.r. study.

In some early crystallographic studies of sodium and other chlorites, Levi & Scherillo (1930) described the morphology and reported the space group of NaClO<sub>2</sub>. More recently, Curti, Rigante & Locchi (1960) attempted to solve the structure, but could not give a full description of it. Two other chlorite structures have been studied; ammonium chlorite at  $-35^\circ\text{C}$  (the compound is unstable at room temperature) by Gillespie, Sparks & Trueblood (1959), and silver chlorite (which is explosive in the dry state) by Cooper & Marsh (1961). The crystal structure of anhydrous NaClO<sub>2</sub> has also been determined recently and will be reported later (Tarimci & Schempp, 1975).

**Experimental.** Sodium chlorite is commercially available as NaClO<sub>2</sub>. $x$ H<sub>2</sub>O. Crystals of the trihydrate in the form of needles or thin distorted hexagonal plates are formed from aqueous solution (to which a small amount of NaOH is added to retard decomposition). Crystallization of the trihydrate takes place below the phase transition temperature of  $38^\circ\text{C}$  (Cunningham & Oey, 1955); above this temperature, only anhydrous

sodium chlorite is obtained. The trihydrate loses water in air and small crystals decompose within a few hours. Therefore, a needle-shaped crystal was sealed in a 0.4 mm capillary with mother liquor during the data collection.

$\text{NaClO}_2 \cdot 3\text{H}_2\text{O}$  crystallizes in space group  $P\bar{1}$ . The unit-cell parameters are  $a=5.492(1)$ ,  $b=6.412(1)$ ,  $c=8.832(1)$  Å,  $\alpha=72.06(5)$ ,  $\beta=87.73(5)$ ,  $\gamma=70.88(5)^\circ$ , and  $Z=2$ . Using graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda=0.7107$  Å), 1850 non-symmetry-related reflections ( $\sin \theta_{\max}/\lambda=0.736$ ) were collected on an

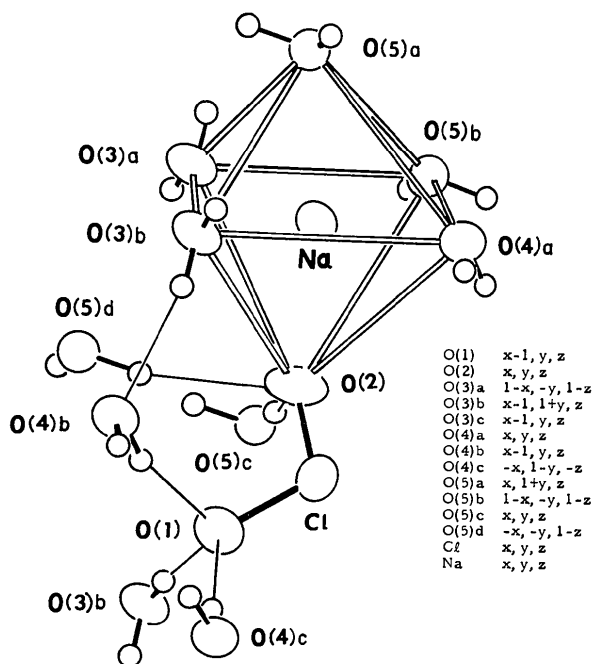


Fig. 1. The water oxygens and one of the oxygens of  $\text{ClO}_2^-$  form a distorted octahedron around the sodium ion. Thin lines represent hydrogen bonds, heavy solid lines the O-H and O-Cl chemical bonds, and double lines describe the octahedron of oxygens in van der Waals contact with the sodium.

automatic diffractometer. Corrections were made for Lorentz and polarizations factors, but no account was taken of absorption and extinction. A three-dimensional Patterson synthesis permitted the structure to be determined by the heavy-atom method. Atomic scattering factors used were those of Cromer & Waber (1965) for Cl, Na and O, and of Stewart, Davidson & Simpson (1965) for H. Counting statistics were used as a weighting scheme [ $w=1/\sigma^2$ , where  $\sigma(I)=\sigma(\text{scan})^2 + \sigma(\text{background})^2$ ], and the trial structure for the non-hydrogen atoms was refined with the ORFLS full-matrix least-squares program with anisotropic temperature factors, down to  $R=(\sum_h |A|/\sum_h |F_{\text{meas}}|)=0.08$ .

A three-dimensional difference map revealed a number of potential hydrogen atom peaks. Those surviving a test for chemically reasonable bond distances and angles were subjected to further refinement. The final refinement terminated at  $R=0.037$  with isotropic temperature factors for the hydrogen atoms and anisotropic temperature factors for the non-hydrogen atoms.\* The atomic positions in the Niggli reduced cell (Santoro & Mighell, 1970) are listed in Table 1.

**Discussion.** The  $\text{ClO}_2^-$  group is found to have an O-Cl-O angle of  $108.23 \pm 0.06^\circ$  which is smaller than that in  $\text{AgClO}_2$  ( $111^\circ$ ) and  $\text{NH}_4\text{ClO}_2$  ( $110.5 \pm 1.4^\circ$ ). As seen in Fig. 1, the two chlorite oxygen atoms have somewhat different environments; the chlorine and three hydrogen atoms make a tetrahedral environment for O(1), while O(2) is involved with the chlorine and only two hydrogen atoms. Thus the Cl-O bond lengths differ slightly ( $7\sigma$ ), Cl-O(1) =  $1.564(1)$  Å and Cl-O(2) =  $1.557(1)$  Å. No other atoms have a close contact with the chlorine, the next closest being H1(O4) at the distance  $2.901(2)$  Å.

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31025 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic parameters

Positional parameters are given as fractions of the lattice translations. Anisotropic and isotropic temperature factors correspond, respectively, to the expressions  $T=\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$  and  $T=\exp(-B \sin^2 \theta/\lambda^2)$ . Estimated standard deviations are given in parentheses. Positional parameters for non-hydrogen atoms  $\times 10^4$ , for hydrogen atoms  $\times 10^3$ ; thermal parameters for non-hydrogen atoms  $\times 10^4$ , for hydrogen atoms  $\times 10$ .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
Cl	944 (1)	1839 (1)	1318 (1)	286 (1)	257 (1)	91 (1)	-76 (1)	20 (1)	-43 (1)
Na	2637 (1)	4586 (1)	3956 (1)	199 (2)	180 (1)	100 (1)	-62 (1)	-7 (1)	-45 (1)
O(1)	8124 (2)	1766 (2)	1329 (1)	306 (4)	228 (3)	134 (2)	-74 (3)	-43 (2)	-17 (2)
O(2)	1710 (2)	1858 (2)	2991 (1)	491 (6)	213 (3)	131 (2)	-137 (3)	-67 (2)	-40 (2)
O(3)	8259 (2)	-2798 (2)	3242 (1)	256 (4)	177 (3)	120 (1)	-77 (3)	-39 (2)	-23 (2)
O(4)	4810 (2)	5981 (2)	1654 (1)	292 (4)	223 (3)	91 (1)	-63 (3)	-30 (2)	-38 (2)
O(5)	2987 (2)	-2524 (2)	5091 (1)	242 (3)	163 (3)	102 (1)	-30 (2)	-3 (2)	-33 (2)
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	
H1(O3)	182 (4)	141 (4)	723 (2)	46 (4)	H2(O4)	412 (4)	663 (4)	92 (3)	44 (5)
H2(O3)	273 (4)	301 (3)	734 (2)	43 (4)	H1(O5)	274 (4)	869 (4)	452 (2)	37 (4)
H1(O4)	434 (4)	540 (3)	844 (2)	39 (4)	H2(O5)	191 (4)	770 (3)	573 (2)	40 (4)

Five water oxygen atoms and one of the chlorite oxygen atoms, O(2), are in van der Waals contact with the sodium atom, forming a distorted octahedron (see Fig. 1 and Table 2). These octahedra are linked by edge-sharing, and thus form zigzag columns along the *a* axis, as shown in Fig. 2. Hydrogen bonds (Table 3) connect the columns to form a three-dimensional framework. The average Na–O distance is 2.409(1) Å. Such edge-sharing octahedral columns are found in the structures of other hydrated sodium salts, *e.g.*, sodium sulfate decahydrate (Ruben, Templeton, Rosenstein & Olovsson, 1961) and borax, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O (Morimoto, 1956). Average Na–O distances in these structures are 2.43 and 2.42 Å, respectively.

Table 2. Distances (Å) and angles (°) of Na<sup>+</sup> coordination octahedron and about the Cl atom

Atomic labels are defined in Fig. 1.

<i>i</i>	<i>j</i>	<i>k</i>	<i>d</i> <sub><i>ij</i></sub>	<i>d</i> <sub><i>jk</i></sub>	∠ <sub><i>ijk</i></sub>
O(2)	Na	O(3) <i>a</i>	2.363 (1)	2.412 (1)	90.81 (4)
O(2)	Na	O(3) <i>b</i>	2.363 (1)	2.491 (1)	94.34 (4)
O(2)	Na	O(4) <i>a</i>	2.363 (1)	2.397 (1)	94.15 (4)
O(2)	Na	O(5) <i>b</i>	2.363 (1)	2.422 (1)	171.89 (4)
O(2)	Na	O(5) <i>a</i>	2.363 (1)	2.372 (1)	100.17 (4)
O(3) <i>a</i>	Na	O(5) <i>b</i>	2.412 (1)	2.422 (1)	82.95 (4)
O(3) <i>a</i>	Na	O(4) <i>a</i>	2.412 (1)	2.397 (1)	101.92 (4)
O(3) <i>a</i>	Na	O(5) <i>a</i>	2.412 (1)	2.372 (1)	168.88 (4)
O(3) <i>b</i>	Na	O(5) <i>b</i>	2.491 (1)	2.422 (1)	80.96 (4)
O(3) <i>b</i>	Na	O(5) <i>a</i>	2.491 (1)	2.372 (1)	83.78 (4)
O(3) <i>b</i>	Na	O(3) <i>a</i>	2.491 (1)	2.412 (1)	93.73 (4)
O(3) <i>b</i>	Na	O(4) <i>a</i>	2.491 (1)	2.397 (1)	162.06 (4)
O(4) <i>a</i>	Na	O(5) <i>a</i>	2.397 (1)	2.372 (1)	79.19 (4)
O(4) <i>a</i>	Na	O(5) <i>b</i>	2.397 (1)	2.422 (1)	92.21 (4)
O(5) <i>a</i>	Na	O(5) <i>b</i>	2.372 (1)	2.422 (1)	85.95 (4)
O(1)	Cl	O(2)	1.564 (1)	1.557 (1)	108.23 (6)
Cl	O(1)	O(2)	1.564 (1)	2.528 (2)	35.79 (6)

Table 3. Hydrogen-bonded distances (Å) and angles (°)

<i>i</i>	<i>j</i>	<i>k</i>	<i>d</i> <sub><i>ij</i></sub>	<i>d</i> <sub><i>jk</i></sub>	∠ <sub><i>ijk</i></sub>
H1(O3)	O(3) <i>c</i>	O(1)	0.846 (23)	2.872 (2)	6.2 (1.5)
H2(O3)	O(3) <i>b</i>	O(4)	0.835 (22)	2.833 (2)	8.1 (1.5)
H1(O4)	O(4) <i>b</i>	O(1)	0.884 (21)	2.813 (2)	7.8 (1.4)
H2(O4)	O(4) <i>c</i>	O(1)	0.701 (23)	2.845 (2)	5.4 (1.9)
H1(O5)	O(5) <i>c</i>	O(2)	0.761 (21)	2.726 (2)	4.6 (1.6)
H2(O5)	O(5) <i>d</i>	O(2)	0.813 (22)	3.014 (2)	12.0 (1.5)

A <sup>35</sup>Cl n.q.r. experiment, using the zero-splitting technique on a large single crystal, has given the asymmetry parameter  $\eta = 0.54$  and the principal axes directions of the e.f.g. tensor at the chlorine site:  $V_{zz}$  is nearly perpendicular to the plane of the ClO<sub>2</sub><sup>-</sup> ion,  $V_{yy}$  bisects the OClO angle in the plane (for  $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$ ) (Tarimci & Schempp, 1975). This orientation of the e.f.g. tensor differs markedly from that found by Curl (1962) in a microwave study of chlorine dioxide,  $V_{xx}$  and  $V_{yy}$  being interchanged in going from the ion to the neutral (paramagnetic) molecule. We have been unable to find a model for the bonds in ClO<sub>2</sub><sup>-</sup> which satisfactorily accounts for the measured field gradients.

The ClO<sub>2</sub><sup>-</sup> ion has a nearly identical configuration

in anhydrous NaClO<sub>2</sub> and the n.q.r. frequencies differ very little in the two compounds. Therefore, the hydrogen bonding and other specifics of the environment of the ClO<sub>2</sub><sup>-</sup> ion have little or no effect on the electron distribution near the chlorine.

*Note added in proof:* – An independent determination of this structure has recently been reported by Tazzoli, Riganti, Giuseppetti & Coda (1975). Their cell parameters **A** can be transformed to our Niggli reduced cell **B** by applying  $\mathbf{TA} = \mathbf{B}$ , where  $\mathbf{T} = 0.0 \ -1/10 \ -1/0 \ 1 \ 0$ ; their atomic positions **X** transform according to  $\mathbf{XT}^{-1} = \mathbf{Y}$  where  $\mathbf{T}^{-1} = 1 \ -1 \ 0/0 \ 0 \ 1/-1 \ 0 \ 0$ . There are no significant differences in the two determinations except that their cell volume is about 0.66 per cent greater than ours, most of which is accounted for in a longer *b* axis (6.441 Å after transformation *vs.* our 6.412 Å). They thus report slightly longer bond distances (+0.003 Å maximum). (Fig 2 in their paper has accidentally reproduced Fig. 1, and therefore does not show a projection down the *b* axis.)

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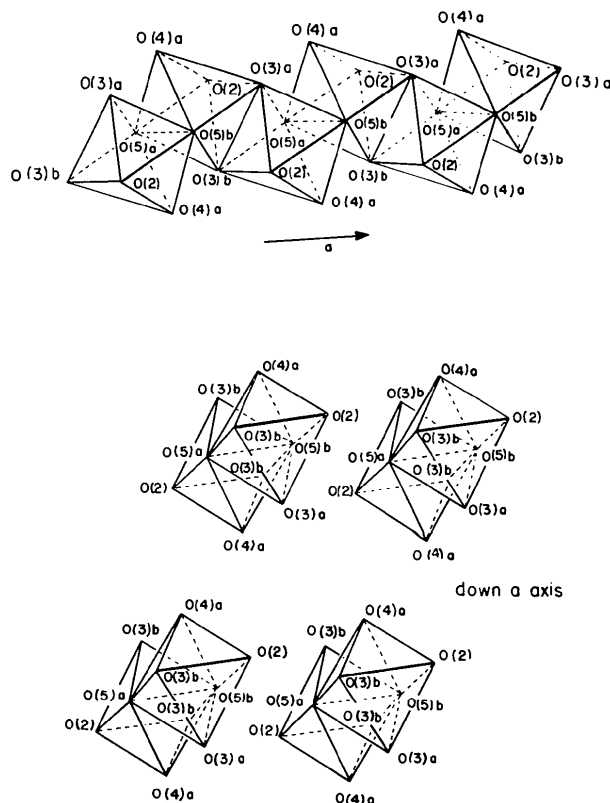


Fig. 2. The octahedra form columns by sharing edges along the *a* axis.

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### Ammonium Tristetrahydroaurate(III) $\mu$ -Chloro-bisdichloroargentate(I)

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(Received 9 December 1974; accepted 17 March 1975)

**Abstract.**  $(\text{NH}_4)_6(\text{AuCl}_4)_3\text{Ag}_2\text{Cl}_5$ , orthorhombic, *Immm*,  $a = 20.86$  (4),  $b = 11.20$  (2),  $c = 6.61$  (3) Å,  $Z = 2$ ,  $D_m = D_c = 3.18$  g cm<sup>-3</sup>. Two of the three  $\text{AuCl}_4^-$  ions stack alternately with the chlorine bridged  $\text{Ag}_2\text{Cl}_3^{2-}$  ion to form a double-stranded analogue of the chain structure previously reported for  $\text{Cs}_2(\text{AuCl}_4)(\text{AgCl}_2)$ .

**Introduction.** Deep-red crystals were prepared as described by Pollard (1920). Intensities were measured visually from Weissenberg photographs taken with Cu  $K\alpha$  radiation for the layers  $hk0$ – $hk5$  and  $h0l$ – $h5l$ , and were corrected for absorption. A set of 677 unique data were obtained, of which 52 were subsequently abandoned as being affected by extinction or as too weak to be reliable. Systematic absences were:  $hkl$ , when  $h+k+l \neq 2n$ . Of the possible space groups the centrosymmetric *Immm* was assumed, and no feature of the structure analysis disagreed with this choice. The structure was solved by Patterson and heavy-atom techniques, and refined by block-diagonal least-squares

calculations to an  $R$  of 0.11 (for 625 data).\* Atom coordinates and temperature factors are listed in Table 1, and interatomic distances and angles shown in Fig. 2.

**Discussion.** Although from its manner of preparation and from its dark colour  $(\text{NH}_4)_6\text{Au}_3\text{Ag}_2\text{Cl}_{17}$  has long been supposed to be analogous to  $\text{Cs}_2(\text{AuCl}_4)(\text{AgCl}_2)$  (Elliott & Pauling, 1938), with a similar chain of alternate  $\text{AuCl}_4^-$  and  $\text{AgCl}_2^-$  ions which would permit intervalence exchange (Hush, 1967), the differing stoichiometry has made the detail of the structure far from obvious. The observed structure is shown in Fig. 1, with particular features amplified in Fig. 2. The main difference lies in the fact that it contains not the  $\text{AgCl}_2^-$  ion but the chlorine bridged ion  $\text{Ag}_2\text{Cl}_3^{2-}$ . These planar

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31000 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atom coordinates and temperature factors*

Anisotropic temperature factors are dimensionless, isotropic factors are in Å<sup>2</sup>

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{150}$
Au(1)	0	0	0	0.036 (5)	0.13 (2)	1.2 (1)			
Au(2)	0.3384 (1)	0	0	0.032 (3)	0.06 (1)	0.43 (5)			
Ag	0.3713 (3)	$\frac{1}{2}$	0	0.18 (1)	0.07 (3)	3.0 (2)			
Cl(1)	0	0.2036 (14)	0	0.16 (3)	0.11 (9)	0.8 (3)			
Cl(2)	0.1098 (8)	0	0	0.08 (3)	0.29 (11)	2.4 (6)			
Cl(3)	0.3433 (4)	0.2869 (10)	0	0.05 (2)	0.32 (7)	0.6 (2)	–0.01 (1)		
Cl(4)	0.2613 (6)	0	0.236 (2)	0.11 (2)	0.45 (9)	1.4 (3)		0.2 (1)	
Cl(5)	0.4135 (6)	0	0.248 (2)	0.11 (2)	0.34 (8)	1.7 (4)		–0.06 (9)	
Cl(6)	$\frac{1}{2}$	$\frac{1}{2}$	0	0.09 (4)	0.12 (15)	3.8 (11)			
N(1)	0.183 (3)	0.268 (6)	0						3.3 (1.1)
N(2)	$\frac{1}{2}$	0.209 (6)	0						1.4 (9)