

seen in Fig. 1, the second apical site in both bipyramids is occupied by the same F atom F(1). It lies 1.819 (2) Å from the equatorial plane of the V(1) complex and 1.812 (2) Å from the equatorial plane of the V(2) complex. The mean bond distance from V atoms to the tetradentate O(2)—O(3) peroxy group [2.011 (2) Å] is significantly longer than the mean bond distance between V atoms and the other equatorial peroxy groups [1.868 (3) Å]. This is easily explained by the weakening of these four V—O bonds as a consequence of the O(2) and O(3) peroxy O atoms being involved in V—O interactions with opposite V atoms within the complex. The additional lengthening of bond distances V(1)—O(2) and V(2)—O(2) [mean 2.047 (3) Å] in comparison with V(1)—O(3) and V(2)—O(3) [mean 1.975 (3) Å] may probably be explained as a *trans* effect. The O(7) and O(5) atoms are *trans* to the O(2) atom in corresponding polyhedra [O(5)—V(1)—O(2) and O(7)—V(2)—O(2) are both 160.7 (2)°], while there are no atoms *trans* to the O(3) atom. The V(1)—F(1) = 2.119 (3) Å and V(2)—F(1) = 2.124 (3) Å bonds are *trans* to V(1)=O(1) and V(2)=O(6), respectively. They are longer than V(1)—F(2) = 1.896 (4) Å and V(2)—F(3) 1.879 (4) Å because F(1) is the bridging apical atom. This lengthening agrees quite well with the general observation that for pentagonal-bipyramidal oxoperoxometallates, the  $M-L_{\text{apical}}$  bonds (*trans* to the  $M=O$  bond) are longer than the  $M-L_{\text{equatorial}}$  bonds (Szentivanyi, 1983). The V=O and O—O bond distances lie in the expected range.

The potassium ions have irregular O and F atom environments. The individual K—O and K—F distances less than 3.2 Å are listed in Table 2. The remaining intermolecular non-bonded contacts in the structure are all longer than the sum of the van der Waals radii for the two atoms involved (Pauling, 1960).

The water molecules are weakly hydrogen bonded to the peroxy atoms O(4) and O(7), the hydrogen

fluoride and to each other [mean 2.97 (1) Å]. The hydrogen fluoride is also weakly hydrogen bonded to the peroxy O atom O(8) with  $F\cdots O = 2.87 (1) \text{ \AA}$ . A higher temperature factor for the hydrogen fluoride and water molecules than for the remaining O and F atoms may be explained by weak bonding and/or partial occupancy for these molecules. The least-squares refinement of occupancy factors for hydrogen fluoride and water molecules shows that the F(4) site is partially occupied [0.78 (2)] while the occupancy of the O(10) and O(9) sites differs from unity within  $1\sigma$ .

The isothermal decomposition of the title compound was shown previously (Schwendt & Joniakova, 1983a) to be accompanied by a simultaneous release of water and hydrogen fluoride. This fact may be interpreted as originating from the above-mentioned peculiarities of the structure which contains both H<sub>2</sub>O and HF molecules.

#### References

- ANDRIANOV, V. I., SAFINA, Z. SH. & TARNOPOLSKY, B. L. (1974). *J. Struct. Chem. (USSR)*, **15**, 911–917.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak National Laboratory, Tennessee, USA.
- CRUICKSHANK, D. W. J. (1965). In *Computing Methods in Crystallography*, edited by J. S. ROLLET, pp. 112–116. London, New York: Pergamon Press.
- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1041–1044.
- OATLEY, S. & FRENCH, S. (1982). *Acta Cryst.* **A38**, 537–549.
- PAULING, L. (1960). *The Nature of the Chemical Bond*. Ithaca, New York: Cornell Univ. Press.
- SCHWENDT, P. & JONIAKOVA, D. (1983a). Proc. 9th Conf. Coordination Chemistry. SCHS, Bratislava, Czechoslovakia, pp. 367–371.
- SCHWENDT, P. & JONIAKOVA, D. (1983b). *Thermochim. Acta*, **68**, 297–303.
- SZENTIVANYI, H. (1983). *Structural Studies on Some Heteroligand Oxoperoxovanadium(V) Compounds*. Dissertation, Chalmers Univ. of Technology and Univ. of Göteborg, Göteborg, Sweden.

*Acta Cryst.* (1990). **C46**, 1755–1759

## Structures of Lead Chlorite, Magnesium Chlorite Hexahydrate and Silver Chlorite

BY MASAMI OKUDA, MAKOTO ISHIHARA, MICHINARI YAMANAKA, SHIGERU OHBA AND YOSHIHIKO SAITO

*Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3, Kohoku-ku, Yokohama 223, Japan*

(Received 27 November 1989; accepted 9 January 1990)

**Abstract.** Pb(ClO<sub>2</sub>)<sub>2</sub> (I),  $M_r = 340.9$ , orthorhombic, *Ccca*,  $a = 6.004 (1)$ ,  $b = 12.504 (2)$ ,  $c = 6.010 (1) \text{ \AA}$ ,  $V = 451.2 (1) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 5.02 \text{ Mg m}^{-3}$ ,  $\text{Mo } K\alpha_1$ ,  $\lambda$

$= 0.70930 \text{ \AA}$ ,  $\mu = 38.76 \text{ mm}^{-1}$ ,  $F(000) = 592$ ,  $T = 300 (1) \text{ K}$ , final  $R = 0.030$  for 502 observed unique reflections. Mg(ClO<sub>2</sub>)<sub>2</sub>·6H<sub>2</sub>O (II),  $M_r = 267.3$ ,

0108-2701/90/101755-05\$03.00

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tetragonal,  $P4_2mc$ ,  $a = 7.471(8)$ ,  $c = 9.980(2)$  Å,  $V = 557.0(1)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.57$  Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71073$  Å,  $\mu = 0.674$  mm<sup>-1</sup>,  $F(000) = 276$ ,  $T = 298(1)$  K, final  $R = 0.041$  for 313 reflections. A redetermination of AgClO<sub>2</sub> (III),  $M_r = 175.3$ , orthorhombic,  $Pcca$ ,  $6.0754(4)$ ,  $b = 6.6796(5)$ ,  $c = 6.1226(4)$  Å,  $V = 248.46(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 4.69$  Mg m<sup>-3</sup>, Mo  $K\alpha_1$ ,  $\lambda = 0.70930$  Å,  $\mu = 8.81$  mm<sup>-1</sup>,  $F(000) = 316$ ,  $T = 298(1)$  K, final  $R = 0.029$  for 302 reflections. In (I), the Pb<sup>2+</sup> ion is surrounded by eight O atoms which form an Archimedean square antiprism; the Pb...O distances range from 2.628(8) to 2.640(9) Å. The structure of (II) consists of [Mg(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> and ClO<sub>2</sub><sup>-</sup> ions without close contacts between Mg<sup>2+</sup> and ClO<sub>2</sub><sup>-</sup> ions. The Ag<sup>+</sup> ion in (III) is surrounded by six O atoms which form a distorted triangular prism; the Ag...O distances range from 2.431(1) to 2.603(1) Å. The metal cations are preferably located above and below the ClO<sub>2</sub><sup>-</sup> plane and near the O atoms. This trend is explained by an *ab initio* molecular-orbital calculation. The effective charge of a chlorite O atom is  $-0.53$  e with a lone-pair orbital perpendicular to the molecular plane.

**Introduction.** The yellow color of crystals (I) and (III) is expected to be due to a spin-orbital enhancement of the spin-forbidden transition of the ClO<sub>2</sub><sup>-</sup> perturbed by post-transition-metal cations, as in case of nitrites (McGlynn, Azumi & Kumar, 1981). The arrangement of the metal cations relative to the nitrite ion has been studied in several crystals involving Pb<sup>2+</sup>, Hg<sub>2</sub><sup>2+</sup>, Ag<sup>+</sup> and Cd<sup>2+</sup> ions. It was shown that the post-transition-metal atoms preferentially lie on the chelated position between two nitrite O atoms (Aoyama, Ohba & Saito, 1988; Ohba, Matsumoto, Takazawa & Saito, 1987; and references therein). On the other hand, for chlorites the relation between coloration and structure has not yet been studied, although the structures of NH<sub>4</sub>ClO<sub>2</sub> (Gillespie, Sparks & Trueblood, 1959), NaClO<sub>2</sub> (Tarimci, Rosenstein & Schempp, 1976), NaClO<sub>2</sub>·3H<sub>2</sub>O (Tarimci & Schempp, 1975; Tazzoli, Riganti, Giuseppetti & Coda, 1975), Zn(ClO<sub>2</sub>)<sub>2</sub>·2H<sub>2</sub>O (Pakkanen, 1979) and AgClO<sub>2</sub> (Cooper & Marsh, 1961) were reported. In the present study the preferred directions of metal cations relative to the ClO<sub>2</sub><sup>-</sup> ion have been investigated and compared with those of the NO<sub>2</sub><sup>-</sup> ion. For AgClO<sub>2</sub>, an incorrect structure was once reported by Curti, Riganti & Locchi (1957) and was corrected by Cooper & Marsh (1961). To obtain precise structural data, a redetermination of the silver salt has also been performed.

**Experimental.** (I): Yellow crystals with forms of {001} and {111} were grown by the diffusion method with Pb(NO<sub>3</sub>)<sub>2</sub> and NaClO<sub>2</sub> aqueous solutions. To

determine a structure containing heavy atoms like Pb, a large absorption error should be avoided. Because an attempt to grind the crystal into a sphere failed, owing to cleavage, a square-pyramidal crystal of 0.10 × 0.10 × 0.10 mm in dimensions was selected taking advantage of the equi-dimensional small crystal to avoid heavy absorption. Rigaku AFC-5 four-circle diffractometer with graphite-monochromatized Mo  $K\alpha$  radiation. Laue group  $mmm$ , cell parameters refined by least squares for 20  $2\theta$  values ( $60 < 2\theta < 70^\circ$ ), intensity measurements performed to  $2\theta = 70^\circ$  ( $h - 9$  to  $9$ ,  $k - 9$  to  $9$ ,  $l 0$  to  $20$ ),  $\theta - 2\theta$  scan with scan speed  $6^\circ \text{ min}^{-1}(\theta)$ . Average ratio of structure factors of five standard reflections  $0.99 < \sum(|F_o|/|F_o|_{\text{initial}})/5 < 1.01$ . 4155 reflections measured, 1043 observed with  $|F_o| > 3\sigma(|F_o|)$ . After absorption correction ( $0.09 < A < 0.16$ ) and averaging equivalent reflections ( $R_{\text{int}} = 0.022$ ), 502 unique reflections were obtained. Systematic absences,  $hkl$  with  $h + k$  odd;  $hk0$  with  $h$  or  $k$  odd;  $h0l$  with  $h$  or  $l$  odd;  $0kl$  with  $k$  or  $l$  odd, showed that the space group is  $Ccca$  (No. 68). Since  $Z = 4$ , the Pb atoms were uniquely fixed to the fourfold special positions. Other atoms were located by Fourier synthesis. The Cl atoms lie on a twofold axis parallel to

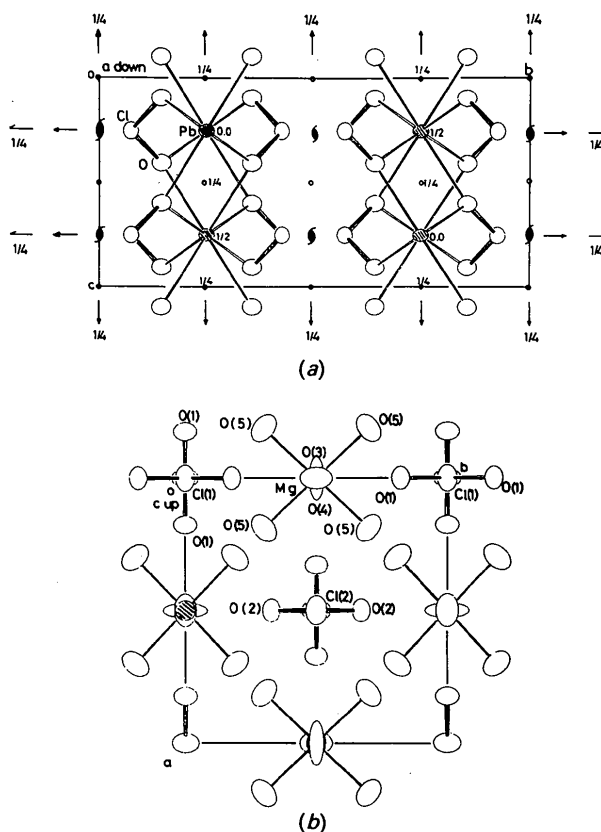


Fig. 1. Projection of the crystal structure of (a) (I) along  $a$  and (b) (II) along  $c$ .

Table 1. Positional parameters ( $\times 10^4$ ; for Ag  $\times 10^5$ )

Compound (I)	x	y	z	B/B <sub>eq</sub> (Å <sup>2</sup> × 10)
Pb	0	2500	2500	13
Cl	0	-736 (2)	2500	17
O	-1551 (14)	-1437 (7)	4036 (14)	19
Compound (II)				
Cl(1)	0	0	44 (2)	40
Cl(2)	5000	5000	-33 (2)	33
Mg	0	5000	2538 (8)	28
O(1)	1715 (5)	0	911 (4)	29
O(2)	3260 (7)	5000	-996 (4)	36
O(3)	0	5000	413 (9)	45
O(4)	0	5000	4503 (8)	51
O(5)	1930 (9)	2978 (9)	2454 (12)	52
Compound (III)				
Ag	0	11313 (4)	25000	24 (1)
Cl	0	6324 (1)	2500	22 (1)
O	3509 (2)	2274 (2)	1056 (3)	28 (1)

Table 2. Bond distances (Å) and bond angles (°)

Compound (I)			
Cl—O	1.577 (9)	O—Cl—O <sup>iii</sup>	112.5 (5)
Pb <sup>iv</sup> ...O	2.628 (8)	Pb <sup>iv</sup> ...O	2.640 (9)
Symmetry code: (i) $\frac{1}{2} - x, y, -\frac{1}{2} + z$ ; (ii) $\frac{1}{2} - x, -y, z$ ; (iii) $-x, y, \frac{1}{2} - z$ ; (iv) $-\frac{1}{2} + x, -y, \frac{1}{2} - z$ ; (v) $-x, -y, -z$ ; (vi) $-\frac{1}{2} + x, y, -z$ ; (vii) $x, -y, \frac{1}{2} + z$ .			
Compound (II)			
Cl(1)—O(1)	1.537 (4)	O(1)—Cl(1)—O(1) <sup>iv</sup>	111.5 (2)
Cl(2)—O(2)	1.607 (5)	O(2)—Cl(2)—O(2) <sup>iv</sup>	106.6 (3)
Mg—O(3)	2.121 (12)	O(3)—Mg—O(4)	180.0 (6)
Mg—O(4)	1.961 (11)	O(3)—Mg—O(5)	87.7 (4)
Mg—O(5)	2.071 (7)	O(4)—Mg—O(5)	92.3 (4)
O(1)...O(5)	2.694 (9)		
Symmetry code: (i) $y, x, z - \frac{1}{2}$ ; (ii) $1 - x, y, z$ ; (iii) $-y, x, z - \frac{1}{2}$ ; (iv) $y, -x, z - \frac{1}{2}$ ; (v) $x, -y, z$ ; (vi) $-x, y, z$ ; (vii) $-y, -x, z - \frac{1}{2}$ .			
Compound (III)			
Cl—O <sup>i</sup>	1.575 (2)	O—Cl—O <sup>ii</sup>	107.0 (1)
Ag...O <sup>iii</sup>	2.431 (1)	Ag...O <sup>iv</sup>	2.479 (2)
Ag...O <sup>v</sup>	2.431 (1)	Ag...O <sup>vi</sup>	2.603 (1)
Ag...O <sup>vii</sup>	2.479 (2)	Ag...O <sup>viii</sup>	2.603 (1)
Symmetry code: (i) $\frac{1}{2} - x, 1 - y, z$ ; (ii) $1 - x, y, \frac{1}{2} - z$ ; (iii) $-x, y, \frac{1}{2} - z$ ; (iv) $-\frac{1}{2} + x, -y, \frac{1}{2} - z$ ; (v) $\frac{1}{2} - x, -y, z$ ; (vi) $-\frac{1}{2} + x, y, -z$ ; (vii) $\frac{1}{2} - x, y, \frac{1}{2} + z$ ; (viii) $x, 1 - y, \frac{1}{2} + z$ ; (ix) $\frac{1}{2} - x, -y, z$ ; (x) $\frac{1}{2} + x, y, -z$ ; (xi) $\frac{1}{2} + x, y, 1 - z$ .			

*b* as shown in Fig. 1(a). Coordinates and anisotropic thermal parameters were refined.  $\sum w(|F_o| - |F_c|)^2$  minimized with weight  $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$ , final  $R = 0.030$ ,  $wR = 0.037$ ,  $S = 1.8$  for 502 unique reflections.\* Reflection/parameter ratio 17.3,  $\Delta/\sigma < 0.1$ ,  $-4.3 < \Delta\rho < 1.8 \text{ e \AA}^{-3}$ . Complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974). UNICSIII program system (Sakurai & Kobayashi, 1979), FACOM M-380 computer of this university.

\* Lists of structure factors and anisotropic thermal parameters for (I), (II) and (III) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52951 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(II): Colorless bipyramidal crystals were grown from the filtrate of a mixture of MgCl<sub>2</sub> and AgClO<sub>2</sub> aqueous solutions. A crystal of 0.40 × 0.40 × 0.45 mm was selected. Laue group 4/*m**m**m*, cell parameters refined by least squares for 18 2θ values (20 < 2θ < 30°), intensity measurement performed to 2θ = 60° (*h* 0 to 10, *k* -10 to 10, *l* -14 to 14), θ-2θ scan. Variation of five standard reflections, 0.98 <  $\sum(|F_o|/|F_o|_{\text{initial}})/5 < 1.01$ , 3248 reflections measured, 1747 observed. After absorption correction (0.82 <  $A < 0.84$ ) and averaging equivalent reflections ( $R_{\text{int}} = 0.017$ ), 313 unique reflections were obtained.  $D_m$  and  $V$  suggested the chemical formula Mg(ClO<sub>2</sub>)<sub>2</sub>·6H<sub>2</sub>O with  $Z = 2$ . From the systematic absences *hk*0 with *h* + *k* odd; *hkl* with *l* odd; and 00*l* with *l* odd, the space group was assumed to be  $P4_2/nmc$  (No. 137) with the Cl atom at the special position  $(-\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ . However, the structure could not be solved. We thought that the space group  $P4_2/nmc$  was incorrect and some of the systematic absences were false. Among the five possible space groups,  $P4_2mc$  (No. 105) brought a successful solution with  $R = 0.041$  and  $wR = 0.058$  (number of parameters 74) for 313 unique reflections. Based on the final atomic coordinates, the initial space group  $P4_2/nmc$  was tested again and rejected by a larger  $R$  value,  $R = 0.066$  and  $wR = 0.148$  (number of parameters 47). The pseudo systematic absences are *hk*0 with *h* + *k* odd, which corresponds to a pseudo *n* glide perpendicular to *c* [see Fig. 1(b)]. Water H atoms could be located on the difference synthesis. The enantiomeric structure gave almost

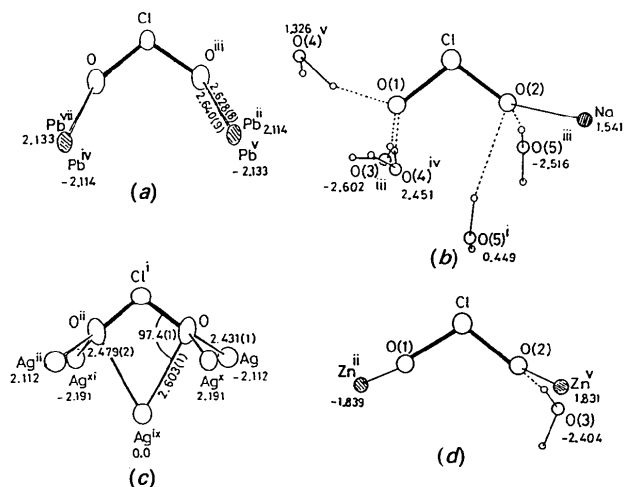


Fig. 2. Arrangement of metal cations and water molecules around the ClO<sub>2</sub><sup>-</sup> ions in (a) (I), (b) (III), (c) NaClO<sub>2</sub>·3H<sub>2</sub>O and (d) Zn(ClO<sub>2</sub>)<sub>2</sub>·2H<sub>2</sub>O. The shifts from the ClO<sub>2</sub><sup>-</sup> plane are indicated by numbers near the atom labels. Distances in Å, angles in °. Symmetry codes in (a) and (b) are given in Table 2. In (c): (i)  $-x, 1 - y, 1 - z$ ; (ii)  $-x, -y, -z$ ; (iii)  $x, 1 - y, z$ ; (iv)  $1 - x, y, z$ ; (v)  $-x, 1 - y, -z$ . In (d): (i)  $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ ; (ii)  $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$ ; (iii)  $-x, -y, -z$ ; (iv)  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ ; (v)  $x, y, 1 + z$ ; (vi)  $-x, -y, 1 - z$ ; (vii)  $1 - x, -y, 1 - z$ .

the same  $R$  values because of the pseudo centrosymmetric structure. Reflection/parameter ratio 4.23,  $\Delta/\sigma < 0.3$ ,  $-0.34 < \Delta\rho < 0.35 \text{ e \AA}^{-3}$ .

(III): Pale-yellow plate-like crystals grown from hot aqueous solution, perfect cleavage parallel to (010). A crystal of  $0.2 \times 0.3 \times 0.4 \text{ mm}$  was selected. Laue group  $mmm$ , cell parameters refined by least squares for 19  $2\theta$  values ( $57 < 2\theta < 60^\circ$ ), intensity measurement performed up to  $2\theta = 60^\circ$  ( $h = -8$  to  $8$ ,  $k = -9$  to  $9$ ,  $l = 0$  to  $8$ ),  $\omega$  scan with scan width  $1.4^\circ$ . No appreciable variation of five standard reflections. 1354 reflections measured, 1011 observed. After absorption correction ( $0.09 < A < 0.21$ ) and averaging equivalent reflections ( $R_{\text{int}} = 0.014$ ), 302 unique were obtained. The space group,  $Pcca$  (No. 54) was confirmed by the systematic absences. Atomic coordinates reported by Cooper & Marsh (1961) were further refined by the full-matrix least-squares program *RADIEL* (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979) introducing an isotropic secondary-extinction parameter,  $g = 0.057$  (5)

$\times 10^{-4}$  (Zachariassen, 1967), final  $R = 0.029$ ,  $wR = 0.036$ ,  $S = 2.15$  for 302 unique reflections. Smallest extinction-correction factor ( $F_o^2/F_c^2$ ) was 0.63 for 002. Reflection/parameter ratio 14.4,  $\Delta/\sigma < 0.01$ ,  $-0.8 < \Delta\rho < 1.4 \text{ e \AA}^{-3}$ .

**Discussion.** Final atomic coordinates and interatomic distances and bond angles are presented in Tables 1 and 2. For (III) the present study confirmed the previous results (Cooper & Marsh, 1961); however, the e.s.d.'s in atomic parameters were reduced to a thirtieth by collecting symmetry-related reflections by diffractometry. Crystal structures of (I) and (II) are shown in Fig. 1. In (I) the  $\text{Pb}^{2+}$  and chlorite ions form two-dimensional networks perpendicular to the  $b$  axis. The  $\text{Mg}^{2+}$  ion in (II) is coordinated octahedrally to six water molecules. The chlorite ion lies at the center of a tetrahedron made up of four  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  complexes. Fig. 2 shows the arrangement of metal cations and water molecules around the chlorite ion in (I), (III),  $\text{NaClO}_2 \cdot 3\text{H}_2\text{O}$  (Tarimci

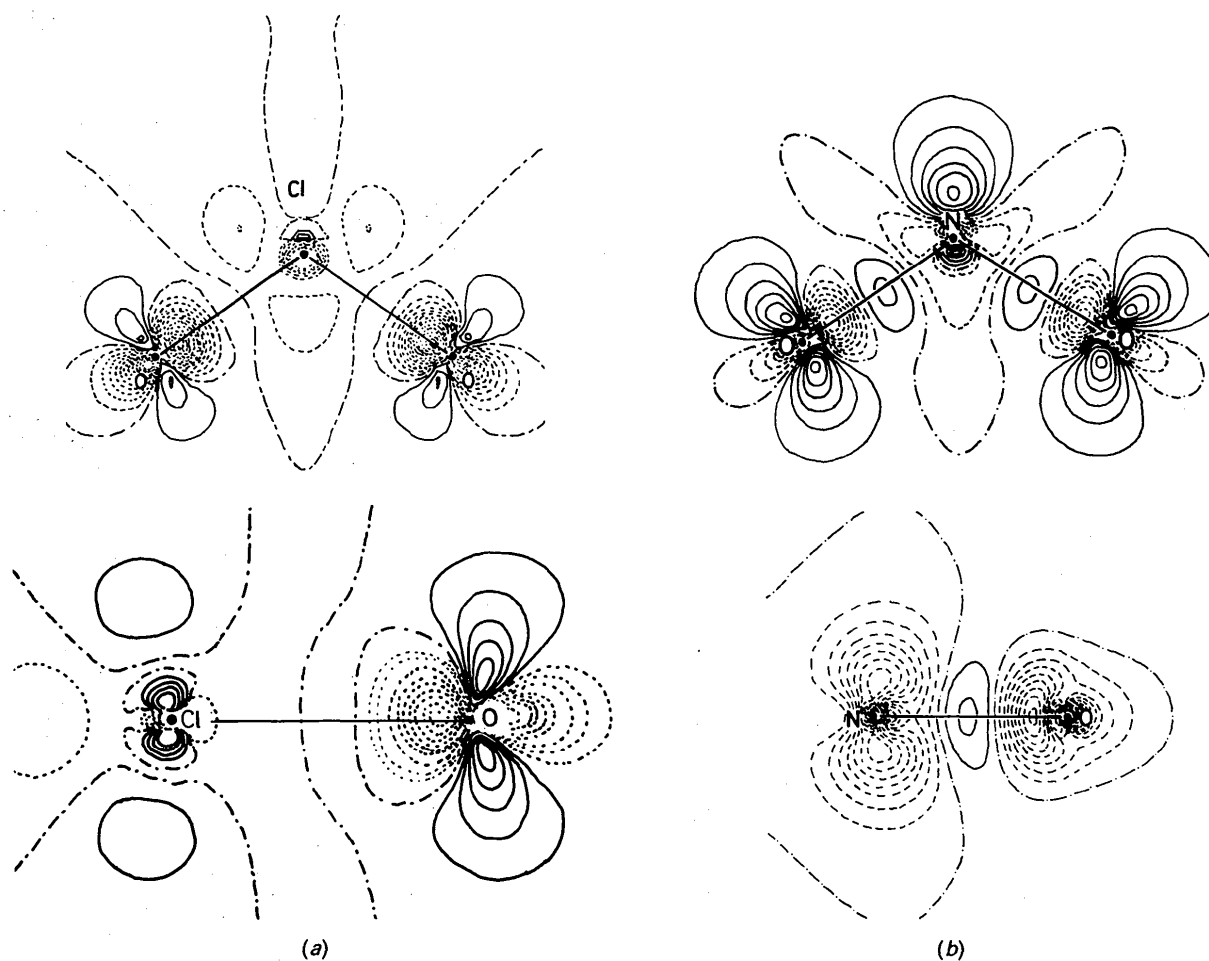


Fig. 3. MIDI4\* deformation densities of (a)  $\text{ClO}_2^-$  (present work) and (b)  $\text{NO}_2^-$  (Kikkawa, Ohba, Saito, Kamata & Iwata, 1987) ions on the molecular plane and on the plane perpendicular to it containing a bond axis. Contour intervals at  $0.20 \text{ e \AA}^{-1}$ .

Table 3. *Electron populations of the O atoms in (a) chlorite and (b) nitrite ions based on the STO-3G basis set*

The *y* axis is perpendicular to the molecular plane and *z* along the twofold axis.

	1s	2s	2p <sub>x</sub>	2p <sub>y</sub>	2p <sub>z</sub>	Total
(a)	1.99960	1.96633	1.01883	2.00000	1.54695	8.53171
(b)	1.99853	1.87826	1.34251	1.50068	1.73160	8.45158

& Schempp, 1975) and Zn(ClO<sub>2</sub>)<sub>2</sub>·2H<sub>2</sub>O (Pakkanen, 1979). The neighboring metal cations are shifted by 1.541 (1)–2.191 (2) Å from the ClO<sub>2</sub><sup>-</sup> plane and the projections of the metal atoms on the ClO<sub>2</sub><sup>-</sup> plane approximately lie on an extension of the Cl—O bond axis. Except for (III) there are no metal cations or water molecules on the ClO<sub>2</sub><sup>-</sup> plane in contrast to the nitrite salts in which there are metal cations nearly on the NO<sub>2</sub><sup>-</sup> plane. Experimental and theoretical deformation density in NO<sub>2</sub><sup>-</sup> suggested that the metal cations approach the *sp*<sup>2</sup> lone-pair lobes of the N and O atoms in the molecular plane (Ohba, Kikkawa & Saito, 1985; Kikkawa, Ohba, Saito, Kamata & Iwata, 1987). In order to investigate the difference in preferred location of the metal cations relative to the chlorite and nitrite ions, the theoretical deformation density of ClO<sub>2</sub><sup>-</sup> was calculated by an *ab initio* molecular-orbital method using the MIDI4\* basis set as reported previously (Kikkawa, Ohba, Saito, Kamata & Iwata, 1987). The theoretical deformation densities of NO<sub>2</sub><sup>-</sup> and ClO<sub>2</sub><sup>-</sup> are compared in Fig. 3, where the reference density is the superposition of the neutral independent atom densities. The positive deformation density of the terminal O atoms in the ClO<sub>2</sub><sup>-</sup> plane is much lower than that of NO<sub>2</sub><sup>-</sup>. On the other hand, electron density in the  $\pi$  region of the O atom is much higher for ClO<sub>2</sub><sup>-</sup>

than for NO<sub>2</sub><sup>-</sup>. The electron populations calculated by using the STO-3G basis set are compared in Table 3. The oxygen 2p<sub>y</sub> orbital perpendicular to the ClO<sub>2</sub><sup>-</sup> plane is fully occupied. This is the electron-rich orbital in the ClO<sub>2</sub><sup>-</sup> ion, to which metal cations or water H atoms preferably approach as seen in Fig. 2. In conclusion, the coloration of chlorite ion seems to be caused by the perturbation of the lone-pair  $\pi$  orbitals of the terminal O atoms by the post-transition-metal cations.

#### References

- AOYAMA, T., OHBA, S. & SAITO, Y. (1988). *Acta Cryst.* **C44**, 1703–1707.
- COOPER, J. & MARSH, R. E. (1961). *Acta Cryst.* **14**, 202–203.
- COPPENS, P., GURU ROW, T. N., LEUNG, P., STEVENS, E. D., BECKER, P. J. & YANG, Y. W. (1979). *Acta Cryst.* **A35**, 63–72.
- CURTI, R., RIGANTI, V. & LOCCHI, S. (1957). *Acta Cryst.* **10**, 687–691.
- GILLESPIE, R. B., SPARKS, R. A. & TRUEBLOOD, K. N. (1959). *Acta Cryst.* **12**, 867–872.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- KIKKAWA, T., OHBA, S., SAITO, Y., KAMATA, S. & IWATA, S. (1987). *Acta Cryst.* **B43**, 83–85.
- MCGLYNN, S. P., AZUMI, T. & KUMAR, D. (1981). *Chem. Rev.* **81**, 475–489.
- OHBA, S., KIKKAWA, T. & SAITO, Y. (1985). *Acta Cryst.* **C41**, 10–13.
- OHBA, S., MATSUMOTO, F., TAKAZAWA, H. & SAITO, Y. (1987). *Acta Cryst.* **C43**, 191–194.
- PAKKANEN, T. (1979). *Acta Cryst.* **B35**, 2670–2672.
- SAKURAI, T. & KOBAYASHI, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69–77.
- TARIMCI, C., ROSENSTEIN, R. D. & SCHEMP, E. (1976). *Acta Cryst.* **B32**, 610–612.
- TARIMCI, C. & SCHEMP, E. (1975). *Acta Cryst.* **B31**, 2146–2149.
- TAZZOLI, V., RIGANTI, V., GIUSEPPETTI, G. & CODA, A. (1975). *Acta Cryst.* **B31**, 1032–1037.
- ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

*Acta Cryst.* (1990). **C46**, 1759–1761

## Structure of Dichlorobis(tetracarbonylcobaltio)tin(IV)(2 Co–Sn)

BY KENNETH M. MACKAY,\* BRIAN K. NICHOLSON\* AND MIRANDA SERVICE

*School of Science and Technology, University of Waikato, Hamilton, New Zealand*

(Received 20 December 1989; accepted 19 January 1990)

**Abstract.** SnCl<sub>2</sub>[Co(CO)<sub>4</sub>]<sub>2</sub>, *M<sub>r</sub>* = 531.5, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 11.716 (4), *b* = 11.486 (4), *c* = 12.765 (8) Å,  $\beta$  = 108.42 (3)°, *U* = 1630 (1) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 2.17 g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha)$  = 0.7107 Å,  $\mu$  =

36.8 cm<sup>-1</sup>, *F*(000) = 1000, *T* = 293 K, *R* = 0.045 for 2558 [*I* > 2 $\sigma$ (*I*)] reflections. The Sn atom is bonded to two Cl atoms [Sn—Cl (av.) = 2.368 (2) Å, Cl—Sn—Cl = 101.3 (1)°] and to two Co(CO)<sub>4</sub> groups [Sn—Co (av.) = 2.534 (1) Å, Co—Sn—Co = 129.3 (1)°].

\* To whom correspondence should be addressed.