

Two alkali metal chlorites, LiClO_2 and KClO_2

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The structures of tetragonal ($P4_2/ncm$) lithium chlorite, LiClO_2 , and orthorhombic ($Cmcm$) potassium chlorite, KClO_2 , have been determined by single-crystal X-ray analyses. In LiClO_2 , the Li atom is at a site of $\bar{4}$ symmetry, while in KClO_2 , the K atom is at a site with $2/m$ symmetry. In both compounds, the unique Cl and O atoms are at sites with mm and m symmetry, respectively. The structure of LiClO_2 consists of layers of Li^+ cations coordinated by ClO_2^- anions. In contrast, the structure of KClO_2 contains pseudo-layers of K^+ and ClO_2^- ions containing four short K—O distances. The Li^+ and K^+ cations are surrounded by four and eight chlorite O atoms in tetrahedral and distorted cubic coordination environments, respectively.

Comment

Previous crystal structure investigations of chlorites include NH_4ClO_2 (Levi & Scherillo, 1931; Gillespie *et al.*, 1959), $\text{NaClO}_2 \cdot 3\text{H}_2\text{O}$ (Tarimci & Schempp, 1975), NaClO_2 (Tarimci

et al., 1976), $\text{Zn}(\text{ClO}_2)_2 \cdot 2\text{H}_2\text{O}$ (Pakkanen, 1979), $\text{Mg}(\text{ClO}_2)_2 \cdot 6\text{H}_2\text{O}$ (Ferrari & Colla, 1937; Okuda *et al.*, 1990; Marsh, 1991), AgClO_2 (Curti *et al.*, 1957; Cooper & Marsh, 1961; Okuda *et al.*, 1990), $\text{Pb}(\text{ClO}_2)_2$ (Okuda *et al.*, 1990) and $\text{La}(\text{ClO}_2)_3 \cdot 3\text{H}_2\text{O}$ (Coda *et al.*, 1965; Castellani Bisi, 1984). It is apparent that alkali metal chlorites have not been investigated systematically. The limited number of studies is probably due to the difficulty of preparation and investigation of these compounds resulting from their low stability. The majority of chlorites quickly decompose to the corresponding chlorates and chlorides under the effect of temperature, sunlight or X-radiation. Besides this, the crystallization of chlorites is often difficult and additional research is required to determine appropriate conditions for single-crystal growth. This paper reports the results of our study of two alkali chlorites, namely LiClO_2 , (I), and KClO_2 , (II).

The structure of lithium chlorite contains separate layers, within which the Li^+ cation is surrounded by four chlorite O atoms forming a tetrahedron which is squashed along a twofold axis (Fig. 1). These layers are parallel to the ab plane and are linked by van der Waals interactions, with the shortest interlayer $\text{Cl} \cdots \text{Cl}$ distance being 3.6339 (9) Å (Fig. 2). The layers are stacked in such way that adjacent layers are rotated by 90° . The ClO_2^- anions serve as tetradentate bridging ligands between the Li^+ cations.

The structure of potassium chlorite contains pseudo-layers parallel to the ac plane consisting of K^+ and ClO_2^- ions with short K—O distances (Fig. 3). The K^+ cations and Cl atoms are nearly coplanar (Fig. 4). The full coordination environment of the K^+ cation involves eight O atoms forming a distorted cube. Four of these O atoms belong to one layer and the other four to the layers above and below.

The structures of LiClO_2 and KClO_2 show some similarities to those of the corresponding hypophosphites. In the case of LiClO_2 , the role of the ClO_2^- anion as a tetradentate ligand is identical to that of H_2PO_2^- in LiH_2PO_2 (Naumov *et al.*, 2004). However, the structures of the layers are different in these

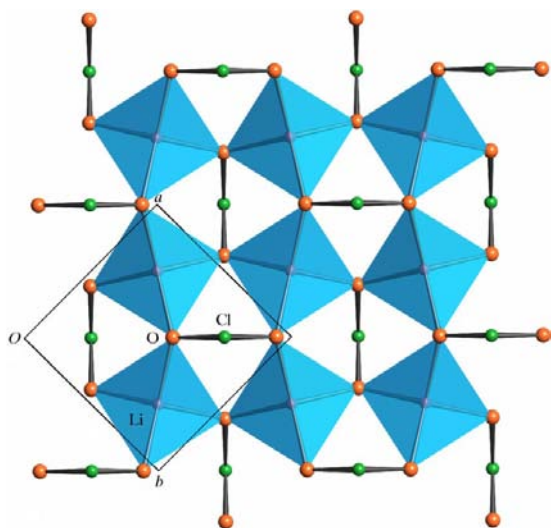


Figure 1
Projection of an (001) layer in LiClO_2 .

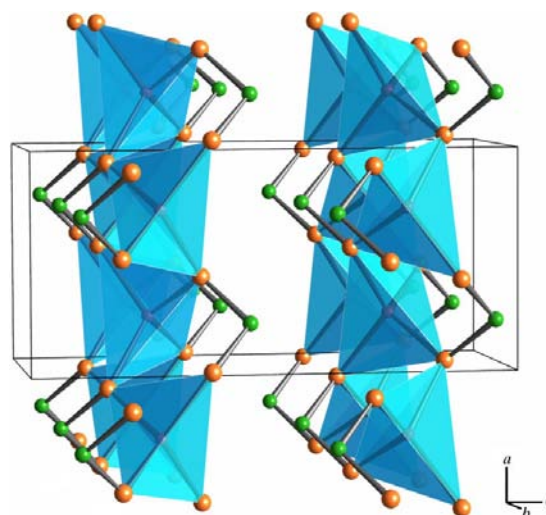


Figure 2
Packing diagram of the LiClO_2 structure.

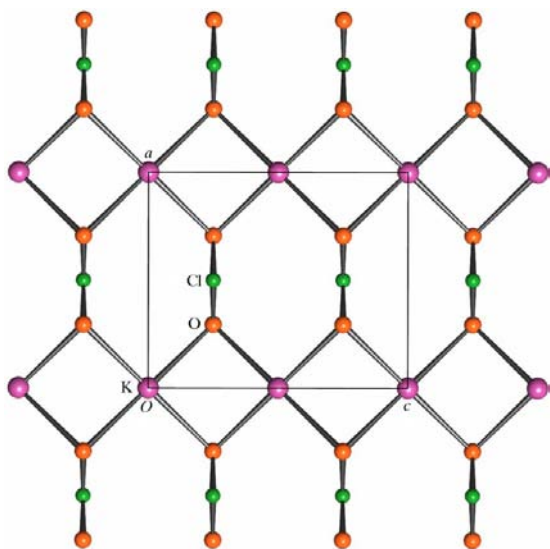


Figure 3
Projection of an (010) layer in KClO_2 .

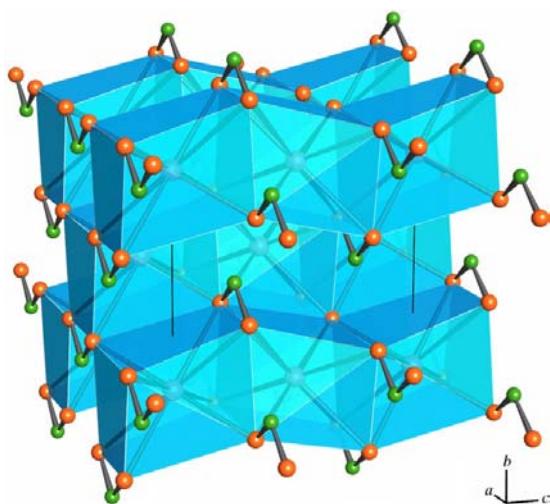


Figure 4
Packing diagram of the KClO_2 structure.

compounds; by sharing edges, the Li^+ -centred tetrahedra form chains linked in different ways within a layer. In KClO_2 , the layers and the immediate environment of the K^+ cations are very similar to those in the K, Rb and Cs hypophosphites (Naumova *et al.*, 2004). The differences arise from the way the layers are joined together and from the K^+ environment, which includes two H atoms in the hypophosphites instead of two O atoms in KClO_2 .

Experimental

Lithium and potassium chlorites were synthesized by mixing aqueous solutions of barium chlorite, $\text{Ba}(\text{ClO}_2)_2$, and the corresponding alkali metal sulfates in equimolar ratios. The reaction mixtures were filtered and crystals were grown by slow evaporation. In the case of potassium chlorite, the compound decomposes at room temperature in a few hours and its crystal growth was carried out at 273–278 K over approximately 24 h. These conditions yielded crystals in the form of

thin plates or needles with a maximum size of 0.5 mm suitable for X-ray diffraction. The decomposition of lithium chlorite seems to occur more slowly, which allowed crystals to be grown at room temperature. The maximum crystal size was 0.3 mm with a plate morphology. The X-ray powder patterns show good agreement between the bulk products and the single crystals. However, in the case of potassium chlorite, additional peaks in the powder pattern indicate the presence of KCl and KClO_3 phases. The precursor used for the preparation of the lithium and potassium chlorites, *viz.* $\text{Ba}(\text{ClO}_2)_2$, was obtained by reaction of an aqueous suspension of BaO_2 with chlorine dioxide and precipitation from solution by adding a 3:1 mixture of ethanol and diethyl ether. It was found that $\text{Ba}(\text{ClO}_2)_2$ is one of the most stable salts of chlorous acid and is a convenient starting material for preparing other chlorites.

Compound (I)

Crystal data

LiClO_2
 $M_r = 74.39$
Tetragonal, $P4_2/ncm$
 $a = 4.7223$ (11) Å
 $c = 10.298$ (3) Å
 $V = 229.65$ (10) Å³
 $Z = 4$
 $D_x = 2.152$ Mg m⁻³

Mo $K\alpha$ radiation
Cell parameters from 20 reflections
 $\theta = 12.6$ – 14.8°
 $\mu = 1.30$ mm⁻¹
 $T = 293$ (2) K
Plate, colourless
 $0.24 \times 0.12 \times 0.04$ mm

Data collection

Enraf-Nonius CAD-4 diffractometer
2 θ/θ scans
Absorption correction: empirical using intensity measurements (CADDAT; Enraf-Nonius, 1989)
 $T_{\min} = 0.746$, $T_{\max} = 0.950$
134 measured reflections
133 independent reflections

87 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.017$
 $\theta_{\text{max}} = 25.9^\circ$
 $h = 0 \rightarrow 5$
 $k = 0 \rightarrow 5$
 $l = 0 \rightarrow 12$
3 standard reflections every 60 min
intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.097$
 $S = 0.91$
133 reflections
13 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0497P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.35$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.33$ e Å⁻³

Table 1

Selected geometric parameters (Å, °) for (I).

Li–O	1.959 (2)	Cl–O	1.578 (4)
O–Li–O ⁱ	121.82 (19)	O–Cl–O ⁱⁱ	110.0 (3)
O–Li–O	103.67 (8)		

Symmetry codes: (i) $-x + \frac{1}{2}, -y + \frac{3}{2}, z$; (ii) $-x + \frac{3}{2}, -y + \frac{3}{2}, z$.

Compound (II)

Crystal data

KClO_2
 $M_r = 106.55$
Orthorhombic, $Cmcm$
 $a = 6.1446$ (9) Å
 $b = 6.3798$ (12) Å
 $c = 7.3755$ (19) Å
 $V = 289.13$ (10) Å³
 $Z = 4$
 $D_x = 2.448$ Mg m⁻³

Mo $K\alpha$ radiation
Cell parameters from 22 reflections
 $\theta = 11.1$ – 11.9°
 $\mu = 2.48$ mm⁻¹
 $T = 293$ (2) K
Plate, colourless
 $0.40 \times 0.24 \times 0.16$ mm

Table 2
Selected geometric parameters (\AA , $^\circ$) for (II).

K—O	2.8120 (18)	Cl—O	1.565 (2)
K—O ⁱ	3.0493 (19)		
O—K—O ⁱⁱ	180.00 (9)	O—K—O ⁱ	98.07 (2)
O—K—O ⁱⁱⁱ	100.14 (7)	O—K—O ⁱ	49.12 (8)
O—K—O	79.86 (7)	O—K—O ^v	81.93 (2)
O—K—O	66.85 (2)	O—Cl—O ^{vi}	108.18 (18)
O—K—O ^{iv}	113.15 (2)		

Symmetry codes: (i) $x - \frac{1}{2}, y + \frac{1}{2}, z$; (ii) $-x, -y, -z$; (iii) $x, -y, -z$; (iv) $x - \frac{1}{2}, -y - \frac{1}{2}, -z$; (v) $-x + \frac{1}{2}, -y - \frac{1}{2}, -z$; (vi) $-x + 1, y, z$.

Data collection

Enraf-Nonius CAD-4 diffractometer	168 reflections with $I > 2\sigma(I)$
$2\theta/\theta$ scans	$R_{\text{int}} = 0.059$
Absorption correction: empirical using intensity measurements (<i>CADDAT</i> ; Enraf-Nonius, 1989)	$\theta_{\text{max}} = 27.5^\circ$
$T_{\text{min}} = 0.494, T_{\text{max}} = 0.672$	$h = 0 \rightarrow 7$
243 measured reflections	$k = -1 \rightarrow 8$
193 independent reflections	$l = -1 \rightarrow 9$
	3 standard reflections
	every 60 min
	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.030$	$\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
$wR(F^2) = 0.074$	$\Delta\rho_{\text{min}} = -1.03 \text{ e \AA}^{-3}$
$S = 1.00$	Extinction correction: <i>SHELXL97</i>
193 reflections	(Sheldrick, 1997)
16 parameters	Extinction coefficient: 0.025 (7)
$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

For both compounds, data collection: *CD4CA0* (Enraf-Nonius, 1989); cell refinement: *CD4CA0*; data reduction: *CADDAT* (Enraf-Nonius, 1989); structure solution: *SHELXS97* (Sheldrick, 1997);

structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *BS* (Ozawa & Kang, 2004); publication software: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1064). Services for accessing these data are described at the back of the journal.

References

- Castellani Bisi, C. (1984). *Acta Cryst.* **C40**, 1120–1121.
 Coda, A., Giuseppetty, G. & Tadini, C. (1965). *Period. Mineral.* **34**, 27–47.
 Cooper, J. & Marsh, R. E. (1961). *Acta Cryst.* **14**, 202–203.
 Curti, R., Riganti, V. & Locchi, S. (1957). *Acta Cryst.* **10**, 687–691.
 Enraf-Nonius (1989). *CD4CA0* (Version 5.0) and *CADDAT* (Version 5.1) in *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
 Ferrari, A. & Colla, C. (1937). *Gazz. Chim. Ital.* **67**, 424.
 Gillespie, R. B., Sparks, R. A. & Trueblood, K. N. (1959). *Acta Cryst.* **12**, 867–872.
 Levi, G. R. & Scherillo, A. (1931). *Z. Kristallogr.* **76**, 431–452.
 Marsh, R. E. (1991). *Acta Cryst.* **C47**, 1775.
 Naumov, D. Yu., Naumova, M. I., Podbereskaya, N. V. & Kuratieva, N. V. (2004). *Acta Cryst.* **C60**, i73–i75.
 Naumova, M. I., Kuratieva, N. V., Podbereskaya, N. V. & Naumov, D. Yu. (2004). *Acta Cryst.* **C60**, i53–i55.
 Okuda, M., Ishihara, M., Yamanaka, M., Ohba, S. & Saito, Y. (1990). *Acta Cryst.* **C46**, 1755–1759.
 Ozawa, T. C. & Kang, S. J. (2004). *Balls & Sticks (BS)*. Version 1.51. (URL: <http://www.softbug.com/toycrate/bs/>)
 Pakkanen, T. (1979). *Acta Cryst.* **B35**, 2670–2672.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
 Tarimci, C., Rosenstein, R. D. & Schempp, E. (1976). *Acta Cryst.* **B32**, 610–612.
 Tarimci, C. & Schempp, E. (1975). *Acta Cryst.* **B31**, 2146–2149.