donné avec les trois atomes j formant les autres sommets du tétraèdre (Tableau 2). En accord avec Louisnathan & Gibbs (1972), qui ont calculé les conditions pour que l'énergie totale de Hückel soit minimum, on constate que la liaison la plus courte nécessite le plus grand espace angulaire: $\mathrm{Si^i{-}O^{iii}}$ = 1,63, $\mathrm{Si^i{-}N^i}$ = 1,78 Å, $\langle \mathrm{O^{iii}{-}Si^i{-}N} \rangle$ = 111,7, $\langle \mathrm{N^i{-}Si^i{-}N} \rangle$ = 107,6°.

L'angle moyen pour l'ensemble du tétraèdre est égal à 109,4°.

Le tétraèdre de coordination du lithium est très déformé. En effet, les distances O—O ou O—N sont comprises entre 3,11 et 3,67 Å. L'atome de lithium est lui-même très excentré dans ce tétraèdre puisqu'il est lié à deux oxygènes à la distance de 1,92 Å alors que la troisième distance Li—O est beaucoup plus grand: 2,07 Å et que la longueur Li—N est égale à 2,25 Å. On observe enfin une dispersion importante (96–123°) de la valeur des angles O—Li—O et O—Li—N.

Références

GRÜN, R. (1979). *Acta Cryst.* B35, 800–804.

LAURENT, Y., GREKOV, F. F., DAVID, J. & GUYADER, J. (1980). *Ann. Chim. (Paris)*, **5**, 647–655.

LOUISNATHAN, J. J. & GIBBS, G. V. (1972). *Mater. Res. Bull.* **7**, 1281–1292.

ROULT, G. & BUEVOZ, J. L. (1977). *Rev. Phys. Appl.* **12**, 581–590.

WORLTON, T. G., JORGENSEN, J. D., BEYERLEIN, R. A. & DECKER, D. L. (1976). *Nucl. Instrum. Methods*, **137**, 331–337.

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The Structure of Potassium Chlorate at 77 and 298 K

BY JACOB DANIELSEN, ALAN HAZELL AND FINN KREBS LARSEN

Department of Inorganic Chemistry, Aarhus University, DK-8000 *Aarhus C, Denmark*

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Abstract. $\mathrm{KClO_3}$, monoclinic, $P2_1/m$, $Z = 2$. 77 K: a = 4·630 (2), b = 5·568 (3), c = 7·047 (3) Å, β = 110·21 (3)°; 298 K: a = 4·6569, b = 5·59089, c = 7·0991 Å, β = 109·648° [Ievin'š & Ozol (1953). *Structure Reports*, Vol. 17, p. 526. Utrecht: Oosthoek]. Full-matrix least-squares refinement of 29 parameters gave $R = 0{\cdot}033$ for 517 reflexions [$I > 3\sigma(I)$] at 77 K and $R = 0{\cdot}023$ for 491 reflexions [$I > 3\sigma(I)$] at 298 K. The structure at 77 K is similar to that at 298 K which is consistent with that reported earlier. The results are compared with the results of ESR measurements on crystals which had been irradiated with X-rays. A mechanism is suggested for the monoclinic–orthorhombic phase transition at 523 K.

Introduction. The structure of $\mathrm{KClO_3}$ has been determined at room temperature by Zachariasen (1929), Aravindakshan (1958) and Bats (1978). ESR spectra of $\mathrm{KClO_3}$ crystals that have been exposed to X-rays at temperatures below 77 K show that $\mathrm{O^-}$ ions formed during irradiation become trapped between pairs of $\mathrm{ClO_3^-}$ ions. The trigonal axis of one member of each pair has the same orientation as found in the X-ray structure determinations whereas that of the other is apparently rotated through 99° around b (Byberg, 1981).

$\mathrm{KClO_3}$ undergoes a phase transition from monoclinic to orthorhombic when heated above 523 K and forms synthetic twins during the subsequent cooling to room temperature (Ramachandran & Lonappan, 1957). The phase transition involves drastic changes in the orientation of the $\mathrm{ClO_3^-}$ ions similar to those observed in the ESR experiments.

Hence, the ESR results might in fact indicate the presence of a disorder in the orientation of $\mathrm{ClO_3^-}$ prior to the X-irradiation in macroscopically untwinned crystals at low temperatures. To test this possibility we have determined the structure at 77 K and have also redetermined the structure at 298 K of the same crystal.

Crystals were obtained by slow evaporation of a saturated aqueous solution of $\mathrm{KClO_3}$ (Merck, p.a.).

A crystal, 0·27 × 0·22 × 0·07 mm, was mounted on a Picker FACS-1 diffractometer. Cell dimensions at 77 K were determined from observed setting angles: three independent sets of measurements were made with 12, 12, and 17 reflexions. For the room-temperature measurements the cell dimensions used were those of Ievin'š & Ozol (1953). Intensities were measured out to 2θ = 45° with Mo $K\alpha$ radiation (graphite monochromator at 298 K, Zr filter at 77 K). The step-scanning technique was used in the ω–2θ mode; the step length was 0·04° and the scan width (3·0 + 0·692 tan θ)°. The counting time per step was 2 s at 77 K and 1 s at 298 K. The crystal was cooled by liquid $\mathrm{N_2}$ with a local modification of the cryostat described by Coppens *et al.* (1974).

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Table 1. *Fractional coordinates* ($\times 10^4$) *and thermal parameters* ($\text{Å}^2 \times 10^{-4}$)

Temperature (K)		x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
77	K	3555 (2)	2500	7086 (1)	161 (4)	124 (4)	176 (4)	0	97 (3)	0
298	K	3537 (1)	2500	7091 (1)	294 (3)	257 (3)	292 (3)	0	144 (2)	0
77	Cl	1210 (2)	2500	1745 (1)	141 (4)	113 (4)	157 (4)	0	64 (3)	0
298	Cl	1216 (1)	2500	1756 (1)	251 (3)	235 (3)	250 (3)	0	81 (2)	0
77	O(1)	4009 (6)	2500	1165 (4)	231 (13)	305 (14)	254 (13)	0	168 (11)	0
298	O(1)	3964 (4)	2500	1152 (3)	412 (10)	574 (12)	418 (11)	0	267 (9)	0
77	O(2)	1456 (4)	4639 (3)	3057 (3)	248 (9)	111 (7)	299 (9)	5 (6)	135 (7)	−52 (7)
298	O(2)	1465 (3)	4614 (2)	3050 (2)	444 (7)	238 (6)	509 (8)	11 (5)	200 (6)	−82 (5)

Table 2. *Bond angles* (°) *in* ClO_3^-

Temperature (K)	O(1)–Cl–O(2)	O(2)–Cl–O(2)
77	106·48 (9)	106·36 (16)
298	106·59 (7)	106·27 (11)

Table 3. Cl—O *lengths* (Å) *corrected for riding motion*

Temperature (K)	O(1)–Cl	O(2)–Cl
77	1·498 (3)	1·495 (2)
298	1·499 (2)	1·491 (1)

With initial parameters as given by Aravindakshan (1958), a least-squares refinement of a scale factor, atomic coordinates, anisotropic thermal parameters, and an isotropic extinction parameter, g, was performed. No corrections were made for absorption. The weighting scheme was $w = \{[\sigma(F_o)^2 + 1{\cdot}02\,F_o^2]^{1/2} - |F_o|\}^{-2}$. The scattering factors were those of Cromer & Mann (1968). The final R values were: at 77 K $R(F) = 0{\cdot}033$, $R_w(F) = 0{\cdot}049$* for 517 reflexions $[I > 3\sigma(I)]$, and at 298 K $R(F) = 0{\cdot}023$, $R_w(F) = 0{\cdot}029$* for 491 reflexions $[I > 3\sigma(I)]$. The values of g which were calculated assuming $\bar{t}$ unity, were $1{\cdot}3\,(2) \times 10^{-7}$ and $1{\cdot}2\,(2) \times 10^{-7}$, corresponding to minimum values of F_o^2/F_o^2(corr.) of 0·82 and 0·84.

Discussion. Coordinates and thermal parameters are given in Table 1 and angles in Table 2; in Table 3 the bond lengths in the ClO_3^- ion corrected for the riding motion of O on Cl at both temperatures (*ORFFE*, Busing, Martin & Levy, 1964) are given. Fig. 1 shows the two K^+ ions in the unit cell together with their nearest ClO_3^- ions.

The results are consistent with those of Bats (1978) if his cell parameters (subscript B) are transformed so that $\mathbf{c}_B = \mathbf{a} + \mathbf{c}$ and $\mathbf{a}_B = -\mathbf{a}$. The angle between the normal to the plane through the O atoms of the ClO_3^- ion and a is 51·9 (1)° at 298 K, in agreement with the value of 52·1 (5)° obtained by Zeldes & Livingstone (1957) from NQR experiments. At 77 K the angle is 52·7 (1)°. The ESR experiments of Byberg (1981) gave angles of 50 (2) and −49 (2)° between a and the O atom planes for the two orientations of the ClO_3^- ions. At both temperatures difference maps of the section in the mirror plane showed maxima within 0·8 Å of Cl and K but no peaks at the expected position of the O atom belonging to the second orientation of ClO_3^-. So no disorder of the type discussed in the *Introduction* could be detected. To obtain the second position suggested by the ESR measurements, the ClO_3^- would have to rotate through 180° about c^*, which makes it unlikely for steric reasons that the second position is obtained as a dynamic rearrangement. However, the apparent rotation of the ClO_3^- ions may be interpreted by assuming that the O^- ions produced during irradiation are originally O(1) atoms which move in the **a** direction from one Cl to the next and that the second Cl then releases its own O(1) as O^- to the next Cl and so on, giving the possibility that the O^- can be trapped between ClO_3^- ions with the two different orientations as observed in the ESR experiments (Byberg, 1981).

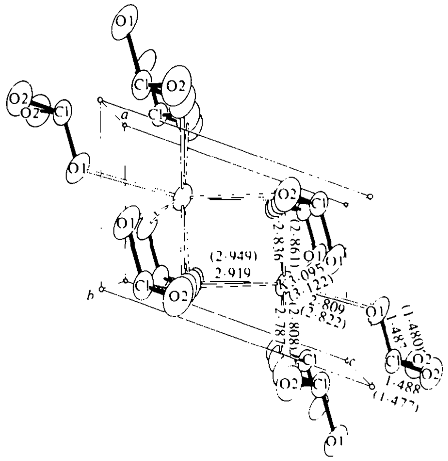

Fig. 1. Perspective view (*ORTEP*, Johnson, 1965) along b of the structure at 77 K. Distances, uncorrected for thermal motion, are in Å; the values in parentheses are for the structure at 298 K. E.s.d.'s are between 0·001 and 0·003 Å.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35731 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

This interpretation is supported by the present work, as O(1) has an average distance to the three nearest K^+ ions of 3·000 Å (77 K) while O(2) is more strongly bonded, with a corresponding average distance of 2·847 Å (77 K). Furthermore, $O^-(1)$ does not have to pass closer than 2·94 Å (77 K) to any K^+ on its way from one Cl to the next.

In the orthorhombic high-temperature phase of $KClO_3$ (Ramachandran & Lonappan, 1957) there are equal amounts of ClO_3^- ions in the same two orientations as observed in the ESR experiments. The ClO_3^- ions are arranged in chains parallel to a. ClO_3^- ions in the same chain have the same orientation. This suggests that the mechanism behind the phase transition at 523 K may be a systematic exchange of O atoms similar to the exchange of O^- ions described above.

Note added in proof: The recent observation (Wadhawan, 1980) of the formation of domain walls on applying a uniaxial stress to crystals of the monoclinic form of $KClO_3$ may be explained as follows.

The stress causes slip to occur at the plane $z = 0$ in the **a** direction. K, Cl, and O(2) with $z > 0$ and the O(1) atom with $z < 0$ will slip relative to K, Cl, and O(2) with $z < 0$ and O(1) with $z > 0$. This slip requires Cl—O(1) bonds to be broken and then re-established, *i.e.* the same mechanism we propose for the monoclinic to orthorhombic phase change. The relative translation, t, is approximately 2·1 Å. If slipping occurs at all planes $z = 0, \pm 1, \pm 2 \ldots$ in the crystal our model gives a slip of $t/c/\cos(\beta - 90) = 2{\cdot}1/7{\cdot}1/0{\cdot}94 = 0{\cdot}31$.

Wadhawan describes four types of domain walls which he describes as DW1, DW2, DW3, and DW4. When the entire plane slides, then only domain wall DW1 appears. If, however, the slip starts at a particular Cl—O(1) bond, then neighbouring Cl—O(1) bonds with the same z value must be broken and Cl—O(1) bonds with the same z value ± 1 may be broken causing planes of fracture to appear. These planes could be $\{100\}$, $\{110\}$ or $\{1\bar{1}0\}$ and may explain the domain walls DW2, DW3, and DW4, respectively. Other planes such as $\{011\}$ and $\{11\bar{1}\}$ are also possible domain walls according to this hypothesis.

Neither Wadhawan nor we attempt to explain the transition to the rhombohedral high-pressure form of $KClO_3$ (Pistorius, 1972). All three forms of $KClO_3$ can be described as having distorted rock-salt structures. A cubic cell with $Z = 4$ and a volume twice that of the monoclinic form, which has $Z = 2$, would have $a = 7{\cdot}05$ Å. The 'tetragonal' prototype phase proposed by Wadhawan has cell edges which are $a/2$, $a/2$, and $2a$.

References

Aravindakshan, C. (1958). *Z. Kristallogr.* **111**, 35–45.
Bats, J. W. (1978). *Acta Cryst.* B**34**, 1679–1681.
Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.
Byberg, J. R. (1981). In preparation.
Coppens, P., Ross, F. K., Blessing, R. H., Cooper, W. F., Larsen, F. K., Leipoldt, J. G., Rees, B. & Leonard, R. (1974). *J. Appl. Cryst.* **7**, 315–319.
Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
Ievin'š, A. F. & Ozol, Ja. K. (1953). *Structure Reports*, Vol. 17, p. 526. Utrecht: Oosthoek.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
Pistorius, C. W. F. T. (1972). *J. Chem. Phys.* **56**, 6263–6264.
Ramachandran, G. N. & Lonappan, M. A. (1957). *Acta Cryst.* **10**, 281–287.
Wadhawan, V. K. (1980). *Acta Cryst.* A**36**, 851–856.
Zachariasen, W. H. (1929). *Z. Kristallogr.* **71**, 501–516.
Zeldes, H. & Livingstone, R. (1957). *J. Chem. Phys.* **26**, 1102–1106.

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Neutron Profile Refinement of $4Na_2SO_4.2D_2O_2.NaCl$

By J. M. Adams and Vijayalakshmi Ramdas

Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth SY23 1NE, Wales

and A. W. Hewat

Institut Laue–Langevin, 38042 Grenoble CEDEX, France

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Abstract. $4Na_2SO_4.2D_2O_2.NaCl$, $P4/mnc$, $a = 10{\cdot}5270$ (2), $c = 8{\cdot}4079$ (3) Å. Neutron powder data (300 K, 1·9 Å) have been refined to give the D atom positions in the title compound. Final $R = 10{\cdot}5\%$. The arrangement and molecular parameters of the disordered peroxide molecules have now been well

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