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Superstructure of α-phase potassium nitrate

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The structure of potassium nitrate, KNO_3, has been redetermined at room temperature. The compound surprisingly shows a $2 \times 2 \times 1$ superstructure and crystallizes in space group $Cmc2_1$. This result contrasts with that found in former investigations, which gave the supergroup *Pmcn*, neglecting the superstructure. The improved results are due to the employment of a CCD area detector.

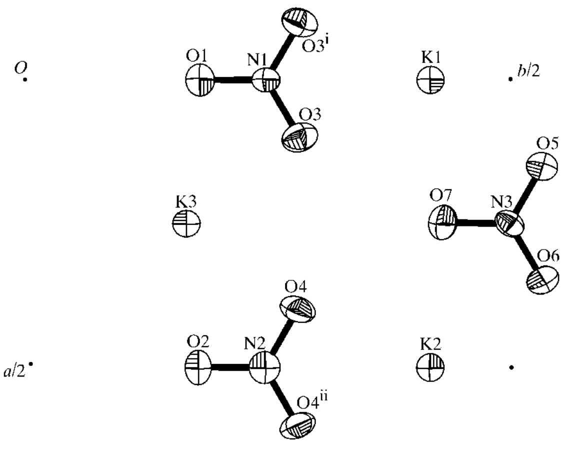

Figure 1
A view along [001] of the α-KNO_3 superstructure, showing an asymmetric unit with N—O bonds. The corners of the cell are indicated with dots. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x, y, z$; (ii) $1 - x, y, z$.]

Comment

Potassium nitrate is known to be both a mineral (niter) and an inexpansive chemical compound. On heating, it undergoes two phase transitions at atmospheric pressure, the first from the α phase to the β phase and the second from the β phase to the melt. These transitions are widely used to calibrate differential thermal analysis (DTA) devices (Barshad, 1952; Greis *et al.*, 1985). The crystal structure of the α phase was determined by Edwards (1931), and redetermined by Nimmo & Lucas (1973) and Holden & Dickinson (1975) using neutrons and X-rays, respectively. All these authors found an aragonite-type structure, with space group *Pmnc*.

For many years, we have used potassium nitrate to calibrate a DTA apparatus and to teach graduate students phase transitions observed by DTA and X-ray powder diffraction. Then, in addition, we advantageously used the same compound to teach structure determination. To study the structure, we employed a Weissenberg camera and an Enraf–Nonius CAD-4 diffractometer. The Weissenberg photographs never showed any sign of superstructure, and therefore the known space group, *Pmnc*, was confirmed. However, the situation was completely different when we used a Nonius KappaCCD diffractometer. In the latter case, space group $Cmc2_1$ was determined, with doubled crystallographic a_0 and b_0 axes. All corresponding reflections with odd h or k indices have weak intensities, thus showing a $2 \times 2 \times 1$ superstructure. On the basis of the criterion $I > 2\sigma(I)$, 1069 reflections are classified as significant, of which 1012 belong to the sublattice and 48 to the superlattice, including 17 Friedel pairs. The intensity of the strongest superlattice reflection is less than 2% of that of the strongest sublattice reflection.

The space group of the superstructure ($Cmc2_1$) is a subgroup of that given in the literature (*Pmcn*) for α-KNO_3. As can be seen from the *International Tables for X-ray Crystallography* (1983, Vol. A), both space groups are connected *via* the minimal supergroup (maximal subgroup) $Pmc2_1$ ($Cmc2_1 < Pmc2_1 < Pmcn$). According to the work of Lima-de-Faria *et al.* (1990), the superstructure of α-KNO_3 and the formerly described aragonite-type structure of this compound are homeotypic. Regarding the geometric properties, the superstructure differs little from the aragonite-type structure. However, the superstructure has a lowered symmetry and hence a higher number of crystallographically independent atoms in the asymmetric unit. While the true aragonite-type structure has one unique K atom and one unique N atom, each of them sitting on a mirror plane, the superstructure contains three unique atoms of both potassium and nitrogen. Each of these elements occupies two unique sites on a mirror plane and one at a general position, as depicted in Fig. 1.

There are seven unique O atoms in the superstructure of α-KNO_3. All seven are bonded to N atoms, forming nitrate ions, of which three are unique (see Table 1 for selected bond lengths and angles). In each nitrate ion, the N atom deviates by 2 s.u. or less from the plane through the O atoms. Each of the three unique potassium ions is surrounded by nine O atoms from six nitrate ions, thereby building an irregular coordination polyhedron.

A face-indexing analytical absorption correction was applied, based on a crystal bound by ten faces, *viz*. $(0\bar{1}1)$, $(01\bar{1})$, (010), $(0\bar{1}0)$, (110), $(\bar{1}\bar{1}0)$, $(0\bar{1}\bar{1})$, $(\bar{1}11)$, $(\bar{1}10)$ and $(1\bar{1}0)$, with face-to-centre distances of 0.11, 0.06, 0.16, 0.17, 0.13, 0.11, 0.12, 0.15, 0.10 and 0.17 mm, respectively. The crystal neither looks orthorhombic nor resembles a sphere, thus making absorption correction extremely difficult.

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Experimental

Crystal data

KNO_3
$M_r = 101.11$
Orthorhombic, $Cmc2_1$
$a = 10.825$ (6) Å
$b = 18.351$ (10) Å
$c = 6.435$ (3) Å
$V = 1278.3$ (12) Å^3
$Z = 16$
$D_x = 2.101$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 2170 reflections
$\theta = 1.0$–$40.3°$
$\mu = 1.46$ mm^{-1}
$T = 293$ (2) K
Irregular, colourless
0.33 × 0.25 × 0.17 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: analytical face-indexing (*COLLECT*; Nonius, 1999)
$T_{\min} = 0.65$, $T_{\max} = 0.78$
3857 measured reflections

3857 independent reflections
1069 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 40.2°$
$h = -19 \rightarrow 19$
$k = -33 \rightarrow 33$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.160$
$S = 1.04$
3857 reflections
101 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0308P)^2 + 2.4843P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.036$
$\Delta\rho_{\max} = 0.46$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0097 (7)
Absolute structure: Flack (1983), 1632 Friedel pairs
Flack parameter = 0.1 (5)

In order to obtain the maximum number of superstructure reflections, we chose a high angle, $\theta_{\max}$, of measured reflections. Therefore, and because of the general weakness of the superstructure reflections, we unavoidably obtained many reflections below the $2\sigma(I)$ threshold, making the refinement a little clumsy. Moreover, the pseudosymmetries imposed by the substructure result in strong correlations of several parameters. Additional correlations are possibly introduced *via* absorption-correction errors (see above). As a result of the correlations, the convergence of the refinement is poor. The use of damping parameters was necessary in the last cycles of refinement, and a final cycle with no damping was added. Because of the presence of a pseudo-centre of symmetry, the absolute structure could not be determined. Simple twinning models based on primitive monoclinic lattices neither resulted in a better convergence of the refinement nor removed the pseudo-centre of symmetry. However, if the transformation of potassium nitrate from the trigonal ferroelectric high-temperature γ phase to the room-temperature α phase is led by symmetry then, in the α phase, a *C*-centred cell lacking a centre of symmetry is desired. Therefore, the pseudosymmetries may be true features of the α-phase structure.

Table 1
Selected geometric parameters (Å, °).

N1—O1	1.241 (12)	N2—O4	1.262 (6)
N1—O3	1.255 (6)	N3—O6	1.235 (8)
N1—O3^{i}	1.255 (6)	N3—O5	1.237 (8)
N2—O2	1.250 (12)	N3—O7	1.253 (9)
N2—O4^{ii}	1.262 (6)		
O1—N1—O3	120.4 (5)	O4^{ii}—N2—O4	120.4 (10)
O1—N1—O3^{i}	120.4 (5)	O6—N3—O5	119.8 (7)
O3—N1—O3^{i}	119.2 (10)	O6—N3—O7	121.5 (6)
O2—N2—O4^{ii}	119.8 (5)	O5—N3—O7	118.6 (6)
O2—N2—O4	119.8 (5)		

Symmetry codes: (i) $-x, y, z$; (ii) $1 - x, y, z$.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *COLLECT*; data reduction: *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1035). Services for accessing these data are described at the back of the journal.

References

Barshad, I. (1952). *Am. Mineral.* **37**, 667–694.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Edwards, D. A. (1931). *Z. Kristallogr.* **80**, 154–163.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881
Greis, O., Bahamdan, K. M. & Uwais, B. M. (1985). *Thermochim. Acta*, **86**, 343–350.
Holden, J. R. & Dickinson, C. W. (1975). *J. Phys. Chem.* **79**, 249–256.
Lima-de-Faria, J., Hellner, E., Liebau, F., Makovicky, E. & Parthé, E. (1990). *Acta Cryst.* A**46**, 1–11.
Nimmo, J. K. & Lucas, B. W. (1973). *Solid State Phys.* **6**, 201–211.
Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.