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Ammonium chlorite, NH_4ClO_2, at 150 K

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The structure of tetragonal ($P\overline{4}2_1m$) ammonium chlorite, NH_4ClO_2, has been redetermined by single-crystal X-ray analysis with higher precision. The $NH_4{}^+$ cation is at a site of $\overline{4}$ symmetry, while the unique Cl and O atoms are at sites with symmetries *mm* and *m*, respectively. The structure consists of corrugated layers of NH_4^+ cations coordinated by ClO_2^- anions. The H atoms of the ammonium cation hydrogen bond to four chlorite O atoms. The resultant coordination is almost ideal tetrahedral.

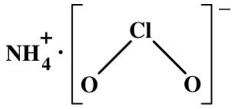
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(Cl–O) = 0.001 Å
R factor = 0.016
wR factor = 0.040
Data-to-parameter ratio = 11.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The salts of chlorous acid were first investigated crystallographically by Levi & Scherillo (1931). However, they attempted a structure determination only for one of the salts studied, *viz*. ammonium chlorite, and because this substance decomposes to ammonium chloride and chlorate in a few hours at ordinary temperatures, they had considerable difficulty in the estimation of intensities. The structure which they proposed could only be regarded as tentative. Later, this incorrect structure was corrected by Gillespie *et al.* (1959). Their experiment was carried out at lower temperature (238 K), but the structural data were of poor quality (R = 0.149; no H atoms located).


(I)

The purpose of the present investigation was to obtain precise structural data for ammonium chlorite, (I). In other words, we tried to produce precise bond lengths and angles (the main goal in the structural study of a simple inorganic compound such as this). Moreover, the number of chlorite structures so far studied is small and, because this compound forms suitable crystals more readily than many other chlorites, it seemed worthwhile searching for a better crystal and redetermining the structure.

The previously determined structure of ammonium chlorite (Gillespie *et al.*, 1959) has been confirmed. It contains separate layers within which the NH_4^+ cation is hydrogen bonded to four chlorite O atoms forming a tetrahedron compressed along a twofold axis (Fig. 1). These layers are parallel to the *ab* plane and are linked by van der Waals interactions (Fig. 2). The ClO_2^- anions serve as tetradentate bridging ligands between the NH_4^+ cations. The structure of the layer is very similar to that found in the $LiClO_2$ structure (Smolentsev & Naumov, 2005). However, the layer packings are different; in

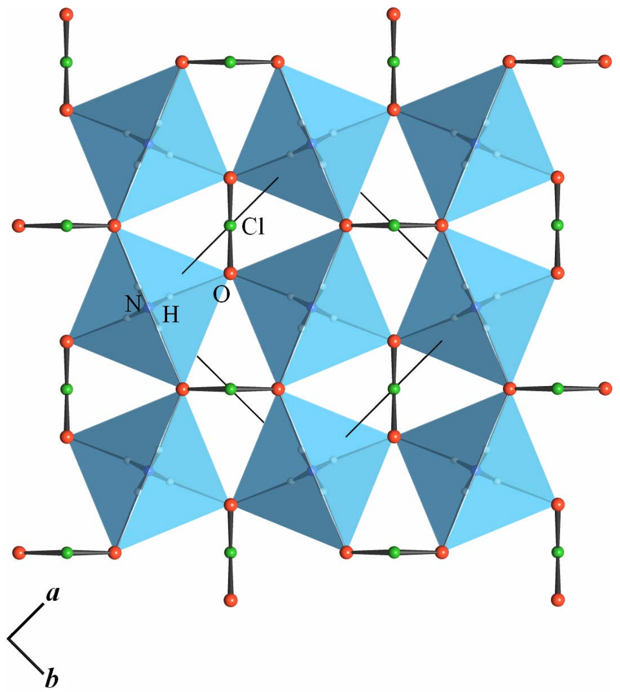


Figure 1
The (001) projection of the layer in NH_4ClO_2.

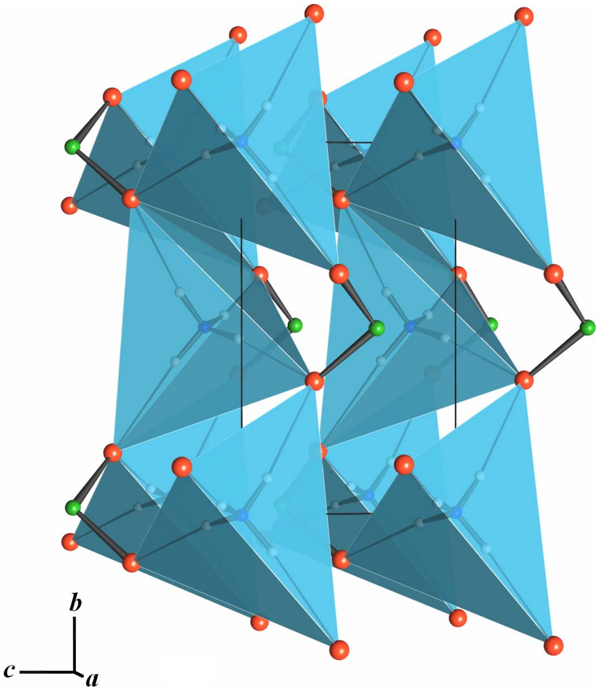


Figure 2
A packing diagram of the NH_4ClO_2 structure.

$LiClO_2$, the layers are stacked in such a way that adjacent layers are rotated by 90°. There are also some similarities to the layers in $NH_4H_2PO_2$ (Naumova *et al.*, 2004) and LiH_2PO_2 (Naumov *et al.*, 2004) which contain chains of cation-centered tetrahedra linked by $H_2PO_2^-$ anions.

The O—Cl—O angle is wider than in the previous determination (Fig. 3): 111.88 (12) *versus* 110.5°. Comparison can be made with other O—Cl—O angles in the literature: 110.0 (3)° in $LiClO_2$ and 108.18 (18)° in $KClO_2$ (Smolentsev & Naumov, 2005), 107.0 (1)° in $AgClO_2$ (Okuda *et al.*, 1990), 111.4 (1)° in $Zn(ClO_2)_2{\cdot}2H_2O$ (Pakkanen, 1979) and 112.5 (5)° in $Pb(ClO_2)_2$ (Okuda *et al.*, 1990). The present Cl—O bond distance [1.5759 (14) Å] is close to the earlier value [1.57 (3) Å] and compares well with the following literature values, in the same order as above: 1.578 (4), 1.565 (2), 1.575 (2), 1.580 (3) and 1.577 (9) Å.

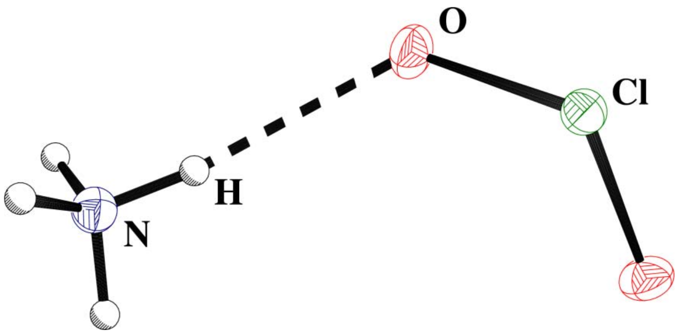


Figure 3
Displacement ellipsoid plot, drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radius. The dashed line indicates a hydrogen bond.

Experimental

Ammonium chlorite was synthesized by mixing aqueous solutions of barium chlorite, $Ba(ClO_2)_2$ and ammonium sulfate in an equimolar ratio. The reaction mixture was filtered and the crystals were grown by evaporation at room temperature. This compound decomposes at room temperature, even after a few hours, and it was necessary to grow crystals quickly from a concentrated solution. Also, it was found that the crystals are stable at low temperatures for a very long time. The crystals were mostly thin colorless needles with a maximum size of 0.5 mm, suitable for X-ray diffraction. Crystals yellowed over time as a result of decomposition. The X-ray powder pattern at room temperature shows good agreement between the bulk product and the single crystal. However, additional peaks indicate the presence of NH_4Cl and NH_4ClO_3 phases. The precursor used for the preparation of ammonium chlorite, $Ba(ClO_2)_2$, was obtained according to the method described by Smolentsev & Naumov (2005).

Crystal data

NH_4ClO_2
$M_r = 85.49$
Tetragonal, $P\bar{4}2_1m$
$a = 6.3397$ (3) Å
$c = 3.7560$ (2) Å
$V = 150.960$ (13) Å^3
$Z = 2$
$D_x = 1.881$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 939 reflections
$\theta = 4.6$–32.6°
$\mu = 1.01$ mm^{-1}
$T = 150$ (2) K
Needle, colorless
0.42 × 0.12 × 0.07 mm

Data collection

Bruker–Nonius X8 APEX CCD area-detector diffractometer
φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
$T_{\min} = 0.676$, $T_{\max} = 0.932$
1087 measured reflections
203 independent reflections
200 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.014$
$\theta_{\max} = 28.2°$
$h = -8 \rightarrow 8$
$k = -8 \rightarrow 8$
$l = -4 \rightarrow 2$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.016$
$wR(F^2) = 0.040$
$S = 1.26$
203 reflections
17 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0174P)^2 + 0.0433P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}
Absolute structure: Flack (1983), 74 Friedel pairs
Flack parameter = −0.02 (1)

Table 1
Selected geometric parameters (Å, °).

Cl—O	1.5759 (14)		
O—Cl—O^{i}	111.88 (12)	O^{ii}—N—O^{iii}	117.33 (5)
O—N—O^{ii}	105.69 (3)		

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N—H···O	0.866 (15)	1.985 (15)	2.8438 (9)	171.2 (18)

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2004); program(s) used to refine structure: *SHELXTL*; molecular graphics: *BS* (Ozawa & Kang, 2004); software used to prepare material for publication: *SHELXTL*.

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