Table 1. *Observed and calculated structure factors*

	h	k	l	$\lvert F_o\rvert$	kF_c*	$\lvert F_o\rvert - \lvert F_c\rvert$	$\sigma(\lvert F_o\rvert)$
($4n\pm1$)							
	5	1	1	60·00	60·29	−0·29	0·23
	5	3	1	59·57	59·47	0·10	0·16
	5	5	1	58·13	57·84	0·29	0·15
	7	1	1	57·73	57·84	−0·11	0·22
	5	5	3	57·26	57·05	0·21	0·42
	7	3	1	56·65	57·05	−0·40	0·20
($4n+2$)							
	4	2	0	23·21	−23·12	0·09	0·23
	4	4	2	20·19	−19·89	0·30	0·32
	6	0	0	19·30	−19·89	−0·59	0·28
	6	2	2	18·95	−18·36	0·59	0·60
	6	4	0	17·17	−16·90	0·27	0·49

* $k=0·316$ (3)

Table 2. *Isotropic thermal parameters*

	B_U	B_O
Present analysis	0·207 (23) Å^2	0·448 (37) Å^2
Willis & Rouse (1966)	0·214 (8)	0·432 (12)

a disappointing result, but it will at least terminate speculation about the use of ^{18}O for this purpose.

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Neutron diffraction study of hydroxylammonium chloride, NH_3OHCl.

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The structure of hydroxylammonium chloride, NH_3OHCl, has been studied with the use of partial three-dimensional neutron diffraction data, to a final $R=8\%$. The heavy atom coordinates reported by Jerslev (1948) by X-ray studies are more or less confirmed. The hydrogen atoms have been located and their positions refined. The N–O distance is 1·383 Å, much shorter than the value 1·47 Å reported by Jerslev. The NH_3 group is in the form of an undistorted triangular pyramid in the crystal. The average of the N–H distances is 1·044 Å. The O–H bond length is 0·996 Å and all the hydrogens are bonded to chlorines of the neighbouring molecules.

The crystal structure of NH_3OHCl has been studied earlier by X-ray methods (Jerslev, 1948). The present neutron diffraction investigation was undertaken primarily for the purpose of locating the hydrogen atoms and it has also resulted in an improvement of all the position parameters.

Crystals of hydroxylammonium chloride were grown by the method described by Jerslev (1948). The crystal used for collecting the data was in the form of a cylinder (1·8 × 5·2 mm) and mounted on a two-circle goniometer set so that the b axis of the crystal was along the φ axis of the goniometer and the scattering vector remained in the χ plane for all reflexions. The space group and unit cell as determined by X-rays and neutrons are $P2_1/c$, $Z=4$, $a=6·95$, $b=5·95$, $c=7·70$ Å, $\beta=120·8°$ in agreement with previous X-ray results. Intensities of 320 $h0l$, $0kl$ and some hkl reflexions were measured on the instrument at the Oak Ridge research reactor, using the θ-2θ scan technique ($\lambda=1·077$ Å). The data were corrected for absorption by the method of Busing & Levy (1957). The intensities were reduced to structure factors in the usual way by comparison with the 400 reflexion from a standard sodium chloride crystal. No correction for extinction was made because of the good agreement between intensity measurements from two different sized crystals. Nuclear density projections were first drawn on (010) and (100) planes, based on neutron amplitudes and phases derived from the parameters of heavy

Table 1. *Positional parameters with estimated standard deviations, and temperature factors*

	x	y	z	x	y	z
					Jerslev (1948)	
N	0·2743 ± 0·009	0·6664 ± 0·0010	0·2252 ± 0·0007	0·283	0·644	0·222
O	0·2650 ± 0·0014	0·8492 ± 0·0015	0·1120 ± 0·0011	0·253	0·870	0·106
Cl	0·2414 ± 0·0006	0·1881 ± 0·0008	0·3972 ± 0·0004	0·233	0·190	0·395
H(1)	0·1310 ± 0·0025	0·6574 ± 0·0028	0·2321 ± 0·0024			
H(2)	0·4103 ± 0·0026	0·6747 ± 0·0029	0·3674 ± 0·0017			
H(3)	0·2890 ± 0·0025	0·5273 ± 0·0041	0·1583 ± 0·0026			
H(4)(OH)	0·2333 ± 0·0020	−0·0171 ± 0·0032	0·1714 ± 0·0018			

Temperature factors ($\times 10^4$)

The temperature factors are the coefficients in the expression

$$\exp \{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\}$$

	β_{11}	β_{12}	β_{33}	β_{12}	β_{13}	β_{23}
N	140	154	116	5	77	66
O	220	96	123	48	109	55
Cl	113	112	96	5	46	−23
H(1)	236	234	276	73	178	161
H(2)	273	268	132	−130	46	−15
H(3)	243	313	231	−40	119	69
H(4)	199	208	135	100	68	43

Table 2. *Bond-lengths and angles*

	Distances		Angles
N——O	1·369 ± 0·007 Å	O——N——H(1)	110·8 ± 0·7°
O——H(4)	0·985 ± 0·016	O——N——H(2)	110·2 ± 0·7
N——H(1)	1·024 ± 0·011	O——N——H(3)	109·2 ± 0·8
N——H(2)	1·017 ± 0·009	H(1)-H(2)-H(3)	60·3 ± 0·7
N——H(3)	1·019 ± 0·009	H(2)-H(3)-H	60·6 ± 0·5
Cl——H(4)	2·109 ± 0·013	H(3)-H(1)-H(2)	59·1 ± 0·9
N——Cl	3·202 ± 0·006	H(1)-N——H(2)	110·2 ± 0·9
O——Cl	3·042 ± 0·009	H(2)-N——H(3)	108·6 ± 0·8
H(1)-H(2)	1·673 ± 0·014	H(1)-N——H(3)	109·5 ± 0·7
H(2)-H(3)	1·648 ± 0·017	N——O——H	107·2 ± 0·6
H(1)-H(3)	1·669 ± 0·019	N——H(1)-Cl_{I}	153·2 ± 0·9
H(1)-Cl_{I}	2·256 ± 0·013	N——H(2)-$\mathrm{Cl}_{\mathrm{II}}$	157·3 ± 0·8
H(2)-$\mathrm{Cl}_{\mathrm{II}}$	2·248 ± 0·016	N——H(3)-$\mathrm{Cl}_{\mathrm{III}}$	156·2 ± 0·9
H(3)-$\mathrm{Cl}_{\mathrm{III}}$	2·260 ± 0·014	O——H(4)-Cl	144·2 ± 0·7

Bond lengths after correction for thermal motion

N-H(1) (riding)	1·047 ± 0·011 Å
N-H(2) (riding)	1·046 ± 0·010
N-H(3) (riding)	1·039 ± 0·010
O-H(4) (riding)	0·996 ± 0·018
N-O (riding)	1·383 ± 0·007

Dihedral angle between the planes containing atoms N, O, H(4) and O, N, H(1) is 53·6°.

Table 3. *Selected* N–O *bond lengths*

Values in parentheses are corrected for thermal vibrations

	N–O length	Reference
Dimethylglyoxime	1·32 Å	Hamilton (1961)
Acetoxime	1·36	Bierlein & Lingafelter (1951)
Trimethylamine oxide	1·388 (1·404)	Caron *et al.* (1964)
Trimethylamine oxide hydrochloride	1·425 (1·438)	Caron & Donohue (1962)
O-Methylhydroxylamine hydrochloride	1·42	Rérat (1964)
Hydroxylammonium chloride	1·369 (1·383)	Present work
	1·450	Jerslev (1948)
Hydroxylamine	1·37	Brockway (1935)
	1·47	Meyers & Lipscomb (1955) Donohue (1958)
Pyridine-*N*-oxide hydrochloride	1·37	Tsoucaris (1961)

Table 4. N–H *bond lengths*

Values in parentheses are corrected for thermal vibrations

	N–H distance	Reference
NH_4I, NH_4Cl	1·03 Å	Levy & Peterson (1953)
$(NH_4)_2SiF_6$	0·985 (1·064)	Schlemper, Hamilton & Rush (1966)
$LiN_2H_5SO_4$	1·03	Padmanabhan & Balasubramanian (1967)
KNH_2SO_3	1·007 (1·044)	Padmanabhan, Cox & Sabine (1966)
NH_3OHCl	1·02 (1·044)	This work

atoms from the X-ray study. The projections served to locate roughly the positions of hydrogen atoms. These positional parameters were refined by the method of least squares with the IBM 7090 computer using the program of Busing & Levy (1959). At later stages of refinement an anisotropic temperature factor for each atom was included. The weighted R index was 0·08, where $R=[\Sigma\, w(F_o-F_c)^2/\Sigma\, wF_o^2]^{\frac{1}{2}}$ where w is the weight for the observed structure factor, calculated from the expression given by Smith & Levy (1962). The refined parameters are listed in Table 1 and the bond distances and angles in Table 2. An interesting point of the study is the N–O distance which is observed to be 1·383 ± 0·007 Å whereas Jerslev (1948) has reported a much higher value, 1·47 Å. Earlier from electron-diffraction studies Brockway (1935) has given the N–O distance as 1·35 Å in crystalline hydroxylamine. In Table 3 we summarize the N–O bond distances in a number of compounds. Caron, Palenik, Goldish & Donohue (1964), after comparing N–O bond lengths in seven or more compounds, suggest that the difference in the formal charges on nitrogen and oxygen is an important factor and that opposite charges across N–O bond do have a shortening effect. In such a case the N–O distance in NH_3OHCl should be much greater than 1·383 Å. A closer study of a few more compounds having N–O bonds is necessary to prove that charges shorten the bond-distance.

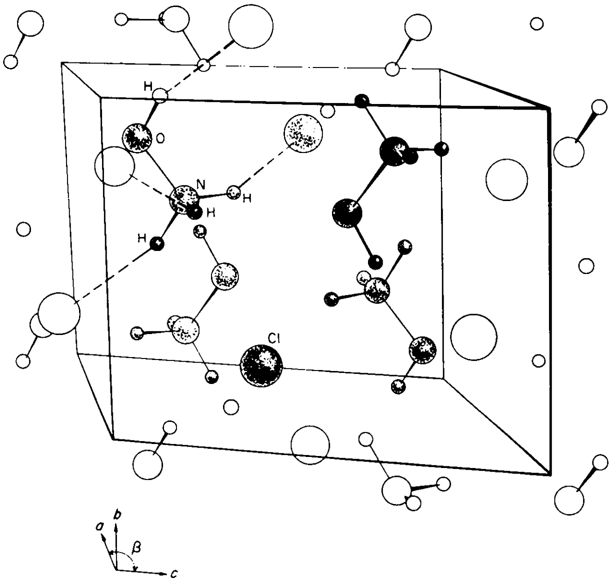

Fig. 1. A perspective view of the atoms in the unit cell of NH_3OHCl. Dashed lines represent hydrogen bonds.

As seen from values in Table 2, the NH_3 group is in the form of an undistorted triangular pyramid in the crystal. The average of the N–H distances is 1·044 ± 0·012 Å and this is compared with distances observed in similar compounds from neutron diffraction studies in Table 4. The H–N–H and O–N–H average bond angles are 109·4 ± 0·7 and 109·9 ± 0·7° respectively, so that within experimental error the nitrogen atoms have the ideal valence angle of 109·5°. All three hydrogen atoms are bonded to chlorine atoms of neighbouring molecules (Fig. 1). The N–H···Cl angles are 153–157° and the three atoms are not collinear. Such a departure from linearity is not uncommon in hydrogen-bonded crystals. The observed O–H(4) bond length, 0·996 ± 0·018 Å, is not significantly different from the values reported in the literature. The hydrogen bond O–H(4)···Cl between oxygen and chlorine atoms is of length 3·042 Å, and the bond is much more bent (144°) than the N–H···Cl bonds mentioned earlier.

This work was done while one of us (V.M.P.) was at Oak Ridge National Laboratory as a participant under the USAID program. The drawing of Fig. 1 was prepared with the aid of Dr W. R. Busing's perspective drawing program for the IBM 7090 computer.

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