

stage. For example, isotropic extinction can result in an anisotropic effect on the intensities depending on the crystal shape. If systematic errors or, rather, systematic effects are detected for which no correction can be made, the obvious conclusion is that the data set is not suitable for high-accuracy work.

Problems in this connexion are the isotropic systematic errors which may be difficult to detect. An example is thermal diffuse scattering which will always affect the data but for which it is difficult to make a correction. The effect of TDS is reduced at low temperatures and low-temperature work is therefore to be preferred.

The agreement among symmetry-related reflexions, as expressed by a discrepancy index R , can also be used as a measure of the quality of the data set. Repeated measurements of identical reflexions should not be included in the calculation of this R value. It is suggested that this number be quoted for all data sets where symmetry-related reflexions have been measured.

We thank S. C. Abrahams for communication of the result of the second harmonic generation test and for valuable comments on the manuscript. This work has been supported by grants from the Swedish Natural Science Research Council which are gratefully acknowledged.

Acta Cryst. (1979). **B35**, 1027–1033

X-ray Structure of Ammonium Perchlorate.

II. Conventional Refinement *versus* Refinement with Multipole Deformation Density Functions

BY JAN-OLOF LUNDGREN

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

(Received 23 November 1978; accepted 2 January 1979)

Abstract

The crystal structure of ammonium perchlorate, $\text{NH}_4^+\text{ClO}_4^-$, has been refined from X-ray data collected at 295 K. A deformation model has proved more successful than a conventional spherical free-atom model in describing the observed structure factors. The deformation refinement with Hirshfeld-type deformation density functions [Hirshfeld (1977). *Isr. J. Chem.* **16**, 226–229] gave a final $R_p(F^2) = 0.0276$ compared with 0.0669 for a conventional refinement. The bias introduced by the bonding density is demon-

References

- ABRAHAMS, S. C. (1969). *Acta Cryst.* **A25**, 165–173.
 ABRAHAMS, S. C. (1973). *Acta Cryst.* **A29**, 111–116.
 ABRAHAMS, S. C. (1974). *Acta Cryst.* **B30**, 261–268.
 ABRAHAMS, S. C. (1976). Private communication.
 ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* **A27**, 157–165.
 ARNDT, U. W. & MATHIESON, A. McL. (1969). *Acta Cryst.* **A25**, 1–276.
 CHOI, C. S., PRASK, H. J. & PRINCE, E. (1974). *J. Chem. Phys.* **61**, 3523–3529.
 CHOI, C. S., PRASK, H. J. & PRINCE, E. (1976). *Acta Cryst.* **B32**, 2919–2920.
 COPPENS, P. (1968). *Acta Cryst.* **A24**, 253–257.
 HELMHOLDT, R. B. & VOS, A. (1977). *Acta Cryst.* **A33**, 38–45.
 HOPE, H. (1975). In *Anomalous Scattering*, edited by S. RAMASESHAN & S. C. ABRAHAMS, pp. 293–305. Copenhagen: Munksgaard.
 MCCANDLISH, L. E., STOUT, G. H. & ANDREWS, L. C. (1975). *Acta Cryst.* **A31**, 245–249.
 NIELSEN, K. (1977). *Acta Cryst.* **A33**, 1009–1010.
 PEYRONEL, G. & PIGNEDOLI, A. (1975). *Acta Cryst.* **B31**, 2052–2056.
 SMITH, H. G. & LEVY, H. A. (1962). *Acta Cryst.* **15**, 1201–1204.

strated by a shift in the refined O atom positions towards the Cl atom in the conventional refinement. The shifts in the positional parameters of O atoms were up to 7σ . No significant changes were found in the thermal parameters. The Cl–O lengths obtained in the two refinements differed by ~ 0.01 Å. A small isotropic extinction correction applied in the conventional refinement proved unnecessary in the deformation refinement. The disordered ammonium ion is described by a model in which the H atoms are randomly distributed on a sphere centred on the N atom. The results from the deformation refinement are compared with a high-order refinement from data with $\sin \theta/\lambda > 0.7$ Å⁻¹.

Introduction

The present paper describes the structure refinement of ammonium perchlorate from X-ray data collected at 295 K. Data collection and reduction has been described in the preceding paper (Lundgren & Liminga, 1979).

Structure refinement

The refinements were made by full-matrix least-squares techniques in the space group $Pnma$. The function minimized was $\sum w(F_o^2 - kF_c^2)^2$, where $w^{-1} = \sigma^2(F_o^2)$ is estimated from Poisson counting statistics and other random errors (Lundgren & Liminga, 1979). All reflexions were included in the calculations. Of the 1123 independent reflexions, 260 had $F_o^2 < 3\sigma(F_o^2)$; 50 of the F_o^2 were negative. The various refinements were allowed to proceed until all parameter shifts were $< 0.1\sigma$. The scattering factors for Cl^0 , O^0 and N^0 were those given by Hanson, Herman, Lea & Skillman (1964). The spherical scattering factors of Stewart, Davidson & Simpson (1965) were used for H. An anomalous-dispersion correction was introduced for the non-hydrogen atoms (Cromer & Liberman, 1970). The programs used for all computations with IBM 370/155 and IBM 1800 computers have been described by Lundgren (1976).

Conventional refinement

A refinement was made for the non-hydrogen atoms with coordinates from Smith & Levy (1962) as starting values. No discrete H positions could be found in a subsequent difference synthesis with data having $\sin \theta/\lambda < 0.45 \text{ \AA}^{-1}$. No convergence could be obtained in a refinement in which the positional parameters for H

were varied from start positions 0.75 \AA from N in directions calculated from the low-temperature neutron diffraction study (Choi, Prask & Prince, 1974). The model used by Smith & Levy for disordered H atoms was therefore applied. Here the H atoms are assumed to be isotropically distributed about the N position on the surface of a sphere. The contribution of a H atom to the structure factor is then

$$f_{\text{H}} \frac{\sin 4\pi rs}{4\pi rs} \exp(-B_{\text{H}} s^2) \cos 2\pi \mathbf{r}_{\text{N}} \cdot \mathbf{h},$$

where $s = \sin \theta/\lambda$ and r is the N–H distance. The quantities r and B_{H} , which were allowed to vary in the refinement, were found to be strongly correlated. B_{H} was therefore constrained to have the same value as B_{N} and only r was varied. The N–H distance then refined to the reasonable value 0.75 \AA . Three H atoms were included to give a total charge of $1+$ on the ammonium ion.

The following 36 parameters were refined: one scale factor, one isotropic extinction parameter, positional and anisotropic thermal parameters for the five non-hydrogen atoms in the asymmetric unit and the N–H distance. The refined extinction correction was very small with a maximum correction of 1.06 (multiplying F_o^2). The final R was rather low (0.028), but R_w , the s value (Table 1) and the δR plot [Fig. 1(a)] were unsatisfactory. Considering the care taken in the data collection, the experimental assessment of variance for the measured intensities, and the good agreement between symmetry-related reflexions, it is likely that the main reason for the unsatisfactory refinement lies in the structural model rather than in the data.

A difference synthesis based on the final parameters showed residual electron density, especially in the Cl–O bonds and around the O atoms.

An attempt to improve the model by including higher cumulants (Johnson, 1970) for the thermal motion of

Table 1. *Some data on the refinements*

	A	B	C	D
<i>k</i> (scale factor $\times F_c$)	1.0000 (23)*	0.9867 (24)	0.9891 (23)	1.0165 (130)
<i>g</i> (isotropic extinction)	$0.6 (2) \times 10^3$	—	—	—
<i>N</i> (number of reflexions)	1123	1123	1123	506
<i>M</i> (number of refined parameters)	36	68	106	34
$s = [\sum w\Delta^2 / (N - M)]^{1/2}$	3.03	1.44	1.29	1.18
$R = \sum \Delta / \sum F_o^2$	0.0278	0.0164	0.0147	0.0740
$R_w = [\sum w\Delta^2 / \sum wF_o^2]^{1/2}$	0.0669	0.0313	0.0276	0.0743
Number of reflexions with $ \Delta /\sigma > 4.0$	95	6	1	0
Maximum $ \Delta /\sigma$	24.1	7.8	4.3	3.2

* This scale factor is (arbitrarily) given the value 1.0000. The scale factors for *B*, *C* and *D* are given relative to this value.

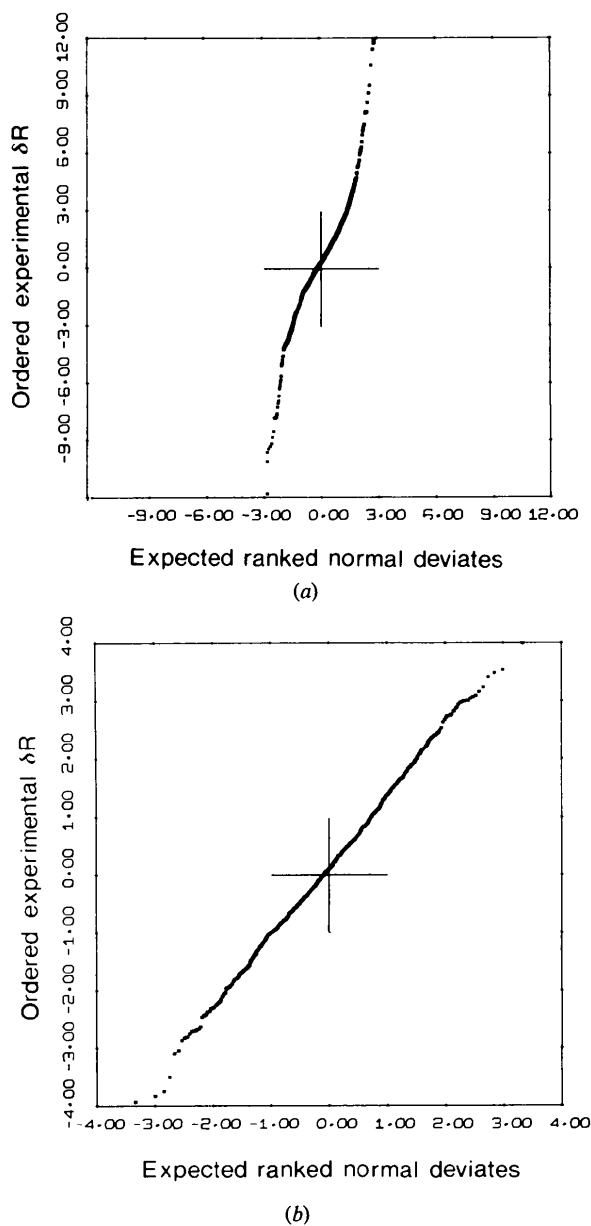


Fig. 1. Normal probability plots. (a) δR plot (Abrahams & Keve, 1971) of the data following the conventional refinement. The slope of the least-squares line through the points is 2.36 and the y intercept is 0.22. The points for nine reflexions fall outside the plot range. The plotted curve is far from the ideal shape: a straight line with slope 1.00. (b) δR plot following the deformation refinement. The slope of the least-squares line through the points is 1.22 and the y intercept is 0.12. The point for one reflexion falls outside the plot range. Note the different plot ranges used in (a) and (b).

the O atoms met with only limited success. The 22 parameters for the γ tensors introduced in the refinement lowered R_w to 0.0620. A Hamilton \mathcal{R} test indicated that this was a significant improvement. The cumulant model did not improve the fit between F_o^2 and

F_c^2 for the low-order data, however, where many large discrepancies still remained.

The positional and thermal parameters from the conventional refinement (series *A*) are given in Table 2.

Deformation refinement

A natural extension of the structural model would be to modify the atomic charge distribution to take account of the non-spherical distribution of the valence electrons about the atomic nuclei. The procedure of Harel & Hirshfeld (1975) and Hirshfeld (1977) was therefore used in a series of deformation refinements. The scattering factor for each atom is computed as

$$f = f_s + \sum c_l \varphi_l,$$

where f_s is the spherical free-atom form factor, and φ_l are the Fourier transforms of the deformation functions centred on the atom. The deformation parameters c_l are included as additional parameters. The functions used for expanding the deformation density were of the form

$$g_{m,n}(r, \theta_k) = N_{m,n} r^m \exp(-\gamma r^2) \cos^n \theta_k.$$

Functions for $n = 0, 1, 2$ and 3 were used in the present case.

To circumvent the problem of assigning deformation functions to the disordered H atoms these atoms were incorporated in the N atom. Deformation functions can be centred on a H atom only if its nuclear position is known (e.g. from a neutron diffraction experiment) and is then not allowed to vary in the deformation refinement. The scattering factor for H was added to that of N with the N–H distance ($r = 0.75 \text{ \AA}$) obtained in the previous refinements [$f_{\text{NH}_4} = f_{\text{N}} + 3f_{\text{H}}(\sin 4\pi rs/4\pi rs)$]. The temperature factors were constrained to be the same for N and H, so that the NH_4^+ ion could be included in the deformation refinement as a single atom.

Two series of deformation refinements were calculated. In the first (Table 1, series *B*), the deformation functions centred on NH_4^+ and O were constrained to m symmetry and on Cl to mm symmetry. Furthermore, the deformation was assumed to be the same for all O atoms. The number of refined deformation parameters was 34. Other refined parameters were as in *A*. It was found, however, that the extinction parameter refined to the value 0.0. The relatively small $F_o^2 - F_c^2$ discrepancies for the strong low-order reflexions were evidently better corrected for by the deformation model which thus made the extinction correction unnecessary. No extinction correction was therefore included in the subsequent refinements. Strong correlation effects meant that the parameter γ , governing the breadth of the deformation function, could not be refined together with other deformation parameters. However, refinements made with different γ values lead to a minimum in R_w for $\gamma = 3.5 \text{ \AA}^{-2}$ for all atoms. This value was then used in all subsequent refinements.

Table 2. Atomic coordinates ($\times 10^5$) and anisotropic thermal parameters ($\text{\AA}^2 \times 10^5$)

The form of the temperature factor is $\exp[-2\pi^2(U_{11}a^{*2}h^2 + \dots + 2U_{12}a^*b^*hk + \dots)]$. Parameters from the conventional refinement are given above parameters from the deformation refinement. The third line gives the difference between the parameters: $(p_1 - p_2)/[\sigma(p_1)^2 + \sigma(p_2)^2]^{1/2}$. The asphericity shift is the distance between the conventional and deformation refinement positions.

	<i>x</i>	<i>y</i>	<i>z</i>	Asphericity shifts (\AA)	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl	43192 (4)	25000	69168 (5)	0.002 (1)	2883 (19)	2969 (20)	2563 (17)	0	109 (16)	0
	43210 (4)	25000	69179 (5)		2837 (12)	2935 (12)	2547 (9)	0	104 (11)	0
	-3.3		-0.9		2.1	1.5	0.8		0.2	
O(1)	42033 (9)	45113 (15)	80365 (11)	0.015 (1)	4850 (53)	3219 (46)	4174 (48)	-91 (35)	-267 (43)	-936 (36)
	41945 (12)	45229 (17)	80506 (17)		4874 (31)	3272 (33)	4134 (28)	-137 (22)	-291 (29)	-883 (27)
	5.7	-5.1	-6.9		-0.4	-0.9	0.7	1.1	0.5	-1.2
O(2)	56795 (15)	25000	60191 (21)	0.015 (3)	4166 (80)	7012 (103)	6324 (95)	0	2534 (73)	0
	56942 (26)	25000	60268 (35)		4216 (59)	7291 (79)	6520 (72)	0	2589 (62)	0
	-5.5		-1.9		-0.5	-2.2	-1.6		-0.6	
O(3)	31490 (15)	25000	56563 (16)	0.013 (2)	5243 (84)	5274 (82)	3425 (65)	0	-1752 (63)	0
	31345 (22)	25000	56565 (21)		5344 (62)	5334 (56)	3380 (40)	0	-1640 (45)	0
	5.5		-0.1		-1.0	-0.6	0.6		-1.5	
NH ₄ ⁺	18074 (15)	75000	66618 (17)	0.002 (2)	3254 (72)	3772 (78)	3256 (71)	0	-100 (57)	0
	18103 (14)	75000	66565 (16)		3094 (37)	3577 (42)	3150 (40)	0	-203 (29)	0
	-1.4		2.2		2.0	2.2	1.3		1.6	

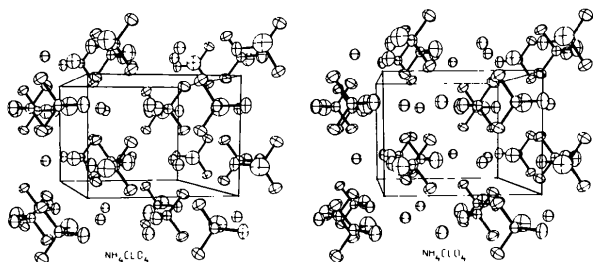


Fig. 2. A stereoscopic ORTEP drawing (Johnson, 1965) of the crystal structure of NH_4ClO_4 . Thermal ellipsoids are scaled to enclose 50% probability. The disordered ammonium ion is drawn as a single atom. *a* is pointing towards the reader and *c* to the left in the plane of the paper.

In a second series of refinements (Table 1, series C), independent deformation functions were centred on each atom. The functions were constrained to the crystallographic site symmetries, resulting in the refinement of 72 deformation parameters. A Hamilton \mathcal{H} test showed that C was significantly better than B, as did the more empirical test suggested by Pawley (1972). The thermal parameters did not differ significantly; the maximum difference was $1.6\sigma_{\text{combined}}$. The *x* coordinate for O(1) changed by 0.005 \AA ($= 4.5\sigma_{\text{combined}}$). Other changes in the coordinates were insignificant. Parameters from C will be used in the following. A δR plot for C is shown in Fig. 1(b). Positional and thermal parameters are given in Table 2.* A

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34189 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

stereoscopic picture of the crystal structure is shown in Fig. 2.

High-order refinement

A high-order (HO) refinement should give the same result as a deformation refinement as far as positional and thermal parameters are concerned. Refinement with 506 reflexions with $\sin \theta/\lambda = 0.70\text{--}0.86 \text{ \AA}^{-1}$ was therefore calculated for comparison (Table 1, series D). Most HO reflexions were rather weak; only one third of the data were stronger than $10\sigma(F_o^2)$. Comparison of the refined parameters from A, C and D reveals the following:

- Significant differences are found for the positional parameters for all O atoms in A and C (Table 2).
- Significant differences are found only for the positional parameters for O(1) in A and D.
- No significant differences are found in C and D.
- The thermal parameters are not significantly different in A, C and D.
- The actual parameter values in D are closer to the conventional refinement than to the deformation refinement except for O(1). This is also seen from the bond distances and angles listed in Table 3. However, the e.s.d.'s in D are 2–5 times larger than in A and C, making most parameters not significantly different.

It is gratifying to note a consistency between the parameters derived from the HO and deformation refinements. However, in view of the large HO standard deviations, this consistency prevails [except for O(1)] in a comparison of the results of the HO and conventional refinements.

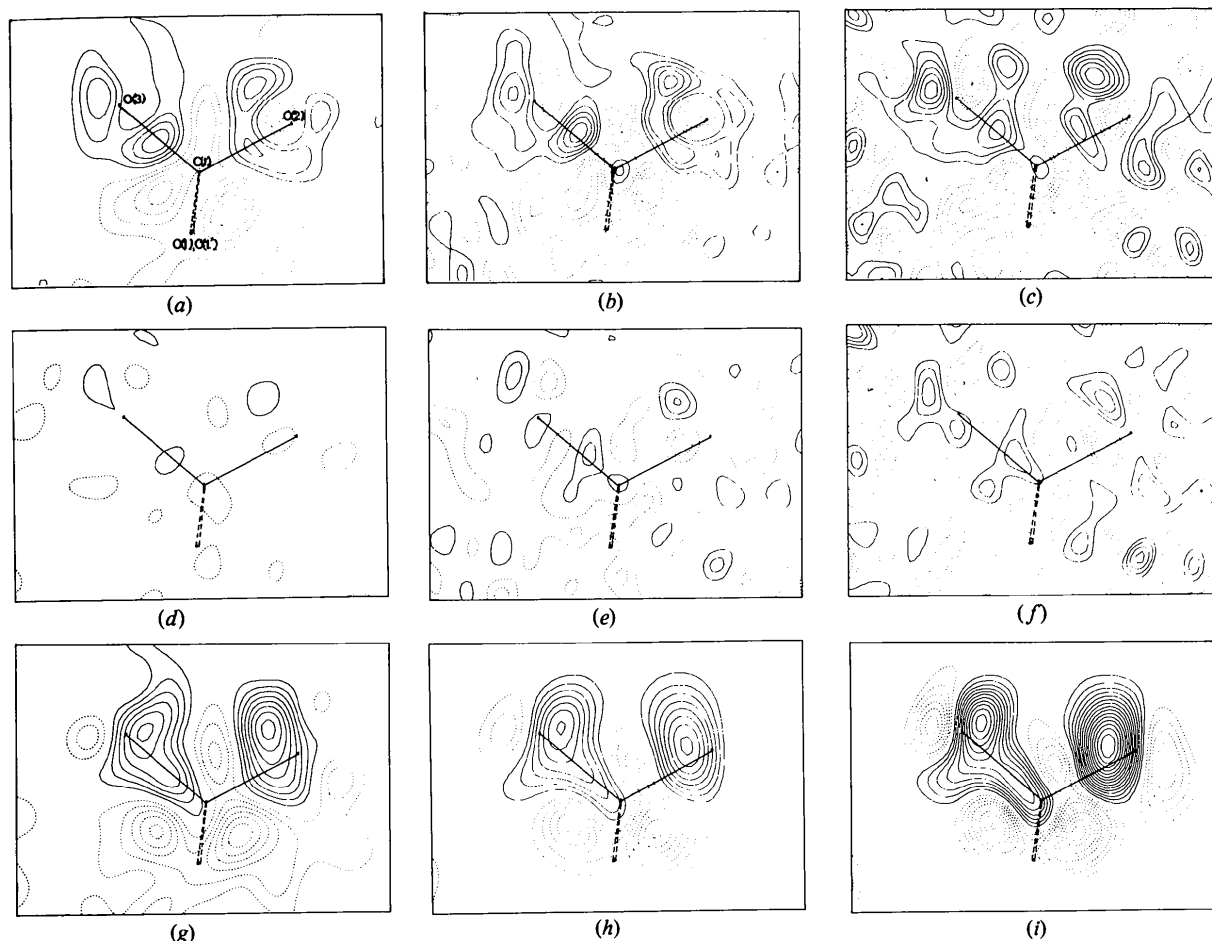


Fig. 3. Residual and model maps. The maps shown are calculated in the plane through Cl, O(2) and O(3). Sections through Cl and other O atoms are very similar. Contours are drawn at intervals of $0.05 e \text{ \AA}^{-3}$. Negative contours are dashed; the zero-level contour is omitted. (a)–(c) Difference densities: parameters from conventional refinement. (a) 543 reflexions with $\sin \theta/\lambda < 0.7 \text{ \AA}^{-1}$ and $F_o^2 > 3\sigma(F_o^2)$, (b) 863 reflexions with $F_o^2 > 3\sigma(F_o^2)$, (c) 1073 reflexions with $F_o^2 > 0$. (d)–(f) Difference densities: parameters from deformation refinement. Data as in (a), (b) and (c), respectively. (g) Difference density: scale factor, positional and thermal parameters from deformation refinement. Deformation functions were not included in the structure factor calculations. Data as in (a). (h) Dynamic model map, i.e. an F_c synthesis calculated with parameters from the deformation refinement, but omitting the spherical free-atom form factors. (i) Static model map, i.e. a plot of the deformation functions. An F_c synthesis as in (h) where all thermal parameters are put equal to zero gives an identical map.

Table 3. Bond distances (Å) and angles (°)

	A	C	D
	A Conventional refinement.		
	C Deformation refinement.		
	D High-order refinement.		
	Values given in square brackets are distances corrected for riding thermal motion.		
Cl–O(1)	1.441 (1) [1.453]	1.453 (1) [1.465]	1.450 (2) [1.462]
Cl–O(2)	1.422 (1) [1.451]	1.431 (2) [1.461]	1.421 (7) [1.452]
Cl–O(3)	1.431 (1) [1.448]	1.443 (2) [1.460]	1.435 (5) [1.452]
O(1)–Cl–O(1)	108.52 (7)	108.11 (10)	108.05 (19)
O(1)–Cl–O(2)	109.76 (5)	109.95 (7)	110.21 (18)
O(1)–Cl–O(3)	108.94 (5)	108.54 (6)	108.70 (14)
O(2)–Cl–O(3)	110.89 (8)	111.68 (13)	110.89 (34)
N...O(1) × 2	2.974 (1)	2.978 (2)	2.981 (3)
N...O(1) × 2	2.993 (1)	2.986 (2)	2.986 (3)
N...O(1) × 2	3.089 (1)	3.078 (2)	3.077 (3)
N...O(2)	3.061 (2)	3.050 (3)	3.054 (7)
N...O(3)	2.979 (2)	2.983 (2)	2.983 (4)

Discussion

The R and s values (Table 1), the δR plots (Fig. 1) and the residual maps [Fig. 3(a) and (d)] all indicate that the deformation model is more successful than the conventional spherical free-atom model in describing the observed structure factors. However, the deformation functions do not merely describe the residual electron densities from the conventional refinement [e.g. Fig. 3(a)]; their inclusion may bring about significant shifts in positional and thermal parameters. In the present case, changes of up to 7σ were observed in the positional parameters, and no significant changes in the thermal parameters (Table 2). The 1% shift in the scale factor is barely significant (3.4σ). Not surprisingly, the

odd ($n = 1, 3$) deformation functions were found to be strongly correlated with the positional parameters (correlation coefficients up to 0.90). The thermal parameters were correlated with the even ($n = 0, 2$) functions.

Some of the peak heights are seen to be increased in maps 3(c) and 3(f), where all high-order reflexions have been included. This increase is the same, however, as the increase in the general noise level. A residual map following a conventional refinement which uses *only* high-order data ($\sin \theta/\lambda > 0.7 \text{ \AA}^{-1}$) is almost identical to 3(f). The deformation refinement thus changes the high-order F_c values very little. The deformation functions were found to give no contribution to F_c for $\sin \theta/\lambda > 0.7 \text{ \AA}^{-1}$. Any changes occurring in these structure factors are therefore a result of changes in positional and thermal parameters in the refinement. If high-order reflexions with $F_o^2 > 3\sigma(F_o^2)$ are added to the low-order reflexions, the residual maps [3(b) and 3(e)] also show a raised noise level.

An error map calculated with the variance-covariance terms for the deformation parameters alone shows rather small errors; a maximum of 0.08 and 0.05 e \AA^{-3} at the nuclear positions of Cl and O, respectively. A detailed analysis of the deformation electron density must clearly include the error contribution from the positional parameters. This has not been done in the present case.

ClO_4^-

The positional parameters obtained for the O atoms from the conventional refinement clearly show the bias introduced by the bonding density. Coordinates for O atoms from the deformation refinement give Cl—O distances $\sim 0.010 \text{ \AA}$ longer than do coordinates from the conventional refinement. A difference map calculated with positional and thermal parameters from the deformation refinement (but *not* including the deformation functions) is shown in Fig. 3(g). This map should be compared with 3(a), where the O atoms have

shifted towards Cl to make the best possible fit to the actual electron density distribution which is centred not exactly at the nuclear positions. The asphericity shifts of the atoms are given in Table 2. The angles Cl—O(conventional)—O(deformation) are 141 (6), 128 (15) and 140 (9)°.

It appears that the electron density maps are very sensitive to changes in atomic positions (*e.g.* Ruysink & Vos, 1974). It is the positional parameters which are responsible for the very different appearances of 3(a) and 3(g). Maps calculated with positional parameters from the conventional refinement, and scale factor and thermal parameters from the deformation refinement have the same general appearance as in 3(a).

No deformation density is observed in the maps [3(h) and 3(i)] in the lone-pair regions of the O atoms.

As a check of the validity of the deformation refinement a rigid-bond test (Hirshfeld, 1976) was applied to the Cl—O bonds (Table 4). This indicated that the relative vibrational motion of the Cl and O atoms is small in the direction of the bond and, even in the conventional refinement, not significantly different from zero. The differences are still smaller, however, in the deformation refinement.

NH_4^+

A map calculated around the ammonium ion indicated very small deviations from spherical symmetry. This can be taken to mean that the model used in the conventional refinement for the disordered H atoms is satisfactory. Some preferred ion orientation would otherwise have been indicated in the deformation model. The eight possible H-bond acceptors are evenly distributed around the ammonium ion at 2.98–3.08 \AA . No choice of four of these atoms can be made to give a tetrahedral arrangement. Some of the H-bonds must therefore be severely bent. This is also observed in the low-temperature neutron study (Choi, Prask & Prince, 1974), where an ordered model was refined. The N—H...O angles are there 180, 159, 138 and 138°.

The formal charge on an atom can be obtained in a deformation refinement by adding the refined values of the coefficients of the even deformation functions centred on that atom. As the deformation functions on neighbouring atoms often overlap (less if Gaussian-type functions, more if Slater-type functions are used) and the coefficients are dependent on the model chosen, the calculated charge for a particular atom has often no physical meaning. The charge on a molecule should, however, be less sensitive to the model. In the present case the refinement gives the reasonable charges ± 0.90 (2) for NH_4^+ and ClO_4^- . The corresponding charges calculated from parameters obtained from *B*, where the model was somewhat different, were virtually identical: ± 0.89 (2).

Table 4. *R.m.s. components (\AA) of thermal motion of Cl and O along Cl—O bonds*

		(a) Conventional refinement.		
		(b) Deformation refinement.		
$Z_{A,B}$ is the r.m.s. component of <i>A</i> in the direction of <i>B</i> .		Cl—O(1)	Cl—O(2)	Cl—O(3)
(a)	$Z_{\text{Cl,O}}$	0.1680 (4)	0.1650 (6)	0.1689 (6)
	$Z_{\text{O,Cl}}$	0.1644 (15)	0.1593 (28)	0.1650 (25)
	Δ	0.0036 (16)	0.0057 (29)	0.0039 (26)
(b)	$Z_{\text{Cl,O}}$	0.1671 (3)	0.1640 (4)	0.1678 (4)
	$Z_{\text{O,Cl}}$	0.1669 (10)	0.1607 (22)	0.1700 (17)
	Δ	0.0002 (10)	0.0033 (22)	−0.0022 (17)

Comparison with previous results

In the three-dimensional X-ray study of Peyronel & Pignedoli (1975) (PP), the structure solution and refinements were made in the space group $Pna2_1$. However, the resulting model showed very small deviations from $Pnma$. Choi, Prask & Prince (1976) showed that, with PP's data, the structure could be refined successfully in $Pnma$, in agreement with the neutron diffraction results. The positional parameters from the present conventional refinement and those obtained by Choi, Prask & Prince are in complete agreement. The maximum difference ($3 \cdot 2\sigma$) is found for the z coordinate of N. This difference may well be explained by the different models used for the disordered H atoms. The thermal parameters are also in agreement except for the U_{33} components, which are all three times larger in the refinement with the PP data. The explanation for this is most likely to be found in the data collection or in the refinements made by PP, where a systematic error was probably introduced into the four-circle diffractometer data since 'the scale factors (K) for each hkl layer were refined'.

In the neutron diffraction study of Choi, Prask & Prince (1974), data were collected at 298, 78 and 10 K. A difference synthesis from the 298 K data gave four clearly localized minima around the N atom for the H positions. The structure refinement would not converge, however, due to the extreme thermal motion of the H atoms. No room-temperature neutron data are thus available for comparison.

Acta Cryst. (1979). **B35**, 1033–1038

A Neutron Diffraction Study of Ammonium Hexachlororhenate

By E. J. LISHER,* N. COWLAM AND L. GILLOTT

Department of Physics, The Hicks Building, The University, Sheffield S3 7RH, England

(Received 7 November 1978; accepted 2 February 1979)

Abstract

The structure of ammonium hexachlororhenate, $(\text{NH}_4)_2\text{ReCl}_6$, has been determined by means of neutron diffraction measurements on powder samples held at room temperature and 4.2 K and analysed using the Rietveld profile-refinement method. The H atoms exhibit the same type of threefold disorder about [111] that has been found in $(\text{NH}_4)_2\text{SiF}_6$, but the

- ### References
- ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* **A27**, 157–165.
 CHOI, C. S., PRASK, H. J. & PRINCE, E. (1974). *J. Chem. Phys.* **61**, 3523–3529.
 CHOI, C. S., PRASK, H. J. & PRINCE, E. (1976). *Acta Cryst.* **B32**, 2919–2920.
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
 HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.
 HAREL, M. & HIRSHFELD, F. L. (1975). *Acta Cryst.* **B31**, 162–172.
 HIRSHFELD, F. L. (1976). *Acta Cryst.* **A32**, 239–244.
 HIRSHFELD, F. L. (1977). *Isr. J. Chem.* **16**, 226–229.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 JOHNSON, C. K. (1970). In *Thermal Neutron Diffraction*, edited by B. T. M. WILLIS. Oxford Univ. Press.
 LUNDGREN, J.-O. (1976). *Crystallographic Computer Programs*. Report UUIC-B13-4-03. Inst. of Chemistry, Univ. of Uppsala, Sweden.
 LUNDGREN, J.-O. & LIMINGA, R. (1979). *Acta Cryst.* **B35**, 1023–1027.
 PAWLEY, G. S. (1972). *Adv. Struct. Res. Diffr. Methods*, **4**, 1–64.
 PEYRONEL, G. & PIGNEDOLI, A. (1975). *Acta Cryst.* **B31**, 2052–2056.
 RUISSINK, A. F. J. & VOS, A. (1974). *Acta Cryst.* **A30**, 503–506.
 SMITH, H. G. & LEVY, H. A. (1962). *Acta Cryst.* **15**, 1201–1204.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

ammonium tetrahedron is orientated in the opposite sense. Additional neutron powder measurements have shown that there is no observable co-operative magnetic alignment of the Re atoms for sample temperatures down to 1.8 K.

1. Introduction

A number of salts of rhenium, iridium and platinum, $X_2\text{Re}Y_6$, $X_2\text{Ir}Y_6$, $X_2\text{Pt}Y_6$, where X is K or NH_4 and Y is Cl or Br, comprise a family of isomorphous

* Now at SRC, Appleton Laboratory, Ditton Park, Slough SL3 9JX, England.