

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

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

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.
 RUYSSINK, 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

©1979 International Union of Crystallography

compounds having a cubic space group ($Fm\bar{3}m$) and a large unit cell, $a_0 \approx 10$ Å. Interest in the magnetic properties of these compounds arises from the fact that the magnetic atoms form a f.c.c. array with clearly defined exchange paths, and also from the possibility of making direct comparisons between similar examples such as $(\text{NH}_4)_2\text{IrCl}_6$ and K_2IrCl_6 (Cooke, Lazenby, McKim, Owen & Wolf, 1959). It is possible to predict the type of antiferromagnetic order from values of the exchange interactions deduced from spin-resonance experiments (Griffiths, Owen, Park & Partridge, 1959; Harris & Owen, 1965) and for K_2ReCl_6 , K_2ReBr_6 and K_2IrCl_6 (Smith & Bacon, 1966; Hutchings & Windsor, 1967; Minkiewicz, Shirane, Frazer, Wheeler & Dorian, 1968) neutron diffraction experiments have established the ordered magnetic structures directly.

The close relationship between the magnetic properties of the $5d$ elements and the chemical bonding, specifically the transfer of appreciable magnetic moment from the $5d$ element on to the neighbouring octahedron of halogens, was established by ESR experiments (Owen & Stevens, 1953). In the earlier neutron diffraction experiments, it was not possible to measure these covalency effects accurately, but experiments with higher neutron fluxes (Lynn, Shirane & Blume, 1976) have been more successful. This latter study on K_2IrCl_6 , together with recent measurements on K_2ReCl_6 – K_2ReBr_6 solid solutions (Hauck & Rossler, 1977) and work in progress on K_2ReCl_6 (Forsyth & Wedgwood, 1977), suggested to us that it would be appropriate to make a neutron diffraction study of $(\text{NH}_4)_2\text{ReCl}_6$, which is being examined in this department by other techniques.

Preliminary measurements of the magnetic susceptibility of $(\text{NH}_4)_2\text{ReCl}_6$ have shown that it exhibits Curie–Weiss behaviour down to at least 40 K with a paramagnetic Néel temperature θ determined by extrapolation to be -80 K and $P_{\text{eff}} = 3.64\mu_B$, which is slightly smaller than the spin-only value ($S = \frac{3}{2}$) for the Re^{4+} ion, namely $3.87\mu_B$. Below 30 K the experimental uncertainties in the measurements were large,

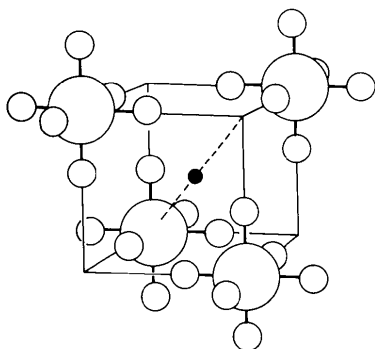


Fig. 1. One eighth of the unit cell of $(\text{NH}_4)_2\text{ReCl}_6$ showing the octahedron of Cl atoms surrounding the Re atom, and the central N atom of the ammonium group.

but there was a suggestion of a peak in the graph of χ vs T around 25 K. It was difficult to deduce a Néel temperature from these data, and this was also complicated by the fact that these compounds show a region of temperature-independent susceptibility above T_N (Cooke *et al.*, 1959). A value for T_N may be estimated, however, from the values of θ/T_N determined for the isomorphous compounds. For K_2ReCl_6 and K_2ReBr_6 , $\theta/T_N \approx 10$ (Busey & Sonder, 1961) and for K_2IrCl_6 and $(\text{NH}_4)_2\text{IrCl}_6$, $\theta/T_N \approx 5$ (Cooke *et al.*, 1959). On this basis T_N for $(\text{NH}_4)_2\text{ReCl}_6$ is estimated to be between 8 and 16 K. In the present study, X-ray and neutron diffraction experiments were undertaken on powder samples to establish details of the atomic and magnetic order.

2. The atomic structure

The structure of this family of salts was first deduced by Wyckoff & Posnjak (1921). The $5d$ element lies on the $4(a)$ sites of the $Fm\bar{3}m$ (O_h^5) space group, surrounded by an octahedron of halogen atoms in the $24(e)$ positions with coordinates $(x,0,0)$ and with $x \approx 0.24$. The N atoms occupy the $8(c)$ ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) sites, as shown in Fig. 1, and the H atoms (by implication) the $32(f)$ (x,x,x) sites. Neutron diffraction experiments on the isomorphous $(\text{NH}_4)_2\text{SiF}_6$ by Schlemper, Hamilton & Rush (1966) have provided information on the orientation and the thermal motion of the ammonium group, and similar models of ordering have been used in this structural refinement of $(\text{NH}_4)_2\text{ReCl}_6$.

2.1. Room-temperature measurements

The neutron diffraction pattern of a 125 μm powder sample of $(\text{NH}_4)_2\text{ReCl}_6$ rotated in a vanadium can at room temperature is shown in Fig. 2. This pattern was obtained using the Curran diffractometer in the Dido Reactor (25 MW) at AERE Harwell. The angular range covered was $10^\circ < 2\theta < 100^\circ$, with a counter

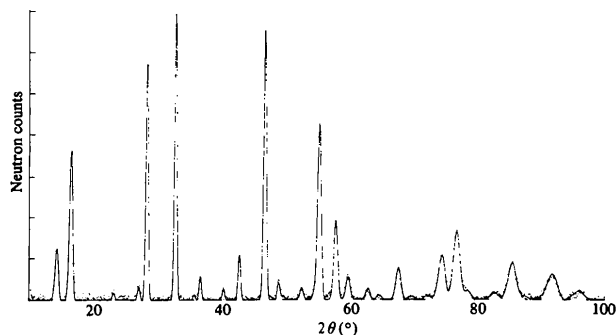


Fig. 2. The neutron diffraction pattern of a 125 μm powder specimen of $(\text{NH}_4)_2\text{ReCl}_6$ rotated in a vanadium can at room temperature, with the profile fitted by the EDINP program. A background level has been subtracted from the neutron counts. Neutron wavelength $\lambda = 1.3687$ Å.

step length of 0.10° in 2θ , and a total run time of 36 h. In this experiment, the incoherent background scattering, which has been subtracted from the powder pattern in Fig. 2, was high due to the large proportion of H in the sample. This background, and the high B factors of the H atoms, considerably reduced the average peak/background ratio, especially at large 2θ . Another effect of the H content was the significant absorption coefficient μ for thermal neutrons. This was corrected for indirectly by introducing an overall negative B factor of -1.0 \AA^2 into the refinement since the uncertainty in the incoherent cross-section for H makes an absolute determination of μ difficult.

Fig. 2 shows that while the Bragg peaks are well resolved at low angles, there is considerable overlap at the higher angles due to the relatively poor resolution of the instrument. In order to obtain the information on the anharmonic and anisotropic thermal vibrations contained in the high-angle data, it was decided to use the profile-refinement method in the analysis. A recent powder-refinement project on alumina (Hewat, 1978) has shown that reliable thermal parameters may be obtained from the profile-refinement technique. The program *EDINP* (Pawley, Mackenzie & Dietrich, 1977) was used throughout the present refinements.

It can be seen from Fig. 1 that the ammonium tetrahedron may be placed in two similar positions with its axis along $[111]$, but with either the base or the apex towards the origin. The H atoms occupy the $32(f)$ positions with $x \simeq 0.19$ and $x \simeq 0.31$, respectively. In the analysis of the low-temperature data (§ 2.2), it was found that the H atoms show a marked preference for the site at $x \simeq 0.19$. This tendency was confirmed in refinement of the room-temperature data, the R factors corresponding to the two sites being 11% and 27%, respectively. The models of H disorder discussed below are therefore based on an ammonium tetrahedron orientated with its apex toward the origin and the corners pointing to the unoccupied corners of the one-eighth cell shown in Fig. 1, rather than to the corners occupied by the Re atoms. The orientation of the ammonium group in $(\text{NH}_4)_2\text{ReCl}_6$ is thus the opposite of that observed in $(\text{NH}_4)_2\text{SiF}_6$ by Schlemper *et al.* (1966).

Following these authors, two models were used to test for hydrogen disorder. In the first, $\frac{1}{3}\text{H}$ was placed in each of the $96(k)$ positions with coordinates (x, x, z) and the final values were $x_{\text{H}} = 0.3183$, $z_{\text{H}} = 0.2636$, $x_{\text{Cl}} = 0.2379$, and $R = 11.2\%$. In the second model $\frac{1}{6}\text{H}$ atom was placed in each of the $192(l)$ general positions and this gave $x_{\text{H}} = 0.2650$, $y_{\text{H}} = 0.2981$ and $z_{\text{H}} = 0.3356$, $x_{\text{Cl}} = 0.2378$ and $R = 11.0\%$, and the other parameters in both models are shown in Table 1. It was considered that the threefold disorder model was adequate to describe the results. This model was preferred by Schlemper *et al.* (1966) since it assigns the same number of H atoms (12) as there are Cl atoms equidistant from a given central nitrogen, and this is, of course, independent of the orientation of the NH_4 group. A difference Fourier map was computed to check the expected threefold disorder of the H atoms about $[111]$. The general form of the H atom scattering density in a plane perpendicular to $[111]$ was found to be similar to that observed for $(\text{NH}_4)_2\text{SiF}_6$ (Schlemper *et al.*, 1966), but the lozenge shape was less well defined on account of the lower resolution obtained from the powder measurements. Any error in the negative overall B factor applied to correct for absorption will cause errors in the absolute values of the thermal parameters given in Table 1. However, the relative values are unaffected and, in fact, comparison of the thermal parameters given here for N with the equivalent values determined for $(\text{NH}_4)_2\text{SiF}_6$ shows remarkably good agreement between powder and single-crystal results. The H–H distance, 0.77 \AA , obtained from the refinement is also in good agreement with the value of 0.75 \AA found for $(\text{NH}_4)_2\text{SiF}_6$.

It was necessary to determine an absolute value of cell dimension a_0 in order to derive the bond distances from the positional parameters given in Table 1. Such a value cannot be obtained from neutron diffraction experiments unless a separate measurement of the neutron wavelength is made (Bacon & Cowlam, 1974) and, in any case, the value obtained is influenced by systematic variations in (both) experiments (Bacon, Cowlam & Self, 1977). A value of a_0 was, therefore, measured independently from Debye–Scherrer photo-

Table 1. Structural and thermal parameters for $(\text{NH}_4)_2\text{ReCl}_6$ for the room-temperature data, where the temperature factors are of the form

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

Model	R value (%)	Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Threefold disorder	11.2	Re	0.0	0.0	0.0	0.00356 (30)	0.00356 (30)	0.00356 (30)	0.0	0.0	0.0
		N	0.25	0.25	0.25	0.00754 (33)	0.00754 (33)	0.00754 (33)	0.0	0.0	0.0
		Cl	0.2379 (3)	0.0	0.0	0.00444 (50)	0.00772 (38)	0.00772 (38)	0.0	0.0	0.0
		H	0.3183 (7)	0.3183 (7)	0.2636 (14)	0.01325 (93)	0.01325 (93)	0.01325 (93)	0.01209 (200)	0.00025 (120)	0.00025 (120)
Sixfold disorder	11.0	Re	0.0	0.0	0.0	0.00353 (25)	0.00353 (25)	0.00353 (25)	0.0	0.0	0.0
		N	0.25	0.25	0.25	0.00785 (35)	0.00785 (35)	0.00785 (35)	0.0	0.0	0.0
		Cl	0.2378 (3)	0.0	0.0	0.00421 (50)	0.00780 (35)	0.00780 (35)	0.0	0.0	0.0
		H	0.2650 (18)	0.2981 (19)	0.3356 (9)	0.01514 (156)	0.01267 (222)	0.00353 (106)	0.00086 (96)	-0.00368 (222)	-0.00119 (161)

graphs using Cu $K\alpha$ radiation. The values calculated were found to be strongly dependent on Bragg angle (see Fig. 3), principally on account of the high linear absorption coefficient of the specimen ($\mu = 37.8 \text{ mm}^{-1}$). Bragg peaks, indexing up to $h^2 + k^2 + l^2 = 164$, were observed and great care was necessary to avoid the indexing becoming 'out of step' at those high angles where the $K\alpha_1, K\alpha_2$ splitting was large. A reliable set of values of a_0 was obtained (Fig. 3), from which a value $9.9265 \pm 0.0005 \text{ \AA}$ at 293 K was derived by extrapolation methods (Nelson & Riley, 1945; Cowlam & Gillott, 1974). The profile-refinement results were normalized to this value to provide the values of bond distances discussed later.

2.2. Low-temperature measurements

The aim of the experiments at low temperature was to investigate antiferromagnetic ordering of the Re atoms. The first experiment was performed on the Curran diffractometer with the specimen at 4.2 K. No magnetic ordering was observed and this was also the case in subsequent experiments made on the Badger spectrometer, Dido reactor, for sample temperatures down to 1.8 K.

The data at 4.2 K, over the angular range $5^\circ < 2\theta < 55^\circ$, in steps of 0.10° , were again analysed using the program *EDINP*. Initially, two possible models were considered. The first model concerned the orientation of the ammonium tetrahedron, as described in § 2.1, and the second model allowed for a distortion of the ReCl_6 octahedron. These refinements were undertaken because it was found that the H—Cl distances for the

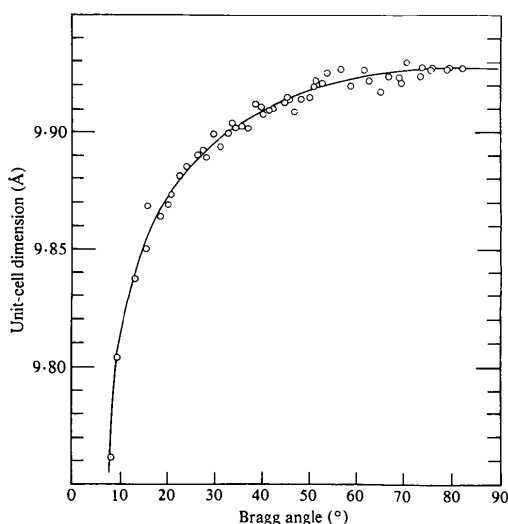


Fig. 3. The apparent variation of unit-cell dimension with Bragg angle for a powder specimen of $(\text{NH}_4)_2\text{ReCl}_6$, obtained using a Debye-Scherrer camera, Cu $K\alpha$ radiation.

two orientations of the ammonium group were very similar (to within 0.3%). Furthermore, these distances could be equalized by allowing a distortion of the ReCl_6 octahedron. Smith & Bacon (1966) had found a displacement of the Cl atoms from $(x, 0, 0)$ to (x, ϵ, ϵ) with $\epsilon \approx 0.012$, in the case of K_2ReCl_6 . In the refinement, therefore, the least-squares routine was constrained. Two sites ($x_{\text{H}}, x_{\text{H}}, x_{\text{H}}$) with $x_{\text{H}1} = 0.25 + X_{\text{H}}$ and $x_{\text{H}2} = 0.25 - X_{\text{H}}$ were specified, and the effective occupation of the two orientations of the ammonium group was determined by refining the scattering lengths on these two sites. The parameters $x_{\text{H}}, x_{\text{Cl}}$, the unit-cell parameter and the instrument parameters were also allowed to vary and the values obtained were: scattering length for site $x_{\text{H}1}$ ($= 0.25 + X_{\text{H}}$) $= -0.351 \pm 0.024 \times 10^{-11} \text{ mm}$; scattering length for site $x_{\text{H}2}$ ($= 0.25 - X_{\text{H}}$) $= -0.029 \pm 0.016 \times 10^{-11} \text{ mm}$; $X_{\text{H}} = 0.0598 \pm 0.0015$.

The hydrogen scattering length on the site $x_{\text{H}2}$ is less than two standard deviations, while that on the site $x_{\text{H}1}$ shows that the occupancy of this site is at least 93%. Possible correlations between the scattering lengths and thermal parameters makes it extremely difficult to ascertain the significance of the small occupancy of site $x_{\text{H}2}$ (<7%). Measurements on deuterated samples would help resolve this point.

No evidence of any distortion of the octahedron was found in the present work, since a refinement of the Cl atoms in the positions (x, ϵ, ϵ) gave a value of ϵ which was within a standard deviation of zero. The value of ϵ which would give equal H—Cl distances ($\epsilon = 0.0035$) is, however, much smaller than that observed for K_2ReCl_6 , and is sufficiently small to be correlated with the thermal parameter of the Cl atom. Since the refinement establishes a strong preference for the orientation of the NH_4 group, the exact equivalence of these H—Cl bonds is probably not of fundamental importance.

Two further refinements were undertaken to test for any evidence of H atom disorder in the 4.2 K data. Firstly, the H atoms were placed in the $32(f)$ positions, representing a static configuration with no disorder, and the final results of this refinement are presented in Table 2. A threefold model for disorder was then tested by placing $\frac{1}{3}\text{H}$ in each of the $96(k)$ positions with coordinates (x, x, z) . This model gave values $x_{\text{H}} = 0.3197$ and $z_{\text{H}} = 0.2838$, but the R value was not significantly different from that obtained in the previous

Table 2. Structural and temperature parameters for $(\text{NH}_4)_2\text{ReCl}_6$ for the 4.2 K data

Model	R factor (%)	Atom	x	y	z	B (\AA^2)
Static (NH_4) group	15.1	Re	0	0	0	0.3 (1)
		N	0.25	0.25	0.25	0.3 (1)
		Cl	0.2412 (6)	0	0	0.3 (1)
		H	0.3072 (9)	0.3072 (9)	0.3072 (9)	1.3 (2)

case and, hence, it was concluded that no H disorder could be detected at 4.2 K.

In the experiments at lower temperatures the specimen, in a vanadium can, was immersed in liquid helium in a cryostat with a vanadium tail. The temperature was adjusted by pumping over the helium surface, and measured by means of the helium vapour pressure. The scans were made over the smaller angular range within which antiferromagnetic superlattice peaks were expected. The two examples $T = 1.8$ K and $T = 3.0$ K, shown in Fig. 4, took approximately 36 h each to record (15 min per point). The nuclear (111) and (200) peaks are shown in these diagrams – there are no detectable non-nuclear peaks, and no statistical difference between the ratio of intensities of the nuclear peaks at the two temperatures. The only difference between the two scans is in the height and slope of the background. This background has contributions from the cryostat, helium and specimen, which was removed between scans to allow the helium to be replenished. The high background makes detection of small magnetic superlattice peaks difficult, but on the assumption that any magnetic peak must be smaller than 2σ of the background, we can estimate the smallest detectable value of moment on the Re atom at $\sim 1.6\mu_B$, in comparison with the larger value ($3.64\mu_B$) indicated by susceptibility measurements. Thus we conclude that the neutron diffraction experiments indicate an absence of magnetic order down to at least 1.8 K.

3. Discussion

Since the critical factors in the analysis of the magnetic interactions are the nearest and next-nearest neighbour distances, it is important that the structure should be known to a reasonable degree of accuracy, especially at low temperatures when the magnetic transitions occur. Unfortunately, in this family of compounds, X_2MY_6 , very little structural work has been undertaken at low temperature and many of the measurements were made before the advent of diffractometers and computers.

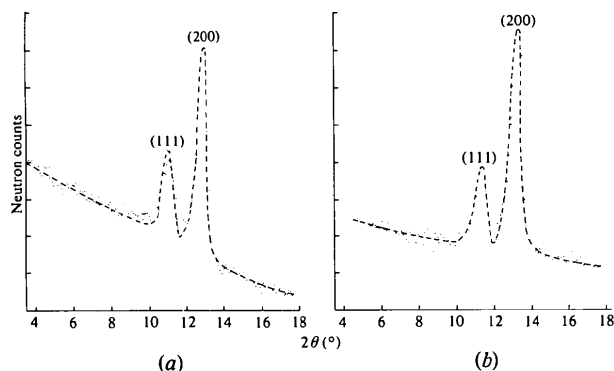


Fig. 4. The low-angle part of the neutron diffraction pattern of $(\text{NH}_4)_2\text{ReCl}_6$ held at (a) 1.8 ± 0.5 K and (b) 3.0 ± 0.5 K.

Hence the following discussion is limited by the inadequacy of the published data on the other materials. The metal–metal ($M-M$) distance is too large for direct exchange and thus the first-nearest neighbour exchange distance is of the form $M-Y-Y-M$ and the second-nearest neighbour is $M-Y-Y-M$ along the cube edge. In the case of the salts $(\text{NH}_4)_2\text{MCl}_6$ and K_2MCl_6 , where M is rhenium and iridium, the cell distance is larger for the ammonium salt by $\sim 1\%$. The Néel temperature is reduced by approximately 30% (3.05 to 2.16 K) in $(\text{NH}_4)_2\text{IrCl}_6$ and, on this basis, T_N for $(\text{NH}_4)_2\text{ReCl}_6$ would be estimated at ~ 8 K as suggested in § 1. On the other hand, if a small aligned moment – below the levels of our detection – occurred (*i.e.* moment $< 1.6\mu_B$), the material might behave magnetically like the iridium salt. A comparison of the exchange paths in K_2IrCl_6 , $(\text{NH}_4)_2\text{IrCl}_6$ and $(\text{NH}_4)_2\text{ReCl}_6$ (Table 3) then gives a value of $T_N \simeq 1.5$ K for the last, which is slightly below the temperature reached in our experiments. Since this would seem to require an unacceptably large suppression of moment from the paramagnetic state, it is perhaps important to consider the role of the H–Cl bonding. If the apex of the tetrahedron points towards (000), as is the case in $(\text{NH}_4)_2\text{SiF}_6$, the H atoms have little effect on the nearest-neighbour $M-Y-Y-M$ paths since their nearest-neighbour Cl atoms are both situated near the same Re. If, however, the apex points toward $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, as in $(\text{NH}_4)_2\text{ReCl}_6$, then the H atoms are equidistant from the two Cl atoms in the Re–Cl–Cl–Re exchange path and they may have an effect on the exchange interaction. The orientation of the ammonium tetrahedron cannot be affected by the H–Cl bond lengths for the two orientations since, as discussed above, these are very similar: H–Cl = 2.56 Å with apex toward (000)

Table 3. Exchange paths in the compounds X_2MY_6

	Positional parameter for Cl ($x_{\text{Cl}}, 0, 0$)	Exchange paths (Å)	
		Nearest neighbour $M-\text{Cl}-\text{Cl}-M$	Next-nearest neighbour $M-\text{Cl}-\text{Cl}-M$ (unit-cell dimension)
$(\text{NH}_4)_2\text{ReCl}_6$	0.2378 (3)	8.402 (10)	9.9265 (5)
K_2ReCl_6	0.240	8.358	9.86
$(\text{NH}_4)_2\text{IrCl}_6$	0.25	8.425	9.87
K_2IrCl_6	0.240	8.277	9.764

Table 4. Bond lengths (Å) in $(\text{NH}_4)_2\text{ReCl}_6$ at room temperature

Re–Cl	2.361 (3)	N–Cl	3.512 (1)
Re–N	4.298 (2)	H–Cl	2.563 (6)
N–H	0.968 (12)	N–H...Cl	166.3 (4)°
H–H	0.768 (30)		

and $H-Cl = 2.55 \text{ \AA}$ with apex toward $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. It is then remarkable that the refinements show quite clearly that one of these two orientations is strongly preferred. We feel that a more comprehensive neutron diffraction investigation of the ammonium-based salts, particularly using deuterated specimens, may be able to provide information on this aspect of the structure.

Table 4 lists the bond lengths at room temperature.

We wish to thank Dr E. A. Harris for providing the powder sample and Dr J. B. Dunlop for making the susceptibility measurements. Financial assistance from the Science Research Council, and the help of the University Support Group at AERE, Harwell, are gratefully acknowledged. We would also like to thank Professor G. E. Bacon for his interest and encouragement throughout this investigation.

References

- BACON, G. E. & COWLAM, N. (1974). *Acta Cryst.* A **30**, 467–469.
- BACON, G. E., COWLAM, N. & SELF, A. G. (1977). *Acta Cryst.* A **33**, 46–49.
- BUSEY, R. H. & SONDER, E. (1961). *J. Chem. Phys.* **36**, 93–97.
- COOKE, A. H., LAZENBY, R., MCKIM, F. R., OWEN, J. & WOLF, W. P. (1959). *Proc. R. Soc. London Ser. A*, **250**, 97–109.
- COWLAM, N. & GILLOTT, L. (1974). *J. Phys. E*, **7**, 725–728.
- FORSYTH, J. B. & WEDGWOOD, F. A. (1977). *Ann. Rep. Inst. Laue–Langevin, Grenoble*, p. 177.
- GRIFFITHS, J. H. E., OWEN, J., PARK, J. G. & PARTRIDGE, M. F. (1959). *Proc. R. Soc. London Ser. A*, **250**, 84–96.
- HARRIS, E. A. & OWEN, J. (1965). *Proc. R. Soc. London Ser. A*, **289**, 122–139.
- HAUCK, J. & ROSSLER, K. (1977). *Acta Cryst.* B **33**, 2124–2128.
- HEWAT, A. W. (1978). Paper presented at the Conference on Profile Refinement, Kraków, Poland.
- HUTCHINGS, M. T. & WINDSOR, C. G. (1967). *Proc. Phys. Soc. London*, **91**, 928–932.
- LYNN, J. W., SHIRANE, G. & BLUME, M. (1976). *Phys. Rev. Lett.* **37**, 154–157.
- MINKIEWICZ, V. J., SHIRANE, G., FRAZER, B. C., WHEELER, R. G. & DORIAN, P. B. (1968). *J. Phys. Chem. Solids*, **29**, 881–884.
- NELSON, J. B. & RILEY, D. P. (1945). *Proc. Phys. Soc. London*, **57**, 160–177.
- OWEN, J. & STEVENS, K. W. H. (1953). *Nature (London)*, **171**, 836.
- PAWLEY, G. S., MACKENZIE, G. A. & DIETRICH, O. W. (1977). *Acta Cryst.* A **33**, 142–145.
- SCHLEMPER, E. O., HAMILTON, W. C. & RUSH, J. J. (1966). *J. Chem. Phys.* **44**, 2499–2505.
- SMITH, H. G. & BACON, G. E. (1966). *J. Appl. Phys.* **37**, 979–980.
- WYCKOFF, R. W. G. & POSNJAK, E. W. (1921). *J. Am. Chem. Soc.* **43**, 2292–2309.

Acta Cryst. (1979). B **35**, 1038–1041

The Crystal Structure of Phase II Ammonium Nitrate

BY B. W. LUCAS

Department of Physics, University of Queensland, St Lucia, Brisbane, Queensland 4067, Australia

M. AHTEE

Department of Physics, University of Helsinki, Siltravuorenpenger 20D, 00170 Helsinki, Finland

AND A. W. HEWAT

Institute Laue–Langevin, avenue des Martyrs, BP 156X, Centre de Tri, 38042 Grenoble CEDEX, France

(Received 4 December 1978; accepted 18 January 1979)

Abstract

On heating dry (without occluded water) ammonium nitrate at atmospheric pressure, a solid-state phase transformation occurs from phase IV to phase II at 328 K. Neutron powder diffractometer data of the deuterated compound have been used with the profile-

refinement method to first verify the reported phase IV structure and then determine the structure of phase II. For phase II, the structure is disordered, with tetragonal space group $P4_2m$, $a = 5.7193(1)$, $c = 4.9326(1) \text{ \AA}$, $Z = 2$. The orientations and disorder of the NH_4 and NO_3 ions in this phase have been determined, there being two equivalent alternative positions for each ion.