Table 3. *Interatomic distances and standard error in* $Rh_{17}S_{15}$

Atom	Neighbors	Distance	σ	Analogous $Pd_{17}Se_{15}$ distance
Rh(b)	6 S(f)	2·336 Å	0·016 Å	2·576 Å
Rh(d)	4 S(j)	2·378	0·009	2·527
	2 Rh(e)	2·588	0·007	2·781
Rh(e)	4 S(i)	2·291	0·008	2·438
	1 Rh(d)	2·588	0·007	2·781
	4 Rh(e)	3·348	0·007	3·566
Rh(m)	1 S(i)	2·261	0·010	2·430
	1 S(f)	2·342	0·010	2·492
	2 S(j)	2·349	0·006	2·509
	1 Rh(m)	2·844	0·004	3·184
	2 Rh(m)	2·846	0·003	3·137
	2 Rh(m)	2·984	0·003	3·029
S(f)	4 S(f)	3·304	0·022	3·643
	4 S(j)	3·406	0·012	3·641
	4 Rh(m)	2·342	0·010	2·492
	1 Rh(b)	2·336	0·016	2·576
S(i)	4 S(i)	3·238	0·009	3·445
	4 S(j)	3·210	0·007	3·440
	2 Rh(e)	2·291	0·008	2·438
	2 Rh(m)	2·261	0·010	2·430
S(j)	2 S(f)	3·406	0·012	3·641
	4 S(i)	3·210	0·007	3·440
	2 S(j)	3·362	0·013	3·572
	1 Rh(d)	2·378	0·009	2·527
	4 Rh(m)	2·349	0·006	2·509

examination of the metal–metal distances indicates a possible reason. The three nearest Rh(m)–Rh(m) distances, although 0·16 Å longer than the elementary distances, are relatively considerably shorter than the analogous Pd–Pd distances; the nearest neighbor Pd(m)–Pd(m) distances average 3·15 Å which is 0·40 Å longer than the elementary distance. Thus it appears that in $Rh_{17}S_{15}$ the Rh–Rh bonds are in general stronger than the Pd–Pd bonds in $Pd_{17}Se_{15}$.

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Neutron Diffraction Study of Ammonium Perchlorate

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A neutron diffraction study of single crystals of NH_4ClO_4 at room temperature has indicated that the orientation of the ammonium ion in the crystal is random, and suggests that it is undergoing free or nearly free rotation.

Introduction

A room temperature single crystal study of ammonium perchlorate was undertaken in order to compare the structure of this compound with the 'isomorphous' compound hydronium perchlorate (also under investigation by the authors). A structure comprising an ordered, hydrogen-bonded arrangement of the ammonium ions had been suggested from X-ray

difference Fourier projections by Venkatesan (1957). This arrangement, however, is not consistent with the present neutron data which suggests that the ammonium ion is undergoing essentially free rotation. The recent infra-red (Waddington, 1958), nuclear magnetic resonance (NMR) (Ibers, 1960, and Richards & Schaefer, 1961), heat capacity (Justice & Westrum, 1961) and cold neutron (Rush, Taylor & Havens, 1961) studies strongly support these results. The OH_3ClO_4 neutron diffraction study in which the OH_3^+ ion is disordered, but not rotating, will be reported at a later date.

Experimental

Neutron diffraction intensities for the $(h0l)$ and $(hk0)$ zones were measured on the instrument at the ORNL graphite reactor $(\lambda = 1.062$ Å). The data were corrected for absorption by the method of Busing & Levy (1957b) for crystals of polyhedral shape. The space group and unit cell as determined by X-rays and neutrons are $Pnma$, $Z = 4$, $a = 9.20$, $b = 5.82$, $c = 7.45$ Å, in agreement with previous X-ray results (Swanson & Tatge, 1957; Venkatesan, 1957).

Analysis of the data

The phases of most of the reflections are reliably determined from the contributions of N, O, and Cl; a nuclear density projection onto the (010) plane based on neutron amplitudes and phases derived from parameters for these atoms from the X-ray study (Venkatesan, 1957) is shown in Fig. 1(a). The smeared-out distribution of negative density around the nitrogen peak, the only density attributable to hydrogen, indicates some type of orientational disorder for the ammonium ion. The (001) projection (Fig. 2(a)) shows similar features. Further, an attempt to fit the data by least squares with Venkatesan's (1957) ordered model was unsatisfactory: in particular, the thermal parameters for H tended to unreasonable values indicating very large displacements. Some other ordered models showed similar, unsatisfactory behavior.

A satisfactory fit has been obtained with a model having an isotropic distribution of the hydrogen atoms about the nitrogen position. The contribution of H to this model was of the form

$$(4f_H/4\pi rs)(\sin 4\pi rs) \exp(-B_H s^2) \cos 2\pi r_N . h$$

with $s = (\sin \theta)/\lambda$ and r the N–H distance. A value of $B_H = 0.4$ Å^2, corresponding to the mean square amplitude of a 3400 cm.$^{-1}$ N–H stretching frequency, was used. Calculated nuclear density projections shown in Figs. 1(b) and 2(b) are quite similar to those based on observed data for both zones.
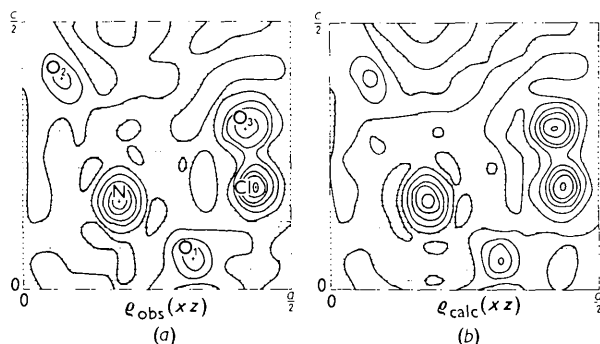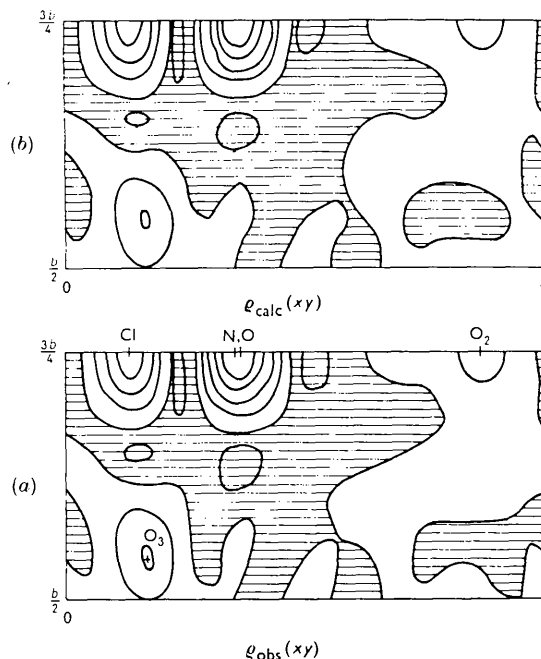

Fig. 2. Nuclear density projection of the [001] zone. The shaded areas represent regions of negative density. (a) Observed density. (b) Calculated density.

A least squares refinement* of the position parameters and the anisotropic thermal parameters of all atoms except H was carried out on the Oracle computer for several fixed values of r, and the fixed value of B_H. (The machine code used did not permit adjustment of r in a simple way.) Equally good fits resulted for $r = 1.03$ and 1.06 Å; a value of 0.97 Å resulted in divergence of the iterative least squares procedure. The refined parameters are listed in Table 1, where the general asymmetric temperature factor was assumed to be of the form

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

The observed and calculated structure factors are listed in Table 2. The weighted R-factor is 0.08, where

$$R = [\Sigma w(F_o - F_c)^2/\Sigma w F_o^2]^{\frac{1}{2}}.$$

The parameters of Table 1 differ somewhat from those of Venkatesan (1957). We have submitted his X-ray data to a least squares refinement, extending the model to anisotropic temperature factors; the resulting position parameters are in good agreement with those of the present study although the thermal

* The weights of the observed structure factors were computed from the expression

$$w(F) = \frac{4C_N^2}{F_o^2[C_N + 2C_B + (0.02C_N)^2]}.$$

Here, F_o is the observed structure factor and w its weight, C_N is the net count (total less background) and C_B is the background count. The justification for this weighting scheme has been discussed elsewhere (Busing & Levy, 1957a).

Fig. 1. Nuclear density projection of the [010] zone. The shaded areas represent regions of negative density. (a) Observed density. (b) Calculated density.

Table 1. *Atomic positions, thermal parameters, and standard deviations*

	Cl	O$_1$	O$_2$	O$_3$	NH$_4$
x	0·432 ± 0·001	0·314 ± 0·002	0·570 ± 0·001	0·418 ± 0·001	0·182 ± 0·001
y	0·250	0·250	0·250	0·053 ± 0·002	0·750
z	0·193 ± 0·001	0·061 ± 0·001	0·107 ± 0·002	0·303 ± 0·001	0·166 ± 0·001
$4a^2\beta_{11}$	1·9 ± 0·2	3·7 ± 0·7	2·7 ± 0·4	3·3 ± 0·3	1·6 ± 0·2
$4b^2\beta_{22}$	1·9 ± 0·4	6·0 ± 3·0	9·5 ± 1·8	2·0 ± 0·4	1·0 ± 0·6
$4c^2\beta_{33}$	2·2 ± 0·2	1·4 ± 0·3	5·6 ± 0·9	2·4 ± 0·2	2·2 ± 0·2
$4ab\beta_{12}$	0	0	0	0	0
$4ac\beta_{13}$	0·4 ± 0·3	0·4 ± 0·5	2·6 ± 0·6	0·4 ± 0·3	0·03 ± 0·3
$4bc\beta_{23}$	0	0	0	*	0

* Not determined from the data.

Table 2. *Observed and calculated structure factors*

hkl	kF_o	F_c	hkl	kF_o	F_c	hkl	kF_o	F_c	hkl	kF_o	F_c
002	4·35	−4·49	403	6·57	−6·43	805	0·67	0·58	210	4·61	4·54
004	2·17	−1·85	404	≤0·67	0·46	806	1·56	−1·44	220	1·16	1·26
006	4·44	4·20	405	5·26	−5·05	807	1·62	−1·97	230	3·40	−3·11
008	5·89	−6·04	406	1·70	−1·61	808	3·14	−3·06	240	≤0·72	−0·66
0,0,10	2·17	1·31	407	4·01	4·68	809	1·48	1·60	250	7·30	7·52
			408	0·77	1·13				260	1·10	−0·30
101	2·87	−2·59	409	2·54	−2·46	902	1·32	1·02	270	≤0·72	−1·92
102	1·03	−0·88	4,0,10	≤0·67	−0·49	903	≤0·67	0·13	280	≤0·72	−1·30
103	1·15	−1·00				904	≤0·67	−9·09			
104	1·40	0·75	501	0·55	0·69	905	≤0·67	0·13	410	2·88	−2·39
105	2·80	2·42	502	3·48	−3·06	906	≤0·67	0·65	420	≤0·72	0·04
106	1·44	−1·06	503	4·13	−3·85	907	1·42	−1·79	430	6·35	6·05
107	1·15	0·68	504	0·87	0·64	908	0·71	1·48	440	2·11	−1·55
108	2·04	−1·88	505	1·21	0·12				450	1·25	1·16
109	≤0·67	−0·06	506	0·76	−0·37	10,0,0	0·65	0·85	460	1·13	1·13
1,0,10	1·87	1·84	507	2·76	2·88	10,0,1	1·89	−1·46	470	1·46	1·79
1,0,11	≤0·67	0·20	508	≤0·67	0·38	10,0,2	≤0·67	−0·27	480	1·14	0·08
			509	0·80	−0·35	10,0,3	2·06	1·96			
200	4·79	4·92	5,0,10	≤0·67	−0·39	10,0,4	0·95	−0·72	610	4·51	4·21
201	5·29	5·61				10,0,5	1·37	−1·60	620	3·36	−2·99
202	3·86	−3·71	600	3·04	−2·89	10,0,6	≤0·67	1·13	630	3·29	−3·56
203	3·08	−2·96	601	≤0·67	−0·15	10,0,7	2·05	−1·42	640	1·12	−0·40
204	1·30	1·39	602	3·37	3·44				650	2·82	2·71
205	3·26	3·28	603	1·46	−1·00	11,0,1	≤0·67	0·67	660	≤0·72	0·64
206	≤0·67	−0·18	604	1·31	−0·97	11,0,2	≤0·67	−0·08	670	1·40	−2·12
207	2·97	2·73	605	1·22	1·70	11,0,3	2·04	−2·26			
208	1·38	−0·60	606	≤0·67	−0·69	11,0,4	1·81	−1·67	810	≤0·72	−0·04
209	3·49	−3·11	607	0·94	0·44	11,0,5	1·69	1·81	820	6·10	6·08
2,0,10	2·44	2·79	609	0·95	−0·84	11,0,6	1·52	1·08	830	1·74	−1·84
2,0,11	1·19	1·50	6,0,10	3·18	−3·19				840	5·90	−5·30
						12,0,0	2·62	3·09	850	1·06	−1·36
301	0·54	0·11	701	1·33	1·55	12,0,1	2·59	−2·43	860	4·38	4·26
302	3·49	3·29	702	5·03	−4·87	12,0,2	1·74	−1·78	870	1·09	−0·96
303	5·04	5·05	703	≤0·67	−0·58	12,0,3	1·71	1·90			
304	0·62	−0·17	704	3·37	3·02	12,0,4	≤0·67	−0·71	10,1,0	3·94	−3·97
305	3·19	−2·56	705	1·40	−1·03	12,0,5	1·55	1·79	10,2,0	1·06	0·54
306	≤0·67	0·18	706	1·61	−1·56				10,3,0	2·33	2·21
307	2·14	−1·69	707	0·47	−0·31	13,0,1	≤0·67	−0·83	10,4,0	≤0·72	0·34
308	0·77	−0·49	708	0·82	−1·15	13,0,2	≤0·67	−0·59	10,5,0	4·21	−4·32
309	≤0·67	0·18	709	≤0·67	−0·06	13,0,3	1·47	1·95	10,6,0	≤0·72	−0·44
3,0,10	≤0·67	−0·20				13,0,4	0·86	−0·83			
3,0,11	1·19	−1·25	800	8·79	−9·37				12,1,0	≤0·72	0·90
			801	3·05	−2·95	020	5·51	−5·76	12,2,0	≤0·72	−0·96
400	3·30	−3·36	802	3·47	3·12	040	9·82	10·43	12,3,0	≤0·72	−0·85
401	6·74	7·41	803	1·61	1·43	060	7·02	−6·80	12,4,0	2·28	1·74
402	2·00	2·08	804	1·43	1·04	080	2·66	1·55			

parameters are less satisfactory. The bond distances and bond angles for the perchlorate ion are

Cl–O$_1$	1·464 ± 0·015 Å	O$_1$–Cl–O$_2$	111·1 ± 1·2°
Cl–O$_2$	1·432 ± 0·014	O$_1$–Cl–O$_3$	108·8 ± 0·5
Cl–O$_3$	1·415 ± 0·011	O$_2$–Cl–O$_3$	109·9 ± 0·6
		O$_3$–Cl–O$_4$	108·1 ± 0·8

The apparent variation in the above Cl–O distances may perhaps be due in part to interactions with the imperfectly described ammonium ion configuration, or to other systematic errors; however, the averaged Cl–O distances (1·43 Å), is in agreement with those distances reported by Truter, Cruickshank & Jeffrey

(1960) for nitronium perchlorate before they have been corrected for thermal motion.

Discussion

The above results indicate that the orientation of the ammonium ion is a highly disordered one, but do not bear directly on the question of whether the disorder is static or dynamic (e.g. a rotating ion). The environment of NH_4^+ in the crystal, namely eight oxygen atoms at 2·94–3·08 Å and four others at 3·25–3·52 Å, (Fig. 3), does not accommodate a static tetrahedral ammonium ion forming four hydrogen bonds to oxygen. An ion undergoing free or nearly free rotation therefore appears likely.
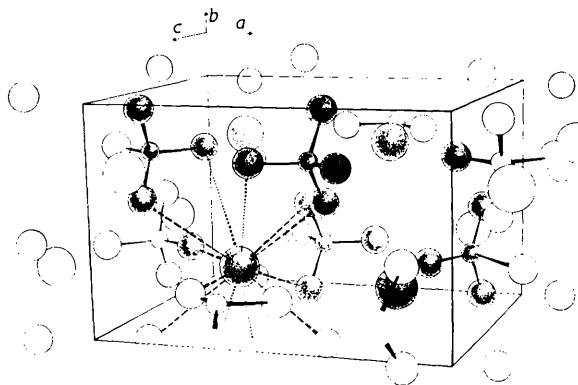

Fig. 3. A perspective view of the atoms in a unit cell of NH_4ClO_4. The largest spheres represent the rotating ammonium ions, the next largest are the oxygen atoms, and the smallest are the chlorine atoms.

A rotating ion is also supported by other evidence. No combination band attributable to torsional oscillation of NH_4^+ has been found in the infra-red spectrum of solid NH_4ClO_4 (Waddington, 1958). In this respect, NH_4ClO_4 resembles NH_4I, for which neutron diffraction (Levy & Peterson, 1953) infra-red (Plumb & Hornig, 1953), and Raman (Couture-Mathieu & Mathieu, 1952) data have indicated single-axis rotation, rather than NH_4Cl and NH_4Br which have been shown to be statistically disordered (Levy & Peterson, 1953b) and to posses the torsional mode (Wagner & Hornig, 1950). An NMR study of the isomorphous compound, NH_4BF_4 (Pendred & Richards, 1955), has indicated a rapid reorientation (frequency greater than $10^5 c/s$) of the ammonium ion at temperatures as low as 20 °K. A recent similar study by Ibers (1960) of NH_4ClO_4 indicates reorientation in this compound at temperatures at least as low as 77 °K. with an activation energy of $2·0 \pm 0·6$ kcal./mole. Ibers predicted a

line width transition between 45° and 55 °K., but Richards & Schaefer (1961) have not observed such a transition at 20 °K. or above, and they estimate the potential barrier to reorientation as less than 1 kcal./mole. Recent measurements of the total neutron cross section of some ammonium salts with very cold neutrons (Rush, Taylor & Havens, 1961) are interpreted to indicate that at room temperature the ammonium ions are rotating in the perchlorate and iodide salts but not in the chloride and bromide salts. Justice & Westrum (1961) have recently reported the results of a heat capacity study of NH_4ClO_4 between 5 and 350 °K. and did not observe any anomalies in the heat capacity curve. They conclude that if random orientation of the NH_4^- ion is to exist at 300 °K. the onset must be a gradual process with increasing temperature and not a cooperative phenomenon.

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