With iodine and chlorine in their standard states of solid and gas, the free energies of formation of the various forms of iodine monochloride as determined by physical chemical methods are as follows: ICl(g), 977 cal.; ICl(l), -867 cal.; ICl(s), -887 cal.

The degree of dissociation of iodine monochloride gas into gaseous iodine and chlorine has the value 0.42% at 25° and 1.58% at 100°.

The entropy of ICl(g) at 25° and one atmosphere is 59.6 cal./deg. (59.2 cal./deg. spectroscopical).

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THE CRYSTAL STRUCTURE OF RHOMBIC AMMONIUM NITRATE

BY C. D. WEST

No x-ray measurements on the rhombic form (IV) of ammonium nitrate have been published other than the three axial lengths. In addition to rounding out the univalent nitrate group, a complete structure is desirable for the interpretation of some of the unusual properties of this compound, such as birefringence, polymorphism and plastic deformation.

Crystallographic.—According to Groth the crystals are of the rhombic bipyramidal class, axial ratios 0.9092 : 1 : 1.0553, density 1.725, optic axial plane (100), acute bisectrix b. Bowen[1] found 2V = 35° and the refractive indices: electric vector parallel to b, $\alpha = 1.41$; parallel to a, $\beta = 1.61$; parallel to c, $\gamma = 1.64$. This form is stable only in the interval -16 to $+32°$.

Methods.—Recrystallization from water at room temperature gave suitable (110) prisms. Molybdenum radiation was employed exclusively; it was filtered in taking powder photographs and a set of 30° oscillation diagrams about the three axes. In a set of Laue patterns with the primary beam nearly parallel to the three axes, the minimum wave length was 0.30 Å. Intensities of reflections were estimated visually. All Miller indices refer to the above axes.

Lattice Constants.—The constants determined from zero lines of accurate rotation photographs are: $a = 4.92_8$, $b = 5.43_4$, $c = 5.73_2$, ratios 0.9069 : 1 : 1.0548, Z = 2, V = 76.7, density = 1.720. The former are identical with Bragg's values to three figures.[2]

Choice of Structure.—The only systematic extinctions noted were for (0kl) when $k + l$ is odd; assuming holohedral symmetry this indicates V_h^{13}. In disposing the atoms in this space-group primary consideration was

[1] N. L. Bowen, *J. Phys. Chem.*, **30**, 722 (1926).

[2] W. H. Bragg, *Trans. Faraday Soc.*, **20**, 59 (1924).

given to intensity data.   It is probable that the nitrate group is a triangle of side 2.10 Å. with the distance between oxygen atoms in different groups greater than 3.2 Å.[3]   It has been shown that some nitrates owe their strong double refraction to the arrangement of the nitrate groups in parallel planes, the ray with the electric vector parallel to these planes being the slower, that with the vector perpendicular to them the faster;   also the molecular birefringence, $R\omega - R\epsilon$, tends to be constant as the metal ion is changed.[4]   Bragg's extended table proves that ammonium nitrate follows this rule;   it is thus to be expected that in it the nitrate planes lie perpendicular to b.

	M/ρ	ω	ϵ	$R\omega$	$R\epsilon$	$R\omega - R\epsilon$
LiNO₃	28.9	1.735	1.435	11.60	7.54	4.06
NaNO₃	37.45	1.587	1.336	12.58	7.75	4.83
KNO₃	47.85	1.506	1.335	14.36	9.90	4.46
NH₄NO₃	46.35	1.625	1.41	16.38	11.48	4.90

There are two orientations of the crystal axes abc in the structure axes XYZ that give the extinctions noted, (A) abc in ZYX and (B) abc in YZX. There are two arrangements which give nitrate groups of the desired configuration;   taking point designations from Wyckoff and indicating ammonium and nitrate nitrogens by Nh and No, respectively, these are (I) Nh in (a), No and O in (b), O in (e) and (II) Nh in (b), No and O in (a), O in (f).   Of the four arrangements IA and IIB have the same structure factor, which is constant for sets of reflections where only l varies by 2; they are excluded by the following sets: 101 absent, 103 vs;   201 vw, 203 vs;   111 vs, 113 w.   Similarly in IB and IIA sets where only k varies by 2 have the same structure factor;   the observed intensities consistently follow this relation through Table I.   IB alone has the too low oxygen–oxygen distance 2.84 Å., depending only on a and the side of the nitrate triangle;   also IIA is more consistent with the abnormal intensity decline of reflections $(h00)$ than IB.   Finally IIA alone has the nitrate planes perpendicular to b.   It was selected and the coördinates rewritten.

Position, V_h^{13}	$k + l$ even	$k + l$ odd
Nh (b) $z^1/_20$, $\bar{z}0^1/_2$	$\pm 2F \cos h2\pi z$ (plus for l even)	$\pm 2F \sin h2\pi z$ (plus for l odd)
No (a) $x00$, $\bar{x}^1/_2{}^1/_2$	$2F \cos h2\pi x$	$2F \sin h2\pi x$
O (a) $y00$, $\bar{y}^1/_2{}^1/_2$	$2F \cos h2\pi y$	$2F \sin h2\pi y$
O (f) $v0u$, $\bar{v}^1/_2{}^1/_2 + u$ $v0\bar{u}$, $\bar{v}^1/_2{}^1/_2 - u$	$4F \cos l2\pi u$, $\cos h2\pi v$	$4F \cos l2\pi u$, $\sin h2\pi v$

Choice of Parameters.—In calculating structure factors F curves for ammonium,[5] nitrogen and oxygen[6] were used.   Since the structure factor

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[3] D. A. Edwards, Z. Krist., **80**, 154 (1931).

[4] W. L. Bragg, Proc. Roy. Soc. (London), A105, 370 (1924);   A106, 346 (1924).

[5] R. W. G. Wyckoff, "The Structure of Crystals," 1931.

[6] R. W. James and G. W. Brindley, Z. Krist., **78**, 470 (1931).

for reflections (0*kl*) depends only on u, their observed intensities offer a check on this parameter, $2cu$ being one side of the nitrate triangle; the value cited showed satisfactory agreement and was retained. It makes the shortest oxygen–oxygen distance independent of x 3.26 Å. Assuming the nitrate triangles are equilateral, only x and z now remain independently
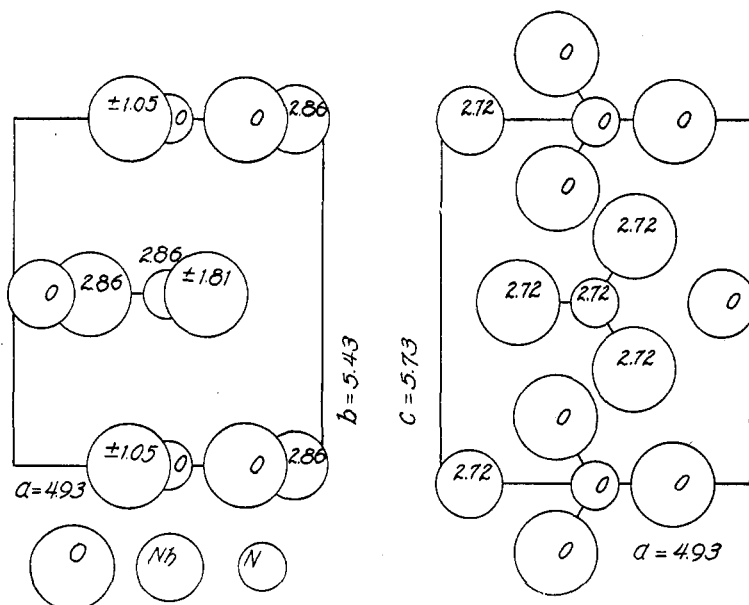

Fig. 1.—Unit cell of ammonium nitrate projected on (001) and (010). The height of each atom is indicated in Ångström units.

variable. The value of x was estimated from the intensities of Laue reflections at large $\sin \vartheta/\lambda$ where F_{Nh} is one-third or less of F_O or F_{No}, and z follows from the intensities of powder and oscillation reflections. The structure factors (F^2) of Table I are calculated for the tabulated values

	Parameters			Distances
u	66°	0.183	1.05 Å.	Nh–No: 3.36, 3.48
x	180	.500	2.47	O–O: 3.08, 3.26, 3.33
y	−90	.750	3.70	Each Nh: 2.96 (two oxygen atoms), 2.96 (two atoms)
v	135	.375	1.85	3.18 (two atoms), 3.21 (two atoms)
z	35	.097	0.48	3.22 (four atoms), average of 12 = 3.13

of the parameters; the disagreements with observed intensities are unsystematic and are not considered prohibitive. The calculated distances are similar to those prevailing in like substances except that the first oxygen–oxygen distance is about 3% below the minimum observed and predicted by Zachariasen.[7]

[7] W. H. Zachariasen, *Z. Krist.*, **80**, 137 (1931).

TABLE I

OBSERVED INTENSITIES OF REFLECTIONS FROM AMMONIUM NITRATE

hkl	$\frac{\sin \vartheta}{\lambda}$	F^2	Intensity Osc.	Intensity Laue	hkl	$\frac{\sin \vartheta}{\lambda}$	F^2	Intensity Osc.	Intensity Laue
020	0.184	665	vs	vs*	033	0.380	0	O	
040	.368	166	s		053	.530	0.2	O	
060	.552	66	m		004	.350	41	s	
011	.127	58	vs	s*	024	.394	32	s	
031	.290	36	s	m*	044	.507	18	m	
051	.468	22	m	m	015	.445	45	s	m
002	.175	54	vs	m*	035	.516	37	m	
022	.254	22	s	m*	006	.524	71	m	
042	.407	8.3	m		026	.554	61	m	
013	.277	30	m		017	.616	7.5		O
100	.101	47	vs	s*	110	.137	2.6	s	O*
120	.210	27	vs	m*	130	.294	0	w	O*
140	.382	19	m		101	.134	2.4	O	O*
111	.162	139	vs	vs*	121	.228	0.4	O	O*
131	.307	42	s	vs	141	.392	0	O	O
151	.479	17	m	s	112	.222	162	vs	
102	.202	61	vs		132	.342	60	s	
122	.273	25	s		152	.502	22	m	s
142	.419	3.6	w	m	172	.674	11		w
162	.587	0.3		O	103	.279	60	vs	m*
113	.294	0.6	w	O*	123	.334	43	s	m*
133	.392	0.1	vw	m	143	.462	22	m	s
153	.539	0	O	w	114	.375	21	s	s
104	.363	0.2	O	O	134	.456	12	m	s
124	.407	0	O	w	154	.586	6.6		m
144	.517	0.4	O	w	105	.448	2	O	O
115	.457	35	s	s	125	.484	1.5	O	O
135	.526	25	m	s	145	.580	0.6		O
155	.641	17		w	210	.222	220	vs	
200	.203	2.3	m		230	.342	75	s	
220	.274	1.0	w		250	.502	28	w	
240	.420	0	vw		270	.674	11		w
211	.239	18	s	w*	201	.221	0.2	vw	O*
231	.353	4	w		221	.288	0	O	O*
251	.509	0.4	O	O	241	.429	0.3	O	O
202	.268	1.3	O	O*	212	.283	5.2	m	O*
222	.324	0.5	O		232	.384	4	w	
242	.455	0	O		252	.531	3.2	O	O
213	.344	28	m	s	203	.331	82	vs	
233	.431	1.4	w		223	.379	55	s	
253	.566	0.2		O	243	.495	27	m	
204	.404	0	w		263	.644	13		m
224	.444	0	w		214	.414	1.2	w	w
244	.546	0	O		234	.489	0.5	w	
215	.490	0.6	O	O	205	.481	7	vw	
235	.554	0.2		O	225	.515	6.8		w
300	.304	6.9	O		310	.318	36	s	

TABLE I   (*Concluded*)

hkl	$\frac{\sin \vartheta}{\lambda}$	F^2	Intensity Osc.	Intensity Laue	hkl	$\frac{\sin \vartheta}{\lambda}$	F^2	Intensity Osc.	Intensity Laue
320	0.356	3.6	O		330	0.411	21	m	
340	.477	0.9	O		301	.317	70	s	s
311	.330	0.6	m	m	321	.366	45	s	vs
331	.420	0	w	m	312	.363	4.3	m	s
302	.350	30	s		332	.446	1.6	w	m
322	.396	25	s		303	.401	0.7	vw	
313	.412	25	s	s	323	.442	0.4	w	
333	.487	19	m		314	.471	0.5	O	w
304	.463	6.5	m		334	.539	0.7	O	
324	.498	6	m	s	410	.416	1.3	vw	m
400	.406	4.5	O		430	.491	0.6	O	
420	.445	2.8	O		401	.414	1.3	m	s
411	.424	13	m	s	421	.454	0.8	m	m
431	.498	9	m	m	412	.451	0.8	O	w
402	.441	40	s		432	.521	0.5		O
422	.478	36	m		403	.483	0.6	m	
413	.491	81	s	s	423	.516	0.5	w	m
433	.556	61		s	510	.515	26	m	s
500	.507	0	O		530	.577	11	m	
520	.539	0		O	501	.515	10	m	s
511	.523	0.2	w	w	521	.546	9	w	m
531	.584	0		O	512	.544	0	w	m
502	.536	21	m	m	532	.603	0		w
522	.567	18	w	m	503	.570	0.5	O	O
513	.578	13	w	w	523	.600	0.4		O

* Powder reflection.

Discussion.—A marked feature of the structures of lithium, sodium and potassium nitrates is the separation into alternate layers of metal ions and nitrate groups which lie parallel to the nitrate planes. In the present form of the ammonium compound this characteristic is absent, although there is a suggestion of such layering in the direction of the *a*-axis perpendicular to the nitrate planes. This structure may be considered as related to the cesium chloride type if the nitrate groups are taken as units.

I am grateful to Professor Albert Sauveur for the use of x-ray apparatus.

Summary

A complete structure is proposed for rhombic ammonium nitrate in the space group V_h^{13}. As in some other univalent nitrates, the strong double refraction is probably to be explained by the arrangement of the nitrate groups in parallel planes.

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