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THE CRYSTAL STRUCTURES OF SODIUM AND POTASSIUM TRINITRIDES AND POTASSIUM CYANATE AND THE NATURE OF THE TRINITRIDE GROUP

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Introduction

The investigation with X-rays of the structures of crystals makes possible in many cases the elucidation of points of chemical interest, especially in regard to atoms connected by non-polar bonds. The tetrahedral arrangement of atoms about a carbon atom has been verified in hexamethylenetetramine,[2] $C_6H_{12}N_4$, but found not to prevail in penta-erythritol,[3] $C(CH_2OH)_4$. The nitrate and carbonate ions are formed of three atoms located about a central atom in positions such that the ions possess a 3-fold symmetry axis. Such information is of use in testing proposed theories of valence and molecular structure. The investigation reported in this paper involved the determination of the structures of three crystals containing triatomic ions which had not previously been studied in this way, namely, the trinitride and cyanate ions.

Sodium trinitride, NaN_3, is described[4] as forming hexagonal plates with prismatic cleavage. Potassium trinitride, KN_3, rubidium trinitride, RbN_3, and thallous trinitride, TlN_3, form apparently isomorphous tetragonal crystals[4] with only slightly different axial ratios, that of potassium trinitrides being given as $a:c = 1:0.5798$. Potassium cyanate, KNCO, is also reported[5] to form tetragonal crystals with $a:c = 1:0.5766$. We have determined the structures of crystals of sodium and potassium trinitride and potassium cyanate by using data obtained from Laue and spectral photographs interpreted with the aid of the theory of space groups.[6] Small basal plates of the two trinitride crystals were prepared by slow crystallization from aqueous solution,[7] and of the cyanate by crystallization from methyl alcohol. Photographs were made of the K-radiation of molybdenum reflected from the basal plane and prism planes of the

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[1] National Research Fellow.

[2] Dickinson and Raymond, THIS JOURNAL, **45**, 22 (1923).

[3] Mark and Weissenberg, *Z. Physik*, 17, 301 (1923); also an unpublished investigation by Huggins and Hendricks in this Laboratory.

[4] Groth, "Chemische Krystallographie," Engelmann, Leipzig, **1908**, vol. 1, p. 204.

[5] Ref. 4, vol. 2, p. 2.

[6] For a detailed description of the experimental methods see R. W. G. Wyckoff, "The Structure of Crystals," The Chemical Catalog Co., New York, **1924**, pp. 109–116 and 161–164.

[7] We wish to thank Mr. Richard Pomeroy for the preparation and crystallization of these compounds.

crystals. Symmetrical and unsymmetrical Laue photographs were made with thin basal plates, using the X-radiation from a tube with a tungsten anticathode operated at a peak voltage of 52 kilovolts. Indices were assigned to the Laue spots with the help of gnomonic projections.

The densities of the sodium and potassium trinitrides, which have not been reported previously, were determined by the suspension method of Retgers to be 1.853 and 2.038 g./cc., respectively.

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The Structure of Sodium Trinitride

The Unit of Structure.—Spectral data for sodium trinitride are given in Table I. The possible axial ratios determined from the positions of spots on Laue photographs are in agreement with these data. The smallest hexagonal unit compatible with these data has $a = 2.100$ Å. and $c = 5.067$ Å. Upon calculating values of $n\lambda$ on the basis of this unit for the X-rays producing the Laue spots for which data are tabulated in Table II, many of these values were much less than 0.24 Å., the short wave-length limit of X-rays present in the incident beam. This def-

TABLE I

SPECTRAL DATA FROM SODIUM TRINITRIDE

hkl	Line[a]	Order	Angle of reflection	d/n	Intensity of reflection[b]
111	β	n	3° 33.7′	5.081 Å.	w
	α	n	4° 0.2′	5.086	m
	β	$2n$	7° 9.5′	5.069	w
	α_1	$2n$	8° 0.7′	5.068	m
	α_2	$2n$	8° 4.0′	5.074	w
	γ	$3n$	10° 35.5′	5.059	vvw
	β	$3n$	10° 47.0′	5.077	mw-w
	α_1	$3n$	12° 5.7′	5.065	ms
	α_2	$3n$	12° 10.5′	5.065	m
	γ	$4n$	14° 9.7′	5.067	vw
	β	$4n$	14° 26.5′	5.061	mw
	α_1	$4n$	16° 14.0′	5.065	s
	α_2	$4n$	16° 20.5′	5.061	ms
$1\bar{1}0$	γ	n	9° 48′	1.819	vw
	β	n	9° 59.5′	1.819	w
	α	n	11° 15′	1.819	m

[a] In tables of spectral data γ indicates MoKγ, $\lambda = 0.6197$ Å.; β, MoKβ, $\lambda = 0.6311$; α_1, MoKα_1, $\lambda = 0.7078$; α_2, MoKα_2, $\lambda = 0.7121$; α, mean of α_1 and α_2, $\lambda = 0.710$.

[b] The abbreviations signify: s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak; vw, very weak; vvw, very very weak.

initely eliminates this unit. Moreover, it can be shown that every possible hexagonal unit with c = 5.067 Å. and every one with c = 10.134 Å. are definitely eliminated by these data. The smallest hexagonal unit not eliminated by the observed reflections has a = 3.638 Å. and c = 15.201 Å., and contains 3 NaN_3.

TABLE II

LAUE PHOTOGRAPHIC DATA FROM SODIUM TRINITRIDE

Incident beam normal to (111)

hkl	d_{hkl}. Å.	$n\lambda$. Å.	Est. intensity	S for u = 0.423	Class
$1\bar{1}0$	1.832	0.46	10.0	36.00	1
$11\bar{1}$	1.578	.40	0.5	4.37	2
$2\bar{1}0$	1.195	.38	.05	4.37	2
$\bar{1}20$	1.195	.45	.05	4.37	2
310	1.145	.37	1.0	17.45	1
$21\bar{1}$	1.117	.28	1.0	29.95	1
320	1.117	.48	1.5	18.50	2
$22\bar{1}$	1.042	.46	0.15	6.30	2
$3\bar{1}0$	0.875	.38	.6	29.95	1
$32\bar{1}$	.862	.35	.12	17.45	1
$23\bar{1}$	.862	.48	.4	17.45	1
410	.846	.47	.3	18.50	2
430	.816	.41	.05	21.62	2
521	.802	.46	.1	11.50	1
541	.762	.46	.2	22.75	1
032[a]	1.117	.34	.2	18.50	2
$\bar{1}\bar{1}2$[a]	1.088	.41	1.3	36.00	1
241[a]	1.058	.39	0.4	21.62	2

[a] Data from another Laue photograph of NaN_3.

The rhombohedral units corresponding to the eliminated hexagonal units are, of course, also eliminated by the Laue data. The rhombohedral unit corresponding to the smallest possible hexagonal unit is, however, in complete agreement with all the observed reflections. This unit has a = 5.481 Å. and α = 38°43′, and contains $1NaN_3$, corresponding to a calculated density of 1.838 g./cc., in good agreement with the directly determined value 1.853 g./cc.

It would be very difficult with any atomic arrangement based on the hexagonal unit to account for the observed absences in the first and second orders of all planes for which $-H + K + L$, $2H + K + L$, and $-H - 2K + L$ are not divisible by three. Accordingly, the rhombohedral unit described is accepted as the correct unit of structure. All indices used in this paper for sodium trinitride are referred to the axes of this unit.

The Space Group.—The observation that a Laue photograph taken with the incident beam normal to (111) shows a trigonal axis and three planes of symmetry requires that the structure be isomorphous with one of the point-groups C_{3v}, D_3, D_{3d}. The only space groups satisfying this requirement and based on a rhombohedral lattice are[8] C_{3v}^5, C_{3v}^6, D_3^7, D_{3d}^5 and D_{3d}^6. Of these C_{3v}^6 and D_{3d}^6 do not provide any arrangement for one sodium and three nitrogen atoms in the unit.

The Atomic Arrangement.—Possible arrangements with the three nitrogen atoms in crystallographically equivalent positions are the following.

C_{3v}^5: Na at uuu; 3N at vvw, vwv, wvv;
D_3^7: Na at 000 or $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; 3N at $u\bar{u}0$, $\bar{u}0u$, $0u\bar{u}$, or $u\bar{u}\frac{1}{2}$, $\bar{u}\frac{1}{2}u$, $\frac{1}{2}u\bar{u}$;
D_{3d}^5: Na at 000 or $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; 3N at $00\frac{1}{2}$, $0\frac{1}{2}0$, $\frac{1}{2}00$, or $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$.

All of these arrangements are eliminated by the observed relative intensities of reflection in different orders from (111), given in Table I; namely, $4 > 3 > 2 > 1$. However, inasmuch as the intensity of reflection at small angles of X-rays from crystal faces is dependent to some extent on the nature of the reflecting surface,[9] some care must be taken in the use of these intensities. Indeed, we found that the intensity of reflection from (111) in the first order was somewhat increased if the crystal face were previously ground with fine emery and oil. Accordingly, we proceeded upon the assumption that the true intensity of the first-order reflection might be greater than that of the second, and attempted to determine the correct arrangement with the use of Laue photographic data, given in Table II. The use made of Laue data throughout our work is independent of quantitative assumptions concerning dependence of intensity of reflection on interplanar distance, and is based on the following principle: if a plane reflects X-rays of a given wave length more strongly than a second plane with a larger value of d/n, the structure factor for the first plane must be greater than that for the second. In this way it was found possible again to eliminate definitely all of the atomic arrangements listed above, without making any assumptions regarding the relative reflecting powers of the different atoms present other than the very safe one that a sodium atom reflects more strongly than a nitrogen atom. Since these arrangements are the only ones placing the three nitrogen atoms in a ring, such a structure cannot be assigned to the trinitride ion.

The only other possible arrangement is the following, derived from space-group D_3^7 or D_{3d}^5: Na at 000; N at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; 2N at uuu, $\bar{u}\bar{u}\bar{u}$.

The structure factor S for any plane (hkl) has the following value.

Class 1; $n\,(h + k + l)$ even; $S = \overline{\mathrm{Na}} + \overline{\mathrm{N}} + 2\overline{\mathrm{N}} \cos 2\pi n\,(h + k + l)\,u$;
Class 2; $n\,(h + k + l)$ odd; $S = \overline{\mathrm{Na}} - \overline{\mathrm{N}} + 2\overline{\mathrm{N}} \cos 2\pi n\,(h + k + l)\,u$.

As is seen from Fig. 1 the observed intensities of reflection from (111) restrict u to the regions 0.083 to 0.105, 0.228 to 0.250 and 0.417 to 0.438. Further restrictions may be made by the use of Laue data. The intensity

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[8] R. W. G. Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," *Carnegie Inst. Publ.*, No. **318** (1922).

[9] W. L. Bragg, James and Bosanquet, *Phil. Mag.*, **41**, 309 (1921). Dickinson and Goodhue, THIS JOURNAL, **43**, 2045 (1921).

inequality (310) > $(2\bar{1}0)$ eliminates the first of these regions, and that of (541) > (521) the second; moreover, the inequality (541) $\geqq$ (430) requires that u be less than 0.425, as is seen from Fig. 2. The parameter is accordingly limited to the region 0.417 to 0.425; the approximate equality of intensities of reflection from (321) and (410) indicates that u is not far from 0.425, and we have taken as the most probable value 0.423.

It is interesting to observe that the comparison $(22\bar{1})$ > $(2\bar{1}0)$ is satisfied for the above range of values of u only if the relative reflecting power of sodium ion is increased by more than 50% above its electron number (Fig. 2). Values of the structure factor S in Table II are calculated for this 50% increase.

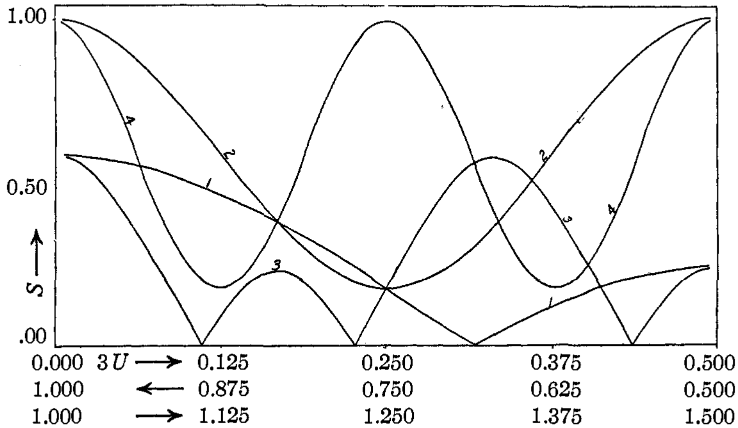

Fig. 1.—Structure-factor curves for the first four orders of reflection from (111) of sodium trinitride. The curves represent three sets of values of the abscissa $3U$; namely, 0 to 0.500, extending from left to right; 0.500 to 1.000, from right to left; and 1.000 to 1.500, from left to right. The numbers on the curves are the orders of reflection.

The Structure of Potassium Trinitride

The Unit of Structure.—Spectral photographic data for potassium trinitride are given in Table III. The possible axial ratios determined by the positions of the spots on Laue photographs are in agreement with these data. The smallest unit of structure compatible with them has d_{100} = 4.308 Å. and d_{001} = 1.764 Å. On calculating values of $n\lambda$ for the Laue spots for which data are given in Table IV on the basis of this unit, some of these values were found to be less than 0.24 Å., the short wave-length limit of X-rays present in the incident beam. This definitely eliminates this unit. In the same way the Laue data eliminate every unit with d_{001} = 1.764 Å., 3.528 Å. or 5.292 Å. The unit with d_{100} = 4.308 Å. and d_{001} = 7.056 Å. is similarly eliminated, but the unit obtained from it by rotation through 45° is in complete agreement with the Laue data; in default of any evidence requiring a still larger unit of structure, this is accepted as the true one. It has $d_{100} = 6.094$ Å. and $d_{001} = 7.056$ Å., and contains 4 KN_3; the density calculated from this information is 2.045 g. per cc., in good agreement with the directly determined value 2.038. All indices used in this paper for potassium trinitride are referred to the axes of this unit.

The Space Lattice and the Space Group.—The observation that a Laue photograph taken with the incident beam normal to (001) of this tetragonal crystal showed a 4-fold axis and four planes of symmetry requires that the structure be isomorphous with one of the point groups V_d, D_{4v}, D_4 and D_{4h}. In the absence of any evidence to the contrary, we have proceeded upon the assumption that the crystals are holohedral, and have considered only structures isomorphous with D_{4h}. This assumption is necessitated by the difficulty which would be introduced if consideration were afforded all of the possible arrangements with lower symmetry, some of which involve more than one parameter, and is justified to a considerable extent by the fact that an atomic arrangement completely explaining all the observed X-ray data was derived by means of it.

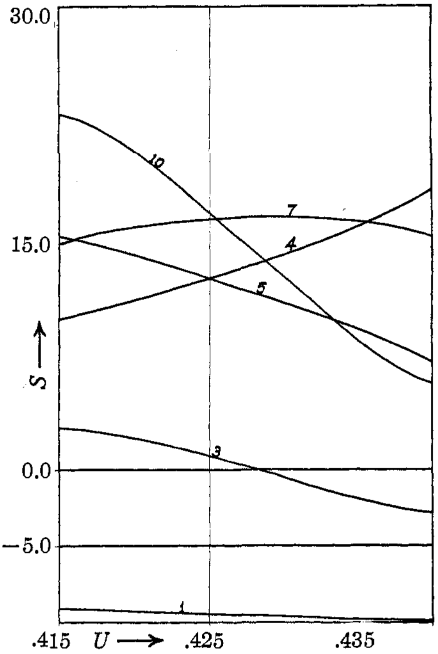

Fig. 2.—Structure-factor curves for first-order reflections from sodium trinitride; the attached numbers are the values of $h + k + l$ for the planes to which the curves correspond.

The absence of any first-order reflections from planes with $h + k + l$ odd makes it very probable that the structure is based on the body-centered tetragonal lattice Γ_t'. The space groups satisfying this requirement and isomorphous with D_{4h} are D_{4h}^{17}, D_{4h}^{18}, D_{4h}^{19} and D_{4h}^{20}. A choice may be made among these through use of the following criteria.[10]

Reflection in odd orders will not occur from these planes:

D_{4h}^{17}:
D_{4h}^{18}; $h = 0$;
D_{4h}^{19}; $h \pm k$, with $(2h + l)/4$ not integral; or $l = 0$;
D_{4h}^{20}; $h = \pm k$, with $(2h + l)/4$ not integral; or $h = 0$; or $l = 0$.

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[10] These are taken from a complete tabulation of criteria for all tetragonal space-groups prepared by Dr. Huggins.

TABLE III

SPECTRAL PHOTOGRAPHIC DATA FROM POTASSIUM TRINITRIDE

hkl	Line	Order	Angle of reflection	Interplanar distance, Å.	Intensity of reflection
001	α	2	5° 45′	7.098	vvw
	γ	4	10° 6′	7.060	w
	β	4	10° 19′	7.046	m
	α_1	4	11° 35′	7.048	m
	α_2	4	11° 37′	7.064	ms
010	γ	2	5° 51′	6.082	w
	β	2	5° 57′	6.088	ms
	α	2	6° 38′	6.094	vs
	β	4	11° 57′	6.094	w
	α	4	13° 28′	6.096	m
110[a]	β	1	4° 12′	4.31	vw
	α	1	4° 42′	4.33	m
	β	2	8° 21′	4.33	w
	α	2	9° 26′	4.32	ms
	α	3	14° 26′	4.28	vw
	β	4	17° 10′	4.29	w
	α	4	19° 22′	4.29	m
	α	5	25° 10′	4.28	vw
	α_1	6	30° 14′	4.25	w
	α_2	6	30° 3′	4.28	w

[a] The data for this plane are less accurate than those for (001) and (010).

TABLE IV

LAUE PHOTOGRAPHIC DATA FROM POTASSIUM TRINITRIDE

Incident beam 30° from normal to (001)

hkl	$\frac{d_{hkl}}{n}$, Å.	λ, Å.	Estimated intensity	S for u = 0.135[a]	Class
132	1.69	0.33	5.0	12.00	2
051	1.20	.46	0	0	1
$\bar{5}21$	1.12	.32	0.25	7.06	1
053	1.10	.24	0	0	1
$\bar{5}32$	1.00	.41	5.0	19.22	2
$\bar{1}61$	0.97	.37	0.12	5.58	1
161	.97	.46	.20	5.58	1
$\bar{1}65$	.82	.43	.08	5.58	1
$7\bar{3}2$	.79	.33	.15	9.77	2
$5\bar{6}1$	.77	.41	.10	6.57	1
$\bar{5}54$	.76	.41	.25	6.23	3
$7\bar{5}2$	.70	.37	.17	12.60	2
$\bar{1}76$	.69	.38	1.0	21.19	2
091	.67	.37	0	0	1
376	.66	.38	.12	9.77	2
$\bar{9}12$	.66	.37	.17	17.40	2
556	.65	.34	.16	17.65	2
$7\bar{7}2$	.60	.36	.17	23.08	2

[a] The structure factor is materially affected by assumptions concerning the relative reflecting powers.

The observed first-order reflection from (110) (Table IV) definitely eliminates D_{4h}^{19} and D_{4h}^{20}. No first-order reflections from planes with $h = 0$ were observed on any Laue photograph, though several such planes were in positions favorable to reflection, as is seen from Tables III and IV. It would be difficult to explain these absences with an arrangement derived from D_{4h}^{17}; accordingly D_{4h}^{18}, which is in complete agreement with the above observations, is accepted as the correct space group.

The Atomic Arrangement.—The following atomic arrangements are provided[11] by D_{4h}^{18}.

4 K or 4 N at (a) $000,\ 00\tfrac12,\ \tfrac12\tfrac12\tfrac12,\ \tfrac12\tfrac12 0;$
(b) $0\tfrac12 0,\ \tfrac12 00,\ 0\tfrac12\tfrac12,\ \tfrac12 0\tfrac12;$
(c) $00\tfrac14,\ 00\tfrac34,\ \tfrac12\tfrac12\tfrac34,\ \tfrac12\tfrac12\tfrac14;$
(d) $0\tfrac12\tfrac14,\ \tfrac12 0\tfrac14,\ \tfrac12 0\tfrac34,\ 0\tfrac12\tfrac34;$
8 N at (e) $\tfrac14\tfrac14 0,\ \tfrac34\tfrac14 0,\ \tfrac34\tfrac34 0,\ \tfrac14\tfrac34 0;$
$\tfrac34\tfrac34\tfrac12,\ \tfrac14\tfrac34\tfrac12,\ \tfrac14\tfrac14\tfrac12,\ \tfrac34\tfrac14\tfrac12;$
(f) $00u,\ \tfrac12\tfrac12 u,\ \tfrac12\tfrac12\ \tfrac12+u,\ 00\ \tfrac12+u,$
$00\bar{u},\ \tfrac12\tfrac12\bar{u},\ \tfrac12\tfrac12\ \tfrac12-u,\ 00\ \tfrac12-u;$
(g) $0\tfrac12 u,\ \tfrac12 0u,\ \tfrac12 0\ \tfrac12+u,\ 0\tfrac12\ \tfrac12+u,$
$0\tfrac12\bar{u},\ \tfrac12 0\bar{u},\ \tfrac12 0\ \tfrac12-u,\ 0\tfrac12\ \tfrac12-u;$
(h) $u\ \tfrac12+u\ \tfrac14,\ \tfrac12-u\ u\tfrac14,\ \bar{u}\ \tfrac12-u\ \tfrac14,\ \tfrac12+u\ \bar{u}\tfrac14,$
$\tfrac12+u,\ u\tfrac34,\ u\ \tfrac12-u\ \tfrac34,\ \tfrac12-u,\ \bar{u}\tfrac34,\ \bar{u}\ \tfrac12+u\ \tfrac34.$

No arrangement with atoms in Position e, f or g is able to give a larger structure-factor to the fifth order from (110) than to the third order; accordingly the observation on a spectral photograph that the fifth order of (110) actually reflects as strongly as the third order eliminates all such arrangements. Arrangements with the 4 potassium and 12 nitrogen atoms in Positions a, b, c and d are similarly eliminated. Of the arrangements with 8 nitrogen atoms at (h), those with 4 nitrogen atoms at (c) or (d) and 4 potassium atoms at (d) or (c) are ruled out by the fact that the fourth-order reflection from (001) is stronger than the second-order one, for the corresponding structure factors are the same. The structure factor for the second order of (001) is $4\overline{K} + 4\overline{N}$ for potassium atoms at (c) or (d) and nitrogen atoms at (a) or (b), and is $4\overline{K} - 4\overline{N}$ for potassium atoms at (a) and nitrogen atoms at (b). Inasmuch as the reflecting powers of potassium and nitrogen atoms are at least approximately proportional to their atomic numbers, 19 and 7, respectively, and previous experimental results indicate that the deviation from strict proportionality is in such directions as to increase the reflecting power of the heavier atom, all of these arrangements are removed from further consideration by their inability to explain the extremely weak observed second-order reflection from (001). The minimum value of the structure factor for the third order of (110) with potassium atoms at (b) and nitrogen at (c) or potassium at (b) and nitrogen at (d) is $4\overline{K} - 4\overline{N}$; with potassium atoms at (a) and

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[11] Ref. 5, p. 100.

nitrogen at (c) it is $4\overline{\mathrm{K}}$. These arrangements, also, are accordingly removed from further consideration, for they are incapable of accounting for the observed very weak third-order reflection from (110).

The only remaining arrangement is that with potassium atoms at (a) and nitrogen atoms at (d) as well as at (h). Changing the origin of coordinates to $00\frac{1}{4}$ for convenience, the arrangement becomes the following.

4K at $00\frac{1}{4}$, $00\frac{3}{4}$, $\frac{1}{2}\frac{1}{2}\frac{1}{4}$, $\frac{1}{2}\frac{1}{2}\frac{3}{4}$;
4N at $0\frac{1}{2}0$, $\frac{1}{2}00$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$;
8N at $\mathrm{u}\ \frac{1}{2}+\mathrm{u}\ 0$, $\frac{1}{2}-\mathrm{u}\ \mathrm{u}\ 0$, $\bar{\mathrm{u}}\ \frac{1}{2}-\mathrm{u}\ 0$, $\frac{1}{2}+\mathrm{u}\ \bar{\mathrm{u}}\ 0$,
$\frac{1}{2}+\mathrm{u}\ \mathrm{u}\ \frac{1}{2}$, $\mathrm{u}\ \frac{1}{2}-\mathrm{u}\ \frac{1}{2}$, $\frac{1}{2}-\mathrm{u}\ \bar{\mathrm{u}}\ \frac{1}{2}$, $\bar{\mathrm{u}}\ \frac{1}{2}+\mathrm{u}\ \frac{1}{2}$.

With this arrangement the structure factor for the second-order reflection from (001) is $4\overline{\mathrm{K}} - 12\overline{\mathrm{N}}$; the extremely weak reflection obtained experimentally shows that the reflecting power of K^+ is almost exactly equal to that of N_3^-. With this information we can easily evaluate the parameter u. All distinct arrangements are provided by giving u values between 0 and 0.25. The only regions explaining the observation that the fifth-order reflection from (110) is as strong as the third order are 0 to 0.063 and 0.125 to 0.187.

All planes may be divided into three classes, which have the following structure factors.

Class 1, l odd, n odd; $S = 4\overline{\mathrm{N}}\ [\cos 2\pi n(h+k)\,\mathrm{u} - \cos 2\pi n(h-k)\mathrm{u}]$;
Class 2, $\frac{nl}{2}$ odd, n odd; or $nl/2$ even, n even; $S = 4\overline{\mathrm{K}} + 4\overline{\mathrm{N}} + 4\overline{\mathrm{N}}\ [\cos 2\pi n(h+k)\mathrm{u} + \cos 2\pi n(h-k)\mathrm{u}]$;
Class 3, $nl/2$ even, n odd; or $nl/2$ odd, n even; $S = 4\overline{\mathrm{K}} - 4\overline{\mathrm{N}} - 4\overline{\mathrm{N}}\ [\cos 2\pi n(h+k)\mathrm{u} + \cos 2\pi n(h-k)\mathrm{u}]$.

Comparisons may be made between planes of the same class with only qualitative assumptions concerning relative reflecting powers. The observation that on a Laue photograph (912) reflects more strongly than (752) accordingly eliminates the first of the above regions and further restricts the second to 0.125 to 0.145. The data did not permit further rigorous restriction of the parameter; however, the observed intensities seem to be in best agreement with the structure factors for $\mathrm{u} = 0.135$, which is accepted as the most probable value.

The Structure of Potassium Cyanate

The Unit of Structure.—Spectral photographic data for potassium cyanate are given in Table V, and Laue data in Table VI. The smallest unit of structure completely accounting for these data has $d_{100} = 6.070$ Å. and $d_{001} = 7.030$ Å., and contains 4 KNCO. The density calculated from these data is 2.065 g. per cc., in good agreement with the directly determined value[5] 2.056 g. per cc. All indices used in this paper for potassium cyanate are referred to the axes of this unit. The elimination of other units of structure was made in the same way as for potassium trinitride.

TABLE V

SPECTRAL PHOTOGRAPHIC DATA FROM POTASSIUM CYANATE

hkl	Line	Order	Angle of reflection	Interplanar distance	Intensity of reflection
001	α	2	5° 51′	6.97 Å.	vvw
	γ	4	10 10.5	7.020	w
	β	4	10 21	7.020	m
	α_1	4	11 36	7.034	vs
	α_2	4	11 41	7.030	s
010	γ	2	5 51	6.075	vvw
	β	2	5 59	6.060	w
	α	2	6 43.3	6.070	m
110[a]	α	1	4 47	4.26	m
	β	2	8 34	4.26	w
	α	2	9 29	4.31	m
	α	3	14 27.5	4.28	vvw
	α	4	19 19	4.26	mw
	α_1	5	24 21	4.30	vw
	α_2	5	25 0.5	4.22	w

[a] These measurements are less accurate than those from (001) and (010).

TABLE VI

LAUE PHOTOGRAPHIC DATA FROM POTASSIUM CYANATE

Incident beam 22.5° from normal to (001)

hkl	$\frac{d_{hkl}}{n}$, Å.	λ, Å.	Estimated intensity	Structure factor for u = 0.135	Class
$3\bar{3}2$	1.32	0.24	0.6	21.21	2
$4\bar{1}3$	1.25	.42	.2	1.60	1
$3\bar{5}0$	1.04	.43	1.0	4.84	3
$5\bar{1}4$	0.99	.46	1.5	10.61	3
$2\bar{3}0$, $n=2$	.84	.37	0.6	14.92	2
$7\bar{1}2$	.83	.26	.1	20.78	2
$\bar{1}72$	.83	.46	3.0	20.78	2
$6\bar{1}5$	.81	.36	0.05	5.58	1
$2\bar{3}2$, $n=2$	.76	.31	.15	14.92	2
$7\bar{5}0$	.71	.45	.3	11.36	3
$7\bar{1}6$	.69	.32	.3	21.19	2
$\bar{2}\bar{4}1$, $n=2$	.67	.46	.3	14.69	3
$7\bar{2}7$	.64	.39	.05	2.64	1
$\bar{3}92$	.63	.36	.15	14.24	2
$1\bar{9}4$	.63	.36	.05	6.64	3
$4\bar{3}0$, $n=2$	.61	.38	.15	18.49	2
$2\bar{4}3$, $n=2$	.59	.37	.07	14.69	3

The Space Lattice and the Space Group.—A Laue photograph taken with the incident beam of X-rays in the plane containing the *a* and *c* axes showed a plane of symmetry, requiring that the crystal be isomorphous with one of the point groups V_d, C_{4v}, D_4 and D_{4h}. As with potassium trinitride, we have preliminarily assumed that the crystals are isomorphous with D_{4h}, in the absence of evidence to the contrary. No first-order reflections were observed from any planes with $h + k + l$ odd, indicating that the structure is based on the lattice Γ_t'. Of the space groups D_{4h}^{17}, D_{4h}^{18}, D_{4h}^{19} and D_{4h}^{20} satisfying these requirements the last two are eliminated by the observed odd-order reflections from (110) (Table V), and the first is made improbable by the absence of any odd-order reflections from planes with $h = 0$. D_{4h}^{18} is, accordingly, temporarily accepted as the correct space group.

The Atomic Arrangement.—The atomic arrangements provided by D_{4h}^{18} are listed in the discussion of potassium trinitride. The only arrangements of 4 potassium, 4 nitrogen, 4 carbon and 4 oxygen atoms are (a), (b), (c) and (d). These arrangements do not permit the structure factor for the fifth-order reflection from (110) to be greater than that for the third-order reflection; the experimental observation that this is true accordingly eliminates these arrangements.

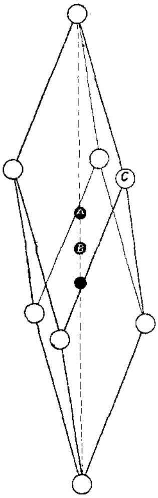

Fig. 3.—The unit of structure of sodium trinitride; the rings denote sodium atoms, the solid black circles nitrogen atoms.

If, however, it is assumed that atoms of two different elements, say oxygen and nitrogen, may be considered to be, as far as the diffraction of X-rays is concerned, in crystallographically equivalent positions, the remaining arrangements discussed for potassium trinitride must be given consideration. Reference to Table V shows that the relative intensities of the spectral reflections in different orders from (001) and (110) are the same as for potassium trinitride; the atomic arrangement is accordingly restricted to that determined for this crystal, the parameter u lying between 0 and 0.063 or 0.125 and 0.187. The observation that $(7\bar{1}6)$ reflects more strongly than $(2\bar{3}2)$, $n = 2$, eliminates the region 0 to 0.063, and the further comparison $(4\bar{3}0)$, $n = 2$, greater than $(\bar{3}92)$ requires that u be less than 0.146. However, throughout the remaining region 0.125 to 0.146 the structure factor for $(7\bar{2}7)$ is less than that for $(6\bar{1}5)$, whereas the observation that $(7\bar{2}7)$ reflects more strongly than $(6\bar{1}5)$ requires the reverse relation to be true. Accordingly, the structure of potassium cyanate is not that of potassium trinitride; the fact that most of the experimental data are satisfied by the same arrangement, with a value of u of about 0.13 shows, however, that the true structure is closely similar to this one.

The experimental data are not sufficiently numerous to permit the deduction of the true structure; indeed, this deduction would be difficult because of the similarity to the structure discussed above, for very small variations in intensities of Laue spots would be of importance. The problem could be more easily solved by a study of the tetragonal crystal thallous thiocyanate, TlNCS, which has the very closely similar axial ratio $a:c = 1:0.5593$.[12]

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[12] Ref. 5, p. 3.

Discussion and Conclusions

Description of the Structures.—The arrangement of atoms in the unit of structure of sodium trinitride is shown in Fig. 3. No NaN_3 molecules can be distinguished in the crystal; however, the nitrogen atoms are seen to be arranged in groups of three, evidently constituting the trinitride ion. Each such ion is surrounded by 6 sodium ions, and each sodium ion by 6 trinitride ions. The determined interatomic distances for this salt are given in Table VII.

TABLE VII

INTERATOMIC DISTANCES FOR THE THREE SUBSTANCES

Substance	N—N (or N—C, C—O) distance, Å.	Metal-metal distance, Å.	Metal-N (or O) distance, Å.
NaN_3	1.17	3.632	2.48
KN_3	1.16	3.528	2.96
KNCO	1.16	3.515	2.95

The similarity of this structure to others is seen by a consideration of Figs. 4, 5 and 6. In Fig. 5 is represented the unit of structure of the cubic crystal sodium chloride, containing 4NaCl, with the zone axis [111] vertical, in Fig. 4 a portion of a crystal of sodium trinitride, the face-centered rhombohedron containing $4NaN_3$, and in Fig. 6 a cleavage rhombohedron of sodium nitrate, containing $4NaNO_3$. It will be observed that in all three crystals the ions are similarly located. By substituting trinitride for chloride ions the atomic arrangement is extended vertically and compressed horizontally; the substitution of nitrate ions has the reverse effect. The shortest distance between sodium ions in a plane parallel to (111) is 3.63 Å. for the trinitride, 3.98 Å. for the chloride, and 4.92 Å. for

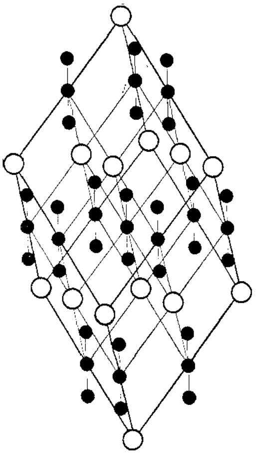

Fig. 4.—The face-centered rhombohedron of sodium trinitride; the rings denote sodium atoms and the solid black circles nitrogen atoms.

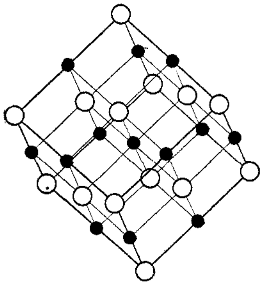

Fig. 5.—The unit of structure of sodium chloride; the rings denote sodium atoms and the solid black circles chlorine atoms.

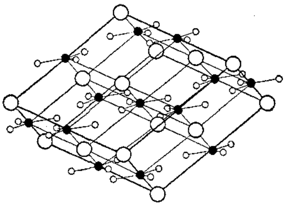

Fig. 6.—The cleavage rhombohedron of sodium nitrate; the large rings denote sodium atoms, the solid black circles nitrogen atoms and the small rings oxygen atoms.

the nitrate; the distances apart of these planes containing sodium ions are 5.07, 3.25 and 2.77 Å., respectively.

The unit of structure of potassium trinitride is shown in Fig. 7. Here also, no molecules of KN_3 can be distinguished, and the nitrogen atoms are in groups of three, forming trinitride ions. Each trinitride ion is equidistant from 8 potassium ions, and each potassium ion equidistant from 8 trinitride ions. The arrangement is closely similar to that of the cubic crystal cesium chloride, the structure of which is represented in Fig. 8. The approximately spherical chloride ions in cesium chloride are replaced by trinitride ions, whose infinite symmetry axes coincide with 2-fold symmetry axes of the crystal. In this figure the *h*- and *k*-axes are rotated 45° from the usual directions. This replacement expands the structure in directions normal to the *l*-axis; the axial ratio c/a becomes 1.158, as compared with the corresponding value 1.414 for crystals with the cesium chloride arrangement.

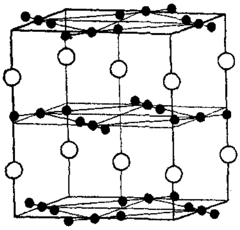
Fig. 7.—The unit of structure of potassium trinitride; the rings denote potassium atoms and the solid black circles nitrogen atoms.

Fig. 7 also represents approximately the structure of potassium cyanate, the trinitride ions being replaced by cyanate ions, NCO^-. Interatomic distances for potassium trinitride and potassium cyanate are included in Table VII. The space group symmetry of potassium cyanate crystals is not that of D_{4h}^{18}, as for potassium trinitride, but something else, presumably of a space group of lower symmetry than point group D_{4h}. The atomic arrangement is closely similar to that assigned potassium trinitride.

Langmuir[13] has stated that, since the trinitride ion and the cyanate ion are isosteric, similar compounds of these ions should be isomorphous, and has quoted morphological data for their potassium salts in support of this contention. While our work has shown that the crystals do not have completely identical structures, and so are not completely isomorphous, the great similarity found makes it probable that solid solutions of every composition could be formed. Any given solid solution could be assigned either the trinitride or the cyanate structure; if less than a certain fraction of cyanate were present, the crystal would be one of potassium trinitride with a number of the trinitride ions replaced by cyanate ions, introduced at random, and with no directional preference shown the nitrogen or carbon end of the group. With a greater fraction of cyanate the influence of the lack of a center of symmetry in the cyanate ions would be felt; the crystal

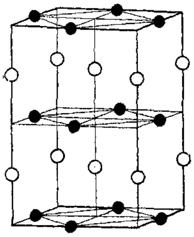
Fig. 8.—The arrangement of atoms in cesium chloride; the rings denote cesium atoms and the solid black circles chlorine atoms.

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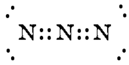
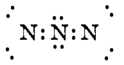
[13] Langmuir, This Journal, 41, 1543 (1919).

would be one of potassium cyanate, with some of the cyanate ions replaced at random by trinitride ions, and with lower point-group symmetry than potassium trinitride.

The Nature of the Trinitride Group.—The present research has shown that the crystals investigated contain trinitride ions composed of three collinear nitrogen atoms. Moreover, the trinitride ions in both sodium and potassium trinitrides are located in positions requiring that they possess centers of symmetry. These facts require that some suggested structures for these ions be discarded; for example, a structure in which the central nitrogen is connected with one end nitrogen by a triple bond and with the other by a double bond is no longer tenable. It is worthy of especial emphasis that this investigation has definitely shown that the trinitride ion does not possess a ring structure.

The trinitride ion consists of 3 nuclei and 22 electrons or, assigning 2 K-electrons to each nucleus, of 3 kernels and 16 outer electrons. We shall represent these kernels by the symbol N, and the electrons, which we shall assume to be paired, by dots. Possible electronic structures of the trinitride ion involving electron sharing and in agreement with our results are these


$${}^{\cdot}_{\cdot}\mathrm{N}::\mathrm{N}::\mathrm{N}{}^{\cdot}_{\cdot}$$
(1)


$${}^{\cdot}_{\cdot}\mathrm{N}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}:\mathrm{N}{}^{\cdot}_{\cdot}$$
(2)


$${}^{\cdot}_{\cdot}:\mathrm{N}:\mathrm{N}:\mathrm{N}:{}^{\cdot}_{\cdot}$$
(3)

It is probable that all trinitride ions in crystals possess one of these arrangements. It is to be understood that the electrons are not necessarily static, but may be in orbits, possibly including, in the case of shared electrons, two nuclei. If, as has been suggested, the double bond does not involve the sharing of four electrons, choice remains to be made between Structures 2 and 3.

We cannot decide between these structures on symmetry considerations. Structure 2 possesses a 2-fold symmetry axis and 3 a 3-fold axis. In the potassium salt the trinitride ion is located on a 2-fold axis, and in the sodium salt on a 3-fold axis; evidently neither of the structures conforms completely with the symmetry of both crystals. It is possible, but very improbable, that the ion has one structure in one crystal and another in the other; the alternative and to us preferable explanation is that the electron arrangement of the group need not conform to the symmetry requirements of the crystals; that is, the group acts as though it had an infinite symmetry axis. That this is a plausible explanation is strikingly shown by the fact that it has been found that even the hydrogen nuclei in ammonia groups and ammonium ions do not conform to the symmetry of the entire crystal.[14] We are accordingly unable to decide between Structures 2 and 3.

The addition of an organic radical to the trinitride group can hardly

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[14] Ref. 6, p. 398.

produce a large change in its structure; we accordingly believe that the azide group has the same collinear structure as the trinitride ion. The original statement of Fischer[15] that the azide group had a ring structure has been criticized also by Thiele,[16] Turrentine,[17] Langmuir[18] and others, but has been included in at least one modern text.[19] A careful investigation of the literature on the reactions of the azide group has led us to the conclusion that these reactions can be satisfactorily explained by the structures given above. It is probable that the aliphatic diazo-amino compounds, $RHCN_2$, have a closely similar structure.[18,19,20]

The Structures of the Acid Fluorides.—The acid fluoride ion, HF_2^-, consists of 3 atomic kernels and 16 outer electrons, and might be expected to have the structure of the trinitride ion, in which case its salts would probably have the crystal structures described in this paper. Crystals of both potassium and sodium acid fluorides have been previously investigated with X-rays.

The tetragonal crystals formed by potassium acid fluoride have an axial ratio only 4% greater than the trinitride. The X-ray data obtained are closely similar to those for the trinitride, and from them the same structure was assigned to the crystal.[21] The data were not as complete as for the trinitride, and assumptions not usually permitted were made in their treatment;[22] however, the agreement of the data with those from potassium trinitride makes it extremely probable that the structure assigned is correct. The hydrogen-fluoride distance was found to be 1.12 Å., with an estimated maximum error of 0.08 Å. The unit of structure has a = 5.67 Å. and c = 6.81 Å.

X-ray powder photographs[23] have been taken of the rhombohedral crystal sodium acid fluoride, $NaHF_2$. With the assumption that the structure of this crystal is similar to that of cesium dichloro-iodide; that is, of sodium trinitride with the center nitrogen replaced by hydrogen and the end nitrogens by fluorine, the variable parameter was evaluated. The structure assigned was in agreement with the data obtained, and is probably correct; the probable hydrogen-fluorine distance is said to be 1.18 Å., with a possible error of about 0.07 Å. The unit of structure has $\alpha = 39°44'$ and a = 5.17 Å.

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[15] Fischer, *Ann.*, **190**, 67 (1878).

[16] Thiele, *Ber.*, **44**, 2522 (1911).

[17] Turrentine, THIS JOURNAL, **36**, 23 (1914).

[18] Langmuir, *ibid.*, **42**, 274 (1920).

[19] Henrich-Johnson and Hahn, "Theories of Organic Chemistry," J. Wiley and Sons, New York, **1922**, p. 149.

[20] See also Staudinger, *Z. angew. Chem.*, **27**, I, 334 (1914); *Helv. chim. Acta*, **5**, 87 (1922); **4**, 228 (1921).

[21] Bozorth, THIS JOURNAL, **45**, 2128 (1923).

[22] See Ref. 6, p. 332, for a criticism of the investigation.

[23] Rinne, Hentschel and Leonhardt, *Z. Krist. Mineralog.*, **58**, 629 (1923).

It seems improbable that a single proton, with unit positive charge, should be able to share more than 4 electrons with other kernels. Structure 3 is, then, to be assigned the acid fluoride ion; representing the proton by H, this is

$$:\underset{..}{\ddot{F}}:H:\underset{..}{\ddot{F}}:$$

Other Groups of Similar Electronic Configuration.—Carbon dioxide, CO_2 and nitrous oxide, N_2O, consist of 3 nuclei and 22 electrons, and might be expected to have the structure of the trinitride ion. X-ray measurements verify this, for crystals of these substances are found to consist of molecules made of three collinear atoms. The previous researches are not in complete agreement, for while one[24] gives the carbon-oxygen distance in a molecule of carbon dioxide as 1.15 Å., the other[25] gives the value 1.59 Å. Moreover, the structure of nitrous oxide[24] with the nitrogen-oxygen distance 1.05 Å., cannot be accepted, for the assumption was made that the molecule has the formula NON, whereas the formula NNO is indicated by a number of facts. These substances are now being investigated in this Laboratory.

Other groups with 3 nuclei and 22 electrons, and probably with the trinitride structure, are the metaborate ion, BO_2^-, the beryllate ion, $BeO_2^=$, the fulminate ion, CNO^-, and the positive nitrogen dioxide ion, NO_2^+.

The distances between adjacent atoms so far determined are listed in Table VIII.

TABLE VIII

DISTANCES BETWEEN ADJACENT ATOMS

Substance	Range, Å.	Prob. distance, Å.
N_3^- in KN_3	1.08 to 1.25	1.16
N_3^- in NaN_3	1.14 to 1.26	1.17
NCO^- in KNCO		1.16
HF_2^- in KHF_2	1.04 to 1.20	1.12
HF_2^- in $NaHF_2$	1.11 to 1.25	1.18
CO_2		1.15
CO_2		(1.59)
N_2O		(1.05)

Summary

The crystal structures of sodium trinitride, potassium trinitride and potassium cyanate have been determined. The rhombohedral unit of structure of sodium trinitride has $\alpha = 38°43'$ and $a = 5.481$ Å., and contains 1 NaN_3. The sodium atom is at 000, the nitrogen atoms at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, uuu, $\bar{u}\bar{u}\bar{u}$, with u equal to 0.423. The tetragonal unit of potassium trinitride has $a = 6.094$ Å. and $c = 7.056$ Å., and contains $4KN_3$. The potassium atoms are at $00\frac{1}{4}$, $00\frac{3}{4}$, $\frac{1}{2}\frac{1}{2}\frac{1}{4}$, $\frac{1}{2}\frac{1}{2}\frac{3}{4}$, and the nitrogen atoms at $0\frac{1}{2}0$,

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[24] Smedt and Keesom, *Proc. Amsterdam Akad.*, **37**, 13 (1924).

[25] Mark and Pohland, *Z. Krist. Mineralog.*, **61**, 293 (1925).

$\frac{1}{2}00$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$; $u\ \frac{1}{2}+u\ 0$, $\frac{1}{2}-u\ u\ 0$, $\bar{u}\ \frac{1}{2}-u\ 0$, $\frac{1}{2}+u\ \bar{u}\ 0$, $\frac{1}{2}+u\ u\ \frac{1}{2}$, $u\ \frac{1}{2}-u\ \frac{1}{2}$, $\frac{1}{2}-u\ \bar{u}\ \frac{1}{2}$, $\bar{u}\ \frac{1}{2}+u\ \frac{1}{2}$, with u equal to 0.135. The structure of potassium cyanate is shown to be closely similar to that of the trinitride; the unit of structure has a = 6.070 Å., and c = 7.030 Å.

Neither sodium nor potassium trinitride shows molecular segregation; the trinitride ion is, however, easily distinguished. This ion is shown to possess not a ring structure, but a linear arrangement of the three nitrogen atoms. Possible electronic configurations are discussed in light of these results.

A consideration of the previously studied structures of sodium and potassium acid fluoride is shown to indicate that the acid fluoride ion is similar in structure to the trinitride ion and the cyanate ion.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WASHINGTON AND LEE UNIVERSITY]

CONTRIBUTIONS TO THE KNOWLEDGE OF RUTHENIUM
VIII. THE ISOMERIC CHLORIDES[1]

BY JAS. LEWIS HOWE AND LAWRENCE P. HAYNES

RECEIVED AUGUST 12, 1925 PUBLISHED DECEMBER 12, 1925

In 1844 the metal ruthenium was discovered by Claus, and its double chloride, K_2RuCl_5 (Claus' formula, $2KCl_2.Ru_2Cl_6$), described and analyzed,[2] attention being called by Claus to the similarity of this to the corresponding rhodium salt, K_2RhCl_5. Later Claus prepared another chloride by the action of aqua regia on ruthenium compounds and naturally ascribed to this the formula K_2RuCl_6 (modern formulation). In 1888 Joly[3] showed that this second chloride was in reality the nitrosochloride, $K_2Ru(NO)Cl_5$. The error of Claus was not unnatural, since the other platinum metals furnished analogous salts under this procedure. He determined the ruthenium and the potassium chloride directly, and the remainder of the chlorine by loss; the difference between the value for $NOCl_3$ and that for Cl_4 is within the limits of his experimental error. He had also noted that potassium pentachlororuthenite, K_2RuCl_5, cannot be directly chlorinated to the hexachlororuthenate, K_2RuCl_6. In 1899 Antony and Lucchesi[4] described the true hexachlororuthenate, K_2RuCl_6, which they formed by the action of concd. hydrochloric acid on potassium ruthenate, K_2RuO_4, though ordinarily the pentachloro-

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[1] This paper is partly based upon the thesis presented by Lawrence P. Haynes in partial fulfilment of the requirements for the degree of Master of Science at Washington and Lee University, June, 1925.

[2] Claus, *Bull. acad. sci. St. Petersburg*, **3**, 367 (1845).

[3] Joly, *Compt. rend.*, **107**, 994 (1888); **108**, 854 (1889).

[4] Antony and Lucchesi, *Gazz. chim. ital.*, **29**, i, 312; ii, 82 (1899).