

[CONTRIBUTION FROM THE RYERSON PHYSICAL LABORATORY, UNIVERSITY OF CHICAGO]

THE STRUCTURE OF GROUPS XO_3 IN CRYSTALS

BY W. H. ZACHARIASEN

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In this paper will be presented the general results of a series of x-ray investigations which have been carried out with the object of determining the structures of radicals XO_3 in crystals.

Previously it was generally believed that the structures of the groups XO_3 were different principally in the absolute dimensions, *i. e.*, that they all were built like the CO_3 -group with the cation situated in the center of an equilateral triangle formed by the 3 oxygens. In 1928 I was able to show from an examination of the atomic arrangement in $KBrO_3$ that the BrO_3 group had the shape of a low trigonal pyramid.¹ As a consequence of this result I classified the groups XO_3 in two classes: one including the co-planar groups and the other including all pyramidal groups. From considerations to be given later I referred to class 1 the $(NO_3)^{-1}$, $(CO_3)^{-2}$ and $(BO_3)^{-3}$ -groups; to class 2 the groups $(PO_3)^{-3}$, $(SO_3)^{-2}$, $(ClO_3)^{-1}$, $(AsO_3)^{-3}$, $(SeO_3)^{-2}$, $(BrO_3)^{-1}$ and $(SbO_3)^{-3}$. The empirical material upon which this classification was founded was very meager; my later investigations have, however, confirmed my predictions completely.

At present we have x-ray data on the following groups: $(NO_3)^{-1}$, $(CO_3)^{-2}$, $(BO_3)^{-3}$, $(ClO_3)^{-1}$, $(SO_3)^{-2}$, $(BrO_3)^{-1}$, $(AsO_3)^{-3}$ and $(SbO_3)^{-3}$. In the following section I will describe the experimental results for the individual groups.

Experimental Data on the Structure of the Individual Groups XO_3

NO_3 Group.—Sodium nitrate and lithium nitrate are the two crystals which have given the most reliable data on the NO_3 group. In the first place the atomic arrangement is characterized by only one degree of freedom, and in the second place the oxygens have a large effect on the intensities of reflection, so their positions can be determined with accuracy.

According to the symmetry of the space group the NO_3 radical in these two crystals is planar with nitrogen in the center of an equilateral oxygen triangle. The dimensions of the group were determined as

$NaNO_3^2$	N-O, 1.22 Å.	O-O, 2.11 Å.
$LiNO_3^3$	N-O, 1.25 Å.	O-O, 2.17 Å.

We have reason to believe that the NO_3 group will not be influenced very much by the surrounding atoms in the lattices because of the strength

¹ W. H. Zachariasen, *Norske Vid. Akad. Skr. Oslo*, No. 4, p. 90 (1928).

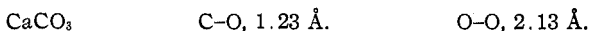
² R. W. G. Wyckoff, *Phys. Rev.*, 16, 149 (1920).

³ W. H. Zachariasen, *Ref. 1*, p. 53.

of the bonds inside the group. V. M. Goldschmidt⁴ has suggested that the dimensions of the group should be greater in compounds containing small cations; *e. g.*, we should expect to find a larger NO_3 group in lithium nitrate than in sodium nitrate. Definite proof of the effect of Goldschmidt's contrapolarization is, however, still lacking. If such an effect exists, it must at any rate be small.

Due to the small scattering power of nitrogen it has been impossible to prove definitely that the NO_3 group always is a planar group. It seems, however, justifiable to assume that the NO_3 group will possess the same structure in all compounds (small deformations may of course be present in some compounds).

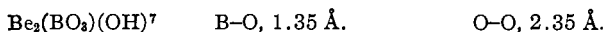
CO_3 Group.—In carbonates with calcite structure a planar CO_3 group follows from the space group symmetry. The dimensions of the group are found to be the same as for the NO_3 group within the limits of error. Wyckoff⁵ determined from calcite:



For the structure of the CO_3 group in other compounds the same considerations that were given for the NO_3 group will be valid.

W. L. Bragg⁶ has determined the dimensions of the CO_3 and the NO_3 groups also from the refractive indices of crystals with calcite or aragonite structure. In the CO_3 group he finds, in agreement with the x-ray data, C-O 1.25 Å. For the NO_3 group, however, he calculated N-O 1.10 Å., which is in definite disagreement with the x-ray determinations 1.24 Å. This result is not surprising when we consider that the center of the oxygen atom determined according to these two methods need not be identical.

BO_3 Group.—Indirect evidence that the BO_3 group is analogous to that of the carbonate group we have from the fact that the two compounds, dolomite, $\text{CaMg}(\text{CO}_3)_2$, and nordenskjöldine, $\text{CaSn}(\text{BO}_3)_2$, are isomorphous. Only one x-ray determination of the BO_3 group exists, namely, from the compd $\text{Be}_2(\text{BO}_3)(\text{OH})$ (the rare mineral hambergite). The atomic arrangement in hambergite is characterized by twenty-one degrees of freedom, so the accuracy necessarily is not very great. A conscientious determination of the parameters led to a planar BO_3 group, however. This result combined with the indirect evidence should be sufficient proof of the analogy to the NO_3 and CO_3 groups. The dimensions of the BO_3 group from hambergite are



⁴ V. M. Goldschmidt, *Geochem. Vert. Ges. VIII Norske Vid. Akad. Skr.* No. 2, p. 64 (1926).

⁵ Wyckoff, *Am. J. Sci.*, 50, 317 (1920).

⁶ W. L. Bragg, *Proc. Roy. Soc. (London)*, A105, 370 (1924); 106, 346 (1924).

⁷ W. H. Zachariassen, *Z. Krist.*, 76, 289 (1931).

ClO_3 Group.—The earlier x-ray investigations on sodium chlorate led to very divergent structures of the ClO_3 group. Kolkmeijer, Bijvoet and Karssen⁸ found Cl-O 0.93 Å., O-O 1.56 Å.; Dickinson and Goodhue,⁹ Cl-O 1.43, O-O 2.34 Å.; Vegard¹⁰ Cl-O 1.85 Å., O-O 1.17 Å. The two former sets of values result in nearly planar groups, while Vegard's ClO_3 values lead to an extremely acute trigonal pyramid. I have determined the atomic arrangement in sodium chlorate with the greatest care, using absolute intensity measurements and applying two-dimensional Fourier analysis of the electron distribution.¹¹ My results were in fairly good agreement with those of Dickinson and Goodhue, but differ in one essential point. My observations show definitely that the ClO_3 group is not planar, but has the shape of a low trigonal pyramid.

From an investigation on potassium chlorate, which has an atomic arrangement completely different from sodium chlorate, I have also determined the structure of the ClO_3 group, making use of the same experimental methods.¹² These two independent determinations of the ClO_3 group agree very well

$KClO_3$	Cl-O, 1.48 Å.	O-O, 2.38 Å.	h , 0.50 Å.
$NaClO_3$	Cl-O, 1.48 Å.	O-O, 2.38 Å.	h , 0.48 Å.

h being the displacement of chlorine out of the oxygen plane.

SO_3 Group.—Recently Mr. Buckley and I have determined the atomic arrangement in sodium sulfite.¹³ Our results for the SO_3 group are

Na_2SO_3	S-O, 1.39 Å.	O-O, 2.24 Å.	h , 0.51 Å.
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It is to be remarked that the dimensions of the SO_3 group in sodium sulfite probably are too small due to the fact that the sodium atoms surround the group in an unsymmetrical way. If the SO_3 group is surrounded by the neighboring ions in a more symmetrical way (as is the case for the ClO_3 group in sodium chlorate and potassium chlorate), we might expect dimensions more close to those of the ClO_3 group.

BrO_3 Group.—The structure of the BrO_3 group was determined from the atomic arrangement in potassium bromate. The results obtained were

$KBrO_3$	Br-O, 1.68 Å.	O-O, 2.76 Å.	h , 0.56 Å.
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AsO_3 Group and SbO_3 Group.—The crystal lattices of arsenic trioxide and antimony trioxide were determined by Bozorth.¹⁴ The lattice can be considered as composed of molecules As_4O_6 or Sb_4O_6 . As the coordination numbers are 3 and 2, each molecule is built up of 4 AsO_3

⁸ Kolkmeijer, Bijvoet, Karssen, *Proc. Roy. Acad. Amsterdam*, **23**, 644 (1921).

⁹ Dickinson and Goodhue, *THIS JOURNAL*, **43**, 2045 (1921).

¹⁰ L. Vegard, *Z. Physik*, **12**, 289 (1922).

¹¹ Zachariasen, *Z. Krist.*, **71**, 517 (1929).

¹² Zachariasen, *ibid.*, **71**, 501 (1929).

¹³ Zachariasen and Buckley in press in *Phys. Rev.*

¹⁴ Bozorth, *THIS JOURNAL*, **45**, 1621 (1923).

or SbO_3 groups, each oxygen being divided between two groups. It is thus not correct to speak of the radicals AsO_3 and SbO_3 existing in these lattices, but only about *groups* of the said composition.

Bozorth's results for the structure of the groups were

As_2O_3	As-O, 2.01 Å.	O-O, 3.28 Å.	h , 0.67 Å.
Sb_2O_3	Sb-O, 2.22 Å.	O-O, 3.62 Å.	h , 0.75 Å.

Among important radicals XO_3 for which experimental data are lacking we have $(\text{PO}_3)^{-3}$ and $(\text{SeO}_3)^{-2}$.

Considerations on the Structure of Groups XO_3 .—The experimental data at once suggest the classification of the groups introduced by the author.¹⁵ The groups examined are divided between the two classes in the following way: Class 1, planar groups, BO_3 , CO_3 , NO_3 ; Class 2, pyramidal groups, SO_3 , ClO_3 , AsO_3 , BrO_3 , SbO_3 .

The following regularity exists: if we consider the groups to have the valence usually ascribed to them (indicated throughout the paper), the number of valence electrons in the groups of class 1 is 3×8 ; in the groups of class 2 the number of valence electrons is $3 \times 8 + 2$. This feature is so striking that it seems natural to seek the cause of the differentiation in planar and pyramidal structures in the number of the valency electrons.

It is not surprising to find that the symmetry of the group has to be correlated with the number of valence electrons. A rigorous explanation of the rule cannot, however, be given until a wave-mechanical treatment of such groups has been carried out. In the meantime we must be content with rough approximations.

It is well known that the greater part of the inorganic non-metallic crystal structures can be treated successfully by introducing the conception of ions, ionic dimensions and polarizability. The results obtained from this point of view may be considered as an approximation to the correct ones. It would be incorrect to consider the bonds within the radicals dealt with here to be of a purely ionic character; therefore we have to take into account also the deformations taking place in the electron clouds of the ions.

Let us consider the ClO_3 group as an example. The constituents are Cl^{+5} and O^{-2} . The polarizability is related to the mole refraction by the well-known expression

$$R = \frac{4\pi}{3} N\alpha$$

α is again defined by the relation $m = \alpha F$, where m is the moment induced in an atom under the influence of the force F . The moment we must consider to be due to a displacement of the centers of the positive and negative charges in the atom. Practically this will mean a displacement

¹⁵ Zachariasen, *Norske Vid. Akad. Skr. Oslo*, No. 4, p. 136 (1928).

of the core relative to the center of the outer electron shell. If there are v valence electrons and if the amount of displacement is d , we have

$$m = dxv \text{ or } d = \frac{3RF}{4\pi Nve}$$

i. e., the displacement is proportional to the molar refraction, and inversely proportional to the number of valence electrons. It is evident therefore that the polarizability constants do not give us directly the degree of deformation in the outer electron shell.

The molar refraction values for O^{-2} and Cl^{+5} are 3.3 and 1.5 cc.¹⁶ If we consider that oxygen has an outer shell of 8 electrons while chlorine has only 2, we derive from our result above that deformation on the outer shell is greatest for Cl^{+5} . It has been shown that groups with a polarizable central ion will have an unsymmetrical structure, so that a pyramidal ClO_3 group is just what we should expect.¹⁷ The deformations taking place are easy to picture. The field intensity due to the three oxygen ions will polarize the chlorine ion, and in such a way that the outer electron density (the two valence electrons) is pushed away from the oxygens. The chlorine ion on the other hand will to some extent attract the electron density corresponding to the valence electrons of oxygen. The relative displacement of core and valence electrons is, however, much greater in the Cl^{+5} ion both because of the stronger force acting upon it and also because of the small number of valence electrons.

As a final result we obtain a ClO_3 group which roughly can be pictured as a tetrahedral arrangement; three of the corners are occupied by oxygen ions, the center by a Cl^{+7} ion and the fourth corner by the two valence electrons of chlorine. If this tetrahedron were accurately regular and if we could consider the ions and the two electrons to be point charges, the center of the positive and negative charges would coincide. It has, however, been definitely shown that unsymmetrical molecules have a permanent dipole moment. The observed moment is very small and corresponds to only a few hundredths of an Ångström unit displacement between the centers of the negative and positive charges. For rough considerations of the structure of such groups we may therefore disregard this displacement. The conception of a tetrahedral ClO_3 group as presented above would give the following relation between the oxygen-oxygen distance (a) and the height h of the Cl^{+7} core above the plane of the oxygens

$$h = \frac{a}{12} \sqrt{6} \quad (1)$$

From x-ray determination we will obtain the position of the Cl^{+7} core, as the two valence electrons have no detectable effect on the scattering power. The centers of the oxygens fixed by the same method on the

¹⁶ From paper submitted to *Phys. Rev.*

¹⁷ Van Arkel and de Boer, *Rec. trav. chim.*, **47**, 593 (1928).

other hand must correspond very closely to the center of electron density as the valence electrons in this case have an appreciable effect. The experimentally determined values of h and a are thus within the limits of error identical with those of Equation (1). In the table is shown how closely the relation I holds for all the groups examined, so that there seems to be justification for the conception of tetrahedral groups.

Group	a	h	$\frac{a}{12} \sqrt{6}$	r
SO ₃	2.24	0.51	0.46	1.39
ClO ₃	2.38	.49	.49	1.48
AsO ₃	3.28	.67	.67	2.01
BrO ₃	2.76	.56	.56	1.68
SbO ₃	3.62	.75	.74	2.22

The picture given for the structure of pyramidal groups XO₃ must not be taken too literally. To say that the two valence electrons of Cl⁺ lie at the fourth corner of the tetrahedral structure is naturally incorrect, and must be interpreted as meaning a concentration of electron density in that region. If we use interpretations of that kind, I believe that the picture can be considered as an approximation toward the true distribution of electron density in the group.

In a following paper¹⁶ I am trying to locate the positions of the displaced electrons in the ClO₃ group from the strength of the birefringence in potassium chlorate. The result of that calculation supports the considerations given here.

A Relation between the Symmetry of Groups and Molecules XY₂, XY₃ and the Number of Valence Electrons

In the previous section we found that groups (XO₃)^{-m} had a co-planar structure if the total number of valence electrons was 24 (3 × 8), while the groups were pyramidal if there were 26 (3 × 8 + 2) valence electrons in the group.

A more general formulation of this empirical rule will now be considered. We will confine ourselves to groups and molecules of the form XY₂ and XY₃, in which all atoms Y are chemically identical and are related to atom X in the group in an identical way. Furthermore, we will make the restriction that the atomic numbers are relatively small.

The existing reliable observations then show:

$$\text{A group or molecule } \left\{ \begin{array}{l} (\text{XY}_2)^{-m} \\ (\text{XY}_3)^{-m} \end{array} \right. \text{ is } \left\{ \begin{array}{l} \text{co-linear} \\ \text{co-planar} \end{array} \right. \text{ if } \left\{ \begin{array}{l} \Sigma v = 2p \\ \Sigma v = 3p \end{array} \right.$$

Σv is the total number of valence electrons in the group or molecule; p represents the number of valence electrons in the inert gas following atom Y in the periodic system. If, on the other hand, the relation between Σv and p takes the form $\left\{ \begin{array}{l} \Sigma v = 2p + \Delta \\ \Sigma v = 3p + \Delta \end{array} \right.$ the group or molecule is $\left\{ \begin{array}{l} \text{angular} \\ \text{pyramidal} \end{array} \right.$

Because these rules have been derived from empirical data, we may with reason use it as a guiding principle until an exact formulation on the basis of wave mechanics can be given, or until we have experimental evidence that the rule does not hold.¹⁸

In the following table I have listed a number of groups and molecules according to the kind of structure which should be expected if the rule holds.

TABLE I

Co-linear	Angular
CO ₂ , ON ₂ , CS ₂ (NN ₂) ⁻ , (HF ₂) ⁻	SO ₂ , NO ₂ , SH ₂ , OH ₂ , OO ₂ ? (ozone) (NO ₂) ⁻
Co-planar	Pyramidal
SO ₃ , BH ₃ , BF ₃ , BCl ₃ , AlF ₃ (BO ₃) ⁻³ , (CO ₃) ⁻² , (NO ₃) ⁻	NH ₃ , PH ₃ , AsH ₃ , PF ₃ , PCl ₃ (OH ₃) ⁺ , (PO ₃) ⁻³ , (SO ₃) ⁻² , (ClO ₃) ⁻ (AsO ₃) ⁻³ , (SeO ₃) ⁻² , (BrO ₃) ⁻

Mr. Ziegler in this Laboratory is at present working on the crystal structure of sodium nitrite. The investigation is not quite completed yet, but his results so far do not seem to be compatible with a co-linear (NO₂)⁻ group.

Groups XO_2 for which $\Sigma v = 2 \times 8 + 2$ can be pictured as an equilateral triangle. The center of the triangle will be occupied by the core of the central ion, two of the corners by oxygens and the third corner by the two displaced valence electrons. The angle between the two cation-oxygen bonds would thus be 120 degrees.

Since the above paper was written, valuable contributions to the quantum mechanical treatment of shared electron bonds have been made by Slater¹⁹ and Pauling.²⁰

Pauling has applied the theory on groups XO_3 with the following results. For groups XO_3 of class 2 in my notation he finds that the angle between the X-O bonds is $109\frac{1}{2}$ (the tetrahedral angle), in excellent agreement with the experimental results I have obtained. In groups of class 1, however, the central atom according to Pauling is oscillating with a very small amplitude perpendicular to the oxygen plane, again in accordance with the results of this paper.

There are thus two ways of interpreting the structure of groups XO_3 , which both lead to the same result: one being the conception of shared electron bonds (naturally in the quantum mechanical treatment), the other being the conception of ions and their deformation in the field of the surrounding ions. These two methods of attack are dualistically related to each other.

¹⁸ It is to be remarked that the above rule for the structure of groups XY_2 and XY_3 can be deduced directly from considerations of ions and their polarizability.

¹⁹ Slater, *Phys. Rev.*, **37**, 481 (1931).

²⁰ Pauling, *THIS JOURNAL*, **53**, 1367 (1931).

Summary

The general results concerning the structure of groups XO_3 in crystals are given. The groups are found to be of two kinds, one kind of groups has a co-planar structure, the other a low pyramidal structure. In the following table a denotes the oxygen to oxygen distance; r the cation to oxygen distance and h the displacement of the cation out of the plane of the oxygens.

Co-planar groups			Pyramidal groups			
	a	r		a	r	h
$(BO_3)^{-3}$	2.35 Å.	1.35	$(SO_3)^{-2}$	2.24	1.39	0.51
$(CO_3)^{-2}$	2.13	1.23	$(ClO_3)^{-}$	2.38	1.48	.49
$(NO_3)^{-}$	2.14	1.23	$(AsO_3)^{-3}$	3.28	2.01	.67
			$(BrO_3)^{-}$	2.76	1.68	.56
			$(SbO_3)^{-3}$	3.62	2.22	.75

It is pointed out that groups $(XO_3)^{-m}$ are co-planar if the number of valence electrons in the groups is 3×8 , while a pyramidal arrangement seems to be connected with $3 \times 8 + 2$ valence electrons. An explanation of the formation of the asymmetrical groups in terms of ions and their polarizability is given. The displacement h is related to the oxygen-oxygen distance a by the expression $h = (a/12) \sqrt{6}$. This relation suggests a simple picture of the pyramidal groups; they can be considered as tetrahedral groups, with three of the corners occupied by oxygen ions, the center by the cation core and the fourth corner by two displaced electrons.

It is shown that the symmetry of groups $(XY_2)^{-m}$ and $(XY_3)^{-m}$ can be correlated with the number of valence electrons. The result is expressed in the following rule: A group or molecule $\begin{Bmatrix} XY_2 \\ XY_3 \end{Bmatrix}$ is $\begin{cases} \text{co-linear} \\ \text{co-planar} \end{cases}$ if the number of valence electrons in the group or molecule (Σv) can be expressed by $\begin{cases} \Sigma v = 2p \\ \Sigma v = 3p \end{cases}$, p being the number of valence electrons in the inert gas following atom Y in the periodic system. If the number of valence electrons has to be written in the form $\begin{cases} \Sigma v = 2p + \Delta \\ \Sigma v = 3p + \Delta \end{cases}$ the group or molecule is $\begin{cases} \text{angular} \\ \text{pyramidal} \end{cases}$.

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