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The Structure of the Hypophosphite Group as Determined from the Crystal Lattice of Ammonium Hypophosphite

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The crystal structure of ammonium hypophosphite was examined in order to determine the size and shape of the hypophosphite group. The crystals are orthorhombic-holohedral with the dimensions of the unit cell; $a=3.98\text{\AA}$, $b=7.57\text{\AA}$, $c=11.47\text{\AA}$. There are 4 molecules $\text{NH}_4(\text{H}_2\text{PO}_2)$ in the cell, and the space group is $A_{cm}m(V_h^{21})$. The complete structure is given by the following parameter values: 4 N in $\pm(0\frac{1}{4}0)$, 4 P in $\pm(u_10\frac{1}{4})$ with $2\pi u_1=195^\circ\pm 5^\circ$; 8 O in $\pm(u_20v_2)$ with $2\pi u_2=125^\circ\pm 5^\circ$ and $2\pi v_2=49^\circ\pm 2^\circ$; 8 H in $\pm(u_3v_3\frac{1}{4})$ with $2\pi u_3=290^\circ$ and $2\pi v_3=51^\circ$; 16 H in $\pm(xyz)$. The parameter values for phosphorus and oxygen were determined directly from the observed intensities of reflections, whereas the hydrogen values are based upon reasonable assumptions. The hypophosphite group has the

shape of a distorted tetrahedron; two of the tetrahedral corners being occupied by oxygen atoms and the other two by hydrogen atoms. The phosphorus to oxygen distance is 1.51\AA and the angle between the phosphorus to oxygen bonds 120° . The distance from phosphorus to hydrogen is 1.5\AA and the angle between the P-H bonds 92° . Each ammonium radical is surrounded by four oxygen atoms at a distance of 2.81\AA and by four hydrogen atoms at a distance of 3.08\AA . There is strong indication that the ammonium radical is not rotating, and that hydrogen atoms of the NH_4 -groups are linked to the surrounding oxygen atoms as well. The hydrogen atoms of the hypophosphite group behave toward ammonium as if they were H^- ions.

FOR a number of years one of us has been making systematic investigations with the purpose of determining the exact shape and dimensions of inorganic groups in crystals. With recent developments in the theory of chemical binding examinations of this kind get additional significance. The experimental data which are available concerning the structures of the oxygenic radicals of atoms in the first two rows of the periodic system are now fairly extensive, although far from complete. Notably the data on boron-oxygen and on phosphorus-oxygen groups are very few. Of the latter groups only the structure of the ortho-phosphate radical has been determined. It is the purpose of the present paper to describe the results of an investigation on the structure of the hypophosphite group.

The ammonium compound was chosen as suitable for the examination. The crystals were prepared for us through the kindness of A. E. Sidwell of the Jones Chemical Laboratory of this university. They conform to the description given by Groth¹ who reports them as orthorhombic bipyramidal with axial ratios: $a : b : c = 0.5276 :$

$1 : 1.5137$. The density was determined by us with the suspension method and gave the value 1.634 .

The x-ray data consisted of Laue and oscillation photographs. For the latter Mo K radiation was used. For the dimensions of the orthorhombic unit cell we found: $a=3.98\text{\AA}$, $b=7.57\text{\AA}$, $c=11.47\text{\AA}$ —accuracy $\frac{1}{2}$ percent. By using the density given above, it is readily seen that the unit cell contains 4 molecules $\text{NH}_4\text{H}_2\text{PO}_2$. The space lattice is base centered since reflections were only observed from planes hkl for which $k+l$ is even. Furthermore, planes $0kl$ reflect only if k and l both are even, indicating that the space group is $A_{cm}m(V_h^{21})$. It was a comparatively easy task to determine the distribution of the atoms among the available positions of the space group. We found:

4 N atoms in $\pm(0\frac{1}{4}0)$, $\pm(0\frac{3}{4}\frac{1}{2})$

4 P atoms in $\pm(u_10\frac{1}{4})$ $\pm(u_1\frac{1}{2}\frac{3}{4})$,

8 O atoms in $\pm(u_20v_2)$, $\pm(u_20\frac{1}{2}-v_2)$,
 $\pm(u_2\frac{1}{2}v_2+\frac{1}{2})$ $\pm(u_2\frac{1}{2}\bar{v}_2)$.

The hydrogen atoms have a negligible influence on the amplitude of the scattered radiation; their positions will therefore be discussed later.

¹ P. Groth, *Chemische Krystallographie*, Vol. 2, p. 770, Leipzig, 1908.

The determination of the three parameter values for phosphorus and oxygen entirely on the basis of the observed intensities of reflections presented no serious difficulties. The values are: $2\pi u_1 = 195^\circ \pm 5^\circ$, $2\pi u_2 = 125^\circ \pm 5^\circ$ and $2\pi v_2 = 49^\circ \pm 2^\circ$.

The good agreement between calculated amplitudes and observed intensities, to be seen in Tables I, II and III, constitutes the ultimate proof of the correctness of the parameter values for nitrogen, phosphorus and oxygen. The scat-

tering powers for phosphorus and oxygen have been experimentally determined by J. West² for potassium dihydrogen-phosphate. The scattering power of nitrogen (or more correctly of the ammonium group) we assumed to be the same as for oxygen.

Two-thirds of the hydrogen atoms per unit cell are associated with nitrogen atoms to form the ammonium ions. These hydrogen atoms will be referred to as H_I atoms. The ammonium radicals may or may not be rotating in the crystal.

TABLE I. Reflections $0kl$.*

$00l$	$\sin \theta/\lambda$	I	F	$02l$	$\sin \theta/\lambda$	I	F	$04l$	$\sin \theta/\lambda$	I	F	$06l$	$\sin \theta/\lambda$	I	F
002	0.087	s	-18	020	0.132	vs	63	040	0.264	vs	69	060	0.396	w+	27
004	.174	m	10	022	.158	vs	-64	042	.278	w+	27	062	.405	w	-28
006	.262	vw-	3	024	.219	w+	-27	044	.316	w	10	064	.433	nil	-7
008	.349	vs	48	026	.293	m	-24	046	.372	vw-	0	066	.475	vw	-16
00.10	.436	w+	-24	028	.373	m	25	048	.437	ms	38				
00.12	.523	vw-	10	02.10	.455	m-	-32	04.10	.510	w-	-16				
				02.12	.540	nil	0								

TABLE II. Reflections $h0l$.*

$00l$	$\sin \theta/\lambda$	I	F	$10l$	$\sin \theta/\lambda$	I	F	$20l$	$\sin \theta/\lambda$	I	F	$30l$	$\sin \theta/\lambda$	I	F
002	0.087	s	-18	100	0.127	s	-39	200	0.251	m	27	300	0.378	tr	16
004	.174	m	10	102	.153	vs	61	202	.266	vw	-5	302	.387	w	20
006	.262	vw-	3	104	.215	vw	13	204	.306	s	39	304	.415	w	-19
008	.349	vs	48	106	.290	s	25	206	.363	w-	-9	306	.459	w+	24
00.10	.436	w+	-24	108	.371	m	-18	208	.430	w+	17	308	.513	nil	6
00.12	.523	vw-	10	10.10	.454	m-	27	20.10	.503	nil	-3				

TABLE III. Reflections $hk0$ and hkl .

$0kl$	$\sin \theta/\lambda$	I	F	$1kl$	$\sin \theta/\lambda$	I	F	$2kl$	$\sin \theta/\lambda$	I	F	$3kl$	$\sin \theta/\lambda$	I	F	$4kl$	$\sin \theta/\lambda$	I	F
011				100	0.127	m	-39	200	0.251	w+	27	300	0.378	tr	16	400	0.503	nil	3
020	0.132	s	63	111	.148	w+	-23	211	.263	nil	10	311	.385	vw-	9	411	.509	vw+	-18
013				120	.182	s+	-77	220	.284	vw-	-5	320	.400	vw	-4	420	.520	nil	-8
022	.158	s	-64	113	.193	m+	-27	213	.291	m	25	313	.404	w+	-14	413	.523	nil	-8
031				122	.202	w+	11	222	.297	m	-31	322	.409	tr	1	422	.527	nil	-12
024	.219	w	-27	131	.239	vw+	-14	231	.323	nil	7	331	.428	vw	9	431	.542	vw-	-17
015				124	.252	m-	-27	234	.333	w	13	334	.436	w+	-35				
033				115	.260	w+	29	215	.339	m	-29	315	.440	w+	15				
040	.264	s-	69	133	.269	w-	-19	233	.346	w+	21	333	.445	w	-13				
042	.278	w	-13	140	.292	w+	-23	240	.364	w+	19	340	.460	nil	10				
026	.293	w+	-24	142	.305	m-	35	242	.375	vw	-5	342	.468	vw	16				
035				126	.319	vw-	2	226	.386	w+	-26	326	.477	vw-	9				
017				135	.320	w+	23	235	.387	w+	-25	335	.478	w-	14				
044	.316	vw	10	117	.337	tr	1	217	.401	tr	4	317	.489	vw+	-9				
051				144	.340	nil	-8	244	.404	w+	30	344	.492	vw+	-16				
053				151	.356	nil	-8	251	.417	nil	4	351	.503	vw-	7				
037				153	.377	vw	-15	253	.435	vw+	17	353	.518	vw	-12				
046	.372	nil	0	137	.385	nil	-1	237	.442	vwv	4	337	.524	tr	-9				
028	.373	w+	25	146	.392	w	22	246	.449	vw	-9	346	.529	vw-	19				
055				128	.393	w+	-35	228	.450	tr	3	328	.530	nil	-6				
060	.396	w+	27	155	.415	vw-	16	255	.469	w-	-20	355	.546	vw	12				
019				160	.415	w+	-34	260	.469	nil	1	360							
062	.405	w	-28	119	.417	nil	-9	219	.471	nil	5	319	.548	vw-	6				
064	.433	nil	-7	162	.424	vw	9	262	.477	vw	-19								
048	.437	w+	38	164	.451	vw	-14	264	.500	vwv	10								
				148	.455	w-	-14	248	.504	vw+	14								

* I =Observed intensity; F =calculated amplitude.² J. West, Zeits. f. Krist. 74, 306 (1930).

Each nitrogen atom is surrounded by four oxygen atoms at a distance of 2.81Å. The four oxygen atoms form an almost regular tetrahedron around nitrogen, the angles between the connection lines N—O being 95°, 113° and 121°. This fact indicates rather strongly that the H_I atoms are linked to the oxygen atoms as well. We shall see later that considerations of the N—O distances support this view. Accordingly the ammonium groups are not rotating and the H_I atoms must be placed in general positions $\pm(xyz)$, etc., with such values of x , y and z as would place the hydrogen atoms somewhere along the connection lines N—O.

Now let us consider the remaining one-third of the hydrogen atoms in the unit cell. These atoms we will refer to as H_{II} . Two possibilities will be considered: (1) $NH_4H_2PO_2$ is a true acid salt (2) the hypophosphite radical is $(H_2PO_2)^-$ with the two hydrogens attached directly to phosphorous. Of course, the chemists have accepted the latter possibility as the correct one, because of the mono-basic character of the hypophosphorous acid. However, we found it to be of interest to disprove case 1 by direct evidence.

We know the crystal lattice of two acid salts (KH_2PO_4 and $NaHCO_3$) and of one acid (H_3BO_3) with great accuracy. The hydrogen atoms are in every case attached to two oxygen atoms forming collinear groups O—H—O with an O—O distance of 2.55Å or 2.71Å (H_3BO_3). Obviously this is the characteristic feature of crystalline oxygenic acids and acid salts. Now in the present crystal the closest distance between two oxygen atoms (which are attached to different phosphorus atoms) is 3.45Å. Consequently there is no possibility for having an O—H—O group of the proper size, and $NH_4H_2PO_2$ is not to be termed an acid salt.

In agreement with chemical evidence we are therefore led to believe that the H_{II} atoms are attached directly to phosphorus.

It is reasonable to suppose that the four bonds of phosphorous are directed more or less toward the corners of a tetrahedron. This means that the H_{II} atoms are lying in positions $\pm(u_3v_3\frac{1}{4})$, $\pm(\bar{u}_3, \frac{1}{2}-v_3, \frac{1}{4})$, $\pm(\bar{u}_3, v_3+\frac{1}{2}, \frac{1}{4})$, $\pm(u_3, \bar{v}_3, \frac{1}{4})$. Assuming a distance of 1.50Å for phosphorus to hydrogen, the ammonium to hydrogen distance becomes about 3.1Å. This indicates a binding

between NH_4 and H_{II} , so that an H_{II} atom is linked to one phosphorus atom and two ammonium groups. It is logical to assume that these three bonds from hydrogen (to one P and two NH_4) are lying in one plane. This latter assumption together with the assumed P—H distance of 1.50Å fix completely the positions of the H_{II} atoms. The parameter values become: $2\pi u_3 = 290^\circ$; $2\pi v_3 = 51^\circ$.

It now remains to be seen if our assumptions lead to a reasonable structure for the hypophosphite group. (It should be emphasized that the phosphorus and oxygen positions were determined directly from the observed intensities of reflections.) Phosphorus is linked to two oxygen atoms at a distance of 1.51Å with a maximum error of 0.11Å. The angle between the P—O bonds is 120° with a maximum error of 8°. The oxygen to oxygen distance is 2.61Å. With the accepted H_{II} parameters one finds the angle between the P—H bonds to be 92°, while the angle between a P—O and a P—H bond becomes 117°. This is a reasonable result: In replacing two of the oxygen atoms in the PO_4 -group by hydrogen atoms it is to be expected that the initial tetrahedral angles between bonds will be modified. On general grounds the repulsion between two oxygen atoms (not linked together) must be greater than between an oxygen and a hydrogen atom, and this again greater than for two hydrogen atoms. Hence we should expect the angle between the P—O bonds to be greater than the tetrahedral angle, the angle between the P—H bonds to be less than the tetrahedral angle. The H—H distance in the group is 2.16Å and the H—O distance 2.45Å.

Around each ammonium group there are four oxygen atoms at a distance of 2.81Å and there are four H_{II} atoms at a distance of 3.08Å. The coordination number thus is 8. The crystal radius of the rotating ammonium ion is 1.44Å.³ The calculated NH_4 —O distance for coordination number 8 (reference 3) is 3.02Å, which is considerably higher than the observed value of 2.81Å. The difference is far greater than can be accounted for by the approximation involved in the conception of ionic radii. It is logical to attribute the cause of the discrepancy to a non-

³ W. H. Zachariasen, *Zeits. f. Krist.* **80**, 137 (1931).

rotating ammonium group, i.e., that the observed distance of 2.81 refers to the N—O distance in group N—H—O, rather than to $(\text{NH}_4)^+ - \text{O}$. It is to be recalled that the presence of nonrotating ammonium radicals was made plausible also by another observation.

It is a well-known fact, tested by scores of observations, that the oxygen atoms in oxygenic radical ions (as $(\text{CO}_3)^{-2}$, $(\text{NO}_3)^-$, $(\text{SO}_4)^{-2}$, $(\text{ClO}_4)^-$, $(\text{ClO}_3)^-$) behave as O^{-2} ions at least with respect to the cations linking the radicals together. We may try if the same applies to the hydrogen atoms in the hypophosphite group. That is to say: Will the H_{II} atoms behave as H^- ions with respect to the $(\text{NH}_4)^+$ ions? From the recent data on the structure of the alkali hydrides⁴ we deduce a radius of 1.52 Å for H^- . With this value we calculate an $(\text{NH}_4)^+ - \text{H}^-$ distance of 3.09 Å (for coordination number 8), while the observed value was 3.08 Å.

Indeed the conception of ions permits fairly accurate predictions of interatomic distances even in radicals, where the binding only in part is

ionic. Thus we may think of the hypophosphite radical as consisting of ions: $(\text{H}_2 - \text{P}^{+5} \text{O}_2^{-2})^-$. The crystal radii of these ions are all known (reference 3) so that we may calculate the interionic distances. We find 1.56 Å and 1.48 Å for $\text{P}^{+5} - \text{O}^{-2}$ and $\text{P}^{+5} - \text{H}^-$, respectively, while we observed 1.51 Å for P—O and assumed 1.50 Å for P—H.

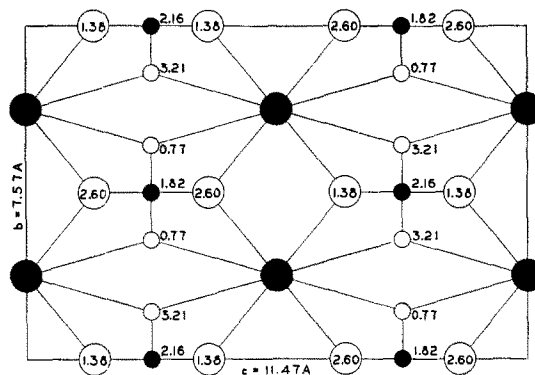


FIG. 1. The drawing shows the structure projected on the a -face. Large filled circles represent ammonium groups, small filled circles phosphorus atoms. Large open circles represent oxygen atoms, while the small open circles represent the hydrogen atoms (H_{II}). The ammonium groups all lie in the plane of the paper. The attached numbers indicate for the other atoms their height in Å above the plane of the paper. Bonds are indicated by connection lines.

⁴ E. Zintl and A. Harder, *Zeits. f. physik. Chemie* **B14**, 265 (1931).