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Crystallographic Study of the Ammonium/Potassium 12-Molybdophosphate Ion-Exchange System

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Ammonium and potassium 12-molybdophosphate crystals obtained by gel-diffusion methods, as well as the products obtained by subjecting the parent compounds to ion exchange in solutions containing the alternate cations, have been studied by single-crystal X-ray diffraction studies, using automatic counting techniques. Details of the structures of five compounds of the type $(K, NH_4, H_3O)_3(PO_4)Mo_{12}O_{36}$, which have all been refined to $R < 0.06$, show that although the various crystals appear to be isomorphous (space group *Pn*3*m*, $a \simeq 11.65$ Å), the incompleteness of exchange observed with these materials can be rationalized in terms of a phase transition consisting of the reorientation during ion exchange of ammonium ions in the exchanger phase. This is probably caused by a reorganization of the bonding pattern in the clathrated anionic unit to compensate for the rupture of bifurcated hydrogen bonds.

Introduction

A well-known but hitherto unexplained feature of cation exchange on ammonium 12-molybdophosphate, $(NH_4)_3PO_4Mo_{12}O_{36}$ (AMP), is its incompleteness, a maximum of about 50% of the ammonium ions being replaceable by the alkali ions (*1*, *2*). One possible reason for this behavior, namely, that the mixed crystal obtained at maximum exchange might represent a state of minimum lattice energy, has been discounted on the basis of "precipitation isotherms" (*2*). These were obtained by adding a solution of the parent acid to a solution of fixed total concentration and which contains ammonium nitrate and the other metal nitrate in varying proportions. The precipitation isotherm for the ammonium/potassium system (Fig. 1) bears no resemblance to the ion-exchange isotherm for this system, shows no evidence of a minimum lattice-energy state, and has a sigmoidal shape reminiscent of ion-exchange isotherms with zeolites (*3*, *4*).

The origin of this selectivity reversal may be threefold (*3*): occupation by cations of sites of different selectivities; interaction between ions in adjacent sites; and the accompaniment of ion exchange by a phase transition.

The second possibility, which usually occurs with di- or trivalent ions, may be discounted as extremely unlikely, and it should be possible to distinguish between the remaining possibilities by means of crystallographic studies of partially exchanged crystals. The results of powder crystallography (*5*, *6*) suggest isomorphous structures for all compositions in the system but leave the position

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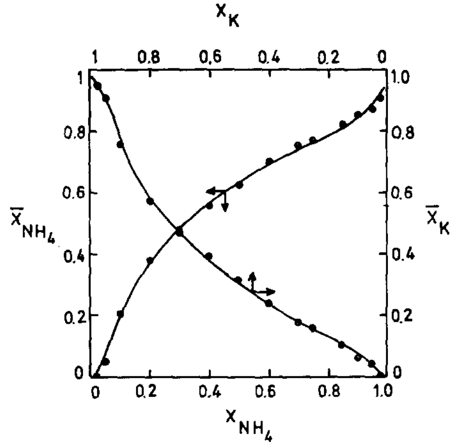

FIG. 1. Precipitation isotherm for the K^+/NH_4^+ 12-molybdophosphate system. X is the ionic fraction in the aqueous phase and $\bar{X}$ is that in the solid phase. Initially the total nitrate concentration was 1 M, and precipitation was brought about by adding 5 ml of 12-molybdophosphoric acid solution dropwise to 50 ml of the nitrate solution.

of the NH_4^+ ions undecided. To resolve the problem, single-crystal studies have now been undertaken.

Experimental and Results

Sample Preparation

Crystalline starting material was obtained by allowing solutions of either ammonium or potassium nitrate and of 12-molybdophosphoric acid to diffuse together over a period of two days through a gelatin plug separating the two solutions contained in the arms of a U-tube. Other compositions were obtained by subjecting good-quality, oriented single crystals of the starting materials, mounted on goniometer heads, to ion exchange by dipping the crystals for about 20 min into 3 M solutions of either potassium or ammonium nitrate. Since the crystals were grown from acid solutions, pure potassium molybdophosphate (KMP) or AMP were not obtained directly, but only after appropriate ion exchange, as just described. Morphologically featureless, diffraction-quality crystals of the following materials were obtained by this method:

(i) $K_x(H_3O)_{3-x}MP$: directly,
(ii) K_3MP: by exchanging (i) in KNO_3,
(iii) $K_x(NH_4)_{3-x}MP$: by exchanging (i) in NH_4NO_3,
(iv) $(NH_4)_x(H_3O)_{3-x}MP$: directly,
(v) $(NH_4)_xK_{3-x}MP$: by exchanging (iv) in KNO_3.

Crystal Data

A preliminary Weissenberg examination of the five types of crystal obtained showed all to be cubic, of space group $Pn3m$, with $Z = 2$, confirming the powder work of Illingworth and Keggin (*7*) on AMP. Cell constants were measured to an accuracy of 0.01 Å on a Weissenberg diffractometer and are given in Table I.

Determination of Structures

Intensity measurements were carried out with a Stoe two-circle automatic Weissenberg diffractometer equipped with a graphite-crystal incident-beam monochromator using molybdenum radiation at room temperature. The intensities of all reflections with positive *hkl* were measured within the sphere $2\theta \leqslant 60°$ using an ω-scan mode over a variable range to compensate for spot-elongation on higher

TABLE I

DETAILS OF STRUCTURE ANALYSIS

Crystal	a (Å)	Number of intensities	R	Refined composition
$K_x(H_3O)_{3-x}MP$	11.60(1)	335	0.052	$K_{2.0}(H_3O)_{1.0}MP$
K_3MP	11.60(1)	178	0.039	$K_{2.7}(H_3O)_{0.3}MP$
$K_x(NH_4)_{3-x}MP$	11.62(1)	173	0.033	$K_{0.9}(NH_4)_{2.1}MP$
$(NH_4)_x(H_3O)_{3-x}MP$	11.70(1)	278	0.048	$(NH_4)_{2.6}(H_3O)_{0.4}MP$
$(NH_4)_xK_{3-x}MP$	11.65(1)	117	0.059	$(NH_4)_{1.8}K_{1.2}MP$

layer lines. Integrated intensities were obtained by counting for 1 sec per 0.01° ω-step.

After correction for Lorentz and polarization factors, internal scaling was attained by averaging the intensities of symmetry-equivalent reflections from different layer lines. The observed discrepancies were less than 4%. The two single crystals used in this study were of approximately the same size (0.05 × 0.03 × 0.03 mm), corresponding to a typical $\mu R = 0.2$, which obviated absorption corrections. After averaging, the unique data sets consisted of 120 to 300 independent measurable intensities. Compare Table I.

TABLE II

FRACTIONAL COORDINATES AND ISOTROPIC THERMAL PARAMETERS FOR THE ATOMS IN THE ASYMMETRIC UNITS, WITH THE ESTIMATED STANDARD DEVIATIONS IN THE LAST ONE OR TWO DECIMAL PLACES GIVEN IN PARENTHESES

Crystal	Asymmetric unit	x	y	z	B (Å^2)
K)$_x$(H$_3$O)$_y$MP	Mo	0.4670(1)	0.4670(1)	0.2587(1)	1.57(2)
	O$_1$	0.6528(6)	0.6528(6)	0.0060(9)	1.56(16)
	O$_2$	0.0689(6)	0.0689(6)	0.7670(9)	2.07(18)
	O$_3$	0.1233(6)	0.1233(6)	0.5398(9)	1.81(18)
	O$_4$	0.3273(8)	0.3273(8)	0.3273(8)	1.01(24)
	P	0.25	0.25	0.25	1.15(18)
	Cations	0.25	0.75	0.75	1.57
(K)$_3$MP	Mo	0.4679(9)	0.4679(9)	0.2584(15)	1.50(3)
	O$_1$	0.6520(9)	0.6520(9)	0.0064(14)	1.63(27)
	O$_2$	0.0688(10)	0.0688(10)	0.7662(15)	2.42(34)
	O$_3$	0.1224(9)	0.1224(9)	0.5415(12)	1.38(25)
	O$_4$	0.3266(14)	0.3266(14)	0.3266(14)	1.46(50)
	P	0.25	0.25	0.25	0.36(25)
	Cations	0.25	0.75	0.75	1.50
(K)$_x$(NH$_4$)$_y$MP	Mo	0.4672(1)	0.4672(1)	0.2589(2)	2.57(5)
	O$_1$	0.6507(11)	0.6507(11)	0.0060(18)	2.68(41)
	O$_2$	0.0672(10)	0.0672(10)	0.7686(16)	2.48(40)
	O$_3$	0.1228(11)	0.1228(11)	0.5395(18)	2.72(46)
	O$_4$	0.3256(16)	0.3256(16)	0.3256(16)	1.24(60)
	P	0.25	0.25	0.25	0.75(45)
	Cations	0.25	0.75	0.75	2.57
	H		Disordered		
(NH$_4$)$_x$(H$_3$O)$_y$MP	Mo	0.4661(8)	0.4661(8)	0.2586(12)	2.44(3)
	O$_1$	0.6522(7)	0.6522(7)	0.0046(9)	2.31(20)
	O$_2$	0.0664(7)	0.0664(7)	0.7677(9)	2.47(22)
	O$_3$	0.1233(7)	0.1233(7)	0.5383(9)	2.59(21)
	O$_4$	0.3257(9)	0.3257(9)	0.3257(9)	1.70(30)
	P	0.25	0.25	0.25	1.77(23)
	Cations	0.25	0.75	0.75	2.44
	H	0.78	0.78	0.32	—
(NH$_4$)$_x$(K)$_y$MP	Mo	0.4671(2)	0.4671(2)	0.2587(4)	3.37(9)
	O$_1$	0.6531(20)	0.6531(20)	0.0069(34)	4.37(78)
	O$_2$	0.0641(16)	0.0641(16)	0.7641(28)	2.57(58)
	O$_3$	0.1205(20)	0.1205(20)	0.5338(30)	4.31(85)
	O$_4$	0.3245(24)	0.3245(24)	0.3245(24)	1.59(94)
	P	0.25	0.25	0.25	0.20(55)
	Cations	0.25	0.75	0.75	3.37
	H	0.80	0.80	0.20	—

Initial characterization indicated isomorphism with the pentahydrate of 12-tungstophosphoric acid (*5*), and this was confirmed by Patterson and Fourier analysis of one of the structures, although water of hydration was not observed. Preliminary full-matrix least-squares refinement of the positional and isotropic thermal parameters of all the structures was followed by difference syntheses to investigate disordering over different lattice sites and test for water content. Detailed refinement by full-matrix least-squares based on F, was done using the program of Finger (*8*), which conveniently allows occupancy refinement. Free atom, analytically approximated scattering factors were obtained from "International Tables for X-Ray Crystallography," Vol. IV, and the weighting scheme was based on counting statistics. Electrical neutrality was used as a constraint to refine the occupancy factors of N, K, and O (for H_3O^+) at the cationic site to give the chemical composition. To avoid correlation problems between occupancy and Debye–Waller factors, the latter for the cationic site was arbitrarily coupled to that of the molybdenum atom. The refined atomic and thermal parameters are listed in Table II. The origin of coordinates was chosen at the center ($\bar{3}m$). The final conventional *R*-factors are given in Table I. Observed and calculated structure factors have been deposited as an NAPS document.[1]

At the termination of refinement after five cycles, virtually featureless difference maps were obtained in most cases. In the case of crystals which had been subjected to exchange before the analysis, some excess electron density was observed beyond the positions of the four oxygen atoms associated with the phosphorous atom (i.e., at positions about 1.9 Å from P), as well as around the phosphorous position. Considered in conjunction with the abnormally low temperature factors of the phosphorus atom in each of these cases, this leads to the conclusion that during ion exchange, another tetrahedral species partially displaces phosphate groups.

Displacement of phosphate by molybdate (MoO_4^{2-}) explains the observed effects rather well. The Mo–O bond in such a species would be longer than the P–O bond, and hence, could account for the electron density beyond the oxygen position, while the heavier Mo causes the apparent Debye–Waller factor of P to be low. The extent of phosphate–molybdate interchange was estimated by approximate occupancy refinement as about 10% of the phosphorus expected in the central position. A related effect has been observed by Fischer and co-workers (*9*) in the structure of another molybdophosphate species, where

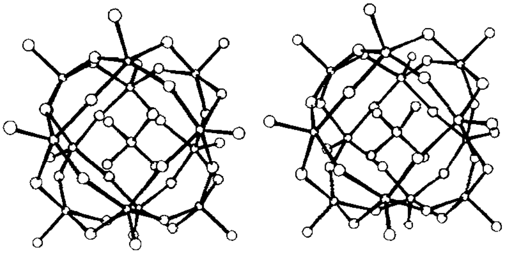

FIG. 2. Stereoscopic view of the $PO_4(MoO_3)_{12}^{3-}$ anionic unit.

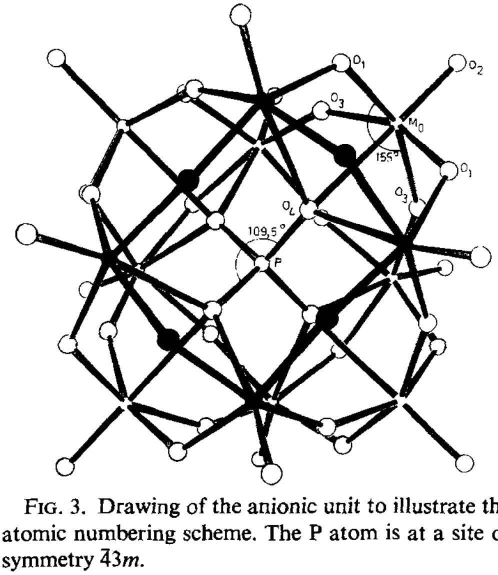

FIG. 3. Drawing of the anionic unit to illustrate the atomic numbering scheme. The P atom is at a site of symmetry $\bar{4}3m$.

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[1] See NAPS document No. 02740 for 16 pages of supplementary material. Order from ASIS/NAPS, c/o Microfiche Publications, 305 East 46th Street, New York, N.Y. 10017. Remit in advance for each NAPS accession number $1.50 for microfiche or $5.00 for photocopies up to 30 pages, 15¢ for each additional page. Make checks payable to Microfiche Publications.

TABLE III

Significant Bond Lengths, Interatomic Distances and Bond Angles in the Various Molybdophosphate Structures, with Estimated Standard Deviations in the Last One or Two Digits in Parentheses

	Bond lengths or interatomic distance (Å)					
	$(K)_{2.0}(H_3O)_{1.0}MP$	$(K)_{2.7}(H_3O)_{0.3}MP$	$(K)_{0.9}(NH_4)_{2.1}MP$	$(NH_4)_{2.6}(H_3O)_{0.4}MP$	$(NH_4)_{1.8}(K)_{1.2}MP$	Ref. (*13*)
Cation–O_1	3.254(8)	3.254(15)	3.270(20)	3.302(9)	3.257(9)	
Cation–O_2	2.983(10)	2.978(12)	3.010(12)	3.055(10)	3.072(8)	
Cation–O_3	3.210(9)	3.200(13)	3.214(19)	3.253(9)	3.307(9)	
Mo–O_1	1.912(7)	1.911(13)	1.914(14)	1.918(10)	1.924(9)	1.914
Mo–O_2	1.701(8)	1.680(12)	1.676(12)	1.686(8)	1.623(8)	1.680
Mo–O_3	1.923(8)	1.934(13)	1.920(16)	1.931(10)	1.907(10)	1.923
Mo–O_4	2.430(10)	2.445(16)	2.456(19)	2.458(10)	2.476(11)	2.433
P–O_4	1.556(10)	1.547(16)	1.516(19)	1.535(10)	1.506(10)	1.542
O_1–O_1	2.610(12)	2.595(18)	2.578(25)	2.597(10)	2.641(10)	2.606
O_1–O_3	2.653(10)	2.670(13)	2.677(20)	2.684(11)	2.688(11)	2.682
O_3–O_3	2.680(13)	2.687(18)	2.672(25)	2.675(14)	2.547(14)	2.645
H–O_3	—	—	—	2.31	—	
H–O_1	—	—	—	—	2.38	
H–O_2	—	—	—	2.745	2.278	
Cation–H	—	—	—	0.96	1.01	
P–Mo	3.567(3)	3.575(3)	3.571(4)	3.583(3)	3.584(3)	3.562
P–O_1	3.376(8)	3.377(12)	3.393(15)	3.397(9)	3.398(9)	
P–O_3	3.959(9)	3.976(12)	3.960(20)	3.978(9)	3.942(9)	
			Bond angles, degrees			
O_4–P–O_4	109.5(5)	109.5(7)	109.5(10)	109.5(5)	109.5(6)	
Cation–H–O_1	—	—	—	—	144	
Cation–H–O_2	—	—	—	99.6	134.6	
Cation–H–O_3	—	—	—	167	—	
H–Cation–H	—	—	—	137	109	
O_1–Mo–O_3	155.3(3)	155.3(4)	155.7(6)	155.5(4)	154.2(4)	

some of the phosphate occurs in positions traditionally occupied by molybdate groups. As discussed in the next section, some unexplained electron density near the cationic site was found to appear in regions most likely to be occupied by the hydrogen atoms of ammonium ions.

Description of Structures

The gross features of the general structure type have been described more or less correctly by Keggin and others (*5*, *7*). The phosphate group, for instance, is centered at a site of $43m$ symmetry and is surrounded by 12 interconnected MoO_4 units in such a way that each of the molybdenum atoms, which together occur in a shell around the phosphate ion, is octahedrally surrounded by oxygen atoms. A stereoscopic view of this arrangement is shown in Fig. 2. Close-packing of the anionic units leaves sufficient space for the cations in orthogonally intersecting channels, but not for any water of crystallization, as surmised by Keggin (*5*).

There are four crystallographically independent oxygen atoms per anionic unit, and our numbering scheme to distinguish between them is shown in Fig. 3. The atoms designated O(1) and O(3) act as bridges between molybdate groups at an average Mo–O bond distance of 1.92 Å, a figure typical for Mo–O–Mo bridge bonds (*10*). The nonbridging O(2) atoms are on average 1.69 Å from the Mo, compared to a typical double-bond length of 1.70 Å (*10*). The average Mo–O(4) distance of 2.45 Å is considerably longer than any known true Mo–O bond length and thus reflects weak coordination. It is therefore not inappropriate to describe the anionic unit as a clathrated phosphate ion, as originally proposed by Pauling (*11*). AMP should then be named ammonium phosphate–12-polymolybdate-(1/1), of formula $(NH_4)_3PO_4(MoO_3)_{12}$, according to the rules of nomenclature for clathrates (*12*).

Individual interatomic distances and angles are shown in Table III. It has been confirmed that the cations occupy only the body-centered $\bar{4}2m$ sixfold set. Multiple-site explanations of the ion-exchange behavior thus need not be considered any further.

Also listed in Table III are corresponding bond lengths and interatomic distances reported by Strandberg (*13*) (after the present work had been completed) for the 12-molybdophosphate anion in the fully hydrated free acid.

Discussion

The actual composition of the various crystals as derived from occupancy refinement is shown in Table I. Sufficient single-crystal material of the potassium acid salt (starting material) was available for the crystallographic result to be compared with chemical analysis, which yielded $(K)_{1.96}(H_3O)_{1.04}MP$. The agreement is sufficiently good for the crystallographic values to be accepted with confidence. According to these, AMP shows only about 40% exchange for K^+, which is in fair agreement with the approximately 50% exchange indicated by chemical studies (*2*). The crystallographic values show the reverse process of NH_4^+ exchange on KMP to have proceeded to 70% of completion. The two processes thus do not yield the same product, and the limited exchange in the two cases cannot be ascribed to a common factor. A detailed comparison of the various structures shows that this anomaly is probably due to a phase transition accompanying ion exchange.

Although the quality of the data does not allow a quantitative description of the structure reorganization that takes place during ion exchange an interesting qualitative picture does emerge. It is emphasized that, particularly in the absence of accurate hydrogen positions which would require a neutron diffraction analysis, the following picture is largely speculative.

The proposed mechanism of transition is based on the differences in the cation–O(1) and cation–O(3) interatomic distances which occur for the partially exchanged (K)AMP and parent AMP crystals. In AMP these distances are 3.30 and 3.25 Å, and after partial exchange for K^+ they are interchanged, being 3.26 and 3.31 Å, respectively. This interchange is accompanied by interchanges of the separations between neighboring O(1)–O(1) and O(3)–O(3) atoms. The respective values of 2.60 and 2.68 Å in AMP becomes 2.64 and 2.55 Å in (K)AMP. At the same time, the O(1)–O(3) distance remains unaffected.

The most obvious factor that could cause these changes is a change in the orientation of the ammonium ion and its interaction with the cagework oxygen atoms, most probably through hydrogen bonds. The first-shell neighbors of the cation are the set of O(2) atoms, but since they occur in square-planar arrangement around the cationic site, they are not likely to be hydrogen-bonded directly to the tetrahedral ammonium ion. The second-nearest shell contains the O(1) and O(3) sets, both tetrahedrally disposed with respect to the cation. In AMP the O(3) set is significantly closer to the nitrogen than the O(1) set, and in (K)AMP the order is reversed. In ammonium sulfate, furcated N–H···O bonds as long as 3.33 Å have been observed by neutron diffraction (*14*). The observed N--O distance of 3.25 Å could represent a similar type of hydrogen bond and, depending on the composition, it is directed preferentially towards either the O(1) or O(3) atoms.

It has been comforting, though not crucial to the argument, to observe, on reexamination of the difference Fourier maps, regions of unexplained electron density (~0.5 e Å^{-3}) around the positions expected to be occupied by hydrogen atoms in terms of the proposed scheme. The two different hydrogen-bond systems, with the "observed" hydrogen positions, are illustrated stereoscopically in Figs. 4 and 5. The lines connecting hydrogen atoms with O(3) and O(1) atoms have been drawn in. Stippled lines are drawn towards O(2) atoms. In both diagrams, and from Table III, the N–H bonds are seen not to be directed straight toward the oxygen atoms but more specifically toward the region between either O(3) or O(1) and a neighboring O(2) atom. As in ammonium sulfate (*14*), such hydrogen bonds would be of the bifurcated type. In AMP the NH_4^+ ion is hydrogen-bonded to both O(2) and O(3), while the bifurcated bonds in (K)AMP involve atoms O(2) and O(1).

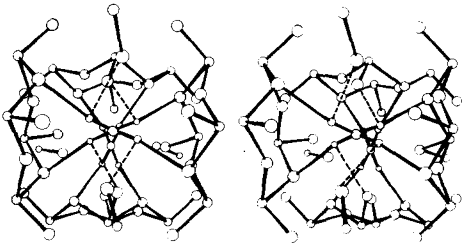

FIG. 4. Stereoscopic diagram to show the environment of NH_4^+ in a crystal of AMP. Hydrogen atoms are connected to O(3) atoms by solid lines and to O(2) by broken lines.

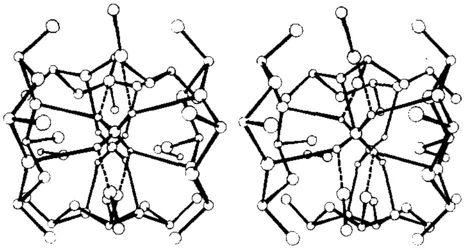

FIG. 5. Stereoscopic diagram to show the environment of NH_4^+ in a crystal of AMP subjected to K^+ ion exchange. Hydrogen atoms are connected to O(1) atoms by solid lines and to O(2) by broken lines.

A reorientation of the ammonium ions remaining in the crystal therefore seems to occur as ion exchange for K^+ proceeds. The exchange is arrested when only reoriented ammonium ions remain in the crystal. Rupture of the hydrogen bonds during exchange of NH_4^+ for K^+ leaves the environment in an excited state, and relaxation occurs through the strengthening of bonds in the anionic unit. Comparison of the Mo–O(2), Mo–O(3), and P–O(4) bonds in AMP with those in (K)AMP shows that these bonds are shortened from 1.69 to 1.62 Å, from 1.93 to 1.91 Å, and from 1.54 to 1.51 Å, respectively, during ion exchange. There is also a decrease from 3.98 to 3.94 Å in the P–O(3) separation. As may be expected, strengthening of the P–O(4) bond is accompanied by a weakening of the Mo–O(4) interaction, as shown by an increase in the interatomic distance from 2.46 to 2.48 Å. Some of these differences are within the limits of experimental error, but they all reflect a consistent pattern.

According to this model, increasing numbers of hydrogen bonds are eliminated as the exchange of NH_4^+ ions for K^+ proceeds, and this leads to a reorganization of the bond pattern in adjacent anionic units. With increased restructuring of the anion, the orientation of the remaining NH_4^+ ions becomes less favorable for bifurcated hydrogen bonding to atoms O(3) and O(2), and they change their orientation to form new hydrogen bonds, which now involve the more favorably disposed atoms O(1) and O(2). At about 50% exchange, the situation is reached where all remaining NH_4^+ ions have reoriented to form new hydrogen bonds. Up to this point it has been possible to compensate for the rupture of hydrogen bonds by a general increase in bond strength within the anionic unit. Beyond this point, no further restructuring can occur and no further compensation for hydrogen-bond rupture in the new phase is possible. Therefore, the exchange of NH_4^+ for K^+ ions becomes energetically unfavorable, and ceases.

The reverse process in which K^+ was exchanged for NH_4^+ in KMP resulted in about 70% exchange. The exchange structure, (NH_4)KMP, approaches the structure of AMP, but no evidence of preferential direction of hydrogen bonds towards any particular set of cagework oxygen atoms was observed. The NH_4^+ ions appear to be disordered over the two possible orientations, although an examination of the bond lengths shows that the AMP structure is favored. The more extensive exchange observed in this case is not surprising, since there is no energy barrier such as the rupture of hydrogen bonds to be overcome.

The incomplete conversion could be due to the random orientation of the incoming NH_4^+ ions. Figures 4 and 5 show that neighboring NH_4^+ ions are oriented at right angles to one another. Unless there is a driving force favoring a certain orientation at a specific site, random exchange cannot be expected to result in any one regular arrangement for the entire crystal. Regions of mismatch between differently oriented ordered domains are more likely to occur, and, unless annealing takes place, this will inhibit further exchange. Therefore, the incomplete conversion in this case probably occurs because of kinetic rather than thermodynamic reasons.

Conclusion

The shape of the precipitation isotherm shown in Fig. 1 can now be explained in terms of the proposed phase transition. The inflection point occurs at $X_{NH_4} \simeq 0.8$, where $\bar{X}_{NH_4}$ is about 0.75. Above this inflection point ($\bar{X}_{NH_4} \geqslant 0.75$), the precipitate has the structure of the ammonium-rich phase, with NH_4^+ ions hydrogen-bonded mainly to O(3) and O(2). In precipitates obtained at $\bar{X}_{NH_4} <$ 0.75, most of the NH_4^+ ions are bonded to O(1) and O(2) in the more relaxed structure-type which favors K^+.

The postulated displacement of phosphate by molybdate groups brought about by ion exchange cannot be explained. It does suggest, however, that gross distortion of the anionic cage occurs during ion exchange and this relates to the tendency of AMP and analogous exchangers to peptise after prolonged elution.

A final aspect, elucidated by this study, concerns the selectivity of AMP for large monovalent cations. Eisenman (*15*; see also *3*) has shown that the selectivity sequence exhibited by an exchanger for ions of a particular group, and the degree to which one ion is preferred over another, depend on the character of the exchanger, i.e., the anionic field strength over the exchanger sites and whether it is anhydrous or not.

The distribution of water in the 12-molybdophosphate compounds between water of crystallization and capillary-condensed water has long been a vexing question (*6*, *7*, *16*, *17*). This study shows conclusively that in contrast to phosphotungstic acid which occurs as the hexahydrate (*18*), AMP, and probably the related structures as well are anhydrous. The water content of microcrystalline AMP is thus entirely due to capillary condensation, and the exchanging cations are fully stripped of their hydration shells upon passing into the exchanger phase. This explains the correlation that exists between the maximum exchange capacities of the monovalent ions and the ionic radius, or hydration energy, of the exchanging cation (*2*).

The selectivity sequence for alkali ions shown by AMP, namely, Cs > Rb > K > Na > Li, is the same as the series I sequence predicted by Eisenman (*3*, *15*) for ion exchangers of low anionic field strength. In fact, AMP is known (*18*) to exhibit an extraordinarily high selectivity for large alkali ions over those proceding them in the series. From a consideration of the structure of AMP it becomes clear that this is due to the fact that AMP is an extreme case of a series I exchanger of unusually low anionic field strength.

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