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A single crystal neutron diffraction study on mixed crystal $(K)_{0.25}(NH_4)_{0.75}H_2PO_4$: tuning of short strong hydrogen bonds by ionic interactions

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Abstract. One of the most intriguing facts about hydrogen bonds is that bonds formed between the same couple of donor and acceptor atoms can have large variation in the geometry as well as energies; this is mainly because hydrogen bonds are highly sensitive to their environment. We report here a comparative study of neutron structures of mixed crystals of potassium–ammonium dihydrogen phosphate. Basic structural framework of crystals belonging to potassium dihydrogen phosphate family is constructed by a network of zigzag O–H–O hydrogen bonded chains of $PO_2(OH)_2$ anions, with cations occupying the interspaces of the zigzagged anionic chains. These crystals having simple crystal structure primarily determined by the O–H–O hydrogen bonds connecting $PO_2(OH)_2$ anions provide us with a unique opportunity to tune the hydrogen bond geometry by varying the cationic occupancy and study the effect of this change on the average structure of the crystal. The cation–anion interaction is found to have a direct influence on the O–H–O hydrogen bonds of the mixed crystals.

Keywords. Neutron crystallography; mixed crystals; hydrogen bonds.

1. Introduction

Hydrogen bond (H-bond) is an important interatomic interaction, which plays an important role in determining the properties of vast range of materials, e.g., hydrogen bonding is central to the unique properties of water, to protein folding and function, to proton transport in proton conductors, to corrosion and crystal engineering [1,2]. Though known for a very long time, no general theoretical model accounting for all the unique features of H-bonds could be proposed until recently. Main difficulty in modelling H-bonds comes from the fact that unlike normal bonds, which have an energy and distance almost exclusively decided by the atoms constituting the bond, there is a large variation in the geometry as well as energies of H-bonds formed between the same couple of donor (D) and acceptor (A) atoms. This is mainly because H-bonds are highly sensitive to their environment [3]. Hence, in order to understand the nature of a given H-bond one needs to closely study the role of other interactions, which the donor and acceptor make with surrounding atoms. A recent study on strongly hydrogen-bonded materials demonstrated that one way of fine-tuning H-bond properties is to tune interionic interactions within crystals by substituting a cation by another cation having similar charge, but different size, e.g., changing K^+ by Na^+ [4]. A thorough understanding of how the environment affects hydrogen bonding is very important from the point of view of improving the properties of existing materials as well as designing new hydrogen-bonded

materials with required properties. Hence, we have undertaken single crystal neutron diffraction investigation on potassium–ammonium dihydrogen phosphate (ADP) mixed crystals and we have tried to analyse how varying cationic occupancy vary with the interionic interactions, which in-turn influences the H-bond properties.

Hydrogen bonding plays a key role in determining the physical properties, including the nature of phase transition in crystals belonging to the potassium dihydrogen phosphate family (KDP family) [5]. The basic structural framework of these crystals is constructed by a network of zigzag hydrogen-bonded chains of $PO_2(OH)_2$ anions along the ab planes, the cations (potassium ion in case of KDP and ammonium ion in case of ADP) occupy the interspaces of the zigzagged anionic chains and they interconnect the adjacent anionic networks along the *c*-axis [6]. Potential energy surface for O–H–O H-bonds connecting adjacent $PO_2(OH)_2$ ions of KDP as well as ADP crystals is known to be having symmetric double-well potential [7]. The cationic site in KDP–ADP mixed crystals $((KDP)_X(ADP)_{1-X})$ is occupied by more than one type of ions [8], structure of these mixed crystals obtained from single crystal diffraction data give time as well as space average picture of the crystal unit cell. Local crystal structures in the mixed crystals vary with the crystal composition and this in turn has an influence on the average crystal structure. For example, any change in the local chemical environment around a given O atom can bring about a change in the potential energy surface of the O–H–O bonds

involving the given O atom and this can lead to a change in the O–O distance of the given O–H–O bond. A number of such variations in the local structure can add up resulting in a change of average crystal structure significantly. Hence, these crystals having simple crystal structure primarily determined by the O–H–O H-bonds connecting $PO_2(OH)_2$ anions provide us with a unique opportunity to tune the H-bond potential surface by varying the cationic occupancy and study the effect of this change on the average structure of the crystal. We had earlier [9] obtained the neutron structure of two mixed crystals with composition $(K)_{0.71}(NH_4)_{0.29}H_2PO_4$ and $(K)_{0.33}(NH_4)_{0.67}H_2PO_4$ along with the structures of pure KDP and ADP under ambient lab conditions. We report here the neutron structure of another mixed crystal having composition $(K)_{0.25}(NH_4)_{0.75}H_2PO_4$ under similar lab conditions. A detailed comparison of the average structure of these crystals namely KDP, $((K)_{0.71}(NH_4)_{0.29}H_2PO_4$, $(K)_{0.33}(NH_4)_{0.67}H_2PO_4$, $(K)_{0.25}(NH_4)_{0.75}H_2PO_4)$ and ADP throws light on how the changing chemical environment influences the O–H–O H-bond and hence, the average crystal structure.

2. Experimental

$KDP_X(ADP)_{1-X}$ mixed crystals are obtained from the aqueous solutions containing AR grade KDP and ADP salts in required stoichiometry. It is difficult to grow good quality big mixed crystals having large levels of substitution [8]. After repeated recrystalization we were able to obtain millimetre size crystals from the aqueous solution containing KDP and ADP salts in a ratio of 0.2:0.8. A clear rectangular crystal of dimensions 2 mm × 1.2 mm × 1 mm was selected for the single crystal neutron diffraction investigation (Although this crystal was smaller than the optimum crystal size of 3 mm × 3 mm × 3 mm required to obtain good data statistics, but still we were able to collect refinable data using it). The crystal was loaded on a goniometer, which was then mounted on a four-circle single crystal neutron diffractometer with BF_3 point detector located at Dhruva Reactor at Trombay. The integrated neutron counts for all unique Bragg reflections up to $\sin\theta/\lambda = 0.7$ Å^{-1} were recorded in the symmetrical setting of the diffractometer using θ–2θ coupled step scan mode ($0.1°$ step in 2θ). The background was scanned for a minimum of 1 Å on either side. A standard reflection was measured after every 25 reflections and the variation of the standard reflection intensity was within 3%. Squared observed structure factors were obtained from integrated intensities after data reduction. Details of the neutron diffraction experiment are given in table 1. The structural parameters obtained from the earlier neutron diffraction study on $KDP_X(ADP)_{1-X}$ crystals [9] were used as the starting parameters; these were subjected to a series of isotropic and anisotropic full-matrix least-square refinements using software SHELXL [10]. All the reflections including negative Fo^2 were used for refinement. Potassium

Table 1. Details of the neutron diffraction experiment.

a (Å) $= b$ (Å), c (Å)	7.452 (3), 7.512 (5)
Space group	I-42d
V (Å^3)	417.16
No. measured, independent, observed ($I > 2\sigma(I)$) Ref.	213, 209, 112
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.1395, 0.41, 1.416

Table 2. Refined structural parameters of $(K)_{0.25}(NH_4)_{0.75}H_2PO_4$.

Atom	x	y	z	U_{iso}
P	0.000	0.000	0.000	0.020(3)
N/K	1/2	0.00	0.2500	0.034(3)
O	0.147(1)	0.085(1)	0.119(2)	0.031(3)
H$_O$	0.153(5)	0.250	0.125	0.114(18)
H$_N$	0.658(14)	0.039(20)	0.203(12)	0.29(5)

as well as ammonium ions were constrains to occupy the same site within the unit cell, their relative site occupancy was varied, lowest R-factor was obtained when potassium ion occupancy was 25% and ammonium ion occupancy was 75%, hence the exact composition of the mixed crystal is taken to be $(K)_{0.25}(NH_4)_{0.75}H_2PO_4$. In the initial stages of refinement, weight (w) was taken to be $1/\sigma(Fo^2)$, which was derived using counting statistics. Table 2 gives the final refined co-ordinates and isotopic thermal parameters for all the atoms in an asymmetric unit; both hydrogen atoms H$_O$ and H$_N$ have large thermal parameters indicating H-atom disorder.

3. Structural comparison

The most striking feature of the structure of $(K)_{0.25}(NH_4)_{0.75}H_2PO_4$ is a very short O–O distance (2.460 Å) for the H-bond connecting adjacent $PO_2(OH)_2$ anions of this crystal. Figure 1a shows the variation of the O–O distance (donor–acceptor distance) with ammonium ions concentration in $(KDP)_X(ADP)_{1-X}$ mixed crystals. Nature of cation–anion interaction in KDP and ADP crystals is known to be different [11]. In KDP, cation–anion interaction is of purely electrostatic nature but for ADP crystals cation–anion has a hydrogen-bonded nature. The H-bond interaction has a complex behaviour, which can vary from primarily Van der Waals type for large donor–acceptor (D–A) distance, to predominantly electrostatic for intermediate D–A distances and finally to a covalent nature for short D–A distances [12]. At any given D–A distance all these above-mentioned components are present making it difficult to make simple predictions regarding the nature of the H-bond interaction. In fact it was demonstrated by Lasave *et al* [13] that in ADP the formation
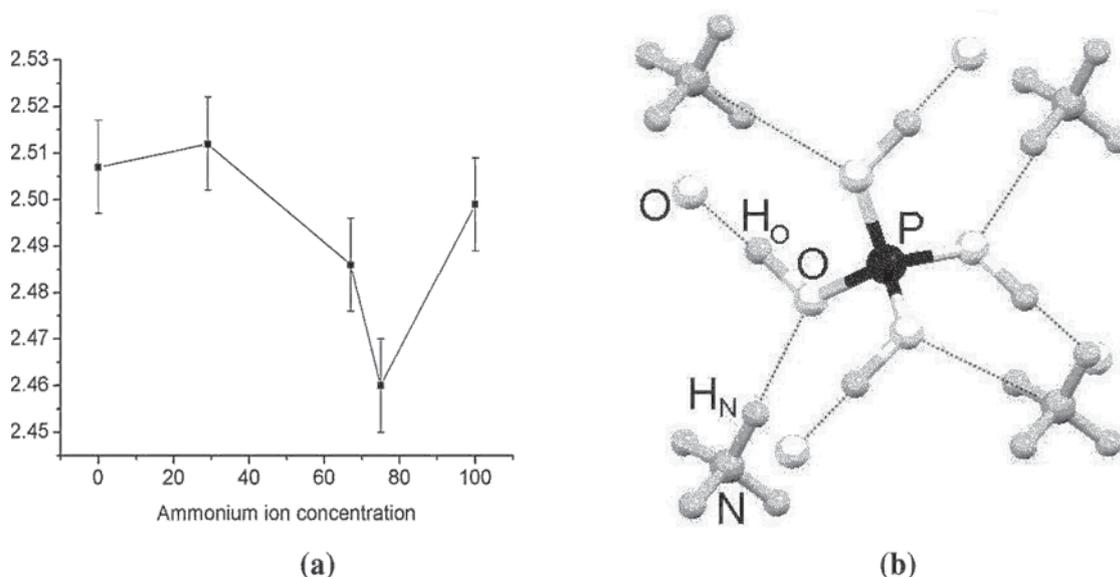
Figure 1. (**a**) Variation of O–O distance with ammonium ion concentration in $(KDP)_X (ADP)_{1-X}$ mixed crystals and (**b**) bifurcated hydrogen bonds in ADP.

of N–H–O H-bond bridges with correlated charge transfers and NH_4 group distortions are essential in stabilizing the anti-ferroelectric configuration against a c-polarized ferroelectric (FE) phase, as well as other FE states polarized perpendicular to the *c*-axis. They clearly indicated that the difference in the nature of ferroelectric phase transition of KDP and anti-ferroelectric phase transition of ADP results from the deference in nature of their respective cation–anion interactions. Phase transition studies [14] on $(KDP)_X (ADP)_{1-X}$ mixed systems have established that as the crystal composition X varies from 1 to 0, the nature of structural phase transition varies as ferroelectric → phase coexistence region → proton glass → phase coexistence region → anti-ferroelectric, i.e., as the nature of cation–anion interaction varies with the crystal composition; the nature of structural phase transition also varies. Curve in figure 1 shows that the changing nature of interionic interactions (cation–anion interactions) in mixed crystals has a direct influence on the O–H–O H-bonds connecting adjacent $PO_2(OH)_2$ anions in the mixed crystals. Main observation from this curve is that the O–H–O H-bond is very sensitive to even small changes in the concentration of ammonium ion in ammonium ion-rich mixed crystals, whereas change in potassium ion concentration in potassium ion-rich mixed crystals does not influence the H-bond that drastically.

O atom of ADP makes P–O, O–H–O and N–H–O bonds, whereas the O atom of KDP makes P–O, O–H–O and K–O bonds, the main difference in the two cases is due to the difference in the nature of K–O interaction and the N–H–O interaction as stated above. The O–H–O bond of ADP is not a commonly encountered two centred H-bond, but it is HXH type three centred H-bond [15] also known as the 'bifurcated acceptor hydrogen bond', acceptor atom (O atom) here acts as an acceptor to not one but two H-bonds simultaneously,

for example, O atom of ADP acts as an acceptor to O–H–O as well as N–H–O H-bonds (figure 1b). Two centred H-bonds like the one found in KDP are energetically superior [15] to the three centred H-bonds like the one found in ADP. Any change in the strength of one of the arms of the bifurcated H-bond influences the other arm directly due to charge redistribution, hence change in the strength of N–H–O H-bonds in ADP crystals will lead to change in the strength of O–H–O H-bonds and vice-versa. Based on the above argument we can explain the rapid decrease in O–O distance as the ammonium ion concentration in mixed crystals falls from 100 to 75% as following: reduction in ammonium ion concentration leads to a change in average strength of N–H–O H-bonds interactions; as a direct consequence of this O–H–O H-bond strength changes as is evident from the significant shortening of O–O distance. However, interestingly this trend is reversed as the ammonium ion concentration decreases further below 75%. There is an increase in O–O distance as the ammonium ion concentration decreases from 75 to 67%. This reversal of behaviour indicates that at ammonium concentration of around 75% the nature of cation–anion interactions within the crystals undergo some sort of change.

Analysing the structure of crystals belonging to the KDP family [8], we find that there are eight O atoms in the close vicinity of a cation, four O atoms lying close to the 'ab' plane are nearest at a distance D1 (figure 2a), remaining four O are located at a slightly longer distance D2 (figure 2a). When we studied the variation of D1 as well as D2 distances with the ammonium ion concentration in the mixed crystals (figure 2b), we noticed an anomalous change in both D1 as well as D2 around the ammonium ion concentration of 75%. Moreover, it is observed (inset of figure 2b) that the c/a ratio (ratio of unit cell dimensions along *c*-axis and *a*-axis) for the
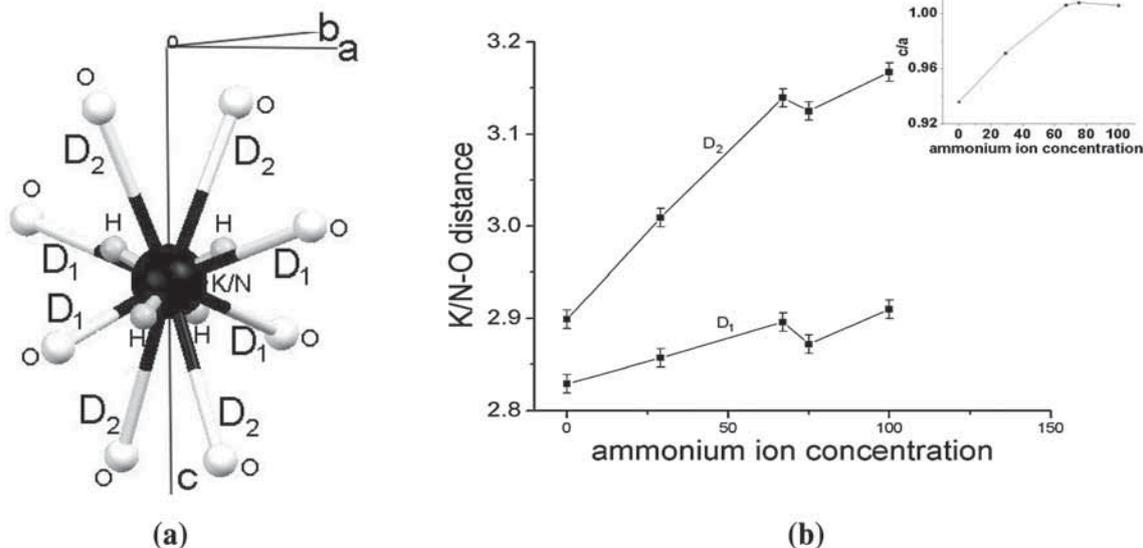
Figure 2. (**a**) Complete co-ordination sphere of the cation in crystal belonging to KDP family and (**b**) variation of D1 and D2 distances with ammonium ion concentration in $(KDP)_X(ADP)_{1-X}$ mixed crystals.

mixed crystals becomes nearly independent of the ammonium concentration around the same ammonium ion concentration. All these observations indicated that the nature of cation–anion interaction in mixed crystals undergoes a change at ammonium ion concentration of around 75%.

Ammonium ion is known to exhibit dual nature in a crystalline environment [16,17], i.e., depending on its environment it can behave either like a pseudo alkali atom or like a H-bond donor. A survey of crystal structures of ammonium salts [17] had shown that the co-ordination number (CN) of the ammonium ion can lie anywhere between 4 and 9, when its CN is small (4 or 5) the hydrogen-bonding tendency of the ammonium ion is predominant and when it is larger (7 to 9) the pseudo alkali character dominates. Difference in c/a ratio of KDP and ADP was explained [11] on the basis of different cationic co-ordination numbers in the two crystals. It was reported that the CN for potassium ion in KDP is 8, but the CN for ammonium ion in ADP is closer to 4. This is mainly due to the formation of reasonably strong N–H–O H-bonds in ADP. Keeping these results in mind we conclude that large and nearly constant c/a ratio for mixed crystals having ammonium ion concentration within the range 100–75% is indicative of higher hydrogen bonding tendency of cations and hence a smaller cationic CN ($\sim$4) in these mixed crystals. Decreasing ammonium ion concentration below 75% results in increasing manifestation of pseudo alkali nature of the ammonium ion, as a result the cationic CN in the mixed crystals increases from 4 to 8. Hence, we can conclude that cation–anion interaction in mixed crystals having ammonium ion concentration below 75% is mainly electrostatic in nature, whereas for crystals having ammonium ion concentration within the range 100–75%, the cation–anion interaction has more of hydrogen bonded nature. The anomalous behaviour

of D1 and D2 as well as the reversal in the trend of variation of O–O distance is due to the change in the nature of ammonium ion from a H-bond donor to pseudo alkali atom, leading to an increase in its cationic co-ordination number.

An interesting observation of our structural comparison is the variation of P–O bond distance with the ammonium ion concentration in mixed crystals (figure 3a), figure 3a shows that changing cation–anion interaction not only affects the O–H–O bonds but also influences the internal geometry of $PO_2(OH)_2$ ions. It is known that P–O bond length in tetrahedral ions can vary anywhere between 1.70 and 1.40 Å depending on the π-orbital contribution to the P–O bond [18]. Ideal geometry for an isolated tetrahedral $PO_2(OH)_2$ ion predicted on the basis of the extended electrostatic valence rule given below [19] has the following bond distances: P–O = 1.501 Å, P–OH = 1.573 Å.

$$d(P–O) = d(P–O)_{mean} + b\Delta p_0$$

Here b is an empirical parameter, Δp_0 is the difference between the bond strength received by individual O atom and the average P–O_{mean} bond strength is 1.537 Å. $PO_2(OH)_2$ ions in KDP as well as ADP form hydrogen bonded chains (figure 3b) and at any location there exists only one H atom between two adjacent $PO_2(OH)_2$ ions. P–O bond lengths of hydrogen-bonded $PO_2(OH)_2$ ions are sensitive to the H atom position within the H-bonds, H atom position in turn depends on the shape of O–H–O H-bond potential energy surface as shown schematically in figure 3b. At room temperature (RT) pure KDP as well as ADP crystals have P–O bond lengths very close to P–O_{mean}, which is an average of P–O and P–OH bond distances for an isolated tetrahedral $PO_2(OH)_2$
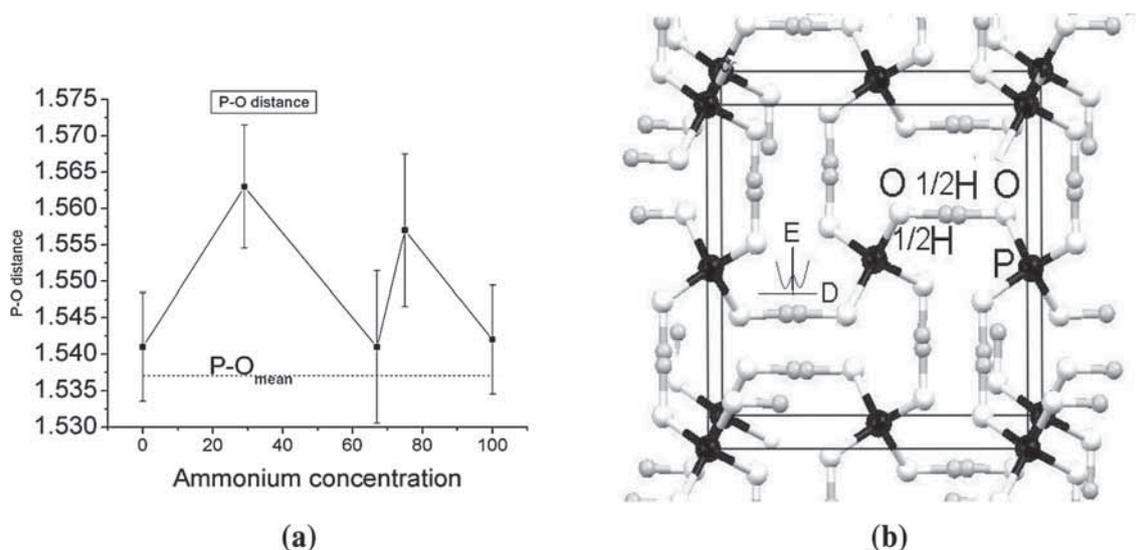
Figure 3. (**a**) Variation of P–O bond distance with the ammonium ion concentration in mixed crystals. (**b**) Hydrogen bonded chains of PO$_2$(OH)$_2$ ions, schematic representation of H-bond potential energy contour for a O–H–O bond in pure crystals.

ion. This is because at RT the H-bonds connecting the adjacent PO$_2$(OH)$_2$ anions of these crystals are symmetrical double-well type (P–O–H$_{1/2}$–~H$_{1/2}$–O–P) with proton spending half the time in each of the two equivalent wells (figure 3b) [7,19]. As a result P–O bond distance obtained from single crystal diffraction is equal to the distance of the P atom to the averaged (apparent) position of the oxygen atoms. P–O bond length in (K)$_{0.33}$(NH$_4$)$_{0.67}$H$_2$PO$_4$ mixed crystal is also very close to P–O$_{mean}$ indicating that just like the cases of pure KDP and ADP crystals, O–H–O H-bonds connecting PO$_2$(OH)$_2$ ions of this mixed crystal are also nearly symmetrical double-well type (P–O–H$_{1/2}$–~H$_{1/2}$–O–P) with H atom spending nearly equal time close to each of the hydrogen bonded O atoms. However, for mixed crystals (K)$_{0.71}$(NH$_4$)$_{0.29}$H$_2$PO$_4$ and (K)$_{0.25}$(NH$_4$)$_{0.75}$H$_2$PO$_4$ the P–O bond length is found to be significantly different from the P–O$_{mean}$ (figure 3a), indicating that average structure in these crystals cannot be simply explained on the basis of symmetrical O–H–O H-bonds connecting adjacent PO$_2$(OH)$_2$ ions. Interestingly if we look into the reported composition–temperature phase diagram (x–T phase diagram) for the KDP$_X$(ADP)$_{1-X}$ mixed systems [14], we realize that the composition of (K)$_{0.71}$(NH$_4$)$_{0.29}$H$_2$PO$_4$ and (K)$_{0.25}$(NH$_4$)$_{0.75}$H$_2$PO$_4$ crystals fall in the phase co-existence region, where competing interactions of ferroelectric/anti-ferroelectric ordering and proton glass random freezing play an important role. The observed average P–O bond lengths for (K)$_{0.71}$(NH$_4$)$_{0.29}$H$_2$PO$_4$ and (K)$_{0.25}$(NH$_4$)$_{0.75}$H$_2$PO$_4$ are 1.563 and 1.557 Å, respectively, which are very close to the bond length of P–O bond with 0.5 π-bond order' (i.e., P–O = 1.55 Å = (1.7 Å + 1.4 Å)/2, here 1.7 Å is the bond length for ideal P–O single bond with π-bond order value 0 and 1.4 Å is the bond length for ideal P=O double bond with π-bond order value 1 [18]). This suggests that H-atom might be spending more time near one of the O atoms as compared to others,

there by modifying the π-bond order of the corresponding P–O bonds; making one bond more like P–O single bond and the other like P=O double bond. Hence, this can be taken as an indication of an asymmetric O–H–O H-bond potential energy surface in these mixed crystals, the main reason for this is the asymmetry in the average local chemical environment around the O–H–O bonds of these mixed crystals.

We conclude that (KDP)$_X$(ADP)$_{1-X}$ mixed crystal system is similar to the alloy systems like (GaN)$_{1-x}$(ZnO)$_x$ [20], where it was found that the compositional fluctuations lead to strong dependence of bond length on the local chemical environment. Understanding the role of order and disorder in determining physical properties such as bond length is complicated by the difficulty in modelling the numerous local chemical environments within the crystal systems.

On the basis of the above-mentioned observations, we suggest that KDP, ADP and (K)$_{0.33}$(NH$_4$)$_{0.67}$H$_2$PO$_4$ crystals having average P–O bond length close to the P–O$_{mean}$ have nearly symmetric double-well average local O–H–O bond potential energy surface. However, K$_{0.71}$(NH$_4$)$_{0.29}$H$_2$PO$_4$ and (K)$_{0.25}$(NH$_4$)$_{0.75}$H$_2$PO$_4$ mixed crystals having P–O bond lengths significantly different from the P–O$_{mean}$ have an asymmetric double-well average local O–H–O bond potential

On the basis of the previously reported x–T phase diagram of the KDP$_X$(ADP)$_{1-X}$ mixed systems [14] and the results of our present structural comparison we can make following predictions: (i) RT phase for all the KDP$_X$ADP$_{1-X}$ crystals is a disordered phase, where hydrogen atom of O–H–O bond continuously moves between the two O atoms, this phase corresponds to the paraelectric phase of x–T phase diagram; (ii) low temperatures phase of the mixed crystals like (K)$_{0.33}$(NH$_4$)$_{0.67}$H$_2$PO$_4$ having nearly symmetric double-well average local O–H–O H-bond potential is the proton glass (PT) phase, where hydrogen atom randomly

freezes into one of the two equivalent positions along the O–H–O bonds; (iii) low temperatures phase of mixed crystals like $K_{0.71}(NH_4)_{0.29}H_2PO_4$ and $(K)_{0.25}(NH_4)_{0.75}H_2PO_4$ having asymmetric double-well average local O–H–O H-bond potential will be a kind of phase coexistence as predicted for phase boundary layers in x–T phase diagram.

4. Conclusions

We have determined the single crystal neutron structure of $(K)_{0.25}(NH_4)_{0.75}H_2PO_4$ mixed crystals and compared the structure with previously determined structures of KDP_X ADP_{1-X} crystals. We have drawn following conclusions from this comparative analysis

(i) The cation–anion interactions have a direct influence on the O–H–O H-bonds in $((KDP)_X(ADP)_{1-X})$ mixed crystals. The O–H–O H-bond connecting $PO_2(OH)_2$ anions is very sensitive to the decrease in the concentration of ammonium ion in predominantly ADP-type crystals, whereas change in the concentration of potassium ion in predominantly KDP-type crystal does not affect the O–H–O H-bond that significantly. Primary reason for this is the difference in the nature of cation–anion interaction in KDP and ADP type crystals.

(ii) The O–O distance of the O–H–O H-bond decreases rapidly as ammonium ion concentration in the crystals falls from 100 to 75% but the trend is reversed as the ammonium ion concentration further decreases from 75 to 67%. This indicated that there is a change in the nature of interactions as the ammonium ion concentration decrease below 75%. We have tried to explain this behavioural change on the basis of change in the average cationic CN. It is argued that CN is 4 for mixed crystals having ammonium ion concentration within the range 100 to 75%, but it increases to 8 as the ammonium ion concentration further decreases below 75%. This change is primarily due to dual nature of ammonium ion, it behaves more like a pseudo alkali atom in crystals with ammonium ion concentration less than 75%, whereas in crystals with ammonium ion concentration more than 75% it behaves like a H-bond donor. This argument is supported by the observed variation of c/a ratio of the mixed crystals with the ammonium ion concentration.

(iii) When we analysed the variation of cation–O distances with the ammonium ion concentration in the mixed crystals (figure 2b), we noticed an anomalous change around the ammonium ion concentration range of 75–67%. This could be attributed to the above-mentioned change in the nature of cation–anion interaction from predominantly H-bond type for crystals having ammonium ion concentration more than 75% to primarily electrostatic for crystals having ammonium ion concentration less than 75%.

(iii) It is known that P–O bond length in tetrahedral ions like in phosphates varies anywhere between 1.70 and 1.40 Å depending on the π-orbital contribution to the P–O bonds. Ideal geometry for isolated $PO_2(OH)_2$ ion has P–O = 1.501 Å and P–OH = 1.573 Å. All the P–O bonds of hydrogen bonded $PO_2(OH)_2$ anionic chains of KDP as well as ADP crystals are close to P–O_{mean} = 1.537Å, which is an average of ideal P–O and P–OH bond lengths indicating that the O–H–O bond connecting $PO_2(OH)_2$ anions is symmetrical double-well type. Of the three mixed crystals studied, one having composition $(K)_{0.33}(NH_4)_{0.67}H_2PO_4$ has average P–O bond lengths close to P–O_{mean} indicating that O–H–O bond linking the $PO_2(OH)_2$ ions of this crystal is also symmetrical double-well type. However, for the remaining two mixed crystals namely $(K)_{0.71}(NH_4)_{0.29}H_2PO_4$ and $(K)_{0.25}(NH_4)_{0.75}H_2PO_4$ the average P–O bond lengths are 1.563 and 1.557 Å, respectively, which are significantly different from P–O_{mean}. Hence, in all likelihood the average potential energy surface for O–H–O bond linking the $PO_2(OH)_2$ ion in these crystals have an asymmetric double form, the main reason for this is the asymmetry in the average local chemical environment around the O–H–O bonds of these mixed crystals.

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