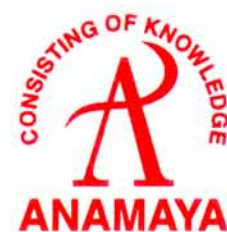


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# X-ray Diffraction Structure Analyses of $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ Mixed Crystals: Nature of H-bonds

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**Abstract:** Structural analyses of  $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$  for  $x = 0.14, 0.33$  and  $0.50$  (TRAHS) single crystals are performed by X-ray diffraction experiments in order to investigate the hydrogen bond (H-bond) connection in  $(\text{SO}_4 \cdot \text{H} \cdots \text{SO}_4'')$  dimers. The H-bond length  $R_{\text{o-o}}$  is determined from the model for H-bond attached to oxygen atoms. In the study, hydrogen bonding is realised with  $R_{\text{o-o}}$  distance being  $2.549 \text{ \AA}$  in  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  and  $2.492 \text{ \AA}$  in  $\text{Rb}_3\text{H}(\text{SO}_4)_2$ . The H-bond length  $R_{\text{o-o}}$  of TRAHS varies with  $x$  and is less than that obtained for pure crystals. The values with  $x = 0.14, 0.33$  and  $0.50$  are  $2.449, 2.522$  and  $2.515 \text{ \AA}$ , respectively. These are close to but still longer than the so-called critical bond length  $R_c$ . The observed lattice parameters vary systematically with  $x$  showing that the mixed crystals are solid solution of two analogues. All these crystals are monoclinic with the space group  $C2/c$  and  $Z = 4$ .

**Keywords:**  $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ , Zero-dimensional hydrogen-bonded crystal, Single crystal X-ray diffraction, Structure analysis.

## Introduction

X-ray structural analyses of  $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$  (TRAHS with  $x = 0.14, 0.33$  and  $0.50$ ) are carried out on P4 four circle diffractometer at room temperature using  $\lambda = 0.71073 \text{ \AA}$  to investigate the H-bond connection in  $(\text{SO}_4 \cdot \text{H} \cdots \text{SO}_4'')$  dimers. The H-atoms positions could not be located directly from the structural refinements of the crystals. The H-bond length  $R_{\text{o-o}}$  is determined from the model for H-bond attached to oxygen atoms [1]. The nature of H-bond and the dynamics of ammonium ions in these crystals is still not unambiguously understood in spite of several efforts. We, therefore, undertook the structural analyses of



$(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  (TAHS) [2] and  $\text{Rb}_3\text{H}(\text{SO}_4)_2$  (TRHS) [4] along with their mixed crystals TRAHS ( $x = 0.14, 0.33$  and  $0.50$ ). The lattice parameters obtained in the recent structure analyses of TAHS and TRHS match well with the earlier reports [3, 5]. In this article, we report the crystal structure analyses of the mixed single crystals TRAHS ( $x = 0.14, 0.33$  and  $0.50$ ) and also suggest the possible H-bond nature from these data. The Fourier map is used to obtain distortion in the electron density distribution around  $\text{O}_1$  atom that supports the H-bond formation. The H-bond is more evident in Fourier map in mixed crystals and the H-atoms positions are localised. This indicates that the H-atom disorder is less in mixed crystals than in pure crystals. The importance of study in relation to tetrahedral orientation dynamics and ordering in low temperature phase is discussed.

## Experiment and Structure Refinements of the Mixed Crystals

### $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$

Single crystals of TRAHS with  $x = 0.14, 0.33$  and  $0.50$  were grown by slow evaporation method from aqueous solutions of  $\text{Rb}_2\text{SO}_4$  (5.25 wt%) and  $(\text{NH}_4)_2\text{SO}_4$  (15.75 wt%) with  $\text{H}_2\text{SO}_4$  (7.0 wt%);  $\text{Rb}_2\text{SO}_4$  (10.5 wt%) and  $(\text{NH}_4)_2\text{SO}_4$  (10.5 wt%) with  $\text{H}_2\text{SO}_4$  (7.0 wt%); and  $\text{Rb}_2\text{SO}_4$  (15.0 wt%) and  $(\text{NH}_4)_2\text{SO}_4$  (5.0 wt%) with  $\text{H}_2\text{SO}_4$  (7.0 wt%), respectively. A spherically-shaped crystal of diameter 0.35 mm with a single domain was used. Intensity datum were collected on Siemens P4 automatic four-circle X-ray diffractometer with graphite monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The measuring time varied from 0.5 to 2.0 s  $\text{step}^{-1}$  in the ranges  $2 < 2\theta < 50^\circ$  for  $-18 \leq h \leq 1, -6 \leq k \leq 1, -11 \leq l \leq 12$  ( $\max \sin\theta/\lambda = 0.8069 \text{ \AA}^{-1}$ ) using  $\lambda = 0.71073 \text{ \AA}$  in TRAHS with  $x = 0.14$ . In case of TRAHS ( $x = 0.33$ ),  $2 < 2\theta < 50^\circ$  for  $-1 \leq h \leq 18, -1 \leq k \leq 6, -12 \leq l \leq 11$  and in TRAHS ( $x = 0.50$ ),  $2 < 2\theta < 50^\circ$  for  $-18 \leq h \leq 1, -6 \leq k \leq 1, -11 \leq l \leq 12$ . After processing the raw data, Lorentz and polarisation corrections are made. 992 measured reflections were averaged to 654 unique observed reflections [ $F_0 > 4\sigma(F_0)$ ];  $R(\text{int}) = 0.1157$ ;  $R(\sigma) = 0.0445$  in TRAHS ( $x = 0.14$ ) and 1141 measured reflections were averaged to 775 unique observed reflections;  $R(\text{int}) = 0.1544$ ;  $R(\sigma) = 0.0465$  in TRAHS ( $x = 0.33$ ). Also 1116 measured reflections were averaged to 762 unique observed reflections;  $R(\text{int}) = 0.1455$ ;  $R(\sigma) = 0.0510$  in TRAHS ( $x = 0.50$ ). Three standard reflections were monitored every hundred reflections. An examination of the diffraction symmetry and systematic absences confirmed the same space group  $\text{C2/c}$  as most of the  $\text{M}_3\text{H}(\text{XO}_4)_2$  type crystals. The unit cell parameters were determined by least-squares fit of the  $\theta$  values of 25 reflections in the range  $10.0^\circ < \theta < 30.0^\circ$ . The function minimised was  $\sum w(|F_0| - |F_c|)^2$ ,  $w = 1/\sigma^2(|F_0|)$ .

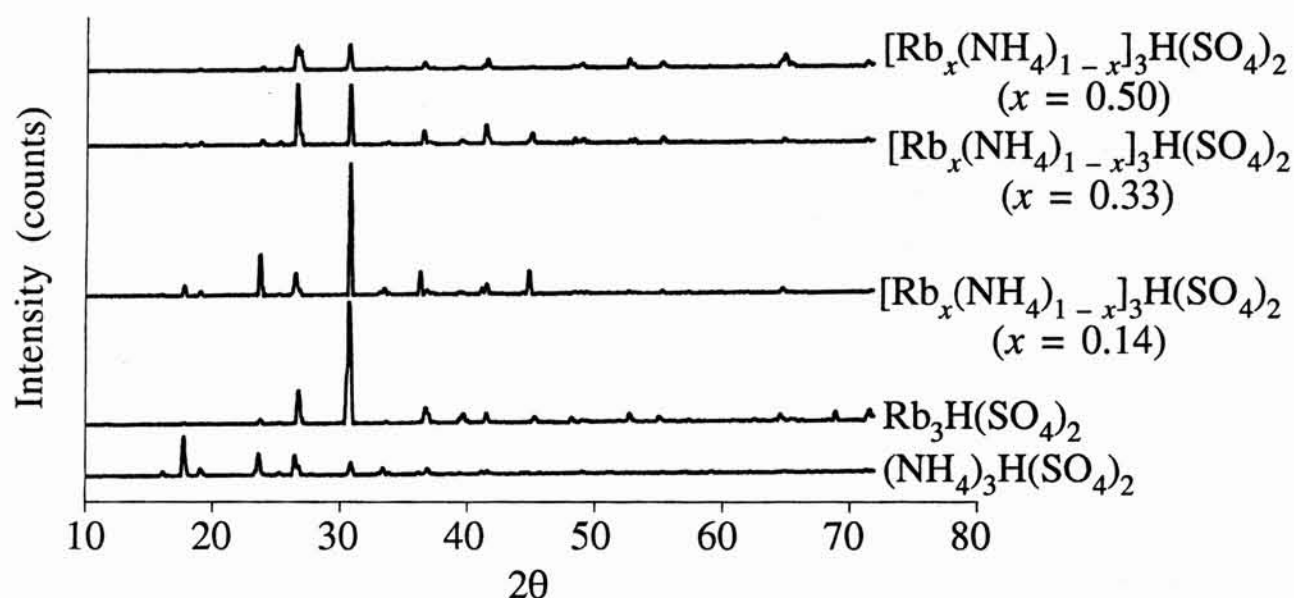
The model summaries concerning unit cell information for mixed crystals TRAHS ( $x = 0.14, 0.33$  and  $0.50$ ) are given in Table 1. The final  $R$ -factor and the weighted  $R$ -factor are 0.161 and 0.221 in TRAHS ( $x = 0.14$ ), 0.112 and 0.258 in TRAHS ( $x = 0.30$ ) and 0.167 and 0.281 in TRAHS ( $x = 0.50$ ), respectively, where these two discrepancy factors are defined as  $R = \sum(|F_0| - |F_c|)/\sum |F_0|$  and  $R_w = \{\sum w(|F_0| - |F_c|)^2/\sum w(|F_0|)^2\}^{1/2}$ . No correction was made for absorption in the present structures.

**Table 1.** Model summaries concerning unit cell information for  $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$  ( $x = 0.14, 0.33$  and  $0.50$ ) mixed crystals

	$[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ ( $x = 0.14$ )	$[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ ( $x = 0.33$ )	$[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ ( $x = 0.50$ )
Cell axes (Å)	15.356 (4) 5.868 (4) 10.159 (5)	15.321 (3) 5.871 (1) 10.176 (3)	15.222 (5) 5.880 (1) 10.168 (6)
Cell angles (°)	101.91 (5)	102.08 (2)	102.43 (5)
Cell volume (Å <sup>3</sup> )	895.71 (97)	895.06 (39)	888.76 (10)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	C2/c
$F(000)$	572.9	623.8	675.8
Density (gcm <sup>-3</sup> )	2.09	2.33	2.60
Formula weight	281.2	314.7	348.4
No. of form units Z	4	4	4
Abs. coeff. (mm <sup>-1</sup> )	3.318	6.019	8.780

## Results and Discussion

An examination of X-ray study on the room temperature structure in  $\text{M}_3\text{H}(\text{XO}_4)_2$  type pure single crystals and mixed crystals reveals that the non-H atoms in mixed crystals lie approximately at the same positions as that in pure crystals. However, the lattice parameters change slightly; this can be thought of as the weighted average of lattice parameters of pure crystal. Thus, the mixed crystal is a sort of solid solution of two pure crystals. The concentration  $x$  was determined by the lattice constants using the relationship in X-ray powder diffraction method. The lattice constants, thus, obtained are consistent with those obtained in the X-ray structure analyses on single crystals. The X-ray powder diffraction patterns of TAHS, TRHS and TRAHS ( $x = 0.14, 0.33, 0.50$ ) at room temperature are shown in Fig. 1. The obtained positional parameters of TRAHS are presented in Tables 2, 3 and 4, respectively.

**Fig. 1.** X-ray powder diffraction patterns of  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ ,  $\text{Rb}_3\text{H}(\text{SO}_4)_2$  and  $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$  ( $x = 0.14, 0.33, 0.50$ ) crystals.

**Table 2.** Atomic positions in  $[\text{Rb}_{0.14}(\text{NH}_4)_{0.86}]_3\text{H}(\text{SO}_4)_2$  at room temperature

Atom	x	y	z
Rb(1)	0.306754	0.767981	0.340903
N(1)	0.306754	0.767981	0.340903
Rb(2)	0.500000	0.237865	0.250000
N(2)	0.500000	0.237865	0.250000
S	0.116921	0.216606	0.463784
O(1)	0.014325	0.175402	0.443064
O(2)	0.148919	0.220568	0.606006
O(3)	0.129392	0.436365	0.397257
O(4)	0.150263	0.023640	0.400001

**Table 3.** Atomic positions in  $[\text{Rb}_{0.33}(\text{NH}_4)_{0.67}]_3\text{H}(\text{SO}_4)_2$  at room temperature

Atom	x	y	z
Rb(1)	0.305485	0.228069	1.348453
N(1)	0.305485	0.228069	1.348453
Rb(2)	0.000000	0.736740	0.750000
N(2)	0.000000	0.736740	0.750000
S	0.114817	0.779543	0.461649
O(1)	0.013568	0.817459	0.442154
O(2)	0.150107	0.770487	0.607535
O(3)	0.129189	0.560161	0.397221
O(4)	0.149405	0.977713	0.400079

**Table 4.** Atomic positions in  $[\text{Rb}_{0.5}(\text{NH}_4)_{0.5}]_3\text{H}(\text{SO}_4)_2$  at room temperature

Atom	x	y	z
Rb(1)	0.000000	0.259475	0.750000
N(1)	0.000000	0.259475	0.750000
Rb(2)	0.193360	0.269143	0.151569
N(2)	0.193360	0.269143	0.151569
S	0.115862	0.221392	0.463119
O(1)	0.015012	0.181298	0.443114
O(2)	0.150321	0.232413	0.611000
O(3)	0.129040	0.441185	0.398448
O(4)	0.149761	0.019886	0.403276

Bond lengths and angles for the sulphate group are given in Tables 5, 6 and 7, respectively. The calculations were performed using a SHELXS-97 [6] and ORTEP-III [7]. The crystal structures are shown in Figs. 2, 3 and 4, respectively.

**Table 5.** Bond lengths and angles of  $\text{SO}_4$  group in  $[\text{Rb}_{0.14}(\text{NH}_4)_{0.86}]_3\text{H}(\text{SO}_4)_2$  at room temperature

Bonds (Å)		Angles (°)	
S-O(1)	1.565	O(1)-S-O(2)	105.40
S-O(2)	1.430	O(1)-S-O(3)	107.07
S-O(3)	1.456	O(1)-S-O(4)	104.94
S-O(4)	1.449	O(2)-S-O(3)	113.35
		O(2)-S-O(4)	112.69
$R_{\text{O(1)-O(1)'}}$	2.449	O(3)-S-O(4)	112.58

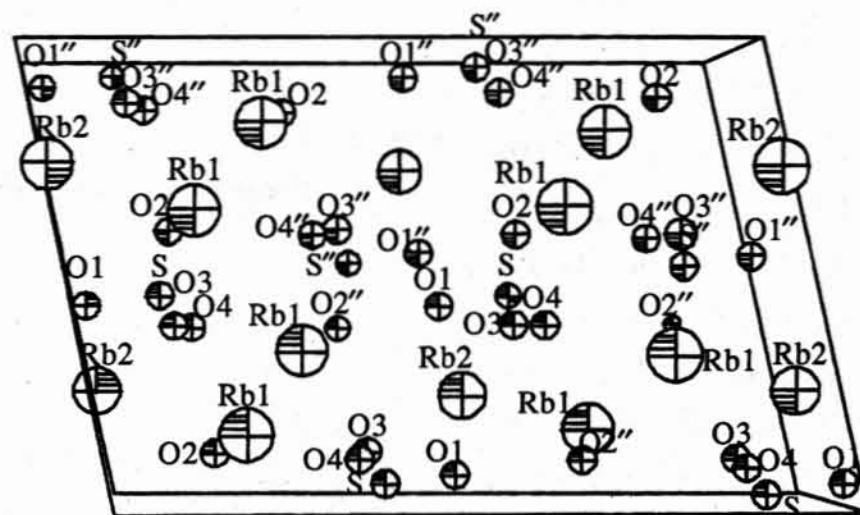
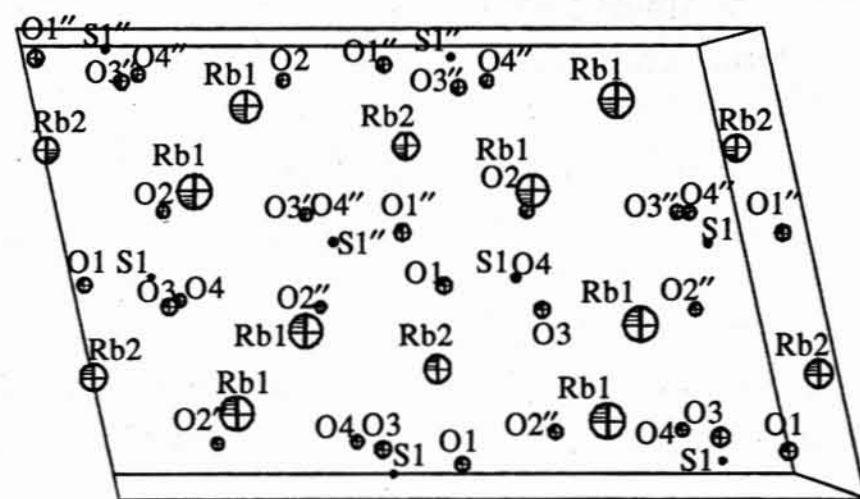
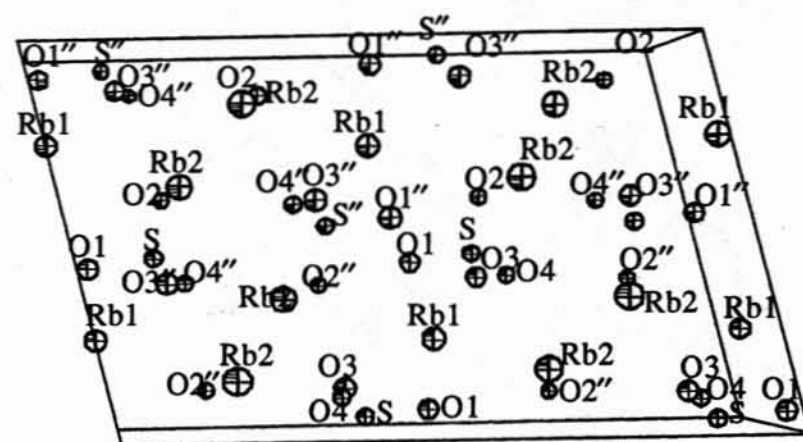
**Table 6.** Bond lengths and angles of  $\text{SO}_4$  group in  $[\text{Rb}_{0.33}(\text{NH}_4)_{0.67}]_3\text{H}(\text{SO}_4)_2$  at room temperature

Bonds (Å)		Angles (°)	
S-O(1)	1.538	O(1)-S-O(2)	106.45
S-O(2)	1.471	O(1)-S-O(3)	107.92
S-O(3)	1.482	O(1)-S-O(4)	105.90
S-O(4)	1.472	O(2)-S-O(3)	110.96
		O(2)-S-O(4)	111.67
$R_{\text{O(1)-O(1)'}}$	2.522	O(3)-S-O(4)	113.49



**Table 7. Bond lengths and angles of  $\text{SO}_4$  group in  $[\text{Rb}_{0.5}(\text{NH}_4)_{0.5}]_3\text{H}(\text{SO}_4)_2$  at room temperature**

Bonds (Å)		Angles (°)	
S-O(1)	1.523	O(1)-S-O(2)	107.55
S-O(2)	1.481	O(1)-S-O(3)	105.53
S-O(3)	1.482	O(1)-S-O(4)	104.90
S-O(4)	1.474	O(2)-S-O(3)	111.09
		O(2)-S-O(4)	115.02
$R_{\text{O}(1)-\text{O}(1)'}$	2.515	O(3)-S-O(4)	112.01

**Fig. 2. Room temperature structure of  $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$  ( $x = 0.14$ ) viewed normal to (010).****Fig. 3. Projection normal to (010) of the room temperature structure of  $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$  ( $x = 0.33$ ).****Fig. 4. Projection normal to (010) of the room temperature structure of  $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$  ( $x = 0.5$ ).**

As the nature of H-bond in two pure systems is not same, the effect on H-bond in mixed crystals will be important. H-bonded dimers that are formed with two different adjacent sulphate groups should have average bond length and strength if structure is an average of the two structures. The obtained bond lengths in TAHS and TRHS are 2.549 and 2.492 Å, respectively [2, 4]. H-bond distance O(1)...O(1)" of TRAHS ( $x = 0.14, 0.33$  and 0.50) are 2.449, 2.522 and 2.515 Å, respectively. These are close to but still longer than the critical bond length  $R_c$ . There is uncertainty in the positional parameter of the H-atom in the present X-ray experiment. It may be due to the electron wave function spread out in H-bond region. Therefore, it is difficult to estimate the atomic scattering factor of H-atoms. The sulphate ion forms a distorted tetrahedron with S-O(1) being longer than the remaining three S-(O) bonds. In these structures, O(1) atom takes part in O(1)-H-O(1)" H-bonds, which link neighbouring  $\text{SO}_4^{2-}$  ions in pairs. This is supported by Fourier maps (Figs. 5 to 7). Further, the position of H-atom seems to be less disordered and localised in mixed crystals in comparison to the pure crystals.

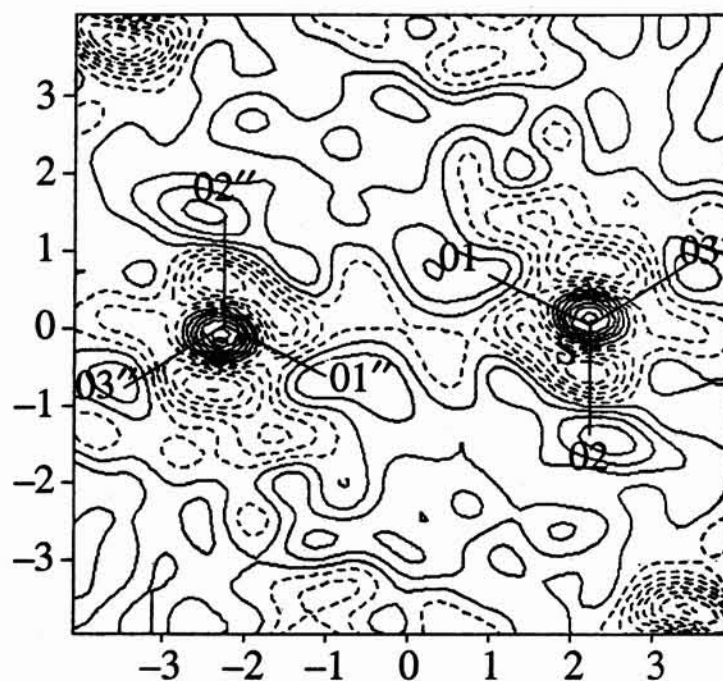


Fig. 5. Fourier map of  $(\text{SO}_4 \cdot \text{H} \cdots \text{SO}_4'')$  dimer in  $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$  ( $x = 0.14$ ).

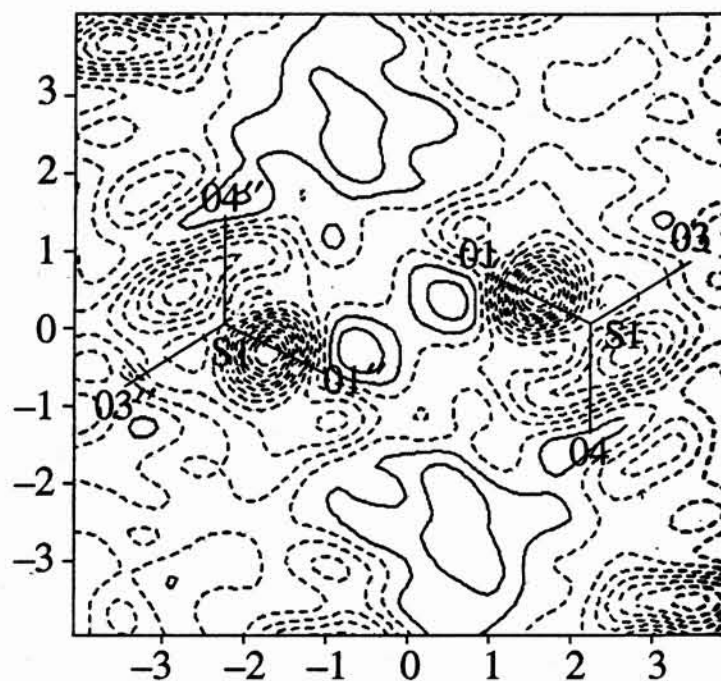


Fig. 6. Contour map of  $(\text{SO}_4 \cdot \text{H} \cdots \text{SO}_4'')$  dimer in  $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$  ( $x = 0.33$ ) for  $(\text{O}_1\text{O}_3\text{O}_4)$ .

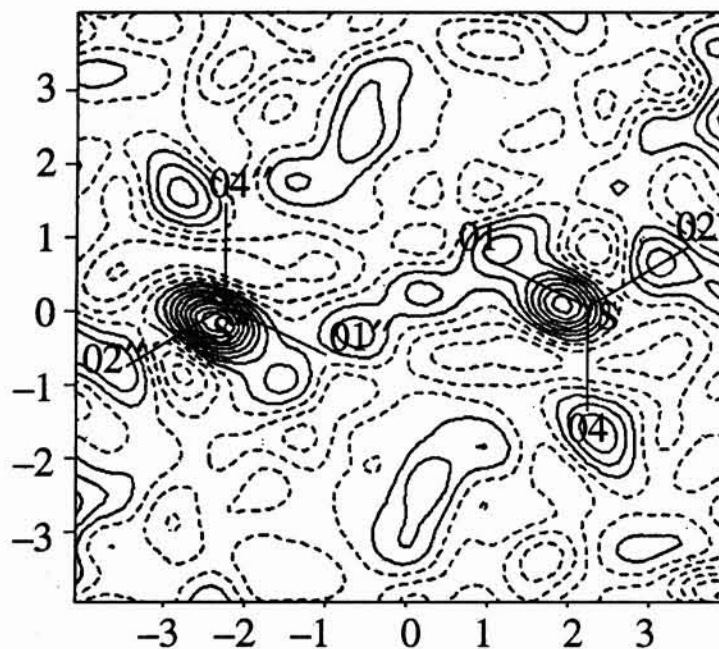


Fig. 7. 2D-contour map of  $(\text{SO}_4 \cdot \text{H} \cdots \text{SO}_4'')$  dimer in  $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$  ( $x = 0.5$ ).

## Conclusions

The precise X-ray structure analyses of TAHS, TRHS and TRAHS ( $x = 0.14, 0.33$  and  $0.50$ ) single crystals were performed to investigate the H-bond nature at room temperature. The observed H-bond lengths at room temperature in TRAHS ( $x = 0.14, 0.33$  and  $0.50$ ) are 2.449, 2.522 and 2.515 Å, respectively, which are longer than the critical bond length. The comparison among Fourier maps for  $SO_4-H-SO_4''$  dimers in different single crystals are observed in the present study. There is no remarkable change in the positional parameters of TAHS, TRHS and TRAHS ( $x = 0.50$ ) at room temperature. The structures of TRAHS ( $x = 0.14$  and  $0.33$ ) are also isomorphous with each other and the difference of positional parameters is extremely small. Observed lattice parameters vary systematically with  $x$  showing that the mixed crystals are solid solutions of two analogues. All these crystals are monoclinic with the space group  $C2/c$  and  $Z = 4$ .

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