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GEOMETRIC ISOTOPE EFFECT AND PHASE TRANSITION ON $(NH_4)_2Co(SO_4)_2 \cdot 6H_2O$ TUTTON SALT

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Abstract

Differential scanning calorimetry (DSC) and X-ray diffraction measurements have been performed on diammonium cobalt disulphate hexahydrate $(NH_4)_2Co(SO_4)_2 \cdot 6H_2O$ and deuterated $(ND_4)_2Co(SO_4)_2 \cdot 6D_2O$ crystals. Several transitions in both compounds at high temperature have been found by the DSC measurements. The structures of both compounds are redetermined accurately at room temperature. The isotope effect in these crystals has been studied. It is confirmed that the changes of O-H-O hydrogen bond length by the substitution of deuterium for hydrogen are in good agreement with that of many crystals with hydrogen bonds as previously reported by Ichikawa.

Keywords and phrases: Tutton salt, isotope effect, crystal structure, X-ray, DSC.

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1. Introduction

It is well known that the Tutton salts have the general formula $A_2M(XO_4)_2{\cdot}6H_2O$, where A is K, Rb, Cs, or NH_4 ions, M is a divalent metal ion, and X is S or Se ions [1]. These crystals have attracted much attention for their associated physical properties [8, 11-13, 15-17]. It also provided a convenient group of compounds for investigating the influence of crystal environments upon the electronic properties and the crystal geometric structures of hexahydrate $[M(H_2O)_6]^{2+}$ complexes. Among these crystals, a diammonium copper (II) disulphate hexahydrate, $(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$, crystal is especially interesting [8, 11-13, 16, 17]. The $[Cu(H_2O)_6]^{2+}$ complex lies on an inversion center and is described as a distorted elongated octahedron with four Cu-O bond lengths of about 2.0Å and two Cu-O bond lengths of about 2.3Å. The Jahn-Teller distortion of the Cu-O system in the complex has an interesting isotope effect. The direction of the Jahn-Teller distortion in the distorted $[Cu(H_2O)_6]^{2+}$ octahedron is switched by 90° in the opposite direction in the *ab*-plane by the substitution of deuterium for hydrogen. Moreover, this change is also accompanied by slight alterations in the orientations of the NH_4 and SO_4 ions and in the hydrogen-bonding interactions between these ions.

A diammonium cobalt disulphate hexahydrate, $(NH_4)_2Co(SO_4)_2{\cdot}6H_2O$, crystal is the other one of the Tutton salts. This crystal belongs to monoclinic system (space group $P2_1/c$) with two molecules in a unit cell of $a = 6.24\text{Å}$, $b = 12.51\text{Å}$, $c = 9.25\text{Å}$, and $\beta = 107.0°$ at room temperature [1, 14]. The crystal structure consists of six Co-O bonds in the $[Co(H_2O)_6]^{2+}$ complex, five N-H-O hydrogen bonds between the NH_4 and SO_4 ions, and six O-H-O hydrogen bonds between the SO_4 ions and H_2O molecules. The $[Co(H_2O)_6]^{2+}$ complex is a nearly regular octahedron with the six Co-O bond lengths of about 2.1Å, and thus does not show the Jahn-Teller distortion as mentioned above.

The geometric isotope effect on the $O \cdots O$ hydrogen bond has been reported by Ichikawa, based on many obtained accurate data of the crystal structures which include hydrogen bonds [9, 10]. The expansion of the hydrogen bond length on deuteration is observed as the bond length is in the range of about 2.43Å to 2.65Å, and the maximum magnitude of the expansion is about 0.03Å at the bond length around 2.5Å (see Figure 3). Therefore, it is also very interesting to study the influence of the hydrogen bonds on deuteration in $(NH_4)_2Co(SO_4)_2{\cdot}6H_2O$. However, since the crystal structure of the deuterated compound has not been reported yet, the isotope effects on the properties in the crystal have not been confirmed.

In this paper, the possible existence of the phase transition in $(NH_4)_2Cu(SO_4)_2{\cdot}6H_2O$ and $(ND_4)_2Co(SO_4)_2{\cdot}6D_2O$ is confirmed by differential scanning calorimetry measurements. The crystal structures of these crystals at room temperature are redetermined. The isotope effect on the hydrogen bonds in $(NH_4)_2Co(SO_4)_2{\cdot}6H_2O$ is studied.

2. Experimental

Single crystals of $(NH_4)_2Co(SO_4)_2{\cdot}6H_2O$ and $(ND_4)_2Co(SO_4)_2{\cdot}6D_2O$ were grown at room temperature by slow evaporation from aqueous solutions containing $(NH_4)_2SO_4$ and $CoSO_4{\cdot}6H_2O$ in the molar ratio of 1:1. The deuterated crystals thus obtained were recrystallized five times from a mixed D_2O solution by an evaporation method in a desiccator over P_2O_5 [4].

Differential scanning calorimetry (DSC) measurements in the temperature range between 112K and 600K were performed with a DSC220 from Seiko Instruments, Inc. The amounts of both kinds of sample crystals for the DSC measurement varied between 0.38mg and 5.91mg. The rates of heating and cooling were 5 or 10K/min with flowing dry N_2 gas at 50ml/min. The X-ray measurements were carried out by using an Enraf-Nonius CAD-4 four-circle automatic diffractometer with an express software and graphite monochromated Mo Kα radiation $(\lambda = 0.71073\text{Å})$ [2]. The intensity data were corrected for both Lorentz-polarization and absorption effects. The structures were refined by the full-matrix least-squares method by using an SDP crystallographic software package on a personal computer [3]. All nonhydrogen atoms were refined with anisotropic thermal parameters. The H (or D) atoms involved in N···O and O···O hydrogen bonds were located by difference Fourier syntheses and refined isotropically. A summary of crystal data, intensity collections, and structure refinements is given in Table 1.

Table 1. Crystal data, intensity collections, and structure refinement parameters

Crystal data		
Compound	$(NH_4)_2Co(SO_4)_2{\cdot}6H_2O$	$(ND_4)_2Co(SO_4)_2{\cdot}6D_2O$
Chemical formula weight Mr	395.22	415.34
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Lattice constants a (Å)	6.2424(5)	6.2417(7)
b (Å)	12.5231(5)	12.5161(12)
c (Å)	9.2565(9)	9.2495(7)
β(°)	107.029(7)	106.996(8)
Volume of unit cell V	691.89(9)	691.02(12)
Formula unit per cell Z	2	2
Calculated density D_X (Mg/m^3)	1.897	1.996
Linear absorption coefficient μ(mm^{-1})	1.614	1.619
Crystal colour	Mahogany	Mahogany
Sample shape	Sphere	Sphere
Size in diameter $2r$ (mm)	0.32	0.34
Intensity collection		
Measurement of temperature (K)	297	297
Data-collection method	$\theta/2\theta$ scans	$\theta/2\theta$ scans
Absorption correction type	Spherical	Spherical
Measurement of θ_{max}(°)	35.0	35.0
Number of reflections measured	6527	6377

Number of unique reflections	3161	3158
R_{int}	0.024	0.017
Range of h, k, and l for measured intensities	h = 0 - - > 10 k = −20 - - > 20 l = −14 - - > 14	h = −10 - - > 9 k = −20 - - > 20 l = 0 - - > 14
Number of standard reflections	3	3
Interval time / intensity decay	120min./−1.55%	120min./−0.83%
Refinement (refinement on F)		
R factor / wR factor	$R = 0.021$ / $wR = 0.031$	$R = 0.021$ / $wR = 0.030$
R / wR factor (all date)	$R = 0.031$ / $wR = 0.040$	$R = 0.030$ / $wR = 0.038$
Goodness of fit S	0.708	0.725
Number of reflections used in refinement	$2658(I > 2\sigma(I))$	$2696(I > 2\sigma(I))$
Number of parameters refined	127	127
Maximum of shift/esd $(\Delta/\sigma)_{\max}$	0.085	0.090
Difference density (peak/hole) $(e\text{Å}^{-3})$	0.447/−0.309	0.401/−0.403
Extinction coefficient	$1.95(8) \times 10^{-6}$	$4.03(7) \times 10^{-6}$

Weighting scheme $w = 1/[\sigma^2(F) + (0.02F)^2 + 1.0]$.

3. Results and Discussion

Figure 1 shows the obtained DSC curves for $(NH_4)_2Co(SO_4)_2 \cdot 6H_2O$ and $(ND_4)_2Co(SO_4)_2 \cdot 6D_2O$ crystals at high temperature on heating and cooling. The rates of heating and cooling were 5K/min. The weights of the proton and deuterated samples were 0.78mg and 1.00mg, respectively. Several DSC peaks were observed at temperatures above 400K and no remarkable peak was observed below room temperature. Large endothermic peaks in the heating charts for the proton and deuterated compounds were clearly recognized at 404K and 408K, respectively. There was a shoulder at temperature of 396K close to the peaks of both compounds, as shown in Figure 1. Thus, this indicates that the observed large peaks consist of two endothermic peaks. Furthermore, one exothermic and two endothermic peaks, respectively, were observed at 496K, 532K, and 550K for the proton compound, and at 496K, 535K, and 552K for the deuterated one. On the other hand, only a small exothermic peak in the cooling chart was detected at 367K and 369K for the proton and deuterated compounds, respectively. It is confirmed that there are distinct differences in the DSC peaks between the heating and cooling charts. By the repeated cycle measurements on heating, only a small but sharp endothermic peak was detected at 417K and 418K for the proton and deuterated compounds, respectively. The widths and intensities of these peaks were very similar to those on the cooling curves shown in Figure 1, except for the difference in the peak temperatures. Thus, it is implied that the peaks on the DSC curves observed by the repeated measurement are corresponding to those on the cooling curves. The hysteresis of the peak temperature between the cooling and repeated heating curves is about 50K in both compounds. After the DSC measurements, the sample crystals were unable to return to their initial state. Moreover, they were destroyed easily by the application of weak pressure.

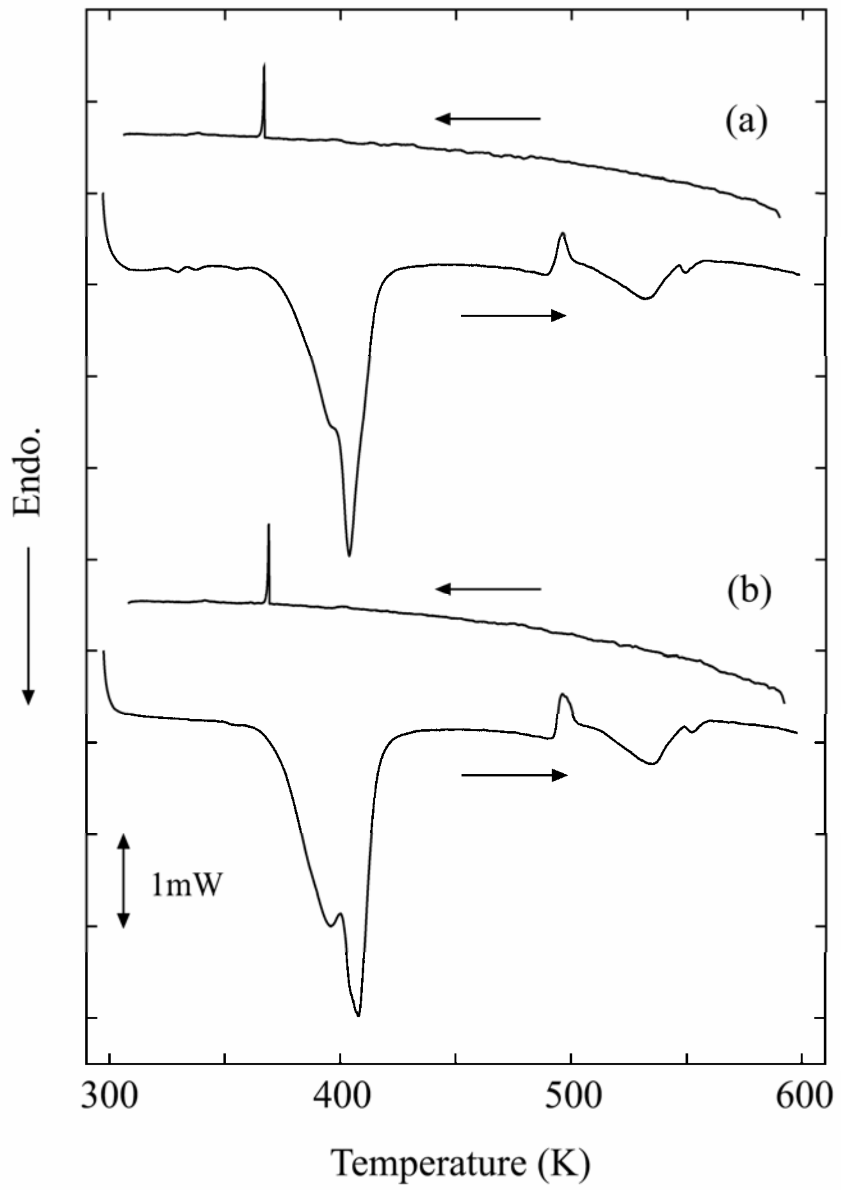


Figure 1. DSC curves for (a) $(NH_4)_2Co(SO_4)_2{\cdot}6H_2O$ and (b) $(ND_4)_2Co(SO_4)_2{\cdot}6D_2O$ crystals on heating and cooling. The sample weights of the $(NH_4)_2Co(SO_4)_2{\cdot}6H_2O$ and $(ND_4)_2Co(SO_4)_2{\cdot}6D_2O$ crystals were 0.78mg and 1.00mg, respectively. The heating and cooling rates were 5K/min.

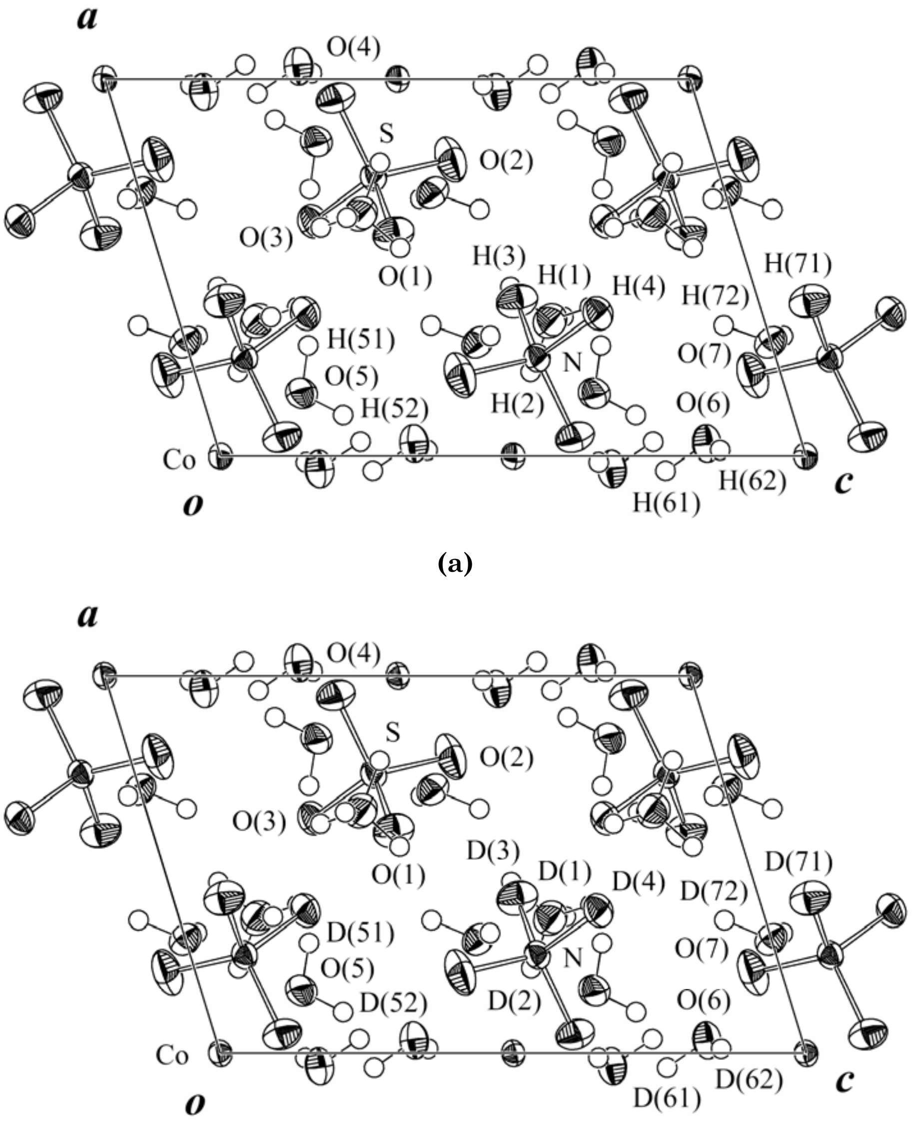
The transition enthalpies ΔH and entropies ΔS for the proton and deuterated compounds with the peak temperatures are shown in Table 2. The obtained results show that there are no large differences in the enthalpies ΔH (entropies ΔS) and the peak temperatures between the proton and deuterated compounds, that is, there are no isotope effects on these properties. However, the width of the endothermic peak around 400K for the deuterated compound is slightly larger than that for the proton one. It is considered that this difference in the width is caused by a 4K upward shift of the peak temperature and no shift of the shoulder temperature by deuteration.

Table 2. Transition enthalpies ΔH and entropies ΔS with endothermic and exothermic peak temperatures T for (a) $(NH_4)_2Co(SO_4)_2 \cdot 6H_2O$ and (b) $(ND_4)_2Co(SO_4)_2 \cdot 6D_2O$ crystals

(a)	Heating (first)				Cooling	Heating (second)
T [K]	404	496	532	550	367	417
ΔH [kJ/mol]	350.0	– 25.0	32.9	2.6	– 3.4	3.8
ΔS [J/(K·mol)]	866.7	– 50.4	61.8	4.8	– 9.4	9.2
(b)	Heating (first)				Cooling	Heating (second)
T [K]	408	496	535	552	369	418
ΔH [kJ/mol]	366.5	– 24.6	28.3	1.9	– 3.2	3.2
ΔS [J/(K·mol)]	898.4	– 49.6	53.0	3.4	– 8.6	7.6

Generally, a peak appeared in DSC chart suggests the change of exchange energy by a phase transition. Thus, the observed DSC curves in both compounds show the existence of several phase transitions at high temperature, and there is no transition in the temperature range between 112K and 400K. There are six water molecules in the crystals, and the onset temperatures (about 370K) of the large endothermic peak in the heating chart are very close to the boiling point (373K) of water. Thus, it is considered that the large peaks at around 400K are attributed to the evaporation of the water molecules from the crystals. The evaporation of water molecules from a crystal is essentially an irreversible process. Therefore, the DSC peak produced by the evaporation of water occurs only once on a first heating curve. The DSC peak corresponding to the large peak at around 400K is not observed in the cooling chart and in the heating chart obtained by the repeated measurements. Thus, this consideration is consistent with the results observed.

The crystal structures of $(NH_4)_2Co(SO_4)_2 \cdot 6H_2O$ and $(ND_4)_2Co(SO_4)_2 \cdot 6D_2O$ at room temperature were analyzed by X-ray diffraction. The observed lattice parameters indicated that they belong to monoclinic system. The comparison between equivalent reflections showed that the Laue class is $2/m$. By the observed systematic extinction condition, the space groups of both crystals were determined to be monoclinic $P2_1/c$. Figure 2 shows the projection of the obtained structures of the $(NH_4)_2Co(SO_4)_2 \cdot 6H_2O$ and $(ND_4)_2Co(SO_4)_2 \cdot 6D_2O$ crystals onto the *ac*-plane. The positional parameters in fractions of the unit cell and the thermal parameters are listed in Table 3. Selected interatomic distances and angles, and hydrogen bond geometries are given in Tables 4 and 5, respectively.



(a)

(b)

Figure 2. ORTEP projection of the crystal structures along the *b*-axis for (a) $(NH_4)_2Co(SO_4)_2{\cdot}6H_2O$ and (b) $(ND_4)_2Co(SO_4)_2{\cdot}6D_2O$ crystals. Displacement ellipsoids are shown at the 50% probability level.

Table 3. Atomic coordinates and thermal parameters of (a) $(NH_4)_2Co(SO_4)_2{\cdot}6H_2O$ and (b) $(ND_4)_2Co(SO_4)_2{\cdot}6D_2O$ crystals at 297K with standard deviations in brackets. The anisotropic thermal parameters $(\text{x}10^4\,\text{Å}^2)$ are defined as $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$. Isotropic thermal parameters for H (or D) atoms are listed under U_{11}

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
(a)									
Co	0	0	0	176.9(6)	185.8(7)	151.6(6)	6.5(6)	49.9(5)	– 8.8(6)
S	0.73981(4)	0.13682(2)	0.40759(3)	210.9(8)	214.3(9)	176.1(8)	– 18.5(8)	52.3(6)	– 25.2(7)
O(1)	0.5900(2)	0.22735(8)	0.4122(1)	298(3)	282(4)	460(4)	18(3)	138(3)	– 87(3)
O(2)	0.7859(2)	0.0762(1)	0.5483(1)	542(5)	469(5)	221(3)	– 64(5)	45(4)	64(4)
O(3)	0.6227(1)	0.06688(7)	0.28037(9)	297(3)	296(3)	226(3)	– 48(3)	61(2)	– 79(3)
O(4)	0.9500(1)	0.17710(8)	0.3845(1)	244(3)	302(4)	417(4)	– 42(3)	131(3)	– 39(3)
O(5)	0.1658(1)	0.10783(8)	0.17125(9)	242(3)	341(4)	256(3)	– 11(3)	55(2)	– 85(3)
O(6)	0.0338(2)	0.11151(7)	0.83759(9)	363(3)	257(3)	222(3)	11(3)	92(2)	20(3)
O(7)	0.3013(1)	0.93123(7)	0.99941(9)	257(3)	261(3)	297(3)	35(3)	126(2)	23(3)
N	0.3579(2)	0.15238(9)	0.6339(1)	308(4)	338(5)	317(4)	– 20(4)	123(3)	– 5(4)
H(1)	0.368(4)	0.090(2)	0.659(2)	0.031(6)					
H(2)	0.223(4)	0.161(2)	0.574(3)	0.035(6)					
H(3)	0.448(4)	0.162(2)	0.584(2)	0.028(6)					
H(4)	0.394(4)	0.189(2)	0.709(3)	0.038(7)					
H(51)	0.293(3)	0.093(2)	0.208(2)	0.021(5)					
H(52)	0.108(3)	0.116(2)	0.231(2)	0.024(5)					
H(61)	– 0.038(3)	0.097(2)	0.753(2)	0.017(5)					
H(62)	0.016(3)	0.177(2)	0.857(2)	0.019(5)					
H(71)	0.318(3)	0.866(2)	0.024(2)	0.014(4)					
H(72)	0.346(3)	0.939(2)	0.928(2)	0.025(5)					

(b)

Co	0	0	0	182.0(6)	181.8(6)	143.0(5)	6.6(5)	43.1(4)	− 9.1(5)
S	0.73952(4)	0.13683(2)	0.40748(2)	213.7(8)	210.6(8)	166.9(7)	− 19.2(7)	45.4(6)	− 25.9(7)
O(1)	0.5899(1)	0.22748(7)	0.4122(1)	307(3)	273(3)	450(4)	17(3)	134(3)	− 91(3)
O(2)	0.7861(2)	0.07613(9)	0.5483(1)	552(5)	466(5)	202(3)	− 60(4)	34(3)	66(3)
O(3)	0.6226(1)	0.06688(7)	0.28019(8)	298(3)	296(3)	212(3)	− 48(3)	54(2)	− 77(3)
O(4)	0.9497(1)	0.17711(7)	0.3844(1)	249(3)	293(3)	408(4)	− 42(3)	121(2)	− 39(3)
O(5)	0.1658(1)	0.10800(7)	0.17105(9)	247(3)	341(3)	245(3)	− 10(3)	49(2)	− 84(3)
O(6)	0.0341(1)	0.11151(7)	0.83761(8)	367(3)	253(3)	211(3)	13(3)	85(2)	24(2)
O(7)	0.3010(1)	0.93124(6)	0.99939(8)	259(3)	257(3)	289(3)	33(2)	119(2)	24(3)
N	0.3577(2)	0.15248(9)	0.6339(1)	314(4)	329(4)	308(4)	− 21(3)	118(3)	− 2(3)
D(1)	0.361(3)	0.092(2)	0.661(2)	0.028(5)					
D(2)	0.225(3)	0.163(2)	0.575(2)	0.029(5)					
D(3)	0.453(3)	0.164(2)	0.586(2)	0.030(6)					
D(4)	0.392(3)	0.191(2)	0.709(2)	0.023(5)					
D(51)	0.292(3)	0.092(2)	0.209(2)	0.018(4)					
D(52)	0.109(3)	0.117(2)	0.231(2)	0.021(5)					
D(61)	− 0.038(3)	0.095(2)	0.755(2)	0.024(5)					
D(62)	0.012(3)	0.179(1)	0.857(2)	0.014(4)					
D(71)	0.318(3)	0.865(1)	0.023(2)	0.012(4)					
D(72)	0.352(3)	0.941(2)	0.930(2)	0.018(4)					

Table 4. Selected interatomic distances (in Å) and angles (in degrees) of (a) $(NH_4)_2Co(SO_4)_2{\cdot}6H_2O$ and (b) $(ND_4)_2Co(SO_4)_2{\cdot}6D_2O$ crystals

	(a)	(b)
Co-O(5)	2.1088(8)	2.1081(8)
Co-O(6)$^{(a)}$	2.1073(9)	2.1063(8)
Co-O(7)$^{(b)}$	2.0701(8)	2.0677(8)
S-O(1)	1.478(1)	1.4781(9)
S-O(2)	1.462(1)	1.462(1)
S-O(3)	1.4778(8)	1.4775(8)
S-O(4)	1.479(1)	1.4783(9)
O(1)-O(2)	2.400(1)	2.402(1)
O(1)-O(3)	2.391(1)	2.391(1)
O(1)-O(4)	2.419(1)	2.418(1)
O(2)-O(3)	2.392(1)	2.393(1)
O(2)-O(4)	2.420(2)	2.418(2)
O(3)-O(4)	2.420(1)	2.419(1)
O(5)-Co-O(6)$^{(a)}$	88.98(3)	88.89(3)
O(5)-Co-O(6)$^{(c)}$	91.02(3)	91.11(3)
O(5)-Co-O(7)$^{(d)}$	91.26(3)	91.26(3)
O(5)-Co-O(7)$^{(e)}$	88.74(3)	88.74(3)
O(6)$^{(a)}$-Co-O(7)$^{(d)}$	89.59(4)	89.57(3)
O(6)$^{(a)}$-Co-O(7)$^{(e)}$	90.41(4)	90.43(3)
O(1)-S-O(2)	109.49(7)	109.60(6)
O(1)-S-O(3)	107.95(5)	108.00(5)
O(1)-S-O(4)	109.77(6)	109.72(5)
O(2)-S-O(3)	108.96(6)	108.98(5)
O(2)-S-O(4)	110.76(6)	110.64(6)
O(3)-S-O(4)	109.86(6)	109.85(5)

Symmetry codes: (a) x, y, z–1; (b) x, y–1, z–1; (c) –x, –y, 1–z; (d) x, y–1, z–1; (e) –x, 1–y, 1–z.

The observed structures of both crystals are very close to that of the previously reported structure of the proton compound [1, 14]. Moreover, the obtained positional parameters, the lengths of the S-O and O-O bonds in the SO_4 tetrahedron, and $N \cdots O$ and $O \cdots O$ hydrogen bonds for the deuterated compound are almost the same as those for the proton compound. The coordination around the Co atom comprises six O atoms of the water molecules, forming a slightly distorted octahedron with the Co-O distances in the range 2.07Å-2.11Å in both compounds. The S-O bond lengths in the SO_4 tetrahedra are 1.48Å in both crystals except one with the S-O(2) bond which has the length of 1.46Å. Thus, the SO_4 tetrahedra are slightly distorted from the regular one. It is considered that this difference in the bond length is attributed to the difference in the number and bond lengths of N-H-O and O-H-O around the O(2) and other oxygen atoms in the SO_4 tetrahedron. All the three O atoms except the O(2) atom are connected to three hydrogen bonds, as shown in Table 5. However, the O(2) atoms have only two hydrogen bonds (the N-H-O(2) and O(2)-H-O(6) hydrogen bonds), and the length of the N-H-O(2) hydrogen bond is longer than that of the other hydrogen bonds as shown in Table 5. There is a bond-stretching force between the O (or N) atoms ended with the hydrogen bonds. When the number and length of the hydrogen bonds, respectively, decrease or become longer, the bond-stretching force between the atoms ended with the bond becomes weaker. Therefore, the bond-stretching force of the hydrogen bond connecting to the O(2) atom is smaller than those of the other O atoms. As the result, the distance between the S and O(2) atoms is shorter than the other S-O bonds in the SO_4 tetrahedron. The difference between the S-O bonds can be also seen in some of deuterated crystals, and in other crystals [5, 6].

Table 5. Hydrogen bond geometry (in Å and degree) of (a) $(NH_4)_2Co(SO_4)_2{\cdot}6H_2O$ and (b) $(ND_4)_2Co(SO_4)_2{\cdot}6D_2O$ crystals

A-H(D)···B	A-H(D)	H(D)···B	A···B	A-H(D)···B
(a)				
N-H(1) ··· O(3)$^{(a)}$	0.81(2)	2.04(2)	2.851(2)	177(2)
N-H(2) ··· O(4)$^{(b)}$	0.87(2)	2.07(2)	2.910(1)	163(3)
N-H(3) ··· O(1)	0.83(3)	2.20(2)	2.989(2)	159(2)
N-H(3) ··· O(2)	0.83(3)	2.47(2)	3.149(2)	139(2)
N-H(4) ··· O(1)$^{(c)}$	0.81(2)	2.18(2)	2.970(1)	163(2)
O(5)-H(51) ··· O(3)	0.79(2)	2.00(2)	2.780(1)	173(2)
O(5)-H(52) ··· O(4)$^{(d)}$	0.75(2)	2.10(2)	2.832(1)	167(2)
O(6)-H(61) ··· O(2)$^{(d)}$	0.80(2)	1.91(2)	2.708(1)	174(2)
O(6)-H(62) ··· O(4)$^{(e)}$	0.86(2)	1.90(2)	2.757(1)	174(2)
O(7)-H(71) ··· O(1)$^{(f)}$	0.85(2)	1.86(2)	2.706(1)	170(2)
O(7)-H(72) ··· O(3)$^{(g)}$	0.79(2)	2.00(2)	2.766(1)	163(2)
(b)				
N-D(1) ··· O(3)$^{(a)}$	0.80(2)	2.05(2)	2.851(1)	176(2)
N-D(2) ··· O(4)$^{(b)}$	0.86(2)	2.08(2)	2.911(1)	163(2)
N-D(3) ··· O(1)	0.85(2)	2.18(2)	2.988(2)	159(2)
N-D(3) ··· O(2)	0.85(2)	2.47(2)	3.151(2)	138(2)
N-D(4) ··· O(1)$^{(c)}$	0.82(2)	2.18(2)	2.966(1)	162(2)
O(5)-D(51) ··· O(3)	0.79(2)	2.00(2)	2.780(1)	171(2)
O(5)-D(52) ··· O(4)$^{(d)}$	0.75(2)	2.10(2)	2.831(1)	168(2)
O(6)-D(61) ··· O(2)$^{(d)}$	0.79(2)	1.92(2)	2.708(1)	172(2)
O(6)-D(62) ··· O(4)$^{(e)}$	0.89(2)	1.87(2)	2.756(1)	176(2)
O(7)-D(71) ··· O(1)$^{(f)}$	0.85(2)	1.86(2)	2.704(1)	170(2)
O(7)-D(72) ··· O(3)$^{(g)}$	0.81(2)	1.99(2)	2.764(1)	159(2)

Symmetry codes: (a) $1-x$, $-y$, $1-z$; (b) $x-1$, y, z; (c) x, $1/2-y$, $1/2+z$; (d) $x-1$, y, z; (e) $x-1$, $1/2-y$, $1/2+z$; (f) $1-x$, $1/2+y$, $3/2-z$; (g) $1-x$, $1-y$, $1-z$.

The Jahn-Teller distortion in the ammonium copper (II) $(NH_4)_2Cu(SO_4)_2{\cdot}6H_2O$ Tutton salt has been found by the deformation of the CuO_6 octahedra [11, 12, 17]. The change of the Jahn-Teller distortion on deuteration in this copper crystal is accompanied with the breaking of the N-H-O(1) hydrogen bond and the formation of the N-D-O(2) hydrogen bond [11, 12, 17]. That is, the O(2) atom in the proton copper salt only forms the O(2)-H-O(6) hydrogen bond, but in the deuterated one it forms the N-D-O(2) and O(2)-D-O(6) hydrogen bonds. Moreover, the expansion of the O(2)-H-O(6) hydrogen bond is also observed by deuteration. However, the presented studies indicate that there is no Jahn-Teller distortion in the $(NH_4)_2Co(SO_4)_2{\cdot}6H_2O$ and $(ND_4)_2Co(SO_4)_2{\cdot}6D_2O$ crystals. The Co-O bond lengths in the deuterated compound are almost equal to that in the proton compound, that is, the bond lengths are not affected by deuteration. It is also confirmed that the changes of the N-H-O(1), N-H-O(2) and O(2)-H-O(6) hydrogen bonds are not produced by deuteration, and there is no expansion of the O(2)-H-O(6) hydrogen bond.

Ichikawa has pointed out the geometric isotope effect on the $O \cdots O$ hydrogen bond, based on many obtained accurate data about the crystal structures and related properties of hydrogen-bonded-crystals (O-H-O bond crystals) [9, 10]. Figure 3 shows the expansion ΔR of the O-H-O hydrogen bond on the deuteration as a function of the hydrogen bond distance [7, 10]. The expansion of the hydrogen bond length on deuteration was reported as the length varied in the range of about 2.43Å to 2.65Å, and the maximum magnitude of the expansion is about 0.03Å at the length slightly above 2.5Å. The changes of the bond lengths on deuteration are obtained to be –0.0001(16), –0.0010(20), –0.0003(16), –0.0011(18), –0.0021(18), and –0.0027(18)Å in the $(NH_4)_2Co(SO_4)_2{\cdot}6H_2O$ crystal. The results are added in Figure 3, and are in good agreement with the expansions for the bond length varied between 2.70Å and 2.85Å. This study strongly shows the support of the expansion range of the O-H-O hydrogen bond on deuteration.

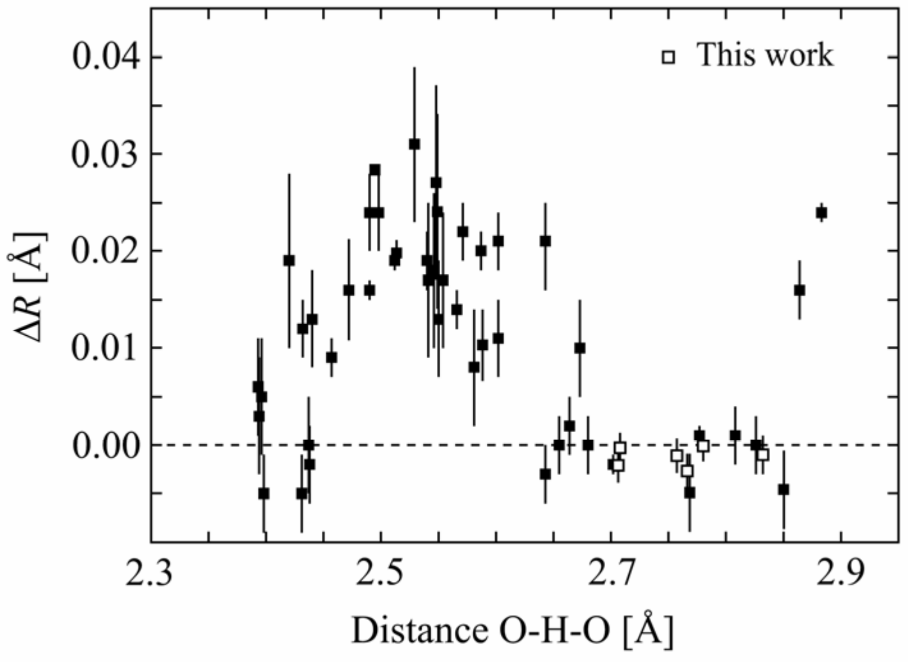


Figure 3. Expansions ΔR [ΔR = (O-D-O)-(O-H-O)] of O-H-O hydrogen bonds on deuteration as a function of hydrogen bond distance [7, 10].

We finally summarize the results from DSC and X-ray measurements for the $(NH_4)_2Co(SO_4)_2 \cdot 6H_2O$ and $(ND_4)_2Co(SO_4)_2 \cdot 6D_2O$ crystals. Several transitions in both crystals produced by the evaporation of the water molecules are found at high temperature. The transition enthalpies ΔH (entropies ΔS) and the transition temperatures are not affected by deuteration. The structures of both crystals at room temperature are determined with the space group symmetry of monoclinic $P2_1/c$. It is found that there are no geometric isotope effects on the S-O and Co-O bonds and on the N-H-O and O-H-O hydrogen bonds. The observed expansions of the O-H-O hydrogen bonds on deuteration are in good agreement with that of other compound data as were previously reported by Ichikawa. Moreover, it is confirmed that there is no existence of the Jahn-Teller distortion in both crystals.

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