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Solid State Sciences 2 (2000) 109–118

Solid State Sciences

www.elsevier.com/locate/ss

Synthesis and crystal structures of yttrium sulfates $Y(OH)(SO_4)$, $Y(SO_4)F$, $YNi(OH)_3(SO_4)$-II and $Y_2Cu(OH)_3(SO_4)_2F \cdot H_2O$

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Received 24 September 1999; accepted 29 November 1999

Abstract

$Y(OH)(SO_4)$, $Y(SO_4)F$, $YNi(OH)_3(SO_4)$-II and $Y_2Cu(OH)_3(SO_4)_2F \cdot H_2O$ are obtained from hydrothermal reactions at 380°C under a pressure of 210 MPa. Their crystal structures were refined from single-crystal X-ray diffraction data. The four compounds have the following space groups and unit cells: $Y(OH)(SO_4)$, $P2_1/n$, $a = 7.9498(6)$, $b = 10.9530(9)$, $c = 8.1447(6)$ Å, $\beta = 93.764(1)°$; $Y(SO_4)F$, $Pnma$, $a = 8.3128(9)$, $b = 6.9255(7)$, $c = 6.3905(7)$ Å; $YNi(OH)_3(SO_4)$-II, $Pnma$, $a = 6.9695(8)$, $b = 7.2615(8)$, $c = 10.292(1)$ Å; $Y_2Cu(OH)_3(SO_4)_2F \cdot H_2O$, $P2_1/n$, $a = 11.6889(7)$, $b = 6.8660(4)$, $c = 12.5280(8)$ Å, $\beta = 97.092(1)°$. The coordination environments of the yttrium atoms in the four structures vary from highly irregular $6+2$, $6+3$, $7+1$ coordination polyhedra to relatively regular dodecahedra.

Keywords: Hydrothermal synthesis; Crystal structure; Yttrium sulfate; Yttrium nickel sulfate; Yttrium copper sulfate

1. Introduction

Yttrium metal sulfates are of interest because superconductivity has been recently observed in some yttrium copper oxides containing sulfate anions [1]. Very little is known, however, about the general structural chemistry of yttrium metal sulfates because of the absence of accurate structural data, although a large number of alkali and alkaline earth metal sulfates have been well characterized [2]. Recently, Wickleder reported crystal structures of $(H_5O_2)Y(SO_4)_2$ [3] and several other rare earth sulfates [4–6]. A number of novel yttrium metal sulfates have been prepared as a result of our exploratory hydrothermal synthesis under conditions near the critical point of water. In a previous paper we reported the structures of $YCu(OH)_3(SO)_4$ and $YNi(OH)_3(SO)_4$-I which are topologically the same [7]. In these two compounds the Y atoms are coordinated by oxygen atoms to form bi-capped trigonal prisms that are connected into infinite chains through sharing common edges. The different local distortions of the CuO_6 and NiO_6 octahedra result in the absence of a center of symmetry in $YNi(OH)_3(SO)_4$-I. In this paper we report the syntheses of the four title compounds and their crystal structures determined from single-crystal X-ray diffraction data.

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PII: S1293-2558(00)00107-2

Table 1
Results of electron microprobe analysis (atomic numbers based on Y atoms)

	Y	S	Cu	Ni	F
$Y(OH)(SO_4)$	1.00	0.82	–	–	0.0
$Y(SO_4)F$	1.00	0.81	–	–	0.7
$YNi(OH)_3(SO_4)$-II	1.00	0.96	–	0.99	–
$Y_2Cu(OH)_3(SO_4)_2F\cdot H_2O$	2.00	1.91	1.03	–	0.9

2. Experimental

2.1. Synthesis

The syntheses were performed using a Leco HR-1B-2 high pressure/high temperature system. Typically, the starting materials were sealed in a flexible Teflon capsule that was subsequently placed into a RENE 41 reaction vessel and heated at 380°C under 210 MPa for 16 h. The products were washed with water, filtered and dried in air. Colorless needles of $Y(SO_4)F$ (~ 5%) and colorless prisms of $Y(OH)(SO_4)$ (~ 10%) together with blue prisms of $Y_2Cu(OH)_3(SO_4)_2F\cdot H_2O$ (~ 10%) were obtained from reactions starting with $Y(NO_3)_3\cdot 5H_2O$ (0.37 g, 1 mmol), $CuSO_4\cdot 5H_2O$ (0.25 g, 1 mmol) and 0.3 ml 45% KOH aqueous solution. The major phase in the product is pale blue needles of $YCu(OH)_3(SO_4)$ (~ 75%). The fluorine content arises from reactions with the Teflon capsules. Blue–green polyhedral crystals of $YNi(OH)_3(SO_4)$-II (~ 30%) formed together with green needles of $YNi(OH)_3(SO_4)$-I (~ 60%) and $Y(SO_4)F$ (~ 10%) from reactions starting with $Y(NO_3)_3\cdot 5H_2O$ (0.37 g, 1 mmol), $NiSO_4\cdot 6H_2O$ (0.26 g, 1 mmol) and 0.2 ml H_2O. Efforts to synthesize single phase products by variations in $Y(NO_3)_3/MSO_4$ ratios and water content were not successful.

2.2. Characterization

The chemical compositions were analyzed using a JEOL 8600 electron microprobe operating at 15 eV with a 10 μm beam diameter and a beam current of 30 nA. The results are listed in Table 1. The measured atomic ratios for $YNi(OH)_3(SO_4)$-II and for $Y_2Cu(OH)_3(SO_4)_2F\cdot H_2O$ are consistent with the for-

Table 2
Crystallographic data for $Y(OH)(SO_4)$ (**1**), $Y(SO_4)F$ (**2**), $YNi(OH)_3(SO_4)$-II (**3**) and $Y_2Cu(OH)_3(SO_4)_2F\cdot H_2O$ (**4**)

	1	**2**	**3**	**4**
Formula	HO_5SY	FO_4SY	H_3O_7SNiY	$H_5FO_{12}S_2CuY_2$
Formula weight	201.98	203.97	294.71	521.52
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Space group	$P2_1/n$	*Pnma*	*Pnma*	$P2_1/n$
Unit cell dimensions				
a (Å)	7.9498(6)	8.3128(9)	6.9695(8)	11.6889(7)
b (Å)	10.9530(9)	6.9255(7)	7.2615(8)	6.8660(4)
c (Å)	8.1447(6)	6.3905(7)	10.292(1)	12.5280(8)
β (°)	93.764(1)			97.092(1)
Volume (Å^3)	707.66(9)	367.90(7)	520.9(1)	997.8(1)
Z	8	4	4	4
$D_{calc.}$ (Mg/m^3)	3.792	3.682	3.758	3.472
Absorption coefficient (mm^{-1})	16.95	16.32	15.08	14.15
Crystal size (mm)	$0.14\times 0.12\times 0.10$	$0.22\times 0.11\times 0.08$	$0.16\times 0.13\times 0.12$	$0.35\times 0.16\times 0.11$
$2\theta_{max}$ (°)	57	57	57	57
Reflections collected	4302	2078	2935	5837
Independent reflections, R_{int}	1644, 0.0229	477, 0.0427	678, 0.0482	2288, 0.0259
Data/restraints/parameters	1644/2/136	477/0/41	678/2/63	2288/5/184
Goodness-of-fit on F^2	1.168	1.067	1.091	1.162
$R_1/wR_2[I>2\sigma(I)]$[a]	0.0285/0.0663	0.0370/0.0894	0.0369/0.0736	0.0265, 0.0686
R_1/wR_2 (all data)	0.0338/0.0680	0.0398/0.0911	0.0491/0.0776	0.0325, 0.0707
Extinction coefficient	0.0027(5)	0.023(4)	0.005(1)	0.0000(2)
Max. Diff. Peak, hole (e Å^{-3})	0.878, −0.529	1.696, −1.332	0.841, −0.909	0.551, −0.587

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. $wR_2=[\Sigma(w(F_o^2-F_c^2)^2)/\Sigma(wF_o^2)^2]^{1/2}$.

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for Y(OH)(SO_4), Y(SO_4)F, YNi$(OH)_3(SO_4)$-II and $Y_2Cu(OH)_3(SO_4)_2F \cdot H_2O$

	x	y	z	U_{eq} [a]
Y(OH) (SO_4)				
Y(1)	1617(1)	9368(1)	3718(1)	7(1)
Y(2)	1881(1)	9244(1)	−913(1)	7(1)
S(1)	5018(1)	8297(1)	−3651(1)	7(1)
S(2)	4567(1)	1909(1)	−1335(1)	7(1)
O(1)	3746(4)	8308(3)	−5032(4)	12(1)
O(2)	3891(4)	2392(3)	−2941(3)	11(1)
O(3)	4841(4)	2924(3)	−184(4)	13(1)
O(4)	4286(4)	8744(3)	−2172(4)	13(1)
O(5)	3343(4)	1040(3)	−742(4)	11(1)
O(6)	1003(4)	427(3)	1294(3)	7(1)
O(7)	1269(4)	114(3)	6416(3)	9(1)
O(8)	3794(4)	8718(3)	1482(3)	10(1)
O(9)	3521(4)	955(3)	3995(4)	14(1)
O(10)	595(4)	7995(3)	1560(3)	11(1)
H(1)	1757(67)	800(26)	6399(68)	27(17)
H(2)	1638(65)	1043(36)	1243(74)	33(18)
Y(SO_4)F				
Y	9455(1)	2500	1519(1)	7(1)
S	926(2)	2500	−3138(2)	7(1)
F	2057(4)	2500	1996(6)	18(1)
O(1)	9388(4)	5816(5)	1734(4)	14(1)
O(2)	7590(5)	2500	−1177(6)	15(1)
O(3)	9798(5)	2500	5130(6)	15(1)
YNi $(OH)_3(SO_4)$-II				
Y	2388(1)	2500	6991(1)	10(1)
Ni	0	0	5000	7(1)
S	6209(2)	2500	4468(2)	7(1)
O(1)	5523(7)	2500	5832(5)	15(1)
O(2)	4598(6)	2500	3549(5)	10(1)
O(3)	2631(4)	−828(5)	5749(3)	14(1)
O(4)	1241(6)	2500	4913(4)	8(1)
O(5)	−465(5)	673(5)	6916(3)	12(1)
H(1)	2130(88)	2500	4396(69)	29(27)
H(2)	−356(70)	−266(50)	7340(50)	16(15)
$Y_2Cu(OH)_3(SO_4)_2F \cdot H_2O$				
Y(1)	3169(1)	2395(1)	5061(1)	6(1)
Y(2)	4906(1)	2481(1)	8059(1)	5(1)
Cu	2538(1)	−108(1)	7488(1)	8(1)
S(1)	5264(1)	2618(1)	10980(1)	6(1)
S(2)	6292(1)	2585(1)	5636(1)	7(1)
O(1)	1540(3)	2188(5)	6045(2)	20(1)
O(2)	4703(2)	2860(4)	9886(2)	11(1)
O(3)	5140(2)	5880(4)	8309(2)	11(1)
O(4)	5003(3)	−707(4)	8604(2)	20(1)
O(5)	5151(3)	2527(4)	4975(2)	16(1)
O(6)	6145(3)	2670(4)	6779(2)	17(1)
O(7)	6959(3)	866(4)	5414(2)	15(1)
O(8)	6930(3)	4302(4)	5350(2)	16(1)
O(9)	2916(2)	2396(4)	8253(2)	8(1)
O(10)	3700(2)	4261(4)	6669(2)	9(1)
O(11)	3801(2)	527(4)	6668(2)	9(1)

Table 3 (Continued)

	x	y	z	U_{eq}[a]
OW	3573(3)	2276(5)	3181(2)	23(1)
F	1626(2)	2520(3)	3913(2)	16(1)
H(1)	2841(48)	2341(69)	8831(41)	18(14)
H(2)	4136(45)	5230(76)	6479(40)	24(14)
H(3)	3881(59)	−434(83)	6699(50)	44(21)
H(4)	4053(61)	2893(98)	2714(54)	56(21)
H(5)	2987(63)	2063(105)	2681(56)	63(23)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

mula ratios derived from the crystal structure refinements. Crystals of $Y(SO_4)F$ and $Y(OH)(SO_4)$ were found to degrade rapidly under the applied electron beam, which may account for the low measured contents of the volatile elements S and F.

Single-crystal X-ray data were measured on a SMART platform diffractometer equipped with a 1 K CCD area detector using graphite-monochromatized Mo K_α radiation at room temperature. For each phase a hemisphere of data (1271 frames at 5 cm detector distance) was collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 30 s/frame. The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability, and the maximum correction applied on the intensities was $< 1\%$. The data were integrated using the Siemens SAINT program, [8] with the intensities corrected for Lorentz factor, polarization, air absorption and absorption due to variation in the path length through the detector faceplate. Absorption correction was made using the program SADABS [9]. The structures were solved by direct methods and refined using SHELXTL [10]. All non-hydrogen positions were derived by direct methods and refined anisotropically in the final refinements. The hydrogen atoms were located from difference maps and refined isotropically with atom distance constraints. Crystallographic and refinement details are summarized in Table 2. Atom coordinates and selected bond lengths and angles are listed in Tables 3 and 4, respectively.

3. Results and discussion

3.1. Structure of $Y(OH)(SO_4)$

Local coordination environment and projections of the structure are shown in Fig. 1. The two symmetry independent yttrium atoms both have 7 + 1 coordination with seven Y–O bond lengths between 2.241 and 2.462 Å and one Y–O(8) bond length of about 2.69 Å. The seven nearest O atoms around each Y atom form mono-capped trigonal prisms that have two edges defined by three hydroxyl groups. The mono-capped trigonal prisms are connected by sharing the hydroxyl edges into infinite double chains parallel to the [001] direction (Fig. 1b). The double chains are interconnected and form a three-dimensional framework by the SO_4 tetrahedra that share all four oxygen corners with the mono-capped trigonal prisms. There are relatively strong hydrogen bonds between the O6 and O5 atoms (O5···H2:2.17 Å, O5···O6:2.658 Å). Weak hydrogen bonds occur between the O7 and O3 atoms (O3···H1:2.38 Å, O3···O7:2.722 Å).

3.2. Structure of $Y(SO_4)F$

Fig. 2 shows the local coordination environments and the [100] projection of the structure. The yttrium atom has a 6 + 2 coordination. Two F and four O atoms are coordinated to the Y atom to form a strongly distorted octahedron with Y–F bond lengths in the range 2.184–2.208 Å and Y–O bond lengths in the range 2.301–2.325 Å. This octahedral coordination of the Y atom is complemented by two further O atoms at Y–O distances of 2.570 Å. The F atoms are located at two opposite corners of the distorted octahedron. The YF_2O_4 octahedra are connected by sharing the F atoms into infinite chains parallel to [100]. The SO_4 tetrahedra are located between the chains. Each tetrahedron is linked to three octahedral chains by sharing their oxygen corners with four YF_2O_4 octahedra. The SO_4 tetrahedron is distorted in such a way that the two S–O bonds linked to the same octahedral chain are shorter and the bond angle between the two bonds is larger than the others. This

Table 4
Selected bond lengths (Å) and bond angles (°) for $Y(OH)(SO_4)$, $Y(SO_4)F$, $YNi(OH)_3(SO_4)$-II and $Y_2Cu(OH)_3(SO_4)_2F{\cdot}H_2O$

$Y(OH)(SO_4)$						
Y1–				Y2–		
O1	2.241(3)			O5	20284(3)	
O9	2.307(3)			O4	2.295(3)	
O6	2.314(3)			O2	2.300(3)	
O3	2.335(3)			O6	2.322(3)	
O7	2.359(3)			O6	2.358(3)	
O7	2.378(3)			O7	2.396(3)	
O10	2.413(3)			O8	2.462(3)	
O8	2.689(3)			O10	2.691(3)	
S1–	Distance	Angles				
O4	1.456(3)					
O1	1.462(3)	109.9(2)				
O9	1.463(3)	109.6(2)	111.5(2)			
O10	1.494(3)	111.1(2)	106.7(2)	108.1(2)		
S2–						
O3	1.461(3)					
O5	1.466(3)	110.9(2)				
O2	1.478(3)	109.0(2)	108.3(2)			
O8	1.485(3)	108.0(2)	109.4(2)	111.4(2)		
$Y(SO_4)F$						
Y–						
F	2.184(3)					
F	2.208(3)					
O1	2.301(3)					
O1	2.301(3)					
O2	2.318(4)					
O3	2.325(4)					
O1	2.570(3)					
O1	2.570(3)					
S–	Distance	Angles				
O3	1.451(4)					
O2	1.451(4)	112.7(3)				
O1	1.495(3)	110.2(2)	110.4(2)			
O1	1.495(3)	110.2(2)	110.4(2)	102.6(3)		
$YNi(OH)_3(SO_4)$-II						
Y–						
O4	2.283(5)					
O5	2.295(3)					
O5	2.295(3)					
O5	2.392(3)					
O5	2.392(3)					
O1	2.489(5)					
O1	2.590(5)					
O3	2.739(4)					
O3	2.739(4)					
Ni–	Distance	Angles				
O4	2.013(2)					
O4	2.013(2)	180.0				
O5	2.057(3)	96.0(2)	84.0(2)			
O5	2.057(3)	84.0(2)	96.0(2)	180.0		
O3	2.078(3)	95.8(2)	84.2(2)	81.5(1)	98.5(1)	
O3	2.078(3)	84.2(2)	95.8(2)	98.5(1)	81.5(1)	180.0

Table 4 (Continued)

S–						
O2	1.468(5)					
O3	1.476(3)	108.8(2)				
O3	1.476(3)	108.8(2)	110.7(3)			
O1	1.484(5)	111.3(3)	108.6(2)	108.6(2)		
$Y_2Cu(OH)_3(SO_4)_2F{\cdot}H_2O$						
Y1–				Y2–		
F	2.166(2)			F	2.157(2)	
O7	2.317(3)			O4	2.292(3)	
O8	2.325(3)			O6	2.293(3)	
O5	2.334(3)			O2	2.345(3)	
O1	2.397(3)			O3	2.366(3)	
O10	2.404(3)			O9	2.370(3)	
O11	2.424(3)			O10	2.431(3)	
OW	2.460(3)			O11	2.440(3)	
Cu–	Distance	Angles				
O10	1.943(3)					
O11	1.949(3)	178.9(1)				
O9	1.990(3)	83.6(1)	97.0(1)			
O9	1.991(3)	93.8(1)	85.6(1)	177.3(1)		
O1	2.568(3)	102.4(1)	78.4(1)	97.4(1)	82.1(1)	
O1	2.737(3)	75.0(1)	104.2(1)	77.8(1)	102.6(1)	174.7(1)
S1–						
O2	1.454(3)					
O4	1.460(3)	110.3(2)				
O3	1.478(3)	110.4(2)	108.2(2)			
O1	1.489(3)	112.0(2)	108.5(2)	107.3(2)		
S2–						
O7	1.460(3)					
O8	1.463(3)	107.7(2)				
O6	1.464(3)	110.4(2)	109.4(2)			
O5	1.481(3)	109.7(2)	109.6(2)	110.0(2)		

compound is isostructural with $Gd(SO_4)F$ reported recently by Wickleder [6].

3.3. Structure of $YNi(OH)_3(SO_4)$-II

In a previous paper we described the structure of $YNi(OH)_3(SO_4)$-I, in which the NiO_6 octahedra share *trans* edges to form infinite chains [7]. As shown in Fig. 3, the structure of $YNi(OH)_3(SO_4)$-II contains infinite chains of NiO_6 octahedra that share common corners. The NiO_6 octahedra in $YNi(OH)_3(SO_4)$-II are quite regular, with Ni–O bond lengths in the range 2.013–2.078 Å. Each NiO_6 octahedron has four hydroxyl groups in a square configuration and two apical oxygen atoms. The octahedra are connected to form infinite chains by sharing opposite hydroxyl corners (O(4)). Adjacent NiO_6 octahedra are bridged by a SO_4 tetrahedron through sharing the apical oxygen corners (O(3)) of the octahedra, to form $[Ni(OH)_3(SO_4)]$ complex chains parallel to [010]. Similar one-dimensional complex chains are found in the sulfate minerals butlerite $Fe(SO_4)(OH)(H_2O)_2$ [11], uklonskovite $Na[Mg(SO_4)(OH)(H_2O)_2]$ [12] and the phosphate mineral childrenite $Mn[Al(PO_4)(OH)_2(H_2O)]$ [13].

The Y atoms in $YNi(OH)_3(SO_4)$-II have a $6+3$ coordination with six Y–O bonds of lengths between 2.283 and 2.489 Å and three Y–O bonds of lengths 2.59–2.74 Å. The six nearest O atoms around each Y atom form a distorted trigonal prism. The YO_6 trigonal prisms share their base edges to form infinite zig–zag chains along [100] direction, perpendicular to the $[Ni(OH)_3(SO_4)]$ complex chains. The $[Ni(OH)_3(SO_4)]$ complex chains are interconnected with the YO_6 trigonal prisms forming a three-dimensional framework with narrow tunnels parallel to

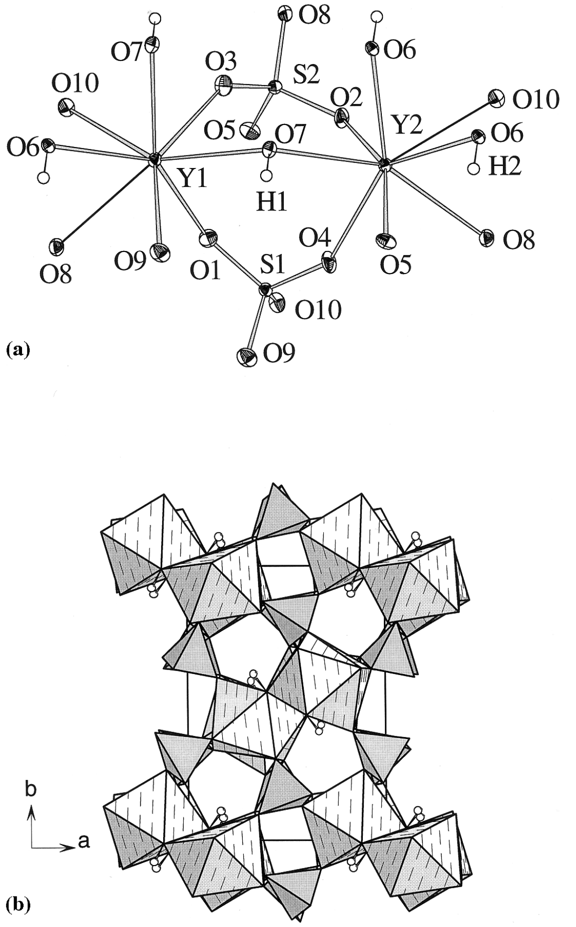

Fig. 1. The structure of Y(OH)(SO_4). (a) The local coordination of cations. Thermal ellipsoids are drawn with 50% probability. (b) Projection on [001]. YO_7 polyhedra are hatched. Open circles represent hydrogen atoms.

[100]. The tunnels have a 1.2 Å diameter window and are filled by hydrogen atoms of the hydroxyl groups. Hydrogen bonds are formed with the terminal O(2) atoms of the SO_4 tetrahedra (H1···O2:1.928 Å, O4···O2:2.729 Å, H2···O2:2.11 Å, O5···O2:2.915 Å).

3.4. *Structure of $Y_2Cu(OH)_3(SO_4)_2F \cdot H_2O$*

The local coordination environments of the cations are shown in Fig. 4a. The Cu atom is coordinated to four O atoms of hydroxyl groups at 1.943–1.991 Å in a square planar arrangement, and to two apical O atoms at 2.568–2.737 Å to form elongated octahedra. The octahedra are linked into infinite chains parallel to [010] by sharing common edges. The $S(1)O_4$ tetrahedra are linked to the octahedral chains with each apical oxygen atom of the CuO_6 octahedra shared by a $S(1)O_4$ tetrahedron forming complex $[Cu(OH)_3SO_4]$ chains (Fig. 4). Similar complex chains are also found in the structure of $YCu(OH)_3(SO_4)$ [7].

Both Y(1) and Y(2) atoms are coordinated by seven oxygen atoms (including a water oxygen) and one fluorine atom to form slightly distorted dodecahedra. The $Y(1)O_7F$ and $Y(2)O_7F$ dodecahedra are connected by sharing a common edge (O(10), O(11)) to form a dimer. The dimers are interconnected by sharing F corners of the dodecahedra into infinite chains parallel to [101]. These dodecahedral chains

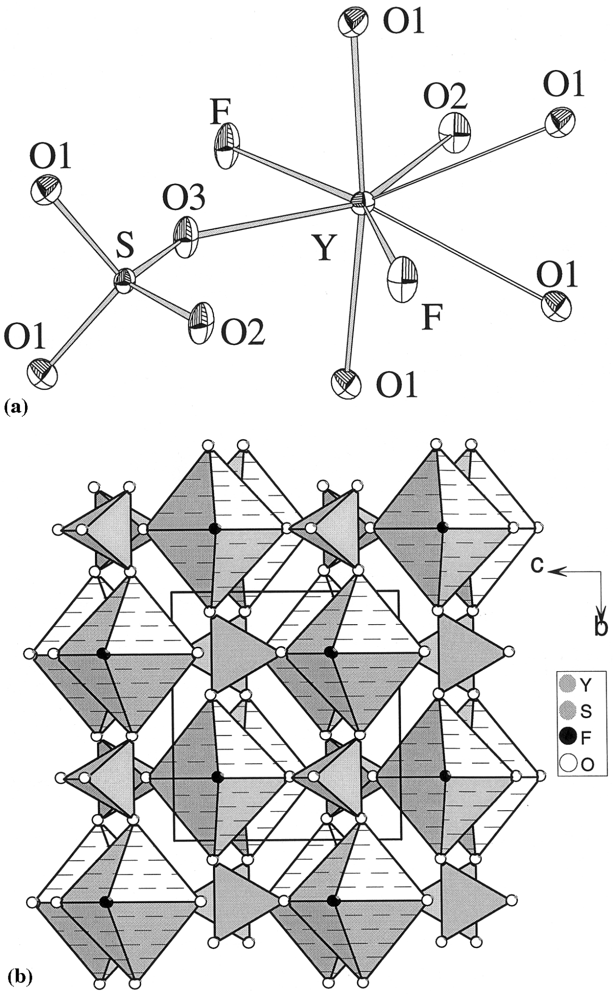

Fig. 2. The structure of $Y(SO_4)F$. (a) The local coordination of cations. Thermal ellipsoids are drawn with 50% probability. (b) Projection on [100]. YO_4F_2 octahedra are hatched. Open and solid circles represent oxygen and fluorine atoms, respectively.

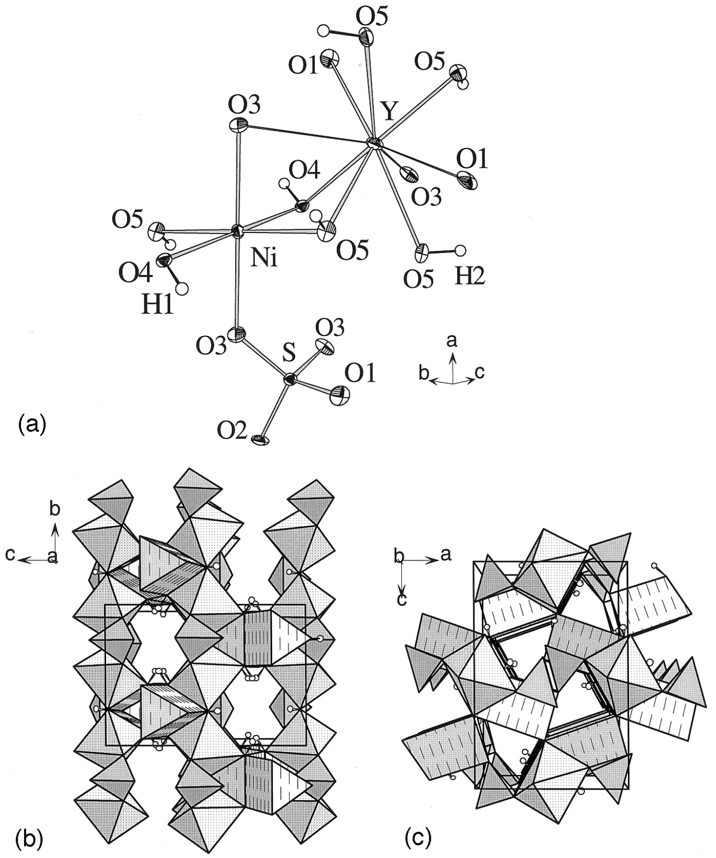

Fig. 3. The structure of YNi(OH)$_3$(SO$_4$)-II. (a) The local coordination of cations. Thermal ellipsoids are drawn with 50% probability. (b) A view along the *a* axis. (c) A view along the *b* axis. The NiO$_6$ octahedra are stippled and YO$_6$ trigonal prisms hatched. Open circles represent hydrogen atoms.

are further linked by the S(2)O$_4$ tetrahedra that share all oxygen corners with the dodecahedra, to form slabs parallel to (10−1). The slabs are connected with the complex [Cu(OH)$_3$SO$_4$] chains to form the three-dimensional structure via corner-sharing between the S(1)O$_4$ tetrahedra and the YO$_7$F dodecahedra and edge-sharing between the CuO$_6$ octahedra and the YO$_7$F dodecahedra. Relatively strong hydrogen bonds are found between the water oxygen atom and the O(3) atom (H4···O3:1.86 Å; Ow···O3:2.84 Å).

4. Discussion

The coordination environments of the yttrium atoms in the four sulfate structures show a large variability, ranging from highly irregular 6 + 2, 6 + 3, 7 + 1 coordination polyhedra to quite regular dodecahedra. In the structure of Y(SO$_4$)F, the YO$_{4+2}$F$_2$ polyhedron is linked to four SO$_4$ tetrahedra by sharing common oxygen corners, and to a fifth SO$_4$ tetrahedron by sharing a common edge (Fig. 2). The Y–O and S–O bonds to the two oxygen atoms defining the common edge (O(1)) are much longer than others because of the repulsion between the Y and S cations. This leads to the strong distortion of both the YO$_{4+2}$F$_2$ polyhedron and the SO$_4$ tetrahedron. From the point of view of the bond-valence theory [14], a S–O bond of a regular SO$_4$ tetrahedron has a bond valence of $6/4 = 1.5$ v.u., and a Y–O bond of a regular YO$_6$ octahedron has a bond valence of $3/6 = 0.5$ v.u. If an oxygen atom of a SO$_4$ tetrahedron is further bonded to only one Y^{3+} cation, a strong Y–O bond would be expected. However, if it is further bonded to more than one Y^{3+} cation, at least one Y–O bond would be relatively weak because the bond valence sum around the oxygen atom should be 2 v.u., and because the S–O bond is relatively rigid. In the case of $Y(SO_4)F$, the O(1) atom is bonded to one S and two Y atoms, therefore, one Y–O(1) bond is substantially weaker than the others. Such bond valence considerations can also be used to understand the diversity of Y–O bond lengths in the structures of $Y(OH)(SO_4)$ and $YNi(OH)_3(SO_4)$-II. In the structure of $Y_2Cu(OH)_3(SO_4)_2F{\cdot}H_2O$, all the oxygen corners of the SO_4 tetrahedra are each bonded to only one Y atom, which gives rise to the occurrence of the rather regular YO_7F dodecahedra.

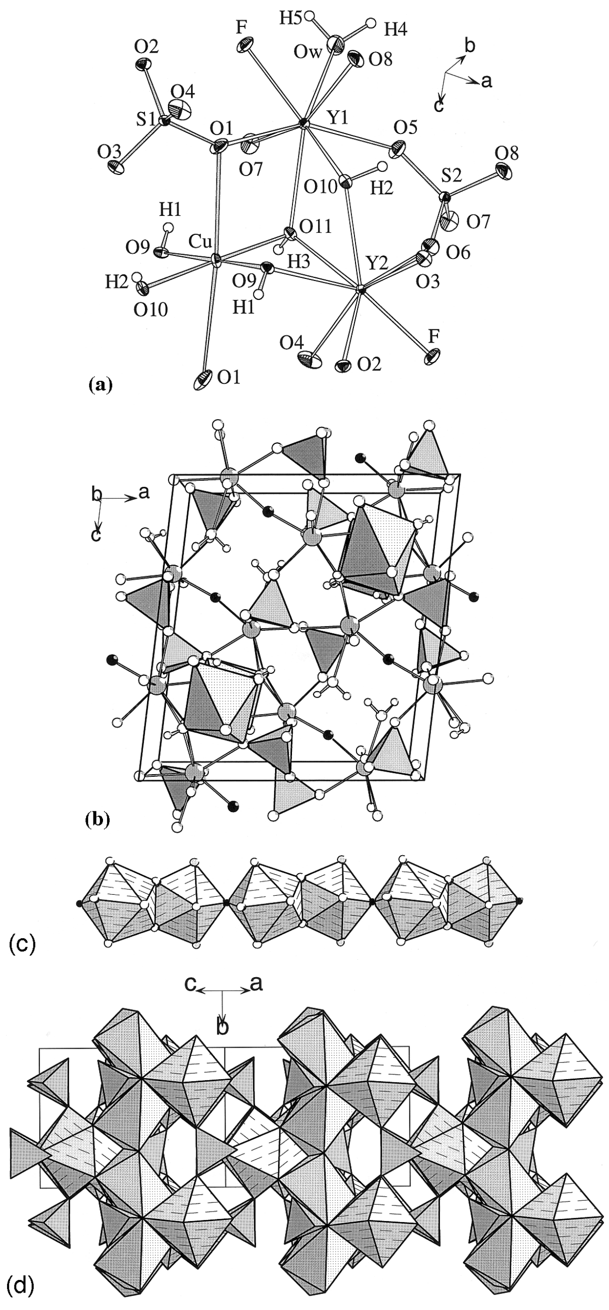

Fig. 4. The structure of $Y_2Cu(OH)_3(SO_4)_2F{\cdot}H_2O$. (a) The local coordination of cations. Thermal ellipsoids are drawn with 50% probability. (b) A view along the *b* axis. (c) The infinite chain of YO_7F dodecahedra. (d) A view along [101]. The CuO_6 octahedra are stippled and YO_7F dodecahedra hatched. Large shaded circles represent Y atoms. Medium sized open and solid circles represent oxygen and fluorine atoms, respectively. Small open circles represent hydrogen atoms.

The NiO_6 octahedra and SO_4 tetrahedra are less distorted in $YNi(OH)_3(SO_4)$-II than in $YNi(OH)_3(SO_4)$-I. In the latter structure containing edge sharing NiO_6 octahedral chains, the apical oxygen atom (O(3)) of the NiO_6 octahedron is shared by a neighboring NiO_6 octahedron and a SO_4 tetrahedron. Both the two Ni–O bonds (2.117–2.162 Å) and the S–O bond (1.502 Å) around the apical oxygen atom are considerably weaker than others. In $YNi(OH)_3(SO_4)$-II with corner sharing NiO_6 octahedral chains, the apical oxygen atom (O(3)) of the NiO_6 octahedron is shared only by a SO_4 tetrahedron. Both the two Ni–O bonds (2.117–2.162 Å) and the S–O bond (1.502 Å) around the apical oxygen atom are considerably weaker than others. In $YNi(OH)_3(SO_4)$-II with corner sharing NiO_6 octahedral chains, the apical oxygen atom (O(3)) of the NiO_6 octahedron is shared only by a SO_4 tetrahedron. The corresponding Ni–O(3) bond (2.078 Å) and S–O(3) bond(1.476 Å) are strong, giving rise to more regular NiO_6 octahedra and SO_4 tetrahedra. The two polymorphs appear in the same synthesis product, indicating that the two structures are energetically similar. $Y_2Cu(OH)_3(SO_4)_2F{\cdot}H_2O$ has the same type of $[Cu(OH)_3SO_4]$ chains as $YCu(OH)_3(SO_4)$ [7]. Distortions of the elongated CuO_6 octahedra and the SO_4 tetrahedra are stronger in the former structure in which the apical oxygen atom of the CuO_6 octahedron is bonded to one S atom, one Y atom and two Cu atoms, while in $YCu(OH)_3(SO_4)$ the corresponding oxygen atom is only bonded to one S atom and two Cu atoms.

Acknowledgements

We thank the National Science Foundation (DMR9214804) and the R.A. Welch Foundation for financial support. This work made use of MRSEC/TCSUH Shared Experimental Facilities supported by the National Science Foundation under Award

Number DMR-9632667 and the Texas Center for Superconductivity at the University of Houston.

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