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Structures and syntheses of four Np^{5+} sulfate chain structures: Divergence from U^{6+} crystal chemistry

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Abstract

Four Np^{5+} sulfates, $X_4[(NpO_2)(SO_4)_2]Cl$ ($X = K$, Rb) (*KS*1, *RbS*1), $Na_3[(NpO_2)(SO_4)_2](H_2O)_{2.5}$ (*NaS*1), and $CaZn_2[(NpO_2)_2(SO_4)_4](H_2O)_{10}$ (*CaZnS*1) were synthesized by evaporation of solutions derived from hydrothermal treatment. Their structures were solved by direct methods and refined on the basis of F^2 for all unique data collected with Mo$K\alpha$ radiation and a CCD-based detector to agreement indices (*KS*1, *RbS*1, *NaS*1, *CaZnS*1) $R_1 = 0.0237$, 0.0593, 0.0363, 0.0265 calculated for 2617, 2944, 2635, 2572 unique observed reflections, respectively. *KS*1 crystallizes in space group $P2/n$, $a = 10.0873(4)$, $b = 4.5354(2)$, $c = 14.3518(6)$, $\beta = 103.383(1)^\circ$, $V = 638.76(5)\,\text{Å}^3$, $Z = 2$. *RbS*1 is also monoclinic, $P2/n$, with $a = 10.5375(8)$, $b = 4.6151(3)$, $c = 16.0680(12)$, $\beta = 103.184(1)^\circ$, $V = 699.33(9)\,\text{Å}^3$, $Z = 2$. *NaS*1 is monoclinic, $P2_1/m$, with $a = 7.6615(5)$, $b = 7.0184(4)$, $c = 11.0070(7)$, $\beta = 90.787(1)^\circ$, $V = 591.81(6)\,\text{Å}^3$, $Z = 4$. *CaZnS*1 is monoclinic, $P2_1/m$, with $a = 8.321(2)$, $b = 7.0520(2)$, $c = 10.743(3)$, $\beta = 91.758(5)^\circ$, $V = 630.1(3)\,\text{Å}^3$, $Z = 2$. The structures of *KS*1 and *RbS*1 contain chains of edge-sharing neptunyl hexagonal bipyramids, with sulfate tetrahedra attached to either side of the chain by sharing edges with the bipyramids. *NaS*1 and *CaZnS*1 both contain chains of neptunyl pentagonal bipyramids and sulfate tetrahedra in which each bipyramid is linked to four tetrahedra, three by sharing vertices and one by sharing an edge. Bipyramids are bridged by sharing vertices with sulfate tetrahedra. Each of these structures exhibits significant departures from those of uranyl sulfates.

Keywords: Neptunyl sulfate; Neptunyl crystal chemistry; Chain structure

1. Introduction

The crystal chemistry of U^{6+} has received a great deal of attention over the past decade owing to its rich structural chemistry [1] as well as its importance in mineralogy [2], nuclear waste management [3–5], transport of uranium in the environment [6], and novel nanostructure materials [7–9]. Far fewer studies have focused on the crystal chemistry of Np^{5+} or Np^{6+}, although it is likely that even greater structural diversity exists in neptunyl compounds because both of these oxidation states are relatively stable and their crystal chemistry is dominated by neptunyl ions [10].

Actinyl ions occur in crystal structures as approximately linear dioxide cations that are coordinated by four, five or six ligands arranged at the equatorial vertices of square, pentagonal and hexagonal bipyramids that are capped by the O atoms of the actinyl ions [1]. The coordination polyhedra about U^{6+}, Np^{6+}, and Np^{5+} have very similar shapes, and differ only in small departures of the bond lengths [10]. As such, it is likely that the crystal chemistry of Np^{6+} will largely parallel that of U^{6+}. However, in the case of Np^{5+}, the lower valence of the neptunyl ion, as compared to the uranyl ion, will probably impact the linkages of the polyhedra, creating novel structure types. For example, structures having uranyl bipyramids and SO_4, MoO_4 or SeO_4 tetrahedra are dominated by the sharing of vertices between the bipyramids and tetrahedra, as edge sharing requires relatively short separations between two hexavalent cations [1]. Given the lower charge of the neptunyl ion in Np^{5+} structures, as compared to the

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uranyl ion, the sharing of edges between neptunyl polyhedra and SO_4, MoO_4 or SeO_4 tetrahedra may be more common, and may result in varied structural topologies. Also, the lower charge of the neptunyl ion containing Np^{5+} may favor more cation–cation interactions [11] than are observed in uranyl compounds. In cation–cation interactions an O atom of an actinyl ion is an equatorial ligand of a second actinyl ion, which results in novel structure types.

We have undertaken an extensive investigation of the crystal chemistry of Np^{5+} in compounds with environmentally relevant compositions. This research is driven not only by the expectation of considerable structural diversity, but also by the importance of Np^{5+} for geologic disposal of nuclear waste. Neptunium has a long half-life (2.14×10^6 years) and Np^{5+} is soluble in groundwater, where it can complex with a variety of ligands such as sulfate, phosphate, and carbonate [12,13]. An improved understanding of the crystal chemistry of Np^{5+} is essential for predicting its behavior in a geologic setting in the solid state, and also as a basis for studying complexation and aggregation of neptunium in solution. The current study presents the synthesis and structures of four Np^{5+} sulfates that contain chains of neptunyl polyhedra and sulfate tetrahedra: $K_4[(NpO_2)(SO_4)_2Cl]$ (*KS*1), $Rb_4[(NpO_2)(SO_4)_2Cl]$ (*RbS*1), $Na_3[(NpO_2)(SO_4)_2](H_2O)_{2.5}$ (*NaS*1) and $CaZn_2[(NpO_2)_2(SO_4)_4](H_2O)_{10}$ (*CaZnS*1).

2. Experimental methods

2.1. Crystal synthesis

The reagents K_2SO_4 (Fisher Scientific Lot # 783390), Rb_2SO_4 (Aldrich Lot # 7488-54-2), $Na_2SO_4(H_2O)_{10}$ (Baker Lot # 28106), $ZnSO_4(H_2O)_7$ (Baker Lot # 25736) and $CaSO_4(H_2O)_{10}$ (Mallinckrodt # 25736) were used as received. A Np^{5+} stock solution was prepared in a 1 M HCl solution. The NpO_2^+ was recovered from early experiments and purified using a cation exchange column containing Dowex-50-X8 resin to create the Np^{5+} stock solution. A UV spectrum was collected for the stock solution to ensure that the neptunium was only present in the pentavalent state. *CAUTION: ^{237}Np represents a serious health risk due to the emission of α- and γ-radiation. Such studies require appropriate equipment and personnel for handling radioactive materials.* All reactions took place in 7 mL Teflon cups with screw-top lids. After loading the reactants, the tightly closed Teflon cups were placed in 125 mL Teflon-lined Parr acid reaction vessels. Fifty milliliters of ultrapure water (18 MΩ resistance) was added to each vessel to provide counter pressure during heating. Heating took place in a gravity convention oven at 150 °C for 1 week. The reactants were allowed to cool slowly to room temperature before removal from the oven. Crystals did not form during the heat cycles; the solutions were allowed to evaporate to near dryness at room temperature to promote crystal growth.

2.2. $K_4[(NpO_2)(SO_4)_2]Cl$

*KS*1 was synthesized from a solution derived from hydrothermal reaction of 0.441 g K_2SO_4 with 0.50 mL of a 0.098 M Np^{5+} solution in 1 M HCl and 0.50 mL of ultrapure water. The pH was adjusted from 0.92 to 4.04 using 455 μL of 1.0 M NH_4OH. Clusters of light green fibrous needles approximately 200 μm in length formed after 2 days of solution evaporation.

2.3. $Rb_4[(NpO_2)(SO_4)_2]Cl$

*RbS*1 was synthesized from a solution derived from hydrothermal reaction of 0.0675 g of Rb_2SO_4 with 0.72 mL of a 0.072 M Np^{5+} solution in 1 M HCl and 0.28 mL of ultrapure water. The pH was adjusted from 0.15 to 2.04 using 200 μL of concentrated NH_4OH and 4 μL of 1 M HCl. The solution was evaporated for 2 days following heating, after which light green acicular crystals approximately 150 μm in length were recovered.

2.4. $Na_3[(NpO_2)(SO_4)_2](H_2O)_{2.5}$

*NaS*1 was synthesized from a solution derived from hydrothermal reaction of 0.082 g $Na_2SO_4(H_2O)_{10}$ with 0.50 mL 0.098 M Np^{5+} solution in 1 M HCl and 0.50 mL of ultrapure water. The pH was adjusted from 1.14 to 3.86 with 750 μL of 1.0 M NH_4OH and 1.5 μL of 1.0 M HCl. The solution was allowed to evaporate to near dryness and small green platy crystals approximately 100 μm in length were recovered.

2.5. $CaZn_2[(NpO_2)_2(SO_4)_4](H_2O)_{10}$

*CaZnS*1 was synthesized from a solution derived by hydrothermal reaction of 0.108 g $CaSO_4(H_2O)_{10}$ and 0.180 g $ZnSO_4(H_2O)_7$ with 0.57 mL 0.089 M Np^{5+} stock solution in 1 M HCl and 0.43 mL of ultrapure water. The pH was adjusted from 0.06 to 3.17 with 128 μL of concentrated NH_4OH and 5 μL of 1.0 M HCl. After evaporation for 2 days, light-green plates approximately 100 μm in length formed.

3. Structure solution and refinement

Single crystals of *KS*1, *RbS*1, and *NaS*1 were mounted on glass fibers and placed on a Bruker PLATFORM three-circle X-ray diffractometer equipped with a 4 K APEX CCD detector. A sphere of three-dimensional data was collected for each crystal at room temperature using monochromatic Mo*K*α X-radiation and frame widths of 0.3° in ω. The counting time per frame was 20 s for *KS*1, 60 s for *RbS*1, and 120 s for *NaS*1. Unit cell parameters for *KS*1, *RbS*1, and *NaS*1 were refined by least-squares techniques using the Bruker SMART software [14]. A single crystal of *CaZnS*1 was mounted on a glass fiber and placed on a Bruker three-circle X-ray diffractometer with a

APEX II CCD detector. A sphere of data was collected with frame widths of 0.3° in ω and 20 s spent counting per step. The Bruker SAINT software [15] was used for data integration. Empirical absorption corrections were applied in each case by modeling the crystals as ellipsoids using the Bruker Program XPREP [16]. Selected data collection parameters and crystallographic data are provided in Tables 1 and 2.

All structures were solved by direct methods and refined on the basis of F^2 for all unique data using the Bruker SHELXTL Version 5 system of programs [17]. Atomic scattering factors for each atom were taken from International Tables for X-ray Crystallography [18]. In each case the heavier cations were found in direct-methods solutions and other cations and anions were located in difference-Fourier maps calculated following refinement of the

Table 1
Selected crystallographic parameters for *KS*1 and *RbS*1

	*KS*1	*RbS*1
Formula	$K_4[(NpO_2)(SO_4)_2]Cl$	$Rb_4[(NpO_2)(SO_4)_2]Cl$
Formula weight	652.97	838.45
Temperature (*K*)	293(2)	293(2)
Crystal system	*P*2/*n*	*P*2/*n*
a (Å)	10.0873(4)	10.5375(8)
b (Å)	4.5354(2)	4.6151(3)
c (Å)	14.3518(6)	16.068(1)
ß (deg.)	103.383(1)	103.184(1)
Volume (Å^3)	638.76(5)	699.33(9)
Z	2	2
D_{calc} (g/cm^3)	3.395	3.982
μ (mm^{-1})	10.0	21.8
F(000)	596	740
Crystal size (mm)	0.20 × 0.05 × 0.04	0.15 × 0.05 × 0.05
θ range	2.24–34.51°	2.16–34.49°
Data collected	$-15<h<15$, $-7<k<7$, $-22<l<22$	$-16<h<16$, $-7<k<7$, $-25<l<25$
Reflections collected/unique	12318/2617 [$R_{int} = 0.061$]	13654/2944 [$R_{int} = 0.098$]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2617/0/83	2944/0/83
Goodness-of-fit on F^2	0.947	0.990
Final *R* indices [$I>2\sigma(I)$]	$R_1 = 0.0237$, w$R_2 = 0.0608$	$R_1 = 0.0593$, w$R_2 = 0.1860$
R indices (all data)	$R_1 = 0.0291$, w$R_2 = 0.0625$	$R_1 = 0.1173$, w$R_2 = 0.2097$
Largest diff. peak and hole (Å^{-3})	1.62 and −2.63	3.11 and −4.95

Table 2
Selected crystallographic parameters for *NaS*1 and *CaZnS*1

	*NaS*1	*CaZnS*1
Formula	$Na_3(NpO_2)(SO_4)_2(H_2O)_{2.5}$	$CaZn_2(NpO_2)_2(SO_4)_4(H_2O)_{10}$
Formula weight	575.10	1273.10
Temperature (*K*)	293(2)	293(2)
Crystal system	*P*2$_1$/*m*	P2$_1$/*m*
a (Å)	7.6615(5)	8.321(2)
b (Å)	7.0184(4)	7.052(2)
c (Å)	11.0070(7)	10.743(3)
ß (deg.)	90.787(1)	91.758(5)
Volume (Å^3)	591.81(6)	630.1(3)
Z	4	2
D_{calc} (g/cm^3)	3.227	3.303
μ (mm^{-1})	9.3	10.7
F(0 0 0)	526	570
Crystal size (mm)	0.08 × 0.05 × 0.05	0.10 × 0.10 × 0.08
θ range	2.66–34.51°	2.45–33.72°
Data collected	$12<h<12$, $-11<k<11$,$-17<l<17$	$-12<h<12$, $-10<k<10$, $-16<l<16$
Reflections collected/unique	12231/2635 [$R_{int} = 0.0507$]	11529/2572 [$R_{int} = 0.0592$]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2635/6/116	2572/0/127
Goodness-of-fit on F^2	1.001	0.850
Final *R* indices [$I>2\sigma(I)$]	$R_1 = 0.0363$, w$R_2 = 0.0822$	$R_1 = 0.0265$, w$R_2 = 0.0393$
R indices (all data)	$R_1 = 0.0453$, w$R_2 = 0.0839$	$R_1 = 0.0420$, w$R_2 = 0.0401$
Largest diff. peak and hole (Å^{-3})	4.43 and −1.46	1.40 and −2.68

partial-structure models. The isostructural compounds *KS*1 and *RbS*1 crystallize in space group $P2/n$, and their final structure models include anisotropic displacement parameters for all atoms. The structures of *NaS*1 and *CaZnS*1 both crystallize in space group $P2_1/m$. The final model for *NaS*1 includes anisotropic displacement parameters for Np, Na, and S. H atom positions were refined with the constraint that O–H bonds be $\sim$0.96 Å. In the case of *CaZnS*1 the final model includes anisotropic displacement parameters for the cations only. The electron density of OW(2) and OW(11), which correspond to H_2O groups that coordinated the Zn cation, are distributed over two sites. These O atoms were modeled as pairs of half-occupied sites with 0.8517(7) Å separating OW(2) and OW(2B) and 1.0710(7) Å separating OW(11) and OW(11B). The H atoms were not included in the model. Miscellaneous crystallographic and refinement parameters for each compound are included in Tables 1 and 2.

The atomic positional parameters are given in Tables 3–6 for *KS*1, *RbS*1, *NaS*1, and *CaZnS*1, respectively. Tables 7–10 contain selected interatomic distances for *KS*1, *RbS*1, *NaS*1, and *CaZnS*1, respectively. Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (Fax: 49 7247 808 666; email crysdata@fiz.karlsruhe.de) on quoting the depository numbers CSD 415684 [$K_4(NpO_2)(SO_4)_2Cl$], 415685 [$Rb_4(NpO_2)(SO_4)_2Cl$], 415686 [$Na_3(NpO_2)(SO_4)_2(H_2O)_{2.5}$], and 415687 [$CaZn_2(NpO_2)_2(SO_4)_4(H_2O)_{10}$].

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for *KS*1

	x	*y*	*z*	*U*(eq)
Np(1)	2500	2561(1)	2500	11(1)
K(1)	5614(1)	−2362(1)	3944(1)	24(1)
K(2)	−655(1)	2285(2)	3705(1)	26(1)
Cl(1)	7500	−2681(2)	2500	27(1)
S(1)	2272(1)	−3415(2)	4312(1)	16(1)
O(1)	4359(3)	2588(4)	2858(2)	20(1)
O(2)	2519(3)	−2294(4)	3387(2)	20(1)
O(3)	947(3)	−2501(4)	4441(2)	28(1)
O(4)	3373(4)	−2536(4)	5104(2)	33(1)
O(5)	2297(3)	−6689(5)	4194(2)	22(1)

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for *RbS*1

	x	*y*	*z*	*U*(eq)
Np(1)	2500	2551(2)	2500	11(1)
Rb(1)	5602(2)	−2365(4)	3960(1)	40(1)
Rb(2)	−656(2)	2304(5)	3719(2)	46(1)
Cl(1)	7500	−2717(14)	2500	31(1)
S(1)	2274(4)	−3429(7)	4262(2)	15(1)
O(1)	4275(9)	2580(20)	2856(7)	21(2)
O(2)	2505(10)	−2270(20)	3353(6)	20(2)
O(3)	1019(11)	−2530(30)	4415(8)	30(2)
O(4)	3302(13)	−2570(20)	5034(7)	36(3)
O(5)	2287(11)	−6660(20)	4162(7)	17(2)

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for *NaS*1

	x	*y*	*z*	*U*(eq)
Np(1)	6418(1)	7500	6858(1)	13(1)
Na(1)	0	0	5000	31(1)
Na(2)	124(5)	7500	2103(3)	34(1)
Na(3)	3466(13)	9538(15)	9683(10)	101(3)
S(1)	6399(2)	2500	5955(2)	14(1)
S(2)	9147(2)	7500	9015(2)	23(1)
O(1)	8166(7)	7500	5732(5)	24(1)
O(2)	4697(7)	7500	7974(5)	22(1)
O(3)	8311(7)	2500	6021(5)	24(1)
O(4)	5692(6)	825(6)	6575(5)	37(1)
O(5)	1050(8)	7500	8869(7)	37(2)
O(6)	8668(10)	7500	271(6)	42(2)
O(7)	5844(9)	2500	4691(5)	42(2)
O(8)	8372(5)	9195(6)	8371(3)	26(1)
OW(9)	1738(6)	218(7)	6891(4)	38(1)
OW(10)[a]	4750(40)	7500	850(20)	102(8)
H(1)[a]	5960(60)	7500	690(160)	50
H(2)	1320(80)	−880(70)	7320(60)	50
H(3)	2910(40)	−200(100)	6730(60)	50
H(4)[a]	4200(200)	7500	80(80)	50

[a] Site 50% occupied.

Table 6
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for *CaZnS*1

	x	*y*	*z*	*U*(eq)
Np(1)	2027(1)	2500	1408(1)	13(1)
Zn(1)	7858(1)	2500	2994(1)	22(1)
Ca(1)	3327(3)	7500	3743(2)	22(1)
S(1)	−859(2)	2500	−1260(1)	15(1)
S(2)	3992(2)	2500	3976(1)	17(1)
O(1)	3949(4)	2500	665(3)	21(1)
OW(2)[a]	7219(9)	178(10)	2071(7)	38(2)
OW(2B)[a]	6772(8)	861(9)	1506(6)	27(2)
O(3)	770(4)	2500	−682(3)	28(1)
O(4)	5752(4)	2500	4050(4)	36(1)
O(5)	−1745(3)	819(3)	−838(3)	26(1)
O(6)	3376(3)	836(4)	3271(2)	28(1)
O(7)	3411(5)	2500	5242(4)	37(1)
O(8)	67(4)	2500	2148(3)	24(1)
O(9)	−747(4)	2500	−2619(3)	26(1)
OW(10)	5054(5)	−7500	−1963(4)	31(1)
OW(11)[a]	8618(7)	936(8)	4553(5)	30(2)
OW(11B)[a]	8605(6)	−153(8)	3858(5)	24(1)

[a] Site 50% occupied.

Table 7
Selected interatomic distances (Å) for *KS*1

Np(1)–O(1)	1.827(2)	K(2)–O(3)^{f}	2.745(3)
Np(1)–O(1)^{a}	1.827(2)	K(2)–O(3)	2.766(3)
Np(1)–O(5)^{b}	2.510(2)	K(2)–O(1)^{a}	2.850(3)
Np(1)–O(5)^{c}	2.510(2)	K(2)–O(3)^{b}	2.921(3)
Np(1)–O(2)	2.541(2)	K(2)–O(5)^{c}	2.934(3)
Np(1)–O(2)^{a}	2.541(2)	K(2)–Cl(1)^{g}	3.168(1)
Np(1)–O(2)^{l}	2.656(2)	K(2)–Cl(1)^{h}	3.190(1)
Np(1)–O(2)^{b}	2.656(2)		
⟨Np(1)–O$_{eq}$⟩	2.569	Cl(1)–K(1)^{i}	3.1240(9)
		Cl(1)–K(2)^{j}	3.1679(11)
S(1)–O(4)	1.449(3)	Cl(1)–K(2)^{a}	3.1679(11)
S(1)–O(3)	1.452(3)	Cl(1)–K(2)^{k}	3.1901(11)
S(1)–O(2)	1.495(2)	Cl(1)–K(2)^{j}	3.1901(11)
S(1)–O(5)	1.495(2)		
⟨S(1)–O⟩	1.473		
K(1)–O(4)^{c}	2.683(2)		
K(1)–O(4)^{d}	2.761(2)		
K(1)–O(1)	2.856(2)		
K(1)–O(1)^{e}	2.891(2)		
K(1)–O(5)^{c}	3.027(3)		
K(1)–O(2)	3.038(3)		
K(1)–O(4)	3.104(4)		
K(1)–Cl(1)	3.1245(8)		

Symmetry transformations used to generate equivalent atoms: a: $-x+1/2, y, -z+1/2$; b: $x, y+1, z$; c: $-x+1, -y, -z+1$; d: $-x+1, -y-1, -z+1$; e: $x, y-1, z$; f: $-x, -y, -z+1$; g: $x-1, y, z$; h: $x-1, y+1, z$; i: $-x+3/2, y, -z+1/2$; j: $x+1, y, z$; k: $-x+1/2, y-1, -z+1/2$; l: $-x+1/2, y+1, -z+1/2$.

Table 8
Selected interatomic distances (Å) for *RbS*1

Np(1)–O(1)^{a}	1.824(9)	Rb(2)–O(3)^{g}	2.870(11)
Np(1)–O(1)	1.824(9)	Rb(2)–O(3)	2.885(12)
Np(1)–O(5)^{b}	2.541(10)	Rb(2)–O(3)^{c}	3.004(12)
Np(1)–O(5)^{c}	2.541(10)	Rb(2)–O(1)^{a}	3.015(10)
Np(1)–O(2)	2.555(9)	Rb(2)–O(5)^{c}	3.058(11)
Np(1)–O(2)^{a}	2.555(9)	Rb(2)–Cl(1)^{h}	3.271(5)
Np(1)–O(2)^{b}	2.702(10)	Rb(2)–Cl(1)^{i}	3.285(5)
Np(1)–O(2)^{c}	2.702(10)		
⟨Np(1)–O$_{eq}$⟩		Cl(1)–Rb(1)^{j}	3.263(2)
		Cl(1)–Rb(2)^{k}	3.271(5)
S(1)–O(4)	1.438(11)	Cl(1)–Rb(2)^{l}	3.271(5)
S(1)–O(3)	1.452(11)	Cl(1)–Rb(2)^{m}	3.285(5)
S(1)–O(5)	1.498(9)	Cl(1)–Rb(2)^{a}	3.285(5)
S(1)–O(2)	1.515(10)		
⟨S(1)–O⟩			
Rb(1)–O(4)^{d}	2.818(11)		
Rb(1)–O(4)^{e}	2.869(11)		
Rb(1)–O(1)	2.964(11)		
Rb(1)–O(1)^{f}	3.002(10)		
Rb(1)–O(5)^{e}	3.167(11)		
Rb(1)–O(2)	3.181(11)		
Rb(1)–O(4)	3.186(15)		
Rb(1)–Cl(1)	3.263(2)		

Symmetry transformations used to generate equivalent atoms: a: $-x+1/2, y, -z+1/2$; b: $-x+1/2, y+1, -z+1/2$; c: $x, y+1, z$; d: $-x+1, -y, -z+1$; e: $-x+1, -y-1, -z+1$; f: x, y—1, z; g: $-x, -y, -z+1$; h: $x-1, y+1, z$; i: $x-1, y, z$; j: $-x+3/2, y, -z+1/2$; k: $x+1, y-1, z$; l: $-x+1/2, y-1, -z+1/2$; m: $x+1, y, z$.

Table 9
Selected interatomic distances (Å) for *NaS*1

Np(1)–O(2)	1.814(5)	Na(1)–O(1)^{a}	2.394(3)
Np(1)–O(1)	1.837(5)	Na(1)–O(1)^{e}	2.394(3)
Np(1)–O(7)^{a}	2.415(6)	Na(1)–OW(9)^{f}	2.460(5)
Np(1)–O(4)^{b}	2.418(4)	Na(1)–OW(9)	2.460(5)
Np(1)–O(4)^{c}	2.418(4)	Na(1)–O(3)^{g}	2.461(4)
Np(1)–O(8)	2.522(4)	Na(1)–O(3)^{h}	2.461(4)
Np(1)–O(8)^{d}	2.522(4)	⟨Na(1)–O⟩	2.438
⟨Np(1)–O$_{eq}$⟩	2.459		
		Na(2)–O(6)^{h}	2.291(7)
S(1)–O(7)	1.449(6)	Na(2)–O(3)^{a}	2.373(6)
S(1)–O(3)	1.466(6)	Na(2)–OW(9)^{i}	2.423(5)
S(1)–O(4)	1.467(4)	Na(2)–OW(9)^{j}	2.423(5)
S(1)–O(4)^{b}	1.467(4)	Na(2)–O(8)^{k}	2.645(5)
⟨S(1)–O⟩	1.462	Na(2)–O(8)^{l}	2.645(5)
		⟨Na(2)–O⟩	2.467
S(2)–O(6)^{m}	1.435(7)		
S(2)–O(5)^{o}	1.469(6)	Na(3)–OW(10)^{m}	2.15(2)
S(2)–O(8)^{d}	1.503(4)	Na(3)–O(5)	2.496(12)
S(2)–O(8)	1.503(4)	Na(3)–O(2)	2.554(9)
⟨S(2)–O⟩	1.477	Na(3)–OW(10)^{k}	2.563(19)
		Na(3)–O(6)^{k}	2.646(12)
		Na(3)–O(8)^{n}	2.729(9)
		⟨Na(3)–O⟩	2.523

Symmetry transformations used to generate equivalent atoms: a: $-x+1, -y+1, -z+1$; b: $x, -y+1/2, z$; c: $x, y+1, z$; d: $x, -y+3/2, z$; e: $x-1, y-1, z$; f: $-x, -y, -z+1$; g: $-x+1, -y, -z+1$; h: $x-1, y, z$; i: $-x, y+1/2, -z+1$; j: $-x, -y+1, -z+1$; k: $-x+1, -y+2, -z+1$; l: $-x+1, y-1/2, -z+1$; m: $x, y, z+1$; n: $-x+1, -y+2, -z+2$; o: $x+1, y, z$.

Table 10
Selected interatomic distances (Å) for *CaZnS*1

Np(1)–O(1)	1.809(3)	Zn(1)–OW(2)*	1.979(7)
Np(1)–O(8)	1.836(4)	Zn(1)–OW(2)^{c}	1.979(7)
Np(1)–O(5)^{a}	2.429(3)	Zn(1)–O(8)^{d}	2.076(4)
Np(1)–O(5)^{b}	2.429(3)	Zn(1)–OW(11)	2.087(5)
Np(1)–O(3)	2.447(4)	Zn(1)–OW(11)^{c}	2.087(5)
Np(1)–O(6)^{c}	2.551(3)	Zn(1)–O(4)	2.116(4)
Np(1)–O(6)	2.551(3)	Zn(1)–OW(2B)	2.149(7)
⟨Np(1)–O$_{eq}$⟩		Zn(1)–OW(2B)^{c}	2.149(7)
		Zn(1)–OW(11B)^{c}	2.171(5)
S(1)–O(9)	1.465(4)	Zn(1)–OW(11B)	2.171(5)
S(1)–O(3)	1.474(4)		
S(1)–O(5)^{c}	1.475(3)	Ca(1)–OW(10)^{e}	2.372(5)
S(1)–O(5)	1.475(3)	Ca(1)–O(6)^{c}	2.407(3)
⟨S(1)–O⟩	1.472	Ca(1)–O(6)^{f}	2.407(3)
		Ca(1)–O(9)^{g}	2.431(4)
S(2)–O(7)	1.458(4)	Ca(1)–O(4)^{h}	2.469(5)
S(2)–O(4)	1.464(4)	Ca(1)–OW(11)^{i}	2.715(7)
S(2)–O(6)	1.480(3)	Ca(1)–OW(11)^{h}	2.715(7)
S(2)–O(6)^{c}	1.480(3)	⟨Ca(1)–O⟩	2.502
⟨S(2)–O⟩	1.470		

Symmetry transformations used to generate equivalent atoms: a: $-x, -y, -z$; b: $-x, y+1/2, -z$; c: $x, -y+1/2, z$; d: $x+1, y, z$; e: $-x+1, -y, -z$; f: $x, y+1, z$; g: $-x, -y+1, -z$; h: $-x+1, -y+1, -z+1$; i: $-x+1, y+1/2, -z+1$.

*Only six sites are occupied locally about each Zn cation.

4. Results

4.1. Structures of KS1 and RbS1

The isostructural compounds *KS*1 and *RbS*1 contain infinite chains of neptunyl and sulfate polyhedra (Fig. 1a). There is one symmetrically independent Np^{5+} cation in each structure that is strongly bonded to two O atoms, giving the nearly linear neptunyl cation $(NpO_2)^+$. The bond lengths of the neptunyl ion are 1.827(2) Å for *KS*1 and 1.826(9) Å for *RbS*1, consistent with Np^{5+}. The $(NpO_2)^+$ ions in both structures are coordinated by six O atoms arranged at the equatorial vertices of a hexagonal bipyramid that is capped by the neptunyl ion O atoms. The Np^{+5}–O_{eq} (eq: equatorial) bond lengths range from 2.510(2) to 2.717(10) Å in the two structures. One symmetrically independent sulfate tetrahedron is present in each structure, with S–O bond lengths ranging from 1.449(3) to 1.503(9) Å.

The neptunyl hexagonal bipyramids in *KS*1 and *RbS*1 share an O(2)–O(2) edge, giving infinite chains of bipyramids that extend in the [010] direction (Fig. 1a). These chains are one bipyramid wide and sulfate tetrahedra are attached to each side by sharing the O(2)–O(5) equatorial edge of the hexagonal bipyramid. The neptunyl sulfate chains are linked through bonds to the K or Rb cations, and there are two symmetrically distinct sites in each case (Fig. 1b). In the structure of *KS*1, the K1 site is coordinated by seven O atoms at distances ranging from 2.683(2) to 3.104(2) Å, and one Cl atom at a distance of 3.1245(8) Å. The K(2) site is coordinated by five O atoms with bond lengths ranging from 2.745(3) to 2.934(3) Å, and two Cl atoms at 3.1680(11) and 3.1899(11) Å. In the case of *RbS*1, the coordination polyhedra are similar to those in *KS*1, but the corresponding bond lengths are ~5% larger due to the larger size of Rb (Table 8).

4.2. Structures of NaS1 and CaZnS1

The structures of *NaS*1 and *CaZnS*1 are closely related. There is one symmetrically independent Np^{5+} cation in each of these structures, and both form strong bonds to two O atoms, giving $(NpO_2)^+$ ions, with bond lengths of 1.814(5) and 1.837(5) Å for *NaS*1 and 1.809(3) and 1.836(4) Å for *CaZnS*1. Each neptunyl ion is coordinated by five atoms of O located at the equatorial vertices of pentagonal bipyramids. The Np^{5+}–O_{eq} bond lengths range from 2.415(6) to 2.551(3) Å, and the polyhedral geometries are consistent with Np^{5+}. Both compounds have two symmetrically distinct sulfate tetrahedra, with individual S–O bond lengths ranging from 1.435(7) to 1.503(4).

The structures of *NaS*1 and *CaZnS*1 contain identical chains of neptunyl pentagonal bipyramids and sulfate tetrahedra (Fig. 2). Each bipyramid shares a single edge with a tetrahedron and the remaining three vertices are shared with three different tetrahedra. As such, each bipyramid is linked to four tetrahedra, one in bidentate and three in monodentate configurations. The S(1) tetrahedron shares three of its vertices with three different bipyramids and provides linkages between the bipyramids along the chain length. The S(2) tetrahedron shares an edge with a bipyramid and two of its vertices do not bridge within the chain.

The neptunyl sulfate chains in *NaS*1 and *CaZnS*1 are linked through bonds to interstitial cations, and by H bonds to interstitial H_2O groups. In *NaS*1, the three unique Na cations are octahedrally coordinated by O atoms, with bond lengths ranging from 2.394(3) to 2.729(9) Å (Fig. 3). The electron density associated with the Na(3) site is elongated along [001], but difference-Fourier maps show no splitting of the site. Two H_2O groups [OW(9) and OW(10)] are located between the neptunyl sulfate chains where they are bonded to Na (Fig. 3). The H bonds extend

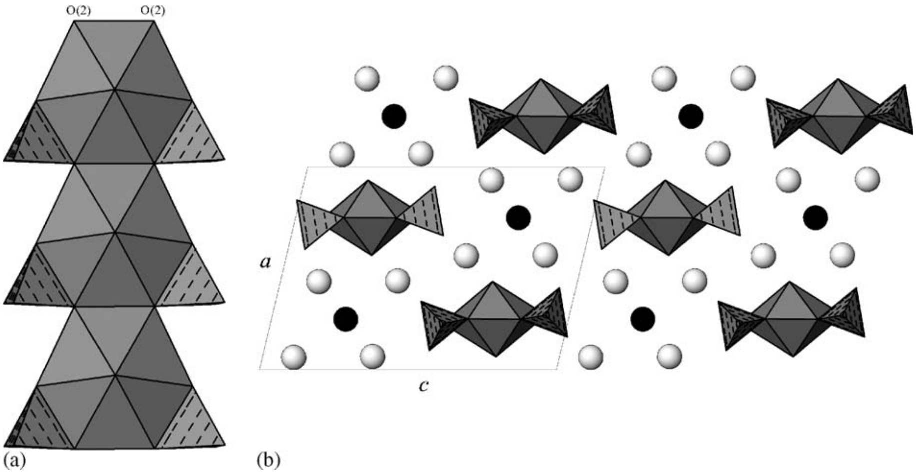

Fig. 1. Polyhedral representations of the structures of *KS*1 and *RbS*1. (a) The chain of neptunyl hexagonal bipyramids and sulfate tetrahedra. (b) Projection of the structure along [010] showing the chains of neptunyl hexagonal bipyramids and sulfate tetrahedra, as well as the locations of K or Rb (open circles) and Cl (black circles).

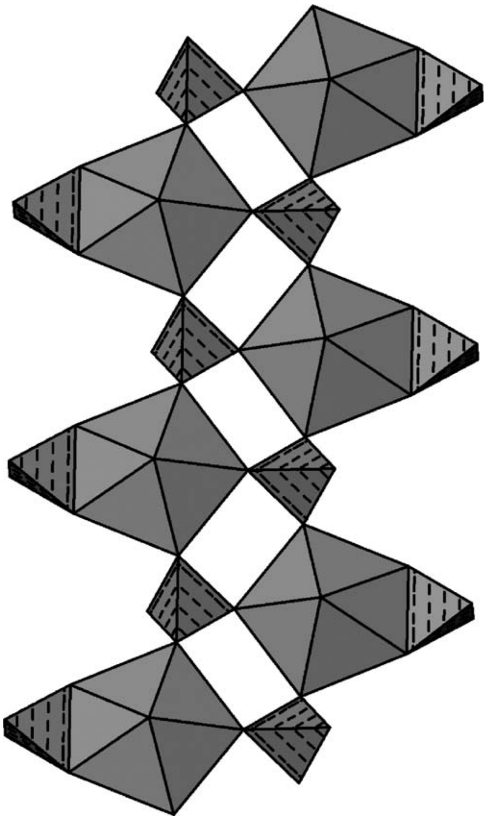

Fig. 2. Polyhedral representation of the chain of neptunyl pentagonal bipyramids and sulfate tetrahedra in the structures of *NaS*1 and *CaZnS*1.

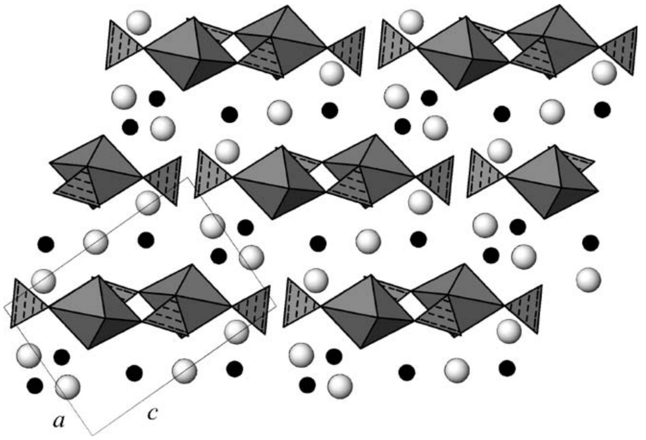

Fig. 3. Polyhedral representation of the neptunyl pentagonal bipyramids and sulfate tetrahedra in the structure of *NaS*1 projected along [010]. The locations of the Na cations are indicated by open circles and those of H_2O groups are shown by black circles.

from OW(9) to O acceptors on the S(1) and S(2) tetrahedra [O(4) and O(5), respectively]. The O acceptor lengths are 2.06 Å for H(2)–O(5) and 2.25 Å for H(3)–O(4). Hydrogen bonds extend from OW(10) to O(12), on the S(2) tetrahedron, and O(6) of a neptunyl ion. The O acceptor lengths are 2.13 Å for H(1)–O(6) and 2.35 Å for H(4)–O(2).

The chains of neptunyl and sulfate polyhedra in *CaZnS*1 are parallel to $[10\bar{1}]$ and are linked into layers by bonds to the Ca cation (Fig. 4a). The Ca site is coordinated by four O atoms and two H_2O groups [OW(10) and OW(11)] with bond lengths ranging from 2.372(5) to 2.715(7) Å. The Zn cation, which is located between the layers, is octahedrally coordinated with an average bond length of 2.09 Å. Zn is coordinated about the equatorial plane by four H_2O groups [OW(2) and OW(11)], and the octahedron is capped by O atoms of the neptunyl ion [O(8)] and the S(2) tetrahedron [O(4)] (Fig. 4b).

5. Discussion

Fifty-five inorganic U^{6+} compounds have structures based on infinite chains of polyhedra containing cations of higher bond-valence [1]. Many of these include uranyl polyhedra and MoO_4, SO_4 or CrO_4 tetrahedra, or cations containing stereoactive lone-pairs of electrons such as Se^{4+} or I^{5+} [1]. The structures are known for 27 uranyl sulfates, eight of which are minerals. Five of these are based upon chains of uranyl and sulfate polyhedra, whereas 17 contain sheets of uranyl polyhedra and sulfate tetrahedra.

There are no reported uranyl sulfate structures that contain chains of edge-sharing uranyl hexagonal bipyramids analogous to that of *KS*1 and *RbS*1. Chains of edge-sharing uranyl hexagonal bipyramids do exist in the structures of studtite, $(UO_2)O_2(H_2O)_4$, where the shared edge is a peroxide group [19], and $(UO_2)(IO_3)_2$, where iodate pyramids are attached to the sides of the chains by sharing equatorial edges of the bipyramids [20]. The sharing of an edge between a sulfate tetrahedron and a uranyl hexagonal bipyramid has not been observed. No other Np^{5+} sulfate structures have been reported that contain chains of edge-sharing neptunyl hexagonal bypramids.

Isolated uranyl sulfate clusters with structural connectivity similar to portions of the chains of *NaS*1 and *CaZnS*1 are found in $Na_6[(UO_2)(SO_4)_4](H_2O)_2$, $Na_{10}[(UO_2)(SO_4)_4(H_2O)_3$ and $KNa_5[(UO_2)(SO_4)_4](H_2O)$ [21–23]. Four sulfate tetrahedra are linked to a uranyl pentagonal bipyramid, with three tetrahedra sharing vertices with the bipyramid and one tetrahedron sharing an equatorial edge of the bipyramid. The resulting $[(UO_2)(SO_4)_4]^{6-}$ clusters are linked by bonds to Na and K cations and by H bonding through the H_2O groups. The same arrangment of sulfate tetrahedra around the neptunyl pentagonal bipyramid occurs in *NaS*1 and *CaZnS*1, but the clusters are further linked into a chain through the sharing of vertices of the sulfate tetrahedra with other neptunyl polyhedra.

In the structures of $(UO_2)(SO_4)(H_2O)(H_2O)_{0.5}$, $(UO_2)(SO_4)(H_2O)(H_2O)_{1.5}$, and $(UO_2)(SO_4)(H_2O)(H_2O)_3$ uranyl pentagonal bipyramids are bridged by sharing vertices with sulfate tetrahedra, creating a chain that is two uranyl polyhedra wide [24–26]. Unlike the chains in *NaS*1 and *CaZnS*1, the exterior of the uranyl sulfate chain is not

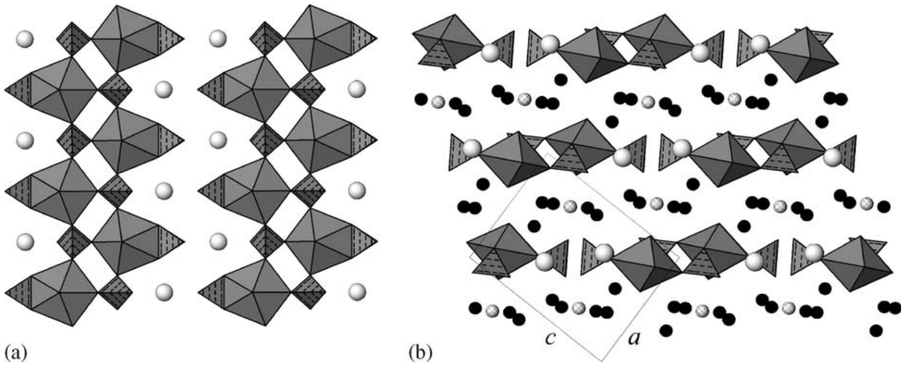

Fig. 4. Polyhedral representation of the neptunyl pentagonal bipyramids and sulfate tetrahedra in the structure of *CaZnS*1 projected along [010]. The locations of the Ca cations are indicated by open circles, those of the Zn cations are shown by cross-hatched circles, and those of H_2O groups are shown by black circles.

decorated with a tetrahedron, and no sulfate tetrahedron shares an edge with a uranyl bipyramid.

The chain of neptunyl pentagonal bipyramids and sulfate tetrahedra found in *NaS*1 and *CaZnS*1 also occurs in the structure of $[Co(NH_3)_6][(NpO_2)(SO_4)_2](H_2O)$ [27]. The chains of composition $[(NpO_2)(SO_4)_2]^{3-}$ are charge-balanced by $[CoNH_3]^{3+}$.

Infinite chains of composition $[(NpO_2)(SO_4)_2]^{3-}$ containing neptunyl pentagonal bipyramids and sulfate tetrahedra occur in $Cs_3[NpO_2(SO_4)_2](H_2O)_2$ [28]. In addition to the sharing of vertices between the sulfate tetrahedra and neptunyl pentagonal bipyramids that constitute the chain, the neptunyl polyhedra are also linked directly by the sharing of edges. The chain thus contains dimers of neptunyl pentagonal bipyramids, edges are shared between the bipyramids and sulfate tetrahedra, and bipyramids are bridged by sharing vertices with sulfate tetrahedral.

The structures of the Np^{5+} sulfates presented herein contain structural units that are unobserved in uranyl sulfates or uranyl phases in general. The sharing of edges between neptunyl bipyramids and sulfate tetrahedra occurs in each of these structures, suggesting that the lower valence of the Np^{5+} cation, as compared to U^{6+}, makes such linkages more favorable than in uranyl sulfates. The reported structures support the hypothesis that Np^{5+} compounds will exhibit a range of structural connectivities absent in uranyl compounds.

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