Journal of Geosciences, 59 (2014), 135–143 DOI: 10.3190/jgeosci.164

Original paper

The modular structure of the novel uranyl sulfate sheet in $[Co(H_2O)_6]_3[(UO_2)_5(SO_4)_8(H_2O)](H_2O)_5$

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A new uranyl sulfate, $[Co(H_2O)_6]_3[(UO_2)_5(SO_4)_8(H_2O)](H_2O)_5$, has been synthesized using mild hydrothermal methods. The structure (monoclinic, $P2_1/c$, $a = 27.1597(14)$, $b = 9.9858(5)$, $c = 22.7803(12)$ Å, $\beta = 106.520(1)°$, $V = 5923.2(5)$ Å^3, $Z = 4$) has been solved by direct methods and refined on the basis of F^2 for all unique reflections to $R_1 = 0.056$, calculated for the 9124 unique observed reflections ($|F_o| \geq 4\sigma_F$). It contains five symmetrically distinct uranyl pentagonal bipyramids and eight sulfate tetrahedra that link via the sharing of vertices between uranyl polyhedra and sulfate tetrahedra, resulting in sheets parallel to (001). Adjacent sheets are linked by hydrogen bonds to $Co^{2+}(H_2O)_6$ octahedra and H_2O groups located in the interlayer. The uranyl sulfate sheet contains four- and five-connected uranyl pentagonal bipyramids and three- and four-connected sulfate tetrahedra. The sheet may be constructed using modules from related structures involving pentagonal bipyramids and tetrahedra, and is readily described using a nodal representation. In general, the uranyl sulfate sheets in $[Co(H_2O)_6]_3[(UO_2)_5(SO_4)_8(H_2O)](H_2O)_5$ are more rigid than the structural units typically found in comparable uranyl molybdates, which involve the sharing of vertices between uranyl pentagonal bipyramids and molybdate tetrahedra.

Keywords: uranyl sulfate, crystal structure, hydrothermal methods, structure topology
Received: 28 December 2013; accepted: 19 March 2014; handling editor: J. Plášil

1. Introduction

Uranyl sulfate hydrates are environmentally important phases that form in oxidation zones of uranium mineral deposits and possibly as alteration products of nuclear waste (Finch and Murakami 1999). Uranyl sulfates were also found in oxidized zones of the Bangombé and Okélobondo natural fission reactors in southeastern Gabon, Africa (Janeczek 1999; Jensen and Ewing 2001). Uranyl sulfate hydrates of divalent metals (Cu, Mg, Co, Ni, and Zn) are especially abundant in nature (Frondel et al. 1976; Finch and Murakami 1999) and several synthetic phases are also known (Gil and Gil 1977; Tabachenko et al. 1979; Serezhkin et al. 1981; Serezhkin and Serezhkina 1982). The structures of the most abundant uranyl sulfates are based upon structural units consisting of uranyl pentagonal bipyramids ($Ur\varphi_5$; $Ur = UO_2^{2+}$, uranyl ion, φ = unspecified ligand) and SO_4 tetrahedra (Burns 2005). $Ur\varphi_5$ bipyramids may polymerize by sharing equatorial edges as in the structures of zippeite-group minerals (Vochten et al. 1995; Brugger et al. 2003; Burns et al. 2003; Brugger et al. 2006; Peeters et al. 2008; Plášil et al. 2011a, b, 2012, 2013a), uranopilite (Burns 2001), johannite (Mereiter 1982) and deliensite (Plášil et al. 2013b). The $Ur\varphi_5$ bipyramids and SO_4 tetrahedra are usually linked by corner-sharing only, although several structures involving edge-sharing between uranyl and sulfate polyhedra have also been described (Mikhailov et al. 1977; Hayden and Burns 2002a, b).

We report the crystal structure of a cobalt uranyl sulfate in which UrO_5 bipyramids do not polymerize with each other, but share their equatorial vertices with SO_4 tetrahedra, resulting in a topologically and geometrically complex uranyl sulfate sheet. This topology may be described using a nodal approach that we developed for the description of uranyl molybdate and uranyl chromate units (Krivovichev et al. 2002a, b, 2005; Krivovichev and Burns 2003a, b, c, d, e).

2. Experimental

2.1. Synthesis

A mixture of $CoSO_4$ (0.123 g), CrO_3 (0.147 g), UO_3 (0.110 g) and 5 ml of ultrapure H_2O was placed in a Teflon-lined 23 ml Parr reaction vessel and heated to 120 °C for 14 days, followed by cooling to ambient temperature. No crystals or precipitates had formed, so the solution was placed in a fume hood to evaporate. After two days, transparent light yellow crystals of $[Co(H_2O)_6]_3[(UO_2)_5(SO_4)_8(H_2O)](H_2O)_5$ were recovered.

2.2. Data collection

The crystal selected for data collection was mounted on a Bruker three-circle diffractometer equipped with a SMART APEX CCD (charge-coupled device) detector with a crystal-to-detector distance of 4.67 cm. Data were collected using monochromated MoK_α X-rays and frame widths of 0.3° in ω. The unit-cell dimensions (Tab. 1) were refined on the basis of 8117 intense reflections using least-squares techniques. More than a hemisphere of data was collected and the three-dimensional data set was reduced and filtered for statistical outliers using the Bruker program SAINT. The data were corrected for Lorentz, polarization and background effects. An empirical absorption correction was done on the basis of 1500 reflections by modeling the crystal as an ellipsoid; this resulted in a decrease of R_{int} from 0.113 to 0.049. Additional information pertinent to the data collection is given in Tab. 1.

Tab. 1 Crystallographic data and refinement parameters for $[Co(H_2O)_6]_3[(UO_2)_5(SO_4)_8(H_2O)](H_2O)_5$

a (Å)	27.1597(14)
b (Å)	9.9858(5)
c (Å)	22.7803(12)
β (°)	106.520(1)
V (Å^3)	5923.2(5)
Space group	$P2_1/c$
F_{000}	4972
μ (cm^{-1})	148.54
Z	4
D_{calc} (g/cm^3)	3.06
Crystal size (mm)	0.08 × 0.04 × 0.01
Radiation	MoK_α
Total Ref.	64514
Unique Ref.	24282
Unique $\lvert F_o \rvert \geq 4\sigma_F$	9124
R_1	0.056
wR_2	0.124
S	0.778

Note: $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$;
$wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$;
$w = 1/[\sigma^2(F_o^2)+(aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$;
$s = \{\Sigma[w(F_o^2 - F_c^2)]/(n - p)\}^{1/2}$ where n is the number of reflections and p is the number of refined parameters

2.3. Structure solution and refinement

Scattering curves for neutral atoms, together with anomalous-dispersion corrections, were taken from Ibers and Hamilton (1974). The Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of the structure. The positions of U, Co and S atoms were determined by direct methods and other atoms were located in the difference-Fourier maps calculated following refinement of the partial-structure model. The Co(4) atom is disordered over two sites, with a Co(4)–Co(4) distance of 2.45 Å. The site occupancy factors and isotropic displacement parameters for the Co(4) positions were fixed at 0.50 and 0.10 Å^2, respectively. Isotropic displacement parameters for several H_2O groups were fixed at 0.15 Å^2. The final model included anisotropic displacement parameters for U, S, and non-disordered Co and S atoms, and isotropic displacement parameters for the anions. The final atomic positional and displacement parameters are in Tab. 2, selected interatomic distances are in Tab. 3.

3. Results

On the basis of the structure determination, the composition of the crystal studied is $[Co(H_2O)_6]_3[(UO_2)_5(SO_4)_8(H_2O)](H_2O)_5$. We note that the synthesis reaction included CrO_3 and it is possible that Cr substitutes at the Co site in the crystal structure. Such substitution, especially at a minor level, would be difficult to discern on the basis of X-ray diffraction.

3.1. Cation coordination polyhedra

There are five independent U^{6+} cations in the structure and each is part of an approximately linear UO_2^{2+} uranyl ion (Ur). The $U(1)O_2^{2+}$, $U(2)O_2^{2+}$, $U(3)O_2^{2+}$ and $U(4)O_2^{2+}$ cations are each coordinated by five O atoms that are arranged at the equatorial vertices of UrO_5 pentagonal bipyramids. The $U(5)O_2^{2+}$ cation is coordinated by four O atoms and one H_2O group, giving a $UrO_4(H_2O)$ pentagonal bipyramid. The $\langle U–O_{Ur} \rangle$ and $\langle U–O_{eq} \rangle$ (O_{eq}: equatorial O atom) bond lengths are in the range of 1.75 to 1.77 and 2.37 to 2.42 Å, respectively. The U(5)–H_2O bond length is 2.43 Å, which is typical for equatorial U^{6+}–H_2O bonds (Burns et al. 1997).

Eight symmetrically independent S^{6+} cations are each tetrahedrally coordinated by four O atoms. The <S–O> bond lengths range from 1.46 to 1.47 Å, in good agreement with the average <S–O> bond length of 1.473 Å reported for sulfates (Hawthorne et al. 2000).

There are four symmetrically independent Co^{2+} cations in the structure, each of which is coordinated by six H_2O groups. The Co(1), Co(2) and Co(3) sites are fully occupied and are in slightly distorted octahedral coordination. In contrast, the coordination environment around the half-occupied Co(4) site is a strongly distorted octahedron. The <Co–O> bond lengths are in the range of 2.03 to 2.12 Å.

3.2. Bond-valence analysis and H_2O groups

The bond-valence sums were calculated using parameters given for U^{6+}–O bonds (Burns et al. 1997) and for S^{6+}–O and Co^{2+}–O bonds (Brown and Altermatt 1985). The

Tab. 2 Atomic coordinates and displacement parameters (× 10^3 Å^2) for $[Co(H_2O)_6]_3[(UO_2)_5(SO_4)_8(H_2O)](H_2O)_5$

Atom	x/a	y/b	z/c	U_{eq}
Co(1)	0.3234(1)	0.5012(2)	0.5331(1)	43(1)
Co(2)	0.5	0.5	0	39(1)
Co(3)	0.1463(1)	0.5065(5)	0.0832(1)	111(2)
U(1)	0.4634(1)	0.6931(1)	0.2073(1)	19(1)
U(2)	0.3316(1)	0.3054(1)	0.2359(1)	18(1)
U(3)	0.1903(1)	0.1991(1)	0.3476(1)	21(1)
U(4)	0.3251(1)	0.8081(1)	0.3379(1)	18(1)
U(5)	0.397(1)	0.7112(1)	0.2598(1)	26(1)
S(1)	0.3283(1)	0.1537(3)	0.3809(2)	20(1)
S(2)	0.3281(1)	0.6578(3)	0.1916(2)	21(1)
S(3)	0.2454(1)	0.5035(3)	0.3043(2)	22(1)
S(4)	0.5862(1)	0.5006(3)	0.2329(2)	21(1)
S(5)	0.4359(1)	0.3448(3)	0.1685(2)	23(1)
S(6)	0.2323(1)	–0.1220(4)	0.4238(2)	23(1)
S(7)	0.0705(1)	0.0297(3)	0.3449(2)	25(1)
S(8)	0.0820(1)	0.3777(4)	0.2467(2)	27(1)
$H_2O(1)$	0.3405(5)	0.7096(13)	0.5362(6)	60(3)
O(2)	0.6269(4)	0.5879(10)	0.2671(4)	33(2)
$H_2O(3)$	0.3080(5)	0.2947(14)	0.5295(6)	67(4)
O(4)	0.3823(3)	0.3786(9)	0.2929(4)	28(2)
O(5)	0.3446(4)	0.6849(10)	0.2573(4)	31(2)
O(6)	0.3760(3)	0.7373(9)	0.3960(4)	27(2)
$H_2O(7)$	0.1671(6)	0.3535(18)	0.1519(8)	105(6)
O(8)	0.2761(4)	0.8813(10)	0.2818(4)	30(2)
O(9)	0.2818(3)	0.1848(9)	0.3989(4)	25(2)
O(10)	0.4686(4)	0.3220(10)	0.2314(4)	32(2)
O(11)	0.1972(4)	0.1615(10)	0.2747(4)	31(2)
O(12)	0.2888(4)	0.5879(11)	0.3376(5)	38(3)
O(13)	0.2307(3)	0.4174(9)	0.3496(4)	23(2)
O(14)	0.2815(3)	0.2328(9)	0.1773(4)	26(2)
O(15)	0.3712(4)	0.2384(10)	0.4149(4)	29(2)
O(16)	0.6028(4)	0.4249(10)	0.1865(4)	31(2)
O(17)	0.5718(4)	0.4083(10)	0.2745(5)	35(2)
O(18)	0.3179(4)	0.1724(9)	0.3150(4)	29(2)
O(19)	0.3725(3)	0.6855(10)	0.1666(4)	29(2)
O(20)	0.3158(4)	0.5141(10)	0.1818(4)	30(2)
O(21)	0.4510(4)	0.2588(10)	0.1249(4)	32(2)
O(22)	0.4603(3)	0.6171(9)	0.2755(4)	27(2)
O(23)	0.4417(4)	0.4862(10)	0.1532(4)	30(2)
O(24)	0.0571(4)	0.8012(12)	0.2029(5)	50(3)
O(25)	0.2029(4)	0.5829(10)	0.2687(4)	35(2)
O(26)	0.3822(3)	0.3159(9)	0.1664(4)	28(2)
O(27)	0.3434(3)	0.0115(9)	0.3963(4)	26(2)
O(28)	0.5423(4)	0.5824(10)	0.2021(4)	29(2)
O(29)	0.2634(4)	0.4144(10)	0.2627(5)	35(2)
O(30)	0.4655(3)	0.7669(9)	0.1380(4)	27(2)
O(31)	0.2846(4)	0.7394(10)	0.1588(4)	31(2)
O(32)	0.0794(3)	0.5218(9)	0.2290(4)	27(2)
O(33)	0.1093(4)	0.0813(11)	0.3191(5)	46(3)
$H_2O(34)$	0.2485(5)	0.5333(13)	0.4726(6)	65(4)
O(35)	0.0336(4)	0.3447(11)	0.2617(5)	40(3)
O(36)	0.2095(4)	–0.0282(11)	0.3738(5)	40(3)
$H_2O(37)$	0.4284(5)	0.5385(13)	0.0141(6)	58(3)
$H_2O(38)$	0.3552(5)	0.4801(13)	0.4607(6)	65(4)
O(39)	0.2753(4)	–0.1902(11)	0.4091(5)	41(3)
O(40)	0.1234(4)	0.3596(11)	0.3008(5)	40(3)
O(41)	0.1941(4)	–0.2189(11)	0.4292(5)	43(3)
O(42)	0.0827(5)	0.0451(15)	0.4120(7)	76(4)
$H_2O(43)$	0.1293(4)	0.6897(12)	0.3189(5)	51(3)
O(44)	0.0612(4)	–0.1121(12)	0.3304(5)	53(3)
O(45)	0.1826(4)	0.2372(10)	0.4208(4)	34(2)
O(46)	0.2515(5)	–0.0512(14)	0.4812(6)	66(4)
$H_2O(47)$	0.2946(5)	0.5199(13)	0.6099(6)	63(4)
O(48)	0.0881(5)	0.2969(12)	0.1948(5)	54(3)
O(49)	0.0209(4)	0.6215(12)	0.3165(5)	50(3)
O(50)	0.0220(4)	0.1029(11)	0.3207(5)	44(3)
$H_2O(51)$	0.5175(5)	0.3579(13)	0.0681(6)	64(4)
$H_2O(52)$	0.3988(5)	0.4721(15)	0.5939(6)	74(4)
$H_2O(53)$	0.5308(5)	0.6499(14)	0.0619(6)	69(4)
$H_2O(54)$	0.1608(8)	0.6550(20)	0.1434(10)	150*
$H_2O(55)$	0.2189(8)	0.5120(20)	0.0792(10)	150*
$H_2O(56)$	0.0714(8)	0.5150(20)	0.0904(10)	150*
$H_2O(57)$	0.1198(8)	0.3380(20)	0.0245(10)	150*
$H_2O(58)$	0.1193(8)	0.6540(20)	0.0197(10)	150*
$H_2O(59)$	0.3490(8)	0.0390(20)	0.5523(10)	150*
$H_2O(60)$	0.4647(8)	0.9980(20)	–0.1001(10)	150*
$H_2O(61)$	0.4600(8)	0.8790(20)	0.0085(10)	150*
$H_2O(62)$	0.0922(8)	0.0420(20)	0.1530(10)	150*
$H_2O(63)$	0.1832(8)	–0.0510(20)	0.1605(10)	150*
Co(4)**	–0.0033(3)	0.8782(8)	0.0043(4)	100*
$H_2O(64)$**	–0.0030(17)	0.6880(40)	0.0420(20)	150*
$H_2O(65)$**	–0.0059(17)	0.6970(40)	–0.0580(20)	150*
$H_2O(66)$**	0.0652(17)	0.9250(50)	0.0470(20)	150*
$H_2O(67)$**	–0.0452(17)	0.8820(50)	0.0730(20)	150*
$H_2O(68)$**	0.0044(17)	1.0190(50)	0.0670(20)	150*
$H_2O(69)$**	–0.0729(17)	0.8650(50)	–0.0320(20)	150*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.
* fixed during refinement; ** s. o. f. = 0.50

bond-valence sums range from 5.84 to 6.17 v.u. for the U sites, from 6.03 to 6.29 v.u. for the S sites, and from 1.91 to 2.21 v.u. for the Co(1), Co(2) and Co(3) sites. The bond-valence sum for the Co(4) atom is 2.60 v.u. However, due to structural disorder, Co(4)–H_2O bond lengths are averages of multiple configurations.

The bond-valence sums for O atoms depend upon their structural role. Oxygen atoms belonging to uranyl ions have bond-valence sums in the range of 1.69 to 1.87 v.u. The bond-valence sums for the O atoms that bridge between U^{6+} and S^{6+} cations are 1.93–2.18 v.u., whereas those for the apical atoms of the SO_4 tetrahedra are 1.47–1.62 v.u. The bond-valence requirements for the apical atoms of the SO_4 tetrahedra are very likely satisfied by one or more hydrogen bonds from the H_2O groups located in the interlayer.

Tab. 3 Selected bond lengths (Å) and angles (°) in the structure of $Co(H_2O)_6]_3[(UO_2)_5(SO_4)_8(H_2O)](H_2O)_5$

U(1)–O(22)	1.753(9)	Co(1)–H_2O(38)	2.08(1)		S(5)–O(21)	1.46(1)
U(1)–O(30)	1.758(9)	Co(1)–H_2O(3)	2.10(1)		S(5)–O(10)	1.47(1)
U(1)–O(10)[a]	2.36(1)	Co(1)–H_2O(47)	2.12(1)		S(5)–O(23)	1.47(1)
U(1)–O(19)	2.380(9)	Co(1)–H_2O(1)	2.13(1)		S(5)–O(26)	1.472(9)
U(1)–O(23)	2.39(1)	Co(1)–H_2O(34)	2.13(1)		<S(5)–O>	1.47
U(1)–O(17)[a]	2.43(1)	Co(1)–H_2O(52)	2.14(1)			
U(1)–O(28)	2.445(9)	<Co(1)–H_2O>	2.12		S(6)–O(46)	1.45(1)
<U(1)–O_{Ur}>	1.76				S(6)–O(41)	1.45(1)
<U(1)–O_{eq}>	2.40	Co(2)–H_2O(51)[e]	2.06(1)	2x	S(6)–O(36)	1.47(1)
		Co(2)–H_2O(53)[e]	2.06(1)	2x	S(6)–O(39)	1.47(1)
U(2)–O(4)	1.761(9)	Co(2)–H_2O(37)[e]	2.10(1)	2x	<S(6)–O>	1.46
U(2)–O(14)	1.768(9)	<Co(2)–H_2O>	2.07			
U(2)–O(18)	2.353(9)				S(7)–O(33)	1.44(1)
U(2)–O(29)	2.37(1)	Co(3)–H_2O(54)	1.98(2)		S(7)–O(44)	1.46(1)
U(2)–O(26)	2.376(9)	Co(3)–H_2O(55)	2.00(2)		S(7)–O(50)	1.47(1)
U(2)–O(20)	2.40(1)	Co(3)–H_2O(58)	2.05(2)		S(7)–O(42)	1.48(1)
U(2)–O(2)[b]	2.46(1)	Co(3)–H_2O(56)	2.09(2)		<S(7)–O>	1.46
<U(2)–O_{Ur}>	1.77	Co(3)–H_2O(57)	2.14(2)			
<U(2)–O_{eq}>	2.39	Co(3)–H_2O(7)	2.15(2)		S(8)–O(40)	1.43(1)
		<Co(3)–H_2O>	2.07		S(8)–O(48)	1.48(1)
U(3)–O(11)	1.765(9)				S(8)–O(35)	1.48(1)
U(3)–O(45)	1.78(1)	Co(4)–H_2O(69)	1.84(4)		S(8)–O(32)	1.49(1)
U(3)–O(36)	2.37(1)	Co(4)–H_2O(66)	1.90(4)		<S(8)–O>	1.47
U(3)–O(33)	2.42(1)	Co(4)–H_2O(68)[h]	1.92(4)			
U(3)–O(40)	2.43(1)	Co(4)–H_2O(64)	2.08(4)		S(4)–O(2)–U(2)[a]	143.4(6)
U(3)–O(9)	2.431(9)	Co(4)–H_2O(67)	2.17(4)		S(2)–O(5)–U(4)	144.3(6)
U(3)–O(13)	2.435(9)	Co(4)–H_2O(65)	2.29(4)		S(1)–O(9)–U(3)	136.1(5)
<U(3)–O_{Ur}>	1.77	<Co(4)–H_2O>	2.03		S(5)–O(10)–U(1)[b]	144.7(6)
<U(3)–O_{eq}>	2.42				S(3)–O(12)–U(4)	142.3(6)
		S(1)–O(18)	1.46(1)		S(3)–O(13)–U(3)	135.7(5)
U(4)–O(8)	1.725(9)	S(1)–O(9)	1.469(9)		S(4)–O(16)–U(4)[b]	145.9(6)
U(4)–O(6)	1.765(9)	S(1)–O(15)	1.47(1)		S(4)–O(17)–U(1)[b]	149.5(6)
U(4)–O(39)[c]	2.39(1)	S(1)–O(27)	1.49(1)		S(1)–O(18)–U(2)	146.6(6)
U(4)–O(5)	2.391(9)	<S(1)–O>	1.47		S(2)–O(19)–U(1)	135.8(5)
U(4)–O(27)[c]	2.400(9)				S(2)–O(20)–U(2)	140.2(6)
U(4)–O(12)	2.41(1)	S(2)–O(31)	1.45(1)		S(5)–O(23)–U(1)	137.2(6)
U(4)–O(16)[a]	2.47(1)	S(2)–O(5)	1.46(1)		S(5)–O(26)–U(2)	137.9(6)
<U(4)–O_{Ur}>	1.75	S(2)–O(20)	1.48(1)		S(1)–O(27)–U(4)[f]	132.5(5)
<U(4)–O_{eq}>	2.41	S(2)–O(19)	1.50(1)		S(4)–O(28)–U(1)	147.3(6)
		<S(2)–O>	1.47		S(3)–O(29)–U(2)	149.8(6)
U(5)–O(24)	1.75(1)				S(8)–O(32)–U(5)	132.6(5)
U(5)–O(49)	1.76(1)	S(3)–O(25)	1.45(1)		S(7)–O(33)–U(3)	141.3(7)
U(5)–O(35)[d]	2.33(1)	S(3)–O(12)	1.47(1)		S(8)–O(35)–U(5)[g]	146.9(7)
U(5)–O(44)[c]	2.35(1)	S(3)–O(29)	1.48(1)		S(6)–O(36)–U(3)	145.1(7)
U(5)–O(50)[d]	2.36(1)	S(3)–O(13)	1.482(9)		S(6)–O(39)–U(4)[f]	142.9(7)
U(5)–O(32)	2.381(9)	<S(3)–O>	1.47		S(8)–O(40)–U(3)	140.5(7)
U(5)– H_2O(43)	2.43(1)				S(7)–O(44)–U(5)[f]	151.3(7)
<U(5)–O_{Ur}>	1.77	S(4)–O(2)	1.45(1)		S(7)–O(50)–U(5)[g]	151.6(7)
<U(5)–O_{eq}>	2.37	S(4)–O(28)	1.45(1)			
		S(4)–O(17)	1.45(1)			
		S(4)–O(16)	1.47(1)			
		<S(4)–O>	1.46			

Note: a = –*x*+1, *y*+1/2, –*z*+1/2; b = –*x*+1, *y*–1/2, –*z*+1/2; c = *x*, *y*+1, *z*; d = –*x*, *y*+1/2, –*z*+1/2; e = –*x*+1, –*y*+1, –*z*; f = *x*, *y*–1, *z*; g = –*x*, *y*–1/2, –*z*+1/2; h = –*x*, –*y*+2, –*z*.

The bond-valence sums incident upon the H_2O sites are in the range of 0.00 to 0.47 v.u., consistent with their assignment as H_2O groups. Note that H_2O groups in the structure are of three types: (i) the H_2O(43) group is bonded to U(5), (ii) the H_2O(1), H_2O(3), H_2O(7), H_2O(34), H_2O(37), H_2O(47), H_2O(51)–H_2O(58) and H_2O(64)–H_2O(69) groups are bonded to Co^{2+} cations and (iii) the H_2O(59)–H_2O(63) groups are held in the structure by hydrogen bonds only. The positions of the H atoms have not been determined.

3.3. Structure description

The structure of the $[Co(H_2O)_6]_3[(UO_2)_5(SO_4)_8(H_2O)](H_2O)_5$ is based upon sheets of UrO_5 and $UrO_4(H_2O)$ pentagonal bipyramids and SO_4 tetrahedra with composition $[(UO_2)_5(SO_4)_8(H_2O)]$ (Figs 1–2). The connectivity is provided by corner-sharing between uranyl bipyramids and SO_4 tetrahedra (Fig. 2). The $[(UO_2)_5(SO_4)_8(H_2O)]$ sheets are parallel to (001) and are strongly distorted (see below). The $[Co(H_2O)_6]^{2+}$ polyhedra and H_2O groups are located in the interlayer, where they provide linkage of the sheets through hydrogen bonds.

3.4. Topology of the uranyl sulfate sheet

The topological structure of sheets composed of uranyl pentagonal bipyramids that share corners with TO_4 tetrahedra (T = S, Cr, Se, and Mo) may be studied using a nodal approach (Krivovichev and Burns 2003a, c, d). Each node corresponds to either an UrO_n bipyramid (n = 4

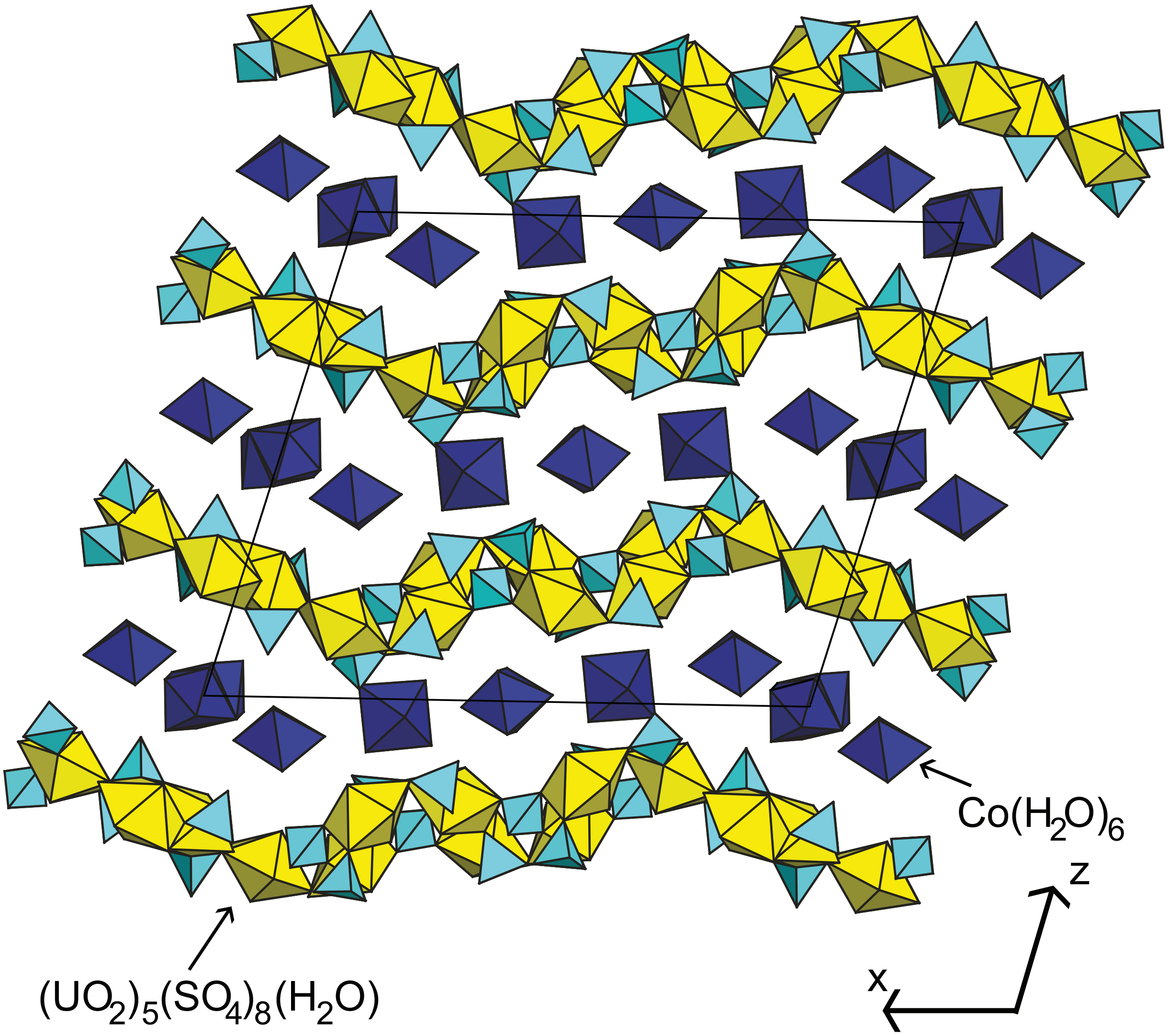

Fig. 1 Polyhedral representations of the structure of $[Co(H_2O)_6]_3[(UO_2)_5(SO_4)_8(H_2O)](H_2O)_5$ viewed along the b axis. Uranyl, cobalt, and sulfate polyhedra are shown in yellow, cyan, and dark blue, respectively.

or 5) (black circle) or a TO_4 tetrahedron (white circle). Nodes are connected if the polyhedra share at least one common vertex, and the number of connecting lines corresponds to the number of anions in common to the polyhedra connected. Each structural unit is associated with a black-and-white graph that represents a topology of polyhedral linkage. In our previous studies (Krivovichev and Burns 2003a, c, d), we demonstrated that many graphs corresponding to polyhedral linkages in uranyl molybdates, sulfates, selenites, selenates and chromates may be derived from a simple one containing only 6-connected black and 3-connected white vertices (Fig. 3b). In contrast, the graph corresponding to the $[(UO_2)_5(SO_4)_8(H_2O)]$ sheet in the structure of $[Co(H_2O)_6]_3[(UO_2)_5(SO_4)_8(H_2O)](H_2O)_5$ (Fig. 2c) cannot be obtained from the parental graph by deletion of lines and vertices. All white vertices in the graph shown in Fig. 3b are 3-connected, whereas the graph shown in Fig. 2c has 4-connected vertices that correspond to $S(4)O_4$ tetrahedra.

Four-connected TO_4 tetrahedra have been found in other layered uranyl compounds. Fig. 3a shows an idealized graph that corresponds to the topology of the $[(UO_2)_2(TO_4)_3]$ sheets in the structures of $Cs_2[(UO_2)_2(SO_4)_3]$ (Ross and Evans 1960) and β-$Cs_2[(UO_2)_2(MoO_4)_3]$ (Krivovichev et al. 2002a). Terminating this graph by the grey lines in Fig. 3a gives a complex chain, which is designated **A** in Fig. 3c. This chain is an important constituent of the $[(UO_2)_5(SO_4)_8(H_2O)]$ sheet in $[Co(H_2O)_6]_3[(UO_2)_5(SO_4)_8(H_2O)](H_2O)_5$ (Figs 2c, 3e). Terminating the graph of Fig. 3b as denoted by the grey lines, chain **B** is obtained (Fig. 3d). The graph corresponding to the $[(UO_2)_5(SO_4)_8(H_2O)]$ sheet is derived by linkage of the chains shown in Figs 3c–d through their black vertices (Fig. 3e). The sequence of chains in the graph is …**ABABAB**… Figure 2 shows that the planes of the **A** and **B** chains in the $[(UO_2)_5(SO_4)_8(H_2O)]$ sheet have slightly different orientations. The plane of the **A** chain is approximately parallel to (102), whereas the plane of the **B** chain is approximately parallel to (–102). In general, the $[(UO_2)_5(SO_4)_8(H_2O)]$ sheet in the structure of $[Co(H_2O)_6]_3[(UO_2)_5(SO_4)_8(H_2O)](H_2O)_5$ has a *modular* structure that consists of two 1-dimensional modules.

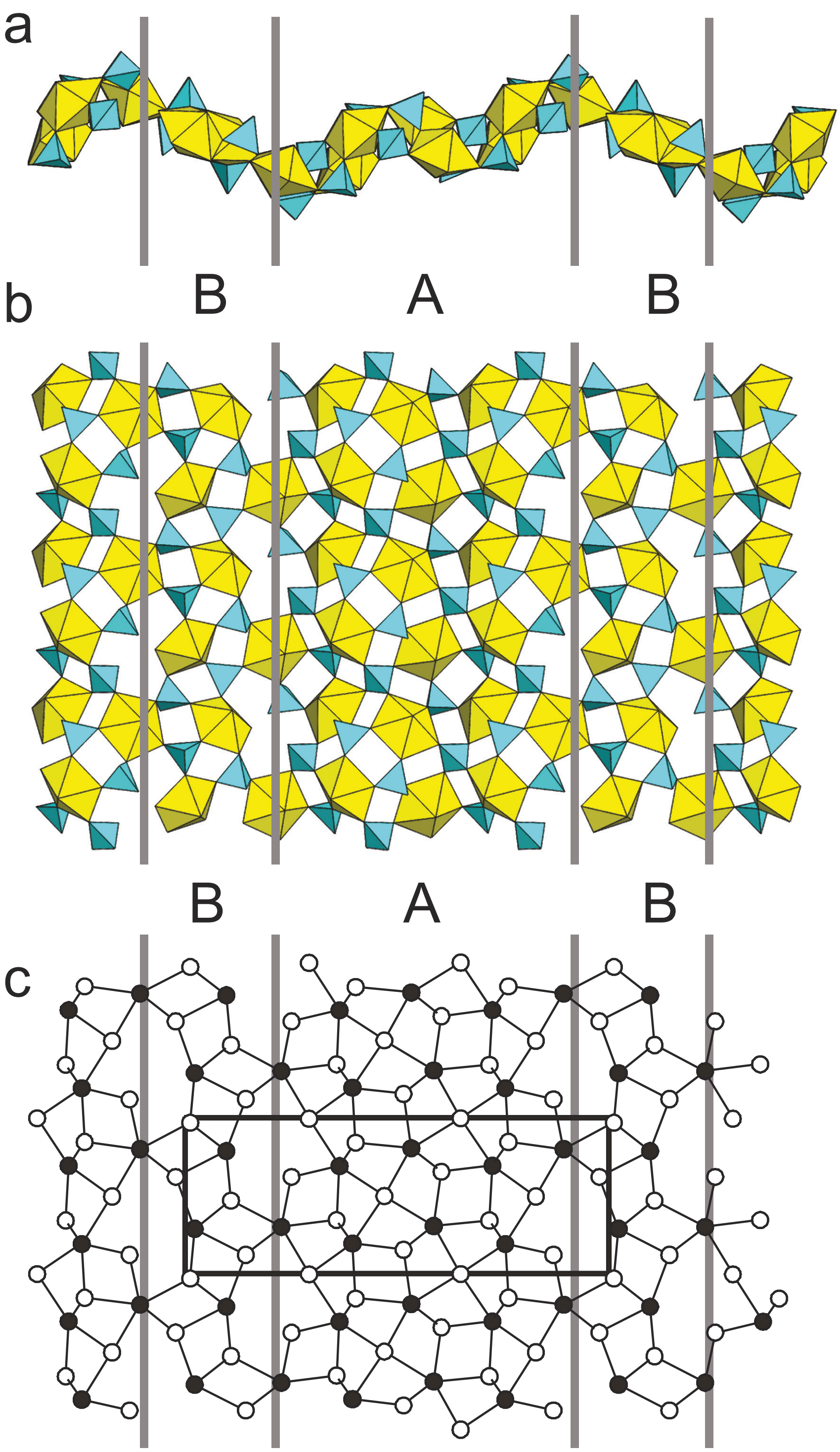

Fig. 2 The $[(UO_2)_5(SO_4)_8(H_2O)]$ sheet in the structure of $[Co(H_2O)_6]_3[(UO_2)_5(SO_4)_8(H_2O)](H_2O)_5$ viewed parallel to its plane (**a**) and perpendicular to its plane (**b**) together with its nodal representation (**c**) (U polyhedra = black circles, S tetrahedra = white circles). The **A** and **B** chains are delineated by grey lines (see text for more details). Color legend as in Fig. 1.

3.5. Flexibility of U–O–S linkages

The U–O–S angles of the bridging O atoms in the structure of $[Co(H_2O)_6]_3[(UO_2)_5(SO_4)_8(H_2O)](H_2O)_5$ are listed in Tab. 3. These angles are in the range of 132 to 152°, which is relatively narrow in comparison with corresponding U–O–Mo linkages in uranyl molybdates (Krivovichev et al. 2007). This is apparently because the S^{6+} cation is smaller than the Mo^{6+} cation, which results in U–O–S linkages that are much less flexible than U–O–Mo linkages. As a result, inorganic uranyl sulfate frameworks are rare, whereas framework structures are common in the case of uranyl molybdates.

3.6. Nickel analogue of $[Co(H_2O)_6]_3[(UO_2)_5(SO_4)_8(H_2O)](H_2O)_5$

Using techniques similar to those described above, crystals of the $[Ni(H_2O)_6]_3[(UO_2)_5(SO_4)_8(H_2O)](H_2O)_5$ were obtained. This phase is also monoclinic, $P2_1/c$, with unit-cell parameters a = 27.1094(17), b = 9.9663(7), c = 22.6054(15) Å, β = 106.465(2)°, and V = 5857.1(5) Å^3. However, crystals of the Ni phase appear to be invariably twinned on (001) and the diffraction patterns involve overlap of at least two reciprocal lattices. As a result, the structure was only refined to R_1 = 0.107 (for 9327 unique observed reflections). It is very similar to that of $[Co(H_2O)_6]_3[(UO_2)_5(SO_4)_8(H_2O)](H_2O)_5$.

4. Discussion and conclusions

Using the concept of the sheet anion topology, it has been demonstrated that structures of many uranyl compounds may be considered as modular, i.e. consisting of smaller blocks taken from other structures (Burns 1999). The current study provides additional evidence in support of this observation, and demonstrates the utility of the nodal approach for comparing structural topologies and establishing topological relationships between structures. The modular composition of the $[(UO_2)_5(SO_4)_8(H_2O)]$ sheet in the structure of $[Co(H_2O)_6]_3[(UO_2)_5(SO_4)_8(H_2O)](H_2O)_5$ shows that combination of modules provides further options for expansion of the rich structural variations possible in uranyl compounds. Note also that this sheet is a graphical isomer of that in a mixed organic–inorganic uranyl sulfate compound (Ling et al. 2010). It is likely that many principles of the modular approach (Eddaoudi et al. 2001) will find applications in the crystal chemistry of uranyl phases.

Acknowledgements. This research was supported by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy, Grant No. DE–FG02–07ER15880 and by the Russian Foundation for Basic Research to S.V.K. (grant 01–05–64883).

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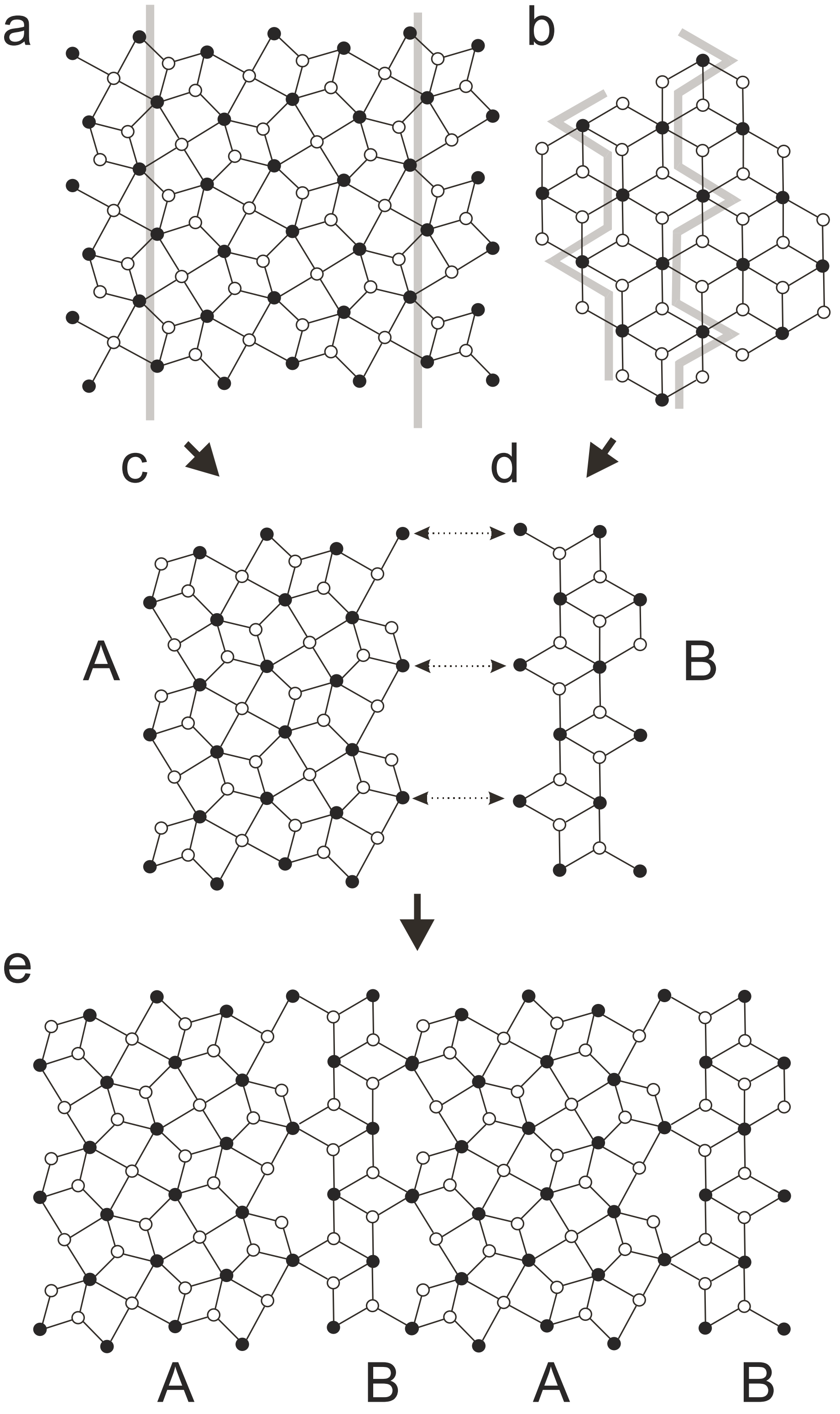

Fig. 3a – The black-and-white graph of the $[(UO_2)_2(TO_4)_3]$ (T = S, Mo) sheet from the structures of $Cs_2[(UO_2)_2(SO_4)_3]$ and β–$Cs_2[(UO_2)_2(MoO_4)_3]$; **b** – the ideal graph consisting of 6-connected black and 3-connected white vertices; **c** – the **A** chain from the graph shown in **a** as delineated by grey lines; **d** – the **B** chain from the graph shown in **b** as delineated by grey lines; **e** – the composite graph obtained by merging the **A** and **B** chains shown in **c** and **d**, respectively. Note that the graph in **e** is an idealized version of that shown in Fig. 2c.

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