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THE CRYSTAL CHEMISTRY OF THE ZIPPEITE GROUP

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ABSTRACT

Single crystals of eight zippeite-group compounds have obtained using mild hydrothermal synthesis techniques. The structure of each has been determined with single-crystal diffraction data collected using Mo$K\alpha$ X-radiation and an APEX CCD-based detector, and refined on the basis of F^2 for all unique data. The structure of zippeite, $K_3(H_2O)_3[(UO_2)_4(SO_4)_2O_3(OH)]$, is monoclinic, $C2$, a 8.7524(4), b 13.9197(7), c 17.6972(8) Å, β 104.178(1)°, V 2090.39(17) Å^3, $R1$ 3.30%, D_c 4.794 g/cm^3. The structure of sodium-zippeite, $Na_5(H_2O)_{12}[(UO_2)_8(SO_4)_4O_5(OH)_3]$, is monoclinic, $P2_1/n$, a 17.6425(11), b 14.6272(9), c 17.6922(11) Å, β 104.461(1)°, V 4421.0(5) Å^3, $R1$ 6.88%, D_c 4.517 g/cm^3. The structure of magnesium-zippeite, $Mg(H_2O)_{3.5}[(UO_2)_2(SO_4)O_2]$, is monoclinic, $C2/m$, a 8.6514(4), b 14.1938(7), c 17.7211(9) Å, β 104.131(1)°, V 2110.24(18) Å^3, $R1$ 2.39%, D_c 4.756 g/cm^3. The structure of zinc-zippeite, $Zn(H_2O)_{3.5}[(UO_2)_2(SO_4)O_2]$, is monoclinic, $C2/m$, a 8.6437(10), b 14.1664(17), c 17.701(2) Å, β 104.041(3)°, V 2102.7(4) Å^3, $R1$ 4.57%, D_c 5.032 g/cm^3. The structure of cobalt-zippeite, $Co(H_2O)_{3.5}[(UO_2)_2(SO_4)O_2]$, is monoclinic, $C2/m$, a 8.650(4), b 14.252(9), c 17.742(10) Å, β 104.092(19)°, V 2122(2) Å^3, $R1$ 5.55%, D_c 4.948 g/cm^3. The structure of $(NH_4)_4(H_2O)[(UO_2)_2(SO_4)O_2]_2$ is monoclinic, $C2/m$, a 8.6987(15), b 14.166(2), c 17.847(3) Å, β 104.117(4)°, V 2132.9(3) Å^3, $R1$ 4.31%, D_c 4.442 g/cm^3. The structure of $(NH_4)_2[(UO_2)_2(SO_4)O_2]$ is orthorhombic, $Cmca$, a 14.2520(9), b 8.7748(5), c 17.1863(10) Å, V 2149.3(2) Å^3, $R1$ 5.11%, D_c 4.353 g/cm^3. The structure of $Mg_2(H_2O)_{11}[(UO_2)_2(SO_4)O_2]_2$ is monoclinic, $P2_1/c$, a 8.6457(4), b 17.2004(8), c 18.4642(9) Å, β 102.119(1)°, V 2684.6(2) Å^3, $R1$ 4.73%, D_c 3.917 g/cm^3. Each structure contains the zippeite-type sheet consisting of chains of edge-sharing uranyl pentagonal bipyramids that are cross-linked by vertex sharing with sulfate tetrahedra, although the compositional details of the sheet are varied. The interlayer configurations are diverse, and are related to the bonding requirements of the sheets.

Keywords: zippeite group, uranyl sulfate, uranium, crystal chemistry, crystal structure.

SOMMAIRE

Nous avons synthétisé par voie hydrothermale légère des monocristaux de huit composés du groupe de la zippéite. Nous en avons établi la structure en utilisant un diffractomètre muni d'un détecteur APEX de type CCD, avec rayonnement Mo$K\alpha$, et nous avons affiné les données uniques en utilisant les facteurs F^2. La structure de la zippéite, $K_3(H_2O)_3[(UO_2)_4(SO_4)_2O_3(OH)]$, est monoclinique, $C2$, a 8.7524(4), b 13.9197(7), c 17.6972(8) Å, β 104.178(1)°, V 2090.39(17) Å^3, $R1$ 3.30%, D_c 4.794 g/cm^3. La structure de la sodium-zippéite, $Na_5(H_2O)_{12}[(UO_2)_8(SO_4)_4O_5(OH)_3]$, est monoclinique, $P2_1/n$, a 17.6425(11), b 14.6272(9), c 17.6922(11) Å, β 104.461(1)°, V 4421.0(5) Å^3, $R1$ 6.88%, D_c 4.517 g/cm^3. La structure de la magnésium-zippéite, $Mg(H_2O)_{3.5}[(UO_2)_2(SO_4)O_2]$, est monoclinique, $C2/m$, a 8.6514(4), b 14.1938(7), c 17.7211(9) Å, β 104.131(1)°, V 2110.24(18) Å^3, $R1$ 2.39%, D_c 4.756 g/cm^3. La structure de la zinc-zippéite, $Zn(H_2O)_{3.5}[(UO_2)_2(SO_4)O_2]$, est monoclinique, $C2/m$, a 8.6437(10), b 14.1664(17), c 17.701(2) Å, β 104.041(3)°, V 2102.7(4) Å^3, $R1$ 4.57%, D_c 5.032 g/cm^3. La structure de la cobalt-zippéite, $Co(H_2O)_{3.5}[(UO_2)_2(SO_4)O_2]$, est monoclinique, $C2/m$, a 8.650(4), b 14.252(9), c 17.742(10) Å, β 104.092(19)°, V 2122(2) Å^3, $R1$ 5.55%, D_c 4.948 g/cm^3. La structure de $(NH_4)_4(H_2O)[(UO_2)_2(SO_4)O_2]_2$ est monoclinique, $C2/m$, a 8.6987(15), b 14.166(2), c 17.847(3) Å, β 104.117(4)°, V 2132.9(3) Å^3, $R1$ 4.31%, D_c 4.442 g/cm^3. La structure de $(NH_4)_2[(UO_2)_2(SO_4)O_2]$ est orthorhombique, $Cmca$, a 14.2520(9), b 8.7748(5), c 17.1863(10) Å, V 2149.3(2) Å^3, $R1$ 5.11%, D_c 4.353 g/cm^3. La structure de $Mg_2(H_2O)_{11}[(UO_2)_2(SO_4)O_2]_2$ est monoclinique, $P2_1/c$, a 8.6457(4), b 17.2004(8), c 18.4642(9) Å, β 102.119(1)°, V 2684.6(2) Å^3, $R1$ 4.73%, D_c 3.917 g/cm^3. Chacune des structures contient un feuillet de type zippéite, fait de chaînes de bipyramides à uranyle pentagonales à arêtes partagées, entre-liées par partage de coins avec des tétraèdres de sulfate, quoiqu'en détail, la composition des feuillets varie. Les agencements interfoliaires sont divers, et résultent des exigeances des feuillets en matière de liaisons.

(Traduit par la Rédaction)

Mots-clés: groupe de la zippéite, sulfate d'uranyle, uranium, cristallochimie, structure cristalline.

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INTRODUCTION

The first description of a yellow earthy uranyl sulfate that probably corresponds to zippeite was provided by John (1821) in is his study of uranyl minerals from Joachimsthal, Czech Republic, although the name did not appear until Haidinger (1845) applied it to the material studied by John. Despite recognition of uranyl sulfate minerals almost two centuries ago, the zippeite group remains poorly characterized. In the 1950s, it was still considered to be a hydrated uranyl sulfate (Nováček 1935, Traill 1952, Frondel 1958), although it is now known that several distinct species contain mono- and divalent cations (Frondel *et al.* 1976). Details of the structures and chemistry of the zippeite-group minerals remain unknown.

Uranyl sulfates, including those of the zippeite group, are rather widespread, although they are not abundant. They typically occur close to actively oxidizing uraninite and sulfide minerals (Smith 1984). Uranyl sulfates usually occur as admixtures of species consisting of fine-grained mats and coatings, making their characterization difficult (Frondel 1958). Although 15 uranyl sulfate species have been described (Mandarino 1999), the structures are known for only four of these; the structures of schröckingerite (Mereiter 1986), johannite (Mereiter 1982), and uranopilite (Burns 2001) were reported for natural crystals, and that of zippeite (Vochten *et al.* 1995) was reported for a synthetic crystal.

We are interested in the structures, chemical compositions and stabilities of uranyl minerals and compounds because they are significant for an understanding of the genesis of uranium deposits (Frondel 1958), the weathering of mine and mill tailings derived from resource utilization, the transport of actinides in contaminated soils (*e.g.*, Buck *et al.* 1996, Roh *et al.* 2000), and the mobility of radionuclides in a geological repository for nuclear waste (Wronkiewicz *et al.* 1992, 1996, Finn *et al.* 1996, Finch *et al.* 1999, Chen *et al.* 1999, 2000, Burns *et al.* 1997a, 2000, Burns 1999). Uranyl sulfates are common in uranium deposits in places such as the U.S. southwest, the Czech Republic, and the United Kingdom. These compounds may also be significant products of the alteration of nuclear waste in a geological repository, owing to the presence of sulfur as an impurity in steel used to construct canisters.

The application of CCD-based (charge-coupled device) detectors of X-rays to mineral-structure analysis (Burns 1998) permits detailed examination of the structures of uranyl compounds that were previously unattainable owing to the small size of the available crystals. We have undertaken an extensive study of the structures of zippeite-group minerals and compounds using hydrothermally grown synthetic crystals and CCD-based diffractometry. In this contribution, we provide complete crystal-structure data for eight zippeite-group compounds.

PREVIOUS STUDIES OF ZIPPEITE-GROUP COMPOUNDS

Frondel *et al.* (1976) examined synthetic and natural specimens of uranyl sulfates, redefined zippeite to be the K-dominant member, and defined sodium-zippeite, cobalt-zippeite, nickel-zippeite, magnesium-zippeite, and zinc-zippeite. They also synthesized NH_4-substituted zippeite, which is not known to occur naturally. Frondel *et al.* (1976) did not provide any crystal-structure information for these minerals owing to the lack of suitable single crystals. Spitsyn *et al.* (1982) reported the structure of a synthetic material that contains zippeite-type uranyl sulfate sheets with Zn cations in the interlayer, and this may correspond to zinc-zippeite. Vochten *et al.* (1995) gave a structure for synthetic zippeite.

Vochten *et al.* (1995) reported the structure of a crystal of synthetic zippeite (grown by hydrothermal techniques) with the composition $K(UO_2)_2SO_4(OH)_3{\bullet}H_2O$. In the course of refinement of the structure, uranyl and sulfate bond-lengths were constrained, and the refinement was done with rigid bond and approximate "isotropicity constraints". Vochten *et al.* (1995) indicated that the uranyl sulfate sheets in the structure contain $\mathit{Ur}O_2(OH)_3$ pentagonal bipyramids. However, reconsideration of their structure using the bond-valence parameters proposed by Burns *et al.* (1997b) leads to a different interpretation: each of the OH groups designated by Vochten *et al.* (1995) are bonded to three U^{6+} cations, and the bond-valence sums incident at these sites (excluding contributions from H atoms) are 1.69 and 1.85 *vu*, which are too high for these sites to contain OH. The bond-valence calculations indicate that the sheets in synthetic zippeite may not contain any OH groups, as all of the other anions are either O_{Ur} atoms (*Ur*: uranyl ion) or are shared between uranyl polyhedra and sulfate tetrahedra. Vochten *et al.* (1995) designated two anions in the interlayer as one OH and one H_2O group, but our bond-valence calculations indicate that each of these is H_2O. Our bond-valence analysis of the structure proposed by Vochten *et al.* (1995) leads to the formula $K(UO_2)_2(SO_4)O_2{\bullet}2H_2O$, which is not neutral.

EXPERIMENTAL

We have synthesized analogues of zippeite, sodium-zippeite, magnesium-zippeite, zinc-zippeite and cobalt-zippeite, and report their crystal structures herein. We have also synthesized single crystals of three zippeite-group compounds that have not been observed in nature: two compounds containing NH_4 (designated $SZIPPNH_4I$ and $SZIPPNH_4II$), and one containing Mg (designated SZIPPMg).

Synthesis of zippeite-group phases

Frondel *et al.* (1976) reported the synthesis of various zippeite-group phases by precipitation from aqueous solution at room temperature, but this approach invariably results in crystals that are too small for single-crystal X-ray-diffraction studies. Spitsyn *et al.* (1982) synthesized a zippeite-like material containing Zn, but they did not give the method of synthesis. Vochten *et al.* (1995) synthesized zippeite by hydrothermal reaction, and obtained crystals large enough for single-crystal studies.

We have done 187 synthesis experiments to obtain crystals of zippeite-group compounds suitable for single-crystal X-ray-diffraction analysis. Most experiments were performed in 23 mL Teflon-lined Parr reaction vessels, which were heated in Fisher Isotemp mechanical convection ovens. Many of the hydrothermal experiments resulted in zippeite-group phases, but only a few provided crystals large enough for single-crystal study. We found that the crystal size is strongly dependent on temperature and pH, as well as the degree of saturation of the mother solution, and that the duration of the experiment is of secondary importance. Our hydrothermal experiments were done at temperatures from 100 to 220°C, and pH from 2 to 10, and experiment durations lasting from 24 h to three weeks. In general, the successful synthesis of zippeite-group crystals large enough for X-ray study involved temperatures in the range of 120 to 150°C, and pH values in the range of 2 to 5. The exception is SZIPPNH_4II, which was grown from a solution with a pH of 10. Techniques used for the synthesis of crystals used for structural analysis are given in Table 1.

Investigations of the relations among marecottite, magnesium-zippeite and SZIPPMg

During the course of our experiments, we obtained the structures of two distinct zippeite-type phases containing Mg. In addition, we recently described the structure of marecottite, a new Mg-rich zippeite-group mineral with the ideal formula $Mg_3(H_2O)_{18}[(UO_2)_8(SO_4)_4O_6(OH)_2]\bullet 10H_2O$ (Brugger *et al.* 2003). We therefore undertook a series of synthesis experiments intended to provide insight into the relative stabilities of these phases. For each experiment, 0.228 g UO_3 was combined with 0.492 g $MgSO_4\bullet H_2O$ in 4 mL of ultrapure H_2O. The pH of the resulting solutions was adjusted to 4 using dilute hydrochloric acid, and each was heated in 23 mL Teflon-lined Parr reaction vessels. Four vessels containing solutions were heated at 150°C, one for 15 h, one for 24 h, one for three days, and one for seven days. The products were strongly dependent upon duration of the experiment. The products heated for up to a day contain considerable fine-grained material, as well as acicular crystals of SZIPPMg up to 200 μm long. The product heated for three days contained only acicular crystals of SZIPPMg ranging up to 400 μm long, whereas the seven-day experiment provided superb acicular crystals of magnesium-zippeite up to 400 μm long. Thus, a transition from SZIPPMg to magnesium-zippeite occurred with time spent heating at 150°C, under otherwise constant conditions.

Five additional vessels, with solution pH = 4, were heated for 24 h at 60, 80, 100, 120 and 180°C. Each of the products heated in the range 60 to 120°C were identified as synthetic marecottite using X-ray powder diffraction, although they are microcrystalline, and the crystallinity, as distinguished on the basis of peak widths in the powder-diffraction patterns, increases with temperature. The product at 150°C is SZIPPMg, and that obtained at 180°C is magnesium-zippeite, although no single crystals were obtained in the latter case. Thus, under otherwise identical conditions and heating for 24 h, a transition from marecottite to SZIPPMg to magnesium-zippeite occurs with increasing temperature.

Single-crystal X-ray diffraction

Single-crystal X-ray-diffraction data were collected using a Bruker three-circle diffractometer equipped with either an APEX or a SMART 1K CCD detector. Unit-cell dimensions were refined using the positions of reflections selected from the data. Specifics of each data

TABLE 1. CONDITIONS OF SYNTHESIS OF ZIPPEITE-GROUP CRYSTALS STUDIED BY X-RAY DIFFRACTION

	Solution*	pH	T (°C)	t (h)	Size (μm)
Zippeite	4 mL 0.2 M uranyl nitrate, 0.261 g K_2SO_4	2	150	72	150
Sodium-zippeite	4mL 0.2 M uranyl nitrate, 0.284 g Na_2SO_4, NaOH	4	150	168	150
SZIPPNH_4I	4 mL 0.2 M UO_3, 0.264 g $(NH_4)_2SO_4$, H_2SO_4	4	150	168	100
SZIPPNH_4II	4 mL H_2O, 0.30 g UO_3, 0.313 g gypsum crystals, NaOH	10	140	168	400
Magnesium-zippeite	4 mL H_2O, 0.229 g UO_3, 0.241 g $MgSO_4$, H_2SO_4	4	150	168	100
Zinc-zippeite	4 mL H_2O, 0.228 g UO_3, 0.576 g $ZnSO_4.7H_2O$, HCl	5	120	24	50
Cobalt-zippeite	4 mL H_2O, 0.228 g UO_3, 0.310 g $CoSO_4$, HCl	3	150	24	30
SZIPPMg	4 mL H_2O, 0.228 g UO_3, 0.492 g $MgSO_4.7H_2O$, HCl	5	150	24	120

*all solutions were heated in 23 mL Teflon-lined Parr reaction vessels in Fisher Isotemp ovens collection are provided in Table 2. The intensities of reflections were integrated and corrected for Lorentz, polarization and background effects using the Bruker program SAINT. Data corresponding to each crystal were corrected for absorption empirically by modeling the crystals as plates; reflections having a plate-glancing angle less that 3° were discarded.

Solution and refinement of the structures

Scattering curves for neutral atoms, together with anomalous-dispersion corrections, were taken from *International Tables for X-Ray Crystallography*, Vol. IV (Ibers & Hamilton 1974). The Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of each structure on the basis of F^2 for all unique data. Solution and refinement of many of the zippeite-group structures were found to be difficult owing to pseudosymmetry and the presence of twinning, which was accounted for using the method of Jameson (1982) and Herbst-Irmer & Sheldrick (1998).

Refinement of the structure of zippeite using space group $C2/c$ and the atomic coordinates given by Vochten *et al.* (1995) gave an $R1$ of 9.4%, as well as partially occupied sites, strongly distorted polyhedra, and a formula that is not electroneutral. Further consideration of the data showed the structure of zippeite to have space group $C2$, and that the crystal studied is twinned.

The structures of magnesium-zippeite, zinc-zippeite and cobalt-zippeite can be solved in space group $C2/c$, and most aspects of the resulting structure models are satisfactory. However, it is impossible to locate one of the H_2O groups of the interlayer $M\phi_6$ octahedra (M: Mg, Zn, Co) in this space group. The correct space-group is $C2/m$, the structures have a pseudo c-glide, and each crystal studied is twinned. This finding is consistent with the results for a synthetic Zn-dominant zippeite-like phase provided by Spitsyn *et al.* (1982).

In the case of cobalt-zippeite, the poor parameter-to-data ratio and the presence of twinning resulted in several U–O_{Ur} and S–O bond-lengths beyond reasonable values. In the final cycles of refinement, U–O_{Ur} and S–O bond-lengths were restrained to be ~1.80 and ~1.48 Å, respectively. Addition of these restraints did not increase the R indices.

Information concerning the refinements is provided in Table 2. Atom parameters and selected interatomic distances are given in Tables 3 through 16. Bond-valence analyses for selected structures are in Tables 17 to 21. Anisotropic displacement parameters, as well as final observed and calculated structure-factors for each structure, are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

TABLE 2. CRYSTALLOGRAPHIC DATA AND REFINEMENT RESULTS FOR ZIPPEITE-GROUP COMPOUNDS

	Zippeite	Sodium-zippeite	SZIPPNH$_4$I	SZIPPNH$_4$II	Magnesium-zippeite	Zinc-zippeite	Cobalt-Zippeite	SZIPPMg
a (Å)	8.7524(4)	17.6425(11)	8.6987(15)	14.2520(9)	8.6514(4)	8.6437(10)	8.650(4)	8.6457(4)
b (Å)	13.9197(7)	14.6272(9)	14.166(2)	8.7748(5)	14.1938(7)	14.1664(17)	14.252(9)	17.2004(8)
c (Å)	17.6972(8)	17.6922(11)	17.847(3)	17.1863(10)	17.7211(9)	17.701(2)	17.742(10)	18.4642(9)
β (°)	104.178(1)	104.461(1)	104.117(4)		104.131(1)	104.041(3)	104.092(19)	102.119(1)
V (Å^3)	2090.39(17)	4421.0(5)	2132.9(3)	2149.3(2)	2110.24(18)	2102.7(4)	2122(2)	2684.6(2)
Space Group	$C2$	$P2_1/n$	$C2/m$	$Cmca$	$C2/m$	$C2/m$	$C2/m$	$P2_1/c$
Twinning	100,010,-10-1	none	100,010,-10-1	none	100,010,-10-1	100,010,-10-1	100,010,-10-1	none
Twin Components	3.6/96.4		49.3/50.7		49.5/50.5	33.4/66.4	45.3/54.7	
F(000)	2592	5192	2456	2416	2616	2760	2736	2776
μ (mm^{-1})	31.80	29.569	30.574	30.336	30.99	33.27	32.27	24.38
D_{calc} (g/cm^3)	4.794	4.517	4.442	4.353	4.756	5.032	4.948	3.917
Crystal size (μm)	140 x 100 x 10	80 x 15 x 10	80 x 80 x 5	140 x 40 x 50	100 x 25 x 10	80 x 15 x 10	30 x 20 x 4	140 x 50 x 40
Radiation	Mo$K\alpha$	Mo$K\alpha$	Mo$K\alpha$	Mo$K\alpha$	Mo$K\alpha$	Mo$K\alpha$	Mo$K\alpha$	Mo$K\alpha$
Frame Width (°)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Count Time (s)	30	40	40	10	60	40	120	30
Detector	APEX	APEX	APEX	1 K	APEX	APEX	APEX	APEX
$2\theta_{max}$(°)	69.0	69.0	69.0	56.6	69.0	69.0	69.0	69.0
Coverage to $2\theta_{max}$	97.9%	97.8%	96.9%	99.2%	97.0 %	98.3%	96.0%	98.0%
Total reflections	19681	81004	19653	11328	19699	19830	19117	50309
Unique reflections	8400	18415	4531	1377	4502	4544	4483	11211
Data with $\|F_o\| > 4\sigma\|F_o\|$	5627	7822	2822	982	2845	1222	1260	5741
$R1$ (%)	3.30	6.88	4.31	5.11	2.39	4.57	5.55	4.73
$wR2$ (%)	5.94	17.7	9.95	12.64	4.61	7.71	7.16	11.13
S	0.81	1.024	0.875	1.14	0.78	0.68	0.62	0.89
Parameters	208	317	79	66	91	97	95	179

Formulae of crystals: Zippeite: $K_3(H_2O)_3[(UO_2)_4(SO_4)_2O_3(OH)]$; Sodium-zippeite: $Na_5(H_2O)_{12}[(UO_2)_8(SO_4)_4O_5(OH)_3]$; SZIPPNH$_4$I: $(NH_4)_4(H_2O)[(UO_2)_2(SO_4)O_2]_2$; SZIPPNH$_4$II: $(NH_4)_2[(UO_2)_2(SO_4)O_2]$; Magnesium-zippeite, Zinc-zippeite and Cobalt-zippeite: $M(H_2O)_{3.5}[(UO_2)_2(SO_4)O_2]$, M = Mg, Zn, Co; SZIPPMg: $Mg_2(H_2O)_{11}[(UO_2)_2(SO_4)O_2]_2$

$R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| \times 100$

$S = [\Sigma w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$, for m observations and n parameters

FORMULAE OF ZIPPEITE-GROUP PHASES STUDIED

The formula of each of the crystal studied, as derived from the crystal-structure analyses and bond-valence considerations, are given in Table 2. The formula of zippeite is $K_3(H_2O)_3[(UO_2)_4(SO_4)_2O_3(OH)]$, *Z* = 4. Frondel *et al.* (1976) provided the formula $K_4(UO_2)_6\,(SO_4)_3(OH)_{10}{\bullet}4H_2O$. The literature does not contain any complete chemical data for natural zippeite, presumably owing to the lack of pure material. Frondel (1958) summarized results of eight chemical analyses of natural and synthetic zippeite, but indicated that all had overlooked K or other cations (Frondel *et al.* 1976). Frondel *et al.* (1976) provided a partial analysis for a sample of zippeite from Joachimsthal; it contains 8.06 wt.% K_2O and 0.62 wt.% Na_2O. They also provided results of an analysis of synthetic zippeite, which may be compared to the values derived from our structural formula (given in parentheses): K_2O 7.89 (9.37), UO_3 75.38 (75.84), SO_3 11.41 (10.61), and H_2O 4.92 (4.18) wt%.

Vochten *et al.* (1995) provided the formula $K(UO_2)_2\,SO_4(OH)_3{\bullet}H_2O$ for synthetic zippeite on the basis of their crystal structure, but as argued above, evaluation of the structure using the bond-valence approach is not consistent with this formula. They provided a chemical composition of synthetic zippeite: K_2O 7.56, UO_3 75.90, SO_3 10.63, H_2O 6.17 wt.%.

The formula for sodium-zippeite is $Na_5(H_2O)_{12}\,[(UO_2)_8(SO_4)_4O_5(OH)_3]$, with *Z* = 4. Frondel *et al.* (1976) proposed the formula $Na_4(UO_2)_6(SO_4)_3(OH)_{10}{\bullet}$

TABLE 3. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC-DISPLACEMENT PARAMETERS FOR ZIPPEITE

	x	*y*	*z*	*U(eq)*
U(1)	0.9214(1)	0.2948(1)	0.0865(1)	0.020(1)
U(2)	0.5874(1)	0.3261(1)	-0.0871(1)	0.018(1)
U(3)	-0.0782(1)	0.3345(1)	-0.4132(1)	0.013(1)
U(4)	-0.4120(1)	0.3028(1)	-0.5868(1)	0.014(1)
S(1)	0.2494(4)	0.3099(4)	-0.2488(2)	0.020(1)
S(2)	-0.7500(4)	0.3230(4)	-0.7491(2)	0.016(1)
K(1)*	0.3091(15)	0.5603(11)	-0.0830(20)	0.063(9)
K(1A)*	0.2957(12)	0.5583(7)	-0.1366(9)	0.035(3)
K(2)*	0.1985(8)	0.5689(6)	-0.3673(6)	0.049(3)
K(2A)*	0.1852(16)	0.5686(12)	-0.4274(9)	0.028(4)
K(3)*	0.6781(9)	0.0586(6)	0.1270(7)	0.029(3)
K(3A)*	0.6138(15)	0.0628(9)	0.0442(9)	0.106(5)
O(1)	-0.8216(12)	0.3818(9)	-0.7007(6)	0.022(3)
O(2)	-0.6749(12)	0.3819(8)	-0.7981(6)	0.020(2)
O(3)	0.3662(10)	0.3742(7)	-0.1956(5)	0.021(2)
O(4)	0.1382(9)	0.3781(7)	-0.2990(5)	0.018(2)
O(5)	-0.8684(10)	0.2635(7)	-0.7974(5)	0.021(2)
O(6)	0.3205(12)	0.2453(9)	-0.2995(6)	0.023(3)
O(7)	0.1742(12)	0.2406(9)	-0.2021(6)	0.021(2)
O(8)	0.8498(8)	0.3066(6)	-0.0444(4)	0.014(2)
O(9)	-0.6282(10)	0.2652(7)	-0.6978(5)	0.021(2)
O(10)	0.9157(14)	0.4190(10)	0.1107(7)	0.029(3)
O(11)	-0.1442(8)	0.2958(6)	-0.5441(4)	0.016(2)
O(12)	0.5819(11)	0.4533(8)	-0.0655(6)	0.023(2)
O(13)	-0.3534(7)	0.3199(5)	-0.4559(4)	0.012(1)
O(14)	0.5840(14)	0.2016(10)	-0.1150(7)	0.031(3)
O(15)	-0.0818(13)	0.2104(9)	-0.3892(7)	0.024(3)
O(16)	-0.4171(14)	0.4253(10)	-0.6171(7)	0.030(3)
O(17)	0.9152(11)	0.1707(8)	0.0676(6)	0.030(3)
OH(18)	0.6447(8)	0.2730(5)	0.0469(4)	0.021(2)
O(19)	-0.4073(11)	0.1831(8)	-0.5610(6)	0.025(2)
O(20)	-0.0642(10)	0.4614(7)	-0.4287(6)	0.022(2)
OW(21)	-0.1515(15)	0.0604(12)	-0.5940(9)	0.061(4)
OW(22)	0.5217(15)	0.5611(14)	-0.2500(8)	0.090(5)
OW(23)	0.0246(12)	0.5619(10)	-0.2549(6)	0.049(3)

* occupancies: K(1) = 0.39(3), K(1A) = 0.52(3), K(2) = 0.70(2), K(2A) = 0.30(2), K(3) = 0.33(1), K(3A) = 0.47(1).

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) FOR ZIPPEITE

U(1)-O(17)	1.758(12)	K(1A)-OW(23)	2.75(2)
U(1)-O(10)	1.784(13)	K(1A)-O(10)c	2.79(2)
U(1)-O(8)	2.253(7)	K(1A)-O(14)i	2.81(2)
U(1)-O(8)a	2.307(7)	K(1A)-O(3)	2.89(1)
U(1)-OH(18)	2.370(7)	K(1A)-O(12)	2.91(2)
U(1)-O(5)b	2.439(9)	K(1A)-O(17)f	2.97(2)
U(1)-O(7)c	2.509(11)	K(1A)-OW(22)	3.14(2)
<U(1)-O$_{Ur}$>	1.771	K(1A)-O(5)j	3.21(2)
<U(1)-ϕ_{eq}>	2.376	<K(1A)-ϕ>	2.93
U(2)-O(14)	1.799(14)	K(2)-O(20)	2.74(1)
U(2)-O(12)	1.815(11)	K(2)-OW(23)	2.79(1)
U(2)-O(8)	2.252(7)	K(2)-O(16)e	2.83(1)
U(2)-OH(18)	2.416(7)	K(2)-O(15)k	2.84(1)
U(2)-OH(18)c	2.426(7)	K(2)-O(19)j	3.01(1)
U(2)-O(3)	2.462(9)	K(2)-O(4)	3.02(1)
U(2)-O(2)e	2.467(11)	K(2)-OW(22)	3.07(1)
<U(2)-O$_{Ur}$>	1.807	K(2)-O(9)j	3.08(1)
<U(2)-ϕ_{eq}>	2.405	<K(2)-ϕ>	2.92
U(3)-O(15)	1.781(13)	K(2A)-O(20)	2.64(2)
U(3)-O(20)	1.795(10)	K(2A)-O(15)k	2.80(2)
U(3)-O(11)	2.311(7)	K(2A)-O(19)k	2.80(2)
U(3)-O(11)e	2.317(7)	K(2A)-O(16)e	2.82(2)
U(3)-O(13)	2.350(6)	K(2A)-O(19)j	2.87(2)
U(3)-O(1)g	2.475(11)	K(2A)-O(20)e	2.92(2)
U(3)-O(4)	2.483(8)	<K(2A)-ϕ>	2.81
<U(3)-O$_{Ur}$>	1.788		
<U(3)-O$_{eq}$>	2.387	K(3)-O(2)l	2.94(1)
		K(3)-O(10)h	2.97(1)
U(4)-O(19)	1.726(11)	K(3)-O(22)d	2.97(2)
U(4)-O(16)	1.786(13)	K(3)-O(12)d	2.98(1)
U(4)-O(13)	2.259(6)	K(3)-O(17)	2.98(1)
U(4)-O(11)	2.281(7)	K(3)-O(7)c	3.00(1)
U(4)-O(13)g	2.367(6)	K(3)-O(14)c	3.01(1)
U(4)-O(9)	2.427(9)	K(3)-OW(23)m	3.20(1)
U(4)-O(6)e	2.473(11)	K(3)-O(18)	3.28(1)
<U(4)-O$_{Ur}$>	1.756	<K(3)-ϕ>	3.04
<U(4)-O$_{eq}$>	2.361		
		K(3A)-O(18)	2.94(1)
S(1)-O(4)	1.488(10)	K(3A)-O(17)	2.97(2)
S(1)-O(3)	1.504(10)	K(3A)-O(12)d	3.01(1)
S(1)-O(6)	1.508(12)	K(3A)-O(14)c	3.06(2)
S(1)-O(7)	1.521(12)	K(3A)-O(10)h	3.06(2)
<S(1)-O>	1.505	K(3A)-O(10)d	3.35(2)
		K(3A)-O(14)	3.37(2)
S(2)-O(5)	1.433(10)	<K(3A)-ϕ>	3.11
S(2)-O(1)	1.436(12)		
S(2)-O(9)	1.461(10)		
S(2)-O(2)	1.461(11)		
<S(2)-O>	1.448		
K(1)-O(10)c	2.74(2)		
K(1)-O(14)i	2.74(2)		
K(1)-O(12)	2.77(2)		
K(1)-O(17)f	2.82(2)		
K(1)-O(12)c	2.97(3)		
K(1)-O(17)i	3.02(3)		
K(1)-O(3)	3.38(3)		
K(1)-OW(23)	3.42(3)		
<K(1)-ϕ>	2.98		

a = -x+2, y, -z; b = x+2, y, z+1; c = -x+1, y, -z; d = -x+1½, y-½, -z; e = -x, y, -z-1; f = -x+1½, y+1/2, -z; g = -x-1, y, -z-1; h = x-½, y-½, z; i = x-½, y+½, z; j = -x-½, y+½, -z-1; k = x+½, y+½, z; l = x+1½, y-½, z+1; m = -x+½, y-1/2, -z

$4H_2O$ for sodium-zippeite on the basis of results of three chemical analyses of synthetic material and two analyses of natural sodium-zippeite. The formula obtained from the crystal-structure analysis may be written as weight percent oxides: Na_2O 5.15, UO_3 76.11, SO_3 10.65, H_2O 8.09. These values are in accord with those determined in two analyses of synthetic material, as given by Frondel *et al.* (1976) [Na_2O 4.96, UO_3 76.79, SO_3 10.39, H_2O 7.43; Na_2O 4.91, UO_3 76.92, SO_3 10.22, H_2O 7.62] and in their analysis of natural material from the Delta mine, Utah [Na_2O 5.25, K_2O 0.47 UO_3 75.86, SO_3 10.43, H_2O 7.99; Na_2O 5.09, K_2O 0.42 UO_3 74.1, SO_3 12.5, H_2O 7.89].

The formula of magnesium-zippeite, zinc-zippeite and cobalt-zippeite is $M(H_2O)_{3.5}[(UO_2)_2(SO_4)O_2]$, Z = 8 (M: Mg, Zn, Co). Note that this differs from the formula $Zn(UO_2)_2(SO_4)(OH)_4(H_2O)_{1.5}$ given by Spitsyn *et al.* (1982), but only in the distribution of hydrogen. Analysis of their structural model using the bond-valence parameters for U provided by Burns *et al.* (1997b) does not support their assignment of hydrogen positions.

TABLE 5. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC-DISPLACEMENT PARAMETERS FOR SODIUM-ZIPPEITE

	x	*y*	*z*	*U(eq)*
U(1)	0.3384(1)	0.2323(1)	0.8377(1)	0.010(1)
U(2)	0.2603(1)	0.2250(1)	1.0096(1)	0.011(1)
U(3)	0.5845(1)	0.2563(1)	0.8347(1)	0.010(1)
U(4)	0.4991(1)	0.2649(1)	1.0090(1)	0.012(1)
U(5)	0.8257(1)	0.2186(1)	0.8326(1)	0.013(1)
U(6)	0.7569(1)	0.2168(1)	1.0078(1)	0.011(1)
U(7)	0.9965(1)	0.2462(1)	1.0091(1)	0.011(1)
U(8)	0.0942(1)	0.2516(1)	0.8329(1)	0.011(1)
S(1)	0.9213(3)	0.2450(4)	1.1710(3)	0.008(1)
S(2)	0.6668(3)	0.2487(4)	0.6713(3)	0.015(1)
S(3)	0.1714(3)	0.2458(4)	0.6728(3)	0.013(1)
S(4)	0.4235(3)	0.2604(4)	1.1748(3)	0.018(1)
Na(1)	0.1795(6)	0.0228(7)	0.6734(6)	0.036(3)
Na(2)	0.9192(6)	0.0301(7)	1.1916(6)	0.032(2)
Na(3)	0.6705(7)	0.0145(8)	0.6745(7)	0.048(3)
Na(4)	0.2360(7)	0.5004(9)	0.9907(7)	0.046(3)
Na(5)	0.5668(6)	-0.0291(8)	0.8133(7)	0.043(3)
O(1)	0.7185(7)	0.2377(9)	0.8768(8)	0.013(3)
O(2)	0.2214(7)	0.2414(9)	0.8779(8)	0.015(3)
O(3)	0.5954(8)	0.3747(10)	0.8692(9)	0.018(3)
O(4)	0.8686(8)	0.2377(10)	0.9643(9)	0.022(3)
O(5)	0.8847(8)	0.3117(10)	1.2154(9)	0.020(3)
O(6)	0.2309(8)	0.1871(10)	0.7202(9)	0.019(3)
O(7)	0.2080(8)	0.3149(10)	0.6278(9)	0.018(3)
O(8)	0.1337(8)	0.3037(10)	0.7213(9)	0.018(3)
O(9)	0.8624(8)	0.1848(10)	1.1255(9)	0.018(3)
O(10)	0.4729(7)	0.2450(9)	0.8799(8)	0.013(3)
O(11)	0.3696(8)	0.2623(10)	0.9683(8)	0.017(3)
O(12)	0.7085(8)	0.3147(10)	0.6280(9)	0.019(3)
O(13)	0.3322(8)	0.3496(11)	0.8121(9)	0.021(3)
O(14)	0.7216(8)	0.1851(10)	0.7140(9)	0.018(3)
O(15)	0.0930(8)	0.3690(10)	0.8667(9)	0.019(3)
O(16)	0.3818(8)	0.3255(10)	1.2160(9)	0.018(3)
O(17)	0.4992(8)	0.1524(10)	1.0407(9)	0.020(3)
O(18)	0.6358(8)	0.3083(10)	0.7252(9)	0.021(3)
O(19)	0.4799(8)	0.2056(10)	1.2320(9)	0.022(3)
O(20)	0.9539(8)	0.3039(10)	1.1201(9)	0.018(3)
O(21)	0.9804(8)	0.1908(10)	1.2249(9)	0.020(3)
O(22)	0.3661(8)	0.2008(10)	1.1288(9)	0.020(3)
O(23)	0.1148(8)	0.1929(10)	0.6148(9)	0.019(3)
O(24)	0.7546(8)	0.0975(11)	0.9966(9)	0.019(3)
O(25)	0.4589(9)	0.3169(11)	1.1254(10)	0.027(4)
O(26)	0.9956(9)	0.3654(10)	0.9767(9)	0.022(3)
O(27)	0.5049(8)	0.3870(9)	0.9916(9)	0.015(3)
O(28)	0.2428(8)	0.3411(10)	1.0265(9)	0.017(3)
O(29)	0.6054(9)	0.2019(11)	0.6121(9)	0.024(4)
O(30)	0.2683(8)	0.1061(11)	0.9993(9)	0.020(3)
O(31)	1.0030(9)	0.1325(11)	1.0427(10)	0.027(4)
O(32)	0.8352(9)	0.3363(11)	0.8148(9)	0.024(4)
O(33)	0.3437(9)	0.1129(11)	0.8528(10)	0.023(4)
O(34)	0.5723(9)	0.1437(11)	0.7954(10)	0.024(4)
O(35)	0.8250(8)	0.0989(11)	0.8445(9)	0.021(4)
O(36)	0.7528(9)	0.3328(12)	1.0271(10)	0.030(4)
O(37)	0.0887(8)	0.1392(10)	0.7969(9)	0.016(3)
OH(1)	0.6162(7)	0.2071(9)	0.9681(8)	0.012(3)
OH(2)	0.1173(7)	0.2052(9)	0.9675(8)	0.010(3)
OH(3)	0.9711(7)	0.2025(9)	0.8742(8)	0.015(3)
OW(1)	0.7841(10)	0.0122(12)	1.1888(10)	0.031(4)
OW(2)	0.0414(10)	0.0053(12)	0.6702(10)	0.027(4)
OW(3)	0.6972(10)	-0.0229(12)	0.8079(11)	0.036(5)
OW(4)	0.5305(10)	0.0063(12)	0.6683(10)	0.031(4)
OW(5)	1.0480(12)	0.0022(15)	1.1788(13)	0.051(6)
OW(6)	0.1412(10)	-0.0129(13)	0.5355(11)	0.038(5)
OW(7)	0.1204(10)	0.5020(12)	1.0309(11)	0.034(4)
OW(8)	0.5990(11)	0.0173(13)	0.9523(12)	0.042(5)
OW(9)	0.3089(10)	0.0227(12)	0.6512(11)	0.033(4)
OW(10)	0.8885(10)	-0.0189(12)	1.0471(11)	0.033(4)
OW(11)	0.7943(11)	0.0069(14)	0.6457(12)	0.041(5)
OW(12)	0.4353(11)	-0.0215(13)	0.8036(12)	0.043(5)

TABLE 6. SELECTED INTERATOMIC DISTANCES (Å) FOR SODIUM-ZIPPEITE

U(1)-O(33)	1.76(2)	U(6)-O(36)	1.74(2)	S(4)-O(22)	1.43(2)
U(1)-O(13)	1.77(2)	U(6)-O(24)	1.75(2)	S(4)-O(25)	1.45(2)
U(1)-O(11)	2.28(1)	U(6)-O(1)	2.27(1)	S(4)-O(19)	1.47(2)
U(1)-O(10)	2.31(1)	U(6)-O(4)	2.31(1)	S(4)-O(16)	1.50(1)
U(1)-O(2)	2.35(1)	U(6)-OH(1)	2.41(1)	<S(4)-O>	1.46
U(1)-O(6)	2.53(1)	U(6)-O(9)	2.47(1)		
U(1)-O(5)a	2.58(1)	U(6)-O(7)c	2.53(1)	Na(1)-OW(9)	2.41(2)
<U(1)-O_{Ur}>	1.76	<U(6)-O_{Ur}>	1.74	Na(1)-OW(1)g	2.42(2)
<U(1)-ϕ_{eq}>	2.41	<U(6)-ϕ_{eq}>	2.40	Na(1)-OW(6)	2.42(2)
				Na(1)-OW(2)	2.44(2)
U(2)-O(30)	1.76(2)	U(7)-O(31)	1.76(2)	Na(1)-O(13)h	2.56(2)
U(2)-O(28)	1.76(1)	U(7)-O(26)	1.83(1)	Na(1)-O(6)	2.63(2)
U(2)-O(2)	2.27(1)	U(7)-O(4)	2.20(1)	Na(1)-O(23)	2.82(2)
U(2)-O(11)	2.29(1)	U(7)-OH(3)	2.40(1)	<Na(1)-ϕ>	2.53
U(2)-OH(2)	2.46(1)	U(7)-O(29)c	2.42(1)		
U(2)-O(22)	2.47(1)	U(7)-O(20)	2.42(1)	Na(2)-OW(5)	2.37(2)
U(2)-O(12)b	2.55(1)	U(7)-OH2e	2.50(1)	Na(2)-OW(1)	2.39(2)
<U(2)-O_{Ur}>	1.76	<U(7)-O_{Ur}>	1.79	Na(2)-OW(2)g	2.43(2)
<U(2)-ϕ_{eq}>	2.41	<U(7)-ϕ_{eq}>	2.39	Na(2)-O(37)g	2.49(2)
				Na(2)-OW(10)	2.58(2)
U(3)-O(34)	1.78(2)	U(8)-O(37)	1.76(1)	Na(2)-O(21)	2.59(2)
U(3)-O(3)	1.83(1)	U(8)-O(15)	1.82(1)	Na(2)-O(9)	2.63(2)
U(3)-O(1)	2.31(1)	U(8)-O(2)	2.19(1)	<Na(2)-ϕ>	2.50
U(3)-O(10)	2.31(1)	U(8)-O(8)	2.38(1)		
U(3)-OH(1)	2.40(1)	U(8)-OH(2)	2.41(1)	Na(3)-OW(3)	2.35(2)
U(3)-O(21)a	2.44(1)	U(8)-O(19)a	2.42(1)	Na(3)-OW(11)	2.37(2)
U(3)-O(18)	2.45(1)	U(8)-OH(3)f	2.56(1)	Na(3)-OW(4)	2.45(2)
<U(3)-O_{Ur}>	1.80	<U(8)-O_{Ur}>	1.79	Na(3)-OW(7)d	2.48(2)
<U(3)-ϕ_{eq}>	2.38	<U(8)-ϕ_{eq}>	2.39	Na(3)-O(32)i	2.62(2)
				Na(3)-O(14)	2.69(2)
U(4)-O(17)	1.74(1)	S(1)-O(9)	1.44(1)	<Na(3)-ϕ>	2.49
U(4)-O(27)	1.82(1)	S(1)-O(21)	1.46(1)		
U(4)-O(11)	2.22(1)	S(1)-O(20)	1.46(1)	Na(4)-OW(7)	2.32(2)
U(4)-O(10)	2.23(1)	S(1)-O(5)	1.50(1)	Na(4)-OW(6)j	2.33(2)
U(4)-O(25)	2.46(2)	<S(1)-O>	1.46	Na(4)-O(28)	2.41(2)
U(4)-O(23)c	2.48(1)			Na(4)-OW(9)j	2.46(2)
U(4)-OH(1)	2.50(1)	S(2)-O(14)	1.42(1)	Na(4)-O(36)k	2.48(2)
<U(4)-O_{Ur}>	1.78	S(2)-O(29)	1.47(2)	Na(4)-OW(11)b	2.68(2)
<U(4)-ϕ_{eq}>	2.38	S(2)-O(18)	1.49(2)	<Na(4)-ϕ>	2.45
		S(2)-O(12)	1.53(1)		
U(5)-O(35)	1.76(2)	<S(2)-O>	1.48	Na(5)-OW(12)	2.29(2)
U(5)-O(32)	1.77(2)			Na(5)-OW(3)	2.33(2)
U(5)-O(1)	2.24(1)	S(3)-O(6)	1.45(1)	Na(5)-OW(8)	2.48(2)
U(5)-O(4)	2.28(1)	S(3)-O(23)	1.46(1)	Na(5)-OW(4)	2.54(2)
U(5)-O(14)	2.47(1)	S(3)-O(8)	1.48(1)	Na(5)-O(34)	2.55(2)
U(5)-OH(3)	2.50(1)	S(3)-O(7)	1.52(1)	Na(5)-O(19)g	2.77(2)
U(5)-O(16)d	2.58(1)	<S(3)-O>	1.477	Na(5)-O(22)g	2.85(2)
<U(5)-O_{Ur}>	1.76			<Na(5)-ϕ>	2.49
<U(5)-ϕ_{eq}>	2.41				

a = x-½, -y+½, z-½; b = x-½, -y+½, z+½, c = x+½, -y+½, z+½; d = x+½, -y+½, z-½; e = x+1, y, z; f = x-1, y, z; g = -x+1, -y, -z+2; h = -x+½, y-½, -z+1½; i = -x+1½, y-½, -z+1½; j = -x+½, y+½, -z+1½; k -x+1, -y+1, -z+2

TABLE 7. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC-DISPLACEMENT PARAMETERS FOR SZIPPNH$_4$I

	x	*y*	*z*	*U(eq)*
U(1)	0.6663(1)	0.2319(1)	0.3347(1)	0.011(1)
U(2)	0.3339(2)	0.2681(1)	0.1654(1)	0.011(1)
S(1)	0	0.2549(7)	0	0.020(2)
S(2)	0	0.2361(5)	½	0.007(1)
N(1)	0.7250(30)	½	0.5051(13)	0.029(5)
N(2)	0.3040(30)	0	0.0118(12)	0.026(5)
N(3)	0.5490(40)	0	0.1598(16)	0.036(8)
N(4)	0.4490(30)	½	0.3265(14)	0.022(5)
O(1)	-0.1139(15)	0.1755(10)	0.4461(7)	0.012(3)
O(2)	-0.1234(18)	0.3177(12)	-0.0481(9)	0.024(4)
O(3)	0.4020(40)	0.2433(9)	0.2947(6)	0.018(3)
O(4)	-0.0690(19)	0.1929(11)	0.0488(10)	0.021(4)
O(5)	-0.0771(18)	0.2973(11)	0.5474(9)	0.015(4)
O(6)	0.6000(20)	0.2395(8)	0.2053(5)	0.008(2)
O(7)	0.6560(20)	0.1050(16)	0.3197(10)	0.021(5)
O(8)	0.3530(20)	0.3950(15)	0.1786(9)	0.019(5)
O(9)	0.3090(20)	0.1461(14)	0.1381(10)	0.021(5)
O(10)	0.6830(20)	0.3549(14)	0.3581(10)	0.021(5)
OW(11)	0.9370(20)	½	0.4011(8)	0.033(3)

TABLE 8. SELECTED INTERATOMIC DISTANCES (Å) FOR SZIPPNH$_4$I

U(1)-O(10)	1.79(2)	S(2)-O(1),f	1.476(14) x2
U(1)-O(7)	1.82(2)	S(2)-O(5),f	1.481(15) x2
U(1)-O(3)	2.24(3)	<S(2)-O>	1.478
U(1)-O(6)	2.241(8)		
U(1)-O(3)a	2.36(3)	N(1)-O(1)b,g	2.878(18) x2
U(1)-O(5)b	2.450(15)	N(1)-O(11)	2.92(3)
U(1)-O(1)c	2.529(13)	N(1)-O(11)k	3.01(3)
<U(1)-O$_{Ur}$>	1.80		
<U(1)-O$_{eq}$>	2.36	N(2)-O(2)h	2.92(2)
		N(2)-O(2)a	2.92(2)
U(2)-O(9)	1.79(2)	N(2)-O(9),i	3.05(2) x2
U(2)-O(8)	1.82(2)		
U(2)-O(3)	2.265(11)	N(3)-O(9),i	2.90(3) x2
U(2)-O(6)	2.28(2)	N(3)-O(8)a,h	2.99(3) x2
U(2)-O(6)d	2.32(2)	N(3)-O(7),i	3.15(3) x2
U(2)-O(4)a	2.492(16)		
U(2)-O(2)c	2.522(16)	N(4)-O(10),j	2.85(3) x2
<U(2)-O$_{Ur}$>	1.80	N(4)-O(7)l,m	2.93(3) x2
<U(2)-O$_{eq}$>	2.38	N(4)-O(8),j	2.97(3) x2
S(1)-O(4),e	1.464(16) x2		
S(1)-O(2),e	1.495(17) x2		
<S(1)-O>	1.479		

a = x+½, -y+½, z; b = -x+½, -y+½, -z+1; c = x+1, y, z; d = x-½, -y+½, z; e = -x, y, -z; f = -x, y, -z+1; g = -x+½, y+½, -z+1; h = x+½, y-½, z; i = x, -y, z; j = x, -y+1, z; k = -x+2, -y+1, -z+1; l = x-½, -y+½, z; m = x-½, y+½, z

TABLE 9. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC-DISPLACEMENT PARAMETERS FOR SZIPPNH$_4$II

	x	*Y*	*z*	*U(eq)*
U(1)	0.2325(1)	0.1268(1)	0.4138(1)	0.014(1)
S(1)	¼	0.3812(5)	¼	0.021(1)
O(1)	0.2434(9)	0.3756(9)	0.4552(7)	0.037(3)
O(2)	0.3086(9)	0.4696(10)	0.3003(6)	0.032(3)
O(3)	0.1868(7)	0.2814(10)	0.2993(5)	0.020(2)
O(4)	0.1070(8)	0.1244(10)	0.4313(7)	0.029(2)
O(5)	0.3527(8)	0.1286(12)	0.3862(7)	0.035(3)
N(1)	0	0.1350(30)	0.2504(17)	0.091(12)
N(2)	0	-0.1650(40)	0.4030(20)	0.119(14)

TABLE 10. SELECTED INTERATOMIC DISTANCES (Å) FOR SZIPPNH$_4$II

U(1)-O(5)	1.78(1)	S(1)-O(2)	1.43(1)
U(1)-O(4)	1.81(1)	S(1)-O(2)c	1.43(1)
U(1)-O(1)a	2.28(1)	S(1)-O(3),c	1.515(9) x2
U(1)-O(1)	2.301(9)	<S(1)-O>	1.472
U(1)-O(1)b	2.341(8)		
U(1)-O(2)b	2.461(9)	N(1)-O(3),d	3.07(2) x2
U(1)-O(3)	2.48(1)	N(1)-O(5)c,e	3.15(3) x2
<U(1)-O$_{Ur}$>	1.79		
<U(1)-O$_{eq}$>	2.37	N(2)-O(5)d,b	2.79(3) x2
		N(2)-O(4),f	3.00(3) x2

a = -x+½, -y+½, -z+1; b = -x+½, y-½, z; c = -x+½, y, -z+½; d = x-½, y-½, z; e = x-½, y, -z+½; f = -x, y, z

TABLE 11. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC-DISPLACEMENT PARAMETERS FOR MAGNESIUM-ZIPPEITE

	x	*y*	*z*	*U(eq)*
U(1)	0.6671(1)	0.2324(1)	0.3349(1)	0.009(1)
U(2)	0.3329(1)	0.2674(1)	0.1651(1)	0.010(1)
S(1)	0	0.2600(3)	0	0.006(1)
S(2)	0	0.2552(3)	½	0.011(1)
Mg(1)	0.6898(12)	½	0.3783(4)	0.027(2)
Mg(2)	0.3070(9)	0	0.1290(4)	0.019(2)
O(1)	0.8791(15)	0.1883(10)	0.4509(7)	0.020(3)
O(2)	-0.1198(13)	0.3168(9)	-0.0505(7)	0.014(3)
O(3)	0.3960(30)	0.2399(5)	0.2944(3)	0.007(1)
O(4)	-0.0757(10)	0.1960(7)	0.0475(6)	0.015(2)
O(5)	0.9339(11)	0.3130(7)	0.5515(6)	0.016(2)
O(6)	0.6010(40)	0.2423(5)	0.2052(3)	0.011(1)
O(7)	0.6558(16)	0.1083(9)	0.3186(6)	0.017(3)
O(8)	0.3420(15)	0.3936(10)	0.1813(7)	0.020(3)
O(9)	0.3156(16)	0.1438(10)	0.1369(7)	0.021(4)
O(10)	0.6855(17)	0.3568(8)	0.3633(6)	0.016(3)
OW(11)	0.7023(13)	½	0.4884(6)	0.028(2)
OW(12)	0.3460(14)	0	0.0103(8)	0.046(4)
OW(13)	0.5522(14)	0	0.1564(6)	0.034(3)
OW(14)	0.4602(13)	½	0.3210(6)	0.031(3)
OW(15)	0.9320(12)	½	0.3873(5)	0.029(2)
OW(16)	0.1713(12)	0	0.2384(6)	0.046(3)
OW(17)	0.0661(12)	0	0.0749(5)	0.033(2)

TABLE 12. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC-DISPLACEMENT PARAMETERS FOR ZINC-ZIPPEITE

	x	*y*	*z*	*U(eq)*
U(1)	0.6667(2)	0.2320(1)	0.3347(1)	0.017(1)
U(2)	0.3332(2)	0.2682(1)	0.1650(1)	0.016(1)
S(1)	0	0.2638(7)	0	0.032(2)
S(2)	0	0.2508(5)	½	0.006(1)
Zn(1)	0.6907(10)	½	0.3768(5)	0.033(2)
Zn(2)	0.3095(10)	0	0.1207(5)	0.039(2)
O(1)	0.8760(20)	0.1891(13)	0.4526(10)	0.015(4)
O(2)	-0.1150(20)	0.3206(15)	-0.0541(12)	0.027(5)
O(3)	0.3950(20)	0.2391(10)	0.2947(7)	0.020(3)
O(4)	-0.0750(20)	0.1982(13)	0.0488(10)	0.017(4)
O(5)	0.9320(20)	0.3155(14)	0.5500(12)	0.024(5)
O(6)	0.6030(20)	0.2392(10)	0.2058(7)	0.016(3)
O(7)	0.6470(30)	0.1046(19)	0.3186(13)	0.023(6)
O(8)	0.3400(30)	0.3930(20)	0.1825(14)	0.027(6)
O(9)	0.3260(20)	0.1417(12)	0.1387(9)	0.017(4)
O(10)	0.6990(20)	0.3560(14)	0.3688(10)	0.024(5)
OW(11)	0.7130(20)	½	0.4919(11)	0.026(4)
OW(12)	0.3500(20)	0	0.0089(13)	0.035(5)
OW(13)	0.5510(20)	0	0.1546(11)	0.024(5)
OW(14)	0.4540(30)	½	0.3217(12)	0.037(6)
OW(15)	0.9350(30)	½	0.3903(10)	0.032(4)
OW(16)	0.1730(20)	0	0.2412(11)	0.045(6)
OW(17)	0.0680(20)	0	0.0762(10)	0.031(5)

URANYL AND SULFATE POLYHEDRA

The structures of all zippeite-group phases studied contain U^{6+} cations that are strongly bonded to two atoms of O, resulting in $(UO_2)^{2+}$ uranyl ions (*Ur*) with U–O bond-lengths of ~1.8 Å. Each U^{6+} cation is also coordinated by five anions arranged at the equatorial vertices of pentagonal bipyramids that are capped by the O_{Ur} atoms. In the structure of zippeite, there are four symmetrically distinct uranyl pentagonal bipyramids: two $Ur\mathrm{O}_5$, one $Ur\mathrm{O}_4(\mathrm{OH})$, and one $Ur\mathrm{O}_3(\mathrm{OH})_2$ polyhedron. In sodium-zippeite, there are eight symmetrically distinct uranyl pentagonal bipyramids: one $Ur\mathrm{O}_5$, five $Ur\mathrm{O}_4(\mathrm{OH})$, and two $Ur\mathrm{O}_3(\mathrm{OH})_2$ polyhedra. SZIPPNH$_4$I and SZIPPNH$_4$II contain two and one symmetrically distinct uranyl pentagonal bipyramids, respectively, and in each case, their composition is $Ur\mathrm{O}_5$. The M^{2+} zippeite-group phases (*M:* Mg, Zn and Co) each contain two uranyl pentagonal bipyramids with the composition $Ur\mathrm{O}_5$. In SZIPPMg, there are four independent $Ur\mathrm{O}_5$ pentagonal bipyramids. The $\langle U–\phi_{eq} \rangle$ (ϕ: O or OH) bond lengths are in the range 2.32 to 2.41 Å, consistent with the grand mean value 2.37(9) Å obtained for numerous uranyl pentagonal bipyramids in well-refined structures (Burns *et al.* 1997b).

TABLE 13. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC-DISPLACEMENT PARAMETERS FOR COBALT-ZIPPEITE

	x	*y*	*z*	*U(eq)*
U(1)	0.6674(5)	0.2317(2)	0.3353(2)	0.019(1)
U(2)	0.3337(5)	0.2684(2)	0.1654(1)	0.010(1)
S(1)	0	0.2467(14)	0	0.020
S(2)	0	0.2400(12)	½	0.020
Co(1)	0.6940(30)	½	0.3737(10)	0.031(5)
Co(2)	0.3080(20)	0	0.1261(10)	0.029(4)
O(1)	-0.8770(50)	0.1790(30)	0.4520(20)	0.022(11)
O(2)	-0.1150(40)	0.3120(30)	-0.0490(20)	0.013(9)
O(3)	0.3920(90)	0.2400(20)	0.2915(17)	0.032(8)
O(4)	-0.0760(30)	0.1992(17)	0.0535(14)	0.012(7)
O(5)	0.9430(30)	0.3145(16)	0.5459(14)	0.014(6)
O(6)	0.6010(50)	0.2414(19)	0.2035(13)	0.006(5)
O(7)	0.6640(50)	0.1098(12)	0.3190(30)	0.015(11)
O(8)	0.3520(70)	0.3905(13)	0.1830(30)	0.028(13)
O(9)	0.3100(50)	0.1445(12)	0.1400(20)	0.016(9)
O(10)	0.6820(50)	0.3527(13)	0.3680(20)	0.020(10)
OW(11)	0.7130(70)	½	0.5010(40)	0.060(18)
OW(12)	0.3340(60)	0	0.0140(30)	0.044(15)
OW(13)	0.5590(70)	0	0.1560(20)	0.032(12)
OW(14)	0.4600(40)	½	0.3230(20)	0.017(9)
OW(15)	0.9350(70)	½	0.3860(18)	0.036(8)
OW(16)	0.1610(40)	0	0.2350(20)	0.060(13)
OW(17)	0.0630(40)	0	0.0726(17)	0.020(7)

The S^{6+} cation in all zippeite-type phases is tetrahedrally coordinated by four atoms of O, with <S–O> bond-lengths ranging from 1.45 to 1.52 Å.

URANYL SULFATE SHEET

The structures of all zippeite-group crystals studied contain topologically identical sheets of uranyl pentagonal bipyramids and sulfate tetrahedra (Fig. 1). However,

TABLE 14. SELECTED INTERATOMIC DISTANCES (Å) FOR MAGNESIUM-ZIPPEITE, ZINC-ZIPPEITE, AND COBALT-ZIPPEITE

	M = Mg	*M* = Zn	*M* = Co		*M* = Mg	*M* = Zn	*M* = Co
U(1)-O(7)	1.783(13)	1.83(3)	1.761(15)	S(2)-O(5)e,f	1.446(10) x2	1.49(2) x2	1.496(16)
U(1)-O(10)	1.833(12)	1.855(19)	1.813(16)	S(2)-O(1)e,f	1.520(14) x2	1.474(18) x2	1.472(17) x2
U(1)-O(6)	2.233(6)	2.216(12)	2.27(2)	<S(2)-O>	1.483	1.482	1.484
U(1)-O(3)	2.28(2)	2.285(18)	2.32(7)				
U(1)-O(3)a	2.30(2)	2.288(17)	2.30(7)	*M*(1)-OW(11)	1.928(12)	2.00(2)	2.22(7)
U(1)-O(5)b	2.467(10)	2.49(2)	2.60(2)	*M* (1)-OW(14)	1.998(15)	2.04(2)	2.01(4)
U(1)-O(1)	2.478(13)	2.486(18)	2.51(4)	*M* (1)-O(10)	2.049(12)	2.048(19)	2.103(19)
<U(1)-O_{Ur}>	1.808	1.842	1.787	*M* (1)-O(10)g	2.049(12)	2.048(19)	2.103(19)
<U(1)-O_{eq}>	2.352	2.353	2.40	*M* (1)-OW(15)	2.062(15)	2.07(2)	2.04(6)
				M (1)-OW(16)h	2.445(12)	2.37(2)	2.40(4)
U(2)-O(8)	1.813(14)	1.80(3)	1.769(16)	< *M* (1)-ϕ>	2.088	2.096	2.146
U(2)-O(9)	1.821(14)	1.848(18)	1.822(15)				
U(2)-O(3)	2.256(5)	2.265(12)	2.21(3)	*M* (2)-O(9)i	2.046(14)	2.032(18)	2.073(16)
U(2)-O(6)	2.28(3)	2.276(17)	2.27(5)	*M* (2)-O(9)	2.046(14)	2.032(18)	2.073(16)
U(2)-O(6)c	2.29(3)	2.306(17)	2.28(5)	*M* (2)-OW(13)	2.058(14)	2.02(2)	2.11(6)
U(2)-O(4)a	2.457(9)	2.425(18)	2.35(2)	*M* (2)-OW(17)	2.070(12)	2.05(2)	2.09(4)
U(2)-O(2)d	2.487(12)	2.48(2)	2.51(4)	*M* (2)-OW(12)	2.210(15)	2.09(2)	2.06(5)
<U(2)-O_{Ur}>	1.817	1.824	1.795	*M* (2)-OW(16)	2.500(13)	2.67(2)	2.52(5)
<U(2)-O_{eq}>	2.354	2.35	2.32	< *M* (2)-ϕ>	2.155	2.149	2.154
S(1)-O(2),d	1.440(12) x2	1.45(2) x2	1.482(17) x2				
S(1)-O(4),d	1.494(10) x2	1.516(19) x2	1.446(15) x2				
<S-O>	1.467	1.483	1.464				

a = x+½, -y+½, z; b = -x+1½, -y+½, -z+1; c = x-½, -y+½, z; d = -x, y, -z; e = x-1, y, z; f = -x+1, y, -z+1; g = x, -y+1, z; h = x+½, y+½, z; i = x, -y, z the symmetry of the uranyl sulfate sheets, as well as their compositional details, are not identical for all members of this group. Each uranyl pentagonal bipyramid is linked to two others by sharing equatorial edges, and to two additional pentagonal bipyramids by sharing equatorial vertices only, resulting in a chain of uranyl pentagonal bipyramids that is two polyhedra wide. Each uranyl pentagonal bipyramid shares three of its equatorial ligands within the chain; the remaining two are linked to SO_4 tetrahedra that cross-link the chains, resulting in uranyl sulfate sheets. Each SO_4 tetrahedron shares all of its vertices with different uranyl pentagonal bipyramids; thus the only anions within the sheet that are not bonded to at least two cations are the O_{Ur} atoms.

The uranyl sulfate sheets in the structures of zippeite-group phases have a variety of compositions (Table 2). The distribution of OH in zippeite and sodium-zippeite is shown in Figures 2 and 3. Each OH group is bonded to two U^{6+} cations, and is located at a common equatorial vertex. In zippeite, OH groups occur at both vertices of a shared edge. In sodium-zippeite, there are three symmetrically distinct OH groups, two of which occur along a shared edge between uranyl pentagonal bipyramids.

INTERLAYER CONFIGURATIONS

The structure of zippeite contains three symmetrically distinct positionally disordered K cations. The K(1) site is coordinated by six O_{Ur} atoms, one O atom that is located at an equatorial position of a uranyl pentagonal bipyramid and shared with a SO_4 tetrahedron (designated $O_{U\text{–}S}$), and one H_2O group located in the interlayer. The <K(1)–ϕ> bond-length is 2.98 Å. The K(1A) site, which is located 0.92(2) Å from K(1), is coordinated by four O_{Ur} atoms, two $O_{U\text{–}S}$ atoms, and two H_2O groups located in the interlayer. The <K(1A)–ϕ> bond-length is 2.93 Å. K(2) is coordinated by four O_{Ur} atoms, two $O_{U\text{–}S}$ atoms, and two H_2O groups located in the interlayer. The <K(2)–ϕ> bond-length is 2.92 Å. K(2A), which is located 1.04(1) Å from K(2), is coordinated by six O_{Ur} atoms and one interlayer H_2O group, with a <K(2A)–ϕ> bond-length of 2.81 Å. K(3) is coordinated by four O_{Ur} atoms, two $O_{U\text{–}S}$ atoms, one (OH) group that is shared between three U atoms, and two interlayer H_2O groups. The <K(3)–ϕ> bond-length is 3.04 Å. The K(3A) site, which is 1.43(2) Å from K(3), is coordinated by six O_{Ur} atoms and one OH group that is bonded to three U atoms, with a <K(3A)–ϕ> bond-length of 3.11 Å.

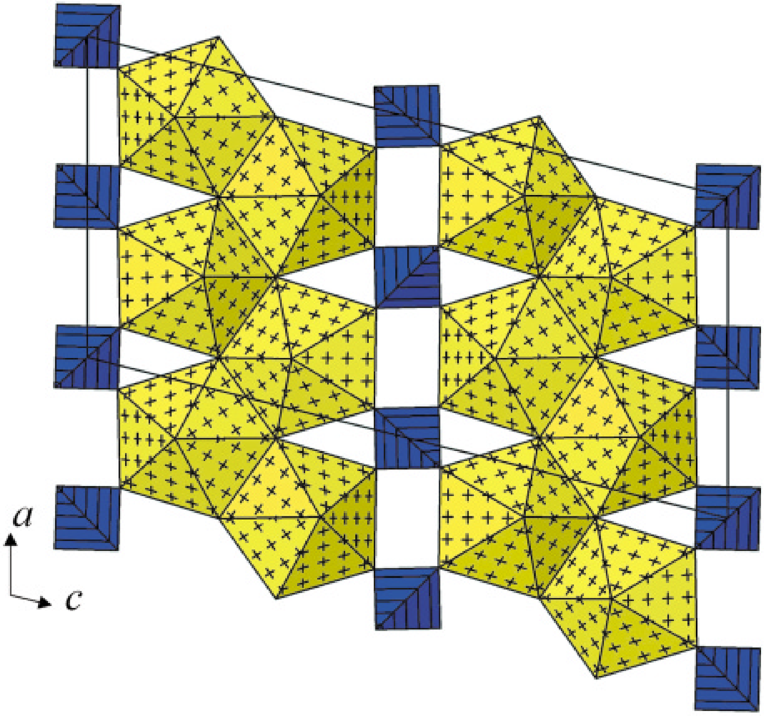

FIG. 1. The zippeite-type uranyl sulfate sheet in the structure of magnesium-zippeite. Uranyl pentagonal bipyramids are shown in yellow, and sulfate tetrahedra are blue.

The structure of zippeite (Fig. 4) contains three symmetrically distinct H_2O groups in the interlayer, each of which is bonded to at least one K cation. Direct linkages between adjacent uranyl sulfate sheets are provided by the K cations, and additional linkages presumably arise through H bonds, although the positions of the H atoms are not known.

The Na sites in sodium-zippeite are coordinated by six or seven ligands. The Na(1), Na(2), and Na(5) sites are each coordinated by one O_{Ur} atom, two $O_{U–S}$ atoms, and four interlayer H_2O groups. The <Na(1)–ϕ>, <Na(2)–ϕ> and <Na(3)–ϕ> bond-lengths are 2.53, 2.50 and 2.49 Å, respectively. Na(3) and Na(4) are each coordinated by four interlayer H_2O groups. In addition, Na(3) is coordinated by one O_{Ur} and one $O_{U–S}$ atom. Na(4) is coordinated by two O_{Ur} atoms. The <Na(3)–ϕ> and <Na(4)–ϕ> bond-lengths are 2.49 and 2.45 Å, respectively.

The structure of sodium-zippeite (Fig. 5) possesses a complex interlayer involving five Na cations and 12 H_2O groups. Of the H_2O groups, eight are shared between two Na cations, whereas four are bonded to only one Na cation. In addition to the Na–ϕ bonds, the interlayer contains a substantial number of H bonds.

There are four symmetrically distinct NH_4 groups in the interlayer of SZIPPNH$_4$I. In the cases of N(1) and N(2), there are four anions located between 2.88(2) and 3.05(2) Å from the N cation (Table 8). It is likely that each of these anions accepts H bonds emanating from the NH_4 groups. The N(3) and N(4) sites are each surrounded by six anions at distances ranging from 2.85(3)

TABLE 15. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC-DISPLACEMENT PARAMETERS FOR SZIPPMg

	x	*y*	*z*	*U(eq)*
U(1)	0.3788(1)	0.5738(1)	0.2579(1)	0.011(1)
U(2)	0.1205(1)	0.4062(1)	0.2373(1)	0.011(1)
U(3)	-0.1358(1)	0.5746(1)	0.2292(1)	0.011(1)
U(4)	0.6337(1)	0.4055(1)	0.2652(1)	0.011(1)
Mg(1)	0.2070(5)	0.3953(2)	0.4503(2)	0.021(1)
Mg(2)	0.2791(5)	0.6082(2)	0.0461(2)	0.019(1)
S(1)	0.6218(3)	0.7404(1)	0.2421(2)	0.014(1)
S(2)	0.1207(3)	0.7403(2)	0.2393(2)	0.016(1)
O(1)	0.7585(10)	0.3084(5)	0.7116(5)	0.023(2)
O(2)	0.3755(9)	0.4449(4)	0.2480(4)	0.014(1)
O(3)	0.6240(10)	0.5331(4)	0.2437(4)	0.019(2)
O(4)	0.3277(9)	0.5966(4)	0.1589(5)	0.019(2)
O(5)	0.0749(9)	0.4163(4)	0.1369(4)	0.016(2)
O(6)	0.1634(9)	0.3857(4)	0.3356(4)	0.017(2)
O(7)	-0.0430(9)	0.2869(4)	0.2115(5)	0.020(2)
O(8)	0.1253(9)	0.5347(4)	0.2490(4)	0.016(2)
O(9)	0.4269(9)	0.5612(4)	0.3579(4)	0.017(2)
O(10)	-0.0910(9)	0.6035(4)	0.3250(4)	0.016(2)
O(11)	0.5910(9)	0.3721(4)	0.1698(4)	0.018(2)
O(12)	0.8078(10)	0.2924(4)	0.3077(5)	0.022(2)
O(13)	0.5047(10)	0.7908(4)	0.1951(5)	0.021(2)
O(14)	0.7371(10)	0.7900(4)	0.2925(5)	0.021(2)
O(15)	0.6773(9)	0.4262(4)	0.3644(5)	0.019(2)
O(16)	0.8759(9)	0.4462(4)	0.2473(4)	0.015(1)
O(17)	-0.1802(9)	0.5573(4)	0.1312(4)	0.018(2)
O(18)	0.0071(9)	0.6891(4)	0.1910(4)	0.018(2)
O(19)	0.6983(9)	0.6933(4)	0.1929(5)	0.021(2)
O(20)	0.5485(9)	0.6898(4)	0.2907(5)	0.019(2)
OW(21)	0.2289(10)	0.6217(5)	-0.0653(5)	0.025(2)
OW(22)	0.2624(10)	0.3983(5)	0.5625(5)	0.025(2)
OW(23)	-0.0281(12)	0.3738(6)	0.4620(6)	0.039(2)
OW(24)	0.2604(12)	0.2781(5)	0.4460(6)	0.035(2)
OW(25)	0.5069(12)	0.5729(6)	0.0387(6)	0.037(2)
OW(26)	0.3551(11)	0.7212(5)	0.0589(5)	0.032(2)
OW(27)	0.0114(14)	0.2414(6)	0.0667(6)	0.050(3)
OW(28)	0.2000(10)	0.4932(5)	0.0298(5)	0.029(2)
OW(29)	0.4470(12)	0.4253(5)	0.4573(6)	0.036(2)
OW(30)	0.1485(11)	0.5127(5)	0.4378(6)	0.037(2)
OW(31)	0.0460(11)	0.6409(5)	0.0460(5)	0.030(2)

TABLE 16. SELECTED INTERATOMIC DISTANCES (Å) FOR SZIPPMg

U(1)-O(9)	1.819(8)	S(1)-O(13)	1.470(8)
U(1)-O(4)	1.830(8)	S(1)-O(14)	1.483(8)
U(1)-O(2)	2.225(7)	S(1)-O(19)	1.473(8)
U(1)-O(8)	2.266(8)	S(1)-O(20)	1.485(8)
U(1)-O(3)	2.299(8)	<S(1)-O>	1.478
U(1)-O(1)a	2.472(8)		
U(1)-O(20)	2.474(8)	S(2)-O(7)d	1.475(8)
<U(1)-O_{Ur}>	1.824	S(2)-O(18)	1.471(8)
<U(1)-O_{eq}>	2.347	S(2)-O(12)c	1.471(9)
		S(2)-O(1)a	1.488(9)
U(2)-O(6)	1.810(8)	<S(2)-O>	1.476
U(2)-O(5)	1.820(8)		
U(2)-O(8)	2.219(7)	Mg(1)-OW22	2.026(10)
U(2)-O(16)b	2.267(7)	Mg(1)-OW24	2.073(10)
U(2)-O(2)	2.271(7)	Mg(1)-O(6)	2.078(9)
U(2)-O(14)c	2.470(8)	Mg(1)-OW30	2.083(10)
U(2)-O(7)	2.481(8)	Mg(1)-OW23	2.121(11)
<U(2)-O_{Ur}>	1.815	Mg(1)-OW29	2.116(11)
<U(2)-O_{eq}>	2.342	<Mg(1)-ϕ>	2.083
U(3)-O(17)	1.795(8)	Mg(2)-OW21	2.025(10)
U(3)-O(10)	1.799(8)	Mg(2)-O(4)	2.046(9)
U(3)-O(16)b	2.233(7)	Mg(2)-OW26	2.050(10)
U(3)-O(3)b	2.265(8)	Mg(2)-OW31	2.092(10)
U(3)-O(8)	2.314(8)	Mg(2)-OW25	2.093(11)
U(3)-O(19)b	2.505(8)	Mg(2)-OW28	2.094(9)
U(3)-O(18)	2.503(7)	<Mg(2)-ϕ>	2.067
<U(3)-O_{Ur}>	1.797		
<U(3)-O_{eq}>	2.364		
U(4)-O(11)	1.815(8)		
U(4)-O(15)	1.826(8)		
U(4)-O(3)	2.229(7)		
U(4)-O(2)	2.291(7)		
U(4)-O(16)	2.297(8)		
U(4)-O(12)	2.483(8)		
U(4)-O(13)c	2.496(8)		
<U(4)-O_{Ur}>	1.820		
<U(4)-O_{eq}>	2.359		

a = -x+1, -y+1, -z+1; b = x-1, y, z; c = -x+1, y-½, -z+½; d = -x, y+½, -z+½; e = -x+1, y+½, -z+½

TABLE 17. BOND-VALENCE* SUMS (*vu*) AT ATOMIC POSITIONS, EXCLUDING CONTRIBUTIONS FROM HYDROGEN ATOMS, IN THE STRUCTURE OF ZIPPEITE

U(1)	6.09	K(2A)	0.98	O(7)	1.75	O(16)	1.80
U(2)	5.69	K(3)	0.80	O(8)	1.94	O(17)	1.99
U(3)	5.89	K(3A)	0.54	O(9)	2.08	OH(18)	1.54
U(4)	6.25	O(1)	2.09	O(10)	1.92	O(19)	2.02
S(1)	5.51	O(2)	2.03	O(11)	1.81	O(20)	1.87
S(2)	6.44	O(3)	1.90	O(12)	1.82	OW(21)	0.00
K(1)	0.96	O(4)	1.92	O(13)	1.74	OW(22)	0.13
K(1A)	0.99	O(5)	2.17	O(14)	1.86	OW(23)	0.25
K(2)	1.00	O(6)	1.80	O(15)	1.83		

*Bond-valence parameters for U^{6+}-O from Burns *et al.* (1997b) and for S^{6+}-O and Na-O from Brese & O'Keeffe (1991)

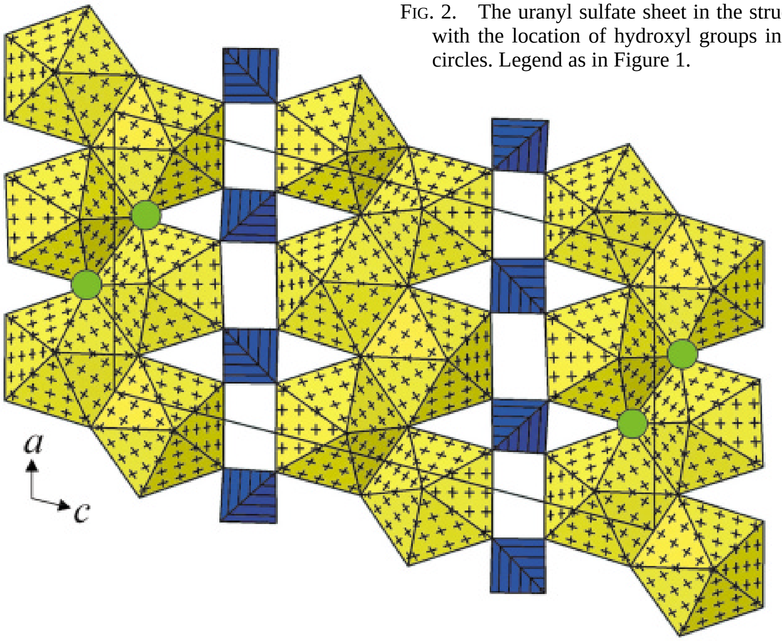

FIG. 2. The uranyl sulfate sheet in the structure of zippeite, with the location of hydroxyl groups indicated by green circles. Legend as in Figure 1.

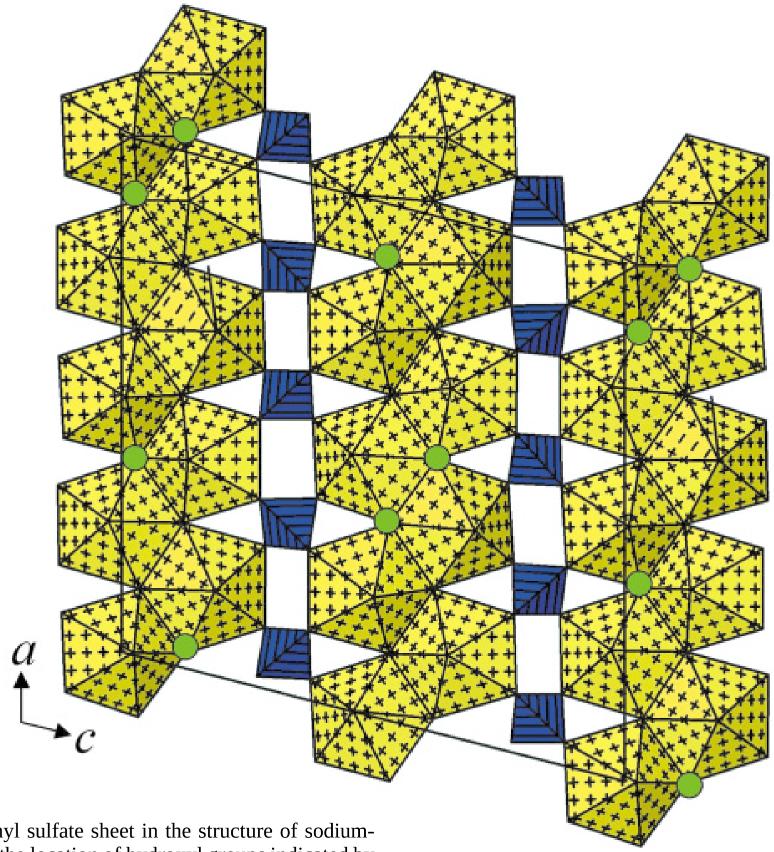

FIG. 3. The uranyl sulfate sheet in the structure of sodium-zippeite, with the location of hydroxyl groups indicated by green circles. Legend as in Figure 1.

to 3.15(3) Å (Table 8). In each case, four of the six ligands presumably accept H bonds from the NH_4 groups.

The structure of SZIPPNH$_4$II involves two symmetrically distinct NH_4 groups, each of which is located in the interlayer in positions surrounded by four anions at distances in the range 2.79(3) to 3.15(3) Å. It is likely that each of these anions accepts a hydrogen bond from the NH_4 groups.

TABLE 18. BOND-VALENCE* SUMS (*vu*) AT ATOMIC POSITIONS, EXCLUDING CONTRIBUTIONS FROM HYDROGEN ATOMS, IN THE STRUCTURE OF SODIUM-ZIPPEITE

U(1)	5.98	O(1)	1.92	O(18)	1.88	O(35)	1.75
U(2)	6.01	O(2)	1.95	O(19)	2.07	O(36)	1.98
U(3)	5.81	O(3)	1.52	O(20)	2.04	O(37)	1.90
U(4)	6.06	O(4)	1.96	O(21)	2.14	OH(1)	1.40
U(5)	5.97	O(5)	1.75	O(22)	2.18	OH(2)	1.34
U(6)	6.15	O(6)	2.09	O(23)	2.05	OH(3)	1.27
U(7)	5.88	O(7)	1.71	O(24)	1.75	OW(1)	0.39
U(8)	5.91	O(8)	1.99	O(25)	2.04	OW(2)	0.36
S(1)	6.16	O(9)	2.18	O(26)	1.52	OW(3)	0.46
S(2)	5.98	O(10)	1.89	O(27)	1.55	OW(4)	0.31
S(3)	5.96	O(11)	1.96	O(28)	1.94	OW(5)	0.21
S(4)	6.20	O(12)	1.66	O(29)	2.00	OW(6)	0.43
Na(1)	1.04	O(13)	1.84	O(30)	1.75	OW(7)	0.40
Na(2)	1.10	O(14)	2.26	O(31)	1.75	OW(8)	0.16
Na(3)	0.97	O(15)	1.55	O(32)	1.82	OW(9)	0.36
Na(4)	1.10	O(16)	1.75	O(33)	1.71	OW(10)	0.12
Na(5)	1.00	O(17)	1.82	O(34)	1.81	OW(11)	0.31
						OW(12)	0.27

*Bond-valence parameters for U^{6+}-O from Burns *et al.* (1997b) and for S^{6+}-O and Na-O from Brese & O'Keeffe (1991)

In addition to four symmetrically distinct NH_4 groups, the interlayer of SZIPPNH$_4$I (Fig. 6) contains one H_2O group. Hydrogen bonds emanating from the

TABLE 19. BOND-VALENCE* ANALYSIS (*vu*) FOR SZIPPNH$_4$I

	U(1)	U(2)	S1	S2	Σ
O(1)	0.39			$1.49^{\times2\downarrow}$	1.88
O(2)		0.39	$1.42^{\times2\downarrow}$		1.81
O(3)	0.68, 0.54	0.65			1.87
O(4)		0.42	$1.54^{\times2\downarrow}$		1.96
O(5)	0.45			$1.47^{\times2\downarrow}$	1.92
O(6)	0.68	0.63, 0.58			1.89
O(7)	1.55				1.55
O(8)		1.55			1.55
O(9)		1.65			1.65
O(10)	1.65				1.65
OW(11)					0.00
Σ	5.94	5.87	5.92	5.92	

*Bond-valence parameters for U^{6+}-O from Burns *et al.* (1997b); for S^{6+}-O from Brese & O'Keeffe (1991).

TABLE 20. BOND-VALENCE* ANALYSIS (*vu*) FOR SZIPPNH$_4$II

	U(1)	S	Σ
O(1)	0.63, 0.61, 0.56		1.80
O(2)	0.44	$1.69^{\times2\downarrow}$	2.13
O(3)	0.43	$1.34^{\times2\downarrow}$	1.77
O(4)	1.59		1.59
O(5)	1.68		1.68
Σ	5.93	6.06	

*Bond-valence parameters for U^{6+}-O from Burns *et al.* (1997b); for S^{6+}-O from Brese & O'Keeffe (1991).

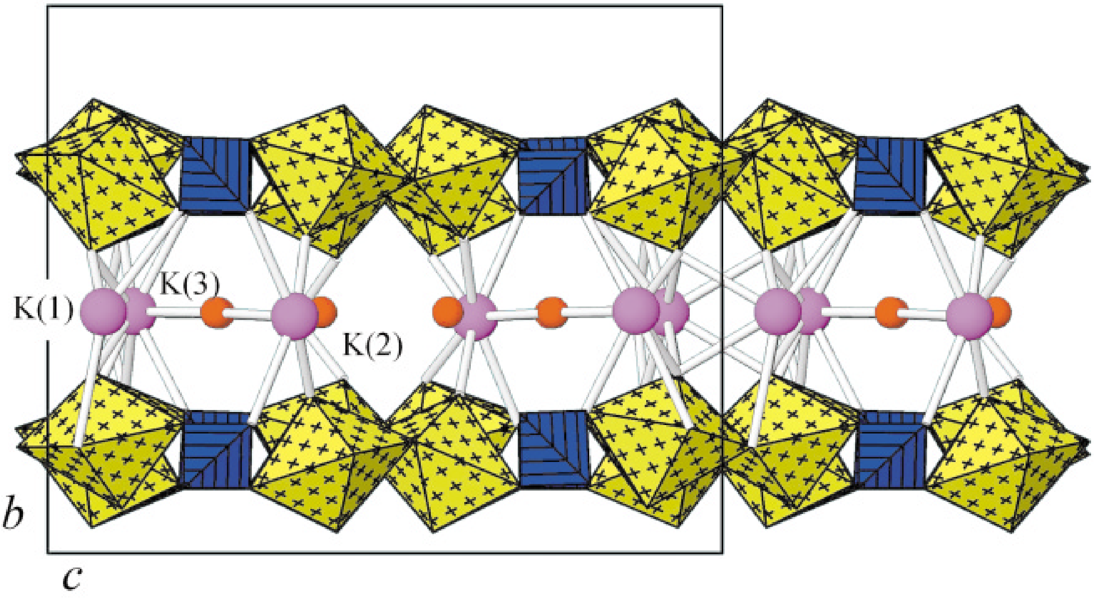

FIG. 4. The structure of zippeite projected along [100]. Legend as in Figure 1. Red circles represent O atoms of H_2O groups. For clarity, the K(1A), K(2A), and K(3A) sites, which are located close to other K sites, are omitted.

NH_4 groups provide direct linkage between the sheets, and are probably accepted both by $O_{U\text{–}S}$ and O_{Ur} atoms within the sheets. The structure of SZIPPNH$_4$II (Fig. 7) contains two distinct NH_4 groups in the interlayer, which provide linkage of the sheets by donating H bonds that are probably accepted by both $O_{U\text{–}S}$ and O_{Ur} atoms.

The structures of magnesium-zippeite, zinc-zippeite and cobalt-zippeite contain two symmetrically distinct *M* sites in the interlayer, each of which is coordinated by six ligands in a distorted octahedral arrangement (Fig. 8). The *M* sites are each coordinated by two O_{Ur} atoms, corresponding to uranyl polyhedra of both adja-

TABLE 21. BOND-VALENCE ANALYSES* FOR M^{2+} ZIPPEITES

	U(1)			U(2)			S(1)			S(2)			*M*(1)			*M*(2)			Σ		
M=	Mg	Zn	Co	Mg	Zn	Co	Mg	Zn	Co	Mg	Zn	Co	Mg	Zn	Co	Mg	Zn	Co	Mg	Zn	Co
O(1)	0.43	0.42	0.40							$1.32^{x2\downarrow}$	$1.50^{x2\downarrow}$	$1.51^{x2\downarrow}$							1.75	1.92	1.91
O(2)				0.42	0.43	0.40	$1.64^{x2\downarrow}$	$1.60^{x2\downarrow}$	$1.47^{x2\downarrow}$										2.06	2.03	1.87
O(3)	0.61	0.62	0.58	0.66	0.65	0.72													1.90	1.89	1.91
	0.63	0.62	0.61																		
O(4)				0.45	0.47	0.55	$1.42^{x2\downarrow}$	$1.34^{x2\downarrow}$	$1.62^{x2\downarrow}$										1.87	1.81	2.17
O(5)	0.44	0.42	0.34							$1.62^{x2\downarrow}$	$1.44^{x2\downarrow}$	$1.41^{x2\downarrow}$							2.06	1.86	1.75
O(6)	0.69	0.72	0.64	0.63	0.64	0.64													1.94	1.96	1.91
				0.62	0.60	0.63															
O(7)	1.67	1.52	1.75																1.67	1.52	1.75
O(8)				1.58	1.62	1.72													1.58	1.62	1.72
O(9)				1.55	1.47	1.55										$0.39^{x2\downarrow}$	$0.41^{x2\downarrow}$	$0.36^{x2\downarrow}$	1.94	1.88	1.91
O(10)	1.52	1.45	1.58										$0.38^{x2\downarrow}$	$0.39^{x2\downarrow}$	$0.33^{x2\downarrow}$				1.90	1.84	1.91
OW(11)													0.53	0.45	0.24				0.53	0.45	0.24
OW(12)																0.25	0.35	0.37	0.25	0.35	0.37
OW(13)																0.37	0.43	0.32	0.37	0.43	0.32
OW(14)													0.44	0.40	0.42				0.44	0.40	0.42
OW(15)													0.37	0.37	0.39				0.37	0.37	0.39
OW(16)													0.13	0.16	0.15	0.11	0.07	0.11	0.24	0.23	0.26
OW(17)																0.36	0.39	0.34	0.36	0.39	0.34
	5.99	5.77	5.90	5.91	5.88	6.21	6.12	5.88	6.18	5.88	5.88	5.84	2.23	2.16	1.86	1.87	2.03	1.86			

*Bond-valence parameters for U^{6+}-O from Burns *et al.* (1997b); for S^{6+}-O from Brese & O'Keeffe (1991).

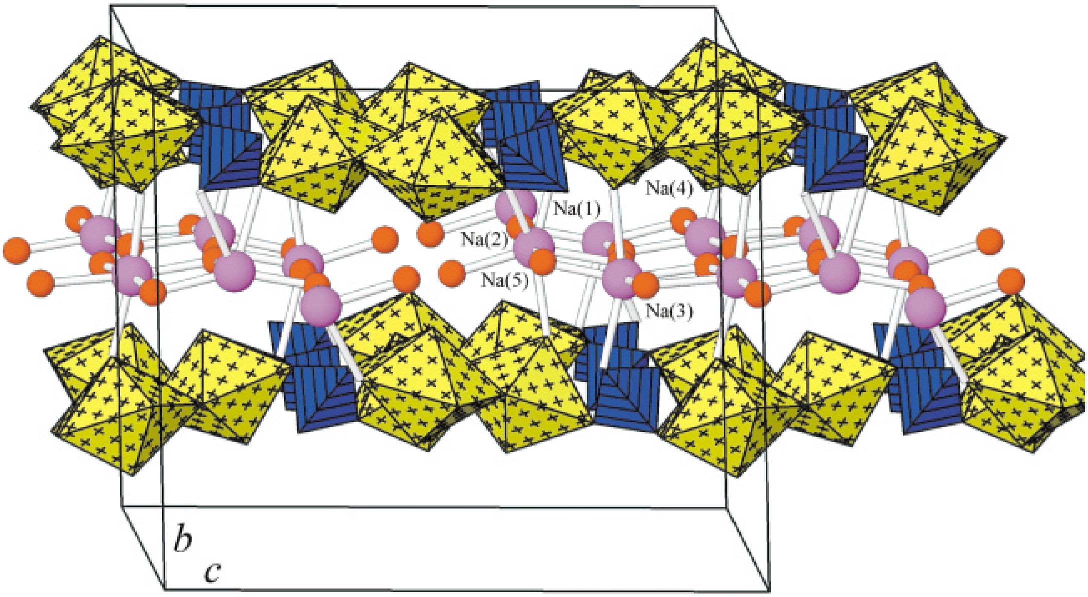

FIG. 5. The structure of sodium-zippeite projected approximately along [100]. Legend as in Figure 1. Red circles represent O atoms of H_2O groups.

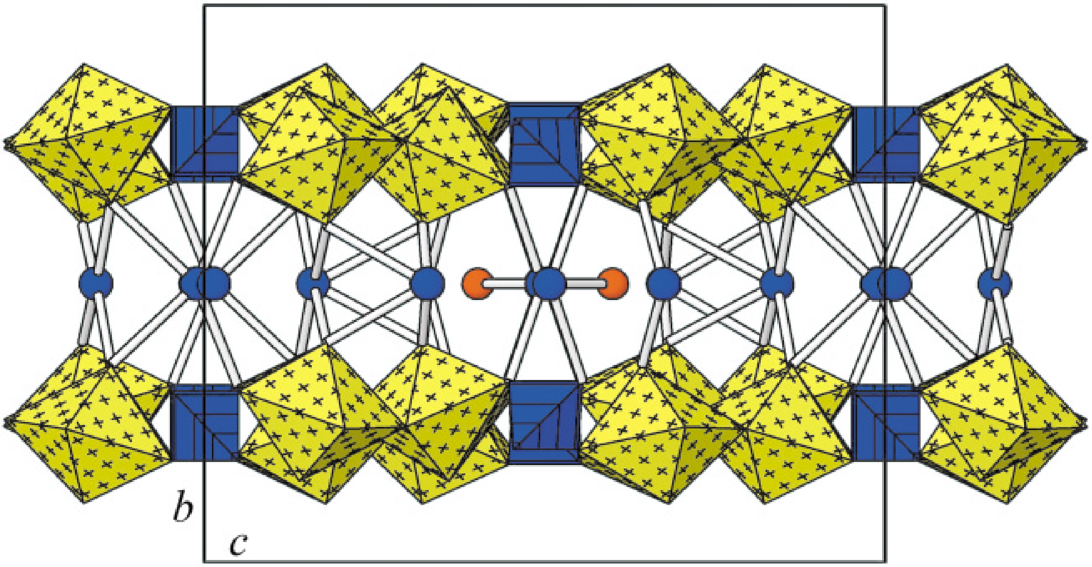

FIG. 6. The structure of SZIPPNH$_4$I projected along [100]. N cations are shown as blue circles; orange circles represent O atoms of H$_2$O groups.

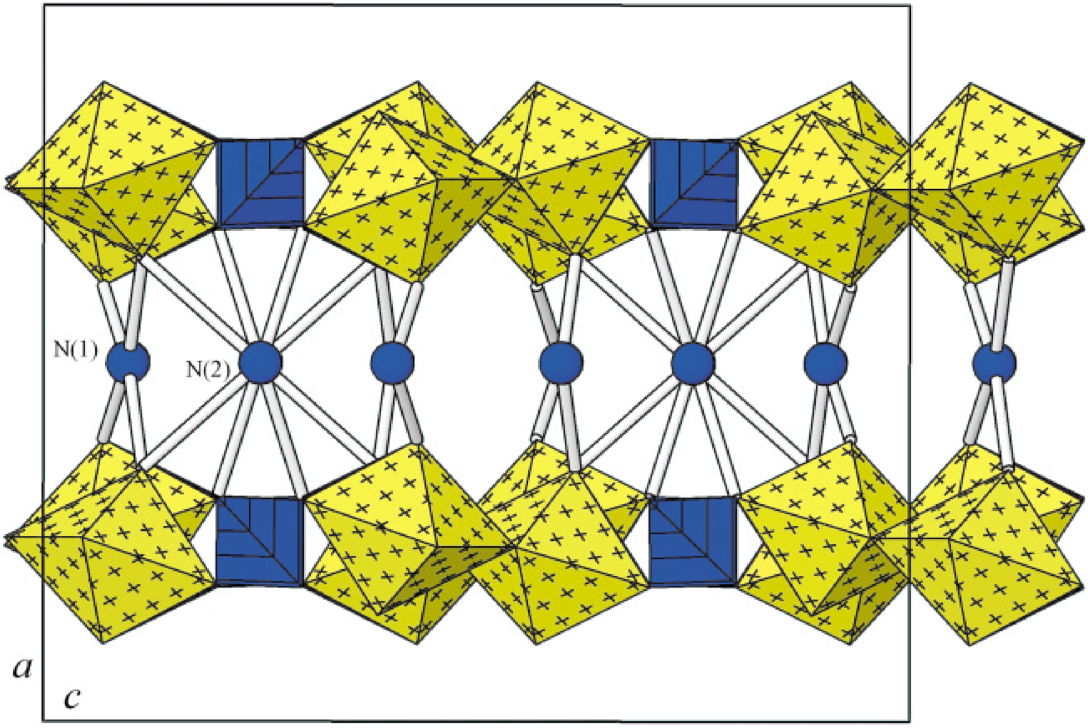

FIG. 7. The structure of SZIPPNH$_4$II projected along [010]. N cations are shown as blue circles.

cent sheets; thus the *M* sites provide a direct bridge between the uranyl sulfate sheets. Each *M* cation is also coordinated by four interlayer H_2O groups, and one H_2O group is shared between adjacent $M\phi_6$ octahedra, resulting in dimers of octahedra of composition $M_2(O_{Ur})_4(H_2O)_7$.

The structure of SZIPPMg (Fig. 9) contains two symmetrically distinct Mg sites, each of which is octahedrally coordinated by five interlayer H_2O groups and one O_{Ur} atom. The $Mg\phi_6$ octahedra do not share polyhedral elements, and are of comparable size.

Comparison of the Structures of Marecottite, Magnesium-zippeite and SZIPPMg

Marecottite, ideally $Mg_3(H_2O)_{18}[(UO_2)_8(SO_4)_4O_6(OH)_2]\bullet10H_2O$, is a new zippeite-group mineral that was recently described by Brugger *et al.* (2003). It is triclinic, *P*1, with *a* 10.815(4), *b* 11.249(4), *c* 13.851(6) Å, α 66.224(7), β 72.412(7), and γ 69.95(2)°. It contains the zippeite-type uranyl sulfate sheet, with composition $[(UO_2)_8(SO_4)_4O_6(OH)_2]$, which is identical to that found for zippeite in the current study. The interlayer of the structure of marecottite contains three M^{2+} cations, as well as 28 symmetrically distinct H_2O groups. Of these, 18 coordinate the M^{2+} cations in distorted octahedral arrangements, and ten are held in the structure by H bonding only. The $M(H_2O)_6$ octahedra in the structure are isolated, and are held in place by H bonds associated with the H_2O groups.

The structure of marecottite is compared to those of magnesium-zippeite and SZIPPMg in Figure 10. Each contains topologically identical uranyl sulfate sheets, although the sheets in magnesium-zippeite and SZIPPMg do not contain any OH groups. The primary difference among these structures is the configuration of the interlayer and the number of H_2O groups within the interlayer. In addition, marecottite contains more Mg than the other two compounds. The $Mg\phi_6$ octahedra in magnesium-zippeite share one vertex (O_{Ur}) with the sheet on either side, those in SZIPPMg only share a vertex (O_{Ur}) with one of the two adjacent sheets, and those in marecottite are not attached to the sheets. All H_2O in the structure of magnesium-zippeite is bonded to Mg, only one of the H_2O groups in SZIPPMg is not bonded to Mg, and 10 H_2O groups in the structure of marecottite are held in place by H bonds only. Thus, the quantity of H_2O in these structures increases both by an increase in the proportion as $Mg\phi_6$ octahedra, and by inclusion of H_2O groups in voids in the interlayer, where they are held in place by H bonds.

Our synthesis experiments described above provide insight into the relative stabilities of marecottite, magnesium-zippeite and SZIPPMg. Under conditions of the hydrothermal synthesis at pH = 4 and 150°C, SZIPPMg crystallizes, but converts to magnesium-zippeite after a few days. This transition involves no significant changes in the uranyl sulfate sheet, but does involve the loss of four H_2O groups from the interlayer, two of which are bonded to Mg. When we heated identical solutions with

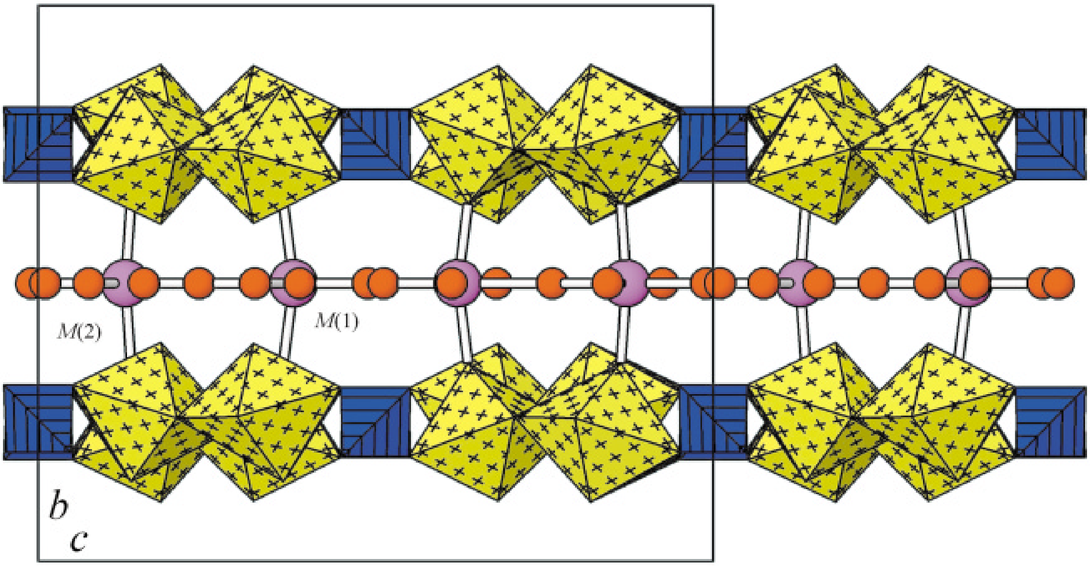

FIG. 8. The structure of magnesium-zippeite projected along [100]. Legend as in Figure 1. Red circles represent O atoms of H_2O groups.

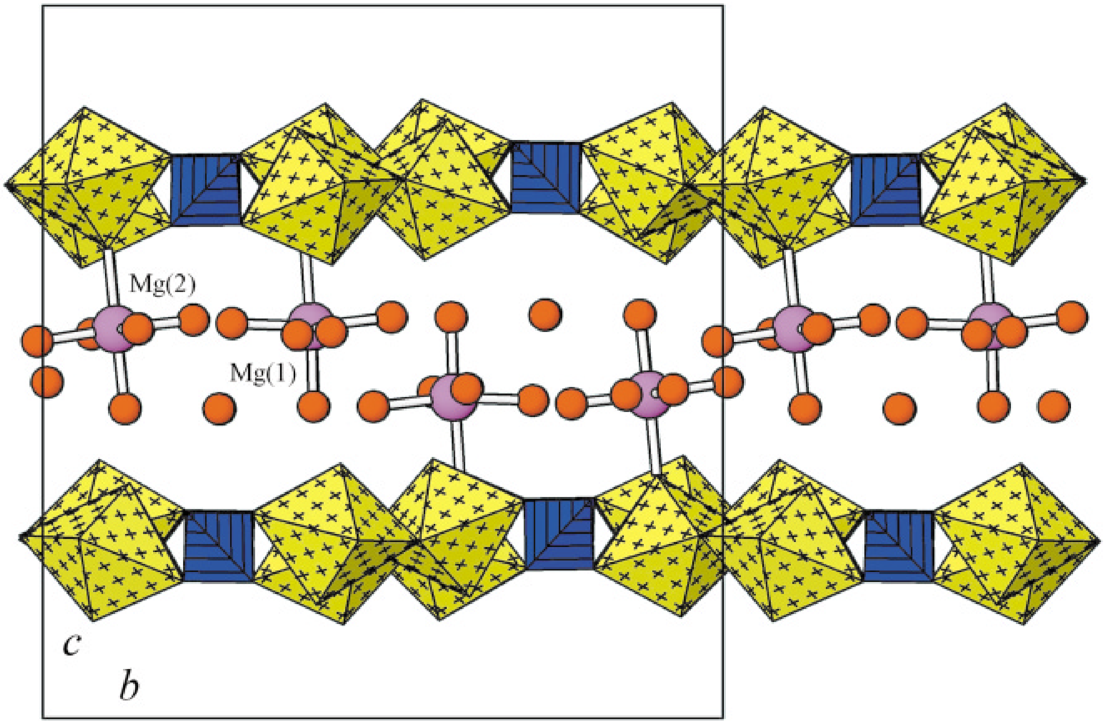

FIG. 9. The structure of SZIPPMg projected along [100]. Legend as in Figure 8.

pH = 4 for 24 h at various temperatures, we obtained marecottite up to 120°C, SZIPPMg at 150°C, and magnesium-zippeite at 180°C. Thus with increasing temperature, we obtained the progressively lower hydrates. The transition from marecottite to SZIPPMg presumably involves recrystallization, as the sheet composition changes, the Mg:U ratio changes, and significant H_2O must be lost from the interlayer.

COMPARISON OF THE STRUCTURES OF SZIPPNH$_4$I AND MAGNESIUM-ZIPPEITE, ZINC-ZIPPEITE, AND COBALT-ZIPPEITE

The structure of SZIPPNH$_4$I is closely related to those of magnesium-zippeite, zinc-zippeite and cobalt-zippeite. All four crystallize in space group $C2/m$, and the structure of SZIPPNH$_4$I may be derived from that of the M^{2+} zippeite by removal of both M^{2+} cations, replacement of four H_2O groups by NH_4 groups, and removal of two of the remaining H_2O groups.

GENERAL ASPECTS OF ZIPPEITE-TYPE STRUCTURES

The uranyl sulfate sheets contain three types of ligands: O_{Ur} atoms, those that are shared between a uranyl pentagonal bipyramid and a sulfate tetrahedron ($O_{U–S}$), and those that are bonded to three U^{6+} cations (O_{3U} or OH_{3U}). The U^{6+}–O_{Ur} bonds are typically 1.8 Å, with corresponding bond-valences of ~1.62 *vu* (valence units). Thus, the O_{Ur} atoms typically form bonds with interlayer cations, or accept H bonds in the structures of zippeite-group phases, as well as other uranyl compounds. The uranyl sulfate sheets in the zippeite group exhibit strongly bimodal distributions of U^{6+}–O_{3U} and U^{6+}–$O_{U–S}$ bonds. In the uranyl sulfate sheets that contain no hydrogen, the U^{6+}–O_{3U} bonds range from 2.21 to 2.36 Å, with an average of 2.275 Å. The U^{6+}–$O_{U–S}$ bonds are considerably longer, in the range 2.35 to 2.60 Å, with an average of 2.483 Å. According to the bond-valence parameters provided for uranyl pentagonal bipyramids by Burns *et al.* (1997b), bond lengths of 2.275 and 2.483 Å correspond to 0.64 and 0.42 *vu*, respectively.

Each uranyl pentagonal bipyramid in the uranyl sulfate sheets that contain no hydrogen involve two O_{Ur} atoms, three O_{3U} atoms, and two $O_{U–S}$ atoms. Summing the typical bond-valences given above for their average geometries results in a bond valence at the U^{6+} site of 6.0 *vu*, which is consistent with its formal valence. The distribution of bond valences at the anion sites within the uranyl sulfate sheet is of significance in determining the nature of the interlayer constituents. The bond valences incident at the O_{Ur}, O_{3U} and $O_{U–S}$ atoms will be about 1.62, 1.92 and 1.92 *vu*, respectively. Consider first the case of magnesium-zippeite, zinc-zippeite and cobalt-zippeite. Each of the M^{2+} interlayer cations is bonded to two O_{Ur} atoms, resulting in about 0.76 *vu* toward their bond-valence requirements. However, there are no additional sheet anions close enough to form significant bonds to the M^{2+} cations. Therefore, H_2O is incorporated into the coordination polyhedron, with ~0.3 *vu* associated with each M^{2+}–H_2O bond, resulting in a bond-valence sum at the M^{2+} cation of ~2.0 *vu*. Hydrogen bonds emanate from the O atoms of the H_2O

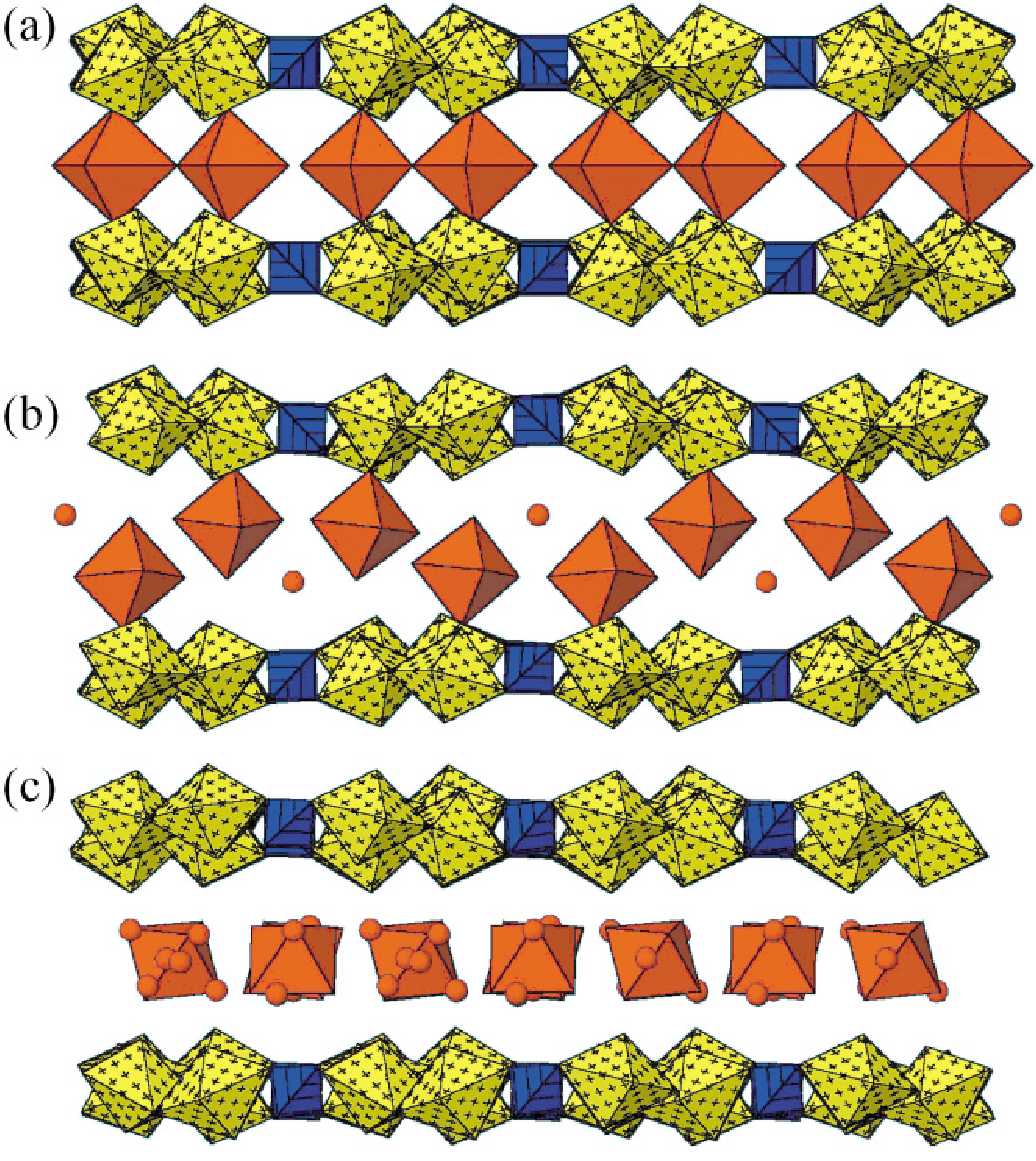

FIG. 10. Polyhedral representations of the structures of magnesium-zippeite (a), SZIPPMg (b), and marecottite (c).

groups, and deliver the 0.3 *vu* received from the M^{2+} cation to the uranyl sulfate sheet. Given that each H bond is ~0.15–0.20 *vu*, they can in principle be accepted by any of the O_{Ur}, O_{3U} and $O_{U–S}$ atoms without excessive incident bond-valence.

In the case of the structures containing a monovalent cation, there are two groups: zippeite and sodium-zippeite contain OH groups within the sheets, whereas the sheets of the two synthetic NH_4 zippeite-group phases do not contain any hydrogen. Consider the structure of SZIPPNH$_4$II, which contains only NH_4 groups within its interlayer. There are two symmetrically distinct N sites, and four hydrogen bonds of ~0.25 *vu* will emanate from each NH_4 group. This is consistent with the observation that six of the H bonds from the interlayer NH_4 groups are probably accepted by O_{Ur} atoms, which can readily accept 0.25 *vu*. The remaining two hydrogen bonds are probably accepted by O(3), which is a $O_{U–S}$ atom. Notably, both the U–O(3) bond and the S(1)–O(3) bond are longer than normal, with values of 2.48 and 1.519(9) Å, respectively. This corresponds to a bond-valence sum at the O(3) site of 1.77 *vu*, which is compatible with acceptance of a ~0.25 H bond. Thus, it is apparent that the relatively strong distortion of the SO_4 tetrahedron in SZIPPNH$_4$II [1.43(1) × 2, 1.519(9) Å × 2] enhances the connectivity between the sheet and the interlayer of the structure.

In the case of SZIPPNH$_4$I, in addition to the four symmetrically distinct NH_4 groups in the interlayer, there is a single distinct H_2O group. The hydrogen bonds associated with the N(3) and N(4) NH_4 groups are probably all accepted by O_{Ur} atoms. In the case of both N(1) and N(2), two H bonds are probably accepted by O_{Ur} atoms, and two by $O_{U–S}$ atoms for each NH_4 group. Although the SO_4 groups are fairly regular in this structure, the $O_{U–S}$ atoms that are candidates for accepting H bonds form long U–O bonds [2.529(13) and 2.522(16) Å]. The bond-valence sums at these sites are 1.88 and 1.81 *vu*, indicating that it is possible for them to accept weak H bonds.

Given the distribution of bond valences at the anion sites within the sheets of uranyl sulfate polyhedra, it seems unlikely that a trivalent cation in octahedral coordination will occur in the interlayer of zippeite and form bonds to at least one anion within the sheet. This is because none of the anions of the sheet are able to accept 0.5 *vu* from the M^{2+} cation.

The zippeite minerals and synthetic compounds show a wide range of compositions. The topology of the zippeite sheet thus is compatible with a wide range of interlayer configurations and H_2O contents. In the case of uranyl minerals in general, it is interesting that many sheets of polyhedra of high bond-valence occur only in one or two structures. For example, the curite, vandendriesscheite, wölsendorfite, fourmarierite, bijvoetite, rutherfordine, haiweeite, and umohoite sheets each only occur in one or two species. The zippeite sheet may be added to the list of notable exceptions, which includes the α-U_3O_8-type sheet of uranyl pentagonal bipyramids, the phosphuranylite sheet of uranyl pentagonal and hexagonal bipyramids and phosphate tetrahedra, the autunite sheet of uranyl square bipyramids and phosphate tetrahedra, and the uranophane sheet of uranyl pentagonal bipyramids and silicate tetrahedra (Burns 1999). Notably, the α-U_3O_8-type sheet occurs in structures with both monovalent and divalent interlayer cations, and with a variety of O:OH ratios within the sheets of polyhedra, in an analogous fashion to the zippeite group.

MINERAL DEFINITIONS OF FRONDEL ET AL. (1976)

Frondel *et al.* (1976) defined zippeite on the basis of re-examination of material from Joachimsthal that was previously studied by Nováček (1935). They provided an X-ray powder-diffraction pattern for the mineral, and showed that their synthetic material had a very similar diffraction pattern. The powder-diffraction pattern calculated from our refined structure is in good agreement with that reported by Frondel *et al.* (1976), showing that the synthetic zippeite we studied is probably the same as the natural and synthetic materials used by Frondel *et al.* (1976) to define the species.

Sodium-zippeite was defined by Frondel *et al.* (1976) on the basis of the chemical composition of a specimen from the Delta mine, Utah, as well as of their synthetic material. They provided an X-ray powder-diffraction pattern for the synthetic material only, and indexed it on an orthorhombic unit-cell with dimensions *a* 8.82, *b* 17.12, *c* 7.32 Å. Comparison of the calculated pattern for sodium-zippeite with that of Frondel *et al.* (1976) reveals reasonable agreement of peak positions, but relatively poor agreement of intensities, possibly owing to preferred orientation. Ondruš *et al.* (1997a) provided an X-ray powder pattern for sodium-zippeite from the Jáchymov (Joachimsthal) district of the Czech Republic; peak positions and, to a lesser extent, peak intensities are in reasonable agreement with the values calculated from our structure. Given the good correspondence between the chemical data given by Frondel *et al.* (1976) for sodium-zippeite (see above), and the reasonable agreement of the powder-diffraction patterns, we conclude that the material we have synthesized and studied may be the same as the sodium-zippeite of Frondel *et al.* (1976).

Frondel *et al.* (1976) provided partial descriptions of magnesium-zippeite, zinc-zippeite and nickel-zippeite on the basis of studies of natural and synthetic material. Their chemical analyses indicate extensive solid-solution between end-member compositions. X-ray powder-diffraction data were provided for nickel-zippeite and magnesium-zippeite, and for synthetic cobalt-zippeite, nickel-zippeite, zinc-zippeite and magnesium-zippeite.

Frondel *et al.* (1976) defined magnesium-zippeite from a fine-grained efflorescence at the Lucky Strike

No. 2 mine in Emery County, Utah. The definition was based upon a poor X-ray powder-diffraction pattern and chemical data on an impure specimen. One of us visited the Harvard Mineralogical Museum and unsuccessfully searched the research collections of Frondel in an attempt to locate the type specimen of magnesium-zippeite. On the basis of chemical and X-ray-diffraction studies, Brugger *et al.* (2003) recommended that magnesium-zippeite be redefined as material identical to that synthesized in the current study. Ondruš *et al.* (1997a, b) examined uranyl sulfates from the Jáchymov (Joachimsthal) district, and provided an X-ray powder-diffraction pattern for magnesium-zippeite that is in excellent agreement with that calculated for our synthetic material. Ondruš *et al.* (1997a, b) also reported a pattern for "pseudo magnesium-zippeite" that corresponds to marecottite.

The synthetic nickel-zippeite and zinc-zippeite of the current study are isostructural with magnesium-zippeite. As in the case of magnesium-zippeite, it seems that samples of nickel-zippeite and zinc-zippeite studied by Frondel *et al.* (1976) contain more than one mineral.

SUMMARY AND CONCLUSIONS

We have determined and refined the structures of eight zippeite-group compounds, five of which had been described as minerals. Each of the structures studied contains topologically identical sheets of uranyl pentagonal bipyramids and sulfate tetrahedra, although the quantity of H in the sheets varies. Details of the interlayer configurations and their relationships to the uranyl sulfate sheets have been established.

We were not able to obtain suitable single crystals of synthetic marecottite or nickel-zippeite for study, although each was obtained in powder form. It is possible that structural analogues of marecottite and SZIPPMg containing Co, Ni and Zn exist, even though we were unable to synthesize them. As is the case with magnesium-zippeite, natural specimens of nickel-zippeite and zinc-zippeite studied by Frondel *et al.* (1976) may contain mixtures of several zippeite-group minerals.

Examination of natural zippeite-group specimens using modern techniques is certainly warranted; it seems likely that several new zippeite-group species await discovery, and the extent of solid solution between end-member compositions is unknown. The current study provides a framework for additional studies of natural specimens.

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