

THE CRYSTAL STRUCTURES OF SYNTHETIC POTASSIUM – TRANSITION-METAL ZIPPEITE-GROUP PHASES

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ABSTRACT

Mixed K–*Me* zippeite-group phases (*Me* = Mn, Co, Ni, Zn) have been synthesized by adjusting a UO₂SO₄ solution containing *Me*SO₄ to a pH of 3.8 by means of KOH. The solution was kept for 75 hours at 150°C and an approximate pressure of 3.5 MPa. Single-crystal X-ray studies, chemical analysis and bond-valence calculations revealed the composition K_{0.5}Me_{0.75}[(UO₂)₂SO₄O₂]•3H₂O. The crystals are monoclinic, space group *C2/c*. For *Me* = Mn, we found *a* 8.661(6), *b* 14.375(8), *c* 17.705(12) Å, β 104.12(5)°; for *Me* = Co, the cell parameters are *a* 8.651(5), *b* 14.188(8), *c* 17.713(13) Å, β 104.14(6)°, for *Me* = Ni, they are *a* 8.662(5), *b* 14.095(8), *c* 17.770(9) Å, β 104.18(5)°, and for *Me* = Zn, they are *a* 8.650(6), *b* 14.180(12), *c* 17.709(13) Å, β 104.14(6)°. The structures were refined to unweighted residuals of 0.0525, 0.0459, 0.0383 and 0.0690, respectively. The structures possess a layer structure parallel to (010) comparable to that of zippeite. We demonstrate that a zippeite-group phase with an interlayer containing monovalent potassium cation and divalent transition metal cations can be synthesized. The interlayer contains two symmetrically distinct *Me* atoms, one K atom and H₂O molecules. Both *Me* atoms (*Me*1, *Me*2) are coordinated by six oxygen atoms forming distorted octahedra. In the *Me*1 octahedron, two O atoms are part of (UO₂)²⁺ of adjacent uranyl oxo sulfate layers, and four are part of four H₂O molecules of the interlayer, which is the same configuration as found in the crystal structure of zinc-zippeite, cobalt-zippeite and magnesium-zippeite. In the *Me*2 octahedron, four O atoms are part of (UO₂)²⁺ of the adjacent uranyl oxo sulfate layers, and two O atoms are part of two equivalent positions of a H₂O group.

Keywords: uranyl sulfate, zippeite-group phases, crystal structure, transition metal.

SOMMAIRE

Nous avons synthétisé des phases du groupe de la zippéite à occupation mixte K–*Me* (*Me* = Mn, Co, Ni, Zn) en ajustant le pH d'une solution de UO₂SO₄ contenant *Me*SO₄ à une valeur de 3.8 par addition de KOH. La solution est laissée pour 75 heures à 150°C et une pression d'environ 3.5 MPa. Nos résultats, obtenus par diffraction X sur monocristal, analyse chimique et calculs de valences de liaisons, révèlent une composition K_{0.5}Me_{0.75}[(UO₂)₂SO₄O₂]•3H₂O. Les cristaux sont monocliniques, groupe spatial *C2/c*. Pour *Me* = Mn, nous avons trouvé *a* 8.661(6), *b* 14.375(8), *c* 17.705(12) Å, β 104.12(5)°; pour *Me* = Co, les paramètres sont *a* 8.651(5), *b* 14.188(8), *c* 17.713(13) Å, β 104.14(6)°, pour *Me* = Ni, ils sont *a* 8.662(5), *b* 14.095(8), *c* 17.770(9) Å, β 104.18(5)°, et pour *Me* = Zn, ils sont *a* 8.650(6), *b* 14.180(12), *c* 17.709(13) Å, β 104.14(6)°. Les structures ont été affinées jusqu'à des résidus non pondérés de 0.0525, 0.0459, 0.0383 et 0.0690, respectivement. Elles possèdent une structure en couches parallèles à (010), tout comme celle de la zippéite. Nous démontrons qu'il est possible de synthétiser une phase du groupe de la zippéite avec un interfeuillet contenant un cation monovalent (potassium) et un cation bivalent d'un métal de transition. L'interfeuillet contient deux atomes *Me* symétriquement distincts, un atome K et des molécules de H₂O. Les atomes *Me*1 et *Me*2 sont entourés de six atomes d'oxygène pour former un octaèdre difforme. Dans le cas de l'octaèdre *Me*1, deux atomes

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d'oxygène font partie du groupe $(\text{UO}_2)^{2+}$ de couches adjacentes à uranyle oxo sulfaté, et quatre font partie de quatre molécules de H_2O de l'interfeuillelet, ce qui est la même configuration que dans la structure de zinc-zippéite, cobalt-zippéite et magnésium-zippéite. Dans le cas de l'octaèdre Me_2 , quatre atomes d'oxygène font partie de groupes $(\text{UO}_2)^{2+}$ de couches adjacentes à uranyle oxo sulfaté, et deux atomes d'oxygène font partie d'une molécule de H_2O en deux positions équivalentes.

(Traduit par la Rédaction)

Mots-clés: sulfate uranilé, phases du groupe de la zippéite, structure cristalline, métal de transition.

INTRODUCTION

Knowledge of chemical composition, structure and stability of uranium minerals or compounds is the basis for understanding the genesis of uranium deposits (Fron del 1958) and the transport of radionuclides in repositories for nuclear waste (Finch *et al.* 1999). The study of uranyl sulfates fits in with these environmental studies because the oxidation of sulfides produces acidic and sulfate-rich waters, which leads to the formation of secondary minerals. Zippeite-group minerals may contain a variety of low-valence cations. They are classified into two subgroups based on the presence of monovalent or divalent cations.

Solid solutions within the divalent zippeite-subgroup phases have been found. Crystal structures of solid solutions between monovalent and divalent cations have not been described.

As the uranyl (hydr)oxo sulfate layers in the end-members zippeite and *Me*-zippeite (*Me* = zinc, nickel, cobalt, magnesium) are very similar, it is quite probable that intermediate *K*-*Me* zippeite-group phases occur in nature. The aim of our research was to synthesize some mixed monovalent cation (*K*) and divalent cation (*Mn*, *Co*, *Ni*, *Zn*) zippeite compounds under moderate pressure and temperature. Well-formed crystals suitable for single-crystal studies were obtained. In the current study, we provide evidence of the existence of such mixed compounds, and describe their crystal structures.

BACKGROUND INFORMATION

A first description of the mineralogy of the zippeite group was published by Fron del *et al.* (1976). Using hydrothermal techniques, Spitsyn *et al.* (1982) were able to synthesize basic uranyl sulfates of divalent cations starting from $Me\text{SO}_4 \cdot n\text{H}_2\text{O}$ (*Me* = *Ni*, *Mg*, *Co*, *Zn*, *Mn*, *Cd*), $\text{UO}_2\text{SO}_4 \cdot 2.5\text{H}_2\text{O}$ and $\text{UO}_2(\text{OH})_2$. They elucidated the crystal structure of the *Zn* member by carrying out a single-crystal study. The cell parameters obtained from the powder patterns for all compounds are close to those refined in the single-crystal study. The powder diagrams resemble those of natural and synthetic zippeite (Fron del *et al.* 1976).

Vochten *et al.* (1995) synthesized zippeite and determined its crystal structure using single-crystal X-ray

diffraction and suggested the formula $\text{K}[(\text{UO}_2)_2(\text{SO}_4)(\text{OH})_3] \cdot (\text{H}_2\text{O})$; they supposed that local charge-balance could be obtained through an OH^- group in the interlayer. Reconsidering bond-valence sum calculations and paying attention to the results of the chemical analysis, the formula could be better rewritten as: $\text{K}_{1.1}[(\text{UO}_2)_2(\text{SO}_4)\text{O}_{1.1}(\text{OH})_{0.9}] \cdot 1.9(\text{H}_2\text{O})$. The formula of zippeite, described by Burns *et al.* (2003) in an extensive study on the crystal chemistry of the zippeite group, can be presented in an analogous way: $\text{K}_{1.5}[(\text{UO}_2)_2(\text{SO}_4)\text{O}_{1.5}(\text{OH})_{0.5}] \cdot 1.5(\text{H}_2\text{O})$, which leads us to suggest that the *K* content of zippeite can be variable and that the formula may be written in a general way as: $\text{K}_x[(\text{UO}_2)_2(\text{SO}_4)\text{O}_x(\text{OH})_{2-x}] \cdot (3-x)(\text{H}_2\text{O})$.

The formula for magnesium-zippeite, zinc-zippeite and cobalt-zippeite is $Me[(\text{UO}_2)_2(\text{SO}_4)\text{O}_2] \cdot 3.5(\text{H}_2\text{O})$, which differs from the formula $\text{Zn}[(\text{UO}_2)_2(\text{SO}_4)(\text{OH})_4] \cdot 1.5(\text{H}_2\text{O})$ given by Spitsyn *et al.* (1982), but only in the distribution of hydrogen atoms (Burns *et al.* 2003).

The zippeite-group minerals contain characteristic topologically identical sheets of uranyl pentagonal bipyramids and sulfate tetrahedra, $(\text{UO}_2)_2(\text{SO}_4)\text{O}_x(\text{OH})_{2-x}$, although with varying quantities of *H* in the sheets. The geometry of the uranyl sulfate sheets (of "zippeite-type") is the defining element of the zippeite group, according to the new structural classification of *U* minerals (Burns 1999, Brugger *et al.* 2003). In the interlayer, monovalent (*Na*, *K*, NH_4) or divalent (*Mg*, *Zn*, *Ni*, *Co*, *Mn*) cations are located beside H_2O molecules. Various authors have described the relationship between the uranyl sulfate sheets and the interlayer configuration in minerals and synthetic compounds (Burns *et al.* 2003, Brugger *et al.* 2003, 2006).

Different types of interlayer configurations have been reported. In the case of $Me^{2+} = \text{Mg}^{2+}$, three different structures have been described (Burns *et al.* 2003, Brugger *et al.* 2003). In one case, the *Mg* octahedra share one vertex (O_{Ur}) with the sheet at either side (magnesium-zippeite, Burns *et al.* 2003), in the second case the octahedra only share a vertex (O_{Ur}) with one of the two adjacent sheets, and in the third case (marecottite, Brugger *et al.* 2003), no vertex is shared with the sheets. The interlayer atoms are commonly disordered, and the distance between the zippeite-type layers depends on the interlayer configuration in the case of a zippeite-group phase containing divalent cations (Brugger *et al.* 2003).

SYNTHESIS

A 100 mL solution of 0.075 M UO_2SO_4 was mixed with 10 mmol of $\text{MeSO}_4 \cdot n\text{H}_2\text{O}$ ($\text{Me} = \text{Mn, Co, Ni or Zn}$) and adjusted to a pH of 3.8 by means of KOH. Of this solution, 50 mL was introduced into a 170 mL teflon-lined bomb, resulting in a 30% degree of filling. The bomb was heated for 75 hours at 150°C, which resulted in an approximate pressure of 3.5 MPa. The crystals obtained were washed several times with distilled water and subsequently air-dried. They were large enough and sufficiently well formed for a single-crystal study.

A representative scanning electron micrograph in Figure 1 shows that the crystals are monoclinic. Each compound occurs with both plate-like and lath-like habits. Etch figures confirm the monoclinic symmetry.

CHEMICAL COMPOSITION

The crystals were analyzed with a Cameca SX-50 electron microprobe, operated in wavelength-dispersion spectrometer mode at 15 kV for the operating voltage, 20 nA for the incident current and 2 μm for the beam diameter. The data for the transition metal, uranium and sulfur were collected at ten different points of each crystal. The standards selected were: barite for sulfur, UO_2 for uranium, metallic manganese for manganese, metallic nickel for nickel, smithsonite for zinc, and corallite for cobalt.

The K content was determined with a Varian Ultra Mass 700 using the ICP-MS technique. The H_2O content was determined by means of a Dupont TGA 951 thermogravimetric analyzer. Results of the analysis are given in Table 1.

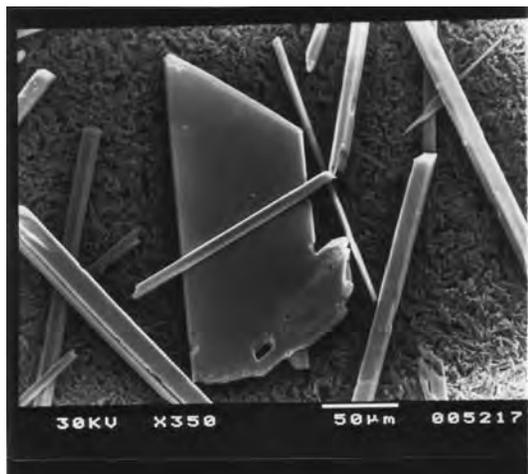


FIG. 1. A representative scanning electron micrograph of the synthetic crystals.

The formula resulting from the analysis based on the oxygen equivalent from the nine oxygen atoms of the mole ratio 2:1 of UO_3 and SO_3 are: 1) $0.68\text{MnO} \cdot 0.19\text{K}_2\text{O} \cdot 2.01\text{UO}_3 \cdot 0.99\text{SO}_3 \cdot 2.58\text{H}_2\text{O}$, 2) $0.63\text{CoO} \cdot 0.22\text{K}_2\text{O} \cdot 2.01\text{UO}_3 \cdot 0.99\text{SO}_3 \cdot 2.87\text{H}_2\text{O}$, 3) $0.62\text{NiO} \cdot 0.23\text{K}_2\text{O} \cdot 2.00\text{UO}_3 \cdot 0.99\text{SO}_3 \cdot 2.72\text{H}_2\text{O}$, and 4) $0.67\text{ZnO} \cdot 0.21\text{K}_2\text{O} \cdot 2.01\text{UO}_3 \cdot 0.99\text{SO}_3 \cdot 2.93\text{H}_2\text{O}$.

X-RAY DIFFRACTION

The selected crystals were mounted on a Stoe STADI4 four-circle diffractometer, equipped with graphite-monochromated $\text{MoK}\alpha$ radiation, and computer controlled by the program DIF4 (Stoe & Cie 1988a). The unit-cell dimensions and orientation matrix were obtained by least-squares refinement of the setting angles of 24 centered reflections. The monoclinic system and C lattice were determined from cell dimensions and observed symmetry. The C lattice was determined from systematic absences on Weissenberg films. The X-ray intensities were collected in the ω -scan mode. The systematically absent reflections due to the C lattice were not measured. Three reflections were used as intensity standards to monitor the measurements at one-hour interval. The data were reduced and corrected for Lorentz and polarization effects using the program REDU4 (Stoe & Cie 1988b). A Gaussian absorption correction was applied with the program PLATON (Spek 1998). Systematic absences revealed the existence of a c glide plane, resulting in a space group $C2/c$. The experimental conditions for data measurements and information about the selected crystals are given in Table 2.

STRUCTURE DETERMINATION

As the K-Me -bearing zippeite-group phases and zippeite have similar cell parameters and content, the structure solution was started with the zippeite coordinates of the uranyl (hydr)oxo sulfate sheet layer (Vochten *et al.* 1995). The refinement of the crystal structure was based on F^2 for all unique data using the program SHELXL (Sheldrick 1997). The model refined isotropically to a rather high R -value, approximately 0.25. Comparing the systematic absences of the

TABLE 1. CHEMICAL COMPOSITION OF SYNTHETIC K-Me -BEARING ZIPPEITE-GROUP PHASES

	K-Mn	K-Co	K-Ni	K-Zn
UO_3 wt%	76.78	75.94	75.98	75.90
SO_3	10.57	10.47	10.54	10.49
MeO	6.32	6.28	6.10	7.20
K_2O	2.40	2.78	2.85	2.64
H_2O	6.20	6.84	6.50	6.97
Total	102.27	102.31	101.97	103.20

synthetic products and zippeite revealed that the pseudo *A* and *B* centering present in zippeite did not conform to the presence of reflections in the odd, odd, even parity-group of those products. The crystals thus seem to be twinned, and the diffraction pattern corresponds to the superposition of two reciprocal lattices. By applying the twin law $[\bar{1}00/0\bar{1}0/101]$, the model containing only the uranyl sheet atoms refined isotropically to an *R* value of approximately 0.11 for each of the four *K-Me* products. The interlayer atoms could be positioned by inspection of difference-Fourier maps. One *K* atom, two *Me* atoms (*Me*1 and *Me*2) on symmetrically distinct positions and three *O* atoms (*O*9, *O*11, *O*12) were found. The fourth *O* atom (*O*10), the one that completes the octahedral configuration of *Me*1, was obtained by splitting the *K* site in a partially occupied *K* site and *O* site. In this model, the *O*12 atom lies on a center of symmetry and is a common vertex of two symmetrically related *Me*1 octahedra. As an H_2O molecule or an OH^- group cannot be positioned on a center of symmetry, this model has been shifted $\frac{1}{4}$ in *x* and *z* so that *Me*2 and *O*12 lie on a twofold axis. The sulfur atom is now in a general position. Such a shift is possible because of the pseudo half-cell translations in the three cell directions. Refine-

ment of this model gave similar results as with the atom coordinates of the uranyl sheet in zippeite. Refinements of the occupancy factors of the interlayer atoms are given in Table 3. The values obtained are in fair agreement with results of the chemical analysis. The results of the final refinement with the occupancy factors set at their ideal values are given in Tables 4, 5, 6 and 7. Tables of calculated and observed structure-factors are available from the Depository of Unpublished Data, MAC website [document Zippeite cm46_173].

DESCRIPTION OF THE STRUCTURE

Like zippeite (Vochten *et al.* 1995, Burns *et al.* 2003), the mixed *K-Me* (*Mn*, *Co*, *Ni*, *Zn*) zippeite-type materials possess a layer structure. The *U* and *S* coordination polyhedra are located in layers parallel to (010) and are interconnected through *K* and *Me* cations, and H_2O molecules in the interlayer.

Sheets of uranyl (hydr)oxo sulfate polyhedra

The structure contains two symmetrically distinct *U* positions related by a pseudo half-cell translation

TABLE 2. CRYSTAL DATA AND RESULTS OF REFINEMENT OF SYNTHETIC *K-Me*-BEARING ZIPPEITE-GROUP PHASES

Compound	K-Mn	K-Co	K-Ni	K-Zn
Crystal size (mm)	0.28×0.28×0.010	0.31×0.036×0.036	0.32×0.038×0.038	0.15×0.15×0.017
Shape	plate	needle	needle	plate
Color	orange	orange	orange	orange
<i>a</i> (Å)	8.661(6)	8.651(5)	8.662(5)	8.650(6)
<i>b</i> (Å)	14.375(8)	14.188(8)	14.095(8)	14.180(12)
<i>c</i> (Å)	17.705(12)	17.713(13)	17.770(9)	17.709(13)
β (°)	104.12(5)	104.14(6)	104.18(5)	104.14(6)
<i>V</i> (Å ³)	2138(2)	2108(2)	2103(2)	2106(3)
Formula weight	782.92	785.92	785.75	790.74
<i>F</i> (000)	2706	2718	2724	2736
Space group	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>Z</i>	8	8	8	8
Formula	$\text{O}_{13}\text{H}_6\text{Mn}_{0.75}\text{K}_{0.5}\text{S}_1\text{U}_2$	$\text{O}_{13}\text{H}_6\text{Co}_{0.75}\text{K}_{0.5}\text{S}_1\text{U}_2$	$\text{O}_{13}\text{H}_6\text{Ni}_{0.75}\text{K}_{0.5}\text{S}_1\text{U}_2$	$\text{O}_{13}\text{H}_6\text{Zn}_{0.75}\text{K}_{0.5}\text{S}_1\text{U}_2$
<i>D_c</i> (g/cm ³)	4.865	4.952	4.962	4.988
<i>D_x</i> (g/cm ³)	4.7(2)	4.8(2)	4.9(2)	4.9(2)
μ (mm ⁻¹)	31.57	32.29	32.52	32.85
$2\theta_{\text{max}}$ (°)	50.01	49.99	54.98	54.99
<i>hkl</i> ranges	-10 ≤ <i>h</i> ≤ 10 -17 ≤ <i>k</i> ≤ 17 -21 ≤ <i>l</i> ≤ 21	-10 ≤ <i>h</i> ≤ 2 -2 ≤ <i>k</i> ≤ 16 -21 ≤ <i>l</i> ≤ 21	-2 ≤ <i>h</i> ≤ 11 -2 ≤ <i>k</i> ≤ 18 -22 ≤ <i>l</i> ≤ 22	-11 ≤ <i>h</i> ≤ 10 0 ≤ <i>k</i> ≤ 18 0 ≤ <i>l</i> ≤ 22
Total reflections	7627	3043	3789	3900
Unique reflections	1879	1835	2394	2420
<i>T_{max}</i>	0.57	0.35	0.36	0.43
<i>T_{min}</i>	0.03	0.28	0.28	0.10
<i>R_{int}</i>	0.0618	0.0430	0.0435	0.110
Observed reflections, <i>F</i> ≥ 4 σ_F	1236	1132	1477	1246
<i>R</i>	0.0525	0.0459	0.0383	0.0690
<i>S</i>	1.068	0.920	0.962	0.882
$\Delta\rho_{\text{max}}$ (eÅ ⁻³)	3.51	4.43	3.55	6.88
$\Delta\rho_{\text{min}}$ (eÅ ⁻³)	-10.09	-2.03	-3.44	-5.37
Twin component	0.8940(4)	0.4307(11)	0.7578(7)	0.1989(12)
Extinction coef.	0.0168(3)	0.00011(1)	0.00013(1)	0.00061(2)

in the *a* direction. The bond-valence sums (Table 8) and polyhedron geometries (Table 9, 10) are consistent with both of these sites containing U^{6+} . Each U^{6+} cation is surrounded by two apical O atoms forming an approximately linear $(UO_2)^{2+}$ uranyl ion (designated *Ur*) and five equatorial O atoms, resulting in an UrO_5 pentagonal bipyramid. Each UrO_5 shares two adjacent equatorial edges with neighboring UrO_5 , resulting in an infinite zigzag chain two UrO_5 polyhedra in width along the *a* direction. This double UrO_5 chain of polyhedra is connected on both sides through S–O tetrahedra, resulting in a sheet with the uranyl ions oriented approximately perpendicular to the sheet (Fig. 2, Bergerhoff 1996). The four O atoms of the sulfate group are part of four different UrO_5 polyhedra, so that the double UrO_5 chain and the (SO_4) tetrahedra polymerize only by corner sharing.

As usual for uranyl phases, it was not possible to determine the positions of the H atoms from the X-ray-diffraction data. Depending on the possible compositions of the sheet, $[(UO_2)_2SO_4(OH)_2]$, $[(UO_2)_2SO_4(OH)O]$ and $[(UO_2)_2SO_4O_2]$, the charge of the structural unit of the sheet must be 0, –1 and –2, respectively. Bond-

valence analysis (Table 8) shows that for the K–*Me* zippeite-group phases, the O3 and O4 atoms, which are both bonded to three U atoms, have bond-valences values close to 2, so that the sheet composition is $[(UO_2)_2SO_4O_2]^{2-}$.

Interlayer constituents

The interlayer occurs at $y \approx 0.25$ and 0.75 and contains two symmetrically distinct *Me* atoms, one K atom and four O atoms. It is known from the refinement that the K and *Me* sites are only half populated, and that *Me*2 lies on a twofold axis. The resulting charge of the interlayer is therefore $0.5 K^+ + 0.5 Me1^{2+} + 0.25$

TABLE 5. FINAL ATOMIC PARAMETERS FOR SYNTHETIC K–Co-BEARING ZIPPEITE-GROUP PHASE

	occupancy	x	y	z	$^*U_{eq}$
U1	1.00	0.41504(10)	0.01901(4)	0.33474(2)	0.0070(1)
U2	1.00	0.91870(13)	-0.01831(5)	0.33490(3)	0.0102(2)
Co1	0.50	0.9448(6)	0.2513(11)	0.37280(19)	0.0225(7)
Co2	0.25	1/2	0.2495(16)	1/4	0.0124(10)
K1	0.50	0.1914(13)	0.251(3)	0.3992(4)	0.0462(19)
S1	1.00	0.7510(17)	0.00202(17)	0.5008(8)	0.0121(5)
O1	1.00	0.405(2)	0.1463(6)	0.3182(6)	0.016(2)
O1'	1.00	0.4316(16)	-0.1037(5)	0.3650(5)	0.0030(19)
O2	1.00	0.932(2)	0.1044(6)	0.3597(8)	0.030(3)
O2'	1.00	0.908(2)	-0.1434(6)	0.3155(6)	0.013(3)
O3	1.00	0.636(2)	0.0008(5)	0.2957(5)	0.000(2)
O4	1.00	0.151(4)	0.0069(9)	0.2941(7)	0.027(3)
O5	1.00	0.8385(15)	-0.0592(9)	0.4542(7)	0.018(3)
O6	1.00	0.6968(13)	-0.0600(7)	0.5541(6)	0.002(2)
O7	1.00	0.6218(13)	0.0525(8)	0.4537(6)	0.010(3)
O8	1.00	0.8650(13)	0.0738(7)	0.5516(6)	0.005(2)
O9	1.00	0.7089(12)	0.248(3)	0.3346(5)	0.023(2)
O10	0.50	0.195(2)	0.242(2)	0.4264(9)	0.014(4)
O11	1.00	0.9537(14)	0.252(5)	0.4968(8)	0.062(4)
O12	0.50	0	0.248(7)	1/4	0.058(5)

* $U_{eq} = \frac{1}{2} \sum_i \sum_j U_i \beta_j \alpha_j' \alpha_j \alpha_j'$ for the U atoms, and $U_{eq} = U_{iso}$ for the other atoms.

TABLE 3. REFINED OCCUPANCY OF INTER-LAYER ATOMS OF SYNTHETIC K–Me-BEARING ZIPPEITE-GROUP PHASES

	K–Mn	K–Co	K–Ni	K–Zn
Me1	0.484(4)	0.484(4)	0.442(3)	0.461(8)
Me2	0.248(3)	0.238(3)	0.199(2)	0.226(4)
K1	0.389(8)	0.385(9)	0.299(6)	0.37(1)
O9	1.00(2)	1.00(2)	1.00(1)	1.00(4)
O10	0.70(2)	0.76(2)	0.77(2)	0.79(4)
O11	1.00(2)	1.00(3)	1.00(2)	1.00(4)
O12	0.54(2)	0.55(2)	0.54(2)	0.37(3)

TABLE 4. FINAL ATOMIC PARAMETERS FOR SYNTHETIC K–Mn-BEARING ZIPPEITE-GROUP PHASE

	occupancy	x	y	z	$^*U_{eq}$
U1	1.00	0.41820(5)	0.01872(2)	0.33547(2)	0.0076(1)
U2	1.00	0.91460(5)	-0.01879(3)	0.33410(2)	0.0049(1)
Mn1	0.50	0.9512(3)	0.2506(5)	0.37572(16)	0.0152(5)
Mn2	0.25	1/2	0.2501(7)	1/4	0.0102(7)
K1	0.50	0.2013(7)	0.2508(10)	0.4049(3)	0.0337(11)
S1	1.00	0.7473(7)	0.00300(14)	0.4989(4)	0.0111(4)
O1	1.00	0.4193(11)	0.1444(5)	0.3179(6)	0.0182(18)
O1'	1.00	0.4333(10)	-0.1056(5)	0.3575(5)	0.0114(15)
O2	1.00	0.9397(11)	0.1012(5)	0.3700(5)	0.0102(16)
O2'	1.00	0.8896(9)	-0.1415(4)	0.3150(5)	0.0038(15)
O3	1.00	0.6469(11)	-0.0067(5)	0.2932(5)	0.0133(16)
O4	1.00	0.1475(10)	-0.0064(5)	0.2957(4)	0.0044(15)
O5	1.00	0.8142(10)	-0.0591(6)	0.4542(5)	0.0171(18)
O6	1.00	0.6730(10)	-0.0560(6)	0.5524(5)	0.0124(18)
O7	1.00	0.6215(10)	0.0595(5)	0.4546(5)	0.0141(17)
O8	1.00	0.8638(9)	0.0679(5)	0.5539(5)	0.0083(16)
O9	1.00	0.7072(10)	0.2484(15)	0.3354(5)	0.0318(17)
O10	0.50	0.2006(19)	0.2423(17)	0.4292(9)	0.025(3)
O11	1.00	0.9498(10)	0.2546(13)	0.4967(5)	0.0324(18)
O12	0.50	0	0.250(3)	1/4	0.046(3)

* $U_{eq} = \frac{1}{2} \sum_i \sum_j U_i \beta_j \alpha_j' \alpha_j \alpha_j'$ for the U atoms, and $U_{eq} = U_{iso}$ for the other atoms.

TABLE 6. FINAL ATOMIC PARAMETERS FOR SYNTHETIC K–Ni-BEARING ZIPPEITE-GROUP PHASE

	occupancy	x	y	z	$^*U_{eq}$
U1	1.00	0.41719(5)	0.01812(3)	0.33493(2)	0.0137(1)
U2	1.00	0.91652(7)	-0.01847(3)	0.33490(2)	0.0148(1)
Ni1	0.50	0.9382(4)	0.2491(11)	0.36853(13)	0.0305(5)
Ni2	0.25	1/2	0.2503(17)	1/4	0.0285(7)
K1	0.50	0.1916(12)	0.250(4)	0.4007(5)	0.089(2)
S1	1.00	0.7509(16)	0.00185(12)	0.5000(9)	0.0179(3)
O1	1.00	0.4169(13)	0.1432(7)	0.3144(5)	0.031(2)
O1'	1.00	0.4250(11)	-0.1080(5)	0.3587(4)	0.0176(16)
O2	1.00	0.9380(14)	0.1050(6)	0.3681(5)	0.026(2)
O2'	1.00	0.9040(12)	-0.1482(6)	0.3182(4)	0.0141(16)
O3	1.00	0.6415(12)	-0.0128(5)	0.2919(4)	0.0149(13)
O4	1.00	0.1537(14)	-0.0086(5)	0.2978(4)	0.0170(15)
O5	1.00	0.8075(10)	-0.0669(6)	0.4468(4)	0.0196(17)
O6	1.00	0.6680(10)	-0.0563(6)	0.5466(5)	0.0195(19)
O7	1.00	0.6257(10)	0.0530(6)	0.4493(4)	0.0188(17)
O8	1.00	0.8693(9)	0.0720(5)	0.5492(4)	0.0107(16)
O9	1.00	0.7029(8)	0.251(3)	0.3353(3)	0.0247(13)
O10	0.50	0.1908(15)	0.249(5)	0.4443(7)	0.027(3)
O11	1.00	0.9540(13)	0.249(6)	0.4991(6)	0.081(3)
O12	0.50	0	0.246(9)	1/4	0.126(8)

* $U_{eq} = \frac{1}{2} \sum_i \sum_j U_i \beta_j \alpha_j' \alpha_j \alpha_j'$ for the U atoms, and $U_{eq} = U_{iso}$ for the other atoms.

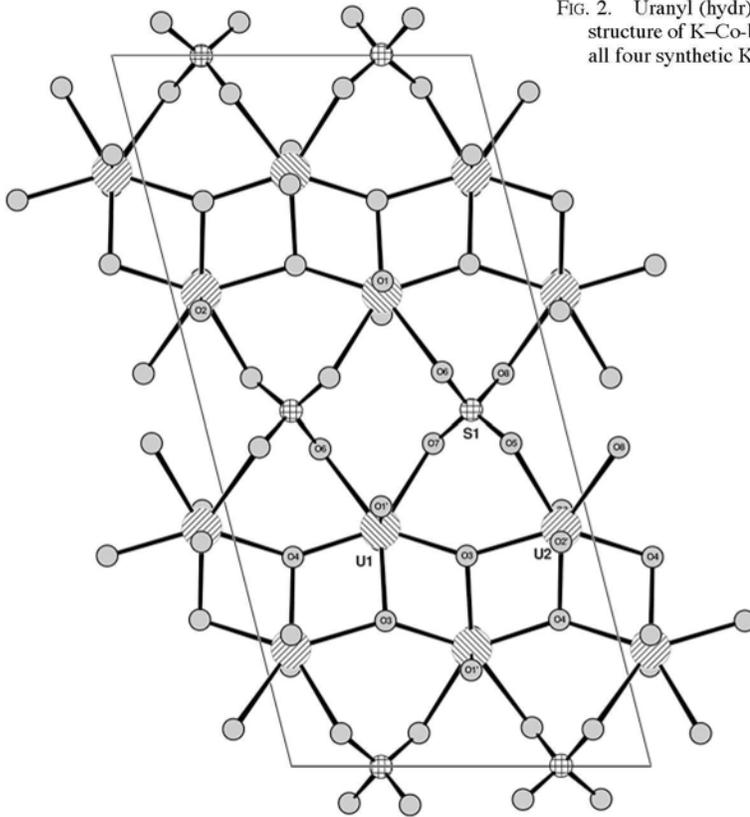


FIG. 2. Uranyl (hydr)oxo sulfate sheet at $\gamma \approx 0$ and $\frac{1}{2}$ in the structure of K-Co-bearing zippeite-group phase, typical of all four synthetic K-Me compounds.

TABLE 7. FINAL ATOMIC PARAMETERS FOR SYNTHETIC K-Zn-BEARING ZIPPEITE-GROUP PHASE

	occupancy	x	y	z	U_{eq}
U1	1.00	0.41884(10)	0.01922(5)	0.33416(4)	0.0099(2)
U2	1.00	0.91483(9)	-0.01826(6)	0.33517(4)	0.0055(2)
Zn1	0.50	0.9478(6)	0.2488(10)	0.3753(3)	0.0238(8)
Zn2	0.25	1/2	0.2480(12)	1/4	0.0145(11)
K1	0.50	0.1923(13)	0.250(2)	0.4001(6)	0.0309(19)
S1	1.00	0.7561(10)	0.0027(2)	0.4980(7)	0.0121(8)
O1	1.00	0.418(2)	0.1445(6)	0.3143(9)	0.014(3)
O1'	1.00	0.4261(16)	-0.1051(6)	0.3605(7)	0.000(2)
O2	1.00	0.943(3)	0.1017(8)	0.3702(14)	0.051(6)
O2'	1.00	0.8910(19)	-0.1438(6)	0.3201(9)	0.010(3)
O3	1.00	0.652(2)	-0.0091(10)	0.2969(10)	0.017(3)
O4	1.00	0.146(2)	-0.0040(8)	0.2935(9)	0.006(3)
O5	1.00	0.8260(18)	-0.0479(10)	0.4518(9)	0.011(3)
O6	1.00	0.6906(17)	-0.0680(9)	0.5526(9)	0.006(3)
O7	1.00	0.616(2)	0.0676(11)	0.4565(10)	0.019(4)
O8	1.00	0.8646(17)	0.0622(10)	0.5519(9)	0.007(3)
O9	1.00	0.7035(17)	0.254(2)	0.3344(8)	0.028(3)
O10	0.50	0.199(3)	0.243(3)	0.4303(14)	0.016(5)
O11	1.00	0.953(2)	0.250(5)	0.4941(11)	0.046(4)
O12	0.50	0	0.252(8)	1/4	0.058(7)

* $U_{eq} = \frac{1}{3} \sum_i \sum_j U_j a_i^2 a_j^2 a_i \cdot a_j$ for the U atoms, and $U_{eq} = U_{oc}$ for the other atoms.

TABLE 8. BOND-VALENCE SUMS* (νu) AT ATOMIC POSITIONS, EXCLUDING CONTRIBUTIONS FROM HYDROGEN ATOMS, IN THE STRUCTURES OF SYNTHETIC K-Me-BEARING ZIPPEITE-GROUP PHASES

	K-Mn	K-Co	K-Ni	K-Zn
U1	5.89	6.07	6.07	5.75
U2	5.87	5.85	5.58	6.15
S1	6.09	5.93	5.83	6.14
O1	1.96	1.89	1.96	2.01
O1'	1.98	1.93	1.91	1.91
O2	1.89	1.98	1.88	1.95
O2'	1.98	1.95	1.81	1.92
O3	1.93	1.90	1.89	1.94
O4	1.91	1.95	1.88	1.90
O5	2.30	1.86	1.90	2.72
O6	1.92	2.16	2.05	1.65
O7	2.13	2.22	2.20	1.62
O8	1.86	1.64	1.66	2.08
Interlayer containing Me1				
Me1	2.28	1.87	1.69	1.90
O9	0.48	0.43	0.42	0.38
O10	0.39	0.30	0.19	0.30
O11	0.38	0.27	0.18	0.35
O12	0.42	0.35	0.35	0.33
Interlayer containing K1 and Me2				
K1	0.84	0.92	1.00	0.95
Me2	2.24	1.86	1.80	1.97
O9	0.48	0.40	0.37	0.43
O11	0.16	0.16	0.16	0.17
O12	0.27	0.37	0.34	0.36

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

$Me2^{2+} = +2$, which counterbalances the -2 charge of the uranyl oxo sulfate sheet. Consequently, the O atoms in the interlayer belong to H_2O molecules, a conclusion strongly supported by the bond-valence calculations for these atoms (Table 8).

The distance between the $Me1$ atom and the K atom is about 2 \AA , so they are mutually exclusive, and only one position is occupied locally. The $Me1$ and $Me2$ atoms are also mutually exclusive, as this situation would result in an interlayer charge of $+3$, whereas the interlayer (as proved, without negative OH^- groups) can only accommodate a maximum charge of $+2$. The crystals are therefore built up of 50% of cells containing the $Me1$ configuration in the interlayer (Fig. 3) and 50% of cells containing the K- $Me2$ combination in the interlayer (Fig. 4). The exact distribution of the cells cannot be revealed from X-ray data.

The K cation is coordinated by an irregular polyhedron of nine O atoms; three are H_2O molecules contained in the interlayer, four are O_{Ur} atoms, and two

are O atoms of sulfate groups. The latter six atoms are part of the two adjacent sheets of uranyl oxo sulfate polyhedra (Fig. 4).

Both Me cations are coordinated by six O atoms forming distorted octahedra. In the $Me1$ octahedron, two O atoms are part of Ur of adjacent uranyl oxo sulfate layers, and four are part of the four H_2O molecules of the interlayer (Fig. 3). The $Me1$ octahedra related by a twofold axis symmetry are connected through the common vertex O12, which is the same configuration as found in the crystal structure of, for example, zinc-zippeite (Spitsyn *et al.* 1982, Burns *et al.* 2003). In the $Me2$ octahedron, four O atoms are part of Ur of the adjacent uranyl oxo sulfate layers and two O atoms are part of two equivalent positions of the O9 H_2O group (Fig. 4).

SUMMARY AND CONCLUSIONS

The crystal structure of four synthetic potassium – transition metal (Zn, Ni, Co, Mn) zippeite-group phases

TABLE 9. SELECTED INTERATOMIC DISTANCES (Å) FOR SYNTHETIC K-*Me*-BEARING ZIPPEITE-GROUP PHASES

	K-Mn	K-Co	K-Ni	K-Zn
U1-O1	1.834(7)	1.828(9)	1.800(10)	1.811(9)
U1-O1'	1.827(7)	1.817(7)	1.825(7)	1.821(9)
U1-O3	2.311(10)	2.201(17)	2.297(10)	2.305(18)
U1-O3,a	2.239(9)	2.259(9)	2.229(7)	2.287(17)
U1-O4	2.306(9)	2.23(3)	2.247(12)	2.317(18)
U1-O6,b	2.370(9)	2.465(11)	2.455(9)	2.515(15)
U1-O7	2.466(9)	2.453(11)	2.416(8)	2.504(17)
U2-O2	1.833(7)	1.792(9)	1.832(9)	1.807(14)
U2-O2'	1.799(6)	1.806(9)	1.851(8)	1.804(9)
U2-O3	2.261(10)	2.389(17)	2.318(10)	2.212(18)
U2-O4,c	2.287(9)	2.32(3)	2.310(12)	2.303(18)
U2-O4,a	2.236(7)	2.245(12)	2.291(7)	2.219(16)
U2-O5	2.553(9)	2.449(12)	2.496(8)	2.410(16)
U2-O8,d	2.501(9)	2.515(11)	2.526(7)	2.483(15)
S1-O5	1.408(10)	1.521(17)	1.517(14)	1.338(18)
S1-O6	1.526(10)	1.451(16)	1.471(15)	1.437(18)
S1-O7	1.430(10)	1.416(17)	1.424(15)	1.556(19)
S1-O8	1.535(10)	1.545(15)	1.534(14)	1.590(17)
Me1-O1',e	2.092(10)	2.063(17)	2.023(17)	2.091(17)
Me1-O2	2.151(10)	2.097(18)	2.031(18)	2.088(18)
Me1-O9	2.059(9)	2.004(12)	1.978(8)	2.061(16)
Me1-O10	2.140(17)	2.145(18)	2.269(13)	2.15(3)
Me1-O11	2.146(9)	2.179(14)	2.291(11)	2.09(2)
Me1-O12	2.365(3)	2.339(4)	2.297(3)	2.370(7)
Me2-O1	2.157(11)	2.18(2)	2.12(2)	2.085(18)
Me2-O1,a	2.157(11)	2.18(2)	2.12(2)	2.085(18)
Me2-O2',f	2.282(10)	2.18(2)	2.168(18)	2.314(18)
Me2-O2',g	2.282(10)	2.18(2)	2.168(18)	2.314(18)
Me2-O9	2.045(9)	2.035(10)	2.020(6)	2.014(15)
Me2-O9,a	2.045(9)	2.035(10)	2.020(6)	2.014(15)
K-O1	3.114(13)	3.00(3)	3.15(3)	3.13(2)
K-O1',f	3.066(14)	3.00(3)	3.01(4)	3.04(2)
K-O2,i	3.075(14)	3.01(3)	2.95(4)	2.97(3)
K-O2',f	2.976(12)	3.05(3)	2.99(3)	2.90(2)
K-O5,f	2.961(16)	3.04(4)	2.82(5)	3.14(3)
K-O6,b	3.033(16)	2.93(4)	3.04(5)	2.82(3)
K-O11,j	3.018(11)	2.992(17)	3.009(15)	2.96(2)
K-O11,j	3.099(11)	3.171(17)	3.149(15)	3.18(2)
K-O12,i	2.868(6)	2.755(8)	2.784(9)	2.770(11)

$a = 1 - x, y, \frac{1}{2} - z$; $b = 1 - x, -y, 1 - z$; $c = 1 + x, y, z$; $d = 2 - x, -y, 1 - z$; $e = \frac{1}{2} + x, \frac{1}{2} + y, z$; $f = -\frac{1}{2} + x, \frac{1}{2} + y, z$; $g = \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; $i = -1 + x, y, z$; $j = \frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.

TABLE 10. SELECTED INTERATOMIC ANGLES (°) FOR SYNTHETIC K-*Me*-BEARING ZIPPEITE-GROUP PHASES

	K-Mn	K-Co	K-Ni	K-Zn
O1-U1-O1'	175.5(4)	172.3(4)	177.7(4)	176.4(6)
O1-U1-O3	93.5(4)	94.4(6)	94.5(4)	94.5(7)
O1-U1-O3,a	89.9(4)	87.7(4)	89.9(3)	89.3(6)
O1-U1-O4	98.6(4)	91.1(6)	98.8(4)	97.1(6)
O1-U1-O6,b	86.3(4)	83.2(5)	88.5(4)	84.3(6)
O1-U1-O7	83.0(4)	86.7(5)	86.3(4)	82.5(6)
O3,a-U1-O4	71.3(30)	74.4(6)	72.9(3)	70.1(6)
O4-U1-O6,b	76.7(3)	72.9(5)	78.0(3)	74.5(5)
O6,b-U1-O7	62.9(3)	67.3(4)	63.5(3)	62.9(5)
O7-U1-O3	79.9(3)	77.7(4)	78.4(3)	80.6(6)
O3-U1-O3,a	70.6(3)	68.5(5)	68.2(3)	73.4(6)
O2-U2-O2'	170.6(4)	178.9(5)	170.7(3)	168.7(9)
O2-U2-O3	93.7(4)	87.8(6)	95.1(4)	95.3(9)
O2-U2-O4,c	89.5(4)	85.3(6)	90.4(4)	88.4(9)
O2-U2-O4,a	105.1(3)	94.6(5)	104.7(3)	104.2(8)
O2-U2-O5	87.7(3)	91.9(5)	91.8(4)	85.1(8)
O2-U2-O8,d	89.3(3)	96.7(5)	91.4(3)	87.0(8)
O3-U2-O5	75.7(3)	78.0(4)	73.3(3)	75.7(6)
O5-U2-O8,d	68.1(3)	63.2(4)	67.3(3)	67.0(5)
O8,d-U2-O4,c	72.3(3)	76.4(5)	74.0(3)	74.0(5)
O4,c-U2-O4,a	72.3(3)	72.3(10)	74.5(4)	70.7(6)
O4,a-U2-O3	72.2(3)	71.6(9)	70.5(4)	73.3(6)
O2-Me1-O1',e	168.1(4)	169.4(5)	174.6(4)	169.8(8)
O2-Me1-O9	86.8(7)	85.3(14)	90.7(14)	90.7(11)
O2-Me1-O10	89.7(7)	90.5(10)	90.1(19)	89.3(14)
O2-Me1-O11	93.6(6)	96(2)	90(2)	93(2)
O2-Me1-O12	88.2(11)	84.(2)	89(3)	89(3)
O9-Me1-O12	94.5(3)	96.4(3)	100.4(2)	94.8(5)
O12-Me1-O10	91.3(4)	89.8(5)	97.9(3)	91.3(7)
O10-Me1-O11	79.1(5)	76.7(6)	65.7(4)	77.0(8)
O11-Me1-O9	95.2(3)	96.9(5)	96.0(4)	97.0(7)
O1-Me2-O2',f	88.1(3)	86.4(4)	86.6(4)	86.3(5)
O2',f-Me2-O2',g	93.8(4)	91.5(10)	97.4(10)	96.9(8)
O1-Me2-O1,a	90.4(5)	95.7(10)	89.4(10)	90.5(8)
O9-Me2-O1	86.0(6)	88.2(10)	86.9(10)	88.7(8)
O9-Me2-O1,a	93.6(6)	91.0(10)	93.5(10)	94.7(9)
O9-Me2-O2',f	91.8(5)	89.1(10)	87.7(9)	88.3(8)
O9-Me2-O2',g	88.6(5)	91.7(10)	91.9(10)	88.5(8)

$a = 1 - x, y, \frac{1}{2} - z$; $b = 1 - x, -y, 1 - z$; $c = 1 + x, y, z$; $d = 2 - x, -y, 1 - z$; $e = \frac{1}{2} + x, \frac{1}{2} + y, z$; $f = -\frac{1}{2} + x, \frac{1}{2} + y, z$; $g = \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; $i = -1 + x, y, z$; $j = \frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.

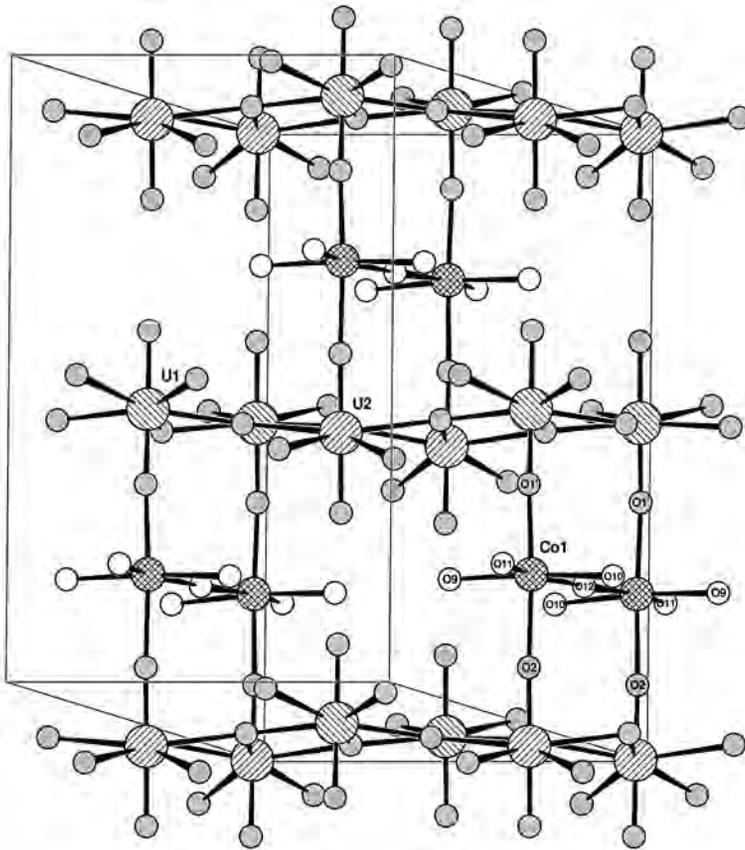


FIG. 3. View of the coordination of the *Me1* cation in the interlayer at $y \approx \frac{1}{4}$ and $\frac{3}{4}$ for the *Me1*-occupied cells in the structures of the K-*Me*-bearing zippeite-group phases (K-Co member shown).

have been determined and refined. The crystal structures obtained are intermediate phases between synthetic zippeite (Vochten *et al.* 1995, Burns *et al.* 2003) and a divalent-transition-metal zippeite-group phase (Spitsyn *et al.* 1982, Burns *et al.* 2003, Brugger *et al.* 2006). The geometry of the uranyl sulfate layers corresponds to the zippeite-type sheets. The interlayer is occupied by two symmetrically distinct divalent atoms (*Me1* and *Me2*), a K atom and H₂O molecules. With the metal atom at the *Me1* position, the structure obtained is isostructural with synthetic zinc-zippeite (Spitsyn *et al.* 1982) and with synthetic magnesium-zippeite and cobalt-zippeite (Burns *et al.* 2003). With the metal at the *Me2* position, a new interlayer disposition shows up, characterized by the binding of the *Me2* atom to four uranyl oxygen atoms and two H₂O molecules. Thus, the interlayer is not only described by the K and *Me1* coordinations as

found in the end members, but also by the coordination of *Me2*.

In this study, we demonstrate that K and divalent transition-metals can occur together in the interlayer between the zippeite-type sheets of uranyl (hydr)oxo sulfate polyhedra. The formula inferred from the crystal structures is: $K_{0.5}Me_{0.75}[(UO_2)_2SO_4O_2] \cdot 3H_2O$.

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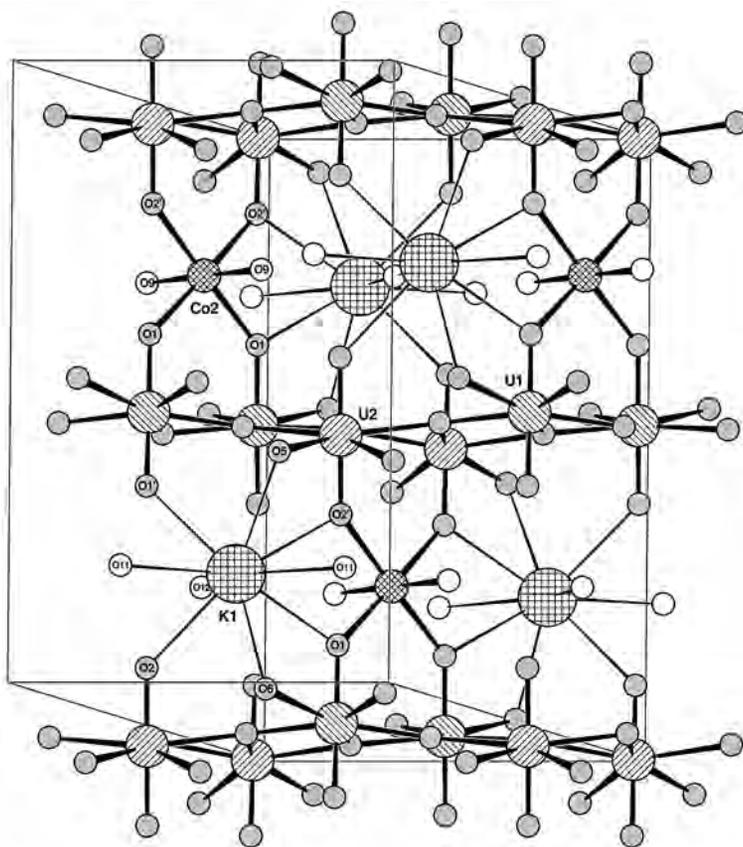


FIG. 4. View of the coordination of the *Me*₂ and K cation in the interlayer at $y \approx \frac{1}{4}$ and $\frac{3}{4}$ for the *Me*₂- and K-occupied cells in the structures of the K-*Me*-bearing zippeite-group phases (K-Co member shown).

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