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Redetermination of dipotassium diuranyl tris(oxalate) tetrahydrate

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The redetermined structure of $K_2(UO_2)_2(C_2O_4)_3 \cdot 4H_2O$ shows significantly improved precision of the positional and displacement parameters. Linear uranyl cations are connected by tetradentate bridging oxalate groups yielding a two-dimensional network. These nets are stacked to form the crystal structure.

Comment

We are currently studying the structure, relative stability, and intramolecular exchange pathways for different configuration isomers of uranyl oxalate complexes in solution, using quantum mechanical *ab initio* methods and EXAFS (Vallet *et al.*, 2002). Accurate structure information on such isomers in the solid state is important for this study. Data for the title compound are available, but they do not have sufficiently high precision to enable us to draw conclusions on structure differences between solution and the solid state and between experimental and theory-based distances. For this reason, we have redetermined the structure of $K_2(UO_2)_2(C_2O_4)_3 \cdot 4H_2O$, for which there exists only a structure determination based on film methods (Jayadevan *et al.*, 1975). In spite of the very high absorption coefficient, only an approximate absorption correction, assuming a cylindrical shape of the crystal, was applied in the previous determination. Furthermore, only the U atom was refined using anisotropic displacement parameters. In the present determination, using diffractometer data and applying numerical absorption corrections, all bond
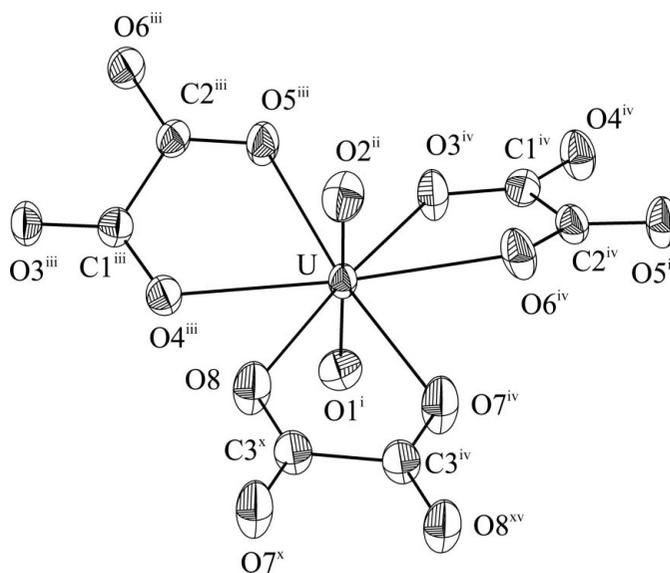

Figure 1
The coordination of the uranyl ion in $K_2(UO_2)_2(C_2O_4)_3 \cdot 4H_2O$. Displacement ellipsoids are drawn at the 70% probability level.
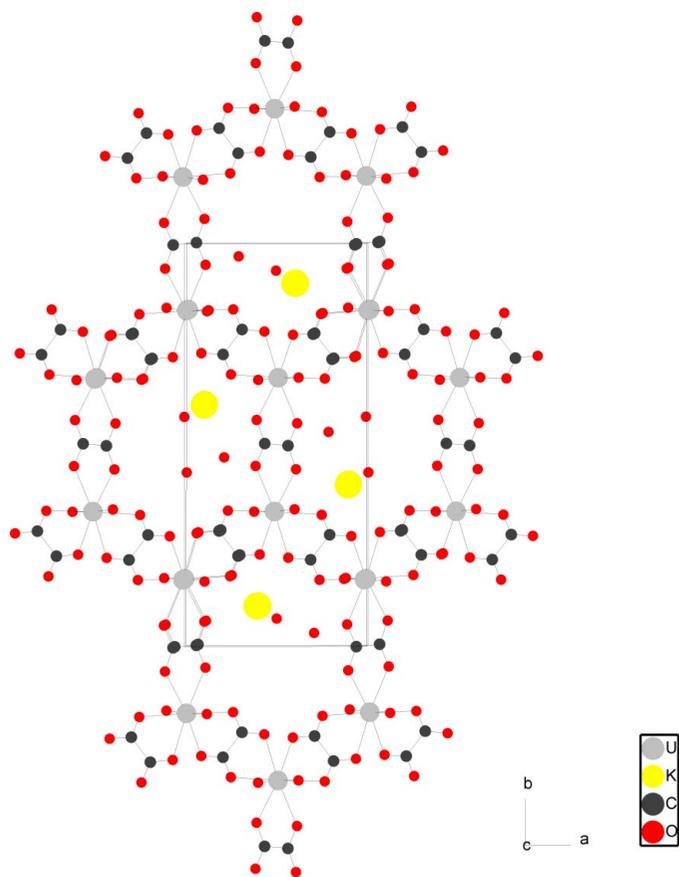
Figure 2
The two-dimensional network in $K_2(UO_2)_2(C_2O_4)_3 \cdot 4H_2O$.

lengths and angles have s.u.'s that are one order of magnitude better than in the original paper. The K atom was refined using a split position, improving the quality of the structural model.

Each uranyl ion is coordinated by three oxalate ions, yielding a coordination of six O atoms in the plane perpendicular to the uranyl ion (Fig. 1). Each of the oxalate ions acts as a tetradentate bridging ligand that connects two uranyl ions, forming a two-dimensional uranyl–oxalate network. These planes are stacked along [102]. As can be seen in Fig. 2, spacious channels are formed due to the geometry of the uranyl-oxalate network. These channels contain the potassium ions and the waters of crystallization. The uranyl complex is similar to that described earlier, but some of the bond lengths deviate significantly from the ones reported before, even taking into account the high s.u. (0.04 Å) of the U—O bond length reported there. The distances within the uranyl group are (within the s.u.'s) identical. The average U—O distance is 1.766 (4) Å, which is slightly longer than in ammonium uranyl tris(oxalate) (Alcock, 1973a), where the average distance is 1.69 (1) Å. However, the longer distance in the title compound is in good agreement with other uranyl oxalates such as ammonium diuranyl tris(oxalate) [1.77 (7) Å; Alcock, 1973b]. In hexapotassium diuranyl oxalate decahydrate (Legros & Jeannin, 1976), much longer U—O bonds are present (1.86 Å).

The other six U—O bonds lie between 2.456 (2) and 2.574 (2) Å in our determination, whereas Jayadevan et al. report a range of 2.31 (4)–2.58 (4) Å. The average bond length is 2.502 Å in our determination and 2.44 Å in the previous structure, thus indicating that the calculated distances were far too short in the previous structure determination. Even the O—U—O angle in the uranyl group shows differences; we obtained an angle of 176.8 (2)°, slightly smaller than the reported angle of 179 (2)°. One oddity is the huge difference between the monoclinic angle determined by us and the one reported by Jayadevan et al.; in our determination β was refined to 99.6283 (7)° whereas Jayadevan et al. report a monoclinic angle of 91.5 (2)°. So far, we have no reasonable explanation for the difference between these two values.

Experimental

0.2325 g (1.26 mmol) $K_2C_2O_4 \cdot H_2O$ was dissolved in 10 ml water and 0.3 g (0.6 mmol) $UO_2(NO_3)_2 \cdot 6H_2O$ was added to the solution. The pH was then adjusted to ca 4.4 by adding aqueous HNO_3. After a couple of hours, yellow crystals of the title compound formed.

Crystal data

$K_2(UO_2)_2(C_2O_4)_3 \cdot 4H_2O$	$D_x = 3.398$ Mg m^{-3}
$M_r = 473.16$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 2170
$a = 8.9277$ (1) Å	reflections
$b = 19.4774$ (3) Å	$\theta = 2.9$–35.0°
$c = 5.3946$ (1) Å	$\mu = 18.03$ mm^{-1}
$\beta = 99.6283$ (7)°	$T = 297$ K
$V = 924.84$ (2) Å^3	Needle, yellow
$Z = 4$	$0.20 \times 0.13 \times 0.08$ mm

Data collection

Nonius KappaCCD diffractometer	2125 independent reflections
φ scans	1980 reflections with $I > 2\sigma(I)$
Absorption correction: numerical	$R_{int} = 0.068$
(*HABITUS*; Herrendorf &	$\theta_{max} = 27.6°$
Bärnighausen, 1997)	$h = -11 \rightarrow 11$
$T_{min} = 0.191$, $T_{max} = 0.498$	$k = -25 \rightarrow 25$
16 994 measured reflections	$l = -7 \rightarrow 7$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.008P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.017$	$+ 1.2824P]$
$wR(F^2) = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.13$	$(\Delta/\sigma)_{max} = 0.001$
2125 reflections	$\Delta\rho_{max} = 1.47$ e Å^{-3}
145 parameters	$\Delta\rho_{min} = -1.65$ e Å^{-3}
H atoms not located	

Table 1
Selected interatomic distances (Å).

U—O1^i	1.759 (3)	U—O8	2.490 (3)
U—O2^{ii}	1.771 (3)	U—O4^{iii}	2.503 (3)
U—O5^{iii}	2.456 (2)	U—O7^{iv}	2.510 (3)
U—O6^{iv}	2.479 (3)	U—O3^{iv}	2.574 (2)

Symmetry codes: (i) $x, y, z - 1$; (ii) $1 + x, y, z$; (iii) $\frac{1}{2} + x -, \frac{1}{2} - y -, z - \frac{1}{2}$; (iv) $1 + x, y, z - 1$.

A numerical absorption correction was applied using a refined crystal shape. All calculations were performed using *maXus* (Mackay et al., 1999).

Data collection: *KappaCCD Software* (Nonius, 1997); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data

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References

Alcock, N. W. (1973a). *J. Chem. Soc. Dalton Trans.* pp. 1610–1613.
Alcock, N. W. (1973b). *J. Chem. Soc. Dalton Trans.* pp. 1616–1620.
Herrendorf, W. & Bärnighausen, H. (1997). *HABITUS*. University of Giessen, Germany.
Jayadevan, N. C., Singh Mudher, K. D. & Chackraburtty, D. M. (1975). *Acta Cryst.* **B31**, 2277–2280.
Legros, J.-P. & Jeannin, Y. (1976). *Acta Cryst.* **B32**, 2497–2503.
Mackay, S., Gilmore, C. J., Edwards, C., Stewart, N. & Shankland, K. (1999). *maXus*. Nonius, The Netherlands, MacScience, Japan, and The University of Glasgow, Scotland.
Nonius (1997). *KappaCCD Software*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G.. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Vallet, V., Moll, H., Szabó, Z., Wahlgren, U. & Grenthe, I. (2002). In preparation.