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The crystal structure of *catena*-poly[(1-(4-carboxybenzyl)pyridin-1-ium-4-carboxylato- $\kappa^1\text{O}$)-(μ_2 -oxalato- $\kappa^4\text{O}:\text{O}':\text{O}'':\text{O}'''$)dioxidouranium(VI)], $\text{C}_{16}\text{H}_{11}\text{NO}_{10}\text{U}$

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Abstract

$\text{C}_{16}\text{H}_{11}\text{NO}_{10}\text{U}$, monoclinic, $P2_1/c$ (no. 14), $a = 16.4675(12)$ Å, $b = 11.7192(8)$ Å, $c = 9.6663(7)$ Å, $\beta = 100.823(2)^\circ$, $V = 1832.3(2)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0277$, $wR_{\text{ref}}(F^2) = 0.0673$, $T = 170.0$ K.

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Table 1: Data collection and handling.

Crystal:	Yellow needle
Size:	$0.20 \times 0.15 \times 0.10$ mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	8.92 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	26.4° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	19,220, 3735, 0.055
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3149
$N(\text{param})_{\text{refined}}$:	254
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was synthesized hydrothermally: 0.50 g uranyl nitrate hexahydrate (0.1 mmol), 0.257 g

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
C1	0.4565 (3)	0.6483 (4)	0.2571 (5)	0.0256 (10)
C2	0.5412 (3)	0.5994 (4)	0.2444 (5)	0.0249 (10)
C3	0.2391 (4)	0.3574 (4)	0.3531 (6)	0.0356 (12)
C4	0.2449 (3)	0.4292 (4)	0.4851 (5)	0.0303 (11)
C5	0.2873 (3)	0.5323 (4)	0.5011 (6)	0.0333 (12)
H5	0.310274	0.562347	0.425699	0.040*
C6	0.2958 (4)	0.5896 (5)	0.6244 (6)	0.0369 (12)
H6	0.324829	0.660047	0.635325	0.044*
C7	0.2214 (4)	0.4508 (5)	0.7187 (6)	0.0470 (15)
H7	0.199181	0.423099	0.796139	0.056*
C8	0.2095 (4)	0.3894 (5)	0.5947 (6)	0.0426 (14)
H8	0.177680	0.321246	0.584797	0.051*
C9	0.2845 (4)	0.6036 (6)	0.8736 (6)	0.0478 (15)
H9A	0.324823	0.555391	0.936843	0.057*
H9B	0.310878	0.678377	0.864104	0.057*
C10	0.2092 (4)	0.6207 (5)	0.9380 (6)	0.0394 (13)
C11	0.1914 (4)	0.5459 (6)	1.0379 (6)	0.0469 (15)
H11	0.228134	0.484513	1.068260	0.056*
C12	0.1202 (4)	0.5590 (6)	1.0954 (6)	0.0486 (15)
H12	0.107835	0.506135	1.163029	0.058*
C13	0.0682 (4)	0.6493 (6)	1.0529 (6)	0.0458 (15)
C14	0.0869 (4)	0.7261 (6)	0.9550 (7)	0.0545 (17)
H14	0.051538	0.789403	0.927077	0.065*
C15	0.1577 (4)	0.7108 (6)	0.8972 (7)	0.0496 (16)
H15	0.170123	0.763329	0.829216	0.059*
C16	−0.0068 (5)	0.6624 (7)	1.1172 (7)	0.0560 (18)
N1	0.2635 (3)	0.5478 (4)	0.7313 (5)	0.0326 (10)
O1	0.3969 (3)	0.3769 (3)	0.0690 (4)	0.0364 (9)
O2	0.4633 (3)	0.3710 (3)	0.4399 (4)	0.0343 (9)
O3	0.3989 (2)	0.5773 (3)	0.2584 (4)	0.0299 (8)
O4	0.5456 (2)	0.4937 (3)	0.2343 (4)	0.0312 (8)
O5	0.4503 (2)	0.7541 (3)	0.2619 (4)	0.0326 (8)
O6	0.5981 (2)	0.6703 (3)	0.2457 (4)	0.0280 (7)
O7	0.2945 (2)	0.3753 (3)	0.2801 (4)	0.0335 (8)
O8	0.1825 (3)	0.2896 (4)	0.3219 (5)	0.0657 (15)
O9	−0.0274 (3)	0.5967 (4)	1.2006 (5)	0.0647 (14)
O10	−0.0480 (4)	0.7575 (6)	1.0751 (7)	0.101 (2)
H10	−0.091437	0.760092	1.108877	0.151*
U1	0.42982 (2)	0.37269 (2)	0.25454 (2)	0.02368 (8)

1-(4-carboxybenzyl)pyridin-1-ium-4-carboxylate, 0.009 g oxalic acid (0.1 mmol), and water (10 mL) were well-mixed, then transferred to a 25 mL teflon-lined stainless steel autoclave and heated at 393 K for 72 h. Yellow needle crystals were obtained by filtration, washed with distilled water and ethanol, and dried in air. Yield: 46% (based on uranyl nitrate hexahydrate).

Experimental details

The structure was solved by direct methods with the SHELXS program. All H-atoms from C atoms were positioned with

idealized geometry and refined isotropic $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ using a riding model with C–H = 0.95 Å. The H-atoms from O refined freely with the distance of O10–H10 = 0.841 Å with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The O10 atom is suggested to be split by OLEX2, but we think the value of $U_{\text{eq}}(\text{O10})$ is just slightly higher than the normal value of $U_{\text{eq}}(\text{O})$ and this suggestion is not adopted.

Comment

Due to the strong chelating coordination ability of oxalate, uranyl is ready to coordinate with it to form various complexes, especially when carboxylate-containing zwitterionic ligands act as co-ligands. Thuery reported some oxalate-based uranyl coordination polymers with cyclic *N*-protonated amino acids acting as co-ligand [5, 6]. Loiseau reported one crystal structure oxalate-containing uranyl coordination polymers with a co-ligand 1,3-bis(carboxylatomethyl)imidazolium [7]. Liu reported a 1D chain oxalate-based uranyl complex with *N*-protonated 4-picolinic acid [8]. Shi reported one 1,1'-(1,3-phenylenebis(methylene))bis(pyridin-1-ium-4-carboxylate)-based oxalate-containing uranyl complex [9] and a series of 1,1'-1,4-phenylenebis(methylene)bis(pyridin-1-ium-4-carboxylate)-based oxalate-containing uranyl complexes [10–13]. It is interesting that in all of the structures mentioned above, the positive charges of the zwitterionic ligands from the protonated N atoms or quaternary ammoniums could be good complements for the negative charges of the uranyl coordination polymers, indicating that zwitterionic ligands played a key role in uranyl complexes. Thus, we report a new oxalate-containing uranyl complex by introducing the zwitterionic ligand 1-(4-carboxybenzyl)pyridin-1-ium-4-carboxylate.

The title compound was obtained hydrothermally as needle yellow crystals. The asymmetric unit of it is made of one uranyl cation, one zwitterionic ligand and one oxalate anion. The U(VI) is seven-coordinated and surrounded by two O atoms from uranyl (O1 and O2), four O atoms from two oxalate ligands (O3, O4, O5#1, and O6#1 (#1 1−*x*, −0.5+*y*, 0.5−*z*)), and one O atom (O7) from one zwitterionic ligand to form a typical slight-distorted pentagonal bipyramid. Uranyl cation coordinates with oxalate anions in a 1:2 ratio to generate a one-dimensional zigzag chain, and all the zwitterionic ligands are hanging on both sides of the chain. The monodentate coordination mode is furnished through one O atom from one carboxyl group from one zwitterionic ligand, left the other carboxyl group freely. The chains are linked by the hydrogen bond O10–H10⋯O8 to generate layers, which are furthermore connected by hydrogen bonds: C5–H5⋯O3, C6–H6⋯O5, C7–H7⋯O8,

C8–H8...O10, and C11–H11...O7; to form a supramolecular three-dimensional structure. All of the bond lengths are comparable with its reported analogs [11–13].

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References

1. Bruker. SAINT (v8.40A); Bruker AXS Inc: Madison, Wisconsin, USA, 2019.
2. Bourhis L. J., Dolomanov O. V., Gildea R. J., Howard J. A. K., Puschmann H. The anatomy of a comprehensive constrained, restrained refinement program for the modern computing environment—Olex2 dissected. *Acta Crystallogr.* 2015, *A71*, 59–75.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
4. Sheldrick G. Using phases to determine the space group. *Acta Crystallogr.* 2018, *A74*, a353.
5. Thuery P. The first crystal structure of an actinide complex of the macrocyclic ligand DOTA: a two-dimensional uranyl-organic framework. *CrystEngComm* 2008, *10*, 808–810.
6. Thuery P. Uranyl-organic assemblies with the macrocyclic ligand 1,4,8,11-tetraazacyclotetradecane-1,4,8,11-tetraacetate (TETA). *CrystEngComm* 2010, *12*, 1905–1911.
7. Martin N. P., Falaise C., Volkringer C., Henry N., Farger P., Falk C., Delahaye E., Rabu P., Loiseau T. Hydrothermal crystallization of uranyl coordination polymers involving an imidazolium dicarboxylate ligand: effect of pH on the nuclearity of uranyl-centered subunits. *Inorg. Chem.* 2016, *55*, 8697–8705.
8. Liu D.-S., Shi T.-Q., Liu S.-F., Ying S.-M., Li X.-F. catena-Poly [[(isonicotinato)uran-yl(VI)]-μ-oxalato]. *Acta Crystallogr.* 2007, *E63*, m385–m387.
9. Xie Z.-N., Mei L., Hu K.-Q., Xia L.-S., Chai Z.-F., Shi W.-Q. Mixed-ligand uranyl polyrotaxanes incorporating a sulfate/oxalate coligand: achieving structural diversity via pH-dependent competitive effect. *Inorg. Chem.* 2017, *56*, 3227–3237.
10. Ge Y.-C., Mei L., Xie Z.-N., Hu K.-Q., Xia C.-Q., Wang X.-L., Chai Z.-F., Shi W.-Q. Supramolecular isomers of coordination-directed side-chain polypseudorotaxanes based on trimeric uranyl oxalate nodes. *Chem. Eur J.* 2017, *23*, 8380–8384.
11. Mei L., Xie Z.-N., Hu K.-Q., Yuan L.-Y., Gao Z.-Q., Chai Z.-F., Shi W.-Q. Supramolecular host-guest inclusion for distinguishing cucurbit[7]uril-based pseudorotaxanes from small-molecule ligands in coordination assembly with a uranyl center. *Chem. Eur J.* 2017, *23*, 13995–14003.
12. Si Wu S., Mei L., Hu K.-Q., Chai Z.-F., Nie C.-M., Shi W.-Q. pH-dependent synthesis of octa-nuclear uranyl-oxalate network mediated by u-shaped linkers. *J. Inorg. Mater.* 2020, *35*, 243–255.
13. Li F.-Z., Mei L., An S.-W., Hu K.-Q., Chai Z.-F., Liu N., Shi W.-Q. Kinked-helix actinide polyrotaxanes from weakly bound pseudorotaxane linkers with variable conformations. *Inorg. Chem.* 2020, *59*, 4058–4067.