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Homoleptic Tris(dithiolene) and Tetrakis(dithiolene) Complexes of Uranium(IV)

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Reaction of UCl_4 with 3 or 4 mol equiv of Na_2dddt (dddt = 5,6-dihydro-1,4-dithiine-2,3-dithiolate) in THF afforded the first example of a tetrakis(dithiolene) metal compound, $[Na_4(THF)_8U(dddt)_4]_\infty$ (**1**). The red crystals of **1** are composed of infinite zigzag chains in which $Na_2(\mu\text{-THF})_3$ fragments ensure the linking of $Na_2(THF)_5U(dddt)_4$ moieties; the uranium atom is in a dodecahedral environment of eight sulfur atoms. Treatment of UCl_4 with 3 mol equiv of Na_2dddt in pyridine gave a mixture of tris- and tetrakis(dithiolene) compounds. After addition of 18c6 (18-crown-6), only the tris(dithiolene) complex was obtained and crystallized as orange crystals of $[Na(18c6)(py)_2]_2[U(dddt)_3]\cdot 2py$ (**2**·2py) in which the isolated $[U(dddt)_3]^{2-}$ anion adopts a slightly distorted trigonal prismatic configuration. A few red crystals of the unsolvated complex **2** and the trinuclear anionic compound $[Na(18c6)(py)_2]_3[Na\{U(dddt)_3\}_2]$ (**3**) were also obtained along with orange crystals of **2**·2py. All the tris(dithiolene) compounds exhibit large folding of the dddt ligand and significant interaction between the C═C double bond and the metal center.

Introduction

We have previously described the synthesis and crystal structure of various neodymium and cerium tris(dithiolene) complexes in which the $Ln(dddt)_3$ unit (dddt = 5,6-dihydro-1,4-dithiine-2,3-dithiolate) is found either in mononuclear species, infinite neutral chains, or two-dimensional neutral or anionic layers.[1] As part of our studies on the differentiation of trivalent lanthanide and actinide complexes,[2] we wanted to prepare analogous compounds of uranium(III) with the expectation that the U^{III} ion, being less hard than the Ln^{III} ions,[3] would lead to the creation of more covalent bonds with the soft sulfur ligand and thus would possibly give dithiolene complexes with distinct structures. Our attempts to synthesize such compounds of uranium(III) have been so far unsuccessful. Nevertheless, we isolated the homoleptic tris(dithiolene) complexes of uranium(IV), $[Na(18c6)(py)_2]_2[U(dddt)_3]$ (18c6 = 18-crown-6), and $[Na(18c6)(py)_2]_3[Na\{U(dddt)_3\}_2]$, and the 1D polymeric derivative $[Na_4(THF)_8U(dddt)_4]_\infty$ which is the first example of a tetrakis(dithiolene) metal compound;[4] here, we present the synthesis and crystal structure of these complexes.

Experimental Section

All reactions were carried out under argon (<5 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a glovebox. Solvents were dried by standard methods and distilled immediately before use. The ^{1}H NMR spectra were recorded on a Bruker DPX 200 instrument and referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0). Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany).

Syntheses. The precursors UCl_4[5] and Na_2dddt[6] were prepared by published methods.

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Table 1. Crystal Data and Structure Refinement Details for Complexes **1**−**3**

	1	**2**·2py	**2**	**3**
empirical formula	$C_{48}H_{80}Na_4O_8S_{16}U$	$C_{66}H_{90}N_6Na_2O_{12}S_{12}U$	$C_{56}H_{80}N_4Na_2O_{12}S_{12}U$	$C_{90}H_{126}N_6Na_4O_{18}S_{24}U_2$
M/g mol^{-1}	1628.07	1828.17	1669.97	2917.67
cryst syst	orthorhombic	monoclinic	triclinic	triclinic
space group	$Pna2_1$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	29.0956(8)	29.0277(13)	10.4901(5)	10.4359(5)
b/Å	15.9080(4)	10.5486(4)	15.5965(13)	16.2555(8)
c/Å	14.3610(4)	29.1026(13)	22.5780(18)	18.9962(10)
α/deg	90	90	83.727(3)	101.530(4)
β/deg	90	116.001(2)	80.084(5)	104.101(5)
γ/deg	90	90	75.523(4)	102.537(4)
V/Å^3	6647.0(3)	8009.3(6)	3514.7(4)	2940.2(3)
Z	4	4	2	1
D_{calc}/g cm^{-3}	1.627	1.516	1.578	1.648
μ(Mo Kα)/mm^{-1}	3.017	2.409	2.736	3.253
F(000)	3296	3720	1692	1464
reflns collected	44816	51508	24028	20231
indep reflns	12603	14996	12311	10294
obsd reflns [$I > 2\sigma(I)$]	9641	9844	8813	6525
R_{int}	0.073	0.114	0.079	0.104
params refined	694	892	784	652
R1	0.044	0.049	0.053	0.068
wR2	0.079	0.107	0.116	0.160
S	0.984	1.006	1.066	1.019
$\Delta\rho_{min}$/e Å^{-3}	−0.60	−0.64	−1.17	−1.13
$\Delta\rho_{max}$/e Å^{-3}	0.48	1.09	1.12	1.24

$[Na_4(THF)_8U(dddt)_4]_\infty$ (1). A flask was charged with UCl_4 (254 mg, 0.67 mmol) and Na_2dddt (613 mg, 2.71 mmol), and THF (30 mL) was condensed in. The reaction mixture was stirred for 12 h at 20 °C, and THF was evaporated off in order to precipitate NaCl. The brown residue was extracted in THF (40 mL); the dark red solution was filtered and evaporated to dryness, leaving a brown powder of $[Na_4U(dddt)_4]\cdot 2THF$. Yield 688 mg (86%). Anal. Calcd for $C_{24}H_{32}O_2S_{16}Na_4U$: C, 24.11; H, 2.70; S, 42.91. Found C, 24.30; H, 2.89; S, 42.70. ^1H NMR (THF-d_8, 23 °C): δ 6.41 (s, $w_{1/2} = 58$ Hz, 16H, dddt); coalescence of this signal was observed at + 5 °C, and two signals of equal intensity ($w_{1/2} = 25$ Hz) were visible at δ 8.75 and 5.80 at −40 °C. ^1H NMR (pyridine-d_5, 23 °C): δ 5.98 (s, $w_{1/2} = 15$ Hz, 16H, dddt), 3.65 (m, 8H, THF), 1.61 (m, 8H, THF); coalescence of the dddt signal was observed at −15 °C, and two signals of equal intensity ($w_{1/2} = 35$ Hz) were visible at δ 7.47 and 4.84 at −40 °C. Dark red crystals of **1** were obtained by crystallization of the powder from THF.

$[Na(18c6)(py)_2]_2[U(dddt)_3]\cdot 2py$ (2·2py). A flask was charged with UCl_4 (185 mg, 0.49 mmol) and Na_2dddt (332 mg, 1.47 mmol), and pyridine (30 mL) was condensed in. The reaction mixture was stirred at −20 °C for 3 h, and pyridine was evaporated off. The black residue was extracted in THF (20 mL); the solution was filtered and evaporated to dryness, leaving a dark brown powder (500 mg). The ^1H NMR spectrum of this powder in pyridine-d_5 at 23 °C showed two signals at δ 5.98 and −2.84 attributed to tetrakis- and tris(dithiolene) uranium complexes, respectively, in the relative molar proportions of 0.6:1. Upon addition of 18c6, these two signals were shifted into a single resonance at δ ca −13.5 which did not collapse and split at lower temperature. Slow diffusion of pentane into a pyridine solution of the dark brown powder and 18c6 (500 mg, 1.89 mmol) afforded orange crystals of **2**·2py. Yield: 480 mg (59%). ^1H NMR (pyridine-d_5, 23 °C): δ −13.55 (s, 12H, dddt), 4.82 (s, 48H, 18c6). The crystals were dried under vacuum to give a dark red powder of **2**. Anal. Calcd for $C_{56}H_{80}N_4O_{12}S_{12}Na_2U$: C, 40.27; H, 4.83; N, 3.36; S, 23.04. Found: C, 39.86; H, 4.86; N, 3.61; S, 22.47. Red crystals of **2** and $[Na(18c6)(py)_2]_3[Na\{U(dddt)_3\}_2]$ (**3**), which are undistinguishable from each other under a microscope, were obtained in very small quantity along with the orange crystals of **2**·2py.

Crystallographic Data Collection and Structure Determination. The data were collected at 110(2) K (**1**) or 100(2) K (**2**·2py, **2**, and **3**) on a Nonius Kappa-CCD area detector diffractometer[7] using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The crystals were introduced in glass capillaries with a protecting "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from 10 frames, then refined on all data. A 180° φ-range was scanned with 2° steps during data collection. The data were processed with *DENZO-SMN*.[8] The structures were solved by Patterson map interpretation (**2**·2py and **2**) or by direct methods (**1** and **3**) with *SHELXS-97* and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with *SHELXL-97*.[9] Absorption effects were corrected empirically with the program *DELABS* from *PLATON*.[10] The absolute structure for compound **1** was determined from the value of the Flack parameter [−0.014(4)].[11] In compound **2**·2py, the C3−C4 bridge of one dithiolene ligand (denoted C) is disordered over two positions which have been refined with occupancy parameters constrained to sum to unity and restraints on bond lengths. Some restraints on bond lengths and/or displacement parameters also had to be applied for some badly behaving atoms, particularly in the crown ether moieties, in compounds **2** and **3**. In **3**, the presence of unresolved disorder on one crown ether is indicated by a short H···H contact involving one of its protons and its image through the symmetry center as well as by the highest residual electron density peak being located near an oxygen atom. All non-hydrogen atoms were refined with anisotropic displacement parameters (except the disordered ones in compound **2**·2py). Hydrogen atoms were introduced at calculated positions (except in disordered parts for compound **2**·2py) and were treated as riding atoms with a displacement parameter equal to 1.2 times that of the parent atom. Crystal data and structure refinement details are given in Table 1.

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The molecular plots were drawn with *SHELXTL*[12] and *ORTEP-3/POV-Ray*.[13]

Results and Discussion

The Tetrakis(dithiolene) Uranium Complex. The reaction of UCl_4 and 3 or 4 mol equiv of Na_2dddt in THF was monitored by ^{1}H NMR spectroscopy which revealed the presence of a single uranium product, characterized by a singlet signal at δ 6.41 corresponding to magnetically equivalent dddt ligands; complete formation of this compound required the addition of 4 mol equiv of Na_2dddt. After usual workup, a red powder was obtained whose general formula $[Na_4U(dddt)_4]\cdot 2THF$ was deduced from the elemental analyses (C, H, S) and the ^{1}H NMR spectrum in pyridine which exhibits the dddt signal at δ 5.98 in addition to the resonances of the two free THF molecules; this product was obtained with an 86% yield. Crystallization of this powder from THF afforded red crystals of $[Na_4(THF)_8U(dddt)_4]_\infty$ (**1**) suitable for X-ray diffraction analysis. The synthesis of **1** is reminiscent of that of $[Li_4(dme)_4U(edt)_4]$ (edt = ethane-1,2-dithiolate)[4] which was the sole isolable compound from the reaction of UCl_4 and Li_2edt, regardless of the reactant ratio. However, the crystal structures of the two compounds are quite different since the edt derivative is monomeric while **1** is polymeric with distinct ligation modes of the alkali metal atoms. Attempts to characterize a monomeric compound containing the $U(dddt)_4$ unit have been unsuccessful; in particular, addition of 18c6 into THF solutions of $[Na_4U(dddt)_4]$ gave very small crystals but these were not suitable for X-ray crystallography.

The asymmetric unit of **1** is shown in Figure 1a, and the structure is outlined in Scheme 1; selected bond distances and angles are listed in Table 2. The crystals are composed of infinite chains in which each $U(dddt)_4$ unit is surrounded by four Na atoms, two of those being involved in bridging $Na_2(\mu\text{-THF})_3$ fragments. The eight-coordinate uranium atom is in a slightly distorted dodecahedral configuration, as can be seen in the simplified view of Figure 2. The S(1) and S(2) atoms of the dddt ligands A and B, and those of ligands C and D, form two trapezia, with mean planar deviations of 0.39 and 0.36 Å, respectively, which both contain the U atom and intersect at an angle of 87.36(4)°; the A and B sites of the dodecahedron are occupied by the S(1) and S(2) atoms, respectively. The U−S distances vary from 2.7900(19) to 2.8654(18) Å with an average value of 2.83(3) Å which is quite similar to that of 2.85(4) Å in $[Li(dme)]_4[U(edt)_4]$. These distances are in the range of U−S bond lengths for uranium(IV) dithiolene complexes which are lying between 2.720(3) Å in $[U(C_8H_8)(mdt)(py)_2]$ and 2.946(6) Å in $[\{U(C_8H_8)(mdt)\}_2]$ (mdt = 2H-1,3-dithiole-4,5-dithiolate).[14]

The folding of the dddt ligands along the S(1)−S(2) axis does not exceed 22.41(8)°, with an average value of 17(5)°, and is much less than that observed in the uranium tris(dithiolene) complex (vide infra); this difference can be explained by the more important steric crowding and negative charge[6,15] around the metal center. The $C(sp^2)$−S and C(1)=C(2) distances within the planar S_4C_2 fragments average 1.767(9) and 1.349(4) Å and are similar to those measured in the lanthanide tris(dithiolene) complexes.[1]

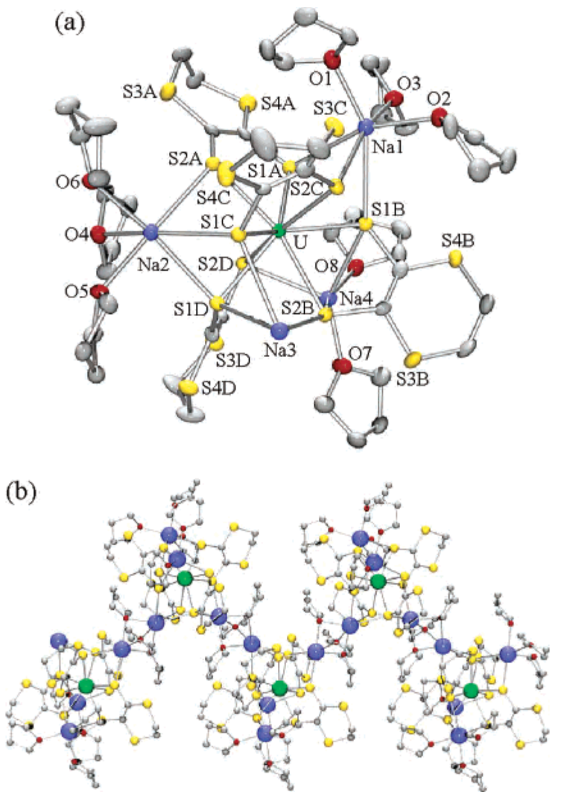

Figure 1. (a) View of the asymmetric unit of **1**. The hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. (b) View of the zigzag chain arrangement along the *c* axis.

In contrast to those observed in $[Li_4(dme)_4U(edt)_4]$, which exhibits a pseudo-S_4 symmetry with each Li atom bridging one A-site and one B-site sulfur atoms of different edt ligands,[4] the U−S distances in **1** cannot be separated into four long and four short distances corresponding to the S(1) and S(2) atoms at the A and B sites, respectively; this difference is due to the dissymmetric attachment of the four Na atoms to the $U(dddt)_4$ unit. The Na(1) atom is bound to two adjacent A-site sulfur atoms, S(1A) and S(1B), and to S(2C). Both Na(2) and Na(3) are linked to the other two A-site sulfur atoms, S(1C) and S(1D), Na(2) being also bound to S(2A) and Na(3) to S(2B). The Na(1), Na(2), and Na(3) atoms are thus bridging three S atoms of three different dddt ligands. A distinct ligation mode is adopted by Na(4) which is attached to three S atoms of two different ligands, S(1B), S(2B), and S(2D), in a manner similar to that found in the tris(dithiolene) lanthanide complexes $\{[Na_3(18c6)_{1.5}Nd(dddt)_3(THF)]\cdot 3THF\}_\infty$ and $\{[Na_2(18c6)Na(py)_2Ce(dddt)_3(py)]\cdot 3py\}_\infty$.[1] The Na(4) atom is also distinct from the others since only two THF molecules instead of three are coordinated to it; however, the sixth coordination site of Na(4) is

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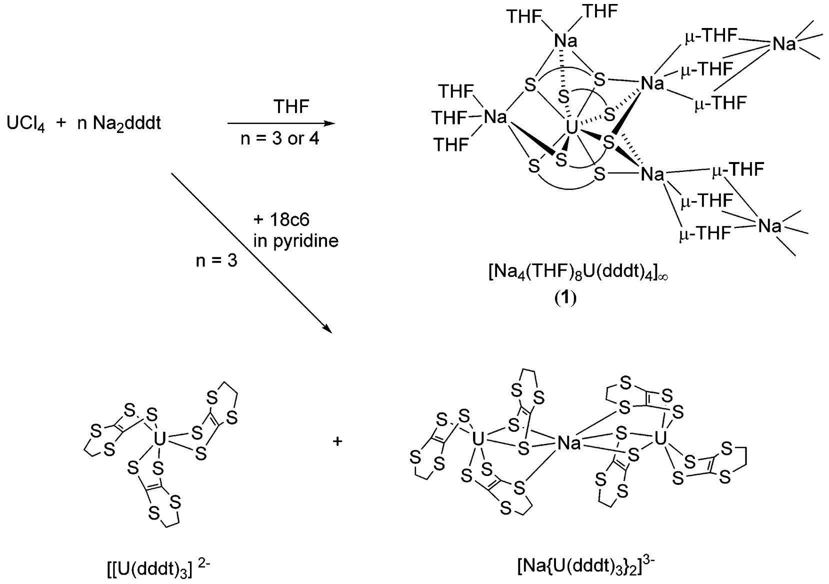
Scheme 1. Synthesis of the Homoleptic Uranium Dithiolene Complexes and Representation of the Environment of the U(dddt)$_3$ and U(dddt)$_4$ Units[a]



[a] For clarity, only the bite of the dddt ligands is represented in the structure of **1**.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex **1**

U−S(1A)	2.7999(19)	Na(1)−S(1A)	3.081(3)
U−S(2A)	2.801(2)	Na(1)−S(1B)	3.022(3)
U−S(1B)	2.8437(19)	Na(1)−S(2C)	2.902(4)
U−S(2B)	2.8548(18)	Na(2)−S(1C)	2.957(3)
U−S(1C)	2.8604(17)	Na(2)−S(1D)	2.905(3)
U−S(2C)	2.7900(19)	Na(2)−S(2A)	2.844(3)
U−S(1D)	2.8654(18)	Na(3)−S(2B)	2.900(3)
U−S(2D)	2.8254(19)	Na(3)−S(1C)	2.993(3)
S(1A)−U−S(2A)	70.63(6)	Na(3)−S(1D)	2.923(3)
S(1B)−U−S(2B)	69.31(5)	Na(4)−S(1B)	2.975(3)
S(1C)−U−S(2C)	70.07(5)	Na(4)−S(2B)	2.872(3)
S(1D)−U−S(2D)	69.91(5)	Na(4)−S(2D)	2.816(3)
θ_A[a]	12.21(9)	θ_C	22.41(8)
θ_B	12.80(10)	θ_D	20.69(7)

[a] θ_A, θ_B, θ_C, and θ_D are the folding angles of the dddt ligands A, B, C, and D, respectively.

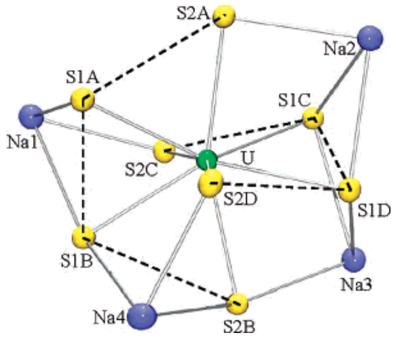


Figure 2. View of the US$_8$Na$_4$ core in **1**. Displacement ellipsoids are drawn at the 50% probability level. The two trapezia in the distorted dodecahedral geometry are shown as dashed lines (- - -).

occupied by the C(1)═C(2) double bond of the dddt ligand, as shown by the Na(4)−C(1B) and Na(4)−C(2B) distances of 3.048(8) and 2.953(8) Å.[16]

The Na(2) atom is linked to the Na(3) atom of another [Na$_4$(THF)$_8$U(dddt)$_4$] unit via the oxygen atoms of three THF molecules, thus giving infinite zigzag chains. While such bridging Na$_2$L$_3$ fragments are known for a variety of neutral oxygen L ligands [L = H$_2$O,[17] MeOH,[18] Me$_2$CO,[19] (Me$_2$N)$_3$PO,[20] Me$_2$NCHO[21]], it seems from the Cambridge Crystallographic Database to have not been previously encountered for L = THF.

The average Na−S distance of 2.93(7) Å and the average Na−O distances of 2.32(3) and 2.43(3) Å for the terminal and bridging THF are unexceptional. These polymeric chains (Figure 1b) are parallel to the crystallographic *c* axis. The distance between two consecutive uranium atoms is 10.8265(4) Å, and the U···U···U angle is 83.094(4)°. A similar arrangement was found in the complex {[Na$_2$(18c6)Na(py)$_2$Ce(dddt)$_3$(py)]·3py}$_\infty$,[1] in which the distance between the metal atoms is only slightly larger [mean value 11.77(18) Å] and the angle less acute [105.610(10)°]. In both cases, two sodium atoms separate the metal atoms, the bridging of these sodium atoms being effected by a 18c6 ligand in the cerium complex.

The magnetic equivalence of the dddt ligands in the ^{1}H NMR spectra of **1** in THF or pyridine at 20 °C indicates that the complex is fluxional in solution, due to rapid exchange of the dithiolene ligands and sodium ions. However, the single, time-averaged dddt resonance was found to broaden as the temperature was lowered and two signals of equal intensity emerged below the coalescence temperature T_c. From line shape analysis of the spectra, the free energies of activation $\Delta G^\ddagger$ corresponding to this fluxional process are 11.9 and 11.5 kcal mol^{-1}, at $T_c = +5$ or -15 °C in THF or pyridine, respectively. These results can be explained by

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the exchange of sulfur atoms between the dodecahedral A and B sites which induces the interchange of the adjacent dithiolene CH_2 groups. This dynamic behavior is identical to that encountered in $[Li_4(dme)_4U(edt)_4]$[4] and a series of tetrakis(mono- or dithiocarbamate) complexes of the group IV and V metals where the barriers $\Delta G^{\ddagger}$ (T_c) to the polytopal rearrangement are lying between 10.2 and 14.7 kcal mol^{-1}.[22]

The Tris(dithiolene) Uranium Complexes. Reaction of UCl_4 with less than 4 mol equiv of Na_2dddt in pyridine led to the formation of two products; the tetrakis(dithiolene) complex was identified by its ^1H NMR signal at δ 5.98, and the other compound, characterized by the resonance at δ −2.84, was assumed to be the tris(dithiolene) derivative $[Na_2(py)_xU(dddt)_3]$. This latter was the major product [tris(dithiolene)/tetrakis(dithiolene) = 1.7] by using 3 mol equiv of Na_2dddt. Upon addition of 18c6, this mixture of tris- and tetrakis(dithiolene) uranium complexes was transformed into a unique compound, according to the NMR spectra which exhibit a single peak at δ ca −13.5; collapse and splitting of this signal was not observed at lower temperature, indicating the presence of a tris(dithiolene) rather than a tetrakis(dithiolene) compound. These observations suggest that the $[U(dddt)_4]^{4-}$ species which would be obtained after encapsulation of the Na^+ ions in 18c6 readily dissociates a dddt ligand for giving the anionic tris(dithiolene) complex $[U(dddt)_3]^{2-}$. The instability of the isolated $[U(dddt)_4]^{4-}$ anion is likely due to the too important negative charge on the complex which is not balanced by the coordination of the alkali metal ions on the outer sphere, as it occurs in **1** and $[Li_4(dme)_4U(edt)_4]$. Slow diffusion of pentane into the pyridine solution of the tris(dithiolene) uranium compound afforded orange crystals of $[Na(18c6)(py)_2]_2[U(dddt)_3]\cdot 2py$ (**2**·2py). A few red crystals of the unsolvated complex **2** and the trinuclear anionic compound $[Na(18c6)(py)_2]_3[Na\{U(dddt)_3\}_2]$ (**3**) were also obtained along with orange crystals of **2**·2py; the crystals of **2** and **3** are indistinguishable from each other under a microscope and were separated by chance.

The crystal structures of the anion in **2**·2py and in **3** are shown in Figures 3 and 4, respectively, and selected bond distances and angles are listed in Table 3; the structure of the anion in **2** resembles that in **2**·2py. The geometrical parameters of the U(dddt)$_3$ units in these three complexes exhibit strong analogies and will be presented together. In each compound, the uranium atom is found in a distorted trigonal prismatic environment defined by the two nearly equilateral triangles S(1A)−S(1B)−S(1C) and S(2A)−S(2B)−S(2C) which are almost parallel with dihedral angles of 0.93(6)°, 0.28(6)°, and 1.07(8)° in **2**·2py, **2**, and **3**, respectively. The metal atom is located between the two triangles on the pseudo-3-fold axis, at the average distance of 1.63(3) Å from these triangles. The distortions of the S_6 polyhedron away from the trigonal prismatic toward the octahedral geometry can be measured by the twist angles of the $S(1)_3$ and $S(2)_3$ triangles from their eclipsed conformation, ca. 7°, 17°, and 20°, and the average *trans* S−U−S angles of 138(4)°, 145.3(6)°, and 148(1)° in **2**·2py, **2**, and **3**, respectively. In the ideal trigonal prism and octahedron, the twist angles are equal to 0° and 60°, whereas the *trans* S−M−S angles, where the two S atoms are from different ligands and are nearly opposite each other, are equal to 136 and 180°, respectively; in the octahedral configuration of a [M(bidentate ligand)$_3$] compound in which the chelate bite

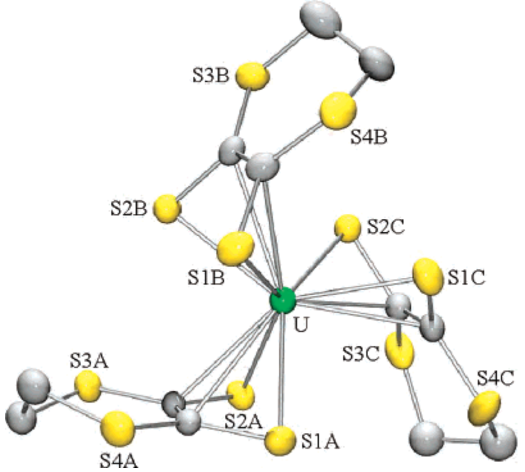

Figure 3. View of the anion in **2**·2py. The hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Only the main component of the disordered ligand C is represented.

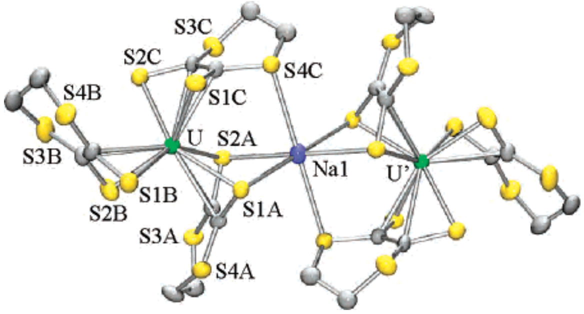

Figure 4. View of the anion in **3**. The hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Symmetry code: ′ = 1 − *x*, 1 − *y*, 1 − *z*.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complexes **2**·2py, **2**, and **3**

	2·2py	**2**	**3**
U−S(1A)	2.7601(16)	2.760(2)	2.774(3)
U−S(2A)	2.7279(16)	2.7398(18)	2.766(3)
U−S(1B)	2.7240(16)	2.7300(18)	2.737(3)
U−S(2B)	2.7368(16)	2.7172(19)	2.734(3)
U−S(1C)	2.7217(17)	2.7343(17)	2.692(3)
U−S(2C)	2.7587(16)	2.7363(19)	2.741(3)
U−C(1A)	2.821(6)	2.944(7)	2.865(10)
U−C(2A)	2.826(6)	2.909(7)	2.895(11)
U−C(1B)	2.826(6)	2.867(7)	2.831(10)
U−C(2B)	2.858(6)	2.854(7)	2.871(11)
U−C(1C)	2.866(6)	2.868(6)	2.838(10)
U−C(2C)	2.880(6)	2.890(7)	2.921(10)
S(1A)−U−S(2A)	73.73(5)	74.82(6)	73.54(8)
S(1B)−U−S(2B)	74.28(5)	76.17(6)	74.71(9)
S(1C)−U−S(2C)	73.73(5)	74.22(5)	76.56(9)
θ_A[a]	85.74(5)	80.21(5)	84.60(7)
θ_B	84.91(5)	81.96(5)	82.09(8)
θ_C	83.38(5)	81.70(4)	79.94(8)

[a] θ_A, θ_B, and θ_C are the folding angles of the dddt ligands A, B, and C, respectively.

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angle of the ligand is 75°, as is the case in these tris(dithiolene) complexes, the expected value of the *trans* S−M−S angles is 165°.[23] From these structural parameters, the amount of trigonal prism → octahedron deviation is ca. 30%, 10%, and 35% in **2**·2py, **2**, and **3**, respectively. The conformational difference between the two $U(dddt)_3$ units of **2**·2py and **2** is difficult to interpret, although lattice packing forces could always be invoked. The structure of these complexes differs markedly from that of the homoleptic uranium hexathiolates $[NEt_2H_2][U(SPh)_6]$,[24] $[\{(Ph_3P)Cu(\mu\text{-}SPh)_3\}_2U]$,[24] and $[\{(THF)_3Na(\mu\text{-}SR)_3\}_2U]$[25] (R = ${}^tBu$ or Ph) which exhibit a quite perfect octahedral geometry, and confirms the tendency of tris(dithiolene) and tris(dithiolate) compounds to adopt preferentially a trigonal prismatic configuration.[23,26]

The average U−S distance in **2**·2py and **2** is 2.737(14) Å; in **3**, the bridging U−S(1A) and U−S(2A) distances of 2.774(3) and 2.766(3) Å are slightly longer than the other U−S distances which average 2.73(2) Å. These values are smaller than those in the tetrakis(dithiolene) compound **1**, in agreement with the variation of the coordination number, and are similar to those of 2.72−2.75 Å in the series of uranium hexathiolates.[24,25] The average U−S distance in **2** is 0.13 Å shorter than the average Nd−S distance in the anion $[Nd(dddt)_3(py)]^{3-}$, in agreement with the variation in the ionic radii of six-coordinate uranium(IV) and seven-coordinate neodymium(III);[27] also, as expected from the difference between the radii of six-coordinate U(III) and Nd(III) ions, the mean bridging U−S distance in **3** is shorter, by 0.09 Å, than the average Nd−S distance in $\{[Na(18c6)(py)_2]_{0.5}[Na(18c6)(py)_{1.5}][Na_{1.5}Nd(dddt)_3]\}_\infty$.

The two $U(dddt)_3$ units in **3** are linked by the sodium atom Na(1) which lies on an inversion center. The ligation mode of Na(1), via S(1A), S(2A), and S(4C), is identical to that encountered in the aforementioned homoleptic tris(dithiolene) neodymium compound; the Na(1)−S(4C) bond length of 3.206(3) Å is longer than the Na(1)−S(1A) and Na(1)−S(2A) distances of 2.878(3) and 2.772(3) Å, as observed in the neodymium complex. These distances can be compared with those of 2.965(8) and 3.060(3) Å in $[\{(THF)_3Na(\mu\text{-}SR)_3\}_2U]$, for R = ${}^tBu$ or Ph, respectively.[25]

The carbon atoms C(1) and C(2) of the dithiolene ligands in the tris(dithiolene) uranium complexes are at an average distance of 2.87(3) Å from the metal center, a value which is similar to or slightly smaller than those of 2.89(1) and 2.97(1) Å in $[U(C_8H_8)(mdt)(py)_2]$ and 2.95(1) Å in $[\{U(C_8H_8)(mdt)\}_2]$.[14] The folding angle of the dddt ligands along the S(1)−S(2) axis, with an average value of 85(1)°, 81.3(8)°, and 82(2)° in **2**·2py, **2**, and **3**, respectively, is slightly smaller than that of 86.7(12)° in the homoleptic tris(dithiolene) neodymium compound; however, the C(1) and C(2) atoms in the uranium complexes are closer to the metal center than in the neodymium complex, by 0.05 Å, due to the shorter U−S distances. The folding of the dddt ligand in the uranium complexes is much larger than that of 15(6)° in the isolated $[Nd(dddt)_3(py)]^{3-}$ anion[1] where the more negative charge disfavors the interaction between the C═C double bond and the metal.[6,15] The characteristics of the planar S_4C_2 fragments of the dddt ligands, with mean $C(sp^2)$−S and C(1)═C(2) bond lengths of 1.768(13) and 1.365(9) Å, are identical to those found in the series of tris(dithiolene) lanthanide compounds; together with the U−S distances, those parameters strongly suggest that the redox active dddt ligands are “innocent” in these complexes and that the uranium atom is formally in the +4 oxidation state.[28]

We underlined in the Introduction that all attempts to obtain dithiolene complexes of uranium(III) were unsuccessful whereas the tris(dithiolene) complexes of neodymium and cerium proved to be very stable.[1] In fact, treatment of $UI_3(THF)_4$ or $U(BH_4)_3(THF)_3$ with Na_2dddt in THF invariably gave the tetrakis(dithiolene) compound of uranium(IV) as the only identified product, while the same reaction in pyridine led to the formation of the tris- and tetrakis(dithiolene) U^{IV} complexes (NMR experiments). The difficulty in isolating uranium(III) thiolate compounds has already been noticed and is obviously due to the facile $U^{III} \rightarrow U^{IV}$ oxidation. Thus, in contrast to its cerium analogue, the uranium(III) complex $[U({}^tBuC_5H_4)_2(SPh)]$ was readily transformed by a ligand and valence redistribution reaction into $[U({}^tBuC_5H_4)_3(SPh)]$ and an unknown uranium species which decomposes.[29] Lanthanide(II) thiolate complexes were found to be similarly unstable toward oxidation, as shown by the reaction of LnI_2 and $LiS{}^tBu$ in the presence of tmeda which afforded the homoleptic Ln(III) thiolates $[Li(tmeda)]_3[Ln(S{}^tBu)_6]$ (Ln = Sm, Yb).[30] In this context, it is noteworthy that oxidation of $UI_3(THF)_4$ also occurred during its reaction with $Li(N\{{}^tBu\}Ar)(OEt_2)$, for giving $[U(I)(N\{{}^tBu\}Ar)_3]$ which was then reduced with Na(Hg) into the expected homoleptic amide of uranium(III).[31] However, no uranium(III) complex was isolated from reactions of the tetrakis- or tris(dithiolene) complexes **1** or **2** with reducing agents; slow decomposition into unidentified products occurred in the presence of sodium amalgam or sodium−potassium alloy.

Conclusion

We have synthesized the first homoleptic dithiolene complexes of uranium, including the first example of a tetrakis(dithiolene) metal compound. While the $U(dddt)_4$ unit of $[Na_4(THF)_8U(dddt)_4]_\infty$ (**1**) is involved in a 1D polymeric chain ensured by $Na_2(\mu\text{-}THF)_3$ bridging fragments, encapsulation of the Na^+ ions in 18c6 permitted us to obtain

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discrete $[U(dddt)_3]^{2-}$ ions in $[Na(18c6)(py)_2]_2[U(dddt)_3]$ (**2**). The ready dissociation of a dddt ligand from the $[U(dddt)_4]^{4-}$ species is likely related to the too important electron richness of this anionic complex. It is noteworthy that the isolated $[U(dddt)_3]^{2-}$ ion was much more easily obtained than the lanthanide ions $[Ln(dddt)_3]^{3-}$ since the tris(dithiolene) lanthanide complexes adopt preferentially 1D or 2D polymeric structures. This difference can also be explained by the greater negative charge on the lanthanide compounds which would favor the coordination of the alkali metal ions on the outer sphere and the formation of chains and layers with Na or $Na_2(18c6)$ bridging fragments. The synthesis of homoleptic uranium(III) dithiolene compounds which could be compared with their lanthanide counterparts remains a challenging goal.

Supporting Information Available: Tables of crystal data, atomic positions and displacement parameters, anisotropic displacement parameters, bond lengths ,and bond angles in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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