ORGANOMETALLICS

Volume 19, Number 2, January 24, 2000

Communications

The First Dithiolene Complexes of an f-Element, Including the Cyclooctatetraene Derivative [$Na(18\text{-crown-}6)(THF)][U(\eta^8\text{-}C_8H_8)(C_4H_4S_4)_2]$, a Unique Example of a Uranium(V) Compound with Metal−Sulfur Bonds

Thérèse Arliguie,*[†] Marc Fourmigué,[‡] and Michel Ephritikhine[†]

Service de Chimie Moléculaire, DSM, DRECAM, CNRS URA 331, CEA Saclay, 91191 Gif sur Yvette, France, and Institut des Matériaux Jean Rouxel, 2, rue de la Houssinière, BP 32229, 44322 Nantes Cedex 03, France

Received September 13, 1999

*Summary: Treatment of [$U(Cp^*)_2Cl_2$] and [$U(COT)X_2(THF)_n$] ($Cp^* = \eta^5\text{-}C_5Me_5$; $COT = \eta^8\text{-}C_8H_8$; $X = BH_4$ and $n = 0$, $X = I$ and $n = 2$) with Na_2dddt (dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate) afforded the (dithiolene)uranium (IV) compounds [$U(Cp^*)_2$(dddt)] (**1**) and [Na(18-crown-6)]$_2$[U(COT)(dddt)$_2$] (**2**); oxidation of **2** with Ag^+ gave the uranium(V) complex [Na(18-crown-6)(THF)][U(COT)(dddt)$_2$] (**3**), the crystal structure of which revealed the exo−endo conformation of the dddt ligands.*

The attractive features of homoleptic metal dithiolene complexes as molecular precursors of novel conducting and magnetic materials[1] have led recently to the development of heteroleptic cyclopentadienyl/dithiolene complexes[2] of the metal groups 4−6, of general formula [$M(Cp)_2$(dithiolene)]$^{0,+}$ or [M(Cp)(dithiolene)$_2$]$^{-,0}$. The introduction of the f-elements in these types of complexes is particularly attractive because their paramagnetism, structural flexibility, and redox behavior are prerequisite qualities for the emergence of collective electronic properties. Here we present the synthesis and characterization of the uranium dithiolene complexes [$U(Cp^*)_2$(dddt)] (**1**), [Na(18-crown-6)]$_2$[U(COT)(dddt)$_2$] (**2**: $Cp^* = \eta^5\text{-}C_5Me_5$; COT = $\eta^8\text{-}C_8H_8$; dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate), and [Na(18-crown-6)(THF)][U(COT)(dddt)$_2$] (**3**), including the crystal structure of **3**. Compounds **2** and **3** are unique examples of heteroleptic cyclooctatetraene/dithiolene metal complexes, and **3** is the first uranium(V) complex with metal−sulfur bonds.

The bis(pentamethylcyclopentadienyl) complex [$U(Cp^*)_2$(dddt)] (**1**) was synthesized by treating [$U(Cp^*)_2Cl_2$] (549.5 mg, 0.948 mmol) with 1 equiv of Na_2dddt (214.6 mg, 0.948 mmol) in THF (25 mL) (Scheme 1). After it was stirred for 2 h at 20 °C, the solution was filtered and evaporated to dryness, giving a brown powder from which **1** was extracted with toluene (458 mg, 70%). The complex is quite stable in the solid state or in THF or benzene solution and crystallized from benzene. The ^{1}H NMR spectra[3] of **1** showed that, even at −80 °C, the two Cp* rings were equivalent, as well as the methylene

---

[†] CEA Saclay.

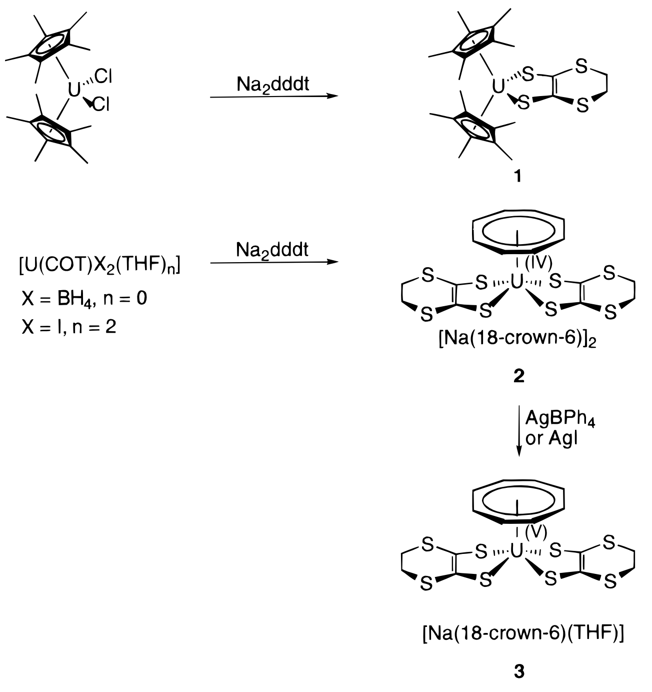
[‡] Institut des Matériaux Jean Rouxel.

(1) (a) Cassoux, P.; Valade, L.; Kobayashi, H.; Kobayashi, A.; Clark, R. A.; Underhill, A. E. *Coord. Chem. Rev.* **1991**, *110*, 115. (b) Olk, R.-M.; Olk, B.; Dietzsch, W.; Kirmse, R.; Hoyer, E. *Coord. Chem. Rev.* **1992**, *117*, 99.

(2) For a recent review see: Fourmigué, M. *Coord. Chem. Rev.* **1998**, *180*, 823.

10.1021/om990719j CCC: \$19.00 © 2000 American Chemical Society
Publication on Web 12/15/1999

Scheme 1. Synthesis of the Compounds



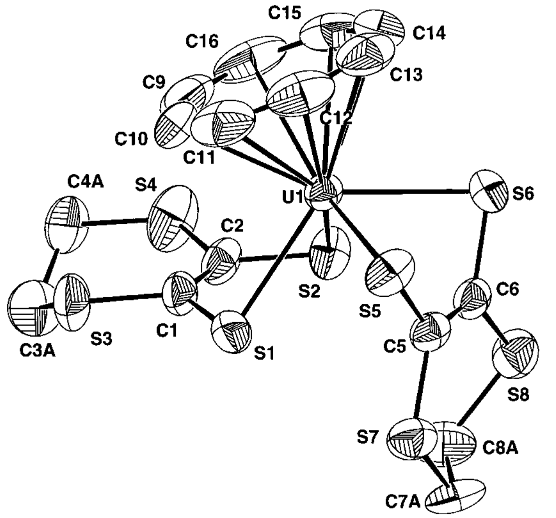


Figure 1. ORTEP drawing of the anion $[U(COT)(dddt)_2]^-$ in **3** with thermal ellipsoids at the 50% probability level. Selected bond distances (Å) and angles (deg): U(1)−COT centroid = 2.033(3), U−C = 2.694(8)−2.746(8), U(1)−S(1) = 2.694(2), U(1)−S(2) = 2.687(2), U(1)−S(5) = 2.700(2), U(1)−S(6) = 2.690(2), S(1)−C(1) = 1.751(7), S(2)−C(2) = 1.744(7), S(5)−C(5) = 1.750(7), S(6)−C(6) = 1.761(7), C(1)−C(2) = 1.357(9), C(5)−C(6) = 1.363(9); S(2)−U(1)−S(1) = 75.15(6), S(6)−U(1)−S(5) = 74.78(6), S(2)−U(1)−S(6) = 79.53(6), S(1)−U(1)−S(5) = 77.75(6). The ethylenic groups of both dddt moieties were found disordered on two positions; only one is represented here.

protons of the dddt ligand, and indicated that the ring inversion process corresponding to the folding of the metallacycle along the S−S axis is much easier than in the group 4 d^0 complexes.[4,5]

Complex **1** was readily reduced in THF with sodium amalgam to the corresponding U(III) anion $[U(Cp^*)_2(dddt)]^-$, which was transformed back into **1** in the presence of $AgBPh_4$ (NMR experiments); **1** was inert toward the silver salt. In that respect this redox behavior is similar to that of the bis(thiolate)uranium(IV) compounds $[U(Cp^*)_2(SR)_2]$ (R = Me, *i*-Pr)[6] and titanocene dithiolenes.[2] A different situation was encountered in the cyclooctatetraene derivative described below.

Reaction of $[U(COT)(BH_4)_2]$ (204 mg, 0.548 mmol) with 2.1 equiv of Na_2dddt (260.7 mg, 1.152 mmol) in THF (25 mL) afforded the bis(dithiolene) derivative $[Na(THF)_n]_2[U(COT)(dddt)_2]$. The mixture was stirred for 5 h at 20 °C and filtered, and after the addition of 2 equiv of 18-crown-6, red crystals of $[Na(18\text{-crown-}6)(THF)_n]_2[U(COT)(dddt)_2]$ were deposited. The crystals were filtered off and dried overnight to remove coordinated THF, leaving **2** as a red powder (520 mg, 77%).[7] The complex is quite stable in THF solution and in the solid state. It is interesting to note that reaction of $[U(COT)(BH_4)_2]$ with Na_2dddt gave the dianionic complex **2**, whereas similar treatment with NaSR afforded the neutral bis(thiolate) complexes $[U(COT)(SR)_2]_2$ (R = *n*-Bu, *i*-Pr).[8]

Complex **2** was oxidized in THF with $AgBPh_4$ to the corresponding U(V) monoanion $[Na(18\text{-crown-}6)(THF)][U(COT)(dddt)_2]$ (**3**; quantitative yield by NMR). The unsolvated uranium(V) bis(dithiolene) compound $[Na(18\text{-crown-}6)][U(COT)(dddt)_2]$ (**4**) was prepared by a one-pot synthesis from $[U(COT)I_2(THF)_2]$ (210 mg, 0.284 mmol), which was treated successively in THF (25 mL) with Na_2dddt (148 mg, 0.653 mmol), AgI (66.6 mg, 0.284 mmol), and, after filtration of the solution, 18-crown-6 (75 mg, 0.284 mmol). After evaporation to dryness, the residue was extracted with the minimum amount of CH_2Cl_2 and black needles of **4** crystallized upon addition of pentane (70 mg, 25% yield). The ^1H NMR spectra[9] showed that the signals of the equivalent dddt ligands were much larger at −90 °C but coalescence and the slow-limit spectrum could not be observed; here again, these facts argue for a facile inversion process of the dddt ligands. The NMR resonances, which are broader than those of the U(IV) precursor **2**, and the dark purple color of the solution were characteristic of a uranium(V) complex.[10]

---

(3) Product **1**: ^1H NMR (THF-d_8, 20 °C) δ 8.0 (s, 30 H, Cp*), −10.45 (s, 4 H, dddt). Anal. Calcd for $C_{24}H_{34}S_4U$: C, 41.85; H, 4.98; S, 18.62. Found: C, 41.60; H, 4.82; S, 18.36.

(4) Guyon, F.; Lenoir, C.; Fourmigué, M.; Larsen, J.; Amaudrut, J. *Bull. Soc. Chim. Fr.* **1994**, *131*, 217.

(5) Guyon, F.; Fourmigué, M.; Audebert, P.; Amaudrut, J. *Inorg. Chim. Acta* **1995**, *239*, 117.

(6) (a) Lescop, C.; Arliguie, T.; Leverd, P. C.; Lance, M.; Nierlich, M.; Ephritikhine, M. *J. Organomet. Chem.* **1999**, *580*, 137. (b) Ventelon, L.; Lescop, C.; Arliguie, T.; Leverd, P. C.; Lance, M.; Nierlich, M.; Ephritikhine, M. *Chem. Commun.* **1999**, 659.

(7) Product **2**: ^1H NMR (THF-d_8, 20 °C) δ 3.74 (s, 24 H, 18-crown-6), −0.24 (m, $w_{1/2}$ = 25 Hz, 4 H, dddt), −3.34 (m, $w_{1/2}$ = 25 Hz, 4 H, dddt), −29.17 (s, $w_{1/2}$ = 8 Hz, 8 H, COT). Anal. Calcd for $C_{40}H_{64}Na_2O_{12}S_8U$: C, 37.61; H, 5.05; S, 20.08. Found: C, 37.41; H, 4.86; S, 20.30.

(8) Leverd, P. C.; Arliguie, T.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **1994**, 501.

(9) Product **4**: ^1H NMR (THF-d_8, 20 °C), δ 4.03 (s, 24 H, 18-crown-6), −0.21 (s, $w_{1/2}$ = 25 Hz, 4 H, dddt), −3.08 (s, $w_{1/2}$ = 35 Hz, 4 H, dddt), −27.35 (s, $w_{1/2}$ = 300 Hz, 8 H, COT). Anal. Calcd for $C_{28}H_{40}NaO_6S_8U$: C, 33.96; H, 4.07; S, 25.91. Found: C, 33.72; H, 3.93; S, 25.65.

(10) Boisson, C.; Berthet, J. C.; Lance, M.; Nierlich, M.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **1996**, 947.

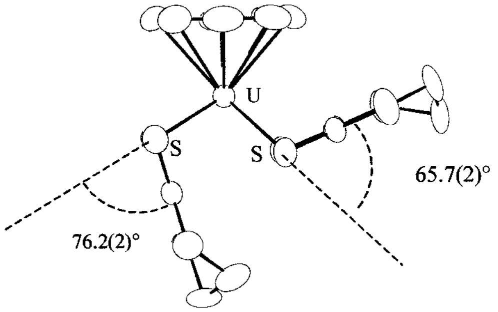


Figure 2. ORTEP drawing showing the folding dihedral angle values observed in **3**.

The crystal structure[11] of **3** shows that the anion $[U(COT)(dddt)_2]^-$ is located in general position in the unit cell, while the solvated cation $[Na(18\text{-crown-}6)(THF)_2]^+$ and the less usual $[Na(18\text{-crown-}6)]^+$ are found on an inversion center. An ORTEP view of the anion is shown in Figure 1 together with selected data. The uranium atom is five-coordinate in a distorted-square-pyramidal arrangement if the cyclooctatetraene is considered as a monodentate ligand. The U atom is 1.286(1) Å above the basal plane formed by the four S atoms (within ±0.0075 Å), the latter being almost parallel to the planar COT ring with an angle of 6.1(2)°. The U−S bond distances (average 2.693(7) Å) are similar to those observed in uranium thiolate complexes.[6,8] The characteristics of the $dddt^{2-}$ ligand, i.e., the C−S (average 1.75(1) Å) and C═C (1.357(9) and 1.363(9) Å) bond lengths, are consistent with those found in $[Ti(Cp)_2(dddt)]$ or $[Ti(Cp)(dmit)_2]^-$ and indicate that the oxidation process is mostly metal-centered with apparently little delocalization on the dithiolene ligands.[4] However, the US_2C_2 rings are strongly folded along the S−S axis, and the dithiolene ligands adopt an exo−endo conformation around the metal atom. The folding dihedral angle values observed in **3** (65.7(2) and 76.2(2)°) (Figure 2) are far more important than those encountered in $[Ti(Cp)(dmit)_2]^-$ (22.00(5) and 62.53(3)°)[4] and $[Ti(Cp)(S_2C_6H_4)_2]^-$ (36.3 and 23.3°)[12] and indicate a stabilization of the metal orbitals through interaction with the dithiolene π orbitals. Determination of the structural characteristics of the U(IV) complex as well as magnetic measurements and molecular calculations are being actively pursued in order to determine the origin of the stabilization of the U(V) species in such a sulfur environment and the extent of spin delocalization on the dithiolene ligands.

Supporting Information Available: Tables giving data collection and refinement details, atomic coordinates, thermal parameters, and bond lengths and bond angles of the crystallographically characterized complex. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990719J

---

[11] X-ray data: black crystal of **3** from THF, $C_{32}H_{48}NaO_7S_8U$, $M = 1062.20$, triclinic ($P\bar{1}$), $a = 10.8696(12)$ Å, $b = 11.4878(12)$ Å, $c = 17.868(2)$ Å, $\alpha = 96.344(12)°$, $\beta = 98.892(12)°$, $\gamma = 107.897(12)°$, $V = 2067.9(4)$ Å^3, $T = 293$ K, $Z = 2$, $\mu = 4.381$ mm^{-1}, 24 937 reflections measured, 9217 independent reflections, 5821 reflections with $I > 2\sigma(I)$. $R1(F) = 0.0405$, $wR2(F^2) = 0.0878$. The structure was solved by direct methods and refined by full-matrix least squares on F^2 with anisotropic thermal parameters for all non-H atoms. H atoms were introduced at calculated positions and constrained to ride on their parent C atoms. All calculations were performed with the SHELTX package: Sheldrick G. M. SHELXS-97 and SHELXL-97; University of Göttingen, Göttingen, Germany.

[12] Köpf, H.; Lange, K.; Pickardt, J. *J. Organomet. Chem.* **1991**, *420*, 345.