Monocyclooctatetraenyl(dithiolene)uranium Compounds

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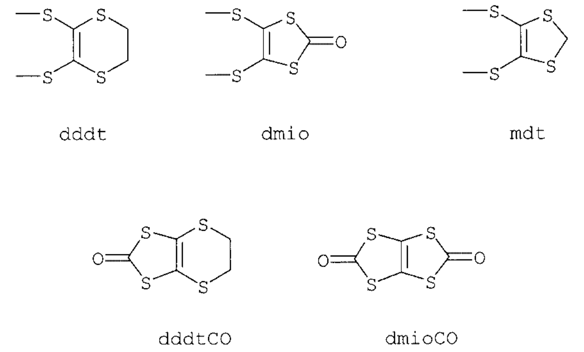
The neutral mononuclear dithiolene compounds [U(cot)(dithiolene)(tppo)$_2$] [cot = η-C_8H_8; dithiolene = dddt (**9**), dmio (**10**), mdt (**11**)], [U(cot)(dithiolene)(hmpa)$_2$] [dithiolene = dddt (**12**), dmio (**13**), mdt (**14**)], [U(cot)(mdt)(bipy)] (**15**) and [U(cot)(mdt)(terpy)] (**16**) were obtained by treating the dimeric complexes [{U(cot)(dithiolene)}$_2$] [dithiolene = dddt (**3**), dmio (**4**), mdt (**5**)] (dddt = 5,6-dihydro-1,4-dithiine-2,3-dithiolate; dmio = 1,3-dithiole-2-one-4,5-dithiolate; mdt = 1,3-dithiole-4,5-dithiolate) with the corresponding Lewis base [triphenylphosphine oxide (tppo), hexamethylphosphoramide (hmpa), 2,2′-bipyridine (bipy), or 2,2′:6′,2′′-terpyridine (terpy)]. Complexes **9**·2THF, **11**·2THF, **12**, **13**, **14**, **15** and **16**·1.5py have been crystallographically characterized. The crystal structures show a significant interaction between the C=C double bond of the dithiolene ligand and the metal centre. The ^{1}H NMR spectra reveal the fluxional behaviour of the compounds in solution in relation to the facile inversion of the dithiolene ring. The variation of the activation energies of the inversion process reflects the steric congestion of the complexes.

Introduction

Dithiolene complexes of the d-block transition metals have received much attention for their remarkable structural features and physicochemical properties, finding applications in the elaboration of novel conducting and magnetic materials.[1] In contrast, such compounds of the f-block elements have been practically neglected,[2] mainly due to the presumption that this type of complex should be unstable. In fact, lanthanides and actinides have proved to have a strong affinity for sulfur,[3−12] and the synthesis of their dithiolene complexes is worth considering since their coordination flexibility, paramagnetism and redox behaviour could favour the emergence of interesting structures and electronic interactions. For these reasons we have started studies on organouranium−dithiolene compounds, in particular bis(pentamethylcyclopentadienyl) and monocyclooctatetraenyl derivatives, for comparison with the heteroleptic cyclopentadienyl/dithiolene complexes of the metals of groups 4−6[13,14] and with the uranium bis(thiolate) complexes [U(cp*)$_2$(SR)$_2$][11] and [{U(cot)(SR)$_2$}$_2$][7] (cp* = η-C_5Me_5; cot = η-C_8H_8). The dithiolene ligands selected for this work are represented in Scheme 1.



Scheme 1. The dithiolene ligands and dithiocarbonates (dddt = 5,6-dihydro-1,4-dithiine-2,3-dithiolate; dmio = 1,3-dithiole-2-one-4,5-dithiolate; mdt = 1,3-dithiole-4,5-dithiolate)

We recently reported that anionic bis(dithiolene) derivatives could be obtained from the metathesis reaction of the uranium bis(borohydride) complex [U(cot)(BH$_4$)$_2$] with 2 mol-equiv. of Na$_2$dddt in THF, affording, in the presence of 18-crown-6, red crystals of a THF solvate of [Na(18-crown-6)(THF)$_2$]$_2$[U(cot)(dddt)$_2$] (**1**). Complex **1** was a unique example of a dianionic monocyclooctatetraenyluranium compound, although the [U(cot)X$_3$]$^-$ anions were found to be stable in the presence of an excess of X$^-$ (X = SR,[7] NR$_2$,[15] BH$_4$ [16]). Its oxidation with AgBPh$_4$ in THF afforded the corresponding monoanionic compound [Na(18-crown-6)(THF)][U(cot)(dddt)$_2$] (**2**), which was structurally characterized.[17] Complex **2** was the first uranium(V) compound with metal−sulfur bonds and, after the cycloheptatrienyl sandwich compound [K(18-crown-

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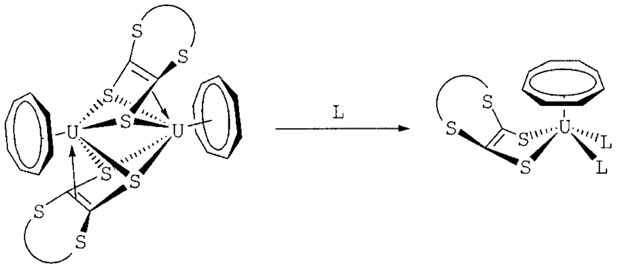
6)][U(η-C_7H_7)$_2$],[18] a new example of an anionic organouranium(V) derivative.

We also disclosed that the same borohydride, [U(cot)(BH_4)$_2$], could act as a hydride reagent in the reductive fission of dithiocarbonates, afording a series of neutral dimetallic dithiolene complexes [{U(cot)(dithiolene)}$_2$] [dithiolene = dddt (**3**), dmio (**4**), mdt (**5**)].[19] Upon dissolution in pyridine, those dimeric compounds could be transformed into the mononuclear complexes [U(cot)(dithiolene)(py)$_2$] [dithiolene = dddt (**6**), dmio (**7**), mdt (**8**)]. The crystal structure of **8** revealed a significant interaction between the dithiolene ligand and the metal centre.[19] With the aim of understanding and controlling this interaction, we have studied the complexation of **3**−**5** with various Lewis bases, such as triphenylphosphine oxide (tppo) or hexamethylphosphoramide (hmpa), and chelating pyridines such as bipyridine or terpyridine.

Here we report the synthesis of a series of adducts of general formula [U(cot)(dithiolene)(L)$_n$] (n = 1 and L = bipy or terpy; n = 2 and L = tppo or hmpa). We describe the X-ray crystal structures of the complexes, paying special attention to the interaction between the dithiolene ligand and the metal centre, and we present the ^{1}H NMR spectra, which reveal the dynamic behaviour of the complexes in solution, related to the facile ring-inversion process of the dithiolene ligand.[17,19]

Results and Discussion

The bis adducts [U(cot)(dithiolene)(tppo)$_2$] [dithiolene = dddt (**9**), dmio (**10**), mdt (**11**)] and [U(cot)(dithiolene)(hmpa)$_2$] [dithiolene = dddt (**12**), dmio (**13**), mdt (**14**)] were obtained by treatment of **3**−**5** with 2 mol-equiv. of tppo or hmpa in THF (Scheme 2). With the exception of **10**, these complexes could also be prepared in a one-pot reaction from [U(cot)(BH_4)$_2$], L and the dithiocarbonates dddtCO or dmioCO, which are the protected forms of the corresponding dithiolene ligands (dddtCO = 5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiine-2-one; dmioCO = 1,3,4,6-tetrathiapentalene-2,5-dione). In the presence of 2,2′-bipyridine (bipy) or 2,2′:6′,2′′-terpyridine (terpy) in THF, **5** was transformed into [U(cot)(mdt)(bipy)] (**15**) and [U(cot)(mdt)(terpy)] (**16**), respectively. Complexes **6**−**16** were isolated as red to dark-brown crystals or powders with yields from 65 to 95%.



dithiolene	
dddt	**3**
dmio	**4**
mdt	**5**

dithiolene \ L	py	tppo	hmpa
dddt	**6**	**9**	**12**
dmio	**7**	**10**	**13**
mdt	**8**	**11**	**14**

Scheme 2. Synthesis of the mononuclear compounds **6**−**14**

At least one example of each type of the Lewis-base adducts of **3**−**5** with tppo or hmpa (**11**, **12** and **13**) was characterized by elemental analysis, as were **15** and **16** , and the X-ray crystal structures of **9**·2THF, **11**·2THF, **12**, **13**, **14**, **15** and **16**·1.5py were also determined.

Crystal Structures of the Complexes

The crystal structure of the dinuclear compound **5** (Figure 1) has already been described in a preliminary report;[19] only the main geometrical features will be recalled for comparison with its congeners.

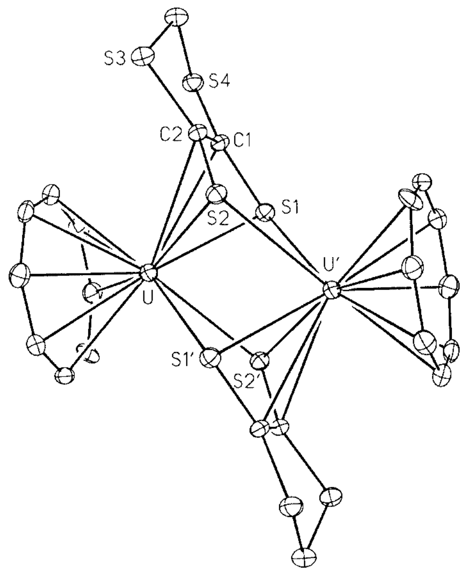


Figure 1. View of the complex [{U(cot)(mdt)}$_2$] (**5**); the hydrogen atoms have been omitted for clarity; the displacement ellipsoids are drawn at the 30% probability level; symmetry code: ′ = − x, 1 −y, −z

The Lewis-base adducts of general formula [U(cot)(dithiolene)(L)$_2$] adopt a four-legged piano-stool configuration, the base of which is defined by the S(1) and S(2) atoms of the dithiolene ligand and the two oxygen [O(1) and O(2)] or the two nitrogen [N(1) and N(2)] atoms of the Lewis base. The structures of **9** (Figure 2), **14** (Figure 3) and **15** (Figure 4), which are representatives of the series, are shown below; selected bond lengths and angles in the complexes [U(cot)(dithiolene)(L)$_2$] are listed in Table 1. Complex **15** has crystallographic mirror symmetry.

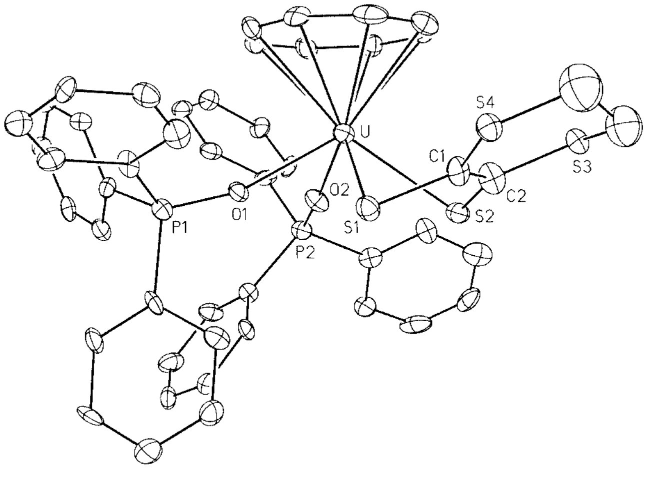


Figure 2. View of the complex [U(cot)(dddt)(tppo)$_2$] (**9**); the hydrogen atoms have been omitted for clarity; the displacement ellipsoids are drawn at the 30% probability level

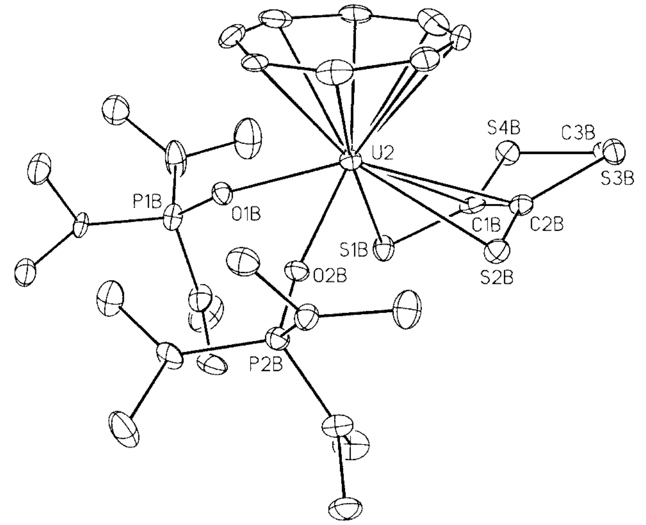


Figure 3. View of one of the two independent molecules of [U(cot)(mdt)(hmpa)$_2$] (**14**); the hydrogen atoms have been omitted for clarity; the displacement ellipsoids are drawn at the 30% probability level

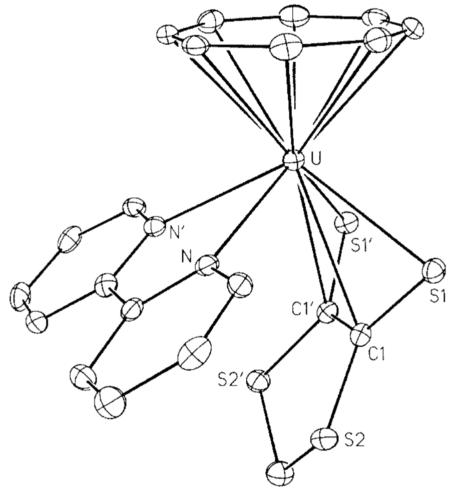


Figure 4. View of the complex [U(cot)(mdt)(bipy)] (**15**); the hydrogen atoms have been omitted for clarity; the displacement ellipsoids are drawn at the 30% probability level; symmetry code: ′ = *x*, 0.5 − *y*, *z*

The cot ligand in all the complexes is planar within ±0.09 Å. The average U−C(cot) distances in the Lewis-base adducts [U(cot)(dithiolene)(L)$_2$], with a typical value of 2.71 Å, are longer than that of 2.640(2) Å in **5**, and are at the upper limit of the range of U−C(cot) bond lengths in monocyclooctatetraenyluranium(IV) compounds, which vary from 2.62(2) Å in the bis(thiolate) complex [{U(cot)(S*i*Pr)$_2$}$_2$][7] to 2.71(4) Å in [U(cot)(NEt$_2$)(THF)$_3$][BPh$_4$].[20]

In the tppo and hmpa adducts, the U−O distances vary from 2.302(8) Å in **13** to 2.444(8) Å in **14** and are unexceptional; they are similar to those of 2.27(1) Å in [U(cot)(BH$_4$)$_2$(tppo)][21] and 2.461(8) Å in [U(cot)(Cp*)(hmpa)].[22] The U−N distance in **15** [2.555(4) Å] can be compared with those in **8** [2.636(9) and 2.691(10) Å], [U(cot)Cl$_2$(py)$_2$] [2.639(5) and 2.644(6) Å],[23] and to the average U−N(bipy) distance of 2.63(2) Å in [NEt$_4$][U(NCS)$_5$(bipy)$_2$],[24] which is the other uranium(IV)−bipy complex to have been crystallographically characterized. The O(1)−U−O(2) or N(1)−U−N(2) angles are quite similar, with an average value of 75(1)°, except for the N−U−N angle of the bidentate bipy ligand, which is equal to 63.12(19)°.

The U−S distances in the series of [U(cot)(dithiolene)(L)$_2$] complexes vary from 2.720(3) Å in **8** to 2.859(3) Å in **13** and are larger than the U−S bond lengths in the monomeric uranium(IV) thiolate compounds, which range between 2.61(5) Å in [U(S*i*Pr)$_2$(hmpa)$_4$][BPh$_4$][9] and 2.744(2) Å in [Na(18-crown-6)][U(Cp*)$_2$(S)(S*t*Bu)].[10] However, as expected for terminal SR ligands, these distances are shorter than the mean bridging SR bond length of 2.88(8) Å in the dimeric compound **5**. The S(1)−U−S(2) angles in the mononuclear compounds are close to 75°, while they are slightly smaller in **5**, with values of 68.29(6) and 71.98(6)°.

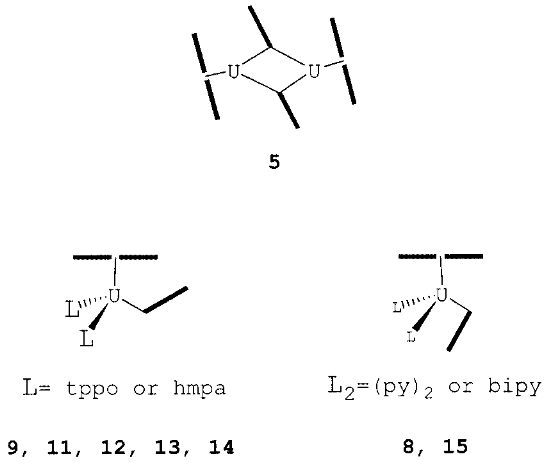
In all the complexes, the characteristics of the dithiolene ligands, such as the average C(sp^2)−S distances, which vary from 1.720(13) Å in **14** to 1.796(17) Å in **9**, and the C=C distances, which lie between 1.343(10) Å in **12** and 1.394(17) Å in **14**, are consistent with those found in [Mo(cp)$_2$(dddt)] [1.76(1) and 1.33(1) Å],[25] [NEt$_4$]$_2$[Ni(dmio)$_2$] [1.75(1) and 1.34(1) Å][26] and [NBu$_4$][Ni(mdt)$_2$] [1.74(2) and 1.36(2) Å].[27]

Special attention should be paid to the folding of the metallacycle as this reflects the interaction of the dithiolene ligand with the metal centre. The S$_4$C$_2$ fragment of the dithiolene ligands is planar within ±0.06 Å and forms a dihedral angle, *θ*, with the corresponding S−U−S plane. Scheme 3 shows the variation of this folding angle and the distinct conformations of the dithiolene ligands in the complexes. Previous studies on dithiolene compounds of the d-block transition metals have shown that *θ* increases upon lowering the electron density at the metal atom, reflecting the strength of the interaction of an empty metal orbital

Table 1. Selected bond lengths [Å] and angles [°] in the neutral mononuclear complexes **8**, **9** and **11−15**

	8[19]	**9**[a]	**11**[a]	**12**	**13**	**14**[b]	**15**
U−C(cot)	2.70(3)	2.70(2)	2.703(17)	2.716(17)	2.71(3)	2.71(2); 2.72(3)	2.686(7)
U−S(1)	2.720(3)	2.745(5)	2.773(2)	2.736(2)	2.801(3)	2.791(3); 2.739(3)	2.7511(14)
U−S(2)	2.751(3)	2.782(5)	2.781(2)	2.793(2)	2.859(3)	2.751(3); 2.821(3)	
U−C(1)	2.889(11)	3.089(15)	3.086(9)	3.181(8)	3.679(15)	3.146(10); 2.969(11)	2.879(5)
U−C(2)	2.965(11)	3.11(2)	3.081(8)	3.179(8)	3.674(14)	3.154(13); 3.020(11)	
U−O(1) or		2.398(10)	2.354(5)	2.363(5)	2.327(8)	2.354(8); 2.444(8)	
U−N(1)	2.691(10)						2.555(4)
U−O(2) or		2.376(12)	2.424(5)	2.353(5)	2.302(8)	2.367(8); 2.312(8)	
U−N(2)	2.636(9)						
C(1)−C(2)[c]	1.389(16)	1.35(2)	1.363(12)	1.343(10)	1.378(16)	1.348(16); 1.394(17)	1.374(10)
C(1)−S(1)	1.732(12)	1.796(17)	1.740(8)	1.757(7)	1.742(15)	1.732(12); 1.720(13)	1.748(5)
C(1)−S(4)[c]	1.781(12)	1.772(19)	1.765(9)	1.774(8)	1.754(14)	1.795(11); 1.762(12)	1.768(6)
C(2)−S(2)	1.749(11)	1.72(2)	1.742(9)	1.757(8)	1.722(14)	1.733(12); 1.742(12)	
C(2)−S(3)	1.749(13)	1.79(2)	1.772(8)	1.774(8)	1.762(13)	1.795(13); 1.772(12)	
S(1)−U−S(2)	77.08(10)	73.67(15)	75.74(7)	73.74(6)	73.89(9)	75.26(9); 75.48(9)	77.13(6)
O(1)−U−O(2) or		74.1(4)	74.2(2)	74.78(19)	77.1(3)	76.1(3); 74.8(3)	
N(1)−U−N(2)	74.3(3)						63.12(19)
θ[d]	75.6(3)	71.89(12)	71.32(6)	65.97(6)	20.93(19)	66.98(9); 75.97(9)	80.60(5)

[a] Complexes **9** and **11** crystallize with two THF molecules. [b] Values are given for the two independent molecules. [c] C(1)−C(2) and C(1)−S(4) are C(1)−C(1′) and C(1)−S(2) in complex **15**. [d] θ is the folding angle as defined in the text.



Scheme 3. Conformation of the dithiolene ligands

with the HOMO of the dithiolene ligand.[13,28] For example, in the series of $[M(Cp^{*})(dmit)_2]^{-1,0}$ compounds, the d^2 complexes $[M(Cp^{*})(dmit)_2]^{-1}$ (M = Mo, W) adopt an *exo-exo* conformation, and the d^0 derivative $[Ti(Cp^{*})(dmit)_2]^{-1}$ is found in an *exo-endo* conformation, while the geometry of the d^1 complex $[M(Cp^{*})(dmit)_2]^{\cdot}$ (M = Mo, W) compounds is intermediate between those of the Mo^{IV} or W^{IV} and Ti^{IV} analogues.[29]

In the series of Lewis-base adducts [U(cot)(dithiolene)(L)$_2$], the dithiolene ligand is found in the *exo* conformation, except in the pyridine and bipyridine derivatives **8** and **15**. The lower steric hindrance of these nitrogen ligands, in comparison with tppo and hmpa, permits the folding of the US_2C_2 fragment towards the *endo* position, with θ being equal to 75.6(3) and 80.60(5)° in **8** and **15**, respectively; the C(1) and C(2) atoms approach the metal centre at less than 3 Å. With the exception of **14**, the folding angles in the tppo and hmpa adducts are smaller than 75°, and are probably limited by the steric interaction between the dithiolene and cot ligands. One of the two independent molecules of **14** presents a θ angle of 75.97(9)° despite the *exo* conformation of the dithiolene ligand. The low value of θ in the dmio complex **13** [20.93(19)°] seems peculiar since the complexes [Ti(Cp)$_2$(dithiolene)] (dithiolene = dddt, dmio or dmit) exhibit quite similar θ angles of 47−50°.[13,14] However, this distinct feature of **13** might be ascribed to the presence in the crystal structure of weak intermolecular O(3)···H−C interactions[30−32] with four H atoms of the hmpa or cot groups of two neighbouring molecules, with O(3)···H distances in the range 2.621−2.893 Å. The structures of the other neutral dithiolene complexes exhibit weak intermolecular C−H···S contacts, shorter than 3 Å and as low as 2.70 Å; such interactions have been observed in a large number of tetrathiafulvalene derivatives.[33]

The crystal structure of the terpy adduct **16** is shown in Figure 5; selected bond angles and distances are given in Table 2. Complex **16** is a unique example of a distorted octahedral monocyclooctatetraenyluranium compound; the apical positions are occupied by the centroid of the cot ring and the S(2) atom, while S(1) and the three nitrogen atoms of the terpy ligand define the equatorial plane, with a mean deviation of ±0.002 Å. This plane is almost parallel to the planar cot ligand, with a dihedral angle of 4.38(13)°, and the U atom is located between the two planes at a distance of 0.8687(13) and 2.0148(15) Å, respectively. The planar dithiolene ligand is practically perpendicular to both the cot ring and equatorial plane, with dihedral angles of 88.93(7) and 84.72(5)°, respectively. The long U−S distances of 2.8203(10) and 2.8304(10) Å and the small folding angle, θ, of 20.40(4)° reflect the electronic and steric saturation of

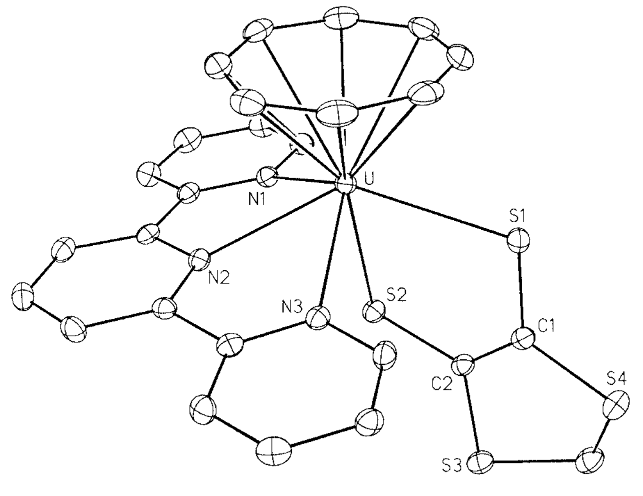


Figure 5. View of the complex [U(cot)(mdt)(terpy)] (**16**); the hydrogen atoms and solvent molecules have been omitted for clarity; the displacement ellipsoids are drawn at the 30% probability level

the complex. The average U−N distance of 2.589(9) Å can be compared with that of 2.63(3) Å in the U^{III} cation $[U(terpy)_3]^{3+}$, the other terpyridine uranium complex to have been crystallographically characterized.[34]

Dynamic Behaviour of the Complexes in Solution

The ^1H NMR spectroscopic data of the complexes are reported in Table 3. Complex **9** is not soluble in THF, while **15** and **16** are not soluble in THF or pyridine; their NMR spectra could therefore not be recorded. The spectra of the tppo and hmpa adducts in pyridine are more complicated, showing partial substitution of the L ligands by solvent molecules. At 20 °C, the cot ligand in all the complexes gives rise to a signal at $\delta \approx -30$ ppm, characteristic of monocyclooctatetraenyluranium compounds.[7,15,21,35] Two signals of equal intensities corresponding to the magnetically non-equivalent methylene protons of the dddt and mdt ligands in the Lewis-base adducts $[U(cot)(dithiolene)(L)_2]$ are visible at 20 °C, or at lower temperature in the case of **12**, as already observed for **6** and **8**.[19] Coalescence of these resonances occurred upon increasing the temperature, and the fast limit spectrum was obtained for complex **12**.

The dynamic behaviour of the complexes can be ascribed to the dithiolene ring inversion represented in Scheme 4; a similar fluxionality has been observed in a variety of $[M(Cp)_2(dithiolene)]$ compounds.[13,14] The ring inversion should proceed via the trigonal bipyramidal intermediate (**A** in Scheme 4) which renders the methylene protons equivalent. It is conceivable that, for the sterically less saturated complexes **6** and **8**, the octahedral intermediate [U(cot)(di-

Table 2. Selected bond lengths [Å] and angles [°] in [U(cot)(mdt)(terpy)]·1.5py (**16**·1.5py)

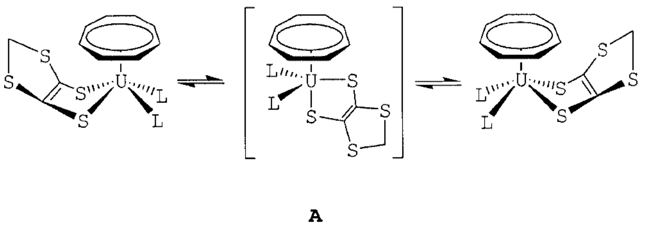
<U−C(cot)>	2.72(2)	U−S(1)	2.8203(10)	U−S(2)	2.8304(10)
U−N(1)	2.582(3)	U−N(2)	2.585(3)	U−N(3)	2.599(3)
C(1)−S(1)	1.743(4)	C(1)−S(4)	1.771(4)	C(2)−S(2)	1.746(4)
C(2)−S(3)	1.783(4)	C(1)−C(2)	1.336(5)		
S(1)−U−S(2)	71.06(3)	N(1)−U−N(2)	62.57(10)	N(1)−U−N(3)	119.58(10)
N(2)−U−N(3)	61.94(10)	S(1)−U−N(1)	125.45(7)	S(1)−U−N(2)	134.27(7)
S(1)−U−N(3)	81.48(7)	S(2)−U−N(1)	64.23(7)	S(2)−U−N(2)	77.15(7)
S(2)−U−N(3)	81.96(7)	cot−U−N(1)[a]	107.9	cot−U−N(2)	113.0
cot−U−N(3)	114.0	cot−U−S(1)	106.3	cot−U−S(2)	163.6

[a] cot is the centroid of the C_8H_8 ring.

Table 3. ^1H NMR spectroscopic data of the complexes[a]

Compound	T [°C]	cot ligand[b]	Dithiolene ligand	L ligands or 18-crown-6[c]
$[U(cot)(dddt)(py)_2]$ (**6**)[19]	+20	−30.98 (12 Hz)	10.87 (33 Hz, 4 H)	
	−40	−38.75 (12 Hz)	20.2 and 15.1 (500 Hz, 2 × 2 H)	
$[U(cot)(dddt)(hmpa)_2]$ (**12**)	+60	−26.13 (6 Hz)	−3.6 (140 Hz, ca 3 H)	1.30 (36 H)
	−80	−45.2 (130 Hz)	1.33 and −5.10 (35 Hz, 2 × 2 H)	−1.60 (36 H)
$[U(cot)(dmio)(py)_2]$ (**7**)[19]	+20	−32.07 (12 Hz)		
$[U(cot)(dmio)(tppo)_2]$ (**10**)	+20	−31.46 (15 Hz)		7.11 (6 H), 6.73 (12 H) 5.30 (45 Hz, 12 H)
$[U(cot)(dmio)(hmpa)_2]$ (**13**)	+20	−30.44 (12 Hz)		1.93 (36 H)
$[U(cot)(mdt)(py)_2]$ (**8**)[19]	+90	−24.82 (8 Hz)	11.21 (35 Hz, 2 H)	
	−30	−37.51 (3 Hz)	17.08 (45 Hz, 1 H)[d]	
$[U(cot)(mdt)(tppo)_2]$ (**11**)	+20	−29.52 (4 Hz)	5.22 and −2.74 (20 Hz, 2 × 1 H)	7.07 (6 H), 6.68 (12 H) 3.78 (45 Hz, 12 H)
$[U(cot)(mdt)(hmpa)_2]$ (**14**)	+20	−28.78 (4 Hz)	3.29 and −4.79 (35 Hz, 2 × 1 H)	0.07 (36 H)

[a] In [D$_8$]THF; **6**, **7** and **8** in [D$_5$]pyridine. The half-height width and the relative integral of the singlet signal are given in parentheses. [b] The cot signal integrates for 8 H. [c] When not specified, the half-height width is between 10 and 30 Hz. [d] The other signal of the mdt ligand is masked by the solvent resonances.



Scheme 4. Ring inversion process of the dithiolene ligand

thiolene)(py)$_3$], with a structure similar to that of the terpy adduct **16**, should be involved in the reaction. However, such an associative mechanism is not likely for the other Lewis-base adducts, since addition of tppo or hmpa has no influence on the fluxional process. The coalescence temperatures, T_c, and the activation energies, $\Delta G^{\ddagger}$, for the dithiolene ring inversion process are given in Table 4. The values of $\Delta G^{\ddagger}$ are in the range of those calculated for the [Ti(Cp)$_2$(dithiolene)] compounds, which vary from 40.5 to 69 kJ·mol^{-1} when the dithiolene is $S_2C_2(CN)_2$ and mdt, respectively;[14] they can also be compared with those measured for the metallacyclopentene ring inversion in bis(cyclopentadienyl)diene complexes of group 4 metals and actinides.[36] In the (dithiolene)titanium compounds, a correlation was found between the activation energy $\Delta G^{\ddagger}$ and the folding angle θ.[14] However, in the [U(cot)(dithiolene)(L)$_2$] derivatives, the variation of $\Delta G^{\ddagger}$ seems better related to the steric congestion of the complex and the difficulty of the ligands to rearrange around the metal centre. The lower barrier in the dddt compounds **6** and **12**, by comparison with the mdt analogues **8** and **14**, respectively, would correspond to a greater steric interaction between the dithiolene and L ligands in the ground state of the complex.

Table 4. Coalescence temperatures and activation energies for the ring-inversion process

Compound	T_c [°C]	$\Delta G^{\ddagger}$ [kJ·mol^{-1}]
[U(cot)(dddt)(py)$_2$] (**6**)[19]	−30	43(1)
[U(cot)(dddt)(hmpa)$_2$] (**12**)	+20	53(1)
[U(cot)(mdt)(py)$_2$] (**8**)[19]	+30	50(1)
[U(cot)(mdt)(tppo)$_2$] (**11**)	+80	63(1)
[U(cot)(mdt)(hmpa)$_2$] (**14**)	+80	63(1)

Conclusion

We have prepared a series of Lewis-base adducts of general formula [U(cot)(dithiolene)(L)$_n$] (n = 1, L = bipy or terpy and dithiolene = mdt; n = 2, L = tppo or hmpa and dithiolene = dddt, dmio, mdt). Crystallographic and NMR studies revealed that the solid-state structure and dynamic behaviour of these dithiolene complexes of an f-block element are similar to those of the d-block transition metal analogues, in particular the mixed cyclopentadienyl/dithiolene derivatives. The interaction between the dithiolene ligand and the metal centre observed in the solid state is favoured with the sterically less demanding Lewis bases which allow an *endo* conformation of the ligand. Still, the characteristics of the dithiolene ligands, such as the average C(sp^2)−S and C=C distances, are not greatly influenced by the nature of the Lewis base. In the whole series, the variable temperature ^{1}H NMR spectra show the fluxionality of the complexes due to the facile dithiolene ring inversion.

Experimental Section

General Remarks: All reactions were carried out under argon (<5 ppm oxygen or water) using standard Schlenk and vacuum-line techniques or in a glove box. Solvents were dried by standard methods and distilled immediately before use. The ^{1}H NMR spectra were recorded with a Bruker DPX 200 instrument and referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ = 0 ppm). Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany). [U(cot)(BH$_4$)$_2$],[21] [U(cot)I$_2$(THF)$_2$],[37] dddtCO,[38] dmioCO[39] and Na$_2$dddt[13] were prepared by published methods. The syntheses of **3**, **4**, **5** and **8** were described in our previous paper.[19]

Synthesis of [U(cot)(dddt)(py)$_2$] (6) and [U(cot)(dmio)(py)$_2$] (7): These complexes were obtained by dissolving **3** and **4**, respectively, in pyridine. After concentration to dryness, a dark-red powder of **6** and a brown powder of **7** were obtained in almost quantitative yield.

Synthesis of [U(cot)(dddt)(tppo)$_2$] (9): An NMR tube was charged with **3** (5.0 mg, 4.6 µmol) and tppo (2.6 mg, 9.2 µmol) in [D$_8$]THF (0.4 mL). Upon standing at 50 °C for 2−3 d, red crystals of **9** suitable for X-ray analysis were deposited.

Synthesis of [U(cot)(dmio)(tppo)$_2$] (10): An NMR tube was charged with **4** (5.0 mg, 4.8 µmol) and tppo (5.3 mg, 19.1 µmol) in [D$_8$]THF (0.4 mL). After 1 h at 20 °C, the spectrum of the brown solution showed the quantitative formation of **10**.

Synthesis of [U(cot)(mdt)(tppo)$_2$] (11). (a): An NMR tube was charged with **5** (5.0 mg, 4.9 µmol) and tppo (5.5 mg, 19.6 µmol) in [D$_8$]THF (0.4 mL). After standing at 65 °C for 3 h, brown crystals of **11** suitable for X-ray analysis were deposited. **(b):** A flask was charged with [U(cot)(BH$_4$)$_2$(THF)] (113 mg, 0.254 mmol) and tppo (142 mg, 0.51 mmol) in THF (25 mL). The reaction mixture was stirred at 20 °C for 15 min and a solution of dmioCO (53 mg, 0.254 mmol) in THF (10 mL) was added to the flask. After refluxing for 3 h, the solution was filtered and the solvents were evaporated to dryness, leaving a brown powder of **11** (276 mg, 90%). **11**·2THF, $C_{55}H_{56}O_4P_2S_4U$ (1209.3): calcd. C 54.63, H 4.67, S 10.61; found C 54.45, H 4.50, S 10.78.

Synthesis of [U(cot)(dddt)(hmpa)$_2$] (12): An NMR tube was charged with **3** (5.0 mg, 4.8 µmol) in [D$_8$]THF (0.4 mL) and hmpa (3.3 µL, 19.1 µmol) was introduced with a microsyringe. After 1 h at 20 °C, the spectrum of the red solution showed the quantitative formation of **12**. After standing at 20 °C overnight, red crystals of **12** suitable for X-ray analysis were deposited. $C_{24}H_{48}N_6O_2P_2S_4U$ (880.93): calcd. C 32.72, H 5.49, S 14.56; found C 32.59, H 5.51, S 14.41.

Synthesis of [U(cot)(dmio)(hmpa)$_2$] (13): A flask was charged with [U(cot)(BH$_4$)$_2$(THF)] (208 mg, 0.56 mmol) and hmpa (201 mg, 1.12 mmol) in THF (30 mL) and dmioCO (233 mg, 1.12 mmol) was added to the solution. After stirring at 20 °C for 24 h, the solution was filtered and the solvents were evaporated to dryness. The dark-red powder of **13** was washed with diethyl ether (50 mL), THF (20 mL) and dried under vacuum (460 mg, 93%). $C_{23}H_{44}N_6O_3P_2S_4U$ (880.88): calcd. C 31.36, H 5.03, S 14.56; found C 31.13, H 5.03, S 14.39.

Synthesis of [U(cot)(mdt)(hmpa)$_2$] (14): An NMR tube was charged with **5** (5.0 mg, 4.9 µmol) in [D$_8$]THF (0.4 mL) and hmpa (3.4 µL, 19.6 µmol) was introduced with a microsyringe. After 1 h at 65 °C, the spectrum of the brown solution showed the quantitative formation of **14**. After standing at 65 °C overnight, the tube was allowed to cool to room temperature and red crystals of **14** suitable for X-ray analysis were deposited.

Synthesis of [U(cot)(mdt)(bipy)] (15): An NMR tube was charged with **5** (21.0 mg, 20.6 µmol) and bipy (6.4 mg, 41.2 µmol) in [D$_8$]THF (0.4 mL). After standing at 5 °C overnight, dark brown crystals of **15** suitable for X-ray analysis were deposited. $C_{21}H_{18}N_2S_4U$ (664.68): calcd. C 37.95, H 2.73, S 19.30; found C 38.10, H 2.85, S 19.05.

Synthesis of [U(cot)(mdt)(terpy)] (16): An NMR tube was charged with **5** (10.0 mg, 9.8 µmol) and terpy (4.6 mg, 19.6 µmol) in [D$_8$]THF (0.4 mL). After standing at 5 °C overnight, dark-brown crystals of **16** suitable for X-ray analysis were deposited. $C_{26}H_{21}N_3S_4U$ (741.76): calcd. C 42.10, H 2.85, S 17.29; found C 41.92, H 2.96, S 17.06.

X-ray Crystallography: The data were collected at 100(2) K with a Nonius Kappa-CCD area-detector diffractometer[40] using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The crystals were placed inside glass capillaries with a protecting "Paratone-N" oil (Hampton Research) coating. The unit-cell parameters were determined from ten frames, then refined on all data. A 180° φ-range was scanned with 2° steps during data collection, with a crystal-to-detector distance fixed at 28 mm, giving complete data sets up to an angle, θ_{max}, of 25.7°. The data were processed with DENZO-SMN.[41] The structures were solved by direct methods with SHELXS-97 and subsequent Fourier-difference synthesis and refined by full-matrix least squares on F^2 with SHELXL-97.[42] Absorption effects were corrected empirically with the program DELABS from PLATON.[43] The correct enantiomorph in compound **13** was determined from the Flack parameter [−0.020(10)].[44] Three compounds crystallize as solvates: **9** and **11** with two tetrahydrofuran molecules and **16** with 1.5 pyridine molecules. A second form of compound **11**, with only one tetrahydrofuran solvent molecule, has been isolated and characterized [crystal data: $C_{51}H_{48}O_3P_2S_4U$, M = 1137.10, triclinic, space group $P\bar{1}$, a = 12.5818(13), b = 12.7381(13), c = 16.4223(14) Å, α = 71.253(6)°, β = 72.669(6)°, γ = 72.573(4)°, V = 2318.0(4) Å^3, Z = 2, D_c = 1.629 g·cm^{-3}, μ = 3.793 mm^{-1}, F(000) = 1128]. As it is essentially similar to the first form, it is not further described here. Some disorder is present in several complexes. In **9**·2THF, the atoms C(3) and C(4) of the dithiolene ligand may be disordered, but the different positions are not resolved and these atoms have been refined with restraints on bond lengths and displacement parameters. In **16**·1.5py, one pyridine solvent molecule is disordered around a symmetry centre and the nitrogen atom has not been located. All non-hydrogen atoms were refined with anisotropic displacement parameters, with some restraints on bond lengths and/or displacement parameters for some disordered or badly behaving atoms, particularly in the solvent molecules. Hydrogen atoms were introduced at calculated positions and were treated as riding atoms with

Table 5. Crystal data and structure refinement details

	9·2THF	**11**·2THF	**12**	**13**	**14**	**15**	**16**·1.5py
Empirical formula	$C_{56}H_{58}O_4P_2S_4U$	$C_{55}H_{56}O_4P_2S_4U$	$C_{24}H_{48}N_6O_2P_2S_4U$	$C_{23}H_{44}N_6O_3P_2S_4U$	$C_{23}H_{46}N_6O_2P_2S_4U$	$C_{21}H_{18}N_2S_4U$	$C_{33.5}H_{28.5}N_{4.5}S_4U$
M [g mol^{-1}]	1223.23	1209.21	880.89	880.85	866.87	664.64	860.38
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_12_12_1$	$P\bar{1}$	$P2_1/m$	$P2_1/n$
a [Å]	17.4062(10)	17.8541(9)	11.2254(8)	10.3673(6)	10.7430(6)	7.4304(5)	14.1685(4)
b [Å]	11.2254(5)	10.8390(5)	16.2142(17)	15.8278(15)	16.2499(10)	14.4901(9)	14.9404(4)
c [Å]	26.2282(17)	25.8930(12)	18.7509(18)	20.0597(18)	20.5468(10)	10.0511(7)	15.3685(5)
α [°]	90	90	90	90	67.938(3)	90	90
β [°]	91.459(5)	91.377(3)	92.248(6)	90	86.563(3)	109.787(4)	105.399(2)
γ [°]	90	90	90	90	87.829(3)	90	90
V [Å^3]	5123.1(5)	5009.4(4)	3410.2(5)	3291.6(5)	3317.8(3)	1018.28(12)	3136.46(16)
Z	4	4	4	4	4	2	4
$D_{calcd.}$ [g cm^{-3}]	1.586	1.603	1.716	1.777	1.735	2.168	1.822
μ(Mo-K_α) [mm^{-1}]	3.440	3.517	5.130	5.317	5.271	8.391	5.474
F(000)	2448	2416	1744	1736	1712	628	1668
Reflections collected	28649	33582	21645	19862	22784	7023	20975
Ind. reflections	9533	9466	6432	6128	11554	2006	5908
Obsd. reflections [$I > 2\sigma(I)$]	3607	6356	4471	4979	8411	1757	4911
R_{int}	0.093	0.094	0.088	0.129	0.074	0.068	0.054
Parameters refined	604	595	364	364	704	130	388
R_1	0.087	0.053	0.050	0.056	0.070	0.030	0.027
wR_2	0.135	0.106	0.094	0.129	0.154	0.059	0.055
S	0.933	1.019	1.019	1.013	1.104	1.023	1.017
$\Delta\rho_{min}$ [e·Å^{-3}]	−1.00	−1.02	−1.03	−1.23	−2.02	−0.91	−0.78
$\Delta\rho_{max}$ [e·Å^{-3}]	0.90	1.24	0.89	1.15	4.41	0.62	0.74

a displacement parameter equal to 1.2 (CH, CH_2) or 1.5 (CH_3) times that of the parent atom. Some short H···H contacts in **11**·2THF involve the protons of disordered parts or of badly behaving solvent molecules. Some short intramolecular contacts in **14** and **16**·1.5py (lower value 2.98 Å), which involve carbon atoms of the cot moiety and S, O or N donor atoms, are likely the result of the steric congestion in these molecules. The large positive and negative residual electron density peaks in **14** are located at 1.32 and 0.95 Å, respectively, from the uranium atom U(1) and may result from an imperfect absorption correction. Crystal data and structure refinement details are given in Table 5. The molecular plots were drawn with SHELXTL.[45] All calculations were performed with a Silicon Graphics R5000 workstation. CCDC-238470 (**9**·2THF), -238471 (**11**·2THF), -238472 (**12**), -238473 (**13**), -238474 (**14**), -238475 (**15**), -238476 (**16**·1.5py) and -238477 (**11**bis) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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