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# Unique crown thioether complexes of f elements: the crystal structure of U(III) and La(III) complexes of 1,4,7-trithiacyclononane

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**The crystal structures of the first U(III) complex of a crown thioether and of its La(III) analog have been determined; a stronger M–S interaction is observed for U(III) with respect to La(III) and Ce(III) in solution and in the solid state.**

The coordination chemistry of crown thioethers has been the subject of great interest in the past decade and has been studied in detail with elements of the p-block[1] and across the transition series.[2–4] However the crown thioether chemistry of lanthanides[5] and actinides is as yet untouched,[6] although a rich and unusual coordination chemistry might be anticipated from the combination of the hard lanthanide and actinide ions with these soft ligands.

Ligands with soft sulfur donors are also of interest in the coordination chemistry of f elements for their potential application in actinide(III)/lanthanide(III) separation, a difficult problem in nuclear waste disposal.[7–9] Indeed, they have been reported to complex actinides(III) more strongly than lanthanides(III), owing to a greater covalent contribution to the metal–sulfur bonding.[10,11] Due to their π-acceptor character[4,12] thioethers appear well suited to assess possible differences in An(III) *vs.* Ln(III) bonding to sulfur donors. The trithia crown 9S3, which offers a six-electron bonding set, is preorganized for facial binding to a metal ion, which explains the large number of studies involving the coordination chemistry of this ligand and makes it a good choice of ligand for this study. In order to relate possible structural differences between Ln(III) and U(III) complexes with the presence of a larger degree of covalency in the U(III)–S interaction we compare isostructural complexes of La and U containing the same iodide counter-ion. La(III) and U(III) have been chosen for their very similar sizes[13] which should minimize steric effects.

Here we report the crystal structure of La(III) and U(III) complexes of 1,4,7-trithiacyclononane (9S3). In addition proton NMR solution competion experiments were carried out with Ce(III) and U(III) which also have similar size[14] and both yield a paramagnetic shift of the proton signals of the coordinated ligand with respect to the free ligand. The proton signals of the coordinated ligand in the diamagnetic La complex are not shifted with respect to the free ligand. The proton NMR of 1 : 1 solutions of 9S3 and $CeI_3(thf)_4$, and of 1 : 1 solutions of 9S3 and $UI_3(thf)_4$ in deuterated acetonitrile show, in addition to the signal of the free ligand, two signals which were attributed to the respective 1 : 1 complexes.† The presence of two signals for the ($–CH_2CH_2–$) backbone of the complexed 9S3 is in agreement with the presence of $C_3$ symmetric rigid solution species. A value of the ratio $K_U/K_{Ce}$ = 3.3 ± 0.5 was obtained by integration of the NMR signals in a competion experiment in which 9S3 was reacted with 1 equiv. of $UI_3(thf)_4$ and 1 equiv. of $CeI_3(thf)_4$. This value indicates a selectivity of 1,4,7-trithiacyclononane for U(III) over Ce(III). Colourless crystals of $[La(9S3)I_3(CH_3CN)_2]$ (**1**), suitable for X-ray analysis‡ were obtained by diffusion of diethyl ether into an acetonitrile solution of 9S3 and $LaI_3{\cdot}(thf)_4$ (0.012 mmol) in a 1 : 1 ratio. Green crystals of $[U(9S3)I_3(CH_3CN)_2]$ (**2**), suitable for X-ray analysis‡ were obtained by leaving concentrated acetonitrile solutions of 9S3 and $UI_3{\cdot}(thf)_4$ (0.013 mmol) in 1 : 1 ratio standing several days at room temperature. Complexes **1** and **2** are isostructural and accordingly only the crystal structure of **2** is shown in Fig. 1. La–L, U–L (L = S, N, I) distances and the parameter $\Delta$ ($d$[La–L] − $d$[U–L]) are given in Table 1. The metal is eight-coordinated by three sulfurs of the trithiacrown 9S3, three iodides and two acetonitrile molecules. The metal environment can be described as a distorted square antiprism with two iodides, one sulfur and one acetonitrile nitrogen forming one square plane and two sulfurs, one iodide and one acetonitrile nitrogen occupying the second plane (Fig. 2). The angle between the two square planes is 6.2° for the U(III) complex and 6.3° for the La(III) complex.

The parameter $\Delta$ given in Table 1 show that the U–S distances are significantly shorter than the La–S distances. Since we are comparing isostructural compounds of ions with very similar ionic radii, these differences indicate the presence of a stronger M–S interaction in the U(III) complex. The differences observed are rather small (0.047(3) Å) but significant since they are larger than the difference found for $d$(M–N) and $d$(M–I) (Table 1).

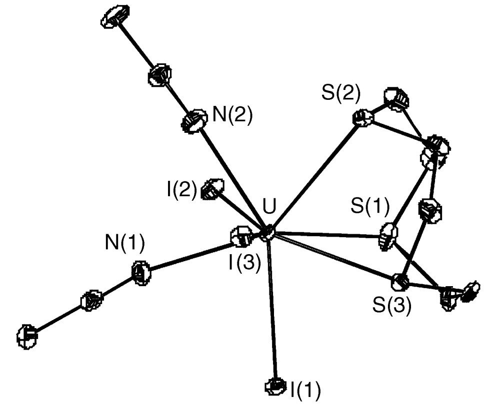

**Fig. 1** Crystal structure of the complex $[U(9S3)I_3(CH_3CN)_2]$ **2** with thermal ellipsoids at 30%.

**Table 1** La–L, U–L distances (Å) and the parameter $\Delta$ ($d$[La–L] − $d$[U–L])

| | $[U(9S3)I_3(MeCN)_2]$ | $[La(9S3)I_3(MeCN)_2]$ | $\Delta$ |
|---|---|---|---|
| M–N(1) | 2.611(3) | 2.6407(16) | 0.0297 |
| M–N(2) | 2.644(3) | 2.6719(16) | 0.0279 |
| M–S(1) | 3.0456(9) | 3.0891(4) | 0.0435 |
| M–S(2) | 3.0146(9) | 3.0635(4) | 0.0489 |
| M–S(3) | 3.0779(9) | 3.1263(4) | 0.0484 |
| M–I(1) | 3.0872(3) | 3.11413(16) | 0.02693 |
| M–I(2) | 3.1488(3) | 3.17696(17) | 0.02816 |
| M–I(3) | 3.1543(3) | 3.18561(16) | 0.03131 |

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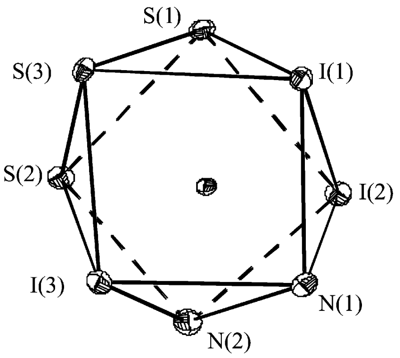

**Fig. 2** Coordination geometry about the metal center in [U(9S3)$I_3$($CH_3CN$)$_2$] **2**.

These crystallographic data (together with the observed selective complexation of U(III) over Ce(III)) could indicate the presence of some uranium to sulfur π-backbonding and therefore the presence of a covalent contribution to the U–S bonding.

In conclusion we have shown that the trithia crown 9S3 can be used to coordinate f elements through three soft sulfur donors. Moreover the uranium complex [U(9S3)$I_3$($CH_3CN$)$_2$] is the first U(III) complex anchored by a neutral polydentate sulfur donor ligand and a very rare example of a U(III) complex containing a U–S bond.[6]

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## Notes and references

† $LnI_3(thf)_4$ (Ln = La, Ce)[15] and $UI_3(thf)_4$[16] were prepared according to described procedures. $^1$H NMR ($CD_3CN$, 400 MHz), $\delta$ (ppm) for the complexes (prepared *in situ*) of 9S3: with Ce(III): 5.11 (6H), 6.80 (6H); with U(III) : 12.67 (6H), 13.65 (6H) . Complexes **1** and **2** were isolated in 30–40% yield by allowing concentrated 1 : 1 acetonitrile solutions of 9S3 and $MI_3(thf)_4$ (M = La, U) to stand for a few days.

‡ *Crystal data* for complex **1**: [La(9S3)$I_3$($CH_3CN$)$_2$], $C_{10}H_{18}I_3N_2S_3La$, $M$ = 782.05, monoclinic, space group $P2_1/c$, $a$ = 15.4185(7), $b$ = 9.1565(4), $c$ = 15.1299(7) Å, $\beta$ = 99.993(10)°, $V$ = 2103.63(16) Å$^3$, $Z$ = 4, $D_c$ = 2.469 g cm$^{-3}$, $\mu$ = 6.722 mm$^{-1}$. 5106 independent reflections ($2\theta_{max}$ = 57.8) were collected at 193(2) K. $R_1[F > 4\sigma(F)]$ = 0.0290, $wR_2$ = 0.0683. Maximum/minimum residual electron density: 1.206/−1.413 e Å$^{-3}$.

*Crystal data* for complex **2**: [U(9S3)$I_3$($CH_3CN$)$_2$], $C_{10}H_{18}I_3N_2S_3U$: $M$ = 881.17, monoclinic, space group $P2_1/c$, $a$ = 15.3393(10), $b$ = 9.1135(6), $c$ = 15.1154(10) Å, $\beta$ = 100.1070(10)°, $V$ = 2080.3(2) Å$^3$, $Z$ = 4, $D_c$ = 2.814 g cm$^{-3}$, $\mu$ = 12.547 mm$^{-1}$. 4996 independent reflections ($2\theta_{max}$ = 57.9) were collected at 193(2) K. $R_1[F > 4\sigma(F)]$ = 0.0404, $wR_2$ = 0.0810. Maximum/minimum residual electron density: 3.095/−1.640 e.Å$^{-3}$.

Both data sets were collected using a Bruker SMART CCD area detector three-circle diffractometer (Mo-Kα radiation, graphite monochromator, $\lambda$ = 0.71073 Å). The structures were solved by direct methods using the SHELXTL 5.03 package, and all atoms were found by difference Fourier syntheses. All non-hydrogen atoms were anisotropically refined on $F^2$. Hydrogen atoms were included in calculated positions and refined isotropically.

To prevent hydrolysis and oxidation, the crystals of **1** and **2** were coated with a light hydrocarbon oil and quickly transferred to a stream of cold nitrogen at 193 K on the diffractometer.

CCDC reference numbers 177594 and 177595. See http://www.rsc.org/suppdata/cc/b2/b200315p/ for crystallographic data in CIF or other electronic format.

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