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Synthesis and crystal structure of $[U(\eta\text{-}C_8H_8)]_2[\mu\text{-}\eta^4{:}\eta^4\text{-}HN(CH_2)_3N(CH_2)_2N(CH_2)_3NH]$, a dinuclear compound with a bridging tetra-amide ligand

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Abstract

The title compound was prepared by the transamination reaction of $[U(COT)(N\{SiMe_3\}_2)_2]$ and $H_2N(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$. The X-ray crystal structure reveals the shortest U–U distance [3.3057(9) Å] ever observed in a molecular compound. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Uranium; Tetra-amide; Dinuclear; Crystal structure

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1. Introduction

Metal amide complexes easily form di-, oligo- and polymeric species resulting from aggregation via nitrogen atom bridges [1]. It has been suggested that these M–N–M bridges will take place more readily in the actinide series than in the early d transition series because the weaker π bonding in the actinides would allow the amide nitrogen atom to more easily become tetrahedral and act as a bridging atom [2]. In uranium(IV) chemistry, two homoleptic $[U(NR_2)_4]$ compounds have been crystallographically characterized: a dimer (R = Et) [2] and a trimer (R = Me) [3]; the number of U–N–U bridges (two or three) and the structure (represented in Scheme 1) depend on the size of the alkyl group R. By using polyamide ligands, one could expect to observe, in addition to the polymers ensured by M–N–M bridges, the formation of polynuclear complexes in which two metals are attached to different nitrogen atoms of the same ligand. Thus, bis(dimethylethylenediamido)uranium $[U(MeNCH_2CH_2NMe)_2]$ was found to crystallize under the form of both a linear trimer [4] and a cyclic tetramer [5]; the metal centres are bridged by three and two nitrogen atoms, respectively (Scheme 1), each of the bridge nitrogen atoms coming from a different diamido ligand. The four homoleptic compounds represented in Scheme 1 are the only polynuclear uranium(IV) amide complexes to have been crystallographically characterized. Here we report on the synthesis and X-ray crystal structure of $[U(COT)]_2[\mu\text{-}\eta^4{:}\eta^4\text{-}HN(CH_2)_3N(CH_2)_2N(CH_2)_3NH]$ (**1**) (COT = $\eta\text{-}C_8H_8$), in which the tetradentate amide ligand is in a bridging position between the two U(COT) fragments. Such dinuclear compounds with the two metals linked by four nitrogen atoms are rather uncommon; in these complexes the nitrogen atoms are those of dinitrogen [6], azobenzene [7], phtalocyanine [8] or Schiff-base ligands [9].

2. Results and discussion

2.1. Synthesis of $[U(COT)]_2[\mu\text{-}\eta^4{:}\eta^4\text{-}HN(CH_2)_3N(CH_2)_2N(CH_2)_3NH]$ (1)

The transamination reaction constitutes a classical method for the synthesis of metal amide complexes.

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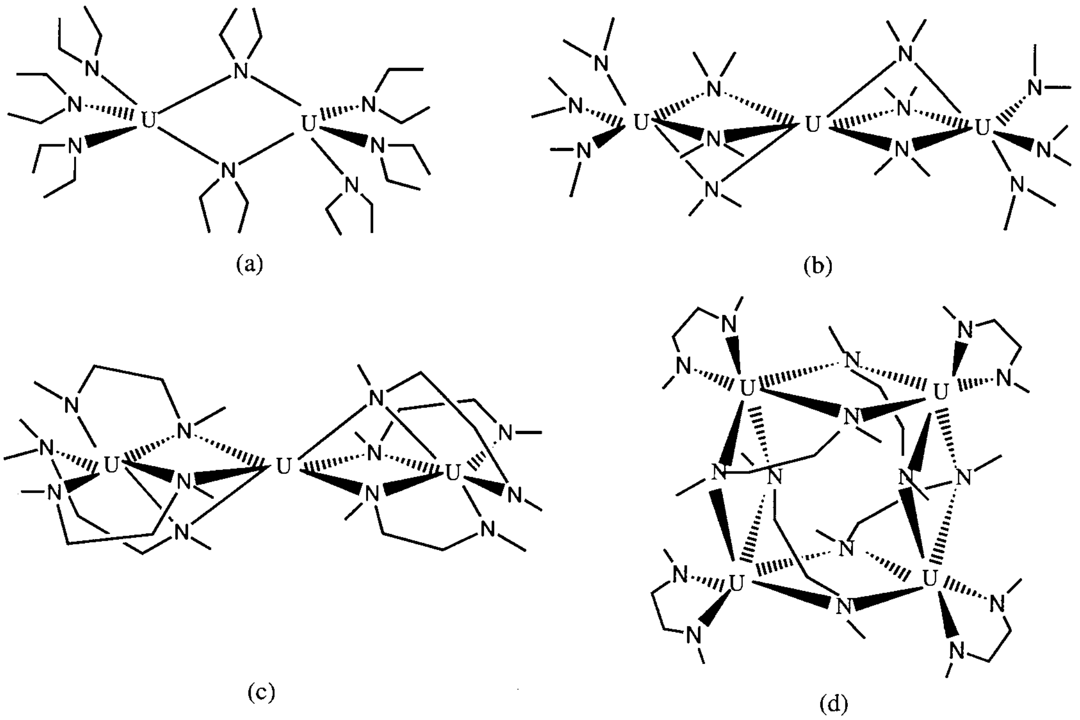
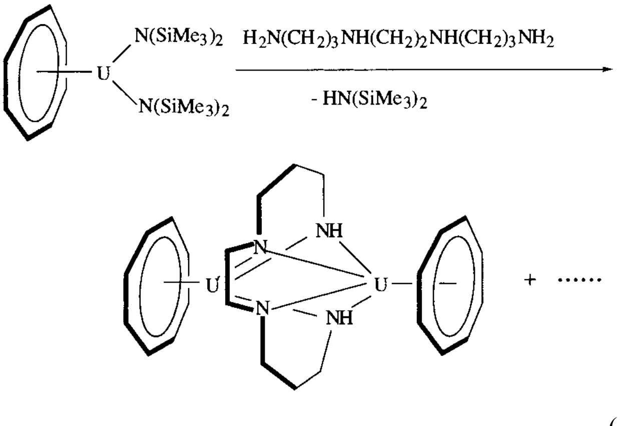


Scheme 1. Representation of the crystal structures of $[U(NEt_2)_4]_2$ (a), $[U(NMe_2)_4]_3$ (b), $[U(MeNCH_2CH_2NMe)_2]_3$ (c) and $[U(MeNCH_2CH_2NMe)_2]_4$ (d).

Thus, the uranium compounds $[U(MeNCH_2CH_2NMe)_2]_3$ [4] and $[U(MeNCH_2CH_2NMe)_2]_4$ [5] were prepared by treatment of $[U(NEt_2)_4]$ with dimethylethylenediamine. A similar reaction of $[U(NEt_2)_4]$ with tetrazadodecane, $H_2N(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$, in tetrahydrofuran (THF) or toluene led to the elimination of NEt_2H, but no product could be characterized by ^{1}H-NMR spectroscopy; attempts to grow crystals from the solution were unsuccessful. In order to reduce the presumed high degree of oligomerization and hence the complexity of the reaction, the transamination of a diamide complex was considered. Treatment of $[U(COT)(N\{SiMe_3\}_2)_2]$ [10] with an excess of the tetra-amine in THF or toluene caused the immediate precipitation of a brown powder in which a few small microcrystals of **1** were visible. The crystal structure of **1** was determined by X-ray diffraction analysis (vide infra), but the insolubility of the product(s) in organic solvents precluded any purification; for the same reason the NMR spectra could not be recorded. Therefore, it cannot be excluded that **1** was formed with other unidentified polymeric species.

It seems likely that the first step in the transamination of $[U(COT)(N\{SiMe_3\}_2)_2]$ with tetraazadodecane (Eq. (1)) is the reaction of the $N(SiMe_3)_2$ ligand with the more reactive primary group of the tetra-amine. Interestingly, 1,4,8,11-tetraazacyclotetradecane (cyclam) was found to be inert towards $[U(COT)(N\{SiMe_3\}_2)_2]$ presumably because of the steric hindrance of the secondary amino groups, which impedes its approach onto the uranium–nitrogen bond.



1 (1)

Moreover, it has been pointed out that amines with pK_a values greater than that of $(Me_3Si)_2NH$ would not react with the bis(trimethylsilyl) amide ligand unless these could be activated by prior coordination to the metal centre [11]. In the case of the formation of **1**, coordination of the secondary amine group to the uranium metal would be facilitated by the chelate effect; this coordination would enhance the acidity of the N–H hydrogen and favour its reaction with the second silylamide ligand.

2.2. X-ray crystal structure of $[U(COT)]_2[\mu\text{-}\eta^4{:}\eta^4\text{-}HN(CH_2)_3N(CH_2)_2N(CH_2)_3NH]$ (**1**)

Two views of the crystal structure of **1** are shown in Figs. 1 and 2 and selected bond distances and angles are listed in Table 1. Each uranium atom is five-coordinate in a quite perfect square-pyramidal arrangement if cyclooctatetraene is considered as a monodentate ligand. The two coordination polyhedra share the common square basis defined by the N atoms of the tetra-amide ligand; in the quadrilateral N(1)N(2)-N(3)N(4), the sides are quite equal with an average distance of 2.57(4) Å and the angles have an average value of 89.9(8)°. All the carbon and nitrogen atoms of the tetra-amide ligand are coplanar within ± 0.06 Å and this plane is almost parallel to the two planar cyclooctatetraene ligands, with dihedral angles of 5.3(5) and 3.6(5)°. The three planes of the tetra-amide and COT ligands are thus nearly perpendicular to the U(1)–U(2) axis, which passes through the centroids of the COT rings and of the nitrogen atoms square (Fig. 2). The COT ligation is similar to that found in uranocene and other monocyclooctatetraene uranium(IV) compounds [12], with an average U–C bond distance of 2.71(5) Å. The U–N bond lengths vary between 2.44(3) and 2.53(1) Å with an average of 2.46(7) Å. Assuming that each uranium is involved in a total of four bonds, each U–N bond in complex **1** can be regarded as a half bond in the terminology previously used by Andersen et al. [4]. Such U–N bridge half bonds have been found in $[U(NEt_2)_4]_2$ [2] and $[U(MeNCH_2CH_2NMe)_2]_4$ [5], with average lengths of 2.51 and 2.49 Å, respectively. In these complexes, the U–N (terminal) single-bond distances are equal to ca. 2.25 Å. By using the same terminology, the central uranium–nitrogen bridge bonds and the terminal uranium–nitrogen bridge bonds in the trinuclear compounds $[U(NMe_2)_4]_3$ [4] and $[U(MeNCH_2CH_2NMe)_2]_3$ [5] are two- and one-third bonds; their average distances are 2.62 and 2.38 Å, respectively. Thus, in complex **1** and the series of homoleptic uranium(IV) amide compounds shown in Scheme 1, the trend in U–N bond distances corresponds nicely to the variation of the bond orders. The U(1)–N–U(2) angles in **1** average 84(1)° and are significantly smaller than in $[U(MeNCH_2CH_2NMe)_2]_4$ [92(2)°] and $[U(NEt_2)_4]_2$ [105.6(3)°]. As a consequence, the U(1)–U(2) distance of 3.3057(9) Å is shorter than the values found in the above complexes, 3.59(1) and 4.004(1) Å respectively. It is also shorter than the U–U distance of 3.543(1) Å in $[U(MeNCH_2CH_2NMe)_2]_3$ [5], which is, to our knowledge, the shortest ever observed in a molecular compound. However, this value is much greater than that of a single U–U bond (2.85 Å) and indicates a non-bonded interaction [13].

Table 1
Selected bond distances (Å) and bond angles (°) in **1**

Bond lengths			
U(1)–N(1)	2.42(1)	U(2)–N(1)	2.43(1)
U(1)–N(2)	2.48(1)	U(2)–N(2)	2.47(1)
U(1)–N(3)	2.44(1)	U(2)–N(3)	2.53(1)
U(1)–N(4)	2.42(1)	U(2)–N(4)	2.44(1)
<U–C>	2.71(5)	U(1)·····U(2)	3.3057(9)
Bond angles			
N(1)–U(1)–N(2)	63.7(5)	N(1)–U(2)–N(2)	63.8(4)
N(2)–U(1)–N(3)	61.2(4)	N(2)–U(2)–N(3)	60.1(4)
N(3)–U(1)–N(4)	64.9(5)	N(3)–U(2)–N(4)	63.3(4)
N(1)–U(1)–N(4)	63.9(4)	N(1)–U(2)–N(4)	63.5(4)
U(1)–N(1)–U(2)	85.8(4)		
U(1)–N(2)–U(2)	83.6(4)		
U(1)–N(3)–U(2)	83.4(4)		
U(1)–N(4)–U(2)	85.5(4)		

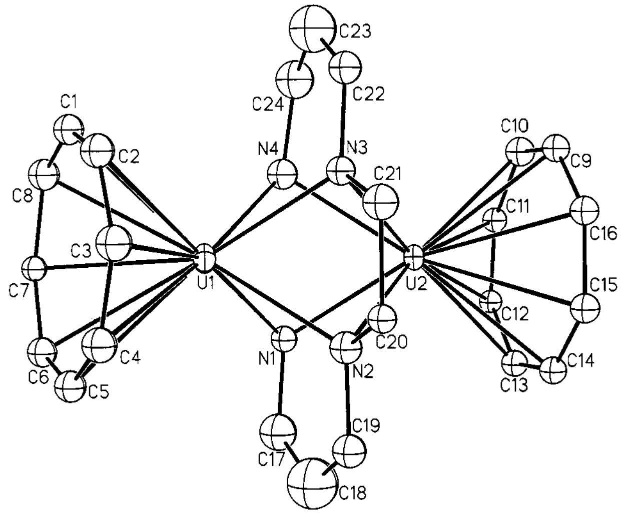


Fig. 1. X-ray crystal structure of **1**.

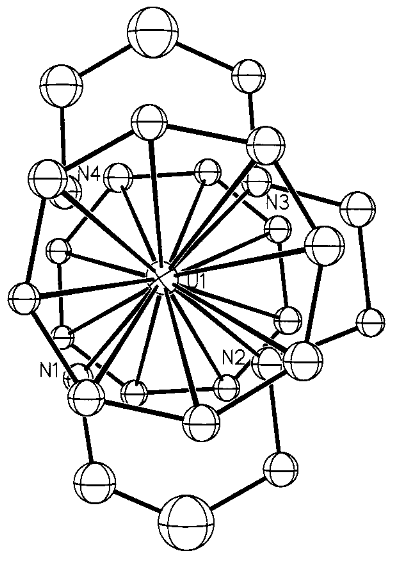


Fig. 2. X-ray crystal structure of **1**, view along the U(1)–U(2) axis.

3. Conclusions

The transamination reaction of the diamide complex $[U(COT)(N\{SiMe_3\}_2)_2]$ with the tetra-amine $H_2N(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$ afforded the first compound in which two metal centres are linked by a tetra-amide ligand in a μ-η^4:η^4 fashion. The crystal structure confirms the half-order of the U–N bonds and exhibits the shortest U–U distance ever observed in a molecular compound.

4. Experimental

4.1. General methods

All preparations and reactions were carried out under argon (less than 5 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a glove box. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately before use. The tetra-amine $H_2N(CH_2)_3$-$NH(CH_2)_2NH(CH_2)_3NH_2$ (Aldrich) was dried over molecular sieves. $[U(COT)(N\{SiMe_3\}_2)_2]$ was prepared as described in Ref. [10].

4.2. Reaction of $[U(COT)(N\{SiMe_3\}_2)_2]$ with $H_2N(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$

A 100 ml round-bottomed flask was charged with $[U(COT)(N\{SiMe_3\}_2)_2]$ (476 mg, 0.7 mmol) and toluene (50 ml) was condensed into the flask at −78°C under vacuum. The tetra-amine $H_2N(CH_2)_3NH(CH_2)_2NH$-$(CH_2)_3NH_2$ (64 μl, 0.35 mmol) was introduced into the flask via a microsyringe. A brown powder was immediately deposited with a few microcrystals of **1**. After 12 h at 20°C, the precipitate was filtered off, washed with THF and dried under vacuum (226 mg). The yield is equal to 75% if it is considered that only **1** was formed. Anal. Found: C, 28.70; H, 3.57; N, 5.50. Calc. for $C_{24}H_{34}N_4U_2$: C, 33.73; H, 4.00; N, 6.50%. The systematic low values of the elemental analyses (calc./found = 1.12–1.18) would reflect the difficult combustion of the product.

4.3. X-ray crystal structure of **1**

Selected single crystals were introduced into thin-walled Lindemann glass tubes in the glove box. Data were recorded on a Nonius Kappa-CCD area detector diffractometer using graphite-monochromatized Mo–K_α radiation. The crystal-to-detector distance was set to 30 cm and the unit cell was determined from all the reflections measured on 10 frames with Φ rotation steps of 1°. A 180° Φ range was scanned during data recording (90 frames, Φ rotation = 2°, exposure time = 30 s by frame). The data were processed with the HKL package [14], the structure was solved by Patterson function and subsequent Fourier differences with SHELXS86 [15] and refined on F^2 with SHELXTL [16] with anisotropic thermal parameters for the U atoms. H atoms were introduced at calculated positions as riding atoms with an anisotropic displacement parameter equal to 1.2 (CH, CH_2) times that of the parent atom. No absorption correction was made.

Crystal data for **1**: formula $C_{24}H_{34}N_4U_2$, crystal dimensions $0.15 \times 0.05 \times 0.05$ mm^3, orthorhombic, space group *Pbca*, $a = 28.051(6)$, $b = 13.298(3)$, $c = 12.235(2)$ Å, $V = 4563.9(16)$ Å^3, $Z = 8$, $\rho_{calc} = 2.488$ g cm^{-3}, $2 < 2\theta < 20.83°$, μ(Mo–K_α) = 14.194 cm^{-1}, $F(000) = 3120$, $T = 123$ K. 17 167 reflections collected, 2329 unique, 1283 with $I > 2\sigma(I)$, $R = 0.0341$. Difference Fourier analysis showed no peaks beyond 0.942 or −1.073 e Å^{-3}.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 135 110. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336022; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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