Journal of Alloys and Compounds 271–273 (1998) 150–153

Journal of
ALLOYS
AND COMPOUNDS

Triamidoamine complexes of the actinides; from mixed-valence bimetallics to dinitrogen activation

Paul Roussel[a], Nigel D. Tinker[b], Peter Scott[a,*]

[a]*Department of Chemistry, University of Warwick, Coventry, CV4 7AL, UK*
[b]*Company Research Laboratory, BNFL, Springfields Works, Preston PR4 0XJ, UK*

Abstract

Reduction of pale green {tris(*tert*-butyldimethylsilylamidoethyl)amino}chlorouranium(IV) $[U(NN'_3)Cl]$ with potassium gives the purple mixed valence (III/IV) dimer $[\{U(NN'_3)\}_2-\mu-Cl]$. Although the two metal atoms in this compound are indistinguishable by X-ray crystallography, other data are consistent with the presence of distinct tri- and tetravalent centres. Careful fractional sublimation of this species allows the 'cracking' of the molecule into $[U(NN'_3)Cl]$ and purple $[U(NN'_3)]$. This latter species reacts with dinitrogen gas to give reversible conversion to $[\{U(NN'_3)\}_2(\mu^2\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$, the first dinitrogen complex of an actinide. The molecular structure as determined by X-ray crystallography shows that the dinitrogen ligand is side-on bonded to the two uranium centres and that the N–N bond length is essentially the same as that in free dinitrogen. This, and variable temperature magnetic data are consistent with the formulation of this compound as a simple Lewis base adduct of uranium(III). The preference for side-on over end-on bonding is explained on the basis that the dinitrogen π_p orbital is a better σ-donor than the σ_p orbital to trivalent uranium. © 1998 Elsevier Science S.A.

Keywords: Uranium; Triamidoamine; Mixed-valence; Dinitrogen; Bonding

1. Introduction

Although the amido ligand (R_2N-) forms complexes with most of the elements, its inherent reactivity limits its use as a spectator ligand [1]. More recently, the use of substituted triamidoamine and tripodal triamido ligands in complexes of the main group elements [2–10] and the transition metals [11–13] has led to an extensive chemistry. Our work on the early actinide elements has shown that the chelate (triamidoamine)uranium fragment is quite robust, tolerating substitution reactions in auxiliary coordination sphere [14,15] and allowing the isolation of otherwise unstable complexes [16].

The recent report that three-coordinate alkylarylamido complexes of molybdenum (III) cleave molecular nitrogen under ambient conditions [17] prompted us to investigate the possibility of synthesising related triamidoamine uranium (III) compounds. Metal complexes of dinitrogen are usually formed from low-valent precursors. For example, the two such lanthanide complexes are derived from Sm(II) starting materials [18,19]. For the actinide elements, no dinitrogen complexes have been detected despite the availability of suitable coordinatively unsaturated trivalent uranium derivatives such as $[U\{N(SiMe_3)_2\}_3]$ [20] and the cyclopentadienyls $[U\{\eta^5\text{-}C_5H_4(SiMe_3)\}_3]$ and $[U(\eta^5\text{-}C_5Me_4H)_3]$ which form adducts with carbon monoxide [21,22].

2. Results and discussion [23]

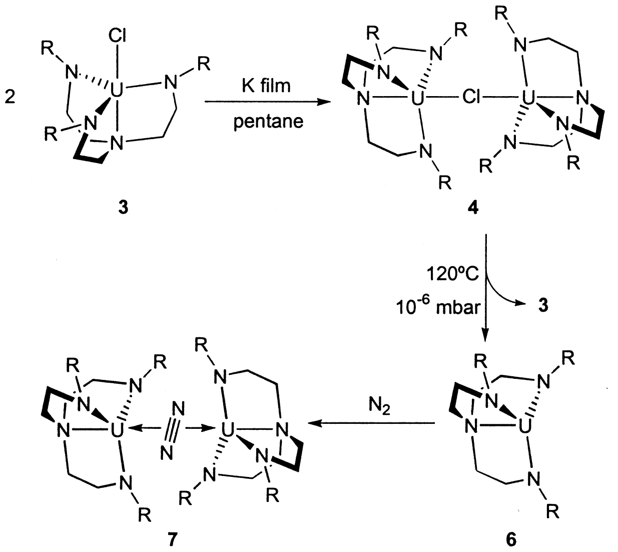
Stirring $[\{U(NN_3)\text{-}\mu\text{-}Cl\}_2]$ **1** [14,15] with a potassium film or sodium/potassium alloy led to no detectable reaction. The more sterically encumbered $MePh_2Si$-substituted analogue $[U(NN_3^{Ph})Cl]$ **2** [24] reacted rapidly to give a dark intractable solution. In contrast, reaction of the $^tBuMe_2Si$-substituted complex $[U(NN'_3)Cl]$ **3** in purified pentane with a potassium mirror gave rise to an extremely sensitive deep purple solution (Scheme 1). Filtration of the solution through thoroughly dry glass microfibre and cooling slowly to −30°C gave long air-sensitive purple needles of mixed valent (III/IV) $[\{U(NN_3)\}_2\text{-}\mu\text{-}Cl]$ **4** in 93% yield (2 crops). Suitable crystals were mounted under purified helium in Lindemann capillaries and the X-ray crystal structure was determined [25].

The molecular structure of **4** is shown in Fig. 1. The principle C_3 axis N(1)-U(1)-Cl-U(1′)-N(1′) and the pres-

---

[*] Corresponding author. Fax: +44 1203 524112; e-mail: peter.scott@warwick.ac.uk

0925-8388/98/$19.00
PII: S0925-8388(98)00043-7



Scheme 1. Synthesis of the dinitrogen complex **7** ($R=SiBu^tMe_2$) *via* the mixed-valent species **4**.

ence of an inversion centre at Cl determines that **4** has the rather rare D_{3d} symmetry. Three-fold symmetric ligation of the triamidoamine ligand is usually observed in complexes of the transition and main-group metals [2–13]; in complexes of the actinides we have observed distorted structures as a consequence of the larger ionic radii [14,15]. While the amido U(1)-N(2) distances of 2.241(11) Å are only slightly larger than the 2.21–2.22 Å observed in trigonal bipyramidal tetravalent [U(NN$_3$)(O-*tert*-C$_4$F$_9$)] [26] the distance N(1)-U(1) of 2.78(2) Å is much longer than the 2.624(11) Å in the latter compound, bringing the U atom well out of the chelate ligand cavity.

Bridging U(IV)-Cl bonds are usually found to be between ca. 2.75 and 2.82 Å [27,28]. In **4** however the U(1)-Cl distance of 3.020(1) Å (vide infra) is longer than the U-Cl bonds in the trivalent trimer [UCl(C$_5$Me$_5$)$_2$]$_3$ [2.901(5) Å] [29]. We cannot, however, discount the possibility that **4** has an unsymmetric U-Cl-U bridge on the X-ray crystallographic timescale and that the molecule is disordered in the crystal such that an average structure with a symmetric bridge is observed. If this is the case, then since the metal centres in the dimer are otherwise structurally indistinguishable, **4** could be compared to the extensive series of linear chain class II mixed valence [30,31], [Pt$^{II/IV}$L$_4$Cl] polymers in which neighbouring metal sites may be interconverted by axial movement of the bridge [32].

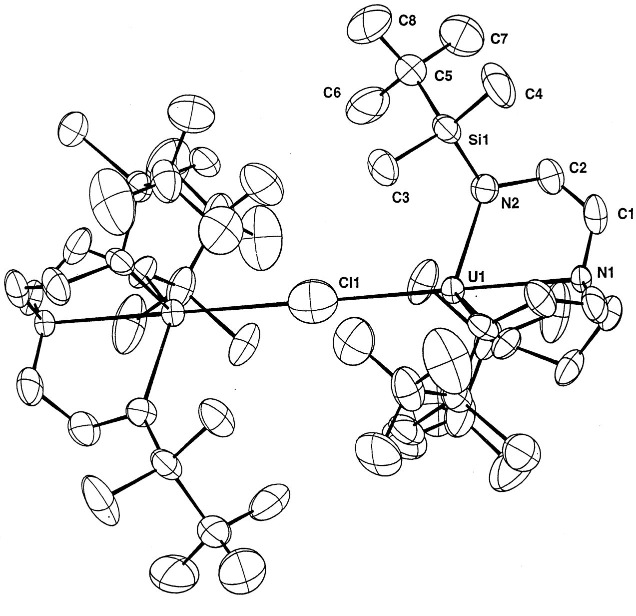


Fig. 1. ORTEP drawing of the molecular structure of **4**; hydrogen atoms omitted.

The UV–visible spectra of **4** measured in cyclohexane solution from 200–1100 nm show strong broad bands typical of trivalent uranium. Toluene solutions of **4** between 225 and 293 K display Curie–Weiss magnetic behaviour ($\Theta=-44.89\pm0.01$ K, $C=1.18$) as determined by the Evans method. This led to a temperature independent value of $\mu_{\mathrm{eff}}=3.08$ BM per uranium atom. Hence, within this temperature range, **4** is behaving as a simple paramagnet. Uranium(IV) amido species exhibit magnetic susceptibilities in the range 2.4–2.8 BM, but are highly dependent on substituent groups and nuclearity [33]. The U(III) amido compound [U{N(SiMe$_3$)$_2$}$_3$] has $\mu_{\mathrm{eff}}=2.51$ BM [34].

We have been able to isolate homogeneous samples of a range of similar materials to **4** of the general type [(NN$'_3$)M-X-M$'$(NN$'_3$)] and will present a full study of their structural, spectroscopic and magnetic properties in due course.

We have found that **4** is a highly reactive source of trivalent uranium. For example, addition of one equivalent of trimethylsilyl azide to a purple pentane solution of **4** at −80°C causes an immediate colour change to red and the formation of **3** along with a new uranium (V) compound [U(NN$'_3$)(NSiMe$_3$)] **5** in the ratio 1:1 (by ^{1}H NMR). Although these compounds can be separated by fractional sublimation and crystallisation, we felt that it would be far more convenient to have access to the pure trivalent species [U(NN$_3$)] in the absence of the tetravalent fragment [U(NN$_3$)Cl] **3**. We subsequently found that careful sublimation of **4** at 120°C and 10^{-6} mbar affords a deep purple solid characterised as the trivalent (and presumably trigonal monopyramidal) complex [U(NN$'_3$)] **6**. At 180°C, pale green **3** can be recovered.

When a sample of pure **6** in d$_6$-benzene is placed under ca. 1 atm of N$_2$ there is colour change from purple to red and new peaks appear in the ^{1}H-NMR spectrum corresponding to a species with three fold symmetry on the NMR timescale. Increasing the pressure of dinitrogen to slightly above 1 atm leads to essentially complete conversion to this new species. When the sample is freeze–thaw degassed, the intense purple colour and ^{1}H-NMR spectrum of **6** is regenerated. So long as rigorously pure dinitrogen is used, this process may be carried out many times on the same sample with little or no decomposition of either **6** or the new complex. Exposure of saturated pentane solutions of **6** to dinitrogen and cooling to −20°C gives dark red crystals of analytically pure $[\{U(NN'_3)\}_2(\mu^2\text{-}\eta^2{:}\eta^2\text{-}N_2)]$ **7**. In the solid state, crystalline samples of **7** are stable for at least three months when stored under an atmosphere of dinitrogen or argon.

The molecular structure of **7** (Fig. 2) shows that the dinitrogen ligand is bound in a side-on bridging mode between two uranium centres [35]. The (triamidoamine)uranium fragments are of approximate trigonal monopyramidal geometry and are arranged in a mutually staggered conformation as found for **4**. The uranium atoms sit out of the planes defined by the three respective amido nitrogen atoms by ca. 0.84 and 0.85 Å. The apical amino N–U bond lengths of 2.555(5) and 2.601(5) Å are unusually short compared to those in tetravalent $U(NN'_3)$ complexes (ca. 2.7 Å) [36] and in **4** [2.78(2) Å]. The U–N(dinitrogen) bond lengths of between 2.39 and 2.44 Å, are slightly longer than typical U–N(amido) bond lengths of ca. 2.28 Å. In contrast, the Sm–N bond lengths in $[\{Cp^*{}_2Sm\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$ are similar to those observed in Sm(III)-NR_2 compounds [1]. The N–N bond length in **7** of 1.109(7) Å is essentially the same as that found in dinitrogen gas (1.0975 Å) [37].

As is expected for this symmetric complex, $^{14}N_2$-**7** and $^{15}N_2$-**7** gave superimposable IR spectra. We have thus far been unable to measure reliable Raman spectra for these isotopomers. The UV/visible spectrum of **7** is virtually indistinguishable from that of trivalent **6**, with intense broad bands typical of trivalent uranium complexes [38].

Similarly, the solution magnetic susceptibility of **7** measured by the Evans method is 3.22 BM per uranium atom between 218 and 293K compared to the value for **6** of 3.06 BM in the same temperature range.

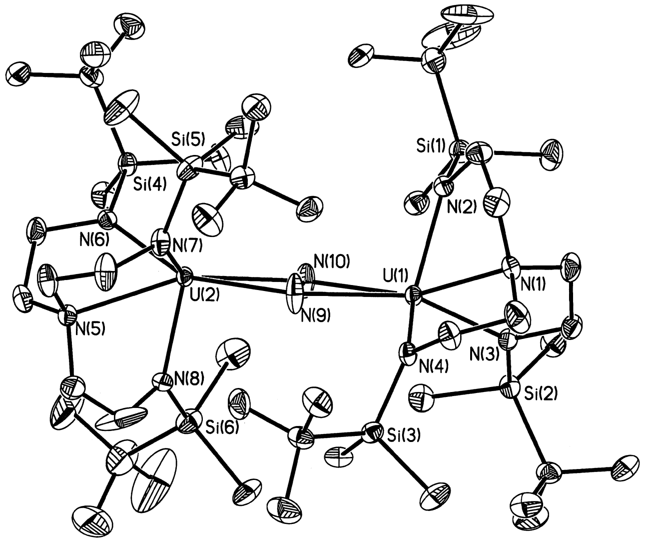


Fig. 2. ORTEP drawing of the molecular structure of **7**; hydrogen atoms omitted.

From these data it does not appear that coordination of dinitrogen to **6** leads to an increase in the valency of the uranium centre. In contrast, ^{13}C-NMR spectroscopic data for $[\{Cp^*{}_2Sm\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$ are consistent with the presence of Sm(III) centres.[7a] Similarly, $[\{Mo(NN'_3)\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)]$ contains a diazenido (N_2^{2-}) ligand and hence tetravalent molybdenum [39].

In the end-on coordination mode of dinitrogen at transition metal centres, two filled metal p-orbitals are utilised in M→N back-bonding. The less commonly observed side-on mode occurs where only one metal p- and one d-orbital are available [40]. The end-on mode is favoured where possible over side-on by virtue of the fact that π-overlap is considerably more efficient than δ. Although there does not appear to be significant M–L π-donation in lanthanide complexes such as $[Cp^*{}_2Yb(\eta^2\text{-}MeCCMe)]$ [41], Bursten has argued that for trivalent uranium, increased 5f-orbital extension can lead to significant covalent bonding character [42]. Were there to be a significant amount of U-N π-bonding in **7** we would expect lowering of the N-N bond order (diazenido character) and concomitant increase in the valency of the uranium centres. Hence we suggest that trivalent **6** contains what are essentially $N_2 \rightarrow U$ σ-bonds and that $[U(NN'_3)]$ is acting as an extremely potent Lewis acid. The preference for side-on over end-on bonding may be explained on the basis that the dinitrogen π_p orbital is a better σ-donor than the σ_p orbital to trivalent uranium.

Acknowledgements

PS wishes to thank the Royal Society for a Research Grant, the Nuffield foundation for a Newly Appointed Science Lecturers Award, EPSRC for an Earmarked Studentship and BNFL for a CASE award (to PR) and for their continued support.

References

[1] M.F. Lappert, P.P. Power, A.R. Sanger, R.C. Srivastava, Metal and Metalloid Amides, Ellis Horwood, Chichester, 1980.
[2] J.G. Verkade, Coord. Chem. Rev. 137 (1994) 233.
[3] J.G. Verkade, Acc. Chem. Res. 26 (1993) 483.
[4] J. Pinkas, T. Wang, R.A. Jacobson, J.G. Verkade, Inorg. Chem. 33 (1994) 4202.
[5] Y. Wan, J.G. Verkade, J. Am. Chem. Soc. 117 (1995) 141.
[6] Z. Duan, V.G. Young, J.G. Verkade, Inorg. Chem. 34 (1995) 2179.
[7] J. Pinkas, J.G. Verkade, Polyhedron 15 (1996) 1567.
[8] B.A. Dsa, J.G. Verkade, J. Am. Chem. Soc. 118 (1996) 12833.
[9] Y.J. Wan, J.G. Verkade, Organometallics 15 (1996) 5769.
[10] W. Plass, J. Pinkas, J.G. Verkade, Inorg. Chem. 36 (1997) 1973.
[11] R.R. Schrock, Acc. Chem. Res. 30 (1997) 9.
[12] C. Rosenberger, R.R. Schrock, W.M. Davis, Inorg. Chem. 36 (1997) 123.

[13] M.B. O'Donoghue, N.C. Zanetti, W.M. Davis, R.R. Schrock, J. Am. Chem. Soc. 119 (1997) 2753.

[14] P. Scott, P.B. Hitchcock, Polyhedron, 13 (1994) 1651.

[15] P. Scott, P.B. Hitchcock, J. Chem. Soc. Dalton Trans., 1995, p. 603.

[16] P. Scott, P.B. Hitchcock, J. Chem. Soc. Chem. Commun., 1995, p. 579.

[17] C. Laplaza, C.C. Cummins, Science 268 (1995) 861.

[18] W.J. Evans, T.A. Ulibarri, J.W. Ziller, J. Am. Chem. Soc. 110 (1988) 6877–6879.

[19] J. Jubb, S. Gambarotta, J. Am. Chem. Soc. 116 (1994) 4477–4478.

[20] R.A. Andersen, Inorg. Chem. 18 (1979) 1507.

[21] J.G. Brennan, R.A. Andersen, J.L. Robbins, J. Am. Chem. Soc. 108 (1986) 335–336.

[22] J. Parry, E. Carmona, S. Coles, M. Hursthouse, J. Am. Chem. Soc. 117 (1995) 2649–2650.

[23] NN_3=N(CH2CH2NSiMe3)3, $NNPh_3$=$N(CH_2CH_2NSiMePh_2)_3$ and NN'_3=$N(CH_2CH_2NSi^tBuMe_2)_3$

[24] The pale green complexes **2** and **3** were prepared in an analogous manner to the trimethylsilyl-substituted analogue **1** (see Refs. 14 and 15) Involatile **2** was purified by recrystallisation from diethyl ether (89% yield), while **3** was purified by sublimation at 180°C/10^{-6} mbar followed by recrystallisation from cold pentane (70% yield). These and all other compounds were characterised spectroscopically and gave satisfactory microanalyses.

[25] Crystal data for **4**. $C_{48}H_{114}ClN_8Si_6U_2$, $M=1483.52$, trigonal, $a=b=12.635(4)$, $c=25.55(8)$ Å, $U=3533(2)$ Å^3, space group $P\bar{3}1c$, $Z=2$, $D_c=1.428$ g cm^{-3}, $F(000)=1520$. Deep purple air and dinitrogen-sensitive tablet 0.25×0.25×0.2 mm in a capillary. Final $R1$, $wR2$ and S were 0.058, 0.147 and 0.884.

[26] P. Roussel, P.B. Hitchcock, P. Scott, unpublished results.

[27] G.C. Campbell, F.A. Cotton, J.F. Haw, W. Schwotzer, Organometallics 5 (1986) 274.

[28] J. Rebizant, M.R. Spirlet, C. Apostolidis, G. Van den Bossche, B. Kanellakopulos, Acta Cryst. 47 (1991) 864.

[29] J.M. Manriquez, P.J. Fagan, T.J. Marks, S.H. Vollmer, C.S. Day, V.W. Day, J. Am. Chem. Soc. 101 (1979) 5057.

[30] K. Prassides (Ed.), NATO Advanced Workshop on Mixed Valency Compounds: Applications in Chemistry, Physics and Biology, Kluwer, Dordrecht 1991.

[31] M.B. Robin, P. Day, Adv. Inorg. Chem. 10 (1967) 247.

[32] R.J.H. Clark, Chem. Soc. Rev. 13 (1984) 219.

[33] J.G. Reynolds, N.M. Edelstein, Inorg. Chem. 16 (1977) 2822.

[34] R.A. Andersen, Inorg. Chem. 18 (1979) 1507.

[35] Crystal data for **7**. C48H114N10Si6U2, $M=1476.09$, Monoclinic, Space group $P21/n$, $a=19.549(2)$, $b=16.2751(14)$, $c=21.517(2)$, $\beta=105.611(3)°$, $U=6593.2(5)$ Å^3, $Z=4$, $D_c=1487$ Mg/m^{-3}, $F(000)=2960$. Dark red air sensitive block 0.24×0.20×0.12 mm. Final $R1$, $wR2$ and S were 0.0494, 0.0756 and 1.023.

[36] P. Roussel, P. Scott, unpublished results.

[37] P.G. Wilkinson, N.B. Houk, J. Chem. Phys. 24 (1956) 528.

[38] L.R. Avens, S.G. Bott, D.L. Clark, A.P. Sattelberger, J.G. Watkin, B.D. Zwick, Inorg. Chem. 33 (1994) 2248–2256.

[39] K.Y. Shih, R.R. Schrock, R. Kempe, J. Am. Chem. Soc. 116 (1994) 8804–8805.

[40] M.D. Fryzuk, T.S. Haddad, M. Mylvaganan, D.H. McConville, S.J. Rettig, J. Am. Chem. Soc. 115 (1993) 2782–2792.

[41] C.J. Burns, R.A. Andersen, J. Am. Chem. Soc. 109 (1987) 941–942.

[42] B.E. Bursten, R.J. Strittmatter, J. Am. Chem. Soc. 109 (1987) 6606–6608.