CHEMCOMM
Communication
www.rsc.org/chemcomm

Synthesis and structure of *N*-heterocyclic carbene complexes of uranyl dichloride

Warren J. Oldham, Jr.,*[a] Susan M. Oldham,[a] Brian L. Scott,[b] Kent D. Abney,[b] Wayne H. Smith[a] and David A. Costa*[a]

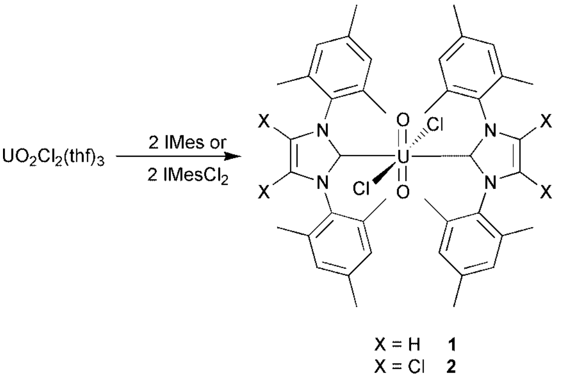
[a] *Nuclear Materials and Technology Division, Los Alamos National Laboratory, MS J514, Los Alamos, New Mexico 87545, USA. E-mail: woldham@lanl.gov; dcosta@lanl.gov*
[b] *Chemistry Division, Los Alamos National Laboratory, MS J514, Los Alamos, New Mexico 87545, USA*

Received (in Irvine, CA, USA) 21st March 2001, Accepted 13th June 2001
First published as an Advance Article on the web 5th July 2001

Treatment of $UO_2Cl_2(thf)_3$ in THF with two equivalents of 1,3-dimesitylimidazole-2-ylidene (IMes) or 1,3-dimesityl-4,5-dichloroimidazole-2-ylidene ($IMesCl_2$) yields novel monomeric uranyl *N*-heterocyclic carbene complexes, representing the first examples of actinyl carbon bonds.

The coordination chemistry of *N*-heterocyclic carbenes (NHC) is a topic of much current interest, motivated in part by promising applications in homogeneous catalysis[1] and materials science.[2] NHC complexes have also been identified as principal species formed upon dissolution of certain metal salts in *N,N′*-dialkylimidazolium-based room-temperature ionic liquids (RTILs).[3] We have recently initiated a general program to characterise the basic coordination chemistry and electrochemical properties of lanthanide and actinide ions dissolved in RTILs with the goal of developing advanced, environmentally responsible, nuclear processing and purification strategies. In support of this effort, the reaction chemistry of isolable and easily handled NHC ligands with lanthanide[4] and actinide complexes is of interest. Given the central role of actinyl ions (*e.g.* MO_2^{2+}, M = U, Np, Pu) in nuclear chemistry,[5] we report here the synthesis and structural characterisation of uranyldichloride complexes stabilised by sterically demanding NHC ligands. Well characterised 1,3-dimesitylimidazole-2-ylidene ligands were chosen in this study in order to favour highly crystalline reaction products, amenable to detailed structural characterisation.

Addition of a THF solution containing two equivalents of IMes[6] or $IMesCl_2$[7] to a bright yellow solution of $UO_2Cl_2(thf)_3$[8] in THF rapidly gives a bleached yellow solution from which pale yellow powders separate that correctly analyse for $UO_2Cl_2L_2$ [L = IMes **1**, $IMesCl_2$ **2**, see eqn. (1)].† The isolated powders are insoluble in aliphatic hydrocarbons, slightly to moderately soluble in THF and toluene, and readily decompose in CH_2Cl_2.



(1)

Crystals suitable for X-ray structural analysis could be obtained for **1** as the THF solvate, by carefully layering a cold solution of $UO_2Cl_2(thf)_3$ in THF with a second solution of IMes, followed by slow diffusion over several days at –30 °C. For **2**, simply cooling a saturated THF solution at –30 °C overnight gave well formed single crystals.‡ Thermal ellipsoid representations of **1** and **2** are shown in Fig. 1. For both complexes the uranium(VI) metal atom lies at the centre of a nearly perfect octahedron. The uranyl U–O bond lengths of 1.761(4) and 1.739(3) Å (**1** and **2**, respectively) are within the range previously observed in $UO_2Cl_2L_2$ complexes.[9–12] The significantly shorter U–O bond length observed for **2** is consistent with $IMesCl_2$ being a weaker σ-donor ligand compared to IMes, which is also reflected in UO_2 vibrational data (*vide infra*). The

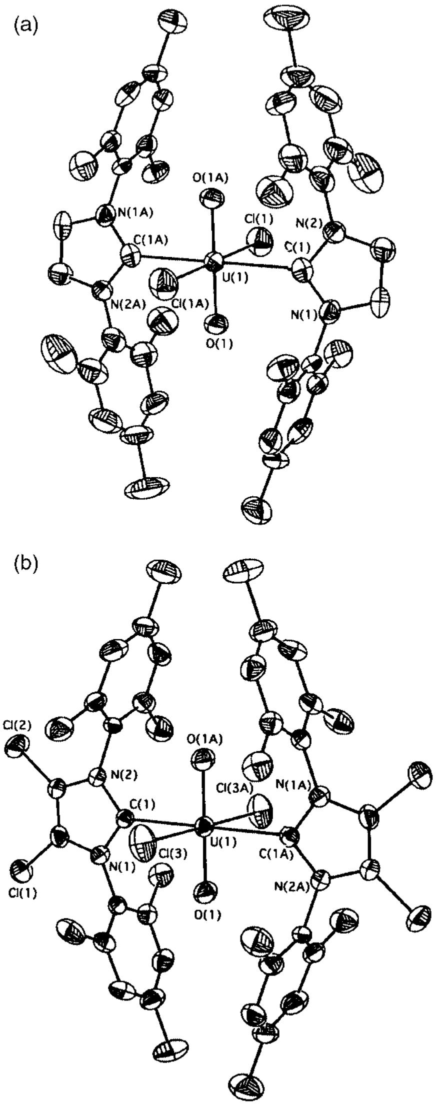


Fig. 1 Thermal ellipsoid representation of (a) **1** and (b) **2** shown at the 50% probability level. THF solvent of crystallisation and hydrogen atoms have been omitted for clarity.

U–Cl bond lengths also fall within the normal range. The uranium–carbene bond lengths are considerably lengthened at 2.626(7) and 2.609(4) Å (**1** and **2**, respectively) compared to the U–L bond lengths in UO$_2$Cl$_2$L$_2$ complexes [L = OPPh$_3$,[9] OC(CHCHPh)$_2$,[10] OP(NMe$_2$)$_3$,[11] or OC(NMe$_2$)$_2$[12]], which are observed between 2.27 and 2.30 Å. The electron-withdrawing 4,5-dichloro substituents of IMesCl$_2$ are expected to reduce the bonding radius of the carbene lone pair, which is reflected in the relative U–C bond lengths of **1** and **2** [2.626(7) and 2.609(4) Å, respectively]. The imidazol-2-ylidene rings lie nearly coplanar, twisted along the C(1)–U(1)–C(1A) axis by *ca.* 6° (**1**) and 8° (**2**). The plane defined by N(1)–C(1)–N(2) eclipses the O–U–O axis [torsion angles: *ca.* 11° (**1**) and 4° (**2**)], thereby minimising steric interaction between the mesityl substituents and the chloride ligands. Instead, the mesityl groups form a basket around the uranyl oxo ligands in which the closest non-bonded oxygen contacts are *ca.* 3.1–3.2 Å to the *ipso*-mesityl carbons.

A measure of the relative donor strength of the NHC ligands in UO$_2$Cl$_2$L$_2$ complexes can be estimated using vibrational spectroscopy. Within an isostructural series of uranyl complexes, the frequency of the symmetric (ν_1) and asymmetric (ν_3) UO$_2$ stretch is inversely proportional to the donor strength of the equatorial ligands which lie orthogonal to the [UO$_2$]$^{2+}$ moiety.[13] For **1** and **2**, the highest intensity peak in the IR spectra (Nujol), assigned to the asymmetric UO$_2$ stretch is observed at 938 and 942 cm^{-1}, respectively. These values are among the highest reported for UO$_2$Cl$_2$L$_2$ complexes,[14] suggesting correspondingly weak electron donation from the NHC ligands. A slightly higher frequency ν_3 observed for **2** is consistent with the electron withdrawing effect of the 4,5-dichloro substituted imidazol-2-ylidene ligand. It should be pointed out that the weak donor ability of NHC ligands in these uranyl complexes is in marked contrast to their exceptionally strong donor strength observed in low valent transition metal complexes.[15] The isolation of uranyl complexes stabilised by soft σ-donor ligands like NHCs is without precedent. Prior to this report, actinyl complexes have been exclusively stabilised by hard donor ligands (*e.g.* halide, oxygen and nitrogen ligation). In fact, even tertiary phosphine complexes are unknown in the actinyl series. A useful comparison can be made to a related tungsten complex, WO$_2$Cl$_2$L$_2$ (L = 1,3-dimethylimidazol-2-ylidene),[16] which further demonstrates the suitability of NHCs as competent stabilising ligands for hard, Lewis acidic metal complexes.

The synthetic and structural results reported in this work suggest that related actinide NHC complexes might reasonably be formed in RTIL solutions. Through control of the effective pH of these media, the concentration of free NHCs could be reversibly adjusted to allow manipulation of the coordination sphere of dissolved metal ions. Novel separations technology based on the imidazolium-RTIL/NHC interconversion is currently under development. Extension of this synthetic and structural investigation to transuranium actinyl complexes and to low valent actinides is being actively pursued.

We thank Dr David L. Clark of the Glenn T. Seaborg Institute for Transactinide Science for providing financial support of this work. Los Alamos National Laboratory is operated by the University of California for the U.S. Department of Energy.

Notes and references

† *Preparation* of UO$_2$Cl$_2$(IMes)$_2$ **1**: to a solution of [UO$_2$Cl$_2$(thf)$_2$]$_2$ (100 mg, 0.103 mmol) dissolved in THF (4 mL) was added a second THF solution (4 mL) of IMes (125 mg, 0.415 mmol). The resulting yellow suspension was stirred for 15 min, diluted with hexanes (5 mL), then filtered off and washed with hexanes (2 × 2 mL). Yield 145 mg (74%). ^{1}H NMR (300 MHz, toluene-d_8): δ 2.08 (s, 6H, *p*-CH$_3$), 2.26 (s, 12H, *o*-CH$_3$), 6.26 (s, 2H, 4,5-imidazole-CH), 6.49 (s, 4H, 3,5-mesityl-CH). IR (Nujol): ν (cm^{-1}) 1304 (w), 1273 (m), 1229 (m), 1160 (w), 1100 (m), 1064 (w), 1033 (w), 962 (w), 938 (vs), 920 (s), 847 (m), 749 (m), 722 (m). Anal. Calc. for C$_{42}$H$_{48}$Cl$_2$N$_4$O$_2$U: C, 53.11; H, 5.09; N, 5.90. Found: C, 53.62; H, 5.76; N, 5.71%.

Preparation of UO$_2$Cl$_2$(IMesCl$_2$)$_2$ **2**: a similar procedure as that described for **1** was followed. Yield 62%. ^{1}H NMR (300 MHz, toluene-d_8): δ 2.02 (s, 6H, *p*-CH$_3$), 2.25 (s, 12H, *o*-CH$_3$), 6.47 (s, 4H, 3,5-mesityl-CH). IR (Nujul): ν/cm^{-1} 1304 (w), 1273 (m), 1195 (w), 1180 (w), 1149 (w), 1131 (m), 1076 (w), 1036 (w), 984 (w), 942 (vs), 851 (m), 733 (w), 722 (w). Anal. Calc. for C$_{42}$H$_{44}$Cl$_6$N$_4$O$_2$U: C, 46.34; H, 4.07; N, 5.15. Found: C, 47.23; H, 4.56; N, 4.63%.

‡ *Crystal data*: for **1**·6THF: C$_{66}$H$_{96}$Cl$_2$N$_4$O$_8$U, M = 1382.40, a = 29.330(1), c = 18.879(1) Å, V = 14065(1) Å^3, trigonal, space group $R\bar{3}$, Z = 9, T = 203 K, $R1(I > 2\sigma)$ = 0.0656, and $wR2(I > 2\sigma)$ = 0.1311.

For **2**·THF: C$_{50}$H$_{60}$Cl$_6$N$_4$O$_4$U, a = 10.1563(5), b = 17.3511(8), c = 13.6466(6) Å, β = 95.162(1)°, V = 2480.2(2) Å^3, monoclinic, space group $P2_1/n$, Z = 2, T = 203 K, $R1(I > 2\sigma)$ = 0.0456, and $wR2(I > 2\sigma)$ = 0.0855.

The reflection data for both structures were collected on a Bruker P4/CCD using a combination of ϕ and ω scans. The structures were solved using standard direct methods techniques (SHELXS-97),[17] and refined using full-matrix least squares based on F^2 (SHELXL-97).[17] Hydrogen atom positions were idealized, and all non-hydrogen atoms were refined anisotropically. Disordered lattice THF molecules in both structures were eliminated from the refinement using PLATON/SQUEEZE.[18] CCDC reference numbers 160347 and 160348 for **1** and **2**, respectively. See http://www.rsc.org/suppdata/cc/b1/b102649f/ for crystallographic data in CIF or other electronic format.

1 A. J. Arduengo III, *Acc. Chem. Res.*, 1999, **32**, 913; W. A. Herrmann and C. Köcher, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2162; T. Weskamp, V. P. W. Böhm and W. A. Herrmann, *J. Organomet. Chem.*, 2000, **600**, 12.

2 R. Faust and B. Göbelt, *Chem. Commun.*, 2000, 919.

3 L. Xu, W. Chen and J. Xiao, *Organometallics*, 2000, **19**, 1123; M. Hasan, I. V. Kozhevnikov, M. R. H. Siddiqui, A. Steiner and N. Winterton, *J. Chem. Res. (S)*, 2000, 392; M. Hasan, I. V. Kozhevnikov, M. R. H. Siddiqui, C. Femoni, A. Steiner and N. Winterton, *Inorg. Chem.*, 2001, **40**, 795.

4 W. A. Herrmann, F. C. Munck, G. R. J. Artus, O. Runte and R. Anwander, *Organometallics*, 1997, **16**, 682.

5 F. Weigel, in *The Chemistry of the Actinide Elements*, ed. J. J. Katz, G. T. Seaborg and L. R. Morss, Chapman and Hall, New York, 2nd edn., 1986, pp. 169–442.

6 A. J. Arduengo, III, H. V. R. Dias, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1992, **114**, 5530.

7 A. J. Arduengo III, F. Davidson, H. V. R. Dias, J. R. Goerlich, D. Khasnis, W. J. Marshall and T. K. Prakasha, *J. Am. Chem. Soc.*, 1997, **119**, 12 742.

8 M. P. Wilkerson, C. J. Burns, R. T. Paine and B. L. Scott, *Inorg. Chem.*, 1999, **38**, 4156.

9 G. Bombieri, E. Forsellini, J. P. Day and W. I. Azeez, *J. Chem. Soc., Dalton Trans.*, 1978, 677; S. B. Akona, J. Fawcett, J. H. Holloway and D. R. Russell, *Acta Crystallogr. Sect. C*, 1991, **47**, 45.

10 N. W. Alcock, P. de Meester and T. J. Kemp, *J. Chem. Soc., Perkin 2*, 1979, 921.

11 J. C. Russell, M. P. du Plessis, L. R. Nassimbeni, J. G. H. du Preez and B. J. Gellatly, *Acta Crystallogr., Sect. B*, 1977, **33**, 2062; P. R. Julien, N. Rodier and P. Khodadad, *Acta Crystallogr., Sect. B*, 1977, **33**, 2411.

12 L. A. Jacobs, C. P. J. van Vuuren and P. H. van Rooyen, *S. Afr. J. Chem.*, 1986, **39**, 174.

13 R. G. Denning, in *Gmelin Handbuch der Anorganischen Chemie Suppl. Ser. Uranium*, 1986, vol. A6, pp. 31–79; A. A. Zazhogin, H. D. Lutz and A. I. Komyak, *J. Mol. Struct.*, 1999, **482–483**, 189.

14 L. V. Kobets and D. S. Umreiko, *Zh. Prikl. Spektrosk. (Engl. Transl)*, 1986, **44**, 643.

15 J. Huang, H.-J. Schanz, E. D. Stevens and S. P. Nolan, *Organometallics*, 1999, **18**, 2370; T. Weskamp, F. J. Kohl, W. Hieringer, D. Gleich and W. A. Herrmann, *Angew. Chem., Int. Ed.*, 1999, **38**, 2416.

16 W. A. Herrmann, G. M. Lobmaier and M. Elison, *J. Organomet. Chem.*, 1996, **520**, 231.

17 SHELXTL/NT Version 5.1, Bruker AXS, Inc., Madison, WI 53719, USA.

18 A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, C34.