Synthesis and Crystal Structure of an Analogue of the Uranyl(vi) Ion, containing a Linear O=U=N- Group

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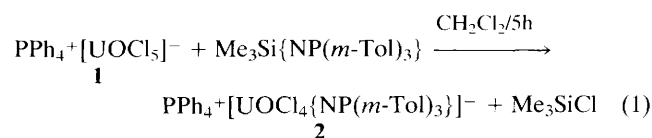The crystal structure of the air-stable compound $PPh_4^+[UOCl_4\{NP(m\text{-}Tol)_3\}]^-$ (m-Tol = $C_6H_4Me\text{-}m$) shows that it contains a linear (179°) O=U=N- group, with U-O and U-N distances of 176 and 190 pm respectively, coordinated by four chlorine atoms; the U-O distance is typical of uranyl compounds, and the U-N distance suggests a bond order >2.

The chemistry of U^{VI} is largely confined to that of the linear uranyl ion, UO_2^{2+}, the stability of the dioxo cation being unparalleled both in the solid state and in solution.[1] A *trans* geometry is always adopted, in contrast to the group VI d-block metals where a *cis*-dioxo group is the norm. Imido compounds are well-known in the d-block,[2] and it is therefore possible that imido analogues of the uranyl ion, maintaining the characteristic linear triatomic unit, may also be stable. We report here the preparation and crystal structure of $PPh_4^+[UOCl_4\{NP(m\text{-}Tol)_3\}]^-$ which we beleive is the first example of a structural analogue of the uranyl ion containing a uranium–nitrogen multiple bond.

In d-block transition metals the similarity between oxo (M=O), and imido (M=N-R) or phosphorane iminato (M=N-PR₃) groups is well-established,[2,3] as are methods for their preparation and interconversion.[2,4] Table 1 lists the small number of uranium compounds known to contain imido or phosphorane iminato groups, of which four are in oxidation state VI. Among these, the pentamethyl–cyclopentadienyl compounds **5** and **6** are approximately tetrahedral,[5,6] and do not resemble the uranyl ion. In **3** and **4** the bulky trimethylsilyl amide ligands occupy the equatorial positions of a trigonal bipyramid whose axis is a linear F–U=N- grouping,[7] but because of the steric bulk in the equatorial positions, it is not clear whether this linearity is related to that of the uranyl ion. The compounds in Table 1 are prepared by oxidative addition to reactive uranium-(iii) or -(iv) organometallics, for which the bulky ligands provide valuable stability, so steric bulk may not be a prerequisite for the isolation of uranium(vi) imido complexes.

The formidable stability of the linear uranyl(vi) ion suggests that imido analogues might be stable even in the absence of bulky ligands, provided that a synthesis can be found that does not attempt to disrupt the uranyl ion itself. Here we start from

the mono-oxo compound $PPh_4^+[UOCl_5]^-$, **1**, prepared by the partial deoxygenation of the uranyl ion in thionyl chloride, following the procedure of Bagnall *et al.*[12] The replacement of a chlorine atom in **1** *via* the formation of Me_3SiCl, a common synthetic strategy,[3] is then employed in the reaction [eqn. (1)].

$$PPh_4^+[UOCl_5]^- + Me_3Si\{NP(m\text{-}Tol)_3\} \xrightarrow{\;CH_2Cl_2/5h\;}$$
$$\mathbf{1}$$
$$PPh_4^+[UOCl_4\{NP(m\text{-}Tol)_3\}]^- + Me_3SiCl \quad (1)$$
$$\mathbf{2}$$

The product **2** is isolated as a red crystalline solid,† stable indefinitely in moist air and soluble in dry polar solvents such as CH_2Cl_2 and MeCN. In moist solvents rapid hydrolysis occurs yielding the uranyl ion. The structure was determined by single-crystal methods.‡ Fig. 1 shows the structure of the anion, and lists selected bond lengths and angles. It consists of an almost linear O–U–N group, surrounded by a square-planar array of chloride ions. Table 2 compares the structural parameters with those of $Cs_2UO_2Cl_4$,[13] and those of the mono-oxo compound **1**.[14]

The uranium–oxo bond length in **2** is similar to that in the reference compounds, and the bond angles at uranium are all within 2.2° of a right angle. The U–N bond is significantly shorter than those in Table 1, except for the trimethylsilyl-imido compound **3**, and the P–N bond length of 163.3 pm is normal for phosphorane iminato complexes.[10] The equatorial chloride bond distances are significant: Replacement of chlorine atoms in UCl_6, where U–Cl is 241 pm, by one or two oxo groups leads to an increase in the *cis* U–Cl distances of *ca.* 13 pm per oxo group, to 254 and 267 pm respectively.[1] This is due to the increased covalency of the oxo groups which lowers the effective positive charge on the uranium atom. On this

Table 1 Imido compounds of uranium

Compound	Oxidation state	U-N/pm	U-N-X angle/°	N-U-N or N-U-O angle/°	Ref.
$[U\{N(SiMe_3)\}\{N(SiMe_3)_2\}_3]$	V	191.0(6)	180	—	8
$[UF\{N(SiMe_3)\}\{N(SiMe_3)_2\}_3]$ **3**	VI	185.4(23)	178.3(11)	—	7
$[UF(NPh)\{N(SiMe_3)_2\}_3]$ **4**	VI	197.9(8)	173.5(7)	—	7
$[U(NPh)(C_5H_4Me)_3]$	V	201.9(6)	167.4(6)	—	9
$[U\{N(PPh_3)\}(C_5H_5)_3]$	IV	207(2)	172(1)	—	10
$[U\{N(CHMeCH=PPh_2Me)\}(C_5H_5)_3]$	V	206(1)	163(1)	—	11
$[U(NPh)_2(C_5Me_5)_2]$ **5**	VI	195.2(7)	177.8(6)	98.7(4)	5
$[UO\{N(C_6H_3Pr^i_2\text{-}2,6)\}(C_5Me_5)_2]$ **6**	VI	198.8(4)	170.5(4)	110.7(2)	6

Table 2 Bond lengths and angles for $CsUO_2Cl_4$, **1** and **2**

Compound	Bond lengths/pm U-O	U-N	U-Cl	O-U-X/°
2	175.9(13)	190.1(14)	262.0(6), 263.5(5) 263.4(5), 263.6(5)	179.0(6)
$Cs_2UO_2Cl_4$	177.4(4)	—	267.1(1)	180
1	176(1)	—	253.6(2)	180
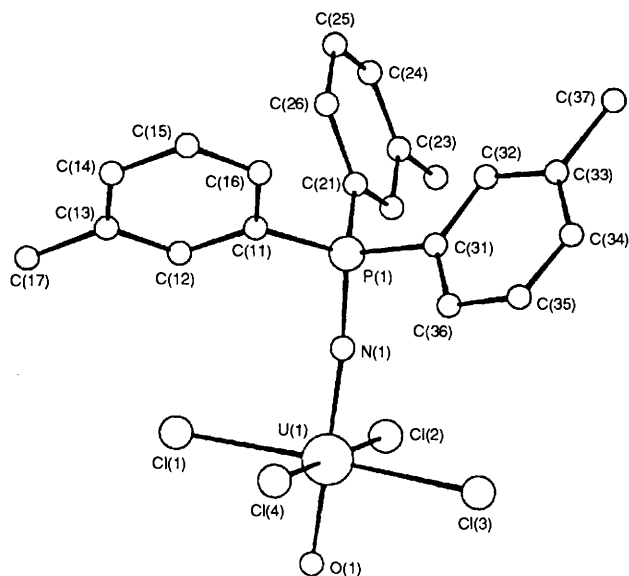
Fig. 1 The structure of the [UOCl₄{NP(m-Tol)₃}]⁻ anion. Selected bond distances (pm) and bond angles (°): U(1)–O(1) 175.9(13), U(1)–N(1) 190.1(14), U(1)–Cl(1) 263.4(5), U(1)–Cl(2) 263.6(5), U(1)–Cl(3) 263.3(5), U(1)–Cl(4) 262.0(6), N(1)–P(1) 163.3(15), O(1)–U(1)–N(1) 179.0(6), U(1)–N(1)–P(1) 171.9(9), N(1)–U(1)–Cl(1) 91.4(4), N(1)–U(1)–Cl(2) 91.0(4), N(1)–U(1)–Cl(3) 90.8(4), N(1)–U(1)–Cl(4) 87.9(4).

basis the U–Cl distance of *ca.* 263 pm in **2** implies a degree of covalency in the U–N bond that is about two-thirds of that in the uranium–oxo bond.

In some electron-rich metal-imido compounds the M=N–R unit is bent, with a nitrogen lone pair excluded from the bonding, and these have a lower formal bond order.[2] In **2** the near linearity (171.9°) of the U–N–P bond indicates full involvement of the ntirogen π-electrons in the uranium–nitrogen bond. The presence of both f and d valence orbitals in uranium allows each uranium oxygen bond in the uranyl ion a formal bond order of three,[1] and it appears that a similarly large U–N bond order applies here. In summary, **2** appears to be a true nitrogen-containing analogue of the uranyl ion.

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Footnotes

† Ph₄P[UOCl₅] (1.8 mmol) and Me₃Si{NP(m-Tol)₃} (2.0 mmol) were allowed to react in dry CH₂Cl₂ (30 cm³) at room temp. for 5 h, forming a clear red solution onto which a layer of an equal volume of toluene was added. After interdiffusion for several weeks, well-

formed needles of **2** were isolated in *ca.* 30% yield. **2** was characterised by IR v/cm⁻¹ 1080vs, U=N–P; 850m, U=O, in addition to the cation and *m*-tolyl bands). Satisfactory microanalytical results were obtained. Triphenylphosphorane- and phenyldimethylphosphorane-iminato analogues were also prepared.

References

1 R. G. Denning, *Struct. Bonding*, 1992, **79**, 215.
2 W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev.*, 1980, **31**, 123.
3 K. Dehnicke and J. Strähle, *Polyhedron*, 1989, **8**, 707.
4 M. L. H. Green, G. Hogarth, P. C. Konidaris and P. Mountford, *J. Chem. Soc., Dalton Trans.*, 1990, 3781.
5 D. S. J. Arney, C. J. Burns and D. C. Smith, *J. Am. Chem. Soc.*, 1992, **114**, 10068.
6 D. S. J. Arney and C. J. Burns, *J. A. Chem. Soc.*, 1993, **115**, 9840.
7 C. J. Burns, W. H. Smith, J. C. Huffman and A. P. Sattelberger, *J. Am. Chem. Soc.*, 1990, **112**, 3237.
8 A. Zalkin, J. G. Brennan and R. A. Andersen, *Acta Crystallogr., Sect. C*, 1988, **44**, 1553.
9 J. G. Brennan and R. A. Andersen, *J. Am. Chem. Soc.*, 1985, **107**, 514.
10 R. E. Cramer, F. Edelmann, A. L. Mori, S. Roth, J. W. Gilje, K. Tatsumi and A. Nakamura, *Organometallics*, 1988, **7**, 841.
11 R. E. Cramer, K. Panchanatheswaran and J. W. Gilje, *J. Am. Chem. Soc.*, 1984, **106**, 1853.
12 K. W. Bagnall, J. G. H. Du Preez, B. J. Gellatly and J. H. Holloway, *J. Chem. Soc., Dalton Trans.*, 1975, 1963.
13 D. J. Watkin, R. G. Denning and K. Prout, *Acta Crystallogr., Sect. C*, 1991, **47**, 2517.
14 J. F. De Wet and J. G. H. Du Preez, *J. Chem. Soc., Dalton Trans.*, 1978, 592.
15 D. J. Watkin, J. R. Carruthers and P. W. Betteridge, CRYSTALS User Guide (Issue 8), Chemical Crystallography Laboratory, University of Oxford, 1985.
16 N. Walker and D. Stuart, *Acta. Crystallogr., Sect. A*, 1983, **39**, 158.