The first actinyl cyanide

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Reaction of $UO_2(OTf)_2$ with 5 molar equivalents of NEt_4CN in acetonitrile led to the formation of the pentacyano uranyl complex $[NEt_4]_3[UO_2(CN)_5]$ which is monomeric in the solid state with the five C-coordinated cyanide ions lying in the equatorial plane perpendicular to the linear $\{UO_2\}$ axis.

The chemistry of f-elements is a particularly active field of research, attracting much attention for both its fundamental aspects and applications.[1] However, it is rather surprising that cyano compounds of these elements are practically unknown, being limited for the actinides to a few U(III) and U(IV) species with only two recently structurally characterized tetravalent organometallic species.[2–8] This situation is in striking contrast to that encountered with the d-transition metal complexes where the CN^- group occupies a prominent position in various domains, from biology to materials science.[9] The strong coordinating ability of the CN^- ion which can adopt several ligation modes,[9] gave rise to a large number of homo- and hetero-polynuclear complexes which exhibit a rich variety of structures and unusual physicochemical properties, as recently highlighted with the fascinating magnetic behaviour of Prussian Blue type complexes.[10] In addition, the strong σ-donating and fair π-accepting capacity of the cyanide ion favour the stabilization of both low- and high-valent ions, that makes it a suitable ligand for uranium which exists in the +3 to +6 oxidation states.

Despite the large number of studies devoted to the halides and pseudohalides (N_3, NCS, NCO) of the ubiquitous *trans* dioxo uranyl(VI) ion, $\{UO_2\}^{2+}$,[11] no isolated or structurally identified uranyl cyanide complex has been so far reported. Yet, the stability of U(VI) cyano compounds has been the subject of recent theoretical debates,[12–14] and the coordination mode of the CN^- group to the uranyl ion $\{UO_2\}^{2+}$, *via* U–C or U–N bonding, was questioned.[12,14] In the gas phase, both $UO_2(CN)_2$ and $UO_2(NC)_2$ were found to be energetically viable species, with the isocyanide U–NC interaction being some 40 kJ mol^{-1} more stable.[13] On the basis of DFT calculations,[14] $[UO_2(NC)_4]^{2-}$ has been predicted to be the most stable species in the gas phase, while $[UO_2(CN)_5]^{3-}$ is predicted to be the most stable species in solution. It was thus highly desirable to confront the theoretical analyses with experimental results. Here we report on the synthesis and crystal structure of $[NEt_4]_3[UO_2(CN)_5]$ (**1**), the first cyano compound of U(VI) and of an $\{AnO_2\}^{n+}$ actinyl ion.

Complex **1** was prepared by reaction of $UO_2(OTf)_2$ (OTf = OSO_2CF_3) with slightly more than 5 molar equivalents of NEt_4CN in acetonitrile (eqn (1)).

$$UO_2(OTf)_2 + 5\ NEt_4CN \xrightarrow[-2\ NEt_4OTf]{\text{acetonitrile}} [NEt_4]_3\,\underset{1}{[UO_2(CN)_5]} \qquad (1)$$

After 24 h at room temperature, a gold–yellow solution and a white precipitate were obtained; evaporation of the solvent and elimination of the salts NEt_4X (X = CN, OTf) by extraction with thf afforded pure **1** as a beige solid in excellent yield (94%).† This compound is insoluble in ethereal (Et_2O, thf) and aromatic solvents but dissolves readily in acetonitrile or pyridine. The ^1H NMR spectrum of **1** in acetonitrile-d_3 exhibits two broad signals corresponding to the ethyl chains of the ammonium counter-ion at δ 3.19 and 1.21.

The IR spectrum of **1** displays a strong absorption band at 911 cm^{-1} assigned to the UO_2 stretching vibration mode. This value is smaller than that found in the neutral parent $UO_2(OTf)_2$ (982 cm^{-1}) but is in the range of frequencies (904–923 cm^{-1}) found in the electron rich species $[UO_2X_4]^{2-}$ (X = Cl, Br).[15] The two major ν(CN) absorption bands at 2190 and 2180 cm^{-1} can be compared with those in the organometallic complexes Cp_2UCN (2112 cm^{-1}),[7] Cp_3UCN (2116 cm^{-1})[7] $(1,2,4\text{-}Bu^t{}_3C_5H_2)_2U(OSiMe_3)(CN)$ (2040 cm^{-1}),[3] Cp_2LnCN (2187 and 2116 cm^{-1} for Ln = Nd; 2198 and 2136 cm^{-1} for Ln = Yb).[7] The highest ν(CN) values for the $5f^0$ uranyl compound can be tentatively explained by the absence of π-back donation from the U^{6+} ion to the cyanide ligand which might occur with the lower valent U^{3+} and U^{4+} ions.

Pale yellow crystals suitable for X-ray diffraction were obtained by slow diffusion of Et_2O into a solution of **1** in pyridine. Large crystals of $[NBu^n{}_4]_3[UO_2(CN)_5]$ (**2**) were also grown from a mixture of $UO_2(OTf)_2$ and excess $NBu^n{}_4CN$ in acetonitrile–diethyl ether, but the poor crystal quality and the disorder affecting the counter-ions did not permit a satisfactory refinement of the structure.‡ The high accuracy of the structure of **1** permits to determine unambiguously the U–C bonding mode of the cyanide ion. A view of the anion $[UO_2(CN)_5]^{3-}$ is shown in Fig. 1 together with selected bond distances and angles. The uranium atom is found in the classical pentagonal-bipyramidal configuration, with the linear UO_2 fragment perpendicular to the equatorial plane containing U and the five C atoms. This structure is familiar in numerous seven-coordinate $UO_2X_2L_3$ compounds[16] and is quite similar to that of the pentaisothiocyanate complex $[DPSH]_3[UO_2(NCS)_5]$ (DPSH = 2-pyridylthio-2-pyridinium).[17] Such $[UO_2X_5]^{3-}$ species are exceedingly rare but some other trianionic uranyl derivatives, all containing the oxalate ligand, have been reported.[18]

The mean U=O distance of 1.7725(5) Å is within the range previously observed in the seven-coordinate halides $UO_2Cl_2(thf)_3$ (1.765(1) Å)[19] and $UO_2Br_2(thf)_3$ (1.76(1) Å)[20] but is larger than that found in the pseudohalide complexes $[DPSH]_3[UO_2(NCS)_5]$

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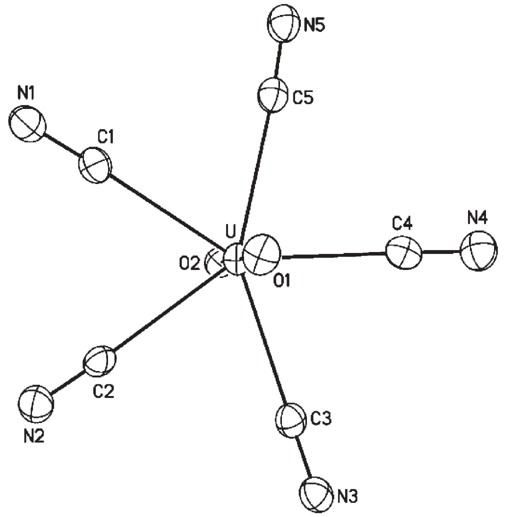

Fig. 1 View of the trianion $[UO_2(CN)_5]^{3-}$ of **1**. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): U–O1 1.772(2), U–O2 1.773(2), U–C1 2.565(3), U–C2 2.563(3), U–C3 2.549(3), U–C4 2.579(4), U–C5 2.577(4), N1–C1 1.166(4), N2–C2 1.158(4), N3–C3 1.163(4), N4–C4 1.172(5), N5–C5 1.156(5); O1–U–O2 178.27(10), C1–U–C2 69.66(10), C2–U–C3 71.70(10), C3–U–C4 74.32(10), C4–U–C5 74.78(10), C5–U–C1 71.21(10).

(1.73(1) Å)[17] or $UO_2(OTf)_2(py)_3$ (1.745(2) Å).[16] The shorter U=O bond lengths in the latter may be consistent with a weaker σ-donor effect of the equatorial ligands.[21]

The U–C distances vary from 2.549(3) to 2.579(4) Å, averaging 2.567(11) Å; they are *ca.* 0.1 Å smaller than those of 2.681(1) Å measured in $[UO_2Cl\{\eta^3\text{-}CH(Ph_2PNSiMe_3)_2\}(thf)]$[22] or in four-coordinate *N*-heterocyclic carbene complexes of uranyl,[21,23] which are in the range 2.61–2.64 Å. The mean U–C(CN) distance in the seven coordinate complex **1** is 0.15–0.25 Å larger than the distances found in the ten- and eight-coordinate organouranium(IV) monocyanides $(C_5Me_4H)_3U(CN)$ [2.31(4) Å][4] and $(1,2,4\text{-}Bu^t{}_3C_5H_2)_2U(OSiMe_3)(CN)$ [2.415(6) Å][3] and is longer than expected[24] by *ca.* 0.3–0.4 Å when compared to the mean U–C(CN) bond length of 2.62(3) Å in the eleven-coordinate and geometrically similar trianionic U(IV) complex $[NEt_4]_3[(C_5Me_5)_2U(CN)_5]$.[2] These observations suggest a stronger U^{IV}–CN interaction, in agreement with the IR data. The mean C–N distance of 1.163(6) Å is quite identical to that in the free cyanide ion [1.16 Å][9] and is unexceptional.

The experimental bond lengths of **1** can be compared with the calculated values on the anion $[UO_2(CN)_5]^{3-}$ with D_{5h} symmetry.[14] The O–U–O angle and U–O bond lengths are in good agreement, while the theoretical mean U–C distance of 2.653 Å is 0.09 Å larger than the real one [2.567(11) Å]. Moreover, in line with the calculated U–C distances, the theoretical vibration frequencies of the cyanide ligands are 16–26 cm^{-1} lower than those experimentally observed, while the calculated $\nu_{as}(UO)$ of 937 cm^{-1} is higher, by 26 cm^{-1}, than that measured in **1**.

In conclusion, the monomeric pentacyano uranyl(VI) complex $[NEt_4]_3[UO_2(CN)_5]$ was readily prepared from uranyl(VI) triflate by simple metathesis reaction in organic medium. This is the sole actinyl cyanide compound and a rare example of an uranyl complex with U–C bonds. The soluble trianionic complex **1** opens attractive perspectives, as precursor for the preparation of new uranyl cyanide derivatives and as metallo-ligand in the building of new assemblages involving U–CN–M (M = d or f-element) bridges which deserve much interest for their peculiar physico-chemical properties. Also of particular interest is their potential in material engineering, for the preparation of new nuclear fuels.

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Notes and references

† *Synthesis and characterizing data.* $[NEt_4]_3[UO_2(CN)_5]$ (**1**): A flask was charged with $UO_2(OTf)_2$ (200 mg, 0.35 mmol) and NEt_4CN (purity 94%, 295 mg, 1.8 mmol) and acetonitrile (15 mL) was condensed in. After stirring for 20 h at 20 °C and 4 h at 70 °C, the gold–yellow solution containing a white precipitate was concentrated to 5 mL. A beige powder was deposited upon addition of thf (15 mL). After filtration, the solvents were evaporated off and the residue was washed with thf (25 mL) by the Soxhlet extraction technique, leaving **1** as a beige powder after drying under vacuum (263 mg, 94%). Found: C, 44.21; H, 7.73; N, 14.07. $C_{29}H_{60}N_8O_2U$ requires C, 44.04; H, 7.65; N, 14.17%.^1H NMR (200 MHz, MeCN-d_3, 20 °C): δ 3.19 (CH_2, broad q, $w_{1/2}$ 25 Hz, 2H), 1.21 (CH_3, broad t, $w_{1/2}$ 18 Hz, 3H). IR (Nujol mulls between KBr pellets): ν(CN): 2190 (m), 2180 (m), 2070 (w); $\nu_{as}(UO)$: 911 (s). Slow diffusion of diethyl ether into a pyridine solution of **1** gave pale yellow crystals of **1**.

Complex **2** was prepared by reaction of $UO_2(OTf)_2$ with 6 equiv. of $NBu^n{}_4CN$ in hot MeCN; slow diffusion of diethyl ether into the yellow solution afforded large pale yellow blocks in a few days.

‡ *Crystal data*: for **1**: $C_{29}H_{60}N_8O_2U$, M = 790.88, monoclinic, space group $P2_1/c$, a = 17.6146(5), b = 12.2593(3), c = 17.4331(3) Å, β = 109.9446(15)°, V = 3538.76(15) $Å^3$, Z = 4, D_c = 1.484 g cm^{-3}, μ = 4.622 mm^{-1}, $F(000)$ = 1592, 72 822 measured reflections, 6707 independent (R_{int} = 0.054), 6039 with $I > 2\sigma(I)$, 373 parameters, R_1 = 0.023, wR_2 = 0.067, S = 1.083, $\Delta\rho_{min}$ = −1.22, $\Delta\rho_{max}$ = 0.54 e $Å^{-3}$. For **2**: $C_{53}H_{108}N_8O_2U$, M = 1127.50, tetragonal, space group $I4_1/a$, a = b = 46.567(2), c = 11.3472(4) Å, V = 24606.2(17) $Å^3$, Z = 16, D_c = 1.217 g cm^{-3}, μ = 2.679 mm^{-1}, $F(000)$ = 9440.

Data were collected at 100(2) K on a Nonius Kappa-CCD area-detector diffractometer with Mo-Kα radiation and processed with HKL2000.[25] The structure was solved by direct methods and refined by full-matrix least squares on F^2 with SHELXTL.[26] All non-hydrogen atoms were refined with anisotropic displacement parameters. CCDC 622766 (for **1**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b614226e

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