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First Structurally Characterized Actinide Isocyanates

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The synthesis and characterization of the neutral uranylisocyanate $UO_2(NCO)_2(OP(NMe_2)_3)_2$ [crystal data: monoclinic, $P2_1/c$, $a = 8.512(2)$ Å, $b = 10.931(2)$ Å, $c = 14.329(3)$ Å, $\beta = 103.923(3)°$, $V = 1294.0(4)$ Å^3, $Z = 2$] and isocyanato uranate $(Et_4N)_6[(UO_2)_2(NCO)_5O]_2 \cdot 2CH_3CN \cdot H_2O$ [crystal data: monoclinic, $P2_1/c$, $a = 17.2787(2)$ Å, $b = 15.560(1)$ Å, $c = 32.7619(4)$ Å, $\beta = 94.0849(5)°$, $V = 8786.5(2)$ Å^3, $Z = 4$] are reported. Not only are these compounds the first unambiguously characterized uranium isocyanates regardless of the oxidation state for uranium, but they are also the first structurally characterized actinide isocyanates. Both compounds show coordination of the OCN moiety through nitrogen to uranium and were characterized using IR and ^{1}H, ^{13}C, ^{14}N, and ^{31}P NMR spectroscopy and X-ray diffraction.

Despite the large number of reports that exist regarding the various uranium halides and uranium pseudohalides,[1] no structurally characterized uranium cyanate or uranium isocyanate has been reported in the literature, and the existence of uranium(VI) isocyanates remains unconvincing. In fact, surprisingly, to the best of our knowledge, no structurally characterized actinide cyanate or isocyanate has been reported. Early reports claiming the syntheses of several uranium(VI) isocyanates exist;[2] however, the authors were unable to provide any unambiguous spectroscopic data. An early report on an isocyanatodioxouranate(VI) $[Et_4N]_2UO_2(NCO)_4(H_2O)$ was published;[3] however, only partial characterization was presented, and the precise nature of the compound remained unclear. In addition, the compounds $(NR_4)_2[UO_2(NCO)_4]$ and $(NR_4)_2[UO_2Cl_3(NCO)]$ were reported to be formed in nonaqueous solvents containing $NR_4[UO_2Cl_3]$ and $NR_4[Ag(NCO)_2]$; however, the compounds were not isolated.[4] Furthermore, the formation of basic carbonato complexes was observed on the attempted preparation of uranyl isocyanato complexes from aqueous solution.[4] In contrast, the tetraazidouranate $UO_2(N_3)_4{}^{2-}$ [5] and pentaisothiocyanatouranate $UO_2(NCS)_5{}^{3-}$ [6] anionic species can be isolated from acidic aqueous solutions. The synthesis and characterization of uranium compounds containing the azide, N_3^-,[5] isothiocyanate, NCS^-,[1,6] and even cyanide, CN^-,[7] pseudohalides for certain oxidation states of uranium have been firmly established and the structures determined using X-ray diffraction. However, for uranium in the +VI oxidation state, only dioxouranium isothiocyanates and azides have been unambiguously characterized.[1,5,6] Very recently, a comprehensive theoretical investigation of the U(VI) series UF_4X_2 (X = CN, NC, OCN, NCO, NCS, SCN, etc.) was reported, and it was predicted for the OCN^- pseudohalide that an isocyanate would be formed preferentially over a cyanate.[8]

Therefore, establishing the existence and structure of a uranium(VI) isocyanato or cyanide complex is obviously a highly desirable target, not only to establish the existence of dioxouranium pseudohalides, which have not been extensively investigated in contrast to their halide counterparts,[1] but also to unequivocally establish the existence of actinide isocyanates. The coordination of the OCN moiety is of particular interest and could be either through the O or N

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† Crystal structure determination.

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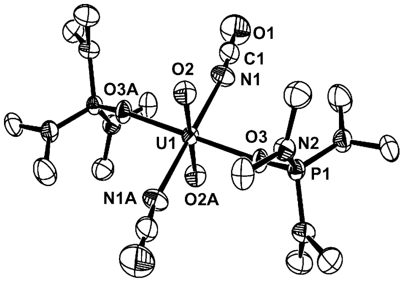

Figure 1. Molecular structure of **1** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): U1−O2 1.765(4), U1−O3 2.277(3), U1−N1 2.336(5), N1−C1 1.145(8), O1−C1 1.214(8), P1−O3 1.501(4), P1−N2 1.624(4), O2−U1−O2A 180.0, N1−U1−N1A 180, O3−U−O3A 180, O2−U1−N1 90.1(2), N1−C1−O1 179.1(7), C1−N1−U1 160.2(5).

atom forming either the uranium cyanate or uranium isocyanate, respectively. In the related isothiocyanate complexes, coordination is through the N atom.[1,6] Herein we report the first unambiguous characterization of uranium isocyanates which have been characterized by both spectroscopic methods and X-ray diffraction.

The reaction of the recently described $UO_2I_2(OP(NMe_2)_3)_2$ [9] with an excess of finely powdered AgOCN resulted in the formation of a pale yellow solution over insoluble AgI and unreacted AgOCN [eq 1].[10]

$$UO_2I_2(OP(NMe_2)_3)_2 + 2AgOCN \rightarrow UO_2(NCO)_2(OP(NMe_2)_3)_2 + 2AgI \quad (1)$$

Slow removal of the acetone from the filtrate under vacuum resulted in yellow crystals which were shown by X-ray diffraction to be diisocyanatobis(hexamethyl-phosphorictriamide)−dioxouranium(VI), (**1**) (Figure 1).[11]

In **1**, the OCN groups are bonded to the dioxouranium center through the N atom and are *trans* with respect to one another. The d(U−N) bond lengths of 2.336(5) Å are comparable with, but significantly shorter than d(U−N) in $UO_2(NCS)_2(OPPh_3)_2$ (d(U−N) = 2.44(2) Å).[6b] The U═O bond lengths of 1.765(4) Å are comparable with those of other dioxouranium species (d(U═O) = 1.78(2), 1.70(2) Å in $UO_2(NCS)_2(OPPh_3)_2{\cdot}OC(CH_3)_2$;[6b] d(U═O) = 1.757(7) Å in $UO_2I_2(OP(NMe_2)_3)_2$).[9] In agreement with the predictions of Straka, Patzschke, and Pyykkö for *trans*-$UF_4(NCO)_2$,[8] the OCN^- group in compound **1** is indeed connected to the central uranium via the nitrogen atom forming an isocyanate.

$UO_2(NCO)_2L_2$ (L = $OP(NMe_2)_3$) (**1**) was characterized by IR,[12] ^1H, ^{13}C, ^{14}N, and ^{31}P NMR spectroscopy[13] as well as X-ray diffraction.[11] The vibrational spectroscopy clearly shows the presence of the NCO group, with ν(CN, NCO) at 2172 cm^{-1} (IR) which compares nicely with the corresponding value for KOCN (ν(CN) = 2167 cm^{-1} (IR)). The band at 2179 cm^{-1} is likely due to the presence of a small amount of AgOCN starting material. The presence of ν_s(OUO) at 911 cm^{-1} (IR) clearly indicates that the UO_2 moiety is intact and is comparable to that observed for the starting material ((ν_s(OUO) = 917 cm^{-1} in $UO_2I_2(OP(NMe_2)_3)_2$).

Having successfully synthesized the neutral compound **1**, the synthesis of an anionic isocyanatouranate species was attempted. The previously reported synthesis[3] was undertaken, and after recrystallization at −28 °C,[14] a fluorescent yellow-green solid, $(Et_4N)_6[(UO_2)_2(NCO)_5O]_2{\cdot}2CH_3CN{\cdot}H_2O$ (**2**), was obtained. The structure determination of **2**[15] showed that the product was not the expected and previously reported salt $(Et_4N)_2UO_2(NCO)_4{\cdot}H_2O$[3] but, rather, a tetranuclear species with bridging and terminal OCN groups, $(Et_4N)_6[(UO_2)_2(NCO)_5O]_2{\cdot}2CH_3CN{\cdot}H_2O$ (**2**) (Figure 2). In **2**, the uranyl bond lengths (d(U═O) = 1.786(6), 1.795 (7) Å) are similar to, but significantly longer than, those observed in **1** (d(U═O) = 1.765(4) Å). In addition, the terminal U−NCO (d(U1−N1) = 2.45(1) Å) and bridging (d(U−NCO) = 2.58(1) Å) bond lengths can be compared to those reported for the related azide compound, $(Me_4N)_4[(UO_2)_3(N_3)_8O]{\cdot}H_2O$, whereby the U−NCO bond lengths in compound **2** are slightly longer (d(U−N) = 2.42(3) Å; d(U−NNN$_{bridging}$) = 2.49(2) Å).[5] As expected, the OUO moiety is almost linear (∠(OUO) = 175.7(3)°), as are both the terminal and bridging NCO groups (∠(NCO$_{terminal}$) = 178(1)°; ∠(NCO$_{bridging}$) = 179(1)°). A tetranuclear isothiocyanate analogue is not known. Compound **2** can however be compared to the related chloride complex $[(UO_2)_2Cl(OH)(OH_2)_3O]_2$ [16] which is also

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(10) The synthesis of $UO_2(NCO)_2(OP(NMe_2)_3)_2$ (**1**) follows: 0.441 g (0.5 mmol) of $UO_2I_2(OP(NMe_2)_3)_2$ and a magnetic stirrer bar were added to a 50 mL Schlenk flask. Under a nitrogen atmosphere, 20 mL of acetone were added, whereby a clear orange-yellow solution formed. To this solution, 3.5 g (23.3 mmol) of freshly prepared AgOCN (excess) were added, and a color change occurred quickly forming a pale yellow solution over a significant amount of yellow AgI solid and unreacted white AgOCN. The reaction vessel was covered in aluminum foil and left stirring vigorously at room temperature for 5 h, after which time the unreacted AgOCN and yellow AgI precipitate were allowed to settle and the filtrate was carefully separated. The volume of the clear, yellow filtrate was slowly reduced under vacuum whereby yellow crystals formed. In order to protect the crystals formed, the vessel was not subjected to dynamic vacuum to remove the last traces of solvent. The vessel was then maintained under a nitrogen atmosphere in the dark at 4 °C.

(11) Crystallographic data collection details for **1** follow: $C_{14}H_{36}N_8O_6P_2U_1$, fw = 712.48, yellow prisms, crystal size 0.2 × 0.2 × 0.2 mm^3, monoclinic ($P2_1/c$), a = 8.512(2) Å, b = 10.931(2) Å, c = 14.329(3) Å, β = 103.923(3)°, V = 1294.0(4) Å^3, Z = 2, T = 193(2) K, final $R(4\sigma)$ = 0.0247, final wR2 = 0.0656.

(12) IR spectrum for **1** (room temperature, RT, KBr plates, resolution = 4 cm^{-1}): 2888 m, 2172 vs, 1711 w, 1454 m, 1300 s, 1189 s, 1082 s, 988 vs, 911 s, 751 s, 632 m, 621 m, 512w, 471m, 377 w.

(13) NMR data (RT, d_6-acetone, δ in ppm) of **1** follow. ^1H (399.78 MHz, TMS): 2.92 (d, J_{PH} = 21.1 Hz, NMe_2). ^{13}C (100.52 MHz, TMS): 37.1 (d, J_{PC} = 3.9 Hz). ^{14}N (28.89 MHz, $MeNO_2$): −220 (br, OC*N*), −352 (br, *N*Me_2). ^{31}P (161.84 MHz, 85% H_3PO_4): 35.2.

(14) Synthesis of $(Et_4N^+)_6[(UO_2)_2(NCO)_5O]_2^{6-}{\cdot}2CH_3CN{\cdot}H_2O$ (**2**) 0.63 g (3.0 mmol) of Et_4NBr were added to 5 mL of ethanol, followed by 0.45 g (3.0 mmol) of AgOCN. After stirring vigorously for 2 h in the dark, a clear, colorless solution over unreacted AgOCN and AgBr precipitate was observed. The filtrate was collected, and a solution of 0.25 g (0.5 mmol) of $UO_2(NO_3)_2{\cdot}6H_2O$ in 2.5 mL of acetone was added. After stirring the reaction mixture for 10 min, 15 mL of acetone were added at RT, whereby a fine, yellow solid slowly precipitated. After the remaining solvent was evaporated, a highly fluorescent yellow-green solid was observed. Dissolving a portion of this solid in a 2:1 (v/v) mixture of CH_3CN/C_2H_5CN, followed by cooling the mixture to −30 °C overnight, resulted in the precipitation of fluorescent yellow-green needles, which quickly became amorphous, if not covered by the CH_3CN/C_2H_5CN solvent mixture.

(15) Crystallographic data collection details for **2** follow: $U_4O_{21}N_{18}C_{62}H_{128}$, fw = 2413.90, crystal size 0.02 × 0.08 × 0.14 mm^3, monoclinic ($P2_1/c$), a = 17.2787(2) Å, b = 15.560(1) Å, c = 32.7619(4) Å, β = 94.0849(5)°, V = 8786.5(2) Å^3, Z = 4, T = 200 K. Final $R(4\sigma)$ = 0.0581, final wR2 = 0.1245.

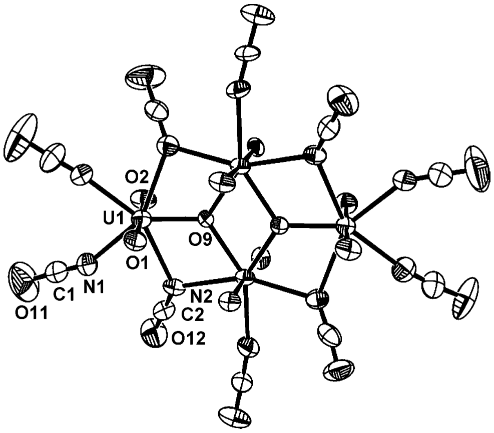

Figure 2. Molecular structure of the anion in **2** with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg): U1−O2 1.795(7), U1−O1 1.786(6), U1−N1 2.45(1), N1−C1 1.17(2), O11−C1 1.19(2), U1−N2 2.58(1), N2−C2 1.19(2), C2−O12 1.17(2), U1−O9 2.279(7), O2−U1−O1 175.7(3), N1−U1−N2 78.7(3), N1−C1−O11 178(1), O12−C2−N2 179(1), N1−U1−O9 144.7(3), N2−U1−O9 66.2(3).

a tetranuclear complex with bridging Cl, O, OH, and H_2O ligands. However, whereas $[(UO_2)_2Cl(OH)(OH_2)_3O]_2$ contains UO_2 groups, all of which are coordinated to at least one OH, H_2O, and Cl ligand as well as the bridging O units, in compound **2** the UO_2 groups are only coordinated to OCN groups in addition to the O bridges. Compound **2** was further characterized by IR[17] and ^1H, ^{13}C, and ^{14}N NMR spectroscopy.[18] In the ^{14}N NMR spectrum, peaks attributable to the bridging OCN groups ($\delta = -260$ ppm) and nonbridging OCN groups ($\delta = -246, -250$) with an intensity ratio of 2:1:2 were observed as would be expected. No decomposition of a solid sample of compound **2** was observed, even after storing the compound for months at room temperature in the dark. However, compound **2** was found to partially decompose in CD_3CN solution if maintained at room temperature for several days.

The synthesis and first structural characterization of a uranium isocyanate and isocyanatodioxouranate(VI) have been achieved, and the existence of a uranyl isocyanate has been unequivocally established for the first time. The synthesis of further uranium isocyanates with lower oxidation states for uranium can now be thought of as likely, as well as the synthesis of other actinide isocyanates.

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Supporting Information Available: Crystallographic files in CIF format for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) IR spectrum of **2** (RT, KBr plates, resolution = 4 cm^{-1}): 2988vw, 2197vs, 1485w, 1455vw, 1438w, 1384s, 1321vw, 1270w, 1184w, 1173w, 1001m, 903m, 884s, 858m, 787m, 659m, 627m, 534m, 502m.

(18) NMR data for **2** (RT, CD_3CN, δ in ppm) follow. ^1H (399.78 MHz, TMS): 1.12 (tt, $^3J_{HH} = 7.3$ Hz, $^3J_{^{14}NH} = 1.9$ Hz, 3H, CH_3), 3.12 (q, $^3J_{HH} = 7.3$ Hz, 2H, CH_2). ^{13}C (100.52 MHz, TMS): 134.3 (t, $^1J_{^{14}NC}$ = 13.7 Hz, N*C*O-terminal); 133.6 (s, N*C*O-bridging), 133.0 (t, $^1J_{^{14}NC}$ = 14.8 Hz, N*C*O-terminal); 52.1 (t, $^1J_{^{14}NC} = 2.9$ Hz, NCH_2), 6.8 (s, Me). ^{14}N (28.89 MHz, $MeNO_2$): −246 (OC*N*-terminal), −249 (OC*N*-terminal), −250 (OC*N*-bridging), −318 (NEt_4^+).