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Nitrate and Perchlorate Complexes of Uranium(IV)

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The solid-state structures of the $[U^{IV}(NO_3)_6]^{2-}$ anions in the $[n\text{-}Pr_4N]_2[U(NO_3)_6]$ (**1**), $[n\text{-}Bu_4N]_2[U(NO_3)_6]$ (**2**), and $[Ph_4P]_2[U(NO_3)_6]\cdot 4NCCH_3$ (**3**) salts were determined using single-crystal X-ray diffraction. For the first time, a nondisordered structure of the hexanitratouranate(IV) dianion with a coordination number of 12 for the central U^{IV} atom was determined. Salts **1**−**3** were prepared in simple metathesis reactions and characterized using IR spectroscopy, C/H/N analysis, and single-crystal X-ray diffraction. Attempts to prepare a salt containing the $[U^{IV}(ClO_4)_6]^{2-}$ anion using the analogous route resulted in the isolation of $U(ClO_4)_4(NCCH_3)_5$ (**4**), which was characterized using single-crystal X-ray diffraction. Compound **4** is the first structurally characterized uranium(IV) perchlorate to be reported in the literature.

Uranium nitrates have been of interest for a long time because of their importance in the PUREX process.[1] Many neutral uranyl nitrate complexes of the type $UO_2(NO_3)_2L_x$ containing uranium(VI) and various neutral coordinating ligands (L) such as H_2O or $OP(NMe_2)_3$,[2] as well as salts of the corresponding $[UO_2(NO_3)_3]^{3-}$ and $[UO_2(NO_3)_4]^{2-}$ anions,[4] have been synthesized and structurally characterized. In the $[UO_2(NO_3)_3]^-$ anion, all of the nitrate groups are bidentate-coordinated, resulting in a coordination number of 8 for the U^{VI} center, whereas in the rubidium[4a] and ammonium[4b] salts of the $[UO_2(NO_3)_4]^{2-}$ anion, only two $[NO_3]^-$ groups are bidentate-coordinated and the other two are monodentate-coordinated, resulting again in a coordination number of 8 for the U^{VI} center.

For the lower IV oxidation state for uranium, several complexes of the type $U(NO_3)_4L_4$ [L = $OPPh_3$, $OP(NMe_2)_3$] have been synthesized and structurally characterized[5] and show high coordination numbers for the central U^{IV} atom. However, attempts to prepare neutral $U(NO_3)_4$, by the reaction of UCl_4 with $AgNO_3$ in an acetone/CH_3CN solution were reported to result in oxidation occurring upon concentration of the solution with the formation of a uranium(VI) compound.[6] Consequently, $U(NO_3)_4$ still has not been isolated in the solid state. Despite this, many reports exist in the literature regarding the hexanitratouranate anion, $[U(NO_3)_6]^{2-}$, which also contains U^{IV} as the central atom and was suggested to show a very high coordination number of 12.[7] Salts of this anion have been isolated as room-temperature-stable solids. However, to the best of our knowledge, only one previous report exists in the literature regarding the structural characterization of a salt containing the $[U(NO_3)_6]^{2-}$ anion in $[Et_4N]_2[U(NO_3)_6]$.[8] Unfortunately, the anion in this salt suffered from disorder, resulting in two possible positions for each of the nitrato O atoms and making the precise structure of the $[U(NO_3)_6]^{2-}$ anion less clear. In this present work, we report on the preparation of three salts of the hexanitratouranate anion, namely, $[n\text{-}Pr_4N]_2[U(NO_3)_6]$ (**1**), $[n\text{-}Bu_4N]_2[U(NO_3)_6]$ (**2**), and $[Ph_4P]_2[U(NO_3)_6]\cdot 4NCCH_3$ (**3**), which were all prepared using a

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Table 1. Selected Structural Parameters of the $[U(NO_3)_6]^{2-}$ Anion in Salts **1**−**3** Determined Using Single-Crystal X-ray Diffraction[10−12]

parameter	$[n\text{-}Pr_4N]_2[U(NO_3)_6]$ (**1**)	$[n\text{-}Bu_4N]_2[U(NO_3)_6]$ (**2**)	$[Ph_4P]_2[U(NO_3)_6]\cdot 4NCCH_3$ (**3**)
$d(U{-}ONO_2)$/Å	2.543(3), 2.497(3), 2.516(3), 2.518(3), 2.508(3), 2.513(3), 2.506(3), 2.511(3), 2.525(3), 2.528(3), 2.535(3), 2.522(3)	2.5307(17), 2.5137(18), 2.5273(17), 2.5313(17), 2.5013(18), 2.5078(18)	2.532(2), 2.5025(18), 2.534(2), 2.4974(18), 2.5283(19), 2.508(2)
$d(O{-}NO_2)_{\text{bidentate}}$/Å	1.255(5), 1.278(5), 1.277(5), 1.281(5), 1.270(5), 1.276(6), 1.273(5), 1.263(6), 1.288(5), 1.267(5), 1.277(5), 1.277(5)	1.266(3), 1.282(3), 1.270(3), 1.272(3), 1.278(3), 1.272(3)	1.244(3), 1.274(3), 1.274(3), 1.259(3), 1.270(3), 1.276(3)
$d(O{-}NO_2)_{\text{terminal}}$/Å	1.210(6), 1.211(5), 1.216(5), 1.206(5), 1.223(5), 1.214(5)	1.211(3), 1.216(3), 1.204(3)	1.237(3), 1.223(3), 1.227(3)
$\angle(U{-}O{-}N)$/deg	96.9(2), 97.0(3), 97.4(2), 97.1(3), 97.4(3), 95.9(2), 97.0(2), 96.1(2), 97.3(2), 96.5(2), 96.8(2), 96.9(2)	96.99(14), 97.34(14), 97.10(13), 96.86(13), 97.18(14), 97.04(14)	96.97(13), 94.66(14), 97.34(14), 96.25(15), 97.41(15), 96.11(14)

procedure[9] similar to that in the literature[8] in a CH_3CN solution as pale-green or emerald crystals (eq 1).

$$M_2UBr_6 + 6AgNO_3 \rightarrow M_2U(NO_3)_6 + 6AgBr \qquad (1)$$

1−**3** were characterized using IR spectroscopy, C/H/N analysis, and the solid-state structures determined using single-crystal X-ray diffraction.[11−13] The homoleptic $[U(NO_3)_6]^{2-}$ anions in **1**−**3** all show, for the first time, a nondisordered arrangement of six bidentate $[NO_3]^-$ ligands around the U^{IV} center. Whereas centrosymmetric $[U(NO_3)_6]^{2-}$ anions are observed for compounds **2** and **3** in the solid state, the $[U(NO_3)_6]^{2-}$ anion in **1** possesses C_1 symmetry. Selected structural parameters of **1**−**3** are summarized in Table 1.

Although **1**−**3** contain uranium(IV), the compounds were not extremely air-sensitive but were handled under inert-gas conditions for the preparation, isolation, and characterization. Characteristic bands in the IR spectra of **1**−**3** indicated the presence of both the cations and $[U(NO_3)_6]^{2-}$ anions.

Since we were interested in the preparation of salts containing homoleptic uranate anions, the investigation was extended to attempt the preparation of a salt containing the $[U(ClO_4)_6]^{2-}$ anion. To the best of our knowledge, no literature report exists prior to our work on the isolation and structural characterization of a uranium(IV) perchlorate compound. Furthermore, although uranium(VI) perchlorates with the general formula $UO_2(ClO_4)_2\cdot nH_2O$ (n = 0, 1, 3, 5, 7) had been extensively investigated,[14] it was only recently that the solid-state structure of $[UO_2(ClO_4)_2(H_2O)_3]$ was determined[15] and showed, for the first time, monodentate coordination of two $[ClO_4]^-$ ligands to the U^{VI} center. Traditionally, nitrate and perchlorate anions were considered to be weakly coordinating, which is in agreement with the formation of salts of the type $[UO_2(H_2O)_n][ClO_4]_2$ (n = 5, 7) reported previously.[14,16]

The reaction according to eq 1 was undertaken by swapping $AgNO_3$ for $AgClO_4$, and a dark-green solution formed,[17] from which only a very small amount of very small emerald-green crystals was obtained in very poor yield. Using single-crystal X-ray diffraction, one of the crystals was shown to correspond to **4**.[18] To the best of our knowledge, this is the first uranium(IV) complex that shows perchlorate ligands coordinated to the U^{IV} center (Figure 2).

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(9) ***Caution!*** *Polynitrates should always be handled with caution as possible energetic materials*. The sensitivities of **1**−**3** were not investigated. General synthesis of $[M]_2[U^{IV}(NO_3)_6]$ (M = n-Pr_4N^+, n-Bu_4N^+, Ph_4P^+): Using the Schlenk line, a 25 mL Schlenk flask was loaded with 0.3 mmol of the corresponding $[M]_2UBr_6$, a magnetic stir bar, and 1.8 mmol (0.306 g) of solid $AgNO_3$. After the reaction vessel was filled with a nitrogen atmosphere, approximately 15 mL of freshly distilled CH_3CN (dried using P_4O_{10}) was added under a N_2 purge. The reaction vessel was covered with aluminum foil and left stirring in the dark for 2 h at room temperature. The dark-green solutions were then filtered off under a N_2 atmosphere into a second 25 mL Schlenk flask, and the volume of the solvent was reduced until the solution was almost saturated. The reaction vessels were then left in the freezer overnight at −28 °C, whereby large peppermint-green (n-Bu_4N^+ and Ph_4P^+ salts) or emerald-green (n-Pr_4N^+ salt) crystals formed overnight. The crystals were removed under a N_2 atmosphere and manipulated in the glovebox.

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(11) Characterization of **1**: 2977w, 2943w, 2883w, 1517s, 1476m, 1456m, 1384w, 1294s, 1284s, 1029s, 986w, 970w, 874vw, 807w, 745m, 671w, 664vw, 465m. C/H/N anal. Calcd (obsd): C, 29.33 (29.77); H, 5.74 (5.78); N, 11.40 (11.20). Crystallographic data collection for **1**: $C_{24}H_{56}N_8O_{18}U_1$, fw = 982.773, crystal size, 0.23 × 0.20 × 0.15 mm, monoclinic ($P2_1/n$), a = 14.6953(2) Å, b = 15.8043(2) Å, c = 16.8333(3) Å, β = 90.6269(14)°, V = 3909.28(10) Å^3, Z = 4, T = 20(2) K, ρ = 1.66983(4) g cm^{-3}, μ = 4.231 mm^{-1}, GOF = 0.951, $R(F_{\text{obs}})$ = 0.0281, $R_w(F^2)$ = 0.0661.

(12) Characterization of **2**: 2961m, 2932w, 2874m, 1612vw, 1512s, 1485s, 1458s, 1415m, 1378m, 1296sh, 1283s, 1177vw, 1155vw, 1143vw, 1127vw, 1108vw, 1065vw, 1038m, 1031m, 972w, 890w, 876w, 806m, 782vw, 745m. C/H/N anal. Calcd (obsd): C, 35.10 (35.37); H, 6.63 (6.48); N, 10.23 (10.10). Crystallographic data collection for **2**: $C_{32}H_{72}N_8O_{18}U_1$, fw = 1094.986, crystal size, 0.37 × 0.13 × 0.07 mm, monoclinic ($P2_1/n$), a = 10.5149(2) Å, b = 19.1166(3) Å, c = 11.7988(2) Å, β = 93.657(2)°, V = 2366.84(7) Å^3, Z = 2, T = 200(2) K, ρ = 1.53647(5) g cm^{-3}, μ = 3.503 mm^{-1}, GOF = 1.154, $R(F_{\text{obs}})$ = 0.0155, $R_w(F^2)$ = 0.0412.

(13) Characterization of **3**: 3087vw, 1821vw, 1777vw, 1733vw, 1613vw, 1586w, 1514s, 1483s, 1443m, 1437m, 1384vw, 1339vw, 1283s, 1186w, 1165w, 1108m, 1032m, 997m, 854w, 806w, 753m, 745s, 723s, 689s, 527s, 454vw. C/H/N anal. Calcd for $(Ph_4P)_2U(NO_3)_6$ (obsd): C, 44.73 (44.50); H, 3.13 (3.26); N, 6.52 (5.84). Crystallographic data collection for **3**: $C_{56}H_{52}N_{10}O_{18}P_2U_1$, fw = 1453.045, crystal size, 0.2 × 0.18 × 0.10 mm, triclinic ($P\bar{1}$), a = 10.6347(4) Å, b = 11.8326(5) Å, c = 13.3839(6) Å, α = 65.904(4)°, β = 85.548(3)°, γ = 77.243(3)°, V = 1499.32(11) Å^3, Z = 1, T = 200(2) K, ρ = 1.60931(12) g cm^{-3}, μ = 2.840 mm^{-1}, GOF = 1.023, $R(F_{\text{obs}})$ = 0.0248, $R_w(F^2)$ = 0.0528.

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(17) ***Caution!*** *Perchlorate-rich compounds should always be handled with caution as possible energetic materials*. The sensitivity of **4** was not investigated. Synthesis of $U^{IV}(ClO_4)_4(NCCH_3)_5$ (**4**): Using the Schlenk line, a 25 mL Schlenk flask was loaded with 0.361 g (0.3 mmol) of $[n\text{-}Bu_4N]_2UBr_6$, a magnetic stir bar, and 0.373 g (1.8 mmol) solid of $AgClO_4$. After it was ensured that a N_2 atmosphere filled the reaction vessel, approximately 15 mL of predried P_4O_{10} and freshly distilled CH_3CN were added under a N_2 purge. The reaction vessel was covered with aluminum foil and left stirring in the dark for 2 h at room temperature. The dark-green solution was filtered off under a N_2 atmosphere into a second 25 mL Schlenk flask, and the volume of the solvent was reduced. Approximately the same quantities of predried CaH_2 and freshly distilled CH_2Cl_2 were added under a N_2 purge, and the reaction vessel was left at 4 °C for several days whereby a very small quantity of very small emerald-green crystals formed.

(18) Crystallographic data collection for **4**: $C_{10}H_{15}Cl_4N_5O_{16}U_1$, fw = 841.10, crystal size, 0.15 × 0.15 × 0.10 mm, tetragonal ($P4nc$), a = b = 10.65500(10) Å, c = 11.1445(2) Å, V = 1265.22(3) Å^3, Z = 2, T = 200 K, ρ = 2.208 g cm^{-3}, μ = 6.916 mm^{-1}, GOF = 1.291, $R(F_{\text{obs}})$ = 0.0165, $R_w(F^2)$ = 0.0578.

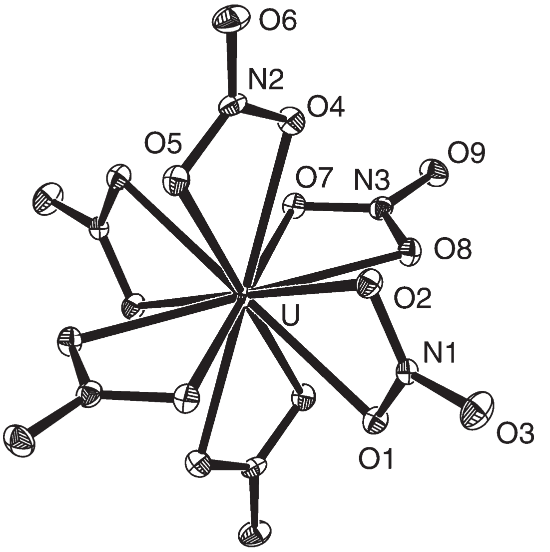

Figure 1. ORTEP representation of the molecular structure of the centrosymmetric $[U(NO_3)_6]^{2-}$ anion in **3** in the solid state determined using single-crystal X-ray diffraction. Thermal ellipsoids are shown with 25% probability. Selected bond lengths and angles for compounds **1−3** are given in Table 1.

Compound **4** shows a U^{IV} center coordinated by four monodentate $[ClO_4]^-$ ligands and five CH_3CN ligands, resulting in a coordination number of 9 for the uranium center. The ligands show a 1:4:4 arrangement around the U^{IV} center with one CH_3CN ligand in the apical position, four $[ClO_4]^-$ ligands in the middle level, and four CH_3CN ligands at the base. The apical CH_3CN ligand shows linear coordination to the U^{IV} center with a significantly longer U−N bond length [2.614(8) Å] in comparison to the U−N bond length of the four CH_3CN ligands at the base [2.489(3) Å], which also show nonlinear coordination to the U^{IV} center [165.2(3)°]. Within the $[ClO_4]^-$ ligands, the O−Cl bond lengths [1.491(12) Å] involving the O atoms that are coordinated to the U^{IV} center are longer than the O−Cl bond lengths involving the noncoordinated O atoms of the perchlorate group [1.399(4), 1.399(4), and 1.403(4) Å].

Other attempts to reproduce the synthesis of **4** and to prepare salts containing the $[U(ClO_4)_6]^{2-}$ anion appear to result in the removal of the perchlorate ligands from the U^{IV} center by substitution of the solvent molecules. Therefore, complex **4** is currently unsuitable for use as a uranium(IV) starting material because its synthesis has so far proven difficult to repeat. Therefore, the possibility of the preparation and isolation of salts containing the $[U(ClO_4)_6]^{2-}$ anion remains open and may be attainable using the correct reaction system and anhydrous conditions.

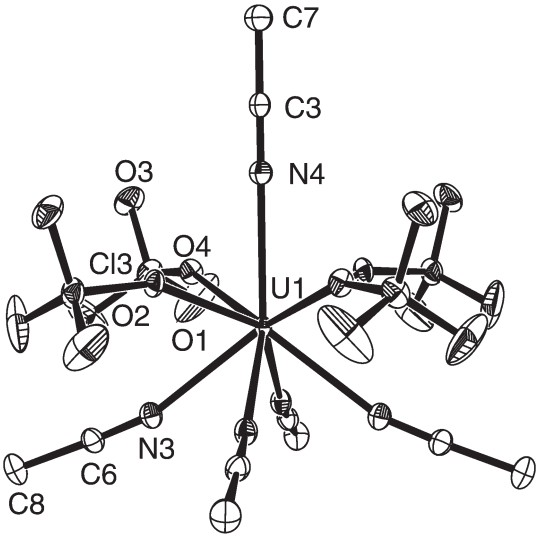

Figure 2. ORTEP representation of the molecular structure of **4** in the solid state determined using single-crystal X-ray diffraction. Thermal ellipsoids are shown with 25% probability, and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): U1−N3 2.489(3), U1−O4 2.335(2), U1−N4 2.614(8), Cl3−O1 1.399(4), Cl3−O2 1.399(4), Cl3−O3 1.403(4), Cl3−O4 1.491(2), N4−C3 1.137(13), C3−C7 1.453(14), N3−C6 1.117(5), C6−C8 1.465(6), U1−O4−Cl3 155.4(2), U1−N3−C6 165.2(3), U1−N4−C3 180.0, N3−C6−C8 177.2(5), N4−C3−C7 180.0, O4−Cl3−O1 107.6(2), O4−Cl3−O2 107.2(2), O4−Cl3−O3 107.0(2), O4−U1−N3 73.12(10), O4−U1−N4 68.68(8), N3−U1−N4 127.81(8).

The preparation and structural characterization of complexes **1−4** provides information of uranium(IV) compounds containing relatively weakly coordinating ligands. For the first time, a nondisordered structure of the homoleptic $[U^{IV}(NO_3)_6]^{2-}$ anion showing the unusual coordination number of 12 for the U^{IV} center has been obtained. The synthesis of the uranium(IV) perchlorate complex **4** shows that, although the perchlorate group is an oxidizer, it is possible to prepare uranium(IV) perchlorate complexes that are room-temperature-stable for some time and in which perchlorate is coordinated to the uranium center. Complexes containing perchlorate ligands coordinated to the uranium center are rare for both the IV and VI oxidation states of uranium.

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Supporting Information Available: Crystallographic files in CIF format for compounds **1−4**. This material is available free of charge via the Internet at http://pubs.acs.org.