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Structurally Characterized Ternary U–O–N Compound, UN_4O_{12}: $UO_2(NO_3)_2 \cdot N_2O_4$ or $NO^+UO_2(NO_3)_3^-$?

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The synthesis and characterization of the ternary U–O–N compound $NO^+UO_2(NO_3)_3^-$ (**1**) using IR and low-temperature and room-temperature Raman spectroscopy as well as ^{14}N and ^{15}N NMR spectroscopy are reported. In addition, solution Raman spectra of compound **1** recorded in various solvents are reported. The structure of compound **1** was determined using single-crystal X-ray diffraction techniques: monoclinic, $C2/c$, $a = 13.3992(4)$ Å, $b = 9.9781(4)$ Å, $c = 7.6455(2)$ Å, $\beta = 115.452(2)°$, $V = 922.98(5)$ Å^3, $Z = 4$. Compound **1** is highly moisture-sensitive and must be handled under an inert atmosphere. It reacts with water with the liberation of NO_2. For the first time, this important precursor for the synthesis of anhydrous uranyl nitrate could be unambiguously identified and has been shown to be an ionic nitrosonium salt and not an adduct between uranyl nitrate and dinitrogen tetroxide, $UO_2(NO_3)_2 \cdot N_2O_4$, as is incorrectly and predominantly cited in the literature.

Introduction

Uranyl nitrates are extremely important in the chemistry of U(VI) and have been widely investigated in various forms for many years.[1] The uranyl nitrate hydrates, for example, $UO_2(NO_3)_2 \cdot 2H_2O$,[2a,b] $UO_2(NO_3)_2 \cdot 3H_2O$,[2c,d] $[UO_2(OH)_2UO_2](NO_3)_2 \cdot 3H_2O$,[2e] $(UO_2)_3O(OH)_3(H_2O)_6NO_3(H_2O)_4$,[2f] and $UO_2(NO_3)_2 \cdot 6H_2O$,[2g−j] have been particularly well investigated and structurally characterized. In addition, $UO_2(NO_3)_2 \cdot 6H_2O$ is one of the most important starting materials in uranium chemistry is a key compound in the PUREX process for the separation of fission products from uranium and plutonium fuels and is a main pollutant in the wastewater produced by nuclear fuel fabrication and processing.[3] In addition to the hydrates, a range of coordination compounds have also been reported such as $UO_2(NO_3)_2(OC(NMe_2)_2)_2$ and $UO_2(NO_3)_2(ONC_5H_4CH_3)_2$.[4]

For U(IV), various coordination compounds of the type $U(NO_3)_4L_2$ (L = neutral Lewis base) have been reported, for example, $U(NO_3)_4(OP(NMe_2)_3)_2$ and $U(NO_3)_4(OPPh_3)_2$.[5] Although the homoleptic U(IV) complex $U(NO_3)_4$ has been characterized in solution, despite many attempts to isolate it in the solid state, only decomposition products were observed.[6] The related U(IV) compound $(Et_4N)_2U(NO_3)_6$ containing the ternary $U(NO_3)_6^{2-}$ dianion was, however, successfully isolated and structurally characterized in the solid state.[7] In addition, uranium oxynitrides have also been investigated and reported in the literature.[8] Further examples of ternary U−O−N anions are the polymeric uranyl azide anions formulated as $(Et_4N)UO_2(N_3)_3$[9a] and $(Et_4N)_4[(UO_2)_3(N_3)_8O] \cdot H_2O$,[9a] as well as the mononuclear $UO_2(N_3)_4^{2-}$

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anion.[9b] The related U(VI) anions $UO_2(NO_3)_3^-$ [10] and $UO_2(NO_3)_4^{2-}$ [11] have also been prepared; however, only three $UO_2(NO_3)_3^-$ salts (Rb,[10a] Cs,[10b] and 4,4′-bipyridinium[10c]) and two $UO_2(NO_3)_4^{2-}$ salts ($(Rb^+)_2$[11a] and $(NH_4^+)_2$[11b]) have been structurally characterized.

Although the isolation of the homoleptic U(IV) compound $U(NO_3)_4$ in the solid-state remains elusive,[7] various synthetic routes and the isolation of the neutral anhydrous uranyl nitrate, $UO_2(NO_3)_2$, in the solid state have been described in the literature.[12] The most widely cited route for the formation of anhydrous uranyl dinitrate employs the thermal decomposition of the dinitrogen tetroxide adduct of uranyl nitrate, $UO_2(NO_3)_2{\cdot}N_2O_4$.[12] Although $UO_2(NO_3)_2{\cdot}N_2O_4$ is reported to be the most useful precursor, the nature of this compound remains unclear, and the question as to whether the compound is an $UO_2(NO_3)_2{\cdot}N_2O_4$ adduct[13] or the ionic nitrosonium salt $NO^+UO_2(NO_3)_3^-$ [14] has not yet been answered. Evidence for both formulations has appeared in the literature,[13,14] and it is interesting to note that both $NO^+UO_2(NO_3)_3^-$ literature,[13,14] and it is and $UO_2(NO_3)_2{\cdot}N_2O_4$ possess the same empirical formula UN_4O_{12}. In addition, UN_4O_{12} is also the same empirical formula for the U(IV) species $U(NO_3)_4$. Establishing whether the U(VI) compound UN_4O_{12} is an ionic or covalent compound is of importance because it is a small and simple ternary system containing only the elements uranium, oxygen, and nitrogen.

The majority of reports in the literature and in inorganic textbooks cite UN_4O_{12} as being $UO_2(NO_3)_2{\cdot}N_2O_4$;[13] however, an early report by Späth[13a] describes the compound as being an NO_2 adduct of the type $UO_2(NO_3)_2{\cdot}2NO_2$. The $UO_2(NO_3)_2{\cdot}N_2O_4$ formulation was supported predominantly by UV absorption spectra of nitromethane solutions of $UO_2(NO_3)_2{\cdot}N_2O_4$, which were reported to indicate that $UO_2(NO_3)_3^-$ ions are not present in significant quantities, in contrast to solutions containing the ionic $R_4N^+UO_2(NO_3)_3^-$ (R = alkyl group) salts.[13] In addition, the IR spectrum was reported and assigned based on the $UO_2(NO_3)_2{\cdot}N_2O_4$ formulation.[13] The presence of the NO^+ group was dismissed, and the weak bands observed in the IR spectrum at 2300 and 2263 cm^{-1} (which correspond to the NO^+ region) were assigned to overtone bands because they were also reported to be observed in the IR spectrum of $K^+UO_2(NO_3)_3^-$. Finally, the authors state that they found no physical or chemical evidence, e.g., the electrical conductivity in CH_3NO_2 solution, that would support the presence of the NO^+ group.[13]

Evidence has also been provided in the literature to support the assignment of the compound to the nitrosonium salt $NO^+UO_2(NO_3)_3^-$,[14] using primarily IR and Raman spectroscopy.[14] Kobets et al. assigned a relatively weak peak at 2300 cm^{-1} (Raman) and a weak band at 2294 cm^{-1} (IR) to the $\nu(NO^+)$, in contrast to the assignments made by Addison et al. In addition, Kobets et al. assigned no peaks in the IR spectrum to bidentate-coordinated N_2O_4.[14] The nature of this compound clearly remained in dispute, with plausible arguments existing for both formulations, and therefore, we wanted to unambiguously establish the nature of this compound using vibrational spectroscopy (IR and Raman) as well as single-crystal X-ray diffraction. In addition, the Raman spectra of compound **1** in various solvents, as well as the ^{14}N and ^{15}N NMR spectra of compound **1** in CH_3NO_2, were investigated.

Experimental Section

General Information. $UO_2(NO_3)_2{\cdot}6H_2O$,[2g−j] $K^+UO_2(NO_3)_3^-$,[15] and $NO^+SbF_6^-$ [16] were prepared according to the literature procedures. Clean uranium turnings (BDH Chemicals) were prepared according to the procedure outlined in the literature.[17] Compound **1**, $NO^+UO_2(NO_3)_3^-$, was prepared by the reaction of uranium metal turnings with a N_2O_4/CH_3NO_2 solution at room temperature with a slightly modified literature procedure.[13b] N_2O_4 (Aldrich) and $K^+NO_3^-$ (Aldrich) were used as supplied without further purification. CH_3NO_2 (Aldrich) was dried over P_4O_{10} and distilled off prior to use. Standard procedures for the handling and disposal of uranium-containing compounds were employed at all times. IR spectra were recorded as solids between KBr plates using a Perkin-Elmer 983G IR spectrometer. Raman spectra were recorded using a Perkin-Elmer FT-IR R2000 spectrometer fitted with a Nd:YAG laser (1064 nm) and a Ventacon low-temperature cell, and the relative peak intensities are given in parentheses. The single-crystal X-ray diffraction study of compound **1** was undertaken using a Nonius Kappa CCD diffractometer. The structure of compound **1** was solved by direct methods using SiR97 and refined by means of full-matrix least-squares procedures with SHELXL-97.[18]

Preparation and Recrystallization of $NO^+UO_2(NO_3)_3^-$ (1). $NO^+UO_2(NO_3)_3^-$ was prepared essentially according to the literature method.[13b] The reaction was facilitated by placing the reaction vessel several times in an ultrasonic bath at room temperature for 0.5−1-min periods. The remaining N_2O_4/CH_3NO_2 solution was then filtered off the solid precipitate under an argon atmosphere using a glass frit, and the yellow-green solid was pumped to dryness using standard Schlenk-line techniques. The highly moisture-sensitive yellow-green solid obtained was isolated under a nitrogen atmosphere in a glovebox. All manipulations of the material were

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undertaken in the glovebox. Yellow-green crystals suitable for X-ray diffraction were grown by preparing a saturated solution of **1** in CH_3NO_2 and maintaining the clear yellow solution at −30 °C for 14 h, after which time highly moisture-sensitive pale yellow crystals formed.

Raman spectrum of $NO^+UO_2(NO_3)_3^-$ (−110 °C, 5 mm glass tube, resolution = 4 cm^{-1}): 2303 (6) ($\nu(NO^+)$), 1605 (1) (NO_3^-), 1510 (2) (ν_1, NO_3^-), 1026 (5) (ν_2, NO_3^-), 872 (10) (ν_s(OUO)), 741 (4) (ν_3, NO_3^-), 713 (2) (ν_5, NO_3^-), 236 (1), 218 (1), 181 (3). Raman spectrum of $NO^+UO_2(NO_3)_3^-$ (RT, 5 mm glass tube, resolution = 4 cm^{-1}): 2301 (6) ($\nu(NO^+)$), 1605 (1) (NO_3^-), 1508 (1) (ν_1, NO_3^-), 1026 (6) (ν_2, NO_3^-), 869 (10) (ν_s(OUO)), 740 (4) (ν_3, NO_3^-), 713 (1) (ν_5, NO_3^-), 236 (3), 162 (5). Raman spectrum of $NO^+UO_2(NO_3)_3^-$ in CH_3CN (RT, NMR tube, resolution = 4 cm^{-1}): 3004 (1), 2944 (10), 2735 (1) (CH_3CN), 2311 (1), 2293 (1), 2253 (5), 1376 (1) (CH_3CN), 1026 (1) (NO_3^-), 920 (3) (CH_3CN), 873 (1) (ν_s(OUO)), 381 (2), 272 (1) (CH_3CN). Raman spectrum of $NO^+UO_2(NO_3)_3^-$ in CH_3NO_2 (RT, NMR tube, resolution = 4 cm^{-1}): 3049 (1), 2967 (7), 2772 (1) (CH_3NO_2), 2282 (2) ($\nu(NO^+)$), 1557 (2), 1402 (4), 1378 (3), 1311 (1), 1100 (1) (CH_3NO_2), 1026 (ν_2, NO_3^-), 918 (10) (CH_3NO_2), 878 (1), 866 (2) (ν_s(OUO)), 821 (1) (CH_3NO_2), 742 (1) (ν_3, NO_3^-), 708 (1) (ν_5, NO_3^-), 656 (3), 607 (1), 481 (2) (CH_3NO_2), 237 (1). Raman spectrum of $NO^+UO_2(NO_3)_3^-$ in SO_2 (RT, NMR tube, resolution = 4 cm^{-1}): 1143 (10) (SO_2). Raman spectrum of $NO^+UO_2(NO_3)_3^-$ in N_2O_4 (RT, NMR tube, resolution = 4 cm^{-1}): 1983 (1), 1853 (1), 1711 (2), 1378 (4), 1325 (1), 1296 (1), 1062 (1), 808 (3), 668 (1), 477 (2), 262 (10), 141 (2) (N_2O_4). IR spectrum of $NO^+UO_2(NO_3)_3^-$ (RT, KBr plates, resolution = 4 cm^{-1}): 2537w ($\nu_2 + \nu_1$, NO_3^-), 2514w (NO_3^-), 2299m ($\nu(NO^+)$), 2044w ($2\nu_2$, NO_3^-), 1981w ($\nu_4 + \nu_5$, NO_3^-), 1960w (NO_3^-), 1761m ($\nu_2 + \nu_3$, NO_3^-), 1727m ($\nu_2 + \nu_5$, NO_3^-), 1630m, 1604m (NO_3^-), 1517vs, br (ν_1, NO_3^-) 1269vs, br (ν_4, NO_3^-), 1022s (ν_2, NO_3^-), 949vs (ν(OUO)), 875vw (NO_3^-), 803s (NO_3^-), 752s, 741s (ν_3, NO_3^-), 710vw (ν_5, NO_3^-), 634w, 532w. ^{14}N NMR (CH_3NO_2, RT, δ/ppm): −13 ($\nu_{1/2}$ = 43 Hz) (NO_3^-). ^{15}N NMR (CH_3NO_2, RT, δ/ppm): −11 (NO_3^-). Crystallographic data collection for **1**, UN_4O_{12}: fw = 486.05; crystal size, 0.10 × 0.05 × 0.03 mm; monoclinic ($C2/c$), a = 13.3992(4) Å, b = 9.9781(4) Å, c = 7.6455(2) Å, β = 115.452(2)°, V = 922.98(5) Å^3, Z = 4, T = 200 K, R1[$I > 2\sigma(I)$] = 0.0228, final wR2 = 0.0515.

Results and Discussion

We are currently interested in the investigation and unambiguous characterization of small and conceptually simple uranium systems, which establish the existence of new, simple classes of uranium compounds for the first time. As was discussed in the Introduction, conflicting views exist in the literature as to the precise nature of the U(VI) compound UN_4O_{12}, which has resulted in the compound being reported to be both the neutral $UO_2(NO_3)_2 \cdot N_2O_4$ and the ionic nitrosonium dioxotrinitratouranate ($NO^+UO_2(NO_3)_3^-$).

The synthesis of $NO^+UO_2(NO_3)_3^-$ was undertaken according to the procedure described in the literature for $UO_2(NO_3)_2 \cdot N_2O_4$,[13b] whereby clean uranium turnings were added to a 30:70 nitromethane/N_2O_4 solution under anhydrous conditions. The highly moisture-sensitive precipitate could be stored for years at room temperature under an inert atmosphere, however addition of a small amount of compound **1** to H_2O, resulted in a vigorous reaction and the evolution of brown NO_2 gas. The synthesis of the air-stable $K^+UO_2(NO_3)_3^-$ was repeated following the literature procedure to enable a direct comparison of the vibrational spectra with that of compound **1**, using the assignments of Bullock for $K^+UO_2(NO_3)_3^-$.[15]

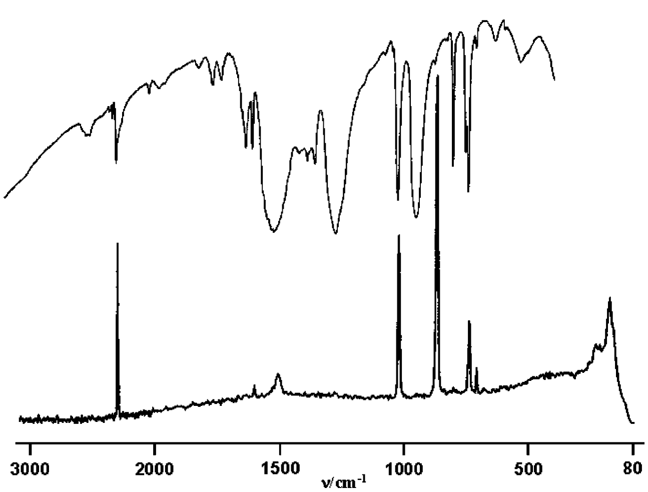

Figure 1. IR (top) and Raman (low-temperature) (bottom) spectra of $NO^+UO_2(NO_3)_3^-$.

In the low-temperature (−110 °C) and room-temperature Raman spectra of compound **1**, the presence of the uranyl group was clearly indicated by the strongest peak in the spectrum at 869 cm^{-1}, nicely in agreement with both ν_s(OUO) observed for $UO_2(NO_3)_2 \cdot 6H_2O$ (869 cm^{-1}) and $K^+UO_2(NO_3)_3^-$ (872 cm^{-1}).[15] This is indicative of the formation of the U(VI) species and excluded the formation of the neutral U(IV) compound $U(NO_3)_4$. The second strongest peak in the Raman spectrum of compound **1** at 2301 cm^{-1} corresponds to the NO^+ group (Figure 1). In contrast to the previously reported spectra, the peak observed at 2301 cm^{-1} is both sharp and strong, does not correspond to an overtone as has been previously suggested. In addition, this peak compares nicely with $\nu(NO^+)$ in other nitrosonium salts, such as $NO^+SbF_6^-$ ($\nu(NO^+)$ = 2348 cm^{-1}).[16] This characteristic peak is the first clear indication that compound **1** is an ionic nitrosonium salt and not an N_2O_4 or NO_2 adduct. The peak at 1026 cm^{-1} (Raman) indicates the presence of the NO_3^- group and is not split in the room-temperature or −110 °C spectra, in agreement with $K^+UO_2(NO_3)_3^-$ (1029 cm^{-1}) and in contrast to $UO_2(NO_3)_2 \cdot 6H_2O$, which shows two peaks (1042 and 1052 cm^{-1}). It is interesting to note that, using higher laser power (200 mW) at room temperature, quick decomposition of a solid sample of compound **1** occurred, with additional peaks at 896 and 1061 cm^{-1} being observed in the Raman spectrum. Compound **1** is soluble in CH_3CN, very soluble in CH_3NO_2, but essentially insoluble in liquid SO_2 and liquid N_2O_4. Attempts to record Raman spectra of compound **1** in liquid SO_2 or N_2O_4, showed only peaks corresponding to SO_2 or N_2O_4.[19] After compound **1** was dissolved in CH_3CN and the Raman spectrum was measured, the CH_3CN was removed under vacuum, leaving behind a pale white/green solid. Peaks corresponding to coordinated CH_3CN were observed in the Raman spectrum; however, no peak for the nitrosonium cation was identified.[21] A saturated CH_3NO_2 solution of compound **1** shows peaks characteristic of CH_3NO_2 as well as a peak at 2282 cm^{-1}, which is considerably shifted from the solid-state spectrum ($\nu(NO^+) = 2301$ cm^{-1}). A comparison of the solid-state Raman spectrum of $NO^+SbF_6^-$ ($\nu(NO^+) = 2342$ cm^{-1}) with the Raman spectrum of $NO^+SbF_6^-$ dissolved in CH_3NO_2 ($\nu(NO^+) = 2283$ cm^{-1}) shows a similar shift to that observed for compound **1**. In addition, a peak at 1026 cm^{-1} corresponding to $\nu_2(NO_3^-)$ was observed, as well as peaks at 878 and 866 cm^{-1}, which correspond to the ν_s(OUO) region. Although two peaks in the uranyl region were observed, after removal of the CH_3NO_2 solvent under vacuum, only peaks characteristic of compound **1** in the solid-state Raman spectrum were observed, and no additional peaks were present.

In the ^{14}N NMR spectrum of compound **1** dissolved in CH_3NO_2, the NO_3^- groups could easily be detected by the peak at −13 ppm, this peak was also clearly observed in the ^{15}N NMR spectrum at −11 ppm; however, in both the ^{14}N and ^{15}N NMR spectra, we were unable to detect the NO^+ moiety. In addition, the solubility of compound **1** in liquid SO_2 was not sufficiently high to obtain ^{14}N or ^{15}N NMR spectra.[22]

To deduce the structure of $NO^+UO_2(NO_3)_3^-$ in the solid state, single crystals suitable for X-ray diffraction of compound **1** were obtained by cooling a saturated CH_3NO_2 solution of compound **1** to −28 °C. From the single-crystal structure determination of the resulting yellow/green crystals, the compound could be determined to be a dioxotrinitratouranate, $UO_2(NO_3)_3^-$, with a structure similar to that of the cesium and rubidium salts $M^+UO_2(NO_3)_3^-$ ($M = Cs^+, Rb^+$)[10] (Figure 2). As would be expected, the uranyl moiety is linear, with d(U═O) bond lengths of 1.753(4) Å, which compare nicely with those observed in $Rb^+UO_2(NO_3)_3^-$ (d(U═O) = 1.746(4) Å). The central uranium atom is eight coordinate, with three bidentate nitrate groups in the equatorial plane. The nitrate groups are slightly twisted out of the equatorial plane. The d(U−ONO_2) bond lengths are within the range 2.456(4)−2.482(4) Å and are similar to those observed for $Rb^+UO_2(NO_3)_3^-$ (d(U−ONO_2) = 2.474(3) Å) but slightly shorter than those observed for $UO_2(NO_3)_2{\cdot}6H_2O$ (d(U−ONO_2) = 2.504(5) and 2.547(6) Å).[2h] It is interesting to note that Pyykkö et al. could show computationally that only a small variation of R_{ax} as a function of R_{eq} is expected for the $UO_2(NO_3)_3^-$ anion.[23] In $NO^+UO_2(NO_3)_3^-$, the O−N bond lengths range from 1.203(9) to 1.291(6) Å, in nice agreement with those of $Rb^+UO_2(NO_3)_3^-$ (d(N−O) = 1.205(6)−1.268(4) Å). The O- - -O contacts between oxygen

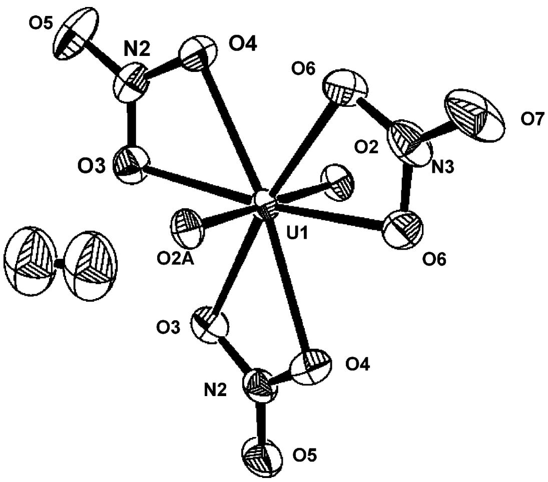

Figure 2. Molecular structure of $NO^+UO_2(NO_3)_3^-$ in the crystalline state. ORTEP representation showing thermal ellipsoids at the 50% probability level. Selected bond lengths [Å] and angles [deg]: U1−O2, 1.753(4); U1−O3, 2.482(4); U1−O4, 2.479(4); U1−O6, 2.456(4); N2−O3, 1.267(5); N2−O4, 1.291(6); N2−O5, 1.208(5); N3−O6, 1.281(5); N3−O7, 1.203(9); O2−U1−O2A, 179.8(2); U1−O3−N2, 96.5(3); O3−N2−O5, 123.0(5).

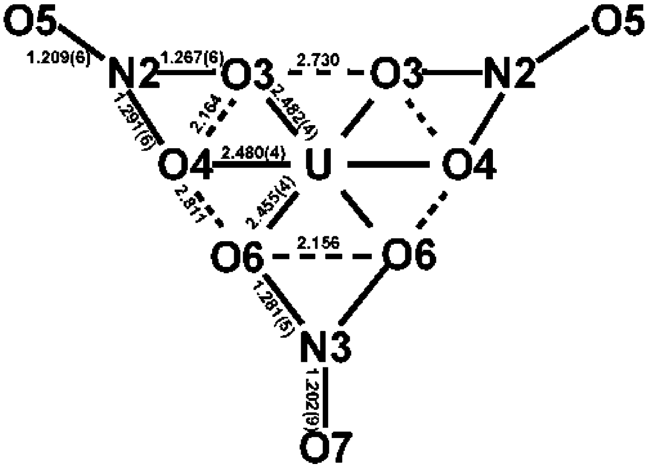

Figure 3. Structure of the $UO_2(NO_3)_3^-$ anion in compound **1**.

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(19) Raman spectra of various concentrations of N_2O_4 were recorded in nitromethane in order to ascertain if a $\nu(NO^+)$ vibration would be observed. In the Raman spectra of the dilute as well as concentrated solutions, essentially only peaks corresponding to N_2O_4 (1710 (1), 811 (3), 480 (2), 269 (5)) and CH_3NO_2 (3049 (1), 2968 (7), 2772 (1), 1558 (1), 1401 (5), 1379 (5), 1100 (1), 918 (10), 656 (3), 607 (1), 480 (2), 152 (1)) were observed. The peak observed at 2283 cm^{-1} in the Raman spectrum of compound **1** may therefore be tentatively assigned to a $\nu(NO^+)$ mode, which is unlikely to arise from the dissociation of N_2O_4 from compound **1**. The effect of various solvents on the precise nature of N_2O_4 has been shown by the isolation of various ionic forms from different solvent systems, such as $NO_2^+NO_2^-{\cdot}BF_3$[20a] and $NO^+NO_3^-$ from an IF_5 solution.[20]

(20) (a) Sprague, R. W.; Garrett, A. B.; Sisler, H. H. *J. Am. Chem. Soc.* **1960**, *82*, 1059. (b) Zhang, X.; Seppelt, K. *Z. Anorg. Allg. Chem.* **1998**, *624*, 667.

(21) The Raman spectrum of the solid obtained after dissolution of compound **1** in CH_3CN and then removal of the solid to yield a pale white/green solid showed a very similar ν_s(OUO) stretch (867 cm^{-1}) to that of solid $NO^+UO_2(NO_3)_3^-$ (ν_s(OUO) = 869 cm^{-1}). However, the peaks at 2312 and 2283 cm^{-1}, are similar to and have the same relative intensities as those of coordinated CH_3CN in $UO_2Cl_2{\cdot}2NCCH_3$ (2308 and 2281 cm^{-1}). No peak could be clearly identified for the presence of the NO^+ group. In addition, there are peaks present in the Raman spectrum that correspond to acetonitrile at 3012, 2943, and 403 cm^{-1}, similar to those observed for noncoordinated CH_3CN. This suggests that compound **1** may have been converted into an acetonitrile adduct of the type $UO_2(NO_3)_2{\cdot}xNCCH_3$.

(22) Relatively few reports exist in the literature regarding ^{14}N NMR spectra of NO^+ compounds; however, the NO^+ group is reported to be very broad and to be observed in the CH_3NO_2 region. For comparison, $NO^+SbF_6^-$ was dissolved in CH_3NO_2 to form a highly concentrated solution, and the ^{14}N NMR spectrum was recorded. However, the close proximity of the NO^+ chemical shift to that of the CH_3NO_2 solvent and the broad nature of the peak are problematic. In the ^{14}N NMR spectrum of compound **1** in CH_3NO_2, we have only been able to identify the presence of NO_3^- groups, and we were unable to prepare a sufficiently concentrated sample to observe the NO^+ moiety in ^{15}N NMR spectroscopy.

(23) Pyykkö, P.; Li, J.; Runeberg, N. *J. Phys. Chem.* **1994**, *98*, 4809.

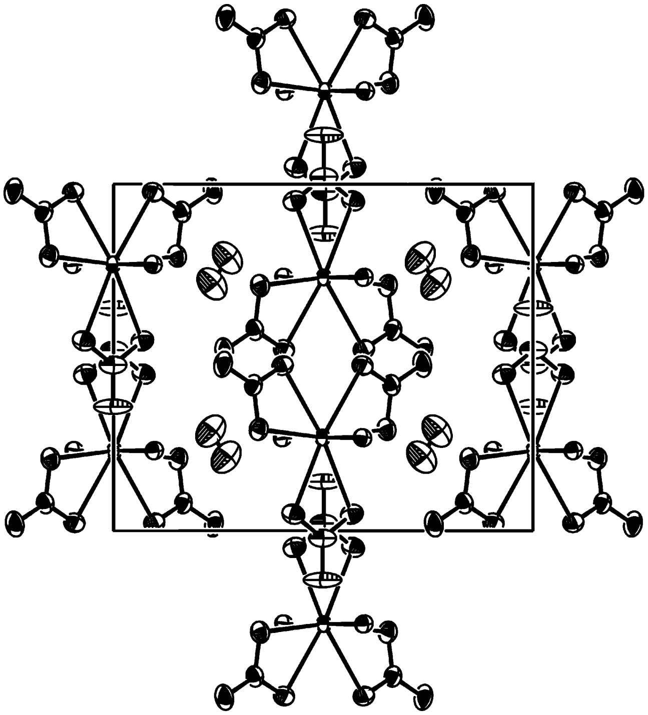

Figure 4. A view of the unit cell of compound **1** viewed along the *c* axis. Thermal ellipsoids are drawn at the 50% probability level.

atoms of the same nitrate group vary between 2.156 and 2.164 Å and between oxygen atoms of neighboring NO_3^- groups in the range 2.730−2.811 Å (Figure 3). In addition, weak contacts exist between the NO^+ cation and the $UO_2(NO_3)_3^-$ anion. Each NO^+ cation shows contacts to the oxygen atom of one uranyl group in one $UO_2(NO_3)_3^-$ anion and the oxygen atom of a nitrate group in a different $UO_2(NO_3)_3^-$ anion. In each $UO_2(NO_3)_3^-$ anion, both uranyl oxygen atoms possess contacts to two different NO^+ cations, and two nitrate groups of one $UO_2(NO_3)_3^-$ anion show contacts to two further NO^+ cations. One of the nitrate groups in the anion does not exhibit any contacts to a NO^+ group. The unit cell of compound **1** viewed along the *c* axis is shown in Figure 4. The N3−O7 bond length (*d*(N3−O7) = 1.203 Å) in the nitrate group that does not show any contacts to a NO^+ cation is essentially the same as the corresponding N2−O5 bond length of the nitrate groups that show cation−anion contacts (*d*(N2−O5) = 1.208 Å). Unfortunately, the NO^+ group was found to be disordered and the N−O bond length unreliably short (0.873 Å), and despite several recrystallizations, the disorder in the NO^+ cation remained.[24] Despite this, the ionic nature of the compound remains clear, and no evidence for the coordination of a bidentate N_2O_4 ligand was observed in the solid state.

Conclusion

The synthesis and characterization of $NO^+UO_2(NO)_3^-$ has been undertaken, and the highly air-sensitive compound obtained was characterized using IR, low-temperature, room-temperature, and solution Raman spectroscopy as well as X-ray diffraction. UN_4O_{12} is an important precursor for the synthesis of anhydrous uranyl nitrate, and the structure has finally been elucidated to be that of an ionic nitrosonium salt $NO^+UO_2(NO_3)_3^-$ and not an N_2O_4 adduct, as is predominantly and incorrectly cited in the literature.

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Supporting Information Available: X-ray crystallographic files for $NO^+UO_2(NO_3)_3^-$ (**1**) are available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[24] Disorder in NO^+ groups has been observed for $NO^+SbCl_6^-{\cdot}C_6Me_6$, $NO^+AsF_6^-{\cdot}C_6Me_6$, and $NO^+SbCl_6^-{\cdot}C_6H_5Me$. See: (a) Brownstein, S.; Gabe, E.; Lee, F.; Tang, L. *J. Chem. Soc., Chem. Commun.* **1984**, 1566. (b) Brownstein, S.; Gabe, E.; Lee, F.; Piotrowski, A. *Can. J. Chem.* **1986**, *64*, 1661. (c) Rosokha, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **2002**, *124*, 5620. (d) Rosokha, S. V.; Lindeman, S. V.; Kochi, J. K. *J. Chem. Soc., Perkins Trans. 2* **2002**, 2123.