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Article

First Actinide Complexes of the Nitrogen-Containing Ligands Dinitramide ($N(NO_2)_2^-$), 4,5-Dicyano-1,2,3-triazolate ($C_4N_5^-$), and Dicyanamide ($N(CN)_2^-$)

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The syntheses and characterization of uranyl complexes of nitrogen-containing ligands are reported. For the first time, an actinide complex containing dinitramide ligands coordinated to the actinide center in $UO_2(N(NO_2)_2)_2(OP(NMe_2)_3)_2$ (**1**) has been isolated and structurally characterized. Using an excess of $OP(NMe_2)_3$, the dinitramide ligands were replaced by $OP(NMe_2)_3$ ligands resulting in the formation of the salt $[UO_2(OP(NMe_2)_3)_4][N(NO_2)_2]_2$ (**2**). Both complexes **1** and **2** were characterized using IR, Raman, as well as ^1H, ^{13}C, ^{14}N and $^{31}P\{^1H\}$ NMR spectroscopy, in addition to C/H/N analysis. The structures of **1** and **2** were determined by single crystal X-ray diffraction. **1**: monoclinic, $P2_1/n$, a=12.5389(3), b=7.9496(2), c=15.8172(4) Å, β=110.842(3)°, V=1473.48(6) Å^3, Z=2. **2**: orthorhombic, *Pbca*, a = 14.5640(6), b = 15.3697(6), c = 45.7789(18) Å, V = 10247.3(7) Å^3, Z = 8. The related complex $[UO_2(N(CN)_2)_2(OP(NMe_2)_3)_2]$ (**3**) containing the dicyanamide ligand ($N(CN)_2^-$) coordinated to the U(VI) center was synthesized and characterized using IR, Raman, ^1H, ^{13}C and $^{31}P\{^1H\}$ NMR spectroscopy. The structure of **3** was determined using single crystal X-ray diffraction and revealed a dinuclear complex containing both terminal and bridging $N(CN)_2^-$ ligands. **3**: monoclinic, $P2_1/c$, a = 15.5873(9), b = 14.2132(6), c = 13.2006(5) Å, β = 100.029(3)°, V = 2879.8(2) Å^3, Z = 2. Finally, in this investigation of the coordination of relatively nitrogen-rich ligands to uranium centers, the synthesis, characterization, and isolation of the first U(VI) complex showing coordination of the triazolate ligand via a ring nitrogen atom is reported in $UO_2((NC)_2C_2N_3)_2(OPPh_3)_3$ (**4**). Complex **4** was characterized using IR, Raman, ^1H, ^{13}C and $^{31}P\{^1H\}$ NMR spectroscopy. The solid state structure of **4** was determined using single crystal X-ray diffraction. **4**: monoclinic, $P2_1/n$, a = 18.9970(2), b = 31.9500(3), c = 20.1133(2) Å, β = 111.4449(4)°, V = 11362.69(19) Å^3, Z = 8. To the best of our knowledge, compounds **1** and **2** are the first structurally characterized complexes where a dinitramide ligand is coordinated to an f-block center. Complex **3** is the first structurally characterized actinide dicyanamide complex and a rare example of a dinuclear uranyl complex showing a 12 membered U−N−C ring formed by bridging dicyanamide ligands between two uranyl centers. Finally, complex **4** is the first isolated and structurally characterized uranium complex containing a triazolate ligand coordinated to the U(VI) center. Complexes **3** and **4** are examples of uranyl complexes containing ligands coordinated via nitrogen atoms to the U(VI) center. Whereas the dinitramide ligand can coordinate via N or O atoms, in complex **1**, the $[N(NO_2)_2]^-$ ligand acts as a bidentate chelate ligand, and only coordination via the oxygen atoms to the U(VI) center was observed in the crystalline state.

Introduction

There are many reports in the literature describing complexes of uranyl nitrates[1] since they are important in the PUREX process.[2] These reports are not only of neutral complexes such as $UO_2(NO_3)_2L_x$ (L = e.g., H_2O, $OP(NMe_2)_3$, $OPPh_3$, dmso, etc.)[3] but also of salts containing the $[UO_2(NO_3)_3]^-$ [4] and $[UO_2(NO_3)_4]^{2-}$ anions.[5] There is a report in the literature

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of a uranyl complex containing nitrite ligands,[6] however, to the best of our knowledge, there are no reports describing the unambiguous characterization of a uranyl complex containing dinitramide ligands, despite the fact that dinitramide ($N(NO_2)_2^-$) and nitrate (NO_3^-) are both binary N−O anions.

Recently, many reports have appeared, describing dinitramide containing compounds, and ammonium dinitramide in particular.[7] This is predominantly as a result of investigations into using $[NH_4][N(NO_2)_2]$ (Ammonium DiNitramide, ADN) as a possible halogen-free replacement for $[NH_4][ClO_4]$ in rocket boosters.[8] In addition, recently many structural reports on nitrogen-rich energetic materials have appeared, which describe metal-free salts containing the dinitramide anion.[9] Although d-block metal complexes containing metal coordinated dinitramide ligands have been reported, for example, *fac*-$Re(bpy)(CO)_3N_3O_4$,[10] to the best of our knowledge, no complex has been structurally characterized whereby an f-block element is directly coordinated to a dinitramide ligand.

The structure adopted by dinitramide complexes is not easy to predict since the dinitramide anion is potentially versatile in the coordination mode it exhibits and may be able either to coordinate via the central nitrogen atom or to act as a bidentate chelate via the two oxygen atoms of one NO_2 group, or via the oxygen atom of one NO_2 group and the central nitrogen atom.[10] Therefore, the dinitramide ligand could coordinate to the uranium(VI) center behaving as a bidentate chelate ligand in a similar manner to the nitrate ligands in the $UO_2(NO_3)_2L_x$ (L = e.g., H_2O, $OP(NMe_2)_3$, $OPPh_3$, dmso, etc.) complexes previously reported in the literature.[3]

The dicyanamide anion ($N(CN)_2^-$) is related to the dinitramide anion ($N(NO_2)_2^-$) since both anions contain a central nitrogen atom with two relatively electronegative groups attached, that is, $[NX_2]^-$ (X = CN, NO_2). However, many more complexes have been reported containing the dicyanamide ligand coordinated to metal centers.[11] The solid state structure of complexes containing dicyanamide ligands is also difficult to predict since it is also versatile in the coordination modes it exhibits.[11] The coordination of the $N(NO_2)_2^-$ and $N(CN)_2^-$ ligands to the uranium(VI) center was of interest to us because we have been interested in the synthesis and characterization of uranium complexes, which show the coordination of ligands via nitrogen atoms, for example, N_3^-,[12] SCN^-,[12] $SeCN^-$[12], and so on. In addition, because uranium azides are of interest as possible precursors for new uranium nitrides,[13] but have the drawback of often involving the use of explosive reagents or formation of explosive products, we have been interested in the synthesis of uranyl complexes which contain ligands with nitrogen donor atoms and relatively high nitrogen contents, but without the hazards commonly associated with azides. Therefore, the dinitramide ($[N_3O_4]^-$) and dicyanamide ($[C_2N_3]^-$) fit these criteria well, as does the 4,5-dicyano-1,2,3-triazolate ($[C_4N_5]^-$) anion.

The 4,5-dicyano-1,2,3-triazolate anion has been known for a long time,[14] but recently it has been investigated again as a possible component of solid polymer electrolytes,[15] or as a component of possible new nitrogen-rich materials.[16] However, relatively little has been described in the literature about its chemistry. In addition, to the best of our knowledge, there is no report in the literature of a uranium complex that shows the direct coordination of the triazolate ring to the uranium center for any oxidation state of uranium. Therefore, there is a large area of uranium coordination chemistry involving the coordination of nitrogen-rich ligands to the uranium center that has hardly been investigated.

Experimental Section

General Information. $Ag[(NC)_2C_2N_3]$,[16] $Ag[N(CN)_2]$,[17] and $K[N(NO_2)_2]$[17] were prepared according to the literature methods. $UO_2Cl_2(OPPh_3)_2$ and $UO_2Cl_2(OP(NMe_2)_3)_2$ were prepared by the addition of 4 equiv of either $OPPh_3$ or $OP(NMe_2)_3$ to 1 equiv of $[UO_2Cl_2(THF)_2]_2$[18] in methanol or acetone, respectively, or by the addition of 2 equiv of $OPPh_3$ to $UO_2Cl_2 \cdot xH_2O$ ($2 < x < 3$). However, the purity of $UO_2Cl_2(OPPh_3)_2$ prepared by the latter method was not determined using C/H analysis and may well contain $OPPh_3$ impurities. Anhydrous $Ag[ClO_4]$ (Aldrich), $OP(NMe_2)_3$ (Fluka), MeOH (Biesterfeld Graen GmbH & Co.

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Table 1. Crystallographic Data for *trans*-$UO_2(N(NO_2)_2)_2(OP(NMe_2)_3)_2$ (**1**), $[UO_2(OP(NMe_2)_3)_2][N(NO_2)_2]_2$ (**2**), $[UO_2(N(CN)_2)_2(OP(NMe_2)_3)_2]_2$ (**3**), and $UO_2((NC)_2C_2N_3)_2(OPPh_3)_3$ (**4**)

	(**1**)	(**2**)	(**3**)	(**4**)
formula mass (amu)	840.464	1198.91	1521.08	1341.04
crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/n$	*Pbca*	$P2_1/c$	$P2_1/n$
a (Å)	12.5389(3)	14.5640(6)	15.5873(9)	18.9970(2)
b (Å)	7.9496(2)	15.3697(6)	14.2132(6)	31.9500(3)
c (Å)	15.8172(4)	45.7789(18)	13.2006(5)	20.1133(2)
α (deg)	90	90	90	90
β (deg)	110.842(3)	90	100.029(3)	111.4449(4)
γ (deg)	90	90	90	90
V (Å^3)	1473.48(6)	10247.3(7)	2879.8(2)	11362.69(19)
Z	2	8	2	8
T (K)	200(2)	153(2)	200(2)	200(2)
crystal size (mm)	0.12 × 0.09 × 0.04	0.22 × 0.18 × 0.13	0.15 × 0.12 × 0.11	0.10 × 0.08 × 0.02
ρ_{calcd} (g cm^{-3})	1.8944	1.554	1.7541	1.5679
μ(Mo Kα) (mm^{-1})	5.688	3.362	5.791	3.001
GOF	1.097	1.382	1.133	0.931
$R(F_{obs})$	0.0473	0.0898	0.0358	0.0425
$R_w(F^2)$	0.1179	0.1438	0.0660	0.0661

KG), acetone (Biesterfeld Graen GmbH & Co. KG), CD_2Cl_2 (Euriso-Top) and CH_3CN (Acros) were used as supplied without further purification. Anhydrous $Ag[ClO_4]$ was only opened and manipulated in the glovebox under an inert atmosphere ($O_2 <$ 1 ppm, $H_2O <$ 1 ppm). Standard procedures for handling and disposal of uranium containing compounds were employed at all times. ***Caution!*** *Uranium compounds are highly toxic and radioactive and should be handled carefully in small quantities and disposed of according to regulations. Although compounds* ***1−4*** *prepared in this work did not appear to be sensitive to friction or shock, the sensitivities of the compounds were not tested. Care should be observed when handling dinitramide or perchlorate complexes since explosive compounds may be formed.* IR spectra were recorded as solids between KBr plates on a Perkin-Elmer FT-IR Spectrum One spectrometer. Raman spectra were recorded using a Perkin-Elmer FT-IR R2000 spectrometer fitted with a Nd:YAG laser (1064 nm) or using a Bruker FT-Raman spectrometer MultiRAM (stand alone version) with a Nd:YAG laser and a high sensitivity Ge detector (cooled with liquid nitrogen). Multinuclear NMR spectra were recorded using a Jeol EX 400 FT-NMR spectrometer operating at 399.78 MHz (^1H), 100.53 MHz (^{13}C), 28.89 MHz (^{14}N), and 161.84 MHz ($^{31}P\{^1H\}$), a Jeol 400 FT-NMR spectrometer operating at 400.18 MHz (^1H), 100.63 MHz (^{13}C), 28.92 MHz (^{14}N), and 161.99 MHz ($^{31}P\{^1H\}$) or a Jeol 270 FT-NMR spectrometer operating at 270.17 MHz (^1H), 67.93 MHz (^{13}C), and 109.37 MHz ($^{31}P\{^1H\}$). Chemical shifts are given with respect to TMS (^1H, ^{13}C), $MeNO_2$ (^{14}N) or 85% aqueous H_3PO_4 ($^{31}P\{^1H\}$) as external standards. C/H/N analyses were performed by the Analytische Laboratorien Dr. H. Malissa and G. Reuter GmbH, Lindlar, Germany. The X-ray diffraction studies for **1**−**3** were carried out using an Oxford Diffraction X-Calibur S instrument and for **4** using a NoniusKappa CCD. The structures of **1**, **3**, and **4** were solved using Sir97[19] and that of **2** by direct methods using SHELXS[19] and refined by means of full-matrix least-squares procedures using SHELXL-97 (Table 1).[19] Further details of the crystal structure determinations are available on request from the Cambridge Crystallographic Data Center, on quoting the depository numbers CCDC *trans*-$UO_2(N(NO_2)_2)_2(OP(NMe_2)_3)_2$ (**1**) (CCDC 743648), $[UO_2(OP(NMe_2)_3)_2][N(NO_2)_2]_2$ (**2**) (CCDC 746821), $[UO_2(N(CN)_2)_2(OP(NMe_2)_3)_2]_2$ (**3**) (CCDC 743649), and $UO_2((NC)_2C_2N_3)_2(OPPh_3)_3$ (**4**) (CCDC 743650), the names of the authors, and the journal citation.

Synthesis of *trans*-$UO_2(N(NO_2)_2)_2(OP(NMe_2)_3)_2$ (1). A 0.699 g portion of *trans*-$UO_2Cl_2(OP(NMe_2)_3)_2$ (1.0 mmol) and a magnetic stirrer bar were placed into a 50 mL beaker. The yellow solid was then dissolved in 30 mL of methanol. To this solution, 0.414 g (1.0 mmol) of solid anhydrous $Ag[ClO_4]$ (which had been weighed out in the drybox under an N_2 atmosphere) were then added with stirring and immediately the solution turned cloudy followed by the formation of a bright yellow solution as well as a white/pale gray precipitate. After stirring at RT for 60 minutes the reaction mixture was allowed to settle, centrifuged, and the supernatant filtered off. To the filtrate, 0.435 g (3.0 mmol, excess) of solid $K[N(NO_2)_2]$ was then added, and the reaction mixture left stirring for approximately 12 h at RT in the dark. After this time, the reaction mixture was centrifuged, and the clear, yellow solution filtered off. The solvent was then removed from the filtrate under reduced pressure, and the sticky yellow mass triturated with Et_2O until a yellow/khaki solid was obtained. The bulk solid was extracted into CH_2Cl_2 and centrifuged for 30 min after which time the clear yellow solution was decanted off and the solvent removed yielding solid **1**, which was used for characterization. Crystals of **1** suitable for X-ray diffraction formed by allowing the Et_2O washings to evaporate slowly at RT. Amount of **1** obtained: 0.442 g, amount of **1** expected: 0.840 g (Yield: 52.6%).

IR [room temperature (RT), KBr plates, res. = 4 cm^{-1}]: 2998 w, 2931 m, 2907 m, 2858 m, 2817 m ($\upsilon(NCH_3)$); 1588 m, 1536 s ($\upsilon_{as}(NO_2)$ in phase); 1486 m ($\delta(NCH_3)$); 1430 s ($\upsilon_{as}(NO_2)$ out of phase); 1343 w ($\upsilon_s(NO_2)$ in phase); 1302 m ($\rho_s(NCH_3)$); 1264 w; 1225 w, 1207 m ($\upsilon_s(NO_2)$ out of phase); 1180 s, 1082 s, 1070 s; 1032 m ($\upsilon_{as}(N_3)$); 991 s ($\upsilon_s(NC_2)$); 957 m; 920 s ($\upsilon_{as}(OUO)$); 888 w; 826 m, 821 m ($\delta(NO_2)$); 754 s ($\upsilon_{as}(PN)$); 731 m ($\delta_{rock}(NO_2)$); 649 w ($\upsilon_s(PN_3)$); 473 m ($\delta(PNC)$).

Raman (res. = 4 cm^{-1}, υ/cm^{-1}): 3006(2), 3000(2), 2942(5), 2914(4), 2863(3), 2816(3) ($\upsilon(NCH_3)$); 1589(1) ($\upsilon_{as}(NO_2)$ in phase); 1486(2), 1446(3), 1419(2) ($\delta(NCH_3)$); 1331(1), 1326(1), 1309(1), 1301(1) ($\upsilon_s(NO_2)$ in phase); 1270(2); 1118(2), 1110(2), 1072(1), 1056(2); 1042(2) ($\upsilon_{as}(NC_2)$); 1038(2); 1008(1); 997(0.5) ($\upsilon_s(NC_2)$); 910(0.5); 849(10) ($\upsilon_s(OUO)$); 833(3); 760(0.5), 746(0.5) ($\delta(NO_2)$); 653(6) ($\upsilon_s(PN_3)$); 507(1) ($\delta(PNC)$); 481(0.5); 467(1) ($\delta(NO_2)$); 350(1) ($\delta_s(PN_3)$); 294(1).

^{1}H NMR (CD_2Cl_2, δ/ppm): 2.86 (d, $^3J_{PH}$ = 9.8 Hz; $OP(N(CH_3)_2)_3$). **^{13}C{^{1}H} NMR** (CD_2Cl_2, δ/ppm): 37.0 (d, $^2J_{PC}$ = 4.8 Hz; $OP(N(CH_3)_2)_3$). **^{14}N{^{1}H} NMR** (CD_2Cl_2, δ/ppm): −23 (s, $\upsilon_{1/2}$ = 38 Hz; $N(NO_2)_2$); −359 (s, br, $\upsilon_{1/2}$ = 363 Hz; $OP(NMe_2)_3$. **^{31}P{^{1}H} NMR** (CD_2Cl_2, δ/ppm): 34.2 (s, $OP(NMe_2)_3$).

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C/H/N Analysis (Calcd for *trans*-$UO_2(N(NO_2)_2)_2(OP(NMe_2)_3)_2$ (Obsd.)); C: 17.15% (18.55%), H: 4.32% (4.19%), N: 20.00% (19.67%).

Synthesis of $[UO_2(OP(NMe_2)_3)_4][N(NO_2)_2]_2$ (2). A 0.699 g portion of *trans*-$UO_2Cl_2(OP(NMe_2)_3)_2$ (1.0 mmol) and a magnetic stirrer bar were placed into a 50 mL beaker. The yellow solid was then dissolved in approximately 30 mL of methanol. To this solution, 0.414 g (2.0 mmol) of solid $Ag[ClO_4]$ (which had been weighed out in the drybox under an N_2 atmosphere) was then added with stirring, and immediately the solution turned cloudy followed by the formation of a bright yellow solution as well as a white/pale gray precipitate. After stirring at RT for 60 min, the reaction mixture was allowed to settle, centrifuged, and the supernatant filtered off. To the filtrate, 0.435 g (3.0 mmol, excess) of solid $K[N(NO_2)_2]$ was added, and the reaction mixture was left stirring at RT for approximately 12 h. The reaction mixture was then centrifuged, the clear yellow supernatant decanted off, and the solvent removed under reduced pressure. The yellow solid was extracted into the minimum amount of CH_2Cl_2. The mixture was centrifuged, the clear yellow solution was filtered off, and the solvent removed under reduced pressure. A 0.42 g portion (0.5 mmol) of the yellow solid prepared above was then redissolved in acetone, and 0.17 mL (1.0 mmol) $OP(NMe_2)_3$ was added and the reaction mixture left stirring for approximately 30 min at RT in the dark. After this time the solvent was removed under reduced pressure yielding yellow solid **2**. Amount of **2** obtained: 0.567 g. Amount expected (based on using 0.5 mmol $UO_2[N(NO_2)_2]_2(hmpt)_2)$): 0.60 g (Yield: 94.5%). Yellow crystals of **2** formed on recrystallization of crude **2** from methanol/isohexane.

IR (RT, KBr plates, res. = 4 cm^{-1}): 3004 w, 2931w, 2902 w, 2858 w, 2815 w ($\nu_s(NCH_3)$); 1508 m ($\upsilon_{as}(NO_2)$ in phase); 1486 m, 1451 m ($\delta(NCH_3)$); 1427 m ($\upsilon_{as}(NO_2)$ out of phase); 1304 m ($\rho_s(NCH_3)$); 1182 s, 1065 s; 995 s ($\upsilon_s(NC_2)$); 918 m ($\upsilon_{as}(OUO)$); 828 w ($\delta(NO_2)$); 756 m ($\upsilon_{as}(PN)$); 717 w; 648 w ($\upsilon_s(PN_3)$); 510 w; 476 m ($\delta(PNC)$).

Raman (res. = 4 cm^{-1}, υ/cm^{-1}): 3007(23), 2945(37), 2911(32), 2863(31), 2816(29) ($\upsilon(NCH_3)$); 1488(20), 1446(26), 1420(19) ($\delta(NCH_3)$); 1332(25), 1309(15) ($\upsilon_s(NO_2)$ in phase); 1187(15) ($\upsilon_s(NO_2)$ out of phase); 1141(16), 1068(22), 1058(20); 1000(17) ($\upsilon_s(NC_2)$); 949(16); 833(100) ($\upsilon_s(OUO)$); 761(19) ($\delta(NO_2)$); 652(89) ($\upsilon_s(PN_3)$); 511(23), 473(22); 351(23) ($\delta_s(PN_3)$).

^{1}H NMR (CD_2Cl_2, δ/ppm): 2.79 (d, $^3J_{PH}$ = 9.5 Hz; $OP(N(CH_3)_2)_3$). **^{13}C{^{1}H} NMR** (CD_2Cl_2, δ/ppm): 36.7 (d, $^2J_{PC}$ = 5.2 Hz; $OP(N(CH_3)_2)_3$). **^{14}N{^{1}H} NMR** (CD_2Cl_2, δ/ppm): −16 (s, $\upsilon_{1/2}$ = 40 Hz; $N(NO_2)_2$); −358 (s, br, $\upsilon_{1/2}$ = 980 Hz; $OP(NMe_2)_3$. **^{31}P{^{1}H} NMR** (CD_2Cl_2, δ/ppm): 33.8 (s, $OP(NMe_2)_3$).

C/H/N Analysis (Calcd for $[UO_2(OP(NMe_2)_3)_2][N(NO_2)_2]_2$ (Obsd.)); C: 24.04% (23.88%), H: 6.05% (6.03%), N: 21.03% (20.88%).

Synthesis of $[UO_2(N(CN)_2)_2(OP(NMe_2)_3)_2]_2$ (3). A 0.699 g portion of *trans*-$UO_2Cl_2(OP(NMe_2)_3)_2$ (1.0 mmol) and a magnetic stirrer bar were placed into a 50 mL beaker. The yellow solid was then dissolved in approximately 25 mL of acetone. To this solution, 0.40 g (2.3 mmol, excess) of solid $Ag[N(CN)_2]$ was then added with stirring and immediately the solution turned cloudy followed by the formation of a bright yellow solution as well as a pale gray precipitate. After stirring the reaction mixture at RT for 12 h it was centrifuged, the clear, yellow supernatant was filtered off, and the solvent was removed from the filtrate under reduced pressure. Crystals of **3** suitable for X-ray diffraction were obtained by redissolving a small portion of the crude solid in acetone and allowing the solvent to slowly evaporate at RT, leaving a small quantity of yellow crystals above a yellow/brown oil. Amount of crude **3** obtained: 0.487 g, amount of **3** expected: 0.745 g (Yield: 65.4%).

IR (RT, KBr plates, res. = 4 cm^{-1}): 2321 m, 2276 s, 2250 m, 2218 s, 2184 sh,s, 2155 vs ($N(CN)_2^-$); 1484 sh,m ($\delta(NCH_3)$); 1353 m; 1303 s ($\rho_s(NCH_3)$); 1269 sh,w, 1190 s, 1100 vs, 1071 s; 990 vs($\nu_s(NC_2)$); 928 vs ($\nu_s(OUO)$); 848 w; 754 s ($\nu_{as}(PN_3)$); 674 w, 660 w; 650 sh,w ($\nu_s(PN_3)$); 511 m; 477 m ($\delta(PNC)$); 419 vw.

Raman (res. = 4 cm^{-1}, υ/cm^{-1}): 3010(18), 2940(40), 2907(32), 2859(32), 2811(25) ($\nu(NCH_3)$); 2250(36), 2219(51), 2185(8), 2172(8), 2165(8), 2158(11), 2146(6) ($N(CN)_2^-$); 1487(17), 1446(22), 1417(12) ($\delta(NCH_3)$); 1349(5), 1305(6), 1153(6), 1134(12), 1120(9), 1109(9), 1101(9), 1072(8); 993(8) ($\nu_s(NC_2)$); 935(5), 918(4), 914(4); 849(100) ($\nu_s(OUO)$); 759(6), 754(6); 650(55) ($\nu_s(PN_3)$); 510(13) ($\delta(PNC)$); 480(10), 356(16), 201(32).

^{1}H NMR (CD_2Cl_2, δ/ppm): 2.89 (d, $^3J_{PH}$ = 8.8 Hz; $OP(N(CH_3)_2)_3$). **^{13}C{^{1}H} NMR** (CD_2Cl_2, δ/ppm): 36.8 (d, $^2J_{PC}$ = 3.8 Hz; $OP(N(CH_3)_2)_3$). **^{31}P{^{1}H} NMR** (CD_2Cl_2, δ/ppm): 33.7 (s, $OP(NMe_2)_3$).

C/H/N Analysis (Calcd. for $[UO_2(N(CN)_2)_2(OP(NMe_2)_3)_2]_2$ (Obsd.)); C: 25.27% (24.63%), H: 4.77% (4.74%), N: 22.10% (21.64%).

Synthesis of $UO_2((NC)_2C_2N_3)_2(OPPh_3)_3$ (4). A 0.898 g portion (1.0 mmol) of *trans*-$UO_2Cl_2(OPPh_3)_2$ (prepared from $UO_2Cl_2 \cdot xH_2O$) and a magnetic stirrer bar were placed into a 50 mL beaker. The yellow solid was then dissolved in a mixture of 30 mL of CH_3CN and 20 mL of methanol. To this solution, 0.620 g (2.74 mmol) of solid $Ag[(NC)_2C_2N_3]$ was then added with stirring and immediately the solution turned cloudy followed by the formation of a bright yellow solution as well as a white/pale gray precipitate. After stirring at RT for 12 h, the reaction mixture was allowed to settle, centrifuged, and the clear yellow supernatant filtered off. The solvent was then removed from the filtrate under reduced pressure yielding a yellow solid. The crude yellow solid was then dissolved in the minimum amount of MeOH and left to slowly evaporate whereby yellow and colorless crystals formed. A very small quantity of the yellow crystals of **4** was isolated. The crystals were suitable for X-ray diffraction and were used for spectroscopic characterization.

IR (RT, KBr plates, res. = 4 cm^{-1}): 2923 w, 2851 w ($\upsilon(CH)$); 2237 w ($\upsilon(CN)$); 1587 w, 1483 w, 1436 m ($\upsilon(CH)$); 1186 w; 1159 w (ss(CH)); 1130 s, 1119 s, 1078 m, 1068 m; 1025 w (ss(CH)); 996 w (Ph-ring); 933 m ($\upsilon_{as}(OUO)$); 747 w ($\gamma(CH)$); 723s, 691 s, 538 s.

Raman (res. = 4 cm^{-1}, υ/cm^{-1}): 3180(0.5), 3149(0.5), 3065(6), 2963(0.5) ($\upsilon(CH)$ $OPPh_3$); 2240(6) ($\upsilon(CN)$ $C_4N_5^-$); 1591(5), 1576(1) ($\upsilon(CC)$ $OPPh_3$); 1492(2) ($C_4N_5^-$); 1439(0.5) ($\upsilon(CC)$ $OPPh_3$); 1395(1), 1294(1) ($C_4N_5^-$); 1189(2), 1161(2) (ss(CH) $OPPh_3$); 1136(1), 1121(1), 1102(0.5), 1093(1), 1083(1), 1072(1); 1030(4) (ss(CH) $OPPh_3$); 1001(10) (Ph-ring, $OPPh_3$); 854(7) ($\upsilon_s(OUO)$ UO_2); 727(0.5) ($\gamma(CH)$ $OPPh_3$); 714(0.5); 688(3) ($\Phi(CC)$ $OPPh_3$), 662(1) ($C_4N_5^-$), 618(2) ($\alpha(CCC)$ $OPPh_3$); 542(0.5); 526(1), 475(0.5), 465(0.5) ($C_4N_5^-$), 417(0.5), 316(0.5), 301(0.5), 273(0.5), 259(3), 232(0.5), 215(0.5), 202(0.5), 194(1), 178(0.5), 156(0.5), 145(0.5).

^{1}H NMR (CD_2Cl_2, δ/ppm): 7.29−7.77 (m, $OPPh_3$). **^{13}C{^{1}H} NMR** (CD_2Cl_2, δ/ppm): 133.2 (d, $^4J_{PC}$ = 2.7 Hz, C-*p*, $OPPh_3$); 132.7 (d, $^2J_{PC}$ = 11.1 Hz, C-*o*, $OPPh_3$); 128.8 (d, $^3J_{PC}$ = 13.1 Hz, C-*m*, $OPPh_3$); 127.8 (s, br, C-*i*); 123.6 (s, $(NC)_2C_2N_3$), 111.6 (s, $(NC)_2C_2N_3$). **^{31}P{^{1}H} NMR** (CD_2Cl_2, δ/ppm): 46.6 (s, $OPPh_3$).

C/H/N Analysis (Calcd. for $UO_2((NC)_2C_2N_3)_2(OPPh_3)_3$ (Obsd.)); C: 55.53% (53.44%), H: 3.38% (3.42%), N: 10.44% (11.21%).

Alternative Synthesis of $UO_2((NC)_2C_2N_3)_2(OPPh_3)_3$ (4). A 0.205 g portion (0.23 mmol) of *trans*-$UO_2Cl_2(OPPh_3)_2$ (prepared from pure $[UO_2Cl_2(THF)_2]_2$) and a magnetic stirrer bar were placed into a 25 mL beaker. The yellow solid was dissolved in a mixture of 8 mL of CH_3CN and 4 mL of methanol. To this solution 0.058 g (0.21 mmol) of solid $OPPh_3$ was added under stirring. Immediately thereafter, 0.113 g (0.50 mmol, slight excess) of freshly prepared, solid $Ag[(NC)_2C_2N_3]$ was added under stirring. The reaction mixture was then stirred at RT in the dark for 2 h. The precipitated AgCl was filtered off, and the remaining yellow solution centrifuged for 5 minutes to remove remaining traces of AgCl. The clear yellow solution was then pumped to dryness, and the remaining yellow product dried in dynamic vacuum and used without further purification for characterization.

IR (RT, KBr plates, res. = 4 cm^{-1}): 3425 vbr, 3059 w (υ(CH)); 2240 m (υ(CN)); 1972 w,br, 1902 w,br, 1821 w,br, 1778 w, br, 1654 w; 1590 w, 1576 w; 1485 w, 1438 m (υ(CH)); 1394 w, 1382 w; 1336 w, 1313 w, 1284 w, 1265 w,sh, 1237 w; 1189 w; 1160 m, sh, 1131 s, 1122 s, 1079 m, 1070 m; 1026 w (ss(CH)); 998 w (Ph-ring); 939 m (υ_{as}(OUO)); 851 w; 748 w (γ(CH)); 725 s, 692 s, 662 w, 637 w, 617 w, 540 s, 462 w.

Raman (res. = 4 cm^{-1}, υ/cm^{-1}): 3182(0.5), 3150(0.5), 3063(10), 3013 (0.5), 2994 (0.5), 2951(0.5) (υ(CH) OPPh$_3$); 2243(10) (υ(CN) $C_4N_5^-$); 1591(6), 1576(2) (υ(CC) OPPh$_3$); 1511(0.5); 1492(2) ($C_4N_5^-$); 1439(0.5) (υ(CC) OPPh$_3$); 1395(0.5) ($C_4N_5^-$); 1288(0.5); 1190(2), 1162(3) (ss(CH) OPPh$_3$); 1123(0.5), 1093(0.5), 1072(0.5); 1029(4) (ss(CH) OPPh$_3$); 1001(10) (Ph-ring, OPPh$_3$); 854(3) (υ_s(OUO) UO$_2$); 688(3) (Φ(CC) OPPh$_3$), 662(0.5) ($C_4N_5^-$), 618(3) (α(CCC) OPPh$_3$); 525(0.5), 466(0.5) ($C_4N_5^-$); 411(0.5), 309(0.5), 256(3), 195(2).

^{1}H NMR (CD$_2$Cl$_2$, δ/ppm): 7.31−7.89 (m, OPPh$_3$). **^{13}C{^{1}H} NMR** (CD$_2$Cl$_2$, δ/ppm): 133.1 (s, br, C-*p*, OPPh$_3$); 132.7 (d, $^2J_{PC}$ = 10.9 Hz, C-*o*, OPPh$_3$); 128.8 (d, $^3J_{PC}$ = 13.0 Hz, C-*m*, OPPh$_3$); 127.6 (s, br, C-*i*); 123.4 (s, (NC)$_2$C$_2$N$_3$), 112.0 (s, (N*C*)$_2$*C*$_2$N$_3$). **^{31}P NMR** (CD$_2$Cl$_2$, δ/ppm): 45.4 (s, O*P*Ph$_3$).

C/H/N Analysis (Calcd. for UO$_2$((NC)$_2$C$_2$N$_3$)$_2$(OPPh$_3$)$_3$ (Obsd.)); C: 55.53% (55.75%), H: 3.38% (3.52%), N: 10.44% (9.88%).

Results and Discussion

The syntheses of new uranium(VI) complexes containing the dinitramide ($N(NO_2)_2^-$), dicyanamide ($N(CN)_2^-$), and 4,5-dicyano-1,2,3-triazolate ($(NC)_2C_2N_3^-$) ligands were investigated. Complex **1** was obtained using a simple metathesis reaction of *trans*-UO$_2$Cl$_2$(OP(NMe$_2$)$_3$)$_2$ with Ag[ClO$_4$], followed by reaction with K[N(NO$_2$)$_2$] (eq 1). This route avoided the synthesis of silver salts of the dinitramide anion. The initial reaction between *trans*-UO$_2$Cl$_2$(OP(NMe$_2$)$_3$)$_2$ and Ag[ClO$_4$] proceeded quickly with the precipitation of AgCl occurring in quantitative yield. Because of the hygroscopic nature of Ag[ClO$_4$], the anhydrous Ag[ClO$_4$] used was only handled in a glovebox and stored in the dark. The solution containing the soluble uranyl complex generated in the first stage was reacted with potassium dinitramide, resulting in the formation of K[ClO$_4$], which was identified using Raman spectroscopy,[20] and *trans*-UO$_2$(N(NO$_2$)$_2$)$_2$(OP(NMe$_2$)$_3$)$_2$ (**1**). The soluble yellow solid (**1**) was obtained in good yields and was manipulated in air at RT without noticeable decomposition occurring. However, if the same reaction was undertaken and 2 equiv of the neutral OP(NMe$_2$)$_3$ ligands were added in addition, the [N(NO$_2$)$_2$]$^-$ ligands coordinated in **1** were replaced by two additional OP(NMe$_2$)$_3$ ligands resulting in the formation of the uranyl salt [UO$_2$(OP(NMe$_2$)$_3$)$_4$][N(NO$_2$)$_2$]$_2$ (**2**) (eq 2). Compounds **1** and **2** were characterized using IR and Raman spectroscopy, and the spectra were tentatively assigned using previous literature assignments for salts of the dinitramide anion,[17] the uranyl group,[20] and for the OP(NMe$_2$)$_3$ ligand.[21] It should be stressed that within the literature, there are inconsistencies in the assignment of the vibrational spectra of uranyl complexes, and therefore, the assignments given in this work are only preliminary and require more detailed investigation.

$$\begin{aligned} &UO_2Cl_2(OP(NMe_2)_3)_2 + 2AgClO_4 + 2KN(NO_2)_2 \\ &\quad \rightarrow UO_2(N(NO_2)_2)_2(OP(NMe_2)_3)_2 \\ &\qquad + 2AgCl + 2KClO_4 \end{aligned} \tag{1}$$

$$\begin{aligned} &UO_2Cl_2(OP(NMe_2)_3)_2 + 2AgClO_4 + 2KN(NO_2)_2 \\ &\quad + 2OP(NMe_2)_3 \rightarrow [UO_2(OP(NMe_2)_3)_4][N(NO_2)_2]_2 \\ &\qquad + 2AgCl + 2KClO_4 \end{aligned} \tag{2}$$

In addition to many of the bands present in the IR spectrum of the starting compound *trans*-UO$_2$Cl$_2$(OP(NMe$_2$)$_3$)$_2$, new bands are present in the IR spectrum of product **1**, which have been tentatively assigned to the dinitramide ligand.[17] The υ_{as}(OUO) stretch at 920 cm^{-1} in **1** shows little change in comparison with that observed in the IR spectrum of *trans*-UO$_2$Cl$_2$(OP(NMe$_2$)$_3$)$_2$ (918 cm^{-1}) and compound **2** (918 cm^{-1}). The corresponding υ_s(OUO) stretch in the Raman spectrum of **1** (849 cm^{-1}) is shifted from 832 cm^{-1} in UO$_2$Cl$_2$(OP(NMe$_2$)$_3$)$_2$ and 833 cm^{-1} in **2**. A small peak is observed in the Raman spectrum of **1** at 833 cm^{-1} which may indicate the presence of small quantities of impurities of **2**. This would also be a possible explanation for the deviations in the C/H/N analysis of **1** from the calculated values. The C/H/N analysis of **2** suggests that **2** is of higher purity than **1**, and there is no peak in the Raman spectrum of **2** at 849 cm^{-1} corresponding to impurities of **1** being present. The coordinated dinitramide ligands in **1** can be replaced forming **2** by simply adding two further equivalents of OP(NMe$_2$)$_3$ to the reaction mixture. In solution, the multinuclear (^{1}H, ^{13}C, ^{14}N and ^{31}P) NMR spectra of **1** and **2** are very similar. In both compounds **1** and **2**, the ^{1}H NMR spectra show the presence of a doublet at 2.86 ppm (**1**) and 2.79 ppm (**2**), and the ^{13}C{^{1}H} NMR spectra also show doublets at 37.0 ppm (**1**) and 36.7 ppm (**2**), which indicates the presence of the OP(NMe$_2$)$_3$ ligands in both compounds. The ^{31}P{^{1}H} NMR spectra of **1** and **2** also both show the presence of signals at 34.2 ppm (**1**) and 33.8 ppm (**2**), which corresponds to the OP(NMe$_2$)$_3$ ligand. The presence of the OP(NMe$_2$)$_3$ ligand in **1** and **2** is also supported by the ^{14}N{^{1}H} NMR spectra, which show broad signals at −360 ppm (**1**) and −358 ppm (**2**). However, the dinitramide ligand could not be clearly identified in the ^{14}N{^{1}H} NMR spectra of **1** and **2** since only one signal was observed in each of the spectra, which corresponds to the nitro groups of $N(NO_2)_2^-$ at −23 ppm (**1**) and −16 ppm (**2**). The previously reported ^{14}N{^{1}H} NMR spectrum of Ag[N(NO$_2$)$_2$] in EtOH[22] showed the presence of two signals, one of which at −73 ppm corresponds to the central nitrogen atom ($\mathit{N}(NO_2)_2^-$) of the dinitramide anion, and the other at −17 ppm, which could be assigned to the nitrogen atoms of the NO$_2$ groups ($N(\mathit{N}O_2)_2^-$). However, the signal at −73 ppm was very broad ($\upsilon_{1/2}$ = 1015 Hz) and therefore difficult to observe, which fits with our observations.

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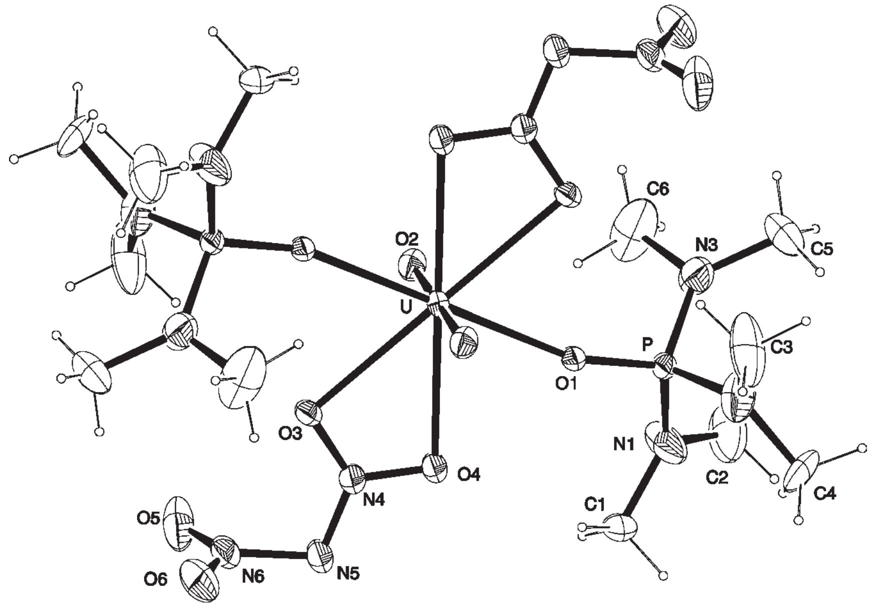

Figure 1. Molecular structure of the centrosymmetric *trans*-$UO_2(N(NO_2)_2)_2(OP(NMe_2)_3)_2$ (**1**) in the crystalline state. ORTEP representation showing thermal ellipsoids at the 50% probability level. The symmetry code for all non-labeled, non-hydrogen atoms is $i = 2-x, -y, -z$ .Selected bond lengths [Å] and angles [deg]: U1−O1 2.332(6), U1−O2 1.750(6), U1−O3 2.551(7), U1−O4 2.574(8), O3−N4 1.260(11), O4−N4 1.254(12), N4−N5 1.290(14), N5−N6 1.438(16), N6−O5 1.235(16), N6−O6 1.186(17), O1−P1 1.484(7), O3−U−O4 49.4(2), U−O3−N4 97.5(6), U−O4−N4 96.5(6), O3−N4−N5 125.4(9), O4−N4−N5 117.9(9), N4−N5−N6 107.3(10), N5−N6−O5 116.8(11), N5−N6−O6 117.2(12), O4−U−O1 65.2(2).

Therefore, the determination of the solid state structures of **1** and **2** was important to identify the presence and the coordination mode of the $N(NO_2)_2^-$ ligands. As would be expected, the solid state structures of **1** and **2** are very different. Whereas two dinitramide ligands are coordinated to the U(VI) center in **1** (Figure 1), in **2** they have been replaced by two further $OP(NMe_2)_3$ ligands. Because the $OP(NMe_2)_3$ ligands are neutral, this results in the formation of a $[UO_2(OP(NMe_2)_3)_4]^{2+}$ dication in **2** with two $N(NO_2)_2^-$ anions (Figure 2). The formation of salts of such $[UO_2L_4]^{2+}$ dications (L = neutral Lewis base coordinating ligand) has been reported in the past with the various anions. Some examples are $[UO_2(OPPh_3)_4][I_3]_2$[23a] and $[UO_2(OSMe_2)_5][CF_3SO_3]_2$.[23b] In the solid state structure of the centrosymmetric **1**, a *trans* arrangement is observed for the $OP(NMe_2)_3$ and $N(NO_2)_2^-$ ligands (Figure 1), similar to the structures observed for *trans*-$UO_2(N_3)_2(OP(NMe_2)_3)_2$[12] and the *trans*-$UO_2Cl_2(OP(NMe_2)_3)_2$ starting material.[24] The two $N(NO_2)_2^-$ ligands are both bidentate coordinated to the uranium(VI) center, each through the two oxygen atoms of one NO_2 group. The NO_2 groups at the other ends of the dinitramide ligands remain non-coordinated. The coordinating atoms of the $N(NO_2)_2^-$ and $OP(NMe_2)_3$ ligands are all found in the equatorial plane perpendicular to the linear uranyl axis, which results in a coordination number of eight for the central U(VI) atom in **1** (Figure 1). A coordination number of eight is relatively high for a neutral uranyl complex, but has also been observed for related uranyl-nitrate complexes such as $UO_2(NO_3)_2(OPPh_3)_2$ and $UO_2(NO_3)_2(OP(NMe_2)_3)_2$.[25] It is worthwhile to mention, however, that in the recently determined structure of the related perchlorate complex $UO_2(ClO_4)_2(H_2O)_3$, a coordination number of seven was observed for the central U(VI) atom, since the perchlorate ligands were only monodentate coordinated to the U(VI) center.[26] In **2**, the lower coordination number of six is observed for the U(VI) center as a result of the coordination of only four $OP(NMe_2)_3$ ligands in the plane perpendicular to the uranyl axis. Compound **2** shows a solid state structure in which the $OP(NMe_2)_3$ ligands are located opposite one another and show deviation from a linear coordination of the $OP(NMe_2)_3$ groups to the U(VI) center with U−O−P angles of 153.8(7), 154.5(8), 156.6(7), and 158.5(8)° (Figure 2), which is in good agreement with the values reported previously for the solid state structure of $[UO_2(OPPh_3)_4][I_3]_2$ ($\angle$(U−O−P) = 159.2(4), 146.9(4)°).[23a]

The uranyl bond lengths are short in both **1** (1.750(6) Å) and **2** (1.775(11), 1.751(11) Å) as would be expected, but do not differ significantly from each other and from the values reported in the literature for the related complexes *trans*-$UO_2(NO_3)_2(OP(NMe_2)_3)_2$ (1.77(1) Å)[25] or $[UO_2(OPPh_3)_4][I_3]_2$ 1.753(5) Å).[23a] The U−$OP(NMe_2)_3$ distances in **1** and **2** are similar, however, they are slightly shorter in **2** (*d*(U−$OP(NMe_2)_3$ = 2.283(12), 2.250(11), 2.301(11), 2.287(11) Å) than in **1** (*d*(U−$OP(NMe_2)_3$ = 2.332(5) Å), but show no significant deviation from the literature values for *trans*-$UO_2(NO_3)_2(OP(NMe_2)_3)_2$ (2.27(2) Å).[25] The most interesting aspects of the solid state structures of **1** and **2** are the structural parameters of the dinitramide ligands. In **1**, the two $[N(NO_2)_2]^-$ ligands are coordinated via the two oxygen atoms of one nitro group to the uranium center resulting in a bidentate coordination mode for the $N(NO_2)_2^-$ ligand. The U−O_2NNNO_2 bond lengths (2.551(6) Å, 2.574(6) Å) in **1** are similar to those observed in *trans*-$UO_2(NO_3)_2(OP(NMe_2)_3)_2$ (2.53(2), 2.56(2) Å)[25] and *trans*-$UO_2(NO_3)_2(OPPh_3)_2$

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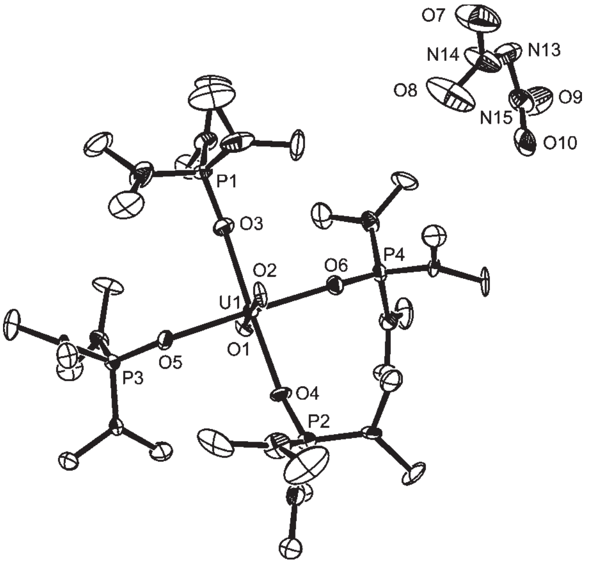

Figure 2. Molecular structure of the $[UO_2(OP(NMe_2)_3)_4]^{2+}$ cation and one $[N(NO_2)_2]^-$ anion of (**2**) in the crystalline state. ORTEP representation showing thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: U1−O1 1.775(11), U1−O2 1.751(11), U1−O3 2.283(12), U1−O4 2.250(11), U1−O5 2.301(11), U1−O6 2.287(11), O3−P1 1.511(13), O4−P2 1.544(12), O5−P3 1.513(12), O6−P4 1.501(12), O7−N14 1.14(3), O8−N14 1.19(3), O10−N15 1.22(2), O9−N15 1.22(2), N14−N13 1.35(3), N13−N15 1.36(3), O2−U1−O1 177.6(5), O2−U1−O4 90.2(5), O1−U1−O4 89.9(5), O2−U1−O3 89.1(5), O1−U1−O3 90.6(5), O4−U1−O3 177.9(4), O2−U1−O6 90.4(4), O1−U1−O6 87.2(5), O4−U1−O6 89.3(4), O3−U1−O6 88.7(4), O2−U1−O5 91.4(4), O1−U1−O5 91.1(5), O4−U1−O5 89.5(4), O3−U1−O5 92.5(4), O6−U1−O5 177.9(4), N14−N13−N15 110(2), O7−N14−O8 121(3), O7−N14−N13 109(3), O8−N14−N13 122(3), O10−N15−O9 117(3), O10−N15−N13 126(2), O9−N15−N13 116(3), P1−O3−U1 158.5(8), P2−O4−U1 154.5(8), P3−O5−U1 153.8(7), P4−O6−U1 156.6(7).

(2.536(11), 2.524(7) Å)[25] and longer than the U−$OP(NMe_2)_3$ bond lengths between the neutral $OP(NMe_2)_3$ ligands and the uranyl center observed in **1** (2.332(5) Å). Within the coordinated $N(NO_2)_2^-$ ligand, the non-coordinated NO_2 group is twisted out of the plane with respect to the coordinated NO_2 group so that the four oxygen atoms of the two NO_2 groups of one dinitramide ligand are almost perpendicular to each other. In addition, since **1** is centrosymmetric, the $N(NO_2)_2^-$ ligands are arranged so that the two non-coordinated nitro groups are oriented *trans* with respect to each other. The N−O bond lengths within the NO_2 groups of the coordinated (1.260(9), 1.255(9) Å) and non-coordinated (1.235(14), 1.186(14) Å) ends of the dinitramide ligand show significant differences, as do the N−NO_2 bond lengths between the central nitrogen atom of the dinitramide ligand and the coordinated (1.290(11) Å) and the non-coordinated (1.437(12) Å) nitro groups. In **2**, the N−O bond lengths within the dinitramide anions vary from 1.14(3)−1.24(3) Å (Figure 2). If the structure of the dinitramide ligands in **1** is compared with that observed in the solid state for *fac*-Re(bipy)-$(CO)_3N_3O_4$,[10] then it is clear that in different coordination modes of the dinitramide ligand are present. In *fac*-Re-$(CO)_3N_3O_4$ coordination of the dinitramide ligand is via the central nitrogen atom,[10] whereas in **1** it is through two oxygen atoms of one of the NO_2 groups. However, in both **1** (1.290(14), 1.438(16) Å) and *fac*-Re(bipy)$(CO)_3N_3O_4$ (1.355(17), 1.431(19)Å),[10] a considerable lengthening of one of the N−N bonds within the dinitramide ligand is observed in comparison with the values for $NH_4^+N(NO_2)_2^-$ (1.376(1), 1.359(1) Å) previously reported in the literature[17c] and compound **2** (1.35(3), 1.36(3) Å).

Despite the fact that both the $N(NO_2)_2^-$ and $N(CN)_2^-$ ligands can be reduced to the general formula $[NX_2]^-$ (X = NO_2, CN), the structures adopted by compounds **1** and **3** are considerably different. Whereas **1** is a mononuclear uranyl complex, **3** is a dinuclear uranyl complex. Despite the fact that the compounds are significantly different, both **1** and **3** were prepared in similar reactions (eqs 1, 3). Because some silver dinitramide salts have been reported to be sensitive to shock and friction and may explode,[22] the preparation of **1** was undertaken using the slightly longer $Ag[ClO_4]/K[N(NO_2)_2]$ route, whereas $Ag[N(CN)_2]$ is not explosive, and therefore **3** was prepared from *trans*-$UO_2Cl_2(OP(NMe_2)_3)_2$ by reaction with $Ag[N(CN)_2]$ in acetone at RT (eq 3).

$$2UO_2Cl_2(OP(NMe_2)_3)_2 + 4Ag[N(CN)_2] \rightarrow [UO_2[N(CN)_2]_2(OP(NMe_2)_3)_2]_2 + 4AgCl \qquad (3)$$

The yellow soluble solid that was obtained after removal of the solvent was redissolved in CD_2Cl_2 for multinuclear NMR spectroscopy. The presence of the $OP(NMe_2)_3$ ligand was indicated by the presence of a doublet in the ^1H NMR spectrum at 2.89 ppm, a doublet in the $^{13}C\{^1H\}$ NMR spectrum at 36.8 ppm, and a signal in the $^{31}P\{^1H\}$ NMR spectrum at 33.7 ppm, which is shifted in comparison with the signal observed for the non-coordinated $OP(NMe_2)_3$ ligand in CD_2Cl_2 (25.4 ppm), but is similar to the values observed for **1** (δ = 34.2 ppm) and **2** (δ = 33.8 ppm).

The IR and Raman spectra of **3** were tentatively assigned based on previous assignments made in the literature for the $OP(NMe_2)_3$[21] and $N(CN)_2^-$[27] ligands as well as the uranyl group.[20] The vibrational spectra showed the presence of the $N(CN)_2^-$ ligand which exhibits characteristic strong bands between 2155−2321 cm^{-1} in the IR spectrum and between 2152−2250 cm^{-1} in the Raman spectrum. The υ_{as} and υ_s uranyl stretches were observed at 928 cm^{-1} (IR) and 845 cm^{-1} (Raman), respectively, which are very similar to those observed for **1** (920 cm^{-1} and 849 cm^{-1}) and **2** (918 cm^{-1} and 833 cm^{-1}), despite the fact that **1** is a neutral mononuclear complex, **2** is a salt containing the $[UO_2(OP(NMe_2)_3)_4]^{2+}$ cation, and **3** is a dinuclear uranyl species.

The differences and similarities in the structures of **1**−**3** were elucidated using X-ray diffraction and showed for **3** an unexpected dinuclear uranyl structure (Figure 3). Compound **3** contains two uranyl groups and is centrosymmetric. Each uranium(VI) center shows a pentagonal bipyramidal arrangement of seven ligands, whereby five ligands are located approximately in the equatorial plane perpendicular to the linear uranyl axis. The uranyl bond lengths in **3** (1.765(3), 1.761(3) Å) show no significant differences to those observed in **1** (1.750(6) Å). The equatorial plane consists of two $OP(NMe_2)_3$ ligands and each uranyl group contributes two $N(CN)_2^-$ ligands, but only one of the $N(CN)_2^-$ ligands per uranyl moiety bridges to the second uranyl center, resulting in the presence of five ligands in the equatorial plane. Therefore, each uranyl group is coordinated to only one terminal, non-bridging dicyanamide ligand and to two bridging dicyanamide ligands. The dicyanamide ligands are only coordinated to the uranium centers via the nitrogen atoms of the CN groups and not through the central nitrogen atoms. In the case of the bridging dicyanamide ligands, both CN nitrogen

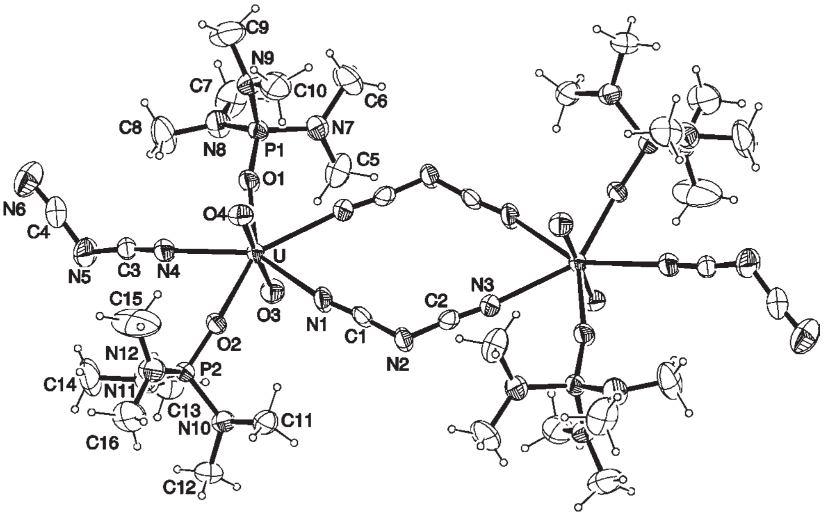

Figure 3. Molecular structure of the centrosymmetric $[UO_2(N(CN)_2)_2(OP(NMe_2)_3)_2]_2$ (**3**) in the crystalline state. ORTEP representation showing thermal ellipsoids at the 50% probability level. The symmetry code for all non-labeled, non-hydrogen atoms is $i = 1-x, 1-y, 2-z$. Selected bond lengths [Å] and angles [deg]:U1−O1 2.323(3), U1−O2 2.321(3), U1−O3 1.765(3), U1−O4 1.761(3), U−N1 2.527(5), U−N3′ 2.533(4), U−N4 2.480(5), N1−C1 1.143(6), C1−N2 1.301(7), N2−C2 1.314(7), C2−N3 1.146(6), C3−N4 1.155(7), N5−C3 1.282(7), C4−N5 1.320(8), N6−C4 1.152(8), O1−P1 1.497(3), O2−P2 1.495(3), O3−U−O4 178.35(14), U−N4−C3 165.6(4), U−O1−P1 163.77(19), U−O2−P2 156.90(19), U−N1−C1 161.3(3), U−N3′−C2’ 169.9(4), U−N4−C3 165.6(4), N4−C3−N5 172.9(5), C3−N5−C4 121.8(5), N5−C4−N6 174.7(6), N1−C1−N2 174.7(5), C1−N2−C2 119.2(4), N2−C2−N3 174.7(5), O1−U−N4 74.44(12), N4−U−O2 74.32(12), O2−U−N172.43(12), N1−U−N3′ 67.55(12), N3′−U−O1 71.26(11).

atoms are coordinated to different uranium centers resulting in the formation of 12 membered U−N−C rings. The U−N−C rings show a non-linear U−N−C coordination (∠(U−N1−C1) = 161.2(4)°; ∠(U′−N3−C2) = 170.0(4)°) and almost linear N−C−N group (∠(N1−C1−N2) = 174.7(5)°; ∠(N2−C2−N3) = 174.7(5)°); however, the angle at the central nitrogen atom of the bridging dicyanamide is bent (∠(C1−N2−C2) = 119.2(4)°) resulting in a distorted parallelogram shape for the 12 membered ring. The terminal dicyanamide ligands also show a slightly non-linear coordination of the CN group to the uranyl center (∠(C3−N4−U) = 165.6(4)°), an essentially linear N−C−N angle of the coordinated (∠(N5−C3−N4) = 173.0(5)°) and non-coordinated (∠(N5−C4−N6) = 174.7(6)°) CN groups and a bent C−N−C angle surrounding the central nitrogen atom of the dicyanamide ligand (∠(C3−N5−C4) = 121.8(5)°). The U−N bond lengths for the coordination of the bridging dicyanamide ligands are similar and slightly longer (*d*(U−N1) = 2.528(4), *d* (U−N3′) = 2.532(4) Å) than those observed between the U(VI) center and the terminal dicyanamide ligands (*d* (U−N4) = 2.480(5) Å). Within the dicyanamide ligands, there are only small differences in both the bond lengths observed for the bridging and terminal dicyanamide ligands and between the coordinated and non-coordinated cyano groups of the terminal dicyanamide ligands. However, there is a considerable difference in the dicyanamide C−N bond lengths, whereby the N_{end}−C bond lengths are much shorter than the C−N_{center} bond lengths. If the bond lengths and angles observed in **3** are compared with the previously reported literature values for the dicyanamide containing salts $[Me_4N][N(CN)_2]$[27] and α-$[C(NH_2)_3][N(CN)_2]$,[27] similar structural parameters for the dicyanamide group are observed, even although the dicyanamide ligand is coordinated to the U(VI) center in **3**. The dimeric structure observed in **3** can be compared with other previously reported compounds in the literature, for example, $Ag[N(CN)_2](PPh_3)_2$[11] which shows bridging dicyanamide ligands forming twelve membered Ag−N−C rings and $[Cu(bipy)N(CN)_2]_n$ (bipy = 2,2′-bipyridine) [11] which shows the presence of bridging and terminal dicyanamide ligands.

Although both the dicyanamide and 4,5-dicyano-1,2,3-triazolate anions contain two CN groups, only the CN groups in the dicyanamide ligands in **3** were observed to take part in coordination to the uranium center, whereas in **4**, the 4,5-dicyano-1,2,3-triazolate ligands were coordinated to the uranyl center only through the central ring nitrogen atom, and no bridged uranyl complexes were observed. In the solid state structure of **4**, two crystallographically independent $UO_2((NC)_2C_2N_3)_2(OPPh_3)_3$ molecules were observed in the asymmetric unit. Since both show similar structures, only one will be discussed in more detail here. The solid state structure of **4** is again different from those of **1**−**3** which show coordination numbers of eight, six, and seven for the central U(VI) atoms, respectively. Although **3** and **4** both show the same U(VI) coordination number (seven), complex **4** is a mononuclear complex and shows no bridging ligands (Figure 4). The ligands coordinated to the central U(VI) atom in **4** comprise two uranyl oxygen atoms, three neutral triphenylphosphineoxide ($OPPh_3$) ligands, and two 4,5-dicyano-1,2,3-triazolate ($C_4N_5^-$) ligands. The $OPPh_3$ and $C_4N_5^-$ ligands are arranged so that the $C_4N_5^-$ ligands are separated by $OPPh_3$ ligands. Therefore, the distorted equatorial plane of the U(VI) atom consists of three oxygen atoms of the three $OPPh_3$ ligands and two nitrogen atoms of two $C_4N_5^-$ ligands. The $C_4N_5^-$ ligands are coordinated by relatively long U−N bond lengths (2.553(4), 2.563(4), 2.536(4), 2.517(4) Å) and are twisted out of the equatorial plane so that the essentially planar $C_4N_5^-$ ring is only slightly twisted with respect to the uranyl axis. The U−$OPPh_3$ bond lengths in **4** (*d*(U−$OPPh_3$) = 2.402(3), 2.361(3),

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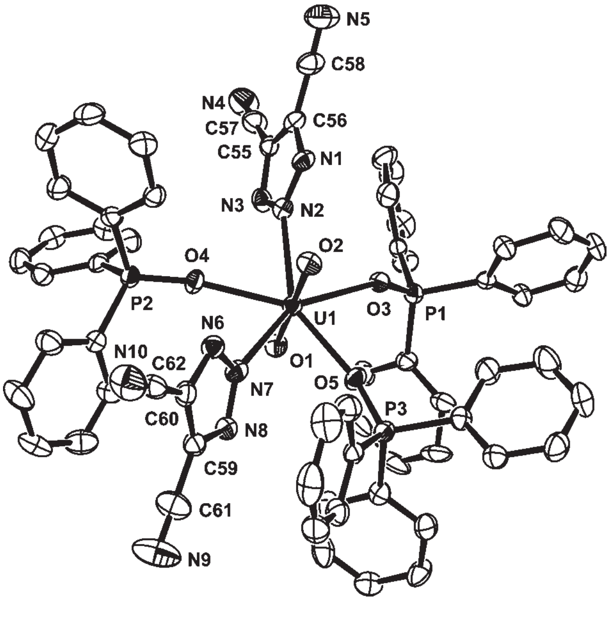

Figure 4. Molecular structure of one of the two crystallographically independent $UO_2((NC)_2C_2N_3)_2(OPPh_3)_3$ molecules found in the asymmetric unit of **4** in the crystalline state. ORTEP representation showing thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: U1−O1 1.760(3), U1−O2 1.763(3), U1−O3 2.402(3), U1−O4 2.361(3), U1−O5 2.360(3), U1−N2 2.563(4), U1−N7 2.553(4), N1−N2 1.352(5), N2−N3 1.340(5), N3−C55 1.353(5), N1−C56 1.330(5), C55−C56 1.389(6), C55−C57 1.421(7), C56−C58 1.438(7), C57−N4 1.147(6), C58−N5 1.139(6), N6−N7 1.352(4), N7−N8 1.331(5), N8−C59 1.353(5), N6−C60 1.342(5), C59−C60 1.368(6), C59−C61 1.446(7), C60−C62 1.454(7), C61−N9 1.131(6), C62−N10 1.142(6), P1−O3 1.511(3), P2−O4 1.515(3), P3−O5 1.512(3), O1−U1−O2 179.80(15), U1−O3−P1 144.20(17), U1−O4−P2 166.64(18), U1−O5−P3 166.12(17), U1−N2−N1 121.8(3), U1−N2−N3 125.7(3), U1−N7−N6 117.9(3), U1−N7−N8 128.8(3), N7−U1−O4 70.29(10), O4−U1−N2 72.20(10), N2−U1−O3 71.38(10), O3−U1−O5 76.92(9), O5−U1−N7 71.46(10).

2.360(3) Å) are slightly longer in comparison with the U−OP(NMe$_2$)$_3$ bond lengths in **3** (d(U−OP(NMe$_2$)$_3$) = 2.323(3), 2.321(3) Å) which is the only other complex reported in this work showing the same coordination number for the central U(VI) atom. The bond lengths within the $C_4N_5^-$ ligand in **4** are very similar to those observed for $Na[(NC)_2C_2N_3]\cdot H_2O$,[16] despite the fact that the triazolate ring is coordinated to the central U(VI) atom via one of the ring nitrogen atoms in **4**. It is difficult to compare the coordination mode observed for the $C_4N_5^-$ ligand in **4** with that of other metal-4,5-dicyano-1,2,3-triazolate containing complexes, since, to the best of our knowledge, there is no other structurally characterized complex of this type in the literature. It is worthwhile to mention that a range of complexes have been reported by Berthet, Nierlich, and Ephritikhine whereby neutral N-donor ligands have been coordinated to uranyl center.[29] The presence of three $OPPh_3$ ligands in **4** was initially unexpected, since $UO_2Cl_2(OPPh_3)_2$ was used as the starting material. However, the starting material used had been prepared from $UO_2Cl_2\cdot xH_2O$ ($2 < x < 3$) and 2 equiv of $OPPh_3$ and had not been recrystallized, and therefore may have contained small quantities of excess $OPPh_3$, because of the imprecise stoichiometry of the uranylchloride hydrate used. However, there may be another cause for the presence of three $OPPh_3$ ligands in **4** instead of the expected two. The reaction between $UO_2Cl_2(OPPh_3)_2$ and $Ag[(NC)_2C_2N_3]$ was repeated (using $UO_2Cl_2(OPPh_3)_2$ prepared from $[UO_2Cl_2(THF)_2]_2$ as the starting material) in the presence of 1 equiv of $OPPh_3$ and the yellow solid obtained investigated using IR, Raman, and multinuclear NMR spectra, as well as C/H/N analysis. The spectra obtained were the same as those obtained for **4** prepared in the initial method.

The multinuclear ^1H, ^{13}C, and ^{31}P NMR spectra of **4** show the presence of the $OPPh_3$ ligands. The presence of the $OPPh_3$ ligands is also shown by the vibrational (IR, Raman) spectra. The $(NC)_2C_2N_3^-$ ligand was identified in the $^{13}C\{^1H\}$ NMR spectrum by weak signals at 111.6 and 123.6 ppm. In addition, the IR and Raman spectra of **4** both show strong vibrations corresponding to υ(CN) of the cyano groups at 2237 and 2240 cm^{-1}, respectively. For the IR and Raman spectra of **4**, preliminary tentative assignments are given in the Experimental Section based on the previous literature assignments for $OPPh_3$.[28] In addition, the characteristic pattern of peaks observed in the Raman spectra of various salts of the 4,5-dicyano-1,2,3-triazolate anion[16] was observed in the Raman spectrum of **4** at 1492, 1395, 1294, 662, 526, and 465 cm^{-1}.

Conclusions

The syntheses and characterization of four new uranyl complexes were reported: *trans*-$UO_2(N(NO_2)_2)_2(OP(NMe_2)_3)_2$ (**1**), $[UO_2(OP(NMe_2)_3)_4][N(NO_2)_2]_2$ (**2**), $[UO_2(N(CN)_2)_2(OP(NMe_2)_3)_2]_2$ (**3**), and $UO_2((NC)_2C_2N_3)_2(OPPh_3)_3$ (**4**). Complexes **1**−**4** contain the dinitramide ($N(NO_2)_2^-$), dicyanamide ($N(CN)_2^-$), or 4,5-dicyano-1,2,3-triazolate ($(NC)_2C_2N_3^-$) ligands and were spectroscopically characterized in the solid state as well as structurally characterized in the solid state using single crystal X-ray diffraction. Complex **1** is the first structurally characterized actinide dinitramide and shows a coordination number of eight with bidentate coordination of two dinitramide ligands via the two oxygen atoms of one nitro group. The related complex **3**, shows the coordination of two dicyanamide ligands per uranyl center, resulting in an unusual dinuclear uranyl complex containing 12 membered U−N−C rings as a result of the presence of both terminal and bridging $N(CN)_2^-$ ligands. Finally, using the 4,5-dicyano-1,2,3-triazolate ligand in combination with $OPPh_3$ ligands, complex **4** was obtained which shows the direct coordination of a triazolate ring to the U(VI) center for the first time. The complexes described in this paper are examples of new uranyl complexes with relatively nitrogen-rich ligands. Because of the significant amounts of nitrogen present in the ligands used, complexes containing ligands of this type may be interesting precursors for new uranium nitrides. The synthesis of many more complexes of this type containing the three ligands used in this work or other related triazolate ligands should now be possible.

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Supporting Information Available: X-ray crystallographic files for *trans*-$UO_2(N(NO_2)_2)_2(OP(NMe_2)_3)_2$ (**1**), $[UO_2(OP(NMe_2)_3)_4][N(NO_2)_2]_2$ (**2**), $[UO_2(N(CN)_2)_2(OP(NMe_2)_3)_2]_2$ (**3**), and $UO_2((NC)_2C_2N_3)_2(OPPh_3)_3$ (**4**) are available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.