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Spectroscopic Evidence for the Direct Coordination of the Pertechnetate Anion to the Uranyl Cation in $[UO_2(TcO_4)(DPPMO_2)_2]^+$

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We report the synthesis and structural characterization of $[UO_2(ReO_4)(DPPMO_2)_2][ReO_4]$ and $[UO_2(Cl)(DPPMO_2)_2][Cl]$ (where $DPPMO_2$ = bis(diphenylphosphino)methane dioxide). In both complexes, the linear uranyl dication is coordinated to two bidentate $DPPMO_2$ ligands in the equatorial plane with one coordinated and one non-coordinated anion (either perrhenate or chloride). We have also prepared the pertechnetate analogue, and, through ^{31}P and ^{99}Tc NMR, we have shown that the cation, $[UO_2(TcO_4)(DPPMO_2)_2]^+$, is stable in solution.

In the PUREX process (plutonium and uranium recovery by extraction) irradiated nuclear fuel is dissolved in nitric acid, and U and Pu are co-extracted into an organic diluent as the tri-*n*-butyl phosphate (TBP) complexes $[UO_2(NO_3)_2(TBP)_2]$ and $[Pu(NO_3)_4(TBP)_2]$, respectively.[1] Most of the unwanted fission products remain behind as unextracted cations, with the notable exception of ^{99}Tc which coextracts with $\{UO_2\}^{2+}$, Pu^{IV}, and Zr^{IV}, as the pertechnetate anion, $[TcO_4]^-$. Despite studies into these solvent extraction processes,[2] and the effect $[TcO_4]^-$ redox chemistry can have on downstream U/Pu separation,[3] there is no spectroscopic evidence as to whether $[TcO_4]^-$ can directly coordinate to another metal center in solution. In addition, there has only been one previously structurally characterized $[TcO_4]^-$ complex, although this was a $\{NpO_2\}^{2+}$ complex in a hydrogen bonded lattice, $[(NpO_2)_2(TcO_4)_4\cdot 3H_2O]$, indicating that direct coordination of pertechnetate to an actinide is possible.[4]

There have been numerous previous studies into the coordination chemistry of the perrhenate anion, $[ReO_4]^-$.[5] We have taken these studies forward and investigated the interaction of $\{UO_2\}^{2+}$ and $\{NpO_2\}^+$ with $[ReO_4]^-$ in the presence of TPPO (triphenyl phosphine oxide)[6] and other monodentate P═O donor ligands (phosphates and phosphine oxides) as analogues of TBP.[7] These results have confirmed direct coordination of $[ReO_4]^-$ to $\{UO_2\}^{2+}$ in the solid state, although it has proved difficult to determine whether $[ReO_4]^-$ remains coordinated in solution, partly due to lability of the P═O donor ligands. Therefore, we have turned our attention to a bidentate chelating ligand, bis(diphenylphosphino)methane dioxide ($DPPMO_2$), in an attempt to increase solution stability.

Convenient synthetic routes have been found to prepare three novel $\{UO_2\}^{2+}/DPPMO_2$ complexes.[8] We have found $UO_2(ReO_4)_2\cdot H_2O$, formed from the dissolution of UO_3 in 2 equiv of aqueous $HReO_4$, to be a good general reagent for $\{UO_2\}^{2+}/[ReO_4]^-/P{=}O$ donor ligand chemistry. The reaction between $UO_2(ReO_4)_2\cdot H_2O$ and 2 equiv of $DPPMO_2$ in MeOH yielded crystals of $[UO_2(ReO_4)(DPPMO_2)_2][ReO_4]$ (**1**) in near quantitative yield. The lack of availability, and difficulty of preparation, of $HTcO_4$ did not allow preparation of the Tc analogue directly. However, reaction of $UO_2Cl_2\cdot H_2O$ with 2 equiv of $DPPMO_2$ yielded the chloride analogue, $[UO_2(Cl)(DPPMO_2)_2][Cl]$ (**2**), again as a crystalline product. Compound **2** could then be added to $AgTcO_4$,[9] forming $[UO_2(TcO_4)(DPPMO_2)_2][TcO_4]$ (**3**) in solution, which we have only been able to isolate as a microcrystalline powder.

Single crystal X-ray data were collected on **1** and **2**, with ORTEP representations given in Figures 1 and 2, respectively.[10] In both cases, monomeric cationic uranyl complexes are formed. The pentagonal bipyramidal cation contains two bidentate $DPPMO_2$ ligands together with one coordinated and one noncoordinated anion ($[ReO_4]^-$ in **1** and Cl^- in **2**).

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(1) (a) *The Nuclear Fuel Cycle*; Wilson, P. D., Ed.; Oxford University Press: Oxford, 1996. (b) Den Auwer, C.; Charbonnel, M. C.; Presson, M. T.; Madic, C.; Guillaumont, R. *Polyhedron* **1998**, *17*, 4507.

(2) (a) Federov, Y. S.; Zilberman, Y. B. *Radiochemistry* **1999**, *41*, 545. (b) Garraway, J.; Wilson, P. D.; *J. Less-Common Met.* **1985**, *106*, 183. (c) Macasek, F.; Kadrabova, J. *J. Radioanal. Nucl. Chem.* **1979**, *51*, 97.

(3) (a) Kemp, T. J.; Thyer, A. M.; Wilson, P. D. *J. Chem. Soc., Dalton Trans.* **1993**, 2601. (b) Kemp, T. J.; Thyer, A. M.; Wilson, P. D. *J. Chem. Soc., Dalton Trans.* **1993**, 2607. (c) Garraway, J.; Wilson, P. D. *J. Less-Common Met.* **1984**, *97*, 191.

(4) Fedosseev, A. M.; Budantseva, N. A.; Grigoriev, M. S.; Guerman, K. E. *Radiochemistry* **2003**, *91*, 147.

(5) Chakravorti, M. C.; *Coord. Chem. Rev.* **1990**, *106*, 205.

(6) John, G. H.; May, I.; Sarsfield, M. J.; Steele, H. M.; Collison, D.; Helliwell, M.; McKinney, J. D. *Dalton Trans.* **2004**, 743.

(7) John, G. H. Ph.D. Thesis, The Chemistry of Uranium and Neptunium Perrhenate Compounds. The University of Manchester, Manchester, U.K., 2003.

10.1021/ic049588r CCC: $27.50

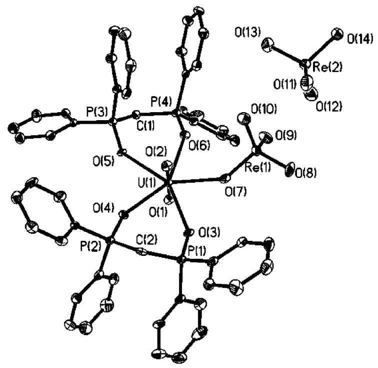

Figure 1. ORTEP representation of $[UO_2(ReO_4)(DPPMO_2)_2][ReO_4]$ (**1**). Selected bond lengths (Å): U(1)−O(1), 1.764(6); U(1)−O(3), 2.395(6); U(1)−O(7), 2.366(6); Re(1)−O(7), 1.761(6); Re(1)−O(9), 1.699(7); Re(2)−O(11), 1.715(7); P(1)−O(3), 1.512(6). Selected bond angles (deg): O(1)−U(1)−O(2), 178.3(3); O(3)−U(1)−O(4), 72.9(2); O(5)−U(1)−O(6), 73.1(2); U(1)−O(7)−Re(1), 142.2(3); U(1)−O(3)−P(1), 140.8(4).

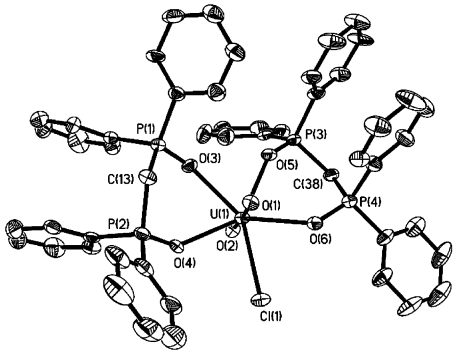

Figure 2. ORTEP representation of the cation $[UO_2Cl(DPPMO_2)_2]^+$ in **2**. Selected bond lengths (Å): U(1)−O(1), 1.754(5); U(1)−O(3), 2.416(5); U(1)−Cl(1), 2.710(2); P(1)−O(3), 1.495(5). Selected bond angles (deg): O(1)−U(1)−O(2), 176.9(2); O(3)−U(1)−O(4), 70.3(2); O(5)−U(1)−O(6), 70.6(2); U(1)−O(3)−P(1), 135.4(3).

Cationic f-element $DPPMO_2$ complexes have also recently been characterized for a series of Ln^{III} ions.[11] The U═O bond lengths in **1** and **2** are as expected for 7-coordinate uranyl complexes although the uranyl bond angle in **2**, 176.9 °, is slightly further bent from linear than would be expected (178−180°).[12] The $U-O_{P=O}$ bond lengths for coordinated $DPPMO_2$ are comparable in **1** and **2** (average of 2.39(4) and 2.39(2) Å) although there are long and short U−O bonds in one coordinated $DPPMO_2$ ligand in **1** (U1−O4, 2.395(6) Å and U1−O5, 2.352(6) Å) and one coordinated $DPPMO_2$ ligand in **2** (U1−O3, 2.416(3) Å and U1−O4, 2.375(6) Å). This phenomenon has previously been observed in $DPPMO_2$ complexes of Ni^{II} and Fe^{II}.[13] The average $DPPMO_2$ bite angle in **2** is slightly less than observed in **1** (70.5(2)° vs 73.0(3)°), which can be explained by the larger radius of the fifth equatorial bound anion/atom (Cl^- in **2** vs O in $[ReO_4]^-$ in **1**) increasing the steric interactions. This effect can be seen more clearly in the related TPPO complexes with only two coordinated P═O donor ligands in the chloride complexes α-*trans*-,[14] *β*-*trans*-,[15] and *cis*-$[UO_2Cl_2(TPPO)_2]$[15] versus three coordinated P═O donor ligands in $[UO_2(ReO_4)_2(TPPO)_3]$.[6]

The coordinated perrhenate in **1** shows deviation from tetrahedral geometry, as previously observed in $[UO_2(ReO_4)_2(TPPO)_3]$.[6] The ligating Re−O bond (1.761(6) Å) is longer than the $Re-O_{terminal}$ bonds, which range from 1.699(7) to 1.731(7) Å. The O−Re−O bond angles are slightly different (range between 108.8(4)° and 110.6(4)°), and the ligating Re−O−U angle is 142.2(3)°. These angles are also comparable to those observed in $[UO_2(ReO_4)_2(TPPO)_3]$[6] and $[Fe(ReO_4)_4(H_2O)_2]^-$.[16]

Solid state vibrational spectroscopy (infrared and Raman) was used to help to determine the structure of **3** in comparison with the spectra of both **1** and **2** (see ESI, Electronic Supporting Information). In all three compounds, bands were assigned to internal $DPPMO_2$ ligand vibrations. These bands moved very little upon coordination, apart from the infrared active P═O stretch, which decreased in energy from 1186 cm^{-1} in the uncomplexed ligand to 1089 cm^{-1} in **1**, 1092 cm^{-1} in **2**, and 1088 cm^{-1} in **3**. By comparing the spectra of **1**−**3**, it has been possible to assign bands for both

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(8) WARNING: ^{99}Tc is a 0.3 MeV *β* emitter with high specific activity (6.37×10^8 Bq g^{-1}), and ^{238}U is an α emitter, 4.20, 4.15 MeV (specific activity 1.24×10^4 Bq g^{-1}). Experimental details follow: $DPPMO_2$ was prepared through the action of H_2O_2 on bis(diphenylphosphino)methane in EtOH. UO_3 (0.70 mmol, 0.20 g) was dissolved in $HReO_4$ (1.40 mmol, 0.192 mL) with stirring. The bright yellow solution was evaporated to dryness in a desiccator over P_2O_5 leading to the formation of a yellow solid, $[UO_2(ReO_4)_2{\cdot}H_2O]$, yield 0.54 g, 98%. (Anal. Calcd for $H_2O_{11}Re_2U$: H, 0.25; Re, 47.34; U, 30.13. Found: H, 0.3; Re, 47.95; U, 29.52%.) $[UO_2(ReO_4)_2(DPPMO_2)_2][ReO_4]$ (0.70 mmol, 0.55 g) was dissolved in MeOH (1 mL), and subsequent dropwise addition of a stoichiometric amount of $DPPMO_2$ (1.40 mmol, 0.582 g) dissolved in MeOH (2 mL) led to the formation of a yellow solution, which was left to stand in air away from direct sunlight. Yellow block crystals of $[UO_2(ReO_4)(DPPMO_2)_2][ReO_4]$ (**1**) formed after 5 days, which were collected by filtration and dried in air, yield 1.03 g, 90%. (Anal. Calcd for $C_{50}H_{44}O_{14}P_4Re_2U$: C, 37.46; H, 2.96; P, 7.58; Re, 22.77; U, 14.56. Found: C, 37.41; H, 2.75, P, 7.73; Re, 23.37; U, 14.46%.) $[UO_2Cl_2{\cdot}H_2O]$ (2.87 mmol, 1.032 g) was dissolved in MeOH (5 mL) and added to $DPPMO_2$ (5.76 mmol, 2.396 g), also dissolved in MeOH (5 mL), to yield a yellow solution, which was stored at 4 °C. Yellow block crystals of $[UO_2(Cl)(DPPMO_2)_2][Cl]$ (**2**) formed after 14 days, which were collected by filtration and dried in air, yield 2.91 g, 86%. (Anal. Calcd for $C_{50}H_{44}O_6P_4Cl_2U$: C, 51.15; H, 3.75; P, 10.57; Cl, 6.05; U, 20.29. Found: C, 51.02; H, 3.82, P, 10.43; Cl, 5.98; U, 20.17%.) Compound **2** (0.032 mmol, 37.9 mg) was dissolved in MeOH (2 mL) and added to a suspension of $AgTcO_4$ (0.064 mmol, 10.9 mg) in MeOH. The resultant mixture was stirred for 1 h to allow the complete precipitation of AgCl, with the supernatant removed after centrifugation. The solution was dried to yield solid $[UO_2(TcO_4)(DPPMO_2)_2][TcO_4]$ (**3**) in near quantitative yield. The radiological hazards associated with ^{99}Tc prevented the collection of elemental analysis or powder X-ray diffraction.

(9) Sarsfield, M. J.; Sutton, A. D.; Livens, F. R.; May, I.; Taylor, R. J. *Acta Crystallogr.* **2003**, *C59*, i45.

(10) Crystal data for **2** follow: $C_{50.75}H_{50}Cl_2O_{8.25}P_4U$, $M = 1224.72$, $a = 14.589(2)$ Å, $b = 19.282(2)$ Å, $c = 19.991(2)$ Å, $\alpha = 73.868(2)°$, $\beta = 87.715(2)°$, $\gamma = 81.923(2)°$; $V = 5348.8(10)$ Å^3, triclinic, space group $P\bar{1}$, $Z = 4$, $T = 100(2)$ K, $\mu = 3.304$ mm^{-1}, reflections collected/unique = 28032/18595 [R(int) = 0.0340], R1($I > 2\sigma(I)$) = 0.0518, and wR2($I > 2\sigma(I)$) = 0.1250. Crystal data for **1** follow: $C_{51}H_{48}O_{15}P_4Re_2U$, $M = 1635.20$, $a = 10.8208(11)$ Å, $b = 14.0952(15)$ Å, $c = 19.307(2)$ Å, $\alpha = 108.702(2)°$, $\beta = 98.098(2)°$, $\gamma = 100.592(2)°$; $V = 2677.9(5)$ Å^3, triclinic, space group $P\bar{1}$, $Z = 2$, $T = 100(2)$ K, $\mu = 7.711$ mm^{-1}, reflections collected/unique = 18919/9307 [R(int) = 0.0245], R1($I > 2\sigma(I)$) = 0.0453, and wR2($I > 2\sigma(I)$) = 0.1132.

(11) (a) Lees, A. M. J.; Platt, A. W. G. *Inorg. Chem.* **2003**, *42*, 4673. (b) Fawcett, J.; Platt, A. W. G. *Polyhedron* **2003**, *22*, 967.

(12) Burns, P. C.; Ewing, R. C.; Hawthorne, F. C. *Can. Mineral.* **1997**, *35*, 1551.

(13) (a) Bermejo, E.; Castineiras, R.; Dominguez, R.; Schule, C. *J. Coord. Chem.* **1994**, *33*, 353. (b) Barclay, J. E.; Evans, D. J.; Hughes, D. L.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1993**, 69.

(14) Bombieri, G.; Forsellini, E.; Day, J. P.; Azeez, W. I. *J. Chem. Soc., Dalton Trans.* **1978**, 677.

(15) Akona, J.; Fawcett, J.; Holloway, J. H.; Russell, D. R. *Acta Crystallogr., Sect. C* **1991**, *47*, 45.

(16) Grigor'ev, M. S.; Kryuchkov, S. V.; Lapitskaya, T. S.; Makarenkov, V. I.; Maksimov, V. G.; Struchkov, Yu. T.; Yanovskii, A. I. *Russ. J. Coord. Chem.* **1998**, *24*, 702.

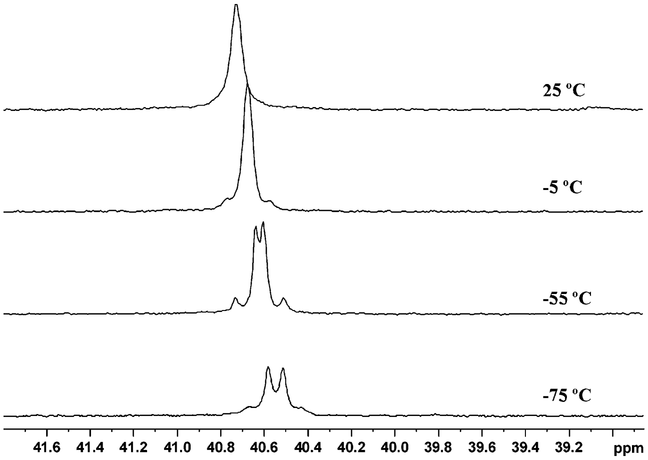

Figure 3. Variable temperature ^{31}P NMR of $[UO_2(TcO_4)(DPPMO_2)_2][TcO_4]$ (**3**) in CD_2Cl_2.

the symmetric (ν_1) and asymmetric (ν_3) stretches of $\{UO_2\}^{2+}$ and $[MO_4]^-$ (where M = Re or Tc) (see ESI). Our assignments were aided by the previous detailed study of coordinated $[ReO_4]^-$ by Chakravorti,[5] and by comparison with the vibrational spectra of $[UO_2(ReO_4)_2(TPPO)_3]$[6] and $AgReO_4$/$AgTcO_4$.[9] Although the presence of both coordinated and uncoordinated $[ReO_4]^-$ complicates the spectra of **1**, the fact that ν_1 is IR active and there are several bands that can be assigned to ν_3 indicates coordination of the anion. The similarities observed for the spectra of **1** and **3**, taking into consideration the lower energy vibrations for $[TcO_4]^-$ versus $[ReO_4]^-$, give good indication that the solid state structures of both complexes are very similar.

While solid state vibrational spectroscopy has indicated that a $[TcO_4]^-$ anion is coordinated to $\{UO_2\}^{2+}$ in **3**, it was hoped that solution vibrational spectroscopy would confirm whether $[TcO_4]^-$ remains coordinated in solution. Unfortunately, the relatively low solubility of **1** and **3** in noncoordinating solvents greatly inhibited such a study, although it was possible to observe bands at 980 and 964 cm^{-1} in the solution spectra of **1** in CD_2Cl_2 which are comparable to ν_1 $[ReO_4]^-$ bands observed in the solid state.

Variable temperature ^{31}P NMR spectra of **1** and **3**, recorded in CD_2Cl_2, were very informative. In each case, the room temperature spectrum revealed one single broad peak (δ = 42.2 ppm in **1**, 40.8 ppm in **3**), which in both cases was significantly downfield shifted from free $DPPMO_2$ (25.1 ppm) indicating that the ligand remained coordinated. In **1** and **3**, as the temperature is lowered the respective peaks sharpen and split into 4 separate peaks (see Figure 3 and Supporting Information). This is consistent with the $DPPMO_2$ ligands being equivalent, but with two different phosphorus environments that are adjacent or distal to coordinated $[ReO_4]^-$ (**1**) or $[TcO_4]^-$ (**3**) in the equatorial plane. Strong coupling between two different ^{31}P environments gives a typical 2nd order spectrum comprising a doublet of doublets in an experimentally observed AB pattern for what is actually an AA′BB′ system. There is a "roof effect" distortion of the intensities within the multiplets that occurs when the chemical shift difference between the ^{31}P resonances is of the order of the coupling constant, and this is clearly visible in the lower temperature measurements. A similar splitting is also observed in the low temperature ^{31}P NMR spectra of **2**. However, due to the very low solubility of this compound in CD_2Cl_2 the spectra were recorded in a coordinating solvent, CD_3OD, leading to additional peaks being observed and no guarentee that Cl^- remains coordinated (see ESI).

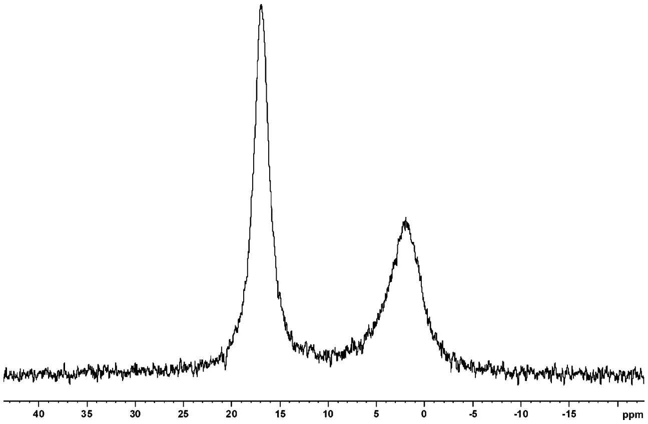

Figure 4. Room temperature ^{99}Tc NMR spectrum of $[UO_2(TcO_4)(DPPMO_2)_2][TcO_4]$ (**3**) in CD_2Cl_2.

Although the ^{31}P NMR variable temperature spectra give very good indirect evidence for coordinated $[TcO_4]^-$ in solution, we also wanted to probe the pertechnetate anion directly and turned to ^{99}Tc NMR ($I = {}^9/_2$) spectroscopy. The pertechnetate anion is often used as an internal standard in ^{99}Tc NMR, and the high (T_d) symmetry of the noncoordinated oxoanion leads to a single, sharp resonance at 0.00 ppm for NH_4TcO_4 in D_2O. The ^{99}Tc NMR spectra of **3** in CD_2Cl_2 gave two peaks of comparable intensity centered at 2.0 and 16.9 ppm, respectively, as would be expected for $[TcO_4]^-$ in two different chemical environments (Figure 4). We assign the first peak to coordinated and the second to uncoordinated $[TcO_4]^-$, because the first peak has the larger width at half-height (353 vs 161 Hz). Increased line width is expected on lowering the symmetry (in this case from T_d to C_{3v} on coordination) for quadrupolar nuclei (although solvent effects and chemical exchange will also contribute).

In conclusion, we have undertaken a systematic structural and spectroscopic study of a series of complexes of general formula $[UO_2(X)(DPPMO_2)_2][X]$ where X = $[ReO_4]^-$, $[Cl]^-$, or $[TcO_4]^-$, and we have been able to show that the pertechnetate anion can directly bond to the uranyl cation in solution. This gives an indication that the co-extraction of this anion in the PUREX process may occur through direct coordination, and perhaps also that selective complexation of $[TcO_4]^-$ may be a route to removing this species from nuclear waste solutions. Future studies will be directed toward evaluating the strength of the $[TcO_4]^-$ interaction with $\{UO_2\}^{2+}$ and other relevant cations in solution, especially in competition with NO_3^-, the dominant anion in most nuclear fuel processing solutions.

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Supporting Information Available: Crystallographic and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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