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Luminescence from Neptunyl(VI) Species in Solution

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Of all the actinyl systems, $\{AnO_2\}^{2+}/\{AnO_2\}^{+}$ (where An = U, Np, Pu, and Am), the chemistry of the $\{UO_2\}^{2+}$ cation has been studied in the most detail, due to a combination of high chemical stability and low radiological hazards.[1] However, uranyl(VI) is the only f^0 actinyl cation and in that key respect is not representative of the series. The absorption and emission spectroscopic properties of $\{UO_2\}^{2+}$ have been studied in great detail,[2] with far less known about the comparable spectroscopic properties of f^1 $\{NpO_2\}^{2+}$. Nevertheless, a detailed solid-state analysis of the absorption spectra of $NpO_2Cl_4^{2-}$ and $NpO_2(NO_3)_3^{-}$ has been undertaken.[4] However, our understanding of the solution-state spectra is not well developed,[4] despite recent advances in computational analysis.[5] Until very recently no luminescence properties of neptunyl(VI) had been reported.

In the past few years, Wilkerson et al. have reported the solid-state emission spectrum Np(VI) doped into a $Cs_2UO_2Cl_4$ phase.[6] The main near-infrared (nIR) observation is ascribed to an intra-5*f* transition giving rise to fluorescence with a lifetime of around 20 μs at room temperature. This spectrum exhibits two bands, corresponding to transitions arising from a single emissive state with an energy of 6881 cm^{-1}. In solution this low-energy emissive state would be susceptible to efficient nonradiative quenching through the X−H vibrational manifold (X = O, C, or N) of the solvent. Over the past 10 years a range of studies on the nIR luminescent lanthanides have been undertaken, for which similar difficulties with nonradiative quenching are encountered, and techniques have been developed by which the photophysical properties of such systems can be studied in detail.[7] We resolved to apply the lessons learned with lanthanides to the case of neptunyl(VI) and to study the luminescence properties of the free ion in deuterated solution and in a series of complexes which exclude solvent and which have no close diffusing X−H oscillators in the ligand structure. Both these approaches should reduce nonradiative quenching of the emissive state. We now report the preliminary results of this study.

Initial studies were carried out in solution in deuterated perchlorate solution in D_2O. We initially studied the photophysical properties of a 21 mM solution of neptunyl(VI) perchlorate in D_2O following excitation using a pulsed light source at 337 nm. The time-resolved emission spectrum in Figure 1a clearly shows two bands at 1490 nm and 1580 nm. This is in close agreement with the observations of Wilkerson et al.[6] in the solid state and represents the first observation of emission by neptunyl(VI) in solution. Even in D_2O, the lifetime of the luminescence is very short, and the time-resolved profile of the decay was found to be indistinguishable from that obtained using a scatterer, implying that the luminescence lifetime of the neptunyl(VI) ion in deuterated aqueous solution is less than 10 ns. This short lifetime implies that all the processes involved in generating and quenching the excited state are short lived. Absorption at 337 nm results in formation of a ligand-to-metal charge state (LMCT) in the NpO_2^{2+} core, and it is reasonable to assume that rapid energy transfer then occurs from this state to the emissive state via the manifold of the neptunium-centered excited state. The same experimental procedure was followed for a solution of neptunyl(VI) perchlorate in H_2O, but no luminescence was observed. This is unsurprising and is almost certainly a consequence of much more effective nonradiative quenching by O−H oscillators, since overlap occurs with a lower harmonic of the O−H vibration.

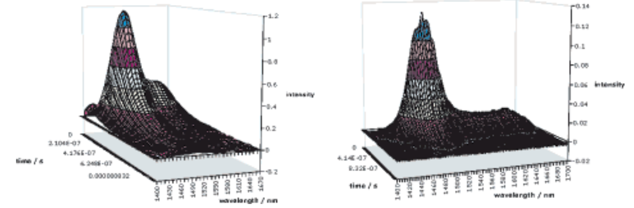

Figure 1. Time-resolved luminescence spectrum for (a) the neptunyl(VI) aquo ion; (b) $[Na_2(Np^{VI}O_2)_2(GeW_9O_{34})_2]^{14-}$. Both spectra were recorded in solution in D_2O following excitation at 337 nm.

The effectiveness of quenching by H_2O was probed further by measuring the intensity of the luminescence at 1490 nm for a series of 15 mM solutions in which the solvent contained varying ratios of H_2O to D_2O. Increasing the mole fraction of H_2O in D_2O resulted in a rapid decrease in the intensity of the luminescence, and no luminescence could be discerned for solvent mixtures containing >15% H_2O. To probe the effect of complexation on the luminescence properties of the neptunyl(VI) moiety we turned to A-type trivacant lacunary heteropolyanions, *A*-α-$[PW_9O_{34}]^{9-}$ and *A*-α-$[GeW_9O_{34}]^{10-}$. It has been shown that oxo clusters such as these form 2:2 cluster complexes with actinyl cations, with two additional monovalent cations enclosed in the structure (e.g., $[Na_2(U^{VI}O_2)_2(PW_9O_{34})_2]^{12-}$, $[Na_2(Np^{V}O_2)_2(PW_9O_{34})_2]^{12-}$).[8] In these systems, the equatorial coordination sphere around each actinyl cation is completely filled by oxo bonds from the ligands, excluding water from the inner coordination sphere without introducing the large numbers of C−H oscillators that would be associated with an organic ligand. It was hoped that this would reduce nonradiative quenching and increase the intensity of emission. Furthermore, these polyoxoanions have strong O → W charge-transfer bands in the UV region which are potentially useful as antennae.

Carefully increasing the pH while adding $[GeW_9O_{34}]^{10-}$ to an aqueous $\{NpO_2\}^{2+}$ solution caused a dramatic color change from

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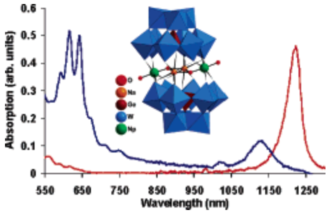

Figure 2. Vis/nIR spectrum of $\{NpO_2\}^{2+}$ (~10 mmol L^{-1}) in 0.5 mol L^{-1} HNO_3 (red) and then after addition of 2 equiv of $[GeW_9O_{34}]^{10-}$ and raising the pH to 8.5 (blue). (Insert) Polyhedral representation of the structure of $[Na_2(Np^{VI}O_2)_2(GeW_9O_{34})_2]^{14-}$.

pale pink to olive green. The solution vis/nIR spectrum (Figure 2) revealed distinct fine structure features (592, 615, 642, 672, 710, and 748 nm) at the tail of a high-energy charge-transfer band. In addition, the major $\{NpO_2\}^{2+}$ transition centered at 1223 nm decreases in intensity and shifts to higher energy, 1130 nm. Similar spectra were obtained when $[GeW_9O_{34}]^{10-}$ was replaced by $[PW_9O_{34}]^{9-}$. Crystallization of the "GeW_9"complex from a pH 7.2 solution yielded diffraction-quality crystals of $Na_{14}[Na_2(Np^{VI}O_2)_2(GeW_9O_{34})_2]\cdot 36H_2O$.[6] The anion, $[Na_2(Np^{VI}O_2)_2(GeW_9O_{34})_2]^{14-}$ ($Np^{VI}GeW_9$), is isostructural to the previously characterized $\{NpO_2\}^+$ and $\{UO_2\}^{2+}$ A-type trilacunary complexes with incorporated Na^+ cations.[1−2] $Np^{VI}GeW_9$ contains two seven coordinate, distorted pentagonal bipyramidal neptunyl cations; each ion is coordinated to four terminal unsaturated oxygen and one bridging oxygen atom in the equatorial plane and linked to two internal sodium cations encapsulated into the sandwich complex (Figure 2 inset).

Bond lengths and angles around the central Np cations for the $Np^{VI}GeW_9$ complex are consistent with the presence of $\{NpO_2\}^{2+}$, but the structural data alone cannot eliminate the possibility of reduction to $\{Np^VO_2\}^+$. However, diffuse reflectance spectrum of the bulk crystalline product reveals a broad band between 500−750 nm with partially resolved intense fine structure, in agreement with the solution spectrum and the literature.[4]

The nIR emission spectrum of both the GeW_9 and PW_9 $\{NpO_2\}^{2+}$ complexes in D_2O were very similar, and more intense than $[NpO_2(D_2O)_5]^{2+}$. In addition, the relative intensities of the two bands in the spectrum were significantly altered on polyoxometalate complexation, as can be seen from the time-resolved emission spectrum in Figure 1b). This change reflects the change in local symmetry at the metal center upon complexation. The increase in intensity is accompanied by a considerable increase in luminescence lifetime, and the time-resolved profile of the emission was fitted to a lifetime of 62 ns. Furthermore, luminescence can be detected in mixtures of H_2O and D_2O with relatively high mole fractions of H_2O (up to around 40%). In a 9:1 mixture of D_2O and H_2O, the luminescence lifetime decreased to 36 ns. If we consider that rate constants are additive in proportion to the number of local oscillators and assume that only the nature of the solvent changes when changing the ratio of H_2O to D_2O, then we can calculate that the lifetime in water would be less than 8 ns. The inner sphere effect of even a single bound water molecule in lanthanide containing systems is very much greater than the whole outer sphere effect.[7] It is therefore reasonable to assume that there is little hope of measuring the solution-state emission from a neptunyl complex with *any* coordinated water molecules using currently available technology. Ligands which exclude inner sphere solvent and which have few high-frequency vibrational modes, such as polyoxometallates, are likely to offer the best option if neptunyl(VI) emission is to be detected in aqueous systems.

In summary, we have studied the luminescence properties of the neptunyl aquo ion and one of its complexes in solution for the first time, and have demonstrated that the nIR luminescence from the metal center can be sensitized through both the LMCT bands of the ion itself and through the absorption bands of a coordinated ligand. We are currently studying a wide range of polyoxometallates with a view to optimizing the ease with which the emission can be detected.

Warning! ^{237}Np is a radionuclide with high specific activity that should only be manipulated in a specifically designated facility in accordance with appropriate safety controls. All spectroscopic and X-ray measurements were undertaken either in controlled facilities and/or using multiple containment procedures.

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Supporting Information Available: Experimental details for synthetic and spectroscopic procedures; energy level diagram for the polyoxometallate complex. Vis/nIR spectrum of $\{NpO_2\}^{2+}$. X-ray data (CIF) for $Na_{14}[Na_2(Np^{VI}O_2)_2(GeW_9O_{34})_2]\cdot 36H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Denning, R. G. *Struct. Bonding* **1992**, *79*, 215−276. (b) Sessler, J. L.; Melfi, P. J.; Pantos, G. D. *Coord. Chem. Rev.* **2006**, *250*, 816−843. (c) Ephritikhine, M. *Dalton Trans.* **2006**, 2501−2506. (d) Grenthe, I.; Drożdżynski, Fujino, T.; Buck, E. C.; Albrecht-Schmitt, T. E.; Wolf, S. F. In *The Chemistry of the Actinide and Transactinide Elements*; Morss, L. R., Edelstein, N. M., Fuger, J., Eds.; Springer, Dordrecht, 2006; pp 253−698. (e) Burns, C. J.; Neu, M. P.; Boukhalfa, H.; Gutowski, K. E.; Bridges, N. J.; Rodgers, R. D. In *Comprehensive Coordination Chemistry II, 3.3*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier Ltd.: Amsterdam, 2003; pp 189−345.

(2) See, for example: (a) Baird, C. P.; Kemp, T. J. *Prog. React. Kinet.* **1997**, *22*, 87−139. (b) Billard, I.; Rustenholtz, A.; Sémon, L.; Lützenkirchen, K. *Chem. Phys.* **2001**, *270*, 345−354. (c) Görller-Walrand, C.; De Houwer, S.; Fluyt, L.; Binnemans, K. *Phys. Chem. Chem. Phys.* **2004**, *6*, 3292−3298. (d) van Besien, E.; Pierloot, K.; Görller-Walrand, C. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4311−4319. (e) Bouby, M.; Billard, I.; Bonnenfant, A.; Klein, G. *Chem. Phys.* **1999**, *240*, 353−370.

(3) (a) Brown, D.; Denning, R. G.; Norris, J. O. W. *Molec. Phys.* **1982**, *46*, 287−324. (b) Denning, R. G.; Norris, J. O. W.; Brown, D. *Molec. Phys.* **1982**, *46*, 325−364. (c) Leung, A. F.; Wong, E. U. *Phys. Rev.* **1969**, *187*, 504−511.

(4) (a) Cohen, D.; Taylor, B. *J. Inorg. Nucl. Chem.* **1961**, *22*, 151−153. (b) Sjoblom, R.; Hindman, J. C. *J. Am. Chem. Soc.* **1951**, *73*, 1744−1751.

(5) (a) Infante, I.; Gomes, A. S. P.; Visscher, L. *J. Chem. Phys.* **2006**, *125*, 074301. (b) Matsika, S.; Zhang, Z.; Brozell, S. R.; Blaudeau, J.-P.; Wang, Q.; Pitzer, R. M. *J. Phys. Chem. A* **2001**, *105*, 3825−3828. (c) Matsika, S.; Pitzer, R. M.; Reed, D. T. *J. Phys. Chem. A* **2000**, *104*, 11983−11992.

(6) Wilkerson, M. P.; Berg, J. M.; Hopkins, T. A.; Dewey, H. J. *J. Solid State Chem.* **2005**, *178*, 584−588.

(7) (a) Faulkner, S.; Burton-Pye, B. P.; Pope, S. J. A. *Appl. Spectrosc. Rev.* **2005**, *40*, 1−39. (b) Parker, D.; Dickins, R. S.; Puschmann, H.; Crossland, C.; Howard, J. A. K. *Chem. Rev.* **2002**, *102*, 1977−2010. (c) Beeby, A.; Dickins, R. S.; Faulkner, S.; Parker, D.; Williams, J. A. G. *Chem. Commun.* **1997**, 1401−1402. (d) Horrocks, W. D.; Bolender, J. P.; Smith, W. D.; Supkowski, R. M. *J. Am. Chem. Soc.* **1997**, *119*, 5972−5973. (e) Werts, M. H. V.; Woudenberge, R. H.; Emmerink, P. G.; van Gassel, R.; Hofstraat, J. W.; Verhoeven, J. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 4542−4544.

(8) (a) Kim, K-C.; Pope, M. T. *J. Am. Chem. Soc.* **1999**, *121*, 8512−8517. (b) Gaunt, A. J.; May, I.; Helliwell, M.; Richardson, S. *J. Am. Chem. Soc.* **2002**, *124*, 13350−13351. (c) Kim, K-C.; Gaunt, A. J.; Pope, M. T. *J. Cluster Sci.* **2002**, *13*, 423−436. (d) Khoshnavazi, R.; Eshtiah-Hossieni, H.; Alizadeh, M. H.; Pope, M. T. *Polyhedron* **2006**, *25*, 1921−1926.

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