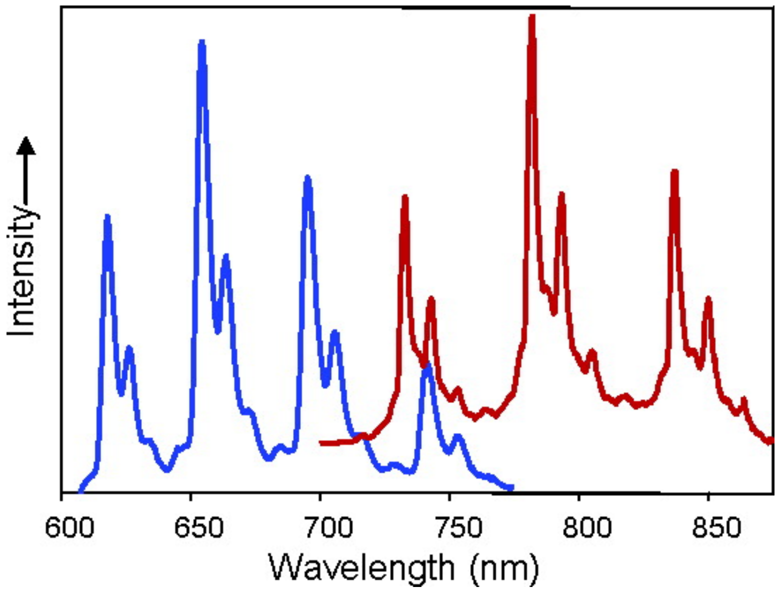
JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

Luminescence from the *trans*-Dioxotechnetium(V) Chromophore

Andrew S. Del Negro, Zheming Wang, Carl J. Seliskar, William R. Heineman, B. Patrick Sullivan, Sean E. Hightower, Timothy L. Hubler, and Samuel A. Bryan

J. Am. Chem. Soc., **2005**, 127 (43), 14978-14979• DOI: 10.1021/ja054906m • Publication Date (Web): 08 October 2005



ACS Publications
High quality. High impact.

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Published on Web 10/08/2005

Luminescence from the *trans*-Dioxotechnetium(V) Chromophore

Andrew S. Del Negro,[†] Zheming Wang,[†] Carl J. Seliskar,[‡] William R. Heineman,[‡] B. Patrick Sullivan,[§]
Sean E. Hightower,[§] Timothy L. Hubler,[*,†] and Samuel A. Bryan[*,†]

Pacific Northwest National Laboratory, Richland, Washington 99352, University of Cincinnati,
Cincinnati, Ohio 45221, and University of Wyoming, Laramie, Wyoming 82071

Received July 21, 2005; E-mail: tim.hubler@pnl.gov; sam.bryan@pnl.gov

We describe the first examples of room-temperature luminescence for Tc complexes. The discovery of luminescence from *trans*-dioxotechnetium(V) complexes provides the first opportunity to directly compare fundamental luminescence properties of second- and third-row d^2 metal−oxo congeners.

Transition metal complexes with metal−oxygen multiple bonds have been well studied since the benchmark work of Winkler and Gray[1] on the photophysical properties of *trans*-$[ReO_2(L)_4]^+$ (L = pyridine (py, **1**) or 4-picoline (pic, **2**)) and *trans*-$[ReO_2(CN)_4]^{3-}$ (**3**) in crystalline and solution forms. These complexes exhibit a broad emission in the visible range at room temperature (ca. 650 nm), and in crystalline form at low temperature, their spectra resolve into distinct vibronic progressions containing O═Re═O and Re−L modes. Others have described the emission properties of the related d^2 dioxoosmium(VI)[2,3] and the oxomolybdenum(IV)[4] chromophores. Recently, the work of Reber et al.[5] has reemphasized the importance of *trans*-$[ReO_2(L)_4]^+$ complexes as fundamental models for understanding excited-state electronic structure and dynamics, for example, the effect of orbital mixing of the in-plane ligands with the linear ReO_2^+ core, vibronic coupling between coordinates on the lowest potential emitting surface, and electronic coupling between the lowest emitting state and higher electronic excited states.[3,5−7]

It is significant that despite well-established studies of the reactivity and spectroscopy of Tc complexes in several oxidation states,[8] luminescence has yet to be reported for a Tc complex until now, although there have been reports of Tc(IV)−halide complexes which luminesce at low temperature and only when isolated in a crystalline host matrix.[9] The room- and low-temperature luminescence studies of the *trans*-$[TcO_2(L)_4]^+$ (L = py (**4**) or pic (**5**)) and *trans*-$[TcO_2(CN)_4]^{3-}$ (**6**) reported here open a new chapter in Tc chemistry, both in a fundamental and practical sense.

Microcrystalline complexes **4**−**6** were prepared by literature methods,[10,11] and their photophysical properties as well as those of the analogous Re complexes[1,12] (**1**−**3**) were studied by variable temperature steady-state emission spectroscopy and time-domain lifetime measurements.[13]

Using 415 nm excitation at room temperature, broad emission spectra with maxima between 745 and 780 nm were observed for complexes **4**−**6**. The suggestion that emission from **4**−**6** would occur in the near-IR was provided by DFT/TDDFT calculations[14] for *trans*-$[MO_2(L)_4]^+$ (M = Re, Tc; L = py) that predicted the dioxotechnetium emission to be 0.41 eV lower in energy.[15] At room temperature, the experimental red-shift from the corresponding Re complex is found to be 0.21 eV (Table 1). Like the Re analogue, the Tc complex luminesces from a ^3E_g excited state. For both, the calculations show that the major contributing excitations are the pair MO 99 (HOMO) to the degenerate pair MO 102 (LUMO+1) and MO 103 (LUMO+1′). MO 99 is mostly $M(d_{xy})$ with some O(p) character, while MOs 102 and 103 are admixtures of $M(d_{xz}, d_{yz})$ and O(p). A small but significant difference is that the excitation MO 86 to MOs 100 and 101 makes a contribution in the Tc case. Since MO 86 is 84.7% pyridine composition, this imparts both LMCT and LLCT character to the transition.

Table 1. Photophysical and Vibronic Data for Tc and Re Complexes

	compound[a]	emission [nm][b]	τ [μs][c]	ν(M═O) Raman [cm^{-1}][d]	$\langle h\omega_{O=M=O}\rangle$ Prog. [cm^{-1}][e]	$\langle h\omega_{M-L}\rangle$ Prog. [cm^{-1}][e]
Re	**1**	610	71	903	903	178
	2	618	48	900	896	221
	3	575	2728	870	866	*f*
Tc	**4**	679	78	858	848	168
	5	733	15	852	853	188
	6	675	1926	826	*f*	*f*

[a] Microcrystalline samples were contained in a quartz cell. [b] Emission energy of the highest energy peak at 8 K. [c] Lifetimes are the average of two runs at 8 K. [d] Raman spectra upon 670 nm laser irradiation. [e] $E_{M=O}$ and E_{M-L} are the average peak to peak separations of the vibronic structure in the 8 K luminescence spectra (see text). [f] The vibronic progressions in the 8 K spectra could not be accurately resolved.

Upon cooling the samples from 278 to 8 K, distinct vibronic features appear in the spectra along with a relative increase in emission intensity. Figure 1 shows the temperature-dependent luminescence spectra for complex **4**. At least two vibronic progressions are observed in the low-temperature spectra, with one clearly

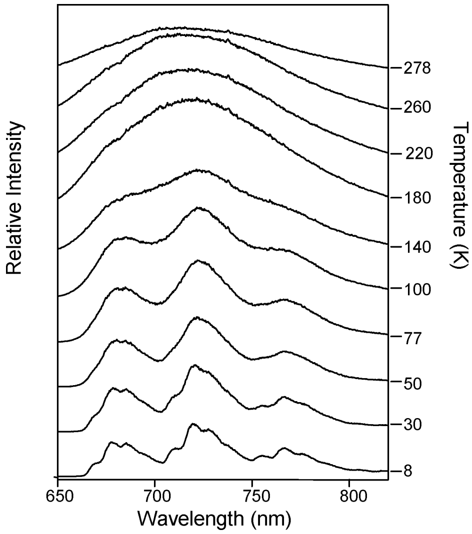


Figure 1. Temperature dependence of $[TcO_2(py)_4](BPh_4)$ luminescence spectra. Spectra shown are not normalized for excitation intensity differences and are not corrected for spectrometer response.

[†] Pacific Northwest National Laboratory.
[‡] University of Cincinnati.
[§] University of Wyoming.

10.1021/ja054906m CCC: $30.25 © 2005 American Chemical Society

visible at temperatures below 100 K and a lower-frequency progression superimposed on the first below 30 K. By analogy to the Re complexes, the low-temperature emission spectra of $[TcO_2(py)_4]BPh_4$ (**4**) and $[TcO_2(pic)_4]BPh_4$ (**5**) appear to display the characteristic progressions of the symmetric O═Tc═O and the Tc−L stretching modes (Table 1). Thus, the O═Tc═O vibronic progression (~850 cm^{-1}) is consistent with the Raman active O═Tc═O symmetric stretch of 858 and 852 cm^{-1} for **4** and **5**, respectively, and is ca. 50 cm^{-1} lower in energy compared to the corresponding Re complexes (see Table 1). Careful inspection of the 77 K spectrum in Figure 1 shows a vibronic progression (801 cm^{-1}) which is not identical to any normal mode in the Raman spectrum and is likely an example of a missing mode effect (MIME).[16] The low-temperature spectrum for **5** (overlaid with the spectrum for **2**) shown in Figure 2 is the best resolved spectrum measured to date and clearly shows the lower energy (~180−200 cm^{-1}) progression that is consistent with a Tc−L mode found for the corresponding *trans*-dioxorhenium analogues. As seen for complex **5**, the three clusters of vibronic transitions have the same relative intensity distributions across the luminescence spectrum (Figure 2). Although vibronic features are apparent in the low-temperature spectrum of complex **6**, we were unable to adequately discern either the O═Tc═O or Tc−L progressions. The O═Tc═O symmetric stretching frequency for **6** was determined by Raman spectroscopy to be 826 cm^{-1} and is consistent with the literature value.[11]

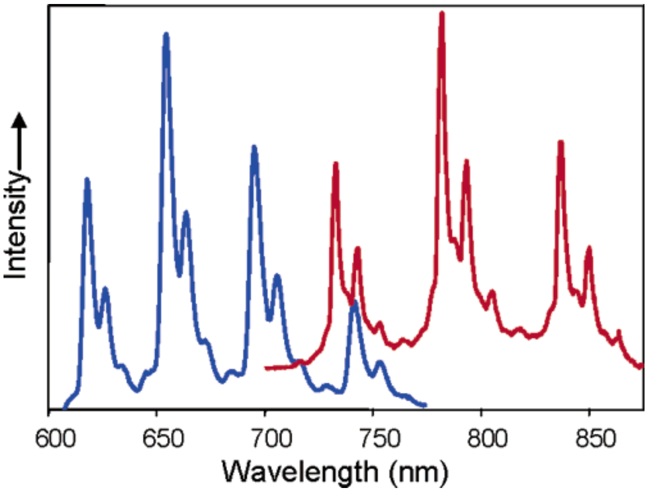


Figure 2. Low-temperature (8 K) luminescence spectra of microcrystalline $[ReO_2(pic)_4](BPh_4)$ (**2**, blue) and $[TcO_2(pic)_4](BPh_4)$ (**5**, red). Spectra are not normalized for excitation intensity differences.

The excited-state lifetimes were measured for the complexes at room and low temperatures. At 8 K, the lifetimes for complexes **4** and **5** were 78 and 15 μs, respectively, and are similar to the 71 and 48 μs lifetimes measured for the corresponding Re(V) complexes. As a standardization, we determined the lifetime of *trans*-$[ReO_2(py)_4]^+$, and our experimental value (LHeT) of 71 μs is close to the lifetime reported recently.[7] Complex **6** exhibits a very long-lived excited-state lifetime (1926 μs) compared to that of **4** and **5**, which is the same trend as the increased lifetime of the corresponding Re−CN complex. In all cases, at 8 K, the excited states were fit to a single exponential decay. The room temperature excited-state lifetimes were more complicated, exhibiting multi-exponential decays. Radiological limitations prevented initial solution measurements to determine quantum yield and absorption spectral data; however, detailed studies of these properties, in addition to the temperature dependence of the photophysical properties of the Tc complexes, are currently underway.

The discovery of luminescence from the *trans*-dioxotechnetium(V) complexes provides the first opportunity to directly compare fundamental luminescence properties of second- and third-row d^2 metal−oxo congeners. In a more practical sense, the analytical applications of the TcO_2 chromophore offer promise for design of dual mode complexes that can correlate luminescence and radioimaging properties into a single agent.[17] For our purposes, luminescent Tc(V) complexes are a significant component in our design of a spectroelectrochemical sensor for detection of pertechnetate in the environment.[18]

Acknowledgment. Financial support was provided by DOE EMSP (Project No. 90076). This research was performed at the Radiochemical Processing Lab and the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the DOE Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory (PNNL). PNNL is operated by Battelle for DOE under Contract DE-AC05-76RL01830.

Supporting Information Available: DFT/TDDFT calculations for $[TcO_2(py)_4]^+$ and $[ReO_2(py)_4]^+$ and complete refs 14 and 16 are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Winkler, J. R.; Gray, H. B. *Inorg. Chem*. **1985**, *24*, 346−355.
(2) (a) Cheng, J. Y. K.; Cheung, K. K.; Che, C. M.; Lau, T. C. *J. Chem. Soc., Chem. Commun*. **1997**, *15*, 1443−1444. (b) Grey, J. K.; Butler, I. S.; Reber, C. *Inorg. Chem*. **2004**, *43*, 5103−5111. (c) Schindler, S.; Castner, E. W.; Creutz, C.; Sutin, N. *Inorg. Chem*. **1993**, *32*, 4200−4208. (d) Yam, V. W. W.; Che, C. M. *Coord. Chem. Rev*. **1990**, *97*, 93−104.
(3) Savoie, C.; Reber, C. *J. Am. Chem. Soc*. **2000**, *122*, 844−852.
(4) (a) Isovitsch, R. A.; Beadle, A. S.; Fronczek, F. R.; Maverick, A. W. *Inorg. Chem*. **1998**, *37*, 4258−4264. (b) Isovitsch, R. A.; May, J. G.; Fronczek, F. R.; Maverick, A. W. *Polyhedron* **2000**, *19*, 1437−1446. (c) Mohammed, A. K.; Maverick, A. W. *Inorg. Chem*. **1992**, *31*, 4441−4443. (d) Da Re, R. E.; Hopkins, M. D. *Inorg. Chem*. **2002**, *41*, 6973−6985.
(5) (a) Savoie, C.; Reber, C. *Coord. Chem. Rev*. **1998**, *171*, 387−398. (b) Savoie, C.; Reber, C.; Belanger, S.; Beauchamp, A. L. *Inorg. Chem*. **1995**, *34*, 3851−3852.
(6) Grey, J. K.; Butler, I. S.; Reber, C. *J. Am. Chem. Soc*. **2002**, *124*, 11699−11708.
(7) Grey, J. K.; Butler, I. S.; Reber, C. *Can. J. Chem*. **2004**, *82*, 1083−1091.
(8) Schwochau, K. *Technetium: Chemistry and Radiopharmaceutical Applications*; Wiley-VCH: New York, 2000 and references therein.
(9) (a) Flint, C. D.; Lang, P. *J. Lumin*. **1981**, *24−25*, 301−304. (b) Flint, C. D.; Lang, P. F. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 465−472. (c) Flint, C. D.; Lang, P. F. *J. Chem. Soc., Dalton Trans*. **1986**, *5*, 921−923. (d) Wendt, A.; Preetz, W. *Z. Naturforsch., A* **1992**, *47*, 882−886.
(10) Kastner, M. E.; Fackler, P. H.; Clarke, M. J.; Deutsch, E. *Inorg. Chem*. **1984**, *23*, 4683−4688. Complexes **1** and **2** were isolated as BPh_4^- salts.
(11) Trop, H. S.; Jones, A. G.; Davison, A. *Inorg. Chem*. **1980**, *19*, 1993−1997.
(12) (a) Beard, J. H.; Casey, J.; Murmann, R. K. *Inorg. Chem*. **1965**, *4*, 797. (b) Sullivan, B. P.; Brewer, J. C.; Gray, H. B. *Inorg. Synth*. **1992**, *29*, 146−150.
(13) Instrumentation for luminescence measurements is described in Wang, Z.; Zachara, J. M.; Yantasee, W.; Gassman, P. L.; Liu, C. X.; Joly, A. G. *Environ. Sci. Technol*. **2004**, *38*, 5591−5597.
(14) Frisch, M. J. et al. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.
(15) Electronic ground state and geometry optimizations were carried out using the B3LYP approximation, followed by TDDFT calculation of the lowest excited states employing the same functional. Calculations utilized the 6-31G* basis set for the ligands and the LANL2 relativistic effective core potential (RECP) for the transition metal.
(16) Tutt, L.; Tannor, D.; Heller, E. J.; Zink, J. I. *Inorg. Chem*. **1982**, *21*, 3859−3860.
(17) Stephenson, K. A. et al. *J. Am. Chem. Soc*. **2004**, *126*, 8598−8599.
(18) (a) Stegemiller, M. L.; Heineman, W. R.; Seliskar, C. J.; Ridgway, T. H.; Bryan, S. A.; Hubler, T. L.; Sell, R. L. *Environ. Sci. Technol*. **2003**, *37*, 123−130. (b) Kaval, N.; Seliskar, C. J.; Heineman, W. R. *Anal. Chem*. **2003**, *75*, 6334−6340.

JA054906M