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First emission studies of $Tc_2X_8^{2-}$ systems (X = Cl, Br)†

Breeze N. Briggs,[a] David R. McMillin,*[a] Tanya K. Todorova,[b] Laura Gagliardi,[c] Frederic Poineau,[d] Kenneth R. Czerwinski[d] and Alfred P. Sattelberger[d,e]

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The emission spectra of the solids [*n*-$Bu_4N]_2Tc_2X_8$ (X = Cl, Br) have been investigated at room temperature and 77 K. In each case, the emission originates in the $^1\delta$–δ^* excited state, as with the rhenium homologues, but has a shorter lifetime.

The development of the chemistry of technetium lags that of its neighbors in the periodic table because all of its isotopes are radioactive. Leads for the exploration of technetium often come from the comparatively well developed chemistry of the heavier congener rhenium, as exemplified by investigations of intriguing octahalodimetalate complexes involving rhenium(III) and technetium(III). Identified first, the $Re_2Cl_8^{2-}$ ion is the prototype quadruply bonded dimetal complex that exhibits D_{4h} symmetry and extraordinary photoluminescence properties.[1–3] A rare δ bond formed by overlap of metal d_{xy} orbitals maintains the eclipsed geometry of the ground state.[4] Exploration of the electronic spectrum began soon after the discovery of the ion, and that led to the assignment of a band in the visible spectrum at about 700 nm as the characteristic $\delta \rightarrow \delta^*$ ($^1A_{1g} \rightarrow {}^1A_{2u}$) transition. Subsequently, investigators reported an emission signal maximizing at *ca.* 780 nm and with a lifetime of *ca.* 140 ns in solution.[5,6] The emission signal displays a remarkably small Stokes shift, and there is now wide agreement that emission originates from the singlet $^1\delta$–δ^* excited state,[2,3] which has an extremely long fluorescence lifetime for a heavy metal system. Characterization of the $Tc_2X_8^{2-}$ analogues, where X = Cl or Br, revealed that the technetium(III) and rhenium(III) complexes are isostructural.[7] Absorption studies and computational results have shown that the electronic structures of the $Tc_2X_8^{2-}$ and $Re_2X_8^{2-}$ ions are very similar, as well.[7,8] The purpose of the studies described herein was to measure photoluminescence spectra and excited-state lifetimes at room temperature and 77 K of the $Tc_2X_8^{2-}$ complexes for comparison with those of the $Re_2X_8^{2-}$ analogues. For containment purposes, the samples of choice were the solids [*n*-$Bu_4N]_2Tc_2Cl_8$ and [*n*-$Bu_4N]_2Tc_2Br_8$. On account of the radiological issues (commercially available ^{99}Tc, $t_{1/2} = 2.1 \times 10^5$ y, is a weak β-emitter), even now the literature includes few reports dealing with technetium-based luminophores, exceptions being detailed studies of the solid materials $Cs_2[TcX_6]$ (X = Cl, Br)[9] and [*trans*-$TcO_2(py)_4]BPh_4$.[10]

At room temperature [*n*-$Bu_4N]_2Tc_2Cl_8$ and [*n*-$Bu_4N]_2Tc_2Br_8$ each exhibit very similar emission spectra with a λ_{max} at about 750 nm. The signal-to-noise ratios in the spectra, shown in Fig. 1, are low because the signals are quite weak even with 20 nm slit settings which may blur any differences between spectra. Also, the true emission maxima conceivably occur at somewhat shorter wavelengths due to the use of the 700 nm long-pass emission filter, which transmits 10% of the intensity at 695 nm and 90% at 705 nm. The choice of an intrusive emission filter is necessary because of the severe light scattering associated with a solid-state sample and the fact that $\delta \rightarrow \delta^*$ excitation occurs so close in energy to the emission (see ESI† for experimental details). The corresponding emission decay times are 25 ns and 30 ns for the chloride and bromide derivatives, respectively. Fig. 2 presents the 77 K emission spectra, along with those of the rhenium analogues run under the same conditions. In the case of the $Tc_2Cl_8^{2-}$ ion, the emission maximum and the bandwidth of the emission remain essentially unchanged at the lower temperature, but the emission intensity approximately doubles as the lifetime extends to 46 ns. In contrast, the emission signal from the $Tc_2Br_8^{2-}$ analogue shows no significant change in the intensity or lifetime; however, the spectrum exhibits a small blue shift and a marginally narrower bandwidth at 77 K. The solid-state emission signals from [*n*-$Bu_4N]_2Re_2Cl_8$ and [*n*-$Bu_4N]_2Re_2Br_8$ are inherently stronger signals, and Fig. 2 reveals the emission spectra of the latter are less noisy even with smaller emission slit settings on the spectrophotometer. For comparison, Trogler *et al.* report emission maxima of 770 nm and 800 nm for $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$, respectively in a KBr disk at 1.3 K.[11] The emission lifetimes are also longer, measured here as 85 ns for the

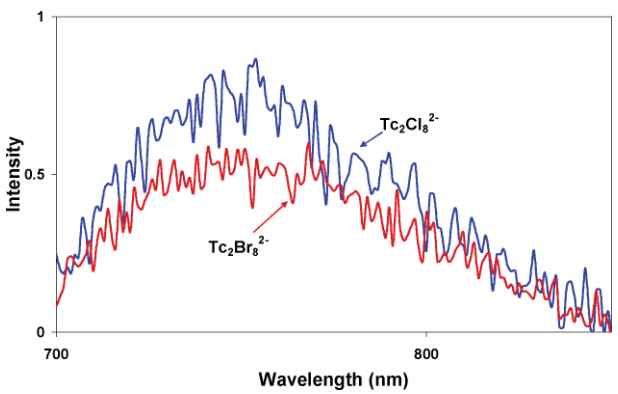

Fig. 1 Room-temperature emission spectra of [*n*-$Bu_4N]_2Tc_2Cl_8$ and [*n*-$Bu_4N]_2Tc_2Br_8$. Arbitrary intensities.

[a]*Department of Chemistry, Purdue University, West Lafayette, IN, 47907-2084, USA. E-mail: mcmillin@purdue.edu*
[b]*Department of Physical Chemistry, University of Geneva, CH-1211, Geneva, Switzerland. E-mail: Tanya.Todorova@unige.ch*
[c]*Department of Chemistry and Supercomputing Institute, University of Minnesota, Minneapolis, MN, 55455, USA. E-mail: gagliard@umn.edu*
[d]*Department of Chemistry, University of Nevada Las Vegas, Las Vegas, NV 89154, USA. E-mail: poineauf@unlv.nevada.edu*
[e]*Energy Engineering and Systems Analysis Directorate, Argonne National Laboratory, Argonne, IL, 60439, USA. E-mail: asattelberger@anl.gov*
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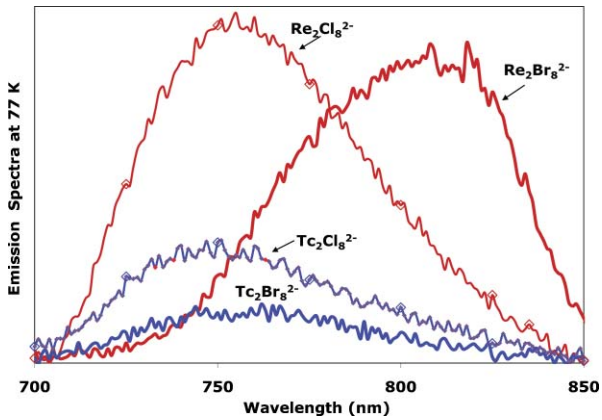

Fig. 2 77 K emission spectra of $[n\text{-Bu}_4\text{N}]_2\text{Tc}_2\text{Cl}_8$, $[n\text{-Bu}_4\text{N}]_2\text{Tc}_2\text{Br}_8$, $[n\text{-Bu}_4\text{N}]_2\text{Re}_2\text{Cl}_8$, and $[n\text{-Bu}_4\text{N}]_2\text{Re}_2\text{Br}_8$. Intensities are arbitrary.

$Re_2Cl_8^{2-}$ compound at room temperature and 145 ns at 77 K. The corresponding lifetimes are 45 ns and 115 ns for the $Re_2Br_8^{2-}$ salt. At 1.3 K the measured lifetimes were 150 ns and 110 ns for the chloride and bromide, respectively.[11]

Fig. 3 and 4 show that the 77 K excitation and emission spectra of the $Tc_2X_8^{2-}$ derivatives overlap, as previously reported for quadruply bonded $Mo_2X_4L_4$ systems.[12] The excitation maximum for $[n\text{-Bu}_4\text{N}]_2\text{Tc}_2\text{Cl}_8$ occurs at around 695 nm whereas the corresponding maximum for $[n\text{-Bu}_4\text{N}]_2\text{Tc}_2\text{Br}_8$ appears at *ca.* 685 nm.

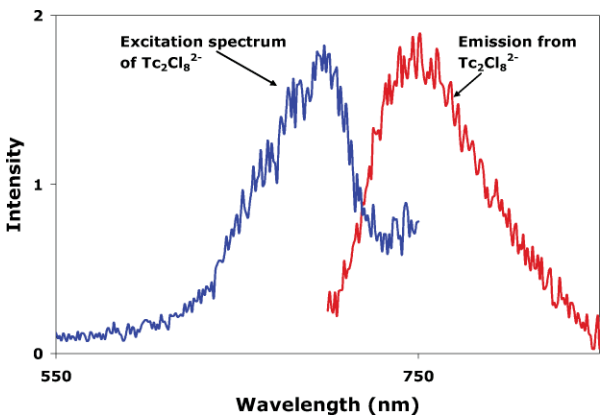

Fig. 3 77 K excitation and emission spectra of $[n\text{-Bu}_4\text{N}]_2\text{Tc}_2\text{Cl}_8$.

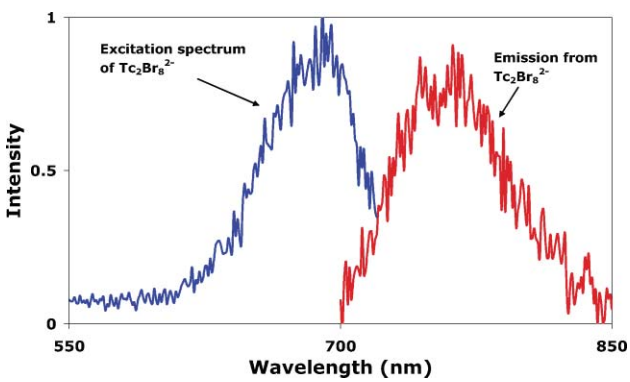

Fig. 4 77 K excitation and emission spectra of $[n\text{-Bu}_4\text{N}]_2\text{Tc}_2\text{Br}_8$.

In room-temperature dichloromethane solution, the maxima for the corresponding $\delta \rightarrow \delta^*$ absorption bands appear at longer wavelengths, namely 680 nm and 730 nm for $Tc_2Cl_8^{2-}$ and $Tc_2Br_8^{2-}$, respectively.[7] The shifts between phases may be real, but there is a possibility that the short-wave pass excitation filter distorts the solid-state excitation spectra by artificially displacing the maxima toward shorter wavelengths. Arguably the shift is small because the experimental configuration actually produces an excitation maximum for $[n\text{-Bu}_4\text{N}]_2\text{Re}_2\text{Br}_8$ at a longer wavelength (705 nm) in the solid state than that reported for the $Re_2Br_8^{2-}$ ion in solution (690 nm).[7]

The broad emission spectra obtained for $[n\text{-Bu}_4\text{N}]_2\text{Tc}_2\text{Cl}_8$ and $[n\text{-Bu}_4\text{N}]_2\text{Tc}_2\text{Br}_8$ are by and large in keeping with results obtained for $[n\text{-Bu}_4\text{N}]_2\text{Re}_2\text{Cl}_8$,[5,6] except the emission of the latter exhibits vibrational structure below 20 K.[11,13] The spectral width may be a consequence of the participation of several low-frequency ν(M—M) and ν(M–Cl) vibrational modes, as well as a tendency to twist away from an eclipsed geometry in the excited state, *vide infra*. The small Stokes shifts observed in the spectra of $[n\text{-Bu}_4\text{N}]_2\text{Tc}_2\text{Cl}_8$ and $[n\text{-Bu}_4\text{N}]_2\text{Tc}_2\text{Br}_8$ are consistent with the emission being spin-allowed fluorescence from the low-energy $^1\delta$–δ^* excited state, again in keeping with results in the literature for quadruply bonded $Re_2Cl_8^{2-}$ and $Mo_2Cl_4X_4$ analogues.[12]

The measured decay time constants, 45 ns for $Tc_2Cl_8^{2-}$ and 150 ns for $Re_2Cl_8^{2-}$ at 77 K, for example, are both surprisingly long for metal-based, singlet excited states of second and third row transition metal complexes. Indeed, the original state assignment proposed for the emission from $Re_2Cl_8^{2-}$ was $^3\delta$–δ^*.[11] However, a great deal of work has revealed that the long singlet lifetime is a consequence of an unusually slow rate of intersystem crossing to the triplet due to an intrinsically wide energy gap separating the $^1\delta$–δ^* and $^3\delta$–δ^* excited states.[14,15] The two excited states actually have very different electronic configurations ultimately due to the small overlap between the d_{xy} orbitals that make up the δ bond. In particular, theory reveals that the emitting $^1\delta$–δ^* state is an "ionic state" state with a comparatively high electron-electron repulsion energy.[2,3] In simple valence-bond theory terms, Re(II)–Re(IV) and Re(IV)–Re(II) resonance structures are very important in the description of the $^1\delta$–δ^* excited state. In contrast, the $^3\delta$–δ^* state has mainly Re(III)–Re(III) character. Early on, Miskowski *et al.* suggested that the emission comes from a $^1\delta$–δ^* state of $Re_2Cl_8^{2-}$ after excitation induces the system to twist away from the characteristic eclipsed geometry of the ground state.[6] However, Peacock and co-workers have argued that the excited state retains an eclipsed geometry, at least in the solid state.[13] The photoexcited $Re_2Cl_8^{2-}$ system is probably no more distorted in solution where the lifetime is even longer than in the solid state. Thus, Morgante and Struve reported a lifetime of 133 ns for the complex in room-temperature acetonitrile and 91 ns in dichloromethane solution.[5] Miskowski, *et al.* also report similar solution results.[6]

Curiously, the fluorescence decay times from the $^1\delta$–δ^* excited states of the $Tc_2X_8^{2-}$ (X = Cl Br) complexes are appreciably shorter than those observed with rhenium analogues. The decrease in lifetimes is surprising because the expectation is that intersystem crossing should be faster in the rhenium complexes due to the fact that the spin–orbit coupling constant of Re(III) is 2500 cm^{-1} compared with 1200 cm^{-1} for that of Tc(III).[16] For optimized geometries, calculations also suggest that the $^3A_{2u}$ states occur at slightly higher energies when rhenium is present. Thus, relative

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to the $^1A_{1g}$ ground state, the calculated triplet energies for $M_2Cl_8^{2-}$ systems are 3650 cm^{-1} (Re) *vs.* 3220 cm^{-1} (Tc), and 3780 cm^{-1} (Re) *vs.* 3390 cm^{-1} (Tc) for the $M_2Br_8^{2-}$ analogues. (See ESI† for theoretical details.) Spin–orbit coupling with a higher energy triplet excited state could still promote intersystem crossing in the $Tc_2X_8^{2-}$ systems if the energy match with the upper triplet is favorable. Alternatively, vibrational overlap factors may promote faster internal conversion to the ground state.

The parallels coming to light in the luminescence properties of analogous rhenium and technetium complexes are impressive and provide impetus for continued exploration. As noted earlier, d^2 dioxo complexes of technetium(V) and rhenium(V) exhibit similar emission behavior,[10] and so do d^3 halide complexes containing technetium(IV) and rhenium(IV).[9] Work described herein deals with the next lower oxidation state and the d^4 configuration. However, the result is the same in that the emissions of the metal–metal quadruply bonded $M_2X_8^{2-}$ (M = Re, Tc) complexes are remarkably similar. Other systems that may be ripe for future studies include paddle-wheel Tc_2(III,III) units bridged by amidinate ligands, should they prove to be accessible. The reason is quadruply bonded dirhenium tetraamidinates contrast $Re_2X_8^{2-}$ systems in having higher energy singlet and triplet excited states and exhibiting emission from what is formally a triplet δ–δ* excited state.[17,18] Another potentially interesting technetium(III) system is the subject of a report by Yoshimura *et al.* who have described hexanuclear clusters of the type $[Tc_6Q_8(CN)_6]^{4-}$ (Q = S, Se).[19] They have also suggested that the clusters may exhibit metal orbital based emissions, but that the signals would appear in the near IR region of the spectrum.[19] The metal-to-ligand charge-transfer excited state of d^6 *fac*-$TcCl(CO)_3(bpy)^+$ (bpy = 2,2′-bipyridine) occurs at higher energy and is potentially more promising.[20] Indeed, Alberto and co-workers have reported observing photoluminescence from the analogous bromide in solution, though they provided few details.[21] Continued expansion of the library of technetium-based luminophores is a worthwhile endeavor because it could facilitate designs of multi-purpose complexes that allow luminescence and radioimaging studies based on a single agent.[10]

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Notes and references

1 F. A. Cotton, C. A. Murillo and R. A. Walton, *Multiple Bonds between Metal Atoms*, Springer, New York, 3rd edn, 2005.
2 F. A. Cotton and D. G. Nocera, *Acc. Chem. Res.*, 2000, **33**, 483.
3 M. D. Hopkins, H. B. Gray and V. M. Miskowski, *Polyhedron*, 1987, **6**, 705.
4 F. A. Cotton, N. F. Curtis, B. F. G. Johnson, J. T. Mague, J. S. Wood, C. B. Harris, W. R. Robinson and S. J. Lippard, *Science*, 1964, **145**, 1305.
5 C. G. Morgante and W. S. Struve, *Chem. Phys. Lett.*, 1979, **63**, 344.
6 V. M. Miskowski, R. A. Goldbeck, D. S. Kliger and H. B. Gray, *Inorg. Chem.*, 1979, **18**, 86.
7 F. Poineau, L. Gagliardi, P. M. Forster, A. P. Sattelberger and K. R. Czerwinski, *Dalton Trans.*, 2009, 5954.
8 F. Ferrante, L. Gagliardi, B. E. Bursten and A. P. Sattelberger, *Inorg. Chem.*, 2005, **44**, 8476.
9 C. D. Flint and P. F. Lang, *J. Chem. Soc., Faraday Trans. 2*, 1986, **82**, 465.
10 A. S. Del Negro, Z. M. Wang, W. R. Seliskar, W. R. Heineman, B. P. Sullivan, S. E. Hightower, T. L. Hubler and S. A. Bryan, *J. Am. Chem. Soc.*, 2005, **127**, 14978.
11 W. C. Trogler, E. I. Solomon and H. B. Gray, *Inorg. Chem.*, 1977, **16**, 3031.
12 M. D. Hopkins and H. B. Gray, *J. Am. Chem. Soc.*, 1984, **106**, 2468.
13 I. F. Fraser and R. D. Peacock, *Chem. Phys. Lett.*, 1987, **137**, 583.
14 L. Gagliardi and B. O. Roos, *Inorg. Chem.*, 2003, **42**, 1599.
15 P. J. Hay, *J. Am. Chem. Soc.*, 1982, **104**, 7007.
16 B. N. Figgis and M. A. Hitchman, *Ligand Field Theory and its Applications*, Wiley-VCH, New York, 2000.
17 M. Q. Dequeant, P. M. Bradley, G. L. Xu, D. A. Lutterman, C. Turro and T. Ren, *Inorg. Chem.*, 2004, **43**, 7887.
18 M. Q. Dequeant, R. McGuire, D. R. McMillin and T. Ren, *Inorg. Chem.*, 2005, **44**, 6521.
19 T. Yoshimura, T. Ikai, T. Takayama, T. Sekine, Y. Kino and A. Shinohara, *Inorg. Chem.*, 2010, **49**, 5876.
20 Y. Tooyama, A. Harano, T. Yoshimura, T. Takayama, T. Sekine, H. Kudo and A. Shinohara, *J. Nucl. Radiochem. Sci.*, 2005, **6**, 153.
21 P. Kurz, B. Probst, B. Spingler and R. Alberto, *Eur. J. Inorg. Chem.*, 2006, 2966.