Inorg. Chem. **1992**, *31*, 4441–4443

Solution Fluorescence and Photoredox Reactions of Molybdenum(V) Oxo Complexes[1]

Abdul K. Mohammed and Andrew W. Maverick*

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803-1804

Received June 9, 1992

Electron-transfer reactions of photoexcited transition-metal complexes continue to attract attention, both as fundamental chemical processes and as potential routes toward photochemical energy storage and artificial photosynthesis.[2] A number of metal complexes have been used as redox photosensitizers.[3] However, with few exceptions,[4] only *phosphorescent* excited states (i.e. with spin multiplicities different from those of the ground states) have lifetimes long enough for bimolecular redox reactions.[5] We now report that molybdenum(V) oxo complexes *fluoresce* in solution at room temperature, yet with lifetimes sufficient for photoredox reactions. These results suggest that a large group of oxo-d^1 species will be useful for solution photochemical study.

Figure 1 shows the room-temperature electronic absorption and fluorescence spectra for $Mo^VOCl_4(CH_3CN)^-$ and $Mo^VOBr_4(CH_3CN)^-$ [6] in CH_3CN solution. Data for these and other oxo-d^1 complexes are summarized in Table I.[7] The lowest-energy absorption bands in these complexes are attributable to $^2B_2 \rightarrow {}^2E$;[8,9] we assign the fluorescences to $^2E \rightarrow {}^2B_2$.[10,11]

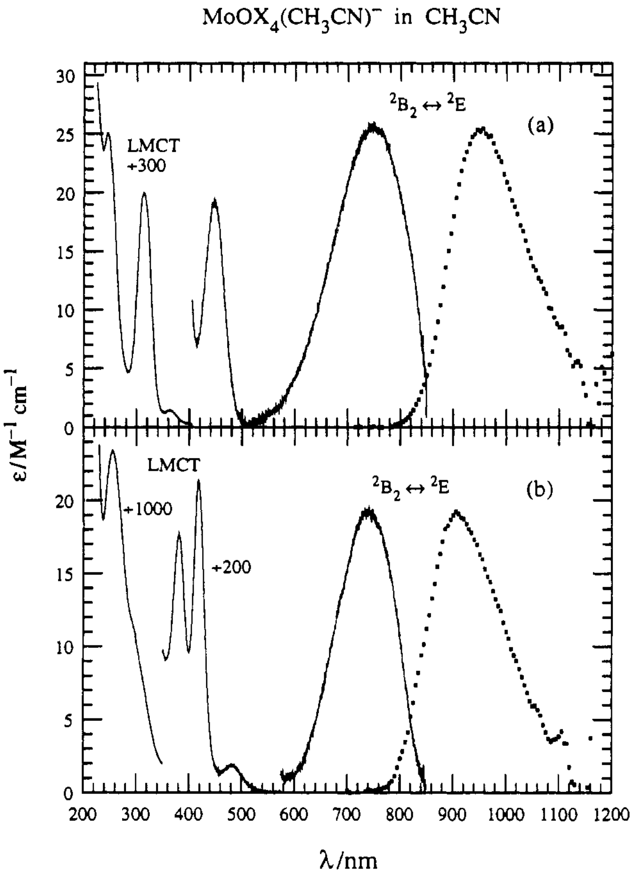


Figure 1. Electronic absorption (—) and corrected fluorescence (• • •) spectra for (a) $MoOCl_4(CH_3CN)^-$ and (b) $MoOBr_4(CH_3CN)^-$ in CH_3CN at room temperature. The fluorescence spectra were recorded using (a) 0.044 M and (b) 8.7×10^{-4} M solutions, with excitation at 436 nm and 15-nm emission bandpass.

The d^1 systems Ti^{3+} [12] and $Mo^VOX_4^-$ (X = Cl, Br)[13] have been reported to fluoresce but only in the solid state. (Winkler found no emission from solutions of $Mo^VOCl_4^-$ in noncoordinating solvents.[13] In our experiments, $(Bu_4N)[MoOCl_4]$ fluoresces in CH_2Cl_2 solution but much more weakly than $Mo^VOCl_4L^-$.)

Oxomolybdenum(V) complexes containing the chelating $Me_3[9]aneN_3$ [14] and $HB(Me_2pz)_3^-$ [15] ligands also fluoresce in solution; see Table I and spectra in the supplementary material.

---

(1) Presented in part at the Fourth Chemical Congress of the North American Continent, New York, NY; Aug 1991; Abstract No. INOR 343.

(2) (a) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401–449. (b) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 364–370.

(3) Hoffman, M. Z.; Bolletta, F.; Moggi, L.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1989**, *18*, 219–543.

(4) Redox reactions of fluorescent excited states have been reported for (a) $Re_2Cl_8^{2-}$ (Nocera, D. G.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7349–7350. Nocera, D. G.; Gray, H. B. *Inorg. Chem.* **1984**, *23*, 3686–3688) and (b) Ce^{3+} (Asbury, R. P.; Hammond, G. S.; Lee, P. H. P.; Poulos, A. T. *Inorg. Chem.* **1980**, *19*, 3461–3465).

(5) Electron spin becomes a poorer quantum number with heavier central metal atoms. However, even in third-row systems such as $Os(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine), the emissions are primarily phosphorescence: Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 3877–3886. In contrast, in the present oxo-d^1 systems, only doublet states are accessible, making phosphorescence impossible.

(6) $(Bu_4N)[MoOX_4(H_2O)]$ complexes were prepared by the methods of Bino and Cotton (*J. Am. Chem. Soc.* **1979**, *101*, 4150–4154; *Inorg. Chem.* **1979**, *18*, 2710–2713), using $(Bu_4N)X$ as a precipitant. They are also obtained on heating $HB(Me_2pz)_3Mo(CO)_3^-$ (Me_2pzH = 3,5-dimethylpyrazole) (Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 6288–6294; *J. Am. Chem. Soc.* **1969**, *91*, 588–595) under reflux for 24 h in concentrated HX(aq), followed by addition of excess $(Bu_4N)X$. The H_2O ligands are retained in CH_2Cl_2 solution, but dissolution in CH_3CN immediately produces $Mo^VOX_4(CH_3CN)^-$. $Mo^VOX_4(CH_3CN)^-$, $Mo^VOX_4(H_2O)^-$, and $Mo^VOX_4^-$ [9b,13] are readily distinguished in solution by their electronic absorption spectra.

(7) Emission spectra were recorded by using a Model F112X Spex Fluorolog 2 spectrophotometer, with Ge photodiode ($HB(3,5\text{-}Me_2pz)_3Mo^VOCl_2$) or Hamamatsu R406 PMT (all others) as detector and were corrected for detector response and differences in refractive indices (Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991–1024. Parker, C. A.; Rees, W. T. *Analyst* **1960**, *85*, 587–600). Quantum yields were measured in deoxygenated solution, by comparison with $Ru(bpy)_3^{2+}$(aq) (Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4853–4858). Lifetimes were measured using Nd:YAG (355 nm, 10 ns) excitation, with deconvolution from the laser pulse response function (Demas, J. N. *Excited State Lifetime Measurements*; Academic: New York, 1983; pp 149–153).

(8) Winkler, J. R.; Gray, H. B. *Comments Inorg. Chem.* **1981**, *1*, 257–263. Gray, H. B.; Hare, C. R. *Inorg. Chem.* **1962**, *1*, 363–368. Ballhausen, C. J.; Gray, H. B. *Inorg. Chem.* **1962**, *1*, 111–122.

(9) (a) Collison, D. *J. Chem. Soc., Dalton Trans.* **1990**, 2999–3006. (b) Garner, C. D.; Hill, L. H.; Mabbs, F. E.; McFadden, D. L.; McPhail, A. T. *J. Chem. Soc., Dalton Trans.* **1977**, 853–858. (c) Garner, C. D.; Hill, L. H.; Mabbs, F. E.; McFadden, D. L.; McPhail, A. T. *J. Chem. Soc., Dalton Trans.* **1977**, 1202–1207.

(10) Although the complexes with chelating ligands (see Table I) do not have full C_{4v} symmetry, we have used the C_{4v} notation for simplicity.

(11) Recent single-crystal MCD spectroscopic studies (Carducci, M. D.; Enemark, J. H.; Solomon, E. I. *Abstracts of Papers*, 203rd National Meeting of the American Chemical Society, San Francisco, CA, April 1992; American Chemical Society: Washington, DC, 1992; Abstract No. INOR 513) suggest that the lowest-energy absorption band in some oxomolybdenum(V) systems may be composite, possibly including a charge-transfer component in addition to $^2B_2 \rightarrow {}^2E$. However, we believe the fluorescence of $MoOX_4L^-$ is essentially localized on the MoO^{3+} unit, since its energy is nearly invariant with X.

(12) Krasser, W.; Koglin, E.; Wiedemann, E.; Brocke, W. A. *Z. Naturforsch, A* **1972**, *27a*, 1119–1123. Gächter, B. F.; Koningstein, J. A. *J. Chem. Phys.* **1974**, *60*, 2003–2006.

(13) Winkler, J. R. Ph.D. Thesis, California Institute of Technology, 1984.

(14) $Me_3[9]aneN_3$ = 1,4,7-trimethyl-1,4,7-triazacyclononane: Backes-Dahmann, G.; Herrmann, W.; Wieghardt, K.; Weiss, J. *Inorg. Chem.* **1985**, *24*, 485–491.

0020-1669/92/1331-4441$03.00/0

Table I. Room-Temperature Fluorescence of Molybdenum(V) Oxo Complexes

complex	medium	λ_{max}/nm ($^2B_2 \leftrightarrow {}^2E$) absorption	fluorescence	Φ_f[a]	τ/ns[a,b]
$MoOCl_4(CH_3CN)^-$	CH_3CN	750	950	4.4×10^{-4}	110
$MoOBr_4(CH_3CN)^-$	CH_3CN	740	905	1.4×10^{-4}	50
$MoOCl_4(H_2O)^-$	CH_2Cl_2	720	950	8.7×10^{-5}	60
$MoOBr_4(H_2O)^-$	CH_2Cl_2	720	900	2.8×10^{-5}	25
$MoOCl_4^-$	crystal	650	890		160[c]
$[(Me_3[9]aneN_3)MoOBr_2]^+$	CH_3CN	665, 780 sh	970		
$[(Me_3[9]aneN_3)MoOI_2]^+$	CH_3CN	662[d]	990		
$HB(Me_2pz)_3MoOCl_2$	CH_2Cl_2	705	1170		

[a] Lifetimes and quantum yields ±20%. Fluorescence from $[(Me_3[9]aneN_3)MoOX_2]^+$ and $HB(Me_2pz)_3MoOCl_2$ was too weak for lifetime or quantum yield determination. [b] Average of values determined in emission and transient absorption. [c] Reference 13. [d] The relatively high intensity of this band (ϵ 1450 M^{-1} cm^{-1}) suggests substantial LMCT character.

We anticipated that these complexes might be more stable than $Mo^VOX_4(L)^-$ and, thus, show more intense and longer-lived fluorescence.[16] Surprisingly, the opposite is true: the emission from these chelates is much weaker than that from the $Mo^VOX_4(L)^-$ species.

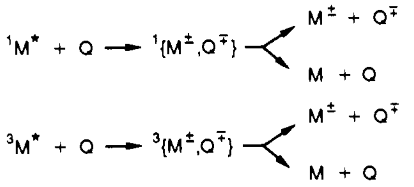
The emissive excited states of these complexes can be characterized further by their transient-absorption spectra. Immediately following 355-nm irradiation, CH_3CN solutions of $Mo^VOX_4(CH_3CN)^-$ show broad absorption in the 370–420-nm (X = Cl) and 450–600-nm (X = Br) regions. These signals decay exponentially, with lifetimes similar to those observed in emission. The transients are attributable to halide-to-metal charge-transfer transitions, as judged by their intensity and by the pronounced red shift for X = Br.

We also carried out cyclic voltammetry experiments on $Mo^VOX_4(CH_3CN)^-$; these revealed one-electron oxidation and reduction processes.[17] This combination of photophysical and redox properties led us to explore excited-state redox reactions, such as

$$Mo^VOX_4(CH_3CN)^{-*} + A \rightarrow Mo^{VI}OX_4(CH_3CN) + A^- \qquad (1)$$

(A = electron acceptor). The fluorescence of the ions in CH_3CN is quenched by the one-electron acceptors tetracyanoethylene (TCNE) and chloranil. Flash irradiation of these mixtures leads to transient-absorption signals attributable to the acceptor radical anions,[18] as expected according to reaction 1. (With $MoOCl_4(CH_3CN)^-$ and chloranil, for example, the excited-state quenching and back-electron-transfer rate constants are 2.1 (2) $\times$ 10^8 and 3.4 (6) $\times$ 10^9 M^{-1} s^{-1}, respectively.) With electron-donor quenchers, photochemical reduction of $Mo^VOX_4(CH_3CN)^-$ is observed.[19]

Both fluorescent and phosphorescent excited states can react with one-electron redox quenchers Q. (These are denoted as $^1M^*$ and $^3M^*$, respectively, in reactions 2a,b and 3a,b, reflecting the predominance of chromophores with diamagnetic ground states in both organic and inorganic systems.)



$$^1M^* + Q \rightarrow {}^1\{M^\pm,Q^\mp\} \rightarrow M^\pm + Q^\mp \qquad (2a)$$
$$^1\{M^\pm,Q^\mp\} \rightarrow M + Q \qquad (2b)$$
$$^3M^* + Q \rightarrow {}^3\{M^\pm,Q^\mp\} \rightarrow M^\pm + Q^\mp \qquad (3a)$$
$$^3\{M^\pm,Q^\mp\} \rightarrow M + Q \qquad (3b)$$

The yield of separated electron-transfer products from singlet excited states (eq 2a) is often low, because of rapid back-electron-transfer (eq 2b) within the $^1\{M^\pm,Q^\mp\}$ complex.[2a,20] A variety of schemes have been employed to make charge separation more efficient; most focus on making reactions 2b and 3b slower. Perhaps the most frequently used is a spin conversion barrier, as in eq 3: if the triplet excited state is involved, then eq 3b is spin-forbidden. Also, back-electron-transfer can be made slower if it occurs in the Marcus "inverted region".[21] Finally, if the charges on the sensitizer and quencher are such that the products are of like charge, they can separate more quickly, inhibiting back-electron-transfer.[4a,22] This principle has been demonstrated with fluorescent doublet states as well.[4b,23] Our experiments extend these conditions by showing that separation of neutral and anionic products can follow fluorescence quenching in transition-metal systems:

$$Mo^VOX_4(CH_3CN)^- \,(^2E) + A \rightarrow Mo^{VI}OX_4(CH_3CN) + A^-$$

In summary, oxomolybdenum(V) complexes fluoresce in solution at room temperature, and several of them possess long-lived excited states that are suitable for bimolecular redox reactions. We are now studying further the scope of luminescence in these and other oxo-d^1 species. A comparison with d^2 metal-oxo and -nitrido complexes[24] will be of interest, in terms of the relative reactivity of structurally similar doublet and triplet excited states. Also, it may be possible to combine the Mo^V photoredox reactions with the photoactivity we have already demonstrated for Mo^{III} [25,26] to achieve overall two-electron photochemical catalytic cycles.

Acknowledgment. We are grateful to Professor Russell H. Schmehl (Tulane University) for numerous helpful discussions

---

(15) Trofimenko, S. *Inorg. Chem.* **1971**, *10*, 504–507. Lincoln, S. E.; Koch, S. A. *Inorg. Chem.* **1986**, *25*, 1594–1602. Lincoln, S. E.; Loehr, T. M. *Inorg. Chem.* **1990**, *29*, 1907–1915.

(16) For example, the phosphorescence of $Ru(bpy)_2(py)_2^{2+}$ (py = pyridine) is much weaker than that of its fully chelated counterpart, $Ru(bpy)_3^{2+}$: Wacholtz, W. M.; Auerbach, R. A.; Schmehl, R. H.; Ollino, M.; Cherry, W. R. *Inorg. Chem.* **1985**, *24*, 1758–1760.

(17) In CH_3CN, quasireversible Mo^{VI}/Mo^V oxidation waves appear at 0.55 V (X = Cl) and 0.60 V (X = Br) vs Fc^+/Fc (Fc = ferrocene). Reduction waves (Mo^V/Mo^{IV}) appear at ca. -0.85 V vs Fc^+/Fc for both complexes.

(18) Webster, O. W.; Mahler, W.; Benson, R. E. *J. Am. Chem. Soc.* **1962**, *84*, 3678–3684. André, J. J.; Weill, G. *Mol. Phys.* **1968**, *15*, 97–99. Solutions of $Mo^VOX_4(CH_3CN)^-$ in the presence of the acceptors are stable in the dark. We also observe no spectroscopic evidence for ground-state complex formation in these experiments.

(19) Irradiation of $Mo^VOX_4(CH_3CN)^-$ and *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine (TMPD) leads to transient-absorption signals characteristic of $TMPD^+$. However, these experiments are complicated by the formation of a TMPD–$Mo^VOX_4(CH_3CN)^-$ charge-transfer complex. We are now exploring the use of less strongly reducing quenchers for Mo^V.

(20) Fox, M. A. *Adv. Photochem.* **1986**, *13*, 237–272. For examples with fluorescent metal complexes, see: Nahor, G. S.; Rabani, J. *J. Phys. Chem.* **1985**, *89*, 2468–2472. Fukuzumi, S.; Nishizawa, N.; Tanaka, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 709–714.

(21) Todd, W. P.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R. *J. Am. Chem. Soc.* **1991**, *113*, 3601–3602. Gould, I. R.; Ege, D.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1987**, *109*, 3794–3796.

(22) Harriman, A.; Porter, G.; Richoux, M.-C. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1175–1187. Holten, D.; Windsor, M. W.; Parson, W. W.; Gouterman, M. *Photochem. Photobiol.* **1978**, *28*, 951–961.

(23) Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396–4403. Johnston, L. C.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6368–6372.

(24) Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 1373–1374. Winkler, J. R.; Gray, H. B. *Inorg. Chem.* **1985**, *24*, 346–355. Thorp, H. H.; Van Houten, J.; Gray, H. B. *Inorg. Chem.* **1989**, *28*, 889–892. Neyhart, G. A.; Bakir, M.; Boaz, J.; Vining, W. J.; Sullivan, B. P. *Coord. Chem. Rev.* **1991**, *111*, 27–32.

(25) Yao, Q.; Maverick, A. W. *J. Am. Chem. Soc.* **1986**, *108*, 5364–5365.

(26) Mohammed, A. K.; Maverick, A. W. Submitted for publication.

and for assistance with measuring luminescence lifetimes. This research was supported by grants from the National Science Foundation (CHE-8601008) and the Louisiana Educational Quality Support Fund (LEQSF(1990-92)-RD-A-06) administered by the Louisiana Board of Regents. Some of the experiments and data analyses were performed at the Center for Fast Kinetics Research, which is supported jointly by grants from the Biomedical Research Technology Program of the Division of Research Resources of the National Institutes of Health (RR00886) and by The University of Texas at Austin.

Supplementary Material Available: Figures showing electronic absorption and fluorescence spectra for $[(Me_3[9]aneN_3)MoOBr_2]^+$, $[(Me_3[9]aneN_3)MoOI_2]^+$, and $HB(Me_2pz)_3MoOCl_2$ (3 pages). Ordering information is given on any current masthead page.