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Near-Infrared Luminescence of Octahedral Molybdenum(III) and Rhenium(IV) Complexes in Solution

Sir:

In recent years, the redox properties of excited states of transition-metal complexes have received widespread attention,[1] owing in part to the possibility of using the complexes as sensitizers for redox transformations of organic and inorganic substrates. However, most of the reactions involve the transfer of only one electron; as a result, the photogenerated species usually react only slowly with substrate molecules. In order to adapt excited-state processes to the generation of multielectron oxidants and reductants, we have examined systems in which an initial photoredox step is followed by a second, spontaneous electron transfer.[2,3] We have focused on early-transition-metal complexes because their stable complexes are found with the photophysically attractive d^3 electronic configuration[4] as well as with several adjacent oxidation states. We now report photophysical and photochemical studies of three such complexes, $Mo(NCS)_6^{3-}$, $MoCl_6^{3-}$, and $ReCl_6^{2-}$, including the first observations of luminescence from these ions in solution at room temperature.

Energy diagrams for the low-lying electronic states of Al_2O_3:Cr^{3+} (ruby),[5] $MoCl_6^{3-}$,[6,7] and $ReCl_6^{2-}$ [8,9] are presented in Figure 1. In all three cases, the ground state is $^4A_{2g}$ and the lowest excited states are ^2E_g and $^2T_{1g}$. (Splitting of the $^2T_{1g}$ and $^2T_{2g}$ states due to spin–orbit coupling is especially apparent in $ReCl_6^{2-}$.[8,9]) The major change in the diagram between ruby and the Mo and Re complexes is the inversion of the $^4T_{2g}$ and $^2T_{2g}$ levels: the ratio of ligand-field strength to interelectronic repulsion is so great for second- and third-row metals, even with weak-field ligands, that all three doublet states lie below $^4T_{2g}$.

We have used a luminescence spectrophotometer optimized for detection in the 1000–1500-nm range[10] to record, for the first time, the phosphorescence spectra for the Mo and Re complexes in solution at room temperature. The results are summarized in

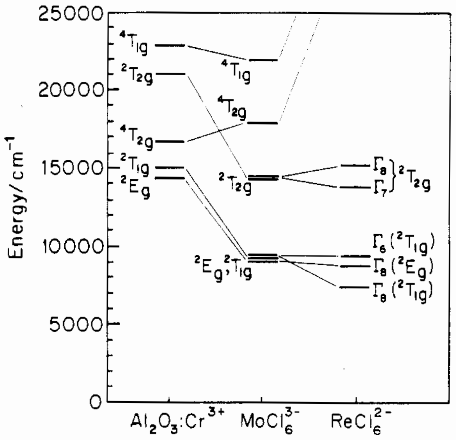

Figure 1. Energy diagrams for ruby (Al_2O_3:Cr^{3+}), $MoCl_6^{3-}$, and $ReCl_6^{2-}$. Equilibrium energies of $^4T_{1g}$ for ruby and $^4T_{2g}$ and $^4T_{1g}$ for $MoCl_6^{3-}$ are estimated from the low-energy "tails" of the corresponding absorption bands; all others are spectroscopic (0–0) energies.[5-9]

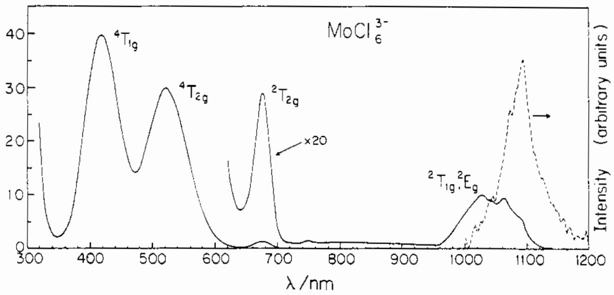

Figure 2. Electronic absorption (—) and near-infrared emission (- -; uncorrected) spectra for 0.05 M K_3MoCl_6 in concentrated HCl(aq) (with 0.1 M $SnCl_2$ added to inhibit oxidation of $MoCl_6^{3-}$) at room temperature.

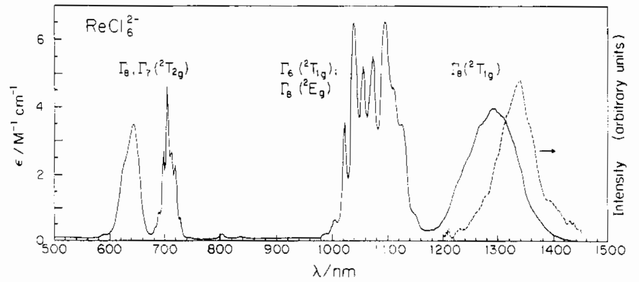

Figure 3. Electronic absorption (—) and near-infrared emission (- -; uncorrected) spectra for 0.1 M $(Bu_4N)_2ReCl_6$ in CH_3CN at room temperature.

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Table I. Luminescence and Transient Absorption Data for Octahedral Molybdenum(III) and Rhenium(IV) Complexes[a]

complex	λ_{exc}	λ_{em}	τ_{em}	λ_{abs}	τ_{abs}
$Mo(NCS)_6^{3-}$[b]	355	1350	760	420	800
	835			425	760
	1279			475	760
$MoCl_6^{3-}$[c]	532	1095	480	340	550
$ReCl_6^{2-}$[d]	355	1330	130		
	620	1340	140	420	140

[a] Abbreviations: exc = excitation, em = emission, abs = transient absorption. Wavelengths are given in nm and lifetimes (±10%) in ns. Excitation was via Nd:YAG laser (532, 355 nm) or Nd:YAG-pumped dye laser (620 nm, with H_2 Raman shifter to generate 835 and 1279 nm). [b] $K_3Mo(NCS)_3 \cdot 4H_2O$ in CH_3CN. [c] K_3MoCl_6 in 6 M HCl/saturated aqueous LiCl (1:1 v/v). [d] $(Bu_4N)_2ReCl_6$ in CH_3CN. The emission maximum is red-shifted slightly by self-absorption in the experiments involving 620-nm excitation, because they require substantially more concentrated solutions of $(Bu_4N)_2ReCl_6$.

Table I; Figures 2 and 3 show the absorption and emission spectra for $MoCl_6^{3-}$ and $ReCl_6^{2-}$ respectively. (The absorption spectrum of $Mo(NCS)_6^{3-}$ in CH_3CN has been reported in ref 2.) The overlap of the absorption and emission spectra can be used to estimate the equilibrium energy of the lowest lying excited state in $Mo(NCS)_6^{3-}$ (7700 cm^{-1}): to our knowledge, an experimental measurement of this energy has not been reported previously. (Excited-state energies obtained for $MoCl_6^{3-}$ and $ReCl_6^{2-}$ by this procedure, 9200 and 7600 cm^{-1} respectively, are in agreement with the high-resolution spectroscopic results of Flint and co-workers.[6,9]) The excitation spectra for these luminescences are very similar to the corresponding absorption spectra. With $ReCl_6^{2-}$, for example, the excitation spectrum for luminescence at 1340 nm shows vibrational structure in the 600–750-nm ($\Gamma_8(^4A_{2g}) \rightarrow \Gamma_7,\Gamma_8(^2T_{2g})$) and 1000–1250-nm ($\Gamma_8(^4A_{2g}) \rightarrow \Gamma_8(^2T_{1g}),\Gamma_8(^2E_g)$) regions comparable to that observed in the absorption spectrum.

The low-lying doublet states in strong-field d^3 complexes are ordinarily relatively long-lived because of the small changes in geometry that accompany the intraconfigurational transitions $\{^2T_{1g},^2E_g\} \rightarrow {}^4A_{2g}$.[4] Excited-state lifetimes well above 1 μs have been observed for $MoCl_6^{3-}$[7] and $ReCl_6^{2-}$[8a] in the solid state. We have now also measured the lifetimes of the lowest excited states for all three complexes in solution, using both emission (τ_{em}; see Table I) and transient absorption techniques (τ_{abs}).[11]

Our previous study of $Mo(NCS)_6^{3-}$[2] showed that the complex is capable of efficient excited-state redox reactions. The new data reported here represent direct measurements of the redox-active state of $Mo(NCS)_6^{3-}$; comparable photophysical properties are now established for the other two ions as well. We have demonstrated by flash kinetic experiments,[12] for example, that photooxidation of $ReCl_6^{2-}$ can be accomplished by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ):

$$ReCl_6^{2-} + DDQ \xrightarrow{h\nu} ReCl_6^{-} + DDQ^{-}$$

The luminescence lifetimes for $ReCl_6^{2-}$ and $Mo(NCS)_6^{3-}$ are reduced in the presence of DDQ and 1,4-dinitrobenzene respectively.[13] Thus, our results from flash irradiation of these two complexes are now confirmed in separate luminescence measurements.

The experiments reported herein strongly suggest that a variety of second- and third-row d^3 complexes will lend themselves readily to photophysical as well as photochemical study. Several aspects of these new photochemical systems are currently under investigation: We are examining the possibility of a spontaneous second electron transfers following initial photoredox processes in $ReCl_6^{2-}$ and $MoCl_6^{3-}$. Also, both our previous study of $Mo(NCS)_6^{3-}$[2] and flash-photolysis experiments now in progress with other acceptors and $ReCl_6^{2-}$[12] suggest that upper excited states may be sufficiently long-lived in these solutions to undergo independent bimolecular redox reactions.

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Registry No. $Mo(NCS)_6^{3-}$, 35215-16-8; $MoCl_6^{3-}$, 15203-34-6; $ReCl_6^{2-}$, 16871-50-4.

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[10] The photomultiplier detector from a Spex Fluorolog 2 Model F112X instrument was replaced with a Ge photovoltaic detector (77 K; Judson J16-D, 2 mm diameter); the emission spectral bandwidth in Figures 2 and 3 was ca. 10 nm. For phosphorescence lifetime measurements, the same detector was used with a Quantel Datachrom 5000 Nd:YAG laser, except that the detector was operated at room temperature (response time <100 ns). Comparison of our lifetimes in solution with those for solids containing $MoCl_6^{3-}$[7] and $ReCl_6^{2-}$ suggests that phosphorescence quantum yields are $<10^{-3}$ in all of our experiments.

[11] Deviations in the order of observed luminescence lifetimes from that expected on the basis of the energy-gap law (see, for example: Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 2444–2453) may be due to differences in solvents and accessible vibrational modes and in the nature of the lowest energy excited states among the three complexes.

[12] Lord, M. D.; Henderson, L. J., Jr.; Maverick, A. W., unpublished work.

[13] The lifetime quenching can only be measured qualitatively with the present apparatus, because both luminescence signals are relatively weak and, in the case of $ReCl_6^{2-}$, because the measured lifetime is close to the response time of the Ge detector.

Kinetics of Hydrolysis of the Chlorosulfate Ion

Sir:

Chlorosulfuric acid ($ClSO_3H$) is a very strong acid that reacts explosively when mixed with water.[1] This has prevented use of chlorosulfuric acid to measure the rate of hydrolysis of the chlorosulfate ion. Recent studies by the pulsed-accelerated-flow method[2,3] show that the reaction between HOCl and SO_3^{2-} is extremely rapid (1.6×10^9 M^{-1} s^{-1} at 25.0 °C).[4] This is 5 orders of magnitude faster than the reaction between OCl^- and SO_3^{2-}.[5] Although the latter reaction has been postulated to occur by oxygen atom transfer,[5] earlier attempts to measure ^{18}O exchange between sulfite and hypochlorous acid gave inconclusive results.[6] The magnitude of the HOCl rate constant and the evidence for Cl^+ transfer in the acid-assisted reactions[7] of NH_2Cl with SO_3^{2-} lead to the proposal that $ClSO_3^-$ is an intermediate for the HOCl reaction as well.[4] The Cl^+-transfer reaction corresponds to a nucleophilic attack by the sulfur of SO_3^{2-} on the chlorine of HOCl to eliminate OH^-.

Direct oxygen atom transfer (eq 1) would give immediate release of acid, whereas Cl^+ transfer will first release base (eq 2) and the subsequent hydrolysis of chlorosulfate will then release acid (eq 3). This study uses indicator reactions, which are

$$HOCl + SO_3^{2-} \rightarrow Cl^- + SO_4^{2-} + H^+ \tag{1}$$

$$HOCl + SO_3^{2-} \rightarrow OH^- + ClSO_3^- \tag{2}$$

$$ClSO_3^- + H_2O \xrightarrow{k_h} Cl^- + SO_4^{2-} + 2H^+ \tag{3}$$

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