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Thermally Driven Intramolecular Charge Transfer in an Oxo-Molybdenum Dithiolate Complex

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The synergistic interactions that can occur between transition metal ions and redox active ligands form the basis for a myriad of complex phenomena including facile redox behavior,[1−3] enzymatic catalysis,[4,5] novel optical properties,[6,7] and valence tautomerism.[8−20] A judicious choice of metal and ligand allows for the occurrence of accessible low-lying electronic states possessing considerable charge-transfer character. This metal−ligand redox interplay can, in principle, be exploited to construct novel molecular and molecule-based multiproperty materials. The fundamental goal is the ability to control these various properties and ultimately "switch" between them via an external perturbation. This is extremely important in the development of all-optical molecular switches[6] and molecular RAM devices. One of the most fascinating properties displayed by transition metal complexes possessing redox active ligands is valence tautomerism (redox isomerism). To date all of the complexes which display valence tautomerism have utilized ene-1,2-diolate (dioxolene) donors,[8,9] or their Schiff-base variants,[10,11] to facilitate a thermally induced intramolecular redox reaction utilizing the catecholato/semiquinonato couple. It has been stated that this redox interconversion is dependent upon a low degree of covalency in the M−L bonding scheme.[9] This initial qualifier for complexes which may display "valence tautomerism" was meant to describe a true metal−ligand electron-transfer process, where a full electron equivalent is transferred between the metal and ligand. Presumably, the metal and ligand wave functions must be localized to facilitate a discrete redox interconversion. However, metallodithiolates possess a *highly delocalized* bonding description[21−24] compared to the corresponding metallodiolates and therefore valence tautomerism has not been anticipated for this class of molecules. Here we show variable-temperature absorption data for the oxomolybdenum dithiolate complex $[\mathrm{MoO(qdt)_2}]$, (qdt = quinoxaline-2,3-dithiolate)$_2$], which clearly reveals the highly thermochromic nature of this compound. Although the observed thermochromism may be explained within the context of valence tautomerism we prefer a more general description, namely thermally driven intramolecular charge transfer, as this reflects more accurately the highly covalent nature of the Mo−S bonds[21−24] and the extreme noninnocence of the qdt ligand.[25,26] Herein, we discuss the unique properties of $[\mathrm{MoO(qdt)_2}]^-$ in terms of molecule-based switching devices and charge redistribution in the catalytic cycle of pyranopterin enzymes.

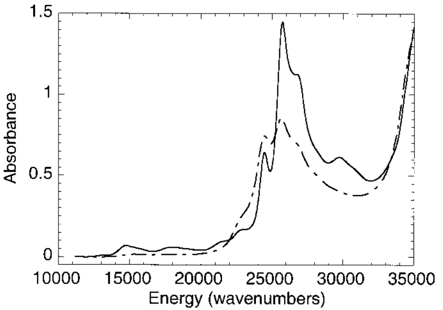

Figure 1. Electronic absorption spectra of $[\mathrm{Mo^VO(qdt)_2}]^-$ in a polystyrene film at 89 (solid line) and 292 K (dashed line).

Substoichiometric addition of ferrocenium hexafluorophosphate to a dry toluene:DMF (70:30) solution of the dark blue Mo(IV) compound $(\mathrm{PPh_4})_2[\mathrm{MoO(qdt)_2}]$ generates the one-electron oxidized $[\mathrm{MoO(qdt)_2}]^-$.[27] Bottle green $[\mathrm{MoO(qdt)_2}]^-$ is highly thermochromic, turning dark orange almost instantaneously upon submersion into liquid nitrogen.[28] The extent of the observed thermochromism is clearly evident in the variable-temperature electronic absorption spectra shown in Figure 1. The 89 K absorption spectrum displays two intense low-energy charge-transfer features at 14 750 and 18 000 cm^{-1}, and these bands are characteristic of all the $[\mathrm{Mo^VO(dithiolate)_2}]^-$ compounds we have studied to date.[24] The observation of magnetic circular dichroism

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(27) An approximate 2:1 mole ratio of $(\mathrm{PPh_4})_2[\mathrm{MoO(qdt)_2}]$ to ferrocenium hexafluorophosphate was used for the chemical oxidation. $[\mathrm{MoO(qdt)_2}]^-$ may also be prepared by aerial oxidation of $(\mathrm{PPh_4})_2[\mathrm{MoO(qdt)_2}]$, and both of these species have been fully characterized by mass spectrometry. The starting material, $(\mathrm{PPh_4})_2[\mathrm{MoO(qdt)_2}]$, was prepared from $\mathrm{H_2qdt}$ (see: Morrison, D. C.; Furst, A. *J. Org. Chem.* **1956**, *21*, 470−471) and $\mathrm{K_4[MoO_2(CN)_4]_6H_2O}$ using a method adapted from the synthesis of $[\mathrm{PPh_4}][\mathrm{MoO(1\text{-}(pyridin\text{-}2\text{-}yl)\text{-}ene\text{-}1,2\text{-}dithiolate)_2}]$ (see: Davies, E. S.; Beddoes, R. L.; Collison, D.; Dinsmore, A.; Docrat, A.; Joule, J. A.; Wilson, C. R.; Garner, C. D. *J. Chem. Soc., Dalton Trans.* **1997**, 3985−3995).

(28) The extinction coefficient of ferrocene is about 2 orders of magnitude lower than that of the $(\mathrm{PPh_4})_2[\mathrm{MoO(qdt)_2}]$ starting material. Residual $(\mathrm{PPh_4})_2[\mathrm{MoO(qdt)_2}]$ starting material undoubtedly contributes to the observed color, but not to any observed color *changes*.

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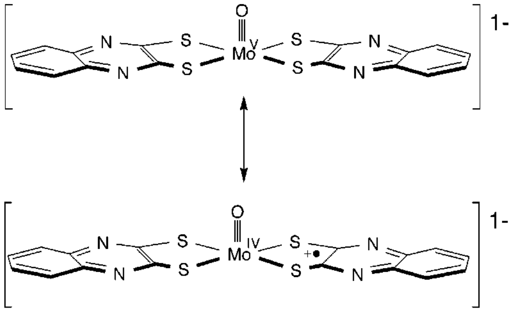
Scheme 1



(MCD) intensity (Figures S1 and S2, Supporting Information) at low temperature (5 K) confirms that the oxidized species is paramagnetic and is best described as $[\mathrm{Mo^{V}O(qdt)_2}]^-$. Furthermore, the one-to-one correspondence between the low-temperature absorption and MCD spectra below ~20 000 cm^{-1} (Figure S1) proves that the observed low-energy charge-transfer bands observed in the absorption spectra arise from a Mo(V) center with electronic configuration $(d_{xy})^1$. Detailed spectroscopic studies of mono-oxo Mo(V) complexes reveal an extremely large splitting of the metal t_{2g} orbitals.[21−24,29] These complexes possess empty $d_{xz,yz}$ acceptor orbitals that are highly destabilized due to their strong Mo≡O π^* antibonding character and lie 14 000−18 000 cm^{-1} to higher energy than the d_{xy} orbital. Thus, all the low-energy charge-transfer bands below ~20 000 cm^{-1} involve one-electron promotions to d_{xy}, and a combination of MCD, electronic absorption, and resonance Raman spectroscopies have been used to assign these bands as S→Mo d_{xy} charge-transfer transitions.[21−24,29]

The observation of tight isosbestic points in Figure 1 indicates that $[\mathrm{Mo^{V}O(qdt)_2}]^-$ interconverts with a single species as the temperature is increased. Interestingly, the low-energy S→Mo d_{xy} charge transfer transitions essentially disappear and the very intense bands at 26 800 and 25 700 cm^{-1} are attenuated by roughly half upon increasing the temperature. The latter transitions have been assigned as qdt $\pi\rightarrow\pi^*$ transitions due to their similarity with bands assigned in (L-*N*$_3$)$\mathrm{Mo^{V}O(qdt)}$.[22,23,30] The lack of low-energy S→Mo d_{xy} charge-transfer transitions in the high-temperature absorption spectrum is very similar to the low−energy spectra of $[\mathrm{Mo^{IV}O(dithiolate)_2}]^{2-}$ complexes, including $[\mathrm{Mo^{IV}O(qdt)_2}]^{2-}$.[31,32] Oxo-molybdenum(IV) complexes possess a $(d_{xy})^2$ electronic configuration and no S→Mo d_{xy} charge-transfer transitions are observed since the d_{xy} orbital is completely filled. Therefore, we propose that a thermally induced intramolecular electron/charge transfer (valence tautomeric) process is operable and responsible for the observed thermochromism. A thermally induced S→Mo d_{xy} charge transfer process would formally result in the conversion of $[\mathrm{Mo^{V}O(qdt)_2}]^-$ to the Mo(IV) species $[\mathrm{Mo^{IV}O(qdt{\cdot})(qdt)}]^-$, and this description is consistent with the attenuation of both the S→Mo d_{xy} charge transfer *and* the dianionic qdt $\pi\rightarrow\pi^*$ bands.The normalized intensity[33] of the 18 000 cm^{-1} band is plotted as a function of temperature in Figure 2, and the $[\mathrm{Mo^{V}O(qdt)_2}]^- \rightarrow [\mathrm{Mo^{IV}O(qdt^{\bullet})(qdt)}]^-$ interconversion is found to be very abrupt ($\Delta T \sim 25$ K) with a $T_{1/2}$ near room temperature (270 K). Since low-energy S→Mo d_{xy} charge transfer transitions are only observed for $[\mathrm{Mo^{V}O(qdt)_2}]^-$, the intensity of this band is directly proportional to the mole fraction ($f_{\mathrm{MO^V}}$) of $[\mathrm{Mo^{V}O(qdt)_2}]^-$ present at a given temperature and the thermodynamic parameters for the thermally induced charge-transfer process may be obtained by fitting the data in Figure 2 to eq 1 . It is clear that this

$$\text{absorption intensity} \propto f_{\mathrm{Mo^V}} = \frac{1}{\exp(\Delta H/RT - \Delta S/R) + 1} \quad (1)$$

interconversion is entropically driven, and the best fit parameters for the $[\mathrm{Mo^{V}O(qdt)_2}]^- \rightarrow [\mathrm{Mo^{IV}O(qdt^{\bullet})(qdt)}]^-$ interconversion are $\Delta H = 74.5$ kJ·mol^{-1} and $\Delta S = 264$ J·K^{-1}·mol^{-1}. This is a relatively large entropic term which falls between that determined for the solid and solution state interconversion of $[\mathrm{Co^{III}(N{-}N)(CAT)_2}]$ and $[\mathrm{Co^{III}(N{-}N)(CAT)(SQ)}]$.[8,11] The origin of this entropic term undoubtedly arises from distortions along Mo−S and intraligand qdt normal modes that occur as a result of the thermally induced charge redistribution.

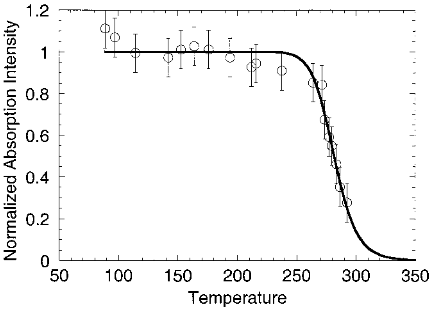
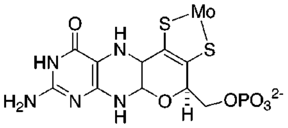


Figure 2. Temperature vs intensity plot for the band at 18 000 cm^{-1}. The solid line represents the best fit of the data to eq 1. The best fit parameters are $\Delta H = 74.5$ kJ·mol^{-1} and $\Delta S = 264$ J·K^{-1}·mol^{-1}.

The observed thermochromism in $[\mathrm{MoO(qdt)_2}]^-$ is most consistent with an induced intramolecular charge transfer between Mo and at least one of the qdt ligands. Therefore, $[\mathrm{MoO(qdt)_2}]^-$ represents the first example of valence tautomerism in a Mo complex and the first example exploiting the inherent redox activity of a dithiolate ligand. Prior to this study valence tautomeric behavior had only been observed in complexes which utilize the catecholato/semiquinonato couple, and it has been suggested that weak metal−ligand bond covalency is a necessary criterion for this interconversion. However, this does not appear to be the case in $[\mathrm{MoO(qdt)_2}]^-$, as the Mo−S bonds are *very* covalent. The results of this study may be significant with respect to the role of the pyranopterin cofactor in various Mo enzymes.



Although the pyranopterin is not covalently linked to the protein, an extensive hydrogen bonding network anchors the cofactor to the protein.[34,35] Therefore, the pyranopterin may function as a transducer, transferring vibrational energy associated with protein conformational changes directly to the active site. This would have the overall effect of mediating substantial charge redistribution at the active site and facilitating crucial atom transfer and electron-transfer processes. Finally, materials based on $[\mathrm{MoO(qdt)_2}]^-$ should possess the desired properties of a molecular switch, namely an abrupt interconversion between two accessible states at ambient temperature.

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Supporting Information Available: Figure S1 (overlay of the 5K/7T MCD and 89 K absorption of $[\mathrm{Mo^{V}O(qdt)_2}]^-$ acquired in a polystyrene thin film) and Figure S2 (MCD spectrum of $[\mathrm{Mo^{V}O(qdt)_2}]^-$ acquired in a 70:30 toluene:DMF glass); collectively, the spectra show spectral features consistent with the presence of a $[\mathrm{Mo^{V}O(dithiolate)_2}]^-$ species (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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