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A Green Heteropoly Blue: Isolation of a Stable, Odd Oxidation Level in a Dawson Molybdate Anion, $[S_2Mo_{18}O_{62}]^{5-}$

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Four consecutive and reversible one-electron reduction processes are observed as the initial reduction steps in the voltammetry of α-$[S_2Mo_{18}O_{62}]^{4-}$ in acetonitrile. This contrasts with the initial four reversible two-electron two-proton reduction processes identified previously in acidified acetonitrile. The one- and two-electron reduction products in acetonitrile have been isolated as the green and blue salts, $(Bu^n_4N)_5[S_2Mo_{18}O_{62}]$ and $(Bu^n_4N)_6[S_2Mo_{18}O_{62}]$ respectively. The disproportionation constant for $[S_2Mo_{18}O_{62}]^{5-}$ has been estimated ($K_{dis} = 8.8 \times 10^{-5}$) and indicates less than 1% disproportionation in acetonitrile solution. In the presence of aqueous acid, $[S_2Mo_{18}O_{62}]^{5-}$ readily disproportionates to give equal concentrations of $[S_2Mo_{18}O_{62}]^{4-}$ and protonated $[S_2Mo_{18}O_{62}]^{6-}$. The microcrystalline EPR spectrum at 253 K (−20 °C) of $(Bu^n_4N)_5[S_2Mo_{18}O_{62}]$ displays at least 91 lines due to hyperfine interaction with the ^{95,97}Mo nuclei ($I = {}^5/_2$; 25.5 atom %). A number of isotopomers contribute to the observed spectrum. These observations, together with the dependence of the EPR linewidth on temperature (E_a, 0.0045 eV), are consistent with intramolecular thermal delocalization of the odd "green" electron over all of the molecular framework in the temperature range 77–253 K. Above 253 K, the temperature dependence increases by a factor of about 20 (E_a, 0.087 eV). This observation is consistent with an intermolecular hopping process at the higher temperatures.

Introduction

There has been a great deal of interest in the redox behavior of heteropolyoxometalates and their ability to form "heteropoly blues" upon reduction.[1,2] In the absence of acid, consecutive reductions usually involve one-electron transfers.[1–11] In the presence of acid, electrons are usually transferred in even numbers due to stabilization of these species by protonation. One-electron reduced heteropolyanions are represented as Robin and Day class II mixed valence species[12] with a thermally mobile electron which can "hop" between the MO_6 octahedra.[1–10,13–15] It is this thermal mobility which accounts for rapid rates of intramolecular electron transfer.[8]

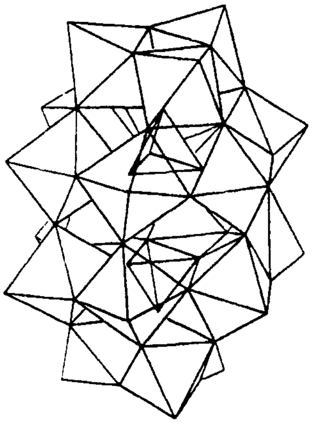

Figure 1. Polyhedral representation of α-$[S_2Mo_{18}O_{62}]^{4-}$. Reprinted with permission from ref 24. Copyright 1989 Royal Society of Chemistry. In the β form, the capping unit of three octahedra is rotated by 60° relative to the rest of the molecule.

In contrast to the above behavior, one class of heterpoly blues commonly has exhibited even oxidation states only. The Dawson anions, α,β-$[X_2Mo_{18}O_{62}]^{6-}$ (X = P, As) (Figure 1), are highly unstable towards disproportionation, so that even in the absence of acid, the two-electron reduction product only is formed.[1,2,16,17] Puckering of the two central Mo_6 rings within these anions[18] reduces the overall point symmetry from a possible D_{3h} to D_3, which in turn gives rise to chirality[19] and even optical activity.[20] Several studies have justified the absence of a stable one-electron state in terms of a loss of this chirality.[20,21] However, interestingly, electrochemical reduction of $P_2Mo_{18}O_{62}{}^{6-}$ in dimethylformamide[22] exhibits evidence for a transient one-electron reduced species, when $Bu^n_4NBF_4$ is used as the supporting electrolyte. When Na^+ is used as the electrolyte cation, the usual reversible two-electron process is observed, so that ion pairing with Na^+ appears to favor disproportionation.

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Recently the synthesis of the new Dawson heteropolyanion α-$[S_2Mo_{18}O_{62}]^{4-}$ was reported.[23] The X-ray structure of the Et_4N^+ salt indicates that it has D_3 symmetry (Figure 1) and is isostructural with α-$[P_2Mo_{18}O_{62}]^{6-}$.[24] Unlike α-$[P_2Mo_{18}O_{62}]^{6-}$, however, the anion displays no optical activity.[24] Electrochemistry for $[S_2Mo_{18}O_{62}]^{4-}$ was examined in acetonitrile in the presence of aqueous $HClO_4$ and indicated that the first four reduction steps involve two-electron transfers.[25] More recently work in these and other laboratories[26,27] has demonstrated that one-electron processes occur in the absence of aqueous perchloric acid. In the present investigation, we report the synthesis of the one-electron-reduced species $[S_2Mo_{18}O_{62}]^{5-}$ and its temperature-dependent EPR signal. This is the first report of a stable isolated odd oxidation level in a Dawson polyoxomolybdate anion.

Experimental Section

Reagents. Sodium molybdate (BDH, AR grade), 70% perchloric acid (BDH, Aristar grade), tetra-*n*-butylammonium and tetra-*n*-hexylammonium perchlorates (Southwestern Analytical, electrometric grade), and sulfuric acid (May and Baker, AR grade) were used as received. The acetonitrile (Mallinckrodt, Chrom AR HPLC grade) was purified as described previously.[28] The tetra-*n*-butylammonium and tetra-*n*-hexylammonium salts of α-$[S_2Mo_{18}O_{62}]^{4-}$ were synthesized via an extension[29] of procedures described previously.[23,25]

Instrumentation. All voltammograms were acquired using a Cypress Systems Model CYSY-1 Computer Controlled Electroanalysis System in the cyclic staircase mode. A single compartment cell with a conventional three-electrode arrangement was used: platinum or glassy carbon-disk working electrode, platinum-wire counter electrode, and an aqueous Ag/AgCl (3.0 M NaCl) reference electrode. The reference provided an $E_{1/2}$ value of 421 mV for a 0.5 mM solution of ferrocene in acetonitrile. Bulk electrolyses and coulometry were carried out using a Bioanalytical Systems 100A Electrochemical Analyzer. For these experiments, platinum-mesh electrodes were used for both counter and working electrodes, and the counter electrode was placed in a separate compartment and connected by a salt bridge. Solutions were degassed with nitrogen for 10 min prior to electrochemical experiments. The EPR measurements were performed on a Varian E-9 spectrometer in conjunction with a Deltron TCm20 temperature controller utilizing cooled nitrogen gas. Temperature measurements were performed with a CRL digital temperature probe (155–353 K). The EPR measurement recorded in acetonitrile was acquired using a thin film quartz cell. The 77 K measurement was made in liquid nitrogen.

Electrosynthesis of $(Bu^n{}_4N)_5[S_2Mo_{18}O_{62}]$. An acetonitrile solution (60 mL) containing $(Bu^n{}_4N)_4[S_2Mo_{18}O_{62}]$ (2.4 mM) and $Bu^n{}_4NClO_4$ (0.24 M) was reduced at 400 mV vs Ag/AgCl. After an hour, the solution had changed color from transparent yellow to a deep transparent green. Upon completion of electrolysis, the green solution was covered with perforated plastic film and placed in a refrigerator at 4 °C. After several weeks, green crystals were present. These were isolated by filtration, washed with EtOH and H_2O, and dried under vacuum. Anal. Found: C, 23.73; H, 4.50; N, 1.87. $C_{80}H_{180}Mo_{18}N_5O_{62}S_2$ requires: C, 24.04; H, 4.54; N, 1.75. Electronic spectrum, λ_{max} (nm) (ϵ (L mol^{-1} cm^{-1})): 296 sh (3.8 × 10^4), 840 sh (2.5 × 10^3), 1040 (4.3 × 10^3). The infrared spectrum showed the characteristic bands that have previously been reported for similar heteropolyoxometalates.[25,29,30] ν_{max} (cm^{-1}): 1169 s and 1069 s (S–O asymmetric and symmetric stretching modes, respectively), 998 s and 946 s, sh (Mo–O_{term} modes), 873 m, sh and 834 s (Mo–O–Mo modes involving corner-sharing octahedra), 784 s and 756 m, sh (Mo–O–Mo modes involving edge-sharing octahedra).

Electrosynthesis of $(Bu^n{}_4N)_6[S_2Mo_{18}O_{62}]$. A similar electrolysis was performed at 0 mV leading to a deep blue solution from which blue crystals were isolated and characterized in a manner similar to that described above. Infrared spectrum, ν_{max} (cm^{-1}): 1166 s, 1067 s, 954 s, 871 m, sh, 724 s, 783 s.

Table I. Voltammetrically Determined $E_{1/2}$ Values for the Reduction of $(Hex^n{}_4N)_4[S_2Mo_{18}O_{62}]$ in Acetonitrile in the Presence and Absence of 0.1 M Aqueous $HClO_4$ with the Number of Electrons Associated with each Process Given in Parentheses

	$E_{1/2}$ (mV vs Ag/AgCl)	
process	acid present[a]	acid absent[b,c]
1st reduction	608 (2)	522 (1)
2nd reduction	507 (2)	282 (1)
3rd reduction	319 (2)	−370 (1)
4th reduction	16 (2)	−650 (1)
5th reduction	−111 (4)	
6th reduction	−140 (4)	

[a] Further details are available in ref 29. [b] See text and Figure 2 for further details. [c] Further processes are observed at more negative potentials, but have not been characterized.

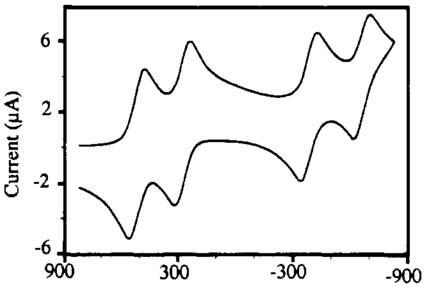

Figure 2. Cyclic voltammogram of $(Bu^n{}_4N)_4[S_2Mo_{18}O_{62}]$ (2.0 × 10^{-3} M) in acetonitrile (0.2 M $Bu^n{}_4NClO_4$): Potential vs Ag/AgCl; scan rate, 200 mV s^{-1}; working electrode, 1 mm diameter glassy-carbon disk.

Results

A cyclic voltammogram of $[S_2Mo_{18}O_{62}]^{4-}$ in acetonitrile containing 0.1 M aqueous $HClO_4$ shows six redox waves between +1000 and −200 mV. Results are independent of whether the cation is $Bu^n{}_4N^+$ or $Hex^n{}_4N^+$. Consistent with the results of Himeno et al,[25] the first four waves (Table I) have peak to peak separations of 28 ± 2 mV, suggestive of two-electron transfer processes. The fifth and sixth reduction processes are barely resolved, but both appear to be four-electron transfer processes. Bulk electrolysis coupled with coulometry for each of the first four redox processes confirms that each couple involves a two-electron transfer and studies as a function of proton concentration indicate that two protons per molecule are also transferred for each of these couples.[29]

The cyclic voltammogram over the potential range +900 to −900 mV vs Ag/AgCl of a solution of $[S_2Mo_{18}O_{62}]^{4-}$ in acetonitrile containing 0.1 M $Bu^n{}_4NClO_4$ and no aqueous acid is shown in Figure 2, and $E_{1/2}$ values are listed in Table I. These results are also independent of the cation. In contrast to the voltammogram in the presence of aqueous acid, the first four redox waves each display peak-to-peak separations of 70 mV suggesting sequential one-electron reductions. A Pt microelectrode (diameter, 10 μm) was used to acquire the steady-state voltammogram[31] for the first two redox processes (Figure 3a). A plot of potential vs $(RT/F)\ln[(i_d - i)/i]$ where i = current and i_d = diffusion-controlled reduction current gives a reciprocal slope of 1.01 and 0.96 for the first and second redox waves, respectively, confirming that each wave involves reversible transfer of a single electron. The limiting current of each of the first four waves show equal limiting currents, confirming each of the first four processes involve one-electron processes.

Bulk electrolysis and coulometry were carried out in acetonitrile (0.1 M $Bu^n{}_4NClO_4$) for the first two redox waves. For the first

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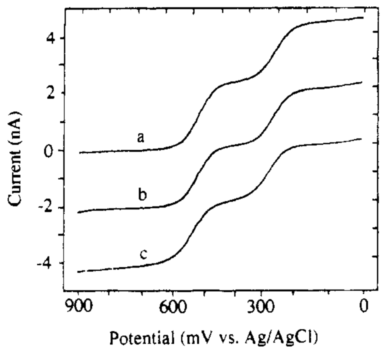

Figure 3. Steady-state voltammograms of 2.0 × 10^{-3} M solutions in acetonitrile (0.2 M $Bu^n_4NClO_4$): (a) $[S_2Mo_{18}O_{62}]^{4-}$; (b) $[S_2Mo_{18}O_{62}]^{5-}$; (c) $[S_2Mo_{18}O_{62}]^{6-}$. Conditions: potential vs Ag/AgCl; scan rate, 10 mV s^{-1}; working electrode, 10 μm diameter platinum disk.

reduction, the potential was held at +500 mV vs Ag/AgCl until the faradaic current decayed to zero. Upon completion, the color of the solution had changed from yellow to green, and the coulometry indicated that 0.95 electron per molecule had been added. Reoxidation was effected by holding the potential at +1000 mV until the current had once again decayed to zero. The coulometry indicated that 1.0 electron per molecule had been removed. For the second reduction, bulk electrolysis at 0 mV provided a deep blue solution after the passage of 2.0 electrons per molecule. The yellow solution characteristic of $[S_2Mo_{18}O_{62}]^{4-}$ was regenerated upon reoxidation at +1000 mV. A cyclic voltammogram was acquired after each bulk electrolysis and showed that no voltammetric degradation had occured. The above observations confirm that the first two redox waves correspond to chemically and electrochemically reversible one-electron transfers, that the electroproducts are stable in bulk solution, and that they can be reversibly oxidized. The data are consistent with the following processes:

$$[S_2Mo_{18}O_{62}]^{4-} + e^- \overset{E_1°}{\rightleftarrows} [S_2Mo_{18}O_{62}]^{5-} \quad (1)$$

$$[S_2Mo_{18}O_{62}]^{5-} + e^- \overset{E_2°}{\rightleftarrows} [S_2Mo_{18}O_{62}]^{6-} \quad (2)$$

As shown clearly in the steady-state voltammograms (Figure 3b,c) taken after **each** reductive bulk electrolysis, the position of zero current is consistent with the stated oxidation level of the sample.

As 0.1 M aqueous $HClO_4$ was added to a solution of the one electron reduction product $[S_2Mo_{18}O_{62}]^{5-}$, the steady-state voltammogram showing two redox couples (compare Figures 3b, 4a) began to change. When enough aqueous acid had been added to give a concentration of 3.8 mM, the steady-state voltammogram shown in Figure 4b was observed. It shows the presence of three redox couples within the potential range scanned. In addition, the limiting currents for each of these three new waves (Figure 4b) are exactly double those of the originally observed two waves (Figure 4a). Consequently, the new couples correspond to three two-electron transfer processes. The waves are much sharper and a plot of potential vs $RT/F \ln [(i_d - i)/i]$ gives a reciprocal slope of 2.0 for each wave. These results are similar to those reported[25,29] for the ($2e^-$, $2H^+$) reduction behavior of $[S_2Mo_{18}O_{62}]^{4-}$ in acidified acetonitrile. In fact, increase of the aqueous acid concentration to 0.12 M and use of the conventional-size working electrode led to cyclic voltammograms which are consistent with eq 3.

$$[S_2Mo_{18}O_{62}]^{4-} + 2H^+ + 2e^- \rightleftarrows [H_2S_2Mo_{18}O_{62}]^{4-} \quad (3)$$

Most interesting of all, the position of zero current in the aqueous acid solution (Figure 4b) bisects the first redox wave.

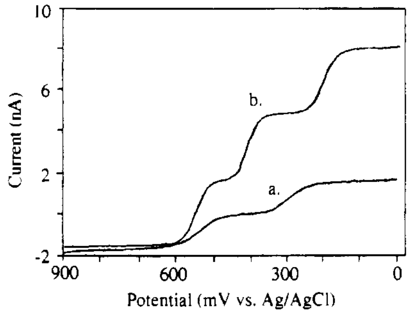

Figure 4. Steady-state voltammograms of $[S_2Mo_{18}O_{62}]^{5-}$ (2.3 × 10^{-3} M) in acetonitrile (0.23 M $Bu^n_4NClO_4$): (a) sample volumn, 1 mL; (b) sample after the addition of 40 μL of 0.1 M $HClO_4$. Conditions: potential vs Ag/AgCl; scan rate, 10 mV/s; working electrode, 10 μm diameter platinum disk.

Since it is known that protons stabilize multiply reduced polyoxomolybdate species,[1,2,16,17] the following disproportionation reactions can be written:

$$2[S_2Mo_{18}O_{62}]^{5-} \rightleftarrows [S_2Mo_{18}O_{62}]^{4-} + [S_2Mo_{18}O_{62}]^{6-} \quad (4a)$$

$$2[S_2Mo_{18}O_{62}]^{5-} + H^+ \rightleftarrows [S_2Mo_{18}O_{62}]^{4-} + [HS_2Mo_{18}O_{62}]^{5-} \quad (4b)$$

$$2[S_2Mo_{18}O_{62}]^{5-} + 2H^+ \rightleftarrows [S_2Mo_{18}O_{62}]^{4-} + [H_2S_2Mo_{18}O_{62}]^{4-} \quad (4c)$$

The position of zero current in Figure 4b indicates the production of equal concentrations of $[S_2Mo_{18}O_{62}]^{4-}$ and protonated $[S_2Mo_{18}O_{62}]^{6-}$ via acid-induced disproportionation of $[S_2Mo_{18}O_{62}]^{5-}$. In addition, the disproportionation constant, K_{dis}, can be defined as

$$K_{dis} = \frac{[S_2Mo_{18}O_{62}{}^{4-}][S_2Mo_{18}O_{62}{}^{6-}]}{[S_2Mo_{18}O_{62}{}^{5-}]^2}$$

and, at 25 °C

$$\log K_{dis} = 16.9(E_2° - E_1°)$$

where $E°_1$ and $E°_2$ are the formal potentials in volts for the first and second redox couples, (1) and (2), respectively. The $E_{1/2}$ values in Table I (taken to approximate the formal potentials) provide an estimate of K_{dis} = 8.8 × 10^{-5}. This value suggests that, in the absence of aqueous acid, the one-electron electroproduct $[S_2Mo_{18}O_{62}]^{5-}$ is relatively stable since less than 1% will disproportionate. However, in the presence of aqueous acid, the anion disproportionates completely due to the stabilization provided by protonation of $[S_2Mo_{18}O_{62}]^{6-}$ to $[HS_2Mo_{18}O_{62}]^{5-}$ and $[H_2S_2Mo_{18}O_{62}]^{4-}$. In strongly acid media the protonation drives the disproportionation equilibrium (4c) to the right and completion.

In order to further confirm the existence of an odd oxidation level for this polyoxometalate system, crystals of the $Bu^n_4N^+$ salt of the $[S_2Mo_{18}O_{62}]^{5-}$ electroproduct were isolated from the one-electron reduced solution obtained by bulk electrolysis. The crystals have so far proven to be unsuitable for X-ray analysis. EPR spectra of the micro-crystalline powder were acquired as a function of temperature. As shown in Figure 5a, the room temperature (22.2 °C) EPR spectrum of the solid shows an intense but broad and symmetric $S = {}^1/_2$ envelope (g, 1.949; peak-to-peak separation W_p, 7.4 mT; cf., $[PMo_{12}O_{40}]^{4-}$, g, 1.945[13]). A similar room-temperature solution EPR spectrum was recorded for 1 mM $[S_2Mo_{18}O_{62}]^{5-}$ in acetonitrile (g, 1.946; peak-to-peak separation W_p, 8.4 mT). No hyperfine splitting is seen at this

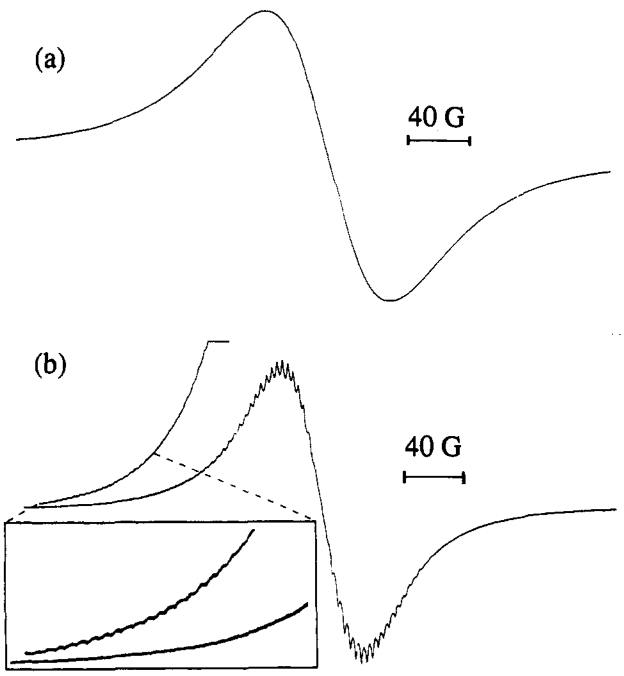

Figure 5. Powder EPR spectra of $(Bu^n_4N)_5[S_2Mo_{18}O_{62}]$: (a, top) 19.6 °C, modulation amplitude 0.005 mT; (b, bottom) –20 °C, modulation amplitude 0.001 mT. Conditions: center field = 334 mT; sweep width = 40 mT; klystron frequency = 9.143 GHz; power = 100 mW. Conditions for inset to part b: modulation amplitude, 0.002 mT; gain, ×1.3.

temperature, but when the solid is cooled to –20 °C, the spectrum narrows and hyperfine structure can be resolved in a symmetric spectrum. Figure 5b shows that at least 91 lines are observed, each with a peak-to-peak separation of about 0.4 mT, contributing to a total envelope width of at least 36 mT.

Assuming that each anion is magnetically isolated within the lattice by the five $Bu^n_4N^+$ cations per anion, isotropic hyperfine coupling of the unpaired electron to 18 magnetically equivalent Mo nuclei each with an $I = {}^5/_2$ nuclear spin (^{95,97}Mo, 25.5 atom % natural abundance) leads to a 91-line spectrum. However, the relative natural abundance of the $^{95,97}Mo_{18}$ isotopomer is negligible (1.5×10^{-9} mol %!). It seems that a number of isotopomers are contributing to the observed pattern. As they must have less than the maximum number of 18 ^{95,97}Mo nuclei, their individual isotropic spectra will feature fewer than 91 lines centered on *g*, 1.949, and with identical hyperfine coupling constants *a*(Mo). A simple splitting diagram indicates that, due to overlap of individual spectra, the peak-to-peak separation in the center of the spectrum will be *a*(Mo)/2 at maximum resolution. Given that observed separation of 0.4 mT may not represent that maximum resolution, the possibilities seem to be[32]

a(Mo), mT	envelope width, 90*a*(Mo), mT
0.8	72
0.4	36
0.2	18

The present data is most consistent with *a*(Mo), 0.4 mT, with the hyperfine structure resolved fortuitously at –20 °C. The number of lines resolved suggests thermal delocalization of the odd electron over the entire ion at this temperature. With a further decrease in temperature, the signal continues to narrow but the resolved hyperfine structure is lost. This narrowing with decrease in temperature is also consistent with a thermal hopping process for the odd electron and the loss of resolved hyperfine coupling can be attributed to spectral density.

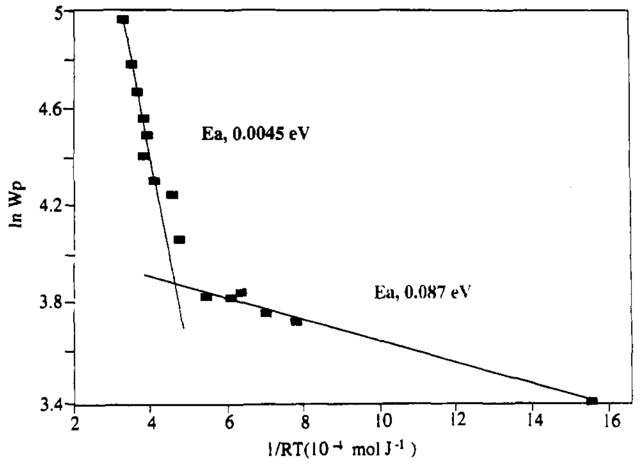

Figure 6. Arrhenius plot of ln W_p vs $(RT)^{-1}$ for $(Bu^n_4N)_5[S_2Mo_{18}O_{62}]$.

An Arrhenius plot of the observed EPR peak-to-peak line width W_p in the temperature range + 86 to –196 °C is presented to Figure 6. Surprisingly, two linear regions are observed on either side of –20 °C. The low temperature relationship (E_a 0.0045 eV[33]) plausibly corresponds to thermal *intra*molecular hopping within the $[S_2Mo_{18}O_{62}]^{5-}$ species as discussed above. The high temperature behavior (E_a, 0.087 eV) would then correspond to an *inter*molecular electron transfer process. The 20-fold increase in E_a is consistent with the greater barrier expected for such a process in the $(Bu^n_4N)_5[S_2Mo_{18}O_{62}]$ lattice. Above 86 °C, the green microcrystals decompose explosively, yielding yellow and blue regions in an inhomogeneous mass. Voltammetry confirmed $[S_2Mo_{18}O_{62}]^{4-}$ as the yellow region and $[S_2Mo_{18}O_{62}]^{6-}$ as the blue region. The observations are consistent with an intermolecular electron hopping mechanism involving electron transfer between green $[S_2Mo_{18}O_{62}]^{5-}$ and the two disproportionation products, yellow $[S_2Mo_{18}O_{62}]^{4-}$ and blue $[S_2Mo_{18}O_{62}]^{6-}$ (cf., eq 3).

A more detailed examination of the EPR properties of this material is warranted. In particular, extension of the temperature range toward 4 K (liquid helium) may allow trapping of the "green" electron on a single Mo site.

Discussion

It has been noted that the redox behavior of the Dawson anions, $[X_2Mo_{18}O_{62}]^{6-}$ (X = P, As), differs from all other types of heteropolyoxometalates in that the odd reduction states have not been observed.[1,2,16,17] The one-electron reduced anion $[S_2Mo_{18}O_{62}]^{5-}$ detected in the present work eliminates this discrepency. The absence of odd oxidation states has been attributed to the extreme distortion of the individual MoO_6 octahedra within the anion. X-ray data for α-$[P_2Mo_{18}O_{62}]^{6-}$ have shown that, in each of the two central rings (consisting of three pairs of edge-sharing MoO_6 octahedra; cf. Figure 1), alternating molybdenum atoms are displaced so that the rings are puckered.[18] This removes the C_{4v} local site symmetry for each MoO_6 octahedron and effectively reduces the overall point symmetry of the anion to D_3. When the anion is reduced, it is believed that the electron enters a MoO_6 LUMO causing the MoO_6 site to relax and attain a symmetry closer to C_{4v}. In turn, this relaxation reduces the off-axis distortion of an adjacent MoO_6 octahedron which facilitates its reduction.[18–21]

The X-ray structure of $(Et_4N)_4[S_2Mo_{18}O_{62}]$ salt has been reported (Figure 1), and the anion is isostructural with α-$[P_2Mo_{18}O_{62}]^{6-}$.[24] This includes the distortion of the MoO_6

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[32] The $18^{95,97}$Mo and $17^{95,97}$Mo isotopomers will feature 91 and 86 lines respectively, and so the maximum number of observable lines is 177; the spectra of the other isotopomers will overlap these. The outermost three lines at the low- and high-field extremes will be separated by *a*(Mo), not *a*(Mo)/2.

[33] This estimate is an apparent high temperature limit as activationless (tunneling) electron transfer may predominate at lower temperatures.[8]

octahedra from C_{4v} site symmetry. However, comparison of the two structures reveals that the alternating displacement of Mo within the six-membered rings (the ring puckering) is much less in $[S_2Mo_{18}O_{62}]^{4-}$ than in α-$[P_2Mo_{18}O_{62}]^{6-}$ although the former does not acquire the C_{4v} site symmetry of α-$[P_2W_{18}O_{62}]^{6-}$.[18,24] According to Hori et al.,[24] the differences in interatomic distances are due to the smaller size of the SO_4 tetrahedron relative to that of PO_4. It seems likely that the differences in geometry are responsible for the differences in redox behavior since the electronic effect of the S^{6+} centers compared to P^{5+} should increase the electron affinity of the anion. It is also plausible that the geometry changes may be linked to the increased Coulombic repulsion between Mo^{6+} and the heteroatom.

The present EPR evidence is consistent with thermal delocalization of the odd electron over the complete polyoxoanion framework in solid $(Bu^n_4N)_5[S_2Mo_{18}O_{62}]$. The "blue" electron in α-$[PW_{12}O_{40}]^{4-}$ is delocalized over all 12 W atoms, but over the two central rings only in α-$[P_2W_{18}O_{62}]^{7-}$ (i.e., 12 of the 18 W atoms).[4] The thermal barrier to intramolecular electron hopping estimated[34] from the EPR line widths (Figure 6) appears to be much smaller in $[S_2Mo_{18}O_{62}]^{5-}$ (E_a, 0.0045 eV) than in $[Mo_6O_{19}]^{3-}$ (E_a, 0.155 eV) and $[PMo_{12}O_{40}]^{4-}$ (E_a, 0.035 eV).[7] Thermal barriers for other polyoxometalates have been estimated to be in the range 0.03 to 0.3 eV,[2-6] so it is perhaps surprising to obtain such a small value, 0.0045 eV, in the present study.

Since cooperative geometrical changes appear to account for the fact that in α-$[P_2Mo_{18}O_{62}]^{6-}$ reduction of one MoO_6 moiety results in the near-instantaneous reduction of a second MoO_6 moiety, it is possible that such an effect could account for the low thermal barrier to intramolecular electron transfer in $[S_2Mo_{18}O_{62}]^{5-}$. By such a mechanism, reduction of a MoO_6 site in $[S_2Mo_{18}O_{62}]^{5-}$ would result in a synergistic lowering of the reduction potential for the adjacent MoO_6. Although the degree of stabilization with respect to reduction might not be enough to immediately facilitate another electron transfer at the electrode surface, it is likely that it would reduce the activation energy required for intramolecular electron-transfer to an adjacent MoO_6 moiety. This effect could then be propagated throughout the anion so that the odd electron appears delocalized at sufficiently high temperatures. The time frame of the process would then be dictated by the frequency of the nuclear motions involved since electron transfer to an adjacent MoO_6 moiety could not occur until geometrical relaxation for the previous transfer had occurred.

On the basis of the disproportionation constant (eq 4) calculated from the redox potentials, about 1% of the $[S_2Mo_{18}O_{62}]^{5-}$ anion will disproportionate in acetonitrile solution. Assuming similar geometries for the 4-, 5-, and 6-anions, it is reasonable that the disproportionate species also may be present in small amounts in solid $(Bu^n_4N)_5[S_2Mo_{18}O_{62}]$. The exact proportions within the crystals is difficult to determine since the solution equilibrium will change even as precipitation occurs. It is just this disproportionation event which appears to be the mechanism of the intermolecular electron transfer responsible for the EPR line broadening in the range −20 to +86 °C. Indeed, the appearance of yellow ($[S_2Mo_{18}O_{62}]^{4-}$) and blue ($[S_2Mo_{18}O_{62}]^{6-}$) regions upon decomposition at 86 °C is evidence for such a mechanism. However, since reversibility of the EPR spectra was possible up to this point, the decomposition may be the result of exceeding the boiling point of acetonitrile molecules of crystallization. These exist in the crytal lattice of $(Et_4N)_4[S_2Mo_{18}O_{62}]\cdot MeCN$[24] and cannot be excluded from $(Bu^n_4N)_5[S_2Mo_{18}O_{62}]$ on the basis of microanalysis.

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(34) We have resisted the temptation for a more sophisticated treatment because of the preliminary nature of the present EPR and electronic spectral data and uncertainties in the theory (discussed in refs 1, 7, and 8).