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IR Spectroelectrochemical Investigation of the Disproportionation of $W_2(SBz)_2(CO)_8^-$

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The UV–vis and IR spectroelectrochemistry of $W_2(SBz)_2(CO)_8^{2-}$ (**1**) in 0.1 M $(TBA)PF_6/CH_2Cl_2$ is reported (where SBz^- = benzyl mercaptide). The reversible 2e⁻ oxidation of $W_2(SBz)_2(CO)_8^{2-}$ is analyzed in terms of the individual 1e⁻ redox potentials, $E^{\circ\prime}_{-/2-}$ and $E^{\circ\prime}_{0/-}$, by measuring the homogeneous disproportionation constant, K_{disp}, of the electrochemically generated $W_2(SBz)_2(CO)_8^-$ radical. At 25 °C, we find K_{disp} equal to 7500 ± 4000. This value places $E^{\circ\prime}_{-/2-}$ at a potential nearly 0.23 V positive of $E^{\circ\prime}_{0/-}$ ($E^{\circ\prime}_{-/2-} = -0.46$ V; $E^{\circ\prime}_{0/-} = -0.69$ V vs aqueous AgCl/Ag). The reversal in positions of the 1e⁻ redox potentials drives the disproportionation reaction and is rationalized to be a consequence of the electronic destabilization of $W_2(SBz)_2(CO)_8^-$ relative to $W_2(SBz)_2(CO)_8^{2-}$ and $W_2(SBz)_2(CO)_8$.

Introduction

Previously, the groups in Indiana studied the electrochemistry of the apparent 2e⁻ oxidation of $W_2(SBz)_2(CO)_8^{2-}$ and related polynuclear thiolate-bridged species by cyclic voltammetry and digital simulation.[1-3] These studies were directed toward understanding the thermodynamic and kinetic barriers involved in the net two-electron reactions. The results suggested that electron transfer occurs in two rapid 1e⁻ steps, with $E^{\circ\prime}$ for the second oxidation lying at potentials more negative than that of the first.

In this paper, we present the results of UV–vis and IR spectroelectrochemical studies of the $W_2(SBz)_2(CO)_8^{2-/-/0}$ system. First, we report detection and characterization of the one-electron intermediate of $W_2(SBz)_2(CO)_8^{2-}$ oxidation. Second, by directly measuring the disproportionation equilibrium constant, K_{disp}, of $W_2(SBz)_2(CO)_8^-$, we have been able to obtain the potentials of the individual 1e⁻ couples, $E^{\circ\prime}_{-/2-}$ and $E^{\circ\prime}_{0/-}$. While in qualitative agreement with the earlier results,[1] the present data suggest that the difference between the two single-electron potentials is greater than that previously indicated.

Experimental Section

Preparation of Compounds. $[Et_4N]_2W_2(SBz)_2(CO)_8$ and $W_2(SBz)_2(CO)_8$ were prepared as described previously.[2]

Electrochemistry. All electrochemical experiments were performed with a Bioanalytical Systems (BAS) Model 100 electrochemical analyzer. Cyclic voltammetry (CV) was performed at 20 ± 2 °C with a normal three-electrode configuration consisting of a highly polished glassy-carbon-disk working electrode ($A = 0.07$ cm²) and a AgCl/Ag reference electrode containing 1.0 M KCl. The working compartment of the electrochemical cell was separated from the reference compartment by a modified Luggin capillary. All three compartments contained a 0.1 M solution of supporting electrolyte.

Dichloromethane (Fischer Scientific Co., HPLC grade) was distilled from P_2O_5 prior to use. Tetrabutylammonium hexafluorophosphate ($(TBA)PF_6$) (Southwestern Analytical) was used as received. Electrolyte solutions were prepared and stored over 80–200-mesh activated alumina (Fisher Scientific Co.) and activated 4-Å molecular sieves.

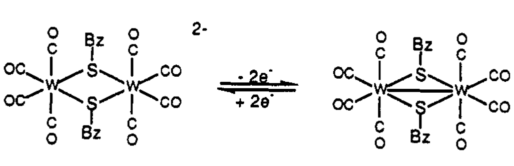
Potentials are reported vs aqueous AgCl/Ag and are not corrected for the junction potential.[4] Under conditions identical to those employed here, the ferrocenium/ferrocene couple[5] has $E^{\circ\prime} = +0.50$ V with $E_{pa} - E_{pc} = 94$ mV.

Spectroelectrochemistry. UV–vis spectroelectrochemistry was performed at an optically-transparent platinum electrode as previously described.[6] Spectral changes were monitored by a Tracor Northern TN-6500 diode array apparatus employing a Xe arc lamp as the light source.

IR spectroelectrochemistry was carried out in specular reflectance mode, using a modified commercial flow-through cell. The working electrode consisted of a highly polished platinum disk similar in design to that reported by Clark et al.[7] Full experimental details will be published elsewhere. Data were collected on a Mattson Galaxy 6080 FTIR spectrometer. Electrolyses were controlled in both UV–vis and IR experiments by the BAS 100 thin-layer bulk electrolysis program.

Results and Discussion

Figure 1 shows the cyclic voltammogram of $W_2(SBz)_2(CO)_8^{2-}$ (**1**) in 0.1 M $TBAPF_6/CH_2Cl_2$. As previously determined by cyclic voltammetry and controlled-potential coulometry,[1,2] **1** undergoes a chemically reversible 2e⁻ oxidation ($E^{\circ\prime}_{0/2-} = -0.57$ V vs AgCl/Ag) to yield the neutral, d⁵–d⁵ complex $W_2(SBz)_2(CO)_8$ (**2**) according to eq 1. As is commonly observed for



1 **2**

(1)

complexes which exhibit multiple changes in oxidation state in a single step,[8-11] the above electron transfer is accompanied by significant structural rearrangement. On the basis of the crystal

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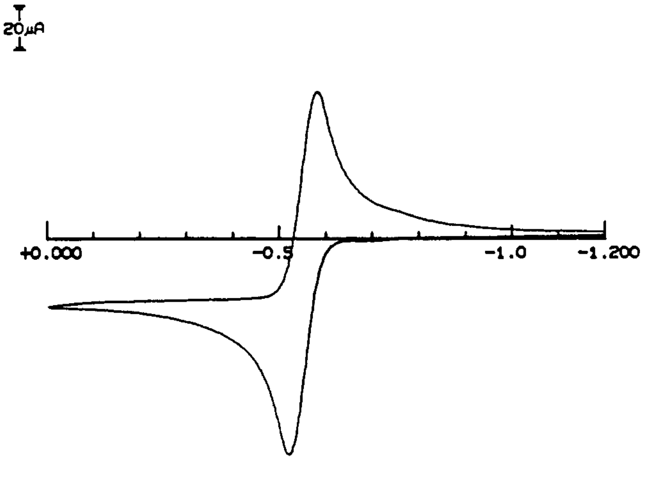

Figure 1. Cyclic voltammogram of $W_2(SBz)_2(CO)_8^{2-}$ in 0.1 M $(TBA)PF_6/CH_2Cl_2$. Scan was initiated in the positive direction at a rate of 100 mV/s.

structures of analogous complexes,[12,13] the intramolecular metal–metal distance is expected to decrease by more than 1 Å upon oxidation of **1** to **2**, and the S–W–S and W–S–W angles are expected to expand and contract, respectively, by more than 25°.

Despite these large nuclear displacements, the heterogeneous electron-transfer rate, $k_{s,h}$, for the oxidation of **1** is large. At a Hg/Au electrode, the apparent $k_{s,h}$ for two-electron transfer has been determined to be 2.2×10^{-2} cm s^{-1}.[1] As discussed within the context of Marcus–Hush theory, this rate is consistent with two, separate one-electron oxidations rather than a single, two-electron transfer.

The net thermodynamics of reaction 1 are related to the relative free energies of the individual electron-transfer events. These energies are expressed as electrochemical potentials for the formal 1e$^-$ couples $E°'_{-/2-}$ and $E°'_{0/-}$. However, the experimentally observed 2e$^-$ electrochemistry of **1** yields only the average potential of these two 1e$^-$ processes, $E°'_{0/2-}$ (eq 2).[14] Initial analysis of

$$E°'_{0/2-} = \frac{E°'_{-/2-} + E°'_{-/2-}}{2} \qquad (2)$$

the cyclic voltammetric response of **1** in terms of two sequential 1e$^-$ oxidations (EE mechanism) gave the qualitative result that the second electron transfer, $E°'_{0/-}$, lies at a potential marginally negative of the first, $E°'_{-/2-}$ ($\Delta E°' = (E°'_{0/-} - E°'_{-/2-}) \approx -0.02$ V).[1] This result was derived from the observation that the cyclic voltammetric peak potential separation $\Delta E_p = E_{p,a} - E_{p,c}$ approached 37 ± 2 mV at slow sweep rates and that the voltammetric traces were qualitatively fit by simulated curves with $\Delta E°' = -0.022$ V and $(k_{s,h})_{0/-} = (k_{s,h})_{-/2-} \approx 10^{-1}$ cm s^{-1}. However, this value of $\Delta E°'$ must be considered an estimate because there is large uncertainty in determining $\Delta E°'$ from ΔE_p values near the Nernstian two-electron limit,[15,16] and the simulations did not account for the known[17,18] dependence of ΔE_p on both $\Delta E°'$ and the *individual* values of the heterogeneous rates.

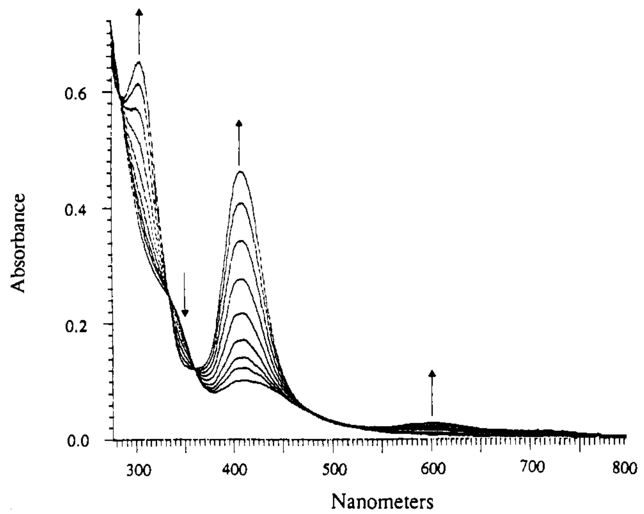

Figure 2. UV–vis spectroelectrochemical oxidation of $W_2(SBz)_2(CO)_8^{2-}$ in 0.1 M $(TBA)PF_6/CH_2Cl_2$ at +0.2 V vs Pt wire pseudoreference electrode. Spectra were recorded in ca. 10-s intervals.

Thus, we determined the relative positions of the individual 1e$^-$ couples directly using spectroelectrochemical techniques.[19] By considering the disproportionation of two $W_2(SBz)_2(CO)_8^-$ radicals, it is possible to relate the potentials of the two 1e$^-$ couples to the equilibrium concentrations of $W_2(SBz)_2(CO)_8^{n-}$ (where n = 2, 1, and 0) present during a bulk oxidation of **1** to **2**.[20] This is shown in expressions 3–5. Experimentally, we measure the

$$2W_2(SBz)_2(CO)_8^- \rightleftharpoons W_2(SBz)_2(CO)_8^{2-} + W_2(SBz)_2(CO)_8 \qquad (3)$$

$$K_{\text{disp}} = \frac{[W_2(SBz)_2(CO)_8^{2-}][W_2(SBz)_2(CO)_8]}{[W_2(SBz)_2(CO)_8^-]^2} \qquad (4)$$

$$\ln K_{\text{disp}} = \frac{nF(E°'_{-/2-} - E°'_{0/-})}{RT} = \frac{-nF(\Delta E°')}{RT} \qquad (5)$$

concentrations of $W_2(SBz)_2(CO)_8^{2-}$, $W_2(SBz)_2(CO)_8^-$, and $W_2(SBz)_2(CO)_8$ present at several points during the spectroelectrochemical oxidation of **1**, determine the value of K_{disp} according to eq 4, and substitute that value into eq 5 to obtain the potential difference, $\Delta E°'$.

Figure 2 shows the UV–vis spectroelectrochemistry of **1** in 0.1 M $TBAPF_6/CH_2Cl_2$. The initial UV absorbance tail due to **1** is replaced by strong bands at 350 and 415 nm and a weak absorbance at 600 nm, in excellent agreement with the previously reported electronic spectrum of complex **2**.[2] Reduction of **2** results in the quantitative regeneration of **1**, establishing the stabilities of compounds **1** and **2** for the duration of the spectroelectrochemical experiment (ca. 3 min). The *apparent* isosbestic behavior depicted in Figure 2 indicates that $W_2(SBz)_2(CO)_8^-$ is not generated in sufficient concentration to be observed under the spectral resolution of the UV–vis experiment.

Figure 3 shows the analogous IR spectroelectrochemical oxidation of $W_2(SBz)_2(CO)_8^{2-}$. The initial spectrum of **1** (ν(CO) = 1788, 1834, 1873, and 1977 cm^{-1}) after oxidation gives the final spectrum of **2** (ν(CO) = 1957, 1989 (sh), and 2035 cm^{-1}). While these spectral changes appear to maintain an isosbestic point at 1910 cm^{-1}, careful examination of the data reveals a transient absorbance at 1912 cm^{-1} which initially grows in, reaches

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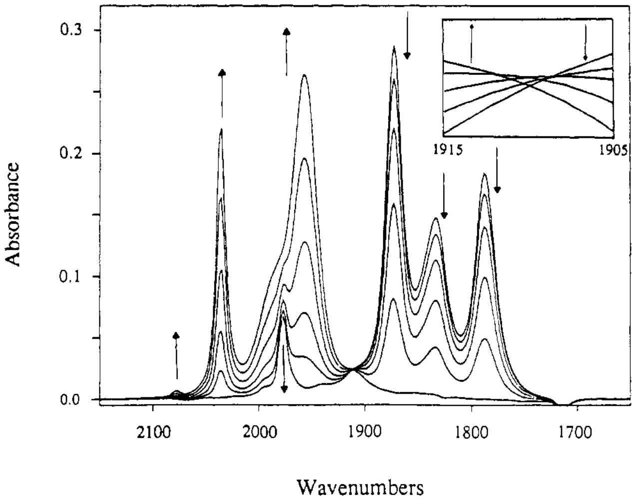

Figure 3. IR spectroelectrochemical oxidation of $W_2(SBz)_2(CO)_8^{2-}$ in 0.1 M (TBA)PF_6/CH_2Cl_2 at +0.2 V vs Pt wire pseudoreference electrode. The inset shows an expansion of the spectral region between 1915 and 1905 cm^{-1}. Spectra were recorded in ca. 15-s intervals.

a maximum value midway through the electrolysis, and eventually disappears (see inset, Figure 3). This feature is both reproducible (observed in five separate experiments) and reversible. The opposite spectral changes occur during reduction of **2**. This behavior is consistent with the existence of a one-electron intermediate and its participation in a radical disproportionation equilibrium.[19,21,22] By subtracting appropriate fractions[23] of pure **1** and **2** from intermediate spectra shown in Figure 3, we were able to generate a spectrum of the d^5–d^6 radical. This spectrum is shown in Figure 4. The absorbances of $W_2(SBz)_2(CO)_8^-$ (ν(CO) = 1875, 1915 (sh), 1958, and 2037 cm^{-1}) lie at energies intermediate between those observed for $W_2(SBz)_2(CO)_8^{2-}$ and $W_2(SBz)_2(CO)_8$.

From the above data, we calculate a disproportionation constant for $W_2(SBz)_2(CO)_8^-$, K_{disp}, of 7500 ± 4000. This relatively large value is near the detection limit of our experiment. However, the ability to detect a small equilibrium concentration (~1%) of the intermediate attests to the high sensitivity of the IR spectroelectrochemical technique. Substituting K_{disp} = 7500 into eq 5 yields a value for ΔE of −0.229 ± 0.022 V; i.e. the potential of the second electron transfer, $E°'_{0/-}$, is approximately 0.23 V negative of the potential of the first, $E°'_{-/2-}$ ($E°'_{-/2-}$ = −0.46 V; $E°'_{0/-}$ = −0.69 V vs AgCl/Ag).

A salient feature of the last result is that the changes which accompany the $2e^-$ oxidation of **1** establish a relative thermodynamic ordering such that the sum of the ΔG_f's of two $W_2(SBz)_2(CO)_8^-$ radicals is nearly 5.5 kcal/mol higher than the sum of the ΔG_f's of **1** and **2**. Conceptually, this ordering could result either from the inherent thermodynamic stability of structures **1** and/or **2** or from the inherent thermodynamic instability of $W_2(SBz)_2(CO)_8^-$. As recently pointed out, these issues can be qualitatively understood in terms of electronic and nuclear structural considerations.[1] Hoffmann and co-workers[24] have performed extended Huckel calculations on a series of edge-sharing binuclear octahedral complexes which predict a $\delta^{*2}\pi^2\delta^2\sigma^2\pi^2\sigma^{*2}$ electronic configuration for d^6–d^6 complexes of the general form, $M_2(\mu\text{-}X)_2(CO)_8$. Within this theoretical framework, complex **1** possesses a formal bond order of zero and exhibits only a minor metal–metal interaction. This results in a long intramolecular distance and relatively small d-orbital splittings. Upon oxidation by one and then two electrons, the metal–metal bond order increases to $^1/_2$ and 1, with concomitant decreases in metal–metal distance and M–X–M bridge angle. The most important effect of this is a sharp increase in the energy of the (M–M)σ^* orbital. Additionally, the energies of σ, π, and δ orbitals decrease, while those of the π^* and δ^* orbitals increase, but to much lesser extents than found for σ^*. Thus, the major effect of the first oxidation of $W_2(SBz)_2(CO)_8^{2-}$ is to raise the energy of the singly-occupied σ^* orbital in the radical. The depopulation of this high-energy σ^* orbital, coupled with the lowering of the bonding orbitals in complex **2**, provides the thermodynamic driving force for the second electron transfer.[25]

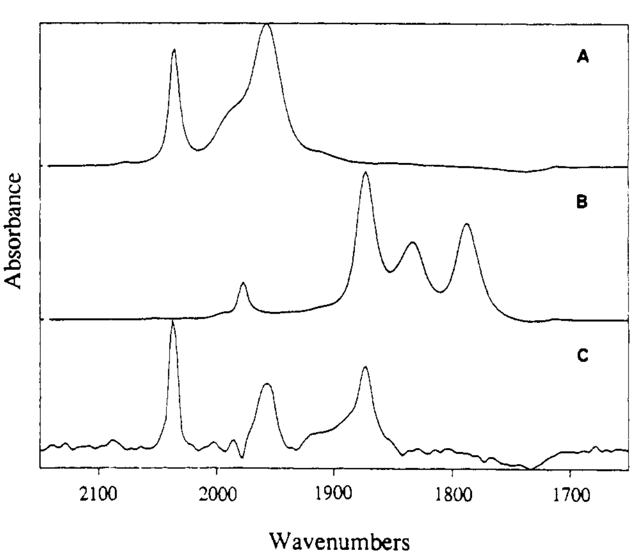

Figure 4. IR spectra of pure $W_2(SBz)_2(CO)_8$ as generated in the spectroelectrochemical cell: A, pure $W_2(SBz)_2(CO)_8^{2-}$; B, $W_2(SBz)_2(CO)_8^-$ as calculated by subtracting appropriate fractions of compounds **1** and **2** from the intermediate spectra recorded in Figure 3 (C). The absorbance scale for spectrum C is roughly $^1/_{100}$ of that for spectra A and B.

It is interesting to compare these results with those reported for the disproportionation of $Rh_2(diisocyanide)_4^{3+}$ (where diisocyanide = 1,8-diisocyanomethane or 2,5-diisocyano-2,5-dime-

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(22) Our analysis assumes that the solutions are at equilibrium. In principle, a relatively large heterogeneous electron-transfer rate for the $E°'_{0/-}$ couple, combined with a slow homogeneous comproportionation rate, could result in a lower concentration of $W_2(SBz)_2(CO)_8^-$ during the time scale of the spectroelectrochemical experiment. Such a situation would result in an overestimation of the magnitude of K_{disp}. To address this possibility, we mixed equimolar amounts of **1** and **2** in 0.1 M (TBA)PF_6/CH_2Cl_2 and monitored the resulting solution by IR. Absorbances matching those of the radical in the spectroelectrochemical experiment were found immediately in the mixing experiment and for periods of up to several minutes. This demonstrates that reaction 3 exists in the mixing experiment and is at equilibrium during the time frame of the spectroelectrochemical experiment. Additional spectral features were generated at longer times (>10 min) in the mixing experiment but were determined to be due either to decomposition of **1** and/or **2** or to side products which exhibited cyclic voltammograms in incompatible with that predicted for $W_2(SBz)_2(CO)_8^-$.

(23) The equilibrium concentrations of **1** and **2** used to calculate K_{disp} were determined by measuring the amounts of pure **1** and **2** which needed to be subtracted from intermediate spectra obtained during the spectroelectrochemical oxidation of **1** such that the absorbances at 1788 cm^{-1} (due to **1**) and 1989 cm^{-1} (due to **2**) were zero. The concentration of $W_2(SBz)_2(CO)_8^-$ was then calculated by integrating the remaining absorbances. In this process, we assumed that the integrated ϵ of $W_2(SBz)_2(CO)_8^-$ was the average of the integrated ϵ's of **1** and **2**.

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(25) In contrast to the disproportionation reactions of coordination compounds such as Cu(I),[26] reaction 3 does not appear to be driven by solvation energies. For example, while an accurate evaluation of K_{disp} for $W_2(SBz)_2(CO)_8^-$ in 0.1 M (TBA)PF_6/CH_3CN was precluded due to partial solvolysis of $W_2(SBz)_2(CO)_8$ during the time scale of the spectroelectrochemical experiments, the IR spectral changes observed at early electrolysis times confirmed that CH_3CN does not significantly shift the disproportionation equilibrium. One explanation for this nonclassical behavior is that, unlike the coordination compounds, the $W_2(SBz)_2(CO)_8^{2-/-/0}$ species do not directly bind solvent within their primary coordination sphere.

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thylhexane).[19,21] Like $W_2(SBz)_2(CO)_8^-$, disproportionation of $Rh_2(\text{diisocyanide})_4^{3+}$ is favorable but for a significantly different reason. Rather than a large destabilization of the $Rh_2(\text{diisocyanide})_4^{3+}$ radical, disproportionation in this case is driven by the large increase in stability afforded by complexation of the 2e$^-$ oxidized form, $Rh_2(\text{diisocyanide})_4^{4+}$, with nucleophiles. Future studies will further refine these ideas as they apply to multielectron reactions and to electron-transfer reactions that occur with chemical bond formation.

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