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Far-Infrared Spectroelectrochemistry: A Study of Linear Molybdenum/Iron/Sulfur Clusters

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Abstract: The far infrared spectroelectrochemistry of linear M/Fe/S (M = Mo, W) complexes was investigated in methylene chloride and dichloroethane. With CsI as spectral windows, bands above 200 cm⁻¹ can be observed in methylene chloride, except for a weak methylene chloride band at 450 cm⁻¹. Substitution of dichloroethane for methylene chloride, solvents of nearly identical electrochemical properties, allows one to observe solute bands in the 450 cm⁻¹ region. The far-infrared spectroelectrochemistry of [MoFe₂S₄Cl₄]²⁻ and its tungsten analogue was investigated. The disappearance of the oxidation bands and the appearance of bands due to the reduced product could be clearly observed. The origin of the vibrational bands could be clearly identified using ³⁴S substituted complexes. In addition

to the far infrared bands, the resonance Raman spectroelectrochemistry of the oxidized and reduced complex, along with the ^{34}S substituted complexes was obtained. Far infrared and resonance Raman spectroelectrochemistry can be combined to understand the electrochemical mechanism of transition metal complexes.

Introduction

Spectroelectrochemistry has been shown over the past several decades to be a powerful tool for the elucidation of electron transfer processes. Initially, the UV/visible region was exploited because common solvents and cell materials were transparent. Interest has shifted to the infrared region because of the additional spectral information that is inherent in this region. For inorganic and organometallic compounds, the most useful region has been the mid-infrared because many important ligands (e.g., CO and NO) absorb in that region [1-4]. For example, Raebiger et al. [1] have used infrared spectroelectrochemistry to monitor variations in the carbonyl vibrations during the reduction or oxidation of Mo/Fe/S cubanes. Solvent absorption, though, generally limits the spectral window available, and vibrations below 1400 cm^{-1} are difficult to observe without significant efforts.

While mid-infrared spectroelectrochemistry is useful for the study of ligand vibrations, metal vibrations commonly occur in the far infrared region. This region typically requires different spectrophotometer optics and cell materials from that normally used in the mid-infrared region. The far infrared region, which has been much less frequently exploited than the mid-infrared region [5], provides important information on the changes in metal cluster vibrations upon oxidation state and ligand changes. The use of far-infrared spectroelectrochemistry can therefore provide important information on the effect of electron transfer on the metal cluster, as well as provide direct information on ligation changes. In order to illustrate the use of far infrared spectroelectrochemistry, the electrochemistry of Mo/Fe/S clusters will be examined. Recent decades have shown the richness of Mo/Fe/S clusters. Depending upon the ligand, metal ratios,

and oxidation state, a large variety of linear and cubane clusters are possible.

The linear Mo/Fe/S clusters are an attractive place to begin this study. Considerable voltammetric and visible/resonance Raman spectroelectrochemical data are available for comparison [6-8]. The purpose of this report will be to demonstrate the use of far infrared spectroelectrochemistry in the study of linear tri-metal clusters, and the results compared with the analogous tungsten clusters. Visible and resonance Raman spectroelectrochemistry of $[\text{Cl}_2\text{FeS}_2\text{MoS}_2\text{FeCl}_2]^{2-}$, *Ia*, has been recently reported [6;7]. Voltammetry of *Ia* indicated that it was reduced reversibly by one-electron to the trianion, which underwent a slow reaction to an unidentified colored cluster [8]. The new cluster, which was probably due to the dimerization of the linear complex, contained only bridging sulfur vibrations, and no terminal Mo-S vibrations. While the voltammetry was irreversible at slow scan rates, coulometric re-oxidation of the one-electron product regenerated the starting material, *Ia*. In this work, the far-infrared spectroelectrochemistry of the linear clusters will be examined in order to illustrate the capabilities of the technique and to provide additional spectroscopic information on the reduced cluster.

Experimental

Chemicals and Equipment.

The spectroelectrochemical cell was constructed from a modified demountable FTIR cell (Wilmad Glass Co.) with CsI plates as the cell windows. The working electrode was a platinum gauze, the pseudo-reference electrode was a silver wire, and the auxiliary electrode was a gold foil. A pseudo-reference electrode was used for ease of construction in that it avoids a separate reference compartment. In that way, the reference electrode could be placed near the working electrode, and between the working and auxiliary electrode. This facilitated greater potential control on the working electrode. The potential of the pseudo-reference electrode was reproducible, and the observed potentials were 400 mV positive of the conventional Ag/AgNO_3 (in ace tonitrile) reference electrode ($E_{\text{Ag wire}} = E_{\text{Ag}/\text{AgNO}_3} + 400 \text{ mV}$). The cell thickness was about 100 μ . The FTIR instrument

was a Nicolet Nexus 670 FT-IR with polyethylene optics for the far infrared region. The linear clusters [8] and $(\text{Ph}_4\text{P})_2\text{Mo}^{34}\text{S}_4$ [9] were synthesized by literature procedures. All the ionic compounds were prepared as tetraphenylphosphonium salts. All solutions were prepared in a glove box prior to use, and the instrument was purged with dinitrogen gas. The supporting electrolyte was 0.2 M tetrabutylammonium perchlorate (TBAP) (G.F.S. Chemical Co.). Methylene chloride and dichloroethane (Sigma Aldrich Chemical Co.) were used as obtained, and continuously maintained under dinitrogen.

The resonance Raman spectra were obtained using Spex 1269 1.26 m single monochromator equipped with a CCD detector. The laser source was a Spectra-Physics (series 2000) Ar^+ laser (488 nm). The sample was contained in an NMR tube. For resonance Raman studies, the samples were reduced either electrochemically or with tetrabutylammonium borohydride. Both procedures yielded identical spectra.

Results and Discussion

Far-Infrared Spectroelectrochemistry.

As with spectroelectrochemistry in other infrared regions, far-infrared spectroelectrochemistry requires a careful choice of solvent and window materials. The most transparent electrochemical solvents are methylene chloride and tetrahydrofuran (THF), which are transparent down to 200 cm^{-1} , with minimal bands at higher energies. For example, methylene chloride has a weak band at 450 cm^{-1} and a strong band at 280 cm^{-1} . The absorbance of the 450 cm^{-1} band can generally be removed by spectral subtraction. Solute bands around 450 cm^{-1} , though, can be observed by repeating the experiment using dichloroethane, a solvent with electrochemical behavior nearly identical to methylene chloride. Window materials such as CsI, Si and polyethylene are transparent in this region. Silicon is transparent to lower energies, but CsI was used because solvent absorption is generally the limiting factor. The tetraphenylphosphonium ion has bands around 530 cm^{-1} , but this region was generally higher than most metal vibrations. Common polar electrochemical solvents such as

dimethylformamide or dimethylsulfoxide are not transparent in the far infrared.

The far-infrared spectrum of *Ia* in methylene chloride is shown in Figure 1 (curve A). Without solvent subtraction, bands could be observed at 473, 350 and 323 cm^{-1} . After the solvent spectrum was subtracted, an additional band at 465 cm^{-1} could be observed (Figure 1, curve B). Such subtraction is more difficult if thicker cells are used. The spectrum of *Ia* in solution obtained compares well with the solid far infrared spectrum of the complex (Table 1). The far infrared spectrum of *Ia* in dichloroethane is shown in Figure 1 (curve C). In dichloroethane, all four bands can be observed without solvent subtraction, though the region below 270 cm^{-1} can only be observed in methylene chloride (*Ia*, though does not have bands in that region). Additional information on the M/Fe/S clusters can be obtained by the frequency shifts of isotopically substituted complexes. The ^{34}S -substituted *Ia* was synthesized, and the results are shown in Table 1. The $\nu(\text{Mo-S})$ bands shifted to lower energies by about 9 cm^{-1} , which was consistent with a Mo-S vibration. On the other hand, no shifts were observed for the 351 and 323 cm^{-1} bands, confirming the assignment as Fe-Cl vibrations.

The complex, *Ia*, was reduced spectroelectrochemically at a platinum gauze electrode. The results are shown in Figure 2. The 473 cm^{-1} band disappeared while a new band at 457 cm^{-1} appeared. The 465 cm^{-1} shoulder in *Ia* appeared as a band in the reduced product. These results are similar, but not identical to the earlier reported isolated product [8]. Differences were also observed in the visible spectra of the isolated product, indicating that some changes in the product occurred upon precipitation. Repetition of the experiment with ^{34}S substituted *Ia* gave the expected shifts in the reduced product (Figure 2 and Table 1). No terminal Mo-S bands were observed indicating that all the sulfur atoms were coordinated in the product. The Fe-Cl bands broadened and weakened considerably.

The tungsten analogue of the molybdenum cluster was also examined (Figure 3). The oxidized complex had sulfur bridging bands at 465 and 454 cm^{-1} (468 and 458 cm^{-1} [8]), and Fe-Cl bands at 347 and 324 cm^{-1} . Reduction at -650 mV vs silver wire electrode caused

the $\nu(\text{M-St})$ (Sbridging) and the $\nu(\text{Fe-Cl})$ bands to disappear, and new bands at 490, 485, 445 and 313 cm^{-1} appeared. The results were quite similar to the molybdenum complex, except for the appearance of the $490/485\text{ cm}^{-1}$ bands. These new bands are indicative of W-S terminal bands.

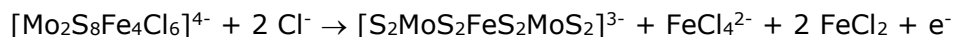
Resonance Raman spectroelectrochemistry.

The resonance Raman spectra of the oxidized and reduced complex, *Ia*, were examined earlier [7]. The effect of ^{34}S -substitution on the starting complex and product was studied in this work. The spectra of *Ia* (natural abundance and ^{34}S substituted complexes) in methylene chloride are shown in Figure 4. The difference spectra between the natural abundance and ^{34}S starting complex showed two isotopically sensitive bands at 437 and 584 cm^{-1} . The latter band has been previously assigned as a combination band between the 437 cm^{-1} vibration, and a $\delta(\text{MoS}_4)$ vibration at 148 cm^{-1} [10]. The 437 cm^{-1} band for the natural abundance complex, which is a Mo-Sb stretching band, shifted to 424 cm^{-1} upon sulfur isotopic substitution. The band at 584 cm^{-1} shifted to 571 cm^{-1} . The difference between the 571 cm^{-1} vibration and the 424 cm^{-1} band was still 147 cm^{-1} , indicating that this band was not isotopically sensitive. As a result, the 147 cm^{-1} band involves Fe-Cl rather than Mo-S or Fe-S vibrations.

Reduction of *Ia* by borohydride has been shown previously to lead to the same product as the electrochemical reduction [7]. The resonance Raman spectrum of reduced *Ia* is shown in Figure 4. The band intensities dropped significantly upon reduction, and two isotopically sensitive bands appear at 453 and 430 cm^{-1} , both bands within the region for Mo-S bridging vibrations. The combination band at 584 cm^{-1} disappeared from the spectrum. Upon isotopic substitution with ^{34}S , these bands decreased to 444 and 418 cm^{-1} , respectively. These correspond to shifts of 8 and 12 cm^{-1} , which are the shifts expected for such isotopic substitution.

In the absence of additional chloride ion, there was no evidence of terminal Mo-S stretching vibrations. When chloride ions are added to the reduced product [7], new bands were observed at 479 and 416 cm^{-1} . These bands correspond to the known resonance Raman

spectrum [7] of $[\text{S}_2\text{MoS}_2\text{FeS}_2\text{MoS}_2]^{3-}$, *II*. Such transformations were also observed when the reduced complex was dissolved in N-methylformamide (NMF). In this case, the reduction product was completely transformed to *II*. The milder transformation due to chloride ion is quite interesting in that the following balanced chemical reaction can be written:



The electron that is released can readily reduce the dimer product, which has a wave about 150 mV negative of *I*. Additional chloride ion would also coordinate to ferrous chloride, maintaining the solubility of the iron species.

The combination of resonance Raman and far infrared spectroelectrochemistry provides important information on the reduced complex. No overlap was observed between the infrared (473, 465, 350 and 323 cm^{-1}) and resonance Raman (437 cm^{-1}) of *Ia*. Similarly, the reduced complex exhibited no overlap in the resonance Raman (453 and 430 cm^{-1}) and infrared (464 and 457 cm^{-1}) bands. The small number of bands and lack of overlap indicates considerable symmetry in the presumed dimeric structure. Work is in progress to use molecular orbital methods in order to calculate the infrared and resonance Raman frequencies of the proposed dimers, and determine which structures are most consistent with the observed spectra.

Conclusions

The use of spectroelectrochemistry in the far infrared region of the spectrum was demonstrated in this work. Electrochemical solvents that are most transparent in the far infrared region are methylene chloride, dichloroethane and tetrahydrofuran. Supporting electrolytes are generally transparent except for tetraphenylphosphonium cations, which have a band around 530 cm^{-1} . Using far infrared spectroelectrochemistry, the spectra of the starting material and the reduction product of the first wave of $[\text{MS}_4\text{Fe}_2\text{Cl}_4]^{2-}$ (where M = Mo, W) in methylene chloride (dichloroethane) were obtained. The combination of the far infrared spectroelectrochemistry with resonance Raman spectroscopy indicated that there was still considerable

symmetry in the reduction product. The use of ^{34}S labeled material in both the infrared and resonance Raman spectroscopy indicated which bands were due to metal sulfur vibrations. The technique is now being exploited in our laboratory for the investigation of Mo/Fe/S cubane structures.

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Table 1
Far-infrared spectra of M/Fe/S complexes^a

Compound	$\nu(\text{M S}_n)$ (cm^{-1})	$\nu(\text{Fe Cl})$ (cm^{-1})	Reference
[MoS ₄ Fe ₂ Cl ₄] ²⁻	473, 465	350, 323	this work
	473, 451(w)	346	[12] ^b
	470, 460(sh)		[8] ^c
[Mo ³⁴ S ₄ Fe ₂ Cl ₄] ²⁻	464, 457	351, 323	this work
[WS ₄ Fe ₂ Cl ₄] ²⁻	465, 454	348, 324	this work
	468, 458		[8] ^c
Reduced [MoS ₄ Fe ₂ Cl ₄] ²⁻	464, 457	341, 322	this work
	475, 465		[8] ^c
Reduced [Mo ³⁴ S ₄ Fe ₂ Cl ₄] ²⁻	455, 448	343, 322	this work
Reduced [WS ₄ Fe ₂ Cl ₄] ²⁻	446	314	this work

^a In methylene chloride, CsI windows, except as noted.

^b CsI pellet.

^c KBr pellet.

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Figure Captions

Figure 1. A: Far infrared spectrum of $[\text{MoS}_4\text{Fe}_2\text{Cl}_4]^{2-}$ in spectroelectrochemical cell with methylene chloride as solvent and 0.2 M TBAP. B: Far infrared spectrum of $[\text{MoS}_4\text{Fe}_2\text{Cl}_4]^{2-}$ after subtraction of the solvent (methylene chloride). C: Far infrared spectrum of $[\text{MoS}_4\text{Fe}_2\text{Cl}_4]^{2-}$ in spectroelectrochemical cell with dichloroethane as solvent and 0.2 M TBAP.

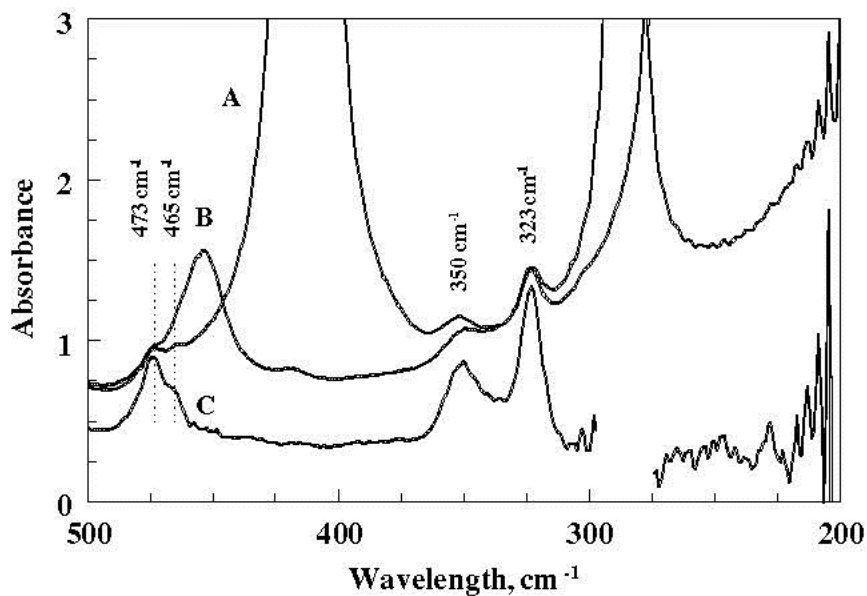


Figure 2. A. Far infrared spectrum of $[\text{Mo}^{\text{na}}\text{S}_4\text{Fe}_2\text{Cl}_4]^{2-}$ reduced at -650 mV vs silver wire pseudoreference electrode using normal abundance sulfur. B. Far infrared spectrum of $[\text{Mo}^{34}\text{S}_4\text{Fe}_2\text{Cl}_4]^{2-}$ reduced at -650 mV vs silver wire pseudo-reference electrode using normal abundance sulfur. C. The difference spectrum between $[\text{MoS}_4\text{Fe}_2\text{Cl}_4]^{2-}$ ($^{\text{na}}\text{S}$) and $[\text{MoS}_4\text{Fe}_2\text{Cl}_4]^{2-}$ (^{34}S), both reduced at -650 mV vs silver wire pseudo-reference electrode. Both solutions contain methylene chloride with 0.2 M TBAP.

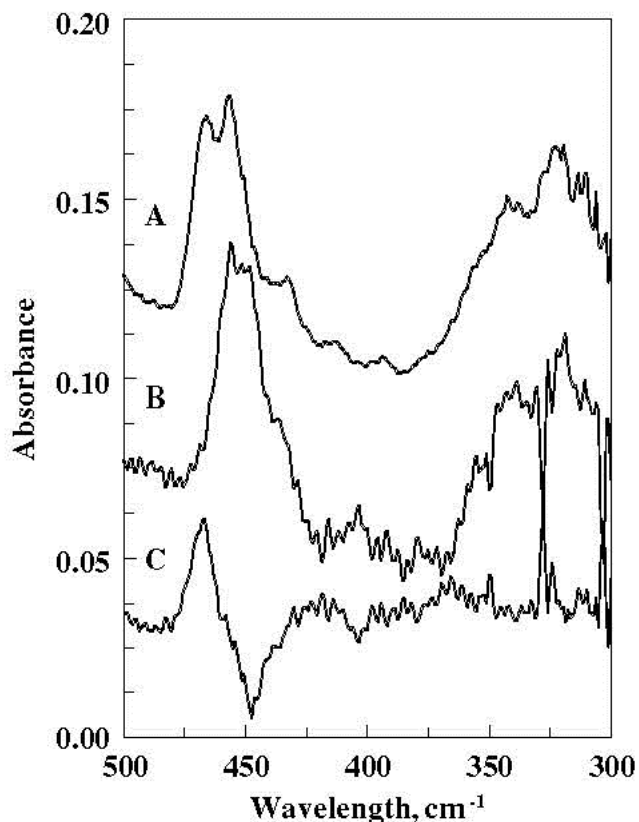


Figure 3. Bold line. Far infrared spectrum of $[\text{WS}_4\text{Fe}_2\text{Cl}_4]^{2-}$ in spectroelectrochemical cell with methylene chloride as solvent. Solvent subtracted from original spectrum. Solid line: Difference spectrum between starting complex and material reduced at -650 mV vs silver wire pseudoreference electrode using normal abundance sulfur. All solutions contain 0.2 M TBAP.

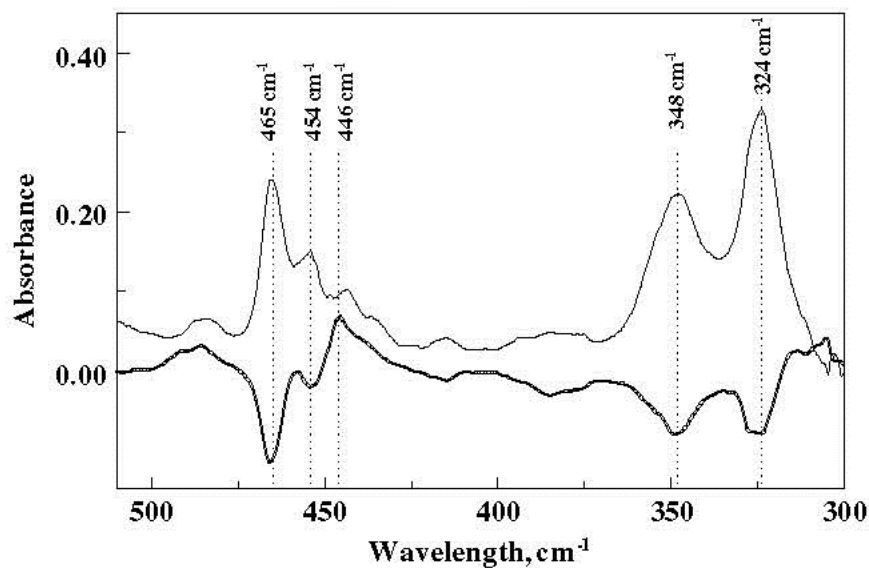


Figure 4. Resonance Raman spectra of *Ia* and its reduction product. Bold lines: natural abundance complexes. Normal lines: ^{34}S complexes. Curves A: $[\text{MoS}_4\text{Fe}_2\text{Cl}_4]^{2-}$ in methylene chloride. Curves B: reduced complex in methylene chloride. Laser excitation: 488 nm.

