

# **Fiber Optical Micro-detectors for Oxygen Sensing in Power Plants**

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## ABSTRACT

$\text{Mo}_6\text{Cl}_{12}$ , a cluster compound whose luminescence depends on the ambient concentration of oxygen, is the basis for a real-time oxygen sensor for combustion applications. Previously, the properties of  $\text{Mo}_6\text{Cl}_{12}$  have largely been studied at room temperature; these studies have now been extended to 200 °C. Optical microscopy shows that  $\text{Mo}_6\text{Cl}_{12}$  undergoes a steady change in color as it is heated from room temperature to 200 °C, changing from canary yellow to crimson and then back to canary yellow. Concurrent thermal gravimetric analyses show a small weight loss for  $\text{Mo}_6\text{Cl}_{12}$  that is consistent with loss of water or HCl from the clusters. These changes are reversible. Absorption and fluorescence emission spectroscopy of  $\text{Mo}_6\text{Cl}_{12}$  heated to 200 °C for two hours shows no change in the photophysical parameters compared to the control sample that was not heat cycled

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## INTRODUCTION

Maximizing the efficiency of the combustion process requires real-time control of the correct fuel/oxygen ratio. This requires the ability to sense oxygen levels over a broad range of concentrations with fast response times.

Mussell, Newsham, and Ruud previously reported preliminary studies of the synthesis and optical properties of  $\text{Mo}_6\text{Cl}_{12}$ -based clusters relevant to this project [1,2,3]. Mussell described the synthesis of the molybdenum clusters, and Newsham gives a good account of the properties of neutral  $\text{Mo}_6\text{Cl}_{12}$  clusters and their salts, in both solution and a sol gel matrix. Newsham's data indicate that the photophysical properties of the clusters are maintained in sol gel matrices. To prepare a fiber optic sensor based on  $\text{Mo}_6\text{Cl}_{12}$ , Ruud dispersed  $\text{Mo}_6\text{Cl}_{12}$  in poly[1-trimethylsilyl-1-propyne] (PTMSP), and used a dipping technique to immobilize the composite at the cleaved end of a silica optical fiber. Ghosh and co-workers [4] demonstrated a fast room temperature fiber optic sensor based on oxygen quenching of the luminescence from the PTMSP/ $\text{Mo}_6\text{Cl}_{12}$  composites. While the PTMSP support is adequate for room temperature applications, is unable to withstand the high temperatures associated with combustion in a power plant. To improve the sensor's high temperature performance, we are replacing PTMSP with a thermally stable sol gel matrix that should be able to withstand the higher temperature requirements of the power plant combustion process. The idea of using a sol gel as the support matrix for high temperature oxygen sensor application is not new. Remillard and coworkers have shown that a sol gel supported copper based oxygen sensor can be used in a combustion process [5]. With these facts in hand, we anticipate promising results from our design.

## EXECUTIVE SUMMARY

Approximately 2 grams of  $\text{Mo}_6\text{Cl}_{12}$  was prepared using the method of Sheldon and co-workers [6]. The absorption, emission, and x-ray powder diffraction results of the new material are similar to that of our previous preparation. To satisfy the material needs of the project additional  $\text{Mo}_6\text{Cl}_{12}$  will be prepared via a method described by McCarley and co-workers [7]. The reason for using this new method is two-fold: 1) our source of molybdenum chloride is no longer available and 2) we would like to compare the spectroscopy of prepared via different techniques to determine the optimum synthesis technique.

TGA data and optical microscopy measurements up to 200 °C were used to assess the thermal properties of  $\text{Mo}_6\text{Cl}_{12}$ . This data indicates that the compound is thermally stable to 200 °C. A small weight loss was observed upon heating, which we attribute to due to the loss of water and our results are consistent with those previously described by Sheldon [6]. The next step will be to determine the thermal and photophysical properties of  $\text{Mo}_6\text{Cl}_{12}$  after cycling to higher temperature (300 °C) in the presence of air and nitrogen.

From optical microscopy performed on a heated stage up to 200 °C we observed a slight change in color of the cluster upon heating (thermo-chromic properties). These results were expected from previous reports[7]. We will continue to use this technique on  $\text{Mo}_6\text{Cl}_{12}$  cluster cycled up to 300 °C.

Initial experiments were performed to assess the high temperature stability of the  $\text{Mo}_6\text{Cl}_{12}$  clusters. A quantity of the newly synthesized material was thermally cycled to 200 °C twice, for a total exposure of two hours at 200 °C. No changes were observed between the emission spectra of the thermally cycled material as compared to the initial compound. Refinements were made to the SPEX spectrometer to enable quantitative comparison of emission spectra taken on different days, by incorporating an optical power meter to monitor the lamp power.

## EXPERIMENTAL

### **Preparation[6]**

Molybdenum chloride (3.0027 g, 3 mmol) from Cerac was dissolved in aqueous 6 M HCl with heating to form a clear yellow solution. The volume was then reduced to one quarter and allowed to cool to room temperature. After placing the flask in a freezer overnight, long yellow needle-like crystals were obtained. The solution was decanted from the flask and the crystals were collected, broken into smaller needles to facilitate drying, and dried on a piece of filter paper. Once dry, some of the crystals were set aside for future analysis, and the remaining crystals were transferred to a Schlenk tube and heated under vacuum at 150 °C for 6 hours. After 6 hours, the temperature was increased to 210 °C for 4 days to obtain approximately 2 g of an orange-yellow powder. The powder changed back to yellow upon cooling to room temperature.

Note: The use of aqueous hydrochloric acid versus other polar solvent is due to the propensity of  $\text{Mo}_6\text{Cl}_{12}$  to undergo ligand exchange. Specifically the chlorine atoms in  $\text{Mo}_6\text{Cl}_{12}$  are known to be somewhat labile, and can be exchanged for a solvent molecule, such as ethanol or acetonitrile. Additionally, the hydrochloric acid will dissolve any metal impurities contained in the molybdenum chloride.

### **Absorption**

The samples were prepared by weighing 8 – 8.5 mg of  $\text{Mo}_6\text{Cl}_{12}$  in a small sample vial. The compound was then dissolved in a small amount of aqueous 6 M HCl and transferred to a volumetric flask. The volumetric flask was filled to the mark, stoppered, and shaken to insure a homogenous solution. Concentration:  $1.7 \times 10^{-4}$  M. Aqueous hydrochloric acid was used in order to compare to the results of Gray and co-workers [8].

Absorption measurements were performed using a Perkin Elmer Lambda 40 Double beam instrument. The data was acquired using UV Winlab software version 2.8 and plotted using Microsoft Excel. Solutions were placed into a 1 cm pathlength quartz cuvette with a separate cell containing only solvent as a reference.

### **Fluorescence**

The samples were prepared by weighing 8 – 8.5 mg of  $\text{Mo}_6\text{Cl}_{12}$  in a small sample vial. The compound was then dissolved in a small amount of aqueous 6M HCl and transferred to a volumetric flask. The volumetric flask was filled to the mark, stoppered, and shaken to insure a homogenous solution. Concentration:  $1.7 \times 10^{-4}$  M.

Fluorescence measurements were performed using a Fluorolog-3 instrument from Instruments S.A., Inc. The system includes a single Czerny-Turner excitation spectrometer with a 1200g/mm ruled grating blazed at 330nm and a single Czerny-Turner emission spectrometer with a 1200g/mm holographic grating blazed at 630 nm. The excitation optics consists of a 450W ozone free Xe lamp, followed by a 270-380 nm bandpass filter (Oriel 1124). A Si photodiode is used to continuously monitor the lamp signal. The detection optics consists of 603.2 nm long wave pass filter (CVI) followed by a multi-alkali photo multiplier tube (Hamamatsu R928) with photon counting electronics. Data processing was performed using the Datamax (version 2.2) software

package supplied with the instrument. Spectra were obtained by exciting at 313 nm with a 5 nm slit width, and scanning the emission monochromatic from 550 to 850 nm.

A Newport 1815-C Power meter with and 818 UV Silicon detector was used to monitor the Xe lamp intensity at the 313 nm pump wavelength, before and after the fluorescence measurements. After an initial warm up time of half an hour, the lamp was found to have a stable output power better than +/- 5% for a period of several hours. These power measurements will allow us to quantitatively compare spectra obtain on different days by accounting for the diminishing output of the Xe lamp due to aging.

Measurements of the cluster fluorescence in solution with different concentrations of dissolved oxygen were performed by placing the solution in a quartz cuvette sealed with an airtight septum. The atmosphere measurements (~20% oxygen) were performed on the original stock solution that was stored under atmospheric pressure under standard lab conditions. To obtain the measurements in a 0.001% oxygen environment, nitrogen gas of purity 99.999% was bubbled through the solution for 10 minutes

### **Microscopy**

Polarized optical microscopy images were acquired using a Nikon Optiphot2-Pol equipped with a Sony Hyper HAD CCD-IRIS/RGB color video camera (model DXC-151A). The camera was connected to a PC using a Sony camera adapter (model CMA-D2). The images were viewed using a Sony Trinitron color video monitor. Images were taken using Hauppauge computer works Win/TV software (version 2.4.17052). Images were collected every 10 °C and analyzed for mean luminosity using Adobe Photoshop, which provides a measure of the light emission from the sample over the entire visible spectrum. The mean luminosity was then plotted as a function of temperature and each sample contained approximately 4 mg of cluster.

### **Thermogravimetric Analysis (TGA)**

The sample size ranged from 6 to 7 mg. The temperature program is shown in Table 1.

<b>Temperature (°C)</b>	<b>Heating Rate (°C/min)</b>	<b>Hold Time (minutes)</b>
30.0	-----	120.0
30.0 – 200.0	10.0	-----
200.0	-----	60.0
200.0 – 30.0	10.0	-----
30.0 – 200.0	10.0	-----
200.0	-----	60.0
200.0 – 30.0	10.0	-----
30.0 – 200.0	10.0	-----
200.0	-----	60.0
200.0 – 30.0	10.0	-----
30.0	-----	240.0

Table 1. Temperature program for thermogravimetric analysis.

Thermogravimetric analysis was performed using a Perkin Elmer TGA-7 system, which consists of a computer, TGA-7 low temperature furnace and balance module, and a TAC7/DX controller. The gas type and flow were adjusted to either nitrogen or air with a separate gas flow regulation system that was attached. The flow-rate of balance and sample gas was 45 and 40 mL/min respectively. The pan, stirrup and hanger wire were made of platinum metal that was connected to a gold balance wire using a quartz hook.



## RESULTS AND DISCUSSION

### Thermogravimetric Analysis

Fig. 1 shows the TGA analysis for  $\text{Mo}_6\text{Cl}_{12}$  during three temperature cycles between 30 °C and 200 °C. Strikingly, there is a weight increase upon cooling followed by a weight decrease upon reheating to 200 °C. Isothermal heating shows very little weight loss. Holding at 30 °C gives rise to an increase in weight. Initially, this behavior was very puzzling and believed to be related to either a reaction and/or a loss of water/aqueous hydrochloric acid. Similar weight changes have been previously observed in the presence of moisture [6].

To determine whether or not this behavior was an oxidative process versus an absorption/desorption of water or aqueous hydrochloric acid, the same compound was heat cycled under nitrogen, Fig. 2. It is readily apparent that the sample loses weight upon heating and then gains weight upon cooling. This difference in weight gain and loss, as compared to Fig. 1, can be attributed to slightly different sample sizes and the fact that the nitrogen purge gas contains much less water.

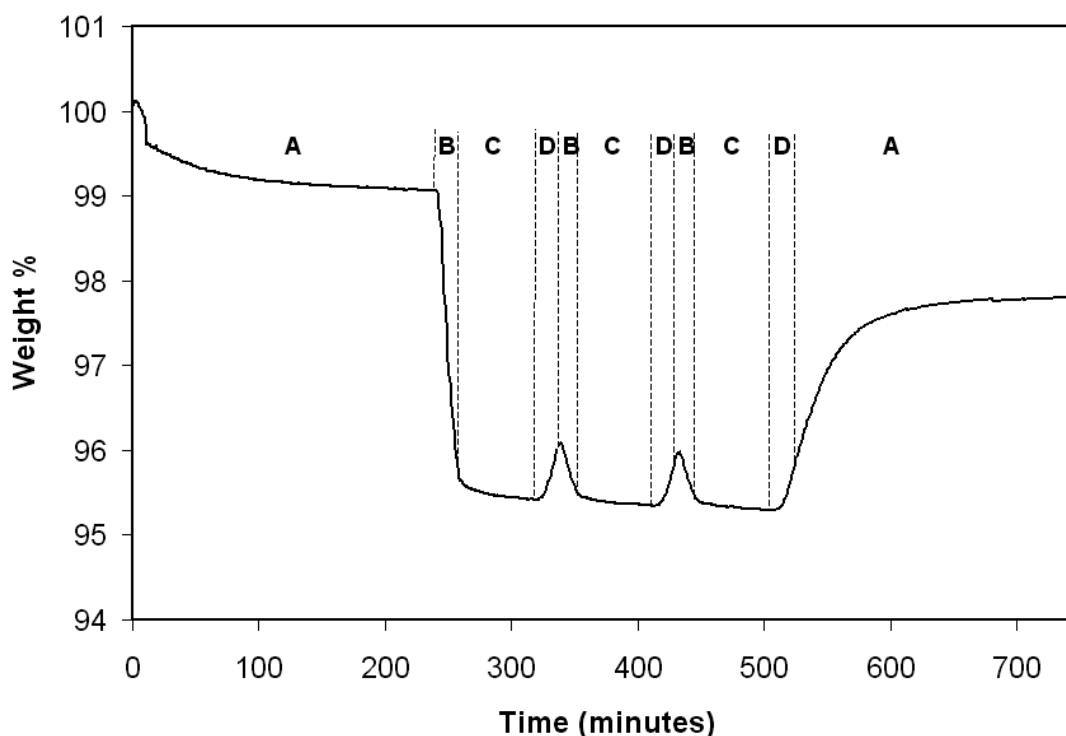


Figure 1. TGA measurements of  $\text{Mo}_6\text{Cl}_{12}$  in air showing weight loss as a function of time. **A** indicates holding at 30 °C. **B** indicates heating from 30 °C to 200 °C. **C** indicates holding at 200 °C. **D** indicates cooling from 30 °C to 200 °C. The heating rate was 10 °C/min for both heating and cooling.

Upon further investigation the weight increase was related to the loss of water/aqueous hydrochloric acid. When run under nitrogen atmosphere the same weight loss and increase is observed, indicating that the weight loss and increase is due to aqueous hydrochloric acid being lost and reabsorbed until finally being completely removed from the sample. There is a net 5% weight loss through the cycling, which remains upon further heating. The aqueous hydrochloric acid is from the purification of the  $\text{Mo}_6\text{Cl}_{12}$ . It appears from the TGA that some of the acid remains after the preparation, even though the sample is heated to 204 °C for 4 days under vacuum.

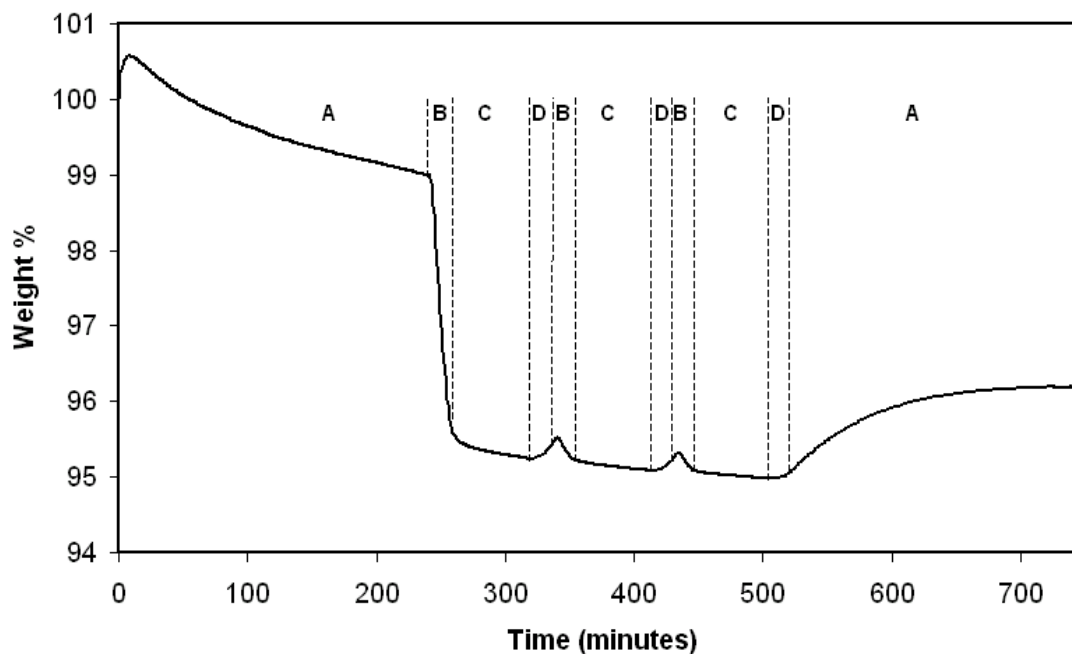


Figure 2. TGA measurements of  $\text{Mo}_6\text{Cl}_{12}$  in nitrogen showing weight loss as a function of time. **A** indicates holding at 30 °C. **B** indicates heating from 30 °C to 200 °C. **C** indicates holding at 200 °C. **D** indicates cooling from 30 °C to 200 °C. The heating rate was 10 °C/minute for both heating and cooling.

### Optical microscopy on a heated stage

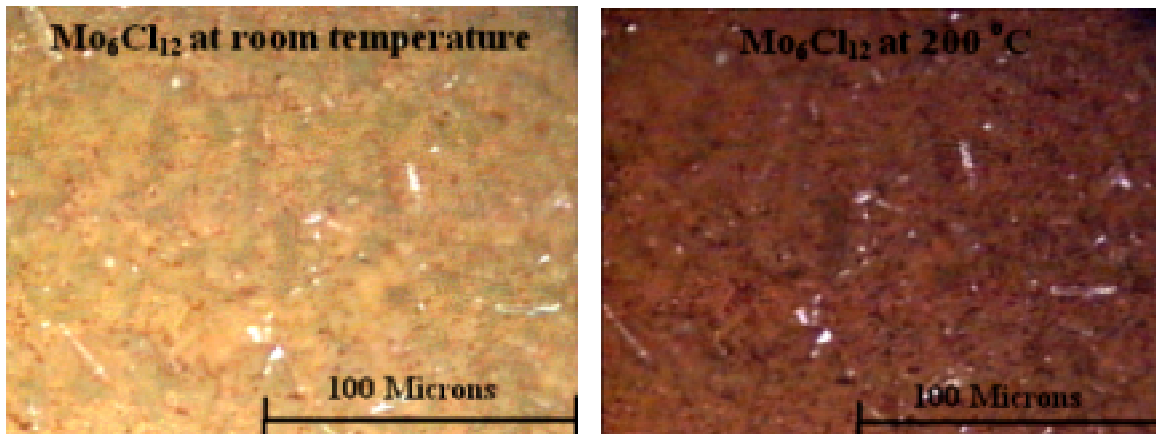


Figure 3. Optical images of Mo<sub>6</sub>Cl<sub>12</sub> at room temperature and at 200 °C illustrating the thermo-chromic properties of the clusters. Samples were heated in air at a rate of 10 °C/min.

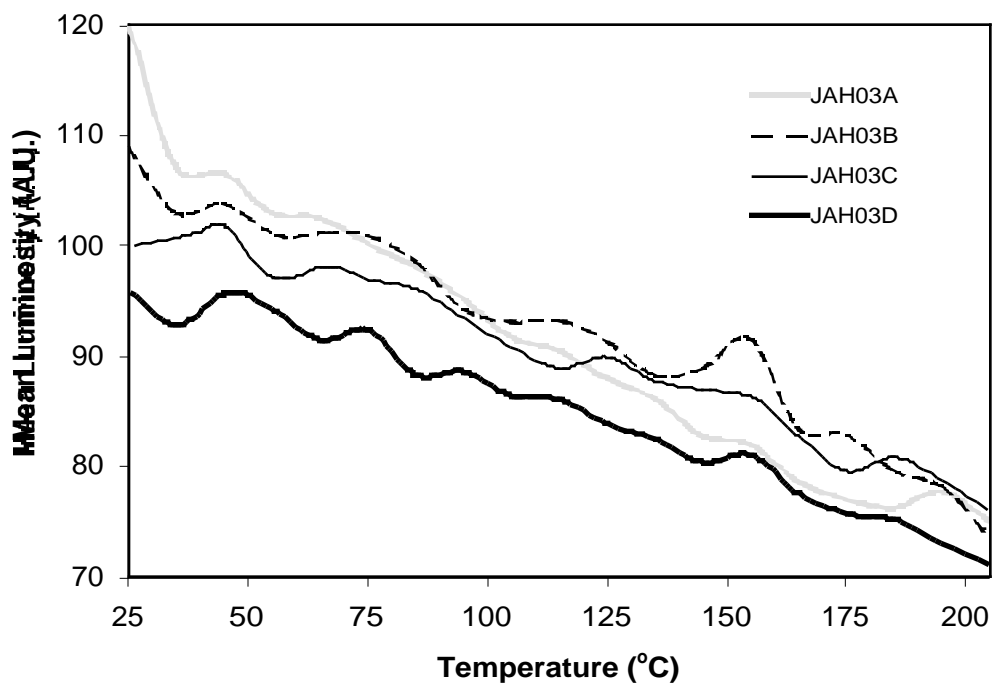


Figure 4. The change in the mean luminosity of Mo<sub>6</sub>Cl<sub>12</sub> as a function of temperature, as defined from the mean luminosity measurements of images analyzed using Adobe Photoshop. Four independent runs are shown.

The optical micrographs (Fig 3) shows that  $\text{Mo}_6\text{Cl}_{12}$  undergoes a steady change in color as it is heated from room temperature to 200 °C, changing from canary yellow to crimson and then back to canary yellow. Quantitative analysis of the intensity of the color change is shown in Fig. 4, where the mean luminosity of the sample is plotted as function of temperature. Note that a change in color associated with a change in temperature was also recognized by Sheldon [6].

### Absorption

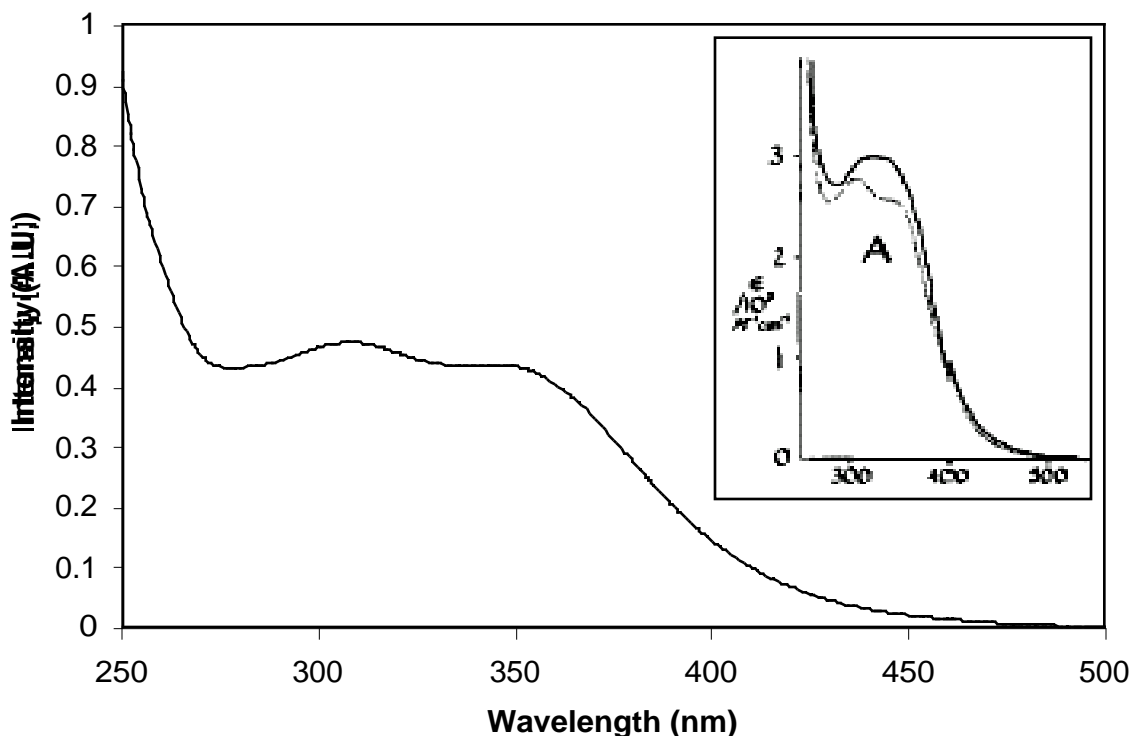


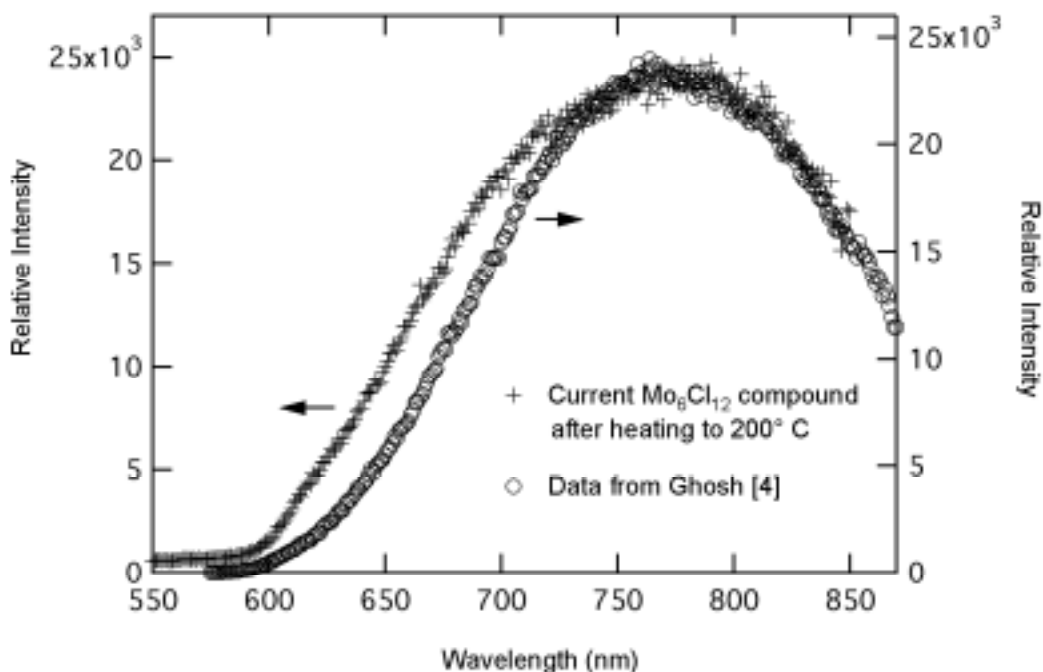
Figure 5. The absorption spectrum of the current  $\text{Mo}_6\text{Cl}_{12}$  compound dissolved in 6M HCl. The spectrum from Gray and co-workers [8] is inserted for comparison, with A indicating their absorption curve taken in 6M HCl.

The absorption spectra of our current cluster compound in the 275 to 450 nm wavelength range is shown in Fig. 5. Our results are in good agreement with previous measurements by Gray [8].

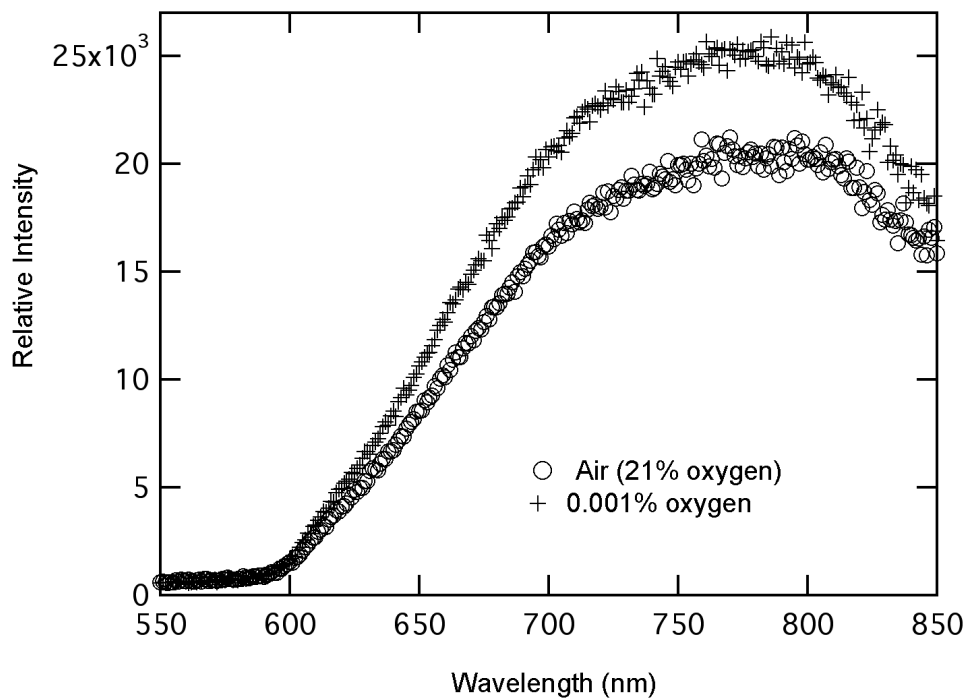
### Emission

The emission spectra of our current  $\text{Mo}_6\text{Cl}_{12}$  compound in (i) air, (ii) 0.001% oxygen, (iii) prior to thermal cycling and (iv) after three thermal cycles to 200 °C are shown in Figures 6, 7 and 8. The data in Fig. 6 demonstrates that the emissions lineshape from our current clusters after heating to 200 °C is similar to that obtained previously by Ghosh.

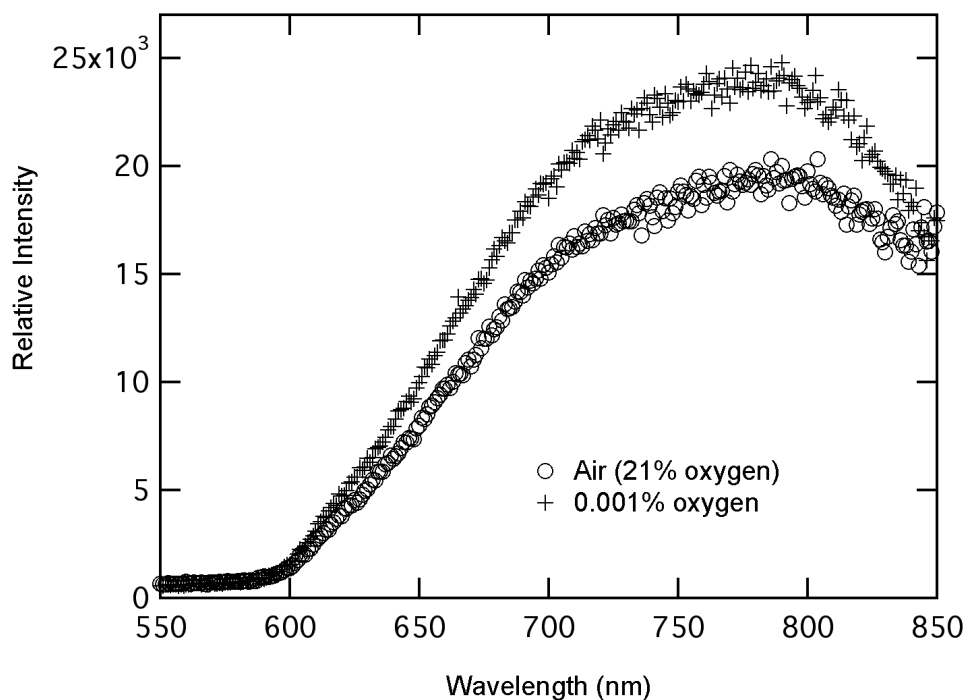
[4]. The differences in the spectra between 550 to 700 nm are attributed to the use of different long wave pass filters to block out the pump beam. Heating to 200 °C appears to have no deleterious effects on the cluster photophysics. Fig. 7 and 8 show the emission spectra of the clusters in both laboratory air (21% oxygen) and 0.001% oxygen, prior to and after cycling to 200 °C, respectively. The luminescence spectra is quenched by ~1.3X between 0.001% and 21% oxygen. This is smaller than the 5.5X quenching we have previously observed [4] with  $\text{Mo}_6\text{Cl}_{12}$  cluster/polymer composite films. We are investigating the physical cause of the reduced quenching, including the lack of molecular dispersion of the clusters in the solvent.



**Fig. 6** Emission spectra from our current cluster compound after thermal cycling to 200 °C and previous results from  $\text{Mo}_6\text{Cl}_{12}$  cluster/polymer composite films. Both spectra were taken in a 0.001% oxygen environment.



**Fig. 7** Emission spectra from our current cluster compound, concentration of  $1.7 \times 10^{-4}$  M in HCl, prior to thermal cycling.



**Fig. 8** Emission spectra from our current cluster compound, concentration of  $1.7 \times 10^{-4}$  M in HCl, after thermal cycling to to 200 °C.

Note that both the room temperature (Fig. 7) and heat treated (Fig. 8) sample had nominally the same cluster concentration of  $1.7 \times 10^{-4}$  M. The difference in the integrated intensity of their respective emission lineshapes is 5%, which is consistent with the experimental uncertainty in preparing the two solutions. These measurements demonstrate that by calibrating the input pump intensity we are now able to quantitatively compare spectra obtained on different days.

### CONCLUSIONS

Our studies have now been extended to 200 °C. TGA results show that our compound still contains water, HCl, or both. The small weight losses are reversible, however and do not affect the luminescent properties of the clusters. The emission spectra of the newly synthesized  $\text{Mo}_6\text{Cl}_{12}$  dissolved in HCl indicates that heating the original material under atmospheric conditions to 200 °C for two hours does not have any deleterious effects on the relevant photophysical parameters. Experiments are in progress to elucidate the physical cause of the smaller quenching (1.3x versus 5x) between a 0.001% and 21% oxygen atmosphere.

### REFERENCES

- [1] R. D. Mussell, Thesis, Michigan State University, 1988
- [2] M. D. Newsham, Thesis, Michigan State University, 1988
- [3] C.R. Ruud, Thesis, Michigan State University, 1999.
- [4] R. N. Ghosh, G. L. Baker, C. J. Ruud, D. G. Nocera, *Appl. Phys. Lett.*, **75**, 2885 (1999)
- [5] Remillard, J.T.; Jones J.R.; Poindexter, B.D.; Narula, C.K.; and Weber, W.H., *Applied Optics*, **38**, no. 25, 5306 (1999)
- [6] J. C. Sheldon, *J. Chem. Soc.*, 1007 (1960)
- [7] W. C. Dorman and R. E. McCarley, *Inorg. Chem.*, **13**, 491 (1974)
- [8] H. B. Gray, *J. Am. Chem. Soc.*, **103**, 1298 (1981)

### BIBLIOGRAPHY

None.

### LIST OF ACRONYMS AND ABBREVIATIONS

HCl – Hydrochloric Acid

MeOH – Methanol

$\text{CH}_3\text{CN}$  – Acetonitrile