On the Electrochemical Synthesis of Metal Acetylacetonates

Scott Browning

The University of Texas at Austin

2006

Abstract

The chemical synthesis of metal acetylacetonates has long been an established procedure, but electrochemical synthesis of these compounds remains unperfected. Through our research, the synthesis of numerous metal acetylacetonates has been achieved using electrolysis. Normally, electrochemical syntheses are accomplished in a solvent, often a nonaqueous solvent. Deviating from traditional electrochemical processes of metal acetylacetonate synthesis, the solution was prepared using the ligand as the solvent. Some metal acetylacetonates are insoluble in acetylacetone. After electrolysis, the solutions not containing precipitates were evaporated to isolate the pure compounds. The yields for the compounds were calculated and the compounds were characterized through UV/VIS spectroscopy, infrared spectroscopy, mass spectrometry, and their melting points. In addition to these spectroscopic measurements, the stereochemical properties of lanthanum acetylacetonate were examined through use of NMR spectroscopy.

On the Electrochemical Synthesis of Metal Acetylacetonates

Introduction

Metal acetylacetonates, formed by a metal and multiple acetylacetonate anions, are prime examples of coordination complexes. The electrochemical synthesis of metal acetylacetonates has been completed with nine metals. Target compounds were those derived from metals with common oxidation states of +2 and +3, thus forming bis and tris chelate complexes with coordination numbers of 4 and 6. Coordination compounds, by definition, arise when a metal cation is bonded to one or more anions through coordinate covalent bonds. Coordination complexes are often studied due to the unique properties that arise in these compounds. One of these unique properties is that of stereoisomerism. Stereoisomerism, in this case present in the tris chelate complexes, occurs due to the fundamental difference in the two possible ligand bonding configurations. With three ligands attached to the metal, there are two possible arrangements for the coordination complex that are mirror images and are not superimposable. This minor difference in structure can create different properties in the compounds and noticeable deviance in NMR spectroscopy. Another common characteristic of coordination compounds is color. In the case of the synthesis of metal acetylacetonates, colored compounds provide a method of visual characterization that can generally be used to predict whether synthesis was successful. In addition to the synthesis of these compounds, characterization was performed through the use of mass spectrometry, UV/VIS spectroscopy, infrared spectroscopy, and melting points. In the case of UV/VIS spectroscopy, the relationship between molar concentration and absorption was studied with copper (II) acetylacetonate.

Procedure

While numerous experiments were conducted, each of these experiments was performed under similar conditions. The typical electrolysis ran consisted of a solution prepared with 50.0 mg tetra-n-butylammonium hexafluorophosphate (electrolyte), 50.0 mL acetylacetone, and two metal electrodes of the desired metal compound. The components of the solution are what differentiate this electrolysis from previously conducted electrolysis. Traditionally, electrochemical synthesis is performed in a solution containing a nonaqueous solvent. In the case of our experiments, the ligand (acetylacetone) was used as the solvent. The solution was placed in a three-neck round bottom flask, the electrodes were positioned in solution, and the flask was sealed with septa. Each electrolysis was run with a maximum voltage of 300 V and most were run until a current could no longer be conducted. With air sensitive compounds, electrolysis was run in a constant flow of nitrogen. Upon completion of the electrolysis, the electrodes were weighed to calculate yield and the solution was rinsed with hexanes and petroleum ether and evaporated or filtered if the solution contained a precipitate.

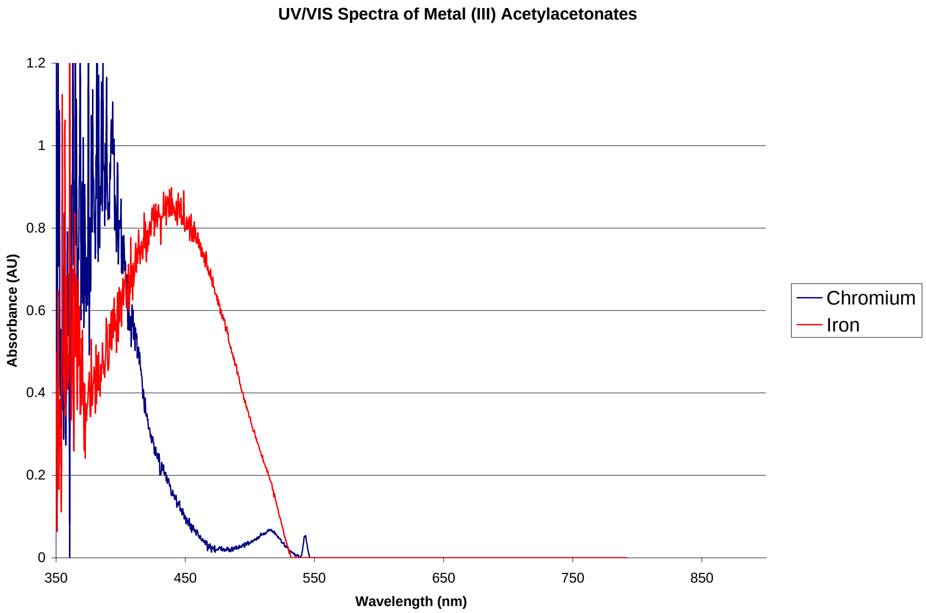
Once the metal acetylacetonates were isolated, characterization was necessary to determine the existence of the product. Preparation for IR spectroscopy involved creating nujol mull placing a small amount between two potassium bromide plates. After preparation, the absorption and transimittance of infrared light was determined. For UV/VIS spectroscopy, compounds were dissolved in chloroform and placed in a transparent cuvette. The machine was blanked with pure chloroform and the absorption and transmittance of ultraviolet and visible light was determined. After all of the compounds were characterized through UV/VIS spectroscopy, the spectroscopic properties of copper (II) acetylacetonate were examined. Absorbance of light at a wavelength of 431 nm was measured as related to the molarity of the solution. An equation for this relationship was generated, providing another potential source of verification of the compound.

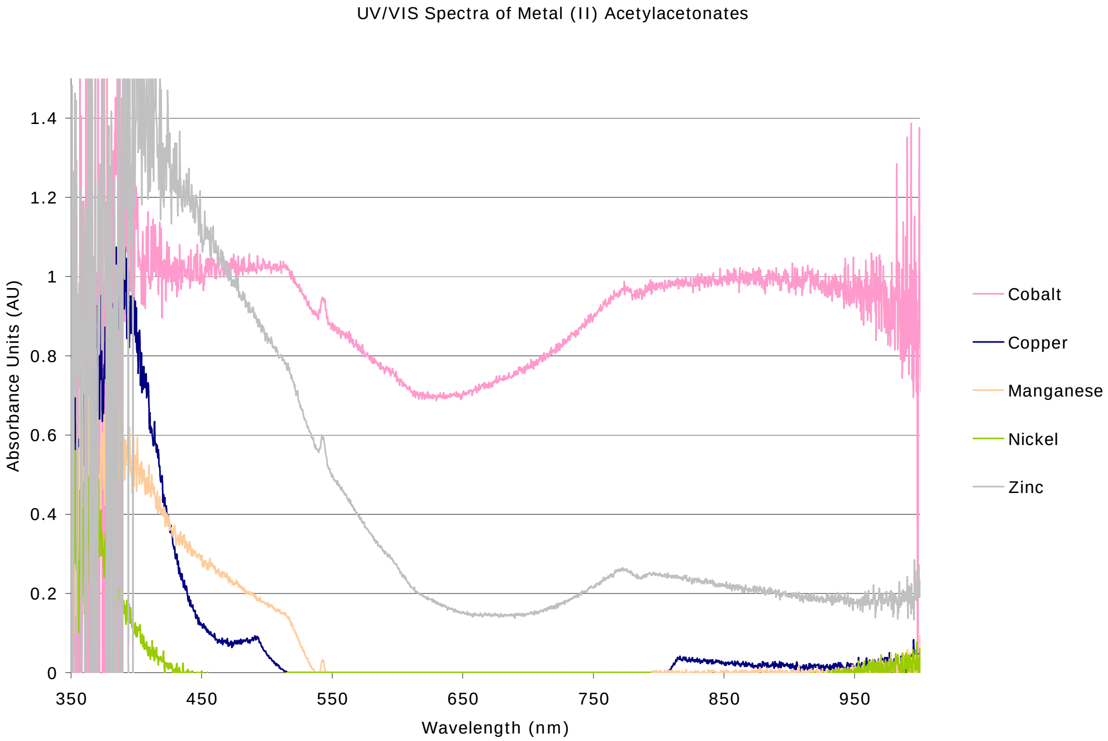
Results and Conclusions

Experimental Data in the Electrochemical Synthesis of Metal Acetylacetonates

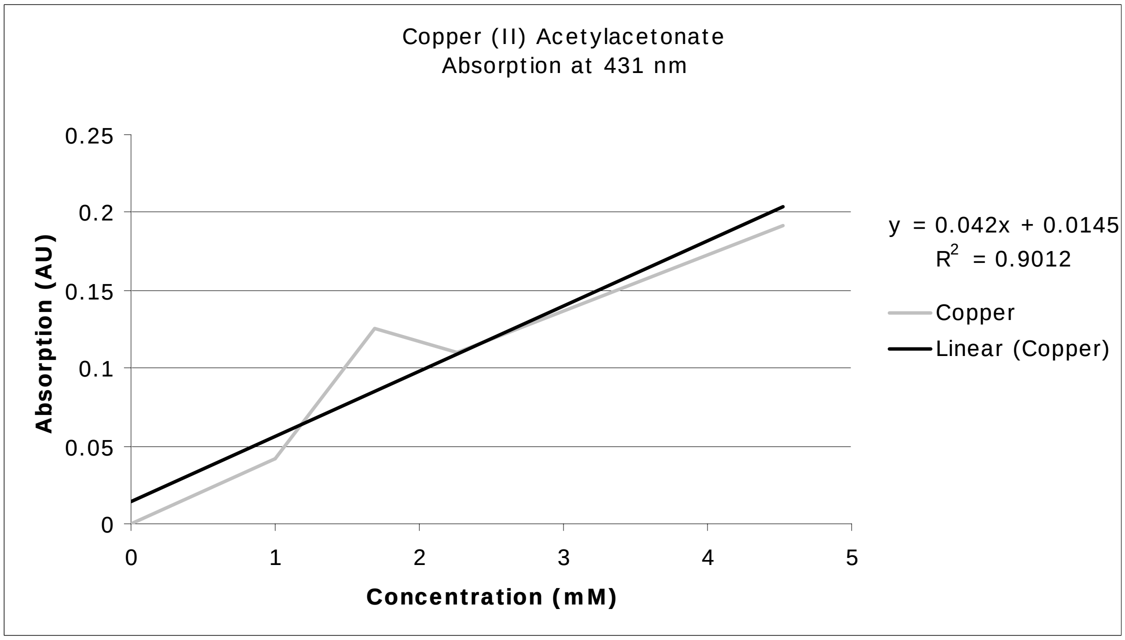
Name	Chemical Formula	Color	Percent of Metal Dissolved	Precipitate	IR	UV/Vis	M.P. (°C)	Mass Spec	NMR	% Yield
Chromium (III)	$Cr(C_5H_7O_2)_3$	Purple	10.8%	No	Yes	Yes	-	(a)	(p)	-
Cobalt (II)	$Co(C_5H_7O_2)_2$	Pink	11.0%	Yes	Yes	Yes	145	(a)	(p)	54.7%
Copper (II)	$Cu(C_5H_7O_2)_2$	Blue	46.0%	Yes	Yes	Yes	235	Yes	(p)	91.2%
Iron (III)	$Fe(C_5H_7O_2)_3$	Dark Red	80.9%	No	Yes	Yes	-	(a)	(p)	Hydrate
Lanthanum (III)	$La(C_5H_7O_2)_3$	White	6.8%	Yes	Yes	Yes	126	(a)	(a)	33.7%
Manganese (II)	$Mn(C_5H_7O_2)_2$	Tan	17.9%	Yes	Yes	Yes	240 d.	(a)	(p)	4.2%
Nickel (II)	$Ni(C_5H_7O_2)_2$	Light Green	20.3%	Yes	Yes	Yes	190	(a)	(p)	Hydrate
Zinc (II)	$Zn(C_5H_7O_2)_2$	White	40.8%	Yes	Yes	Yes	136	(a)	(p)	Hydrate
Vanadyl (II)	$VO(C_5H_7O_2)_2$	Brown	-	No	Yes	Yes	-	(a)	(p)	-
(a) - pending	(p) - paramagnetic									

The extensive experimental data and results from our research can be best summarized in the above spreadsheet. The following UV/VIS spectra were used to characterize the metal acetylacetonates. The UV/VIS spectra are divided between the bis and tris chelates. Several characteristic trends were observed through UV/VIS spectra including a distinctive absorbance spike near 550 nm. Also evident in the UV/VIS spectra are shifts in absorbance that correlate with change in mass. In general, the heavier compounds will exhibit greater absorption at higher wavelengths of light and thus an apparent shift to the right will be visible on the spectra. For example, the spectrum pictured below contrasts the absorbance of chromium (III) acetylacetonate and iron (III) acetylacetonate. The iron chelate weighs slightly more than that of chromium and there is a difference of about 100 nm between the two absorption spikes. In the second set of UV/VIS spectra pictured, the trend still remains although there are some spikes that diverge from this trend. This divergence could be due to a couple of the compounds being hydrates instead of pure metal acetylacetonates.

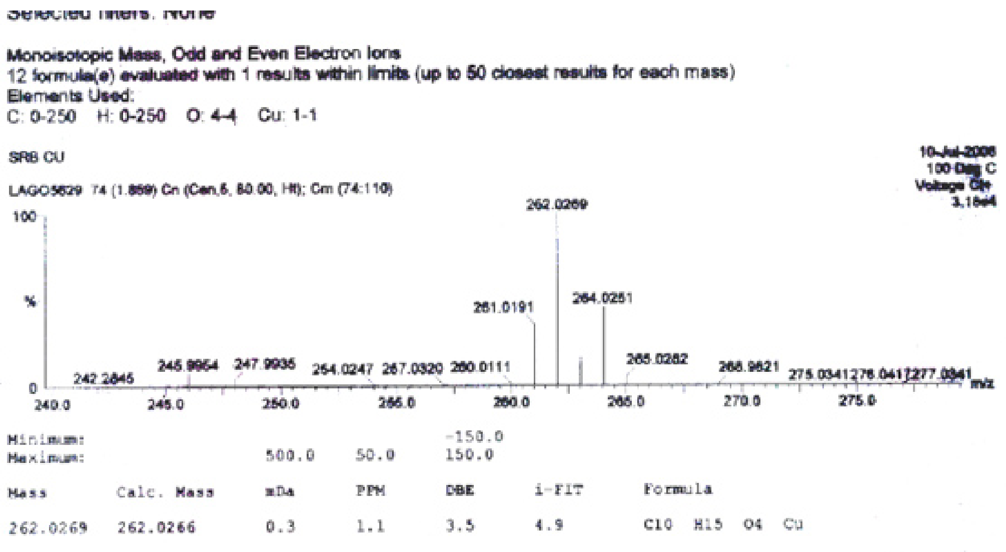




Following the UV/VIS spectra, the relationship between copper (II) acetylacetonate molar concentration and absorption was examined. Although data could have been more precise had an automatic pipette been used, an equation and graph (pictured below) were still generated with a slope of .042.



In addition to data retrieved from UV/VIS spectroscopy, data from mass spectrometry also validates the existence of our products. The high resolution mass analysis of copper (II) acetylacetonate is pictured below, the calculated mass was 262.0266 and the found mass was 262.0269. The significant spikes near that of copper (II) acetylacetonate are common in any mass analysis and represent common changes in the compound such as the loss of a methyl group and proton ionization.


Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
12 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-250 H: 0-250 O: 4-4 Cu: 1-1

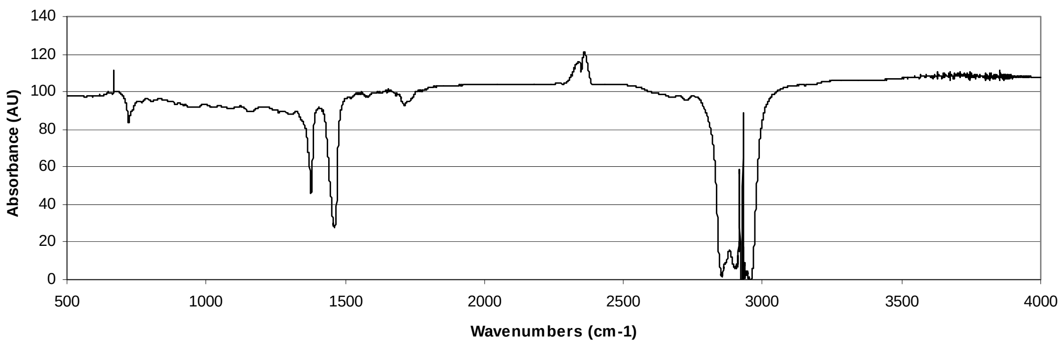
SRB CU

LAGO5629 74 (1.859) Cn (Cen,6, 80.00, Ht); Cm (74:110)

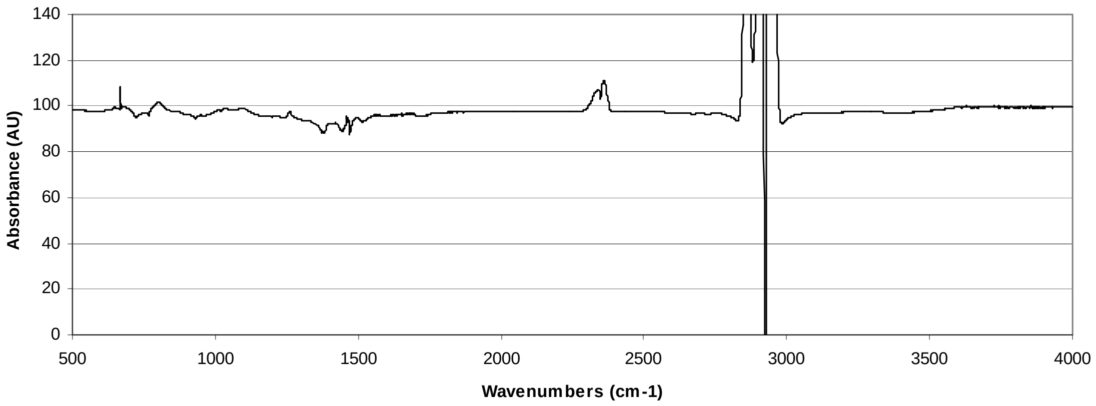
```
Minimum:                              -150.0
Maximum:                 500.0  50.0   150.0

Mass       Calc. Mass    mDa    PPM    DBE     i-FIT    Formula

262.0269   262.0266      0.3    1.1    3.5     4.9      C10  H15  O4  Cu
```

The IR spectra of eight metal acetylacetonates are pictured below. Each spectrum exhibits similar characteristics such as spikes caused by fundamental carbonyl stretching frequencies near the 1600 cm^{-1} region and another distinguishing spike near 2400 cm^{-1}. The spike near 2900 cm^{-1} appeared larger than expected. This could be an outcome of water or electrolyte interference.

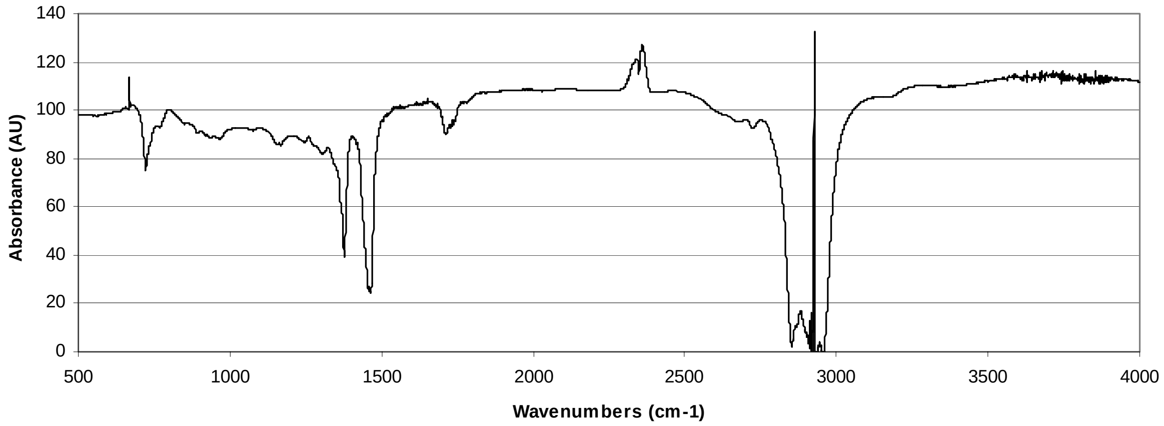
Chromium (III) Acetylacetonate IR Spectrum

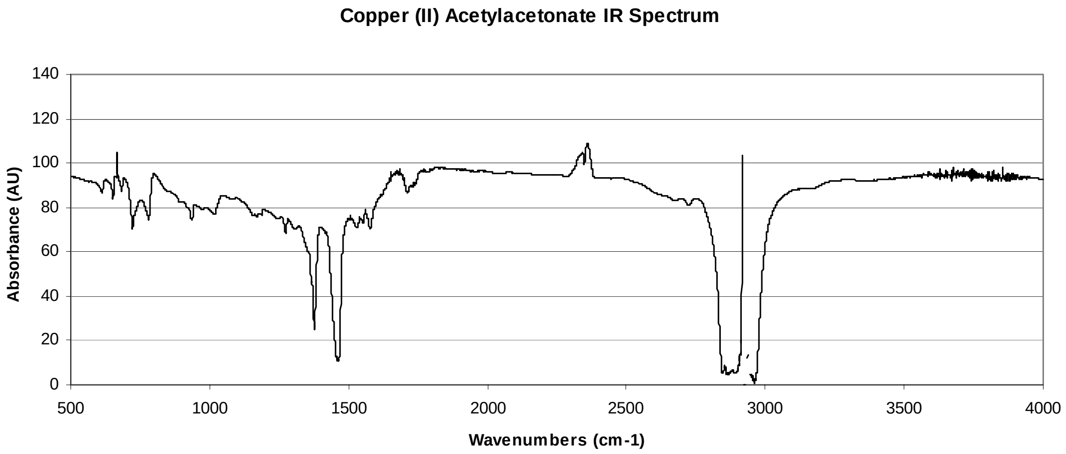


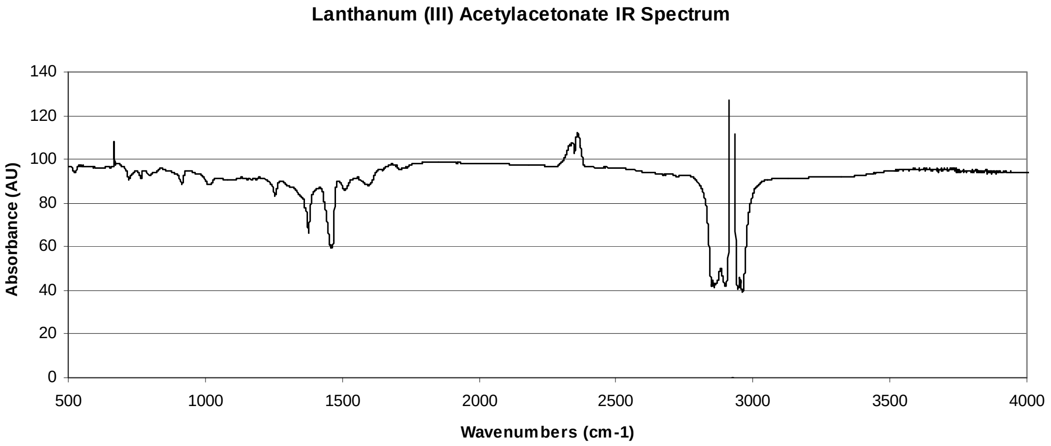
Cobalt (II) Acetylacetonate IR Spectrum

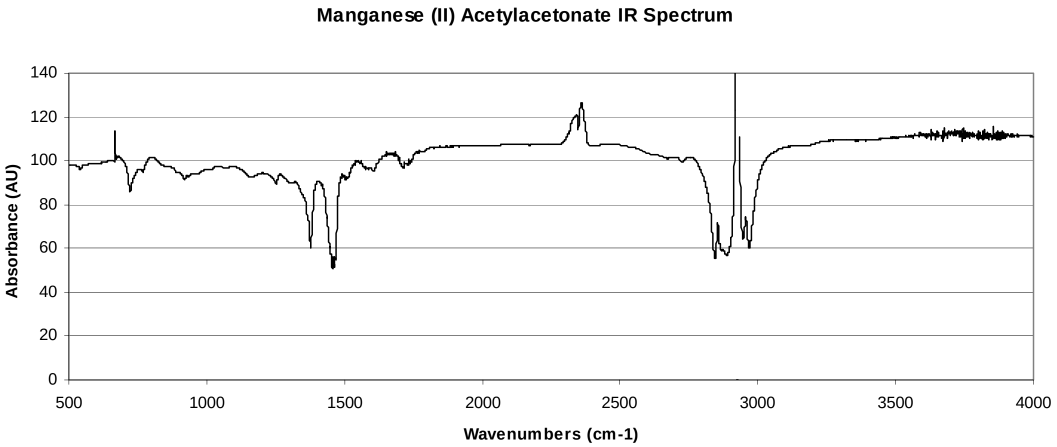


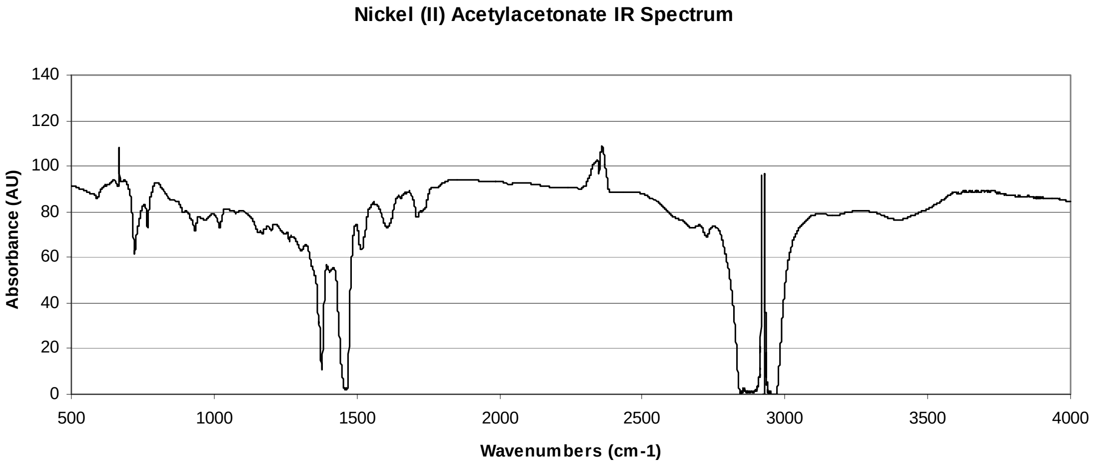
Iron (III) Acetylacetonate IR Spectrum

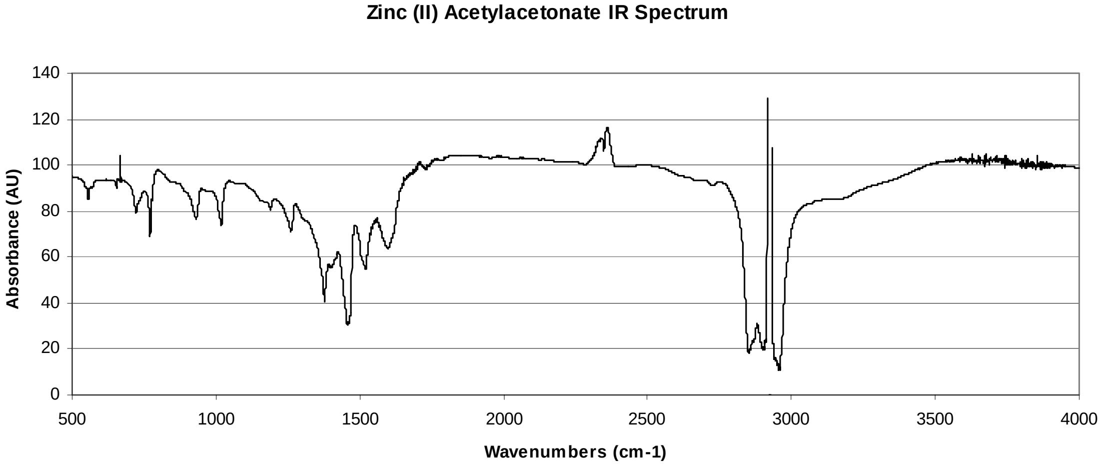



Copper (II) Acetylacetonate IR Spectrum


Lanthanum (III) Acetylacetonate IR Spectrum


Manganese (II) Acetylacetonate IR Spectrum





The melting points of the compounds tested are similar to those from literature. Differences occurred in some melting points as a result of a hydrate being formed. Although every compound did not undergo melting point check and mass analysis, the collaboration of all characteristic data supports the notion that all of the compounds were synthesized.

Through our research we can conclude that in electrochemical synthesis the ligand can be effectively used as the solvent. Spectral data served as confirmation that our reactions were successful and our products were present. Throughout the research process, numerous possibilities for further research became evident. Among these is the electrochemical synthesis of air sensitive and rare-earth metal acetylacetonates. Also, due to NMR results being pending, further study of the stereochemical properties of lanthanum (III) acetylacetonate and other diamagnetic chelates would be ideal.

Works Cited

1. Habeeb, Jacob J., Dennis G. Tuck, and Frederick H. Walters. "Direct Electrochemical Synthesis of Some Metal Chelate Complexes." Journal of Coordination Chemistry 8 (1978): 27-33.

2. Nakamoto, Kazvo. “Infrared Spectra of Inorganic and Coordination Compounds.” New York. 1963

Acknowledgments

I would like to sincerely thank the Robert A. Welch Foundation for funding this research and providing me with the opportunity to expand my scientific horizons. My utmost appreciation goes to Dr. Lagowski for accepting me into his research laboratory and appointing me to such a fascinating project. This research could not have been completed without Reid Long, who took me under his wing and taught me everything I needed to be successful in the research process. Thanks also go to Rita Wilkinson for organizing events, finalizing the preparation of our papers, and much other work behind the scenes. I also must thank my fellow scholars for making this experience both enjoyable and memorable. I would also like to express my gratitude to Mr. TenEyck, Mrs. Rice, and Mrs. Breeding for igniting my interest in science and academics and for nominating/recommending me for this program. Lastly, I would like to thank my parents for providing unending support and motivation as I go about my scientific endeavors.