On the Electrochemical Synthesis of Metal Acetylacetonates

Scott Browning, Reid Long, Dr. Lagowski

The Department of Chemistry and Biochemistry, The University of Texas at Austin

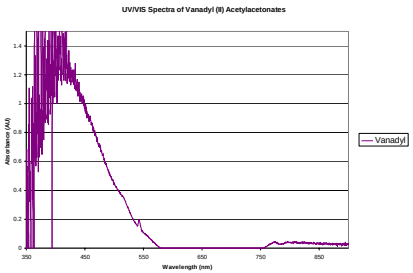
1. Introduction

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. Chemical syntheses can often require more steps than the direct route of electrochemical syntheses. Metal acetylacetonates are used as catalysts and gasoline additives. Beyond the synthesis of the compounds, comprehensive characterization of the metal acetylacetonates was necessary in order to prove the existence of the product. NMR spectroscopy was also used to examine the stereochemical characteristics of lanthanum actetylacetonate.

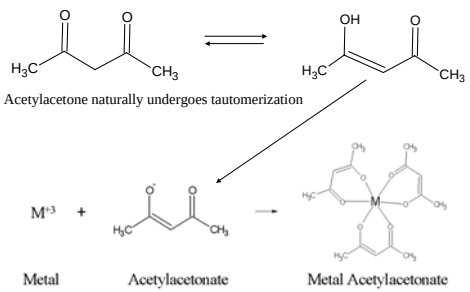
Experimental Data in the Electrochemical Synthesis of Metal Acetylacetonates

Name	Chemical Formula	Color	% of Metal Diss.	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									

UV/VIS Spectrum of Vanadyl (II) Acetylacetonate



2. Molecular Interactions



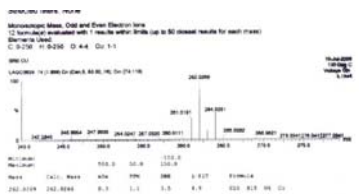
4. Experimentation

The typical electrolysis conducted in these experiments consisted of the following:

- two metal electrodes (of the desired metal compound)
- 50.0 mL Acetylacetone
- 50.0 mg tetra-n-butylammonium hexafluorophosphate (electrolyte)

A solution containing acetylacetone and the electrolyte was placed in a round bottom three-neck flask. The two electrodes were weighed, attached to wires connected to a current generator, and placed in the solution. The flask was sealed with septa and the electrolysis was initiated with a maximum voltage of 300 V. The electrolysis was run with the constant cooling of an ice bath. With air sensitive compounds, electrolysis was run in a nitrogen atmosphere. After electrolysis, the electrodes were weighed to calculate theoretical yield. The solutions not containing precipitate were rinsed with hexanes and petroleum ether and then evaporated. Solutions containing precipitate were filtered to isolate the metal acetylacetonates.

High Resolution Mass Spec of Copper (II) Acetylacetonate



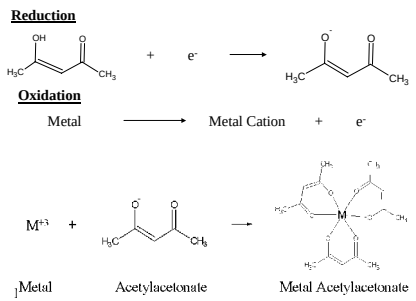
10. Conclusions

Electrochemical syntheses of metal acetylacetonates can be effectively conducted in a solution containing the ligand as the solvent. Spectral data confirmed the existence of the desired metal acetylacetonates. A minor discrepancy in characterization occurred with some melting points being low due to the product being a hydrate.

11. Future Work

- Electrochemical synthesis of air sensitive metal acetylacetonates
- Electrochemical synthesis of more rare-earth acetylacetonates
- Further examination of stereochemical behavior of diamagnetic metal acetylacetonates through NMR data

3. Electrochemical Synthesis

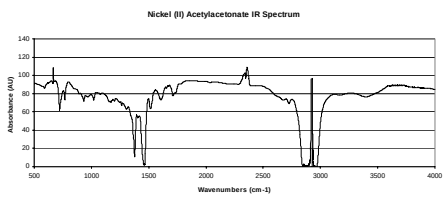


5. Characterization

In order to verify the presence of the metal acetylacetonates, multiple methods of characterization were employed. The following methods were utilized in the identification of our products:

- **Mass Spectrometry** – analyzes the mass of all components present in the sample
- **UV/VIS Spectroscopy** – determines the absorption and transmittance of visible and ultraviolet light through a solution
- **IR Spectroscopy** – determines the absorption and transmittance of infrared light through a solution
- **NMR Spectroscopy** – exploits the magnetic properties of the compound, measures the resonance frequency as related to the magnetic field strength to help identify fundamental carbon and hydrogen atoms
- **Melting Points** – the melting points of the compounds are checked and compared to known values

IR Spectrum of Nickel (II) Acetylacetonate



12. References

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

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