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# The Direct Electrochemical Synthesis of Transition Metal Acetylacetonates

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Acetylacetonates were prepared electrochemically in good yield using the pure liquid ligand, acetylacetonone, as the solvent, in which the supporting electrolyte, tetra-*n*-butylammonium hexafluorophosphate, was dissolved; the metal of interest served as the electrodes. The products were characterized by UV-visible spectrometry (color) and mass spectrometry. Both a lower,  $M(\text{AcAc})_2$ , and a higher,  $M(\text{AcAc})_3$ , oxidate state were formed for the cobalt and manganese systems; the identity of the product(s) could be biased by a careful choice of the potential used for the synthesis.

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**Keywords** acetylacetonone, transition metals, synthesis, electrolysis

## INTRODUCTION

Electrochemical methods represent one of the less well-known techniques in the arsenal of synthetic strategies available to chemists. From one point of view, the electrochemical approach to synthesis is one of the most direct methods available to carry out redox reactions because it eliminates the attendant product complications involved in the use of chemical redox reagents. In electrochemical synthesis, the electrodes act as sinks for, or sources of, electrons which can react with solution species; electrode-derived species, such as cations produced at the anode, can enter into the synthesis reactions. In the latter instance, the electrodes are described as sacrificial electrodes since they lose mass, which can be used as a measure of the “efficiency” of the reaction. Electrochemical syntheses are most often successful when conducted in non-aqueous solvents, in which case an

appropriate supporting electrolyte is necessary to make the solution conducting.

Tuck and his students<sup>[1]</sup> have provided us with the details of the synthesis of a variety of inorganic and organometallic compounds, ranging from anhydrous transition metal halides and their coordinate covalently bonded solvates, derivatives of weak acids, as well as sigma-bonded organometallic compounds. Others have described the electrochemical synthesis of  $\pi$ -complexed organometallic substances.<sup>[2]</sup>

We have become interested in the possibility of using liquid ligands as the solvents in electrochemical synthesis, which, in principle, would make the isolation of the product even simpler since the number of species present had been decreased, i.e., no solvent with which to contend. Here we describe the successful electrochemical synthesis of some transition metal acetylacetonates using acetylacetonone as the electrolytic solvent.

## EXPERIMENTAL

In a typical experiment, ~50.0 mg of tetra-*n*-butylammonium hexafluorophosphate, the supporting electrolyte, was added to 50 ml of dry acetylacetonone contained in a 500 ml three-necked round-bottomed flask; the flask necks were sealed with septa. The two furthest septa carried the electrodes. Stout copper wires pierced these septa; a mechanical clip was attached at each end of each copper wire. The working electrodes were attached mechanically to the copper wire using the interior clips and the clips, which were outside of the flask, could be attached to the power supply at the appropriate time in the experiment. The central neck of the flask was generally unused, but was useful occasionally where the electrolytic solution could be removed or more solvent added with a syringe; the flask could be purged with a dry inert gas (nitrogen or argon) using a needle attached to the gas source with flexible tubing. The power source (Daigger 300) could produce either constant current or constant voltage output.

In a typical experiment, the power source was attached to the reaction flask after the latter had been assembled and was

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TABLE 1  
Experimental data in the electrochemical synthesis of metal acetylacetonates

Formula	Color	Solubility in acetyl- acetone	Yield (%) <sup>a</sup>	Mass expected	Mass found	$\nu$ CO		UV-vis, (nm) major peak	
						Literature	Found		
Vanadyl (IV)	VO(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>2</sub>	Brown	Yes	47.7	266.0359	266.0357	1541 <sup>c</sup>	1540	278
Chromium (III)	Cr(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>3</sub>	Red-purple	Yes	71.7	350.0821	350.0823	1524 <sup>d</sup>	1512	338
Manganese (II)	Mn(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>2</sub>	Tan	Yes <sup>b</sup>	4.2	254.0351	254.0352	1520 <sup>e</sup>	1520	274
Manganese (III)	Mn(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>3</sub>	Brown/black	Yes	95.1	352.0715	352.0719	1590 <sup>e</sup>	1578	262
Iron (III)	Fe(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>3</sub>	Dark red	Yes	75.7	354.0766	354.0764	1526 <sup>d</sup>	1464	272
Cobalt (II)	Co(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>2</sub>	Pink	No	54.7	258.0302	258.0303	1601 <sup>d</sup>	1522	281
Cobalt (III)	Co(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>3</sub>	Green	Yes	95.1	356.0669	356.067	1580 <sup>e</sup>	1575	260
Nickel (II)	Ni(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>2</sub>	Light green	No	97.3	257.0324	257.0325	1598 <sup>d</sup>	1606	276
Copper (II)	Cu(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>2</sub>	Blue	No	91.2	262.0266	262.0269	1554 <sup>d</sup>	1554	300
Zinc (II)	Zn(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>2</sub>	White	No	86.8	263.0262	263.0265	1592 <sup>d</sup>	1600	275

<sup>a</sup>Calculated from the mass loss of the anode and the mass of the dry product.

<sup>b</sup>Precipitated from solution with hexanes.

<sup>c</sup>Lawson, K. E. *Spectrochimica Acta* **1961**, *17*: 248–258.

<sup>d</sup>Nakamoto, Kazuo, the infrared absorption spectra of metal acetylacetonates, infrared spectra of inorganic and coordination compounds. The Direct Electrochemical Synthesis of Transition Metal Acetylacetonates, John Wiley, New York, 1963.

<sup>e</sup>Aldrich Spectrum Library.

set to produce a constant voltage of 300 volts with the current “floating” between 10–50 mA. Most experiments were conducted at 300 V until a current would no longer pass. Generally, the time for electrolysis was ~10 hours (over night); however, useful amounts of product, ~50 mg, could be obtained after ~1 hour. When air-sensitive products were involved, the electrolysis was conducted under a constant flow of inert, dry nitrogen gas, which could be introduced through a needle piercing the septum covering the central neck of the flask. Of course, the increase in pressure must be relieved using an additional needle piercing one of the other septa.

If an insoluble product formed, the precipitate was vacuum-filtered and washed twice with hexanes and petroleum ether; the electrolyte, tetra-n-butylammonium hexafluorophosphate, is soluble in the wash solvents whereas the desired products are not. When the product was soluble in the electrolyte solution the solvent (excess acetylacetonate) was removed *in vacuo* and the resulting solid mixture of the desired product—metal acetylacetonate—and electrolyte was washed twice with hexanes and twice with petroleum ether.

## RESULTS

The acetylacetonates of the first row transition metals produced in this investigation are listed in Table 1, together with pertinent details and properties that characterize these compounds.

## DISCUSSION

The compounds produced using the general protocol described here—the ligand as solvent—are identical with the equivalent compounds produced by chemical means<sup>[3]</sup> and electrochemically using a solvent.<sup>[4]</sup>

Among the products formed (Table 1, column 2) we see evidence (Mn and Co) for the production of the 3+ oxidation state, M(AcAc)<sub>3</sub>, of the metal compound in addition to the expected 2+ state M(AcAc)<sub>2</sub>. At least two possibilities exist for these kind of results: the 2+ product (M(AcAc)<sub>2</sub>) is oxidized by atmospheric oxygen, a process that would be expected to form the 3+ compound which would form M(AcAc)<sub>3</sub> readily since the solvent is the ligand. The second possibility is that the higher oxidation state is produced electrochemically together with, or after, the lower oxidation state product. Most of our experiments on this question were focused on the cobalt system. The electrochemical oxidation hypothesis seems to be supported by the observation that, in the initial stage of the electrolysis, the solution is distinctly pink, a color characteristic of Co(AcAc)<sub>2</sub>, but it quickly changes to the green color characteristic of Co(AcAc)<sub>3</sub> while a current is still passing. The hypothesis that oxidation by atmospheric oxygen is probably *not* the culprit is supported by the observation that the pink compound does not turn green when air is passed through the mixture. Finally, we were able to show that below a voltage in the range of 50–75 V the product is always pink, but above this range, a mixture of pink and green products form. The yields for the cobalt compounds were obtained from experiments in which

the conditions (voltage) were adjusted to favor the green or the pink compound. Interestingly, the higher oxidized product in the case of cobalt,  $\text{Co}(\text{AcAc})_3$ , was isolated as an oil; dissolution of this product in chloroform produced a green solution from which a green solid was obtained by evaporation of the solvent.

Similar results for the manganese system strongly suggest that the production of  $\text{Mn}(\text{AcAc})_2$  and  $\text{Mn}(\text{AcAc})_3$  is also electrochemically controlled.

The formation of the unexpected vanadyl acetylacetonate,  $\text{VO}(\text{AcAc})_2$ , arises from the air oxidation of the expected lower valent production which is a characteristic process in the general chemistry of vanadium.<sup>[5]</sup>

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