

Synthesis, Electrochemical, and Spectroscopic studies  
of a series a of tris(Acetylacetonato) M(III) complexes

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## **Abstract**

During our research, we studied the cyclic voltammetry of a series of coordination complexes of M(III)tris(acac). In our first electrochemical experiments, we used Cyclic Voltammetry. In this experiment, a varying potential voltage is run through the system and the resulting current is measured. We scanned our complexes with different scan rates to find the average  $E^{(1/2)}$  value. We used the currents to find the diffusion coefficient from the Randles-Sevcik equation. For our second electrochemical experiments, we did a Controlled Potential Coulometry on one of our complexes,  $\text{Ru}(\text{acac})_3$  to observe the features of both of its reversible redox couples.

## **Introduction**

At the beginning of the semester, we got introduced to Coordination compounds. In order to thoroughly understand the theory behind our research, our advisor, Dr. Ghosh, lectured us on Electrochemistry, Spectroscopy, Coordination Chemistry, Ligand Field Theory, and NMR. In our research, we worked with coordination complexes. We studied the ligand of acetylacetonone and its interaction with Metal(III) ions.

When we began Cyclic voltammetry, we practiced with  $\text{Fe}(\text{C}_5\text{H}_5)_2$ ,  $\text{K}_3\text{Fe}(\text{CN})_6$ , and  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ . We aimed to reproduce literature results for different compounds, using various solvents and supporting electrolytes. This represents much of our learning curve for our understanding of electrochemistry, its techniques, and the software that we used throughout our research. From here onwards, we solely devoted our time to studying the electrochemical and spectroscopic properties of our tris(acac)M(III) complexes.

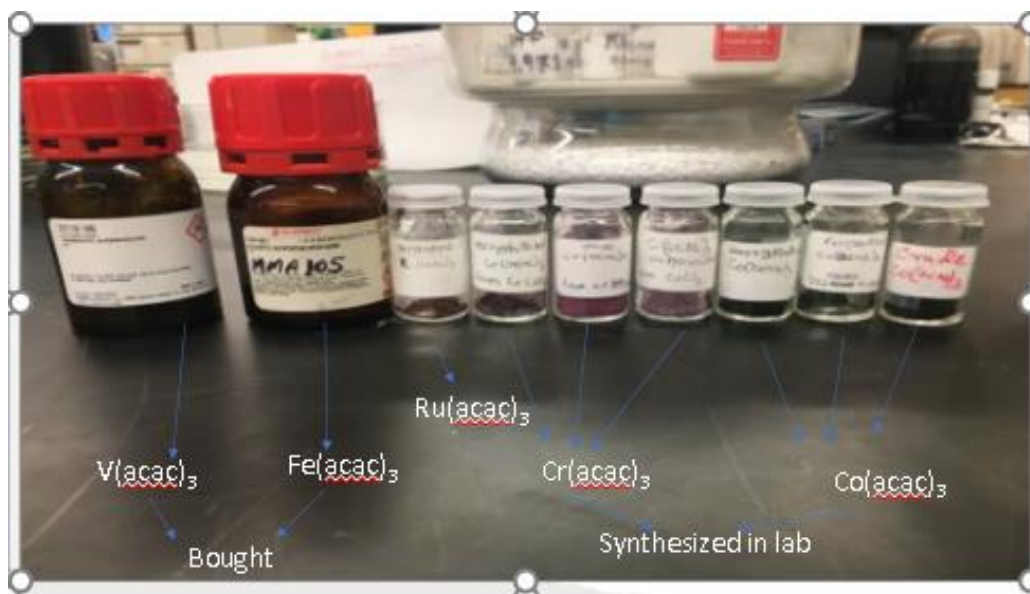
## **Equipment and Materials**

The material we used throughout this research were the spectrophotometer Genesys 10S UV-Vis, the IR PerkinElmer FT-IRspectrometer and BASi Epsilon Eclipse electrochemical analyzer.

For our CV studies, we used a 3-electrode cell Working, Counter, and Reference electrodes. The Working electrode sends the potential voltage through the system, the Counter electrode completes the circuit, and the Reference electrode acts as a reference point for the potential voltages. For Cyclic Voltammetry, we mostly used a glassy carbon working electrode, acetonitrile as a solvent, and tetrabutylammonium hexafluorophosphate as a supporting electrolyte. For Controlled Potential Coulometry, we used a platinum working electrode. We used an Ag/AgCl reference electrode. We purge with nitrogen because oxygen comes in very fast and can accept electrons. The purging pushes the oxygen from the system by forcing Nitrogen in throughout the experiment. The solvent is used to make the solution dissolve the analyte. The Supporting Electrolyte is used to prevent various issues including Ohmic Drop and Mass Diffusion. Both must be chosen to be able to both work with the analyte and not be reactive under the voltage range that we measure.

## **Procedure**

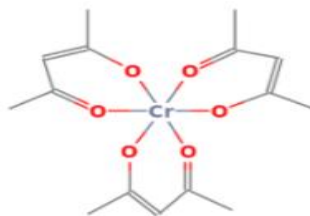
We worked with  $\text{Cr}(\text{acac})_3$ ,  $\text{Co}(\text{acac})_3$ ,  $\text{Ru}(\text{acac})_3$ ,  $\text{Fe}(\text{acac})_3$  and  $\text{V}(\text{acac})_3$ . We bought  $\text{Fe}(\text{acac})_3$  and  $\text{V}(\text{acac})_3$ . We synthesized  $\text{Cr}(\text{acac})_3$ ,  $\text{Co}(\text{acac})_3$ , and  $\text{Ru}(\text{acac})_3$ .



We initially synthesized  $\text{Cr}(\text{acac})_3$  according to a literature method. We used  $\text{CrCl}_3$  anhydrous as a starting material. Our product did not look like the literature pictures that we found of  $\text{Cr}(\text{acac})_3$ , and we suspect that the error is from our  $\text{CrCl}_3$  being anhydrous when the literature method used  $\text{CrCl}_3$  hexahydrate. We then synthesized  $\text{Cr}(\text{acac})_3$  again using a method that our advisor came up with and we were able to get a compound that looked the same as the literature pictures. Our final method consisted of heating a solution of  $\text{Cr}(\text{NO}_3)_3$ , Urea, acetylacetonate, and water under reflux for several hours. We then vacuum filtered it to get the product on the right. After that, we recrystallized it using ethanol to purify it for our research.



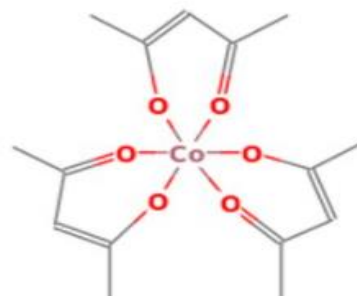
Starting Material:  $\text{CrCl}_3$  Anhydrous



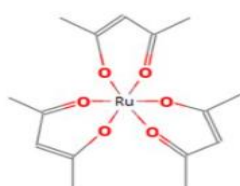
Starting Material:  $\text{Cr}(\text{NO}_3)_3$

For the  $\text{Co}(\text{acac})_3$  synthesis we also followed a reference. We heated the solution of Cobalt carbonate and acetylacetonate. We kept it under nitrogen and

dripped hydrogen peroxide into the solution. We then recrystallized it in ethanol and we got our solution.

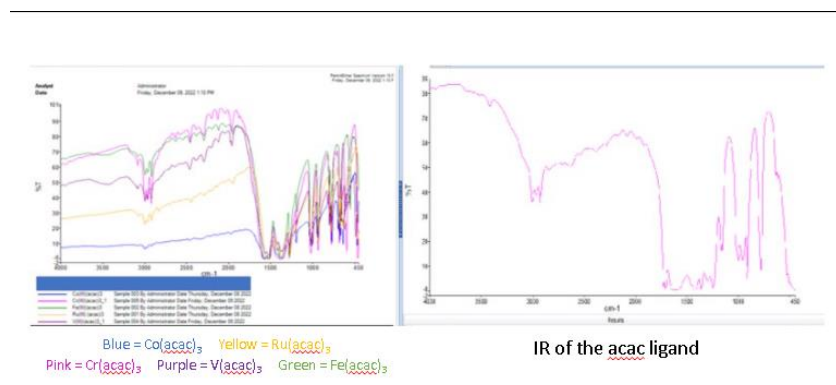


We synthesized  $\text{Ru}(\text{acac})_3$  according to a literature method. We dissolved  $\text{RuCl}_3$  trihydrate in a water/ethanol solution. We refluxed it for several hours and then added acetylacetonate. We refluxed it for another hour and then added  $\text{KHCO}_3$  (potassium bicarbonate). We then refluxed it for one more hour. To isolate the pure ruthenium, we decided to do a flask chromatography. We dissolved our solution in toluene and let it run through aluminum oxide -- our stationary phase. Only pure  $\text{Ru}(\text{acac})_3$  should be able to dissolve in toluene and go through the stationary phase. Once we got our product, we distilled it and recrystallized it in ethanol.



In order to prove that our products --including the bought ones-- were pure, we decided to check the IR and a UV-Visible spectrum of all the acac compounds.

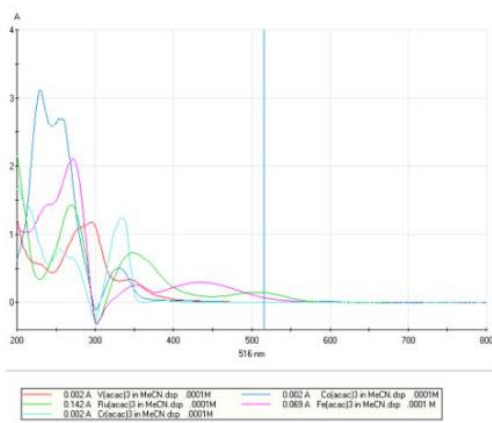
The IR was done with a KBr palatte. The IR of all the acac compounds match with the acac ligand, and these values were the same as the ones recorded in the literature.



We dissolve our compound with acetonitrile in a molarity of  $10^{-4}$  in order to do the spectral studies of the compounds. The UV-Visible spectrum done with a baseline of acetonitrile shows us a higher region and a lower region. The higher region has characteristics of the ligand band meanwhile the lower region has the metal and ligand charge transfer change. These values match the literature values. Due to all our values matching in IR and UV visible spectrum, our compounds were proven to be pure.

UV-Vis Spectrum of  
M(III) tris(acac)<sub>3</sub>  
compounds

- Red = V(acac)<sub>3</sub>
- Green = Ru(acac)<sub>3</sub>
- Light Blue = Cr(acac)<sub>3</sub>
- Blue = Co(acac)<sub>3</sub>
- Purple = Fe(acac)<sub>3</sub>



Green – Co(acac)<sub>3</sub>

Red – Ru(acac)<sub>3</sub>

Orange – Fe(acac)<sub>3</sub>

Yellow – V(acac)<sub>3</sub>

Purple – Cr(acac)<sub>3</sub>

We succeeded in synthesizing our acac compounds proven by the IR and UV-Visible spectrum, therefore we started with the investigation of the electrochemical properties of these compounds with cyclic voltammetry and controlled potential coulometry.

When we began Cyclic Voltammetry of our M(III)Tris(acac) complexes, we were interested in seeing the variation of the diffusion coefficients. The diffusion coefficient can be calculated using the Randles-Sevcik equation. Although there are many variables in the equation, we held most of them at a constant, and only changed  $v$ , the scan rate. This is the rate of how many Volts of Potential Voltage pass through the system over time. By changing just the scan rate we were able to calculate the average diffusion coefficients of each of our complexes. We scanned each of our complexes multiple times with different scan rates to find an average diffusion coefficient.

- $i_p$  - current peak
- $N$  - amount of electrons transferred in redox
- $F$  - Faraday's Constant
- $A$  - Area of working electrode
- $D$  - Diffusion Coefficient
- $C$  - Concentration of Analyte in Solvent
- $V$  - scan rate
- $R$  - Gas Constant
- $T$  - Temperature

$$i_p = 0.4463 n^{3/2} F^{3/2} A \frac{D^{1/2} c v^{1/2}}{(RT)^{1/2}}$$

In most of our Cyclic Voltammeteries we scanned the system with six scan rates: 100, 200, 300, 400, 500, and 1000 mV. We then overlaid the six voltammograms to get a better visual representation of how the system is reacting.

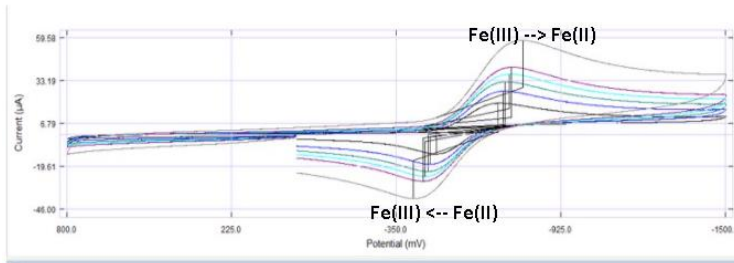
Using this overlay, you can also find the  $E^{(1/2)}$  value. The  $E^{(1/2)}$  value is found using the average of the average reduction potential and the average oxidation potential.

In the graph of two of our complexes –  $\text{Co}(\text{acac})_3$  and  $\text{Cr}(\text{acac})_3$ —you can see that they only get reduced to  $\text{M}(\text{II})$ , but they do not get oxidized back to  $\text{M}(\text{III})$ . This is what makes those two irreversible systems. This contrasts to  $\text{Fe}(\text{acac})_3$  which does get oxidized back to  $\text{M}(\text{III})$ . This is what makes  $\text{Fe}(\text{acac})_3$  a reversible System. As a side note, although there are small oxidation peaks on the left side of the voltammogram for  $\text{Co}(\text{acac})_3$  and  $\text{Cr}(\text{acac})_3$ , we believe that those are just the oxidation of the product of the decomposition of the  $\text{M}(\text{II})$ . The other two complexes –  $\text{Ru}(\text{acac})_3$  and  $\text{V}(\text{acac})_3$ — have two fully reversible



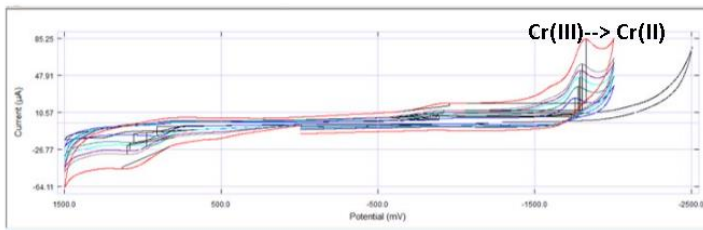
redox couples. They are definitely reversible systems.

### CV $\text{Fe}(\text{acac})_3$



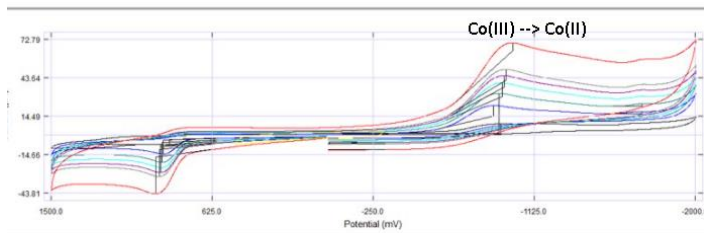
Reversible  $E^{\circ} = -596 \text{ mV}$  in reference to  $\text{Ag}/\text{AgCl}$

### CV Of $\text{Cr}(\text{acac})_3$



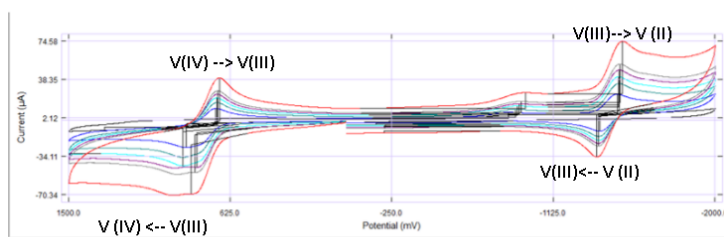
Irreversible  $E_c = -1785 \text{ mV}$

### CV Of $\text{Co}(\text{acac})_3$



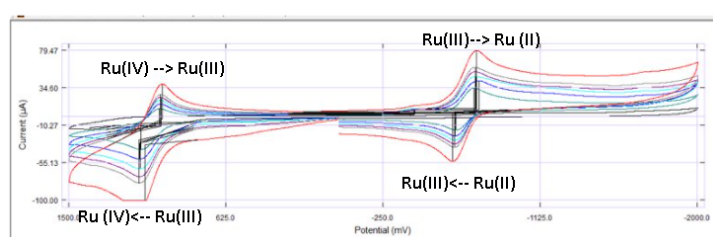
Irreversible E  $E_c = -951 \text{ mV}$

### CV Of $V(acac)_3$



Two Reversible  $Ip_1 E^{1/2} = -1423 \text{ mV}$   
 $Ip_2 E^{1/2} = 756 \text{ mV}$

### CV of $Ru(acac)_3$



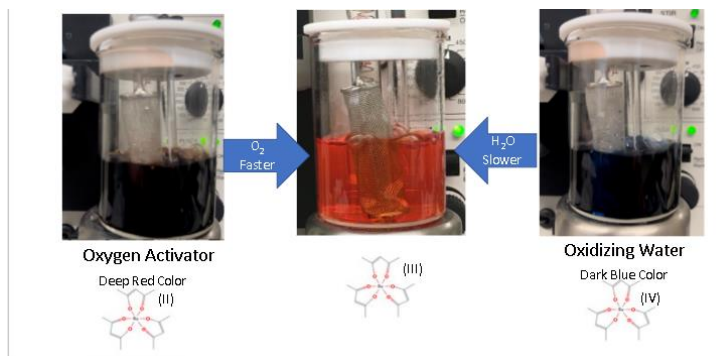
Two Reversible peaks  $Ip_1 E^{1/2} = -704 \text{ mV}$   
 $Ip_2 E^{1/2} = 1046 \text{ mV}$

This concluded the acquisition of data from Cyclic Voltammetry experiments for the purpose of the calculation of the diffusion coefficient using the Randles-Sevcik equation. We then moved on to our second electrochemical technique: Controlled Potential Coulometry. We had hoped to experiment with both  $Ru(acac)_3$  and  $V(acac)_3$  -- the two complexes that displayed multiple fully reversible redox couples—, but we only had time for  $Ru(acac)_3$ .

Controlled Potential Coulometry differs from Cyclic Voltammetry in that in Controlled Potential Coulometry a steady Voltage is applied across a fixed period of time. This quantitatively changes the oxidation state of the compound.

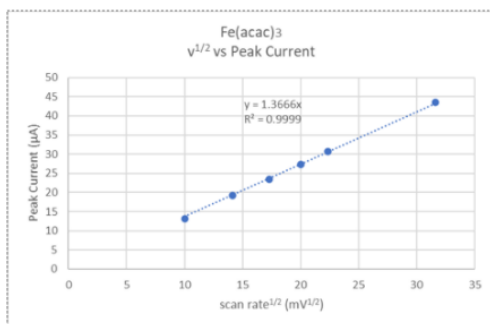
We began by reducing  $Ru(III)$  to  $Ru(II)$ . We observed a color change from orange to deep red. Immediately after cutting off the Nitrogen Purge, we saw the compound oxidize back to  $Ru(III)$  within seconds. We believe that  $Ru(II)$  is a Molecular Oxygen Activator. We then oxidized  $Ru(III)$  to  $Ru(IV)$ . We observed a color change from orange to deep blue. Immediately after cutting of

the Nitrogen Purge, we saw the compound reduce back to Ru(III) within minutes. We believe that Ru(IV) is oxidizing water.



## Results

Using this data, we now calculate the diffusion coefficients. The Randles-Sevcik equation can also be reformatted as a slope-intercept equation. We plot our results and find the slope of the best-fitted trend line. From that slope, we calculate the diffusion coefficients using the components of the slope from the reformatted Randles-Sevcik equation. We also calculated the average diffusion coefficients by finding the average of each individual value diffusion coefficient.

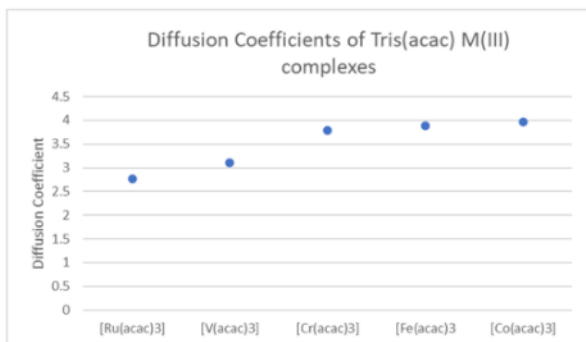


$$i_p = 0.4463 n^{3/2} F^{3/2} A \frac{D^{1/2} c v^{1/2}}{(RT)^{1/2}}$$

Above Equation in the form of  $y=mx$ :

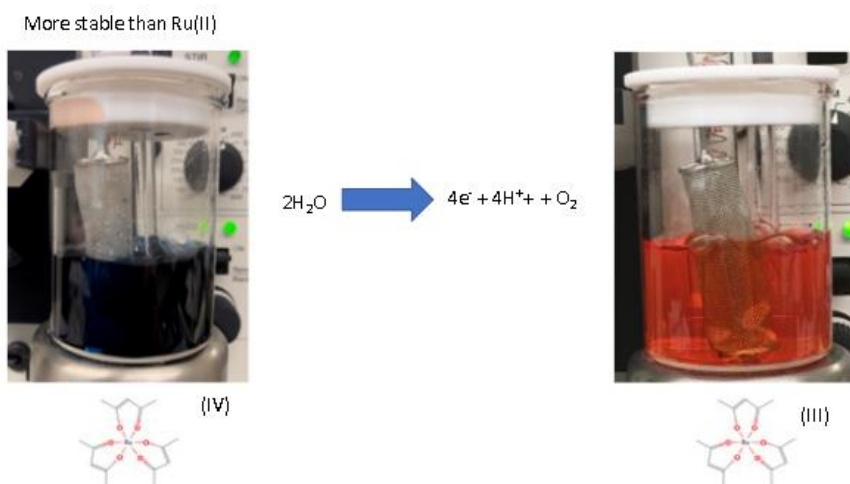
$$I_p = (.4463(nF)^{3/2}Ac(D/RT)^{1/2}) * v^{1/2}$$

Diffusion Coefficient = 3.88 (cm<sup>2</sup>/s)



One interesting part of our diffusion coefficient data was the grouping of the values.  $\text{Co}(\text{acac})_3$ ,  $\text{Cr}(\text{acac})_3$ , and  $\text{Fe}(\text{acac})_3$  all were together at a higher value, while  $\text{Ru}(\text{acac})_3$  and  $\text{V}(\text{acac})_3$  were close together at a lower value.  $\text{Ru}(\text{acac})_3$  and  $\text{V}(\text{acac})_3$  also were similar in that they both had two fully reversible redox couples.

From the Coulometry Experiment, we thought that Ru (IV) is oxidizing water in order to go back to Ru (III). This is especially interesting, that Ru(acac) in both its Ru (II) and Ru (IV) oxidation states is reacting with the environment to return to Ru (III). We ran the cycle of Ru (III) and Ru (IV) five times and successfully oxidized water each time, with minimal decomposition. We have not yet had time to investigate the decomposition, but we plan to do so as soon as possible.



## Conclusion

Working with Cyclic Voltammetry, we learned about the diffusion coefficient and how to calculate it. We could also observe that the lower diffusion coefficient was the acac compounds with a double reversible system like V and Ru. We are not saying that these two things are related but it was an observation we made. Using Controlled Potential Coulometry, we made the observation of the molecular activation of oxygen by Ru(II)(acac)<sub>3</sub> and the Oxidation of Water by Ru(IV)(acac)<sub>3</sub>.

There are several possible paths to continue this research:

1. What are the spectroscopic properties and kinetics of Ru(acac) in its various oxidation states? We have to find a way to efficiently observe Ru(II) and Ru(IV) without them switching back to Ru(III). With our current setup this is extremely difficult.
2. Can Ru(II)(acac) and Ru(IV)(acac) be made synthetically? We had only made them electrochemically, but can they be made synthetically as well?
3. To explore Controlled Potential Coulometry experiments of V(acac). V(acac) was similar to Ru(acac) in that the both had two fully reversible redox couples and lower diffusion coefficients. We wonder if V(acac) has similar features when it changes oxidation states.
4. How do other Ru coordination complexes --- with ligands other than acac compare to Ru(acac)?
5. What is the nature and degree of the decomposition of Ru(IV) in the Ru(IV) Ru(III) couple?
6. Is the Ru(II) Ru(III) couple repeatable? If there is decomposition, what is the degree and nature of its decomposition?

## Acknowledgements

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### **Reference**

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