

METHINE-SELECTIVE DEUTERATION OF $V(\text{acac})_3$, $[\text{Co}(\text{acac})_2]_4$, AND $\text{Al}(\text{acac})_3$

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SUMMARY

In solid state NMR studies of transition metal acetylacetonate complexes, peak assignments required complexes deuterated at methine or methyl positions. The preparation of methine-deuterated complexes— $V(\text{acac}-3\text{-}^2\text{H})_3$, $[\text{Co}(\text{acac}-3\text{-}^2\text{H})_2]_4$, and $\text{Al}(\text{acac}-3\text{-}^2\text{H})_3$ —is presented. This method is applicable to preparations of methyl-deuterated complexes as well.

Key words: deuteration, acetylacetonate, vanadium(III), cobalt(II), aluminum(III)

INTRODUCTION

The blood of some species of tunicates contains polyphenolic tripeptide pigments (tunichromes) and very high concentrations of oxygen-sensitive V^{III} (up to 1 M), originally accumulated from sea water as vanadate, V^{V} .¹ During our ongoing efforts to clarify the biological roles of tunichromes and vanadium, solid state NMR analysis was desirable for insoluble complexes produced in reactions between tunichrome and vanadium ions. Analysis of paramagnetic V^{III} complexes was especially interesting because V^{III} generally acts as a shift reagent. For V^{III} complexes in solution, the shifted NMR peaks are relatively sharp; however, the analysis of paramagnetic complexes by solid state NMR is a relatively new pursuit. In the development of solid state NMR techniques to study paramagnetic transition metal complexes, acetylacetonate (acac) complexes of V^{III} , Co^{II} , and Al^{III} have been studied.² To assign the NMR peaks, complexes specifically deuterated at methyl or methine positions were desired.

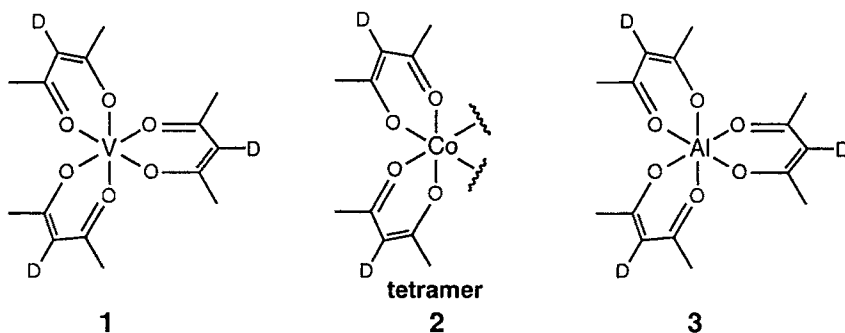
RESULTS AND DISCUSSION

In the initial approach, specifically deuterated ligands $\text{acac}-3\text{-}^2\text{H}_2$ and $\text{acac}-1,5\text{-}^2\text{H}_6$ were prepared according to literature procedures.³ Synthetic schemes for the corresponding V^{III} complexes $V(\text{acac}-3\text{-}^2\text{H})_3$ **1** and $V(\text{acac}-1,5\text{-}^2\text{H}_6)_3$ using conventional bases were avoided, as base is likely to promote deuterium scrambling. A preparation using $V\text{Cl}_3$ in dry toluene and no base was followed (with a KOH trap above the reflux condenser);⁴ however, the HCl or DCl liberated in the complexation reaction led to $V(\text{acac}-^2\text{H}_n)_3$ products showing completely scrambled deuterium.⁵

The successful incorporation of deuterium at selected positions was based on the reported exchange properties of $[\text{Co}(\text{acac})(\text{en})_2]^{2+}$ ions (en = ethylenediamine).⁶ When this complex is dissolved in D_2O , the methine proton of acac is selectively exchanged, whereas all protons of acac are exchanged when NaOD is added. For test purposes, a solution of $\text{V}(\text{acac})_3$ in THF was treated with D_2O and monitored by mass spectrometry (MS). Over several hours at 25°C , deuterium exchange of only the methine protons was indicated. Preparative scale reactions for $\text{V}(\text{acac-3-}^2\text{H})_3$ **1**, $[\text{Co}(\text{acac-3-}^2\text{H})_2]_4$ **2**,⁷ and $\text{Al}(\text{acac-3-}^2\text{H})_3$ **3** were run for at least 3 days and repeated for further enrichment. The complexes were selectively deuterated at methine positions as determined by MS and ^1H NMR. Deuterium incorporation for the hygroscopic Co complex **2**, although adequate for NMR studies, would certainly be higher if the commercially obtained $[\text{Co}(\text{acac})_2]_4$ were made anhydrous prior to the first exchange reaction.

Parallel reactions were carried out for $\text{Fe}(\text{acac})_3$ and $\text{Cr}(\text{acac})_3$, but without success. Mass spectrometry showed that the Fe product was a mixture of Fe^{II} and Fe^{III} complexes, $\text{Fe}(\text{acac-3-}^2\text{H})_2$ and $\text{Fe}(\text{acac-3-}^2\text{H})_3$. The $\text{Cr}(\text{acac})_3$ product did not show any detectable deuterium incorporation by mass spectrometry. This result is not surprising for Cr^{III} complexes in which the ligands are substitutionally inert. For exchange to occur at methine positions, one imagines that the bidentate acac ligand is transiently labile, perhaps to the monodentate form.

As a corollary to the deuterium exchange reported here, complexes specifically deuterated at methyl positions— $\text{V}(\text{acac-1,5-}^2\text{H}_6)_3$, $[\text{Co}(\text{acac-1,5-}^2\text{H}_6)_2]_4$, and $\text{Al}(\text{acac-1,5-}^2\text{H}_6)_3$ —can be prepared from the fully deuterated complexes by methine exchange with water.



EXPERIMENTAL

Metal acetylacetonates were purchased from Aldrich Chemical Company. Tetrahydrofuran (THF) was distilled under argon from sodium benzophenone ketyl prior to use. Deuterium oxide (D_2O) was degassed by freeze/pump/thaw cycles (4x) under argon. All manipulations of $\text{V}(\text{acac})_3$ and $[\text{Co}(\text{acac})_2]_4$ were performed under pre-purified argon or nitrogen (glove box).

$V(acac-3-^2H)_3$ (1). A solution of $V(acac)_3$ (~5 g) in benzene was passed through a 5 x 15 cm column of alumina (Activity III) under argon to remove traces of blue oxovanadium(IV) chelates.⁴ The dark brown eluent was evaporated under vacuum using a large pre-trap (a 250 mL Schlenk flask, in line) cooled in dry ice/acetone to afford $V(acac)_3$ as a brown solid.

In a 100-mL Schlenk flask, a solution was prepared of the purified $V(acac)_3$ (~1 g) in THF (25 mL) and D_2O (10 mL). The sealed flask sat at 25°C for 3 days. The solvents were evaporated under vacuum using a pre-trap as before. After the THF had mostly evaporated, the solid precipitated in the D_2O . The slurry was frozen and kept under vacuum to freeze-dry the complex. The deuterium exchange and evaporation procedures were repeated. The product was 85% $V(acac-3-^2H)_3$ and 15% $V(acac)(acac-3-^2H)_2$ according to integration of the major MS peaks (for 50 scans): MS (CI, CH_4) m/z (relative intensity) 380 ($M_a + 29$, 100.0), 379 ($M_b + 29$, 17.4). The position of deuterium incorporation was determined by solution 1H NMR analysis of the product mixture (compared to the original $V(acac)_3$):^{8,9} 1H NMR (400 MHz, $CDCl_3$) δ 47.64 (s, CH_3), 41.52 (s, CH) (trace).

$[Co(acac-3-^2H)_2]_4$ (2). The deuterium exchange procedure for $V(acac-3-^2H)_3$ was followed. The starting material $[Co(acac)_2]_4$ (~2 g) did not completely dissolve in THF (25 mL). (The purchased material contains $\leq 3\%$ water). Addition of D_2O (10 mL) precipitated the pink dihydrate.¹⁰ After each exchange reaction, the solid was made anhydrous by warming under vacuum at 45-50°C overnight (~12 hr) using an oil bath. (Some decomposition was observed by warming at 62°C). The anhydrous, magenta solid completely dissolved in THF. The product was 55% $Co(acac-3-^2H)_2$, 37% $Co(acac)(acac-3-^2H)$, and 8% $Co(acac)_2$ according to integration of the major MS peaks (for 58 scans): MS (CI, CH_4) m/z (relative intensity) 288 ($M_a + 29$, 100.0), 287 ($M_b + 29$, 66.0), 286 ($M_c + 29$, 14.7). The position of deuterium incorporation was determined by solution 1H NMR analysis of the product mixture (compared to the original $Co(acac)_2$):⁸ 1H NMR (400 MHz, pyridine- 2H_5) δ 27.65 (s, CH_3), 25.02 (s, CH) (small peak).

$Al(acac-3-^2H)_3$ (3). The deuterium exchange procedure for $V(acac-3-^2H)_3$ was followed using 5 g of $Al(acac)_3$ in THF (75 mL) and D_2O (30 mL), except the reaction times were ca. 5 days. The product was 100% $Al(acac-3-^2H)_3$ according to integration of the major MS peaks (for 32 scans): MS (CI, NH_3) m/z (relative intensity) 345 ($M + 18$, 100.0). The position of deuterium incorporation was determined by solution 1H NMR analysis of the product (compared to the original $Al(acac)_3$): 1H NMR (400 MHz, $CDCl_3$) δ 2.00 (s, CH_3), (no methine peak at δ 5.49 was observed).

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