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Synthesis and Characterization of a New Tc(IV) Cation: Tris(acetylacetonato)technetium(IV) Tetrafluoroborate

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Introduction

Over the last four years, several reports concerning tris(acetylacetonato)technetium(III) (Tc(acac)$_3$) have appeared in the literature [1, 2, 3]. The preparation of this complex directly from the pertechnetate ion [2, 3] is of interest to diagnostic nuclear medicine because neutral complexes of ^{99m}Tc have been proposed as potential brain imaging agents [2]. In the course of our electrochemical investigations on Tc(acac)$_3$ we found that the complex undergoes a reversible oxidation at 0.30 V *vs.* SCE in acetonitrile solution. This result led to the preparation of [Tc(acac)$_3$]BF$_4$ described below.

Experimental

Technetium as NH$_4$^{99}TcO$_4$ was obtained as a gift from New England Nuclear, Billerica, MA. All manipulations were carried out in laboratories approved for low-level radioactivity (^{99}Tc is a weak β-emitter with a half life of 2.12×10^5 years and a particle energy of 0.292 MeV) and all precautions followed have been detailed elsewhere [4, 5]. Field desorption mass spectra (FDMS) were measured with a Varian MAT 731 instrument described elsewhere [6] and ^{1}H NMR spectra were made on a JEOL FX-90Q 90 MHz spectrometer in either chloroform-d$_1$ or acetonitrile-d$_3$ solution with TMS as internal calibrant. Voltammetric studies were carried out by using a PAR model 174 polarographic analyzer with a stationary Pt electrode. All potentials were referenced to a saturated calomel electrode; ferrocene was used as an internal calibrant and tetra-n-butylammonium perchlorate was used as the supporting electrolyte in spectrograde acetonitrile.

Preparation of Tris(acetylacetonato)technetium(III)

To a mixture of 15 ml of acetylacetone (Aldrich), 30 ml of ethanol and 25 ml of 1% aqueous sodium hydroxide, 1.5 ml of 0.399 *M* NH$_4$TcO$_4$ (0.60 mmol) was added. As the solution was heated, 0.21 g (1.21 mmol) of sodium dithionite (Fisher) in 5 ml of 1% aqueous sodium hydroxide was added dropwise to the stirred reaction mixture (solutions of sodium dithionite must be prepared immediately before use). The resulting deep red solution was refluxed for 45 min at which time an additional 0.02 g of sodium dithionite in aqueous base (5 ml) was added to the reaction mixture which was then refluxed for another 45 min. The volume of the solution was reduced to ~20 ml by heating on a hot plate and 30 ml of cold water was added. The red crystalline product was collected, washed with water (5 ml) and dried *in vacuo.* Yield of Tc(acac)$_3$, 0.28 mmol, 47% based on Tc; mp 175–180 °C dec, (lit. 170 °C dec [1]). *Anal.* Calcd for $C_{15}H_{21}O_6Tc$: C, 45.43; H, 5.35. Found: C, 45.48; H, 5.34. Optical spectrum (acetonitrile): 535 nm (4.6×10^3 Lmol^{-1} cm^{-1}), 505 (4.6×10^3), 375 (7.3×10^3), 348 (10.3×10^3), 283 (16.5×10^3), 270 (18.0×10^3). IR (KBr): 2990 (w), 2960 (w), 2915 (w), 1515 (broad, vs), 1420 (m), 1365 (broad, vs), 1335 (s), 1265 (s), 1190 (w), 1015 (s), 930 (s), 795 (m), 775 (s), 655 (m), 645 (sh), 615 (s), 605 (s), 435 (s), 415 (m), 310 (m) cm^{-1}. The optical and IR spectra of this material are in good agreement with literature values [1]. ^{1}H NMR (chloroform-d): 7.43 ppm (γ-H), 10.89 ppm (-CH$_3$). (+)FDMS: m/z 396 (calcd for $C_{15}H_{21}O_6Tc = 396$). $E_{1/2}$(anodic) = 0.30 V *vs.* SCE (1 e, reversible). $E_{1/2}$(cathodic) = −1.46 V *vs.* SCE (1 e, reversible).

Preparation of Tris(acetylacetonato)technetium(IV) Tetrafluoroborate

To a solution of 0.08 g of Tc(acac)$_3$ (0.20 mmol) in N$_2$ purged acetonitrile (15 ml) was slowly added solid ferricenium tetrafluoroborate [7] (0.05 g, 0.18 mmol). The color of the stirred solution changed from red-violet to orange-brown. Addition of ether (200 ml) precipitated a brown, crystalline solid. This material was dissolved in acetonitrile (5 ml) and reprecipitated with ether (150 ml). The product was collected, washed with ether (10 ml) and dried *in vacuo.* Yield of [Tc(acac)$_3$]BF$_4$, 0.06 g, 1.2 mmol, 60% based on Tc; mp 215–220 °C dec. *Anal.* Calcd for $C_{15}H_{21}BF_4O_6Tc$: C, 37.29; H, 4.39. Found: C, 37.39; H, 4.28. Optical spectrum (methylene chloride): 400 (4.5×10^3), 267 (2.2×10^4). IR (KBr): 3100 (w), 3010 (w), 2920 (w), 1530 (broad, vs), 1420 (s), 1365 (m), 1310 (s), 1285 (s), 1050 (broad, s), 940 (s), 805 (m), 680 (s), 600 (s), 530 (m), 520 (m), 475 (s), 420 (m), 325 (m) cm^{-1}. ^{1}H NMR (acetonitrile-d$_3$): 56.67 ppm (-CH$_3$), 46.42 ppm

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(γ-H). Conductivity (acetonitrile, 10^{-3} *M*): $\Lambda_M = 155$ ohm^{-1} cm^2 mol^{-1}. Magnetic moment: (measured by the Evans NMR method in methylene chloride solution [8]) μ_{eff} (308 K) = 3.5 B.M. (+)FDMS: m/z 396 (calcd for $[C_{15}H_{21}O_6Tc]^+$ = 396). Cyclic voltammetry: identical to Tc(acac)$_3$.

Results and Discussion

The reaction of Tc(acac)$_3$ and ferricenium tetrafluoroborate in acetonitrile yields the Tc(IV) species, [Tc(acac)$_3$]BF$_4$ in 60% yield. This brown, crystalline compound has been characterized by elemental analysis, optical, IR and ^{1}H NMR spectroscopy, conductivity, magnetic susceptibility, cyclic voltammetry and field desorption mass spectrometry.

The salt [Tc(acac)$_3$]BF$_4$ is a 1:1 electrolyte in acetonitrile solution [9] and has a magnetic moment (3.5 B.M. at 308 K) consistent with its formulation as a monomeric complex of Tc(IV) [10]. The ^{1}H NMR spectrum of the cationic Tc(IV) complex is qualitatively similar to the spectrum of the isoelectronic Mo(III) species, Mo(acac)$_3$, in that both the CH$_3$ and γ-H proton resonances are shifted markedly downfield with respect to the comparable resonances in the diamagnetic complex, Rh(acac)$_3$ [11]. The ^{1}H NMR spectrum of Tc(acac)$_3$ (a complex with a low-spin d^4 configuration) is different from that of Mo(acac)$_3$ (d^3) and Ru(acac)$_3$ (low-spin d^5) in that the γ-H resonance is shifted downfield from its diamagnetic position while the CH$_3$ resonance is shifted upfield. In Ru(acac)$_3$ both resonances are shifted upfield [11].

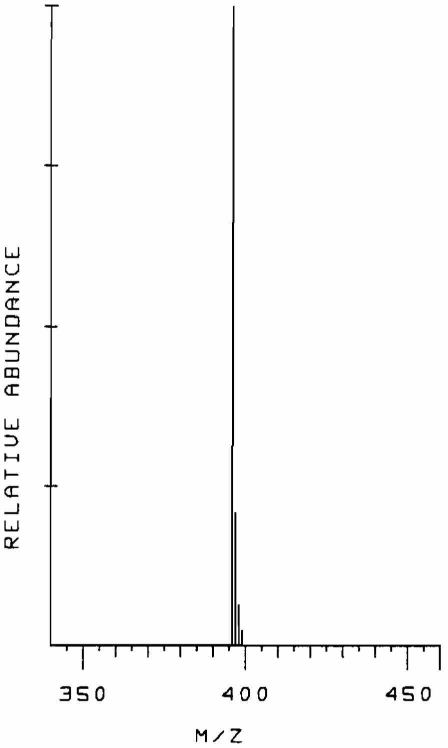

Fig. 1. Positive Ion FDMS of Tc(acac)$_3$.

Both Tc(acac)$_3$ and [Tc(acac)$_3$]BF$_4$ exhibit a signal at m/z 396 (corresponding to the C$^+$ species) as the only feature in their (+)FD mass spectra (Fig. 1). This demonstrates that characterization of electrochemically active species by (+)FDMS can sometimes give ambiguous results.

In addition to the readily obtainable [Tc(acac)$_3$]$^+$ cation, the one electron reduction of Tc(acac)$_3$ at −1.46 V *vs.* SCE provides evidence for the existence of the Tc(II) species [Tc(acac)$_3$]$^-$. Patterson and Holm have shown that the electrochemical properties of ruthenium tris(β-diketonates) are strongly influenced by the nature of substituents on the chelate ring [12]. Therefore it is reasonable to expect that by using different β-diketonate ligands a variety of anionic, cationic and neutral technetium tris(β-diketonate) complexes can be prepared.

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