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Reaction of erbium(III) carbonate with thenoyltrifluoroacetone: the molecular structure of hydrate hydroxonium tetrakis(thenoyltrifluoroacetonato)erbate(III)

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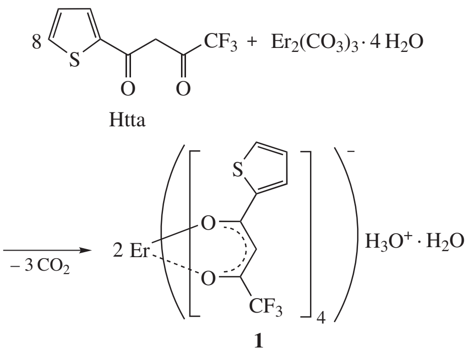
The reaction of erbium(III) carbonate with thenoyltrifluoroacetone in ethanol leads to the formation of hydrate hydroxonium tetrakis(thenoyltrifluoroacetonato)erbate(III) $(H_3O)^+[Er(tta)_4]^-\cdot H_2O$, whose molecular structure has been determined by X-ray analysis.

The rare-earth β-diketonates Ln(β-dik)$_3\cdot n$H$_2$O and Na$^+\cdot$[Ln(β-dik)$_4$]$^-\cdot n$H$_2$O are usually prepared by the interaction of sodium β-diketonates with lanthanide salts LnX$_3\cdot n$H$_2$O in aqueous–alcoholic solutions.[1] In the synthesis of tetrakis derivatives, an excess of the sodium salt is used. Anhydrous complexes are prepared from alkoxides Ln(OR)$_3$, bis(trimethylsilyl)amides Ln[N(SiMe$_3$)$_2$]$_3$ and anhydrous salts LnCl$_3$.[2]

Carbonates Ln$_2$(CO$_3$)$_3\cdot n$H$_2$O are convenient reagents for the synthesis of lanthanide β-diketonates. Because of their low solubility in organic solvents, the interaction of carbonates with β-diketones should be performed in a highly ionizing medium with intense stirring and heating. It should be expected that yields in such reactions would depend on the acidity of a CH acid.[3]

Here, we report the interaction of erbium(III) carbonate tetrahydrate with thenoyltrifluoroacetone (Htta), which does not lead to the formation of expected tris(thenoyltrifluoroacetonato)erbium(III) Er(tta)$_3\cdot n$H$_2$O. Only tetrakis derivative **1** has been obtained (Scheme 1). In its molecule, the anion [Er(tta)$_4$]$^-$ is counterbalanced with the hydroxonium cation H$_3$O$^+$ (Zundel cation[4]). The reaction was carried out in an aqueous–alcoholic solution at room temperature with intense stirring; the erbium(III) carbonate : Htta ratio was varied from 1 : 6 to 1 : 5.

The formation of tetrakis derivative **1** in an excess of erbium(III) carbonate in the reaction mixture was unexpected. Hydrate hydroxonium tetrakis(thenoyltrifluoroacetonato)erbate(III) is precipitated as large pale pink crystals[†] from a CH$_2$Cl$_2$–hexane solution.



Scheme 1

We suppose that the formation of (H$_3$O)$^+\cdot$[Er(tta)$_4$]$^-\cdot$H$_2$O is explained by the high acidity of the reaction mixture due to thenoyltrifluoroacetone (pK = 6.23).[1] Rare-earth metal acylpyrazolonates containing the Zundel ions H$_3$O$^+$ and H$_5$O$_2^+$ were synthesized previously.[7,8] The cation H$_3$O$^+$ is situated in the external coordination sphere of the metal atom and stabilized by H-bonding to the pyridine nitrogen of acylpyrazolonate. The hydroxonium cation H$_3$O$^+$ in compound **1** is located in the external coordination sphere of the metal atom, but it is connected *via* hydrogen bonding with the oxygen and fluorine atoms of β-diketonate ligands.[8]

Our attempts to detect the presence of tris(thenoyltrifluoroacetonato)erbium(III) Er(tta)$_3\cdot n$H$_2$O by TLC in mother solution after the separation of compound **1** were unsuccessful. The test solution did not contain unreacted thenoyltrifluoroacetone because of the use of an excess of erbium(III) carbonate. The solid fine-crystalline product was obtained after the removal of hexane and methylene chloride from the mother solution. The mass spectra of compound **1** and the fine-crystalline product are identical.

[†] Thenoyltrifluoroacetone and erbium(III) carbonate (Acros) were used without additional purification. The IR spectra were recorded on a Bruker-Vertex 70 instrument. The composition of **1** was determined using a Polaris Q/Trace GC Ultra GC-MS instrument. UV spectra were recorded using a Perkin Elmer Lambda 25 UV-VIS spectrometer.

Thenoyltrifluoroacetone (2.04 g, 9.2 mmol) and Er$_2$(CO$_3$)$_3\cdot$4H$_2$O (0.89 g, 1.5 mmol) were dissolved in 20 ml of EtOH, and the solution was stirred magnetically at 60 °C for 4 h. Ethanol was distilled off from the filtrate. Light pink crystals (0.52 g) and pink powder (0.90 g) of **1** were obtained after the recrystallization of a crude product from a CH$_2$Cl$_2$–hexane mixture (57% total yield). IR (Nujol, ν/cm^{-1}): 3639, 3437, 3341, 1605, 1582, 1539, 1509, 1413, 1353, 1304, 1247, 1184, 1145, 1059, 933, 856, 787, 684, 644, 582. UV [λ/nm (ε/dm^3 mol^{-1} cm^{-1})]: 264 (21000), 335 (40000). Found (%): C, 35.80; H, 2.04. Calc. for C$_{32}$H$_{21}$ErF$_{12}$O$_{10}$S$_4$ (%): C, 35.33; H, 1.93.

Crystallographic data for **1**: C$_{32}$H$_{21}$ErF$_{12}$O$_{10}$S$_4$ (M = 1088.99), triclinic, space group $P\bar{1}$, Z = 2; a = 9.976(2), b = 12.136(3) and c = 17.086(4) Å, α = 101.330(4)°, β = 94.413(5)°, γ = 103.146(4)°, V = 1958.9(8) Å^3, d_{calc} = 1.846 g cm^{-3}, μ = 2.466 mm^{-1}, $2\theta_{max}$ = 52°; 16532 reflections collected (7566 independent reflections, R_{int} = 0.0249), R_1 [$I > 2\sigma(I)$] = = 0.0346, wR_2 (for all data) = 0.0921, GOOF (F^2) = 1.074, largest difference peak and hole 2.615/–0.985 e Å^{-3}.

The X-ray data for **1** were collected on a Bruker Smart Apex diffractometer [graphite-monochromated MoKα radiation, ω-scan technique, λ = 0.71073 Å, T = 100(2) K]. The structures were solved by direct methods and refined on F^2 using the SHELXTL package.[4] All non-hydrogen atoms were found from a Fourier syntheses of electron density and refined anisotropically. All hydrogen atoms were placed in calculated positions and refined in the riding model. SADABS was used to perform area-detector scaling and absorption corrections.[5]

CCDC 927808 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2014.

The IR spectrum of compound **1** exhibits three absorption bands at 3640, 3440 and 3342 cm^{-1} due to the valence vibrations of the O–H bond. The narrowest of them can be attributed to the vibrations of unassociated water molecules and two others, to the hydroxonium cation. It is well known[9] that two absorption bands attributed to vibrations $\nu_3(E)$ and $\nu_1(A_1)$ are observed in the spectrum of such a particle in a range of 3470–3390 cm^{-1}. The most intense absorption bands relate to a β-diketonate fragment associated with the Er cation (1605, 1582 cm^{-1}).

The UV spectrum consists of two absorption bands at 264 and 335 nm due to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions in the β-diketonate ligand, respectively.

The analysis of the mass spectra shows that the defragmentation of compound **1** begins with the removal of CF_3C (*m/z* 81), $CF_3C(O)CH$ (*m/z* 110), $C_4H_3SC(O)$ (*m/z* 111) and diketone $C_4H_3SC(O)CHC(CF_3)(O)$ (*m/z* 221) groups. In the field of heavy fragmentation ions, the most intense peaks are at *m/z* 761, 830 and 982, corresponding to the $[C_4H_3SC(O)CHC(CF_3)(O)]_2Er[C_4H_3SC(O)CHC(O)]$, $[C_4H_3SC(O)CHC(CF_3)(O)]_3Er$ and $[C_4H_3SC(O)CHC(CF_3)(O)]_3Er[C_4H_3SC(O)CHC(O)]$ fragments, respectively.

Erbium(III) carbonate interacts with thenoyltrifluoroacetone under conditions of a topochemical reaction initiated by the addition of a small amount of 96% ethanol.‡ FTIR, UV-VIS, mass spectrometry, TLC and elemental analysis of the product confirmed the formation of tetrakis derivative **1**.

Thus, complex **1** is formed in a reaction of erbium(III) carbonate with thenoyltrifluoroacetone in spite of an excess of erbium(III) carbonate.

Figure 1 shows the molecular structure of the $[Er(tta)_4]^-$ anion in **1**. The erbium atom is situated at the center of a distorted quadrangular prism formed by the eight oxygen atoms of β-diketonate ligands. The coordination number of Er is 8. The Er–O distances are 2.290(3)–2.345(3) Å, and they are comparable to the related distances in the erbium phenanthroline complex $Er^{III}(tta)_3Phen$ [2.288(2)–2.315(2) Å].[10] β-Diketonate fragments of ligands in **1** are nearly planar (maximum deviations of the atoms from a plane are 0.05 Å). The C–O bond distances in β-diketonate ligands are 1.252(6)–1.284(5) Å, which are slightly shorter than those in the $(C_4H_3S)C(O)C{=}C(OH)CF_3$ molecule [1.269(4)–1.310(4) Å]. The C–C bond distances in OCCCO fragments in **1** [1.368(6)–1.428(6) Å] are comparable to the related distances in the $(C_4H_3S)C(O)C{=}C(OH)CF_3$ molecule [1.343(4)–1.432(5) Å].[11] β-Diketonate and thiophene fragments are almost coplanar. The angles between them are 1.8–15.2°. It can be explained by the presence of intermolecular interactions like S···H (2.83 Å) and S···F (3.15 Å).

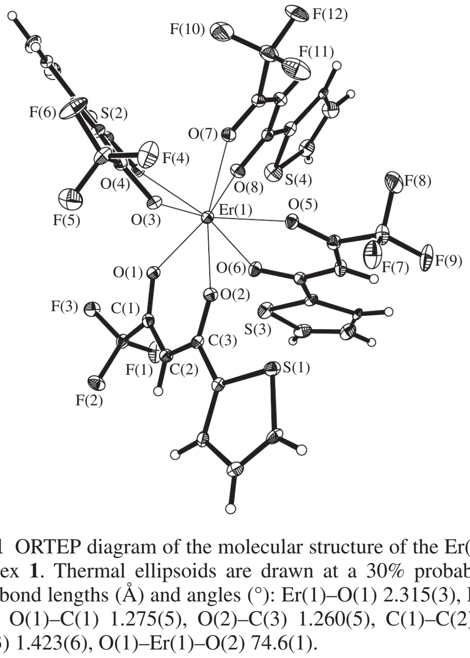


Figure 1 ORTEP diagram of the molecular structure of the $Er(tta)_4^-$ anion in complex **1**. Thermal ellipsoids are drawn at a 30% probability level. Selected bond lengths (Å) and angles (°): Er(1)–O(1) 2.315(3), Er(1)–O(2) 2.314(3), O(1)–C(1) 1.275(5), O(2)–C(3) 1.260(5), C(1)–C(2) 1.369(6), C(2)–C(3) 1.423(6), O(1)–Er(1)–O(2) 74.6(1).

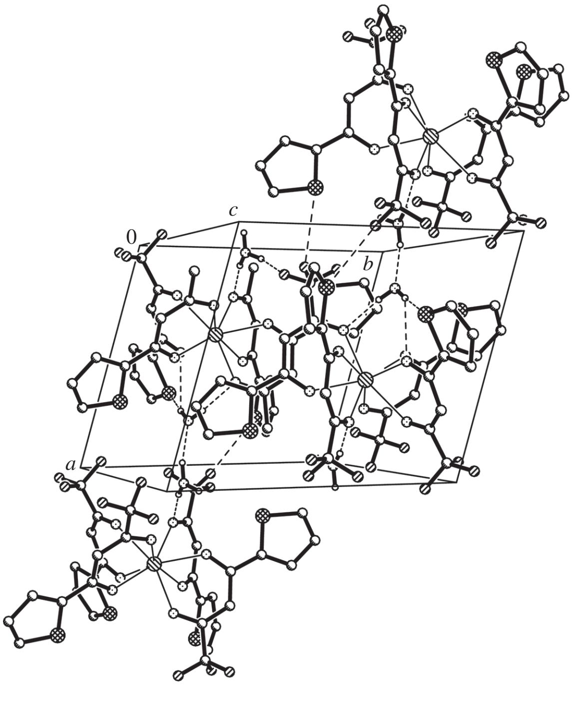


Figure 2 ORTEP diagram of molecular packing in complex **1**. Hydrogen atoms of β-diketonate ligands are omitted for clarity. The H-bonds are shown as dashed lines.

In addition to the $Er(tta)_4^-$ anion, the asymmetric unit cell of **1** contains the H_3O^+ cation and the molecule of water (Figure 2). In each H_3O^+ particle, one hydrogen atom is linked with the O atom of the β-diketonate ligand (1.91 Å), the second, with the F atom of another $Er(tta)_4^-$ anion (2.32 Å) and the third, with the O atom of a water molecule (1.84 Å). The hydrogen atoms of water molecules, in turn, are linked with the O atoms of β-diketonate ligands (1.96, 2.56 Å) and the S atom of the thiophene fragment (2.83 Å).

Thenoyltrifluoroacetone is a ligand commonly used in the chemistry of coordination compounds of rare-earth metals. Three structurally characterized complexes of erbium with β-diketones are known; they are tris derivatives having additional neutral ligand $Er(tta)_3{\cdot}L$, where L is 9,10-phenanthroline[10] or substituted phenanthroline.[12]

Thus, the complex $(H_3O^+){\cdot}[Er(tta)_4]^-{\cdot}H_2O$ was synthesized from thenoyltrifluoroacetone and erbium(III) carbonate even in spite of an excess of the salt. Apparently, the formation of complex **1** is resulted from the high acidity of the reaction mixture due to thenoyltrifluoroacetone. In each molecule of complex **1**, one hydrogen atom of the cation H_3O^+ is linked with the O atom of the β-diketonate ligand, the second, with the F atom of another $Er(tta)_4^-$ anion and the third, with the O atom of water.

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‡ Thenoyltrifluoroacetone (1.74 g, 7.8 mmol) and $Er_2(CO_3)_3{\cdot}4H_2O$ (0.77 g, 1.3 mmol) were mixed and triturated in a mortar. Five drops of EtOH were added, and the mixture was triturated once again. Gas liberation was observed. The mixture turned gradually to the slush. The crude products were dissolved in ethanol, and the solution was filtered. Light pink crystals and pink powder (1.0 g, 48%) of **1** were obtained after recrystallization from a CH_2Cl_2–hexane mixture. Found (%): C, 35.67; H, 2.06. Calc. for $C_{32}H_{21}ErF_{12}O_{10}S_4$ (%): C, 35.33; H, 1.93.

Synthesis of Substances with Required Properties and Creation of Functional Materials Based on Them'.

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