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The first perfluoroacetylacetonate metal complexes: as unexpectedly robust as tricky to make†

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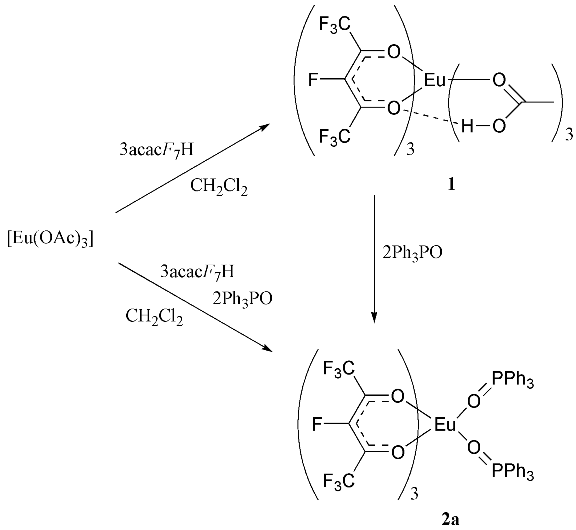
First metal complexes containing the perfluoroacetylacetonato ligand have been prepared by the reaction of anhydrous Ln(OAc)$_3$ (Ln = Eu, Tb, Tm) with heptafluoroacetylacetone, optionally in the presence of other ligands Ph$_3$PO, bpy, and PyO.

Metal complexes containing β-diketonate ligands represent a broad and important class of compounds.[1] Polyfluorination of the simplest β-diketonate (acetylacetonate, acac) provides its metal complexes with enhanced volatility, lipophilicity, solubility in low-polar media, and other important properties.[2] While hexafluoroacetylacetonate (acac-F$_6$) derivatives of metals are well-known and widely used, no perfluoroacetylacetonate (acac-F$_7$) metal complexes have been reported. Since heptafluoroacetylacetone (acac-F$_7$H) was first described two decades ago,[3] acac-F$_7$ metal complexes have been proposed a few times,[4] but, to the best of our knowledge, never isolated nor characterized in solution.

In this paper we report the first examples of metal complexes containing acac-F$_7$, the *fully fluorinated acac ligand*. We also describe herein the unexpected, remarkably facile degradation reaction of acac-F$_7$H, involving both C–C and C–F bond cleavage, and show how this undesired process can be avoided. This project was undertaken in continuation of our luminescent materials research program,[5] in order to develop new red (Eu) and green (Tb) emitters.

Conventional techniques for the preparation of acac and acac-F$_6$ lanthanide complexes could not be extended to syntheses with acac-F$_7$H. Thus, the rapid reaction of freshly precipitated Eu(OH)$_3$·nH$_2$O with acac-F$_7$H led to europium trifluoroacetate rather than an acac-F$_7$ Eu species. Treatment of Eu(OAc)$_3$·nH$_2$O with acac-F$_7$H in the presence of 1,10-phenanthroline (phen) gave rise to polynuclear complexes [Eu$_4$(phen)$_4$(acac-F$_7$)$_4$(μ^3-F)$_4$(μ-F)$_2$(μ-OCOCF$_3$)$_2$] and [Eu$_2$(phen)$_2$(acac-F$_7$)$_2$(μ-OCOCF$_3$)$_4$] (both crystallographically characterized, see ESI).†‡ Obviously, complete or partial decomposition of acac-F$_7$H took place in these reactions, resulting in C–C bond cleavage and formation of the F and CF$_3$COO ligands.

The problem of acac-F$_7$H degradation was solved by reacting dry [Eu(OAc)$_3$] with acac-F$_7$H in CH$_2$Cl$_2$ under rigorously anhydrous conditions. At room temperature, quick dissolution of the Eu salt occurred to produce [Eu(acac-F$_7$)$_3$(HOAc)$_3$], **1**, [eqn. (1)], whose structure was established by single crystal X-ray diffraction (Fig. 1).‡ Reaction (1) may be formally regarded as acac-F$_7$H addition to [Eu(OAc)$_3$] *via* proton transfer from the β-diketone to the coordinated AcO ligands, with hydrogen bond formation to one of the two O atoms of each of the acac-F$_7$ ligands. Remarkably, the molecule of **1** contains three acetic acid rather than acetato ligands. It is the C=O oxygen atoms of the AcOH ligands that are coordinated to Eu, as indicated by the C–O bond distances within the moieties EuO–C [1.227(3) Å] and C–OH···O$_{acac}$ [1.305(3) Å]. This AcOH coordination mode is completely different from the one found in [Eu$_2$(OAc)$_6$-(OH$_2$)$_2$(HOAc)$_2$]·3HOAc, *i.e.* Eu–O(H)–C(CH$_3$)=O.[6] Of the two O atoms of each acac-F$_7$ ligand on **1**, the oxygen involved in hydrogen bonding forms a longer Eu–O bond, Eu1–O1 = 2.522(2) Å *vs.* Eu1–O2 = 2.388(2) Å.



(1)

All three weakly bound AcOH ligands of **1** are easily displaced by other ligands, *e.g.* Ph$_3$PO, to produce [Eu(acac-F$_7$)$_3$(OPPh$_3$)$_2$], **2a**. More conveniently, **2a** and its Tb (**2b**) and Tm (**2c**) analogues were prepared in one step by reacting [Ln(OAc)$_3$] (Ln = Eu, Tb, Tm) directly with both acac-F$_7$H and Ph$_3$PO [eqns. (1) and (2)]. This one-step method was successfully extended to the preparation of similar acac-F$_6$ complexes **3** [eqn. (2)]; anhydrous conditions were not necessary for the acac-F$_6$ complex syntheses.

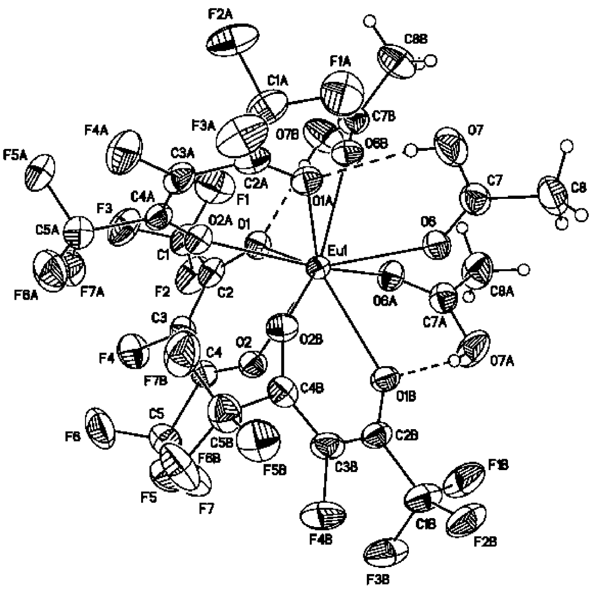


Fig. 1 An ORTEP drawing of [Eu(acac-F$_7$)$_3$(HOAc)$_3$], **1**, with thermal ellipsoids drawn to the 50% probability level.

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† Electronic supplementary information (ESI) available: details of the preparation of the complexes, analytical, NMR spectroscopical, and crystallographic data. See: http://www.rsc.org/suppdata/cc/b1/b111249j/

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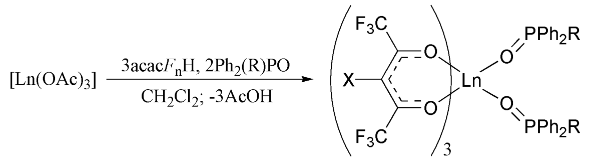


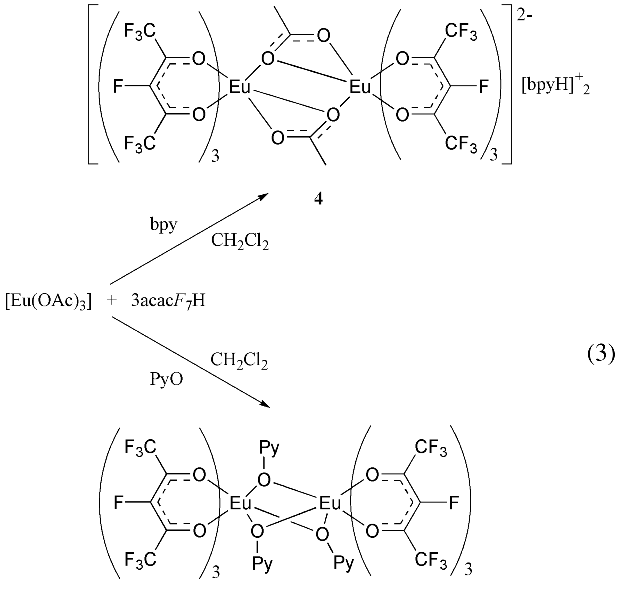
2a: Ln = Eu, X = F, R = Ph
2b: Ln = Tb, X = F, R = Ph
2c: Ln = Tm, X = F, R = Ph
2d: Ln = Eu, X = F, R = N=PPh$_3$
3a: Ln = Eu, X = H, R = Ph
3b: Ln = Tb, X = H, R = Ph
3c: Ln = Eu, X = H, R = CH$_2$CH$_2$PPh$_2$
3d: Ln = Eu, X = H, R = CH$_2$PPh$_2$
3e: Ln = Eu, X = H, R = N=PPh$_3$

2 (n = 7; X = F)
3 (n = 6; X = H)

60-88%

(2)

Dinuclear acac-F$_7$ complexes **4** and **5** were obtained upon treatment of [Eu(OAc)$_3$] with acac-F$_7$H in the presence of 2,2′-bipyridyl (bpy) and pyridine *N*-oxide, respectively [eqn. (3)]. X-Ray analysis of **4** (see ESI‡) indicated that bpy acted as a base rather than a coordinating ligand. Complex **5** was formulated as [(acac-F$_7$)$_6$Eu$_2$(μ-PyO)$_3$], based on elemental analysis and X-ray data‡ of its acac-F$_6$ analogue which was prepared similarly.



4

5

(3)

X-Ray structures of **2a** (Fig. 2), **2b**, **2c** (all isostructural), **3a** (previously reported[7]), and **3b** showed the lanthanide atom in a square antiprism formed by eight O atoms. The Ln(OP)$_2$ plane and one of the three acac ligands are almost co-planar. The thus defined mean plane is orthogonal to the other two equivalent, 'side' acac ligands. The central (O)C–C(X)–C(O) bond angles are more obtuse in **2a** [X = F; 123.6(2)–124.6(2)°] than in **3a** [X = H; 120.5(3)–121.6(3)°], likely due to the electron-withdrawing effect of the central fluorine. In contrast with the X-ray data, ^{19}F and ^{31}P NMR spectra for all **2** and **3** (see ESI) indicated that all three β-diketonate ligands on each molecule were magnetically equivalent in solution at ambient temperature, possibly due to fluxionality.

Once isolated, the acac-F$_7$ complexes can be handled in moist air and analyzed by NMR in solvents that have not been dried. This is in sharp contrast with the very poor hydrolytic stability of acac-F$_7$H during the synthesis (see above). The difference is believed to be due to facile S$_N$-type hydrolysis of the central C–F bond, likely aided by pre-coordination of the Ln^{3+} electrophile to an O atom of acac-F$_7$H before chelation. The resulting carbinol (CF$_3$C(O))$_2$CHOH then rearranges[8] to CF$_3$COO-CH$_2$C(O)CF$_3$ which is hydrolyzed to CF$_3$COO$^-$. However, once acac-F$_7$ is η^2-coordinated, nucleophilic attack of water or OH$^-$ on the central carbon is impeded for both steric and electronic reasons.

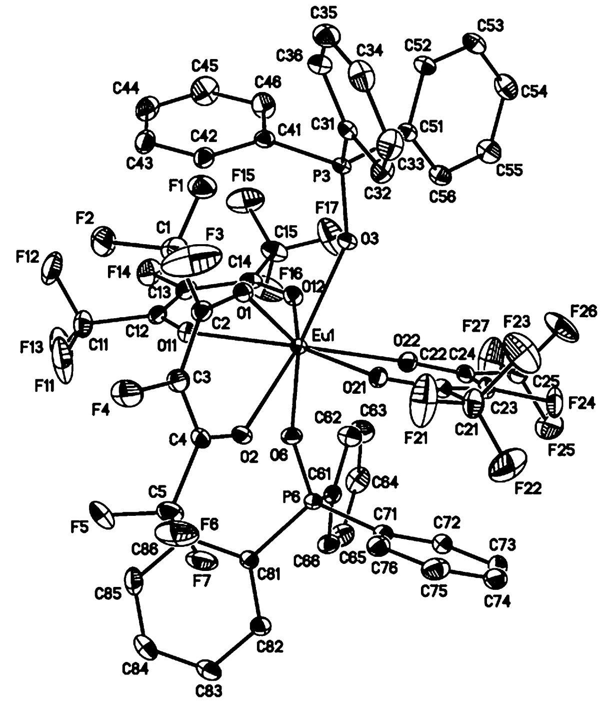


Fig. 2 An ORTEP drawing of [Eu(acac-F$_7$)$_3$(OPPh$_3$)$_2$], **2a**, with all hydrogen atoms omitted and thermal ellipsoids drawn only to the 20% probability level for clarity.

In **3c** and **3d** the hemilabile Ph$_2$P(CH$_2$)$_n$P(O)Ph$_2$ ligands (dppeO, $n = 2$; dppmO, $n = 1$),[9] are coordinated to Eu entirely through the hard O-center (see ESI for NMR data), in accord with a previous report[10] on dppmO Nd species. Owing to the two dangling PPh$_2$ groups, molecules **3c**,**d** may be regarded as exotic bidentate phosphine ligands. We successfully used **3c** for ligand-exchange co-polymerization with [Pd(PhCN)$_2$Cl$_2$] to produce [(μ-dppeO)Eu(acac-F$_6$)$_3$(μ-dppeO)PdCl$_2$]$_n$.

Notes and references

‡ Crystallographic data available (CCDC numbers in parentheses) for: [Eu$_4$(phen)$_4$(acac-F$_7$)$_4$(μ^3-F)$_4$(μ-F)$_2$(μ-OCOCF$_3$)$_2$] (171067), [Eu$_2$(phen)$_2$(acac-F$_7$)$_2$(μ-OCOCF$_3$)$_4$] (171064), **1** (171072), **2a** (171065), **2b** (171066), **2c** (171068), **3a** (171069), **3b** (171070), **4** (171284), and [(acac-F$_6$)$_6$Eu$_2$(μ-PyO)$_3$] (171071) (see ESI†). See http://www.rsc.org/cc/b1/b111249j/ for crystallographic data in CIF or other electronic format.

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