



Dedicated to Prof. Bogdan C. Simionescu
on the occasion of his 75th anniversary

SYNTHESIS AND CRYSTAL STRUCTURES OF YTTRIUM AND DYSPROSIUM TETRAKIS(HEXAFLUOROACETYLACETONATO) COMPLEX ANIONS WITH TETRAMETHYLAMMONIUM COUNTERIONS**

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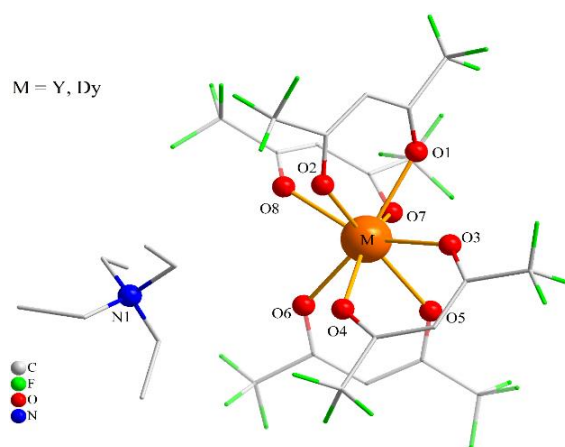
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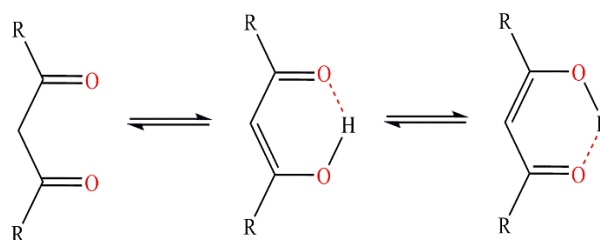
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The isostructural mononuclear complexes $(\text{Et}_3\text{NH})[\text{M}(\text{hfac})_4]$, where $\text{M} = \text{Y}$ (**1**) and Dy (**2**), $\text{Hhfac} = \text{hexafluoroacetylacetonate}$, have been synthesized and structurally characterized. The two compounds crystallize in monoclinic crystal system ($P2_1/n$ space group). The purity of the crystalline phases was investigated by X-ray powder diffraction. The analysis of the packing diagram reveals the segregation of the fluorine atoms from the CF_3 groups.



INTRODUCTION

β -Diketones are known for their keto-enolic tautomerism (Scheme 1).^{1–3} The simplest members of this class of compounds are malondialdehyde and acetylacetonate (Hacac). While Hacac is present 81% in enol form, its perfluorinated equivalent, hexafluoroacetylacetonate (Hhfac), presents only the enolic form.^{4–6}



Scheme 1 – Keto-enolic tautomerism of β -diketones.

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** Supplementary information on <https://www.icf.ro/rrch/> or <https://revroum.lew.ro>

The presence of the CF_3 electron withdrawing groups determines the structural effects which induces the enolization that is further stabilized by intramolecular hydrogen bonding.⁷ Moreover, the hfac⁻ anion coordinated to a metal ion increases the Lewis acidity of the metallic center, hence the metal ion becomes more susceptible to be coordinated by ligands with lower coordination abilities. In particular, this property of the hexafluoroacetylacetonato complexes has been fruitfully utilized, for example, in the chemistry of the nitronyl nitroxide radicals,^{8–10} which are weak Lewis bases, thus contributing to the development of a rich variety of molecular magnets materials.^{11–15}

Tetrakis (hexafluoroacetylacetonato) complexes of lanthanides have been reported in the literature with tetraethylammonium counterions, exhibiting similar structural features.^{16–18}

The structures presented herein offer a useful reference to the byproducts that could appear during the reaction between tris (hexafluoroacetylacetonato) complexes of lanthanides with various substrates in the presence of triethylamine. For example, we have previously shown that such byproduct, i.e. $(\text{Et}_3\text{NH})[\text{Tb}(\text{hfac})_4]$, is formed when the complexation between a nitronyl nitroxide ligand and $[\text{Tb}(\text{hfac})_4(\text{H}_2\text{O})_2]$ takes place in excess of triethylamine.¹⁹

RESULTS AND DISCUSSION

Description of the structures

The synthesis and the crystal structure of $(\text{Et}_3\text{NH})[\text{Tb}(\text{hfac})_4]$ have been previously reported.¹⁹

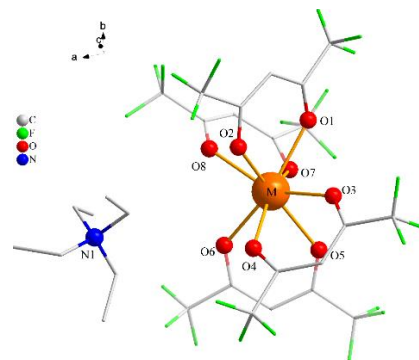


Fig. 1 – Perspective view of the molecule $(\text{Et}_3\text{NH})[\text{M}(\text{hfac})_4]$, where $\text{M} = \text{Y}$ (**1**) and Dy (**2**). Hydrogen atoms have been removed for clarity.

The complexes $(\text{Et}_3\text{NH})[\text{M}(\text{hfac})_4]$, where $\text{M} = \text{Y}$ (**1**) and Dy (**2**) are isostructural (see Table 1), hence just one will be further detailed.

Compound **1** crystallizes in a monoclinic crystal system, $P2_1/n$ space group. The purity of the crystalline phase for all compounds has been verified via powder X-ray diffraction (XRPD) showing a good agreement between the experimental patterns and the simulated ones (see Figs. S1–S3). Based on comparable relative heights of patterns on the XRD powder diffractograms, the quantitative analysis (Table S1) demonstrates that the simulated diffractogram in general fits the experimental data well, the WPPF (Whole Powder Pattern Fitting) parameters R_{wp} (<10) and S (around 1), as well as χ^2 values, support the above assertion. In the case of compound **1**, the high value of S (“goodness-of-fit”) can be explained by preferential orientation (high χ^2) due to the high crystallite size.

Table 1

Crystallographic data and structures refinement for **1** and **2**

Compound	$(\text{Et}_3\text{NH})[\text{Y}(\text{hfac})_4]$	$(\text{Et}_3\text{NH})[\text{Dy}(\text{hfac})_4]$
Chemical formula	$\text{C}_{26}\text{H}_{20}\text{F}_{24}\text{NO}_8\text{Y}$	$\text{C}_{26}\text{H}_{20}\text{F}_{24}\text{NO}_8\text{Dy}$
M (g mol ⁻¹)	1019.34	1092.93
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	<i>Monoclinic</i>	<i>Monoclinic</i>
Space group	$P2_1/n$	$P2_1/n$
a (Å)	12.0600(5)	12.0242(4)
b (Å)	16.4519(7)	16.4786(5)
c (Å)	20.9390(8)	20.9820(8)
α (°)	90	90
β (°)	101.087(4)	101.149(4)
γ (°)	90	90
V (Å ³)	4077.0(3)	4078.9(2)
Z	4	4
D_c (g cm ⁻³)	1.661	1.780
μ (mm ⁻¹)	1.582	1.984
$F(000)$	2008	2116
GOF	1.042	1.062
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0798, 0.2380	0.0535, 0.1588
R_1, wR_2 (all data)	0.0994, 0.2621	0.0667, 0.1732
$\Delta\rho_{\text{min}}/\Delta\rho_{\text{max}}$ (e Å ⁻³)	1.30 –0.49	1.14 –0.73

The yttrium ion shows a coordination number of 8, with a square antiprism stereochemistry (the SHAPE^{20,21} parameters for compounds **1** and **2** are presented in Table S2). The coordination sphere is made by 8 oxygen atoms arising from four chelating hfac⁻ ligands, with Y-O distances varying between 2.310(4) Å and 2.361(4) Å. The Tb-O distances vary between 2.323(4) Å and 2.375(5) Å. The shortest distance between two adjacent Y ions is 11.13 Å, while for Dy ions is 9.63 Å, respectively. The fluorine atoms form an outer shell for the Y(hfac)₄⁻ anion (Fig. 2), illustrating the tendency of the fluorinated groups to segregate.^{22,23} Intermolecular F...F interactions are

established between the closest CF₃ groups with distances of 2.938 Å for **1** and 2.906 Å for **2**, in agreement with the other reported distances.^{24,25} The corresponding angles are $\theta_1 = 145.3^\circ$ for **1** and 139.3° for **2**, and $\theta_2 = 109.8^\circ$ for **1** and 111.1° for **2** (Fig. 3).

The three ethyl groups are disordered over four crystallographic positions, each carbon atom presenting an occupancy of $\frac{3}{4}$. The triethylammonium cations occupy in the lattice positions that describe a herring bone pattern (Figure S4). The distances between two adjacent nitrogen atoms are 11.60 Å and 13.15 Å, in the *bc* plane, and 12.97 Å between two consecutive *bc* planes.

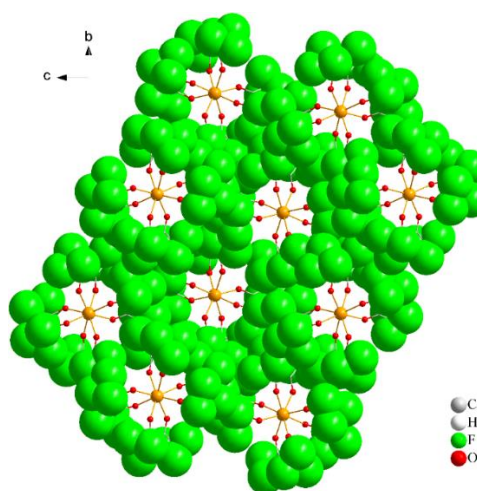


Fig. 2 – Packing diagram for crystal **1** (view along the crystallographic *a* axis). The fluorine atoms are represented in the space filling mode. HNEt₃ cations are not represented.

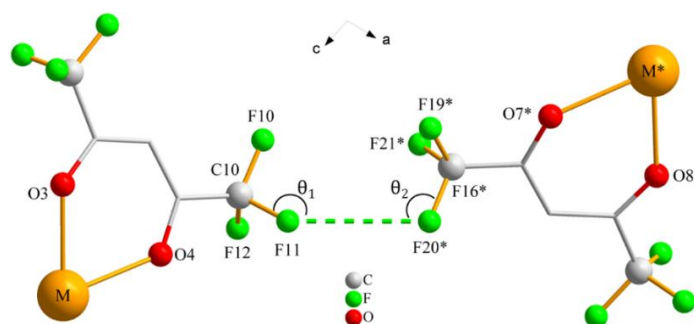


Fig. 3 – Detail of the packing diagram for crystal **1**, showing intermolecular F...F interactions. Symmetry operation: * = $1/2 + x, 1/2 - y, -1/2 + z$.

EXPERIMENTAL

Materials. All starting materials were of reagent grade and used without purification. All manipulations were performed under aerobic conditions. The syntheses of Y(III) and Dy(III) tris(hexafluoroacetylacetonato) compounds were performed following the reported procedure.²⁶

Compounds (Et₃NH) [M(hfac)₄], where M = Y, Dy, have been synthesized using the following procedure.

Synthesis of (Et₃NH) [Y(hfac)₄] (1**).** Over a hot solution of *n*-heptane (15 ml) containing [Y(hfac)₃(H₂O)₂], (0.04 mmol) two drops of triethylamine and 3 ml CHCl₃ were added. The mixture was stirred for another minute and then it was let to cool down. White crystals appeared after 1–2 days. Yield: 33%. Selected FTIR ATR peaks (cm⁻¹): 3623(w), 3555(w), 3054(w), 2892(w), 2818(w), 2720(w), 2105(w), 1650(s), 1519(s), 1499(s), 1401(s), 1349(s), 1262(vs), 1199(vs), 1133(vs), 796(s).

(Et₃NH) [Dy(hfac)₄] (**2**) has been prepared following the same procedure described for (Et₃NH)[Y(hfac)₄] using [Dy(hfac)₃(H₂O)₂], (0.04 mmol). Yield: 31%. Selected FTIR ATR peaks (cm⁻¹): 3551(w), 3056(w), 2820(w), 2217(w), 2122(w), 1647(vs), 1499(s), 1402(s), 1343(m), 1250(vs), 1202(vs), 1135(vs), 797(s).

X-Ray crystallography. Single crystal X-ray diffraction measurements were performed on a Rigaku XtaLAB Synergy-S diffractometer operating with Mo-K α ($\lambda=0.71073$ Å) micro-focus sealed X-ray tube. The crystals were kept at 293(2) K during data collection. Using Olex2,²⁷ the structure was solved with the SHELXS²⁸ structure solution program using Direct Methods and refined with the SHELXL²⁹ refinement package using Least Squares minimization. The non-H atoms were refined with anisotropic displacement parameters.

X-ray diffraction measurements on powder were performed on a Rigaku Miniflex 600 diffractometer with Cu-K α emission ($\lambda = 1.5406$ Å) in the angular range (2θ) of 5 to 35°, at a scanning step of 0.01 and a recording rate of 1/min. The background subtraction, smoothing and WPPF (Whole Powder Pattern Fitting) refinement were processed using SmartLab II v.4 software, while the powder patterns were simulated using the specific crystallographic information files (.cif) obtained in single crystal X-ray by Rigaku XtaLAB Synergy-S diffractometer.

A summary of the crystallographic data and the structures refinement are given in Table 1. Deposition numbers 2266359 for **1** and 2266344 for **2** contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Physical measurements. The IR spectra were recorded on an FTIR Bruker Vertex 70 spectrometer in the 4500–400 cm⁻¹ range using the ATR technique. The following abbreviations were used: w = weak, m = medium, s = strong, v = very, br = broad.

CONCLUSIONS

In this article we described the synthesis and the X-ray structure of mononuclear complexes (Et₃NH) [M(hfac)₄], where M = Y (**1**) and Dy (**2**), and their structural features. The analysis of the packing diagram has shown the segregation of the fluorine atoms from the CF₃ groups.

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