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# New NIR-emissive tetranuclear Er(III) complexes with 4-hydroxo-2,1,3-benzothiadiazolate and dibenzoylmethanide ligands: synthesis and characterization†

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New tetranuclear heteroleptic complexes [Er$_4$(dbm)$_6$(O-btd)$_4$(OH)$_2$] (**1**) and [Er$_4$(dbm)$_4$(O-btd)$_6$(OH)$_2$] (**2**) (O-btd = 4-hydroxo-2,1,3-benzothiadiazolate and dbm = dibenzoylmethanide) and their solvates with toluene, THF and CH$_2$Cl$_2$ were prepared using two synthetic approaches. The structures of the products were confirmed by single-crystal X-ray diffraction. Magnetic properties of **1** and **2** are in good agreement with X-ray data. The effective magnetic moment ($\mu_{eff}$) values at 300 K for **1** and **2** corresponds to a system of 4 non-interacting Er(III) ions in the ground state $^4J_{15/2}$ with $g$ = 6/5. At ambient temperature and upon excitation with $\lambda_{exc}$ = 450 nm, complexes **1** and **2** exhibit luminescence at ~1530 nm, *i.e.* in the near infra-red (NIR) region. The luminescence intensity grows with increasing the number of the (O-btd)$^-$ ligands in the complexes. This observation suggests (O-btd)$^-$ as a new efficient antenna ligand for the lanthanide-based NIR luminescence.

## Introduction

Over last few years, lanthanide (Ln) compounds have been attracting much attention because of their actual or candidate applications as luminescent materials for light-emitting diodes (LEDs), together with those in biomedicine and telecommunications.[1–4] Among them, Ln complexes with 8-quinolinolate and β-diketonate ligands are of special interest

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due to their significant antenna effect on the Ln(III)-centered near infra-red (NIR) luminescence.[3,5–7] NIR-emitting ions have recently gained much popularity due to application in telecommunications, sensor technology,[8,9] solar energy conversion[10,11] and biomedical analysis.[12,13] Among these NIR-emitting lanthanide ions, Er(III) plays a key role both for active and passive optical architectures in telecom technologies.[3,14,15]

The synthesis of complexes with controlled composition, structure and properties is a serious challenge requiring the search for new synthetic routes. For example, Ln complexes with 8-quinolinolate ligands have been expected to be Ln(RQ)$_3$ ones (RQ = 8-quinolinolate and its derivatives). Depending on the reaction conditions, however, [Ln(RQ)$_4$]$^-$ and [Ln$_3$(RQ)$_9$] were obtained along with the target [Ln(RQ)$_3$].[3,16–18] Structural chemistry of Ln β-diketonate complexes is also sophisticated. Under variable conditions, one can synthesize mono-, di-, tetra-, penta- and dodecanuclear complexes containing both β-diketonate and other bidentate ligands.[5–7,19–28]

The 2,1,3-benzothiadiazole derivatives attract current attention particularly because of their potential use in the design and synthesis of organic LEDs (*i.e.* OLEDs) and low-band gap polymers for photovoltaic applications.[29–37] Their coordination and supramolecular chemistry is also in progress.[29,38–41]

For OLED applications, 2,1,3-benzothiadiazole derivatives are promising not only as structural units of polymers but also as ligands for transition metal complexes.[30] In this context,

the 4-hydroxo-2,1,3-benzothiadiazole (OH-btd) ligand is of particular interest especially taking into account that its structure and acid–base properties are similar to those of 8-quinolinol. Importantly, this ligand can be deprotonated giving rise to a stable anion (O-btd)$^-$. From a structural point of view, this heterocycle offers the possibility of several coordination modes[38] which can lead to the formation of polynuclear coordination compounds. From a photophysical standpoint, it can act as an efficient antenna ligand in Ln complexes.

To date, just a few examples of transition metal complexes with the (O-btd)$^-$ ligand have been synthesized,[38,42–44] and most of them were characterized only by elemental analysis (EA) and IR spectroscopy. To the best of our knowledge, the rare earth complexes with this ligand have not been described until now.

It is known that luminescence of Ln compounds is seriously complicated by non-radiative deactivation through energy transfer from luminescent metal centres to vibrational levels of C–H, N–H, and O–H bonds of both ligands and solvent molecules. The formation of rigid complex structures and the use of sterically hindered ligands are well-known approaches to minimize the aforementioned radiationless decay. For these aims, dibenzoylmethanide (dbm)$^-$ can particularly be used.[7]

Herein, we report on the synthesis, structural characterization and luminescence and magnetic properties of new heteroleptic tetranuclear erbium complexes [Er$_4$(dbm)$_6$-(O-btd)$_4$(OH)$_2$] (1) and [Er$_4$(dbm)$_4$(O-btd)$_6$(OH)$_2$] (2) and their solvates with toluene, THF and CH$_2$Cl$_2$.

## Results and discussion

### Syntheses of the complexes

In this work, two approaches to synthesise the target compounds, *i.e.* Er complexes containing both (O-btd)$^-$ and (dbm)$^-$ ligands, were tried. The first one was based on the reaction of OH-btd and dibenzoylmethane (Hdbm) with ErCl$_3$·6H$_2$O in the presence of an organic base. A similar

method has already been used by P.W. Roesky *et al.* for the preparation of Ln complexes with *o*-nitrophenolato and (dbm)$^-$ ligands.[45] The second approach was based on the ligand substitution reaction between (O-btd)$^-$ and the complex [Er$_5$(dbm)$_{10}$(OH)$_5$]. The latter was known before being prepared in two steps from ErCl$_3$·6H$_2$O.[7] To synthesize this pentanuclear complex, we used a modified one-step procedure reported for other [Ln$_5$(dbm)$_{10}$(OH)$_5$] complexes (Ln = Y, Nd, Eu, Gd, Tb, Ho)[5,19,23,46,47] which consists in reacting LnCl$_3$·6H$_2$O with Hdbm in the presence of a base.

### Preparation of [Er$_4$(dbm)$_6$(O-btd)$_4$(OH)$_2$] (1) and its solvates

With the first approach, the 1:1:1 reaction between ErCl$_3$·6H$_2$O, OH-btd and Hdbm in the presence of triethylamine yielded a mixture of compounds. Extraction of the mixture with toluene and slow evaporation of toluene solution gave a crystalline complex [Er$_4$(dbm)$_6$(O-btd)$_4$(OH)$_2$]·7C$_7$H$_8$ (1·7C$_7$H$_8$) in low yield (Scheme 1). The structure of the product was established by single-crystal XRD. Drying of 1·7C$_7$H$_8$ *in vacuo* afforded the complex [Er$_4$(dbm)$_6$(O-btd)$_4$(OH)$_2$] (1) whose composition was confirmed by EA. A similar complex was also prepared by the second approach. One might expect that reacting [Er$_5$(dbm)$_{10}$(OH)$_5$] with OH-btd would lead to the substitution of OH$^-$ or (dbm)$^-$ ligands at the unchanged Er$_5$ core. However, the reaction of [Er$_5$(dbm)$_{10}$(OH)$_5$] with 5 equivalents of OH-btd in methylene chloride resulted in 1 with a good yield (~70%). Recrystallization of 1 from toluene gave crystalline 1·7C$_7$H$_8$.

### Preparation of [Er$_4$(dbm)$_4$(O-btd)$_6$(OH)$_2$] (2) and its solvates

Of interest is whether the Er$_4$ core of 1 would be retained when the complex is treated with coordinating solvents. In this context, 1 was dissolved in THF and the solution was slowly evaporated. The residue was a complex [Er$_4$(dbm)$_4$(O-btd)$_6$-(OH)$_2$]·6THF (2·6THF) in the form of orange crystals. Thus, formally two (O-btd)$^-$ ligands substituted two (dbm)$^-$ ligands whereas the Er$_4$ core remained unchanged. However, we suppose that actually the tetranuclear complex [Er$_4$(dbm)$_6$-
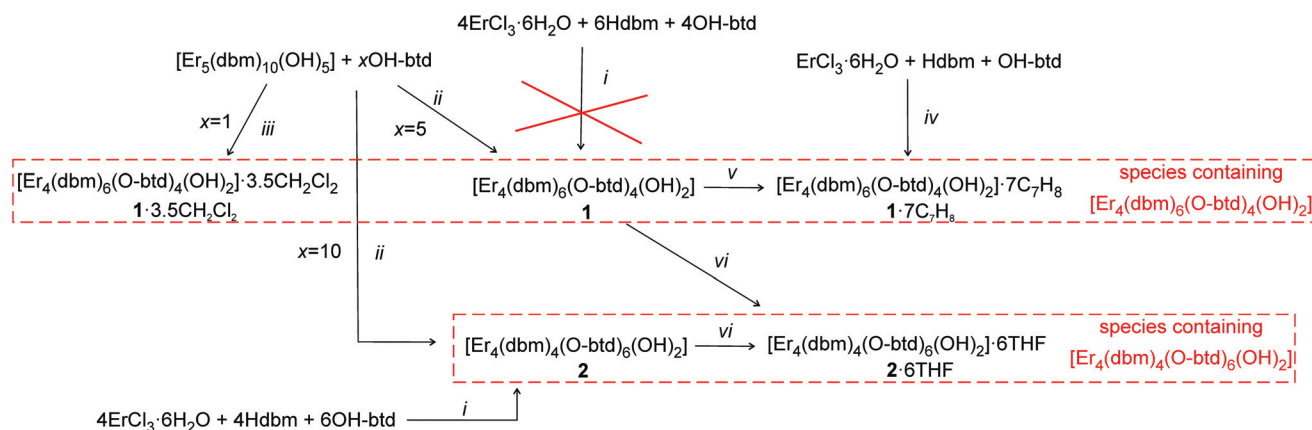


**Scheme 1** Synthetic pathways to complexes 1, 1·7C$_7$H$_8$, 1·3.5CH$_2$Cl$_2$, 2, and 2·6THF. Reactions conditions: (i) methanol, NEt$_3$; (ii) CH$_2$Cl$_2$; (iii) (1) CH$_2$Cl$_2$, (2) *n*-hexane; (iv) (1) methanol, NEt$_3$, (2) toluene; (v) toluene; (vi) THF.

(O-btd)$_4$(OH)$_2$] got decomposed in the solution and another complex was formed during the crystallization from THF. Upon drying *in vacuo*, complex **2**·6THF loses all solvate molecules to form [Er$_4$(dbm)$_4$(O-btd)$_6$(OH)$_2$] (**2**).

For direct preparation of **2**, the first approach with ErCl$_3$·6H$_2$O, Hdbm and OH-btd reacting in the 4 : 4 : 6 stoichiometric ratio was used. Target complex **2** was obtained in nearly quantitative yield (~95%) and its authenticity was confirmed by EA. Crystalline solvate **2**·6THF was prepared by crystallization of complex **2** from THF. It should be noted that reaction of ErCl$_3$·6H$_2$O with Hdbm and OH-btd in the 4 : 6 : 4 ratio does not yield **1** but only a mixture of undefined compounds (Scheme 1).

Overall, one can conclude that the composition of the heteroleptic complexes under discussion depends on the ratio of the starting compounds. Special experiments of reacting [Er$_5$(dbm)$_{10}$(OH)$_5$] with OH-btd were carried out by varying their ratio from 1 : 1 to 1 : 10. At a ratio 1 : 1, the reaction in methylene chloride did not yield any precipitate. Layering *n*-hexane onto the reaction solution gave however a crystalline complex [Er$_4$(dbm)$_6$(O-btd)$_4$(OH)$_2$]·3.5CH$_2$Cl$_2$ (**1**·3.5CH$_2$Cl$_2$) whose structure was established by single-crystal XRD. This finding indicates the higher thermodynamic stability of [Er$_4$(dbm)$_6$(O-btd)$_4$(OH)$_2$] as compared to other complexes even under low concentration of OH-btd. As mentioned above, the 1 : 5 reaction of [Er$_5$(dbm)$_{10}$(OH)$_5$] and OH-btd resulted in the precipitation of individual **1**. Changing the ratio to 1 : 6 led to **1** contaminated by some impurities as indicated by EA. Performing the reaction of [Er$_5$(dbm)$_{10}$(OH)$_5$] and ten-fold excess of OH-btd resulted in the formation of **2** whose composition was confirmed by EA. One can conclude that the [Er$_4$(dbm)$_6$(O-btd)$_4$(OH)$_2$] (**1**) and [Er$_4$(dbm)$_4$(O-btd)$_6$(OH)$_2$] (**2**) are the most stable species under the conditions employed, and that they can be selectively prepared with the use of specific ratios of [Er$_5$(dbm)$_{10}$(OH)$_5$] and OH-btd.

### Structures of the complexes synthesized

Compounds **1**·7C$_7$H$_8$, **1**·3.5CH$_2$Cl$_2$ and **2**·6THF are not isostructural but have the same {Er$_4$(OH)$_2$} core (Fig. 1). Complexes **1**·7C$_7$H$_8$ and **2**·6THF are centrosymmetric. The complex **1**·3.5CH$_2$Cl$_2$ possesses lower symmetry as compared to **1**·7C$_7$H$_8$ but differences in the structures are minimal. The {Er$_4$(OH)$_2$} complex core consists of 4 Er atoms bridged by 2 μ$_3$-OH$^-$ groups which are located on both sides of the metal parallelogram. The presence of the hydroxyl groups is confirmed by a broad peak around 3400 cm$^{-1}$ in the IR spectra. The Er atoms adopt four different types of strongly distorted square-antiprismatic coordination geometries. The first type is observed for the Er atoms defining the shorter diagonal of the Er$_4$ parallelogram in **1**·7C$_7$H$_8$ and **1**·3.5CH$_2$Cl$_2$ complexes, and includes 6 O atoms of 2 (dbm)$^-$ and 2 (O-btd)$^-$ ligands in addition to 2 O atoms of μ$_3$-OH– groups. The two remaining Er atoms have the coordination environment which consists of 3 O atoms of 2 (dbm)$^-$ ligands, 2 N and 2 O atoms of 2 (O-btd)$^-$ ligands, and 1 O atom of μ$_3$-OH$^-$ groups. In the case of **2**·6THF, the Er atoms lying on the shorter diagonal of the par-
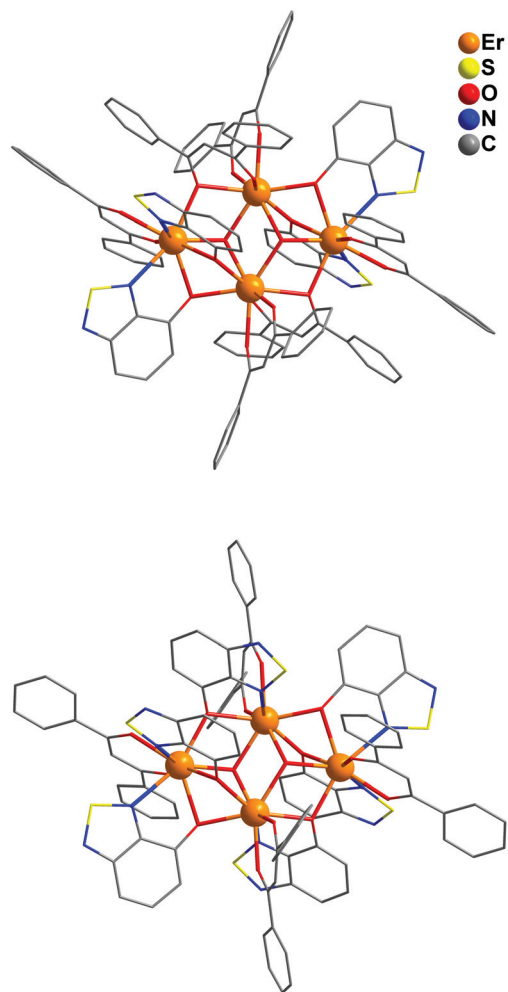


**Fig. 1** XRD molecular structures of the complexes **1**·7C$_7$H$_8$, **1**·3.5CH$_2$Cl$_2$ (top), and **2**·6THF (bottom). Solvate molecules and hydrogen atoms of the ligands have been omitted for clarity.

allelogram are eight-coordinated by 2 O atoms of 2 (dbm)$^-$ ligands, 1 N and 3 O atoms of 3 (O-btd)$^-$ ligands, and 2 O atoms of μ$_3$-OH$^-$ groups. The other two Er atoms are coordinated by 2 O atoms of (dbm)$^-$ ligands, 2 N and 3 O atoms of 3 (O-btd)$^-$ ligands, and 1 O atom of μ$_3$-OH$^-$ groups.

A similar Ln$_4$ core was observed earlier in [Ln$_4$(dbm)$_{10}$(OH)$_2$], Ln = Pr, Nd, Sm, Eu.[47,48] The coordination types of organic ligands in these complexes are different from those in the **1**·7C$_7$H$_8$, **1**·3.5CH$_2$Cl$_2$ and **2**·6THF. In [Ln$_4$(dbm)$_{10}$(OH)$_2$], the (dbm)$^-$ ligand is known to have 3 types of coordination modes chelating and/or bridging metal cations: (a) one metal centre chelating mode, (b) one metal centre chelating/bridging mode, and (c) two metal centres chelating and bridging mode. In contrast, the (O-btd)$^-$ ligand possesses 1 coordination mode shown in Scheme 2. On the whole, the molecules of the complexes discussed contain 4 chelating (dbm)$^-$ ligands and 6 chelating/bridging ligands consisting of 2 (dbm)$^-$ and 4 (O-btd)$^-$ ones in **1**·7C$_7$H$_8$ and **1**·3.5CH$_2$Cl$_2$; and 6 (O-btd)$^-$ ligands in **2**·6THF. Thus, there are no ligands possessing the c mode in these complexes.
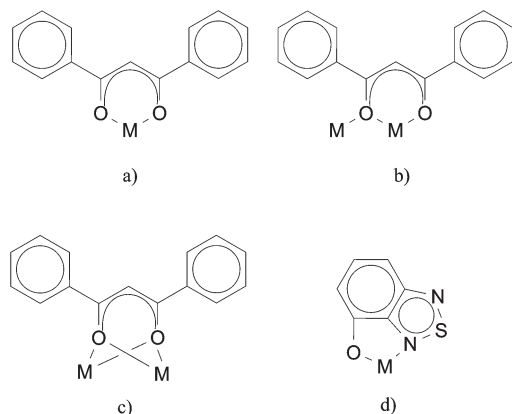
**Scheme 2** The bonding modes of (dbm)⁻ and (O-btd)⁻ ligands.

The average Er–O and Er–N bond lengths for chelating/bridging ligands are 2.36 Å and 2.52 Å, respectively. The average Er–O bond length for chelating the (dbm)⁻ ligand is 2.28 Å. These distances are in the expected range.[49] For Er atoms linked *via* 2 bridging atoms the average Er···Er distance and Er–O–Er angle are 3.81 Å and 109° respectively. The Er atoms linked *via* 3 bridging atoms have the average Er···Er distance and Er–O–Er angle of 3.54 Å and 97°, respectively.

It should be noted that crystal packing of **2**·6THF features infinite chains in which the molecules are linked by pairs of shortened intermolecular S···N contacts of 2.893(4) Å (Fig. S1†). These distances are noticeably shorter than the sum of the corresponding van der Waals radii of 3.35 Å. According to the CSD they belong to the shortest intermolecular S···N contacts observed for the complexes with 2,1,3-benzothiadiazole ligands. On the other hand, neither **1**·7C₇H₈ nor **1**·3.5CH₂Cl₂ has the S···N contacts shorter than 3.35 Å.

## Magnetic properties of the complexes

Solvent-free complexes **1** and **2** show similar temperature dependences of their effective magnetic moment ($\mu_{\text{eff}}$) (Fig. S2a,b†). At 300 K, values of $\mu_{\text{eff}}$ equal to 19.19 and 19.14$\mu_{\text{B}}$ for **1** and **2**, respectively, are in good agreement with the theoretical value 19.16$\mu_{\text{B}}$ for a system of 4 non-interacting Er(III) ions in the ground state $^4J_{15/2}$ with $g$ = 6/5. The $\mu_{\text{eff}}$ gradually decreases by lowering temperature down to 14.01 and 13.65$\mu_{\text{B}}$ at 5 K for **1** and **2**, respectively. In the temperature range 5–300 K, the temperature dependences of the molar magnetic susceptibility ($\chi$) obey the Curie–Weiss law with $C$ = 47.0(±0.1) cm³ K mol⁻¹ and $\theta$ = −7.6(±0.3) K for **1**, and $C$ = 46.7(±0.2) cm³ K mol⁻¹ and $\theta$ = −6.5 K for **2**. The negative values of the Weiss constants $\theta$ and decreasing of $\mu_{\text{eff}}$ by lowering temperature may be associated with a weak antiferromagnetic interactions or depopulation of the $m_J$ sublevel arising from the ligand field effects.

## Spectral properties of the complexes

The previously reported complex [Er₅(dbm)₁₀(OH)₅] reveals efficient Er(III)-centered luminescence in the NIR range.[7]

Therefore, spectral properties of complexes **1** and **2** were studied in comparison with those of [Er₅(dbm)₁₀(OH)₅]. The electronic absorption spectrum (EAS) of the latter is characterised by the main band at 350 nm assigned to (dbm)⁻ intraligand transition. The excitation at this wavelength sensitizes the Er(III)-centered NIR luminescence associated with the $^4I_{13/2}{\to}^4I_{15/2}$ transition.[7] The EAS of complexes **1** and **2** (Fig. 2a) reveal the main band at 360 nm together with the shoulders at 310–330 and 430–450 nm.

The shoulders should be assigned to (O-btd)⁻ intraligand transitions. The origin of the electronic absorption of complexes **1** and **2** at 450 nm is worth noting. The intensity of the electronic absorption at 450 nm is *ca.* 100-fold less than the intensity of the main band at 360 nm arisen from π→π* transition (Fig. 2a). The n→π* transition associated with the imine N atoms of O-btd is the probable reason of the shoulder at 450 nm.[42]

The fluorescence properties of complexes **1** and **2** are also quite different from those of [Er₅(dbm)₁₀(OH)₅]. In particular, the excitation by the wavelength of the main band, $\lambda_{\text{exc}}$ =
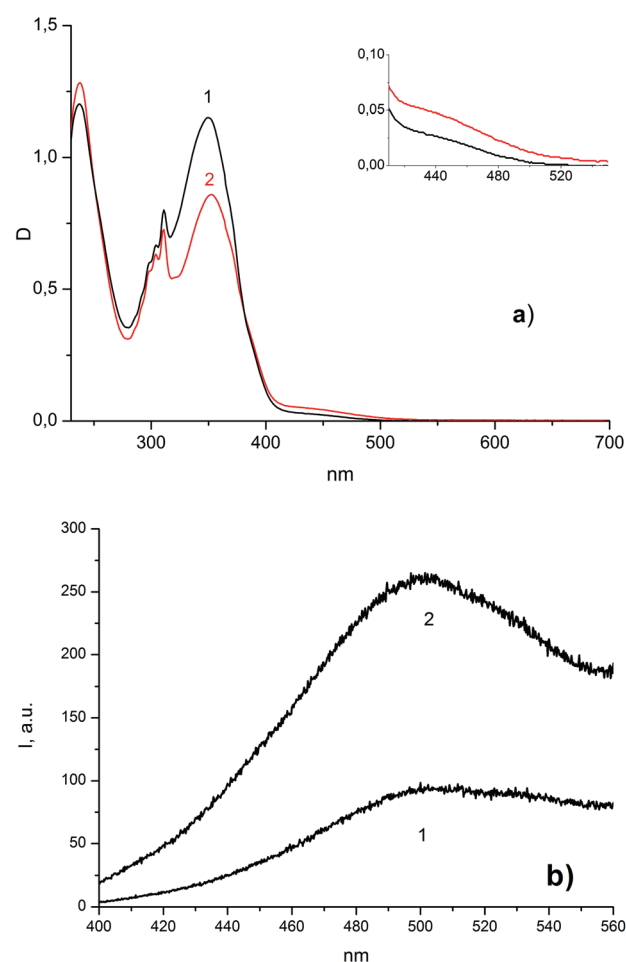


**Fig. 2** Electronic absorption (a) and emission (b) spectra of complexes **1** and **2** (0.01 mM in CH₂Cl₂), $\lambda_{\text{exc}}$ = 360 nm, the slit width is 14 nm. The detailed representation of the shoulder at 450 nm is in the inset of Fig. 2a.
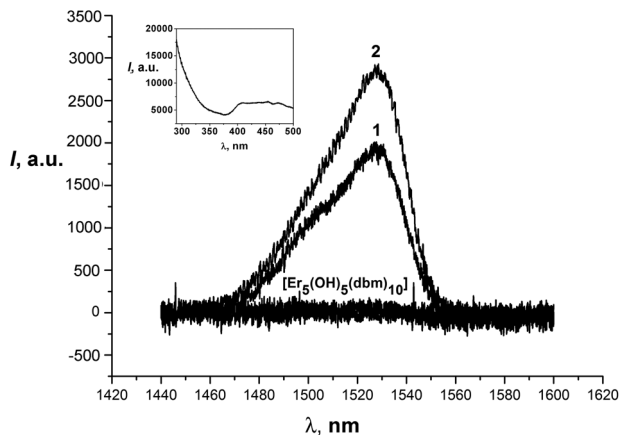
**Fig. 3** The normalized luminescence spectra of complexes **1** and **2** obtained with $\lambda_{exc}$ = 450 nm, and the spectrum of complex [Er$_5$(dbm)$_{10}$(OH)$_5$] obtained with $\lambda_{exc}$ = 350 nm. Conditions: 0.1 mM solutions of the complexes in CH$_2$Cl$_2$. The excitation spectrum of **2** is in the inset.

360 nm, induces the emission at 510 nm only, while no detectable luminescence in the NIR range occurs at the concentrations (Fig. 2b) and instrument conditions employed. The emission at 510 nm excited at 360 nm (Fig. 2b) should be assigned to the intraligand fluorescence. The excitation at 450 nm arisen from O-btd-centered transitions results in the Er(III)-centered NIR luminescence of complexes **1** and **2** at ~1530 nm (Fig. 3). Fig. 2b and 3 show that the metal-centered emission is significantly greater than the ligand-centered one. The IR-luminescence is quite strong (the spectra were recorded under aerated conditions). Unfortunately low solubility of the compounds **1** and **2** (0.1 mM concentration can be achieved) did not allow us to obtain accurate data of decay curves.

The luminescence spectra of complexes **1**, **2** and [Er$_5$(dbm)$_{10}$(OH)$_5$] have been measured under identical concentrations and instrumental conditions. Comparison revealed that the emission intensity was higher for complex **2** than for complex **1**, while for [Er$_5$(dbm)$_{10}$(OH)$_5$] the intensity was practically at the noise level under the applied conditions (Fig. 3). This finding indicates that the (O-btd)$^-$ ligand acts as a more efficient antenna for the Er(III)-centered NIR luminescence than (dbm)$^-$ ligands. One can think that this effect of the (O-btd)$^-$ ligand results from its structure influencing greatly both the ligand-to-metal energy transfer and the radiationless decay through the deactivation *via* vibrational excitation.[3,12] However, further research is necessary towards understanding the ligand-to-metal energy transfer mechanism in complexes **1** and **2**.

## Conclusions

To summarize, two synthetic approaches were applied to prepare new heteroleptic tetranuclear complexes [Er$_4$(dbm)$_6$(O-btd)$_4$(OH)$_2$] (**1**) and [Er$_4$(dbm)$_4$(O-btd)$_6$(OH)$_2$] (**2**) based on the reaction of OH-btd and Hdbm with ErCl$_3$·6H$_2$O in the presence

of an organic base, and on ligand substitution reaction between (O-btd)$^-$ and a known complex [Er$_5$(dbm)$_{10}$(OH)$_5$]. It has been shown that the first method gives only complex **2**, whereas the second one gives **1** or **2** depending on the reaction conditions. Crystalline complexes **1**·7C$_7$H$_8$, **1**·3.5CH$_2$Cl$_2$, and **2**·6THF were also prepared and their structures were confirmed by single-crystal XRD. The {Er$_4$(OH)$_2$} core is similar in all compounds, and differences in their structures are related to the (dbm)$^-$/(O-btd)$^-$ ligand ratio and nature of solvate molecules (where present). The magnetochemical study of **1** and **2** is in good agreement with the structures. The high temperature $\mu_{eff}$ values and Curie constants for **1** and **2** correspond to the theoretical ones for four non-interacting Er(III) ions.

At ambient temperature, the complexes synthesized exhibit strong NIR luminescence upon excitation of the (O-btd)$^-$ ligand. This observation allows us to suggest it as a new efficient antenna ligand for the lanthanide-based luminescence. Taking into account the high potential of 2,1,3-benzothiadiazole derivatives for various photodevices[29–37] the Er(III) complexes might be applied to extend this potential to the infrared scale.

## Experimental

### General

All reagents and solvents were of analytical grade and were used as received without further purification except for the CH$_2$Cl$_2$ solvent which was distilled before use. OH-btd[50] and [Er$_5$(dbm)$_{10}$(OH)$_5$][5] were synthesized by known methods, in the latter case a modified procedure was used.

EA data were obtained with a Eurovector EuroEA3000 analyzer. The Er : S ratio in the samples was determined by energy-dispersive X-ray spectroscopy (EDX) with a JSM-6700F scanning electron microscope.

### Spectral measurements

IR spectra were recorded on a Bruker IFS28 spectrometer for KBr pellets, and EAS (UV-Vis) spectra on a Shimadzu UV-3000 instrument using 10 mm quartz cuvettes. The steady-state emission spectra were measured with a Jobin Yvon FL3-221-NIR spectrofluorometer using excitation lines of 350, 380 and 450 nm and 10 mm quartz cuvettes. The excitation and emission slits were 14/14 nm in all measurements. All samples were measured under aerated conditions without preliminary deoxygenation.

### X-ray diffraction

Single-crystal XRD data were collected with a Bruker Nonius X8 APEX diffractometer equipped with a 4 K CCD area detector at 150(2) K using the graphite-monochromated MoK$_\alpha$ radiation ($\lambda$ = 0.71073 Å). The φ-scan technique was employed to measure intensities. Absorption corrections were applied using the SADABS program.[51] The crystal structures were solved by direct methods and refined by full-matrix least squares techniques with the use of the SHELXTL package.[52]

Atomic thermal displacement parameters for non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated corresponding to their geometrical conditions and refined using the riding model.

## Magnetic measurements

The magnetic susceptibility $\chi$ of the polycrystalline samples was measured with a Quantum Design MPMS*XL* SQUID magnetometer in the temperature range 5–300 K in magnetic fields up to 5 kOe. None of the complexes exhibited any field dependence of molar magnetization at low temperatures. Diamagnetic corrections were made using the Pascal constants. The effective magnetic moment was calculated as $\mu_{eff}(T) = [(3k/N_A\mu_B^2)\chi T]^{1/2} \approx (8\chi T)^{1/2}$.

## Syntheses

**Synthesis of [Er₅(dbm)₁₀(OH)₅] (modified procedure.[5]).** At ambient temperature, KO*t*Bu (0.151 g, 1.34 mmol) and Hdbm (0.204 g, 0.910 mmol) were dissolved in methanol (7 mL). The solution of ErCl₃·6H₂O (0.177 g, 0.464 mmol) in 5 mL of methanol was then added. A yellowish precipitate was formed immediately. The reaction mixture was stirred overnight, the solvent was distilled off under reduced pressure, and the residue was treated with methylene chloride (10 mL). The suspension obtained was centrifuged to remove the solid and hexane (15 mL) was added to the resulting solution. The precipitate formed was collected and dried. An additional portion of the compound was obtained by evaporation of the mother solution to ~15 mL. Overall yield was 0.200 g (80%); IR, $\nu$ (cm⁻¹): 3630 w, 3400 w, 3058 w, 3027 w, 1598 s, 1553 s, 1521 s, 1480 s, 1456 s, 1397 s, 1313 m, 1282 m, 1223 m, 1180 w, 1069 m, 1023 m, 941 w, 784 w, 748 m, 718 s, 685 s, 609 m; C₁₅₀H₁₁₅Er₅O₂₅ (3153.8): calcd C 57.1, H 3.7; found C 57.3, H 3.9.

**Synthesis of [Er₄(dbm)₆(O-btd)₄(OH)₂] (1) and its solvates with toluene (1·7C₇H₈) and methylene chloride (1·3.5CH₂Cl₂).** (a) At ambient temperature, Hdbm (0.075 g, 0.34 mmol) and OH-btd (0.051 g, 0.34 mmol) were dissolved in methanol (5 mL). Triethylamine (0.18 mL) was added, and the solution was stirred for 1 h. Then the solution of ErCl₃·6H₂O (0.128 g, 0.335 mmol) in methanol (5 mL) was added, and an orange precipitate was formed immediately. The reaction mixture was stirred for 1 day, the precipitate was filtered off, washed with several portions of methanol and dried *in vacuo*. Extraction of the product with toluene (25 mL) followed by slow evaporation of the solution at room temperature gave orange crystals of 1·7C₇H₈. Drying of this compound *in vacuo* resulted in individual 1, yield 0.026 g (10%); C₁₁₄H₈₀Er₄N₈O₁₈S₄ (2647.2): calcd C 51.7, H 3.0, N 4.2, S 4.8; found C 51.2, H 3.4, N 4.2, S 4.5.

(b) [Er₅(dbm)₁₀(OH)₅] (0.082 g, 0.026 mmol) was dissolved in methylene chloride (3 mL) and a solution of OH-btd (0.020 g, 0.13 mmol) in the same solvent (3 mL) was added. An orange precipitate of 1 formed after 2 days was collected, washed with small amounts of methylene chloride and dried *in vacuo*, yield 0.060 g (70%); IR, $\nu$ (cm⁻¹): 3615 w, 3480 w, 3400 w, 3060 w, 1598 s, 1553 s, 1522 s, 1479 s, 1454 s, 1399 s, 1314 m, 1289 m, 1224 m, 1180 w, 1096 m, 1070 w, 1024 w, 941 w, 904 w, 860 w, 784 w, 723 m, 690 m, 619 m; C₁₁₄H₈₀Er₄N₈O₁₈S₄ (2647.2): calcd C 51.7, H 3.0, N 4.2, S 4.8; found C 51.0, H 3.4, N 4.3, S 4.5. The Er : S ratio is 1 : 1 according to the EDX analysis. Recrystallization of 1 from toluene gave crystalline 1·7C₇H₈.

(c) [Er₅(dbm)₁₀(OH)₅] (0.058 g, 0.018 mmol) was dissolved in methylene chloride (5 mL) and OH-btd (0.0028 g, 0.018 mmol) was added. The solution obtained was stirred for 4 days, and 10 mL of *n*-hexane were layered onto it. The two-layered system was left at ambient temperature until mutual diffusion of solvents ceased. The liquid was removed and orange crystals of 1·3.5CH₂Cl were obtained, being slightly contaminated with unreacted [Er₅(dbm)₁₀(OH)₅]. Washing the product with a small amount of methylene chloride gave pure 1·3.5CH₂Cl₂. Drying of this compound in vacuum resulted in the formation of 1, yield 0.010 g (80% on OH-btd weight). C₁₁₄H₈₀Er₄N₈O₁₈S₄ (2647.2): calcd C 51.7, H 3.0, N 4.2, S 4.8; found C 51.3, H 2.9, N 4.1, S 4.7.

**Synthesis of [Er₄(dbm)₄(O-btd)₆(OH)₂] (2) and its solvate with THF (2·6THF).** (a) At ambient temperature, solution of OH-btd (0.040 g, 0.26 mmol) in methylene chloride (3 mL) was added to a stirred solution of [Er₅(dbm)₁₀(OH)₅] (0.188 g, 0.0588 mmol) in the same solvent (3 mL). An orange precipitate formed after 2 days was collected, washed with small amounts of methylene chloride, dried *in vacuo* and dissolved in hot THF (10 mL). Slow evaporation of the solution at ambient temperature gave orange crystals of 2·6THF. Drying of this compound *in vacuo* resulted in the formation of individual 2, yield ~5%. C₉₆H₆₄Er₄N₁₂O₁₆S₆ (2557.1): calcd C 46.0, H 2.6, N 6.7, S 7.7; found C 45.5, H 2.8, N 6.3, S 7.4.

(b) Hdbm (0.074 g, 0.33 mmol) and OH-btd (0.075 g, 0.49 mmol) were dissolved in 7 mL of methanol. Triethylamine (0.24 mL) was added, and the solution was stirred at ambient temperature for 1 h. Then a solution of ErCl₃·6H₂O (0.126 g, 0.329 mmol) in 5 mL of methanol was added, and an orange precipitate was formed immediately. The mixture was stirred overnight, the precipitate of 2 was collected, washed with several portions of methanol and dried *in vacuo*, yield 0.193 g (95%); IR $\nu$ (cm⁻¹): 3630 w, 3428 w, 3062 w, 1596 s, 1552 s, 1536 s, 1524 s, 1481 s, 1454 m, 1390 s, 1321 m, 1287 m, 1225 w, 1180 w, 1165 w, 1095 m, 1072 w, 1025 w, 942 w, 904 m, 853 w, 802 w, 784 w, 740 m, 723 m, 692 m, 620 m; C₉₆H₆₄Er₄N₁₂O₁₆S₆ (2503.0): calcd C 46.0, H 2.6, N 6.7, S 7.7; found C 45.5, H 2.7, N 6.3, S 7.6. The Er : S ratio is 2 : 3 according to the EDX analysis. Recrystallization of 2 from THF gives crystalline 2·6THF.

(c) [Er₅(dbm)₁₀(OH)₅] (0.041 g, 0.013 mmol) was dissolved in methylene chloride (1.5 mL) and the solution of OH-btd (0.020 g, 0.13 mmol) in the same solvent (1.5 mL) was added. An orange precipitate of 2 formed after 1 day was collected, washed with small amounts of methylene chloride and dried *in vacuo*, yield 0.028 g (70%). C₉₆H₆₄Er₄N₁₂O₁₆S₆ (2503.0): calcd C 46.0, H 2.6, N 6.7, S 7.7; found C 45.7, H 2.7, N 6.5, S 7.6.

## Acknowledgements

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