DOI: 10.1002/zaac.200600150

The Octanuclear Europium Cluster $[\mathrm{bmpyr}]_6[\mathrm{Eu}_8(\mu_4\text{-O})(\mu_3\text{-OH})_{12}(\mu_2\text{-OTf})_{14}(\mu_1\text{-Tf})_2](\mathrm{HOTf})_{1.5}$ Obtained from the Ionic Liquid [bmpyr][OTf][1)]

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Received May 5th, 2006.

Dedicated to Professor Glen B. Deacon on the Occasion of his 70th Birthday

Abstract. The octanuclear europium cluster compound $[\mathrm{bmpyr}]_6[\mathrm{Eu}_8(\mu_4\text{-O})(\mu_3\text{-OH})_{12}(\mu_2\text{-OTf})_{14}(\mu_1\text{-OTf})_2](\mathrm{HOTf})_{1.5}$ has been crystallized from the ionic liquid [bmpyr][OTf]. Structural characterization by single crystal X-ray diffraction revealed an Eu_8 cluster unit which is centered by an oxide anion. The Eu_8-cluster polyhedron can be described as a bicapped octahedron or a triangulated dodecahedron. Each of the triangular faces of the cluster is capped by one μ_3-hydroxo group. Fourteen μ_2-triflate ($\mathrm{CF_3SO_3^-}$) anions bridge via oxygen the cluster edges. Together with two μ_1-terminal coordinating triflate anions they complete the cluster unit. Six cations from the ionic liquid counterbalance the cluster charge. Additionally, 1.5 HOTf molecules per Eu_8-cluster unit are incorporated in the crystal structure of the title compound.

Keywords: Rare-earth metals; Ionic liquids; Cluster compounds

Lanthanide polyoxometallate cluster compounds offer a high potential as luminescent, magnetic and catalytic functional materials [1]. However, because of the high charge and the polarizing power of the trivalent rare earth cations, it is generally difficult to control the process of oligomerization. In addition, the trivalent rare earth ions generally show highly variable coordination numbers and geometries with only small energy differences leading to a large number of different polyoxometallates. In case of (trivalent) europium, hexa-, octa-, nona- and pentadecanuclear polyhydroxometallate cluster compounds have been described [2]. Here, we report on the synthesis and structural characterization of an oxygen-centered octanuclear europium cluster compound obtained from the ionic liquid [bmpyr][OTf] (bmpyr = 1-butyl-1-methylpyrrolidinium, OTf = trifluoromethanesulfonate, $\mathrm{CF_3SO_3^-}$).

Results and Discussion

The europium cluster compound $[\mathrm{bmpyr}]_6[\mathrm{Eu}_8(\mu_4\text{-O})(\mu_3\text{-OH})_{12}(\mu_2\text{-OTf})_{14}(\mu_1\text{-OTf})_2](\mathrm{HOTf})_{1.5}$ (**1**) has been obtained from acidic europium(III)-triflate in the ionic liquid [bmpyr][OTf] as a colorless compound. Single crystal X-ray structure analysis reveals an octanuclear unit of europium atoms which can be understood as a bicapped octahedron (see Fig.1, left). Such a $[\mathrm{Eu}_8(\mu_4\text{-O})(\mu_3\text{-OH})_{12}]^{10+}$ cluster core has been previously described for $\mathrm{Eu}_8(\mathrm{DMF})_8(\mu_4\text{-O})(\mu_3\text{-OH})_{12}(\mathrm{Se}_3)(\mathrm{Se}_4)_3(\mathrm{Se}_5)_2$ [3]. In case of the mixed valent octanuclear cluster compound $\mathrm{H}_{10}[\mathrm{Eu}_8\mathrm{O}_8(\mathrm{OC}_6\mathrm{H}_3\mathrm{Me}_2\text{-}2,6)_{10}(\mathrm{O}^i\mathrm{Pr})_2(\mathrm{THF})_6]$ a distorted cubic arrangement of the eight europium atoms was found [4]. The Eu-Eu distances in **1** with a mean value of 393.0(4) pm are well beyond the Eu-Eu bonding region and significantly higher as in $\mathrm{Eu}_8(\mathrm{DMF})_8(\mu_4\text{-O})(\mu_3\text{-OH})_{12}(\mathrm{Se}_3)(\mathrm{Se}_4)_3(\mathrm{Se}_5)_2$. The arrangement of the europium cations can alternatively be described as a Eu_4 butterfly sandwiched between two perpendicular Eu_2 dimers. Such a structural unit is known for octanuclear clusters like $\mathrm{B_8H_8}^{2-}$ and $\mathrm{B_8Cl_8}$ [5]. In case of **1** the central Eu_4 butterfly is centered by an oxide anion with a mean Eu-O interatomic distance of 254.4(3) pm. Surpisingly this interatomic distance is about 18 pm longer than in $\mathrm{Eu}_8(\mathrm{DMF})_8(\mu_4\text{-O})(\mu_3\text{-OH})_{12}(\mathrm{Se}_3)(\mathrm{Se}_4)_3(\mathrm{Se}_5)_2$ but similar to the one in $[\mathrm{Eu}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(\mathrm{H_2O})_{24}]\mathrm{I}_8(\mathrm{H_2O})_8$ (257 pm) [2c]. In order to describe the hydroxide anion arrangement around the Eu_8 cluster unit it is useful to view the cationic arrangement as a triangulated dodecahedron. Each of the triangular faces of this polyhedron is capped by a μ_3-hydroxide anion with a mean Eu-O interatomic distance of 237.1(3) pm which lies in the same region as found for $\mathrm{Eu}_8(\mathrm{DMF})_8(\mu_4\text{-O})(\mu_3\text{-OH})_{12}(\mathrm{Se}_3)(\mathrm{Se}_4)_3(\mathrm{Se}_5)_2$ (241(6) pm) and $[\mathrm{Eu}_6(\mu^6\text{-O})(\mu^3\text{-OH})_8(\mathrm{H_2O})_{24}]\mathrm{I}_8(\mathrm{H_2O})_8$ (239(1) pm). Sixteen triflate (OTf) anions fill the coordination sphere of the europium cations. Fourteen of the triflate anions coordinate in a bidentate chelating mode through two oxygen atoms along the edges of the Eu_8 cluster. Two additional triflate anions coordinate only monodentately to europium. The mean Eu-OTf interatomic distance of 239.8(3) pm is in the expected range. All europium cations are crystallographically independent. Six of them are coordinated by nine oxygen atoms in the form of a monocapped square antiprism whereas two europium

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[1)] Paper presented at the XVIIIth Tage der Seltenen Erden (Terrae Rarae 2005) at Bonn-Röttgen/Germany, November 30th – December 2nd, 2005 (www.Terrae-rarae.de).

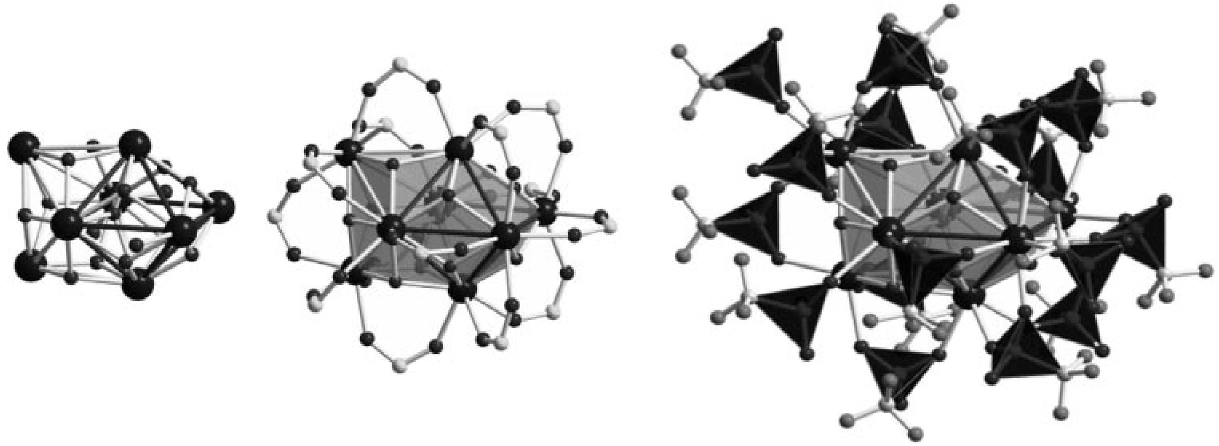

Fig. 1 Parts of the crystal structure of $[bmpyr]_6[Eu_8(\mu_4\text{-O})(\mu_3\text{-OH})_{12}(\mu_2\text{-OTf})_{14}(\mu_1\text{-OTf})_2](HOTf)_{1.5}$ (**1**): $Eu_8(\mu_4\text{-O})(\mu_3\text{-OH})_{12}$ cluster core (left), $\{[Eu_8(\mu_4\text{-O})(\mu_3\text{-OH})_{12}(\mu_2\text{-OTf})_{14}\}^{4-}$, one oxygen and CF_3 groups omitted for clarity (middle), $\{[Eu_8(\mu_4\text{-O})(\mu_3\text{-OH})_{12}(\mu_2\text{-OTf})_{14}(\mu_1\text{-OTf})_2]\}^{6-}$cluster unit (right).

cations are surrounded by just eight oxygen atoms in the form of a square antiprism. The coordination of the europium cations belonging to the inner Eu_4 butterfly (Fig. 2, left) is accomplished by one oxide anion, five hydroxide anions and three oxygen atoms belonging to triflate anions that form a bridge to neighbouring europium cations. In case of the perpendicular Eu_2 units one europium ion of each unit has the coordination number nine, which is accomplished by four hydroxide anions, four triflate anions that bridge to other europium cations and one terminal triflate ligand. The other half of the europium cations has a coordination number of eight with the terminal triflate ligand missing. The anionic charge of the cluster is counterbalanced by six [bmpyr] cations from the ionic liquid. Additionally, 1.5 HOTf molecules per Eu_8-cluster unit are incorporated in the crystal structure of **1**. Despite the plethora of polynuclear hydroxo lanthanide clusters it seems that certain cluster cores have a pronounced stability. In case of oxygen centred hydroxo lanthanide clusters the hexanuclear cluster unit $[Ln_6(\mu^6\text{-O})(\mu^3\text{-OH})_8]^{8+}$ (Ln = lanthanide) with a Ln_6 octahedron has been described for a plethora of different counter anions and ligands [2, 6, 7]. The existence of $Eu_8(DMF)_8(\mu_4\text{-O})(\mu_3\text{-OH})_{12}(Se_3)(Se_4)_3(Se_5)_2$ and together with the new example of $[bmpyr]_6[Eu_8(\mu_4\text{-O})(\mu_3\text{-OH})_{12}(\mu_2\text{-OTf})_{14}(\mu_1\text{-OTf})_2](HOTf)_{1.5}$ may justify the assumption that the $[Ln_8(\mu_4\text{-O})(\mu_3\text{-OH})_{12}]^{10+}$ cluster unit is also common to oxygen centred hydroxo lanthanide cluster compounds.

Experimental Section

All operations were carried out under argon using standard Schlenk-line and glovebox techniques.

$[bmpyr]_6[Eu_8(\mu_4\text{-O})(\mu_3\text{-OH})_{12}(\mu_2\text{-OTf})_{14}(\mu_1\text{-OTf})_2](HOTf)_{1.5}$ (1)

500 mg Eu_2O_3 (99.9 %, Chempur) were suspensed in 10 ml H_2O and trifluoromethanesulfonic acid (CF_3SO_3H = HOTf; 98 % Sigma-Aldrich) was added dropwise until a transparent acidic (pH < 1) solution of europium(III)-triflate was obtained. Water was removed *in vacuo* and the remaining colorless solid was dried for 12 h at 300 °C under reduced pressure (10^{-2} mbar).

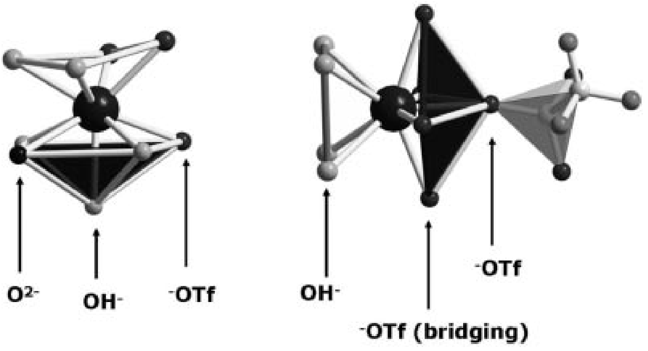

Fig. 2 Europium coordination in $[bmpyr]_6[Eu_8(\mu_4\text{-O})(\mu_3\text{-OH})_{12}(\mu_2\text{-OTf})_{14}(\mu_1\text{-OTf})_2](HOTf)_{1.5}$. Coordination of Eu cations belonging to the central Eu_4 butterfly (left). Coordination of one half of Eu-cations belonging to the perpendicular Eu_2 units (right), in case of the other half the terminal monodentate triflate ligand is absent.

The ionic liquid 1-butyl-1-methylpyrrolidinium triflate, [bmpyr][OTf], was synthesized following a literature procedure [7].

To obtain $[bmpyr]_6[Eu_8(\mu_4\text{-O})(\mu_3\text{-OH})_{12}(\mu_2\text{-OTf})_{14}(\mu_1\text{-Tf})_2](HOTf)_{1.5}$ 120 mg of the acidic europium(III)-triflate and 0.2 ml of [bmpyr][OTf] were placed in a silica tube which was sealed under vacuum. The reaction mixture was heated at 393 K for 36 h. Colorless, transparent single crystals of **1** form as an insoluble product after cooling the reaction mixture to room temperature (2 K/min). The product was separated by cannula-filtration from the ionic liquid. Estimated yield: 20 %.

Crystal structure determination of 1

After checking the crystal quality via Laue photographs a colorless fragment (0.3 × 0.3 × 0.2) mm^3 of **1**, $C_{71.5}H_{133.5}Eu_8F_{52.5}N_6O_{65.5}S_{17.5}$ (4899.57 g mol^{-1}) was selected for data collection. Triclinic, P-1, a = 1557.05(5) pm, b = 1915.14(6) pm, c = 2798.37(8) pm, α = 104.950(2)°, β = 92.324(2)°, γ = 107.107(2)°, V = 7644.0(4) $Å^3$, Z = 2, ρ_{calcd} = 2.129 g cm^{-3}, μ = 3.620 mm^{-1}.

X-ray diffraction data were collected on an IPDS II diffractometer with Mo-Kα radiation (graphite monochromator, $\lambda = 0.71073$ Å) at -150 °C, $\theta_{min}/\theta_{max} = 1.38°/27.00°$. Indices: $-19<=h<=19$, $-24<=k<=24$, $-35<=l<=35$; F(000) = 4770; 122252 reflections collected, 33371 unique [R(int) = 0.0471]. The X-Area program package was used for data collection, unit cell refinement and data reduction [8]; numerical absorption correction after crystal shape optimization was performed using the programs X-Red 1.01 and X-Shape 1.01 [9, 10]. Structure solution with direct methods (SHELXS-97) [11] and refinement against F_0^2 with SHELXH-97 [12] led to $R_1 = 0.0571$, $wR_2 = 0.1598$ [$I > 2\sigma(I)$] and $R_1 = 0.0665$, $wR_2 = 0.1653$ for all data.

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre, CCDC 604289. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code +(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

Acknowledgements. This work has been supported by the Deutsche Forschungsgemeinschaft (SPP 1166: Lanthanoidspezifische Funktionalitäten) and the Fonds der Chemischen Industrie. The authors thank *Prof. Dr. Gerd Meyer* for his continuous support.

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[1] Z. Zheng, *Chem. Commun.* **2001**, 2521 and literature cited therein.
[2] (a) R. Wang, H. D. Selby, H. Liu, M. D. Carducci, T. Jin, Z. Zheng, J. W. Anthis, R. J. Staples, *Inorg. Chem.* **2002**, *41*, 278; (b) M. Addamo, G. Bombieri, E. Foresti, M. D. Grillone, M. Volpe, *Inorg. Chem.* **2004**, *43*, 1603; (c) T. Timofte, A. Babai, A.-V. Mudring, *Inorg. Chem.* submitted.
[3] Ch. G. Pernin, J. A. Ibers, *Inorg. Chem.* **1997**, *36*, 3802.
[4] W. J. Evans, M. A. Greci, J. W. Ziller, *Inorg. Chem.* **2000**, *39*, 3213.
[5] L. J. Guggenberger, *Inorg. Chem.* **1969**, *8*, 2771; R. A.Jacobson, W. N. Lipscomb, *J. Am. Chem. Soc.* **1958**, *80*, 5571.
[6] Z. Zheng, *Chem. Commun.* **2001**, 2521 and literature cited therein; Z. Zheng, *Inorg. Synthesis* **2004**, 184; A. Babai, A.-V. Mudring, *Z. Anorg. Allg. Chem.* **2005**, *631*, 261.
[7] L. Crowhurst, N. L. Lancaster, J. M. Pérez Arlandis, T. Welton, *J. Am. Chem. Soc.* **2004**, *126*, 11549.
[8] X-Area, Stoe & Cie, Darmstadt, Germany, 2002.
[9] X-Red 1.01, Stoe & Cie, Darmstadt, Germany, 2002.
[10] X-Shape 1.01, Stoe & Cie, Darmstadt, Germany, 2002.
[11] G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, **1997**, Göttingen.
[12] G. M. Sheldrick, *SHELXH-97, Program for Crystal Structure Refinement*, **1997**, Göttingen.