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A heterometallic hexanuclear $\{Fe_4Sm_2\}$ cluster supported by pivalate and phenyldiethanolamine ligands

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Abstract. A new hexanuclear heterometallic $[Fe_4Sm_2(OH)_2(piv)_4(phdea)_4(N_3)_2(H_2O)_2]Cl_2 \cdot 3MeCN$ (**1**) cluster has been synthesized using a μ-oxo $[Fe_3O(piv)_6(H_2O)_3](piv)\cdot Hpiv$ (Hpiv = pivalic acid) precursor, $SmCl_3 \cdot 6H_2O$, NaN_3, and N-phenyldiethanolamine (H_2phdea). Single-crystal X-ray diffraction analysis reveals that **1** possesses a nonplanar butterfly-type core with an open-dicubane topology. Continuous Shape Measure (CShM) and Bond Valence Sum (BVS) analyses confirm the distorted octahedral geometry for six-coordinate Fe(III) centers and square-antiprismatic geometries for eight-coordinate Sm(III) ions, consistent with trivalent oxidation states.
Keywords: 3d metal, lanthanide, heterometallic clusters, amino-polyalcohol ligands, single-crystal X-ray diffraction, SHAPE analysis.

Cluster heterometalic hexanuclear $\{Fe_4Sm_2\}$ în bază de liganzi pivalat și fenildietanolamină

Rezumat. A fost sintetizat un cluster heterometalic hexanuclear $\{Fe_4Sm_2\}$, $[Fe_4Sm_2(OH)_2(piv)_4(phdea)_4(N_3)_2(H_2O)_2]Cl_2$, utilizând precursorii $[Fe_3O(piv)_6(H_2O)_3](piv)\cdot Hpiv$, $SmCl_3\cdot 6H_2O$, NaN_3 și N-fenildiethanolamină (H_2phdea). Structura cristalină evidențiază un nucleu de tip „butterfly" neplanar, cu topologie de dicuban incomplet. Analiza SHAPE și calculele BVS confirmă geometrii distorsionate și stări de oxidare +3 pentru toate centrele metalice.
Cuvinte-cheie: metal 3d, lantanid, cluster heterometalice, liganzi amino-polialcoolici, difracție de raze X pe monocristal, analiza SHAPE.

1. Introduction

Heterometallic Fe–Ln clusters constitute an important class of compounds in molecular magnetism, as the combination of 3d transition metals with 4f lanthanide ions enables magnetic properties that are difficult to achieve in homometallic systems [1]. In such assemblies, Fe(III) ions provide high-spin configurations and efficient super exchange pathways through O- and N-donor ligands, while Ln(III) ions contribute large magnetic moments and pronounced single-ion anisotropy [2]. This complementarity promotes

slow magnetic relaxation and enhanced magneto-structural correlations, which are central to the development of single-molecule magnets [3]. Ligand design is fundamental to the controlled assembly of these Fe–Ln architectures. Carboxylate ligands serve as versatile bridging units stabilizing metal–oxygen cores, while amino-polyalcohol ligands offer flexible, multidentate coordination environments suitable for both Fe(III) and Ln(III) ions [4]. Among these systems, hexanuclear $\{Fe_4Ln_2\}$ clusters have attracted particular interest as model compounds for investigating 3d–4f magnetic interactions and structure–property relationships [5]. In continue of our work on the synthesis and investigation of heterometallic polynuclear Fe-Ln coordination compounds [4]–[10], we report the synthesis and structural characterization of a new hexanuclear heterometallic $[Fe_4Sm_2(OH)_2(piv)_4(phdea)_4(N_3)_2(H_2O)_2]Cl_2{\cdot}3MeCN$, (**1**) cluster (where Hpiv = pivalic acid, H_2phdea = N-phenyldiethanolamine).

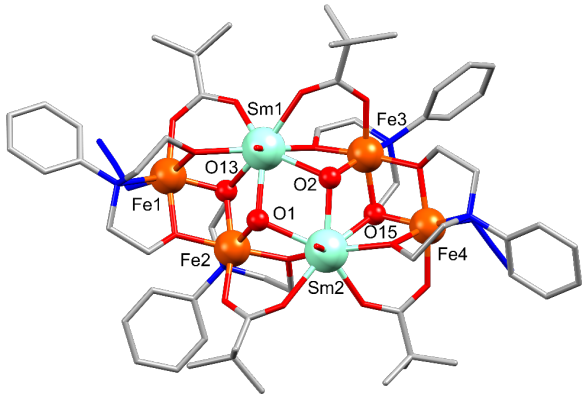
2. Results and discussion

The heterometallic $[Fe_4Sm_2(OH)_2(piv)_4(phdea)_4(N_3)_2(H_2O)_2]Cl_2{\cdot}3MeCN$, (**1**) cluster (where Hpiv = pivalic acid, H_2phdea = N-phenyldiethanolamine) has been synthesized by the ultrasonic treatment of an *i*-PrOH/MeCN mixture containing the trinuclear $[Fe_3O(piv)_6(H_2O)_3](piv){\cdot}Hpiv$ precursor, hexahydrate samarium(III) chloride, sodium azide, and *N*-phenyldiethanolamine.

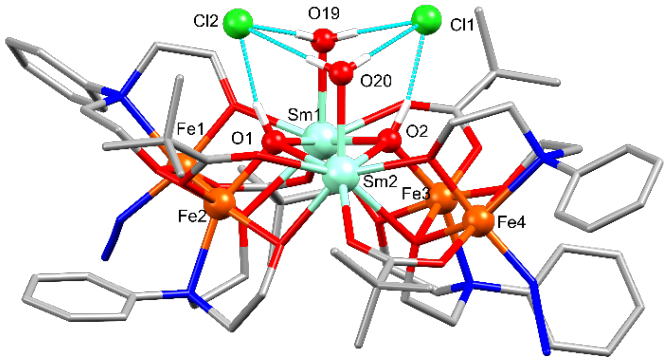
Compound **1** crystallizes in the orthorhombic space group *Pbca* with the following unit cell parameters: $a = 27.9608(8)$, $b = 16.9448(4)$, $c = 36.3593(9)$ Å, $\alpha = \beta = \gamma = 90°$ and $V = 17226.7$ Å^3. A single crystal X-ray diffraction analysis reveals that **1** comprises a dicationic $[Fe_4Sm_2(OH)_2(piv)_4(phdea)_4(N_3)_2(H_2O)_2]^{2+}$ unit with overall charge balanced by two chloride anions, and three acetonitrile solvate molecules. The cationic complex in **1** consists of a hexanuclear $\{Fe_4Sm_2\}$ core fragment of four Fe(III) and two Sm(III) ions and can be regarded as two nearly identical Fe_2Sm triangles fused via two μ_3-hydroxo groups with the observed Sm$\cdots$Sm distance of 3.983(1) Å (Figure 1).

Within these triangular subunits, the Sm$\cdots$Fe distances range from to 3.4421(9) to 3.501(1) Å [Sm1$\cdots$Fe1, 3.486(1); Sm1$\cdots$Fe3, 3.442(1); Sm2$\cdots$Fe2, 3.436(1); Sm2$\cdots$Fe4, 3.501(1) Å]. This metal arrangement is reminiscent of a butterfly-like topology, where the two Sm(III) ions define the body of the butterfly and the four Fe(III) ions occupy the wingtip positions. Unlike planar butterfly cores frequently observed in homometallic iron clusters, the $\{Fe_4Sm_2\}$ unit in **1** is distinctly nonplanar, with a dihedral angle of 36.39° between the two Fe_2Sm triangular subunits. This distortion leads to an open dicubane-type framework, characterized by the absent of one vertex in each cubane-like unit. The central $[Fe_4Sm_2(\mu_3\text{-}O)_2(\mu_3\text{-}OH)_2]$ fragment can alternatively be

decomposed into four edge-sharing [$M_2M'(\mu_3$-O)] triangles: Fe1Fe2Sm1, Sm1Sm2Fe2, Sm1Sm2Fe3, and Fe3Fe4Sm2.



(a)



(b)

Figure 1. (a) Stucture of the dicationic $[Fe_4Sm_2(OH)_2(piv)_4(phdea)_4(N_3)_2(H_2O)_2]^{2+}$ cluster in **1**. Hydrogen atoms are omitted for clarity (b) Side view of the cluster showing the trifurcated O–H$\cdots$Cl hydrogen bonding motive. Hydrogen atoms not involved in H-bonding are omitted for clarity. Hydrogen bonds are shown as blue dotted line

The structural assembly of the cluster is strongly governed by the versatile coordination behavior of the phdea^{2-} ligand. Each Fe(III) center is chelated by a fully deprotonated phdea^{2-} ligand, which facilitates the core's connectivity through various alkoxo-bridging modes: μ_2 at Fe1 and Fe4, or a combination of μ_2- and μ_3-alkoxo bridging modes at Fe2 and Fe3. These bridges effectively link Fe–Fe and Fe–Sm edges within the core, stabilizing the heterometallic framework and enforcing the observed hexanuclearity.

Additional stabilization is provided by four *syn,syn*-bridging pivalate ligands that span peripheral Sm–Fe edges.

All Fe(III) ions reside in distorted six-coordinate environments, as confirmed by Continuous Shape Measure (CShM) analysis [11], [12]. The calculations yield the lowest CShM values for an octahedral geometry (*OC-6*) of 2.745 (Fe1), 4.230 (Fe2), 2.332 (Fe3), and 4.047 (Fe4) (Table 2). Specifically, the Fe1 and Fe4 centers exhibit an N_2O_4 environment composed of one carboxylate oxygen atom, three alkoxy oxygen atoms (one μ_3-O and two μ_2-O) from two phdea^{2-} groups, one phdea^{2-}-nitrogen atom and one azide nitrogen atom. The Fe2 and Fe3 atoms are N_2O_4 coordinated by a μ_3-OH group, a carboxylate oxygen as well as three alkoxo oxygen atoms (one μ_3-O and two μ_2-O) from two phdea^{2-} groups, and one nitrogen atom from the polyalcoholamine ligand. The Fe–O bond distances are in the range of 1.964(4)–2.083(4) Å and Fe–N bond distances are 1.980(5)–2.287(5) Å (Table 1). The Sm(III) centers are eight-coordinate and exhibit geometries best described as square-antiprismatic geometries (*SAPR-8*), with minimum CShM values of 0.843 (Sm1) and 0.854 (Sm2), these are closely followed by biaugmented trigonal prismatic configurations (Table 2).

Table 1. Selected bond distances in **1**

Atom1	Atom2	Length/Å	Atom1	Atom2	Length/Å	Atom1	Atom2	Length/Å
Sm1	O1	2.413(4)	Sm2	O18	2.343(4)	Fe3	O2	1.970(4)
Sm1	O2	2.494(4)	Sm2	O20	2.460(4)	Fe3	O5	1.987(4)
Sm1	O4	2.354(4)	Fe1	O3	2.039(4)	Fe3	O15	2.074(4)
Sm1	O6	2.369(4)	Fe1	O11	2.003(4)	Fe3	O16	1.964(4)
Sm1	O12	2.340(4)	Fe1	O12	1.966(4)	Fe3	O17	1.965(4)
Sm1	O13	2.625(4)	Fe1	O13	2.083(4)	Fe3	N3	2.271(5)
Sm1	O16	2.369(4)	Fe1	N1	2.272(5)	Fe4	O9	2.050(4)
Sm1	O19	2.470(4)	Fe1	N5	2.004(5)	Fe4	O15	2.069(4)
Sm2	O1	2.489(4)	Fe2	O1	1.970(4)	Fe4	O17	2.007(4)
Sm2	O2	2.434(3)	Fe2	O7	1.975(4)	Fe4	O18	1.970(4)
Sm2	O8	2.387(4)	Fe2	O11	1.969(4)	Fe4	N4	2.287(5)
Sm2	O10	2.360(4)	Fe2	O13	2.079(4)	Fe4	N8	1.980(5)
Sm2	O14	2.358(4)	Fe2	O14	1.964(4)			
Sm2	O15	2.595(4)	Fe2	N2	2.273(5)			

The coordination sphere of each Sm(III) ion is defined by an O_8 donor set, comprising two μ_3-OH$^-$ groups, two oxygen atoms from two carboxylates, two alkoxy μ_2-O and one μ_3-O atoms from two phdea^{2-} ligands. The coordination environments are further

fulfilled by a terminal water molecule, reflecting the preference of lanthanide ions for high coordination numbers. The Sm–O bond distances range from 2.340(4) to 2.625(4) Å (Table 1). These assignments are consistent with the observed ligand arrangements and metal-donor distances (Table 2). Bond valence sum (BVS) calculations yield values close to 3.0 v.u. for all Fe and Sm centers, confirming their trivalent oxidation states and the absence of mixed-valence behavior. The combined SHAPE and BVS analyses thus provide a coherent description of both the coordination geometries and oxidation states of the metal centers in compound **1**.

Table 2. Continuous shape measure (CShM) values for the metal centers in **1***

Geometry	**Fe1**	**Fe2**	**Fe3**	**Fe4**	**Geometry**	**Sm1**	**Sm2**
OC-6	**2.745**	**4.230**	**2.332**	**4.047**	*SAPR-8*	**0.843**	**0.854**
TPR-6	8.697	5.888	9.786	6.157	*BTPR-8*	1.655	1.619
PPY-6	21.572	19.846	21.268	19.617	*JBTPR-8*	2.144	2.243
JPPY-6	25.377	22.819	25.976	22.623	*TDD-8*	2.178	2.433
HP-6	32.442	33.291	32.762	32.954	*JSD-8*	4.381	4.692
					CU-8	9.758	10.070
					TT-8	10.176	10.536
					JGBF-8	14.755	14.931
					HBPY-8	16.383	16.407
					HPY-8	21.040	20.551
					ETBPY-8	22.018	21.773
					JETBPY-8	25.484	25.257
					OP-8	29.578	29.232

* bold entries denote the lowest CShM values for each metal center, indicating the closest proximity to the ideal coordination geometry

Table 3. Details of the hydrogen bonding interactions in **1**

D–H. . .A	**d(D–H)**	**d(H. . .A)**	**d(D. . .A)**	**∠(DHA)**
O1–H1. . .Cl2	1.00	2.08	3.061(4)	168.3
O2–H2. . .Cl1	1.00	2.09	3.068(4)	167.0
O19–H19A. . .Cl1	0.87	2.24	3.094(4)	167.3
O19–H19B. . .Cl2	0.87	2.23	3.101(4)	174.4
O20–H20A. . .Cl2	0.87	2.23	3.088(5)	167.3
O20–H20B. . .Cl1	0.87	2.24	3.102(4)	173.5

The coordinated water molecules, μ_3-hydroxo ligands and the outer-sphere chloride anions engage in hydrogen bonds in **1**. Each chloride counterion forms a trifurcated hydrogen-bonding motif, acting as an acceptor for O–H$\cdots$Cl interactions involving two coordinated water molecules and one μ_3-hydroxo ligand (Figure 1b, Table 3).

3. Conclusions

A new hexanuclear heterometallic $[Fe_4Sm_2(OH)_2(piv)_4(phdea)_4(N_3)_2(H_2O)_2]Cl_2 \cdot 3MeCN$ cluster has been synthesized via the reaction of a μ-oxo trinuclear iron(III) pivalate precursor with N-phenyldiethanolamine and auxiliary ligands under ultrasonic irradiation. Single-crystal X-ray diffraction reveals a non-planar butterfly-type core that can be described as an open-dicubane framework. In this arrangement, four Fe(III) and two Sm(III) ions are interconnected through μ_3-hydroxo, alkoxo, and carboxylate bridges. The amino-polyalcohol ligand acts as a structure-directing agent, defining the nuclearity and connectivity of the cluster by simultaneously stabilizing Fe–ligand and Sm–ligand interactions. Quantitative SHAPE analysis indicates that all Fe(III) centers adopt distorted octahedral coordination environments (*OC-6*), while the Sm(III) ions exhibit eight-coordinate square-antiprismatic geometries (*SAPR-8*). These assignments are fully supported by Bond Valence Sum calculations confirming the trivalent oxidation states for all metal centers. The well-defined structural features of this $\{Fe_4Sm_2\}$ system provide a suitable platform for extending this synthetic strategy to related Fe–Ln clusters and for probing systematic structure–property relationships within heterometallic 3d–4f assemblies.

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