

# A Novel Europium Carbodiimide that Contains Isolated Europium Tetrahedra and Parallel Chains of Edge-Sharing Open Handbag-Like $\text{Eu}_6$ Units

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$\text{Eu}_2\text{I}_2(\text{NCN})$  is the first compound to contain discrete empty europium tetrahedra and infinite metal chains that are constructed from edge-sharing  $\text{Eu}_6$  units with an open handbag-like motif. The europium tetrahedra and chains are bridged

by coordinating carbodiimide ( $\text{NCN}^{2-}$ ) anions in a three-dimensional network.

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## Introduction

Within the past three decades, solid-state (metal) cluster phases have drawn significant attention due to their interesting structural features and physical properties. There are many examples of both empty metal clusters and those filled by interstitial atoms; the differing cluster connectivities result in a large variety of structural motifs.<sup>[1]</sup> For instance,  $\text{Ln}_6\text{Z}$  octahedra ( $\text{Z}$  = main-group elements such as H, B–O, Si, Ga, and  $\text{C}_2$  units but also transition metals such as Mn–Cu, Ru–Pd, and Re–Au) serve as characteristic building blocks in the metal-rich rare-earth halides.<sup>[2]</sup> On the other side,  $\text{Ln}_4\text{Z}$  ( $\text{Z}$  = N, O) tetrahedra are found for a couple of rare-earth halides and sulfides. The different linkages of these  $\text{Ln}_4\text{Z}$  tetrahedra, by corners and/or by edges, lead to a large structural richness that involves oligomeric units, chains, or layers.<sup>[3]</sup> The polymorph number V of  $\text{PrI}_2$  was recently reported to contain empty tetrahedral  $\text{Pr}_4$  units.<sup>[4]</sup>

Our own research has resulted in novel europium carbodiimide compounds that contain discrete, but also oligomeric,  $\text{Eu}_4$  tetrahedra and 1D chains that are constructed from the tetrahedra by vertex- and face-sharing  $\text{Eu}_4$ .<sup>[5]</sup> Nonetheless, there are few reports that outline the coexistence of empty metal clusters and 1D metal chains except for  $\text{Ln}_{13}\text{Br}_{18}\text{B}_3$  ( $\text{Ln}$  = Gd, Tb)<sup>[6]</sup> which contains both discrete  $\text{Ln}_{10}\text{B}_2$  biocuboctahedra and 1D metal chains that are constructed from edge-sharing  $\text{Ln}_6\text{B}$  octahedra. In this communication, we present the novel phase  $\text{Eu}_2\text{I}_2(\text{NCN})$ , which is another example of a compound that contains discrete metal clusters and chains; the latter are constructed from edge-sharing handbag-like  $\text{Eu}_6$  units.

## Results and Discussion

The crystal structure of  $\text{Eu}_2\text{I}_2(\text{NCN})$  reveals isolated empty  $\text{Eu}_4$  tetrahedra and parallel 1D metal chains that are bridged by  $\text{NCN}^{2-}$  anions in a 3D network in which the iodide anions are located in the interstices (Figure 1, top). To the best of our knowledge, this is the first example of a crystal structure that contains both isolated empty metal tetrahedra and infinite metal chains. Another characteristic feature of  $\text{Eu}_2\text{I}_2(\text{NCN})$  is given by the uncommon open handbag-like  $\text{Eu}_6$  entity (Figure 1, bottom) which embraces one  $\text{NCN}^{2-}$  anion (either located centrally or shifted to the left or right side with partial occupancies) and is capped by another two  $\text{NCN}^{2-}$  anions. As mentioned above, an octahedral  $\text{Ln}_6$  entity would be a more typical structure for this type of compound, and the open handbag-like configuration is quite rare and has only been observed in molecular chemistry, namely to describe one of the lowest-energy structures of the water hexamer.<sup>[7]</sup>

There are four different crystallographic positions found for the Eu units: two fully occupied sites (Eu1 and Eu2) and two other disordered sites (Eu3 and Eu4); all four of the Eu sites differ in their coordination environments with coordination numbers between 6 and 8. While the first two Eu atoms generate the empty  $(\text{Eu}1)_2(\text{Eu}2)_2$  tetrahedron, the other two are responsible for the open handbag-like  $(\text{Eu}3)_4(\text{Eu}4)_2$  entity. The isolated  $\text{Eu}_4$  tetrahedra are capped over all triangular faces by two kinds of  $\text{NCN}^{2-}$  anions (Figure 2, top), which is a typical structure. The open handbag-like  $\text{Eu}_6$  entity, however, is capped by two other  $\text{NCN}^{2-}$  units as described above (Figure 1, bottom). The  $\text{Eu}_6$  entities are interconnected to each other by edge-sharing to result in an infinite 1D chain (Figure 1, middle). Note that the encapsulated  $\text{NCN}^{2-}$  anion excludes the interpretation of the 1D chain as a row of neighboring  $\text{Eu}_4$  tetrahedra (Figure 2, top) because the filled monomer is nonexistent. The capping  $\text{NCN}^{2-}$  anions interconnect the  $\text{Eu}_4$  tetrahedra and the 1D chains into a 3D network that contains quasihexag-

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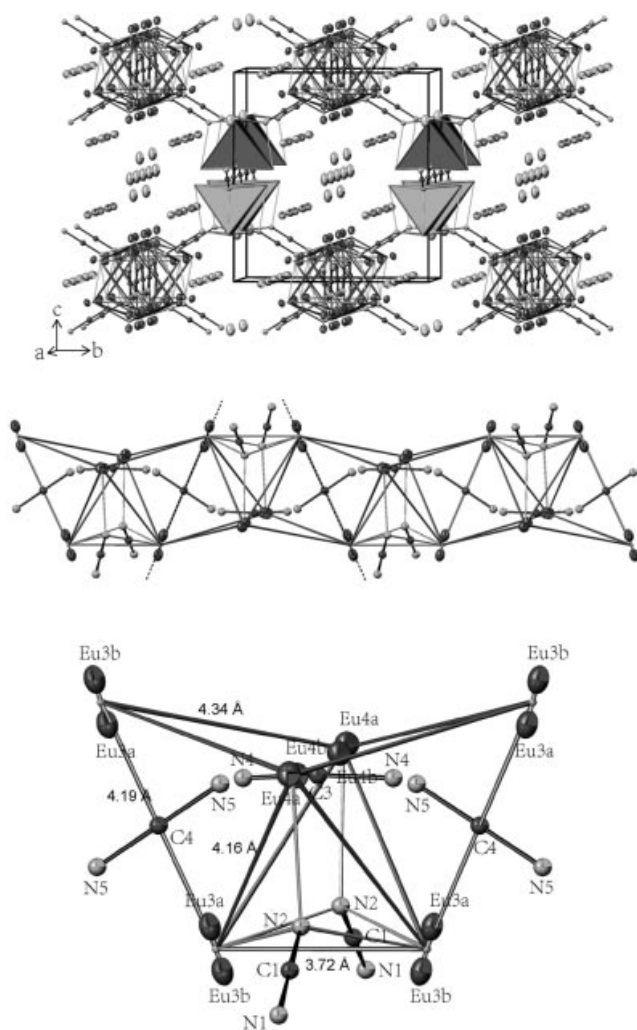


Figure 1. View of the structure of  $\text{Eu}_2\text{I}_2(\text{NCN})$  along the  $a$  axis which shows isolated  $\text{Eu}_4$  tetrahedra and 1D metal chains (top), a single 1D metal chain with encapsulated and capping  $\text{NCN}^{2-}$  anions (middle), and the open handbag-like  $\text{Eu}_6$  unit coordinated by  $\text{NCN}^{2-}$  anions (bottom). The I atoms are given as isolated grey spheres, Eu atoms as dark-grey spheres whereas N atoms are shown as small grey and C atoms as small dark-grey spheres.

onal and orthorhombic channels for the iodide anions (Figure 1, top). Alternatively, the structure can be viewed as the alternate stacking of one layer of metal chains and two layers of isolated  $\text{Eu}_4$  tetrahedra along the  $c$  axis. As a result, one  $\text{Eu}_4$  tetrahedron is simultaneously interconnected to two metal chains and two other  $\text{Eu}_4$  tetrahedra (Figure 2, bottom).

The Eu–Eu distances in the isolated  $(\text{Eu}_1)_2(\text{Eu}_2)_2$  tetrahedron cover a range of 3.97–4.10 Å, which is comparable to 3.98 Å in  $\text{LiEu}_2(\text{NCN})\text{I}_3$  and 3.99–4.12 Å in  $\text{LiEu}_4(\text{NCN})_3\text{I}_3$ .<sup>[5]</sup> The Eu–N bond for isolated  $(\text{Eu}_1)_2(\text{Eu}_2)_2$  is 2.60–2.62 Å, which is also comparable to 2.62 Å in  $\text{LiEu}_2(\text{NCN})\text{I}_3$  and 2.61–2.66 Å in  $\text{LiEu}_4(\text{NCN})_3\text{I}_3$ . In the  $(\text{Eu}_3)_4(\text{Eu}_4)_2$  entities, the distance between the barycenters of the electron densities of the europium sites cover a range of 3.72–4.45 Å (Figure 1, bottom, the Eu4–Eu4

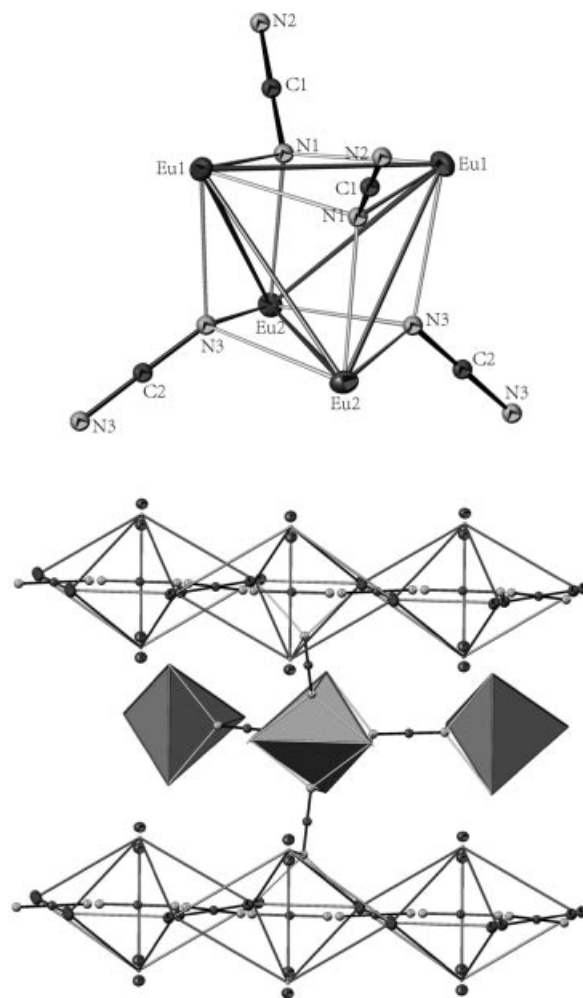


Figure 2. An isolated  $\text{Eu}_4$  tetrahedron capped by  $\text{NCN}^{2-}$  anions (top) and its coordination (bottom).

distance is neglected). The bottom Eu3–Eu3 distance is much shorter (3.72 Å), which might be due to an ionic matrix effect of the nonmetal atoms<sup>[8]</sup> because there are two N atoms from the  $\text{NCN}^{2-}$  anions bonded to this edge. The longer distance of the Eu4–Eu4 (4.45 Å) bond and also the Eu3–Eu4 (4.34 Å) bond might be due to the steric effect of the incorporated carbodiimide anion. The Eu–N distances (between the barycenters of Eu and N sites) lie in the range of 2.51–2.72 Å. The wide range goes back, in part, to the distortion of the Eu3 and Eu4 sites. The split positions of the Eu3 and Eu4 sites mirror the two possible sites of the encapsulated carbodiimide anion, either central or shifted to the left or right side of the  $\text{Eu}_6$  unit. Nonetheless, there is no indication of any Eu valence instability (see Figure 3) and all europium atoms are clearly divalent in nature.

There are four different crystallographic sites for the C atoms which indicate that there are four different  $\text{NCN}^{2-}$  anions (Table 1). Two of the anions are spatially separated and two are spatially correlated; the latter two correspond to alternatively occupied split positions. All four  $\text{NCN}^{2-}$  anions have two double C=N bonds with (almost) equiva-

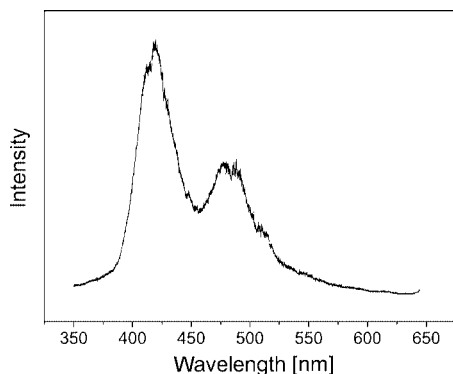


Figure 3. Photoluminescence of Eu<sub>2</sub>I<sub>2</sub>(NCN) excited at 330 nm which indicates that europium is divalent.

lent distances such that they adopt the classic carbodiimide shape. The shape can be confirmed by analysis of the IR spectra in which characteristic carbodiimide frequencies (around 1958 cm<sup>-1</sup> for the asymmetric stretch and 665, 656, and 621 cm<sup>-1</sup> for the deformation vibration) are clearly detected. Different from the alternatively occupied N4–C3–N4 and N5–C4–N5 units, which are located in the interstices of the metal chain, the N2–C1–N1 and N3–C2–N3 units bridge all isolated Eu<sub>4</sub> tetrahedra and the metal chains in a 3D network. In particular, the N2–C1–N1 unit bridges the chain (by the N2 atom) and the Eu<sub>4</sub> tetrahedron (by the N1 atom), whereas the N3–C2–N3 unit connects two isolated Eu<sub>4</sub> tetrahedra. The N4–C3–N4 unit is slightly bent [176(3)°] whereas the other three NCN<sup>2-</sup> anions are linear (with N–C–N angles of 180°). Note again that an NCN<sup>2-</sup> unit (with 68% site probability, named N4–C3–N4) is located in the center of the spatially restricted Eu<sub>6</sub> entity, but it may also appear (with 32% occupancy, named N5–C4–N5) slightly shifted to the left or right. The very presence of these dislocated NCN<sup>2-</sup> units indicates the source for the distortion of the Eu3/Eu4 sites.

Table 1. C=N bond lengths [Å] and N=C=N angles [°].

C1–N1	1.24(2)	N1–C1–N2	180(1)
C1–N2	1.23(2)	N3–C2–N3 <sup>i[a]</sup>	180
C2–N3	1.24(2)	N4–C3–N4 <sup>ii[a]</sup>	176(3)
C3–N4	1.29(2)	N5–C4–N5 <sup>iii[a]</sup>	180
C4–N5	1.28(5)		

[a] Symmetry codes: (i)  $-x, -y, -z + 1$ ; (ii)  $-x + 1/2, -y + 1, z$ ; (iii)  $-x, -y + 1, -z$ .

In conclusion, a novel europium carbodiimide iodide serves as the first example of a structure that contains both isolated empty M<sub>4</sub> tetrahedra and infinite 1D metal chains. In Eu<sub>2</sub>I<sub>2</sub>(NCN), the metal chains are constructed from uncommon Eu<sub>6</sub> entities that adopt an open handbag-like motif. All metal chains and isolated tetrahedra are bridged by carbodiimide anions in a 3D network with the iodide anions held in the interstices – a structural richness never seen before within europium cluster chemistry.

## Experimental Section

**Synthesis of Eu<sub>2</sub>I<sub>2</sub>(NCN):** As recently reported, different thermal treatment of identical reactants may lead to the formation of up to three different compounds.<sup>[5d]</sup> The synthesis of Eu<sub>2</sub>I<sub>2</sub>(NCN) is another example of a largely temperature-controlled synthesis. Typically, yellow single-crystals of Eu<sub>2</sub>I<sub>2</sub>(NCN) are synthesized from the reaction of EuI<sub>2</sub>, NaCN, NaN<sub>3</sub>, and InI in a 2:1:1:1 ratio at elevated temperatures. EuI<sub>2</sub> (99.9%) and InI (99.999%) were used as purchased from Aldrich, and NaCN (95%, Merck) and NaN<sub>3</sub> (99%, Alfa) were thoroughly dried in vacuo heated at 160 °C for 3 d. It is important to follow this procedure because even traces of moisture or oxygen will lead to the immediate formation of Eu<sub>4</sub>OI<sub>6</sub>. The mixtures were transported in tantalum ampoules which were sealed with an arc welder and jacketed with quartz; both tasks were performed under an argon atmosphere. The sample was heated to 750 °C at a rate of 6 °C/min. The sample was heated at 750 °C for a week and then slowly cooled to 600 °C at a rate of 2 °C/min. After the sample was annealed at 600 °C for 2 weeks, the mixture was cooled to room temperature at a rate of 2 °C/min. The crystals of the target phase were easily separated from the surplus fluxes because the crystals were of different colors and shapes, and the yield was more than 50%. A single-crystal with a fresh surface was used for X-ray fluorescence (XRF) analysis. It revealed that the Eu and I molar percentiles – Eu/(Eu+I) and I/(Eu+I) – are 51.67% and 48.33%, respectively, which is comparable to the calculated values of 50% and 50%. The elements Na and In were not detected.

Photoluminescence emission spectra excited at 330 nm were recorded at room temperature with a spectrofluorometer (SPEX, DM3000F) equipped with two 0.22 m double monochromators (SPEX, 1680) and a 450 W xenon lamp. Two broad bands were detected with maxima at 417 and 483 nm, which can be assigned to the 4f<sup>6</sup>5d<sup>1</sup>→4f<sup>7</sup> transition of Eu<sup>2+</sup>. These two independent broad bands indicate two different coordinations of the Eu atoms (either from the isolated Eu<sub>4</sub> tetrahedra or from the metal chain). The small splitting of the broad bands may be attributable to the non-identity of chemically similar atoms such as Eu3 and Eu4.

**Crystal data:** Eu<sub>2</sub>I<sub>2</sub>(NCN), *M* = 597.75 g/mol, orthorhombic, *a* = 11.0056(10) Å, *b* = 10.8921(11) Å, *c* = 11.5947(11) Å, *V* = 1389.9(2) Å<sup>3</sup>, *T* = 120(2) K, Space group *Pnma* (no. 51), *Z* = 8, *μ*(Mo-*K*<sub>α</sub>) = 26.655 mm<sup>-1</sup>; diffraction data collected with a Bruker SMART APEX CCD diffractometer with graphite-monochromatized Mo-*K*<sub>α</sub> radiation (*λ* = 0.71073 Å), empirical absorption correction, 38036 reflections measured, 1920 unique (*R*<sub>int</sub> = 0.0771) which were all used in the refinements. The final values for *wR*<sub>2</sub> (all data) and *R*<sub>1</sub> [*I* > 2σ(*I*)] were 0.0733 and 0.0312, respectively. Crystal structure solution/refinement was processed by means of SHELX programs.<sup>[9]</sup> The disordered sites of Eu3, Eu4, and I4 were refined to site occupation factors of 0.757(2) for Eu3a, 1–0.757(2) = 0.243(2) for Eu3b, 0.483(2) for Eu4a, 1–0.483(2) = 0.517(2) for Eu4b, 0.911(3) for I4a, and 1–0.911(3) = 0.089(3) for I4b, respectively. There is no indication whatsoever for a higher symmetry or a superstructure despite the presence of split positions for the Eu3/Eu4 sites. The partially occupied anions N4–C3–N4 and N5–C4–N5 were also refined with a charge constraint (all europium atoms are divalent indicated by the PL spectra), and their site occupation factors arrive at 0.68(3) and 1–0.68(3) = 0.32(3). We believe that the two possible carbodiimide locations induce the aforementioned europium split positions because of the spatial confinement of the Eu<sub>6</sub> unit. Further details of the crystal-structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344

Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-416668.

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