Eu$_8$(NCN)$_{5-\delta}$I$_{6+2\delta}$ (δ = 0.05): a novel rare-earth carbodiimide iodide containing oligomeric tritetrahedral Eu$_8$ clusters†

Wuping Liao, Boniface P. T. Fokwa and Richard Dronskowski*

Received (in Cambridge, UK) 29th March 2005, Accepted 16th May 2005
First published as an Advance Article on the web 9th June 2005
DOI: 10.1039/b504235f

Eu$_8$(NCN)$_{4.95}$I$_{6.10}$ is the first compound with discrete tritetrahedral Eu$_8$ clusters which are interconnected by coordinating NCN^{2-} carbodiimide anions on their triangular faces to form separated layers, the latter being bridged by iodide and carbodiimide anions.

Within the last three decades, solid-state (metal) cluster compounds have received particular attention owing to their fascinating structural features and physical properties. The literature reveals both empty metal clusters and those filled by interstitial atoms, and the connectivities (isolated clusters, oligomeric units, chains *etc.*) may be interpreted in terms of the concept of condensed clusters.[1] For example, the metal-rich rare-earth halides show an exceedingly rich cluster chemistry, and most compounds contain *octahedral* Ln$_6$Z units (Z = main-group elements such as H, B–O, Si, Ga, C$_2$ units but also transition metals like Mn–Cu, Ru–Pd, and Re–Au).[2] On the other hand, Ln$_4$Z (Z = N, O) *tetrahedra* are characteristic for a couple of rare-earth halides and sulfides, and the different linkages of these Ln$_4$Z tetrahedra *via* corners and/or edges lead to a large structural variety with oligomeric units, chains or layers.[3] Nonetheless, there are very few reports on empty Ln$_4$ tetrahedra such as those found in the recent PrI$_2$-V polymorph containing tetrahedral Pr$_4$ units.[4] Other exceptions are the recently synthesized compounds LiEu$_2$(NCN)X$_3$ (X = Br, I)[5,6] in which isolated Eu$_4$ tetrahedra are connected by NCN^{2-} anions into a three-dimensional network while in LiEu$_4$(NCN)$_3$I$_3$ the Eu$_4$ tetrahedra are corner- and face-sharing to yield one-dimensional chains which are bridged by NCN^{2-} anions.[5] Despite the topological findings of metal clustering, there is no reason to assume significant metal–metal bonding in these (and related) phases as shown by quantum-chemical calculations.[7] Yet another (still unpublished) example is given by Eu$_6$I$_5$(NCN)$_2$N$_2$ with *both* discrete Eu$_4$ tetrahedra and edge-sharing tetrahedral [Eu$_{4/2}$N] chains. Here we present a novel europium carbodiimide iodide, Eu$_8$(NCN)$_{4.95}$I$_{6.10}$, which exhibits a tritetrahedral Eu$_8$ unit that may well be considered as a missing link of cluster condensation.‡

The crystal structure was determined by single-crystal X-ray diffraction§ and reveals Eu$_8$–NCN^{2-} layers separated by iodide and NCN^{2-} anions (Fig. 1, top). There are six different crystallographic positions found for Eu (four on 4*i* and two on 8*j* sites) which all differ in their coordination environments, with coordination numbers between 7 and 9. Eight adjacent europium atoms form an empty tritetrahedral unit which is linked to neighboring ones by bridging NCN^{2-} anions, thereby forming layers (Fig. 1, bottom). All the layers are stacked along the *c* axis but with a small shift between the layers in the (*ab*) plane. The iodide anions are located in the interstices of the layers or between the layers.

The essential feature of Eu$_8$(NCN)$_{4.95}$I$_{6.10}$ is given by *tritetrahedral* Eu$_8$ clusters which result from three empty Eu$_4$ tetrahedra through face- and vertex-sharing (Fig. 2, top right). We note that the term "tritetrahedral" is used for triphosphate or vanadium mono-phosphate compounds due to the presence of P$_3$O$_{10}$ or P$_2$VO$_{10}$ units that are indeed corner-sharing but further connected into layers or networks by other octahedra.[8] The only *isolated* tritetrahedral unit is given by the complex Sn$_3$Se$_8$$^{4-}$ anion which contains three edge-sharing SnSe$_4$ tetrahedra.[9] To the best of our

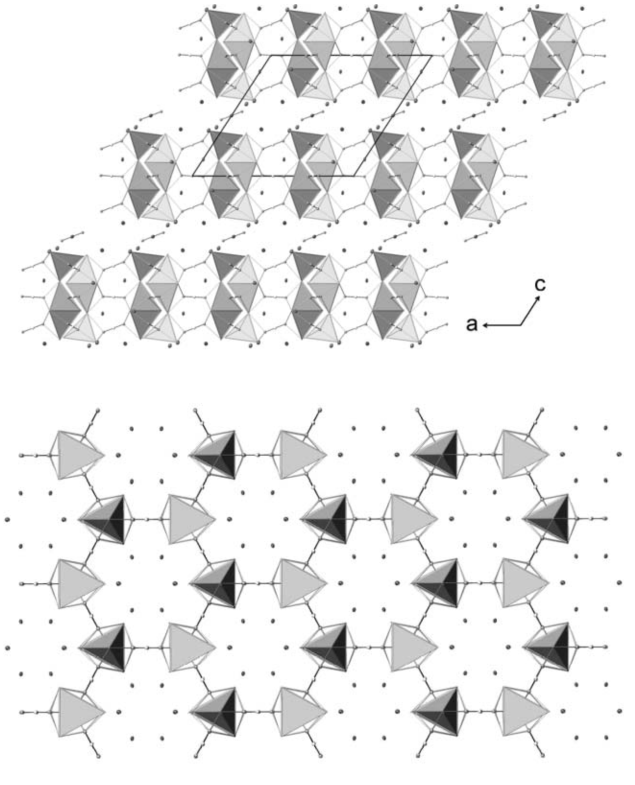

Fig. 1 View of the Eu$_8$(NCN)$_{4.95}$I$_{6.10}$ structure along the *b* axis (top) and a single layer structure looked along the perpendicular direction (bottom).

---

† Electronic supplementary information (ESI) available: Graphical representation of the six crystallographically independent Eu sites including their coordination spheres. See http://www.rsc.org/suppdata/cc/b5/b504235f/

Institut für Anorganische Chemie der RWTH Aachen, Landoltweg 1, D-52056 Aachen, Germany.
E-mail: drons@HAL9000.ac.rwth-aachen.de; Fax: +49-241-80 92642; Tel: +49-241-80 93642
*drons@HAL9000.ac.rwth-aachen.de

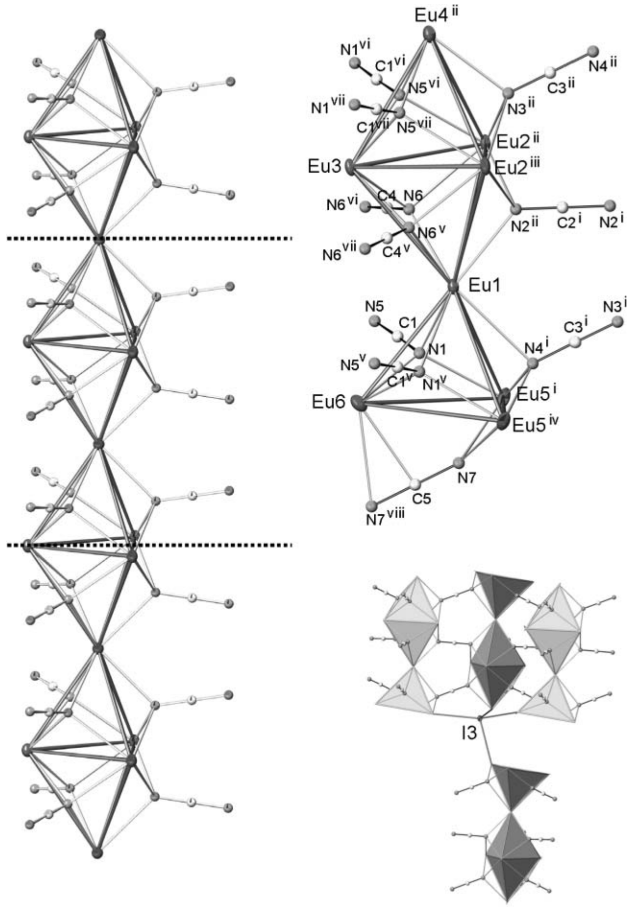

Fig. 2 Tritetrahedral Eu_8 unit in $Eu_8(NCN)_{4.95}I_{6.10}$ (top right) compared with the tetrahedral metal chains capped by carbodiimide anions in $LiEu_4(NCN)_3I_3$ (left); coordination of I3 (bottom right). The symmetry codes are: (i) $x + ½, y - ½, z$; (ii) $-x + ½, y - ½, -z$; (iii) $-x + ½, -y + ½, -z$; (iv) $x + ½, -y + ½, z$; (v) $x, -y, z$; (vi) $-x + ½, -y - ½, -z$; (vii) $-x + ½, y + ½, -z$; (viii) $-x + 1, -y, -z + 1$.

knowledge, $Eu_8(NCN)_{4.95}I_{6.10}$ is the first example with an empty tritetrahedral metal-cluster unit. If we compare this unit with the infinite chain of condensed tetrahedra found in $LiEu_4(NCN)_3I_3$,[5] it is clear that the tritetrahedral unit formally derives from cutting the infinite chain at the dashed lines (Fig. 2, left). Within a tritetrahedral unit, a single Eu_4 tetrahedron is connected to the other two by simultaneous face- and vertex-sharing. Otherwise, *trans*-edge sharing was found for the trimer units of condensed Mo_6 octahedra in oxomolybdates.[10]

All tritetrahedral units are capped by NCN^{2-} anions on their triangular faces with Eu–N bonds of 2.49–2.93 Å, to be compared with 2.61–2.66 Å in $LiEu_4(NCN)_3I_3$. The wider range goes back, in part, to the NCN^{2-} anion capping the bottom face of the Eu_8 cluster because its function is quite different from the other carbodiimide anions. These units connect the tritetrahedral clusters into layers, and a single layer with interstitial iodide anions looks similar to the one in $LiEu_4(NCN)_3I_3$ along the *c* axis (Fig. 1, bottom). Again, there is the formation of one-dimensional hexagonal channels.

The Eu–Eu distances cover the range 3.91–4.13 Å except for the (bottom) Eu6–Eu5 distance which is slightly longer (4.266(2) Å). This longer distance is clearly due to the ionic matrix effect of the non-metal atoms[11] because there are two N atoms bonded to the other cluster edges but only one for the Eu6–Eu5 edge. With respect to the iodide anions, five different crystallographic sites exist which are located in the layer (I1 and I2) or between the layers (I3, I4, I5). As has been said, their arrangement in a single layer is similar to that in $LiEu_4(NCN)_3I_3$ since they show the same connectivity to the Eu_4 tetrahedral units. I1 and I2 are located over the "saddle" bitetrahedron [(Eu2,Eu2,Eu3)(Eu1)(Eu5,Eu5,Eu6)] of one tritetrahedral unit and therefore connect to both the saddlepoint and the upper/lower tetrahedra. At the same time, they coordinate to two neighboring tritetrahedral units by I^{a}. Atom I3 bridges the different layers by connecting *four* tritetrahedral units (three from one layer and one from another) with the $I^{a\text{-}a\text{-}a\text{-}a}$ functionality[12] (Fig. 2, bottom right). The site I4 is split into two different sites while site I5 is partially occupied (see below). They also bridge the different layers.

There are five different crystallographic sites for the C atoms, indicating five different NCN^{2-} anions. All C=N distances are in the typical range 1.21–1.26 Å, and the N=C=N angles are close to 180° (Table 1). This indicates that all NCN^{2-} units adopt the carbodiimide shape which is confirmed by the IR spectra in which characteristic carbodiimide frequencies (around 1963 cm^{-1} for the asymmetric stretching and 666, 655 and 621 cm^{-1} for the deformation vibration) are clearly detected. Four of these NCN^{2-} units are bonded to the side faces of the tritetrahedral unit by one end while the fifth one (N7–C5–N7) coordinates to the bottom face (Eu6–Eu5–Eu5) by *two* ends, that is, one end N atom bonds to two Eu5 atoms and the other bonds to the Eu6 atom, with Eu–N distances of 2.78(2) and 2.68(3) Å for Eu5–N7 and Eu6–N7, respectively. Also, the C5 atom is rather near to Eu6 (2.550(1) Å) which suggests some bonding between these two atoms. Fig. 3 indicates that the N7–C5–N7 unit and iodine atom I5 are located in a plane parallel to the (*ab*) plane between the layers, and a careful inspection of the electron-density distribution reveals that there is a slight sub-occupation of this particular carbodiimide unit. At the same time, the occupation of the I5 site exactly complements the NCN^{2-} charge loss such that the phase is an electron precise europium(II) compound in accord with a formal formulation such as $(Eu^{2+})_8(NCN^{2-})_{4.95}(I^-)_{6.10}$.

In conclusion, a novel europium-rich compound has been synthesized containing the first empty tritetrahedral metal unit ever reported. These discrete Eu_8 units are bridged by carbodiimide NCN^{2-} anions into layers which are separated by iodides and an additional NCN^{2-} anion. There must be other oligomeric metal units within this europium cluster chemistry.

It is a pleasure to thank Resi Zaunbrecher from the Institute of Physical Chemistry (RWTH) for the EDS analyses and the Fonds der Chemischen Industrie (Frankfurt) for their support.

Table 1 C=N bond lengths (Å) and N=C=N angles (°)[a]

C1–N1	1.21(2)	N1–C1–N5	180(2)
C1–N5	1.23(2)	N2–C2–N2^{ix}	180
C2–N2	1.22(2)	N3–C3–N4	178(2)
C3–N3	1.26(2)	N6–C4–N6^{vi}	180
C3–N4	1.22(2)	N7–C5–N7^{viii}	180
C4–N6	1.22(1)		
C5–N7	1.25(3)		

[a] Same symmetry codes as in Fig. 2 plus (ix) $-x, -y + 1, -z$.

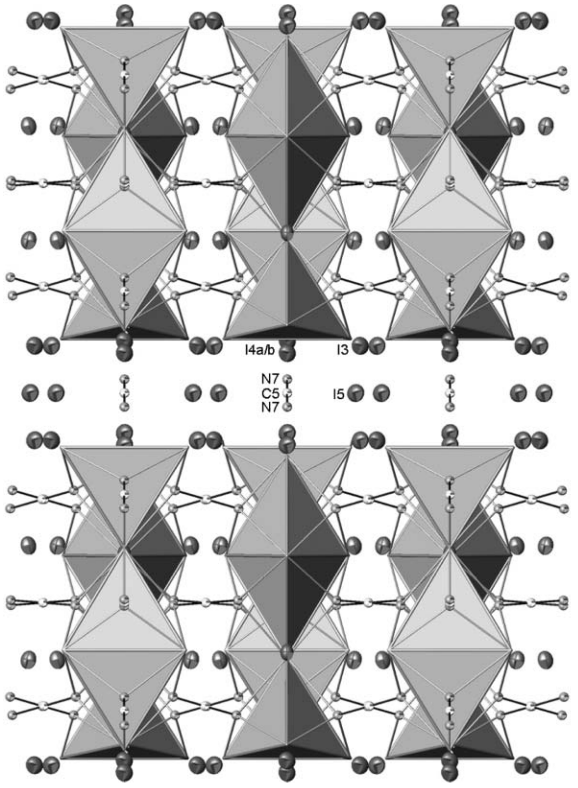

Fig. 3 N7–C5–N7 units and iodide anions I5 located between two layers.

Notes and references

‡ Orange-red single crystals of $Eu_8(NCN)_{4.95}I_{6.10}$ were synthesized from the reaction of EuI_2, KCN, CsN_3, and InI in a 2 : 1 : 1 : 1 ratio at elevated temperatures. All physical manipulations were performed in a glovebox (MBraun) under dry argon with oxygen and moisture levels well below 1 ppm. EuI_2 (99.9%), CsN_3 (99.99%) and InI (99.999%) were used as purchased from Aldrich, and KCN (96%, Merck) was thoroughly dried at 160 °C for 3 days *in vacuo*. It is important to follow this procedure because even traces of moisture or oxygen will lead to the formation of Eu_4OI_6. The mixtures were transported into tantalum ampoules which were sealed with an arc welder and jacketed with quartz, both under argon. The samples were heated to 750 °C at 6 °C min^{-1}, kept at 750 °C for a week and then slowly cooled to 490 °C at 2 °C min^{-1}. After annealing at 490 °C for 2 weeks, the mixture was cooled to room temperature by turning off the oven. A single crystal with a fresh surface was used for energy-dispersive X-ray spectrometer (EDS) analysis. It reveals that the Eu and I molar percentages—Eu/(Eu + I) and I/(Eu + I)—are 56.81% and 43.19%, respectively, such that the analytical Eu : I ratio is 8 : 6.08 compared with an X-ray analytical ratio of 8 : 6.10. Additional heavy elements (K, Cs, In) were not detected.

§ Crystal data: $Eu_8(NCN)_{4.95}I_{6.10}$, M = 2187.92 g mol^{-1}, monoclinic, a = 18.321(3) Å, b = 10.6557(16) Å, c = 16.405(3) Å, β = 122.950(3)°, V = 2687.5(7) $Å^3$, T = 293(2) K, space group $C2/m$ (no. 12), Z = 4, μ(Mo-Kα) = 25.392 mm^{-1}; diffraction data collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å), empirical absorption correction, 36060 reflections measured, 3581 unique (R_{int} = 0.1192) which were all used in the refinements. The final values for w$R2$ (all data) and $R1$ [$I > 2\sigma(I)$] were 0.1041 and 0.0429 respectively. Crystal structure solution/refinement by means of SHELX programs.[13] The partially occupied sites of I5 and the anion N7–C5–N7 were refined with a charge constraint (the material is transparent and non-conducting) and the site occupation factors of I5 and N7–C5–N7 arrive at 0.048(2) and 0.226(1). CCDC 267791. See http://www.rsc.org/suppdata/cc/b5/b504235f/ for crystallographic data in CIF or other electronic format.

1 A. Simon, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 1; A. Simon, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 159; A. Simon, in *Clusters and Colloids – From Theory to Applications*, ed. G. Schmid, Verlag Chemie, Weinheim, 1994, pp. 373; A. Simon, *J. Alloys Compd.*, 1995, **229**, 158; S. V. Krivovichev and S. K. Filatov, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1999, **55**, 664; J. D. Corbett, *Inorg. Chem.*, 2000, **39**, 5178.
2 For example: G. Meyer, *Chem. Rev.*, 1988, **88**, 93; M. Lulei, J. D. Martin, L. M. Hoistad and J. D. Corbett, *J. Am. Chem. Soc.*, 1997, **119**, 513; M. Lulei, *Inorg. Chem.*, 1998, **37**, 777; Hj. Mattausch, O. Oeckler and A. Simon, *Inorg. Chim. Acta*, 1999, **289**, 174; M. Köckerling and J. D. Martin, *Inorg. Chem.*, 2001, **40**, 389; C. Zheng, O. Oeckler, Hj. Mattausch and A. Simon, *Z. Anorg. Allg. Chem.*, 2001, **627**, 2151; Hj. Mattausch, C. Zheng, L. Kienle and A. Simon, *Z. Anorg. Allg. Chem.*, 2004, **630**, 2367.
3 For example: P. E. Caro, *J. Less-Common Met.*, 1968, **16**, 367; A. Simon and T. Köhler, *J. Less-Common Met.*, 1986, **116**, 279; T. Schleid, *Eur. J. Solid State Inorg. Chem.*, 1996, **33**, 227; M. Lulei and J. D. Corbett, *Eur. J. Solid State Inorg. Chem.*, 1996, **33**, 241; G. M. Ehrlich, M. E. Badding, N. E. Brese, S. S. Trail and F. J. DiSalvo, *J. Alloys Compd.*, 1996, **235**, 133; F. Lissner and T. Schleid, *Z. Anorg. Allg. Chem.*, 2003, **629**, 1027; W. Liao and R. Dronskowski, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2004, **60**, i23; G. Meyer, N. Gerlitzki and S. Hammerich, *J. Alloys Compd.*, 2004, **380**, 71.
4 N. Gerlitzki, G. Meyer, A. V. Mudring and J. D. Corbett, *J. Alloys Compd.*, 2004, **380**, 211.
5 W. Liao, C. Hu, R. K. Kremer and R. Dronskowski, *Inorg. Chem.*, 2004, **43**, 5884.
6 W. Liao and R. Dronskowski, *Z. Anorg. Allg. Chem.,* in press.
7 W. Liao, J. von Appen and R. Dronskowski, *Chem. Commun.*, 2004, 2302.
8 G. J. McCarthy, W. B. White and D. E. Pfoertsch, *Mater. Res. Bull.*, 1978, **13**, 1239; M. T. Averbuch-Pouchot and A. Durif, *C. R. Acad. Sci., Ser. II*, 1993, **316**, 609; K. Rissouli, K. Benkhouja, A. Sadel, M. Bettach, M. Zahir, M. Giorgi, M. Pierrot and M. Drillon, *Eur. J. Solid State Inorg. Chem.*, 1997, **34**, 221; M. M. Borel, A. Leclaire, J. Chardon, M. Daturi and B. Raveau, *J. Solid State Chem.*, 2000, **149**, 149; A. Guesdon, E. Daguts and B. Raveau, *J. Solid State Chem.*, 2002, **167**, 258.
9 W. S. Sheldrick, *Z. Naturforsch., B: Chem. Sci.*, 1988, **43**, 249.
10 R. Dronskowski and A. Simon, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 758; G. L. Schimek, S. C. Chen and R. E. McCarley, *Inorg. Chem.*, 1995, **34**, 6130; T. G. Gray, *Coord. Chem. Rev.*, 2003, **243**, 213.
11 J. D. Corbett, *J. Chem. Soc., Dalton Trans.*, 1996, 575.
12 H. Schäfer and H. G. Schnering, *Angew. Chem.*, 1964, **76**, 833.
13 G. M. Sheldrick, *SHELXS/SHELXL computer programs*, Universität Göttingen, Germany.