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Crystal Structures of Extended Europium Cyanamide–Carbodiimide Compounds Derived from Different Reaction Conditions: Temperature-Controlled Syntheses of $In_{0.08}Eu_4(NCN)_3I_3$, $Eu_8I_9(CN)(NCN)_3$, and $In_{0.28}Eu_{12}(NCN)_5I_{14.91}$

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A different thermal treatment of identical reactants (EuI_2, NaCN, NaN_3, and InI) leads to the formation of the three title compounds. $In_{0.08}Eu_4(NCN)_3I_3$ is isotypic with the reported $LiEu_4(NCN)_3I_3$, $Eu_8I_9(CN)(NCN)_3$ represents the first mixed cyanide–cyanamide rare-earth compound, and $In_{0.28}Eu_{12}(NCN)_5I_{14.91}$ is characterized by a sandwichlike stacking motif involving Eu_4–NCN double layers stuffed by a layer of vertex-sharing InI_6 octahedra. The redox behavior of In is the main factor that leads to alternative product formation as a function of the temperature.

Our group has recently reported a new flux route on the basis of a mixture of the simple metal halides, sodium (or potassium) cyanide, and sodium (or cesium) azide, which serves as a lucrative precursor for the synthesis of complex, extended rare-earth metal cyanamides and carbodiimides.[1−6] By using this route, several new products have either been synthesized for the first time or fabricated at significantly lowered temperatures. For example, the quasi-binary Eu(NCN) made originally by Reckeweg and DiSalvo[7] can be synthesized at just 700 °C, in contrast to the formerly reported 1030 °C. The flux route is also characterized by the fact that different metal halides induce the formation of sometimes strongly differing target compounds. For instance, M(NCN) (with M being either Eu or Sr) is easily synthesized using the iodides as precursors, whereas the metal chlorides lead, under otherwise identical conditions, to the formation of $M_2Cl_2(NCN)$.[4] Trivially, the thermal conditions also play an important role in the product formation, easily illustrated from the syntheses of α- and β-Sr(NCN). In fact, the α phase is prepared at 880 °C, while the β phase is obtained at 800 °C.[3] Likewise, the phases $LiEu_2(NCN)I_3$ and $LiEu_4(NCN)_3I_3$ may be synthesized using the same educts (EuI_2, NaCN, NaN_3, and LiI in a 2:1:1:2 molar ratio) but at a different temperature.[1] We now present another example that illustrates the role of the reaction temperature but that also rests on the fascinating redox behavior of the In-containing reactive melt.

As reported,[1] the Li^+ cations in $LiEu_4(NCN)_3I_3$ are located in one-dimensional (1D) hexagonal channels of I^- anions. The attempt to substitute Li^+ with In^{3+} leads to the formation of the title compounds. The richness in compound formation is a direct consequence of the presence of InI, which induces the temperature-dependent reactions. Upon replacement of InI by other fluxes (involving TlI or SnI_2), only *one* reaction product is obtained even at very different thermal conditions. For example, a mixture of EuI_2, NaCN, NaN_3, and TlI (2:1:1:1 molar ratio) always results in the formation of $Eu_8I_9(CN)(NCN)_3$, while the presence of SnI_2 (instead of TlI) always yields the synthesis of $Eu_4(NCN)_3I_3$. We believe that the reason for the special role of In goes back to the low stability of InI or, alternatively expressed, by the ease with which monovalent In is oxidized to In^{3+} (as demonstrated by the In redox potentials, i.e., −0.444 V for $In^{3+} \rightarrow In^+$, −0.126 V for $In^+ \rightarrow In$, and −0.338 V for $In^{3+} \rightarrow In$). Although the exact reaction mechanism is unknown up to now, the structural analysis reveals In^{3+} to be present for the two products made at higher temperatures (see below), whereas the one made at lowest temperature is In-free.

The presence of carbodiimide−cyanamide units in these compounds is easily deduced from the characteristic NCN^{2-} vibrational frequencies (around 1959 cm^{-1} for the asymmetric stretching and 662 cm^{-1} for the deformation vibration) as given by the corresponding infrared spectra (Supp-Figure 1 in the Supporting Information). Nonetheless, only the phase $Eu_8I_9(CN)(NCN)_3$ exhibits an additional peak at 2010 cm^{-1}, which presumably goes back to the *differing* C−N bonds in

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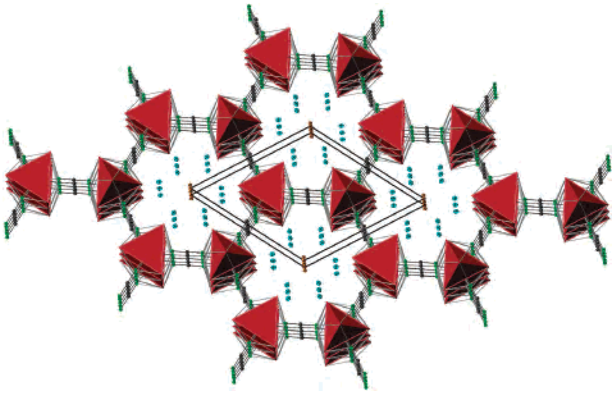

Figure 1. View of the $In_{0.08}Eu_4(NCN)_3I_3$ crystal structure along [001] showing the hexagonal iodine channels and the guest In cations inside, with Eu_4 tetrahedra given in red, I atoms in cyan, N atoms in green, C atoms in gray, and In atoms in brown.

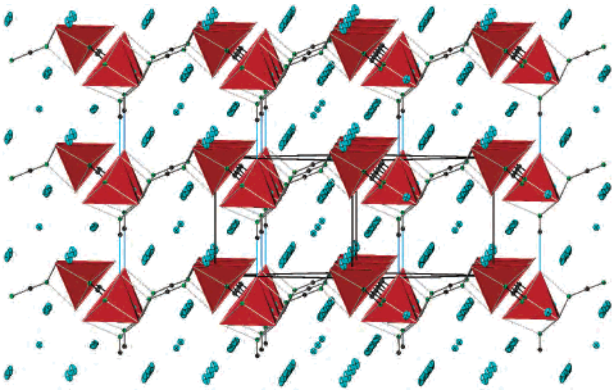

Figure 2. View of the $Eu_8I_9(CN)(NCN)_3$ crystal structure along [110] showing the Eu_4−NCN layers separated by the I^- and CN^- anions.

the NCN^{2-} units and the presence of CN^- (cyanide) units also. The X-ray single-crystal structural refinements further reveal that all N−C−N angles are close to 180°. In the phase $Eu_8I_9(CN)(NCN)_3$, we can find an asymmetrically shaped $N{-}C{\equiv}N^{2-}$ (cyanamide) unit instead of the often found $N{=}C{=}N^{2-}$ (carbodiimide) shape with C=N around 1.2 Å, for example, in $In_{0.08}Eu_4(NCN)_3I_3$ and $In_{0.28}Eu_{12}(NCN)_5I_{14.91}$. The cyanamide unit formally exhibits a C−N "single" bond, 1.32(2) Å, and a C≡N "triple" bond, 1.16(2) Å. The true triple C≡N bond of the CN^- anion in $Eu_8I_9(CN)(NCN)_3$ lies at an even shorter but quite typical 1.07(3) Å.

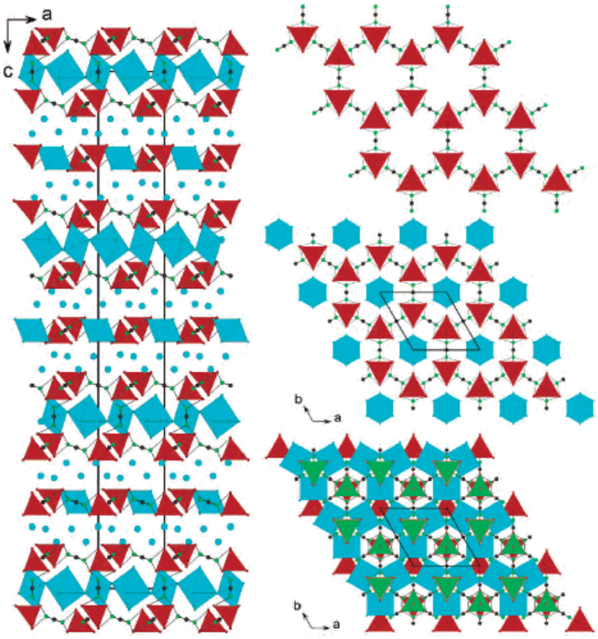

Figure 3. Crystal structure of $In_{0.28}Eu_{12}(NCN)_5I_{14.91}$ viewed along the *b* axis with Eu_4 tetrahedra in red and InI_6 octahedra in cyan (left), the common Eu_4−NCN motif in all three structures (upper right), a single Eu_4−NCN layer comprising isolated $[(In2)(I4)_6]$ octahedra (middle right), and a sandwich motif made from a Eu_4−NCN double layer and a layer of vertex-sharing InI_6 octahedra (in cyan) in between (bottom right) found in the $In_{0.28}Eu_{12}(NCN)_5I_{14.91}$ crystal structure. The Eu_4 tetrahedra in the upper and lower layers are shown in green and red, respectively.

All three extended structures are shown in Figures 1−3, and the common Eu_4 tetrahedra capped by NCN^{2-} anions, *the* characteristic feature of this particular class of materials, are clearly visible. The first phase, $In_{0.08}Eu_4(NCN)_3I_3$ (Figure 1), is isotypic with $LiEu_4(NCN)_3I_3$ such that the attempted replacement of Li^+ by In^{3+} was successful. The tetrahedral Eu_4 units (from *two* symmetry-distinct Eu atoms) are connected by face- and vertex-sharing to generate 1D metal chains, which are coordinated by carbodiimide units on all of their triangular faces. The NCN^{2-} anions also bridge the metal chains in a three-dimensional network and 1D hexagonal iodine channels, which are filled by octahedrally coordinated In cations. Taking into account the radius of the I^- anion for octahedral coordination (2.20 Å),[8] the experimental $In^{3+}{-}I^-$ distance (3.06 Å) is quite close to the theoretical one (3.00 Å); in other words, In is indeed found in its trivalent state. Puzzling, however, is the small site occupation factor (SOF) of In. One would have naively predicted, using charge-balance arguments, a maximum In content of 0.3333 (compared to unity for Li^+), but the experimental value lies at only 0.08(2). This clearly means that the Eu atom *must* be charged a bit higher (+2.19) than in the divalent state, indicating the presence of Eu^{3+}, but this has been observed already in the Li-containing phase also. The latter $LiEu_4(NCN)_3I_3$ also exhibits a slight suboccupation of the Li atom with SOF = 0.7(2), and the presence of Eu^{3+} clearly manifests from the magnetic data.[1] The synthetic observations further let us assume to regard the mixed-valent compound $In_{0.08}Eu_4(NCN)_3I_3$ solely as a high-temperature phase because it cannot be isolated whenever the reaction mixture is kept at lower temperatures for 2 weeks (see the Experimental Section) but requires "quenching" to room temperature, at which it seems to be kinetically stable.

When the reactants are tempered at a much "colder" 420 °C, the phase $Eu_8I_9(CN)(NCN)_3$ is formed, and its crystal structure (Figure 2) consists of *four* different crystallographic Eu atoms per formula unit. The chemical formula already implies a precisely divalent state for Eu. Four adjacent Eu atoms build *two* kinds of empty Eu tetrahedra, one of (Eu4)(Eu1)$_3$ and the other of (Eu2)(Eu3)$_3$. All Eu_4 tetrahedra are connected by cyanamide anions into a layerlike substructure (Figure 3, upper right), and upon comparison of this structural motif with the Eu−NCN substructure of $In_{0.08}Eu_4(NCN)_3I_3$, it is obvious that the former results from slicing of the latter perpendicular to the *c* axis, with a thickness of *one*

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[8] Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

tetrahedron. All of the layers derived as such are stacked along *c* but connected to each other by I^- and CN^- anions (Figure 2). The latter anions are coordinated to the Eu cations in an “end-on” fashion, where the N atom is capping the bottom $(Eu3)_3$ triangular face of the $[(Eu2)(Eu3)_3]$ tetrahedron in one layer and the C atom coordinates the vertex Eu2 atom of another layer. We note that, in other mixed cyanide−cyanamide units,[9] the cations are coordinated by the CN^- anions in *both* end-on and side-on fashions. There are three different crystallographic sites for the I atoms, one (I2) located in the layer and the other two (I1 and I3) between the layers. Viewed along the *c* axis, the structure of $Eu_8I_9(CN)(NCN)_3$ is very similar to that of $In_{0.08}Eu_4(NCN)_3I_3$ (Supp-Figure 2 in the Supporting Information).

In $Eu_8I_9(CN)(NCN)_3$, the Eu−Eu distances arrive at 4.33 Å for Eu1−Eu1, 3.99 Å for Eu1−Eu4, 4.23 Å for Eu3−Eu3, and 3.93 Å for Eu2−Eu3. That means that the tetrahedral side edges are much shorter than those at the bottom. Also, the bottom-edge Eu3−Eu3 is slightly shorter than Eu1−Eu1, and the side-edge Eu2−Eu3 is also slightly shorter than Eu1−Eu4. This is very probably a simple ionic matrix effect of the nonmetal atoms[10] because there are two N atoms from NCN^{2-} anions bonded to one side edge but only one for the bottom one. As has been said already, the bottom face $(Eu3)_3$ is capped by a CN^- anion, such that the Eu3−Eu3 distance is shorter than Eu1−Eu1. In addition, the asymmetric N1−C1≡N2 cyanamide anions are capping the tetrahedra $[(Eu2)(Eu3)_3]$ and $[(Eu4)(Eu1)_3]$ through their N1 and N2 atoms, respectively. In other words, the singly bonded N1 atom coordinates to the triangular side face $[(Eu2)(Eu3)_2]$ using its three lone pairs of the cyanamide Lewis formula, while the triply bonded N2 atom coordinates to $[(Eu4)(Eu1)_2]$ using its one electron pair, such that the former may be expected to be somewhat stronger than the latter. Consequently, the closest Eu−N1 distance is shorter than the Eu−N2 distance.

The phase $In_{0.28}Eu_{12}(NCN)_5I_{14.91}$ (Figure 3) crystallizes in the trigonal system (rhombohedral axes) with a large unit cell. The sandwichlike motifs containing (a) a Eu_4−NCN double layer stuffed by a layer of vertex-sharing InI_6 octahedra and (b) a Eu_4−NCN single layer with isolated InI_6 octahedra in its hexagonal pores are stacked along the *c* axis in an alternating sequence, with additional interstices for the isolated I^- anions. Its crystal structure may also be considered a combination of the europium carbodiimide and In−I substructures (Supp-Figure 3 in the Supporting Information).

Eu atoms from six different crystallographic sites form three different Eu_4 tetrahedra, namely, $[(Eu1)(Eu2)_3]$, $[(Eu3)(Eu5)_3]$, and $[(Eu6)(Eu4)_3]$, with significantly differing Eu−Eu distances. The side-edge distances Eu1−Eu2 (3.99 Å) and Eu3−Eu5 (3.99 Å) are much shorter than the corresponding bottom edges Eu2−Eu2 (4.22 Å) and Eu5−Eu5 (4.37 Å), while Eu6−Eu4 (3.94 Å) is close to Eu4−Eu4 (4.02 Å). An ionic matrix effect by the nonmetal atoms may also be present in this case. If we consider all tetrahedra to be arranged along the *c* axis, all of them—including $[(Eu6)(Eu4)_3]$, which is capped by carbodiimide anions on all of its faces—are capped by carbodiimide anions on their side faces. The $[(Eu1)(Eu2)_3]$ tetrahedron is bridged by the N1−C1−N1 unit to form a single layer with hexagonal pores (Figure 3, middle right), as are the tetrahedra $[(Eu3)(Eu5)_3]$ and $[(Eu6)(Eu4)_3]$ but through the N2−C2−N3 units to also give a layer with hexagonal pores; both layers are bridged by N4−C3−N4 units to eventually result in a double-layer motif (Supp-Figure 4 in the Supporting Information). In the upper and lower layers, the tetrahedra $[(Eu6)(Eu4)_3]$ are oriented in opposite directions; two bottoms face each other with a rotation of 60°. The N4 atoms are capping the bottom faces $(Eu4)_3$ so that N4−C3−N4 anions bridge two layers.

There are six crystallographic sites for the I^- anions, three of them (I1, I3, and I4) bonded to the In atoms and the other three being isolated (except for the Eu−I bonds). The suboccupation of the I1, I4, and I6 sites leads to a chemical formula that matches the suboccupation of the In1 and In2 sites in the sense of $In_{0.28(2)}Eu_{12}(NCN)_5I_{14.91(2)}$ such that the phase, incorporating Eu^{2+}, appears as nicely charge-balanced. The two partially occupied In atoms experience octahedral I coordination with In−I bonds between 2.93 and 3.12 Å, again indicating In^{3+}. The $[(In1)(I1)_4(I3)_2]$ octahedron is connected with the other four by sharing all four I1 vertexes to form a layer with trigonal and hexagonal pores (Supp-Figure 5 in the Supporting Information). This layer is inserted into the Eu_4−NCN double-layer motif to form a sandwich unit (Figure 3, bottom right), and two Eu_4 tetrahedra from both the upper and lower layers are located over the *hexagonal* pore, while only one Eu_4 tetrahedron is located over the *trigonal* pore; in other words, the N4−C3−N4 carbodiimide units bridging the layers spike through the hexagonal pores. The isolated $(In2)(I4)_6$ octahedron fill into the hexagonal pores of the single $[(Eu1)(Eu2)_3]$−NCN layers (Figure 3, middle right). The multilayer sandwich motif (constructed from Eu_4−NCN double layers stuffed by one layer of vertex-sharing InI_6 octahedra) and the condensed single layer (one Eu_4−NCN layer with isolated InI_6 octahedra filling its hexagonal pores) are alternately stacked along the *c* axis (Figure 3).

In summary, different thermal treatments of the same reactants lead to three different europium cyanamide−carbodiimide compounds, and the reactive InI flux plays a crucial role in the compound formation. All three compounds are structurally closely related, and their characteristic features are empty Eu_4 tetrahedra capped by carbodiimide or cyanamide anions.

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Supporting Information Available: X-ray crystallographic data in CIF format, a synthetic section, and a table of selected bonds and angles plus other figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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