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Syntheses and Structural Properties of Rare Earth Carbodiimides

Michael Neukirch, Sonja Tragl, and H.-Jürgen Meyer*

Abteilung für Festkörperchemie und Theoretische Anorganische Chemie, Institut für Anorganische Chemie, Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

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Crystalline samples of rare earth carbodiimides were synthesized by solid-state metathesis reactions of rare earth trichlorides with lithium cyanamide in sealed silica ampules. Two distinct structures were determined by single-crystal X-ray diffraction. The structure determined for $Sm_2(CN_2)_3$ [$C2/m$, $Z = 2$, $a = 14.534(2)$ Å, $b = 3.8880(8)$ Å, $c = 5.2691(9)$ Å, $\beta = 95.96(2)°$, $R_1 = 0.0267$, and $wR_2 = 0.0667$] was assigned for $RE_2(CN_2)_3$ compounds with RE = Y, Pr, Nd, Sm, Gd, Tb, Dy, Ho, and Er, and the structure determined for $Lu_2(CN_2)_3$ [$R32$, $Z = 3$, $a = 6.2732(8)$ Å, $c = 14.681(2)$ Å, $R_1 = 0.0208$, and $wR_2 = 0.0526$] was assigned for the smallest rare earth ions with RE = Tm, Yb, and Lu by powder X-ray diffraction. Both types of crystal structures are characterized by layers of $[NCN]^{2-}$ ions whose arrangements can be derived from the motif of a closest packed layer of sticks. These layers alternate with layers of rare earth ions in a one-by-one sequence. Different tilting arrangements of the N–C–N-axes relative to the stacking directions (c) and different arrangements of RE^{3+} ions within metal atom layers account for the two distinct structures in which Sm^{3+} and Lu^{3+} ions adopt the coordination numbers 7 and 6, respectively.

Introduction

After the discovery of nitridoborate compounds with linear $[NBN]^{3-}$ ions, their structural chemistry has been widely explored for alkali (A), alkali earth (AE), and divalent rare earth (RE) nitridoborates with formulas $A_3(BN_2)$,[1−3] $AE_3(BN_2)_2$,[4−10] and $RE_3(BN_2)_2$,[11] respectively. Great progress has been achieved by extending this chemistry toward the trivalent rare earth elements. Especially, lanthanum compounds have been synthesized and structurally characterized with different types of nitridoborate anions, including $[BN]^{n-}$, $[B_2N_4]^{8-}$, $[B_3N_6]^{9-}$, and $[BN_3]^{6-}$.[12−17] A key for the development of the chemistry of rare earth nitridoborates was the successful implementation of solid-state metathesis reactions between rare earth trichloride and lithium nitridoborate $[Li_3(BN_2)]$.[18,19]

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* To whom correspondence should be addressed. Phone: 49-7071-29-76226. Fax: 49-7071-29-5702. E-mail: juergen.meyer@uni-tuebingen.de.

(1) Yamane, H.; Kikkawa, S.; Koizumi, M. *J. Solid State Chem.* **1986**, *65*, 6−12.
(2) Yamane, H.; Kikkawa, S.; Koizumi, M. *J. Solid State Chem.* **1987**, *71*, 1−11.
(3) Evers, J.; Münsterkötter, M.; Oehlinger, G.; Polborn, K.; Sendlinger, B. *J. Less-Common Met.* **1990**, *162*, 17−22.
(4) Goubeau, J.; Anselment, W. *Z. Anorg. Allg. Chem.* **1961**, *310*, 248−260.
(5) Hiraguchi, H.; Hashizume, H.; Sasaki, S.; Nakano, S.; Funkunaga, O. *Acta Crystallogr., Sect. B* **1993**, *49*, 478−483.
(6) Womelsdorf, H.; Meyer, H.-J. *Z. Anorg. Allg. Chem.* **1994**, *620*, 262−265.
(7) Somer, M.; Herterich, U.; Curda, J.; Carrillo-Cabrera, W.; Peters, K.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1997**, *623*, 18−24.
(8) Wörle, M.; Meyer zu Altenschildesche, H.; Nesper, R. *J. Alloys Compd.* **1998**, *264*, 107−114.
(9) Reckeweg, O.; DiSalvo, F. J.; Somer, M. *J. Alloys Compd.* **2003**, *361*, 102−107.
(10) Häberlen, M.; Glaser, J.; Meyer, H.-J. *J. Solid State Chem.* **2005**, *178*, 1478−1487.
(11) Carrillo-Cabrera, W.; Somer, M.; Peters, K.; von Schnering, H. G. *Z. Kristallogr.* **2001**, *216*, 43−44.
(12) Cava, R. J.; Takagi, H.; Zandbergen, H. W.; Krajewski, J. J.; Peck, W. F., Jr.; Siegrist, T.; Batlogg, B.; van Dover, R. B.; Felder, R. J.; Mizuhashi, K.; Lee, J. O.; Eisaki, H.; Uchida, S. *Nature* **1994**, *367*, 253−253.
(13) Cava, R. J.; Zandbergen, H. W.; Batlogg, B.; Eisaki, H.; Takagi, H.; Krajewski, J. J.; Peck, W. F., Jr.; Gyorgy, E. M.; Uchida, S. *Nature* **1994**, *372*, 245−247.
(14) Zandbergen, H. W.; Jansen, J.; Cava, R. J.; Krajewski, J. J.; Peck, W. F., Jr. *Nature* **1994**, *372*, 759−761.
(15) (a) Reckeweg, O.; Meyer, H.-J. *Angew. Chem.* **1999**, *111*, 1714−1716. (b) Reckeweg, O.; Meyer, H.-J. *Angew. Chem., Int. Ed.* **1999**, *38*, 1607−1609.
(16) Reckeweg, O.; Meyer, H.-J. *Z. Anorg. Allg. Chem.* **1999**, *625*, 866−874.
(17) (a) Blaschkowski, B.; Jing, H.; Meyer, H.-J. *Angew. Chem.* **2002**, *114*, 3468−3483. (b) Blaschkowski, B.; Jing, H.; Meyer, H.-J. *Angew. Chem., Int. Ed.* **2002**, *41*, 3322−3336.
(18) Gibson, K.; Ströbele, M.; Blaschkowski, B.; Glaser, J.; Weisser, M.; Srinivasan, R.; Kolb, H.-J.; Meyer, H.-J. *Z. Anorg. Allg. Chem.* **2003**, *629*, 1863−1870.
(19) Blaschkowski, B.; Meyer, H.-J. *Z. Anorg. Allg. Chem.* **2003**, *629*, 129−132.

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Compounds with $[NCN]^{2-}$ ions have been known much longer than those with $[NBN]^{3-}$ ions. Examples of well-known $A_2(CN_2)$ and $AE(CN_2)$ compounds include alkali[20−23] and alkali earth[24−30] elements, with $Ca(CN_2)$[27] being presumably the most striking example, because of its applications, for example, in organic synthesis and in soil treatments. Compounds with analogous compositions to those of the alkali or alkali earth elements are known for group 11 and 12 elements,[31−34] and recently, $Mn(CN_2)$ was reported to adopt the $Ca(CN_2)$ structure.[35]

The chemistry of rare earth carbodiimide compounds is not yet well-established. The successful synthesis of $RE_2(CN_2)_3$ compounds with RE = La and Ce was already reported long ago, departing from reactions of RE_2O_3 with HCN.[36,37] Products were, however, not well-characterized at that time, and no structural or spectroscopic data are available. The structure of $Eu(CN_2)$ was recently refined from a single crystal, being obtained from a reaction mixture of EuN, C, and NaN_3 reacted at 1300 K.[38] In addition, rare earth dicyanamides $RE(N(CN)_2)_3$ for RE = La, Ce, Pr, Nd, Sm, and Eu were recently synthesized from aqueous solutions.[39]

Attempts are being undertaken in our laboratory to synthesize rare earth nitridocarbonate compounds by using a similar synthetic approach to that employed earlier for the development of the rare earth nitridoborates. Solid-state metathesis reactions between rare earth trichloride and $Li_2(CN_2)$ have been already successfully applied to synthesize members of the rare earth series $RECl(CN_2)$,[40] $RE_2Cl(CN_2)N$,[41] and $RE_2O(CN_2)_2$.[42] Here, we report on a reliable high-yield synthesis of trivalent pseudo-binary rare earth carbodiimides $RE_2(CN_2)_3$, their crystal structures, and their structural properties.

Experimental Section

Synthesis. All manipulations for the synthesis of $RE_2(CN_2)_3$ were performed in an Ar-filled glovebox (Braun LabMaster 130, M. Braun GmbH) with commercial or synthesized starting materials. $SmCl_3$ was purchased (ABCR, 99.9%), and $LuCl_3$ was synthesized from Lu_2O_3 (Rhone Poulenc, 99.99%) and NH_4Cl (Merck, p.a.) as described in the literature.[43] The obtained $LuCl_3$ was sublimed at 820−850 °C under a dynamic vacuum below 1×10^{-3} mbar. $Li_2(CN_2)$ was made from $Li_2(CO_3)$ (Alfa, ultrapure) under flowing ammonia at 650 °C (12 h).

Reactions were performed with $RECl_3$ and $Li_2(CN_2)$ in a 2:3 molar ratio together with KCl/LiCl as a flux. Mixtures with total masses around 400 mg were carefully homogenized in an agate mortar under argon. Each mixture was sealed into an evacuated silica ampule and then placed into a tube furnace.

Reactions at lower temperatures (e.g., 500 °C) and with shorter reaction times (e.g., 48 h) yielded light gray to yellow crystalline powders, later identified as $RE_2(CN_2)_3$ for RE = Sm and Lu, according to the indexed powder X-ray diffraction (XRD) patterns. When samples were treated at 650 °C for 3 weeks, some gray and brown powders were obtained, containing colorless crystals of $RE_2(CN_2)_3$. The silica ampules were opened in the air, and the products were washed twice with water and then with acetone to remove the coproduced LiCl and the flux. Homologous $RE_2(CN_2)_3$ compounds for RE = Y and Pr−Lu (except Pm and Eu) were synthesized under analogous conditions and investigated by powder XRD.

X-ray Diffraction Studies. Single crystals of $RE_2(CN_2)_3$ with RE = Sm and Lu were selected and mounted on the tips of glass fibers for intensity measurements using a single-crystal X-ray diffractometer (Stoe, IPDS, Darmstadt, Germany), equipped with (graphite) monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The intensity data were corrected for Lorentz, polarization, and absorption effects by the IPDS software X-Red/X-Shape. The crystal structure solutions and refinements were obtained with the program package SHELX-97.[44] Crystals of $Lu_2(CN_2)_3$ were obtained as racemic twins. Therefore, the structure of the Lu compound was refined using the TWIN instruction with the matrix (−1 0 0 1 0 −1 0 1 0 0 −1). Anisotropic refinements were performed for all atoms. Selected data of the crystal structures and refinement parameters are given in Table 1. Atom positions and isotropic displacement parameters are provided in Table 2, and selected interatomic distances and angles are given in Table 3. More detailed crystallographic data and the anisotropic displacement parameters are provided in the Supporting Information.

The carefully washed $RE_2(CN_2)_3$ powders were inspected with an X-ray powder diffractometer (Stoe, StadIP, Darmstadt, Germany) using monochromatic Cu $K\alpha_1$ radiation ($\lambda = 1.54051$ Å). The powder XRD patterns of $RE_2(CN_2)_3$ with RE = Sm and Lu were indexed with the aid of the program system WinXPow,[45] and the lattice parameters were refined therefrom. The powder pattern of $Sm_2(CN_2)_3$ was indexed (using 33 single indexed lines) with a monoclinic cell yielding $a = 14.578(2)$ Å, $b = 3.8978(5)$ Å, $c = 5.2781(7)$ Å, and $\beta = 95.883(8)°$. The pattern of $Lu_2(CN_2)_3$ was

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(20) Pulham, R. J.; Hubberstey, P.; Down, M. G.; Thunder, A. E. *J. Nucl. Mater.* **1979**, *85−86* (A), 299−303.

(21) Down, M. G.; Haley, M. J.; Hubberstey, P.; Pulham, R. J.; Thunder, A. E. *J. Chem. Soc., Dalton Trans.* **1978**, *10*, 1407−1411.

(22) Harper, A.; Hubberstey, P. *J. Chem. Res., Synop.* **1989**, *7*, 194−195.

(23) Becker, M.; Nuss, J.; Jansen, M. *Z. Anorg. Allg. Chem.* **2000**, *626*, 2505−2508.

(24) Dehlinger, U. *Z. Kristallogr.* **1927**, *65*, 286−290.

(25) Bredig, M. A. *J. Am. Chem. Soc.* **1942**, *64*, 1730−1731.

(26) Yamamoto, Y.; Kinoshita, K.; Tamaru, K.; Yamanaka, T. *Bull. Chem. Soc. Jpn.* **1958**, *31*, 501−502.

(27) Vannerberg, N. G. *Acta Chem. Scand.* **1962**, *16*, 2263−2266.

(28) Berger, U.; Schnick, W. *J. Alloys Compd.* **1994**, *206*, 179−184.

(29) Reckeweg, O.; DiSalvo, F. J. *Angew. Chem.* **2000**, *39*, 412−414.

(30) Liao, W.; Dronskowski, R. *Acta Crystallogr., Sect. E* **2004**, *60*, 124−126.

(31) Bowden, F. P.; Montagu-Pollock, H. M. *Nature* **1961**, *191*, 556−559.

(32) Becker, M.; Nuss, J.; Jansen, M. *Z. Naturforsch. B* **2000**, *55*, 383−385.

(33) Baldinozzi, G.; Malinowska, B.; Rakib, M.; Durand, G. *J. Mater. Chem.* **2002**, *12*, 268−272.

(34) Becker, M.; Jansen, M. *Acta Crystallogr., Sect. C* **2001**, *57*, 347−348.

(35) Liu, X.; Krott, M.; Müller, P.; Hu, C.; Lueken, H.; Dronskowski, R. *Inorg. Chem.* **2005**, *44*, 3001−3003.

(36) Hartmann, H.; Eckelmann, W. *Z. Anorg. Allg. Chem.* **1948**, *257*, 183−194.

(37) Hartmann, H.; Dobek, G. *Z. Anorg. Allg. Chem.* **1953**, *271*, 138−143.

(38) Reckeweg, O.; DiSalvo, F. J. *Z. Anorg. Allg. Chem.* **2003**, *629*, 177−179.

(39) Jürgens, B.; Irran, E.; Schnick, W. *J. Solid State Chem.* **2005**, *178*, 72−78.

(40) Srinivasan, R.; Glaser, J.; Tragl, S.; Meyer, H.-J. *Z. Anorg. Allg. Chem.* **2005**, *631*, 479−483.

(41) Srinivasan, R.; Ströbele, M.; Meyer, H.-J. *Inorg. Chem.* **2003**, *42*, 3406−3411.

(42) Srinivasan, R.; Tragl, S.; Meyer, H.-J. *Z. Anorg. Allg. Chem.* **2005**, *631*, 719−722.

(43) Meyer, G.; Morss, L. R. *Synthesis of Lanthanide and Actinide Compounds*; Kluwer Academic Publishers: Hannover, Argonne, 1990.

(44) Sheldrick, G. M. *SHELX-97*: *Program Package for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1997.

(45) *WinXPow, version 1.10: Diffractometer Software*; Stoe & Cie GmbH: Darmstadt, Germany, 2001.

Table 1. Crystal Data from the Structure Refinements of $Sm_2(CN_2)_3$ and $Lu_2(CN_2)_3$

formula	$Sm_2(CN_2)_3$	$Lu_2(CN_2)_3$
fw (g/mol)	420.79	470.03
syst, space group, *Z*	monoclinic,*C*2/*m* (No. 12), 2	trigonal, *R*32 (No. 155), 3
unit cell dimensions (Å, deg)	$a = 14.534(2)$	$a = 6.2732(8)$
	$b = 3.8880(8)$	
	$c = 5.2691(9)$	$c = 14.681(2)$
	$\beta = 95.96(2)$	
unit cell vol (Å^3)	$V = 296.1(1)$	$V = 500.3(1)$
d_{calcd} (g/cm^3)	4.719	4.680
μ (mm^{-1}) (Mo Kα)	19.55	29.35
R_1, $wR_2{}^a$(all data)	0.0267, 0.0667	0.0208, 0.0526

^{a} $R_1 = \sum_{hkl}||F_o| - |F_c|\sum_{hkl}|F_o||$. $wR_2 = \sum_{hkl}w(|F_o|^2 - |F_c|^2)^2/[\sum_{hkl}w(F_o{}^2)]^{1/2}$.

Table 2. Atom Positions and Isotropic Displacement Parameters for $Sm_2(CN_2)_3$ and $Lu_2(CN_2)_3$

atom	multiplicity, symmetry	*x*	*y*	*z*	$U_{eq}{}^a$
$Sm_2(CN_2)_3$					
Sm	4, m	0.1348(1)	0	0.0705(1)	0.0063(2)
C(1)	4, m	0.3283(5)	0	0.404(1)	0.009(1)
C(2)	2, 2/m	0	0	$^1/_2$	0.011(2)
N(1)	4, m	0.1590(4)	$-^1/_2$	0.362(1)	0.010(1)
N(2)	4, m	0.1901(4)	$-^1/_2$	−0.170(1)	0.009(1)
N(3)	4, m	0.118(5)	0	−0.266(1)	0.014(1)
$Lu_2(CN_2)_3$					
Lu	6, 3	0	0	0.1716(1)	0.0080(1)
C	9, 2	0.369(2)	$^1/_3$	$^1/_3$	0.013(2)
N	18, 1	0.338(1)	0.264(1)	0.255(5)	0.018(1)

^{a} U_{eq} (Å^2) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Interatomic Distances (in Å) and Angles (in deg) in the Crystal Structures of $Sm_2(CN_2)_3$ and $Lu_2(CN_2)_3$

$Sm_2(CN_2)_3$			$Lu_2(CN_2)_3$		
Sm−N(3)	2.382(6)	1x	Lu−N	2.282(7)	3x
Sm−N(3)	2.460(7)	1x			
Sm−N(1)	2.479(4)	2x			
Sm−N(2)	2.498(4)	2x	Lu−N	2.325(6)	3x
Sm−N(2)	2.544(6)	1x			
C(1)−N(1)	1.227(9)	1x	C−N	1.216(7)	2x
C(1)−N(2)	1.235(9)	1x			
C(2)−N(3)	1.229(7)	2x			
N(3)−C(2)−N(3)	180.0				
N(1)−C(1)−N(2)	176.2(8)		N−C−N	178.0(3)	

Table 4. Lattice Parameters (in Å and deg), Unit Cell Volumes (in Å^3), and Number of Single Indexed Reflections of $RE_2(CN_2)_3$ Compounds

RE	*a*	*b*	*c*	β	*V*	indexed reflns
Y	14.278(9)	3.781(6)	5.209(3)	95.73(3)	279.8(5)	29
Pr	14.853(2)	3.9907(6)	5.3243(9)	96.125(8)	313.8(1)	32
Nd	14.754(2)	3.9563(5)	5.3084(6)	96.027(5)	308.15(9)	32
Sm	14.578(2)	3.8978(5)	5.2781(7)	95.883(8)	298.3(1)	33
Gd	14.453(2)	3.8472(5)	5.2586(6)	95.762(7)	290.92(8)	27
Tb	14.369(3)	3.8201(9)	5.243(1)	95.70(2)	286.4(2)	31
Dy	14.287(5)	3.7901(9)	5.224(1)	95.66(1)	281.5(2)	23
Ho	14.214(9)	3.766(2)	5.210(3)	95.60(4)	277.5(4)	28
Er	14.184(2)	3.7471(3)	5.2051(5)	95.559(6)	275.34(7)	46
Tm	6.3393(7)		14.766(1)		513.9(1)	30
Yb	6.294(2)		14.723(3)		505.1(3)	21
Lu	6.2723(8)		14.708(2)		501.1(1)	23

indexed trigonal-rhombohedrally (using 23 single indexed lines) with lattice parameters of $a = 6.2723(8)$ Å and $c = 14.708(2)$ Å. In each case, few weak lines of unknown phases were present and, occasionally, very little Li_2O. Homologous $RE_2(CN_2)_3$ compounds with RE = Y and Pr−Lu (except Pm and Eu) were indexed correspondingly with a monoclinic crystal system for Y and Pr−Er and trigonal-rhombohedrally for Tm−Lu. All refined lattice parameters are presented in Table 4.

Infrared Spectroscopy. The infrared spectra were recorded on a Perkin-Elmer FT-IR spectrometer in a range from 400 to 4000 cm^{-1}. The samples were measured as KBr pellets. Characteristic bands of the $[NCN]^{2-}$ ions were observed at 1954 cm^{-1} (Sm ν_{as}) and 1967 cm^{-1} (Lu ν_{as}). The C−N bending vibrations were found at 706, 669, 635, and 616 cm^{-1} for $Sm_2(CN_2)_3$ and at 681 and 641 cm^{-1} for $Lu_2(CN_2)_3$.

Results and Discussion

The solid-state metathesis reaction between $RECl_3$ and $Li_2(CN_2)$ was successfully applied for the synthesis of the novel rare earth carbodiimides $RE_2(CN_2)_3$. The discovery and identification of these novel compounds allows us to extend the group of already known rare earth carbodiimides. The carbodiimides $RE_2(CN_2)_3$, $RECl(CN_2)$,[40] $RE_2Cl(CN_2)N$,[41] and $RE_2O(CN_2)_2$[42] were all obtained by the same general synthesis route, following eqs 1−4.

High purity of the starting materials, the absence of oxygen or associated traces of water, and strict handling under a dry, inert atmosphere turned out to be important for successful and high-yield syntheses of $RE_2(CN_2)_3$ compounds following eq 1. Because of the stability of the produced $RE_2(CN_2)_3$ against air and moisture, the coproduced LiCl and the flux can be easily washed out with water.

$$2RECl_3 + 3Li_2(CN_2) \rightarrow RE_2(CN_2)_3 + 6LiCl \qquad (1)$$

$$RECl_3 + Li_2(CN_2) \rightarrow RECl(CN_2) + 2LiCl \qquad (2)$$

$$2RECl_3 + Li_3N + Li_2(CN_2) \rightarrow RE_2Cl(CN_2)N + 5LiCl \qquad (3)$$

$$RECl_3 + REOCl + 2Li_2(CN_2) \rightarrow RE_2O(CN_2)_2 + 4LiCl \qquad (4)$$

The employment of a KCl/LiCl flux has been reported previously for the synthesis of $RECl(CN_2)$ compounds (RE = La, Ce, and Pr) and usually allows for the obtainment of better crystal growth and for reactions to proceed at lower temperatures. According to our experiments and to differential thermal analyses, reaction 1 can proceed at temperatures below 400 °C in a KCl/LiCl melt.

Single-crystal structure refinements were performed for $Sm_2(CN_2)_3$ (**I**) and $Lu_2(CN_2)_3$ (**II**). Both structures are closely related by their nearly hexagonal [NCN] stick packing modes displayed in Figure 1. The monoclinic (*C*2/*m*) structure of **I** contains one layer of Sm^{3+} ions and one layer of $[NCN]^{2-}$

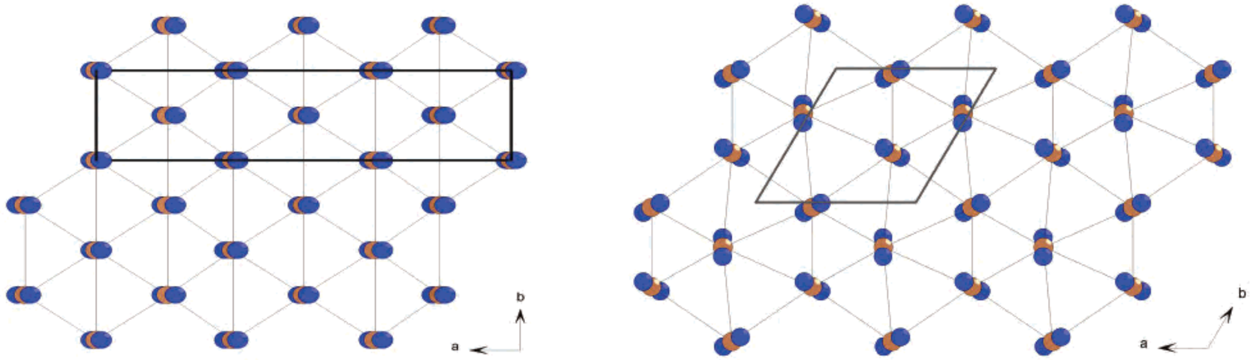

Figure 1. Top view of two distorted hexagonal stick packings of $[NCN]^{2-}$ ions ("sticks") in the crystal structures of $Sm_2(CN_2)_3$ (left) and $Lu_2(CN_2)_3$ (right). Corresponding unit cells are projected onto their *ab* planes. Nitrogen atoms of $[NCN]^{2-}$ ions are shown with blue color.

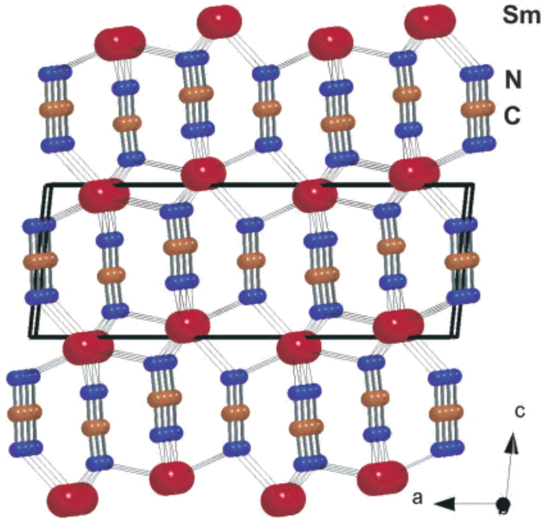

Figure 2. Crystal structure of $Sm_2(CN_2)_3$.

ions within the *c*-axis repeat (Figure 2). The coordination number of Sm^{3+} with nitrogen atoms of the carbodiimide ions is seven (Figure 3), with Sm−N distances ranging from 2.38 to 2.54 Å (Table 3). The structure contains two different types of carbodiimide ions with their coordination environments by Sm^{3+} displayed in Figure 3.

The trigonal-rhombohedral (*R*32) structure of **II** is represented by single layers of Lu^{3+} ions alternating with single layers of $[NCN]^{2-}$ ions three times along the *c*-axis repeat (Figure 4). The structure contains only one carbodiimide ion in the asymmetric unit, being surrounded by four Lu^{3+} ions. The Lu^{3+} ions are surrounded by six nitrogen atoms of the carbodiimide ions (Figure 5) with Lu−N distances ranging between 2.28 and 2.33 Å (Table 3).

The C−N bond lengths within the $[NCN]^{2-}$ ions are nearly equivalent in both of the refined crystal structures, leading to the assignment of these anions to occur with the carbodiimide (N=C=N) rather than the cyanamide (N−C≡N) structure. Refined C−N distances of the two distinct $[NCN]^{2-}$ ions in **I** are at $d_{C-N} = 1.227(9)$, 1.235(9), and 1.229(7) Å, whereas for the $[NCN]^{2-}$ ion in **II**, they are at $d_{C-N} = 1.216(7)$ Å (Table 3). For comparison, the C−N distances of the $[NCN]^{2-}$ ion in $La_2Cl(CN_2)N$ amount to similar values of $d_{C-N} = 1.234(3)$ and 1.238(6) Å. A more pronounced difference of these distances with values of $d_{C-N} = 1.202(6)$ and 1.251(6) Å was obtained in the $[NCN]^{2-}$ ion of $LaCl(CN_2)$.

Slight deviations of the N−C−N angles in the $RE_2(CN_2)_3$ structures from linearity (see values of 176−180° in Table 3**)** can be considered as matrix effects, as well-known from many other structures containing triatomic anions.

After the single-crystal structures were solved for $Sm_2(CN_2)_3$ **I** and $Lu_2(CN_2)_3$ **II**, corresponding syntheses were performed in order to synthesize more RE compounds. Inspections of their powder XRD patterns revealed that RE = Y, Pr, Nd, Sm, Gd, Tb, Dy, Ho, and Er are represented by the structure of **I**, and the smallest RE = Tm, Yb, and Lu are represented by the structure of **II**, as listed in Table 4.

Both structures are composed of alternating layers of RE^{3+} and $[NCN]^{2-}$ ions. The [NCN] layers can be considered as being derived from a hexagonal closest packed layer of

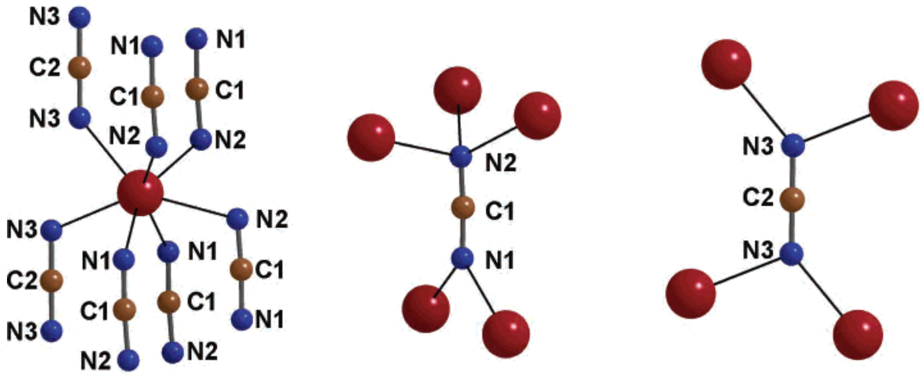

Figure 3. Environments of Sm^{3+} with $[NCN]^{2-}$ ions (left) and of the two distinct $[NCN]^{2-}$ ions with Sm^{3+} ions (right).

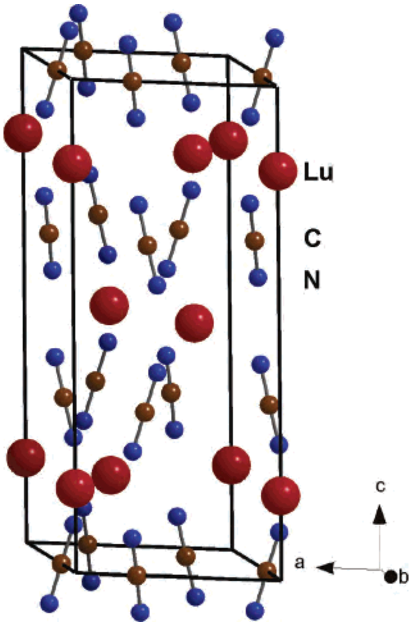

Figure 4. Crystal structure of $Lu_2(CN_2)_3$.

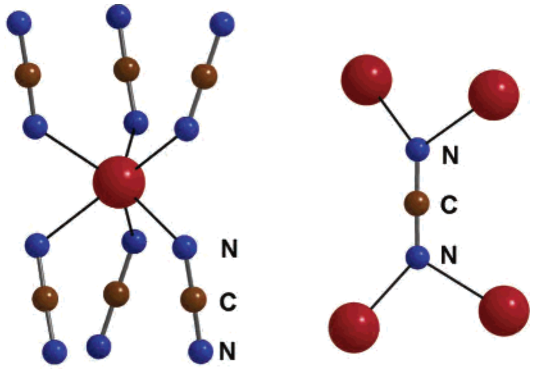

Figure 5. Environments of Lu^{3+} with $[NCN]^{2-}$ ions (left) and of $[NCN]^{2-}$ with Lu^{3+} ions (right).

[NCN] sticks. In the refined crystal structures, we note distortions. Most remarkable is the opposite tilting of the $[NCN]^{2-}$ ions in the structure of **II**, shown in Figure 4, and deviations of layers from planarity in the structure of **I**, shown in Figure 2.

In a Gedankenexperiment, we derive a simplified structure model in order to relate both refined crystal structures with each other. The starting motif is an idealized hexagonal closest packed layer of [NCN] sticks which is the prototype of those presented in Figure 1. A primitive stacking sequence of such layers creates trigonal-prismatic voids between the layers which can be occupied with metal atoms. Occupations of half of the trigonal-prismatic voids by metal atoms lead to the composition "$RE(CN_2)$", displayed in Figure 6 (center), which merits the topology of a WC-type structure. Occupations of only $^1/_3$ of the trigonal-prismatic metal atom sites allows the establishment of various structural possibilities of $RE_2(CN_2)_3$ structures, depending on the ordering of metal atoms on these sites. In our idealized structure of **I**, the Sm ions are ordered over $^1/_3$ of the voids within one layer of the *ab* plane, whereas in the idealized structure of **II**, the ordering of Lu ions alternates over three layers of the *ab* plane along the (*c*-)stacking direction.

In the modeled structures, our metal atoms would have a coordination number of six (Figure 6), which is rather low for compounds of the rare earth elements, although known from rock-salt structured REN compounds. Partial occupations of trigonal-prismatic voids do not only create superstructures that are displayed in Figure 6 (left and right) but can also explain the alignments or distortions of [NCN] ions in the structures of **I** and **II**. However, the distinct distortions being present in the structures of **I** and **II** do not only bring up different coordination numbers for Sm (CN = 7) and Lu (CN = 6) but also create very strong differences in the molar volumes of both structures. We note that opposite tilting of the [NCN] sticks in the structure of **II** creates a significantly larger *ab* plane than in **I**. Three [NCN] ions in the structure of $Lu_2(CN_2)_3$ are packed with each other to make up an average *ab* area of 34.1 $Å^2$, which is about 21% larger than the corresponding value of 28.1 $Å^2$ obtained in $Sm_2(CN_2)_3$. The larger *ab* area of **II** is not overcompensated when the *c* lattice parameters are taken into account, for example, by the impact of the smaller Lu^{3+} ion, and we note that the volume of the Lu compound ($V/Z = 166.8$ $Å^3$) still remains about 11% larger than that of the Sm compound ($V/Z = 148.1$

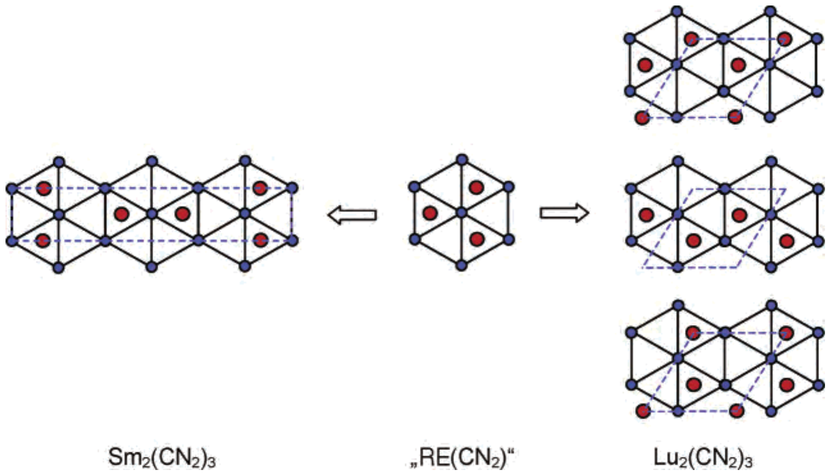

Figure 6. Archetype structure of hexagonal primitive "$RE(CN_2)$" (center). Atoms drawn in blue represent nitrogen atoms of the linear [NCN] units (top view). Idealized structures with $^1/_3$ of the metal positions (in red) being occupied are shown at left for $Sm_2(CN_2)_3$ and at right for $Lu_2(CN_2)_3$, which is decomposed into three layers. All projections are shown onto ab planes. Unit cells are shown as dashed lines.

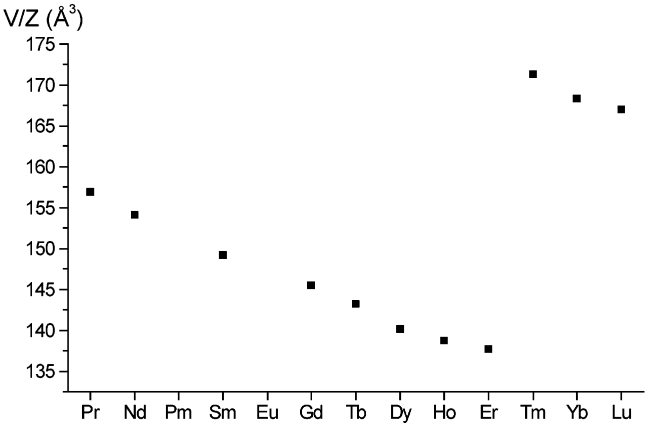

Figure 7. Volume per formula unit (*V*/*Z*) for various of $RE_2(CN_2)_3$ compounds with RE = Pr−Lu.

Å^3). Considering the influence of the lanthanide contraction, a smaller volume is usually regarded for the compound with the smaller RE^{3+} ion, which would be $Lu_2(CN_2)_3$ (**II**) in this case.

The occurrence of more than one phase along a series of homologous lanthanide compounds is not unexpected. Well-known examples among many are rare earth sesquioxides and oxide-halides. Generally, a volume change of this large of an extent is quite seldom within a series of rare earth compounds. One example is, however, the series of rare earth compounds REOCl. These are reported to crystallize with the PbFCl-type structure for RE = La−Ho and with the SmSI-type structure for RE = Tm, Yb, and Lu. ErOCl is reported to be dimorphic, occurring with both structures.[46] The transition of ErOCl from the PbFCl type into the SmSI type involves a volume increase of about 15%.

A projection of the volume per formula unit (*V*/*Z*) versus the RE elements of the homologous $RE_2(CN_2)_3$ series is shown in Figure 7. The well-known trend of the lanthanide contraction is evident for $RE_2(CN_2)_3$ compounds between RE = Pr and Er and between RE = Tm and Lu. The pronounced jump in volume of these compounds is related to the structural change being obtained between RE = Er and Tm. Between these two structures, the volume increases (from $V/Z = 137.7$ to 171.3 Å^3) by a remarkable 24%. Therefore, it may be assumed that the crystal structure of **II** represents the low-pressure modification, whereas the structure of **I** represents the high-pressure modification of $RE_2(CN_2)_3$ compounds.

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Supporting Information Available: Additional tables and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(46) (a) Beck, H. P. *Z. Naturforsch. B* **1976**, *31*, 1562−1564. (b) Beck, H. P. *Z. Naturforsch. B* **1977**, *32*, 1015−1021.