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► **To cite this version:**

Hans-Juergen Meyer. The Many Faces of Rare Earth Carbodiimide Compounds. *Journal of Inorganic and General Chemistry / Zeitschrift für anorganische und allgemeine Chemie*, 2009, 635 (12), pp.1947. 10.1002/zaac.200900221 . hal-00520636

HAL Id: hal-00520636

<https://hal.science/hal-00520636>

Submitted on 24 Sep 2010

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**The Many Faces of Rare Earth Carbodiimide Compounds**

Journal:	<i>Zeitschrift für Anorganische und Allgemeine Chemie</i>
Manuscript ID:	zaac.200900221.R1
Wiley - Manuscript type:	Article
Date Submitted by the Author:	13-May-2009
Complete List of Authors:	Meyer, Hans-Juergen
Keywords:	Rare earth, Carbodiimide , Fluoride, Metathesis



The Many Faces of Rare Earth Carbodiimide Compounds

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Dedicated to Professor Martin Jansen on the Occasion of his 60th Birthday

Keywords: Rare earth; Fluoride; Carbodiimide; Metathesis

Abstract. Solid state metathesis reactions have been established as a successful tool in syntheses of rare earth carbodiimide compounds. Current results evidence the new compounds $\text{LiRE}(\text{CN}_2)_2$ with $\text{RE} = \text{La}, \text{Ce}$ and the carbodiimide nitride $\text{Ce}_3(\text{CN}_2)_3\text{N}$. $\text{LiRE}(\text{CN}_2)_2$ compounds were synthesized by solid state metathesis reactions between REF_3 and $\text{Li}_2(\text{CN}_2)$ in 1 : 2 molar ratio. $\text{Ce}_3(\text{CN}_2)_3\text{N}$ was obtained via thermal conversion of $\text{LiCe}(\text{CN}_2)_2$.

Crystal structures of $\text{LiLa}(\text{CN}_2)_2$ and $\text{Ce}_3(\text{CN}_2)_3\text{N}$ were determined from X-ray single crystal data ($\text{LiLa}(\text{CN}_2)_2$: $P2_1/m$, $a = 542.4(2)$ pm, $b = 379.16(7)$ pm, $c = 1013.0(3)$ pm, $\beta = 101.35(3)^\circ$; $\text{Ce}_3(\text{CN}_2)_3\text{N}$: $P2_12_12_1$, $a = 672.97(9)$ pm, $b = 1309.8(2)$ pm, $c = 1697.7(3)$ pm) and $\text{LiCe}(\text{CN}_2)_2$ was assigned from indexed X-ray powder diffraction data ($\text{LiCe}(\text{CN}_2)_2$: $a = 541.9(1)$ pm, $b = 374.50(8)$ pm, $c = 1008.8(2)$ pm, $\beta = 101.21(1)^\circ$).

The crystal structure of $\text{LiLa}(\text{CN}_2)_2$ represents a layer-like arrangement of ions as typical for this type of compounds. The crystal structure of $\text{Ce}_3(\text{CN}_2)_3\text{N}$ reveals chains of $[\text{NCe}_4]$ tetrahedra running parallel to each other, and trigonal prismatic to trigonal antiprismatic arrangements of six distinctly interconnected $[\text{Ce}_3\text{-NCN-Ce}_3]$ units. Both structures contain $(\text{CN}_2)^{2-}$ ions deviating from their ideal $D_{\infty h}$ symmetry, with C–N distances ranging between 121 and 126 pm and N–C–N angles near 180° .

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Introduction

Rare earth (RE) carbodiimides are an emerging and rapidly growing group of compounds. Dioxide monocarbodiimides were reported in 1994 presumably synthesized under fortuitous conditions with the aid of a graphite container serving as a carbon source for the carbodiimide ion of $\text{La}_2\text{O}_2(\text{CN}_2)$ [1]. Two distinct structures are reported for $\text{RE}_2\text{O}_2(\text{CN}_2)$. Tetragonal $\text{La}_2\text{O}_2(\text{CN}_2)$ is reported to contain axially-parallel disordered $[\text{N}=\text{C}=\text{N}]^{2-}$ ions, whereas in trigonal $\text{RE}_2\text{O}_2(\text{CN}_2)$ with RE = Ce – Gd, Dy, Ho, Er, Tm, Yb [2,3] the alignment of $[\text{N}=\text{C}=\text{N}]^{2-}$ ions follows the threefold axis.

A great deal of rare earth carbodiimide or infrequently cyanamide compounds was synthesized following solid state metathesis reactions between rare earth trihalides and lithium carbodiimide. Upon heating these mixtures, solid state metathesis reactions reveal their characteristics, with an ignition coming about in a temperature regime around 450 to 550 °C when double exchange of ions is being completed. A flux can be used in reactions to lower the reaction temperature and to improve the crystal growth of products.

A series of quasi-binary carbodiimides $\text{RE}_2(\text{CN}_2)_3$ [4-6] with trivalent rare earth ions (RE = Y – Lu, except Pm, La) has been established by this route as well as some families of multinary carbodiimides (or in some cases cyanamides) represented by the formulas $\text{REX}(\text{CN}_2)$ (X = Cl, F) [7,8], $\text{RE}_2\text{X}(\text{CN}_2)\text{N}$ (X = Cl, Br, I) [9,10], $\text{ARE}_2\text{X}_3(\text{CN}_2)_2$ (A = Li, X = F), and two more compositions being reported in this work.

Carbodiimides or cyanamides containing divalent europium ions were obtained for $\text{Eu}(\text{CN}_2)$ [11] through high temperature reactions, and through halide-based flux reactions for a number of multinary europium compounds [12].

The synthesis of new rare earth compounds containing nitrides or carbodiimides has received considerable attention due to the luminescence properties of doped compounds and their potential in solid state lighting, but also for other perspectives. The luminescence behaviour of lanthanide-doped carbodiimide compounds has been studied for $\text{RE}_2\text{O}_2(\text{CN}_2):\text{Ln}$ [13] and $\text{Y}_2\text{O}_2(\text{CN}_2):\text{Eu}$ [14] in relation to the well-known red light emitter $\text{Y}_2\text{O}_2\text{S}:\text{Eu}$. For compounds $\text{Gd}_2(\text{CN}_2)_3:\text{Ln}$ with Ln = Ce, Tb a broad yellow emission has been obtained. Furthermore, the dimorphic character of structures has been demonstrated for $\text{Y}_2\text{O}_2(\text{CN}_2)$ and by pressure induced phase transition for $\text{Tm}_2(\text{CN}_2)_3$ [6].

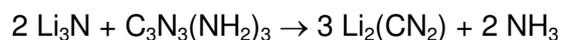
Still there are some homologous examples of RE compounds missing in carbodiimide containing families. Some of them can be assumed isotopic and others have just not been attempted to make. A challenging example may be the missing compound $\text{La}_2(\text{CN}_2)_3$ [15].

The rational approach of solid state metathesis reactions has been successfully used as a conceptual tool for the discovery of some novel [16] compounds and turns out to be a promising endeavour in solid state synthesis.

Experimental Section

Synthesis of Li₂(CN₂)

Li₂(CN₂) was prepared via reaction of 700 mg (ca. 20 mmol) Li₃N (Alfa Aesar, 99.5 %) with an excess of 1400 mg (ca. 11 mmol) melamine (Fluka, >99 %, purum) [17] following the reaction equation:



The reaction mixture was carefully homogenized in an agate mortar under argon atmosphere (glove box) and placed into a silver boat. An argon flooded transfer shuttle was used to replace the silver boat from the glove box into a silica tube, being inserted into the silica tube under nitrogen counter current.

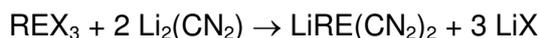
The reaction mixture was heated up (ca. 10 °C/min) in a silica tube under nitrogen flow (ca. 200 ml/min) to 270 °C and remained at this temperature for about ten minutes before it was further heated up very slowly (1 °C/min.) to 330 °C. From 330 °C the temperature was further raised (10 °C/min.) to 600 °C to remove the excess of melamine from the product. Afterwards the reaction was allowed to cool down to room temperature and the crystalline powder was inspected by XRD.

The beginning of the reaction was obtained at 150 °C, as indicated by the development of NH₃ at the exhaust pipe of the silica tube. Note that faster heating-up rates may generate a strongly exothermic reaction when reaching temperatures near 270 – 300 °C, thereby expelling material from the reaction vessel. If Li₂NH was present in the product, the mixture was carefully ground with ca. 150 mg melamine and heated (5 °C/min.) to 600 °C. Preparations of Li₂(CN₂) proceeded quantitatively and yielded a single phase product according to powder XRD.

Synthesis of LiLa(CN₂)₂ and LiCe(CN₂)₂

Rare earth trifluorides (REF₃) were synthesized as previously reported [8]. Solid state metathesis reactions were performed between REX₃ (X = F, Cl) and Li₂(CN₂). Reactions of LaCl₃ (ABCR, 99.9 %) were carried out in flame sealed silica ampoules and reactions with trifluorides in copper ampoules (4 cm long pieces, inner diameter ca. 5 mm, thickness of the wall ca. 1 mm, cleaned with HCl). Copper tubes were sealed first from one side by arc-melting, loaded with starting materials under argon (glove box) and then sealed from the other side, before they were flame sealed into silica tubing.

Reaction containers were charged with 1 : 2 molar mixtures of REX₃ (RE = La, Ce; X = F, Cl) and Li₂(CN₂) under dry argon atmosphere inside a glove box. The reaction vessels were placed into a tube furnace and reacted at 450 – 650 °C for two days before they were allowed to cool down to room temperature. The course of reactions can be specified by the following equation:



Reactions departing from REF_3 yielded colourless powders of $\text{LiLa}(\text{CN}_2)_2$ and yellow powders of $\text{LiCe}(\text{CN}_2)_2$ at 500 °C besides coproduced LiF. Reactions with LaCl_3 and $\text{Li}_2(\text{CN}_2)$ yielded $\text{LiLa}(\text{CN}_2)_2$ in the temperature range 450 – 550 °C. Product treatments of $\text{LiCe}(\text{CN}_2)_2$ and LiF above 650 °C gave rise to the decomposition into a crystalline product containing the new compound $\text{Ce}_3(\text{CN}_2)_3\text{N}$.

All compounds behave moderately stable in air and against hydrolysis. Reaction products were washed in water, dried with acetone, and inspected by powder XRD.

X-Ray Powder Diffraction

The XRPD patterns of the reaction products were collected with a Stadi-P (Stoe, Darmstadt) powder diffractometer using $\text{Cu-K}_{\alpha 1}$ radiation (germanium monochromator). No significant reflections of any side phase could be identified after indexing the patterns of $\text{LiLa}(\text{CN}_2)_2$ and $\text{LiCe}(\text{CN}_2)_2$ by using the program system WinXPow [18]. The patterns were indexed monoclinically with $a = 541.5(2)$ pm, $b = 378.2(2)$ pm, $c = 1010.6(4)$ pm, $\beta = 101.38(2)^\circ$ yielding $V = 202.9(2) \text{ \AA}^3$ based on 30 single indexed lines for $\text{LiLa}(\text{CN}_2)_2$; and $a = 541.9(1)$ pm, $b = 374.50(8)$ pm, $c = 1008.8(2)$ pm, $\beta = 101.21(1)^\circ$ yielding $V = 200.8(1) \text{ \AA}^3$ based on 33 single indexed lines for $\text{LiCe}(\text{CN}_2)_2$.

X-Ray Single-Crystal Diffraction

Colourless needle shaped single-crystals of $\text{LiLa}(\text{CN}_2)_2$ and orange crystals of $\text{Ce}_3(\text{CN}_2)_3\text{N}$ were selected and mounted on the tips of glass fibers for single-crystal X-ray diffraction measurements (Stoe, IPDS I diffractometer, graphite monochromated Mo-K_{α} radiation, $\lambda(\text{Mo-K}_{\alpha}) = 71.073$ pm) performed at 210(2) K for $\text{LiLa}(\text{CN}_2)_2$ and at room temperature for $\text{Ce}_3(\text{CN}_2)_3\text{N}$ (Table 1). Intensities were corrected for Lorentz factors, polarization and absorption effects by the IPDS software X-Red/X-Shape. The crystal structure solutions and anisotropic refinements of all atoms of $\text{LiLa}(\text{CN}_2)_2$ and $\text{Ce}_3(\text{CN}_2)_3\text{N}$ were obtained with the program SHELX-97 package [19]. Crystallographic data are given in Table 1, atom positions are listed in Table 2, and selected bond lengths are displayed in Table 3.

Further details on the crystal structure investigations can be obtained from Fachinformationszentrum Karlsruhe, 76334 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de on quoting the CSD number 420440 of $\text{LiLa}(\text{CN}_2)_2$ and CSD number 420507 of $\text{Ce}_3(\text{CN}_2)_3\text{N}$.

Results and Discussion

During the past, the synthesis of $\text{Li}_2(\text{CN}_2)$ has been accomplished in several ways, i.e. through ammonolysis of $\text{Li}_2(\text{CO}_3)$ [20, 8], from Li_2C_2 and Li_3N [21], or by reaction of $\text{Li}(\text{NH}_2)$ or

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3 Li₃N with melamine [17]. According to our experiments, the synthesis from Li₃N and
4 melamine described by *Becker* and *Jansen* is a useful and time efficient route for the
5 preparation of Li₂(CN₂).
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8 A selective choice of starting materials, i.e. pure rare earth trihalide and Li₂(CN₂) is of course
9 crucial in order to drive solid state metathesis reactions towards desired products. The
10 employment of various compositions of these starting materials has been successfully
11 applied to synthesize various compositions of rare earth carbodiimide compounds such as
12 RE₂(CN₂)₃, REX(CN₂) (X = Cl, F), ARE₂X₃(CN₂)₂ (A = Li, X = F), and RE₂X(CN₂)N (X = Cl, Br,
13 I), now being attributed by the new composition ARE(CN₂)₂ (A = Li; RE = La, Ce). This
14 composition was indeed expected to exist, not only with lithium but also with other
15 monovalent cations. On the other hand, the carbodiimide nitride RE₃(CN₂)₃N was obtained
16 unintentionally from thermal decomposition of LiCe(CN₂)₂. Corresponding rare earth
17 nitridoborate nitrides, e.g. Ce_{3+x}(B₂N₄)N_x with x = 1, 2, where synthesized under multilateral
18 solid state metathesis conditions departing from appropriate amounts of RECl₃, Li₃(BN₂), Li₃N
19 and Li as reducing agent [22].
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22 Many carbodiimide compounds appear to be thermally labile at temperatures above 600 °C.
23 This is of course one reason that these compounds can hardly be obtained from high
24 temperature reactions of elements – but there are some exceptions [11, 23].
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27 LaCl(CN₂) was previously shown to transform into La₂Cl(CN₂)N on heating up to
28 temperatures above 750 °C. A direct synthesis of RE₂X(CN₂)N (X = Cl, Br, I) compounds was
29 accomplished by using multilateral metathesis reactions departing from REX₃, Li₂(CN₂), and
30 Li₃N, or from other combinations of compounds [10]. A similar decomposition as for
31 LaCl(CN₂) is obtained for LiCe(CN₂)₂ after being heated at temperatures around 650 °C. As
32 noted from the previous example, a decomposition of only a portion of (CN₂)²⁻ ions is the
33 result of the reaction to yield crystalline powder and single-crystals of Ce₃(CN₂)₃N. A feasible
34 solid state metathesis synthesis for this type of rare earth carbodiimide nitride compounds is
35 at hand.
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38 Most rare earth carbodiimide compounds known to date can be considered to contain nearly
39 linear and nearly symmetrical [N=C=N]²⁻ ions, but there can be deviations from the ideal D_{∞h}
40 symmetry in structures, frequently due to non-equivalent environments of the two terminal
41 nitrogen atoms. Departing from the two non-equivalent bond lengths within the cyanamide
42 molecule H₂C–C≡N of roughly 131 pm and 115 pm we note less distinct or sometimes
43 equivalent C–N distances within [NCN]²⁻ ions of rare earth carbodiimide compounds, typically
44 around 123 pm as present in the structure of lithium carbodiimide. A pronounced difference
45 was found in the [NCN]²⁻ ion of LaCl(CN₂) with C–N bond lengths of 120.2(6) and 125.1(6)
46 pm, pointing out that it is difficult to make up a fixed borderline for the notation as a
47 carbodiimide or cyanamide ion.
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3 The crystal structure of $\text{LiLa}(\text{CN}_2)_2$ resembles layers of La^{3+} ions and two differently aligned
4 $(\text{CN}_2)^{2-}$ ions, as displayed in Figure 1. A similar difference in C–N bond lengths as in
5 $\text{LaCl}(\text{CN}_2)$ is obtained in one of the two crystallographically distinct $[\text{NCN}]^{2-}$ ions contained in
6 the structure of $\text{LiLa}(\text{CN}_2)_2$, of which one set of N(1)–C(1)–N(2) bond lengths is 122.0(8) and
7 123.8(8) pm and the second set N(3)–C(2)–N(4) being 120.8(8) and 125.5(8) pm. In
8 addition, the N–C–N bond angles of both ions are refined near 177° being close to 180°
9 which is regarded for a carbodiimide ion (Table 3).

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11 Lithium ions are situated in a slightly distorted tetrahedral environment of nitrogen atoms
12 having Li–N distances within the interval of 209 – 211 pm. The lanthanum ion is surrounded
13 by eight nitrogen atoms forming a bicapped trigonal prism, shown in Figure 2, having La–N
14 distances of 259 – 268 pm.

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16 $\text{Ce}_3(\text{CN}_2)_3\text{N}$ is the first example of a rare earth carbodiimide nitride. In the light of more
17 $\text{RE}_3(\text{CN}_2)_3\text{N}$ compounds having this composition, the structure of this compound will be
18 presented here only briefly. The crystal structure of $\text{Ce}_3(\text{CN}_2)_3\text{N}$ was refined in the non-
19 centrosymmetric space group $P2_12_12_1$, being rare in solid state chemistry. The unit cell of
20 $\text{Ce}_3(\text{CN}_2)_3\text{N}$ contains eight formula units, accommodating six crystallographically
21 independent cerium ions, six independent carbodiimide anions, and two independent nitride
22 ions (Figure 3). The two nitride ions (N(13) and N(14)) are surrounded tetrahedrally by
23 cerium ions with Ce–N distances between 229.5(7) and 247.3(8) pm. These tetrahedra are
24 interconnected in an alternating fashion by shared corners and edges to form chains parallel
25 to the crystallographic y direction. The six $[\text{NCN}]^{2-}$ ions exhibit C–N distances ranging from
26 121 to 125 pm, being almost linear with N–C–N angles around 179° (Table 3). Environments
27 of $[\text{NCN}]^{2-}$ ions compromise more or less distorted trigonal prismatic or trigonal antiprismatic
28 surroundings with cerium ions, all displayed in Figure 4. The six crystallographically distinct
29 cerium ions are shown in Figure 5, with coordination numbers between seven and eight with
30 N atoms of both types, N^{3-} and $[\text{NCN}]^{2-}$. Displayed Ce–N distances with nitrogen atoms of
31 $[\text{NCN}]^{2-}$ ions range from 250.3(8) to 302.6(9) pm, but there are also short contacts with
32 carbon atoms in the order of 300 pm. Only one cerium ion (Ce(5)) remains without a contact
33 to a nitride ion.

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52 *Acknowledgement.* Support of this research by the Deutsche Forschungsgemeinschaft
53 (Bonn) through the project *Nitridocarbonate* is gratefully acknowledged.
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Table 1 Single-crystal data from structure refinements of LiLa(CN₂)₂ and Ce₃(CN₂)₃N.

Empirical formula	LiLa(CN ₂) ₂	Ce ₃ (CN ₂) ₃ N
Formula weight / g/mol	225.91	554.46
Crystal system	monoclinic	orthorhombic
Space group	P 2 ₁ /m (No. 11)	P 2 ₁ 2 ₁ 2 ₁ (No. 19)
Unit cell dimensions /pm	<i>a</i> = 542.4(2)	<i>a</i> = 672.97(9)
	<i>b</i> = 379.16(7)	<i>b</i> = 1309.8(2)
	<i>c</i> = 1013.0(3)	<i>c</i> = 1697.7(3)
Angle/°	<i>β</i> = 101.35(3)	
Volume / 10 ⁶ pm ³	204.26(8)	1496.4(4)
Z	2	8
Temperature /K	210(2)	293(2)
Density (calculated) / g·cm ⁻³	3.673	4.922
Absorption coefficient /mm ⁻¹	10.285	17.894
F(000)	200	1928
Crystal description	colourless needle	orange-red needle
Crystal size /mm ³	0.12 x 0.04 x 0.04	0.24 x 0.08 x 0.08
Θ range for data collection /°	3.83 to 25.89	2.40 to 25.83
Index range	-6 ≤ <i>h</i> ≤ 6; -4 ≤ <i>k</i> ≤ 4; -12 ≤ <i>l</i> ≤ 12	-8 ≤ <i>h</i> ≤ 8, -16 ≤ <i>k</i> ≤ 16, -20 ≤ <i>l</i> ≤ 20
Reflections collected	2273	16256
Independent reflections	434	2870
R _{int}	0.0299	0.0584
Data / Parameters	434 / 49	2870 / 236
Goodness-of-fit on F ²	1.112	0.998
R indices [<i>I</i> > 2σ(<i>I</i>)]	R1 = 0.0188, wR2 = 0.0423	R1 = 0.0224, wR2 = 0.0509
R indices (all data)	R1 = 0.0199, wR2 = 0.0426	R1 = 0.0247, wR2 = 0.0514
Largest diff. peak and hole e·Å ⁻³	1.099 and -0.909	1.691 and -0.892
CSD-Number	420440	420507

Table 2 Atom positions and isotropic displacement parameters (\AA^2) of $\text{LiLa}(\text{CN}_2)_2$ and $\text{Ce}_3(\text{CN}_2)_3\text{N}$.

	x	y	z	U_{eq}
$\text{LiLa}(\text{CN}_2)_2$				
La(1)	0.9832(1)	1/4	0.1934(1)	0.0102(1)
N(1)	0.6502(9)	-1/4	0.1585(5)	0.0131(9)
C(1)	0.426(1)	-1/4	0.1093(6)	0.014(1)
N(2)	0.8038(9)	1/4	-0.0658(5)	0.014(1)
N(3)	0.7576(9)	1/4	0.4048(5)	0.016(1)
C(2)	0.220(1)	-1/4	0.4741(6)	0.012(1)
N(4)	0.2071(9)	-1/4	0.3491(5)	0.014(1)
Li(1)	0.595(2)	-1/4	0.357(1)	0.020(2)
$\text{Ce}_3(\text{CN}_2)_3\text{N}$				
Ce(1)	0.8365(1)	0.0794(1)	0.3986(1)	0.0138(1)
Ce(2)	0.6181(1)	0.1212(1)	0.1663(1)	0.0136(1)
Ce(3)	0.4035(1)	-0.0815(1)	0.3169(1)	0.0139(1)
Ce(4)	0.3583(1)	0.2139(1)	0.3328(1)	0.0138(1)
Ce(5)	0.4149(1)	0.0691(1)	0.5663(1)	0.0137(1)
Ce(6)	0.1319(1)	0.2459(1)	0.1101(1)	0.0138(1)
N(1)	0.328(1)	0.0934(6)	0.0578(4)	0.016(2)
C(1)	-0.109(1)	0.4096(7)	0.0107(5)	0.015(2)
N(2)	-0.048(1)	0.4150(7)	0.0777(4)	0.018(2)
N(3)	0.296(1)	0.3098(6)	-0.0278(4)	0.016(2)
C(2)	0.365(1)	0.3815(7)	0.0093(5)	0.017(2)
N(4)	0.435(1)	0.4531(6)	0.0480(4)	0.018(2)
N(5)	0.414(1)	-0.0927(7)	0.1631(4)	0.022(2)
C(3)	0.560(1)	-0.0819(7)	0.1184(5)	0.017(2)
N(6)	0.705(1)	-0.0706(8)	0.0759(5)	0.028(2)
N(7)	0.580(1)	0.1992(6)	0.4597(4)	0.018(2)
C(4)	0.122(1)	0.2219(7)	0.5040(5)	0.015(2)
N(8)	0.165(1)	0.1433(6)	0.4693(4)	0.017(2)
N(9)	-0.029(1)	0.2743(7)	0.3490(5)	0.021(2)
C(5)	-0.88(1)	0.2740(7)	0.2804(5)	0.018(2)
N(10)	-0.145(1)	0.2747(6)	0.2115(4)	0.016(2)
N(11)	0.125(1)	0.0611(6)	0.2979(4)	0.017(2)
C(6)	0.057(1)	0.0632(6)	0.2306(5)	0.011(2)
N(12)	0.506(1)	-0.0673(7)	0.6631(4)	0.018(2)
N(13)	0.394(1)	0.2617(6)	0.1956(4)	0.018(2)
N(14)	0.584(1)	0.0790(7)	0.3006(4)	0.018(2)

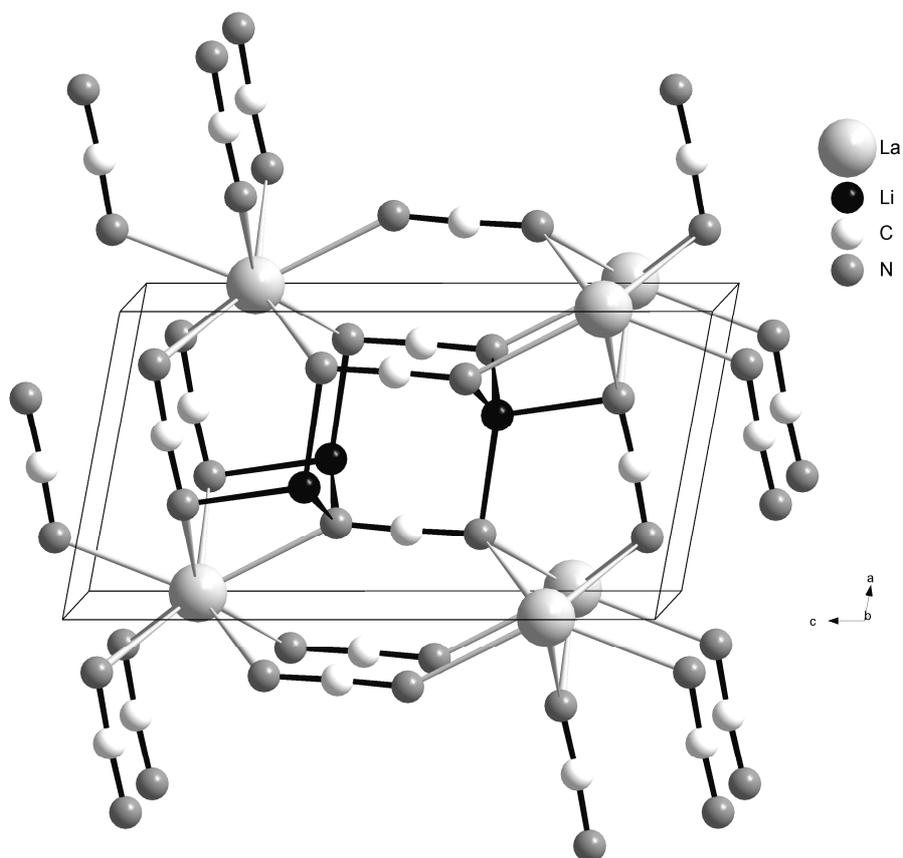
Table 3 Selected bond lengths (in pm), angles (\angle , in $^\circ$), and multiplicities in $\text{LiLa}(\text{CN}_2)_2$ and $\text{Ce}_3(\text{CN}_2)_3\text{N}$.

$\text{LiLa}(\text{CN}_2)_2$

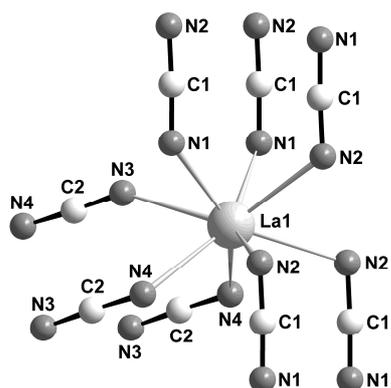
La(1) – N(1)	259.4(3) 2x		
La(1) – N(2)	261.4(5) 1x, 268.1(3) 2x		
La(1) – N(3)	266.7(5)		
La(1) – N(4)	260.8(4) 2x		
Li(1) – N(1)	210(1)		
Li(1) – N(3)	210.7(5) 2x		
Li(1) – N(4)	209(1)		
N(1) – C(1) – N(2)	122.0(8), 123.8(8)	\angle N(1) – C(1) – N(2)	176.8(6)
N(3) – C(2) – N(4)	120.8(8), 125.5(8)	\angle N(3) – C(2) – N(4)	177.6(6)

$\text{Ce}_3(\text{CN}_2)_3\text{N}$

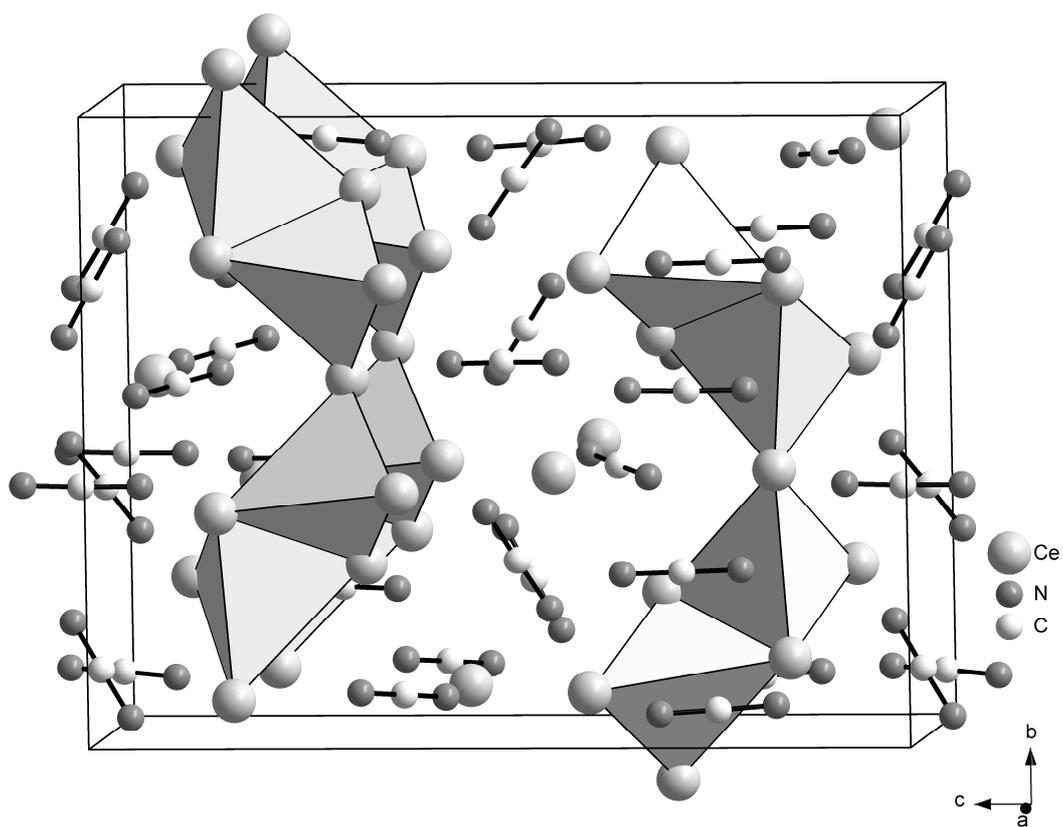
Ce(2) – N(13)	243.0(8)		
Ce(3) – N(13)	247.3(8)		
Ce(4) – N(13)	242.5(7)		
Ce(6) – N(13)	229.5(7)		
Ce(1) – N(14)	238.0(7)		
Ce(2) – N(14)	235.8(7)		
Ce(3) – N(14)	244.2(8)		
Ce(4) – N(14)	239.1(8)		
Ce – N (NCN)	250.3(8) – 302.6(9)		
N(1) – C(1) – N(2)	124(1), 121(1)	\angle N(1) – C(1) – N(2)	178(1)
N(3) – C(2) – N(4)	122(1), 124(1)	\angle N(3) – C(2) – N(4)	178.9(9)
N(5) – C(3) – N(6)	125(1), 122(1)	\angle N(5) – C(3) – N(6)	179(1)
N(7) – C(4) – N(8)	124(1), 122(1)	\angle N(7) – C(4) – N(8)	178.8(9)
N(9) – C(5) – N(10)	123(1), 123(1)	\angle N(9) – C(5) – N(10)	179(1)
N(11) – C(6) – N(12)	123(1), 122(1)	\angle N(11) – C(6) – N(12)	178(1)



33 **Figure 1.** Monoclinic crystal structure of $\text{LiLa}(\text{CN}_2)_2$.



56 **Figure 2.** Environment of the lanthanum ion in $\text{LiLa}(\text{CN}_2)_2$.



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Figure 3. Orthorhombic crystal structure of $\text{Ce}_3(\text{CN}_2)_3\text{N}$.

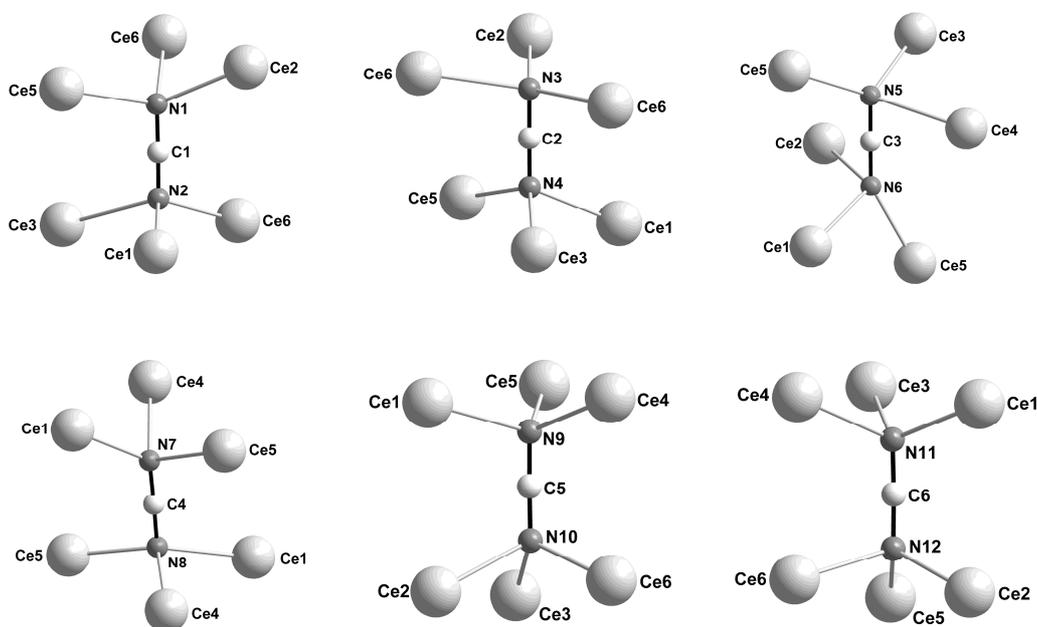


Figure 4. Environments of the six independent carbiimide ions in $\text{Ce}_3(\text{CN}_2)_3\text{N}$.

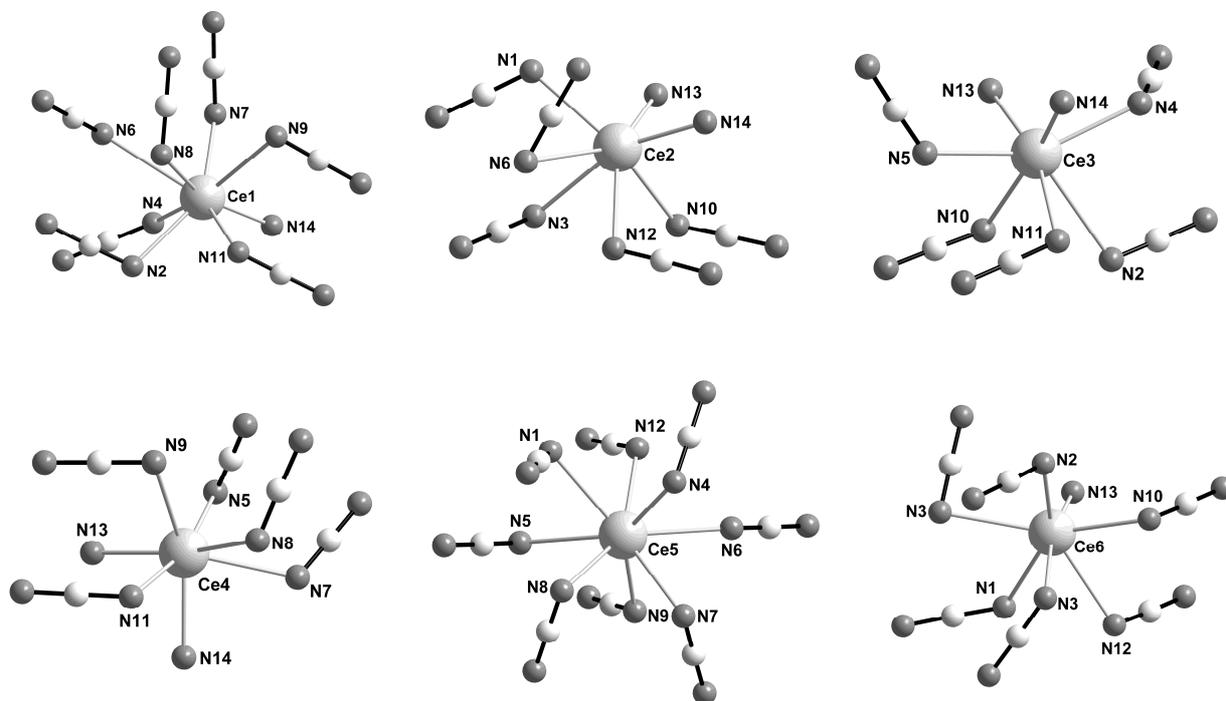


Figure 5. Environments of the six independent cerium ions in $\text{Ce}_3(\text{CN}_2)_3\text{N}$.