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The Versatility of Solid-State Metathesis Reactions: From Rare Earth Fluorides to Carbodiimides

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Abstract. The new carbodiimide compounds $LaF(CN_2)$ and $LiPr_2F_3(CN_2)_2$ were obtained as crystalline powders by solid-state metathesis reactions from 1:1 molar ratios of REF_3 (RE = rare earth) and $Li_2(CN_2)$ at temperatures between 500 and 700 °C over 4 days in fused copper ampoules. Higher proportions of $Li_2(CN_2)$ in reactions yielded $RE_2(CN_2)_3$ compounds, including the new $Eu_2(CN_2)_3$. Single-crystal structure refinements were performed for $LaF(CN_2)$ and $LiPr_2F_3(CN_2)_2$. Homologous $LiRE_2F_3(CN_2)_2$ compounds with RE = Ce, Pr, Nd, Sm, Eu, Gd were assigned by isotypic indexing of their XRD patterns. The crystal structure of $LaF(CN_2)$ contains planar $[La_3F_3]$ layers being interconnected by carbodiimide ions, and is related with that of the mineral bastnäsite ($REF(CO_3)$).

Introduction

During the past years several carbodiimide compounds of rare earth (*RE*) metals have been established by rational approach using solid-state metathesis reactions. Reactions between $RECl_3$ and $Li_2(CN_2)$ were performed to synthesize compounds of the families $RE_2(CN_2)_3$ [1], $RECl(CN_2)$ [2], and $RE_2Cl(CN_2)N$ [3] just by changing the molar ratios of starting materials and the reaction temperature, respectively. $RE_2(CN_2)_3$ compounds with RE = Y, Ce–Tm (except Pm, Eu) adopt the monoclinic structure type ($C2/m$), whereas the $RE_2(CN_2)_3$ compounds with RE = Tm, Yb, Lu crystallize in the rhombohedral structure type ($R\bar{3}c$). Among these, $Tm_2(CN_2)_3$ occurs dimorphic adopting both structure types [7].

Other carbodiimide compounds were obtained by using additives such as oxides [4] or silicates [5] in multilateral metathesis reactions, in which the choice of appropriate reaction partners appears to be important. Metathesis reactions with two or more reaction partners are exothermic reactions, in which the exothermicity is driven not only by the stability of the desired product but also by the lattice energy of the co-produced salt [6]. Most metathesis reactions in the field of rare earth carbodiimides have been performed by using $Li_2(CN_2)$ and rare earth chlorides leading to LiCl as a co-product, in spite of the higher lattice energy of LiF, which could be formed in a metathesis reaction starting from rare earth fluorides.

A comparative study of the employment of rare earth fluoride instead of rare earth chloride with $Li_2(CN_2)$ was, therefore, a likely task for the exploration of metathesis reactions, and for the search of missing compounds [7].

Experimental Section

Synthesis

The rare earth trifluorides were synthesized by reacting rare earth oxides such as RE_2O_3, CeO_2, Pr_6O_{11}, Tb_4O_7 (La_2O_3 from Merck, 99.99 %; other *RE* oxides from Ventron, 99.99 %) with NH_4F in 1:10 molar ratio (with respect to RE_2O_3) at 100 °C in a corundum beaker in air. The excess of NH_4F was removed by sublimation and the resulting complex ammoniumfluoridometallate was decomposed at 380 °C under vacuum to obtain pure REF_3 [8]. $Li_2(CN_2)$ was synthesized by treating $Li_2(CO_3)$ (Alfa, ultrapure) in flowing ammonia at 600 °C (ca. 18 h) several times, inclusive regrinding, until a single phase product was obtained [9].

A copper tube (inner diameter ca. 5 mm, thickness of the wall ca. 1 mm) was cut into 4 cm long pieces and each piece was sealed from one side by with an arc melter under vacuum. A copper container was charged with a carefully homogenized 1:1 molar mixture of REF_3 and $Li_2(CN_2)$ (total amount about 250 mg) under dry argon inside a glovebox. Afterwards, the copper container was evacuated and sealed from the other side with an arc melter. The copper ampoule was jacketed into an evacuated silica ampoule in order to prevent oxidation with air during the heating process in the furnace. Afterwards, the ampoule was placed into a tube furnace and heated at 500–700 °C for 4 d. After reaction, the copper container was allowed to cool down to room temperature and opened in air. The products were washed with water, dried with acetone, and inspected by powder XRD.

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Table 1. Lattice parameters /pm, monoclinic angles /°, unit cell volumes /10^6 pm^3, and number of single indexed reflections of $\mathrm{LaFCN_2}$ (*Cmcm*) and $\mathrm{Li}RE_2\mathrm{F_3(CN_2)_2}$ (*C2/c*).

	a	*b*	*c*	*β*	*V*	indexed reflections
$\mathrm{LaFCN_2}$	388.64(4)	872.37(9)	782.48(8)	–	265.29(7)	40
$\mathrm{LiCe_2F_3(CN_2)_2}$	1166.2(1)	664.16(7)	855.51(9)	115.431(5)	598.4(2)	40
$\mathrm{L}i\mathrm{Pr_2F_3(CN_2)_2}$	1159.7(1)	658.3(1)	849.8(1)	115.381(6)	586.17(2)	43
$\mathrm{LiNd_2F_3(CN_2)_2}$	1155.2(2)	653.7(1)	845.5(1)	115.330(8)	577.2(2)	47
$\mathrm{LiSm_2F_3(CN_2)_2}$	1146.5(3)	645.6(2)	838.1(2)	115.31(1)	560.9(4)	33
$\mathrm{LiEu_2F_3(CN_2)_2}$	1141.7(4)	642.2(3)	834.3(3)	115.377(2)	552.7(6)	30
$\mathrm{LiGd_2F_3(CN_2)_2}$	1140.1(3)	638.9(2)	832.2(3)	115.28(1)	548.2(3)	30

$\mathrm{LaF(CN_2)}$ was synthesized at 500 °C. Single crystals of $\mathrm{LaF(CN_2)}$ were obtained after reaction at 750–800 °C (1:1 molar ratio). Single crystals of $\mathrm{LiPr_2F_3(CN_2)_2}$ were found after the reaction was performed at 750 °C.

X-ray Powder Diffraction

The XRD patterns of the reaction products were collected with a Stadi-P (Stoe, Darmstadt) powder diffractometer using Cu-$K_{\alpha1}$ radiation (germanium monochromator). After the single crystal refinements were successfully performed for $\mathrm{LaF(CN_2)}$ and $\mathrm{Li}RE_2\mathrm{F_3(CN_2)_2}$ their calculated X-ray patterns were used to inspect unknown reflections in the XRD powder patterns resulting from analogous reactions of other rare earth elements. Lattice parameters of homologous *RE* compounds were indexed and calculated with the aid of the program system WinXPow [10] with the results listed in Table 1. The powder pattern of the new $\mathrm{Eu_2(CN_2)_3}$ was indexed isotypic to monoclinic $RE_2\mathrm{(CN_2)_3}$ (*C2/m*) compounds revealing lattice parameters of a = 1450.4(2) pm, b = 387.08(6) pm, c = 526.8(1) pm, and β = 95.815(9)°.

X-ray Single-Crystal Diffraction

Transparent needle shaped single-crystals of $\mathrm{LaF(CN_2)}$ and transparent green rodlike crystals of $\mathrm{LiPr_2F_3(CN_2)_2}$ 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) at room temperature (Table 2). Intensities were corrected for Lorentz factors, polarization and absorption effects by using the IPDS software X-Red/X-Shape. The crystal structure solutions and anisotropic refinements of all atoms were obtained by using the SHELX-97 program package [11].

Further details on the crystal structure investigation 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 419916 of $\mathrm{LaF(CN_2)}$ and CSD number 419925 of $\mathrm{LiPr_2F_3(CN_2)_2}$.

Infrared Spectroscopy

Infrared spectra were recorded from KBr pellets in the spectral region between 4000 and 350 cm^{-1} with a Perkin-Elmer FT-IR spectrometer (SPEKTRUM 1000).

Results and Discussion

Solid-state metathesis reactions may be regarded as a straightforward tool for target orientated syntheses, which have been proven to be efficient in syntheses of rare earth compounds containing nitridoborate [12], carbodiimide [1–3, 7], and tetracyanamidosilicate [5] ions. During the past, most reactions of this type were performed starting from rare earth trichlorides.

Reactions between $RE\mathrm{F_3}$ compounds and $\mathrm{Li_2(CN_2)}$ in 1:1 molar ratio resulted in three distinct main products, as shown in Equations (1)–(3). Formations of crystalline powders of new compounds $\mathrm{LaF(CN_2)}$ and $\mathrm{Li}RE_2\mathrm{F_3(CN_2)_2}$ may be described according to Equations (1) and (2), with respect to the results of indexed powder patterns. $RE_2\mathrm{(CN_2)_3}$ compounds given in Equation (3) were already known from previous experiments, originally synthesized from 2:3 molar ratios of $RE\mathrm{Cl_3}$ and $\mathrm{Li_2(CN_2)}$ [Equation (4)] [1, 7]. All reported carbodiimide products behave stably in air and can be purified by washing with water.

$$\mathrm{LaF_3 + Li_2(CN_2) \rightarrow LaF(CN_2) + 2\ LiF} \qquad (1)$$

$$2\ RE\mathrm{F_3} + 2\ \mathrm{Li_2(CN_2)} \rightarrow \mathrm{Li}RE_2\mathrm{F_3(CN_2)_2} + 3\ \mathrm{LiF} \qquad (2)$$

with *RE* = Ce, Pr, Nd, Sm, Eu, Gd

$$3\ RE\mathrm{F_3} + 3\ \mathrm{Li_2(CN_2)} \rightarrow RE_2\mathrm{(CN_2)_3} + \mathrm{Li}RE\mathrm{F_4} + 5\ \mathrm{LiF} \qquad (3)$$

with *RE* = Tb, Dy, Ho, Er, Tm, Yb, Lu

$$2\ RE\mathrm{F_3} + 3\ \mathrm{Li_2(CN_2)} \rightarrow RE_2\mathrm{(CN_2)_3} + 6\ \mathrm{LiF} \qquad (4)$$

with *RE* = Y, Ce – Lu (except Pm)

Rare earth trifluorides appear to be easier in synthesis (from oxides) and handling than the corresponding chlorides. In the course of our reactions with $\mathrm{Li_2(CN_2)}$ we noted that the co-produced LiCl (from $RE\mathrm{Cl_3}$ reactions) can be easily washed away with water from air stable products. This is not the case with LiF (from $RE\mathrm{F_3}$ reactions) as the solubility of LiF in $\mathrm{H_2O}$ is only about 0.15 % at 20 °C, making a separation process, if desired, more difficult.

The synthesis of the $\mathrm{LaF(CN_2)}$ parallels the already reported formation of $RE\mathrm{Cl(CN_2)}$ with *RE* = La, Ce, Pr from reactions of $RE\mathrm{Cl_3}$ and $\mathrm{Li_2(CN_2)}$ [2]. In contrast, the formation $\mathrm{LaF(CN_2)}$ was obtained only for *RE* = La.

Reactions of rare earth trifluorides with *RE* = Ce, Pr, Nd, Sm, Eu, Gd lead to the formation of compounds with the formula $\mathrm{Li}RE_2\mathrm{F_3(CN_2)_2}$. The employment of the second half series of rare earth elements with *RE* = Tb, Dy,

Table 2. Crystal data from single crystal structure refinements on $LaF(CN)_2$ and $LiPr_2F_3(CN_2)_2$.

Empirical formula	$LaF(CN)_2$	$LiPr_2F_3(CN_2)_2$
Formula weight /g·mol^{-1}	197.94	425.82
Crystal system	orthorhombic	monoclinic
Space group	*Cmcm* (No. 63)	*C 2/c* (No. 15)
Unit cell dimensions /pm	a = 387.72(8), b = 869.3(2), c = 780.3(2)	a = 1156.2(2), b = 656.3(1), c = 847.1(1), β = 115.32(2)
Volume /10^6 pm^3	263.00(9)	581.1(2)
Z	4	4
Density (calculated) /g·cm^{-3}	4.999	4.867
Absorption coefficient /mm^{-1}	15.973	16.560
F(000)	344	752
Crystal description	Colorless needle	Green block
Crystal size /mm	0.34 × 0.10 × 0.06	0.18 × 0.14 × 0.07
θ for data collection /°	4.69 to 30.26	3.67 to 32.84
Index range	$-5 \le h \le 5$, $-12 \le k \le 12$, $-11 \le l \le 11$	$-17 \le h \le 17$, $-9 \le k \le 9$, $-12 \le l \le 12$
Reflections collected	2153	6182
Independent reflections	238	1028
R_{int}	0.0571	0.0372
Data /parameters	238 /20	1028 /57
Absorption correction	Numerical	Numerical
Min. and max. transmission	0.1186 and 0.4338	0.1902 to 0.4047
Extinction coefficient	0.108(8)	0.0151(4)
Goodness-of-fit on F^2	1.356	1.060
R indices [$I > 2\sigma(I)$]	$R1$ = 0.0231, $wR2$ = 0.0651	$R1$ = 0.0172, $wR2$ = 0.0427
R indices (all data)	$R1$ = 0.0231, $wR2$ = 0.0651	$R1$ = 0.0223, $wR2$ = 0.0438
Largest diff. peak and hole e$^-$ /10^6 pm^3	1.545 and −1.522	1.947 and −0.799
Temperature /K	293(2)	293(2)
λ (Mo-K_α) /pm	71.073	71.073
Diffractometer	STOE IPDS I	STOE IPDS I
CSD-Number	419916	419925

Ho, Er, Tm, Yb, Lu yielded the already known $RE_2(CN_2)_3$ compounds plus $LiREF_4$ [13, 14] as side phases.

Pure $RE_2(CN_2)_3$ compounds were already obtained previously, by using the appropriate 2:3 molar ratio of starting materials. From these results we note that $RE_2(CN_2)_3$ compounds can be synthesized by using rare earth chlorides or fluorides [Equation (4)]. This is also the case for the first half series of *RE* elements when the appropriate 2:3 molar ratio of reactants is employed. However, our experiments suggested that there were some differences with respect to products and yields of reactions, sometimes favoring a metathesis reaction with rare earth fluoride and sometimes with chloride. For example, $Ce_2(CN_2)_3$ was obtained as a low yield product when synthesized from $CeCl_3$, but appeared in high yields when synthesized from CeF_3. Monoclinic $Eu_2(CN_2)_3$ was a missing member of the $RE_2(CN_2)_3$ [1, 7] series, which was successfully synthesized as a single phase product (besides LiF) by metathesis reaction starting from EuF_3 and identified from indexed XRD patterns [$Eu_2(CN_2)_3$: *C2/m*, a = 1450.4(2) pm, b = 387.08(6) pm, c = 526.8(1) pm, β = 95.815(9)°]. The unit cell volume of $Eu_2(CN_2)_3$ [$V = 294.3(1) \cdot 10^6$ pm^3] nicely fits into the series of $RE_2(CN_2)_3$ compounds [7].

Rhombohedral $Tm_2(CN_2)_3$ (II) was previously synthesized from $TmCl_3$ and $Li_2(CN_2)$. Pressure experiments have shown that $Tm_2(CN_2)_3$ is dimorphic, and that monoclinic $Tm_2(CN_2)_3$ (I) is obtained as moderately crystalline powder after applying pressure on rhombohedral $Tm_2(CN_2)_3$ (II) [7]. Crystalline powder of monoclinic $Tm_2(CN_2)_3$ (I) was obtained as a high yield product according to Equation (4), starting from TmF_3 and $Li_2(CN_2)$.

The crystal structure of $LaF(CN_2)$ is shown in Figure 1. A common pattern of the crystal structures of $LaCl(CN_2)$ and $LaF(CN_2)$ is their arrangement of $[LaX]^{2+}$ (X = Cl, F) and $(CN_2)^{2-}$ layers alternating along the stacking directions. The carbodiimide groups in the structure of $LaCl(CN_2)$ are not fully symmetrically with respect to their coordination environments with lanthanum atoms, yielding C−N distances of d = 125.1(6) and 120.2(6) pm, respectively. Carbon atoms of the carbodiimide group in the

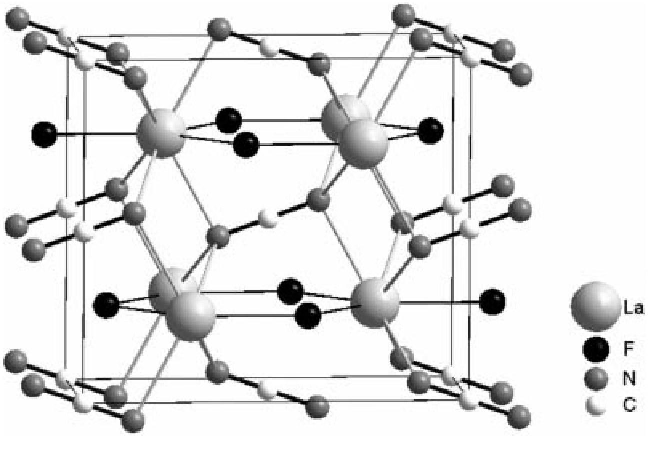

Figure 1. View along the approximate [100] direction of the crystal structure of $LaF(CN_2)$.

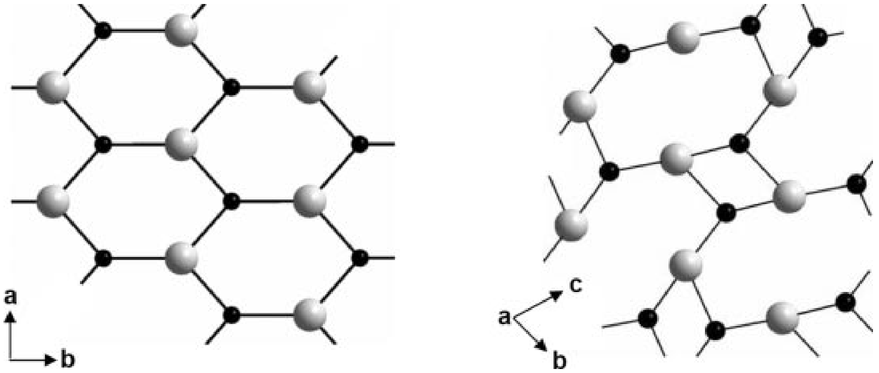

Figure 2. Section of [LaF] layers in the structures of $LaF(CN_2)$ (left) and $LiPr_2F_3(CN_2)_2$ (right). Note that the layer at right is not fully planar.

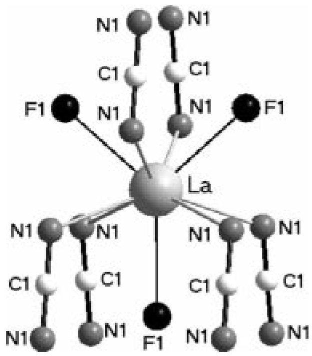

Figure 3. Coordination environment of La in the structure of $LaF(CN_2)$.

$LaF(CN_2)$ structure occupy positions at the center of inversion and the C−N distances are refined at d = 122.0(6) pm. The linear [N=C=N] unit is surrounded by six La atoms in a nearly trigonal antiprismatic fashion. Infrared spectra of $LaCl(CN_2)$ revealed a strong asymmetrical vibration signal (ν_{asym}) at 2033 cm^{-1} and strong deformation vibration signals (δ) at 660 and 648 cm^{-1}. For $LaF(CN_2)$ the corresponding signals were obtained at 1981 cm^{-1} (ν_{asym}), 661, and 685 cm^{-1} (δ). These values are closely related to many other $(CN_2)^{2-}$ containing compounds [15].

A striking feature in the crystal structure of $LaF(CN_2)$ is the planar arrangement of [LaF] layers, constructed from six membered $[La_3F_3]$ rings, displayed in Figure 2 (left), which can be related to the arrangement of boron and nitrogen atoms in the structure of hexagonal boron nitride. These layers are interconnected by nitrogen atoms of the carbodiimide ions. Lanthanum atoms in the structure are surrounded in a nine fold $[LaN_6F_3]$ environment formed by six nitrogen atoms [$d_{\mathrm{La-N}}$ = 259.7(4)−267.8(5) pm] of [N=C=N] groups forming a trigonal prism, which is tricapped by fluorine atoms [$d_{\mathrm{La-F}}$ = 258.7(4)−263.3(6) pm] as shown in Figure 3. A related structure pattern is known from the structure of the most common fluoride carbonate mineral bastnäsite [16]. The relation between these two compounds, $LaF(CN_2)$ and REF(CO_3), exists also in a chemical matter, because $(CN_2)^{2-}$ ions can hydrolyze to form $(CO_3)^{2-}$, and vice-versa, $(CO_3)^{2-}$ can be converted into $(CN_2)^{2-}$ by ammonolysis reaction, as shown for $Li_2(CO_3)$ in the synthesis part.

RE atoms in the bastnäsite structure (usually combinations of cerium, lanthanum and yttrium) have a nine fold $[REO_6F_3]$ coordination as well, resulting from six oxygen atoms of carbonate groups, and three fluorine atoms connecting the *RE* atoms into [*RE*F] layers. However, adjacent layers are shifted relative to each other, resulting in a trigonal prismatic environment for the carbonate groups.

The crystal structure of $LiPr_2F_3(CN_2)_2$, can be considered as an adduct, $LiF \cdot 2PrF(CN_2)$(Figure 4), and is closely related with the structure of $LiLa_2F_3(SO_4)_2$ [17]. The structure is constructed from buckled 4.8^2 [PrF] layers of praseodymium atoms and one third of fluorine atoms per formula unit (Figure 2, right). These layers are interconnected by [N=C=N] and the remaining two-thirds of fluorine atoms. The [N=C=N] group in $LiPr_2F_3(CN_2)_2$ is not fully symmetrically having an N−C−N angle of 178.3(3)° and C−N distances of d = 123.4(4) and 121.7(4) pm, respectively. The monitored infrared spectra of $LiPr_2F_3(CN_2)_2$ revealed frequencies of 2024 cm^{-1} (ν_{asym}) and 682, 673, 646 cm^{-1} (δ) but also the frequency of the *pseudo* symmetrical vibration at 1260 cm^{-1} indicating the small asymmetry of the [N=C=N] group.

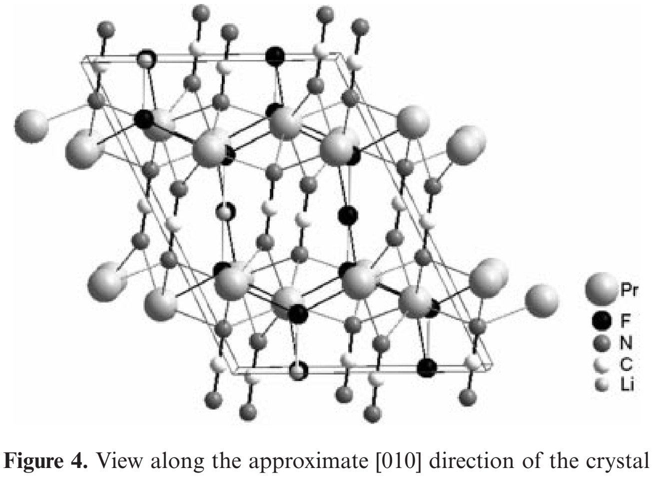

Figure 4. View along the approximate [010] direction of the crystal structure of $LiPr_2F_3(CN_2)_2$.

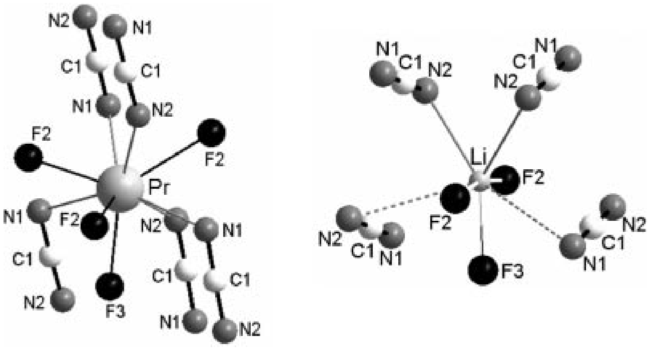

Figure 5. Coordination environment of Pr (left) and Li (right) in the structure of $LiPr_2F_3(CN_2)_2$.

Table 3. Atom positions and equivalent isotropic displacement parameters /10^4 pm^2 in structures of $LaF(CN)_2$ and $LiPr_2F_3(CN_2)_2$.

	x	y	z	U_{eq}
$LaF(CN)_2$				
La(1)	0	0.2222(1)	1/4	0.0124(4)
F(1)	1/2	0.4193(6)	1/4	0.016(1)
N(1)	1/2	0.1322(6)	0.4475(7)	0.015(1)
C(1)	1/2	0	1/2	0.011(1)
$LiPr_2F_3(CN_2)_2$				
Pr(1)	0.2869(1)	0.0042(1)	0.1670(1)	0.0066(8)
F(2)	0.1861(2)	0.1223(2)	−0.1342(2)	0.0117(3)
F(3)	1/2	0.1020(3)	1/4	0.0120(5)
N(1)	0.1377(2)	−0.2982(3)	0.0377(3)	0.0098(4)
N(2)	−0.0867(2)	−0.2024(3)	−0.1321(3)	0.0134(5)
C(1)	0.0245(3)	−0.2498(3)	−0.458(4)	0.0101(5)
Li(1)	0	0.0940(12)	−1/4	0.030(2)

Praseodymium atoms in the structure have the coordination number nine, resulting from four fluoride [d_{Pr-F} = 234.37(7)−256.3(2) pm] and five nitrogen atoms [d_{Pr-N} = 254.9(2)−262.4(2) pm] of carbodiimide ions (Figure 5, left). The lithium ions are localized between metal layers, in which metal atoms from adjacent layers form a distorted trigonal prismatic cage, bridged along the prism axes by four [N=C=N] and one fluorine. Together with the fluorine atoms from each [PrF_2] layer, there are three short Li−F [d_{Li-F} = 195.5(8)−199.5(8) pm] and two short Li−N contacts [d_{Li-N} = 257.7(6) pm]. But there are more nitrogen and even carbon neighbors from two nearly side-on arranged [N=C=N] groups in the vicinity of lithium, as shown in Figure 5.

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Table 4. Atomic distances /pm, (multiplicity) and angles /° in structures of $LaF(CN_2)$ and $LiPr_2F_3(CN_2)_2$.

$LaF(CN_2)$	
La(1)−F(1)	258.7(4) (2x), 263.3(6) (1x)
La(1)−N(1)	259.7(4) (4x), 267.8(5) (2x)
C(1)−N(1)	122.0(6) (2x)
N(1)−C(1)−N(1)	180
$LiPr_2F_3(CN_2)_2$	
Pr(1)−F(3)	234.37(7)
Pr(1)−F(2)	243.4(2), 250.1(2), 256.3(2)
Pr(1)−N(1)	254.9(2), 261.4(2), 262.4(2)
Pr(1)−N(2)	256.0(2), 261.3(2)
N(1)−C(1)	123.4(4)
N(2)−C(1)	121.7(4)
Li(1)−F(2)	195.5(2) (2x)
Li(1)−F(3)	199.5(8)
Li(1)−N(2)	257.7(6) (2x), 303.5(3) (2x)
Li(1)−N(1)	316.5(4) (2x), 343.3(6) (2x)
N(2)−C(1)−N(1)	178.3(3)

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