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Chains of [RE_6] Octahedra Coupled by (NCN) Links in the Network Structure of $RE_2Cl(CN_2)N$. Synthesis and Structure of Two Novel Rare Earth Chloride Carbodiimide Nitrides with Structures Related to the RE_2Cl_3 Type

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Solid state metathesis reactions between $RECl_3$ (RE = La, Ce) and Li_2CN_2 at 800 °C have led to the discovery of the rare earth chloride carbodiimide nitrides $La_2Cl(CN_2)N$ (**1**) and $Ce_2Cl(CN_2)N$ (**2**), respectively. Single crystal X-ray diffraction analyses revealed that **1** and **2** crystallize isotypic in an orthorhombic system (*Cmmm*, $Z = 4$, $a = 13.3914(8)$ Å, $b = 9.6345(7)$ Å, $c = 3.9568(2)$ Å for **1** and $a = 13.340(1)$ Å, $b = 9.5267(8)$ Å, $c = 3.9402(5)$ Å for **2**). The crystal structures of **1** and **2** contain linear chains of edge-sharing octahedra built from rare earth metal atoms. Similar to [M_6X_8] type clusters, the [RE_6] octahedra are capped by eight nitrogen atoms above their faces, of which four are from N^{3-} ions and the other four are from $(CN_2)^{2-}$ ions. The chains are interconnected by bridging $(CN_2)^{2-}$ to form a three-dimensional network with Cl^- ions in linear channels. Compounds **1** and **2** are surprisingly stable toward air and water. They have been characterized by thermal analysis, infrared spectroscopy, and magnetic susceptibility studies.

Introduction

Carbodiimides or cyanamides are an important class of compounds, useful in synthetic solid state chemistry as well as in molecular chemistry. There are several alkali,[1] alkaline earth,[2] transition metal,[3] and main group metal[4] cyanamides and dicyanamides[5] known from the literature. The first crystal structure refinement with good precision was obtained for calcium cyanamide,[6] which has applications in industry and in other fields such as organic synthesis and in soil treatments. Later on, many transition metal cyanamides and other derivatives of cyanamides were synthesized. Zinc cyanamide[7] was found to be useful in nonpolluting anticorrosive white pigments. In the rare earth system, there are many carbide nitrides available in the literature, but cyanamides or carbodiimides of rare earths are not available and are unexplored. Some of the rare earth carbide nitrides known in the literature have interesting properties and structures. Hence, our interests increased in studying the behavior of rare earth compounds having C−N bonds.

The discovery of gadolinium sesquichloride was the first window on the chemistry of metal-rich halides.[8] Its remarkable structure contains infinite chains constructed of metal octahedra as could be generated by condensing [Gd_6Cl_8] clusters via trans-edges. Isostructural sesquihalides are known

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for Y_2Cl_3,[9] Gd_2Br_3, Tb_2Cl_3, and Tb_2Br_3.[10] The existence of La_2Cl_3, once reported as a low yield product, remains unconfirmed.[11]

The occurrence of discrete or condensed [M_6X_8] and [M_6X_{12}] type clusters does, however, not necessarily require the presence of cluster electrons, e.g., in β-$PdCl_2$ (=Pd_6Cl_{12}). Yttrium sesquichloride nitride has been reported to occur with two structures. The structure of β-Y_2Cl_3N is closely related to rare earth sesquihalide structure, with additional N^{3-} ions residing in tetrahedral voids above and below the shared edge of condensed chains of yttrium octahedra.[12] Here, the building block is the [$Y_6Cl_4N_4$] derivative of a [M_6X_8] type cluster. In (α-)Y_2Cl_3N, the N^{3-} ions reside in tetrahedral voids formed by yttrium tetrahedra linked via shared edges into linear chains.[13]

Investigations in the system RE−X−N−C (RE = rare earth metal, X = halide) with nitride (REN) and graphite have yielded products that resemble both typical halide nitride and typical halide carbide structures. The halide carbide structures reported in the literature usually contain discrete or condensed octahedral [RE_6] clusters with C or C_2 units as interstitial atoms. Examples of carbide nitrides are $Y_6X_9C_2N$, RE_4X_6CN (RE = La, Gd; X = Br, I),[14] and $RE_7I_{12}C_2N$ (RE = Y, Ho)[15] with C_2 centered [M_6X_{12}] type clusters and N atoms in tetrahedral voids of metal atom arrangements. These compounds occur as colored transparent air-sensitive materials. The conditions employed in the synthesis for these compounds did not lead to the formation of stable C−N bonds. To our knowledge, the only rare earth compounds known to have C−N bonds are $RE_2O_2CN_2$ (RE = La, Ce, Pr, Nd, Sm, Eu, Gd).[16] These rare earth oxide cyanamides are prominent for their luminescence properties.[17]

Our reactions with carbodiimide ions have now created a novel structure pattern with $[NCN]^{2-}$ bridges in $RE_2Cl(CN_2)N$. Crystalline samples of **1** were first obtained in an attempt to synthesize the yet unknown compound “$La_2(CN_2)_3$” from a solid state reaction between $LaCl_3$ and $Li_2(CN_2)$ in 2:3 molar ratio at 950 °C. The strategy employed in this reaction followed the concept of the solid-state nitridoborate metathesis reaction[18] between $LaCl_3$ and $Li_3(BN_2)$ that yields $La_3(B_3N_6)$, with cyclic trimers of $(BN_2)^{3-}$ in its structure.[19] Hence, the C−N bonds in $Li_2(CN_2)$ may also be stable enough to sustain high temperature solid state reactions such as B−N bonds.

Here in this paper, we describe the preparation and crystal structure of **1** and **2**, as well as the magnetic properties of **2**.

Experimental Section

Synthesis. All manipulations of compounds were performed in a glovebox under dry argon with oxygen and moisture levels below 1 ppm. $Li_2(CN_2)$[20] was synthesized from a finely ground mixture of Li_3N (99.5%, Strem) and melamine (≥99%, Fluka) in a 2:1 molar ratio with a slight excess of melamine. A molybdenum boat with the ground mixture was preheated at 250 °C for 2−3 h under flowing argon by placing it in quartz tube. Then, the preheated mixture was heated slowly to 650 °C and kept at this temperature for 3 h to obtain X-ray pure $Li_2(CN_2)$ which was suitable for further synthesis without any purification.

All the following reactions were carried out in sealed tantalum ampules made from tantalum tube (Plansee, 99.99%). The tantalum tube was cut into pieces of 3 cm length, cleaned with a mixture of H_2SO_4 (97%), HNO_3 (65%), and HF (38%), and dried in air at 100 °C. Afterward, the tantalum pieces were sealed under 600 mbar argon pressure with an arc welder, first at one side and after loading with starting materials on the other side.

The tantalum capsule containing starting material $RECl_3$ (99.9% Alfa, sublimed) and Li_2CN_2 in the ratio 2:3 was jacketed with quartz under vacuum and placed into a furnace which was heated with a rate of 2 °C/min to 950 °C. After 4 days, the temperature was slowly (within 6 h) reduced to room temperature. The crystals were obtained as yellow needles **1** for RE = La and as black needles **2** for RE = Ce along with LiCl as a side product, that can be washed off with water. After the compositions of the new products were established from single crystal diffraction, high purity phases of **1** and **2** were obtained from stoichiometric 2:1:1 molar reactions of $RECl_3$, Li_3N, and $Li_2(CN_2)$, respectively, at 800 °C for 1 day. The purity of Li_2CN_2 was vital to obtain the title compounds, since even small amounts of oxygen impurities drove reactions toward $RE_2O_2CN_2$ (RE = La, Ce) and resulted low yields of **1** and **2**. The synthesis can be well performed in the temperature range 750−800 °C for 1 or 2 days to obtain good crystalline powders of **1** and **2**.

Phase Analysis. Phase analysis was done by X-ray powder diffraction techniques. The powder patterns were recorded on a StadiP diffractometer (Stoe, Darmstadt), using germanium monochromated Cu Kα_1 radiation ($\lambda = 1.540598$ Å). The samples were mounted between two pieces of aluminum foil for the X-ray powder measurement. The powder patterns of **1** and **2** were successfully indexed with an orthorhombic unit cell that could not be addressed to any known compound in a related system. Consequently, the crystal structures of **1** and **2** were determined from single crystal X-ray diffraction data. The X-ray diffraction patterns of the products were consistent with the calculated pattern from the single crystal structure refinements and contained a few weak unidentified reflections besides those of LiCl.

Physical Measurements. Infrared spectra were recorded on Perkin-Elmer FT-IR spectrometer. The measurements were done in the range 200−4000 cm^{-1} using KBr pellets of the compounds. Differential thermal analysis (DTA) was performed using a Netsch STA 409C thermal analyzer between 25 and 800 °C with the sample

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Table 1. Some Crystal and Refinement Data for $RE_2Cl(CN_2)N$

formula	$La_2Cl(CN_2)N$	$Ce_2Cl(CN_2)N$
f_w	367.32	368.68
syst, space group, *Z*	orthorhombic, *Cmmm* (No. 65), 4	orthorhombic, *Cmmm* (No. 65), 4
unit cell dimensions (Å, Å^3)		
a	13.3914(8)	13.340(1)
b	9.6345(7)	9.5267(8)
c	3.9568(2)	3.9402(5)
V	510.50	500.73
d_{calcd} (g/cm^3)	4.779	4.904
μ, mm^{-1} (Mo Kα)	16.86	18.33
R1, wR2^a [$F_o > 4\sigma(F_o)$]	0.0232, 0.0467	0.0276, 0.0505

^{a} $R1 = \Sigma||F_o| - |F_c|/\Sigma|F_o|$; $wR2 = \Sigma w(|F_o|^2 - |F_c|^2)^2/[\Sigma w(F_o^2)]^{1/2}$.

Table 2. Atomic Coordinates and Isotropic-Equivalent Displacement Parameters (Å^2) for $RE_2Cl(CN_2)N$

atom	multiplicity, symmetry	*x*	*y*	*z*	$U_{eq}{}^a$
		$La_2Cl(CN_2)N$			
La1	4, 2*mm*	0.36132(2)	0	0	0.00866(9)
La2	4, *m*2*m*	$^1/_2$	0.71113(3)	$^1/_2$	0.0095(1)
C	4, 2/*m*	$^1/_4$	$^1/_4$	$^1/_2$	0.0108(9)
N1	4, *m*2*m*	$^1/_2$	0.8434(5)	0	0.0093(8)
N2	8, *m*	0.3226(3)	0.1713(3)	$^1/_2$	0.0128(6)
Cl	4, 2*mm*	0.1222(1)	0	0	0.0228(3)
		$Ce_2Cl(CN_2)N$			
Ce1	4 2*mm*	0.36240(4)	0	0	0.0111(2)
Ce2	4 *m*2*m*	$^1/_2$	0.71059(4)	$^1/_2$	0.0119(2)
C	4, 2/*m*	$^1/_4$	$^1/_4$	$^1/_2$	0.014(2)
N1	4, *m*2*m*	$^1/_2$	0.8428(7)	0	0.013(2)
N2	8, *m*	0.3238(5)	0.1710(5)	$^1/_2$	0.015(1)
Cl	4, 2*mm*	0.1225(2)	0	0	0.0299(6)

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

fused in a self-made quartz ampule container. The magnetic susceptibility data were obtained with a SQUID (superconducting quantum interference device, MPMS, Quantum Design) magnetometer in the temperature range between 22 and 285 K with a 50 mg sample of **2** in a gelatin capsule. The data obtained have been corrected for the diamagnetic moments of the gelatin capsule and all atoms. Measurements were performed using a magnetic field of $H = 0.05$ T.

Crystal Structure Determination. Single crystals were mounted in glass capillaries inside a glovebox for the X-ray measurements. The crystal dimensions were approximately 0.02 × 0.02 × 0.1 mm^3 for **1** and 0.02 × 0.15 × 0.02 mm^3 for **2**. Measurements were performed on an IPDS (Stoe, Darmstadt) X-ray diffractometer in the θ range between 4.23° and 32.86° for **1** and between 4.28° and 32.94° for **2** at 293 K, using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The intensity data were corrected by XRED/XSHAPE for Lorentz, polarization, and absorption effects. Out of the total 5224 reflections for **1** and 4387 reflections for **2** that were collected, 552 and 422 reflections, respectively, were merged as unique reflections. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares calculations on F^2 (SHELXL-97). Anisotropic refinements of all atoms with fixed full occupancies yielded $R1 = 0.0232$, $wR2 = 0.0467$ for **1** and $R1 = 0.0276$, $wR2 = 0.0505$ for **2** with all reflections. The largest residual peak and deepest hole in the ΔF map were 1.12 and -1.78 e/Å^{-3} for **1** and 1.37 and -1.62 e/Å^{-3} for **2**. Some selected crystallographic data and details on the refinement are listed in Table 1. The atomic positions and isotropic-equivalent displacement parameters are given in Table 2. A summary of selected bond lengths is given in Table 3. More detailed crystallographic data and the anisotropic thermal displacement parameters are in the Supporting Information.

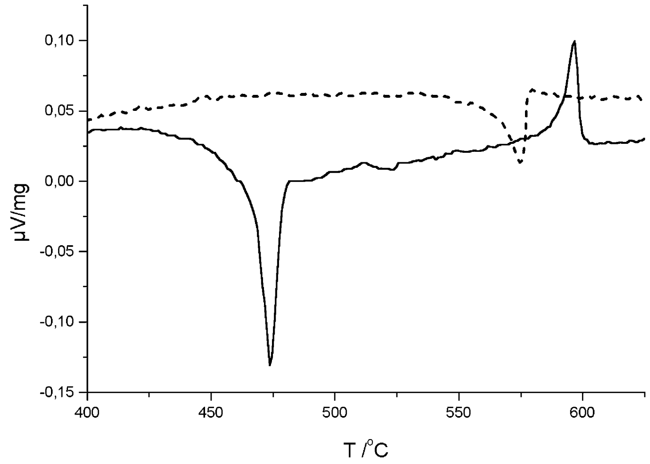

Figure 1. DTA for the reaction between $LaCl_3$, $Li_2(CN_2)$, and Li_3N in 2:1:1 molar ratio, measured in a cyclic procedure (heating rate 5 K/min) up to 800 °C. The temperature interval between 400 and 625 °C is only shown here. The exothermic effect on heating (—) and the endothermic effect on cooling (- - -) around 600 °C correspond to melting and recrystallization of LiCl.

Table 3. Selected Bond Lengths (Å) in $RE_2Cl(CN_2)N$

$La_2Cl(CN_2)N$		$Ce_2Cl(CN_2)N$		
La1−La2	3.8870(3)	Ce1−Ce2	3.8538(4)	×4
La1−La1	3.7142(6)	Ce1−Ce1	3.671(1)	×1
La1−N1	2.393(3)	Ce1−N1	2.369(4)	×2
La1−N2	2.628(2)	Ce1−N2	2.608(3)	×4
La1−Cl	3.203(2)	Ce1−Cl	3.201(3)	×1
La2−N1	2.353(2)	Ce2−N1	2.338(4)	×2
La2−N2	2.632(3)	Ce2−N2	2.608(6)	×2
La2−Cl	3.2754(8)	Ce2−Cl	3.252(2)	×4
C−N2	1.234(3)	C−N2	1.238(6)	×2

Results and Discussion

$Li_2(CN_2)$ can be considered as a good carbodiimide source even in high temperature environments because it can be recrystallized in a sealed tantalum ampule after reaching temperatures as high as 800 °C without any major decomposition. The metathesis reaction between $LaCl_3$ and $Li_2(CN_2)$ in 2:3 molar ratio leads to the title compound $La_2Cl(CN_2)N$ instead of the hypothetical "$La_2(CN_2)_3$". Due to the presence of $LaCl_3$ in the reaction, part of the $Li_2(CN_2)$ decomposes to form La_2NCl_3. The formation of intermediate La_2NCl_3 can be also considered with Li_3N in the stoichiometric reaction performed between $LaCl_3$, $Li_2(CN_2)$, and Li_3N in 2:1:1 molar ratio at 800 °C.

$$2RECl_3 + Li_3N + Li_2(CN_2) \rightarrow RE_2Cl(CN_2)N + 5LiCl \quad (1a)$$
$$(RE = La, Ce)$$

A differential thermal analysis (DTA) of reaction 1a exhibits an exothermic effect near 475 °C, as shown in Figure 1, that is consistent with results on the formation of LaN or La_2NCl_3.[21] An endothermic effect near 600 °C corresponds to the melting of LiCl, and the X-ray powder pattern of the

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reaction mixture heated at 600 °C indicated the presence of LiCl and La_2NCl_3 along with (nearly) X-ray amorphous material. The supposed intermediate La_2NCl_3,[22] prepared from a 2:1 molar mixture of $LaCl_3$ and Li_3N at 600 °C, was successfully reacted with $Li_2(CN_2)$ to form $La_2Cl(CN_2)N$ plus LiCl at 800 °C after 1 day (eq 1b).

$$La_2NCl_3 + Li_2(CN_2) \rightarrow La_2Cl(CN_2)N + 2LiCl \quad (1b)$$

Well developed single crystals of **1** and **2** are obtained through annealing in the flux of the coproduced LiCl at 800 °C or slightly higher. Compounds **1** and **2** are stable in air and water. The lanthanum compound was obtained as yellow crystalline material, and crystals of the cerium compound were obtained black. As a result of the lanthanide contraction, the corresponding cell parameters and the distances in **2** are shortened by typically 1−2%.

The crystal structures of **1** and **2** contain linear chains of edge-sharing octahedra built from rare earth metal atoms. The individual chains are closely related to those in the rare earth sesquihalide structures. The building blocks are [RE$_6$] octahedra surrounded by ligands corresponding to the well-known [M_6X_8] type moiety, with face-capping atoms. All the octahedral faces of the title compounds are capped by eight nitrogen atoms resulting from four N^{3-}, and from four $(NCN)^{2-}$ ions. The octahedra are linked via trans-edges to form chains, similar to those in Y_2Cl_3, or rather (β-)Y_2Cl_3N as illustrated in Figure 2 for comparison with structures of **1** and **2**. In the structures of (β-)Y_2Cl_3N, as well as in the title compounds, the nitride ions occupy tetrahedral interstices above and below the shared edge along the chain of [RE$_6$] octahedra. The $[RE_2RE_{4/2}N_{4/2}(CN_2)_4]$ chains of **1** and **2** run parallel to each other along the *c* direction, being linked via shared $(N{=}C{=}N)^{2-}$ to open up channels in the structure that are occupied by chloride ions in the projected *ab* plane of the structure as shown in Figure 3. The C−N distances in **1** and **2** are 1.234(3) and 1.238(6) Å, respectively. Relatively long RE−Cl distances (1 × 3.203(2) Å, 4 × 3.2754(8) Å for **1** and 1 × 3.201(3) Å, 4 × 3.252(2) Å for **2**) indicate that these tunnels are rather big for the accommodation of chloride ions.[23]

In **1** and **2**, RE1 and RE2 have coordination numbers 5 and 8, respectively, when the adjacent RE atoms are neglected. As shown in Figure 4, the RE1 atom has a strongly distorted square pyramidal coordination environment by one chloride atom and four nitrogen atoms (two from nitrides, N1, and two from carbodiimides, N2) and RE2 is surrounded by a square antiprismatic arrangement of four chlorine atoms from one side and four nitrogen atoms (two from nitrides, N1, and two from carbodiimides, N2) from the other side.

The characteristic vibrational frequencies of carbodiimide ions (around 2085 cm^{-1} for asymmetric stretching of NCN; 1090 cm^{-1} for symmetric stretching of NCN) were clearly detected from the infrared spectra of the compounds and thereby confirmed the presence of the $(CN_2)^{2-}$ ions.

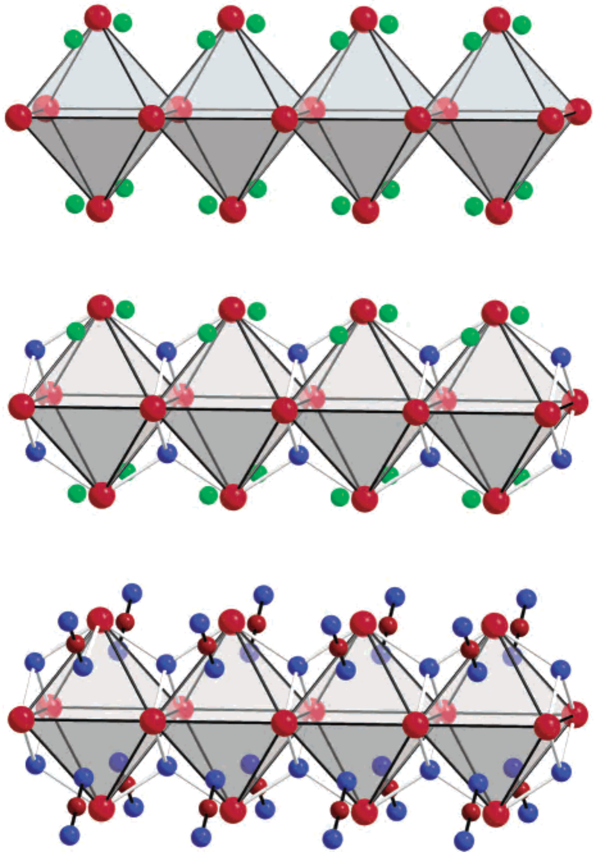

Figure 2. Sections of individual chains in the structures of Y_2Cl_3 (top), β-Y_2Cl_3N (center), and $RE_2Cl(CN_2)N$ (below). Terminal chloride atoms over the corners of metal octahedra are always suppressed in the drawings. Metal atoms are shown in red, chlorides are in green, nitrogen atoms are in blue, and carbon atoms are in brown.

We have already noted that the title compounds occur as yellow (**1**) and black (**2**) crystalline materials. We consider saltlike conditions for **1** with La^{3+}. For **2**, the configuration may be addressed analogous to that of binary CeN, with a saltlike $4f^15d^0$ or with a metallic $4f^05d^1$ configuration. CeN adopts the NaCl type structure and would likely be described with the saltlike notation as $Ce^{3+}N^{3-}$. However, CeN is a conductor showing Pauli paramagnetism and is therefore better described as $Ce^{4+}N^{3-}{\bullet}e^-$ with one delocalized electron in the 5d conduction band. Band structure calculations on CeN have revealed Ce−Ce bonding interactions (at a bond distance of 3.57 Å) with the remaining electron $Ce^{4+}{\bullet}e^-$ in a hybrid 5d−4f energy band.[24] The shortest Ce−Ce interatomic distance along the shared edge in **2** is slightly longer (3.671(1) Å) than that in CeN. The obtained magnetic moment of $\mu = 1.8\ \mu_B$ for **2** is smaller than would be expected for a free Ce^{3+} ion with the 5d^1 configuration ($\mu_{exp} = 2.5\ \mu_B$). In addition, a small temperature independent portion was assigned to the total susceptibility when a fit according to the formula $\chi = C/(T - \Theta) + \chi_{TIP}$ is used. This temperature independent contribution on the order of 10^{-3} emu/mol leads to the nonlinear temperature dependence of $1/\chi$ as shown in Figure 5.

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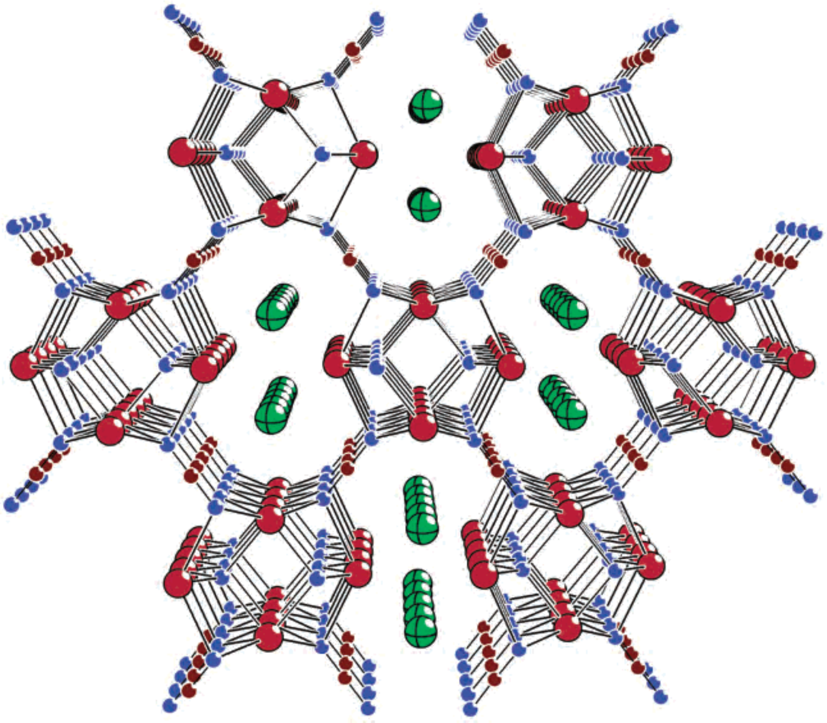

Figure 3. View of the $RE_2Cl(CN_2)N$ (RE = La, Ce) structure parallel to the short *c* repeat of the chain direction showing the isolated chloride ions in tunnels of the framework structure. Atom colors are as in Figure 2.

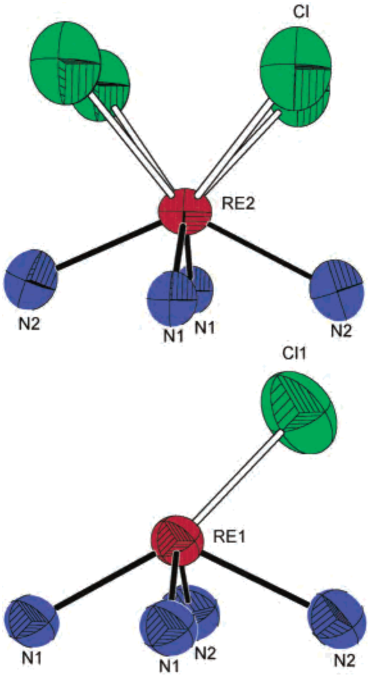

Figure 4. Coordination environment of RE1 and RE2 in the crystal structure of **1** and **2**.

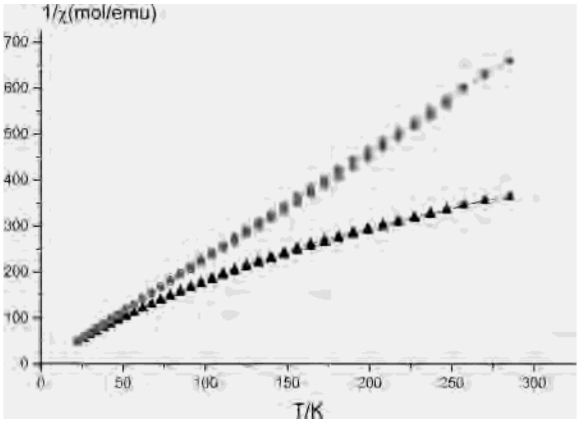

Figure 5. Temperature dependence of the magnetic susceptibility of **2** shown as $1/\chi$ vs T plot measured in a cyclic procedure. The total susceptibility (including TIP) is shown by black triangles (▲), and the temperature dependent contribution is indicated by gray dots (●).

Conclusions

The structures of the new carbodiimide nitride chlorides exhibit an interesting relationship with structures of the rare earth sesquihalides. In addition, the structures of **1** and **2** feature channels in their structures with feasibilities for anion exchange reactions, to be performed even in aqueous media. The work on the synthesis of analogous compounds having bromide or iodide ions instead of chloride in the structure is in progress. Also, it will be interesting to study the electronic structure of such compounds and to learn if RE−RE interactions are possible as in sesquihalides.

Thus, solid state chemistry of rare earth compounds with carbodiimide nitride (or nitridocarbonate) ions as bridging ligands may open up a new and attractive field of materials that could compete with already discovered carbidoborate (RE−B−C) and nitridoborate compounds (RE−B−N).[25,26]

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Supporting Information Available: X-ray crystallographic data for **1** and **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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