

# Synthesis and characterization of the rare-earth dicyanamides $Ln[N(CN)_2]_3$ with $Ln = La, Ce, Pr, Nd, Sm,$ and $Eu$

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## Abstract

The rare-earth dicyanamides  $Ln[N(CN)_2]_3$  ( $Ln = La, Ce, Pr, Nd, Sm, Eu$ ) were obtained via ion exchange in aqueous medium and subsequent drying. The crystal structures were solved and refined based on X-ray powder diffraction data and they were found to be isotypic:  $Ln[N(CN)_2]_3$ ;  $Cmcm$  (no. 63),  $Z = 4$ ,  $Ln = La$ :  $a = 799.88(9)$  pm,  $b = 1158.2(1)$  pm,  $c = 1026.7(1)$  pm;  $Ce$ :  $a = 794.94(3)$  pm,  $b = 1152.15(4)$  pm,  $c = 1020.96(4)$  pm;  $Pr$ :  $a = 790.45(5)$  pm,  $b = 1146.19(6)$  pm,  $c = 1016.74(6)$  pm;  $Nd$ :  $a = 787.79(3)$  pm,  $b = 1144.59(4)$  pm,  $c = 1015.54(4)$  pm;  $Sm$ :  $a = 781.30(5)$  pm,  $b = 1138.64(6)$  pm,  $c = 1012.04(5)$  pm;  $Eu$ :  $a = 776.7(1)$  pm,  $b = 1135.1(1)$  pm,  $c = 1013.7(1)$  pm). The compounds represent the first dicyanamides with trivalent cations. The  $Ln^{3+}$  ions are coordinated by three bridging N atoms and six terminal N atoms of the dicyanamide ions forming a three capped trigonal prism. The structure type is related to that of  $PuBr_3$ . The novel compounds  $Ln[N(CN)_2]_3$  have been characterized by IR and Raman spectroscopy ( $Ln = La$ ) and the thermal behavior has been monitored by differential scanning calorimetry ( $Ln = Ce, Nd, Eu$ ).

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**Keywords:** Coordination chemistry; Dicyanamides; Powder diffractometry; Rare-earth elements;  $PuBr_3$  structure type

## 1. Introduction

The rapidly growing interest in the synthesis of the hitherto unknown binary nitride  $C_3N_4$  has provided several investigations on ternary nitridocarbonates (IV), e.g., cyanamides and dicyanamides. In the last few years a number of cyanamides and dicyanamides containing  $[CN_2]^{2-}$  and  $[N(CN)_2]^-$  ions have been synthesized [1]. The alkali and alkaline earth compounds  $M(I)_2[CN_2]$  ( $M(I) = Li, Na, K$ ) [2–5],  $M(I)[N(CN)_2]$  ( $M(I) = Na, K, Rb, Cs$ ) [6–8],  $M(II)[CN_2]$  ( $M(II) = Mg, Ca, Sr, Ba$ ) [9–11] and  $M(II)[N(CN)_2]_2$  ( $M(II) = Mg, Ca, Sr, Ba$ ) [12] were structurally characterized. Furthermore, the lead salts  $Pb[CN_2]$  [13] and  $Pb[N(CN)_2]_2$  [14,15] were obtained. Apart from this the transition metal cyana-

mides  $Ag_2[CN_2]$  [16,17],  $Zn[CN_2]$  [18,19],  $Cd[CN_2]$  [20],  $Hg_2[CN_2]$  [21–24] and the transition metal dicyanamides  $M(II)[N(CN)_2]_2$  ( $M(II) = Cr, Mn, Co, Ni, Cu, Zn, Cd$ ) [25–31] were characterized. Surprisingly, up to now only a few rare-earth compounds were described which contain  $Ln \cdots N-CN$  bonds, e.g.,  $Ln_2O_2[CN_2]$  ( $Ln = La, Ce, Pr, Nd, Sm, Eu, Gd$ ) [32,33] and  $Eu[CN_2]$  [34]. In an attempt to synthesize the ternary rare-earth cyanamides  $Ln_2[CN_2]_3$  by metathesis of  $LnCl_3$  and  $Li_2[CN_2]$  at 950 °C, the mixed compounds  $Ln_2Cl[CN_2]N$  ( $Ln = La, Ce$ ) were synthesized [35].

For the respective dicyanamides only coordination compounds crystallizing with solvent molecules have been described: For  $Ln[N(CN)_2]_3 \cdot 3OP(NMe_2)_3$  ( $Ln = Nd, Er$ ) [36] and  $Nd[N(CN)_2]_3 \cdot 2OP(NMe_2)_3$  [37] structural data have been reported. Very recently, the crystal structures of the rare-earth complexes  $\{Ln[N(CN)_2]_2(phen)_2(H_2O)_3\}[N(CN)_2](phen)$  ( $Ln = Pr,$

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Sm, Gd) and  $[Ln[N(CN)_2]_3(2,2'\text{-bipy})_2(H_2O)]_n$  ( $Ln = La, Sm, Gd$ ) were presented [38].

In the past years, we found a convenient synthetic approach towards metal dicyanamides by ion exchange in aqueous solution. In this work, we report about the application of this method to prepare the compounds  $Ln[N(CN)_2]_3$  ( $Ln = La, Ce, Pr, Nd, Sm, Eu$ ), which represent the first rare-earth dicyanamides with trivalent cations.

## 2. Experimental

### 2.1. Syntheses

The rare-earth dicyanamides  $Ln[N(CN)_2]_3$  ( $Ln = La, Ce, Pr, Nd, Sm, Eu$ ) were synthesized via ion exchange in aqueous medium: a column with an ion exchange resin (Merck, Ionenaustauscher I, Art. 4765) was completely filled with a solution of the respective rare-earth chloride ( $LaCl_3 \cdot 7H_2O$  (Alfa Aesar),  $Ln(III)Cl_3 \cdot xH_2O$  ( $Ln = Ce, Pr, Nd, Sm, Eu$ ), all received from Alfa Aesar, 99.9% (REO)). An excess of these chlorides was removed by washing with water. Subsequently, a solution of  $Na[N(CN)_2]$  (Fluka, >96%) was poured onto the column and the eluate was collected. By drying at room temperature hydrated phases  $Ln[N(CN)_2]_3 \cdot xH_2O$  remained. These powders were heated in vacuo (ca. 1 Pa) up to 150 °C. After cooling to room temperature, the obtained microcrystalline powders were handled under argon to prevent hydration. The compounds show characteristic colors: white ( $Ln[N(CN)_2]_3$  with  $Ln = La, Ce, Eu$ ), light green ( $Pr[N(CN)_2]_3$ ), pink ( $Nd[N(CN)_2]_3$ ), and light yellow ( $Sm[N(CN)_2]_3$ ).

### 2.2. X-ray structure determination

Because single crystals were not obtained, the dicyanamides  $Ln[N(CN)_2]_3$  were characterized using powder diffractometry. Powder diffraction patterns of the salts were obtained on a STOE Stadi P diffractometer in Debye-Scherrer geometry. Due to the absorption of the rare-earth elements monochromated  $MoK\alpha_1$  radiation was used.

Owing to the similar appearance of the powder patterns of the six phases, they were supposed to be isotypic. In some diffractograms a small amount of the starting material  $Na[N(CN)_2]$  was detected. All patterns were indexed on the basis of orthorhombic cells with similar lattice parameters. The extinction conditions indicated  $Cmcm$ ,  $Cmc2_1$ , or  $C2cm$  as possible space groups.

The crystal structure of the compounds was determined by using the diffraction pattern of  $Nd[N(CN)_2]_3$ . Initially, the integrated intensities were extracted by the Le Bail method and subsequently used for a structure

solution with direct methods utilizing the program EXPO [39]. In the space group  $Cmcm$  all atom positions were localized immediately. With this structural model the structures of the rare-earth dicyanamides  $Ln[N(CN)_2]_3$  ( $Ln = La, Ce, Pr, Sm, Eu$ ) were refined by the Rietveld method using the program GSAS [40]. For  $Nd[N(CN)_2]_3$  the result of the Rietveld refinement is given in Fig. 1. Details of the structure refinements are listed in Table 1. The refined atomic coordinates of  $Ln[N(CN)_2]_3$  with  $Ln = La, Ce, Pr, Nd, Sm, Eu$  are given in Table 2. Details of all crystal structures reported in this paper may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, e-mail [crysdata@FIZ-karlsruhe.de](mailto:crysdata@FIZ-karlsruhe.de), by quoting the depository numbers CSD-391272 ( $La[N(CN)_2]_3$ ), CSD-391271 ( $Ce[N(CN)_2]_3$ ), CSD-391270 ( $Pr[N(CN)_2]_3$ ), CSD-391269 ( $Nd[N(CN)_2]_3$ ), CSD-391268 ( $Sm[N(CN)_2]_3$ ), and CSD-391267 ( $Eu[N(CN)_2]_3$ ).

### 2.3. Vibrational spectroscopy

Infrared spectra were recorded on a Bruker IFS 66v/S spectrometer scanning a range from 400 to 4000  $cm^{-1}$ . The samples were thoroughly mixed with dried KBr (5 mg sample, 500 mg KBr). Raman spectra were excited by a Bruker FRA 106/S module with an Nd-YAG laser ( $\lambda = 1064$  nm) scanning a range up to 3500  $cm^{-1}$ . All preparation procedures were performed in a glove box under an atmosphere of dried argon.

### 2.4. Thermal behavior

Differential scanning calorimetry (DSC) curves of the salts  $Ln[N(CN)_2]_3$  were recorded with a Mettler DSC 25

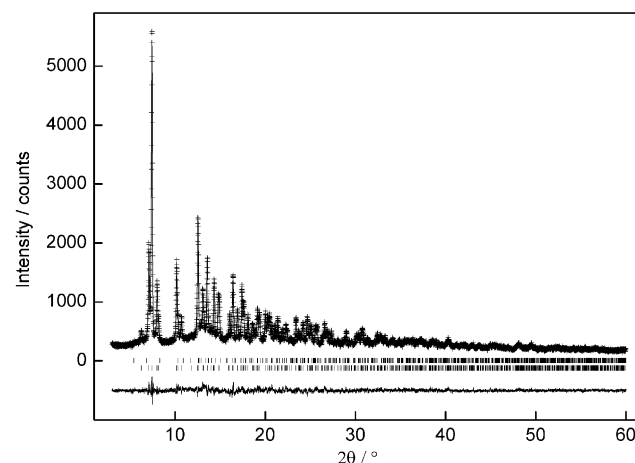


Fig. 1. Observed (crosses) and calculated (line) X-ray powder diffraction pattern as well as difference profile of the Rietveld refinement of  $Nd[N(CN)_2]_3$ . The upper row of vertical lines indicates possible peak positions of  $Nd[N(CN)_2]_3$ , the lower row indicates an impurity of  $Na[N(CN)_2]$ .

Table 1  
Crystallographic data of the rare-earth dicyanamides  $Ln[N(CN)_2]_3$  ( $Ln = La, Ce, Pr, Nd, Sm, Eu$ )

$Ln[N(CN)_2]_3$	$Ln = La$	$Ln = Ce$	$Ln = Pr$	$Ln = Nd$	$Ln = Sm$	$Ln = Eu$
Formula weight	337.04	338.25	339.04	342.37	348.49	350.09
Crystal system			Orthorhombic			
Space group			$Cmcm$ (no. 63)			
Radiation ( $\lambda$ , pm)			MoK $\alpha_1$ (70.93)			
<i>Lattice parameters</i>						
$a$ (pm)	799.88(9)	794.94(3)	790.45(5)	787.79(3)	781.30(5)	776.7(1)
$b$ (pm)	1158.2(1)	1152.15(4)	1146.19(6)	1144.59(4)	1138.64(6)	1135.1(1)
$c$ (pm)	1026.7(1)	1020.96(4)	1016.74(6)	1015.54(4)	1012.04(5)	1013.7(1)
$V$ ( $10^6$ pm $^3$ )	951.2(2)	935.08(6)	921.16(9)	915.71(6)	900.33(9)	893.7(2)
$Z$			4			
$\rho_c$ (g cm $^{-3}$ )	2.353	2.402	2.444	2.483	2.571	2.602
Profile range			$3^\circ \leq 2\theta \leq 60^\circ$			
No. of data points			5700			
No. of reflections	787	770	764	755	739	736
Positional parameters	21	21	21	21	21	21
Profile parameters	19	19	18	18	17	19
<i>R-values</i>						
$wR_p$	0.084	0.051	0.071	0.055	0.046	0.047
$R_p$	0.064	0.040	0.055	0.044	0.036	0.037
$R_F$	0.054	0.042	0.045	0.032	0.042	0.044

from room temperature to 500 °C (heating rate: 10 °C min $^{-1}$ ). Samples of Nd[N(CN) $_2$ ] $_3$  were heated up in glass ampoules under argon atmosphere to different temperatures between 200 and 400 °C. After cooling to room temperature, yellow–brown powders remained. The samples were characterized by X-ray powder diffractometry and IR spectroscopy.

### 3. Results

#### 3.1. Crystal structure

The rare-earth dicyanamides  $Ln[N(CN)_2]_3$  ( $Ln = La, Ce, Pr, Nd, Sm, Eu$ ) were found to be isotypic. According to the lanthanide contraction, the lattice parameters and volumes of the orthorhombic unit cells decrease with decreasing ionic radius of the rare-earth elements (Table 1).

The crystal structure consists of the rare-earth cations  $Ln^{3+}$  coordinated by dicyanamide anions  $[N(CN)_2]^-$ , which are planar and bent (Figs. 2 and 3).

There are two kinds of crystallographically different  $[N(CN)_2]^-$  anions occurring in a 2:1 ratio. The more abundant type of anions, labeled  $[N4-C2-N3-C2-N4]^-$ , are arranged in sheets perpendicular to [010]. The point symmetry of these ions is  $C_s$ , coming however close to  $C_{2v}$ . The distances and angles of the ions resemble closely those of other dicyanamide ions (Table 3) though they are not as accurate as single-crystal data.

The less abundant type of dicyanamide anions  $[N2-C1-N1-C1-N2]^-$ , forming sheets perpendicular to [001], show point symmetry  $C_{2v}$ , which is the ideal

symmetry of the  $[N(CN)_2]^-$  ions. Up to now, this ideal symmetry of the anions has only been observed for the room-temperature modification of  $Zn[N(CN)_2]_2$  [30]. However, in  $Zn[N(CN)_2]_2$  the anions with symmetry  $C_{2v}$  are disordered and thus, the high point symmetry is avoided. Since it cannot be fully excluded that the  $[N2-C1-N1-C1-N2]^-$  anions of the  $Ln[N(CN)_2]_3$  are disordered as well, we performed refinements with different disorder models. In three models one of the three atomic positions of the anion (C1, N1 or N2) was kept on the same special position but the other two positions were refined with the  $z$  coordinates being slightly smaller or larger than 1/4. In the fourth disorder model all three positions were refined with  $z$  slightly different from 1/4. The structure refinements with disordered anions showed no improvement of either  $R$ -values, distances or angles. Obviously, the low accuracy of the X-ray powder diffraction data caused by severe overlap of the diffraction peaks and the low scattering power of C and N compared to the rare-earth elements does not allow an unambiguous decision between order and disorder of these anions. When  $Zn[N(CN)_2]_2$  is cooled below  $-100^\circ\text{C}$ , a phase transition occurs which is accompanied by the locking of the disordered dicyanamide ions on sites with point symmetry  $C_s$ . In this work, temperature-dependent investigations of  $Ce[N(CN)_2]_3$  on an X-ray powder diffractometer (STOE Stadi P) were performed. However, during cooling from room temperature to  $-150^\circ\text{C}$ , no phase transition was observed.

In the crystal structure of  $Ln[N(CN)_2]_3$ , every N atom of both anions is bound to one rare-earth ion. The coordination of the cations within the structure of

Table 2  
Atomic coordinates and displacement factors (in pm<sup>2</sup>) of  $Ln[N(CN)_2]_3$   
( $Ln = La, Ce, Pr, Nd, Sm, Eu$ )

Atom	Wyckoff position	x	y	z	$U_{iso}^a$
La	4c	0	0.2896(3)	1/4	126(4)
Ce		0	0.2885(1)	1/4	134(2)
Pr		0	0.2891(1)	1/4	160(5)
Nd		0	0.2883(1)	1/4	137(2)
Sm		0	0.2873(1)	1/4	110(5)
Eu		0	0.2871(2)	1/4	109(3)
C1 (La)	8g	0.122(4)	0.596(2)	1/4	20(50)
C1 (Ce)		0.133(2)	0.590(1)	1/4	390(60)
C1 (Pr)		0.140(2)	0.590(1)	1/4	100(50)
C1 (Nd)		0.134(2)	0.589(1)	1/4	230(50)
C1 (Sm)		0.128(3)	0.588(1)	1/4	350(80)
C1 (Eu)		0.142(5)	0.611(3)	1/4	1110(200)
C2 (La)	16h	0.149(3)	0.135(2)	0.556(2)	20(50)
C2 (Ce)		0.147(1)	0.138(1)	0.554(1)	570(50)
C2 (Pr)		0.144(2)	0.141(1)	0.551(1)	210(40)
C2 (Nd)		0.137(1)	0.1399(8)	0.5498(9)	330(40)
C2 (Sm)		0.135(2)	0.140(1)	0.550(1)	430(60)
C2 (Eu)		0.149(3)	0.132(2)	0.562(3)	900(100)
N1 (La)	4c	0	0.495(3)	1/4	510(50)
N1 (Ce)		0	0.522(1)	1/4	120(60)
N1 (Pr)		0	0.511(1)	1/4	400(80)
N1 (Nd)		0	0.517(1)	1/4	280(60)
N1 (Sm)		0	0.512(1)	1/4	160(80)
N1 (Eu)		0	0.527(3)	1/4	140(100)
N2 (La)	8g	0.265(3)	0.625(2)	1/4	510(50)
N2 (Ce)		0.271(1)	0.627(1)	1/4	450(50)
N2 (Pr)		0.265(2)	0.634(1)	1/4	220(50)
N2 (Nd)		0.269(1)	0.6315(8)	1/4	250(40)
N2 (Sm)		0.267(2)	0.628(1)	1/4	240(60)
N2 (Eu)		0.288(4)	0.621(2)	1/4	370(100)
N3 (La)	8f	0	0.173(2)	0.491(2)	510(50)
N3 (Ce)		0	0.1597(8)	0.485(1)	150(40)
N3 (Pr)		0	0.161(1)	0.485(1)	100(40)
N3 (Nd)		0	0.1629(8)	0.4800(9)	140(40)
N3 (Sm)		0	0.167(1)	0.474(2)	190(50)
N3 (Eu)		0	0.164(2)	0.499(2)	30(80)
N4 (La)	16h	0.260(3)	0.135(2)	0.598(2)	510(50)
N4 (Ce)		0.265(1)	0.1335(7)	0.5923(8)	280(30)
N4 (Pr)		0.271(1)	0.1346(8)	0.601(1)	350(40)
N4 (Nd)		0.2718(9)	0.1354(6)	0.5939(6)	180(30)
N4 (Sm)		0.276(2)	0.1375(9)	0.595(1)	390(40)
N4 (Eu)		0.294(3)	0.146(2)	0.593(2)	1000(100)

<sup>a</sup>  $U_{iso}$  is defined as  $\exp(-8\pi^2 U_{iso} \sin^2 \theta / \lambda^2)$ .

$Ln[N(CN)_2]_3$  can thus be classified as tris-monodentate bridging (Scheme 1). A similar coordination situation has been found for the dicyanamides  $M[N(CN)_2]_2$  ( $M(II) = Mg, Cr, Mn, Co, Ni, Cu, Cd$ ) which exhibit a Rutile-type structure [12,25–28,31].

The rare-earth ions are surrounded by nine nitrogen atoms in the form of a tricapped trigonal prism. Four N4 and two N2 form the trigonal prism, while two N3

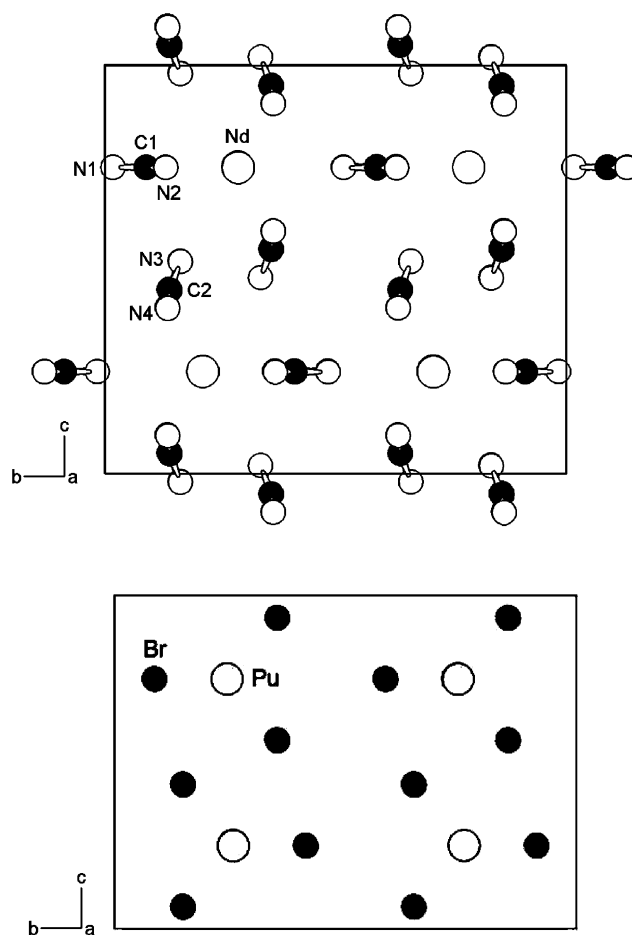


Fig. 2. Crystal structure of  $Nd[N(CN)_2]_3$  (top, Nd: white, C: black, N: small white circles) in comparison to that of  $PuBr_3$  (bottom, Pu: white, Br: black), view along [100].

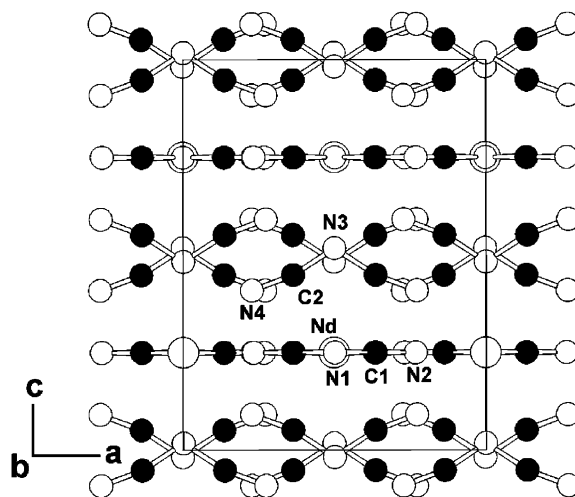
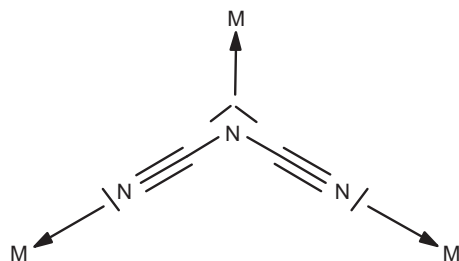


Fig. 3. Crystal structure of  $Nd[N(CN)_2]_3$ , view along [010] (Nd: white, C: black, N: small white circles). The structures of  $Ln[N(CN)_2]_3$  ( $Ln = La, Ce, Pr, Sm, Eu$ ) are isotypic.

Table 3

Bond distances (in pm) and angles (in°) in  $Ln[N(CN)_2]_3$  ( $Ln = La, Ce, Pr, Nd, Sm, Eu$ ).

$Ln$	La	Ce	Pr	Nd	Sm	Eu
$Ln-N1$ (1 ×)	238(4)	269(1)	255(2)	262(1)	256(2)	272(3)
$Ln-N2$ (2 ×)	268(2)	260(1)	257(1)	255.4(9)	257(1)	250(2)
$Ln-N3$ (2 ×)	282(3)	282(1)	281(1)	274(1)	265(2)	288(2)
$Ln-N4$ (4 ×)	262(2)	262.3(8)	252(1)	255.1(7)	250(1)	238(2)
$C1-N1$	152(4)	132(2)	143(2)	134(1)	132(2)	146(4)
$C1-N2$	120(4)	117(2)	111(2)	117(1)	118(2)	114(5)
$C2-N3$	144(2)	139(1)	134(1)	132.0(9)	134(1)	137(2)
$C2-N4$	98(3)	102(1)	113(1)	115(1)	119(2)	118(3)
$N1-C1-N2$	146(4)	165(2)	169(2)	167(2)	162(3)	145(4)
$N3-C2-N4$	161(3)	170(2)	173(2)	167(1)	162(2)	154(3)
$C1-N1-C1$	80(3)	107(2)	102(2)	104(2)	99(3)	99(4)
$C2-N3-C2$	112(3)	116(2)	117(2)	110(1)	104(2)	116(3)

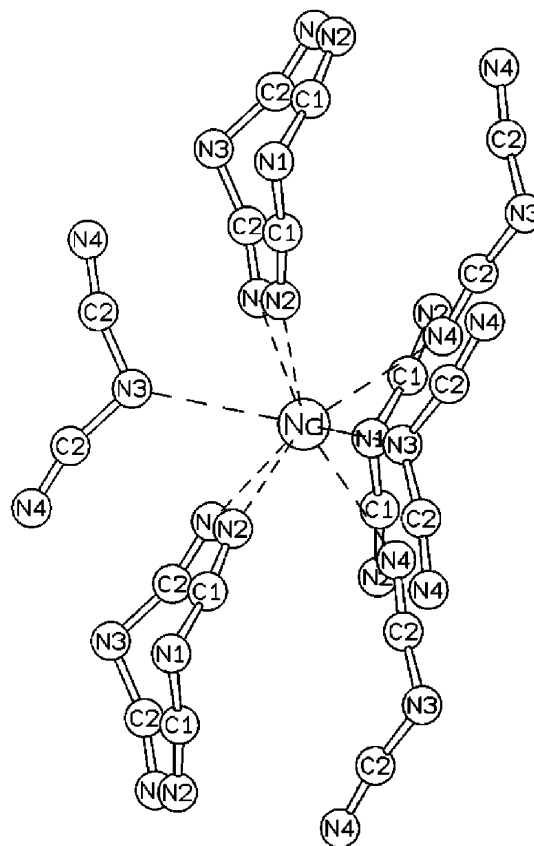


Scheme 1.

and N1 cap the prism planes (Fig. 4). The coordination of the  $Ln^{3+}$  ions is realized by all three N atoms of both types of dicyanamide ions. The distances between  $Ln$  and N3 in all  $Ln[N(CN)_2]_3$  ( $Ln = La, Ce, Pr, Nd, Sm, Eu$ ) are slightly longer than those to the other N atoms. Similar coordination polyhedra of dicyanamide ions were found for the divalent metal ions in  $Ba[N(CN)_2]_2$  [12] and the isotopic compound  $Pb[N(CN)_2]_2$  [14]. In nitrides the rare-earth ions are usually bound to fewer N atoms, e.g., in the nitrides  $LnN$  ( $Ln = La-Nd, Sm-Lu$ ) [41,42] they are coordinated to six neighbors, in  $Ln_3Si_6N_{11}$  ( $Ln = Ce, Pr, Sm$ ) [43,44] to eight, and in  $Ln_3B_2N_4$  ( $Ln = La-Nd$ ) [45] both to six and eight. The  $Ln[N(CN)_2]_3$  structure type can be derived from that of  $PuBr_3$ , which is frequently encountered for rare-earth halogenides [46,47], by replacing the  $Br^-$  by  $[N(CN)_2]^-$  ions (Fig. 2).

### 3.2. Spectroscopic and thermal behavior

The vibrational spectra (Fig. 5) of anhydrous  $La[N(CN)_2]_3$  show the typical signals of the  $[N(CN)_2]^-$  ion [48,49]. The splitting of some signals can be explained by the existence of two crystallographically

Fig. 4. Coordination sphere of the  $Nd^{3+}$  ion in  $Nd[N(CN)_2]_3$ .

different anions which occur in a ratio of 2:1. A similar splitting was observed in the IR spectra of  $M(II)[N(CN)_2]_2$  ( $M = Ba, Pb$ ) where two crystallographically different anions occur as well.

The dicyanamide ions  $[N(CN)_2]^-$  of the alkali dicyanamides  $M(I)[N(CN)_2]$  ( $M = Na, K, Rb$ ) trimerize forming tricyanomelaminates ions  $[C_6N_9]^{3-}$  [6,7,49]. Depending on the heating conditions, the  $[N(CN)_2]^-$  ions of  $Li[N(CN)_2]$  either trimerize as well or polymerize [50]. For the dicyanamides  $M(II)[N(CN)_2]_2$  ( $M(II) = Mg, Ca, Sr, Ba, Pb$ ) which have divalent cations no analogous formation of the respective tricyanomelaminates  $M(II)_3[C_6N_9]_2$  was found. Instead, oligomerization of their anions seems to take place [12,14].

Obviously, the nature and the ionic radius of the cation seems to have a significant influence on the thermolysis of the dicyanamides. In this context, the thermal behavior of a dicyanamide with a trivalent cation is of interest and was studied for  $La[N(CN)_2]_3$ .

DSC curves of the compounds  $Ln[N(CN)_2]_3$  ( $Ln = Ce, Nd, Eu$ ) show broad exothermic peaks between 300 and 450 °C. During heating above 400 °C, the samples become X-ray amorphous. Accordingly, the occurring transformations are irreversible and, thus, the further

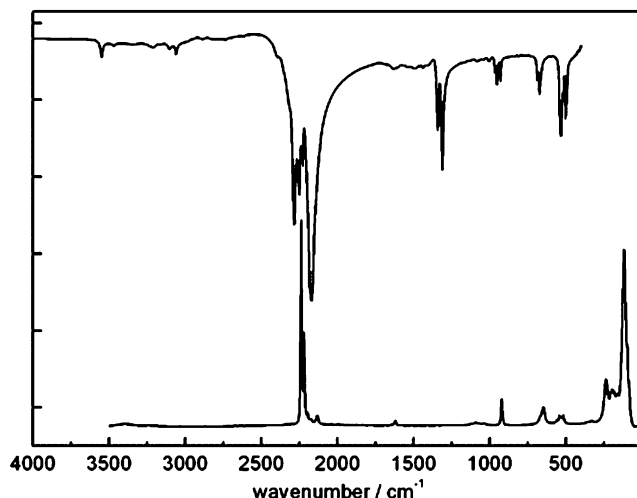


Fig. 5. IR (top) and Raman (bottom) spectra of  $\text{La}[\text{N}(\text{CN})_2]_3$ .

characterization of the reaction products by X-ray diffractometry is not possible.

The IR spectrum of a sample of  $\text{La}[\text{N}(\text{CN})_2]_3$  that was heated up to  $400^\circ\text{C}$  shows a sharp peak at  $804\text{ cm}^{-1}$  which cannot be observed in the spectrum of pure and unreacted  $\text{La}[\text{N}(\text{CN})_2]_3$ . This peak is observed in the IR spectra of salts containing *s*-triazine ring systems, as found for instance in the isolated tricyanomelaminato ions  $[\text{C}_6\text{N}_9]^{3-}$ .

#### 4. Conclusion

The compounds  $\text{Ln}[\text{N}(\text{CN})_2]_3$  ( $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}$ ) represent the first dicyanamides with trivalent cations as well as the first rare-earth dicyanamides. The dicyanamides  $\text{Ln}[\text{N}(\text{CN})_2]_3$  ( $\text{Ln} = \text{Gd}–\text{Lu}$ ) of the heavier rare-earth elements crystallize in another structure type, which will be presented in a forthcoming paper.

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#### References

- [1] S.R. Batten, K.S. Murray, *Coord. Chem. Rev.* 246 (2003) 103.
- [2] M.G. Down, M.J. Haley, P. Hubberstey, R.J. Pulham, A.E. Thunder, *J. Chem. Soc., Chem. Comm.* (1978) 52.
- [3] M.G. Down, M.J. Haley, P. Hubberstey, R.J. Pulham, A.E. Thunder, *J. Chem. Soc., Dalton Trans.* (1978) 1407.
- [4] M. Becker, J. Nuss, M. Jansen, *Z. Anorg. Allg. Chem.* 626 (2000) 2505.
- [5] M. Becker, M. Jansen, *Solid State Sci.* 2 (2000) 711.
- [6] B. Jürgens, E. Irran, J. Schneider, W. Schnick, *Inorg. Chem.* 39 (2000) 665.
- [7] E. Irran, B. Jürgens, W. Schnick, *Chem. Eur. J.* 7 (2001) 5372.
- [8] P. Starynowicz, *Acta Crystallogr. C* 47 (1991) 2198.
- [9] M.A. Bredig, *J. Am. Chem. Soc.* 64 (1942) 1730.
- [10] U. Berger, W. Schnick, *J. Alloys Compounds* 206 (1994) 179.
- [11] K.G. Strid, N.G. Vannerberg, *Naturwissenschaften* 52 (1965) 258.
- [12] B. Jürgens, E. Irran, W. Schnick, *J. Solid State Chem.* 157 (2001) 241.
- [13] X. Liu, A. Decker, D. Schmitz, R. Dronskowski, *Z. Anorg. Allg. Chem.* 626 (2000) 103.
- [14] B. Jürgens, H.A. Höpfe, W. Schnick, *Solid State Sci.* 4 (2002) 821.
- [15] Y.-J. Shi, X.-T. Chen, Y.-Z. Li, X.-Z. You, *New J. Chem.* 26 (2002) 1711.
- [16] D. Britton, Y.M. Chow, *Acta Crystallogr. B* 33 (1977) 697.
- [17] D. Britton, *Acta Crystallogr. C* 46 (1990) 2297.
- [18] M. Becker, M. Jansen, *Acta Crystallogr. C* 57 (2001) 347.
- [19] M. Becker, H. Bender, M. Jansen, L. Kienle, W. Assenmacher, *J. Phys. Chem. Solids* 62 (2001) 1431.
- [20] G. Baldinozzi, B. Malinowska, M. Rakib, G. Durand, *J. Mater. Chem.* 12 (2002) 268.
- [21] X. Liu, P. Mueller, P. Kroll, R. Dronskowski, *Inorg. Chem.* 41 (2002) 4259.
- [22] H. Liu, W. Klein, H. Bender, M. Jansen, *Z. Anorg. Allg. Chem.* 628 (2002) 4.
- [23] M. Becker, M. Jansen, *Z. Anorg. Allg.* 626 (2000) 1639.
- [24] X. Liu, P. Müller, P. Kroll, R. Dronskowski, W. Wilmann, R. Conradt, *Chem. Phys. Chem.* 4 (2003) 725.
- [25] J.L. Manson, C.R. Kmety, A.J. Epstein, J.S. Miller, *Inorg. Chem.* 38 (1999) 2552.
- [26] M. Kurmoo, C.J. Kepert, *New J. Chem.* 22 (1998) 1515.
- [27] S.R. Batten, P. Jensen, B. Moubaraki, K.S. Murray, R. Robson, *Chem. Commun.* (1998) 439.
- [28] J.L. Manson, C.R. Kmety, Q.-Z. Huang, J.W. Lynn, G.M. Bendele, S. Pagola, P.W. Stephens, L.M. Liable-Sands, A.L. Rheingold, A.J. Epstein, J.S. Miller, *Chem. Mater.* 10 (1998) 2552.
- [29] J.L. Manson, D.W. Lee, A.L. Rheingold, J.S. Miller, *Inorg. Chem.* 37 (1998) 5966.
- [30] P. Jensen, S.R. Batten, G.D. Fallen, B. Moubaraki, K.S. Murray, D.J. Price, *Chem. Commun.* 177 (1999).
- [31] B. Jürgens, E. Irran, H.A. Höpfe, W. Schnick, *Z. Anorg. Allg. Chem.* 630 (2004) 219.
- [32] Y. Hashimoto, M. Takahashi, S. Kikkawa, F. Kanamaru, *Chem. Lett.* (1994) 1963.
- [33] Y. Hashimoto, M. Takahashi, S. Kikkawa, F. Kanamaru, *J. Solid State Chem.* 114 (1995) 592.
- [34] O. Reckeweg, F.J. DiSalvo, *Z. Anorg. Allg. Chem.* 629 (2003) 177.
- [35] R. Srinivasan, M. Ströbele, H.-J. Meyer, *Inorg. Chem.* 42 (2003) 3406.
- [36] V.V. Skopenko, A.A. Kapshuk, F.G. Kramarenko, *Dopov. Akad. Nauk Ukr. RSR, Ser. B: Geol. Khim. Biol. Nauk.* 4 (1982) 48.
- [37] A.A. Kaphsuk, V.V. Skopenko, *Koord. Khim.* 12 (1986) 380.
- [38] A.-Q. Wu, F.-K. Zheng, W.-T. Chen, L.-Z. Cai, G.-C. Guo, J.-S. Huang, Z.-C. Dong, Y. Takano, *Inorg. Chem.* 43 (2004) 4839.
- [39] A. Altomare, M.C. Burla, M. Camalli, B. Carrozzini, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Rizzi, *J. Appl. Crystallogr.* 32 (1999) 339.



- [40] A.C. Larson, R.B. von Dreele, General structure analysis system, Report LAUR 86-748, Los Alamos National Laboratory, Los Alamos, NM, 1990.
- [41] W. Klemm, G. Winkelmann, *Z. Anorg. Allg. Chem.* 288 (1956) 87.
- [42] P. Ettmayer, J. Waldhart, A. Vendl, *Z. Anorg. Allg. Chem.* 317 (1962) 25.
- [43] T. Schlieper, W. Schnick, *Z. Anorg. Allg. Chem.* 621 (1995) 1535.
- [44] M. Woike, W. Jeitschko, *Inorg. Chem.* 34 (1995) 5105.
- [45] O. Reckeweg, H.-J. Meyer, *Z. Anorg. Allg. Chem.* 625 (1999) 866.
- [46] W.H. Zachariasen, *Nat. Nucl. Energy Ser. Div. Iv. Sec. B* 14 (1949) 1473.
- [47] D. Hake, W. Urland, *Z. Anorg. Allg. Chem.* 586 (1990) 99.
- [48] M. Kuhn, R. Mecke, *Chem. Ber.* 94 (1961) 3010.
- [49] B. Jürgens, W. Milius, P. Morys, W. Schnick, *Z. Anorg. Allg. Chem.* 624 (1998) 91.
- [50] A.P. Purdy, E. Houser, C.F. George, *Polyhedron* 16 (1997) 3671.