Synthesis and Structure of the New Compound $La_2O(CN_2)_2$ Possessing an Interchanged Anion Proportion Compared to the Parent $La_2O_2(CN_2)$

Synthese und Kristallstruktur der neuen Verbindung $La_2O(CN_2)_2$ mit einem vertauschten Anionenverhältnis gegenüber der Bezugsverbindung $La_2O_2(CN_2)$

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Abstract. $La_2O(CN_2)_2$ was synthesized from a 1:1:2 molar reaction mixture of $LaCl_3$, LaOCl, and $Li_2(CN_2)$ at 650 °C. Well developed single crystals were grown from a LiCl-KCl flux. The crystal structure was refined as monoclinic (space group $C2/c$, Z = 2, a = 13.530(2) Å, b = 6.250(1) Å, c = 6.1017(9) Å, β = 104.81(2)°) from single crystal X-ray diffraction data. The La^{3+} and $(CN_2)^{2-}$ ions in the crystal structure of $La_2O(CN_2)_2$ can be compared to Fe^{3+} and S_2^{2-} ions in the cubic pyrite structure, being arranged like in a distorted NaCl type structure with their centers of gravity. In addition, the O^{2-} ions in $La_2O(CN_2)_2$ are occupying 1/4 of the tetrahedral voids formed by the arrangement of metal ions.

Keywords: Lanthanum; Oxides; Cyanamides; Carbodiimides

Introduction

Research interest in C-N containing compounds of the lanthanides has been growing recently with the discovery of new $(NCN)^{2-}$ compounds such as $Eu(CN_2)$ [1], $LiEu_2(CN_2)I_3$, $LiEu_4(CN_2)_3I_3$ [2], $LnCl(CN_2)$ with Ln = La, Ce, Pr [3], and $Ln_2Cl(CN_2)N$ with Ln = La, Ce [4]. Stimulated by research on lanthanide compounds with BN_x anions [5], referred as to nitridoborates (in agreement with the designation of oxoborates) and after the discovery of oxide nitridoborates of the formula type $Ln_6O_6(BN_3)$ with Ln = La [6], Pr, Nd [7], we have now synthesized the new *oxide di-nitridocarbonate* $La_2O(CN_2)_2$. The authors note here that the designation of a $(NCN)^{2-}$ containing compound as cyanamide or carbodiimide is sometimes ambiguous. The composition of $La_2O(CN_2)_2$ is related to the known compound $La_2O_2(CN_2)$, marked by an interchanged number of anions.

The known lanthanide (Ln) compounds with the $Ln_2O_2(CN_2)$ composition were characterized from X-ray powder diffraction studies reported by Hashimoto et al. [8]. $La_2O_2(CN_2)$ was originally synthesized by treating La_2O_3 with flowing NH_3 at 950 °C for 12 h in a graphite boat. The carbon in the obtained $La_2O_2(CN_2)$ was considered to originate from the graphite boat. All the homologous $Ln_2O_2(CN_2)$ compounds were synthesized following the same procedure, and their crystal structures have been reported as tetragonal for Ln = La and trigonal for Ln = Ce, Pr, Nd, Sm, Eu, and Gd [9]. Both types of structures are represented by an alternating sequence of $[La_2O_2]^{2+}$ and $(CN_2)^{2-}$ layers along their crystallographic c-axis. For tetragonal $La_2O_2(CN_2)$ the alignment of the $(CN_2)^{2-}$ ions has been reported perpendicular to the c-axis, and for trigonal $Ln_2O_2(CN_2)$ the $(CN_2)^{2-}$ ions have been refined parallel to the c-axis.

Lanthanide doped $La_2O_2(CN_2)$:Ln compounds with Ln = Eu^{2+} or Pr^{3+} were studied for their luminescence properties [10−12]. The presence of $[La_2O_2]^{2+}$ layers in the structure of $La_2O_2(CN_2)$:Ln compounds has been accounted for the efficient luminescence behaviour [13].

In the course of our studies of metathesis reactions [14] between lanthanide chlorides and lithium cyanamide, we have synthesized new $(NCN)^{2-}$ containing compounds. With the employment of lanthanum oxide chloride, we here report the synthesis for the new $La_2O(CN_2)_2$, a route that has been analogously applied for the synthesis of $La_6O_6(BN_3)$ [6].

Experimental Section

Preparation methods

All reactions were performed in fused silica tubes or in sealed copper ampoules fused in silica tubes. Copper ampoules were obtained from a copper tube that was cut into pieces of 5-6 cm length, cleaned with HCl, and rinsed in distilled water before being air dried at 100 °C in an oven. The pieces were welded under Ar in an electric arc, first from one side, and then from the other side after loading with the reaction mixture. The reaction containers were

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fused in evacuated silica tubes and heated in a commercial (Carbolite) furnace up to temperatures between 500 and 650 °C, using heating and cooling durations of about 24 h.

$La_2O(CN_2)_2$ was synthesized from mixtures of $LaCl_3$, LaOCl, and $Li_2(CN_2)$. $LaCl_3$ was obtained by the ammonium chloride route from La_2O_3 (Ventron, 99.9 %) and NH_4Cl (Merck, 99.8 %, sublimed) [15]. LaOCl was synthesized according to [6], and $Li_2(CN_2)$ was synthesized as described in [4]. The purity of all phases was controlled by X-ray powder diffraction.

Synthesis of $La_2O(CN_2)_2$

$La_2O(CN_2)_2$ was first obtained as a minor phase, when mixtures with different stoichiometries of $LaCl_3$ and $Li_2(CN_2)$ were reacted in silica ampoules at 500−650 °C. The oxygen contamination may have been due to water or oxygen impurities of the employed $LaCl_3$ or from the wall of the silica tube. Yields were increased, when oxygen sources were introduced into the reaction externally. Therefore, a homogeneous mixture of $LaCl_3$, LaOCl, and $Li_2(CN_2)$ was reacted in a 1:1:2 molar ratio at 650 °C and yielded a light brown powder, later known to be $La_2O(CN_2)_2$, besides LiCl.

$$LaCl_3 + LaOCl + 2\ Li_2(CN_2) \rightarrow La_2O(CN_2)_2 + 4\ LiCl \qquad (1)$$

$La_2O(CN_2)_2$ appeared quite stable against air and water, so that water could even be used to wash off LiCl from the product.

In a separate attempt, the same mixture (total mass: 225 mg) was combined with a LiCl-KCl mixture (29 mg) and reacted similarly as in reaction (1). The mixture was heated in a sealed copper ampoule at 600 °C for ten days before being cooled down slowly to 300 °C first and then to room temperature. From this reaction well developed needle-shaped colourless crystals were grown and afterwards selected for X-ray single crystal diffraction studies.

X-ray Diffraction

All phase analyses were done by X-ray powder diffraction. The powder patterns were recorded on a StadiP diffractometer (STOE, Darmstadt), using germanium monochromated Cu-$K_{\alpha 1}$ radiation (λ = 1.540598 Å) and a position sensitive X-ray detector (opening angle: $2\theta = 6°$). The powdered samples of $La_2O(CN_2)_2$ were washed in ethanol, dried overnight, and placed in between two mylar foils for the X-ray powder pattern measurement. Routine analyses were done in the 2θ range between 10 and 60°. As a new structure was evident from the powder pattern, a measurement in the 2θ range of 5−130° was performed with step increments of 0.2° and exposure periods of 120 seconds. The powder pattern was indexed using Louer's algorithm (DICVOL) consistent with a C-centred monoclinic cell (a = 13.507(2) Å, b = 6.2432(9) Å, c = 6.1002(7) Å, β = 104.833(8)°, V = 497.3(2) Å^3) for 75 selected peaks. The composition of the title compound was first derived from a Rietveld refinement. The refined composition of $La_2O(CN_2)_2$ was the key information for the straight forward synthesis. In favour of the better accuracy, we here present the single crystal structure refinement studies only.

Suitable colourless transparent single crystals of $La_2O(CN_2)_2$ were selected under a microscope and mounted on the tips of glass fibres for X-ray diffraction studies. Single crystal measurements were performed on an IPDS (STOE, Darmstadt) X-ray diffractometer using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å).

Table 1 Crystallographic details and structure refinement data of $La_2O(CN_2)_2$.

Space group (no.), Z	C2/c (15), 4
Unit cell dimension (in Å)	a = 13.530(2), b = 6.250(1), c = 6.1017(9), β = 104.81(2)°
Cell volume (in Å^3)	498.9(1)
Density calc. (in g cm^{-3})	4.978
Molecular weight (in g·mol^{-1})	373.88
Crystal appearance	transparent colourless, needle shaped
Crystal size (in·mm^3)	0.1 x 0.04 x 0.04
Diffractometer	STOE, IPDS
Radiation, Temperature	Mo-K_α (λ = 71.073 pm), graphite monochromator, 293(2) K
Range: θ	5.27 to 30.35°
Range: h, k, l	$-19 \leq h \leq 19$, $-8 \leq k \leq 8$, $-8 \leq l \leq 8$
Data correction	Lorentz, polarisation and absorption
μ (in mm^{-1})	16.78
Unique reflections	734
Collected reflections ($F_0 > 2\sigma(F_0)$)	4289
Parameters refined	42 (all atoms refined anisotropically)
R indices [a] (all data)	R1 = 0.0283, wR2 = 0.0679
Final R indices [a] [$I > 2\sigma(I)$]	R1 = 0.0266, wR2 = 0.0671
GooF (all reflections)	1.141
Res. peak: max.; min. (in e/Å^3)	3.17; −1.19

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

Table 2 Atomic coordinates and isotropic-equivalent displacement parameters (in Å^2) for $La_2O(CN_2)_2$.

Atom	Wyckoff position	x	y	z	U_{eq} [a]
La1	8 f	0.10072(2)	0.21443(3)	0.07542(4)	0.0096(1)
O1	4 e	0	0.0260(6)	$^3/_4$	0.0118(8)
N1	8 f	0.2915(3)	0.3423(7)	0.2473(6)	0.0143(6)
N2	8 f	0.0923(3)	0.6174(6)	0.9698(6)	0.0133(7)
C1	8 f	0.1530(3)	0.2739(6)	0.6112(8)	0.0111(8)

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

Table 3 Bond lengths (in Å) and N-C-N bond angle (in °) in $La_2O(CN_2)_2$.

La1−O1	2.409(2)	La1−N2	2.655(3)
La1−O1	2.448(2)	La1−N2	2.762(4)
La1−N1	2.650(4)	C1−N1	1.227(6)
La1−N1	2.756(3)	C1−N2	1.233(6)
La1−N1	2.811(4)	N1−C1−N2	176.1(5)
La1−N2	2.595(4)		

Some crystallographic data and measurement parameters are provided in Table 1. The atomic positions along with the isotropic-equivalent displacement parameters are given in Table 2. Selected bond distances and the N-C-N bond angle are shown in Table 3. Details on the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, Germany, D-76344 Eggenstein-Leopoldshafen (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number 391255 for $La_2O(CN_2)_2$.

Results and Discussion

As $La_2O_2(CN_2)$ is known for a long time, the new $La_2O(CN_2)_2$ represents the second composition in this system.

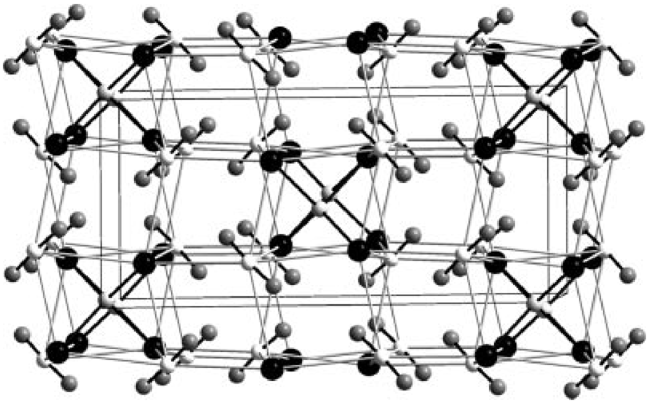

Fig. 1 Unit cell of $La_2O(CN_2)_2$. Lanthanum atoms are shown black, carbon atoms white, nitrogen atoms dark grey, and oxygen atoms light grey.

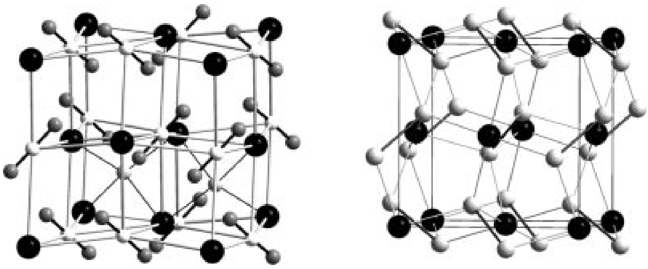

Fig. 2 Relation of cubic FeS_2 (Pyrite) with a substructure of $La_2O(CN_2)_2$ in which the oxide ions occupy $^1/_4$ of the tetrahedral voids. Metal atoms are shown black, carbon atoms white, nitrogen atoms dark grey, sulphur and oxygen atoms light grey.

The synthesis route employed here to obtain $La_2O(CN_2)_2$ (1) may be also considered for (doped) $La_2O_2(CN_2)$ compounds following (2) instead of the former synthesis where graphite serves as a carbon source for the $(CN_2)^{2-}$ formation.

$$2\ LnOCl + Li_2(CN_2) \rightarrow Ln_2O_2(CN_2) + 2\ LiCl \qquad (2)$$

This synthesis may also be useful for a reinvestigation of the crystal structure of $La_2O_2(CN_2)$, as to take a closer look at the reported disorder of NCN groups in this structure.

The crystal structure of $La_2O(CN_2)_2$ shown in Figure 1 may occur complicated on the first glance. However, the arrangements of La^{3+} and $(CN_2)^{2-}$ ions can be well derived from the positions of ions in a NaCl type structure. In addition, the oxygen atoms of $La_2O(CN_2)_2$ occupy 1/4 of the tetrahedral voids created by the La^{3+} ions. Such relations with the NaCl structure are frequently used to explain the structures of pyrite (FeS_2) or CaC_2. A comparison of a section of the $La_2O(CN_2)_2$ structure with the cubic pyrite (FeS_2) structure [16] having $S_2{}^{2-}$ ions similar to the linear $(CN_2)^{2-}$ ions in $La_2O(CN_2)_2$ is illustrated in Figure 2. For better understanding the structure principle, the lanthanum ions are connected with carbon instead of nitrogen atoms of the $(CN_2)^{2-}$ units in the Figures 1 and 2.

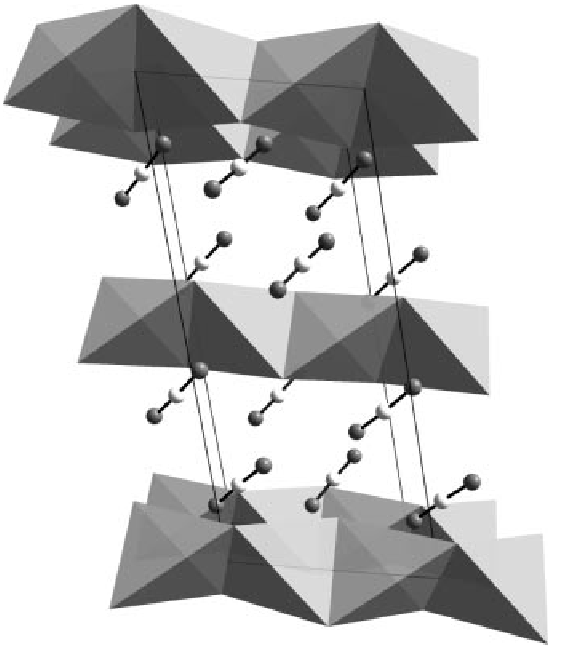

Fig. 3 Perspective view of edge sharing $[OLa_{4/2}]$ tetrahedral chains in the structure of $La_2O(CN_2)_2$ running along the *c* axis.

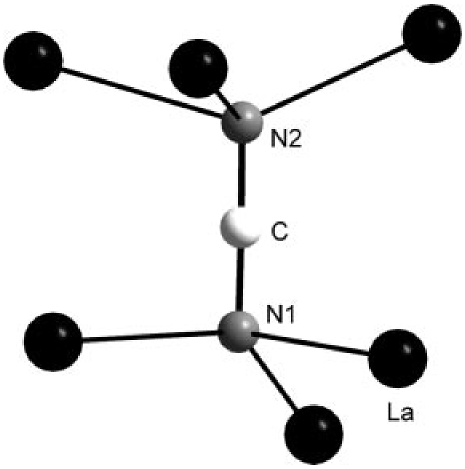

Fig. 4 Coordination environment around the $(CN_2)^{2-}$ ion in $La_2O(CN_2)_2$.

In a different view, the crystal structure of $La_2O(CN_2)_2$ contains one-dimensional chains composed of edge sharing $[OLa_{4/2}]$ tetrahedra running along the *c*-axis. A perspective view of the cyanamide ions being situated in between the chains of tetrahedra is shown in Figure 3.

The $(N\text{-}C\text{-}N)^{2-}$ ion in $La_2O(CN_2)_2$ has two crystallographically distinct nitrogen positions. However, with calculated values of 1.227(6) Å and 1.233(6) Å, the C−N bond lengths do not differ much from each other, meaning that the $(N\text{-}C\text{-}N)^{2-}$ ion is clearly closer to a carbodiimide than to a cyanamide. A symmetrical $(N\text{-}C\text{-}N)^{2-}$ ion may also be regarded from the drawing in Figure 4 where three La^{3+} ions contact the $(N\text{-}C\text{-}N)^{2-}$ ion from both sides, with

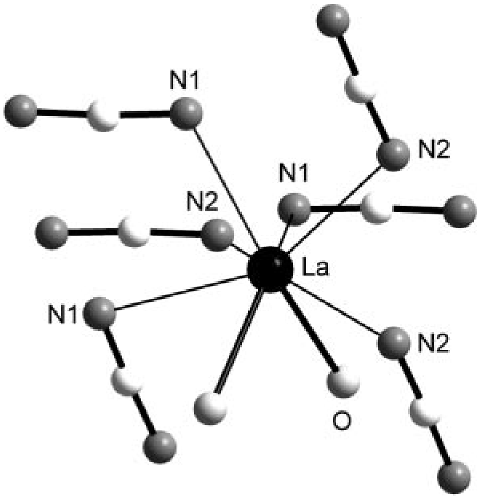

Fig. 5 Coordination environment of the La^{3+} ion in $La_2O(CN_2)_2$.

slightly deviating La−N bond lengths given in Table 3. The average La−O bond length of 2.428(5) Å in $La_2O(CN_2)_2$ is slightly longer than the corresponding value of 2.39 Å reported for $La_2O_2(CN_2)$. The La atom is eight-coordinated being situated in a polyhedron formed by six nitrogen atoms (3 x N1 and 3 x N2) of the cyanamide ions and two oxide ions as shown in Figure 5.

The infrared spectrum (Perkin Elmer FT-IR spectrometer) of $La_2O(CN_2)_2$ (in a KBr pellet) also suggests the presence of a carbodiimide ion with a strong absorption peak ν_{as} at 1979 cm^{-1} and strong δ peaks at 661 and 684 cm^{-1} for $(CN_2)^{2-}$. Corresponding characteristic signals were reported at 1950 cm^{-1} and 670 cm^{-1} for $La_2O_2(CN_2)$ [8].

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