

CRYSTAL STRUCTURE OF $\{[La_2(CNCH_2COO)_6(H_2O)_4]\cdot H_2O\}_n$ COMPLEXAna Lazarescu^{a*}, Elena Melnic^b, Sergiu Shova^a, Victor Kravtsov^b, Constantin Turta^a^aInstitute of Chemistry of Academy of Sciences of Moldova, 3, Academiei str., Chisinau MD-2028, Republic of Moldova^bInstitute of Applied Physics of Academy of Sciences of Moldova, 5, Academiei str., Chisinau, MD-2028, Republic of Moldova

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Abstract. The lanthanum(III) cyanoacetate complex of formula $\{[La_2(CNCH_2COO)_6(H_2O)_4]\cdot H_2O\}_n$ (**1**), has been prepared and characterized by X-ray diffraction analysis. Compound crystallizes in the triclinic centrosymmetric space group *P*-1 (No.2), $a=8.997(5)$ Å, $b=9.251(5)$ Å, $c=9.728(5)$ Å, $\alpha=67.849(5)^\circ$, $\beta=84.224(5)^\circ$, $\gamma=81.351(5)^\circ$. Single-crystal X-ray diffraction study reveals that crystals of **1** exhibits one-dimensional coordination polymer structure, which is composed of cyanoacetate bridged lanthanum(III) ions. The O₉ coordination surrounding of La cation is completed by oxygen atoms of six carboxylate ligands that are coordinated in the bidentate bridging and tridentate-chelating bridging mode and two water molecules. The cations are bridged in a polymeric chain by four exo-bidentate cyanoacetate ligands or through μ_2 -O function of two other chelato-bridging cyanoacetate ligands. The La...La separation along the polymer is equal to 4.754(3) Å and 4.608(2) Å.

Keywords: coordination polymers, lanthanum (III), cyanoacetic acid, crystal structure.

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Introduction

The synthesis of functional rare-earth coordination polymers with various N- and / or O-donor ligands has attracted increasing interest, due to their various topologies [1-3] and potential applications as optical, electronic and magnetic materials [4-7].

The carboxylate ligands are attractive candidates for construction of the polymeric networks due to their versatile functions as bridges or terminal groups, which lead to generation of dimers [8, 9], 1D chains [10], 2D-layers [11], and 3D- polymeric structures [12].

However, investigation of lanthanide complexes with cyanoacetic acid anion as ligand is very scarce [13,14]. Our previous investigations of 3d and 4f metal complexes with cyanoacetate anions have demonstrated that copper(II) ion has $\{O_4^{(carbox.)}N^{(CN)}\}$ coordination node, while neodymium(III) ion – $\{O_7^{(carbox./O_2(H_2O))}\}$, respectively [15, 16]. The study of magnetic properties of gadolinium(III) cyanoacetate complex has shown that external magnetic field induces two slow relaxation processes, while heat capacity and direct current susceptibility measurements at very low temperatures has indicated strong single ion anisotropy, due to the Kramer's doublet of the ground state [17].

In continuation of our research on the use of cyanoacetic acid with both O- and N- potential donor atoms as a ligand for 4f cations [16, 17] and d-block transition metal [15], we have synthesized and structurally characterized the $\{[La_2(CNCH_2COO)_6(H_2O)_4]\cdot H_2O\}_n$ compound by single crystal X-ray method.

Experimental

Synthesis

All reagents of analytical grade were commercially purchased and used without further purification. Elemental analyses (C, H, N) were performed on a Elemental Analyzer vario EL(III). The lanthanum content in the complex was determined gravimetrically as stable oxide by precipitating lanthanide (III) ions with ammonium hydroxide [18].

$\{[La_2(CNCH_2COO)_6(H_2O)_4]\cdot H_2O\}_n$ (**1**). Solution of cyanoacetic acid (0.51 g, 6 mmol) in water (10 mL) was added to La₂O₃ (0.32 g, 1 mmol). After stirring the resulting solution was passed through a glass filter. The filtrate was stored at room temperature for some weeks, whereupon the suitable for X-ray analysis colorless crystals of the product appeared. The crystals were collected by filtration, dried under reduced pressure and kept in desiccator. Yield: 52 %. Anal. found (calc.)%: for $\{C_9H_{12}N_3O_9La\}_n$, C, 23.99 (24.29); H, 2.43 (2.69); N 9.07 (9.45); La, 30.89 (31.22). IR data (Nujol, cm⁻¹): 3545br, 3430br, 3250br, 2265sh, 1705s, 1600vs, 1580s, 1545s, 1410s, 1264m, 1195m, 955w, 930m, 915m, 700m, 570m, 515m.

Physical measurements

IR spectrum of polycrystalline sample was recorded on Perkin Elmer spectrum 100 FT IR Spectrometer in the range of 4000-400 cm⁻¹.

X-ray crystallography

The X-ray data for **1** were collected at room temperature on an Oxford Diffraction Xcalibur diffractometer equipped with CCD area detector and a graphite monochromator utilizing MoK α radiation. The crystals were placed at 40 mm from the CCD detector. The data were processed using the CrysAlis package of Oxford Diffraction [19]. The final unit cell dimensions were obtained and refined on an entire data set. The structures were solved by direct methods using SHELX-97 program package [20] and refined with full-matrix least squares method with anisotropic thermal parameters for the non-hydrogen atoms. The C(sp²)-bound H atoms were placed in calculated positions and were treated

using a riding model approximation with $U_{iso}(H) = 1.2U_{eq}(C)$, while the hydrogen atoms of water molecules were refined with isotropic displacement parameter $U_{iso}(H) = 1.5U_{eq}(O)$ using DFIX restrain instruction. The figures were produced using MERCURY [21]. The X-ray data and details of the refinement for **1** are summarized in Table 1, the selected geometric parameters are given in Table 2 and the hydrogen-bonding geometry is given in Table 3. CCDC 1032624 contains the crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1

Crystal and structure refinement data for **1**.

Parameter	Value
Compound	1
Empirical formula	$C_9H_{12}N_3O_9La$
Formula weight	445.13
T (K)	293(2) K
Crystal system	Triclinic
Space group	$P-1$
Z	2
a , Å	8.997(5)
b , Å	9.251(5)
c , Å	9.728(5)
α , (°)	67.849(5)
β , (°)	84.224(5)
γ , (°)	81.351(5)
V , Å ³	740.5(7)
D_{calc} (g cm ⁻³)	1.996
μ (mm ⁻¹)	2.934
$F(000)$	432
Crystal size (mm)	0.30 x 0.20 x 0.15
θ_{min} , θ_{max} (°)	2.62 - 25.99
Reflections collected/unique	5555 / 2899
Reflections with $[I > 2\sigma(I)]$	2810
Data/restraints/parameters	2899 / 9 / 217
Goodness-of-fit (GOF) on F^2	1.000
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0182, 0.0464
$R1$, $wR2$ (all data)	0.0190, 0.0468
$\Delta\rho_{max}$, $\Delta\rho_{min}$ ($e \times \text{Å}^{-3}$)	0.416, -0.689

Table 2

Selected bond lengths (Å) and angles (°) in coordination metal environment in **1**.

Bond	d , (Å)	Bond	d , (Å)
La-O(1)	2.511(2)	La-O(3) ⁱⁱ	2.804(2)
La-O(2)	2.456(2)	La-O(6) ⁱ	2.490(2)
La-O(3)	2.525(2)	La-O(1w)	2.578(2)
La-O(4)	2.451(2)	La-O(2w)	2.667(2)
La-O(5)	2.639(2)	-	-
Angle	ω , (deg)	Angle	ω , (deg)
O(1)-La-O(2)	117.39(7)	O(3)-La-O(3) ⁱⁱ	60.38(6)
O(1)-La-O(3) ⁱⁱ	121.23(5)	O(3)-La-O(1w)	74.69(7)
O(1)-La-O(3)	79.09(6)	O(3)-La-O(2w)	78.71(6)
O(1)-La-O(4)	75.31(7)	O(4)-La-O(3) ⁱⁱ	114.09(6)
O(1)-La-O(5)	138.55(7)	O(4)-La-O(5)	77.08(6)
O(1)-La-O(6) ⁱ	73.48(7)	O(4)-La-O(6) ⁱ	117.37(7)
O(1)-La-O(1w)	143.16(6)	O(4)-La-O(1w)	138.48(7)
O(1)-La-O(2w)	67.33(6)	O(4)-La-O(2w)	68.49(7)
O(2)-La-O(3)	141.97(6)	O(5)-La-O(3) ⁱⁱ	47.66(5)
O(2)-La-O(3) ⁱⁱ	120.81(7)	O(5)-La-O(6) ⁱ	147.68(6)
O(2)-La-O(4)	73.24(7)	O(5)-La-O(1w)	75.17(7)
O(2)-La-O(5)	82.64(7)	O(5)-La-O(2w)	74.06(6)
O(2)-La-O(6) ⁱ	75.29(7)	O(6) ⁱ -La-O(3) ⁱⁱ	128.54(6)
O(2)-La-O(1w)	73.10(7)	O(1w)-La-O(3) ⁱⁱ	65.62(6)

Continuation of Table 2

Angle	ω , (deg)	Angle	ω , (deg)
O(2)-La-O(2w)	138.57(6)	O(1w)-La-O(2w)	130.08(6)
O(3)-La-O(4)	144.14(6)	O(1w)-La-O(6) ⁱ	75.99(7)
O(3)-La-O(5)	108.01(6)	O(2w)-La-O(3) ⁱⁱ	64.55(6)
O(3)-La-O(6) ⁱ	77.77(6)	O(2w)-La-O(6) ⁱ	137.25(6)

Symmetry code: ⁱ -x+1, -y, -z+1; ⁱⁱ -x+1, -y+1, -z+1

Table 3

Geometric parameters of hydrogen bonds (Å, deg) in **1**.

D-H...A	d(H...A)	d(D...A)	D(DHA)	Symmetry transformation for acceptor
O1w-H1w1...N3	2.28(2)	3.106(4)	168(3)	x, y, z
O1w-H2w1...O2w	1.92(2)	2.771(3)	161(3)	-x+1, -y+1, -z+1
O2w-H2w2...O3w	1.90(2)	2.770(3)	164(3)	x, y, z
O2w-H1w2...O3w	2.02(2)	2.809(3)	153(2)	-x+1, -y+1, -z
O3w-H1w3...N1	2.29(3)	2.951(4)	136(3)	-x+2, -y+1, -z
O3w-H2w3...N2	1.95(2)	2.802(3)	176(3)	x, y+1, z

Results and discussion

The reaction of lanthanum(III) oxide with cyanoacetic acid in a molar ratio of 1:3 in water solution leads to polymeric complex with the composition $\{[\text{La}_2(\text{CNCH}_2\text{COO})_6(\text{H}_2\text{O})_4] \times \text{H}_2\text{O}\}_n$ (**1**). The complex is a colorless, air hygroscopic crystalline solid, readily dissolves in water, but is insoluble in organic solvents, such as methanol, acetone and acetonitrile. The IR spectrum shows the absorption band at 2265 cm^{-1} , which is characteristic to the $\nu(\text{C}\equiv\text{N})$ vibrations of the ligand.

Here we report the results of X-ray study of the lanthanum(III) compound with cyanoacetate ligands, which is a linear polymer of composition $\{[\text{La}_2(\text{CNCH}_2\text{COO})_6(\text{H}_2\text{O})_4] \times \text{H}_2\text{O}\}_n$. Compound crystallizes in the triclinic centrosymmetric space group $P\bar{1}$, $a = 8.997(5)$ Å, $b = 9.251(5)$ Å, $c = 9.728(5)$ Å, $\alpha = 67.849(5)^\circ$, $\beta = 84.224(5)^\circ$, $\gamma = 81.351(5)^\circ$, $V = 740.5(7)$ Å³ and is isostructural to the reported earlier Nd analog [16]. The inversion centers related to La cations are linked in 1D structure by carboxylic groups of cyanoacetate ligands, which exhibit different binding modes (Figure 1).

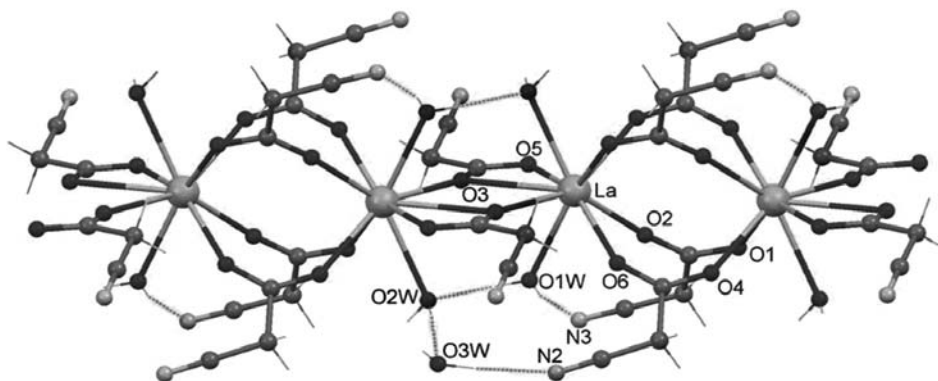


Figure 1. View of polymeric chain.

The La cation is linked to the center of symmetry related neighboring La cations either by four cyanoacetic ligands, acting as *syn-syn* (c-2-c) bidentate bridges (La-O2, 2.455(2); La-O6, 2.490(2); La-O1', 2.511(2); La-O4', 2.450(2) Å), or through two tridentate (3₂-c) chelate-bridging ligands with the La-O3 bond lengths of 2.524(2) and 2.806(2) Å, respectively.

Two different La...La separations in the polymer chain alternate and are equal to 4.755 and 4.608 Å, respectively. The shorter of the La...La distance is related with monoatomic bridging function of carboxylic group in the second case. The coordination surrounding of lanthanum is completed to nine by two coordinated water molecules O(1w) and O(2w) (La-O(1w), 2.579(2) and La-O(2w), 2.664(2) Å). The coordination polyhedron of lanthanum is a monocapped tetragonal antiprism. The comparison of average La-O distances for acting as *syn-syn* (c-2-c) bidentate bridges (2.477 Å) ligands, chelate-bridging ligands (2.525, 2.639 and 2.804 Å) and coordinated water molecules (2.623 Å) in **1** with the corresponding values in related Nd analog [16] (2.420, 2.463, 2.587 Å and 2.831, 2.590 Å) revealed well agreement

with the difference in ionic radii of nine coordinated La^{III} (1.36 Å) and Nd^{III} (1.30 Å) [22]. The cyano group of the cyanoacetate ligands does not coordinate to the lanthanide cation. The coordinated water molecules are involved in intra- and inter-chain hydrogen bonds (Table 3).

In the crystal, the parallel polymer chains run along a crystallographic axis and are united into a three-dimensional network through a system of hydrogen bonds involving water molecules and nitrogen atoms of cyanoacetic ligands (Figure 2).

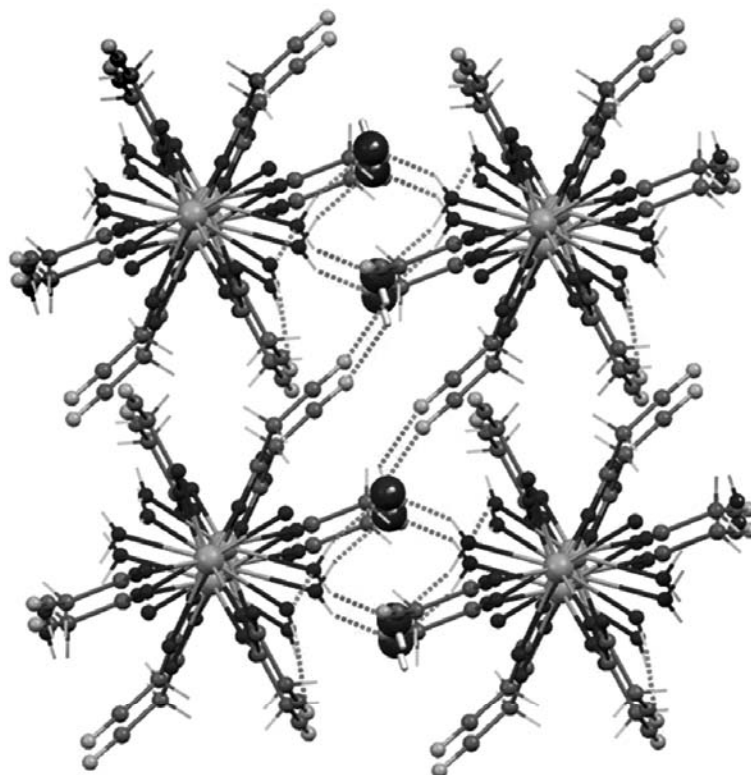


Figure 2. Hydrogen bonded parallel polymer chains in the crystal structure of $\{[La_2(CNCH_2COO)_6(H_2O)_4] \cdot H_2O\}_n$. Solvent water molecules O3w are shown by bigger radii red spheres.

Conclusions

The lanthanum(III) cyanoacetate polymer of formula $\{[La_2(CNCH_2COO)_6(H_2O)_4] \cdot 2H_2O\}_n$ (**1**) has been synthesized and characterized by single-crystal X-ray diffraction. The complex was found to be isostructural to Nd analog. The cyano-group of the ligand is not coordinated to the lanthanide ion.

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