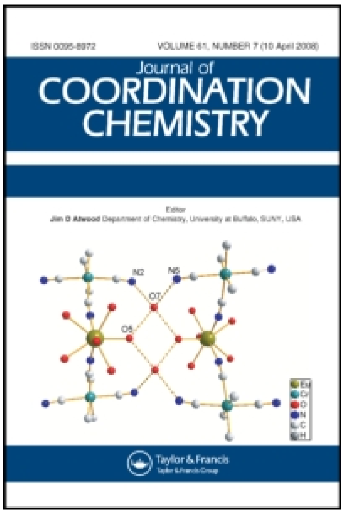

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Coordination polymer of lanthanum: synthesis, properties and crystal structure of [La(4,4'-bipyridine)$(CCl_2HCOO)_3(H_2O)]_{<b><i>n</i>}$

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Coordination polymer of lanthanum: synthesis, properties and crystal structure of $[La(4,4'\text{-bipyridine})(CCl_2HCOO)_3(H_2O)]_n$

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A new mixed ligand complex of general formula $[La(H_2O)(4,4'\text{-bpy})(CCl_2HCOO)_3]_n$ has been synthesized and characterized by elemental and thermal analysis, IR spectroscopy and conductivity studies. The crystal and molecular structure was determined. The lanthanum atom is ten coordinate by four oxygen atoms from two chelating tridentate dichloroacetate substituents, two oxygen atoms from two bidentate bridging dichloroacetate groups, two oxygen atoms from two bridging tridentate dichloroacetate substituent, one oxygen atom of water molecule and one nitrogen atom from 4,4′-bipyridyl substituent. The coordination polyhedron of central atom can be described as tetradecahedron. The molecules are built up by O–H ··· N hydrogen bonds to a two-dimensional network.

Keywords: Lanthanide(III); 4,4′-Bipyridine; Dichloroacetate; Thermal decomposition

1. Introduction

Lanthanides have versatile applications in diagnostic medicine (*e.g.* contrast agents for magnetic resonance imaging [1, 2], radiotherapeutic drugs [3], fluoroimmunoassay [4]), in hetero- and homogeneous catalysis [5, 6], as components of permanent magnet materials [7] or as non-toxic alternatives to cadmium and lead in inorganic pigments for special plastics.

4,4′-Bipyridine, 4-bpy, has a huge and versatile use in creating polymeric species [8–11]. Coordination polymers possessing rigid or flexible chains/nets [12–15], which can create nanoporous channels, are especially of interest due to their properties of physical gas adsorption [16–31], chemical adsorption [17, 21, 32–36], ion exchange [37–40] and heterogeneous catalysis [41–43]. Mixed-ligand complexes with 4-bpy and carboxylate ligands form also species of unusual structures and properties [44–48]. Only a few publications on halogenoderivates of lanthanide acetates can be found [49–54]. Thus, the synthesis and analytical characterisation of the title compound was undertaken, especially the determination of its structure and thermal properties.

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Thermal studies of compounds of this type are very important because during thermal liberation of water a microporous material with active metal sites is created, and during pyrolysis different solid products are formed as important reagents in heterogeneous catalysis [5, 6].

2. Experimental

2.1. *Chemicals*

4,4′-Bipyridine (m.p. 342.9 K), dichloroacetic acid p.a. and La_2O_3 (99.99%) were obtained from Aldrich; methanol (anhydroscan), dimethylformamide p.a. (DMF) and dimethylsulfoxide p.a. (DMSO) from Lab.Scan, Reachim and VEB Jano-pharm Labochem Apolda, respectively. The solution of lanthanide(III) dichloroacetate was prepared by dissolving freshly precipitated $La(OH)_3$ in 2 mol dm^{-3} dichloroacetic acid in ca stoichiometric quantities (pH $\sim$ 4.0). The lanthanide content in this solution was determined complexometrically with a standard EDTA solution, against xylenol orange as indicator. Other chemicals were analytical reagent grade from POCh-Gliwice.

2.2. *Preparation of complex*

A solution of 4-bpy (6.2 mmol) in 96% v/v ethanol ($v = 11\,cm^3$) was added to a freshly obtained solution of lanthanide(III) dichloroacetate (3.1 mmol) in water (29 cm^3) at room temperature. Over a period of several days a crystalline complex was obtained. The white product was collected by filtration, washed with cold EtOH and then with ethanol–diethyl ether mixture (1 : 1) v/v and dried in open air. The C, H and N contents were determined by elemental analysis with V_2O_5 as oxidizing agent; La(III) was determined complexometrically. Anal. Calcd for $[La(H_2O)(C_{10}H_8N_2)(C_6H_3O_6Cl_6)_3]$%; La, 19.33; C, 27.58; H, 1.88; N, 4.02. Found: La, 19.93; C, 27.40; H, 1.81; N, 3.82.

2.3. *Crystal structure determination*

A colorless rectangular prism was mounted on a KM-4-CCD automatic diffractometer equipped with CCD detector, and used for data collection. X-ray intensity data were collected with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293.0(2) K, with ω scan mode. A 31 s exposure time was used and reflections inside the Ewald sphere were collected up to $2\theta = 50.2°$. The unit cell parameters were determined from least-squares refinement of the setting angles of the 10126 strongest reflections. Details concerning crystal data and refinement are given in table 1. Examination of reflections on two reference frames monitored after each 40 frames measured showed 8.38% loss intensity. During the data reduction above decay correction coefficient was taken into account. Lorentz, polarization, and numerical absorption [55] corrections were applied. The structure was solved by direct methods. All the non-hydrogen atoms were refined anisotropically using full-matrix, least-squares on F^2. All the hydrogen atoms were found from difference Fourier synthesis after four cycles of anisotropic refinement, and refined as "riding" on the adjacent atom with

Table 1. Crystal data and structure refinement details for title compound.

Empirical formula	$(C_{16}H_{13}Cl_6N_2O_7La)_n$
Formula weight	696.89
Temperature (K)	291.0(3)
Wavelength, λ(Mo-Kα) (Å)	0.71073
Crystal system, space group	Monoclinic, $C2/c$
Unit cell dimensions (Å, °)	
a	19.4803(11)
b	16.3220(8)
c	15.9661(14)
β	113.678(7)
Volume (Å^3)	4649.2(6)
Z, Calculated density (Mg m^{-3})	8, 1.991
Absorption coefficient (mm^{-1})	2.569
$F(000)$	2704
Crystal size (mm^3)	$0.391 \times 0.252 \times 0.219$
° range for data collection	2.84–25.18
Index ranges	$-23 \le h \le 23$, $-19 \le k \le 19$, $-19 \le l \le 16$
Reflections collected/unique	24211/4172 [R(int) = 0.0412]
Completeness to $2\theta = 25.11°$	98.0%
Refinement method	Full-matrix least-squares on F^2
Max. and min. transmission	0.625 and 0.435
Data/restraints/parameters	4172/0/301
Goodness-of-fit on F^2	1.173
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0314$, $wR_2 = 0.0720$
R indices (all data)	$R_1 = 0.0342$, $wR_2 = 0.0734$
Largest diff. peak and hole (e Å^{-3})	1.183 and −0.663

individual isotropic displacement factor equal 1.2 times the value of equivalent displacement factor of the bound carbon atom. The SHELXS-97 [56], SHELXL-97 [57] and SHELXTL [58] programs were used for all calculations. Atomic scattering factors were those incorporated in the computer programs. Selected interatomic bond distances and angles are listed in table 2.

2.4. *Other measurements*

Elemental analysis was carried out using a Carbo-Erba C, H, N-analyser. La(III) was determined chelatometrically. IR spectra were obtained using KBr pellets on a Schimadzu spectrophotometer (4000–400 cm^{-1}). Conductivity measurements were performed on an OK-102/1 conductivity meter equipped with an OK 902 electrode at 298.14 ± 0.05 K. Molar conductivity (Λ_M) of the complex was measured using 10^{-3} M solutions in MeOH, DMF and DMSO. Thermal decomposition studies were carried out on a Q-1500 derivatograph over the temperature range 293–1273 K at a heating rate of 10 K min^{-1}, in static air. The sample mass was 100 mg; α-Al_2O_3 served as the reference. Thermal decomposition products were confirmed by recording IR spectra of sinters prepared by heating samples to fixed temperatures.

3. Results and discussion

The title compound is air stable at room temperature. Its molar conductances (Ω^{-1} cm^{2}mol^{-1}) in MeOH (51.5) and DMF (59.6) indicate behaviour intermediate

Table 2. Selected structural data for title compound. Distances in (Å), angles in (°).

La(1)–O(7)	2.542(2)
La(1)–O(4)#1	2.542(2)
La(1)–O(6)#2	2.556(2)
La(1)–O(1)	2.566(2)
La(1)–O(2)#2	2.579(2)
La(1)–O(3)	2.608(2)
La(1)–O(5)	2.630(3)
La(1)–O(2)	2.779(2)
La(1)–N(1)	2.792(3)
La(1)–O(4)	2.822(2)
O(1)–C(11)	1.246(4)
O(2)–C(11)	1.266(4)
O(3)–C(13)	1.248(4)
O(4)–C(13)	1.265(4)
O(5)–C(15)	1.236(4)
O(6)–C(15)	1.257(4)
O(7)–La(1)–O(4)#1	68.68(8)
O(7)–La(1)–O(6)#2	135.38(8)
O(4)#1–La(1)–O(6)#2	86.40(8)
O(7)–La(1)–O(1)	77.98(8)
O(4)#1–La(1)–O(1)	81.89(8)
O(6)#2–La(1)–O(1)	136.12(8)
O(7)–La(1)–O(2)#2	130.85(8)
O(4)#1–La(1)–O(2)#2	158.16(7)
O(6)#2–La(1)–O(2)#2	72.41(7)
O(1)–La(1)–O(2)#2	109.62(8)
O(7)–La(1)–O(3)	77.91(9)
O(4)#1–La(1)–O(3)	108.68(7)
O(6)#2–La(1)–O(3)	75.97(8)
O(1)–La(1)–O(3)	147.68(8)
O(2)#2–La(1)–O(3)	71.84(8)
O(7)–La(1)–O(5)	129.73(8)
O(4)#1–La(1)–O(5)	70.11(8)
O(6)#2–La(1)–O(5)	67.38(8)
O(1)–La(1)–O(5)	68.85(8)
O(2)#2–La(1)–O(5)	96.16(8)
O(3)–La(1)–O(5)	143.35(8)
O(7)–La(1)–O(2)	118.87(8)
O(4)#1–La(1)–O(2)	120.09(7)
O(6)#2–La(1)–O(2)	105.55(7)
O(1)–La(1)–O(2)	48.84(7)
O(2)#2–La(1)–O(2)	63.03(8)
O(3)–La(1)–O(2)	131.23(7)
O(5)–La(1)–O(2)	62.31(7)
O(7)–La(1)–N(1)	67.53(8)
O(4)#1–La(1)–N(1)	133.52(8)
O(6)#2–La(1)–N(1)	137.25(8)
O(1)–La(1)–N(1)	74.62(8)
O(2)#2–La(1)–N(1)	68.29(8)
O(3)–La(1)–N(1)	76.44(8)
O(5)–La(1)–N(1)	132.30(9)
O(2)–La(1)–N(1)	70.73(8)
O(7)–La(1)–O(4)	70.15(8)
O(4)#1–La(1)–O(4)	61.75(8)
O(6)#2–La(1)–O(4)	65.46(8)
O(1)–La(1)–O(4)	138.09(7)
O(2)#2–La(1)–O(4)	111.72(7)
O(3)–La(1)–O(4)	47.90(7)
O(5)–La(1)–O(4)	112.63(7)
O(2)–La(1)–O(4)	170.98(6)
N(1)–La(1)–O(4)	115.02(8)

(*Continued*)

Table 2. Continued.

C(11)–O(1)–La(1)	98.43(19)
C(11)–O(2)–La(1)#2	153.6(2)
C(11)–O(2)–La(1)	87.9(2)
La(1)#2–O(2)–La(1)	106.13(8)
O(1)–C(11)–O(2)	124.0(3)
C(13)–O(3)–La(1)	99.2(2)
C(13)–O(4)–La(1)#1	152.1(2)
C(13)–O(4)–La(1)	88.7(2)
La(1)#1–O(4)–La(1)	118.25(8)
O(3)–C(13)–O(4)	123.5(3)
C(15)–O(5)–La(1)	149.6(2)
C(15)–O(6)–La(1)#2	128.3(2)
O(5)–C(15)–O(6)	128.1(3)
O(5)–C(15)–C(16)	118.1(3)
O(6)–C(15)–C(16)	113.8(3)

Symmetry transformations used to generate equivalent atoms: #1: $-x$, $-y$, $-z+1$; #2: $-x$, y, $-z+1/2$.

between non- and 1 : 1 electrolytes [59]. The molar conductivity value in DMSO (59.6) corresponds to that of 1 : 1 electrolyte. Higher than anticipated Λ_M values are probably due to displacement of dichloroacetate ligands by molecules of solvent.

Among lanthanide halogenoacetate polymers only two compounds containing N-donor ligands in the inner coordination sphere are known: $[La(C_{12}H_8N_2)(CCl_2HCOO)_2\ (H_2O)(NO_3)]_n$ [60] and $[Sm(C_{10}H_8N_2)(CCl_2HCOO)_3\ (H_2O)]_n$ [49]; the second can be considered as an analogue of the title compound. A perspective view of the title compound structure, occupying the asymmetric unit of the unit cell, together with the atom numbering scheme is shown in figure 1 (displacement ellipsoids are plotted with 50% probability). One chlorine of the dichloroacetate substituent indicated by C(16) atom is disordered over two positions. All atoms lie in general positions. The planar, within the experimental error, pyridine rings are inclined at 22.60(17)°. The lanthanum atom is ten coordinate by four oxygen atoms from two chelating tridentate dichloroacetate substituents, two oxygen atoms from two bidentate bridging dichloroacetate groups, two oxygen atoms from two bridging tridentate dichloroacetate substituent, one oxygen atom of water molecule and one nitrogen atom from 4,4′-bpy substituent, which means that every tridentate dichloroacetate substituent is bridging toward one lanthanum atom and chelating toward another. This is different than in Sm analogue [49] where samarium was nine coordinate by two oxygen atoms from one chelating tridentate dichloroacetate substituent, four oxygen atoms from four bidentate bridging dichloroacetate groups, one oxygen atoms from one bridging tridentate dichloroacetate substituent, one water molecule and one nitrogen atom from 4,4′-bpy. Both carboxylic groups of title compound are bonded unsymmetrically to the central atom. The coordination polyhedron of La can be described as tetradecahedron (figure 2) [61]. The existence of an inversion centre and twofold rotation axis around lanthanum (special positions *a* and *e* of $C2/c$ space group at 0, 0, ½ and 0, *y*, ¼ respectively [62]) expands the molecule to the one dimensional coordination polymer along *c* (figure 3). The polymer scheme (figure 4a) is distinctly different than in the Sm analogue (figure 4b) [49], because the main chain is created via chelating-bridging tridentate groups (with bridging bidentate groups stabilizing every second polymer mesh) instead of bridging bidentate groups in Sm analogue (with chelating-bridging tridentate groups stabilising

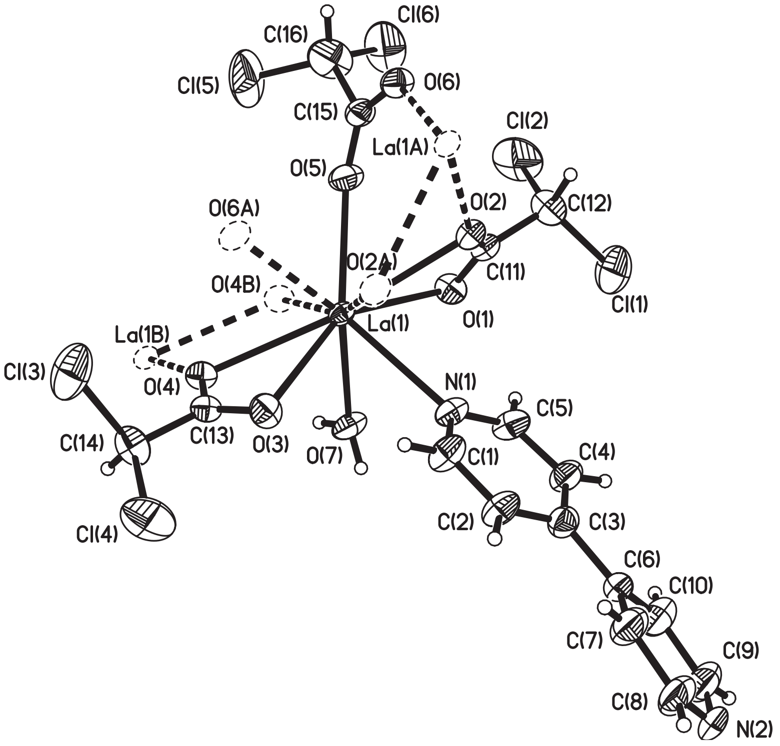

Figure 1. The molecular conformation with atom numbering, plotted with 50% probability of displacement ellipsoids. The hydrogen atoms and disordered chlorine atoms are omitted for clarity. The symmetry generated atoms are indicated by dashed lines.

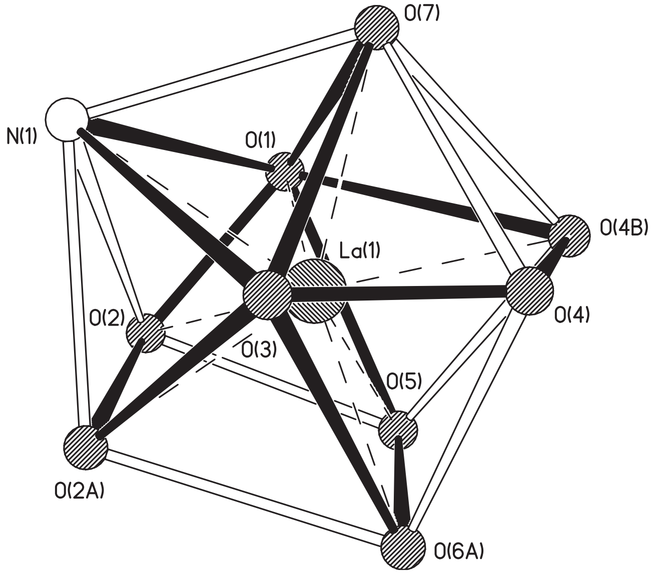

Figure 2. The lanthanum coordination polyhedron.

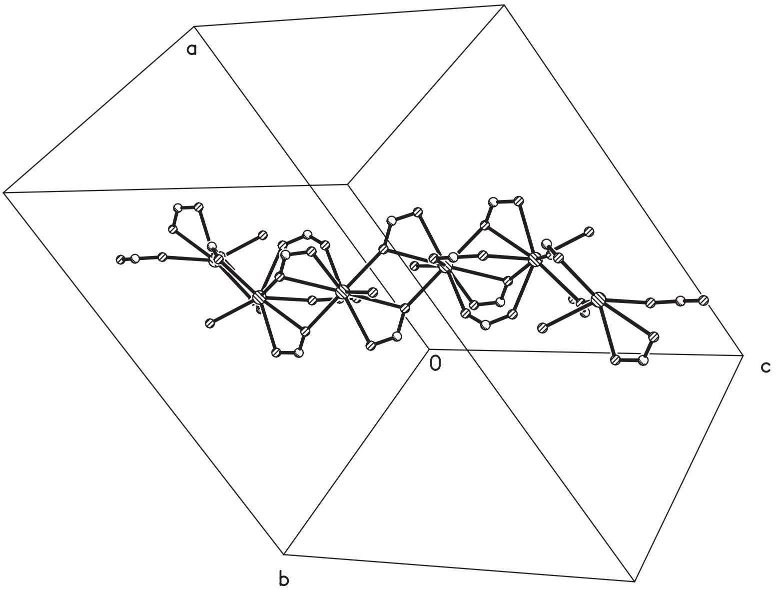

Figure 3. The coordination polymer main chain created along *c* direction.

every second polymer mesh). In the title compound each main chain mesh is created from four atoms (two samarium and two oxygen) in opposition to eight in Sm analogue. This is the first known lanthanide 1D coordination polymer with such arrangement of carboxylate groups.

The bond valences were computed as $\nu_{ij} = \exp[(R_{ij} - d_{ij})/b]$ [63–67], where R_{ij} is the bond-valence parameter (in the formal sense R_{ij} can be considered as an parameter equal to the idealised single-bond length between *i* and *j* atoms for given *b*) and *b* was taken as 0.37 Å [64]. The $R_{\mathrm{La-O}}$ and $R_{\mathrm{La-N}}$ were taken as 2.148 [70] and 2.261 [71] respectively. The computed bond valences of the lanthanum are $\nu_{\mathrm{La(1)-O(1)}} = 0.323$, $\nu_{\mathrm{La(1)-O(2)}} = 0.182$, $\nu_{\mathrm{La(1)-O(3)}} = 0.228$, $\nu_{\mathrm{La(1)-O(4)}} = 0.162$, $\nu_{\mathrm{La(1)-O(5)}} = 0.272$, $\nu_{\mathrm{La(1)-O(7)}} = 0.345$, $\nu_{\mathrm{La(1)-O(2\#-}x,y,-z+1/2)} = 0.312$, $\nu_{\mathrm{La(1)-O(4\#)}} = 0.345$, $\nu_{\mathrm{La(1)-O(6\#-}x,y,-z+1/2)} = 0.332$, $\nu_{\mathrm{La(1)-N(1)}} = 0.283$ v.u. (valence units), thus the computed valence of the La(1) atom is 2.80 v.u. The deviation of valence sum rule can be explained by constraints imposed by the tridentate carboxylate group. The weakest are La–O chelating bonds created by bridging O atoms; the almost two times stronger La–O(water) bond is the strongest bond and La-bipyridyl bond strength lies in the middle. In the structure intramolecular O(water)–H $\cdots$ O(carboxyl) hydrogen bonds exist (table 3) which provide additional conformational stabilization to the polymer chains. Additionally O(water)–H $\cdots$ N hydrogen bonds (table 3) can be found, and in this way a two dimensional network is created. Approximately rectangular channels (figure 5) are created along the [1 1 0] direction. These channels have two different sizes 11.5 × 3.7 Å and 11.0 × 4.3 Å, and are bordered by π electrons, which create a possibility to utilise title compound in both selective absorption and heterogeneous catalysis.

IR spectra exhibit several bands characteristic for 4-bpy and dichloroacetate groups. The infrared spectrum of free 4-bpy undergoes a change upon coordination with La(III). The characteristic ring stretching vibrations ν(CC), ν(CN), $\nu(\mathrm{CC})_{\mathrm{inter\,ring}}$

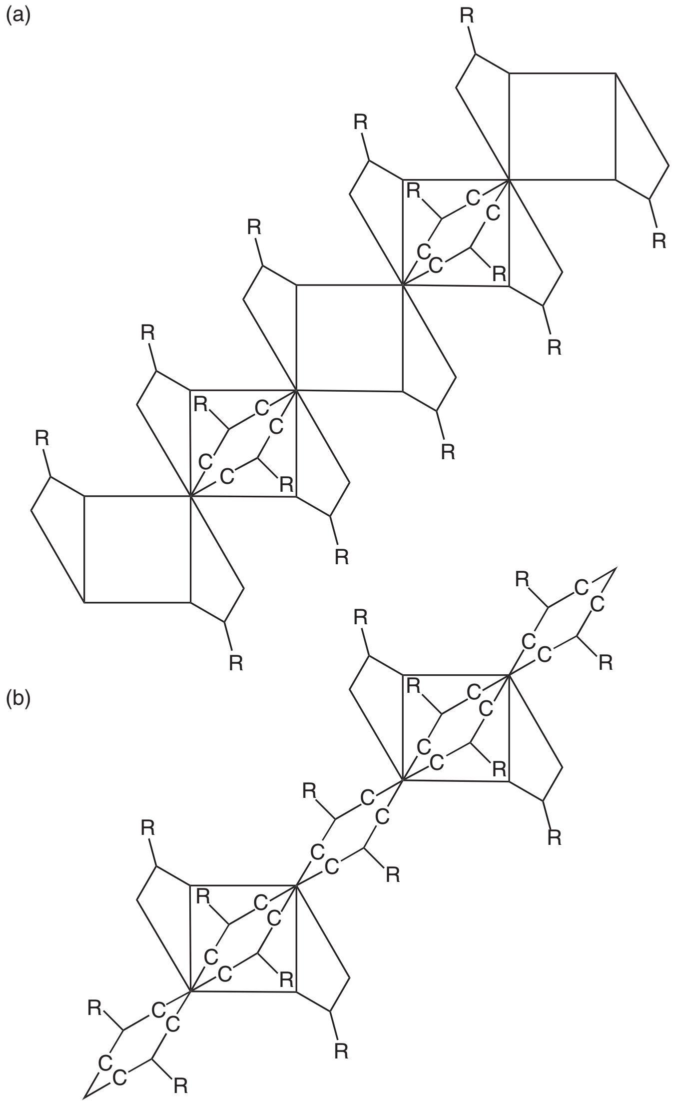

Figure 4. The [Ln(4,4′-bipy)(CCl_2HCOO)$_3$(H_2O)]$_n$ polymer scheme, Ln = La (A), Ln = Sm (B).

(A_1 symmetry) and ν(CC), ν(CN) (B_1 symmetry) appear at 1588 and 1530 cm^{-1} in free ligand [68]; in the title compound they are observed at 1600.0 and 1589.2 (A_1 symmetry) and 1533.3 cm^{-1} (B_1 symmetry), respectively. The ring "breathing" mode is shifted by 3.9 cm^{-1} towards higher frequency in comparison to free 4-bpy.

The asymmetric stretching modes (ν_{as}OCO) are split and appear at 1652.9 and 1622.0 cm^{-1}. The frequency of the symmetric stretching mode (ν_sOCO) is 1377.1 cm^{-1}. These bathochromic shifts of principal absorption bands shows that 4-bpy and COO$^-$ groups were coordinated [69]. The compound exhibits a band in the water stretching region at ca 3460 cm^{-1}. The H_2O wagging vibrations for coordinated water were not observed.

Table 3. Hydrogen-bonds for title compound. Distances in (Å), angles in (°).

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(7)–H(7O)···O(6)#1	0.88	2.06	2.929(3)	172.5
O(7)–H(7P)···N(2)#2	0.83	2.06	2.881(4)	173.2

Symmetry transformations used to generate equivalent atoms: #1: $x, -y, z+1/2$; #2: $-x, -y+1, -z+1$.

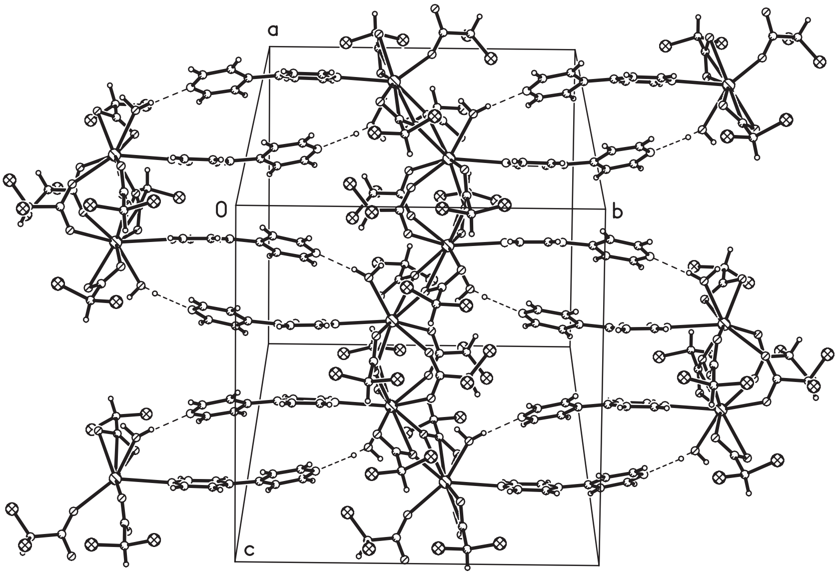

Figure 5. A part of molecular packing showing the two dimensional hydrogen-bonded network and approximately rectangle channels created along [1 1 0] direction. Intermolecular hydrogen bonds are indicated by dashed lines.

Thermal decomposition of the La(III) complex in air is a multi-stage process. The compound is stable to 373 K. The first mass loss is assigned to 1 mol water evolution (Calcd 2.58%, found 3.0% in the temperature range 373–433 K. With increasing temperature (433–543 K) partial decomposition of the dichloroacetate ligands take place. During this process La(4-bpy)(Cl_2CHCOO)Cl_2 is probably formed (Calcd 26.55%, found 27.0%). Next in the range 543–1013 K $LaCl_3$ begins to form. Above 1013 K La_2O_3 was identified as a final product of decomposition (Calcd 11.76%, found 12.0%). Pyrolysis of the investigated compound is accompanied by several exo- and endothermic effects in the DTA curve (given in the scheme below).

$$[\mathrm{La(4\text{-}bpy)(CCl_2HCOO)_3}]\cdot\mathrm{H_2O} \xrightarrow[\text{423 K endo}]{\text{373–433 K}} [\mathrm{La(4\text{-}bpy)(CCl_2HCOO)_3}] \xrightarrow[\text{513 K exo}]{\text{433–543 K}}$$

$$\longrightarrow [\mathrm{La(4\text{-}bpy)(CCl_2HCOO)Cl_2}] \xrightarrow[\text{733, 833 K exo}]{\text{543–1013 K}} \mathrm{LaCl_3} \xrightarrow[\text{1073 K exo}]{\text{1013–1153 K}} \mathrm{La_2O_3}$$

Supplementary data

Tables of crystal data and structure refinement, anisotropic displacement coefficients, atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms, H-atom coordinates and isotropic displacement parameters, bond lengths and interbond angles have been deposited with the Cambridge Crystallographic Data Centre under No. CCDC631906.

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