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**LANTHANIDE COORDINATION COMPOUNDS  
WITH MONODENTATE COORDINATED  
 $\beta$ -DIKETONE HETEROANALOGUE - (2,2,2-  
TRICHLORO-N-(DIPERIDIN-1-YL-  
PHOSPHORYL)ACETAMIDE: SYNTHESIS AND  
SPECTRAL INVESTIGATIONS**

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## LANTHANIDE COORDINATION COMPOUNDS WITH MONODENTATE COORDINATED $\beta$ -DIKETONE HETEROANALOGUE - (2,2,2-TRICHLORO-N-(DIPERIDIN-1-YL-PHOSPHORYL)ACETAMIDE: SYNTHESIS AND SPECTRAL INVESTIGATIONS

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**Abstract.** 14 new mononuclear six-coordinate lanthanide coordination compounds of general formula  $[\text{Ln}(\text{HL})_3\text{Cl}_3]$  (Ln = La-Nd, Sm-Lu; HL = (2,2,2-trichloro-N-(dipiperidin-1-yl-phosphoryl)acetamide  $\text{CCl}_3\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})[\text{N}(\text{CH}_2)_5]_2$ , carbacylamidophosphate (CAPH) type ligand) have been synthesized from non-aqueous solutions. The complexes have been characterized by elemental analysis, FTIR,  $^1\text{H}$ - and  $^{31}\text{P}$ -NMR, and UV-vis spectroscopy. The structure of  $[\text{Sm}(\text{HL})_3\text{Cl}_3]$  (**1**) has been further confirmed by single crystal X-ray diffraction analysis. Crystal data: trigonal,  $R\bar{3}$ , with  $a = 24.098 \text{ \AA}$ ,  $c = 18.025 \text{ \AA}$ ,  $V = 9065.0 \text{ \AA}^3$ ,  $Z = 6$ ,  $R_1 = 0.0327$ , and  $wR_2 = 0.0404$ . The crystal structure was solved as two crystallographically independent fragments  $\text{Sm}(\text{HL})\text{Cl}$ : A and B that exist in the crystalline lattice due to the differences in some geometrical parameters.

**Keywords:** lanthanide, carbacylamidophosphate, phosphoryl ligand, six-coordinate lanthanide complex, electronic spectrum.

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### Introduction

Due to the remarkable and unmatched optical and magnetic properties of lanthanides, these compounds are of interest when it comes to high technology [1-8]. These elements are used in strategic applications such as telecommunications, production of optical glasses and lasers, lights and displays, magnetic materials, hard-disk drives, security inks and counterfeiting tags, as well as in catalysis, biosciences, and medicine.  $\beta$ -Diketones and their structural analogues are among the most investigated ligands that are applied for binding lanthanides (III) ions [9-13]. Carbacylamidophosphates (CAPH) – compounds, containing the functional fragment  $\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})$ , have been of special interest, because of their useful properties as urease inhibitors [14], enzyme inhibitors [15,16], their antibacterial properties [17,18], and anticancer activity [19,20]. The lanthanide chelates of CAPHs exhibit biological activities and in vitro tests show their strong anticancer properties [21]. The presence in the CAPH's composition of the

phosphoryl group provides a high affinity towards highly charged metal ions, such as lanthanides and actinides [22-24]. CAPH compounds may be regarded as powerful chelating systems and for this reason they are used as extractants, namely those of them containing the long alkyl chains ( $n\text{-C}_5\text{H}_{11}$  –  $n\text{-C}_{10}\text{H}_{21}$ ) near the carbonyl carbon atom [25,26].

The ability of deprotonated CAPH ligands to form stable complexes with both transition and non-transition metals has been extensively investigated [27-31]. Previous studies revealed that the monodentate coordination for the molecular form of CAPH ligands is realized mainly via phosphoryl oxygen for 3d metals, rare earth elements, and for  $\text{Sn}^{2+}$  ions [32-35].

This work presents a study of metal complexes of the composition  $[\text{Ln}(\text{HL})_3\text{Cl}_3]$  (Ln= La-Nd, Sm-Lu, HL=  $\text{CCl}_3\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})[\text{N}(\text{CH}_2)_5]_2$  -2,2,2-trichloro-N-(dipiperidin-1-yl-phosphoryl)acetamide) and crystal structure of trichlorotriss[2,2,2-trichloro-N-(dipiperidinophosphoryl)acetamide]samarium

(III)] [Sm(HL)<sub>3</sub>Cl<sub>3</sub>] (**1**). The spectral characteristics of synthesized complexes in non-aqueous solutions and solid state were investigated.

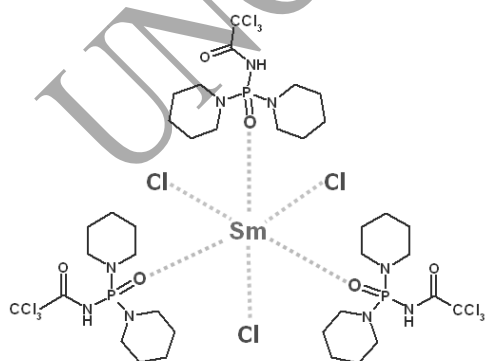
## Experimental

### Chemicals

All chemicals were purchased from commercial sources and used as received unless otherwise stated. Basic solvents for synthesis were dried using literature methods. Solvents for spectroscopic investigations were of the highest purity available.

Carabacylamidophosphate ligand 2,2,2-trichloro-N-(dipiperidin-1-yl-phosphoryl)acetamide HL was synthesized *via* the three-step procedure based on the Kirsanov reaction [32, 36], and its structure was identified using FTIR and NMR spectroscopy. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, RT): δ = 1.51 (d, 4H, β-CH<sub>2</sub>), 1.58 (d, 2H, γ-CH<sub>2</sub>), 3.16 (s, 4H, α-CH<sub>2</sub>), 9.37 (s, 1H, NH). <sup>31</sup>P NMR (162 MHz, DMSO-*d*<sub>6</sub>, RT): δ = 10.18 (s, P=O).

Trichlorotriss[2,2,2-trichloro-N-(dipiperidinophosphoryl)acetamide]samarium (III) [Sm(HL)<sub>3</sub>Cl<sub>3</sub>] (**1**) (Figure 1) and coordination compounds [Ln(HL)<sub>3</sub>Cl<sub>3</sub>] were synthesized as follows: hydrated rare earth chloride (1 mmol) was dissolved in methanol (15 mL), then heated to a boiling temperature for 2 minutes and after that the mixture was added to the solution of HL (3 mmol) in methanol (15 mL). The obtained solution was left under vacuum in a desiccator over CaCl<sub>2</sub>. Crystals of the complexes were formed in 1-2 days, filtered, washed with cooled 2-propanol, and air-dried (yield 78-82%). The complexes, as prepared, are soluble in non-polar aprotic solvents, acetone, acetonitrile, alcohols, and toluene; and insoluble in water, hexane, and cyclohexane (m.p. 175-188°C). Crystalline powder of **1** was recrystallized from a 2-propanol/methanol mixture (3:1, v/v) to get colorless prisms.



**Figure 1.** Representation of CAPH-ligand coordination mode in [Sm(HL)<sub>3</sub>Cl<sub>3</sub>].

For C<sub>36</sub>H<sub>63</sub>N<sub>9</sub>O<sub>6</sub>P<sub>3</sub>Cl<sub>12</sub>Sm the elemental composition was determined, %: C 32.04, H 4.87, N 9.22, Sm 10.24; and calculated, %: C 31.18, H 4.58, N 9.09, Sm 10.84.

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, RT): [La(HL)<sub>3</sub>Cl<sub>3</sub>]: δ = 1.63 (d, 4H, β-CH<sub>2</sub>), 1.68 (d, 2H, γ-CH<sub>2</sub>), 3.24 (s, 4H, α-CH<sub>2</sub>), 9.87 (s, 1H, NH); [Lu(HL)<sub>3</sub>Cl<sub>3</sub>]: δ = 1.65 (d, 4H, β-CH<sub>2</sub>), 1.7 (d, 2H, γ-CH<sub>2</sub>), 3.25 (s, 4H, α-CH<sub>2</sub>), 9.85 (s, 1H, NH). <sup>31</sup>P NMR (162 MHz, DMSO-*d*<sub>6</sub>, RT): [La(HL)<sub>3</sub>Cl<sub>3</sub>]: δ = 9.21 (s, P=O). Lu: δ = 9.28 (s, P=O).

### Characterization

The composition of the complexes was determined by the elemental analysis of carbon, hydrogen, and nitrogen using EL III Universal CHNOS Elemental Analyzer. The concentration of lanthanide ions in lanthanides was quantified by standard titrimetric methods.

<sup>1</sup>H and <sup>31</sup>P NMR spectra in DMSO-*d*<sub>6</sub> solutions were recorded on a Varian 400 NMR spectrometer at room temperature (RT). <sup>1</sup>H chemical shifts were determined relative to the internal TMS, whereas <sup>31</sup>P chemical shifts were calculated relatively to an external standard of 85% H<sub>3</sub>PO<sub>4</sub>.

Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Perkin-Elmer Spectrum BX spectrometer using KBr pellets with resolution of 1 cm<sup>-1</sup>, in the range 4000–400 cm<sup>-1</sup>.

UV-vis absorption spectra of [Nd(HL)<sub>3</sub>Cl<sub>3</sub>] solutions were measured at RT in absolute non-aqueous solvents on a KSVU-23 “LOMO” spectrometer using 3 cm<sup>3</sup> stoppered quartz cell of 1 cm pathlength. The concentrations of complexes were 1·10<sup>-2</sup> mol/L.

Single crystal X-ray diffraction (XRD) data for [Sm(HL)<sub>3</sub>Cl<sub>3</sub>] (**1**) was collected at 20°C using Xcalibur-3 diffractometer (Mo-Kα radiation, CCD-detector, graphite monochromator, ω-scan). The size of a single crystal was 0.4×0.2×0.1 mm. The structure was solved by direct method and refined against F<sup>2</sup> by full-matrix least-squares method using the SHELXTL package [37]. All non-hydrogen atoms were refined within anisotropic approximation. Positions of the hydrogen atoms were located from electron density difference maps and refined by “riding” model with *U*<sub>iso</sub> = 1.2*U*<sub>eq</sub> of the carrier atom. The chlorine atoms of one of the trichloromethyl groups in molecules A and B are disordered due to rotation around the Csp<sup>2</sup>-Csp<sup>3</sup> bond with a ratio of 0.54:0.46% in molecule A and 0.52:0.48 % in molecule B. Crystallographic data for the structure have been deposited to the Cambridge Crystallographic Data Centre with CCDC number

869525. Copies of the data can be obtained free of charge by an application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(122) 333-6033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk); website: <http://www.ccdc.cam.ac.uk>).

## Results and discussion

### FTIR spectra

The FTIR spectra of HL and the complexes contain characteristic bands corresponding to vibrations of the phosphoryl and carbonyl groups which are sensitive to the coordination mode of CAPH ligand. According to our previous studies, the neutral forms of carbacylamidophosphates are coordinated mostly in a monodentate manner *via* the oxygen atom of the phosphoryl group [23,32] whereas the deprotonated forms – in a bidentate manner *via* the oxygen atoms of the phosphoryl and carbonyl groups forming six-membered

chelate cycles [38]. Infrared spectroscopic investigations revealed a bathochromic shift ( $\Delta\nu$ ) of these bands in the sodium salt NaL spectrum equal to 119–126  $\text{cm}^{-1}$  for C=O and 72–86  $\text{cm}^{-1}$  for P=O compared to the ligand HL spectrum [39].

The presence of the coordinated HL molecules in 1 is confirmed by characteristic IR spectroscopic bands:  $\nu_{as}(\text{C=O})$ ,  $\nu_{as}(\text{P=O})$ ,  $\nu(\text{NH})$ ,  $\nu(\text{Amide II})$  and  $\rho(\text{PNC})$  (Table 1) [40,41]. The 48–54  $\text{cm}^{-1}$  shift of the absorption band of stretching vibrations  $\nu(\text{P=O})$  to lower frequencies was used as a criterion of the ligand coordination to the  $\text{Ln}^{3+}$  ions. There is also a small high-frequency shift for the C=O band in the spectra of coordination compounds in comparison to HL spectrum. The shift may be caused by a slight increase of CO bond order under coordination.

Table 1

FTIR* data ( $\text{cm}^{-1}$ ) of the HL and its coordination compounds $[\text{Ln}(\text{HL})_3\text{Cl}_3]$ .				
Compound	$\nu(\text{NH})$	$\nu(\text{CO})$	$\nu(\text{PO})$	$\rho(\text{PNC})$
HL	3027 m, b	1729 vs, sp	1194 s, sp	498 w, sp
La	2983 m, b	1733 vs, sp	1146 s, sp	523 w, sp
Ce	2990 m, b	1733 vs, sp	1142 s, sp	518 w, sp
Nd	2975 sh, b	1733 vs, sp	1141 s, sp	520 w, sp
Sm	2981 m, b	1734 vs, sp	1140 s, sp	519 m, sp
Eu	2973 m, b	1733 vs, sp	1143 s, sp	520 w, sp
Gd	2972 sh, b	1732 vs, sp	1144 s, sp	520 m, sp
Tb	2994 sh, b	1734 vs, sp	1140 s, sp	523 m, sp
Dy	2962 m, b	1735 vs, sp	1142 s, sp	525 w, sp
Ho	2970 m, b	1735 vs, sp	1143 s, sp	522 w, sp
Er	2970 m, b	1736 vs, sp	1143 s, sp	520 w, sp
Yb	2968 m, b	1735 vs, sp	1142 s, sp	523 m, sp
Lu	2972 m, b	1736 vs, sp	1140 s, sp	523 m, sp

\*s- strong, vs- very strong, m- medium, w- weak, sh- shoulder, b- broad, sp- sharp.

### UV-vis spectroscopy

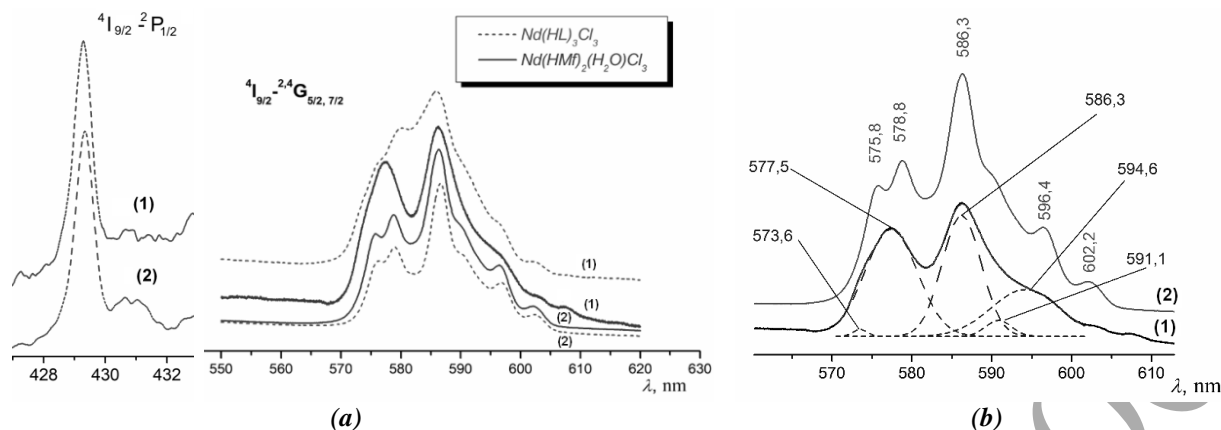
Absorption and luminescence of lanthanide ions as useful structural probes for biomolecular systems have been widely studied. The form and intensity of  $^4\text{I}_{9/2} \rightarrow ^2,4\text{G}_{5/2, 7/2}$  (560–620 nm) transitions are often used as a probe of structural peculiarity. The bands shape in this region is known to be sensitive to the coordination environment around the Nd(III) center [42,43]. Figure 2 shows the characteristic neodymium *f-f* transitions split by a crystal field for  $[\text{Nd}(\text{HL})_3\text{Cl}_3]$  solutions in acetonitrile and toluene. The precise analysis of the band splitting, mainly those of  $^4\text{I}_{9/2} \rightarrow ^2\text{P}_{1/2}$  and the hypersensitive  $^4\text{I}_{9/2} \rightarrow ^2,4\text{G}_{5/2, 7/2}$  transitions allows us to assume the existence of exactly one Nd(III) ion site in the structure  $[\text{Nd}(\text{HL})_3\text{Cl}_3]$ . The number of components of the Kramer's doublet  $^4\text{I}_{9/2} \rightarrow ^2\text{P}_{1/2}$  transition is directly

related to the number of metal sites. Thus, only one component is observed for  $[\text{Nd}(\text{HL})_3\text{Cl}_3]$  (Figure 2(a)). The splitting of the  $^4\text{I}_{9/2} \rightarrow ^2,4\text{G}_{5/2, 7/2}$  transition into six bands when Nd(III) is complexed in an octahedral environment (*e.g.*,  $[\text{NdCl}_6]^{3-}$ ) has been previously reported [42].

From the positions and band shapes observed for  $[\text{Nd}(\text{HL})_3\text{Cl}_3]$  in the absorption spectra we can conclude that the central atom nearest environment in both polar and non-polar solutions has similar octahedral geometry. As shown in Figure 2, the spectrum of acetonitrilic solution contains three asymmetric broadened bands. Decomposition of these bands using Gaussian approximation gives 5 symmetric peaks with the line maxima similar to ones in the spectrum of acetonitrilic solution but with a slight hypsochromic shift (Figure 2(b)).

The electronic spectra of  $[\text{Nd}(\text{HL})_3\text{Cl}_3]$  are identified as alike to that of the six-coordinate  $\text{Nd}^{3+}$  O,O-chelates  $\text{Nd}(\text{thd})_3$  in  $\text{CHCl}_3$  and  $\text{Nd}(\text{DPPD})_3$  in  $\text{C}_6\text{H}_6$  (where thd - is  $(\text{CH}_3)_3\text{CCOCHCO}(\text{CH}_3)_3$ , DPPD - is  $\text{C}_6\text{H}_5\text{CCOCHCOCC}_6\text{H}_5$ ) [43]. Electronic absorption spectra of 0.01 M toluene and

acetonitrile solutions of  $[\text{Nd}(\text{HL})_3\text{Cl}_3]$  and  $[\text{Nd}(\text{HMf})_2(\text{H}_2\text{O})\text{Cl}_3]$  (six-coordinate carbacylamidophosphate complex with similar structure where HMf is 2,2,2-trichloro-N-(dimorpholin-1-yl-phosphoryl)acetamide  $\text{CCl}_3\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})[\text{NC}_4\text{H}_8\text{O}]_2$ ) are given for comparison in Figure 2(a).



**Figure 2.** Absorption spectra of  $[\text{Nd}(\text{HL})_3\text{Cl}_3]$  and  $[\text{Nd}(\text{HMf})_2(\text{H}_2\text{O})\text{Cl}_3]$  in acetonitrile (1) and toluene (2) at room temperature (a) and absorption spectra of  $[\text{Nd}(\text{HL})_3\text{Cl}_3]$  in acetonitrile (b) which have been empirically convoluted by Gaussian functions in order to produce an envelope compared with the experimental measurement (1) and absorption spectra of the  $[\text{Nd}(\text{HL})_3\text{Cl}_3]$  in toluene (2).

### Structural description of $[\text{Sm}(\text{HL})_3\text{Cl}_3]$ (1)

We succeeded in confirming the conclusions regarding the structures of the obtained compounds (based on spectroscopic data) by the results of full X-ray analysis of the  $[\text{Sm}(\text{HL})_3\text{Cl}_3]$  compound (1). Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) are listed in Table 2, the hydrogen bonds parameters are given in Table 3 and the crystal data and structure refinement for  $[\text{Sm}(\text{HL})_3\text{Cl}_3]$  are given in Table 4.

The X-ray analysis reveals that compound **1** crystallizes in the trigonal system with space group  $R\bar{3}$ , samarium atoms are in the special position on a 3-fold rotation axis. The complex **1** was solved as two crystallographically independent fragments  $\text{Sm}(\text{HL})\text{Cl}$ : A and B that exist in the crystalline lattice due to the differences in their similar torsion angles  $\text{Sm}-\text{O}-\text{P}-\text{N}$  ( $27.49^\circ$  and  $25.18^\circ$  in molecules A and B respectively) (Figure 3). The central Sm atom of  $[\text{Sm}(\text{HL})_3\text{Cl}_3]$  in A and B has a distorted octahedral environment (*facial* isomer) coordinated by three Cl anions and three O atoms of CAPH ligands phosphoryl groups (Figure 4(b)). Slightly distorted octahedral  $\text{LnO}_3\text{Cl}_3$  geometry with a *fac*-arrangement of the donor atoms was fixed earlier for the complexes  $[\text{Ln}(\text{CAPH})_3\text{Cl}_3]$  type with carbacylamidophosphates  $\text{CCl}_3\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})[\text{NC}_4\text{H}_8]_2$  and  $\text{CCl}_3\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})[\text{NET}_2]_2$  [44,45]. Triclinic symmetry was shown for  $[\text{Er}(\text{CCl}_3\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})[\text{NC}_4\text{H}_8]_2)_3\text{Cl}_3]$  (space

group  $P\bar{1}$ ) and trigonal one, like **1** for  $[\text{Pr}(\text{CCl}_3\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})[\text{NET}_2]_2)_3\text{Cl}_3]$  (space group  $R\bar{3}$ ). In contrast to these structures, the coordination polymer of  $\text{Ln}^{\text{III}}$  in the structure of  $[\text{Pr}(\text{HMPA})_3\text{Cl}_3]$  (HMPA – is phosphorylic ligand hexamethylphosphoramide) is realized as a meridional isomer [46].

The Sm-O distances are 2.323(5)  $\text{\AA}$  and 2.307(5)  $\text{\AA}$  for molecules A and B (Table 2), respectively, which falls within the bond length range typical of lanthanide complexes with CAPH ligands [22,23]. The Sm-Cl distances are 2.673(2)  $\text{\AA}$  and 2.669(2)  $\text{\AA}$  for molecules A and B, respectively.

The P=O bond lengths in ligands of **1** are 1.495(4)  $\text{\AA}$  and 1.496(4)  $\text{\AA}$  for molecules A and B, respectively, which is longer than the mean value of the P=O bond length (1.45  $\text{\AA}$ ) and the bond in the corresponding ligand HL (see Table 2) [47,48]. Also, the phosphorus atoms conserved a slightly distorted tetrahedral configuration. The angles around P atom in **1** range between  $119.1^\circ$  and  $103.0^\circ$ , for the angles  $\text{O1}-\text{P1}-\text{N3}$  and  $\text{O1}-\text{P1}-\text{N1}$ , respectively.

The P- $\text{N}_{\text{amide}}$  bond lengths are longer than the P- $\text{N}_{\text{pip}}$  bond lengths (bond of phosphorus with the piperidine nitrogen), because of the resonance interaction of the  $\text{N}_{\text{amide}}$  with the C=O system that causes the contribution of  $\pi$ -component into the C- $\text{N}_{\text{amide}}$  bond (the C- $\text{N}_{\text{amide}}$  bond lengths are shorter than the C- $\text{N}_{\text{pip}}$  bond lengths, Table 2).

Table 2

Selected bond lengths (Å) and angles (°) for 1.			
Bond lengths			
Sm1A O1A	2.323(5)	Sm1B O1B	2.307(5)
Sm1A C14A	2.673(2)	Sm1B C14B	2.6684(19)
P1A O1A	1.494(5)	P1B O1B	1.496(5)
P1A N3A	1.610(5)	P1B N3B	1.620(6)
P1A N2A	1.615(6)	P1B N2B	1.623(5)
P1A N1A	1.692(6)	P1B N1B	1.692(5)
O2A C1A	1.197(9)	O2B C1B	1.177(7)
Angles			
O1A-Sm1A-O1A <sup>a</sup>	85.52(16)	O1B-Sm1B-O1B <sup>c</sup>	84.21(17)
O1A-Sm1A-C14A	82.83(12)	O1B-Sm1B-C14B	84.64(12)
O1A <sup>a</sup> -Sm1A-C14A	167.86(12)	O1B <sup>c</sup> -Sm1B-C14B	168.22(13)
O1A <sup>a</sup> -Sm1A-C14A <sup>a</sup>	167.86(12)	O1B <sup>c</sup> -Sm1B-C14B <sup>c</sup>	84.64(12)
O1A <sup>b</sup> -Sm1A-C14A	96.97(12)	O1B <sup>d</sup> -Sm1B-C14B	90.91(13)
O1A-Sm1A-C14A <sup>a</sup>	96.97(12)	O1B-Sm1B-C14B <sup>c</sup>	90.91(13)
C14A-Sm1A-C14A <sup>a</sup>	95.14(7)	C14B-Sm1B-C14B <sup>c</sup>	99.32(6)
C14A <sup>a</sup> -Sm1A-C14A <sup>b</sup>	95.13(7)	C14B <sup>c</sup> -Sm1B-C14B <sup>d</sup>	99.32(6)
O1A-P1A-Sm1A	160.6(3)	O1B-P1B-Sm1B	159.2(3)
O2A-C1A-N1A	124.6(8)	O2B-C1B-N1B	123.2(7)
O1A-P1A-N3A	119.1(3)	O1B-P1B-N3B	110.6(3)
O1A-P1A-N2A	109.9(3)	O1B-P1B-N2B	117.3(3)
N3A-P1A-N2A	106.2(3)	N3B-P1B-N2B	107.5(3)
O1A-P1A-N1A	103.0(3)	O1B-P1B-N1B	103.9(3)
N3A-P1A-N1A	105.5(3)	N3B-P1B-N1B	112.0(3)
N2A-P1A-N1A	113.3(3)	N2B-P1B-N1B	105.5(3)

Symmetry transformations used to generate equivalent atoms:

<sup>a</sup>  $1-x+y+2, -x+1, z$

<sup>b</sup>  $-y+1, x-y-1, z$

<sup>c</sup>  $-y, x-y-1, z$

<sup>d</sup>  $-x+y+1, -x, z$

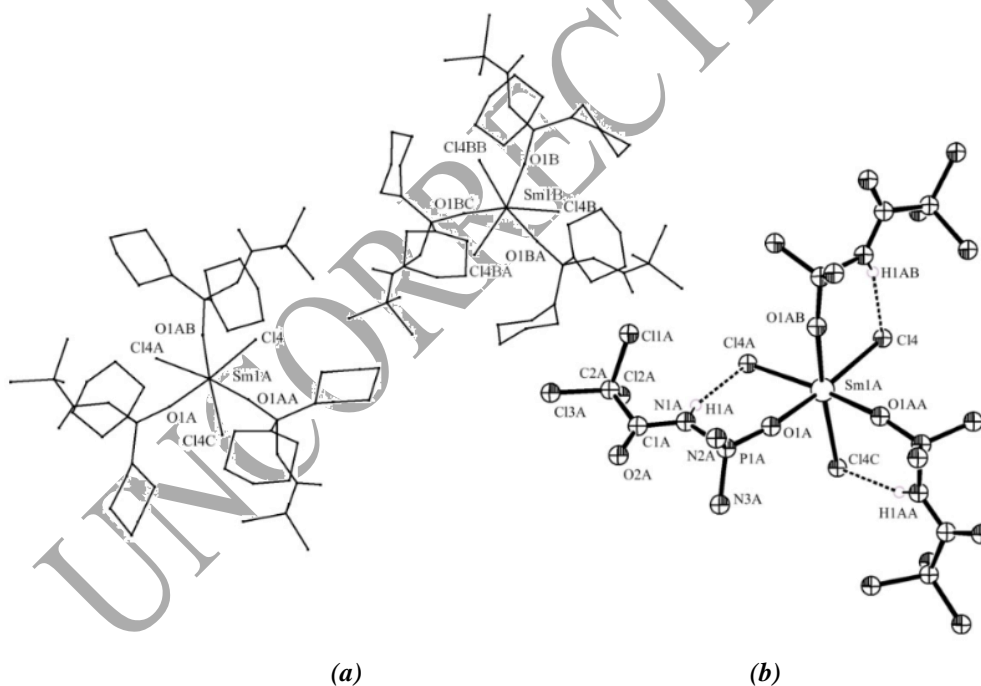


Figure 3. View of the molecules A and B in the unit cell of [Sm(HL)<sub>3</sub>Cl<sub>3</sub>] along to 001. Hydrogen atoms of piperidine rings are omitted for clarity (a). ORTEP visualization of [Sm(HL)<sub>3</sub>Cl<sub>3</sub>] along 001 with partial atom-numbering scheme. Displacement ellipsoids are shown at 30% probability level (b). Dashed lines denote H-bonds. Piperidine rings are omitted for clarity.

All these P–N bonds are shorter than the typical P–N single bond (1.77 Å) [47]. This is probably caused by the electrostatic effects (polar bonds) which overlap with P–N  $\sigma$  bond. The sum of surrounding angles around N1A and N1B atoms are 359.8° and 359.9°, respectively. Similar results were obtained for the nitrogen atoms of other CAPH structures [22–24,39] that confirm the  $sp^2$  hybridization for the N atoms under

consideration, although due to the repulsion and steric interactions, some angles are larger, and others are less than 120°.

In a crystal phase, the molecules of compound **1** form columns along the crystallographic direction (001), which are connected to each other by C(O)⋯Cl short contacts (Figure 5).

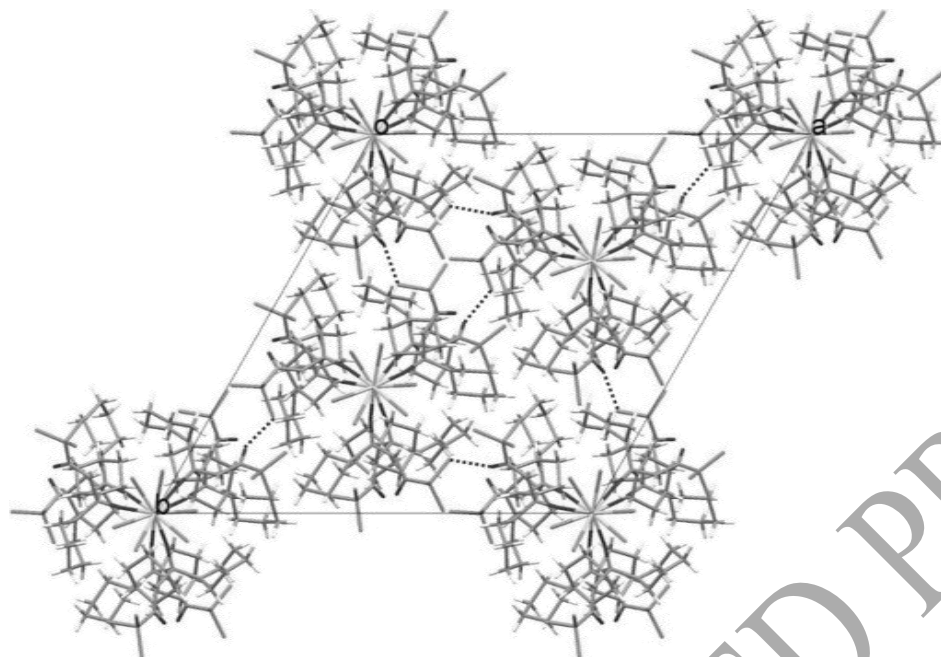


Figure 5. The crystal packing of **1**. The view along the crystallographic *c* axis.

Table 3

<i>D</i> - <i>H</i> ⋯ <i>A</i>	Hydrogen bonds for <b>1</b> .			Angle <i>D</i> - <i>H</i> ⋯ <i>A</i> (°)
	<i>d</i> [Å]			
	<i>D</i> - <i>H</i>	<i>A</i> ⋯ <i>H</i>	<i>D</i> ⋯ <i>A</i>	
N(1A)-H(1A)⋯Cl4	0.86	2.50	3.317(6)	159.9
N(1B)-H(1BA)⋯Cl4B	0.86	2.51	3.337(6)	161.4

Table 4

Crystal data and structure refinement for <b>1</b> .			
Parameter	Value	Parameter	Value
Empirical formula	C <sub>36</sub> H <sub>63</sub> N <sub>9</sub> O <sub>6</sub> P <sub>3</sub> Cl <sub>12</sub> Sm	<i>F</i> (000)	4206
Crystal color	colorless	Crystal size, mm	0.400×0.200×0.100
Formula weight, g·mol <sup>-1</sup>	1386.61	$\theta$ , °	2.819 to 27.498
Temperature, K	293(2)	Reflections collected/unique	29113 / 9160
Wavelength, Å	0.71073	Data/restraints/parameters	9160 / 31 / 459
Crystal system	trigonal		-31 ≤ <i>h</i> ≤ 31
<i>Z</i>	6	Limiting indices	-29 ≤ <i>k</i> ≤ 31
Absorption coefficient, mm <sup>-1</sup>	1.628		-23 ≤ <i>l</i> ≤ 23
Space group	<i>R</i> 3 (146)	GOF	0.679
<i>a</i> , Å	24.098	<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0327
<i>b</i> , Å	24.098		<i>wR</i> <sub>2</sub> = 0.0404
<i>c</i> , Å	18.025		
$\alpha$ , °	90.00	<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	<i>R</i> <sub>1</sub> = 0.1043
$\beta$ , °	90.00		<i>wR</i> <sub>2</sub> = 0.0449
$\gamma$ , °	120.00		
Volume, Å <sup>3</sup>	9065.0	Largest diff. peak and hole, e·Å <sup>-3</sup>	1.164 and -0.398
<i>d</i> , mg·m <sup>-3</sup>	1.524		

## Conclusions

This work showed that the carbacylamidophosphate (CAPH) ligand HL as a heterosubstituted analogue of the  $\beta$ -diketones forms stable coordination compounds of the  $[\text{Ln}(\text{HL})_3\text{Cl}_3]$  type. The coordination of the phosphoryl oxygen atoms of HL to the  $\text{Ln}^{\text{III}}$  ions can be established by the  $\nu(\text{P}=\text{O})$  and  $\nu(\text{C}=\text{O})$  stretching vibrations shifts in the FTIR spectra of the complexes compared to the spectra of “free” CAPH ligand. The precise analysis of the absorption band splitting, mainly those of hypersensitive  $^4\text{I}_{9/2} \rightarrow ^2,4\text{G}_{5/2,7/2}$  transitions of  $[\text{Nd}(\text{HL})_3\text{Cl}_3]$ , allows us to assume that the central atom nearest environment in both polar and non-polar solutions has similar octahedral geometry. This conclusion was indirectly confirmed by X-ray diffraction measurements for  $[\text{Sm}(\text{HL})_3\text{Cl}_3]$ . Due to the peculiar system of intramolecular H-bonds in the structure of  $[\text{Sm}(\text{HL})_3\text{Cl}_3]$  all three CAPH ligands are on the opposite faces of coordination octahedron of Sm(III).

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