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

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Abstract. 14 new mononuclear six-coordinate lanthanide coordination compounds of general formula \([\text{Ln}(H\text{L})Cl]_3\) (\(\text{Ln} = \text{La}-\text{Nd}, \text{Sm}-\text{Lu}\); \(H\text{L} = (2,2,2\text{-trichloro-N-(dipiperidin-1-yl-phosphoryl)})\text{acetamide}\)) carbycylamidophosphate (CAPh) type ligand) have been synthesized from non-aqueous solutions. The complexes have been characterized by elemental analysis, FTIR, \(^1\)H- and \(^{31}\)P-NMR, and UV-Vis spectroscopy. The structure of \([\text{Sm}(H\text{L})Cl]_3\) (1) has been further confirmed by single crystal X-ray diffraction analysis. Crystal data: trigonal, \(R_3\), with \(a = 24.098\ \text{Å}, c = 18.025\ \text{Å}, V = 9065.0\ \text{Å}^3\), \(Z = 6, R_f = 0.0327,\) and \(wR_f = 0.0404.\) The crystal structure was solved as two crystallographically independent fragments \(\text{Sm}(H\text{L})\text{Cl}_2\): A and B that exist in the crystalline lattice due to the differences in some geometrical parameters.

Keywords: lanthanide, carbycylamidophosphate, 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]. Carbycylamidophosphates (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 anti-cancer activity [19,20]. The lanthanide chelates of CAPHs exhibit biological activities and in vitro tests show their strong anti-cancer 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 (\(n\text{-C}_3\text{H}_{11}\) – \(n\text{-C}_{10}\text{H}_{21}\)) 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 \([\text{Ln}(H\text{L})\text{Cl}_3]\) (\(\text{Ln} = \text{La}-\text{Nd}, \text{Sm}-\text{Lu}\); \(H\text{L} = \text{CCl}_3\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})\text{N}(\text{CH}_2)_3\text{Cl}_2\)-2,2,2-trichloro-N-(dipiperidin-1-yl-phosphoryl)acetamide) and crystal structure of trichlorotris[2,2,2-trichloro-N-(dipiperidinophosphoryl)acetamide]samarium (III) \([\text{Sm}(H\text{L})_3\text{Cl}_3]_\text{str.}\) (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).* 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. $^1$H NMR (400 MHz, DMSO-d$_6$, RT): $\delta$ = 1.51 (d, 4H, $\beta$-CH$_3$), 1.58 (d, 2H, $\gamma$-CH$_2$), 3.16 (s, 4H, $\alpha$-CH$_2$), 9.37 (s, 1H, NH). $^{31}$P NMR (162 MHz, DMSO-d$_6$, RT): $\delta$ = 10.18 (s, P=O).

*Trichlorotris[2,2,2-trichloro-N-(dipiperidinophosphoryl)acetamide]samarium (III) [Sm(HL)$_3$Cl]$_2$ (1) (Figure 1)* and coordination compounds [Ln(HL)$_3$Cl]$_2$ 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$_2$. 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.

For C$_{36}$H$_{60}$N$_{10}$O$_{6}$P$_{3}$Cl$_{12}$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.

$^1$H NMR (400 MHz, DMSO-d$_6$, RT): [La(HL)$_3$Cl]$_2$: $\delta$ = 1.63 (d, 4H, $\beta$-CH$_2$), 1.68 (d, 2H, $\gamma$-CH$_2$), 3.24 (s, 4H, $\alpha$-CH$_2$), 9.87 (s, 1H, NH); [Lu(HL)$_3$Cl]$_2$: $\delta$ = 1.65 (d, 4H, $\beta$-CH$_2$), 1.7 (d, 2H, $\gamma$-CH$_2$), 3.25 (s, 4H, $\alpha$-CH$_2$), 9.85 (s, 1H, NH). $^{31}$P NMR (162 MHz, DMSO-d$_6$, RT): [La(HL)$_3$Cl]$_2$: $\delta$ = 9.21 (s, P=O); Lu: $\delta$ = 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.

$^1$H and $^{31}$P NMR spectra in DMSO-d$_6$ solutions were recorded on a Varian 400 NMR spectrometer at room temperature (RT). $^1$H chemical shifts were determined relative to the internal TMS, whereas $^{31}$P chemical shifts were calculated relatively to an external standard of 85% H$_3$PO$_4$.

*Fourier transform infrared spectroscopy (FTIR)* spectra were recorded on a Perkin–Elmer Spectrum BX spectrometer using KBr pellets with resolution of 1 cm$^{-1}$, in the range 4000–400 cm$^{-1}$.

*UV-Vis absorption spectra* of [Nd(HL)$_3$Cl]$_2$ solutions were measured at RT in absolute non-aqueous solvents on a KSVU-23 “LOMO” spectrometer using 3 cm$^3$ stopped quartz cell of 1 cm pathlength. The concentrations of complexes were 1·10$^{-2}$ mol/L.

*Single crystal X-ray diffraction (XRD)* data for [Sm(HL)$_3$Cl]$_2$ (1) was collected at 20°C using Xcalibur-3 diffractometer (Mo-$\text{K}\alpha$ radiation, CCD-detector, graphite monochromator, $\omega$-scan). The size of a single crystal was 0.40×0.20×0.1 mm. The structure was solved by direct method and refined against $F^2$ 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 $U_{iso} = 1.2U_{eq}$ 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$^3$-Csp$^3$ 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...

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*Figure 1. Representation of CAPh-ligand coordination mode in [Sm(HL)$_3$Cl]$_2$.***
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 carboxylamidophosphates 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 cm$^{-1}$ for C=O and 72–86 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: $\nu_{\text{as}}$(C=O), $\nu_{\text{as}}$(P=O), $\nu$(NH), $\nu$(Amide II) and $\rho$(PNC) (Table 1) [40,41]. The 48–54 cm$^{-1}$ shift of the absorption band of stretching vibrations $\nu$(P=O) to lower frequencies was used as a criterion of the ligand coordination to the 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.

**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 $^5_{2g} \rightarrow ^4_{2g}$ (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 [Nd(HL)$_2$Cl$_3$] solutions in acetonitrile and toluene. The precise analysis of the band splitting, mainly those of $^4_{2g} \rightarrow ^2_{2g}$ and the hypersensitive $^4_{2g} \rightarrow ^2_{4g}$ transitions allows us to assume the existence of exactly one Nd(III) ion site in the structure [Nd(HL)$_2$Cl$_3$]. The number of components of the Kramer’s doublet $^2_{2g} \rightarrow ^2_{2g}$ transition is directly related to the number of metal sites. Thus, only one component is observed for [Nd(HL)$_2$Cl$_3$] (Figure 2(a)). The splitting of the $^4_{2g} \rightarrow ^2_{4g}$ transition into six bands when Nd(III) is complexed in an octahedral environment (e.g., [NdCl$_6$]$^{3-}$) has been previously reported [42].

From the positions and band shapes observed for [Nd(HL)$_2$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 [Nd(HL)$_2$Cl$_3$] are identified as alike to that of the six-coordinate
**Nd**$^{3+}$ O,O-chelates Nd(thd)$_3$ in CHCl$_3$ and Nd(DPPD)$_3$ in C$_6$H$_6$ (where thd - is (CH$_3$)$_2$CCOCHCOC(CH$_3$)$_3$, DPPD - is C$_6$H$_5$CCOCHCOC(C$_6$H$_5$)$_3$) [43]. Electronic absorption spectra of 0.01 M toluene and acetonitrile solutions of [Nd(HL)$_2$Cl$_3$] and [Nd(HMF)$_2$(H$_2$O)Cl$_3$] (six-coordinate carbacylamidophosphate complex with similar structure where HMF is 2,2,2-trichloro-N-(dimorpholin-1-yl-phosphoryl)acetamide CCl$_3$C(O)N(H)P(O)[NC$_6$H$_4$(O)$_2$] are given for comparison in Figure 2(a).

![Figure 2](image)

**Figure 2.** Absorption spectra of [Nd(HL)$_2$Cl$_3$] and [Nd(HMF)$_2$(H$_2$O)Cl$_3$] in acetonitrile (1) and toluene (2) at room temperature (a) and absorption spectra of [Nd(HL)$_2$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 [Nd(HL)$_2$Cl$_3$] in toluene (2).

**Structural description of [Sm(HL)$_2$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 [Sm(HL)$_2$Cl$_3$] compound (1). Selected bond lengths (Å) and angles (°) are listed in Table 2, the hydrogen bonds parameters are given in Table 3 and the crystal data and structure refinement for [Sm(HL)$_2$Cl$_3$] are given in Table 4.

The X-ray analysis reveals that compound 1 crystallizes in the trigonal system with space group R3, samarium atoms are in the special position on a 3-fold rotation axis. The complex 1 was solved as two crystallographically independent fragments Sm(HL)Cl: A and B that exist in the crystalline lattice due to the differences in their similar torsion angles Sm–O–P–N (27.49° and 25.18° in molecules A and B respectively) (Figure 3). The central Sm atom of [Sm(HL)$_2$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 LnO$_6$Cl$_3$ geometry with a face-arrangement of the donor atoms was fixed earlier for the complexes [Ln(CAPH)$_2$Cl$_3$] type with carbacylamidophosphates CCl$_3$C(O)N(H)P(O)[NC$_6$H$_4$I$_2$] and CCl$_3$C(O)N(H)P(O)[NET$_2$]$_2$ [44,45]. Triclinic symmetry was shown for [Er(CCl$_3$C(O)N(H)P(O)[NC$_6$H$_4$I$_2$])$_2$Cl] (space group P-1) and trigonal one, like 1 for [Pr(CCl$_3$C(O)N(H)P(O)[NET$_2$])$_2$Cl] (space group R3). In contrast to these structures, the coordination polymer of Ln$^{III}$ in the structure of [Pr(HMPA)$_2$Cl$_3$] (HMPA – is phosphoryl ligand hexamethylphosphoramide) is realized as a meridional isomer [46].

The Sm-O distances are 2.323(5) Å and 2.307(5) Å 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) Å and 2.669(2) Å for molecules A and B, respectively.

The P=O bond lengths in ligands of 1 are 1.495(4) Å and 1.496(4) Å for molecules A and B, respectively, which is longer than the mean value of the P=O bond length (1.45 Å) 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° and 103.0°, for the angles O1–P1–N3 and O1–P1–N1, respectively.

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

Selected bond lengths (Å) and angles (°) for 1.

<table>
<thead>
<tr>
<th>Bond lengths</th>
<th>Sm1A O1A 2.323(5)</th>
<th>Sm1B O1B 2.307(5)</th>
<th>Sm1A Cl4A 2.673(2)</th>
<th>Sm1B Cl4B 2.6684(19)</th>
<th>P1A O1A 1.494(5)</th>
<th>P1B O1B 1.496(5)</th>
<th>P1A N3A 1.610(5)</th>
<th>P1B N3B 1.620(6)</th>
<th>P1A N2A 1.615(6)</th>
<th>P1B N2B 1.623(5)</th>
<th>P1A N1A 1.692(6)</th>
<th>P1B N1B 1.692(5)</th>
<th>O2A C1A 1.197(9)</th>
<th>O2B C1B 1.177(7)</th>
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<td>Bond lengths</td>
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<td>Angles</td>
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<tr>
<td>O1A-Sm1A-O1A</td>
<td>85.52(16)</td>
<td>O1B-Sm1B-O1B</td>
<td>84.21(17)</td>
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<tr>
<td>O1A-Sm1A-Cl4A</td>
<td>82.83(12)</td>
<td>O1B-Sm1B-Cl4B</td>
<td>84.64(12)</td>
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<tr>
<td>O1A'-Sm1A-Cl4A</td>
<td>167.86(12)</td>
<td>O1B'-Sm1B-Cl4B</td>
<td>168.22(13)</td>
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<tr>
<td>O1A'-Sm1A-Cl4A</td>
<td>96.97(12)</td>
<td>O1B'-Sm1B-Cl4B</td>
<td>90.91(13)</td>
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<tr>
<td>O1A-Sm1A-Cl4A</td>
<td>96.97(12)</td>
<td>O1B-Sm1B-Cl4B</td>
<td>90.91(13)</td>
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<tr>
<td>O1A-Sm1A-Cl4A</td>
<td>95.14(7)</td>
<td>Cl4B-Sm1B-Cl4B</td>
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<tr>
<td>Cl4A'-Sm1A-Cl4A</td>
<td>95.13(7)</td>
<td>Cl4B'-Sm1B-Cl4B</td>
<td>99.32(6)</td>
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</tbody>
</table>

Symmetry transformations used to generate equivalent atoms:

- $1: x+y+2, -x+1, z$
- $2: -y+1, x-y, 1-z$
- $3: -y, z, -y, -1, z$
- $4: -x+y+1, -x, z$

Figure 3. View of the molecules A and B in the unit cell of [Sm(HL)₃Cl₃] along to 001. Hydrogen atoms of piperidine rings are omitted for clarity (a). ORTEP visualization of [Sm(HL)₃Cl₃] 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 σ 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.](image)

### Hydrogen bonds for 1.

<table>
<thead>
<tr>
<th>D-H···A</th>
<th>(d) (Å)</th>
<th>(A-H)</th>
<th>(D-A)</th>
<th>Angle D-H···A (°)</th>
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<tbody>
<tr>
<td>N(1A)-H(1A)···Cl4</td>
<td>0.86</td>
<td>2.50</td>
<td>3.317(6)</td>
<td>159.9</td>
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<tr>
<td>N(1B)-H(1BA)···Cl4B</td>
<td>0.86</td>
<td>2.51</td>
<td>3.337(6)</td>
<td>161.4</td>
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</table>

### Crystal data and structure refinement for 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>(C_{36}H_{63}N_9O_6P_3Cl_2)Sm</td>
<td>F(000)</td>
<td>4206</td>
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<td>colorless</td>
<td>Crystal size, mm</td>
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<td>Formula weight, g·mol(^{-1})</td>
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<td>(\theta) °</td>
<td>2.819 to 27.498</td>
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<td>Reflections collected/unique</td>
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<td>Wavelength, Å</td>
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<td>Data/restraints/parameters</td>
<td>9160 / 31 / 459</td>
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<td>Crystal system</td>
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<tr>
<td>(Z)</td>
<td>6</td>
<td>Limiting indices</td>
<td>-31 (\leq h \leq 31)</td>
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<tr>
<td>Absorption coefficient, mm(^{-1})</td>
<td>1.628</td>
<td></td>
<td>-29 (\leq k \leq 31)</td>
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<td></td>
<td></td>
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<td>-23 (\leq l \leq 23)</td>
</tr>
<tr>
<td>Space group</td>
<td>R3 (146)</td>
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<tr>
<td>(a), Å</td>
<td>24.098</td>
<td>(R_1, wR_2 [I &gt; 2\sigma(I)])</td>
<td>(R_1 = 0.0327)</td>
</tr>
<tr>
<td>(b), Å</td>
<td>24.098</td>
<td></td>
<td>(wR_2 = 0.0404)</td>
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<td>(c), Å</td>
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<td>(\alpha), °</td>
<td>90.00</td>
<td>(R_1, wR_2) (all data)</td>
<td>(R_1 = 0.1043)</td>
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<td>(\beta), °</td>
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<td>(wR_2 = 0.0449)</td>
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<td>(\gamma), °</td>
<td>120.00</td>
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<tr>
<td>Volume, Å(^3)</td>
<td>9065.0</td>
<td>Largest diff. peak and hole, e·Å(^3)</td>
<td>1.164 and -0.398</td>
</tr>
<tr>
<td>(d), mg·m(^{-3})</td>
<td>1.524</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Conclusions
This work showed that the carbacylamidophosphate (CAPh) ligand HL as a heterosubstituted analogue of the β diketones forms stable coordination compounds of the [LnHL3][Cl]. The coordination of the phosphoryl oxygen atoms of HL to the LnIII ions can be established by the ν(P=O) and ν(C=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 4G5/2 → 2G9/2,7/2 transitions of [NdHL3][Cl], allows us to assume that the central atom nearest environment in both polar and nonpolar solutions has similar octahedral geometry. This conclusion was indirectly confirmed by X-ray diffraction measurements of [SmHL3][Cl]. Due to the peculiar system of intramolecular H-bonds in the structure of [SmHL3][Cl] all three CAPh ligands are on the opposite faces of coordination octahedron of Sm(III).

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