

New carbacylamidophosphates (CAPH) and CAPH-containing coordination compounds: structural peculiarities

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Abstract The new carbacylamidophosphate derivative **HL1** (**1**) with general formula $\text{Cl}_3\text{CC}(\text{O})\text{N}(\text{H})\text{P}(\text{O})(\text{CH}_2\text{C}_5\text{H}_4\text{N})_2$ named 2,2,2-trichloro-N-(3-(aminomethyl)pyridine)-1-yl-phosphoryl)-acetamide), the potassium, lanthanide and uranyl (VI) complexes with the different CAPH ligands: $\text{KL2}\cdot\text{H}_2\text{O}$ (**2**) and $\text{Eu}(\text{L2})_3\cdot\text{H}_2\text{O}$ (**3**) with 2,2,2-trichloro-N-(dimorpholinophosphoryl)acetamide ($\text{CCl}_3\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})(\text{N}(\text{C}_2\text{H}_4)_2\text{O})_2$, **HL2**), $\text{Ce}(\text{L3})_3(i\text{-PrOH})_2\cdot i\text{-PrOH}$ (**4**) with N-(bis(phenylamino)phosphoryl)-2,2,2-trichloroacetamide ($\text{CCl}_3\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})(\text{NHC}_6\text{H}_5)_2$, **HL3**), $\text{Nd}(\text{NO}_3)_3(\text{HL4})_2$ (**5**), $\text{Nd}(\text{NO}_3)_3(\text{HL5})_2$ (**6**) and $\text{UO}_2(\text{NO}_3)_2(\text{HL5})_2$ (**7**) ($\text{HL4}=\text{CH}_3(\text{C}_4\text{H}_3\text{N})\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})(\text{N}(\text{CH}_3)_2)_2$ —N-(bis(dimethylamino)phosphoryl)-1-methyl-1H-pyrrole-2-carboxamide, $\text{HL5}=\text{CH}_3(\text{C}_4\text{H}_3\text{N})\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})(\text{N}(\text{C}_2\text{H}_5)_2)_2$ —N-(bis(diethylamino)phosphoryl)-1-methyl-1H-pyrrole-2-carboxamide) have been synthesized. Obtained compounds were characterized by means of FTIR, ¹H and ³¹P NMR spectroscopy. Crystal structures of **1–7** have been determined. Compound **2** represents the first structure of the deprotonated CAPH compounds with bridging function of both carbonyl and phosphoryl groups. Structural

peculiarities of CAPH ligands in the composition of the synthesized coordination compounds are discussed.

Keywords Carbacylamidophosphates · Heterosubstituted β -diketones · Lanthanide complexes · Coordination polyhedra · Lanthanide-oxygen bond

Introduction

Carbacylamidophosphates (CAPH)—substances with $\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O}) = \text{core}$ —belong to the new powerful ligand systems [1]. Many compounds of this type are already known as drugs, insecticides, acaricides, fungicides, herbicides, growth regulator for plants, defoliants, extractants, antioxidants and anti-corrosive additives [2, 3]. It should be noted that CAPH compounds can be considered like a structural analogous of the widely studied bidentate-chelating ligands— β -diketones, whose complexes have been practically applied for a long time [4–9]. Heterosubstitution of carbon atoms of chelating core often leads to useful new properties untypical for β -diketones. For example, replacing of one carbonyl group in β -diketone functional fragment to phosphoryl allows to find a new class of effective extractants able to extracting of uranium(VI), americium(III) and europium(III) from acidic radioactive solutions [10–12] since the phosphoryl group has the very high affinity to the majority of metal ions, and especially to the lanthanides and actinides [13]. Many representatives of this type complexes have been synthesized and investigated at the moment [14–21]. The possibility of involving in the coordination sphere both in the molecular and acidic forms makes the coordination chemistry of CAPH extremely diverse and interesting and

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allows to use CAPH ligands in the lanthanides and actinides coordination chemistry [8, 14].

The influence of substituents nature near $-C(O)N(H)P(O)=$ functional fragment on the structural parameters of compounds under consideration and on the peculiarity of the intramolecular interactions in the crystal state of CAPH compounds gives us an additional information for the purposeful synthesis of new coordinational compounds with useful properties.

In this work, we report structures and properties of some new carbacylamidophosphates and CAPH-containing coordination compounds. Structural peculiarities of the synthesized compounds will be discussed.

Experimental

General

$Ln(NO_3)_3 \cdot nH_2O$ ($Ln=Ce, Nd, Eu$), $UO_2(NO_3)_2 \cdot 2H_2O$ were of “puriss. p.a.” grade and used without further purification. 2,2,2-trichloro-N-(dimorpholinophosphoryl)acetamide ($Cl_3CC(O)N(H)P(O)[N(CH_2)_4O]_2$, **HL2** [17]) and N-(bis(phenylamino)phosphoryl)-2,2,2-trichloroacetamide ($CCl_3C(O)N(H)P(O)(NHC_6H_5)_2$, **HL3** [18]) were prepared according to the previously described methods and were identified using IR and NMR spectroscopy.

1H and ^{31}P NMR spectra in DMSO- d_6 solutions were recorded on a Varian 400 NMR spectrometer at room temperature. 1H chemical shifts were determined on 400-MHz frequency relative to the internal TMS, whereas ^{31}P chemical shifts on 162.1-MHz frequency relative to 85 % H_3PO_4 as an external standard. Infrared (FTIR) spectra were recorded on a PerkinElmer Spectrum BX spectrometer using KBr pellets. Resolution of the FTIR spectra is 1 cm^{-1} .

Syntheses

2,2,2-trichloro-N-(3-(aminomethyl)pyridine)-1-yl-phosphoryl)-acetamide, **HL1** (1)

The solution of the dichloride of trichloroacetylaminodiphosphoric acid (14 g, 0.05 mol) [19] in 150 ml of dioxane was added slowly with stirring to the solution of 3-(aminomethyl)pyridine (10.8 g, 0.1 mol), triethylamine (15.2 g, 0.15 mol) and dioxane (100 ml). The mixture was cooled by ice to 268 K. The temperature was not allowed to rise above 278 K. Stirring was continued for about 1 h, and the solution was left under ambient conditions for 1 day. The resulting mixture was evaporated. Then, the solid residue was treated with water and filtered off. The solid precipitate of 2,2,2-trichloro-N-(3-(aminomethyl)pyridine)-1-yl-phosphoryl)-acetamide (**HL1**) was recrystallized from 2-propanol as a white crystalline powder (80 % yield). The compound is air-stable, soluble in alcohols and hot acetone, and insoluble in nonpolar aprotic solvents and water, M.p. 120 °C.

White crystals of **1** suitable for X-ray analysis were obtained from the 2-propanol solution slow evaporation.

The structural formulas of **1** and of all the compounds synthesized are shown in Scheme 1.

Poly- $[\mu\text{-aqua}[2,2,2\text{-trichloro-N-(dimorpholinophosphoryl)acetamido]sodium(I)] [KL2 \cdot H_2O]_n$ (2)

The 0.38 g (1 mmol) of 2,2,2-trichloro-N-(dimorpholinophosphoryl)acetamide (**HL2**) was dissolved in methanol (10 ml) and added to 10 ml of potassium hydroxide solution in methanol (0.056 g, 1 mmol of KOH in methanol). The obtained solution was heated to boiling and was left at ambient temperature for crystallization in air. After 36 h, the crystals precipitated from the solution and were separated by filtration. Yield: 76 %. The compound **2** is quite stable in air for a long time, like a majority of the “simple” CAPH salts with sodium, rubidium and cesium [20, 21], M.p. 173 °C. The $[KL2 \cdot H_2O]_n$ is soluble in acetone, acetonitrile, alcohols, toluene, soluble in water by heating and insoluble in hexane and cyclohexane. Colorless monocystals of **2** suitable for X-ray analysis were obtained from the methanol solution slow evaporation.

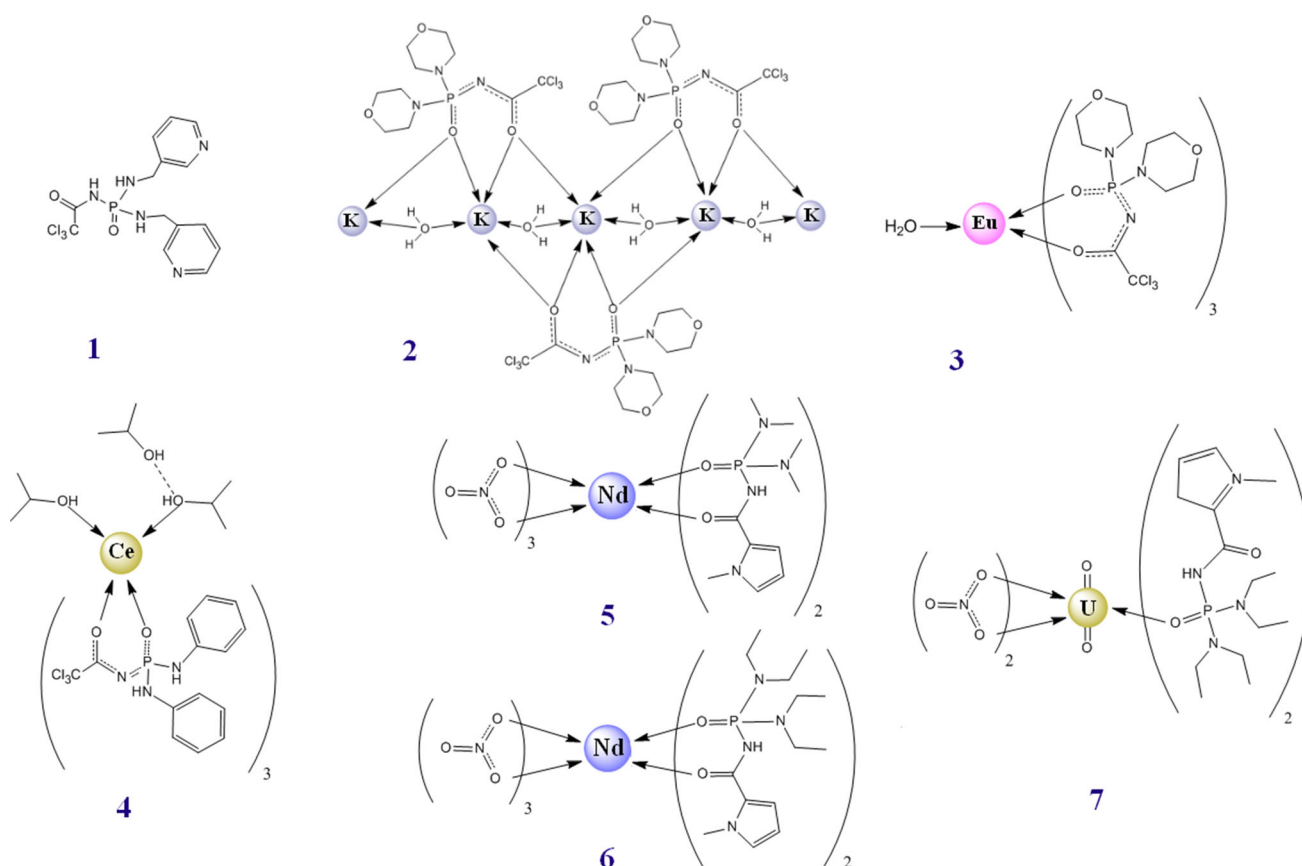
Tris(2,2,2-trichloro-N-(dimorpholin-1-yl-phosphoryl)acetamido-O, O')-diaqua-europium(III) $Eu(L2)_3 \cdot H_2O$ (3)

The solution of $Eu(NO_3)_3 \cdot 6H_2O$ (1 mmol) was dissolved in isopropanol (15 ml) and added to the solution of **NaL2** (3 mmol) in 20 ml of acetone and heated to the boiling point. After cooling for 15 min, the precipitated $NaNO_3$ was filtered off. The resulting clear solution was left at ambient temperature in desiccator over $CaCl_2$. In a day, the coordination compound precipitated as powder was filtered, washed with suction by acetone cooled to 15 °C and finally dried on air (Yield 80 %). The obtained $Eu(L2)_3 \cdot H_2O$ is stable on air and is soluble in nonpolar aromatic solvents, acetone, chloroform, DMFA, DMSO, soluble poorly in isopropanol and insoluble in water.

Single crystals of **3** were prepared by slow recrystallization from the acetone solution.

Tris(N-(bis(phenylamino)phosphoryl)-2,2,2-trichloroacetamido-O, O')-bis(isopropanol)-cerium(III) isopropanole solvate $Ce(L3)_3(i\text{-}PrOH)_2 \cdot i\text{-}PrOH$ (4)

The sodium salt of N-(bis(phenylamino)phosphoryl)-2,2,2-trichloroacetamide **NaL3** was prepared by the reaction



Scheme 1 Structural formulas of synthesized compounds

between equimolar amounts of sodium isopropylate (0.069 g, 3 mmol of Na was dissolved in isopropanol) and **HL3** (1.181 g, 3 mmol) in isopropanol medium and was used for the preparation of the complex without isolation from the reaction mixture.

A solution of **NaL3** heated up to 55 °C (1.247 g, 3 mmol) in isopropanol (10 ml) was added to a $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ solution heated up to 55 °C (0.434 g, 1 mmol, previously it was dehydrated by the boiling with 6 mmol $\text{HC}(\text{OC}_2\text{H}_5)_3$ in 20 ml of acetone). After 15 min, the resulting mixture was filtered from the sodium nitrate and the filtrate was left above CaCl_2 at room temperature.

The crystals of the complexes were formed after 2 days, filtered and washed with cooled-to-10 °C isopropanol (yield 82 %). The complex $\text{Ce}(\text{L3})_3(i\text{-PrOH})_2 \cdot i\text{-PrOH}$ (**4**) is soluble in acetone, methanol and nonpolar aprotic solvents, is less soluble in isopropanol and is insoluble in the water. Single crystals of **4** were prepared by slow crystallization from the isopropanol solution, but

they are unstable in air because of coordinated solvent molecules losing.

*Bis(N-(bis(dimethylamino)phosphoryl)-1-methyl-1H-pyrrole-2-carboxamido-O, O')-neodymium(III) $\text{Nd}(\text{NO}_3)_3(\text{HL4})_2$ (**5**) and bis(N-(bis(diethylamino)phosphoryl)-1-methyl-1H-pyrrole-2-carboxamido-O, O')-neodymium(III) $\text{Nd}(\text{NO}_3)_3(\text{HL5})_2$ (**6**)*

$\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (1 mmol) was dissolved in isopropanol (15 ml) and was heated to the boiling point to dissolve the salt completely and then added to the solution of carbacylamidophosphate ligand **HL4** or **HL5** (2 mmol) in acetone (15 ml). The reaction mixture was allowed to stand in a vacuum desiccator over CaCl_2 . After precipitation, the crystals were filtered off, washed with cooled isopropanol and dried over CaCl_2 (yield 78 %). The complexes **5** and **6** are soluble in acetone and methanol and are insoluble in water. The single crystals of

$\text{Nd}(\text{NO}_3)_3(\text{HL4})_2$ and $\text{Nd}(\text{NO}_3)_3(\text{HL5})_2$ were prepared by slow crystallization from isopropanole.

Bis(N-(bis(diethylamino)phosphoryl)-1-methyl-1H-pyrrole-2-carboxamido-O, O')-dioxo-uranium(VI) $\text{UO}_2(\text{NO}_3)_2(\text{HL5})_2$ (7)

To solution of 0.215 g (0.5 mmol) of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in 10 ml of acetonitrile, 0.18 ml (1 mmol) of $\text{HC}(\text{OC}_2\text{H}_5)_3$ was added as a dehydration reagent. The solution was heated to the boiling within two minutes to dissolve the uranyl nitrate completely and then was added to the solution of 0.388 g (1 mmol) of **HL5** in 10 ml of methanol. The resulting mixture was heated to boiling and was left at ambient temperature for crystallization in a vacuum desiccator over CaCl_2 for 24 h. The compound **7** was obtained in a form of well-faceted yellow-green crystals, which were filtered, washed with cooled diethyl ether and dried over CaCl_2 . The yield was 83 %. The compound is air-stable, soluble in alcohols and acetone, and insoluble in nonpolar aprotic solvents and water.

Compound **1**: IR (cm^{-1}): 1706 vs, sp (ν_{CO}), 1236 s, sp (ν_{PO}). ^1H NMR (DMSO- d_6): 4.08 (m, 4H, 2CH₂); 5.60 (m, 2H, 2NH); 7.32 (dd, 1H of C₅H₄ N), 7.76, 8.42 (d, 2H of C₅H₄ N), 8.54 (s, 1H of C₅H₄ N); 9.95 (s, 1H, NH of C₅H₄ N). ^{31}P NMR (DMSO- d_6): 11.64 (m, PO).

Compound **2**: IR (cm^{-1}): 1628 vs, sp (ν_{CO}), 1338 s, sp (Amide II), 1182 s, sp (ν_{PO}), 960 s, sp (ν_{PN}), 678 s, sp (ν_{CCl}), 530 m, sp (δ_{PNC}). ^1H NMR (DMSO- d_6): 3.4 (m, 4 H, 2,6-CH₂), 3.03 (m, 4 H, 3,5-CH₂). ^{31}P NMR (DMSO- d_6): 12.83 (s, PO).

Compound **3**: IR (cm^{-1}): 1605 vs, sp (ν_{CO}), 1355 s, sp (Amide II), 1120 s, sp (ν_{PO}), 1012 s, sp (ν_{PN}), 698 s, sp (ν_{CCl}), 524 m, sp (δ_{PNC}).

Compound **4**: IR (cm^{-1}): 1590 vs, sp (ν_{CO}), 1350 s, sp (Amide II), 1130 s, sp (ν_{PO}), 1010 s, sp (ν_{PN}), 694 s, sp (ν_{CCl}), 528 m, sp (δ_{PNC}).

Compound **5**: IR (cm^{-1}): 1629 vs, sp (ν_{CO}), 1177 s, sp (ν_{PO}).

Compound **6**: IR (cm^{-1}) 1633 vs, sp (ν_{CO}), 1174 s, sp (ν_{PO}).

Compound **7**: IR (cm^{-1}) 1681 vs, sp (ν_{CO}), 1150 s, sp (ν_{PO}).

X-ray structural study

Crystal data for **1–7** were measured on an Xcalibur-3 diffractometer (graphite-monochromated Mo- K_α radiation, CCD detector, φ and ω -scanning, $\lambda = 0.71073 \text{ \AA}$) at the room temperature. The structures were solved by the direct method using SHELXTL package [22]. Full-matrix least-squares refinement against F^2 in anisotropic approximation was used for non-hydrogen atoms. All H atoms were

placed in idealized positions with constrained distance of 0.96 Å (RCH₃), 0.97 Å (R₂CH₂), 0.98 Å (R₃CH), 0.82 Å (O–H), 0.93 Å for aromatic and 0.86 Å for amide group. Uiso(H) values set to either 1.2_{eq} or 1.5_{eq} (RCH₃, OH) of the attached atom. In the structure **2**, one of the morpholine rings is disordered on two positions with 0.7 occupancy for main residual. The CCl₃ group is rotationally disorder with main residual 0.6. In both disordered fragments, standard bond lengths C–C, N–C, C–O and C–Cl were fixed. In the structure **3**, the C12 O7 C13 atoms of the morpholine ring are disordered on two positions with 0.75 occupancy for main residual with standard bond length fixed. In the structure **5**, two dimethylamide groups of one of the phosphoryl ligands are disordered on two positions with 0.6 occupancy for main residual and N–C bonds are fixed. In the structure **6**, four-terminal carbon–carbon bond lengths in diethylamide groups were fixed. Refinement on F^2 was carried out against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , and conventional R-factors R are based on F, with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt), etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

CCDC 1063113-18 and 1401193 (CCDC numbers according to the Table 1) contain the supplementary crystallographic data for **1–7**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Experimental details of the structures **1–7** refinements are presented in Table 1, while the crystal structure data, selected bond lengths and angles are listed in Tables 2, 3 and 4. DIAMOND plots of the structures **1–7** are displayed in Figs. 1, 2, 3, 4, 5 and 6.

Results and discussion

Structural analysis of **1–7**

Several general structural features have been found for the crystal structures of the CAPH derivatives in our previous studies [17, 18, 21]. Most of the established regularities are characteristic also for the structure **1**:

In the fragment=P(O)N(H)C(O)- the PO and NH bonds are in *syn* position to each other, and the PO and CO groups are in *anti*-position to each other (Fig. 1). Generally, this disposition differs from the ideal *anti*-conformation [17, 18, 23]. So, the O(2)-P(1)-C(2)-O(1) torsion angles are equal to 170.9° and 169.9° in **1A** and **1B**, respectively.

Table 1 Experimental details: crystallographic data and refinement parameters

	1	2	3	4
Empirical formula	C ₁₄ H ₁₅ Cl ₃ N ₅ O ₂ P	C ₁₀ H ₁₈ Cl ₃ KN ₃ O ₅ P	C ₃₀ H ₅₀ Cl ₉ EuN ₉ O ₁₃ P ₃	C ₅₁ H ₆₀ CeCl ₉ N ₉ O ₉ P ₃
<i>M_r</i>	422.63	436.69	1308.71	1495.16
Crystal system, space group	Orthorhombic, <i>Pbcn</i>	Monoclinic, <i>P2₁/c</i>	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$
<i>a</i> (Å)	39.3110(13)	10.087(3)	10.9384(4)	12.278(5)
<i>b</i> (Å)	10.1730(3)	25.064(2)	12.0444(5) 21.2292(9)	14.560(5)
<i>c</i> (Å)	18.6430(6)	7.671(3)		18.725(5)
α (°)		108.94(3)	78.110(4) 81.180(3)	93.316(5)
β (°)			73.354(4)	103.211(5)
γ (°)				97.899(5)
<i>V</i> (Å ³)	7455.5(4)	1834.3(10)	2608.9(2)	3214.1(19)
<i>Z</i> , <i>D_x</i> (g/cm ³)	16, 1.506	4, 1.581	2, 1.666	2, 1.545
μ (mm ⁻¹)	0.596	0.838	1.817	1.215
<i>F</i> (000)	3456	896	1316	1514
Crystal size (mm)	0.40 × 0.20 × 0.20	0.40 × 0.20 × 0.20	0.60 × 0.40 × 0.20	0.30 × 0.20 × 0.20
Theta range for data collection (°)	2.68–27.50	2.923–24.989	2.91–27.5	2.54–27.50
Limiting indices	−50 ≤ <i>h</i> ≤ 51, −13 ≤ <i>k</i> ≤ 11, −21 ≤ <i>l</i> ≤ 24	−11 ≤ <i>h</i> ≤ 11, −29 ≤ <i>k</i> ≤ 29, −9 ≤ <i>l</i> ≤ 9	−14 ≤ <i>h</i> ≤ 14, −15 ≤ <i>k</i> ≤ 11, −27 ≤ <i>l</i> ≤ 27	−15 ≤ <i>h</i> ≤ 15, −18 ≤ <i>k</i> ≤ 18, −24 ≤ <i>l</i> ≤ 23
Reflections collected/ unique	48,742/8554 [<i>R</i> _(int) = 0.0914]	12,111/3091 [<i>R</i> _(int) = 0.034]	22,476/11,942 [<i>R</i> _(int) = 0.044]	23,652/14,524 [<i>R</i> _(int) = 0.0269]
Completeness (%)	99.8	0.961	99.7	98.5
Max. and min. transmission	0.8901 and 0.7965	0.846 and 0.747	1.000 and 0.894	0.7932 and 0.7120
Data/restraints/parameters	48,742/0/451	12,111/60/280	22,476/10/608	23,652/0/763
Goodness of fit on <i>F</i> ²	1.160	1.11	0.983	0.911
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0538, w <i>R</i> 2 = 0.0750	<i>R</i> 1 = 0.0726, w <i>R</i> 2 = 0.1916	<i>R</i> 1 = 0.0851, w <i>R</i> 2 = 0.1127	<i>R</i> 1 = 0.0353, w <i>R</i> 2 = 0.0743
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1499, w <i>R</i> 2 = 0.1016	<i>R</i> 1 = 0.0773, w <i>R</i> 2 = 0.1916	<i>R</i> 1 = 0.0537, w <i>R</i> 2 = 0.1259	<i>R</i> 1 = 0.0575, w <i>R</i> 2 = 0.0774
Largest diff. peak and hole (eÅ ⁻³)	0.377 and −0.420	1.03 and −0.396	1.63 and −1.17	1.083 and −0.596
CCDC Number	1,063,116	1,063,117	1,063,118	1,063,113
	5	6	7	
Empirical formula	C ₂₀ H ₃₈ N ₁₁ NdO ₁₃ P ₂	C ₂₈ H ₅₄ N ₁₁ NdO ₁₃ P ₂	C ₁₄ H ₂₇ N ₅ O ₆ PU _{0.50}	
<i>M_r</i>	846.79	959.00	511.39	
Crystal system, space group	Monoclinic, <i>P2</i> (1)	Monoclinic, <i>P2₁/c</i>	Triclinic, <i>P</i> $\bar{1}$	
<i>a</i> (Å)	10.6302(14)	20.1362(19)	9.3453(19)	
<i>b</i> (Å)	29.020(2)	19.9507(11)	10.4875(16) 12.033(2)	
<i>c</i> (Å)	11.9607(9)	21.727(2)		
α (°)	106.491(9)	92.256(7)	71.986(15)	
β (°)			80.786(16)	
γ (°)			68.488(16)	
<i>V</i> (Å ³)	3538.0(6)	8721.6(12)	1041.9(3)	
<i>Z</i> , <i>D_x</i> (g/cm ³)	4, 1.590	8, 1.461	2, 1.630	
μ (mm ⁻¹)	1.629	1.331	4.037	
<i>F</i> (000)	1716	3944	510	
Crystal size (mm)	0.30 × 0.30 × 0.20	0.40 × 0.20 × 0.20	0.40 × 0.30 × 0.20	
Theta range for data collection (°)	2.67 to 30.00	2.93 to 27.50	2.87 to 30.00	

Table 1 continued

	5	6	7
Limiting indices	$-14 \leq h \leq 14,$ $-40 \leq k \leq 40,$ $-16 \leq l \leq 16$	$-25 \leq h \leq 26,$ $-25 \leq k \leq 25,$ $-24 \leq l \leq 28$	$-13 \leq h \leq 10,$ $-14 \leq k \leq 14,$ $-16 \leq l \leq 12$
Reflections collected/ unique	34,275/18,246 [$R_{\text{int}} = 0.0186$]	49,651/19,008 [$R_{\text{int}} = 0.0357$]	11,403/6010 [$R_{\text{int}} = 0.0202$]
Completeness (%)	99.3	94.9	99.0
Max. and min. transmission	0.7364 and 0.6406	0.7766 and 0.6180	0.4990 and 0.2951
Data/restraints/parameters	34,275/9/909	49,651/5/995	11,403/0/241
Goodness of fit on F^2	1.010	1.076	0.945
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0294, wR2 = 0.0548	R1 = 0.0502, wR2 = 0.1280	R1 = 0.0211, wR2 = 0.0403
R indices (all data)	R1 = 0.0424, wR2 = 0.0578	R1 = 0.0883, wR2 = 0.1384	R1 = 0.0221, wR2 = 0.0405
Largest diff. peak and hole ($e\text{\AA}^{-3}$)	1.087 and -0.959	1.321 and -0.847	0.455 and -0.860
CCDC Number	1,063,114	1,401,193	1,063,115

The *anti*-conformation of the carbonyl and phosphoryl groups is stabilized by the intermolecular N–H...O=P hydrogen bonds between two CAPH molecules [17, 18, 23–25]. The CAPH compounds containing only one amidic hydrogen atom usually are connected in dimeric aggregates. However, the intermolecular hydrogen N–H...O=C bond and the weak interaction of N–H...N type (3.15 Å) formed by the NH groups of the 3-(aminomethyl)pyridine substituents near the phosphorus atoms in addition to the N–H...O=P bond type lead to the formation of two-dimensional network (HL1)_n along (100) in the crystalline lattice of **1** (Fig. 1B). The parameters of the hydrogen bonds are listed in Table 2.

The phosphorus atom environment of the CAPH compounds has a distorted tetrahedral configuration [1, 23–26]. The OPN angles have the largest deviation from tetrahedral angle of 109.4°, compared to the NPN angles. This fact can be explained by the steric repulsion of the amide substituents near the phosphorus atom. The largest angles in the phosphorus environment are O2A–P1A–N2A (119.32(13)°) and O2B–P1B–N4B (120.79(12)°) for the molecules **1A** and **1B**, respectively. The smallest angles have values 101.13(13)° (N2A–P1A–N1A) and 102.40(12)° (N4B–P1B–N1B), as shown in Table 3.

The P=O bond length in the carbacylamidophosphates is longer than usual P=O bond length (1.45 Å) [27], and its value is determined by the nature of the substituents near the phosphorus atom. In **1**, the average value of P=O bond length in the two independent molecules **1A** and **1B** is equal to 1.47 Å and it is typical for compounds with alkylamide type of substituents [18, 23, 24].

The lengths of the carbonyl C=O and the amide bonds were determined by the nature of the carbonyl carbon atom substituents (R). The C=O distances as a rule lie in the range of 1.22–1.23 Å for the crystal structures of CAPH compounds with the R having aromatic nature [24–26]. For the structure **1**, the $d(\text{C2A–O1A}) = 1.203(3)$ Å and the $d(\text{C2B–O1B}) = 1.197(3)$ Å (Table 3), which corresponds to the structural parameters of the CAPH with the R = CHAl₃ [18, 23, 25].

All of the PN bonds (P–N_{amide} with the nitrogen atom of P(O)NR moiety and P–N_{imide} with the nitrogen atom of P(O)NHC(O) moiety) in the CAPH compounds are shorter than the typical P–N single-bond length (1.77 Å) and are longer than P=N double-bond lengths (1.57 Å) [27–31].

The P–N_{amide} distances are shorter than the P–N_{imide} one, because of the resonance interaction of the N_{imide} with the carbonyl π system that causes a partial multiple-bond character in C–N_{imide}. So, in the structure **1** the P–N_{imide} bond length is equal to 1.693(2) Å in the **1A** molecule and to 1.696(2) Å in the **1B** one. The P–N_{amide} average value in HL1 is 1.61 Å (Table 3).

The sums of the surrounding angles for nitrogen atom of P(O)NHC(O) moiety are close to 360°. The trigonal-planar bond angles observed for these compounds suggest the sp²-hybridization of the nitrogen atom and support the conclusion about the possibility of interaction of the unshared electron pair of nitrogen with π-bond of carbonyl group. According to X-ray structural data for HL1, the angles C(2)–N(1)–P(1) have values of 122.3(2)° and 123.46(19)° in the **1A** and **1B** molecules, respectively (Table 3).

Table 2 Hydrogen bonds D–H...A in compounds **1–7**

D–H...A	d[Å]			Angle DHA (°)
	D–H	H...A	D...A	
1				
N(4A)–H(4NA)···O(1B)	0.86	2.10	2.943(3)	167.7
N(2B)–H(2NB)···O(1A)	0.86	2.15	2.977(3)	160.7
N(1A)–H(1NA)···O(2B)#1	0.86	1.98	2.798(3)	158.8
N(2A)–H(2NA)···N(5A)#2	0.86	2.41	3.245(5)	164.7
N(1B)–H(1NB)···O(2A)#3	0.86	1.89	2.722(3)	161.4
N(4B)–H(4NB)···N(3B)#4	0.86	2.46	3.151(4)	137.9
Symmetry transformations used to generate equivalent atoms: #1 x, y + 1, z; #2 x, –y + 1, z – 1/2; #3 x, y – 1, z; #4 x, –y, z + 1/2				
2				
O(1 W)–H(1 W)···O(3)#5	0.89	1.93	2.817(5)	174.7
O(1 W)–H(2 W)···N(1)#1	0.89	2.55	3.440(6)	178.9
Symmetry transformations used to generate equivalent atoms: #1 x, y, z + 1; #5x + 1, y, z + 1				
3				
O(13)–H(13A)···O(3)#1	0.8789	2.18	2.938	144
O(13)–H(13B)···O(11)#2	0.8772	1.81	2.627	157
C(25)–H(25B)···Cl(5)#4	0.9700	2.78	3.494	131
C(28)–H(28A)···O(4)#5	0.9700	2.32	3.094	136
Symmetry transformations used to generate equivalent atoms: #1 –x, –y, 1 – z; #2 – 1 + x, y, z; #3 x, y, z; #4 1 – x, –y, –z; #5 x, –1 + y, z				
4				
N33–H33···O11	0.86	2.32	3.034(3)	139.9
N23–H23···O3	0.86	2.14	2.986(3)	167.7
O2–H2···O3	0.82	1.94	2.721(3)	157.8
O3–H3···O31	0.82	1.99	2.752(3)	155.0
5				
N(6B)–H(6BA)···O(11A)#1	0.86	2.19	2.984(4)	153.0
N(2A)–H(2AA)···O(11B)#2	0.86	2.06	2.878(4)	159.5
N(6A)–H(6AA)···O(7B)#3	0.86	2.15	2.957(3)	156.4
N(2B)–H(2BA)···O(12A)	0.86	2.38	3.134(4)	147.3
Symmetry transformations used to generate equivalent atoms: #1x + 1, y, z + 1 #2 – x – 1, y – 1/2, –z – 3 #3 –x, y – 1/2, –z – 2				
6				
N(9A)–H(9AA)···O(9B)#1	0.86	2.33	3.167(5)	163.6
N(5A)–H(5AA)···O(11B)#2	0.86	2.13	2.955(5)	161.0
N(4B)–H(4BA)···O(1B)#2	0.86	2.18	3.021(4)	164.3
N(7B)–H(7BA)···O(10A)#3	0.86	2.46	3.226(5)	149.5
Symmetry transformations used to generate equivalent atoms: #1 –x, –y, –z – 1 #2 x, –y – 1/2, z – 1/2 #3 –x – 1, –y, –z – 1				
7				
N(2)–H(2A)···O(6)	0.86	2.19	2.945(14)	147.1

As it was demonstrated in our previous works [1, 14, 25], carbacylamidophosphates are ambidentate ligands, having two potential donor centers (PO and CO). Because of high affinity of phosphoryl oxygen to the 3d and 4f metal ions, the CAPH ligands in the molecular form (HL)

coordinate mostly in a monodentate manner via the oxygen atom of PO group [32], whereas in the deprotonated form (L[–]), CAPHs demonstrate a bidentate manner (via oxygen atoms of phosphoryl and carbonyl groups) of coordination to the metal ions, with formation of six-membered chelate

Table 3 Selected interatomic distances (d , Å) and angles between interatomic vectors for **1–7** with standard deviations in parentheses

Bond	1	2	3	4	5	6	7
C=O	1.203(3); 1.197(3)	1.236(5)	1.248(3) 1.261(3) 1.266(3)	1.252(6) 1.259(5) 1.249(6)	1.230(4) 1.231(4); 1.240(4) 1.250(3)	1.235(4) 1.240(4); 1.225(5) 1.227(5)	1.217(2)
C–N _{imide}	1.344(3); 1.347(3)	1.291(5)	1.315(4) 1.302(4) 1.309(4)	1.280(6) 1.296(7) 1.288(6)	1.368(4) 1.376(4); 1.374(4) 1.366(4)	1.373(5) 1.353(5); 1.370(5) 1.362(5)	1.383(2)
P=O	1.4668(17); 1.4740(17)	1.477(3)	1.497(2) 1.498(2) 1.503(2)	1.496(4) 1.506(3) 1.496(4)	1.478(2) 1.480(2); 1.478(2) 1.479(2)	1.482(3) 1.481(3); 1.467(3) 1.506(3)	1.4932(12)
P–N _{imide}	1.693(2); 1.696(2)	1.639(4)	1.633(2) 1.631(2) 1.639(3)	1.631(4) 1.638(5) 1.635(5)	1.679(3) 1.681(3); 1.678(3) 1.675(3)	1.664(4) 1.681(3); 1.687(3) 1.690(3)	1.6721(16)
P–N _{amide}	1.602(2) 1.608(3); 1.615(2) 1.614(2)	1.660(4) 1.645(3)	1.634(3)– 1.655(3)	1.628(5)– 1.649(4)	1.604(4)–1.619(3); 1.600(4)–1.617(3)	1.614(4)– 1.625(5); 1.625(4)– 1.667(6)	1.6216(14) 1.6248(16)
Angle ω (°)							
O–C– N _{imide}	124.3(3); 125.2(3)	131.0(4)	130.6(3)	131.2(5) 131.0(5) 132.6(5)	120.7(3) 120.5(3); 122.1(3) 121.4(3)	121.8(4) 121.3(4); 121.8(4) 122.0(3)	120.97(17)
O–P– N _{imide}	108.14(11); 106.52(10)	114.8(2)	117.27(12)	116.4(2) 116.4(2) 115.1(2)	110.02(13) 110.70(14); 109.67(14) 108.94(13)	109.27(18) 109.46(16); 109.50(16) 108.68(16)	103.20(7)
O–P– N _{amide}	119.32(13) 109.82(12); 111.67(12) 111.67(12)	115.39(19) 107.50(18)	114.06(13) 107.48(12)	106.9(2)– 115.8(2)	109.98(17)– 115.11(18); 110.95(15)–115.61(15)	110.34(19)– 119.8(3); 109.50(16)– 116.88(19)	109.02(7) 117.27(8)
N _{amide} –P– N _{imide}	111.95(13) 101.13(13); 102.40(12) 111.76(12)	113.80(19) 100.76(17)	109.49(13) 102.70(13)	103.6(2)– 109.0(2)	103.02(17)– 108.43(17); 103.91(17)–108.96(17)	100.81(18)– 109.73(19); 102.53(19)– 110.0(2)	115.22(8) 107.39(8)

metallocycles. The last coordination mode is typical for the deprotonated structural analogs of β -diketones, CAPH and SAPH (sulfonylamidophosphates) especially [33–37]. The cases of ligand bridging function via the one of the oxygen atoms have also been observed. The bridging function of the phosphoryl oxygen atom was shown for the “simple” CAPH salts [21], the 3d [38] and the RE complexes with CAPH [39]. The bridging carbonyl atom was fixed earlier

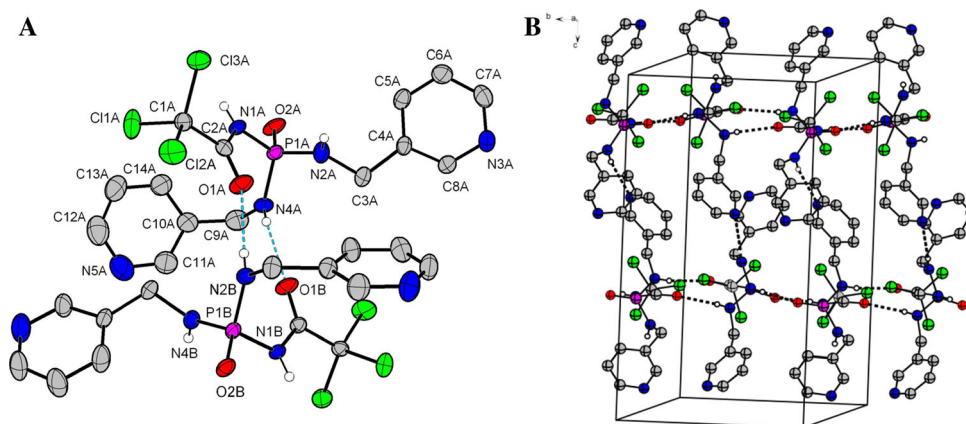
for the poly- $[\mu$ -aqua[2,2,2-trichloro-*N*-(dimorpholin-4-yl-phosphoryl)acetamide]sodium(I)] ([NaL2·H₂O]_n) only [20].

In this work, the bridging type of coordination through the μ -O atoms of carbonyl and phosphoryl groups simultaneously has been observed for the first time for deprotonated CAPH ligands in the structure of [KL2·H₂O]_n (2). Each potassium atom is six-coordinated by 6 O atoms

Table 4 Selected bond lengths (d , Å) for coordination polyhedrons in **2–7** with standard deviations in parentheses

Bond	2	3	4	5	6	7
M–O _C	2.658(3) 2.704(3)	2.389(3) 2.371(3) 2.333(4)	2.496(2) 2.434(2) 2.460(2)	2.634(2) 2.449(2); 2.499(2) 2.454(2)	2.497(3); 2.508(3); 2.536(3) 2.464(3)	–
M–O _P	2.671(3) 3.120(4)	2.287(3) 2.325(3) 2.371(3)	2.448(2) 2.4223(19) 2.496(2)	2.413(2) 2.377(2); 2.377(2) 2.373(2)	2.422(3) 2.374(3); 2.404(3) 2.355(3)	2.356(8) 2.316(9)
M–O _W	2.821(4) 2.830(4)	2.417(4)	–	–	–	–
M–O(<i>i-prOH</i>)	–	–	2.517(3) 2.498(2)	–	–	–
M–O(NO ₃)	–	–	–	2.523(3)–2.671(3); 2.563(3)–2.623(2)	2.512(4)–2.669(4); 2.525(4)–2.830(4)	2.563(9) 2.519(9) 2.577(7) 2.517(7)
C.N. of the central ion	6	7	8	10	10	8

Fig. 1 **A** Thermal ellipsoid plot and atom labeling of the HL1 dimeric aggregate representation at 50 % probability level; **B** the 1 cell edge representation. Hydrogen atoms of 3(aminomethyl)pyridine substituents have been omitted for clarity



($3(\mathbf{L2})^- + 2\text{H}_2\text{O}$). The coordination polyhedron of the K atoms can be described as a distorted tetragonal bipyramid (Fig. 2). The O–K bond lengths vary from 2.659(3) Å (the bond of K atom with carbonyl oxygen atom O(1)) to 2.831(4) Å (K(1)–O(1 W)); the O–K–O angles change from 65.32(11)° to 166.07(12)° (Table 4).

The bridging water molecules complete the formation of a one-dimensional (1D) infinite coordination polymeric chains of **2** associated with hydrogen-bonded layers parallel to (1 0 1) crystal plane. There are two types of intramolecular hydrogen bonds realized in $[\text{KL2}\cdot\text{H}_2\text{O}]_n$ with water hydrogen atoms H(1 W) and H(2 W) participation: first is O–H...O type created with the oxygen atom

of morpholine group (Table 2) and second one is O–H...N type—via the imide nitrogen atom of ($\mathbf{L2}$)[–] molecule.

The imide nitrogen atom of the 2,2,2-trichloro-*N*-(dimorpholin-4-yl-phosphoryl)acetamide is in deprotonated form that leads to decrease in the CN_{imide} and NP_{imide} and increase in the CO bond length values (Table 3) of ($\mathbf{L2}$)[–] compared with those for HL2 [17]. But opposite to the respective parameters of other analogous chelating structures described earlier [14, 25], in **2** structure the PO distance is not changed upon coordination in comparison with free HL2 [17]. Other bond lengths of chelate cycle, being regular, are decreased upon coordination, indicating π -conjugation in the coordinated anion. Carbonyl and

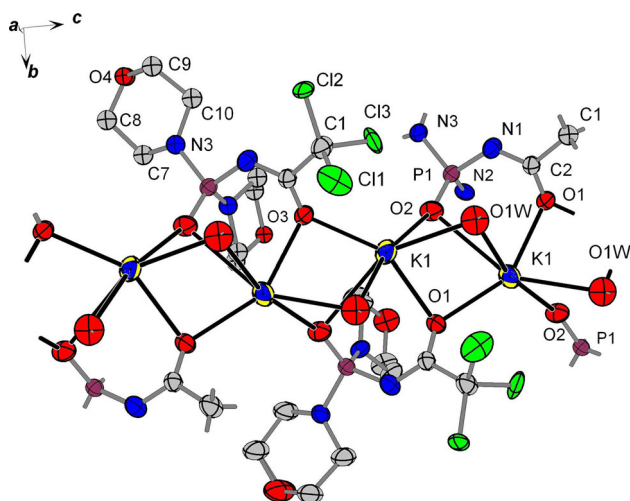


Fig. 2 Structural representation of **2** with the atom numbering scheme; H atoms are omitted for clarity

phosphoryl group oxygen atoms form two types of bonds with K: intrachelating bonds O1–K and O2–K are longer than the ones with neighboring potassium atoms (Table 4).

The phosphorus atoms of (**L2**)[−] adopt an distorted tetrahedral configurations (Table 3). Oxygen atoms of the phosphoryl and the carbonyl groups of the OCNPO structural fragment have *syn* conformation (the dihedral angle between O(1)–C(2)–P(1) and O(2)–P(1)–C(2) planes is 66.4°) in contrast to the *anti*-conformation of the free HL2 [17]. Tris-complexes of lanthanides were based on deprotonated CAPH ligands [40].

Thus, decrease in the CN_{imide} and NP_{imide} distances in the coordinated ligands (**L2**)[−] and (**L3**)[−] and increase in the P=O and C=O distances compared to ones in the crystal structures of the free ligands HL2 and HL3 [17, 18]

demonstrate the presence of π -conjugation in the chelate fragments of the Eu(**L2**)₃·H₂O (**3**) and Ce(**L3**)₃(*i*-PrOH)₂·*i*-PrOH (**4**). Three six-membered metal chelating rings are formed with the participation of both the phosphoryl and the carbonyl oxygen atoms of three (CAPH)[−] ligands (Fig. 3), similar to previously obtained CAPH complexes [40]. The chelating (O)PNC(O) frames of all phosphoryl ligands are planar, whereas six-membered rings with Ln central atom are far from planar, and maximum deviations from the least-squares plane are in average 0.21 Å for phosphoryl oxygen atoms in **3** and in average 0.17 Å for imide nitrogen atoms in **4**. The Ln–O bond lengths of the **3** and **4** are in the presumed range (Table 4). The Ln–O_P bonds are shorter than the Ln–O_C bonds because of stronger affinity of the phosphoryl group for lanthanides. A similar difference in bond lengths was observed for the complexes with deprotonated CAPH ligands described earlier. The selected bond angles are given in Table 3.

The phosphorous atoms of the **3** and **4** have a slightly distorted tetrahedral geometry. The maximum deviations from the ideal value (109.4°) are observed for the NPO angles: 116.34(16) and 116.35(19)° for **3** and **4**, respectively (Table 3). They are involved in the formation of the six-membered chelate rings, whereas in the free ligands, this angle is less than that in the tetrahedron because of the formation of hydrogen bonds of the P=O···H–N type and equals 105.13(13)° and 105.5(3)° for HL2 and HL3, respectively [17, 18]. The carbonyl atom has a sp²-character.

The central cerium(III) ion of **4** has eight-coordinated oxygen environment (6O from the 3 (**L3**)[−] and 2O from 2-propanole), Fig. 4B. But the C.N. of europium(III) ion is equal to 7 (6O from the 3 (**L3**)[−] and 1O from H₂O) in line with the cation hardness effect.

Fig. 3 **A** Structural representation of **3** with the atom numbering scheme; H atoms are omitted for clarity; **B** the coordination polyhedron around the Eu(III) central atom in the **3**

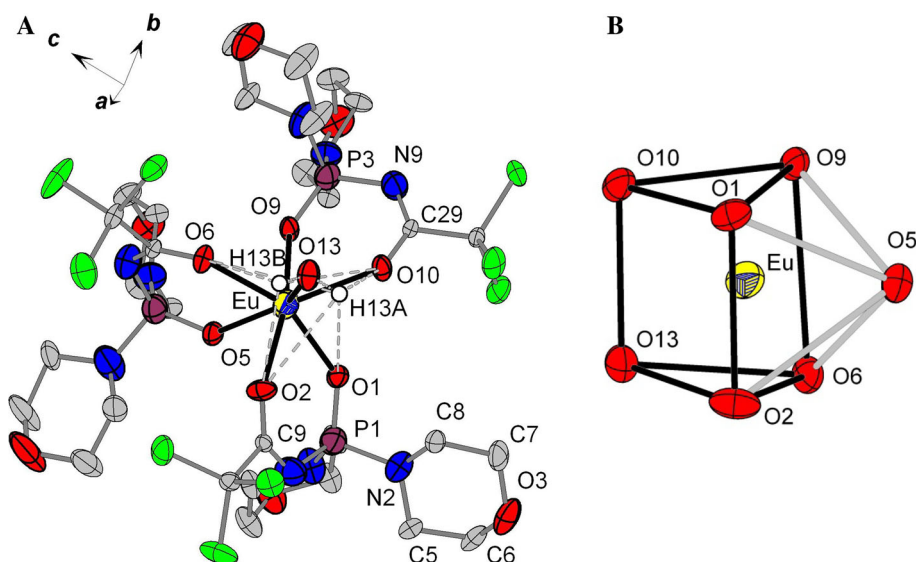


Fig. 4 **A** Structural representation of **4** with the atom numbering scheme; H, Cl atoms and the C₆H₅ substitutes are omitted for clarity; **B** the coordination polyhedron around the Ce(III) central atom in the **4**

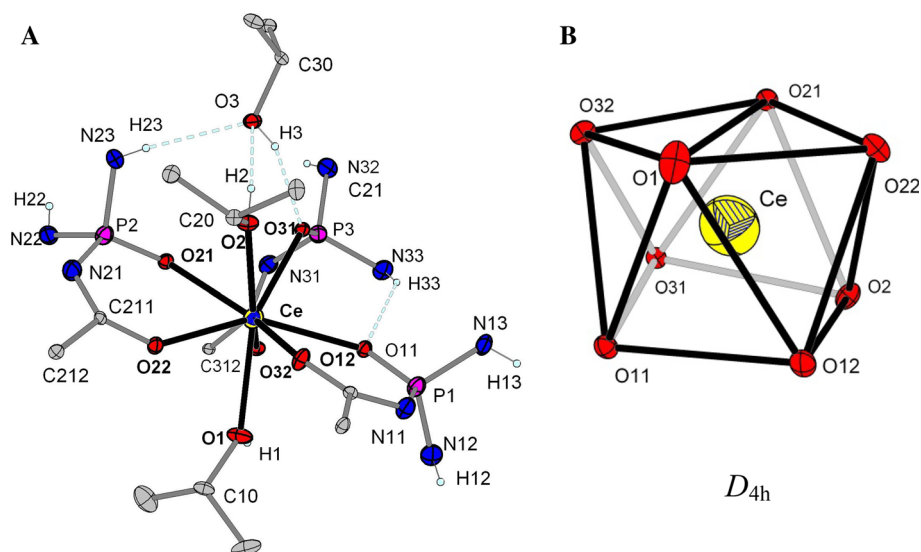
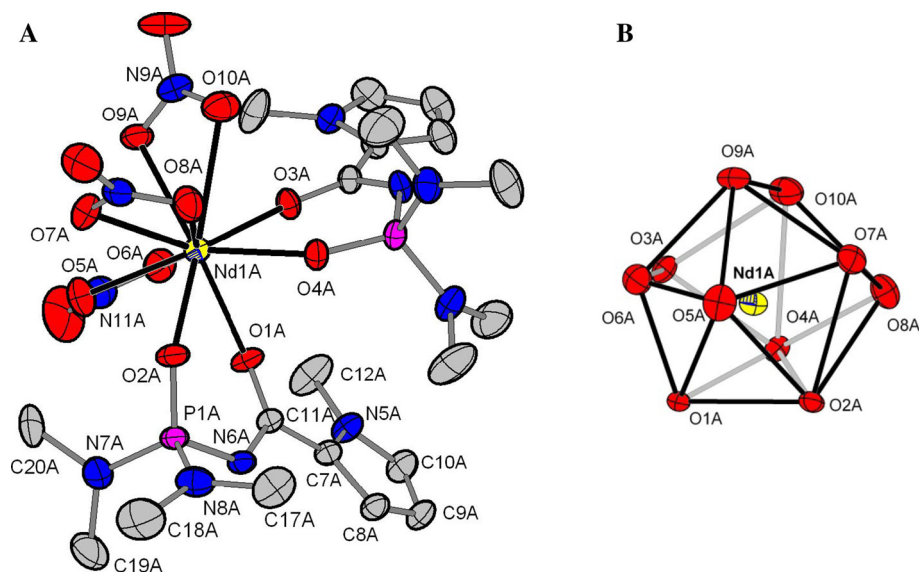


Fig. 5 **A** Structural representation of the one of **5** independent unit with the atom numbering scheme; H atoms of pyrrole substituents are omitted for clarity; **B** the coordination polyhedron around the Nd(III) central atom in the **5**

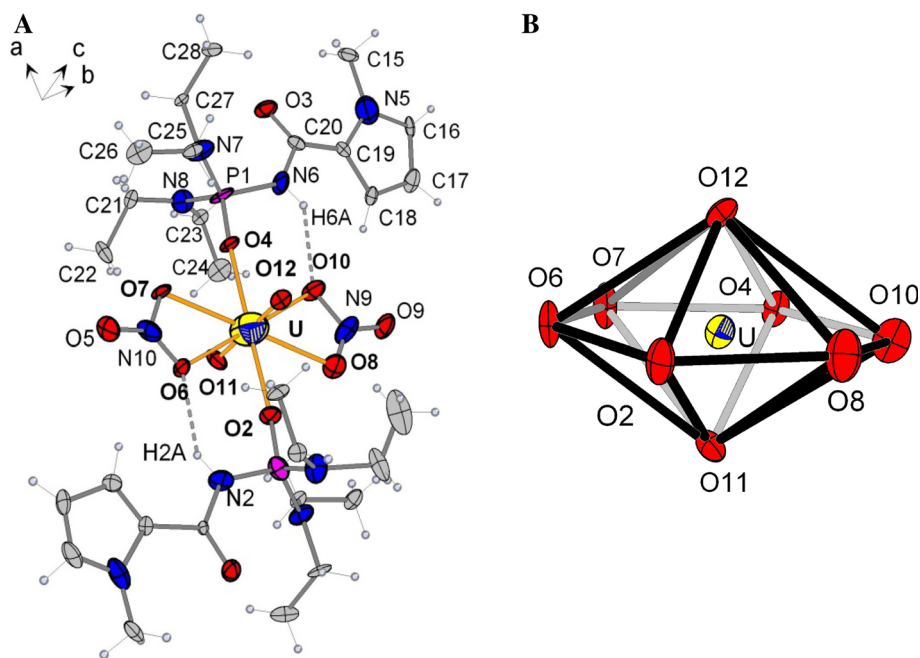


According to the geometrical criteria proposed for the determination of the eight-vertex polyhedron form [41], the resulting polyhedra of Ce(III) in **4** can be described as a distorted tetragonal anti-prism, D_{4d} . The angle ω between the non-planar body-diagonal trapezoids O32-O1-O12-O2 and O22-O21-O31-O11 of the **4** polyhedron is equal to 83.21°.

The asymmetric unit in the crystals of **4** is created by one Ce(III) ion, which coordinates three deprotonated (**L3**)[−] CAPH ligands and two isopropanole molecules (Fig. 4A). There is one isopropanole molecule connecting to the CAPH ligands through the H-bonds in the second coordination sphere. An intramolecular N33-H33...O11 hydrogen bond is also presented in structure **4**, and all the hydrogen bond parameters are listed in Table 2.

Previous investigations allowed us to assume a definite regularity in the coordination-chemical behavior of carbamylamidophosphates: chelate coordination was observed for deprotonated forms of ligands only, while in molecular form, they were coordinated exclusively monodentately via the oxygen atom of the phosphoryl group [25, 42, 43]. The formation of six-membered metallocycles on chelate coordination is accompanied by essential changes in the bond lengths which could be related to the formation of π -electron systems. The first example for O, O'-chelating CAPH coordination in its molecular form was fixed for a cerium (III) complex on the base of N-(bis(dimethylamino)phosphoryl)benzamide (C₆H₅C(O)NHP(O)[N(CH₃)₂]₂) [44].

Fig. 6 **A** Structural representation of $\text{UO}_2(\text{NO}_3)_2(\text{HL5})_2$ independent unit with the atom numbering scheme. *Dashed lines* denote hydrogen bonds; **B** the coordination polyhedron around the U(VI) central atom in the **7**



In the present work, the similar neodymium (III) coordination compounds of $\text{Nd}(\text{NO}_3)_3(\text{HL})_2$ type on the base of **HL4** (**5**) and **HL5** (**6**) having the 1-methyl-1H-pyrrole substituent near the carbonyl atom were synthesized.

Selected structural parameters of **5** and **6** are listed in Table 4. Figure 5 show the molecular structure, the coordination polyhedron type and the view of unit cell for **5** and **6**. In fact, these structures differ by substituents of amido groups (NMe_2 for **5** and NEt_2 for **6**) only, and their structures are very similar.

In both structures, CAPH ligands are coordinated in molecular form via the oxygen atoms of phosphoryl and carbonyl groups. A comparison of complex and free ligands geometry shows that coordination in the molecular form does not lead to essential changes neither in bond lengths nor in the electron density distribution in the fragment $-\text{OCNPO}-$. As a result, the metalocycles for **5** and **6** have non-planar structures. The symmetry level of the unit cell is increased when the coordinated ligand changes from **HL4** to **HL5** (space group $P2(1)$ and $P2_1/c$ for **5** and **6**, respectively).

The coordination sphere of Nd^{3+} in **5** and **6** is a distorted sphenocorona (C.N. = 10: 4 O[HL] + 6 O[NO₃]) (Fig. 5B). Four oxygen atoms of two bidentate nitrate groups and two phosphoryl oxygen atoms ligand form a distorted hexagon in the equatorial plane of the polyhedron.

The phosphorus atom in both structures has a slightly distorted tetrahedral geometry. The angles OPN in the units C(O)NHP(O) are practically similar to tetrahedral (average 110.1 for **5** and 109.3 for **6**), while the average value of

other two OPN are a little bit bigger (in average 113.0 for **5** and 114.4 for **6**).

The environment of nitrogen atoms of C(O)NHP(O) fragments is nearly planar (sum of angles at those atoms for **5** and **6** is in the range 358–360°). The CN_{imide} distance of C(O)NHP(O) core is shortened with respect to the typical values for the “free” carbacylamidophosphates (1.371 (**5**) and 1.365 (**6**) Å). The PN_{imide} bonds have particularly the same lengths in the range of 1.678(3)–1.681(3) Å.

The values of the C=O and P=O bonds in the C(O)NHP(O) cores in both structures are typical for carbacylamidophosphates (in average 1.479 Å (PO), 1.238 (CO) Å for **5**, and 1.484 Å (PO), 1.232 Å (CO) for **6**).

The planar pyrrole rings lie practically in one plane with six-membered metalocycles (NdOCNPO), which evidence strong π -interaction inside of these parts of ligand molecule.

The hydrogen atoms of the NH groups of the coordinated **HL4** and **HL5** molecules take part in the formation of hydrogen bonds with nitrate group oxygen atoms of neighboring molecules (Table 2, Fig. 6).

The crystal structure of **7** is composed of centrosymmetric molecules $\text{UO}_2(\text{NO}_3)_2(\text{HL5})_2$, analogous to the previously reported complexes [45, 46] and in contrast to the crystal structure on the base of **HL3** [47] which contains asymmetric molecules. The U^{VI} ion of **7**, located on an inversion center, is eight-coordinated by two axial oxo ligands and six equatorial O atoms from the phosphoryl and nitrate groups in distorted hexagonal-bipyramidal

geometry (see Fig. 6B). It is interesting that in the similar structure on the base of 2,2,2-trichloro-N-(dipiperidine-1-yl-phosphoryl)acetamide $\text{Cl}_3\text{CC}(\text{O})\text{N}(\text{H})\text{P}(\text{O})[\text{N}(\text{CH}_2)_4\text{O}]_2$, the coordination number of the U^{VI} ion is equal to seven [45, 46]. Two coordination modes of the phosphoryl ligands were found in this structure: monodentate in the neutral form, HL (via oxygen atom of the phosphoryl group), and bidentate in the deprotonated form, (L^-) (via oxygen atoms both of the phosphoryl and carbonyl groups). The coordination polyhedron of the uranium ion in this case was completed by two oxo-ligands and the bidentately coordinated nitrate group, and represents a distorted pentagonal bipyramid.

Traditionally to the structures described earlier, the nitrate groups in **7** take part in formation of intramolecular hydrogen bonds with the hydrogen atoms of the HL5 ligands N–H groups (Table 2).

In the crystal structure of **7**, the phosphoryl and carbonyl groups of the neutral CAPH ligands HL5 are in *trans* positions to each other, which was typical for the crystal structures of the free carbacylamidophosphates. The PO bond length in complex $\text{UO}_2(\text{NO}_3)_2(\text{HL5})_2$ is larger than those in the non-coordinated molecules of CAPH compounds, for example to HL1, but the and PN_{imide} bond lengths show an opposite result, Table 3. The PN bond distances between the phosphorus and nitrogen atoms of the 1-methyl-1H-pyrrole-2-carboxamide substituents are 0.05 Å shorter than PN_{imide} , which can be explained by the increasing π -donor bonding in the $(\text{N}_{\text{amide}})_2\text{P}(\text{O})$ fragment due to the coordination.

Conclusions

As discussed above, the structural parameters of the HL1 $\text{C}(\text{O})\text{NP}(\text{O})\text{N}'$, N' -core are typical for all the free carbacylamidophosphates. The **1** interatomic distances and angles have been taken for comparing with ones in the CAPH coordination compounds **2–7**. The structural alterations in the $\text{C}(\text{O})\text{NP}(\text{O})\text{N}'$, N' -core occur due to polarization effects and electron donation to the central atom (CA). The PO distances vary from ~ 1.47 Å in the free HL1 to the range 1.477(3)–1.508(10) Å in the different complexes types, such as **2–7**. The same was observed for carbonyl bond lengths: the average value of $d(\text{CO})$ in HL1 is 1.195 Å, and in compounds **2–7**, this parameter was changed from 1.216(17) to 1.266(3) Å.

The values of PO bond length are less sensitive to the type of CAPH ligand coordination (monodentately via the phosphoryl oxygen and bidentately or bidentately chelating both via the carbonyl and phosphoryl oxygen atoms). Due to the π -conjugation on the six-membered metallocycle formed under coordination CAPH ligands in the

deprotonated form, the orders of respective bonds are changed. The lengths of CO and PO bonds decreases by the value of 0.016–0.03 Å, but the CN_{imide} and PN_{imide} increases by the value of 0.06–0.03 Å compared to the HL1 structural data. It was established that the polarization of the PO bond in the electrostatic field of the cation leads to an increase in the charge difference between phosphorus and nitrogen atoms and a decrease in the degree of lone pair (O_P) $\rightarrow \sigma^*(\text{P}-\text{N})$ electronic delocalization [48]. These electronic effects may be reasonable for decreased $\text{P}-\text{N}_{\text{imide}}$ distances in the structures of complexes with monodentate type of CAPHs coordination, in agreement with the increase in $\nu(\text{P}-\text{N}_{\text{imide}})$ values in the IR spectra. The maximum decrease in this bond compared to HL1 is equal to 0.02 Å.

The $\text{M}-\text{O}_\text{P}$ bond lengths for the compounds **3–7** with the chelate type of ligand coordination are in 2.287(3)–2.496(2) Å range. The $\text{M}-\text{O}_\text{C}$ bond lengths for these complexes are longer, 2.333(4)–2.634(2) Å. This fact can be explained by the stronger affinity of the phosphoryl group to metal ions compared to the carbonyl group.

Comparing the geometry of the free carbacylamidophosphates with their complexes, it was found that the bidentate chelate coordination of ligands via the O_P and O_C atoms leads to the increase in $\text{OPN}_{\text{imide}}$ angles (they are not changed for coordinated CAPH in HL form) and $\text{OCN}_{\text{imide}}$ angles (they were decreased for coordinated HL).

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