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ORIGINAL PAPER

Trivalent Holmium in an Octahedral Cl_3O_3 Environment: Synthesis, Crystal Structure and Hirshfeld Surfaces of Coordination Compound with 2,2,2-Trichloro-*N*-(dimorpholinophosphoryl)acetamide

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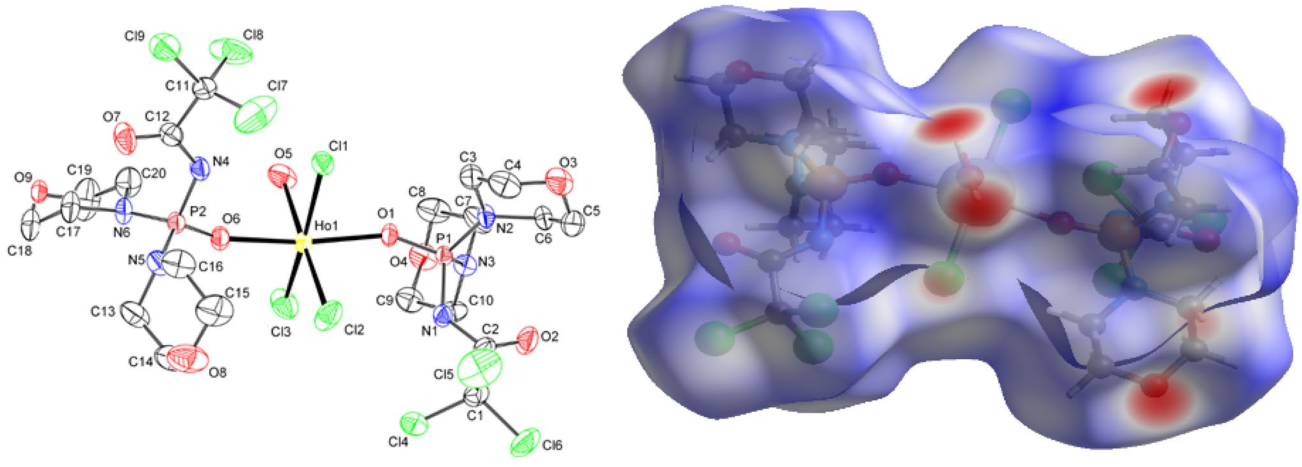
Abstract

The reaction of $HoCl_3{\cdot}6H_2O$ with 2,2,2-trichloro-*N*-(dimorpholinophosphoryl)acetamide (carbacylamidophosphate (CAPh) type ligand, $C_{10}Cl_3H_8N_3O_4P$, HL) in acetone-isopropanolic solution produces the title coordination compound $[Ho(HL)_2(H_2O)Cl_3]$ (**1**). The complex with a low for lanthanides coordination number 6 crystallizes in the triclinic space group $P\,\bar{1}$. The unit cell parameters are a = 11.0587(11) Å, b = 14.2224(12) Å, c = 14.2520(11) Å, α = 116.192(9)°, β = 104.170(8)°, γ = 91.342 (8)°, V = 1927.8(3) $Å^3$ and Z = 2. The Ho^{III} ion is octahedrally coordinated by three chlorine ions, two O atoms of CAPh ligands phosphoryl groups and one O atom of water molecule. The $[Ho(HL)_2(H_2O)Cl_3]$ molecules are linked via $O_{water}–H{\cdots}O_{morpholine}$ hydrogen bonds, forming chains along [100] crystallographic direction. These chains are bound into a three-dimensional framework due to the $C_{morpholine}–H{\cdots}Cl$ intermolecular hydrogen bonds. Hirshfeld surface analysis and two-dimensional fingerprint plots have been used to identify the intermolecular interactions presented in the crystal.

Graphic Abstract

The X-ray structure of hexacoordinate holmium(III) complex with the carbacylamidophosphate (CAPh) ligand 2,2,2-trichloro-*N*-(dimorpholinophosphoryl)acetamide ($CCl_3C(O)N(H)P(O)[N(CH_2)_4O]_2$) is reported and compare with the similar complex structures. Hirshfeld surface analysis employed to identify intermolecular interactions within the structure.



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Keywords Ho^{3+} complex · Carbacylamidophosphate · Phosphoryl ligand · Six-coordinate geometry · Hirshfeld surface analysis · Fingerprint plots

Introduction

Coordination compounds of lanthanides have attracted considerable attention because of possessing a number of useful properties: from the creation of up-lighting to usage as biomedical sensors for biological objects imaging [1–9]. Among the most widely investigated groups of lanthanide complexes there are *β*-diketonates due to easy synthesis of the ligands and unique luminescence properties of their complexes [10–14]. Carbacylamidophosphates (CAPh) are the best known structural analogues of *β*-diketones having similar coordination ability [15]. The presence of peptide and phosphoramide groups combined together in the fragment C(O)N(H)P(O) determines their interaction with biological molecules and cell membranes. Variation of substituents near phosphoryl and carbonyl groups gives possibility to modulate CAPh stereochemical and pharmacological properties. In particular, different CAPh representatives were shown to possess antineoplastic [16, 17], antibacterial activity [18, 19] and enzyme inhibitor properties [20, 21]. The lanthanide chelates of CAPhs exhibit biological activities and in vitro tests show their strong anticancer properties [22]. The presence of the phosphoryl group provides a high affinity towards majority of metal ions, including lanthanides and actinides [21, 23, 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-C_5H_{11}–n-$C_{10}H_{21}$) near the carbonyl carbon atom [25, 26].

The possibility of inclusion into the coordination sphere both in the molecular and acidic forms makes the coordination chemistry of CAPh extremely diverse and interesting and allows to use these ligands both for the 4*f* and 3*d*-metals bonding [27–35].

As a part of our study of the trichloro-bis[2,2,2-trichloro-*N*-(dimorpholinophosphoryl)acetamide coordination ability we described herein the synthesis, structural features and Hirshfeld surface analysis of a new aqua-trichloro-bis[2,2,2-trichloro-*N*-(dimorpholinophosphoryl)acetamide] holmium(III)] $[Ho(HL)_2(H_2O)Cl_3]$ (**1**). This work is a part of the project dedicated to explore the coordination behavior of the molecular forms of CAPh ligands with respect to Ln(III) ions and to determine the structure of the CAPh-complexes with octahedral geometry of Ln(III) center.

Experimental

Elemental analyses (Ln, C, H, N) were performed using standard titrimetric method for lanthanide ions [36] and the EL III Universal CHNOS elemental analyzer.

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Perkin–Elmer Spectrum BX spectrometer using KBr pellets with resolution of 1 cm^{-1}.

X-ray Crystallography

Crystal data for $[Ho(HL)_2(H_2O)Cl_3]$ (**1**) was measured at 294 K on a "Xcalibur-3" diffractometer (graphite monochromated MoK_α radiation with $\lambda = 0.71073$ Å, CCD detector, *ω*-scanning).

Refinement

The structure was solved by the direct method using SHELXTL package [37]. Full-matrix least-squares refinement against F^2 in anisotropic approximation was used for non-hydrogen atoms. Positions of hydrogen atoms were determined from electron density difference maps and refined by "riding" model with $U_{iso} = nU_{eq}$ of the carrier atom (n = 1.5 for hydrogens of water and n = 1.2 for other hydrogen atoms). Crystallographic data (excluding structure factors) for the structure **1** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC 1943482. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: + 44-(0)1223–336,033 or e-mail: deposit@ccdc.cam.ac.uk, website: https://www.ccdc.cam.ac.uk).

Structural and refinement parameters are given in Table 1. Bond lengths are given in Supplementary Information, angles and atomic displacement parameters—in the.cif file.

Chemistry General Information

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.

Carbacylamidophosphate ligand 2,2,2-trichloro-*N*-(dimorpholinophosphoryl)acetamide (HL) was synthesized via the three-step procedure based on the Kirsanov

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

Parameter	Value
Empirical formula	$C_{20}H_{36}Cl_9HoN_6O_9P_2$
CCDC number	1943482
Crystal color	Yellowish white
Formula weight, g mol^{-1}	1050.47
Temperature, K	294
Crystal system	Triclinic
Z	2
Density (calculated), g cm^{-3}	1.810
Absorption coefficient, mm^{-1}	2.810
Space group	$P\bar{1}$
a, Å	11.0587(11)
b, Å	14.2224(12)
c, Å	14.2520(11)
α, °	116.192(9)
β, °	104.170(8)
γ, °	91.342(8)
Volume, Å^3	1927.8(3)
d, mg m^{-3}	1.810
F(000)	1040
Crystal size, mm	0.500 × 0.400 × 0.300
2*Θ* range for data collection, °	6.228 to 59.998
Reflections collected/unique	11,211/8692
Data/restraints/parameters	11,211/0/424
GOF	0.928
R_1, wR_2 [$I > 2\sigma(I)$]	$R_1 = 0.0320$
	$wR_2 = 0.0659$
R_1, wR_2 (all data)	$R_1 = 0.0459$
	$wR_2 = 0.0683$

reaction [38, 39], and its structure was identified using FT-IR and NMR spectroscopy.

Synthesis and Crystallization of Compound 1

Aqua-trichloro-bis[2,2,2-trichloro-*N*-(dimorpholinophosphoryl)acetamide]holmium(III)] $[Ho(HL)_2(H_2O)Cl_3]$ (**1**) (Fig. 1a) was synthesized as follows: hydrated holmium chloride $HoCl_3{\cdot}6H_2O$ (0.1 mmol) was dissolved in 15 mL of acetone/isopropanol mixture (1:1, v/v), then heated to a boiling temperature for 2 min after what the mixture was added to the solution of HL (0.2 mmol) in isopropanol (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 isopropanol, and air-dried (yield 76%). The complexes, as prepared, are soluble in non-polar aprotic solvents, acetone, acetonitrile, alcohols, and toluene; and insoluble in water, hexane, and cyclohexane. Yellowish white SC-XRD quality prismatic crystals were obtained by slow evaporation of a solution of **1** in acetone/isopropanol mixture (1:1, v/v) over 2 days.

IR (KBr, cm^{-1}): 3390 *vs*, b ($\nu_{O\text{–}H}$), 3013 m, *b* ($\nu_{N\text{–}H}$), 1725 *vs*, *sp* ($\nu_{C=O}$), 1635 m, sp (δ_{HOH}), 1450 s, *sp* (Amide II), 1201 s, *sp* ($\nu_{P=O}$), 975 s, *sp* ($\nu_{P\text{–}N}$), 674 s, *sp*($\nu_{C\text{–}Cl}$), 507 m, *sp* (ρ_{PNC}), where *s* is strong, *vs* is very strong, *m* is medium, *b* is broad, *sp* is sharp (Fig. 1b).

For $C_{20}H_{36}Cl_9HoN_6O_9P_2$ the elemental composition was determined, %: C, 22.10; H, 3.57; N, 8.12; Ho, 15.56, and calculated, %: C, 22.87; H, 3.45; N, 8.00; Ho, 15.70. Excessive content of Hydrogen and Oxygen in the real analysis may indicate the presence of extrasphere water in complex composition (in this case the contents of elements are, %: C, 22.48; H, 3.58; N, 7.87; Ho 15.44.

Structural Analysis

The three-dimensional Hirshfeld surfaces (HSs) and twodimensional fingerprint plots for **1** were generated using Crystal Explorer 3.0 [40, 41]. The d_{norm} plots were mapped with color scale in between − 0.649 au (blue) and 1.554 au (red). The fingerprint plots were displayed by using the expanded 0.4–2.4–3.0 Å view with the d_e and d_i distance scales displayed on the graph axes. When the.cif files of **1** was uploaded into the CrystalExplorer software, all bond lengths to hydrogen were automatically modified to typical standard neutron values, i.e., *d*(C–H) = 1.083 and *d*(O–H) = 0.983 Å.

Results and Discussion

Molecular and Crystal Structure of $[Ho(HL)_2(H_2O)Cl_3]$

In the asymmetric part of the unit cell is one molecule of $[Ho(HL)_2(H_2O)Cl_3]$ (**1**) (Fig. 1, Table 1). The complex **1** contains one Ho (III) center, two CAPh ligands, one water ligand and three chloride ligands. The structure of $[Ho(HL)_2(H_2O)Cl_3]$ (**1**) are rather similar to the previously studied [Er(**HL1**)$_3$Cl$_3$] (triclinic symmetry, $P\bar{1}$, CCDC: 774162), [Pr(**HL2**)$_3$Cl$_3$] (trigonal, *R*3, CCDC: 1316528) and [Sm(**HL3**)$_3$Cl$_3$] (trigonal, *R*3, CCDC: 869525) complexes [42–44] with the different CAPh ligands $CCl_3C(O)N(H)P(O)[NC_4H_8]_2$ (**HL1**, CCDC: 240149), $CCl_3C(O)N(H)P(O)[NEt_2]_2$ (**HL2**, CCDC: 1276961) and $CCl_3C(O)N(H)P(O)[N(CH_2)_5]_2$ (**HL3**, CCDC: 871746) respectively. In all complexes the molecules of CAPh ligand are coordinated to the metal center monodentately via the O atom of the phosphorylic group. The next common feature of all the complexes is disposition of the phosphoryl group in an anti-position to the carbonyl one similarly to the crystal structure of the free ligands **HL**, CCDC: 1254024 [38], **HL1** [45, 46], **HL2** [47] and **HL3** [32] described recently.

The central Ho atom of $[Ho(HL)_2(H_2O)Cl_3]$ has a distorted octahedral environment (*mer* isomer) coordinated by

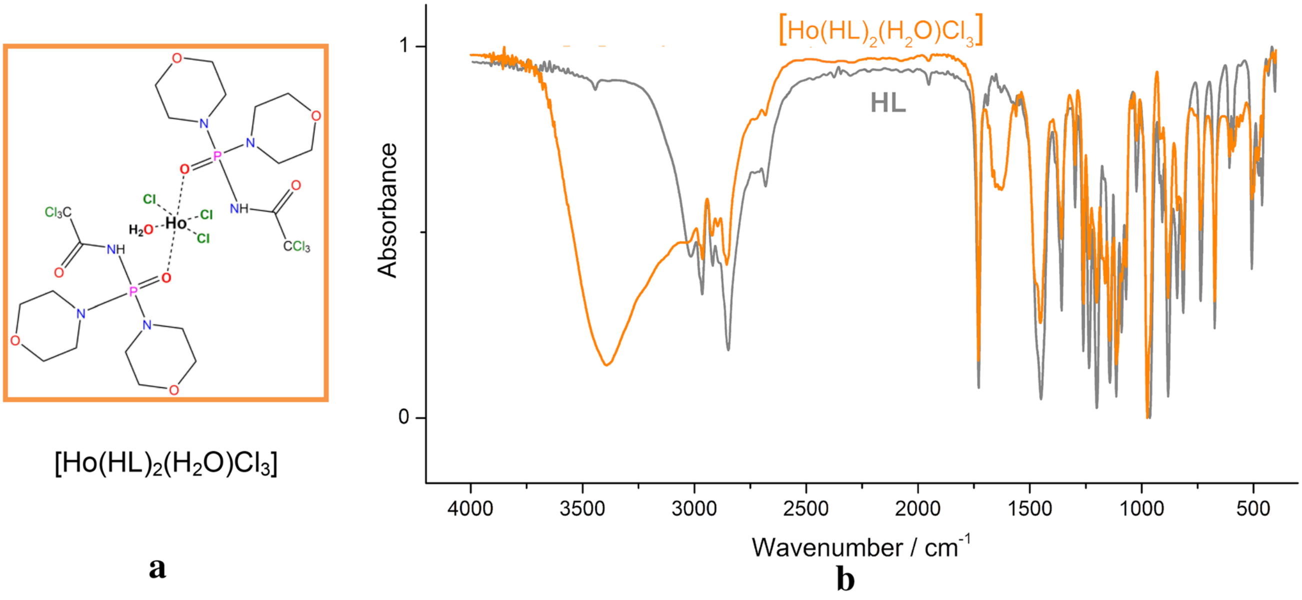

Fig. 1 **a** Representation of the CAPh-ligand coordination mode in [Ho(HL)$_2$(H$_2$O)Cl$_3$]. **b** FT-IR spectra of HL and [Ho(HL)$_2$(H$_2$O)Cl$_3$] (KBr pellet)

three chloride ions, two O atoms of two 2,2,2-trichloro-*N*-(dimorpholinophosphoryl)acetamide molecules and one O atom of water molecule (Fig. 2). Similar slightly distorted octahedral LnO$_3$Cl$_3$ geometry with a *meridional* arrangement of the donor atoms was fixed earlier for the complex [Pr(HMPA)$_3$Cl$_3$], CCDC: 1177132 (HMPA: is phosphorylic ligand hexamethylphosphoramide) [48]. However, Ln (III) environment in most known LnO$_3$Cl$_3$-core complexes realized in the form of a *facial* isomer, in contrast to these mentioned two structures (for example, in the complexes

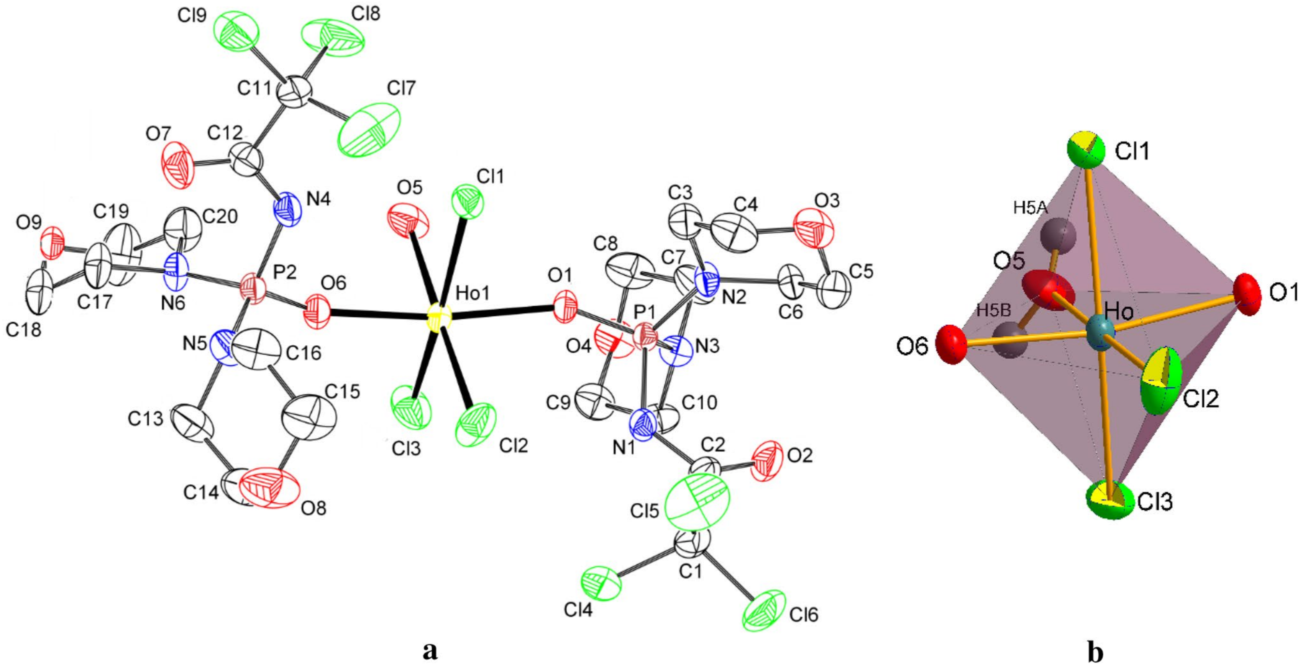

Fig. 2 **a** Representation of the molecular structure of **1**. Thermal ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity. **b** Coordination polyhedron around the Ho atom

Table 2 Selected geometric parameters of the coordination polyhedron of Ho(**HL**)$_2$(H$_2$O)Cl$_3$ (**1**) (Å, °)

Ho1–O6	2.2366(17)	Cl1–Ho1–O5	85.04(6)
Ho1–O1	2.2467(16)	Cl1–Ho1–O6	86.74(5)
Ho1–O5w	2.343(2)	Cl2–Ho1–Cl3	96.69(3)
Ho1–Cl3	2.5712(8)	Cl2–Ho1–O1	88.07(6)
Ho1–Cl2	2.5821(9)	Cl2–Ho1–O6	92.95(6)
Ho1–Cl1	2.6152(6)	Cl3–Ho1–O1	93.44(6)
O1–Ho1–O6	170.48(7)	Cl3–Ho1–O5	82.48(6)
Cl2–Ho1–O5	178.54(6)	Cl3–Ho1–O6	95.83(6)
Cl1–Ho1–Cl3	167.17(3)	O5–Ho1–O6	88.34(8)
O1–Ho1–O6	170.48(7)	Cl3O5O6–Cl1O5O6	60.2
O1–Ho1–O5	90.78(8)	Cl3Cl2O6–Cl1Cl2O6	72.3
Cl1–Ho1–Cl2	95.72(3)	Cl3O1Cl2–Cl1O1Cl2	71.5
Cl1–Ho1–O1	83.74(5)	Cl3O5O1–Cl1O5O1	56.0

Table 3 Hydrogen-bond geometry for [Ho(HL)$_2$(H$_2$O)Cl$_3$] (symmetry codes: $^1-x, -y+1, -z$; $^2-x+1, -y+1, -z$; $^3x, y+1, z+1$; $^4-x+1, -y, -z$; $^5-x, -y, -z$)

D–H···*A*	H···*A*, Å	*D*···*A*, Å	*D*–H···*A*, °
O5–H5*A*···O3^1	1.90	2.788 (3)	165
O5–H5*B*···O4^2	1.77	2.720 (3)	161
N1–H1···Cl2	2.54	3.318 (2)	152
N4–H4···Cl1	2.39	3.221 (2)	163
C5–H5*D*···Cl9^3	2.89	3.804 (3)	158
C6–H6*A*···Cl1^2	2.68	3.609 (3)	160
C13–H13*B*···Cl3^4	2.86	3.588 (3)	132
C15–H15*B*···Cl1^5	2.78	3.652 (4)	150

[Er(**HL1**)$_3$Cl$_3$], [Pr(**HL2**)$_3$Cl$_3$] and [Sm(**HL3**)$_3$Cl$_3$] [41–43]). The Ho–Cl distances are in the range 2.57–2.61 Å, the Ho–O$_P$ distances are shorter than Ho–O$_w$ (Table 2). Such ranges of bond lengths are typical for complexes of lanthanides with neutral form of CAPh ligands [23]. The valence angles in coordination polyhedron deviate from ideal values 90° and 180° for octahedron (see Table 2), but the dihedral angles between the faces clearly demonstrate the distortion of the octahedron. In contrast to regular value 109.47° real ones are in the range of 56.0°–72.3° (Table 2).

In the crystal phase the molecules of **1** are linked via O$_{water}$–H···O$_{morpholine}$ hydrogen bonds (Table 3) and form chains along [100] crystallographic direction (Figs. 3, 4). These chains are bound into a three-dimensional framework due to the C$_{morpholine}$–H···Cl intermolecular hydrogen bonds (Table 3). The H atoms of the amino group ligand participate in the intramolecular hydrogen bonding with Cl$^-$ ligands (Table 3), similarly to the chlorido-complexes [Er(**HL1**)$_3$Cl$_3$], [Pr(**HL2**)$_3$Cl$_3$] and [Sm(**HL3**)$_3$Cl$_3$] described earlier [42–44].

Hirshfeld Surface Analysis and Fingerprint Plots

Hirshfeld surface analysis is an effective tool for exploring packing modes and intermolecular interactions in molecular crystals [48], as they provide a visual picture of intermolecular interactions and of molecular shapes in a crystalline environment. Surface features characteristic of different types of intermolecular interactions can be identified, and these features can be revealed by color coding distances from the surface to the nearest atom exterior (d_e plots) or interior (d_i plots) to the surface. This gives a visual picture of different types of interactions present, and also reflects their relative contributions from molecule to molecule. Further, 2D fingerprint plots (FP), in particular the breakdown of FP into specific atom···atom contacts in a crystal, provide a quantitative idea of the types of intermolecular contacts experienced by molecules in the bulk and presents this information in a convenient color plot. Hirshfeld surfaces comprising d_{norm} surface plots and FP were generated and analyzed for the crystal of **1** in order to explore their packing modes and intermolecular interactions. The d_{norm} surfaces of molecules **1** are shown in Fig. 5, and the FP for the overall contacts and individual atom···atom contacts in **1** are shown

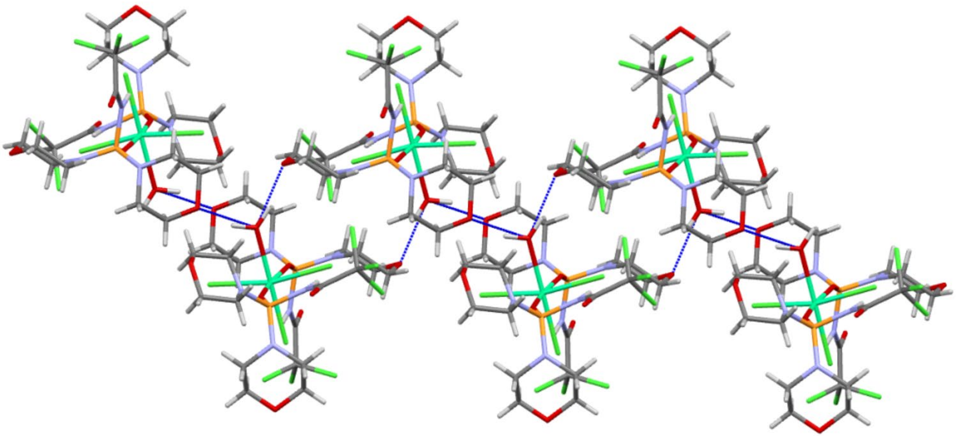

Fig. 3 The fragment of hydrogen bonded chains with hydrogen bonds highlighted in bold blue line (Color figure online)

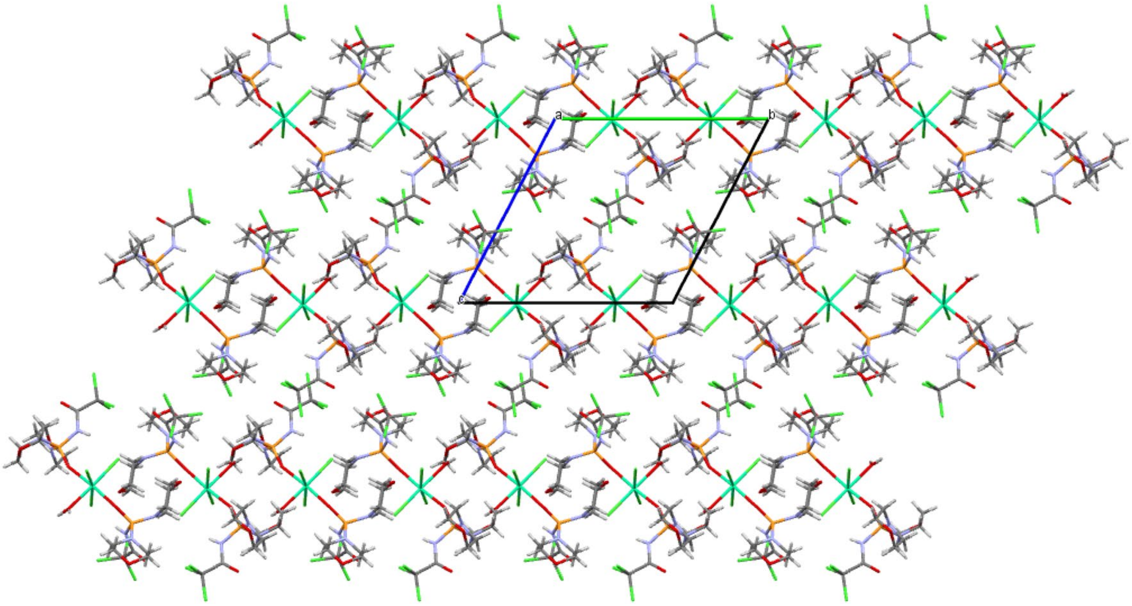

Fig. 4 General view of a three-dimensional framework; view along the crystallographic axis *a*

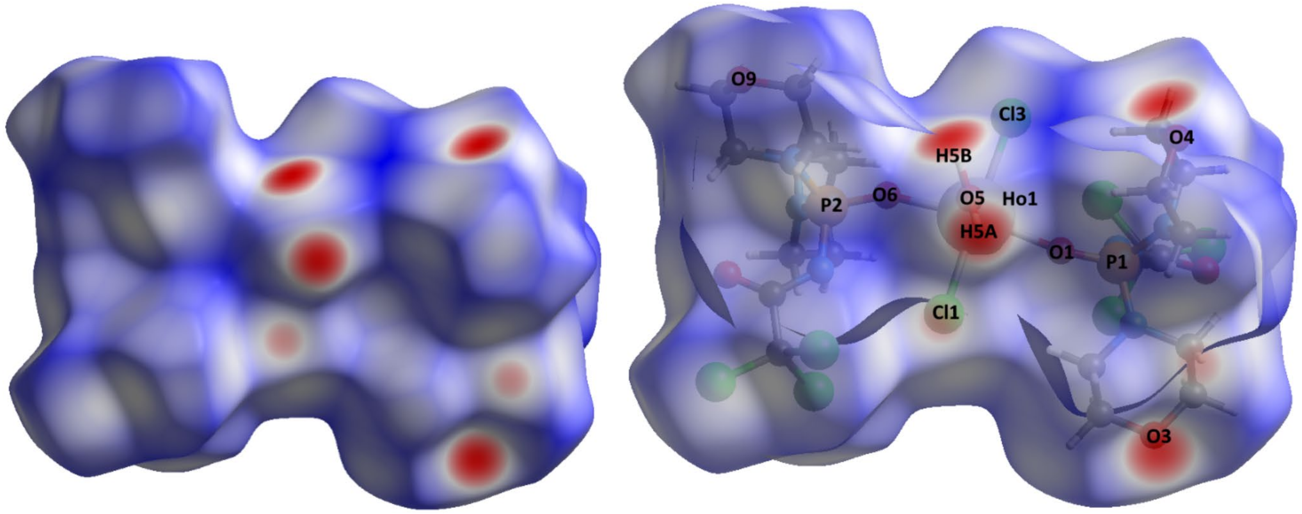

Fig. 5 d_{norm} mapped on the Hirshfeld surface to visualize the intermolecular interactions in **1**

in Fig. 6. The dark-red spots on the d_{norm} surface arise as a result of the short interatomic contacts, i.e., strong hydrogen bonds, while the intermolecular interactions appear as light-red spots. The analysis of the d_{norm} surface and FP gives a pictorial conformation (both qualitatively as well as quantitatively) to the nature and geometries of the hydrogen bonds and intermolecular interactions described in the crystal structure of **1**. The d_{norm} and FP of **1** are consistent with the observed intermolecular interactions.

The analysis of the FP of **1** (Fig. 6) shows that the major contribution to the Hirshfeld surface is from Cl···H contact, with a 44.1% contribution, the closest Cl···H contact occurs at $d_i + d_e = 2.6$ Å. The light red spots on the d_{norm} surface of **1** located near the coordinated chlorine atoms and CCl_3 group chlorine atoms (Fig. 6) can be attributed to the Cl···H contacts displayed in **1**. The smallest of which are 2.68 and 2.78 Å for Cl1···H6A and Cl1···H15B respectively.

The second largest contribution comes from the closest H···H contact, with a 28.4% contribution occurs at $d_i + d_e = 2.4$ Å.

H···O/O···H contacts (15.9%), the closest one observed at $d_i + d_e = 1.8$ Å, which are closely to the interatomic

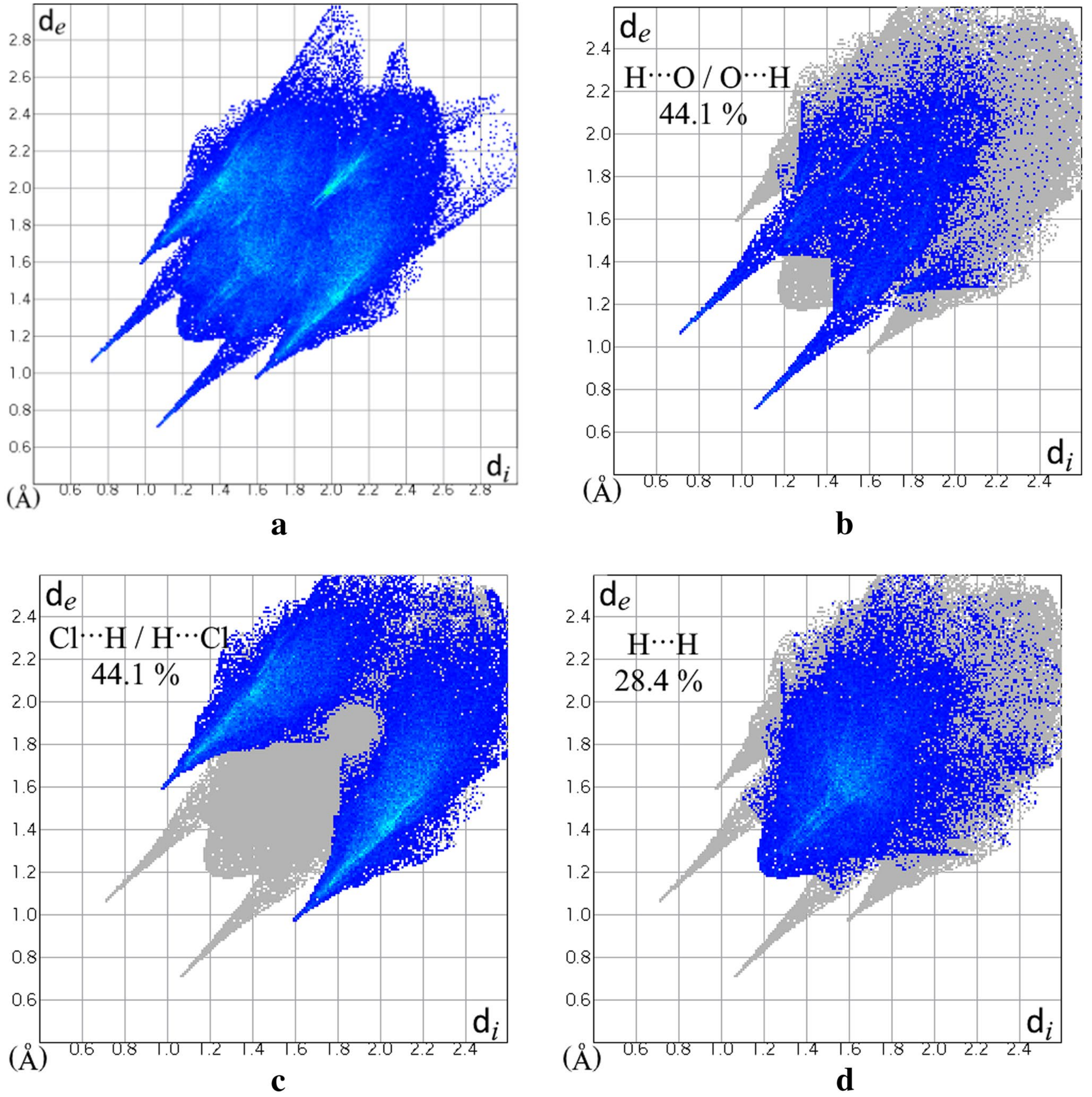

Fig. 6 Hirshfeld fingerprint plots for **a** all intermolecular interactions. **b** H···O/O···H interactions. **c** Cl···H/H···Cl interactions. **d** H···H interactions

distances of 1.77 and 1.95 Å (Table 3) observed for the H10B···O4 and H10A···O3 contacts in the crystal structure of **1** respectively.

The four red bright spots in the d_{norm} surface around the H10B, H10A of coordinated water molecule, O4 and O3 oxygen atoms of morpholine groups (Fig. 5) gives conclusive evidence for the participation of the lone pair of electrons of oxygen atom of morpholine rings as bifurcated hydrogen bond acceptors in the crystal structure of **1**.

Thus, the Hirshfeld surface and FP analysis of **1** give conclusive evidence, both qualitatively and quantitatively, of the various hydrogen bonds/intermolecular interactions displayed in the crystal structure of **1**.

Conclusions

Here, we have presented the solid-state structural analysis of a new hexacoordinate holmium(III) complex with the carbacylamidophosphate (CAPh) ligand 2,2,2-trichloro-*N*-(dimorpholinophosphoryl)acetamide. The central Ho atom of $[Ho(HL)_2(H_2O)Cl_3]$ has a distorted octahedral environment (*mer* isomer) coordinated by three chloride ions, two O atoms of two CAPh ligand molecules and one O atom of water molecule. Intramolecular H-bonding is present in the structure, and Hirshfeld surface analysis has been used to reveal intermolecular interactions that would otherwise have been difficult to elucidate.

References

1. Bünzli J-CG (2014) Review: lanthanide coordination chemistry: from old concepts to coordination polymers. J Coord Chem 23–24:3706–3733. https://doi.org/10.1080/00958972.2014.957201
2. Reddy MLP, Divya V, Pavithran R (2013) Visible-light sensitized luminescent europium(III)-β-diketonate complexes: bioprobes for cellular imaging. Dalton Trans 42:15249–15262. https://doi.org/10.1039/C3DT52238E
3. Bünzli J-CG, Wong K-L (2018) Lanthanide mechanoluminescence. J Rare Earths 36:1–41. https://doi.org/10.1016/j.jre.2017.09.005
4. Ramos TJS, Berton GH, Júnior SA, Cassol TM (2019) Photostable soft materials with tunable emission based on sultone functionalized ionic liquid and lanthanides ions. J Lumin 209:208–216. https://doi.org/10.1016/j.jlumin.2019.01.007
5. Kasprzycka E, Trush VA, Amirkhanov VM, Jerzykiewicz L, Malta OL, Legendziewicz J, Gawryszewska P (2017) Contribution of energy transfer from the singlet state to the sensitization of Eu^{3+} and Tb^{3+} luminescence by sulfonylamidophosphates. Chem Eur J 23:1318–1330. https://doi.org/10.1002/chem.201603767
6. Mariichak OYu, Rozantsev GM, Radio SV (2017) Synthesis and investigation of heteropoly decatungstosamarates(III) with anion of Peacock-Weakley structure. Voprosy Khimii i Khimicheskoi Tekhnologii 2017–6:23–31 https://udhtu.edu.ua/public/userfiles/file/VHHT/2017/6/Mariichak.pdf
7. Døssing A, Kadziola A, Gawryszewska P, Watras A, Melchior A (2017) Structure, stability and spectroscopic features of the neodymium(III) complex of the octadentate polypyridine ligand 6,6′-bis[bis(2-pyridylmethyl)aminomethyl]-2.2′-bipyridine. Inorg Chim Acta 467:93–98. https://doi.org/10.1016/j.ica.2017.07.040
8. Smola S, Rusakova N, Martsinko E, Seifullina I, Korovin Y (2007) Spectroscopic properties of the Ln–Ge complexes with diethylenetriaminepentaacetic acid. Chem J Moldova 2:83–87. https://doi.org/10.19261/cjm.2007.02(1).10
9. Kariaka N, Litsis O, Kolomzarov Y, Gawryszewska P, Smola S, Rusakova N, Trush V, Sliva T, Amirkhanov V (2018) Luminescent thin films based on N-(diphenylphosphoryl)benzamide Eu III and Tb III complexes for light emitting diode technology. Chem J Moldova 13:54–62. https://doi.org/10.19261/cjm.2018.473
10. Skopenko VV, Amirkhanov VM, Sliva TYu, Vasilchenko IS, Anpilova EL, Garnovskii AD (2004) Various types of metal complexes based on chelating β-diketones and their structural analogues. Russ Chem Rev 8:737–752
11. Gawryszewska P, Sokolnicki J, Legendziewicz J (2005) Photophysics and structure of selected lanthanide compounds. Coordin Chem Rev 249:2489–2509. https://doi.org/10.1016/j.ccr.2005.06.021
12. Olyshevets IP, Dyakonenko VV, Shyshkina SV, Trush VO, Sliva TYu, Amirkhanov VM (2018) Synthesis, structural and spectral studies of anionic tetrakis-complexes of lanthanides CsLNL4 with SAPh-ligand: dimethyl(phenylsulfonyl)amidophosphate. Voprosy khimii i khimicheskoi tekhnologii 6:56–62. https://doi.org/10.32434/0321-4095-2018-121-6-56-62
13. Savchenko I, Berezhnytska A, Fedorov Y, Trunova E (2014) Copolymers of rare earth elements complexes with unsaturated β-diketones and N-vinylcarbazole for OLEDs. Mol Cryst Liq Cryst 590:49–57. https://doi.org/10.1080/15421406.2013.873847
14. Savchenko I, Berezhnytska A, Smola S, Ivakha N (2013) Synthesis and characterization of copolymers of lantanide complexes with styrene. French-Ukrainian J Chem 1:94–99
15. Amirkhanov V, Ovchynnikov V, Trush V, Gawryszewska P, Jerzykiewicz LB (2014) Powerful new ligand systems: carbacylamidophosphates (CAPh) and sulfonylamidophosphates (SAPh) in ligands. Synthesis, characterization and role in biotechnology. NOVA Publishers, New York, ISBN-13: 978-1631171437
16. Dorosti N, Delfan B, Gholivand K, Ebrahimi-Valmoozi AA (2016) Synthesis, crystal structure, biological evaluation, electronic aspects of hydrogen bonds, and QSAR studies of some new N-(substituted phenylurea) diazaphosphore derivatives as anticancer agents. Med Chem Res 25:769–789. https://doi.org/10.1007/s00044-016-1527-9
17. Vahdani Alviri B, Pourayoubi M, Saneei A, Keikha M, van der Lee A, Crochet A et al (2018) Puckering behavior in six new phosphoric triamides containing aliphatic six- and seven-membered ring groups and a database survey of analogous ring-containing structures. Tetrahedron 74:28–41. https://doi.org/10.1016/j.tet.2017.11.030
18. Oroujzadeh N, Gholivand K, Jamalabadi NR (2017) New carbacylamidophosphates containing nicotinamide: synthesis, crystallography and antibacterial activity. Polyhedron 122:29–38. https://doi.org/10.1016/j.poly.2016.10.024
19. Grynyuk II, Prylutska SV, Kariaka NS, Sliva TY, Moroz OV, Franskevych DV, Amirkhanov VM, Matyshevska OP, Slobodyanik MS (2015) Computer prediction of biological activity of dimethyl-*N*-(benzoyl)amidophosphate and dimethyl-*N*-(phenylsulfonyl)amidophosphate, evaluation of their cytotoxic activity against leukemia cells in vitro. Ukr Biokhim Zh+ 6:154–161. https://doi.org/10.15407/ubj87.06.154
20. Jaroslav K, Swerdloff F (1985) *N*-acyl phosphoric triamide urease inhibitors and urease inhibited urea based fertilizer compositions. USA Patent No. 4517003A
21. Grimes KD, Lu Y-J, Zhang Y-M, Luna VA, Hurdle JG, Carson EI, Qi J, Kudrimoti S, Rock ChO, Lee RE (2008) Novel acyl phosphate mimics that target PlsY, an essential acyltransferase in gram-positive bacteria. ChemMedChem 12:1936–1945. https://doi.org/10.1002/cmdc.200800218
22. Amirkhanov V, Ovchinnikov V, Legendziewicz J, Graczyk A, Hanuza J, Macalik L (1996) Spectroscopic studies of neodymium and europium phosphoro-azo β-diketonates. Acta Phys Pol A 90:455–460. https://doi.org/10.12693/APhysPolA.90.455
23. Litsis OO, Shatrava IO, Amirkhanov OV, Ovchynnikov VA, Sliva TYu, Shishkina SV, Dyakonenko VV, Shishkin OV, Amirkhanov VM (2016) New carbacylamidophosphates (CAPh) and CAPh-containing coordination compounds: structural peculiarities. Struct Chem 1:341–355. https://doi.org/10.1007/s11224-015-0701-x
24. Kariaka NS, Trush VA, Medviediev VV, Dyakonenko VV, Shishkin OV, Smola SS, Fadeyev EM, Rusakova NV, Amirkhanov VM (2016) Coordination compounds based on CAPh type ligand:

synthesis, structural characteristics and luminescence properties of tetrakis-complexes $CsLnL_4$ with dimethylbenzoylamidophosphate. J Coord Chem 1:123–134. https://doi.org/10.1080/00958972.2015.1115024

25. Tananaev IG, Letyushov AA, Safiulina AM, Goryunova IB, Glibov LA, Myasoedov BF (2008) Search strategy for new efficient organophosphorus extractants for concentrating radionuclides. Dokl Chem 422:260–264. https://doi.org/10.1134/S0012500808100054
26. Yizhak RV, Znovjyak KO, Ovchynnikov VA, Sliva TY, Konovalova IS, Medviediev VV, Shishkin OV, Amirkhanov VM (2013) Synthesis and crystal structures of new dioxouranium(VI) complexes based on carbacylamidophosphates (CAPh). Investigation of extraction properties of some CAPh ligands in respect of dioxouranium(VI) nitrate. Polyhedron 62:293–299. https://doi.org/10.1016/j.poly.2013.06.043
27. Yakovlev OO, Kariaka NS, Trush VA, Smola SS, Siczek M, Amirkhanov VM (2018) Luminescent properties and structure of new CAPh-based lanthanide complexes [LnL_3Q], containing additional bis-heterocyclic aromatic ligand-antenna 2-(1,3,4-oxadiazole-2-yl)pyridine. Opt Mater 75:459–464. https://doi.org/10.1016/j.optmat.2017.10.044
28. Zhang W, Tan M, Liu W, Yu K (1992) Synthesis and structure of *N*-(*O*,*O*-diethylphosphoryl)-*N*′-benzoylurea samarium perchlorate complex. Polyhedron 11:1581–1585. https://doi.org/10.1016/S0277-5387(00)83710-9
29. Gubina KE, Maslov OA, Trush EA, Trush VA, Ovchynnikov VA, Shishkina SV, Amirkhanov VM (2009) Novel heteroligand complexes of Co(II), Cu(II), Ni(II) and Mn(II) formed by 2,2′-dipyridyl or 1,10-phenanthroline and phosphortriamide ligands: synthesis and structure. Polyhedron 28:2661–2666. https://doi.org/10.1016/j.poly.2009.06.004
30. Trush VA, Domasevitch KV, Amirkhanov VM, Sieler J (1999) Structure of Tl(18-crown-6){$Cl_3CC(O)NP(O)(OCH_3)_2$}: coordination of the ionic multidentate weakens the interaction of the metal atom with the crown ether. Z Naturforsch Pt B 54:451–455
31. Litsis O, Sliva TY, Kolomzarov YV, Minakova IE, Amirkhanov VM (2016) Nanodimension thin films based on lanthanide coordination compound for light-emitting devices. CAOL Proc Intl Conf Adv Optoelectron Lasers. https://doi.org/10.1109/CAOL.2016.7851409
32. Litsis OO, Ovchynnikov VA, Shishkina SV, Sliva TY, Amirkhanov VM (2013) Dinuclear 3D metal complexes based on a carbacylamidophosphate ligand: redetermination of the ligand crystal structure. Transit Metal Chem 38:473–479. https://doi.org/10.1007/s11243-013-9713-9
33. Gholivand K, Salami R, Shahsavari Z, Torabi E (2016) Novel binuclear and polymeric diorganotin(IV) complexes with *N*-nicotinylphosphoramides: synthesis, characterization, structural studies and anticancer activity. J Organomet Chem 819:155–165. https://doi.org/10.1016/j.jorganchem.2016.05.008
34. Znovjyak KO, Ovchynnikov VA, Moroz OV, Shishkina SV, Amirkhanov VM (2010) Bis{*N*-[bis(pyrrolidin-1-yl)phosphoryl]-2,2,2-trichloroacetamide}dinitratodioxidouranium(VI). Acta Crystallogr E E 66:m322. https://doi.org/10.1107/S1600536810006422
35. Shatrava I, Gubina K, Ovchynnikov V, Dyakonenko V, Amirkhanov V (2016) Crystal structure of aquatris-*μ*-*N*-[bis(diethylamino)phosphoryl]-2,2,2-trichloroacetamidato-κ^3O, *O*':*O*}calciumsodium. Acta Crystallogr E 72:1683–1686. https://doi.org/10.1107/S2056989016017035
36. Schwarzenbach G, Flaschka H (1969) Complexometric titrations. Methuen, London
37. Sheldrick GM (2015) Crystal structure refinement with SHELXL. Acta Crystallogr C C71:3–8. https://doi.org/10.1107/S2053229614024218
38. Kirsanov AV, Derkach GI (1955) Trichlorophosphazotrichloroacetyl chloride and cloro anhydride of *N*-phosphoric acid trichloroiminoacetyl chloride. Zh Obshch Khim+ 2009–2014 (**in Russian**)
39. Ovchynnikov VA, Amirkhanov VM, Timoshenko TP, Glowiak T, Kozlowski H (1998) Carbacylamidophosphates: synthesis, properties, and structure of dimorfolido-*N*-trichloroacetylphosphorylamide. Z Naturforsch Pt B 53:481–484
40. Wolff SK, Grimwood DJ, McKinnon JJ, Turner MJ, Jayatilaka D, Spackman MA (2012) Crystal Explorer 3.0. University of Western Australia, Perth
41. Spackman MA, Jayatilaka D (2009) Hirshfeld surface analysis. Cryst Eng Comm 11:19–32. https://doi.org/10.1039/B818330A
42. Znovjyak KO, Ovchynnikov VA, Shishkina SV, Sliva TYu, Amirkhanov VM (2010) Tris{*N*-[bis(pyrrolidin-1-yl) phosphoryl]-2,2,2-trichloroacetamide}trichloridoerbium(III). Acta Crystallogr 66:m447. https://doi.org/10.1107/S1600536810010408
43. Amirkhanov VM, Ovchynnikov VA, Kapshuk AA, Skopenko VV (1995) Synthesis and study of coordination compounds of rare-earth chlorides with bis(diethylamido)trichloroacetylamidophosphoric acid. Russ J Inorg Chem+ 40:1800–1804 (**in Russian**)
44. Litsis O, OvchynnikovV. Sliva T, Shishkina S, Amirkhanov V (2018) Lanthanide coordination compounds with monodentate coordinated β-diketone heteroanalogue—(2,2,2-trichloro-*N*-(dipiperidin-1-yl-phosphoryl)acetamide: synthesis and spectral investigations. Chem J Moldova. General, Industrial and Ecological Chemistry 13:15–23. https://dx.doi.org/10.19261/cjm.2017.466
45. Znovjyak KO, Moroz OV, Ovchynnikov VA, Sliva TYu, Shishkina SV, Amirkhanov VM (2009) Synthesis and investigations of mixed-ligand lanthanide complexes with *N*,*N*′-dipyrrolidine-*N*″-trichloracetylphosphortriamide, dimethyl-*N*-trichloracetylamidophosphate, 1,10-phenanthroline and 2,2′-bipyrimidine. Polyhedron 28:3731–3738. https://doi.org/10.1016/j.poly.2009.08.017
46. Gholivand K, Alizadehgan AM, Arshadi S, Firooz AA (2006) Conformational, structural analysis and vibrational spectra of a new carbacylamidophosphate compound: experimental and theoretical study. J Mol Struct 791:193–200. https://doi.org/10.1016/j.molstruc.2006.01.029
47. Amirkhanov VM, Ovchinnikov VA, Trush VA, Skopenko VV (1996) Properties and structure of bis(diethylamido)trichloracethylamido phosphoric acid. Zh Org Khim+ 32:376–380 (**in Russian**)
48. Radonovich LJ, Glick MD (1973) Structure of a six-coordinate rare earth complex: trichlorotris(hexamethylphosphoramide) praseodymium(III). J Inorg Nucl Chem 35:2745–2752. https://doi.org/10.1016/0022-1902(73)80505-6

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