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SYNTHESIS AND CHARACTERIZATION OF NEW LUMINESCENT TETRAKIS-COMPLEXES $NEt_4[LnL_4]$ WITH DIPHENYL-N-TRICHLOROACETYLAMIDOPHOSPHATE

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The manuscript reports the synthesis and investigation of new carbacylamidophosphate-based tetrakis-complexes of rare earth elements $NEt_4[LnL_4]$, where Ln = Eu, Tb, Y and HL is diphenyl-N-trichloroacetylamidophosphate. The work contributes to the study of the influence of the outer-sphere cation on the properties of tetrakis-complexes with carbacylamidophosphate, a promising class of ligands for the design of highly luminescent coordination compounds. The obtained complexes were characterized by elemental analysis and IR spectroscopy. The yttrium complex was additionally characterized by ^{1}H NMR, absorption, and diffuse reflectance spectroscopies. According to X-ray single-crystal analysis of $NEt_4[TbL_4]\cdot$iPrOH, the central ion in the complex is eight-coordinate by oxygen atoms of four carbacylamidophosphate ligands and has a coordination polyhedron in the form of a square antiprism, while 2-propanol is a solvated molecule. PXRD analysis reveals the isostructural nature of the obtained complexes. According to TG analysis, the decomposition of the europium complex begins at approximately 190^{0}C. Luminescence measurements of the complexes allowed the evaluation of the ligands' lowest triplet state (22780 cm^{-1}) as well as observation of Eu^{3+} and Tb^{3+} f–f emission with decay times in the range of 1.73–1.93 ms. Excitation spectra of the europium and terbium complexes showed that more efficient sensitization of f–f emission occurs in the «tail» of the absorption of the complexes.

Keywords: lanthanide, coordination compounds, carbacylamidophosphate, tetrakis-complex luminescence, crystal structure.

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Introduction

The lanthanide tetrakis-complexes of general formula $Q[LnL_4]$, where L and Q are bidentate organic ligands (e.g., β-diketonates carbamoylmethylphosphine oxides, carbacylamidophosphonate, sulfonylamidophosphonate, alkyldithiocarbamate, carboxylate, etc.), and counterion, respectively, are known molecular light emitters [1]. Such type of complexes is characterized by saturated coordination sphere of the lanthanide ion and high structural rigidity, that usually results in efficient *f–f* luminescence. The Ln^{3+} tetrakis β-diketonate

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complexes is one of the most investigated classes of Ln^{3+} based complexes, which exhibit high-intensity luminescence, making them suitable for efficient luminescent materials creation. Therefore, such type of tetrakis complexes can act as promising applications: lighting activators (LEDs and OLEDs), optical thermometers, mechanoluminescent sensors, biological markers, nano particle synthesis, luminescent solar concentrators, functionalized organic-inorganic hybrid materials, and quantum technologies [1].

The reports on the tetrakis compounds with other then β-diketonates kinds of ligands are still scarce therefore, needs more investigation. The design of new tetrakis-complexes is important for improvement of their luminescence properties. Recently, it was shown that carbacylamidophosphates (CAPh) can be considered as a promising class of ligands for the design of highly luminescent coordination compounds. CAPh-based Sm^{3+}, Eu^{3+}, Tb^{3+}, and Dy^{3+} complexes possess intense, long lasting luminescence with high intrinsic quantum yield [1].

Although the properties of Ln^{3+} based tetrakis-compounds mainly depend on the ligand nature, they can also depend on the counterion, which can influence much on the complex geometry, rigidity and intermolecular interactions resulting in change of thermodynamic stability, melting point, solubility, luminescent intensity and decay time, etc. [2–4].

This study is devoted to the synthesis and investigation of new tetrakis-CAPh complexes $NEt_4[LnL_4]$, where Ln=Eu, Tb, Y and HL is diphenyl-N-trichloroacetylamidophosphate (Fig. 1).

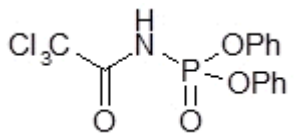


Fig. 1. Structural formula of HL

Experimental

Synthesis

The sodium salt of diphenyl-N-trichloroacetylamidophosphate NaL was obtained and identified according to previously described procedure [5] and used in the synthesis of the tetrakis-complexes, which can be described by the following scheme:

$$Ln(NO_3)_3{\cdot}6H_2O+6HC(OC_2H_5)_3+4NaL+NEt_4Cl\rightarrow$$
$$\rightarrow NEt_4[LnL_4]+3NaNO_3+NaCl+6HC(O)OC_2H_5+$$
$$+12C_2H_5OH,\ Ln=Eu,\ Tb,\ Y$$

The mixture of hydrated rare earth nitrates (0.2 mmol) and triethyl orthoformate (1.2 mmol) were dissolved in 2-propanol (4 mL) upon refluxing and heating to the solvent boiling temperature. NaL (0.8 mmol) was dissolved in acetone (4 mL) upon heating. NEt_4Cl (0.2 mmol) was dissolved in 2-propanol (2 mL) upon heating. The obtained three solutions were combined and refluxed upon heating for a minute and then left to cool down to the room temperature. Then, the precipitations of $NaNO_3$ and NaCl were filtered off and the clear solution was left at room conditions for slow evaporation of the solvents. In few days, when the majority of the solvent was evaporated, the precipitation of the target complexes appeared. The complexes were filtered off, washed with 2-propanol and dried on air.

$NEt_4[EuL_4]$: Yield 76%. Calculated for $EuC_{64}H_{60}N_5P_4O_{16}Cl_{12}$ (1856.48) (%): C 41.41; H 3.26; N 3.77. Found: C 41.52; H 3.67; N 3.80. IR (KBr): 3100–2850w (ν(C–H)), 1620vs (ν(C=O)), 1585s, 1490s, 1370s, 1220m, 1192vs (ν(P=O)), 1163m, 1072w, 1020s, 947vs (ν(P–N)), 876m, 819m, 775m, 717w, 690m, 676m, 615w, 587w, 528m, 506m cm^{-1}.

$NEt_4[TbL_4]$: Yield 78%. Calculated for $TbC_{64}H_{60}N_5P_4O_{16}Cl_{12}$ (1863.44) (%): C 41.25; H 3.25; N 3.76. Found: C 41.32; H 3.64; N 3.81. IR (KBr): 3100–2850w (ν(C–H)), 1622vs (ν(C=O)), 1585s, 1490s, 1370s, 1220m, 1192vs (ν(P=O)), 1163m, 1071w, 1021s, 947vs (ν(P–N)), 878m, 819m, 775m, 718w, 690m, 676m, 615w, 590w, 528m, 506m cm^{-1}.

$NEt_4[YL_4]$: Yield 79%. Calculated for $YC_{64}H_{60}N_5P_4O_{16}Cl_{12}$ (1793.42) (%): C 42.86; H 3.37; N 3.91. Found: C 42.98; H 3.77; N 3.94. IR (KBr): 3100–2850w (ν(C–H)), 1622vs (ν(C=O)), 1585s, 1490s, 1370s, 1220m, 1192vs (ν(P=O)), 1163m, 1072w, 1021s, 947vs (ν(P–N)), 879m, 819m, 775m, 717w, 690m, 676m, 615w, 587w, 528m, 506m cm^{-1}. ^1H NMR (DMSO-d6): 7.31t (16H, Ph), 7.22d (16H, Ph), 7.10t (8H, Ph), 3.18q (8H, CH_2), 1.14t (12H, CH_3).

Methods

Elemental analysis was performed using a CHNS Vario EL Cube Elemental Analyzer.

Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum BX spectrometer in the range of 400–4000 cm^{-1} using KBr pellets.

^1H NMR spectrum of NaL and $NEt_4[YL_4]$ was measured on a AVANCE 400 Bruker NMR spectrometer.

Diffuse reflectance and absorption spectra of $NEt_4[YL_4]$ were recorded on a Shimadzu UV-2600i spectrophotometer. The solution of the complex in methanol was prepared for measuring the absorption spectrum.

Photoluminescence excitation and emission spectra of the solid europium and terbium complexes

were measured at 298 K on a Fluorolog FL 3−22 (Horiba Jobin Yvon) spectrofluorimeter coupled to a R928 Hamamatsu photomultiplier, using the right-angle detection mode. The excitation source was a 450W Xe arc lamp. The emission spectra were corrected for detection and optical spectral response of the spectrofluorimeter and the excitation spectra were corrected for the spectral distribution of the lamp intensity using a photodiode reference detector. All the spectra were acquired through an UV filter (350 nm cut-off). The luminescence lifetime measurements were acquired with the same instrument using a pulsed Xe−Hg lamp (6 mcs pulse at half width and 20−30 mcs low-intensity tail). The luminescence lifetime values are averages of at least three independent measurements which were made by monitoring the decay at the maxima of the emission spectra. The decays were analyzed with Origin 9.2.257. The decay time values were estimated with an error of 10%. The phosphorescence spectrum was registered for the solid Y^{III} complex at 77 K enforcing a 1 ms delay, and repeating measurements at least 3 times.

The thermal stability of $NEt_4[EuL_4]$ has been studied on a derivatograph Mettler-Toledo TGA/DSC 3+STARe System in the temperature range up to 600^0C in argon atmosphere with a heating rate equal to 5^0C/min.

Powder X-ray diffraction (PXRD) patterns were obtained using a Shimadzu XRD-6000 diffractometer with CuKa radiation (λ=1.5418 Å) over a 2θ range of $5-50^0$ with a step size of 0.05^0.

Single-crystal X-ray diffraction data were collected on a Bruker APEX-II CCD diffractometer with graphite-monochromated MoKa radiation (λ=0.71073 Å). The structure was solved with the ShelXT [6] solution program using the intrinsic phasing method and by using Olex2 [7] as the graphical interface. The model was refined with ShelXL program [8] using full matrix least squares minimization on F^2. Restrictions on the thermal ellipsoids in the disordered tetraethylammonium cation found in the special position at the center of symmetry were applied. All non-hydrogen atoms were refined within anisotropic approximation. Positions of the hydrogen atoms were located from electron density difference maps and refined using a "riding" model with U_{iso}=nU_{eq} (n=1.5 for methyl groups and 1.2 for other atoms) of the carrier atom. CCDC 2558134.

The crystals $NEt_4[TbL_4]$·iPrOH (M=1923.46 g/mol) monoclinic crystal system, space group C2/c, *a*=25.189(3) Å, *b*=15.177(3) Å, *c*=42.307(6) Å, β=96.264(15)^0, V=16077(4) Å^3, Z=8, T=173(2) K, μ(MoKα)=1.425 mm^{-1}, D_{cacl}=1.589 g/cm^3, gathered 94585 reflections, (15780 independent reflections, R_{int}=0.1702), wR_2=0.2381 (R_1=0.1180, F>4s(F), S=1.229).

Results and discussion

Structure of $NEt_4[TbL_4]$·iPrOH

The obtained tetrakis-complexes crystallize from the 2-propanol solutions as a solvate with one 2-propanol molecule. The 2-propanol molecule is involved in O−H...π hydrogen bonds with the C23...C28 aromatic ring (O17−H...C25' and O17−H...C26' interactions; symmetry operation is 1/5−x, 1/5−y, 1−z; H...C distances are 2.47 Å and 2.79 E; O−H...C angles are 154^0 and 166^0).

In the anionic tetrakis-complexes the ligands are coordinated towards Tb^{3+} ion in a bidentate chelating way, forming TbO_8 polyhedron in form of a square antiprism (D_{4d}) (Fig. 2). The geometry of the coordination polyhedron was analyzed using SHAPE 2.1 program [9], which gives the convergence factor for square antiprism geometry equal 0.159. The Tb−O bonds are not equivalent, being shorter with oxygen atoms of P=O groups compared to C=O groups (Table 1). Such nonequivalence of the Ln−O bonds is typical for CAPh based complexes and can be explained by higher affinity of phosphoryl group toward metal ions. The The P=O and C=O bonds in the structure of $NEt_4[TbL_4]$·iPrOH are elongated compared to the free ligand HL (C−O_{HL}=1.207(2) Å, P−O_{HL}=1.475(1) Å [7]), whereas the P−N and C−N bonds are shorterned compared to the free ligand (N−C_{HL}=1.338(2) Å, P−N_{HL} =1.696(2) Å) due to deprotonation and electron density redistribution in the chelating core −C−O−N−P−O−. The chelating metallacycles −C−O−N−P−O−Tb in the complex anion $[TbL_4]^-$ have different conformations. The cycle Tb1...O2...P1...N1...C2...O1 is planar with an accuracy of 0.026 Å. The cycle Tb1...O6...P2...N2...C16...O5 adopts a sofa conformation (the puckering parameters are as follows: S=0.38 Å, Θ=30.35^0, Ψ=5.91^0 [10]). The O6, P2, N2, C16 and O5 atoms lie within a plane with an accuracy of 0.010 Å, while the Tb1 atom deviates from this plane by −0.544(13) Å. The cycle Tb1...O10...P3...N3...C30...O9 adopts a half-chair conformation (the puckering parameters are as follows: S=0.33 Å, Θ=31.34^0, Ψ=28.31^0). The O10, P3, N3, C30 atoms lie within a plane with an accuracy of 0.00 Å while the Tb1 and O9 atoms deviate from this plane by 0.36(2) Å and −0.083(17) Å, respectively. The cycle Tb1...O14...P4...N4...C44...O13 adopts a boat conformation (the puckering parameters are as follows: S=0.24 Å, Θ=68.57^0, Ψ=2.50^0). The P4, N4, C44 and O13 atoms lie within a plane with an accuracy of 0.005 Å, while the Tb1 and O14 atoms deviate from this plane by 0.47(2) Å and 0.235(13) Å, respectively.

The atoms of the metallacycles are not involved in intermolecular interactions. However, there are numerous intermolecular interactions with participation of CAPh ligands' substitutes in crystal. In particular, the CCl_3 groups participate in Cl···C and Cl···H interactions, and the phenyl groups are involved in Cl···C, Cl···H, H···H, and C···H contacts.

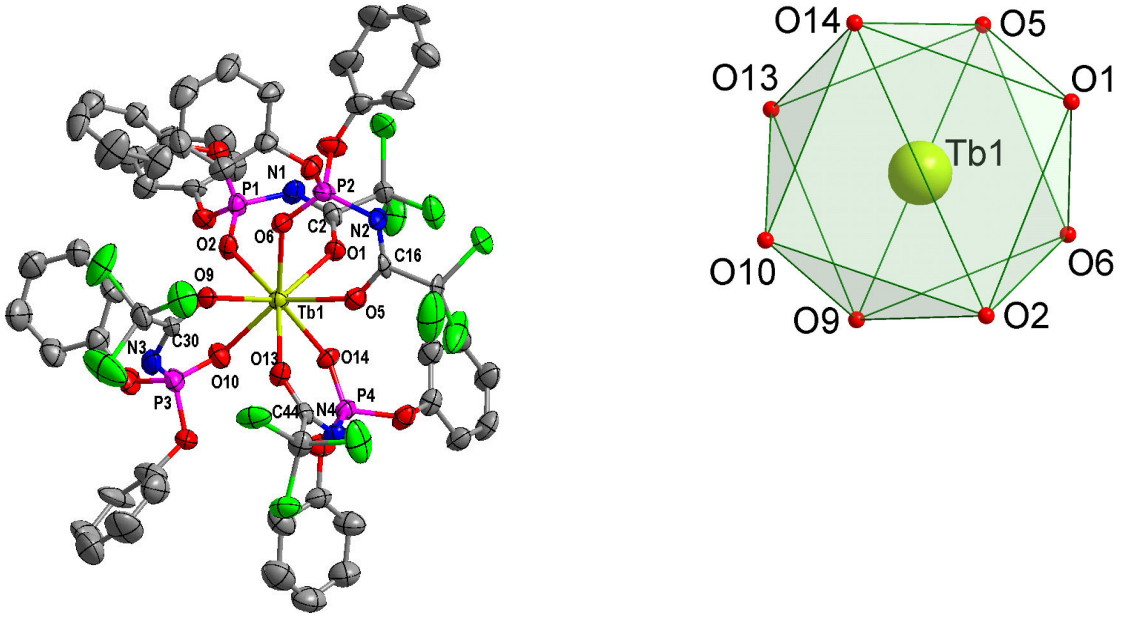
According to the data of PXRD analysis, the obtained complexes are isostructural.

IR spectroscopy

All the obtained complexes $NEt_4[LnL_4]$ have almost identical IR spectra. The assignment of the main bands of the spectra is given in Table 2. The IR spectra of the complexes are characterized by an absence of ν(N−H) band, confirming the ligands deprotonation. The bands of the carbonyl and phosphoryl groups valence vibrations in the spectra of $NEt_4[LnL_4]$ compounds are typically shifted towards low frequencies compared to the spectrum of HL (1740 cm^{-1} ν(C=O), 1280 cm^{-1} ν(P=O) [7]). The ν(P−N) band for the complexes is blue-shifted compared to HL (900 cm^{-1}).

Thermal gravimetric analysis

The TG and DTA curves of $NEt_4[EuL_4]$ are



a b

Fig. 2. a − The structure of $[TbL_4]^-$ complex anion (H-atoms are omitted); b − the coordination polyhedron of the Tb^{3+} ion

Table 1

Selected bond lengths in the complex of $NEt_4[TbL_4]$

Bond	Length, Å	Bond	Length, Å
Tb1–O1(C)	2.412(8)	Tb1–O2(P)	2.347(7)
Tb1–O5(C)	2.385(8)	Tb1–O6(P)	2.329(8)
Tb1–O9(C)	2.379(7)	Tb1–O10(P)	2.376(8)
Tb1–O13(C)	2.398(8)	Tb1–O14(P)	2.323(7)
O1–C2	1.244(14)	O2–P1	1.482(8)
O5–C16	1.258(13)	O6–P2	1.474(8)
O9–C30	1.227(13)	O10–P3	1.446(9)
O13–C44	1.246(13)	O14–P4	1.470(8)
C2–N1	1.309(15)	P1–N1	1.587(10)
C16–N2	1.262(14)	P2–N2	1.621(10)
C30–N3	1.302(15)	P3–N3	1.600(11)
C44–N4	1.293(14)	P4–N4	1.605(10)

shown in Fig. 3. The TG curve is characterized by absence of weight loss in the temperature range 27–100°C pointing on the absence of solvents in the sample, which is in agreement with elemental analysis. The DTA curve exhibit endothermal extremum at 110°C, which is not accompanied by melting or destruction, thus, can be a phase transition. At further heating, the complex stays stable until the decomposition begins at approximately 190°C. The decomposition is an exothermic process, which occurs in several steps with total weight loss of 73.2% of the sample in the temperature region of 27–600°C, pointing on the europium metaphosphate being the main product of the complex decomposition.

Diffuse reflectance spectrum of $NEt_4[YL_4]$

The diffuse reflectance and absorption spectra of $NEt_4[YL_4]$ are shown in Fig. 4. The ligands possess absorption in the region 200–300 nm. The diffuse reflectance spectrum shows two maxima at 235 and 264 nm. The absorption spectrum shows the maxima at 213 and 264 nm.

Luminescence

Considering the importance of the ligands' lowest triplet state (LLTS) level in the process of *f–f* emission sensitization we have estimated the value of energy of LLTS (22780 cm^{-1}) from the phosphorescence spectrum of solid $NEt_4[YL_4]$. The LLTS energy in $NEt_4[LnL_4]$ is for approximately 1490 cm^{-1} lower compared to the $PPh_4[LnL_4]$ (24270 cm^{-1} [7]), which points on notable involvement of the outer sphere cations in the formation of molecular orbitals of the ligands in the complexes. The found value of the LLTS is high enough for efficient energy transfer from the ligands to Eu^{III} and Tb^{III} ions.

The excitation spectra of $NEt_4[EuL_4]$ and $NEt_4[TbL_4]$ (Figs. 5 and 6) were measured by monitoring emission at 613 and 544 nm, respectively. The obtained spectra consist of the narrow bands of Eu^{III} and Tb^{III} ions *f–f* transitions and a broad band of relatively small intensity in the region of 275–325 nm. Unlike excitation spectra of $PPh_4[LnL_4]$ (Ln=Eu, Tb), the spectra of $NEt_4[EuL_4]$ and $NEt_4[TbL_4]$ do not contain a sensitization band in the region of 240–275 nm. The possible explanation of this phenomenon can be either the presence of energy transfer from PPh_4^+ cation to the lanthanides in $PPh_4[LnL_4]$ or quenching of this energy of excitation in the complexes $NEt_4[LnL_4]$. From the

Table 2

Main bands assignment in the IR spectra of the $NEt_4[LnL_4]$ compounds (cm^{-1})

Assignment/compound	$NEt_4[EuL_4]$	$NEt_4[TbL_4]$	$NEt_4[YL_4]$
ν(C=O)	1620	1622	1622
ν(P=O)	1192	1192	1192
ν(P–N)	947	947	947

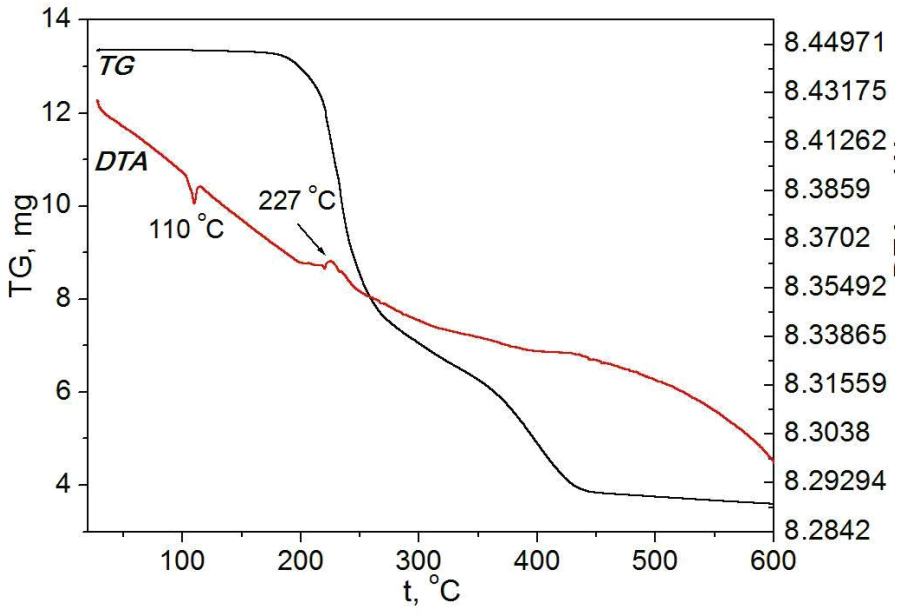


Fig. 3. TG and DTA curves for $NEt_4[EuL_4]$

other side, it is interesting to note, that similar to the previously studied tetrakis-complexes of lanthanides with dimethyl-N-trichloroacetylamidophosphate [4], the presence of a broad band in the region of 275–325 nm in the excitation spectra of the complexes $NEt_4[EuL_4]$ and $NEt_4[TbL_4]$ correlates with presence of planar metallacycle in the structure of the compounds. The nature of the profile of excitation spectra for these two series of compounds is yet unclear and requires further study.

Upon excitation of the complexes $NEt_4[EuL_4]$ and $NEt_4[TbL_4]$ by UV light they exhibit typical emission bands of *f–f* transitions of Eu^{III} and Tb^{III} ions in the visible region (Figs. 5 and 6). The band of hypersensitive transition $^5D_0 \rightarrow {}^7F_2$ dominates in the emission spectrum of $NEt_4[EuL_4]$ and the band of $^5D_0 \rightarrow {}^7F_0$ forbidden transition is of the lowest intensity. The intensities ratio $^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_2$ (red/orange

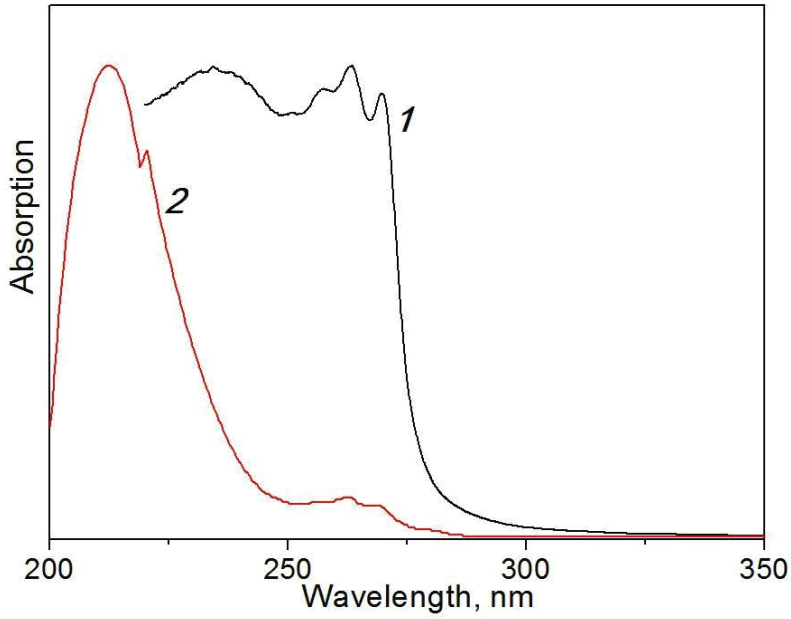


Fig. 4. Normalized diffuse reflectance (1) and absorption (2) spectra of $NEt_4[YL_4]$ in UV range

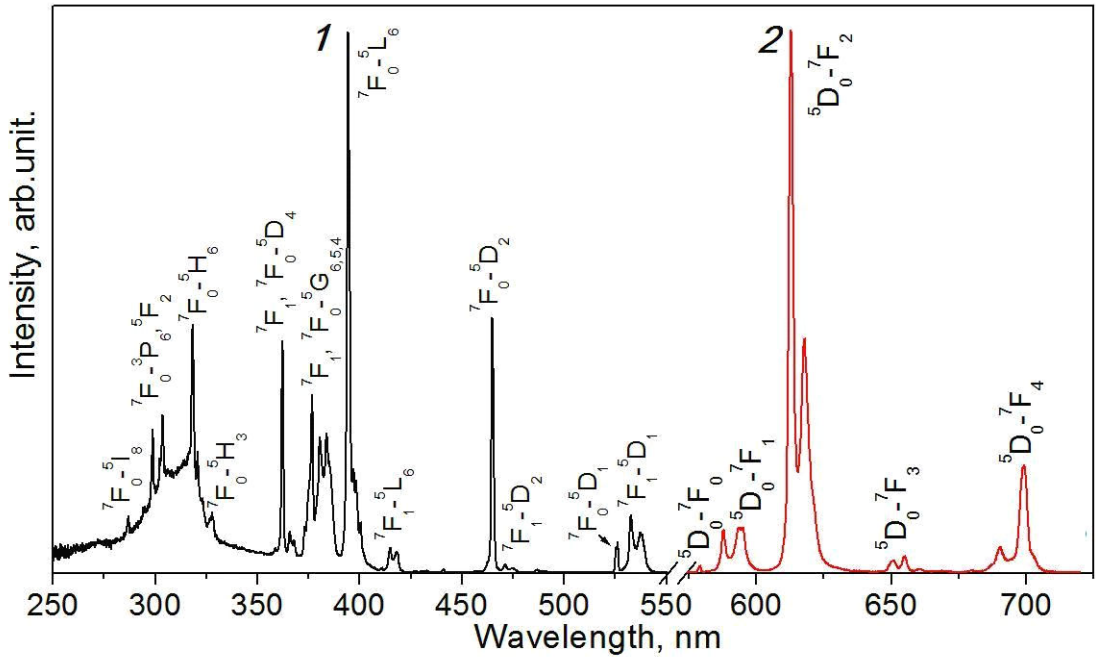


Fig. 5. Excitation (1) and emission (2) spectra of $NEt_4[EuL_4]$

ratio) equals 6.5. The band of transition $^5D_4 \rightarrow {}^7F_5$ dominates in the spectrum of $NEt_4[TbL_4]$. The rest of the bands are approximately of the same intensity. The ligands fluorescence is absent in the spectra. The emission decay curves of $NEt_4[EuL_4]$ and $NEt_4[TbL_4]$ are monoexponential. The emission decay time of $NEt_4[EuL_4]$ equals 1.93 ms and 1.73 ms at λ_{exc}=310 nm and at λ_{exc}=294 nm, respectively. The radiative lifetime of $^5D_0$ state of $NEt_4[EuL_4]$ was estimated from emission data using the following equation: $1/\tau_{RAD}=A_{MD,0}\cdot n^3\cdot(I_{tot}/I_{MD})$ [11,12], where $A_{MD,0}$ is equal to 14.65 s^{-1}, n is considered to be 1.5, and (I_{tot}/I_{MD}) is the ratio of the total integrated emission from the Eu ($^5D_0$) level to the integrated intensity of MD transition $^5D_0 \rightarrow {}^7F_1$ [13]. The radiative lifetime equals 2.14 ms. The $^5D_0$ intrinsic quantum yield (Q^{Ln}_{Ln}) can be estimated from the observed and radiative decay times ($Q^{Ln}_{Ln}=\tau_{obs}/\tau_{RAD}$) and equals 81%. The emission decay time of $NEt_4[TbL_4]$ is less dependent on excitation wavelength and equals 1.85 ms and 1.77 ms at λ_{exc}=295 nm and at λ_{exc}=396 nm, respectively.

Conclusions

In search of efficient lanthanide based luminophores, new three isostructural tetrakis-complexes $NEt_4[LnL_4]$ (Ln=Eu, Tb, Y) with diphenyl-N-trichloroacetylamidophosphate were successfully obtained with aim to study the influence of the outersphere cation on the properties of the compounds.

The X-ray analysis of $NEt_4[TbL_4]\cdot iPrOH$ reveals that the ligands are coordinated towards Tb^{3+} ion in a bidentate chelating way, forming LnO_8 polyhedron in form of a square antiprism.

The complexes are solvent-free. The complex $NEt_4[EuL_4]$ is thermally stable up to approximately 190^{0}C, however, demonstrates a phase transition at approximately 110^{0}C.

Being excited by UV light, the complexes $NEt_4[EuL_4]$ and $NEt_4[TbL_4]$ exhibit photoemission with luminescence decay times of approximately of 1.8 ms. The complex $NEt_4[EuL_4]$ possesses rather high intrinsic quantum yield of 81%.

The introduction of NEt_4^+ cation instead of PPh_4^+ one into the complexes $[LnL_4]^-$ leads to decrease of LLTS for approximately 1490 cm^{-1}, decrease of the complexes' decomposition temperature from 220 to 190^{0}C, increase in europium and terbium *f–f* luminescence decay time for 0.5 ms and decrease of sensitization the *f–f* emission.

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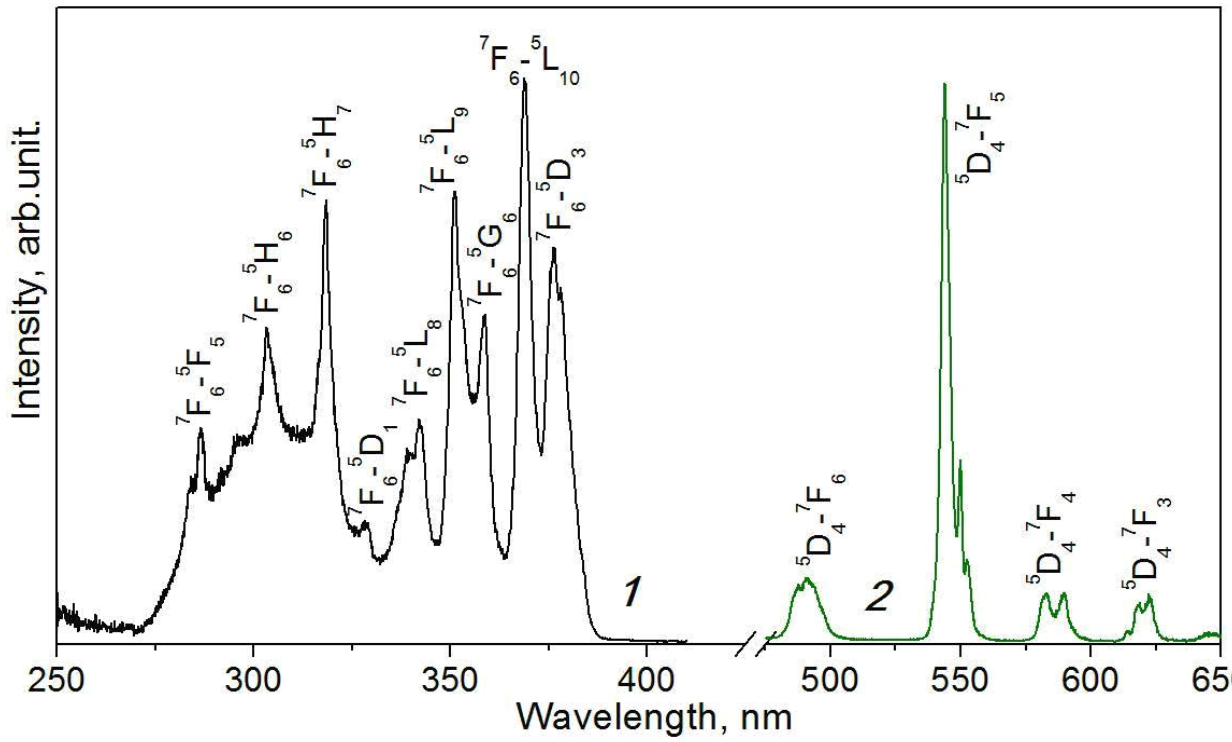


Fig. 6. Excitation (1) and emission (2) spectra of $NEt_4[TbL_4]$

and sulfonylamidophosphates as a basis for novel polyfunctional compounds and materials»).

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СИНТЕЗ І ХАРАКТЕРИСТИКА НОВИХ ЛЮМІНЕСЦЕНТНИХ ТЕТРАКІС-КОМПЛЕКСІВ $NEt_4[LnL_4]$ З ДИФЕНІЛ-N-ТРИХЛОРАЦЕТИЛАМІДОФОСФАТОМ

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У статті описано синтез і наведено результати досліджень нових тетракіс-комплексів рідкісноземельних елементів $NEt_4[LnL_4]$ на основі карбациламідофосфатного ліганду, де Ln=Eu, Tb, Y та HL − дифеніл-N-трихлорацетиламідофосфат. Робота сприяє дослідженню впливу позасферних катіонів на властивості тетракіс-комплексів лантаноїдів з карбациламідофосфатами − перспективними сенсибілізаторами люмінесценції лантаноїдів. Одержані комплекси досліджені методами елементного аналізу та ІЧ спектроскопії. Комплекс ітрію досліджений також методами ПМР та електронної спектроскопії. Згідно з даними рентгеноструктурного аналізу комплексу $NEt_4[TbL_4]\cdot$iPrOH центральний іон у сполуці є восьми-координованим чотирма карбациламідофосфатними лігандами та має координаційний поліедр у формі квадратної антипризми, а молекула 2-пропанолу є сольватованою. Рентгенофазовий аналіз вказує на ізоструктурність одержаних комплексів. Згідно з даними термогравіметричного аналізу комплекс європію розкошлається при близько 190^{0}C. Із допомогою люмінесцентних досліджень синтезованих комплексів знайдено енергію найнижчого триплетного рівня лігандів (22780 см$^{-1}$), а також показано, що для комплексів Eu^{3+} та Tb^{3+} спостерігається *f−f* люмінесценція з часом життя збудженого стану в діапазоні 1,73−1,93 мс. Спектри збудження люмінесценції комплексів європію та тербію вказують на більш ефективний процес сенсибілізації *f−f* люмінесценції в діапазоні «хвоста» смуги поглинання комплексів.

Ключові слова: лантаніди, координаційна сполука, карбациламідофосфат, люмінесценція тетракіс-комплексів, кристалічна структура.

SYNTHESIS AND CHARACTERIZATION OF NEW LUMINESCENT TETRAKIS-COMPLEXES $NEt_4[LnL_4]$ WITH DIPHENYL-N-TRICHLOROACETYLAMIDOPHOSPHATE

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The manuscript reports the synthesis and investigation of new carbacylamidophosphate-based tetrakis-complexes of rare earth elements $NEt_4[LnL_4]$, where Ln = Eu, Tb, Y and HL is diphenyl-N-trichloroacetylamidophosphate. The work contributes to the study of the influence of the outer-sphere cation on the properties of tetrakis-complexes with carbacylamidophosphate, a promising class of ligands for the design of highly luminescent coordination compounds. The obtained complexes were characterized by elemental analysis and IR spectroscopy. The yttrium complex was additionally characterized by ^{1}H NMR, absorption, and diffuse reflectance spectroscopies. According to X-ray single-crystal analysis of $NEt_4[TbL_4]\cdot$iPrOH, the central ion in the complex is eight-coordinate by oxygen atoms of four carbacylamidophosphate ligands and has a coordination polyhedron in the form of a square antiprism, while 2-propanol is a solvated molecule. PXRD analysis reveals the isostructural nature of the obtained complexes. According to TG analysis, the decomposition of the europium complex begins at approximately 190^{0}C. Luminescence measurements of the complexes allowed the evaluation of the ligands' lowest triplet state (22780 cm^{-1}) as well as observation of Eu^{3+} and Tb^{3+} f−f emission with decay times in the range of 1.73−1.93 ms. Excitation spectra of the europium and terbium complexes showed that more efficient sensitization of f−f emission occurs in the «tail» of the absorption of the complexes.

Keywords: lanthanide; coordination compounds; carbacylamidophosphate; tetrakis-complex luminescence; crystal structure.

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