UDC 546.3+543.4+543.572 doi: 10.33609/2708-129X.91.11.2025.22-34

CATION EFFECT ON THERMAL STABILITY AND LUMINESCENT PROPERTIES OF BINUCLEAR RARE EARTH ANIONIC COMPLEXES WITH BISCARBACYLAMIDOPHOSPHATE.

Nataliia Kariaka[1,*], Viktor Trush[1], Igor Fesych[1], Olena Gnatyuk[2], Ivan Gnatyuk[2], Galyna Dovbeshko[2], Volodymyr Amirkhanov[1]

[1]Taras Shevchenko National University of Kyiv, Department of Chemistry,
64 Volodymyrska str., 01601 Kyiv, Ukraine;
[2] Department of Physics of Biological Systems, Institute of Physics of the National Academy of Sciences of Ukraine,
46 Prospekt Nauki, 03028 Kyiv, Ukraine
e-mail: natka04@i.ua

A series of new binuclear anionic coordination compounds of yttrium (III) and europium (III) with bis-carbacylamidophosphate ligand tetramethyl N,N′-(2,2,3,3,4,4-hexafluoro-1,5-dioxopentane-1,5-diyl)bis(phosphoramidate) and six different cations has been obtained with an aim to study the cation influence on the thermal and spectral properties of the complexes. The synthesis of coordination compounds was carried out using standard techniques based on the exchange reaction between lanthanide nitrates and the sodium or triethylammonium salt of the ligand in non-aqueous solutions. The complexes' composition was established by means of elemental and thermal gravimetric analyses as well as ^1H NMR spectroscopy. The chelating type of metal binding with participation of both chelating cores of the bis-carbacylamidophosphate was confirmed by IR spectroscopy. It was shown that the cation nature greatly influences the properties of complexes, such as solubility, thermal stability, and luminescence characteristics, as well as determines the degree of the complexes' hydration. The europium (III) complexes exhibit f-f emission, which is sensitized by the ligands. The luminescence intensity, bands splitting, and bands intensity ratios, as well as luminescence decay time and intrinsic quantum yield, were found to be strongly dependent on the cation in the complexes under study. The red/orange ratio for the europium (III) complexes varies from 2.6 to 7.6, the luminescence decay time varies from 0.76 to 2.74 ms, and the intrinsic quantum yield varies from 24 to 90 %. The temperature of decomposition varies in the range near 155–190 °C, depending on the cation. The manuscript contributes to the studies of influence of outer sphere interactions on the luminescence of lanthanides' complexes, which is important for design of luminescent compounds with suitable for practical application properties.

Key words: rare earth element, bis-carbacylamidophosphate, coordination compounds, luminescence, thermal gravimetric analysis.

INTRODUCTION. Coordination compounds of lanthanides are objects of intensive research due to their specific spectral and magnetic properties, which are of interest for modern technologies [1–6]. Organic ligands in the coordination compounds of lanthanides play an important role, being used to enhance or modulate properties of Ln^{III} ions as well as to adjust other useful properties of compounds such as solubility, conductivity, biological activity, etc. An additional significant effect on luminescent and magnetic properties of lanthanides can result from outer-spherical ions and intermolecular interactions in the complex [7–13]. Such an influence occurs due to changes in the geometry and electronic properties of the ligand. As a result, the geometry of the coordination polyhedron of the lanthanide, the "rigidity" of the complex, or the energy of the triplet state of the ligand can vary. These affect the efficiency of energy transfer from the ligand to the metal as well as the efficiency of excited states deactivation. The influence of the second coordination domain on the photophysical properties of Ln^{III} coordination compounds is difficult to predict, and the relationships found are often not well understood. Therefore, research aimed at a deeper understanding of the mechanisms of influence of the second coordination sphere of lanthanide complexes on their properties is relevant. The knowledge gained will make it possible to design and improve the photophysical characteristics of electromagnetic radiation converters based on lanthanide complexes.

This study is devoted to the synthesis and investigation of new anionic binuclear rare earth complexes of general formula $(Cation)_2Ln_2L_4$ (where Ln = Y, Eu) with biscarbacylamidophosphate ligand H_2L (Figure 1) and different cations ($[Cation_2]^{2+} = [Na_2]^{2+}$, $[Cs_2]^{2+}$, $[(NH_4)_2]^{2+}$, $[(NMe_4)_2]^{2+}$, $[NaNEt_4]^{2+}$, and $[(HNEt_3)_2]^{2+}$). Different radii and different nature of the cations cause different polarizability and affect the possibility of hydrogen bond formation and their strength, thus can significantly affect the geometry of the complex, spectral properties, and ability to crystallize.

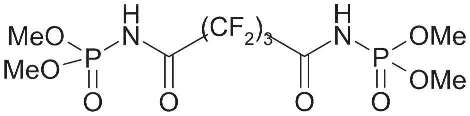

Fig. 1. The structural formula of H_2L

EXPERIMENT AND DISCUSSION OF THE RESULTS.

Synthesis of the complexes.

The H_2L and its sodium salt were synthesized and identified as described earlier [14, 15]. The complexes were obtained according to the following schemes:

$$2Ln(NO_3)_3\times 6H_2O + 4Na_2L = Na_2[Ln_2L_4]\cdot 3H_2O + 6NaNO_3 + 6H_2O$$

$$2Ln(NO_3)_3\times 6H_2O + 4Cs_2L = Cs_2[Ln_2L_4]\cdot H_2O + 6CsNO_3 + 6H_2O$$

$$2Ln(NO_3)_3\times 6H_2O + 4Na_2L + 2NH_4NO_3 = (NH_4)_2[Ln_2L_4]\cdot 4H_2O + 8NaNO_3 + 6H_2O$$

$$2Ln(NO_3)_3\times 6H_2O + 4Na_2L + 2NMe_4Cl = (NMe_4)_2[Ln_2L_4]\cdot H_2O + 6NaNO_3 + 2NaCl + 6H_2O$$

$$2Ln(NO_3)_3\times 6H_2O + 4Na_2L + NEt_4Cl = NEt_4[NaLn_2L_4]\cdot H_2O + 6NaNO_3 + NaCl + 6H_2O$$

$$2Ln(NO_3)_3\times 6H_2O + 4H_2L + 8NEt_3 = (HNEt_3)_2[Ln_2L_4]\cdot 3H_2O + 6HNEt_3NO_3 + 6H_2O$$

Ln = Eu, Y.

To obtain $Na_2[Ln_2L_4]\cdot3H_2O$ and $Cs_2[Ln_2L_4]\cdot{}\cdot H_2O$ the mixture of hydrated rare earth nitrates (0.2 mmol) and triethyl orthoformate (1.2 mmol) were dissolved in acetone (4 mL) upon refluxing and heating to acetone boiling temperature. Separately, Na_2L or Cs_2L (0.4 mmol) were dissolved in a mixture of acetone and 2-propanol (1:1, 10 mL) upon heating. The obtained solutions were mixed, refluxed upon heating for a minute and left to cool down to the room temperature. Then, the precipitation of $NaNO_3$ or $CsNO_3$ was 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. It was, filtered off, washed with 2-propanol and left on air to dry for a day and then for 8 hours in drying closet at 40 °C. The yield of the complexes was 70–76 %.

The complexes $(NH_4)_2[Ln_2L_4]\cdot4H_2O$, $(NMe_4)_2[Ln_2L_4]\cdot H_2O$, and $NEt_4[NaLn_2L_4]\cdot H_2O$ were obtained in a similar way as described above by combining three solutions at the initial stage. The NH_4NO_3 was dissolved in ethanol, while NMe_4Cl and NEt_4Cl were dissolved in 2-propanol. The yield of the complexes was 57–75 %.

To obtain $(HNEt_3)_2[Ln_2L_4]\cdot3H_2O$ the solution of mixture of hydrated rare earth nitrates (0.2 mmol) and triethyl orthoformate (1.2 mmol) in acetone was combined with the solution of mixture of H_2L (0.4 mmol, 0.18166 g) and NEt_3 (0.8 mmol, 0.111 ml) in 2-propanol. The obtained final solution was refluxed upon heating for a minute, then, cooled down to the room temperature and left to stand in air for slow evaporation of the solvents. The polycrystalline precipitate of the target complexes appeared in two days. It was filtered off, washed with 2-propanol and dried as described above. The yield of the complexes was near 80 %.

The obtained compounds are polycrystalline or amorphous powders, which are stable in air and have different solubility depending on the outer-sphere cations. All the complexes are soluble in methanol and insoluble in 2-propanol. The compounds $Cs_2[Ln_2L_4]\cdot H_2O$, $(NH_4)_2[Ln_2L_4]\cdot{}\cdot4H_2O$ and $(NMe_4)_2[Ln_2L_4]\cdot H_2O$ are soluble in water, while the rest of the obtained complexes ($Na_2[Ln_2L_4]\cdot3H_2O$, $NEt_4[NaLn_2L_4]\cdot H_2O$, and $(HNEt_3)_2[Ln_2L_4]\cdot3H_2O$) do not dissolve in water. All the obtained complexes, except of $(NMe_4)_2[Ln_2L_4]\cdot H_2O$ are slightly soluble in acetone. The complexes $(HNEt_3)_2[Ln_2L_4]\cdot3H_2O$ are soluble in dichloromethane as well.

Compound $Na_2[Y_2L_4]\cdot3H_2O$ ($Na_2Y_2C_{36}H_{54}N_8P_8O_{35}F_{24}$). Elemental anal. Calcd (%): H 2.61%, C 20.72%, N 5.37%; found H 2.46%, C 21.54%, N 5.47%. NMR - ^1H (DMSO-d6): $[L]^-$ 3.56 (d) 48H; ^{31}P (DMSO-d6): 10.74 (s)

Compound $Na_2[Eu_2L_4]\cdot3H_2O$ ($Na_2Eu_2C_{36}H_{54}N_8P_8O_{35}F_{24}$). Elemental anal. Calcd (%): H 2.46%, C 19.54%, N 5.06%; found H 2.26%, C 19.50%, N 5.31%.

Compound $Cs_2[Y_2L_4]\cdot H_2O$ ($Cs_2Y_2C_{36}H_{50}N_8P_8O_{33}F_{24}$). Elemental anal. Calcd (%): H 2.22%, C 19.05%, N 4.94%; found H 2.12%, C 18.88%, N 5.04%. NMR - ^1H (DMSO-d6): $[L]^-$ 3.56 (d) 48H; ^{31}P (DMSO-d6): 10.57 (s).

Compound $Cs_2[Eu_2L_4]\cdot H_2O$ ($Cs_2Eu_2C_{36}H_{50}N_8P_8O_{33}F_{24}$). Elemental anal. Calcd (%): H 2.10%, C 18.04%, N 4.68%; found H 2.06%, C 17.81%, N 4.80%.

Compound $(NH_4)_2[Y_2L_4]\cdot4H_2O$ ($Y_2C_{36}H_{64}N_{10}P_8O_{36}F_{24}$). Elemental anal. Calcd (%): H 3.08%, C 20.64%, N 6.69%; found

H 2.99%, C 21.46%, N 6.85%. NMR - ^{1}H (DMSO-d6): $[L]^-$ 3.55 (d) 48H, $[NH_4]^+$ 7.12 (m) 8H; ^{31}P (DMSO-d6): 10.57 (s)

Compound $(NH_4)_2[Eu_2L_4]\cdot 4H_2O$ ($Eu_2C_{36}H_{64}N_{10}P_8O_{36}F_{24}$). Elemental anal. Calcd (%): H 2.91%, C 19.47%, N 6.31%; found H 2.68%, C 19.74%, N 6.46%.

Compound $(NMe_4)_2[Y_2L_4]\cdot H_2O$ ($Y_2C_{44}H_{74}N_{10}P_8O_{33}F_{24}$). Elemental anal. Calcd(%): H 3.46%, C 24.55%, N 6.51%; found H 3.37%, C 24.28%, N 6.62%. NMR - ^{1}H (DMSO-d6): $[L]^-$ 3.54 (d) 48H, $[NMe_4]^+$ 3.08 (s) 24H; ^{31}P (DMSO-d6): 10.99 (s).

Compound $(NMe_4)_2[Eu_2L_4]\cdot H_2O$ ($Eu_2C_{44}H_{74}N_{10}P_8O_{33}F_{24}$). Elemental anal. Calcd (%): H 3.27%, C 23.19%, N 6.15%; found H 3.22%, C 22.90%, N 6.24%.

Compound $NEt_4[NaY_2L_4]\cdot H_2O$ ($NaY_2C_{44}H_{70}N_9P_8O_{33}F_{24}$). Elemental anal. Calcd (%): H 3.27%, C 24.49%, N 5.84%; found H 3.24%, C 24.18%, N 5.97%. NMR - ^{1}H (DMSO-d6): $[L]^-$ 3.56 (d) 48H, $[NEt_4]^+$ 1.14 (m) 12H, 3.18 (m) 8H; ^{31}P (DMSO-d6): 10.74 (s).

Compound $NEt_4[NaEu_2L_4]\cdot H_2O$ ($NaEu_2C_{44}H_{70}N_9P_8O_{33}F_{24}$). Elemental anal. Calcd (%): H 3.09%, C 23.14%, N 5.52%; found H 3.08%, C 22.90%, N 5.60%.

Compound $(HNEt_3)_2[Y_2L_4]\cdot 3H_2O$ ($Y_2C_{48}H_{86}N_{10}P_8O_{35}F_{24}$). Elemental anal. Calcd (%): H 3.86%, C 25.68%, N 6.24%; found H 3.76%, C 25.96%, N 6.41%. NMR - ^{1}H (DMSO-d6): $[L]^-$ 3.57 (d) 48H, $[HNEt_3]^+$ 1.15 (m) 18H, 3.13 (m) 12H; ^{31}P (DMSO-d6): 10.96 (s).

Compound $(HNEt_3)_2[Eu_2L_4]\cdot 3H_2O$ ($Eu_2C_{48}H_{86}N_{10}P_8O_{35}F_{24}$). Elemental anal. Calcd (%): H 3.66%, C 24.31%, N 5.91%; found H 3.55%, C 24.36%, N 6.09%.

Methods

Elemental analysis was performed on a Perkin-Elmer 2400 CHN elemental analyzer.

The thermal stabilities of the complexes have been studied on a derivatograph Mettler-Toledo TGA/DSC 3+ STARe System and on a synchronous TG / DTA analyzer Shimadzu DTG-60H in the temperature range up to 600 °C in argon atmosphere with a heating rate equal to 5 °C/min.

^{1}H and ^{31}P NMR spectra for solutions in dimethyl sulfoxide were obtained on an AVANCE 400 Bruker NMR spectrometer at room temperature.

Infrared spectra were recorded using a TENSOR 27 (Bruker) infrared spectrometer with an ATR attachment, which was developed specifically for the study of solid and powdery samples. All spectra were recorded in the wide spectral region from 4000 to 400 cm^{-1}. For spectra processing, the Opus 8.0 program was used. All spectra were baselined and normalized by the intensity of a band near 1600 cm^{-1}.

Diffuse reflection spectra were recorded on a Shimadzu UV-2600i spectrometer.

The luminescence spectra and luminescence decay time were measured using a spectrofluorometer FS5 (Edinburgh Instruments). It is a high-tech, all-in-one solution that allows the measurement of fluorescence spectra, UV and visible absorption spectra, and fluorescence decay times. This system has a guaranteed signal-to-noise ratio of > 6000:1 at 350 nm excitation and 397 nm emission, with an integration time of 1 s. A special vertically inclined and linearly positioned solid sample holder was used to record the spectra to maximize the signal from the sample. The fluorescence decay times were measured using the Time-Correlated Single-Photon Counting Technique, which is a quantum-based, highly sensitive method that is less sensitive to noise. This allows the measurement of decay times of less than 30 ps. The resolution of the TCSPC matrix is 305 ps. The continuous light source was a 150W xenon arc lamp. For fluorescence decay time, the EPL laser at 375 nm was used. The spectra were measured using identical conditions for each sample.

Spectroscopic studies of the complexes

IR and NMR spectroscopy

The ^1H NMR spectroscopy of the diamagnetic Y^{III} complexes allowed establishing the ratio between the organic cations and the ligand's protons. The ^1H NMR spectra of the complexes contain the doublet signal of methylate groups of $[L]^{2-}$ at 3.54–3.57 ppm. This signal is shifted compared to the spectrum of H_2L (3.74 ppm [15]) towards the high field. The signal of the amide proton is absent in the spectra of the complexes, confirming the ligands' deprotonated form in the complex compositions. The residual solvent 2-propanol can be observed in the ^1H NMR spectra of $Na_2[Y_2L_4]\cdot 3H_2O$ and $(NH_4)_2[Y_2L_4]\cdot 4H_2O$. The ^{31}P NMR spectrum of each Y^{III} complex contains a singlet band with the maximum in the range 10.57–10.99 ppm. This testifies the equivalence of the phosphorus atoms in the composition of the complexes, and also confirms their individuality.

IR spectra of all the complexes are very similar to each other (Figure 2). In the high wavelength part of the spectra, one can observe a series of narrow ν(CH) bands in the region 3060–2830 cm^{-1} and broad bands ν(OH) in the region 3600–3200 cm^{-1}. The latter has different intensity depending on the complex and appears due to the presence of the small amount of moisture and residual 2-propanol solvent in the samples. A band ν(NH) at near 3250 cm^{-1} is also observed for the complexes $(NH_4)_2[Ln_2L_4]\cdot 4H_2O$ and $(HNEt_3)_2[Ln_2L_4]\cdot 3H_2O$ due to respective cations' vibrations. The ν(NH) band of the ligand is not observed in the IR spectra of the coordination compounds, confirming the double deprotonated form of the ligands in the complexes' composition. There are numerous narrow bands in the region 1800–400 cm^{-1} of the IR spectra of the complexes. The most intense are bands of C=O valence vibrations (at near 1600 cm^{-1}), P=O valence vibrations (at near 1250 cm^{-1}), and POC deformational vibrations (at near 1030 cm^{-1}). The bands of C=O and P=O valence vibrations are shifted significantly towards lower frequencies compared to the spectrum of H_2L (Table 1), indicating coordination of both carbonyl and phosphoryl oxygen atoms to the metals. The blue shift of ν(PN) band results from distribution of electron density in the ligands' chelating cores OCNPO.

Table 1.

Positions of the main characteristic bands in the IR spectra of the complexes.

Compound/ Assignment of bands	ν(C=O)	ν(P=O)	ν(P-N)
H_2L [15]	1746	1212	877
$Na_2[Y_2L_4]\cdot 3H_2O$	1603	1149	964
$Na_2[Eu_2L_4]\cdot 3H_2O$	1606	1147	962
$Cs_2[Y_2L_4]\cdot H_2O$	1598	1154	961
$Cs_2[Eu_2L_4]\cdot H_2O$	1597	1154	960
$(NH_4)_2[Y_2L_4]\cdot 4H_2O$	1605	1155	959
$(NH_4)_2[Eu_2L_4]\cdot 4H_2O$	1602	1158	959
$(NMe_4)_2[Y_2L_4]\cdot H_2O$	1615	1160	965
$(NMe_4)_2[Eu_2L_4]\cdot H_2O$	1612	1158	963
$NEt_4[NaY_2L_4]\cdot H_2O$	1604	1152	963
$NEt_4[NaEu_2L_4]\cdot H_2O$	1611	1159	963
$(HNEt_3)_2[Y_2L_4]\cdot 3H_2O$	1607	1149	963
$(HNEt_3)_2[Eu_2L_4]\cdot 3H_2O$	1607	1148	963

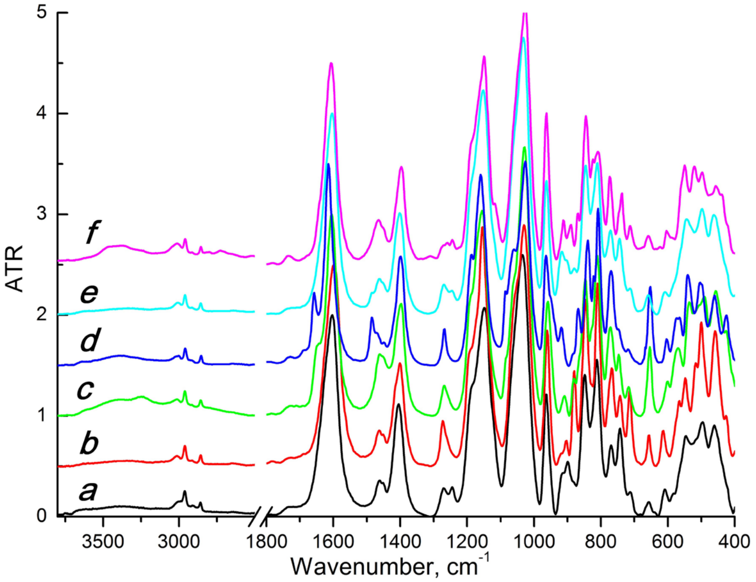

Fig. 2. IR spectra of $Na_2[Eu_2L_4]\cdot 3H_2O$ (a), $Cs_2[Eu_2L_4]\cdot H_2O$ (b), $(NH_4)_2[Eu_2L_4]\cdot 4H_2O$ (c), $(NMe_4)_2[Eu_2L_4]\cdot H_2O$ (d), $NEt_4[NaEu_2L_4]\cdot H_2O$ (e), and $(HNEt_3)_2[Eu_2L_4]\cdot 3H_2O$ (f).

The diffuse reflectance spectra of the complexes.

The diffuse reflectance spectra of the synthesized compounds were measured in the UV region and are presented in Figure 3. The broad band of the ligands' absorption is observed in the 220–340 nm region with a maximum near 250 nm. The Eu^{III} f-f transitions are also observed in the long-wavelength part of the spectra.

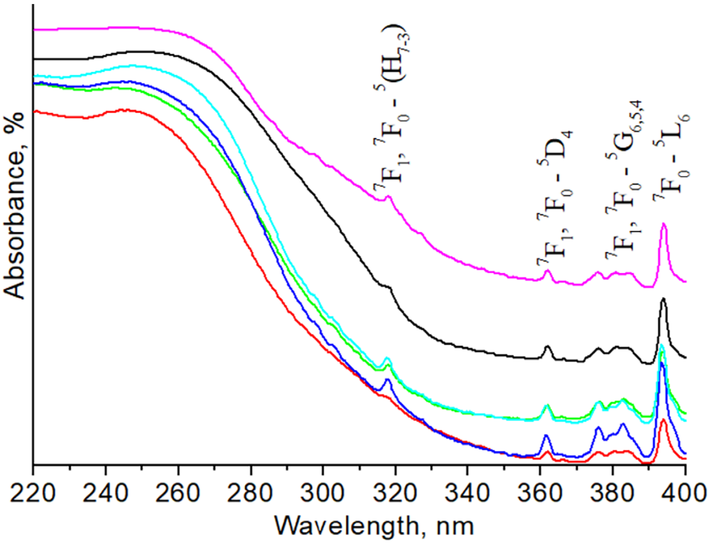

Fig. 3. Diffuse reflectance spectra of $Na_2[Eu_2L_4]\cdot 3H_2O$ (black line), $Cs_2[Eu_2L_4]\cdot H_2O$ (red line), $(NH_4)_2[Eu_2L_4]\cdot 4H_2O$ (green line), $(NMe_4)_2[Eu_2L_4]\cdot H_2O$ (blue line), $NEt_4[NaEu_2L_4]\cdot H_2O$ (light blue line), and $(HNEt_3)_2[Eu_2L_4]\cdot 3H_2O$) (pink line).

Luminescence spectroscopy.

All the obtained europium complexes exhibit red emission under UV lamp irradiation. The luminescence excitation spectra (Figure 4) were recorded by monitoring the emission of $^5D_0 \rightarrow ^7F_2$ transition. The spectra consist of a broad band of the ligands' absorption in the region 230–280 nm and numerous f-f transitions of the Eu^{III} ion. The identical conditions of measurements of the compounds' excitation spectra allow us to roughly compare the intensity of Eu^{III} emission. The intensity of bands is the highest in the spectrum of $(NMe_4)_2[Eu_2L_4]{\cdot}H_2O$ and the lowest in the spectrum of $(HNEt_3)_2[Eu_2L_4]{\cdot}3H_2O$. The band of transition $^7F_0 \rightarrow ^5L_6$ dominates in the excitation spectra of all the obtained europium complexes. From the intensity ratio between ligand absorption band and the band of $^7F_0 \rightarrow ^5L_6$ transition one can conclude that the most efficient sensitization of Eu^{III} emission by the ligands takes place in the $Cs_2[Eu_2L_4]{\cdot}H_2O$ and the lowest sensitization efficiency is observed for $Na_2[Eu_2L_4]{\cdot}3H_2O$.

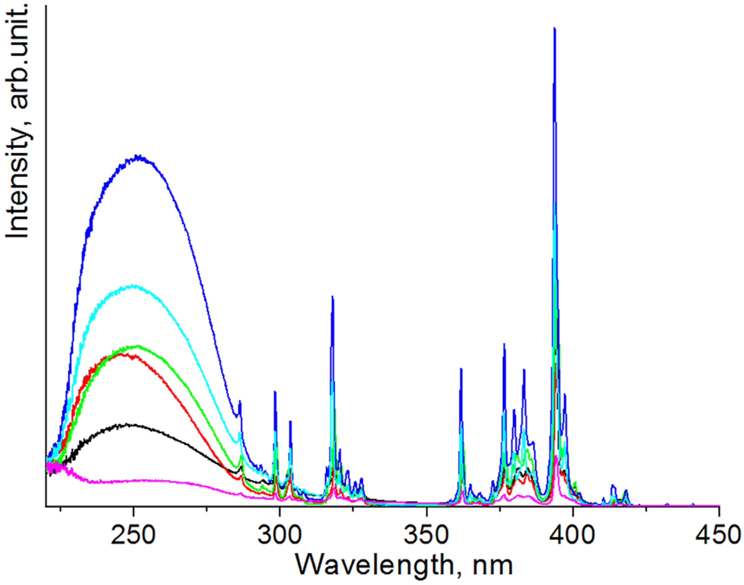

Fig. 4. Luminescence excitation spectra (emission at 611,4-612 nm) of $Na_2[Eu_2L_4]{\cdot}3H_2O$ (black line), $Cs_2[Eu_2L_4]{\cdot}H_2O$ (red line), $(NH_4)_2[Eu_2L_4]{\cdot}4H_2O$ (green line), $(NMe_4)_2[Eu_2L_4]{\cdot}H_2O$ (blue line), $NEt_4[NaEu_2L_4]{\cdot}H_2O$ (light blue line), and $(HNEt_3)_2[Eu_2L_4]{\cdot}3H_2O$) (pink line).

Upon excitation by UV light, the complexes exhibit typical Eu^{III} ion f-f emission with narrow bands assigned to transitions $^5D_0 \rightarrow ^7F_j$ (j=0-4) (Figure 5). The emission spectra recorded upon excitation of the complexes into Eu^{III} f-f transition and the ligands' absorption bands are identical. It was found that the cations' nature significantly affects the splitting of f-f transition bands in luminescence spectra, their positions, and the ratio of their intensities. The weak band of transition $^5D_0 \rightarrow ^7F_0$ is observed for all the obtained europium complexes. The observation of this transition is an indication that the Eu^{III} ion occupies a site with C_{nv}, $C_{n,}$ or C_s symmetry [16]. The maximum of the band of $^5D_0 \rightarrow ^7F_0$ transition varies depending on the cation from 577.9 nm (for $(NMe_4)_2[Eu_2L_4]·H_2O$) to 578.9 nm (for $Na_2[Eu_2L_4]·3H_2O$ and $(NH_4)_2[Eu_2L_4]·4H_2O$). The transition $^5D_0→^7F_1$ appears in the complexes' emission spectra as a band with different splitting. There are two separated bands in the region of $^5D_0→^7F_1$ transition observed for $Cs_2[Eu_2L_4]·H_2O$, $(NMe_4)_2[Eu_2L_4]·H_2O$ and $NEt_4[NaEu_2L_4]·H_2O$. The spectrum of $(NH_4)_2[Eu_2L_4]·4H_2O$ exhibits three components in this region, pointing to the lower Eu^{III} site symmetry in this complex compared to the previously mentioned three compounds. For $Na_2[Eu_2L_4]·3H_2O$ and $(HNEt_3)_2[Eu_2L_4]·3H_2O$ the band of $^5D_0→^7F_1$ transition is broadened. The band of hypersensitive transition $^5D_0→^7F_2$ is the most intensive in all the recorded emission spectra; however differs by splitting depending on the cation. The biggest number of components of the $^5D_0→^7F_2$ band is observed for $Cs_2[Eu_2L_4]·H_2O$ and $(NH_4)_2[Eu_2L_4]·4H_2O$. The relative integral intensities ratio $I(^5D_0→^7F_2)/I(^5D_0→^7F_1)$, so-called ratio, varies much (from 2.6 to 7.6) depending on the cation (Table 2). The highest values of red/orange ratio are observed for the complexes $Cs_2[Eu_2L_4]·H_2O$ and $(NH_4)_2[Eu_2L_4]·4H_2O$. Thus, the lowest symmetry of the Eu^{III} ion coordination environment can be concluded for these two compounds. A known feature of many mononuclear tetrakis-complexes with CAPh ligands is the high intensity of transition $^5D_0→^7F_4$ [9, 17]. The nature of this phenomenon was explained by the presence of the P=O group in the ligand structure, which is more polarizable compared to the C=O one. However, the dependence of this band's intensity on the cation nature of the tetrakis-complexes has not been explained yet and requires further studies. Among obtained in this work binuclear Eu^{III} tetrakis-complexes only two – $(NMe_4)_2[Eu_2L_4]·H_2O$ and $NEt_4[NaEu_2L_4]·H_2O$ – exhibit a high intensity of transition $^5D_0→^7F_4$. The contribution of this band to the total integral intensity of the spectra of the two mentioned complexes is more than 30%. While for the rest of the obtained compounds, the contribution of $^5D_0→^7F_4$ band equals only 17–23%.

Table 2.

Some photoluminescence characteristics of the complexes $(Cation)_2[Eu_2L_4]$.

(Cation)$_2$ =		**Na_2**	**Cs_2**	**$(NH_4)_2$**	**$(NMe_4)_2$**	**NEt_4Na**	**$(HNEt_3)_2$**
Photoluminescence intensity distribution (%)	**$^5D_0→^7F_0$**	0.19	0.15	0.15	0.08	0.10	0.24
	$^5D_0→^7F_1$	12.25	9.26	10.06	16.35	16.59	15.63
	$^5D_0→^7F_2$	66.20	70.37	67.56	42.64	43.66	59.23
	$^5D_0→^7F_3$	1.79	2.76	2.77	3.51	3.41	1.48
	$^5D_0→^7F_4$	19.57	17.46	19.46	37.42	36.24	23.42
$I(^5D_0→^7F_2)/I(^5D_0→^7F_1)$		5.4	7.6	6.7	2.6	2.6	3.8
$τ_{RAD}$ (ms)		2.48	1.87	2.03	3.31	3.36	3.16
$τ_{obs}$ (ms)		1.33	1.69	1.57	2.74	1.91	0.76
Q^{Ln}_{Ln} (%)		54	90	77	83	57	24

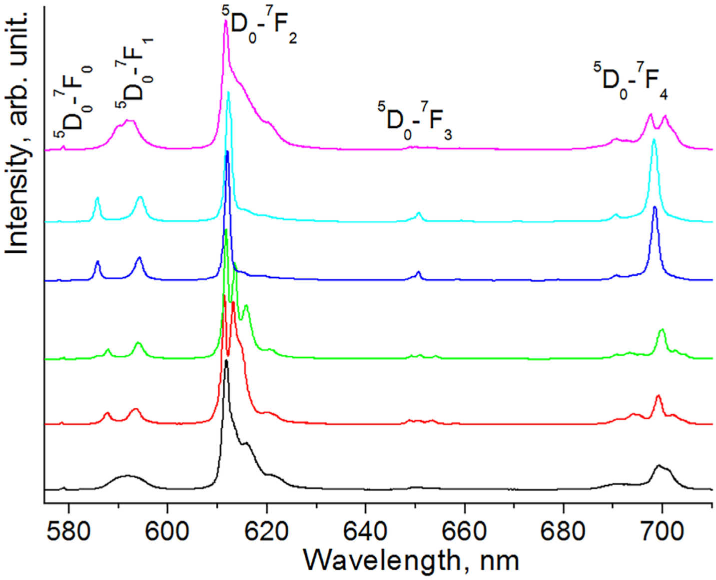

Fig. 5. Normalized luminescence spectra of $Na_2[Eu_2L_4]\cdot 3H_2O$ (black line), $Cs_2[Eu_2L_4]\cdot H_2O$ (red line), $(NH_4)_2[Eu_2L_4]\cdot 4H_2O$ (green line), $(NMe_4)_2[Eu_2L_4]\cdot H_2O$ (blue line), $NEt_4[NaEu_2L_4]\cdot H_2O$ (light blue line), and $(HNEt_3)_2[Eu_2L_4]\cdot 3H_2O)$ (pink line) measured at 300 K and λ_{exc} = 394 nm.

The luminescence decay times were measured for the europium complexes by monitoring the emission of $^5D_0 \rightarrow {}^7F_2$ transition and excitation at a wavelength of 372 nm, which corresponds to the f-f transition of the Eu^{III} ion. The obtained decay curves were fitted by a monoexponential function and yielded values of τ_{obs} equal to 0.76–2.74 ms, depending on the cation (Table 3). The radiative lifetime of $^5D_0$ state τ_{RAD} was estimated from emission data using the following equation: $\tau_{RAD} = 1/(A_{MD,0}\cdot n^3\cdot(I_{tot}/I_{MD}))$ [18, 19], with $A_{MD,0}$ being equal to 14.65 s^{-1}, n considered to be 1.5 and (I_{tot}/I_{MD}) the ratio of the total integrated emission from the $Eu(^5D_0)$ level to the integrated intensity of MD transition $^5D_0 \rightarrow {}^7F_1$ [20, 21]. The $^5D_0$ intrinsic quantum yield (Q^{Ln}_{Ln}) for the europium complexes was estimated from the emission spectrum and measured $^5D_0$ lifetime: $Q^{Ln}_{Ln} = \tau_{obs} / \tau_{RAD}$. The obtained values of τ_{RAD} agree with the values of red/orange ratios, being changed in the opposite way. The values of τ_{obs} are not directly proportional to τ_{RAD}, which results in very different Q^{Ln}_{Ln} for the studied complexes. The lowest intrinsic quantum yield was found for $(HNEt_3)_2[Eu_2L_4]\cdot 3H_2O$. This can be evidence of efficient quenching of Eu^{III} f-f emission due to the non-rigid structure of the complex and high-energy vibrations of the cations. The complexes $Cs_2[Eu_2L_4]\cdot H_2O$ and $(NMe_4)_2[Eu_2L_4]\cdot H_2O$ demonstrated the highest intrinsic quantum yield.

Thermal gravimetric studies of the complexes. The thermal gravimetric studies of the Y^{III} complexes (Figure 6) have shown that the main weight loss of the samples takes place at a temperature close to 200 °C. However, some minor weight losses preceded the compounds' decomposition for the majority of the samples studied. One can observe for $Na_2[Y_2L_4]\cdot 3H_2O$ and $(NH_4)_2[Y_2L_4]\cdot 4H_2O$ two small weight losses. The first one takes place at a temperature below 100 °C and is connected with the evaporation of

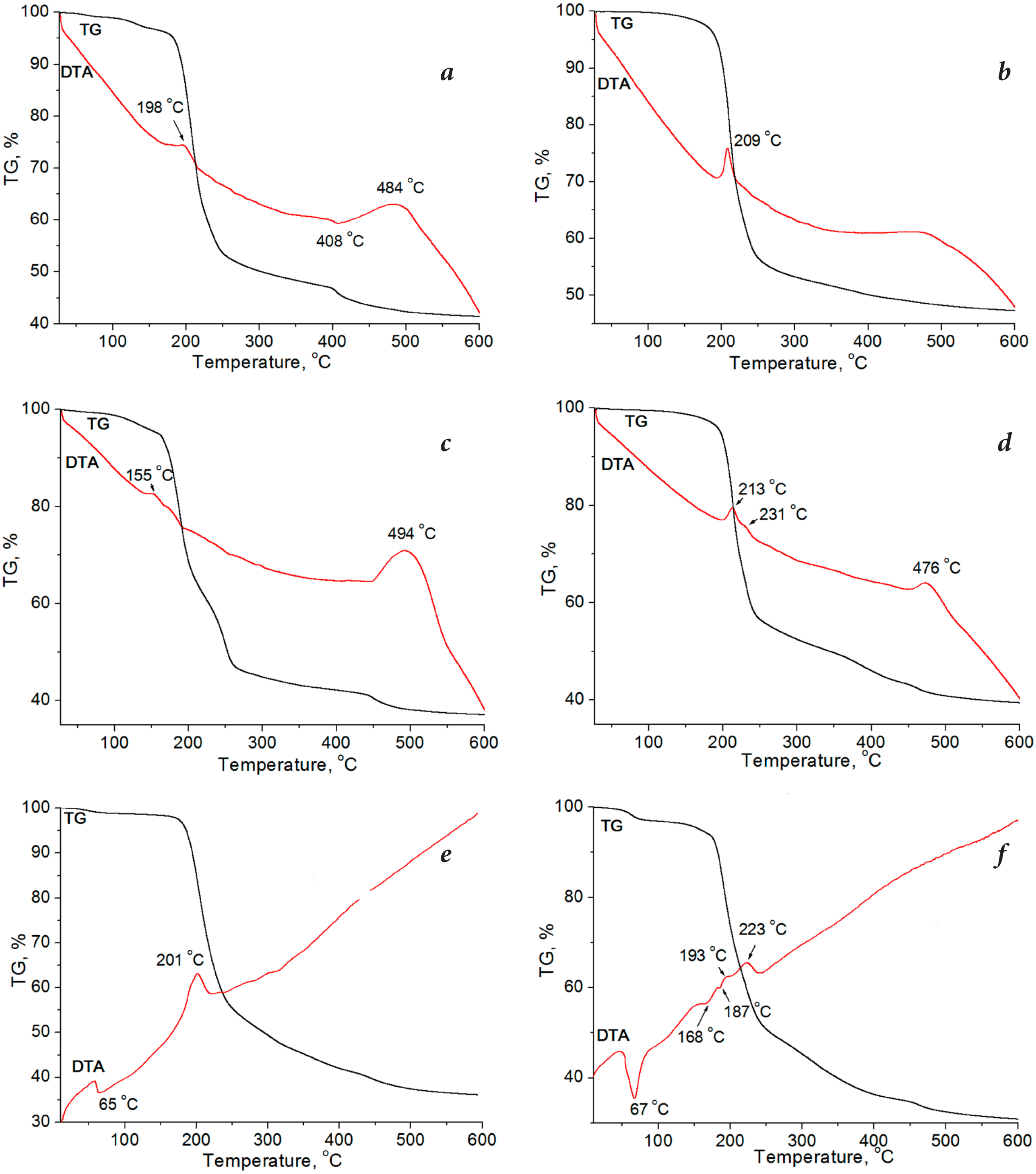

Fig. 6. Thermal gravimetric analysis of of $Na_2[Eu_2L_4]\cdot 3H_2O$ (a), $Cs_2[Eu_2L_4]\cdot H_2O$ (b), $(NH_4)_2[Eu_2L_4]\cdot 4H_2O$ (c), $(NMe_4)_2[Eu_2L_4]\cdot H_2O$ (d), $NEt_4[NaEu_2L_4]\cdot H_2O$ (e), and $(HNEt_3)_2[Eu_2L_4]\cdot 3H_2O$ (f).

residues of 2-propanol solvent, which was used for the synthesis of complexes. This conclusion correlates with the NMR spectra of these complexes. The second weight loss at a temperature higher than 100 °C can be due to evaporation of water molecules. Earlier, it was shown that a molecule of water can be encapsulated into the negatively charged environment of the ligand fluorine and carbonyl oxygen atoms of the helicate structure of lanthanide binuclear *tetrakis*-complexes with $[L]^{2-}$ [14]. Also, water molecules tend to bind the outersphere sodium cation in $Na[NaNd_2L_4(H_2O)]\cdot 2H_2O$ [14]. For the compounds $NEt_4[NaY_2L_4]\cdot H_2O$ and $(HNEt_3)_2[Y_2L_4]\cdot 3H_2O$, one can observe a small weight loss, which is accompanied by an endothermic effect at 65 and 67 °C, respectively. As there is no organic solvent in the complexes, which was confirmed by ^1H NMR analysis, the observed weight loss was assigned to the water molecules evaporation. Evaporation of solvents is followed by decomposition of organic part of the complexes, which takes place at 200 °C for the $Cs_2[Eu_2L_4]\cdot H_2O$, $(NMe_4)_2[Eu_2L_4]\cdot H_2O$, and $NEt_4[NaEu_2L_4]\cdot H_2O$ and at slightly lower temperature for $Na_2[Eu_2L_4]\cdot 3H_2O$ (198 °C), $(NH_4)_2[Eu_2L_4]\cdot 4H_2O$ (184 °C) and $(HNEt_3)_2[Eu_2L_4]\cdot 3H_2O$ (192 °C). The total weight loss upon heating of the samples till 600 °C equals 52–65 %.

*CONCLUSIONS***.** The new binuclear tetrakis-complexes of Y^{III} and Eu^{III} with tetramethyl N,N′-(2,2,3,3,4,4-hexafluoro-1,5-dioxopentane-1,5-diyl)bis(phosphoramidate) and different cations have been successfully obtained and characterized. The variation of the cations has allowed obtaining compounds with different solubility, i.e., soluble in water or in organic solvents. It was found that complexes contain different amounts of moisture depending on the cation and the temperature of decomposition varies in the range near 155–190 °C. The highest thermal stability among Y^{III} compounds was observed for the complexes $Cs_2[Y_2L_4]\cdot H_2O$ and $(NMe_4)_2[Y_2L_4]\cdot H_2O$. The luminescence studies of the obtained compounds allowed us to conclude the lowest symmetry of Eu^{III} ion coordination environment for $Cs_2[Eu_2L_4]\cdot H_2O$ and $(NH_4)_2[Eu_2L_4]\cdot 4H_2O$, which results in the highest values of red/orange ratio and lowest values of radiative luminesce decay time. The highest Eu^{III} intrinsic quantum yield (90 and 83%, respectively) has been observed for $Cs_2[Eu_2L_4]\cdot H_2O$ and $(NMe_4)_2[Eu_2L_4]\cdot H_2O$, which can be partially explained by the absence of moisture in these complexes. The rather high intensity of transition $^5D_0 \rightarrow {}^7F_4$ observed for $(NMe_4)_2[Eu_2L_4]\cdot H_2O$ and $NEt_4[NaEu_2L_4]\cdot H_2O$ is an interesting feature, which needs further investigations.

ACKNOWLEDGMENTS. This work was supported by the Ministry of Education and Science of Ukraine (grants no. 22BF037-04, and B/218 (0123U100990)).

ВПЛИВ КАТІОНІВ НА ТЕРМІЧНУ СТІЙКІСТЬ ТА ЛЮМІНЕСЦЕНТНІ ВЛАСТИВОСТІ БІЯДЕРНИХ КОМПЛЕКСІВ РІДКОЗЕМЕЛЬНИХ ЕЛЕМЕНТІВ ІЗ БІС-КАРБАЦИЛАМІДОФОСФАТАМИ

Наталія Каряка[1,*], Віктор Труш[1], Ігор Фесич[1], Олена Гнатюк[2], Іван Гнатюк[2], Галина Довбешко[2], Володимир Амірханов[1]

[1]Хімічний факультет Київського національного університету ім. Тараса Шевченка,
вул. Гетьмана Павла Скоропадського, 12,
Київ 01033, Україна;
[2] Відділ фізики біологічних систем, Інститут фізики Національної академії наук України,
проспект Науки, 46, Київ, Україна
e-mail: natka04@i.ua

Було одержано серію комплексних сполук ітрію (III) та європію (III) з біс-карбациламідофосфатом тетраметил-N,N′-(2,2,3,3,4,4-гексафлуоро-1,5-діоксопентан-1,5-диіл)біс(фосфорамідатом) та різними катіонами з метою вивчення впливу природи катіона на термічні та спектральні властивості комплексних сполук. Було показано, що природа катіона значно впливає на такі властивості комплексів, як розчинність, термічна стійкість та люмінесцентні характеристики. Комплекси європію (III) демонструють сенсибілізовану лігандами f-f люмінесценцію. Інтенсивність люмінесценції, розщеплення та співвідношення інтенсивностей смуг у спектрах, а також час життя люмінесценції і власний квантовий вихід для досліджених сполук суттєво залежали від природи катіона. Червоно/помаранчеве співвідношення для синтезованих комплексів європію (III) варіюється від 2.6 до 7.6, час життя люмінесценції – від 0.76 до 2.74 мс, а власний квантовий вихід – від 24 до 90 %. Температура розкладання комплексів залежно від природи катіона варіюється в діапазоні 155–190 °С.

Ключові слова: рідкоземельні елементи, біс-карбациламідофосфат, координаційні сполуки, люмінесценція, термогравіметричний аналіз.

REFERENCES

[1] Long J., Guari Y., Ferreira R.A., Carlos L.D., & Larionova J. Recent advances in luminescent lanthanide based Single-Molecule Magnets. *Coord Chem Rev.* 2018. **363**: 57–70. https://doi.org/10.1016/j.ccr.2018.02.019

[2] Jia J.H., Li Q.W., Chen Y.C., Liu J.L., & Tong M.L. Luminescent single-moleculemagnets based on lanthanides: Design strategies, recent advances and magneto-luminescent studies. *Coord Chem Rev.* 2019. 378: 365-381. https://doi.org/10.1016/j.ccr.2017.11.012

[3] Bünzli J-C.G., Rising Stars in Science and Technology: Luminescent Lanthanide Materials. *Eur J Inorg Chem.* 2017. 44: 5058-5063. https://doi.org/10.1002/ejic.201701201

[4] Kaczmarek M.T., Zabiszak M., Nowak M., & Jastrzab R. Lanthanides: Schiff base complexes, applications in cancer diagnosis, therapy, and antibacterial activity. *Coord Chem Rev.* 2018. 370: 42-54. https://doi.org/10.1016/j.ccr.2018.05.012

[5] Teo R.D., Termini J & Gray H.B. Lanthanides: applications in cancer diagnosis and therapy: miniperspective. *J Med Chem.* 2016. 59: 6012-6024. https://doi.org/10.1021/acs.jmedchem.5b01975

[6] Parker D., Fradgley J.D., Wong K.L. The design of responsive luminescent lanthanide probes and sensors. *Chem Soc Rev.* 2021. **50**: 8193–8213. https://doi.org/10.1039/D1CS00310K

[7] Costa I.F., Blois L., Paolini T.B., Assunção I.P., Teotonio E.E.S., Felinto M.C.F.C., Moura R.T. Jr., Longo R.L., Faustino W.M., Carlos L.D., Malta O.L., Carneiro Neto A.N., & Brito H. F. Luminescence properties of lanthanide tetrakis complexes as molecular light emitters. *Coord Chem*

Rev. 2024. **502**: 215590.
https://doi.org/10.1016/j.ccr.2023.215590

[8] Kofod N., Thomsen M.S., Nawrocki P. & Sørensen T.J. Revisiting the assignment of innocent and non-innocent counterions in lanthanide (III) solution chemistry. *Dalton Trans.* 2022. 51: 7936-7949.
https://doi.org/10.1039/D2DT00565D

[9] Struhatska M.B., Kariaka N.S., Dyakonenko V.V., Shishkina S.V., Smola S.S. , Rusakova N.V., Gawryszewska P., Malta O.L., Carneiro Neto A.N., Trush V.O. and Amirkhanov V.M. The influence of different cations on the structure and spectral properties of Ln^{3+} tetrakis-complexes with the CAPh-type ligand dimethyl- N-trichloroacetylamidophosphate, *New J Chem.* 2024. 48: 11886–11898.
https://doi.org/10.1039/D4NJ01700E

[10] Paolini T.B., Assunção I.P., Costa I.F., Blois L., Felinto M.C.F., Moura R.T. Jr, Teotonio E.E.S., Malta O.L., Carneiro Neto A.N., & Brito H.F. The influence of imidazolium counterions on the luminescence properties of Cnmim[Eu(tta)$_4$] tetrakis complexes in solid-state and ionic liquid solutions. *J Lumin.* 2023. 263 120158.
https://doi.org/10.1016/j.jlumin.2023.120158

[11] Lunkley J.L, Shirotani D., Yamanari K., Kaizaki S., & Muller G. Chiroptical spectra of a series of tetrakis ((+)-3-heptafluorobutylyrylcamphorato) lanthanide (III) with an encapsulated alkali metal ion: circularly polarized luminescence and absolute chiral structures for the Eu(III) and Sm(III) complexes. *Inorg Chem.* 2011. 50: 12724-12732.
https://doi.org/10.1021/ic201851r

[12] Basal L.A., Kajjam A.B., Bailey M.D., & Allen M.J. Systematic tuning of the optical properties of discrete complexes of EuII in solution using counterions and solvents. *Inorg Chem.* 2020. 59: 9476-9480.
https://doi.org/10.1021/acs.inorgchem.0c01516

[13] Liu C.M., Sun R., Wang B.W., Hao X., & Li X.L. Effects of counterions, coordination anions, and coordination solvent molecules on single-molecule magnetic behaviors and nonlinear optical properties of chiral Zn$_2$Dy Schiff base complexes. *Inorg Chem.* 2022. **61**: 18510–18523.
https://doi.org/10.1021/acs.inorgchem.2c02743

[14] Horniichuk O.Y., Trush V.A., Kariaka N.S., Shishkina S.V., Dyakonenko V.V., Severinovskaya O.V., Gawryszewska P., Domasevitch K.V., Watras A., Amirkhanov V.M. Novel quadruple-stranded heterometallic Ln2Na complexes hosting sodium ions inside the cryptand-like cavity, *New J Chem.* 2021. **45**: 22361–22368.
https://doi.org/10.1039/D1NJ04353F

[15] Horniichuk O.Y., Kariaka N.S., Trush V.O., Smola S.S., Sliva T.Y., Rusakova N.V., Amirkhanov V.M. Synthesis and investigation of binuclear rare earth complexes based on bis-chelating carbacylamidophosphate (in Ukr.), *Issues of Chemistry and Chemical Technology.* 2019. **5**: 27–33.
http://dx.doi.org/10.32434/0321-4095-2019126-5-27-33

[16] Binnemans K. Interpretation of europium(III) spectra. *Coord Chem Rev.* 2015. **295**: 1–45.
https://doi.org/10.1016/j.ccr.2015.02.015

[17] Kariaka N.S., Lipa A., Carneiro Neto A.N., Malta O.L., Gawryszewska P. and Amirkhanov V.M. Eu^{3+} and Tb^{3+} coordination compounds with phenyl-containing carbacylamidophosphates: comparison with selected Ln^{3+} β-diketonates, *Front. Chem.* 2023. **11**: 1188314.
https://doi.org/10.3389/fchem.2023.1188314

[18] van der Tol E.B., van Ramesdonk H.J., Verhoeven J.W., Steemers F.J., Kerver E.G., Verboom W., Reinhoudt D.N. Tetraazatriphenylenes as Extremely Efficient Antenna Chromophores for Luminescent Lanthanide Ions. *Chem Eur J.* 1998. **4**: 2315–2323.
https://doi.org/10.1002/(SICI)1521-3765(19981102)4:11<2315::AID-CHEM2315>3.0.CO;2-E

[19] Werts M.H.V., Jukes R.T.F., Verhoeven J.W. The emission spectrum and the radiative lifetime of Eu^{3+} in luminescent lanthanide complexes, *Phys. Chem Chem Phys.* 2002. **4**: 1542–1548.
https://doi.org/10.1039/B107770H

[20] Bünzli J.C.G., Eliseeva S.V. Basics of Lanthanide Photophysics. In: Hänninen, P., Härmä, H. (eds) Lanthanide Luminescence. Springer Series on Fluorescence, Springer. *Berlin, Heidelberg*. 2010. **7**: 1–46.
https://doi.org/10.1007/4243_2010_3

[21] de Sa G.F., Malta O.L., de Mello Donega C., Simas A.M., Longo R.L., Santa-Cruz P.A., da Silva E.F. Spectroscopic properties and design of highly luminescent lanthanide coordination complexes, *Coord Chem Rev.* 2000. **196**: 165–195.
https://doi.org/10.1016/S0010-8545(99)00054-5

Стаття надійшла 25.08.2025.