**Introduction**

Rare earth elements are enablers and vitamins of modern living. For a long time, REs remained laboratory curiosities, although Carl Auer von Welsbach (1858 – 1929) initiated some applications in lighting and took patents out for the famous Auer mantle for gas lamps (1891) and for flint stones (1903). There is no doubt that the inherent properties of these metals and their compounds have been understood more quantitatively with the improvement of research tools and technologies. Investigation on molecular coordination complexes of 4f-ions has attracted significant attention owing to their outstanding properties and considering the growing levels of lanthanoids present in the technosphere as well as the numerous applications. The coordination chemistry of lanthanoids in conjunction with modern analytical chemistry plays an important role in developing new compounds for technological, industrial and biological applications.

4-Acylpyrazolones are a class of chelating agents that have received great attention in recent years in the fields of coordination chemistry, solvent extraction and separation of s-, d- and f-elements. Many structural modifications in this type of O-donor molecule exist and as a consequence they are very attractive for complex formation with metals. The nature of the substituent in the fourth position of the pyrazolone ring causes significant variations in the electronic, steric, and solubility parameters of the ligand having different low \( pK_a \) values (2.56 \( \pm \) 4.26), thereby affecting complexation, extraction and separation of ions with similar chemical properties as 4f- and 5f-elements. The acidity of a ligand depends on the substituents; electron-withdrawing groups increase the acidity, whereas electron-donating groups decrease it. Another advantage is the harmless chemical composition consisting of fully incinerable elements adhering to the CHON principle. The use of these “environmentally friendly extractants” is in accordance with some of the principles of green chemistry. Thus, this family of complexes has developed rapidly and attracted long-lasting interest, due partially to their easy synthesis, but mainly to their promising prospects in widespread applications, ranging from materials science to biomedical analysis (Gd(III) based contrast agents for magnetic resonance imaging). The \( \beta \)-dicarbonyl compounds have been recognized as efficient sensitizers, as so called “antenna”, to achieve high harvest lanthanoid emissions owing to the effectiveness of the energy transfer from the \( \beta \)-dicarbonylate to the Ln\(^{3+}\) cation. A novel poly-ligand europium complex Eu(TTA)\(_2\)(PMBBP)Phen (1,10-phenanthroline, 1-phenyl-3-methyl-4-(4butylbenzoyl)-5-pyrazolone, 2-thienyltrifluoroacetone) was synthesized by Zhu et al. and its photoluminescence and electroluminescence properties indicate that this new Eu-complex can be used as a novel red-emitting material in electroluminescent devices. Yang et al. synthesized seven complexes of REs with the general formula Ln(III)-3.5H\(_2\)O (Ln: La, Eu, Ga, Th, Dy, Ho and Er; HL: 4-hydroxy-3-methyl-1-phenyl-4-pyrazolyl phenyl ketone isonicotinoyl hydrazone) and the test results showed that La and Eu complexes possess antitumoral activity for hepatic carcinoma (HTC-8) and leukemia cells (L1210).

In a fundamental view, this prompted us to synthesize two new europium(III) complexes with different or similar architecture as those formed in solution during liquid-liquid extraction (molecular diluent and ionic liquid) is discussed.

**Keywords** Lanthanoids, europium solid complex, 4-acyl-5-pyrazolones, ionic liquid

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The white solid product was treated as described above. The white solid product formed was separated by liquid extraction process by applying two acylpyrazolones possessing methyl (+I) or Ph (±M) substituent at the 4-position of the aroyl group. Their structure may be a hint for the determination of the extraction mechanism in ionic liquids (ILs).

**Experimental**

**Reagents and chemicals**

The compounds 3-methyl-4-(4-methylbenzoyl)-1-phenylpyrazol-5-one (HPMPBP) and 3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one (HPPMBP) were obtained according to an optimized procedure described in the literature. The full characterization of HPMMBP was recently published. A detailed description of the synthesis and characterization of the compound 3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one will be published in a separate paper: 71 – 76% yield; m.p. 151.1 – 151.5°C. The NMR spectra were recorded in chloroform-d₃ as 0.01 M solutions, see Supporting Information. All apparatus used in the study are described in the Supporting Information as well. All reagents were purchased from Merck, Aldrich and Fluka and were used without any further purification. Fluka silica gel/TLC-cards 60778 with fluorescent indicator 254 nm were used for TLC chromatography.

**Procedure**

**Preparation of metal complex of Eu(III) with 3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one (1:3).** A solution of 164.88 mg (0.15 mmol) of EuCl₃·6H₂O in 2 cm³ of absolute ethanol was added at room temperature to a solution of 395.5 mg (0.45 mmol) of 3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one (HPMPBP) in 2 cm³ of absolute ethanol in the presence of NaOH 540 mg (0.45 mmol) and stirred for 10 h. The white solid product formed was separated by centrifugation and washed three times with absolute ethanol, water and then with ethanol. It was dried in a high vacuum over P₂O₅. The crystal (solid) product melts at 273 – 274°C. Yield: 72.5%.

**Analysis for EuL₃·3H₂O (M 1266.19 g/mol), Calc. %: C, 65.45; H, 4.54; N, 6.64.** Found, %: C, 64.386; H, 4.238; N, 6.350, Fig. S1 (Supporting Information).

**Results**

The elemental analysis, IR, TG-DSC and NMR studies of the isolated solid complexes give a possibility to make conclusions about the composition and the structure of the complex. Since the relatively large europium ion usually has a coordination number in the range 7 – 9, Eu(PPPMBP) is an unsaturated six-coordinated species with three L⁻ ligands that can accommodate additional ligands, probably one molecule C₂H₅OH in the present case according to elemental analysis. Generally, complexes with empirical formula LnL₃·xH₂O, LnL₃·EtOH or LnL₃·H₂O·EtOH were reported. However, a series of anhydrous six-coordinate derivatives LnL₃ (Ln: Y, La, Nd, Eu, Gd, Dy, Er, Lu) was prepared and studied by UV, IR and NMR spectroscopy. On the basis of the elemental analysis, we found that the three HPPMBP ligands are coordinated to the central europium ion as well in an O₂-bidentate form. Three water molecules are coordinated perhaps in this case, giving a nine-coordinated Eu atom: Eu(PPMBP)₃·3H₂O (Fig. S1, Supporting Information).

**IR spectra of europium complexes**

HPMPB and HPPMBP contain a large number of bands in the region 1700 - 450 cm⁻¹. A broad characteristic band at around 2810 cm⁻¹ for intramolecular hydrogen bond of the free ligand (HPMPBP) is not observed in the complex as HO group is deprotonated as a result of the complex formation. A broad band in the complex observed at 3400 cm⁻¹ (νO-H) is due to the ethanol molecule in the adduct type chelates: Eu(PPMBP)₃·C₂H₅OH, Fig. S2 (Supporting Information). The ligand band at 1613 cm⁻¹ shifts to 1606 cm⁻¹ in the metal chelate and thus can be related to the C=O stretching. The ligand band at 1540 cm⁻¹ (N-N=C) gets displaced to 1578 cm⁻¹ and a band 1499 (νC=O) appears at 1480 cm⁻¹ in the coordination compound. The vibrations in the free ligand at 1216 and 1171 cm⁻¹ due to the O-C=O vibrations in the free ligand at 1700 cm⁻¹ shifts to 1606 cm⁻¹ in the metal chelate and thus can be related to the C=O stretching. The ligand band at 1540 cm⁻¹ (N-N=C) gets displaced to 1578 cm⁻¹ and a band 1499 (νC=O) appears at 1480 cm⁻¹ in the coordination compound. The vibrations in the free ligand at 1216 and 1171 cm⁻¹ due to the O-C=O vibrations in the free ligand at 1700 cm⁻¹ shifts to 1606 cm⁻¹ in the metal chelate and thus can be related to the C=O stretching. The ligand band at 1540 cm⁻¹ (N-N=C) gets displaced to 1578 cm⁻¹ and a band 1499 (νC=O) appears at 1480 cm⁻¹ in the coordination compound. The vibrations in the free ligand at 1216 and 1171 cm⁻¹ due to the O-C=O vibrations in the free ligand at 1700 cm⁻¹ shifts to 1606 cm⁻¹ in the metal chelate and thus can be related to the C=O stretching. The ligand band at 1540 cm⁻¹ (N-N=C) gets displaced to 1578 cm⁻¹ and a band 1499 (νC=O) appears at 1480 cm⁻¹ in the coordination compound. The vibrations in the free ligand at 1216 and 1171 cm⁻¹ due to the O-C=O vibrations in the free ligand at 1700 cm⁻¹ shifts to 1606 cm⁻¹ in the metal chelate and thus can be related to the C=O stretching. The ligand band at 1540 cm⁻¹ (N-N=C) gets displaced to 1578 cm⁻¹ and a band 1499 (νC=O) appears at 1480 cm⁻¹ in the coordination compound. The vibrations in the free ligand at 1216 and 1171 cm⁻¹ due to the O-C=O vibrations in the free ligand at 1700 cm⁻¹ shifts to 1606 cm⁻¹ in the metal chelate and thus can be related to the C=O stretching. The ligand band at 1540 cm⁻¹ (N-N=C) gets displaced to 1578 cm⁻¹ and a band 1499 (νC=O) appears at 1480 cm⁻¹ in the coordination compound. The vibrations in the free ligand at 1216 and 1171 cm⁻¹ due to the O-C=O vibrations in the free ligand at 1700 cm⁻¹ shifts to 1606 cm⁻¹ in the metal chelate and thus can be related to the C=O stretching. The ligand band at 1540 cm⁻¹ (N-N=C) gets displaced to 1578 cm⁻¹ and a band 1499 (νC=O) appears at 1480 cm⁻¹ in the coordination compound. The vibrations in the free ligand at 1216 and 1171 cm⁻¹ due to the O-C=O vibrations in the free ligand at 1700 cm⁻¹ shifts to 1606 cm⁻¹ in the metal chelate and thus can be related to the C=O stretching. The ligand band at 1540 cm⁻¹ (N-N=C) gets displaced to 1578 cm⁻¹ and a band 1499 (νC=O) appears at 1480 cm⁻¹ in the coordination compound.
689 and 693 cm\(^{-1}\) monosubstituted Ar as well as the bands at 754 and 760 cm\(^{-1}\) (\(\nu\) (Ar)). The three peaks of HPPMBP at 1058, 1028 and 1006 cm\(^{-1}\) do not move in the spectra of the complex but in the last, a band at 1071 appears and was overlap with the band at 1058 cm\(^{-1}\).

NMR spectra of europium complexes

The proton spectra of the obtained Eu(III) complex with HPPMBP (1:3) were recorded in CD\(_3\)OD:DMSO-d\(_6\) 1:1 as 1 × 10\(^{-3}\) M solution due to the very limited solubility of the complex. Unfortunately, carbon spectrum, where the shift of...
quaternary nuclei would be very informative, cannot be recorded in a reasonable time-scale. The proton spectrum of the complex shows broad HPMPBP resonances, the most part being shifted upfield, as seen on Fig. 2, which is typical for Eu-complexes. The protons CH-2 and CH-4 of the 4-MePh group give separate signals with dramatic shift difference. One is significantly upfielded (5.761 ppm vs. 7.174 ppm in pure ligand), while the second is only slightly influenced (7.173 ppm). This behavior can be explained by keto form with fixed rotations due to coordination, where one proton lies in the shielding zone of the carbonyl group and the other in the deshielding area. From the other side, two of the CH-3 protons are significantly shifted upfield (0.525 ppm vs. 2.296 ppm), which is incompatible with such structure and most probably is due to transmolecular shielding.

The NMR spectra of the Eu(III) complex with HPPMBP (1:3) in benzene-d6 and in CDCl3 (Fig. S4, Supporting Information), recorded in 1 × 10−3 M concentration, showed very broad significantly shifted overlapped signals. The suggested presumable structures of the two complexes are presented in Fig. 3.

**DSC–TG analyses**

In the Figs. 4 and S4 (Supporting Information) the results from DSC–TG analyses of the complexes are presented. One clearly outlined sharp exothermic peak in the DSC curve is observed for the compound Eu(PMMBP)3·C2H5OH in the temperature range of 437.8 – 485.8°C with $T_{\text{max}} = 458.3°C$, while for Eu(PPMBP)3·3H2O the exothermic peak is with $T_{\text{max}} = 499.8°C$. For the first compound’s exothermic peak effect, enthalpy change $\Delta H' = 19523.62$ J/g (delta-cp 29.0122 J/gK) is calculated using DSC data. For the second compound, enthalpy change $\Delta H' = 16178.62$ J/g (delta-cp 29.6272 J/gK) is obtained. Large exothermic features are commonly evidenced during decompositions of various compounds in air and are generally associated with the oxidation process. Thus, the compound may decompose to the final product Eu2O3.19–21 The thermal steps of the decomposition of (Eu(PMMBP)3·C2H5OH) was not completed until 620°C, Fig. 4. Within the temperature range of 239 – 496°C in the TG curve a mass loss of 6.22 mg (calc. 79.7%) is registered. Initial temperature of decomposition indicates that the thermal stability of the complex is higher than that of the free ligand, which has a melting point of 92 – 94°C. Yang et al.19 determined three exothermic peaks appearing around 361, 473 and 642°C during the thermal analysis data of the Eu(HL)3·3.5H2O complex (HL: 1-phenyl-3-methyl-5-hydroxy-4-pyrazolyl phenyl ketone isonicotinoyl hydrazone), as well.

A mass loss of 0.1 mg is observed in Fig. S5 (Supporting Information) until 281°C probably resulting mainly from the coordinated water of the complex, which is stable up to 349°C and then decomposes in the temperature range from 349 to 652°C. Within the temperature range of 349 – 652°C in the TG curve a mass loss of 6.56 mg is registered. Initial temperature of decomposition indicates that the thermal stability of the complex Eu(PPMBP)3·3H2O is higher than that of the free ligand, which has a melting point of 151.1 – 151.5°C.

**Discussion**

Coordination numbers (C.N.) of mononuclear β-dicarbonyl lanthanoid complexes are generally high, varying from 6 to 12, and depend on the ionic radii of ions (La3+, Gd3+ and Lu3+: 103.2, 93.8 and 86.1 pm, respectively), the ligand, the reaction medium, diluent, and conditions, such as temperature or ligand to metal ratio, with 8 and 9 being rather common.22,23 Another fact responsible for the large C.N. is the large ionic radius of the lanthanoid elements, (Eu3+: 94.7 pm). Three main types of lanthanoid complexes in solid state and in solution can be considered:1,7

i) Tris complexes containing three 4-acylpyrazolone ligands (HL) for an ion Ln3+. However, the coordination sphere of the trivalent ion is unsaturated in this six-coordinate chelate complex, so the lanthanoid ion can expand its coordination sphere by adduct formation, depending on the preparation protocol, with water for example LnL3·(H2O)x, x = 2 or 3.22,23 The two solid europium(III) complexes synthesized in the present work using HPPMBP and HPMBP as chelating ligands are of type a) as described above, with a change from water to EtOH for completion of the coordination sphere, when passing from one ligand to another, Fig. 3. But there is no so clear evidence for the coordination of the solvent molecules to
central ion based on the applied analytical methods. In our recent work, it was shown that La(III) was extracted with 3-methyl-1-phenyl-4-(4-trifluoromethylbenzoyl)-pyrazol-5-one in 1-butyl-3-methylimidazolium-bis(trifluoromethanesulfonyl)-imide, ([C1C4im][Tf2N]), as neutral LaL3 chelate but at the same time, the composition of the extracted species was established as LaL3-HL in CHCl3.14 In ILs, it has been shown that lanthanoids maintain the usual coordination number they display in molecular diluents.25 It is well known that hydrophobic ILs have higher water dissolving ability than conventional organic hydrophobic diluents.26,27 For instance, the average value of H2O dissolved in [C1C4im][Tf2N] after mixing equal volumes for 2 h is 122000 ppm (Karl-Fischer titration).28,29 One may consider water as a possible candidate for the Ln coordination sphere, but another possibility is the introduction of Tf2N– anions. Using time-resolved laser-induced fluorescence and IR spectroscopies Okamura et al.,30 demonstrated that not only Eu(TTA)3 but also Eu(TTA)3(H2O)3 synthesized as a solid crystal were almost completely dehydrated in water saturated [C6H5C6H4][Tf2N]. So, the significant amount of water present in the IL extracting phase does not favor the coordination of water molecules.

i) Formation of self-adduct species LnL3-HL including one unprotonated acidic ligand.31,32 Albinsson has established that in the organic phase (C6H6) at least two complexes exist, LnAA3 and the self-adopt LnAA-HAA as well as for the lower lanthanoids (especially La) a second self-adduct, LnAA(HAA)2 was supposed to be extracted with acetylacetone (HAA).32 The solvent extraction behavior of all 4f-elements has been investigated in aqueous-benzene medium using 3-methyl-1-phenyl-4-benzoyl-5-pyrazolone (HP) and the composition of the species has been determined as Ln3+HP.33

ii) It is also possible to arrange four bidentate ligands around a single ion; in this way, tetrakis anionic complexes with general formula [Ln4+L4]− are formed and the electroneutrality is achieved by a counter cation.23,34 Formation of an anionic mixed complex of the type Q−[Mn+Ln+1]− (L− is the anion of the chelating agent) is the quaternary ammonium salt cation, QCI: Aliquat 336, which is an IL, actually) in molecular diluents (C6H6, CCl4, C6H12) was firstly established by Dukov et al.35,36 Studies of Ln4+ extraction to [C6H5C6H4][Tf2N]− by 2-thienyl-trifluoroacetone revealed the existence of [C6H5C6H4][Ln(TTA)3] using high HTTA concentrations, while for low concentrations of HTTA neutral complexes were extracted Ln(TTA)3(H2O)4.37,38 However, the extraction of anionic complexes is possible by the exchange of the [Tf2N]− anions into the aqueous phase:

\[
\text{Ln}^{4+} + 4\text{HTTA} + [C_6\text{H}_5\text{C}_6\text{H}_4]_4\text{[Tf}_2\text{N}]_{12}^{-} \leftrightarrow [C_6\text{H}_5\text{C}_6\text{H}_4][\text{Ln(TTA)3}]_{12} + 4\text{H}^+ + [\text{Tf}_2\text{N}]_{12}^{-}.
\]

So, according to the reaction for each extracted Ln4+ ion to IL, one [Tf2N]− ion is lost by transfer to the aqueous phase. The quantities of the IL’s entities transferred in the aqueous phase have been measured recently for five hydrophobic ILs of the type [C6H5C6H4][Tf2N] (1-alkyl, 3-alkyl-imidazolium bis(trifluoromethylsulfonyl)imide) by Q-NMR (1H and 19F NMR spectra).29 The results show that 15 mM of [C6H5C6H4][Tf2N] are solubilized in the aqueous phase (DCI/0.1M NaCl at pH6 from 1 to 7) without the presence of a metal. But the amount of transferred Tf2N− due to the extraction mechanism itself is in the order of the metallic ion concentration, which, most of the time, is very low as compared to the mM range. Furthermore, depending on the IL nature, the Tf2N− transfer may be below the detection limits of the NMR technique.29 Another way that is different from the classical slope analysis11,14,22,23 to determine the stoichiometry of the extracted species and can give insight into the first coordination sphere, is EXAFS. Distinction between oxygen atoms arising from H2O or Tf2N− or the ligand could be made provided model compounds with known X-ray structure and EXAFS spectra.

Conclusions

Two Eu(III) complexes were synthesized applying 4-acylpyrazolone ligands (HL) with methyl and Ph substituent at the 4-position of the aryl group. Tris-chelate complexes were obtained (EuL3), which completed their unsaturated six coordination sphere by adduct formation probably with one molecule C2H5OH and three water molecules reaching coordination numbers 7 and 9, respectively, according to the data from elemental analysis. This type of lanthanoid complex (LnL3) can be considered as a main in solid state and in the IL phase.14 The existence of the two types of complexes (chelates and self-adduct species LnL3-HL) formed by 4-acylpyrazolone ligands in molecular diluents during the solvent extraction process has been reported. This family of extractants was not widely used in extraction chemistry applying “the green” IL medium. So, at the moment, the existence of anionic tetrakis complexes [LnL4]− was not established in IL phase, although this kind of entity with typical β-dicarbonyl compounds was already specified (thenoyltrifluoroacetone)33 as well as when an IL (Aliquat 336) was used as a synergistic agent in volatile organic compounds (VOCs).34,35 The synthesis of these two europium compounds is the first step before X-ray analysis in view of EXAFS data acquisition for further insights into extraction mechanisms in ILs.

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Figures S1 – S5: elemental analysis, IR spectra, NMR spectrum and DSC-TG analysis of the complexes. This material is available free of charge on the Web at http://www.jsac.or.jp/asnlsc/index.html.

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