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Spectral and Thermochemical Properties of the $[Na(H_2O)_4]$ $[EuL_4]\cdot 0.775CH_2Cl_2$ Complex, HL = 1,3-Bis(1,3-dimethyl-1*H*-pyrazol-4-yl)-1,3-propanedione

I. V. Taidakov[a], B. E. Zaitsev[b], S. S. Krasnosel'skii[b], and R. S. Borisov[c]

[a] *Petrov Institute of Plastics, Perovskii proezd 35, Moscow, 111024 Russia*
e-mail: taidakov@gmail.com

[b] *Russian Peoples' Friendship University, ul. Mikluho-Maklaya 6, Moscow, 117198 Russia*

[c] *Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences,*
Leninskii pr. 29, Moscow, 119991 Russia

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Abstract—Reaction of $Eu(NO_3)_3\cdot 6H_2O$ with 1,3-bis(1,3-dimethyl-1*H*-pyrazol-4-yl)-1,3-propanedione (HL) in the presence of NaOH affords the complex compound $[Na(H_2O)_4]$ $[EuL_4]\cdot 0.775CH_2Cl_2$ (**I**). The spectral (UV, IR, ^{1}H NMR spectroscopy), and thermo-luminescent (TG–DSC–MS) properties of the complex **I**, as well as its fragmentation at the laser desorption ionization (LDI–MS) were studied.

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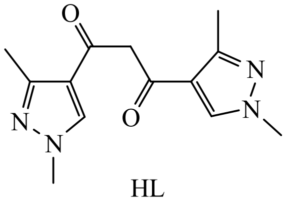
We have previously described [1] the synthesis of a new anionic Eu(III) complex with a pirazole-containing diketone, 1,3-bis(1,3-dimethyl-1*H*-pyrazol-4-yl)-1,3-propandione (HL), whose structure was confirmed by XRD analysis. In this paper, we describe an improved method for the synthesis of this compound and also compile the data on its spectral and thermochemical properties.

The synthesis of the target compound **I** was carried out as follows:



HL

$$\xrightarrow[(2)\ \text{DMSO–}CH_2Cl_2]{(1)\ Eu(NO_3)_3\cdot 6H_2O/\text{NaOH}} Na(H_2O)_4[EuL_4]\cdot 0.775CH_2Cl_2$$

I

We found that traditional synthesis in solution [2] has some advantages over earlier procedures implementing mechanochemical [3] method: the reaction is carried out in a homogeneous environment and leads to the formation of purer product. In addition, changing the molar ratio of reactants to 1:4:4 (Eu:LH:NaOH) increased markedly the yield of the desired compound. The method of isolation of the product was not changed: the slow diffusion of the CH_2Cl_2 vapor to the solution of the complex in DMSO yields **I** as well-formed crystals.

The UV absorption spectra of solutions of the ligand and complex are given in Fig. 1. Since 1,3-dimethylpyrazole itself has only slight absorption in the region below 220 nm [4], the observed pattern is caused primarily by the fragment C(=O)CH=C(O). Both peak may correspond to π→π* transitions in the conjugated system of the enol isomer of the free diketone and coordinately bound ligand. Slight bathochromic shift of the long-wave maximum (343 nm in the complex compared to 340 nm in the free ligand) of the compound **I** can be associated with an increase in the degree of conjugation at the complex formation. This is also reflected by an increase of the molar extinction coefficient (log ε = 4.2 and 4.7 at 251 nm for the ligand and complex, respectively). Significant absorption in the visible region due to the *d*–*d* transitions in the central atom is not observed.

In the IR spectrum of free ligand there is a band of the stretching vibrations of carbonyl group at 1652 cm^{-1} characteristic of the enol form of the β-diketones [5].

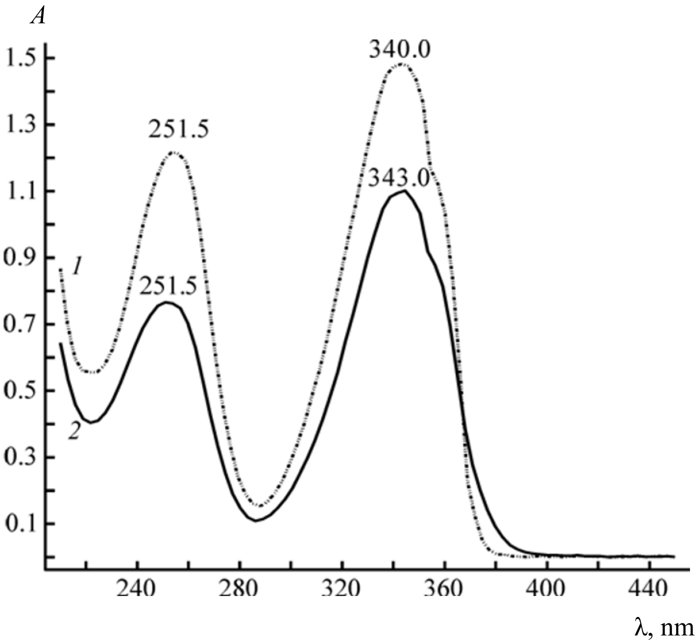


Fig. 1. Absorption spectra of solutions in acetonitrile at 25°C: (*1*) the ligand (8.1×10^{-5} M , (*2*) complex (1.5×10^{-5} M).

Absorption at 1720 cm^{-1} characteristic of the keto form is not observed that allows an assumption that free ligand exists mostly as the enol isomer.

A shift of the absorption maximum of carbonyl group to the low-frequency region in the spectrum of diketone as compared with that in mono-ketones (1690 cm^{-1}) indicates the presence of hydrogen bonding of the carbonyl and hydroxyl groups of the enol isomer. Existence of the hydrogen bonds is affirmed also by the presence of the absorption bands of OH groups (3406 and 2334 cm^{-1}), the strong shift of the absorption maxima to lower frequencies (approximately $\Delta\nu$ = 230 and 1300 cm^{-1}, respectively) relatively to the absorption frequency free OH group in alcohols (3635 cm^{-1}) suggests the presence of hydrogen bonds of two types: of moderate strength and a very strong.

Stretching vibrations of CH bond of the heterocyclic fragments induces the bands at 3125 and 3085 cm^{-1} and of the methyl groups at the 2928 cm^{-1}.

The IR spectrum of complex **I** (Fig. 2) contains fewer absorption bands than the spectrum of the ligand. A very strong and broad band at 3376 cm^{-1} is attributable to the absorption of coordinationally bound water. Small peak at 2928 cm^{-1} may be due to the stretching vibrations of the C–H bonds of methyl group. A very strong band at 1584–1316 cm^{-1} according to [6] corresponds to the deformation vibrations of the fragments C=O and C=C. There are multiple absorption bands in the *fingerprints* region, arose from the stretching and bending vibrations of various C–O, C–H and C=C bonds. The absorption bands corresponding to the Eu–O vibrations must be in the region of 400–350 cm^{-1}, but examination of this area is difficult because of the signal of water absorption.

The complex **I** in solid form and in solution shows a bright orange-red fluorescence. Complete data on the dependence of $\lambda_{em}/\lambda_{exc}$ can be represented graphically by a surface and are very cumbersome. Therefore, Fig. 3 shows the cross-section of this surface for the exciting radiation wavelengths 240 and 370 nm (at the emission maxima).

The emission spectrum is quite typical for the europium(III) diketonate derivatives and is due to the $^5D_0\rightarrow{}^7F_n$ (n = 0–4) transitions [7]. Increase in the wavelength of the exciting radiation increases intensity of luminescence and simultaneously shifts the emission wavelengths maximum from 440 to 600 nm.

Increasing the intensity of luminescence can be caused by so-called *antenna effect*, which essentially consists in the transfer of energy from the excited molecules of ligand to the central europium atom.

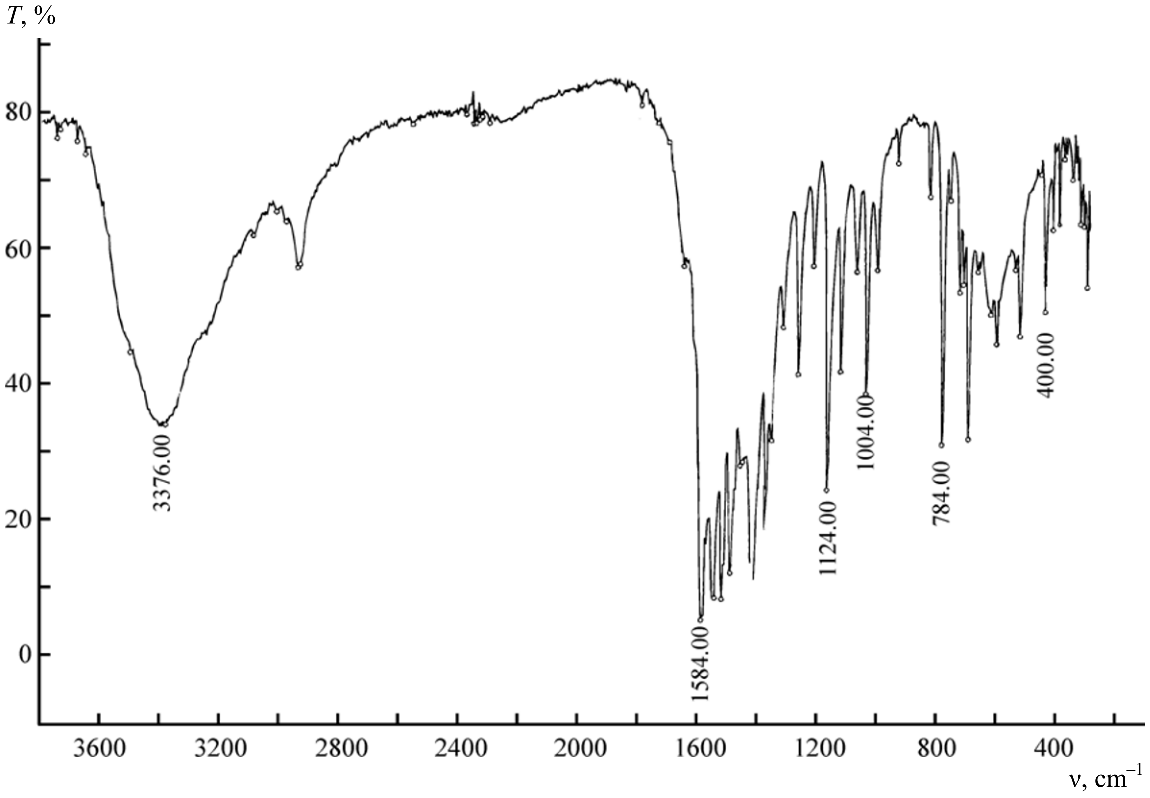


Fig. 2. IR spectrum of complex **I** in KBr pellet.

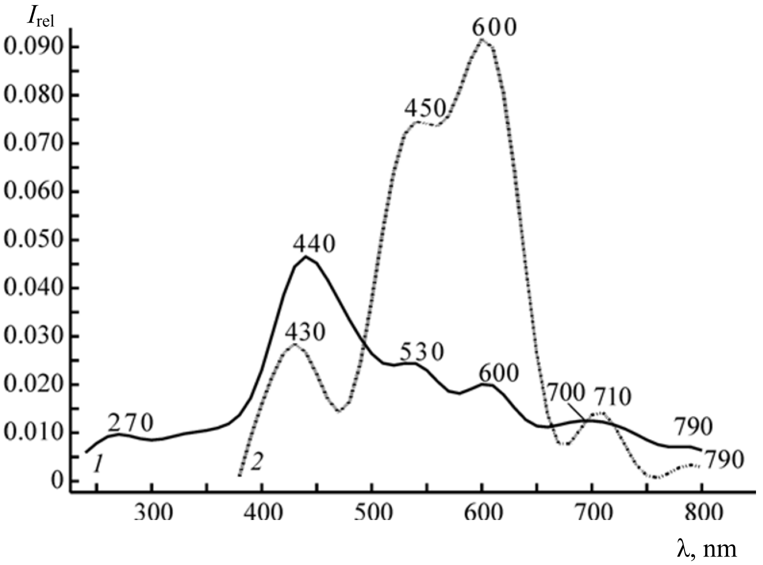
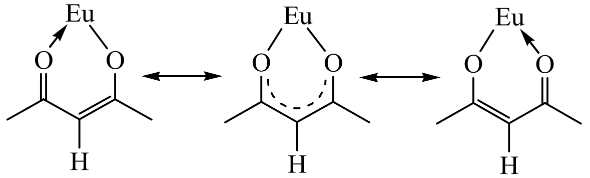


Fig. 3. Luminescence spectra of 2×10^{-3} M solution of the complex **I**. The wavelength of the exciting radiation is (*1*) 240 and (*2*) 370 nm.

Indeed, as shown above, both the free ligand and the complex exhibit a significant absorption at 340 nm.

Another interesting feature of the luminescence of this complex is a very long decay time (Fig. 4). Usually, the europium(III) diketonate complexes are characteriszed by the decay time of the order of hundreds of microseconds [8]. For compound **I**, this time is more than 3000 μs. The reason for such a long luminescence (here we can speak about phosphorescence), most likely, is a complex multistep mechanism of energy transfer from the excited part of the molecule to the emitting metal atom.

The ^{1}H NMR spectrum of compound **I** dissolved in DMSO-d_6 is shown in Fig. 5. The observed broadening of all signals is due to both the dynamic equilibrium between the boundary structures of the enol form of the ligand and the influence of the paramagnetic Eu^{+3} ion.



The narrow singlet at 5.75 ppm corresponds to the signals of CH_2Cl_2, broad singlet at 3.36 is the signals of protons of water (both coordinationally bound and residual in the solvent), and a weak multiplet at 2.5 ppm corresponds to the methyl groups of non-deuterated dimethylsulfoxide in the solvent. The assignment of other signals (δ, ppm): 7.12 (8H, CH pyrazole), 4.72 (24H, N–CH_3), 4.35 (HC=C), 3.64 (24H, CH_3 pyrazole). Note that the chemical shifts of the methyl groups differ markedly from those of the original ligand (shifted downfield by 0.5–1 ppm), which is caused by the influence of the europium atom [9]. Thus, the ^{1}H NMR spectrum of compound **I** is fully consistent with the proposed structure.

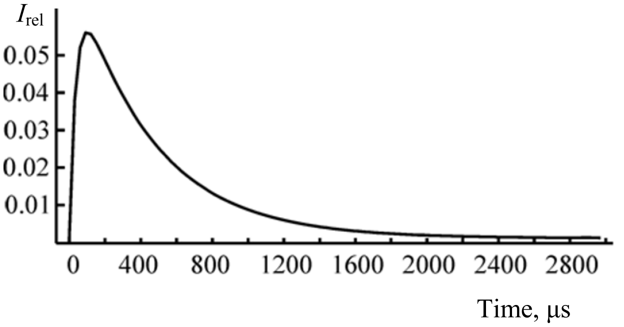


Fig. 4. The kinetics of luminescence decay of 2×10^{-3} M solution of complex **I**.

We carried out comparative studies of the ionization process of compound **I** under the action of laser radiation in the presence of standard matrices (e.g., 2,5-dihydroxybenzoic acid), and without them. The

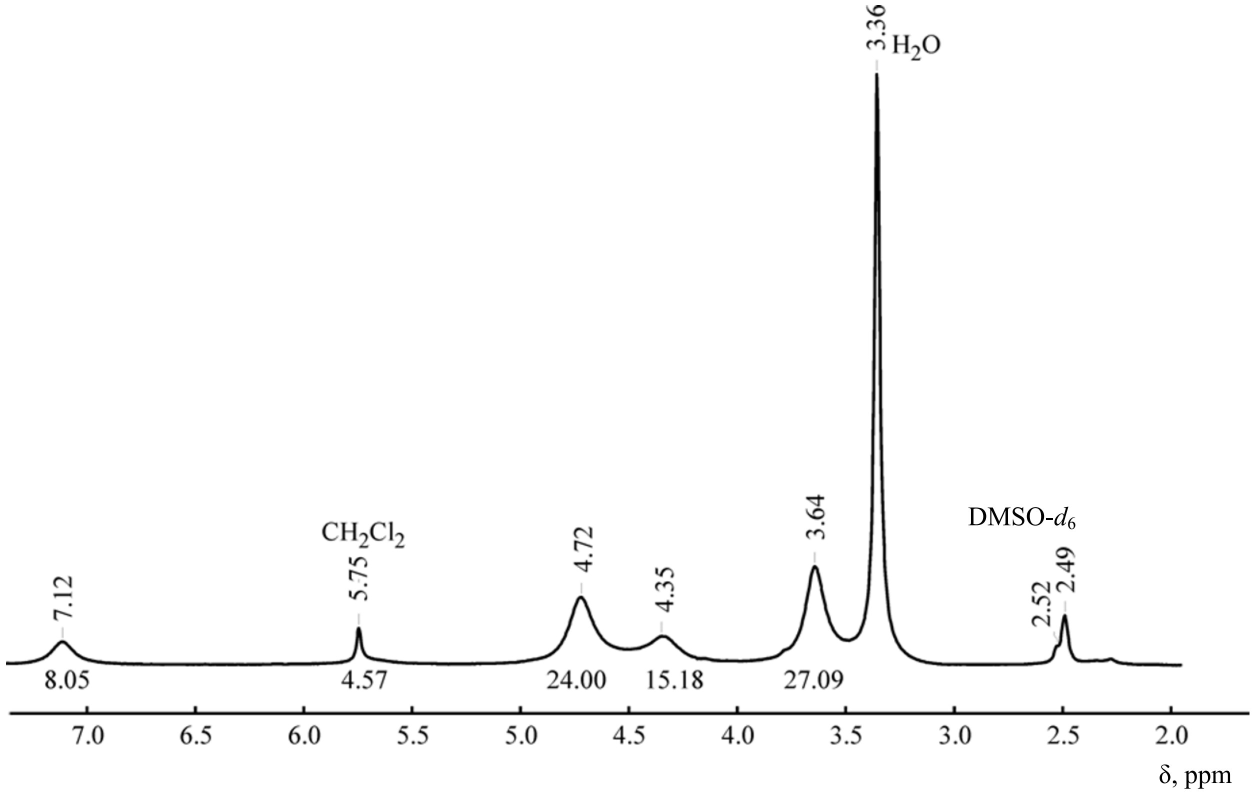


Fig. 5. ^{1}H NMR spectrum of compound **I** in DMSO-d_6 (300K, 300 MHz). The figures above the peaks correspond to the chemical shifts, below to the integral intensities of the signals.

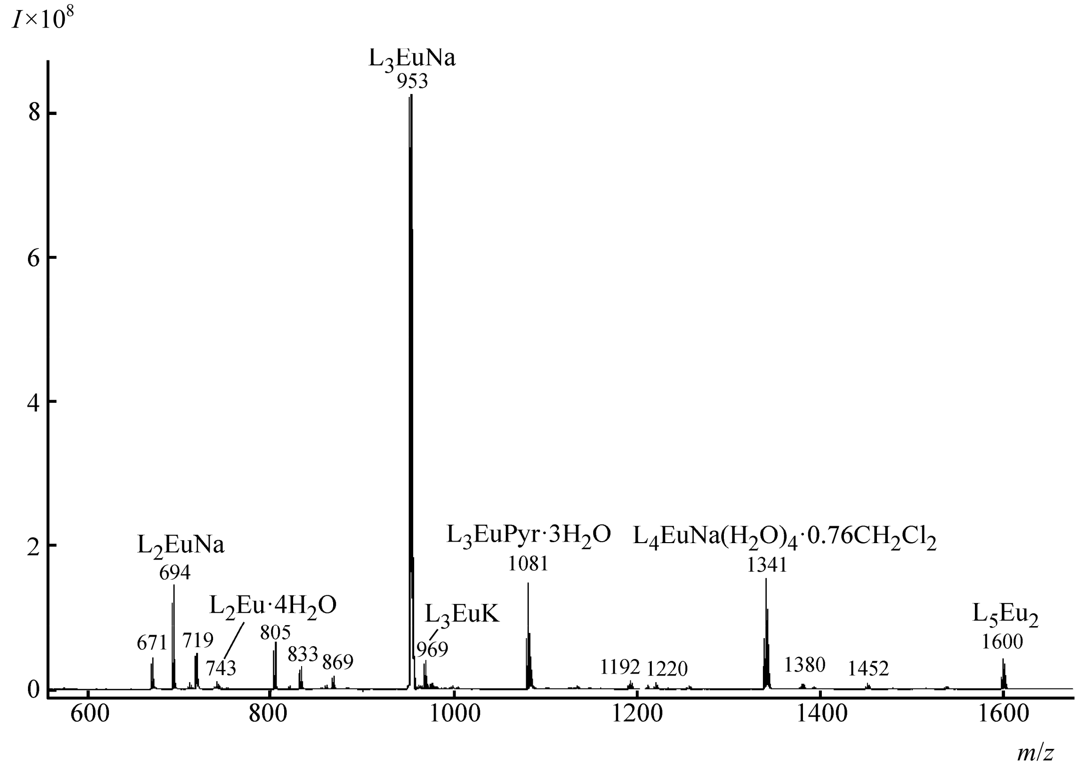


Fig. 6. Mass spectrum (LDI–TOF) of compound **I** without a matrix.

best results were achieved using sodium acetate as a buffer salt without adding the organic matrix. The presence of the matrix leads to a considerable complication of the spectrum and increased fragmentation. The mass spectrum of the complex is shown in Fig. 6.

An interesting feature of this spectrum is the absence of peaks of the molecular ion cluster corresponding to the empirical formula, as well as evidence of a significant fragmentation, usually not typical for this method of ionization.

The main signal (*m*/*z* = 953) in the spectrum corresponds to the L_3EuNa cluster appearing at the decay of the initial complex. Also there are much weaker signals of the L_3EuK cluster (*m*/*z* = 969). Common source of potassium in this case is the impurities in the reagents, as well as the products of the glass leaching.

The isotope distribution in the clusters agree well with the predicted using the Isoform program and the data on the natural content of isotopes.

Noteworthy the presence of heavy clusters with a ratio *m*/*z* = 1600. They have been attributed to the composition of Eu_2L_5, but additional experiments (MS/MS) are needed for the reliable proof. Similarly (based on the *m*/*z* ratio and isotopic distribution) were identified some other clusters.

The LDI–MS experiments showed that with a high probability the compound **I** is not volatile and decomposes when heated. For a more detailed study of this process we implemented the method of TGA with the mass-spectrometric identification of the products of decomposition. The TG–DSC data are shown in Fig. 7.

The first endothermic effect is recorded at 167.3°C. It corresponds to the beginning of melting. Simultaneously occur a weight loss and appearance in the mass spectrum of intense peaks of the ions with *m*/*z* = 18 and 85, which correspond to the elimination of water and CH_2Cl_2, respectively. The mass loss corresponds to the removal of all bound CH_2Cl_2 and H_2O.

At further increase in temperature begins destruction of the ligand, the most intensively occurring in the temperature range of 376–410°C. Destruction ends at a temperature of 476°C. Simultaneously, in the mass spectrum occur intense peaks *m*/*z* = 18 and 44 (H_2O and CO_2, respectively) and a weak peak *m*/*z* = 85 (the CH_2Cl_2 residual). Also

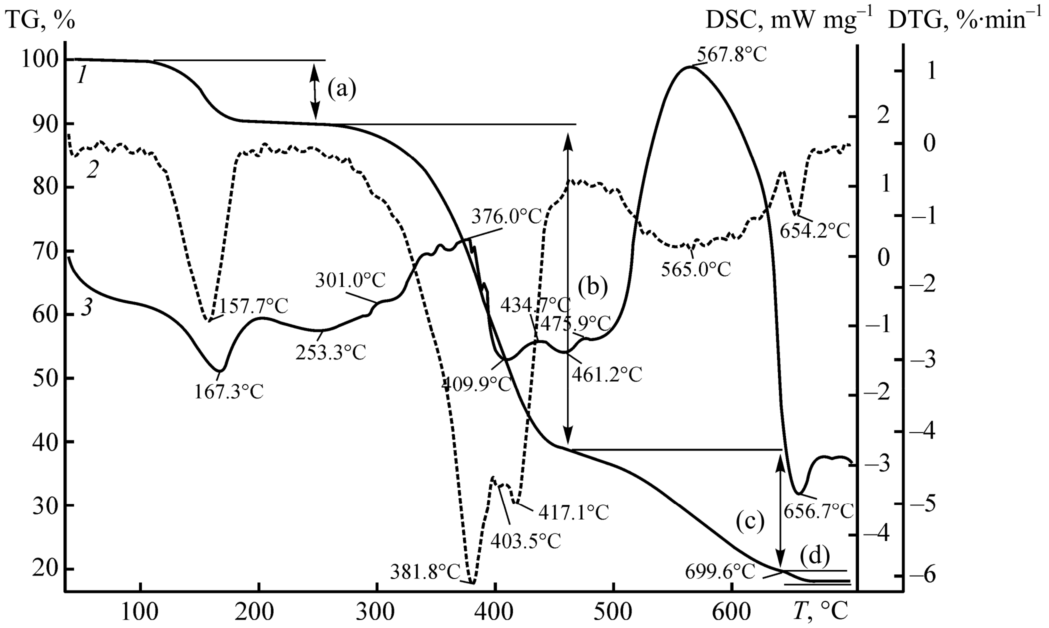


Fig. 7. The curves of (*1*) TG, (*2*) DTG, and (*3*) DSC for the complex **I**. The change in weight, %: (a) –10.32, (b) –51.38, (c) –18.87, and (d) –1.92; the residual weght is 17.51% (699.6°C).

identified a heavy ion with $m/z = 138$, corresponding to the molecular ion of 1-(1,3-dimethyl-1*H*-pyrazol-3-yl) ethanone, the a product of the ligand decomposition. Noteworthy that no formation of heavier fragments (m/z above 139) was observed.

At the temperature above 500°C starts burning out of carbon, which is accompanied by a strong exothermic effect and further weight loss. The mass spectrum contains intense peaks $m/z = 44$ (CO_2), while the peaks with $m/z = 18$ (H_2O) are virtually absent. Heavier ions are not observed.

The remaining mixture of oxides and salts presumably melts or crystallizes at 654°C, which is registered as a small endothermic effect. The residue corresponds to the formula $Eu_2O_3{\cdot}Na_2CO_3$ (theoretical weight of the residue should be 16.9% of the initial, experimental 17.5%).

Thus, we showed that the thermal decomposition of **I** proceeds stepwise: above the melting point (167.3°C) are removed water and occluded dichloromethane, and then proceeds the ligand pyrolysis, presumably with the formation of free carbon or carbon-rich resin, burnable at a temperature above 500°C. At 700°C the decomposition ends with the formation of a mixture of europium oxide and sodium carbonate.

EXPERIMENTAL

Synthesis of compound I. The diketone (1.04 g, 4 mmol) was dissolved in 15 ml of ethanol and 4 ml of NaOH 1N solution in water was added. Then to the solution was poured with stirring a solution of 0.34 g (1 mmol) of $Eu(NO_3)_3{\cdot}6H_2O$ in 5 ml of water. The mixture was heated to 40–50°C and pH = 7 was set by adding a few drops of glacial acetic acid (initially the solution was strongly alkaline). A few minutes later from the clear solution begins to drop a precipitate. The mixture was heated for 20 min and left for 10 h at room temperature, and then evaporated in vacuo to dryness.

The precipitate was washed successively with CH_2Cl_2, 50% aqueous ethanol, 96% ethanol and diethyl ether using centrifugation at 4000 rpm. The product was dried in a vacuum. Yield 0.65 g.

Weighed 0.3 g sample of the product was mixed with 0.7 ml of water-free dimethyl sulfoxide (DMSO), centrifuged for 5 minutes at 12000 rpm, the liquid over the precipitate was placed into a tube and kept in a closed desiccator over CH_2Cl_2 till complete crystallization of the product (5–7 days). The mother liquor was decanted, the crystals were washed with a small amount of CH_2Cl_2 and dried in a vacuum at 20°C. The overall yield (from three separate crystallization) is 0.39 g of pure **I**, light brown transparent crystals, mp 196–198°C (decomp.). Found, %: C 47.23, H 5.36, N 16.07. $C_{52.77}H_{69.54}Cl_{1.53}EuN_{16}NaO_{12}$. Calculated, %: C 46.98, H 5.19, N 16.61.

The UV absorption spectra were recorded in the range of 210–450 nm from the solutions in acetonitrile of the free ligand and the complex, on a Shimadzu UV-160 spectrophotometer in quartz cuvettes with the layer 1 cm, relatively to the pure solvent. Concentration of solutions of the free ligand and the complex were 8.1×10^{-5} and 1.5×10^{-5} M , respectively.

The IR spectra were recorded in the range of 400–4000 cm^{-1} on the Specord 75 IR and Specord M80 instruments (Carl Zeiss, Jena, Germany) from the samples mixed with KBr.

The fluorescence spectra were recorded for 2×10^{-3} M solution of the complex in a mixture of DMSO–ethanol (1:1 by volume) using a scanning spectrofluorimeter Fluorat Panorama (produced by Lyumeks, Russia) in cells with 1 cm layer. The excitation source was a pulse xenon lamp. The width of the *forbidden zone* ($\Delta = \lambda_{em} - \lambda_{exc}$) was to 10 nm. Radiation in the *anti-Stokes* region ($\lambda_{em} < \lambda_{exc}$) was not recorded. The excitation range 210–400 nm (step 10 nm), the range of recording fluorescence is (λ_{exc} + 10)–800 nm (step 10 nm).

In studying the kinetics of the luminescence decay was used the same solution, λ_{exc} = 260 nm, λ_{em} = 600 nm, pulse delay 0.05 to 3000 μs (step 30 μs), pulse width 3.0 μs.

The ^{1}H NMR spectra were recorded on a Bruker AC-300 spectrometer (operating frequency for the ^{1}H nuclei 300 MHz). We used a 0.9% solution of **I** in the fully deuterated DMSO (DMSO-d_6). The chemical shifts (δ) are expressed in ppm relative to the reference tetramethylsilane (δ = 0.00 ppm). The measurements were carried out at 300K with ampoules of 5 mm diameter.

Mass spectra of laser desorption/ionization (LDI) were obtained on a Bruker Autoflex II (TOF) instrument operating in the reflectron mode with the registration of positively charged ions. As the excitation source was used a nitrogen laser (λ 337 nm), the measuring range is from 400 Da to 10 kDa, with suppression of the signal below 400 Da. On the target was applied a mixture (1:1 by volume) of the sample (2 mg ml^{-1}) and sodium acetate (5 mg ml^{-1}) solutions in THF. The data were processed using the software packages Bruker DataAnalysis for TOF 1.6g and Isoform.

The thermogravimetry with mass-spectral registration of products (TG-DSC-MS) was performed on a Netzsch STA 449C instrument with attached quadrupole mass spectrometer Aeolos QMS 403C. For measurement, a weighed sample in a corundum crucible (Al_2O_3) was placed in the oven. Volumetric flow rate through the sample was maintained at 60 ml min^{-1} (mixture of air 50 ml min^{-1} and argon 10 ml min^{-1}). The measurement was carried out in the temperature range from 42 to 700°C. The heating rate was 10°C min^{-1}. As a reference was used an empty crucible. The mass of the sample relative to the mass of empty crucible was measured with an accuracy of 10^{-6}, the accuracy of measuring thermal effects (DSK) was 3%. The results of the measurements were processed using the software NETZSCH-analysis. The ionization method is electron impact (EI, 70 eV).

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REFERENCES

1. Taidakov, I.V., Zaitsev, B.E., Krasnosel'ski, S.S., Polyakova, I.N., and Sergienko, V.S., *Zh. Neorg. Khim.*, 2010, vol. 56, no. 3, p. 345.
2. Melby, L.R., Rose, N.J., Abramson, E., and Caris, J.C., *J. Am. Chem. Soc.*, 1964, vol. 86, no. 23, p. 5117.
3. Kalinovskaya, I.V., Karasev, V.E., Romanchenko, A.M., and Kuryavyi, V.G., *Zh. Neorg. Khim.*, 2007, vol. 52, no. 4, p. 574.
4. Pretsch, E., Büllmann, P., and Affolter, C., *Structure Determination of Organic Compounds*, Berlin: Springer-Verlag, 2000.
5. Silverstein, R.M, Webster, F.X., and Kirmle, D., *Spectrometric Identification of Organic Compounds*, New York: Wiley, 2005.
6. Nakamoto, K. and Martell, A.E., *J. Phys. Chem.*, 1960, vol. 32, p. 588.
7. Murray, G.M., Pesterfield, L.L., Stump, N.A., and Schweitzer, G.K., *Inorg. Chem.*, 1989, vol. 28, p. 1994.
8. Watson, M.M., Zerger, R.P., Yardley, J.T., and Stusky, G.D., *Inorg. Chem.*, 1975, vol. 14, p. 2675.
9. Peters, J.A., Huskens, J., and Raber, D.J., *Prog. Nucl. Magn. Reson. Spectrosc.*, 1996, vol. 28, p. 283.