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Mixed-Ligand Lanthanide Complexes with Acylpyrazolones and Phosphorus-Containing Ligands

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Abstract—The reactions of lanthanum acetylacetonate with various phosphorus-containing pesticides, toxic gases, and products of their hydrolysis are modeled by quantum-chemical methods. In the most cases, the enthalpy of substitution for water by organophosphorus compounds is negative. The complexes are studied in solutions using ethyl (diethoxyphosphoryl) acetate as a model compound. The mixed-ligand lanthanide complexes with acylpyrazolones and ethyl (diethoxyphosphoryl) acetate are synthesized. The crystal structure is determined for the samarium complex.

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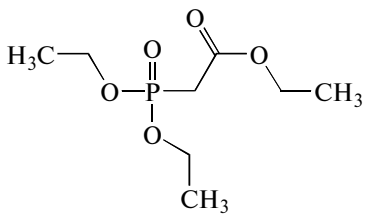
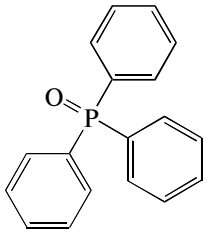
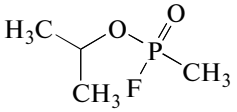
Luminescent coordination compounds of lanthanides attract attention as promising materials for light-emitting devices and fluorescence sensors. Among the latter there are compounds, whose luminescence response is attained by the direct coordination of an additional ligand to the central metal ion. The widely studied lanthanide complexes with phosphorus acid esters [1, 2] and phosphine oxide [3–8] are structurally similar to the known pesticides, toxic gases, and products of their hydrolysis. The europium complexes were studied as a basis of sensors for the determination of the hydrolysis products of toxic gases [9, 10]. A drawback of the approach applied in these works is the use of uncharged ligands, such as divinyl methyl benzoate, because of which these materials are less resistant to solvents including water. In this work, the possibility of the reversible coordination of neutral molecules of phosphorus-containing pesticides and toxic gases to lanthanum acetylacetonate was theoretically modeled and the complex formation of ethyl (diethoxyphosphoryl) acetate (LP) with samarium, europium, terbium, and dysprosium acyl pyrazolonates was experimentally studied. Compound LP was chosen because of its structural similarity to molecules of some phosphorus-containing pesticides and military poison gases at a low toxicity.



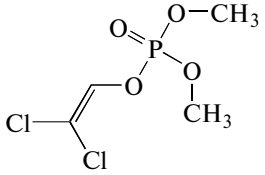
(LP)



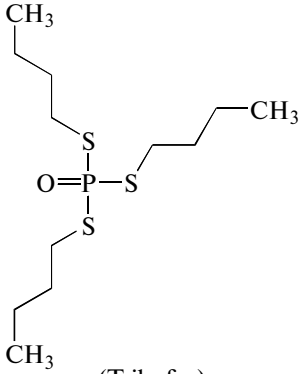
(Triphenylphosphine oxide)



(Sarin)

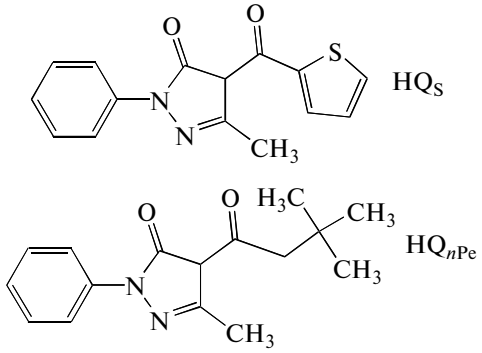


(Dichlorvos)



(Tribufos)

The purpose of this work is the quantum-chemical study of the mixed-ligand lanthanide complexes with acetylacetone and various phosphorus-containing compounds (pesticides and model objects), as well as the synthesis and study of the luminescence properties of the Sm, Eu, Tb, and Dy complexes with acylpyrazolones and ligand LP. 1-Phenyl-3-methyl-4-thienylcarbonylpyrazol-5-one (HQ_S) [3, 11, 12] and 1-phenyl-3-methyl-4-neopentylcarbonylpyrazol-5-one ($HQ_{n\mathrm{Pe}}$) [4], $Ln(Q)_3(LP)(EtOH)$ ($Q = HQ_{n\mathrm{Pe}}$, HQ_S; Ln = Sm, Eu, Tb, Dy), were used as acylpyrazolones.



EXPERIMENTAL

The Firefly 7.1.G calculation complex [13] in the DFT method with the B3LYP hybrid exchange correlation functional was used. Calculations were performed in the 6-31G Pople basis set [14–16] for atoms different from lanthanum. The SBK basis set [17] was used to describe the lanthanum atom. The Hesse matrix was calculated to check the correspondence of the optimized structures of the local minimum points on the potential energy surface for all compounds. No imaginary frequencies were found.

For simplification the calculations were performed for the lanthanum acetylacetonate complexes. The geometry of molecules of the $La(Acac)_3(EtOH)(X)$, $La(Acac)_3(H_2O)(X)$, and $La(Acac)_3(X)$ complexes, where X are different ligand molecules, was optimized. The initial geometry of the complexes was taken from the X-ray diffraction data for lanthanum acetylacetonate dihydrate [18], after which the water molecule was replaced by the ligand molecule in the preoptimized geometric configuration. Then the energies of the reactions

$$La(Acac)_3(EtOH)(H_2O) + X \rightleftarrows La(Acac)_3(EtOH)(X) + H_2O, \quad (1)$$

$$La(Acac)_3(EtOH) + X \rightleftarrows La(Acac)_3(X) + EtOH, \quad (2)$$

were determined using the difference scheme.

The IR spectra of the complexes were recorded on a FTIR Spectrum One spectrometer (PerkinElmer) in the attenuated total internal reflectance mode in the range from 400 to 4000 cm^{-1} (resolution 0.5 cm^{-1}). Excitation and luminescence spectra were recorded on a Perkin-Elmer LS55 spectrometer.

The CHN analysis was carried out on a Fision Instruments 1108 CHN microanalyzer. The lanthanide content was determined by complexonometry.

Commercially accessible 1-phenyl-3-methylpyrazol-5-one (Fluka), α-thenoyl chloride and *tert*-butylacetyl chloride (Sigma-Aldrich), and KOH (Mosreaktiv, IMP) were used as received. Calcium oxide (Reakhim, analytical grade) was calcined in a muffle furnace at 1200°C. Lanthanide nitrates were prepared by the dissolution of the corresponding oxides (reagent grade) in nitric acid (high-purity grade). Dioxane (Komponent-Reaktiv, analytical grade) was purified and dried according to a standard procedure using metallic sodium and benzophenone. Ethanol (Ferein) was purified by distillation over KOH.

Ligands HQ_S and $HQ_{n\mathrm{Pe}}$ were synthesized according to a standard procedure of 1-phenyl-3-methylpyrazol-5-one acylation with the corresponding carboxylic acid chloride in dioxane [3–5]. Ligand LP was synthesized using a described procedure [19].

Synthesis of $Eu(Q_S)_3(EtOH)(LP)$. A solution of $Eu(NO_3)_3 \cdot 6H_2O$ (52.29 mg, 0.1172 mmol) in ethanol (2 mL) and a solution of LP (26.28 mg, 0.1172 mmol) in ethanol (1 mL) were added dropwise to a solution of a mixture of HQ_S (100.00 mg, 0.3517 mmol) and KOH (19.73 mg, 0.3517 mmol) in ethanol (5 mL). The mixture was refluxed for 15 min and cooled to ambient temperature. Potassium nitrate was salted-out with chloroform (2 mL). Precipitated KNO_3 was filtered off. After the solution was evaporated by 3/4 of the volume, a yellow precipitate of the complexes was formed, filtered off, washed with cool ethanol (two times, 2 mL each washing) and ether, transferred to a vacuum desiccator, and dried over P_2O_5 for 12 h.

IR (ν, cm^{-1}): 3072 ν(O–H); 1604, 1592, 1576; 1470, 1456, 1417 ν(C=O, C=C, C=N); 1186 ν(P=O); 1059, 1044, 1014, 902, 858, 817, 779, 751.

Other complexes were synthesized similarly from the corresponding acylpyrazolone and metal nitrate. The elemental analysis results are given in Table 1.

IR of $Sm(Q_S)_3(EtOH)(LP)$ (ν, cm^{-1}): 3075 ν(O–H); 1604, 1591, 1578; 1472, 1457, 1440 ν(C=O, C=C, C=N); 1192 ν(P=O); 1044, 1015, 816, 780, 759, 738.

IR of $Tb(Q_{n\mathrm{Pe}})_3(EtOH)(LP)$ (ν, cm^{-1}): 3069 ν(O–H); 1612, 1593, 1580, 1536; 1498, 1479, 1426 ν(C=O, C=C, C=N); 1188, 1176 ν(P=O); 1093, 1075, 1063, 1014, 840, 754, 730.

IR of $Dy(Q_{n\mathrm{Pe}})_3(EtOH)(LP)$ (ν, cm^{-1}): 3069 ν(O–H); 1612, 1589, 1581, 1535; 1493, 1472 ν(C=O, C=C, C=N); 1175 ν(P=O); 1160, 1092, 1070, 1060, 1011, 831, 730.

Single crystals of complex $Sm(Q_S)_3(EtOH)(LP)$ were obtained as yellow needles by the slow evaporation of a solution of the complex in an ethanol–chloroform mixture in a sealed L-type ampule. It should be mentioned that crystals coinciding, according to the X-ray diffraction data, with the complex described above precipitate from a solution containing $Sm(NO_3)_3 \cdot 6H_2O$, HQ_S, KOH, and LP in a molar ratio of 1 : 1 : 1 : 2 upon gradual evaporation.

Table 1. Elemental analysis results for the complexes

Compound/empirical formula	Content (found/calculated), %			
	C	H	N	M
$Eu(Q_S)_3(EtOH)(LP)$ $C_{55}H_{56}EuN_6O_{12}PS_3$	52.12/51.92	4.32/4.44	6.75/6.61	11.27/11.94
$Sm(Q_S)_3(EtOH)(LP)$ $C_{55}H_{56}N_6O_{12}PS_3Sm$	52.21/51.99	4.37/4.44	6.79/6.61	11.99/11.83
$Tb(Q_{n\text{Pe}})_3(EtOH)(LP)$ $C_{58}H_{80}N_6O_{12}PTb$	55.72/56.04	6.61/6.49	6.83/6.76	12.63/12.78
$Dy(Q_{n\text{Pe}})_3(EtOH)(LP)$ $C_{58}H_{80}DyN_6O_{12}P$	55.63/55.87	6.52/6.47	6.80/6.74	12.99/13.03

X-ray diffraction analysis. A single crystal of complex $Sm(Q_S)_3(EtOH)(LP)$ ($0.44 \times 0.08 \times 0.06$ mm) was used. A set of diffraction reflection intensities was obtained on a Bruker SMART APEX2 automated diffractometer ($\lambda Mo K_\alpha$, graphite monochromator) at 160 K. The structure was solved by a direct method. Positions of hydrogen atoms were found in the difference Fourier synthesis. Non-hydrogen atoms were refined by least squares in the anisotropic approximation, and all hydrogen atoms were refined in the isotropic approximation. The APEX2, SAINT, SADABS, and XPREP programs [20] were used for the collection and processing of the $I(hkl)$ array. The calculations were performed using the SHELX-97 program package [21].

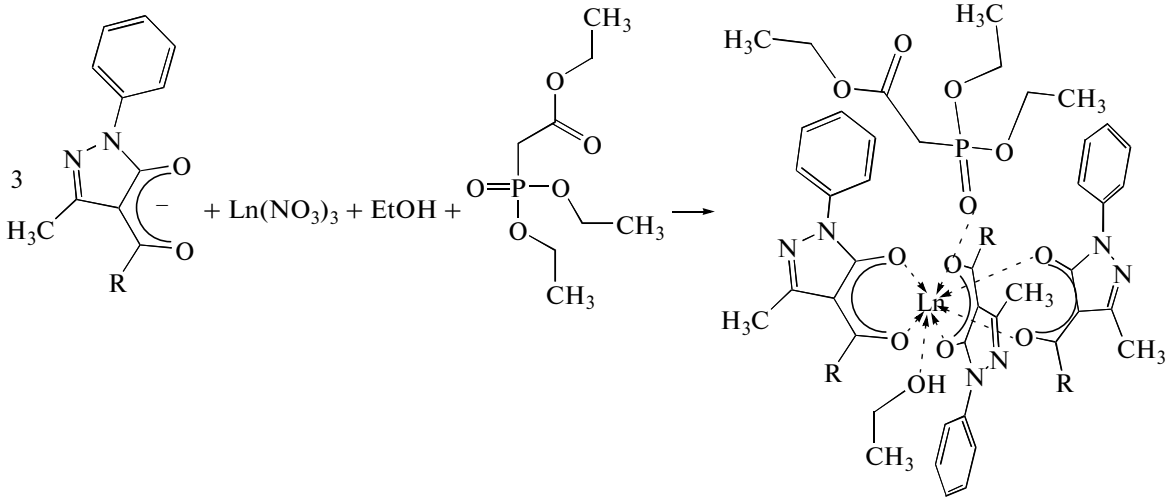
Selected crystallographic data and experimental and structure refinement parameters are listed in Table 2. The coordinates of atoms and other parameters were deposited with the Cambridge Crystallographic Data Centre (no. 906743; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The results of quantum-chemical calculations showed that the enthalpies of reactions (1) and (2) are the following: −6.06 and −19.74 (dichlorvos), −11.95 and −29.55 (tribufos), −28.64 and −34.19 (TPPO), −7.64 and −18.99 (LP), and −13.35 and −18.01 (sarin) kJ/mol, respectively. These data indicate that the reactions of substitution for an out-of-sphere solvent molecule by LP, dichlorvos, and sarin are thermodynamically allowed.

The negative values of enthalpies of reactions (1) and (2) for the model object and for the phosphorus-containing toxic substances (dichlorvos and sarin) are quite expected, since the affinity of the diketonate rare-earth metal complexes to the addition of oxygen-donating additional ligands is well known. The complexes with TPPO known from literature were studied by modeling in order to compare the calculation results with the published data on the stability of the complexes. The calculation data suggest LP as a model object for chemical luminescence sensors to phosphorus-containing toxic substances.

The mixed-ligand complexes of lanthanides with LP and acylpyrazolones are prepared in high yields using the method for the synthesis of the diketonate complexes by the reaction



The crystal structure of complex $Sm(Q_S)_3(EtOH)(LP)$ is formed by molecules closely packed due to weak stacking interactions (Fig. 1). The central samarium atom is coordinated by eight oxygen atoms forming a distorted archimedean antiprism. Six oxygen atoms in the vertices of the antiprism belong to three bidentate-chelating acylpyrazolone molecules, and other two atoms belong to the alcohol molecule and ligand LP. The Sm–O bond lengths are as follows: Sm–O(1) 2.408, Sm–O(2) 2.374, Sm–O(3) 2.458, Sm–O(4) 2.317, Sm–O(5) 2.391, Sm–O(6) 2.389, $Sm–O_{LP}(7)$ 2.390, and $Sm–O_{EtOH}(12)$ 2.464 Å. It is remarkable that the Sm–O(7) distance is close to the average value of Sm–O of acylpyrazolone, which is characteristic of the adducts of lanthanide β-diketonates with phosphorus-containing ligands. The hydrogen bond between the proton of the alcohol molecule and the O(10) atom of the ester group of ligand LP (O···O 2.782 Å) stabilizes the molecule of the complex.

The IR spectra of the complexes exhibit broad bands with a maximum at 3070 cm^{-1}related to the out-of-sphere alcohol molecules. The bands of stretching vibrations of the C=C, C=N, and C=O bonds of the coordinated acylpyrazole anion are obtained in a region of 1612–1510 cm^{-1}. The bands at 1470–1440, 1200–1100, and 1044 cm^{-1} can be attributed to vibrations of the P–OEt and P=O bonds and alkyl groups in molecule LP, respectively. The shift of the band corresponding to the P=O bond from 1165 cm^{-1} in free molecule LP to 1170–1192 cm^{-1} in the complexes indicates the coordination of this additional ligand through oxygen bound to the phosphorus atom.

The samarium and europium complexes exhibit the luminescence properties only on cooling to the temperature of liquid nitrogen, emitting in the orange and red spectral ranges, respectively. The dysprosium complex emits in the blue-green range, and the maximum of the broad band is observed at 490 nm. This band is assigned, most likely, to the emission of the ligand and, hence, no significant ligand-to-metal energy transfer is observed for this compound. Contrary to the Sm, Eu, and Dy compounds, the terbium complex exhibits the luminescence properties in the solid state already at ambient temperature, and luminescence is observed in both the solid state and solution. Its luminescence spectrum is typical of the terbium complexes with ligands manifesting the antenna properties. The excitation and luminescence spectra of $Tb(Q_{n\text{Pe}})_3(EtOH)(LP)$ and dihydrate $Tb(Q_{n\text{Pe}})_3(H_2O)_2$ are shown in Fig. 2. Luminescence arising (at λ_{exc} = 356 nm for the transition $^5D_4–^7F_5$ (556 nm) by 1.39 times) is observed for $Tb(Q_{n\text{Pe}})_3(EtOH)(LP)$. This can be explained by the substitution for water by LP and alcohol molecules (quenching can be performed through stretching vibrations of the OH bonds) and also by a slight decrease in symmetry of the nearest coordination environment of the terbium atom. The peak with the maximum at ~356 nm in the coinciding excitation spectra for complexes $Tb(Q_{n\text{Pe}})_3(EtOH)(LP)$ and $Tb(Q_{n\text{Pe}})_3(H_2O)_2$ suggests that the acylpyrazolone anion acts as a single "antenna," whereas the LP molecule is not directly involved in the energy transfer.

Thus, the quantum-chemical studies proved that LP can be used as a model object for the further investigation of the sensor response upon the interaction of phosphorus-containing compounds with terbium acyl pyrazolonates. The structural and spectroscopic data, as well as the chemical analysis results, showed the possibility of formation of mixed-ligand lanthanide complexes with acylpyrazolones and triethoxyphosphoacetate. Luminescence arising for the terbium complex suggests the use of these compounds and their structural analogs as sensors for phosphorus-containing toxic substances. Further we are planning

Table 2. Crystallographic data and experimental and refinement parameters for complex $Sm(Q_S)_3(LP)(EtOH)$

Parameter	Value
FW	1270.56
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	9.1911(4)
b, Å	15.1695(7)
c, Å	20.985(1)
α, deg	76.148(1)
β, deg	85.905(1)
γ, deg	78.541(1)
V, Å^3	2783.25
ρ_{calcd}, g/cm^3	1.516
Z	2
θ Range, deg	1.41–30.42
Index range	$-13 \le h \le 13$, $-20 \le k \le 21$, $-29 \le l \le 29$
Number of measured/independent reflections (R_{int})	33727/16622 (0.0370)
Number of reflections with $I > 2\sigma(I)$	13709
Goodness-of-fit on F^2	0.986
Number of refined parameters	927
R_1 and wR_2, $I > 2\sigma(I)$	0.0388 and 0.0772
R_1 and wR_2 for all reflections	0.0517 and 0.0821
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	1.070, –0.664

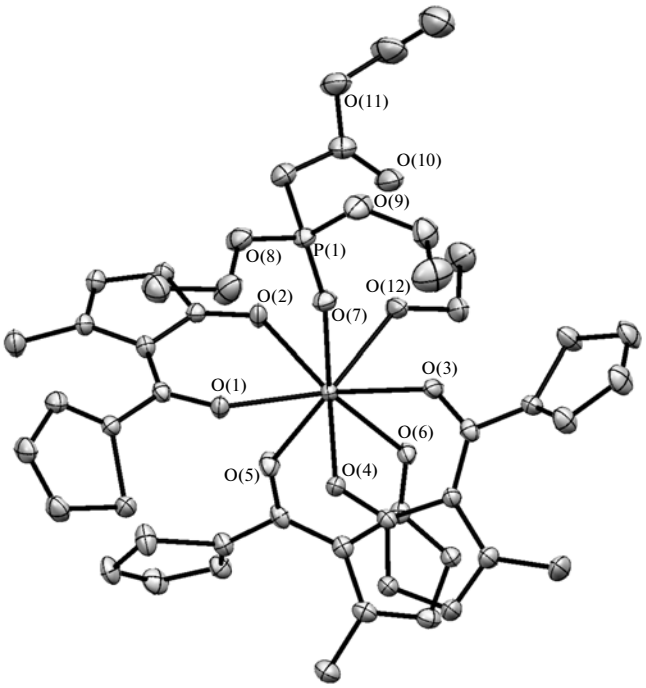


Fig. 1. Structure of complex $Sm(Q_S)_3(EtOH)(LP)$ according to the X-ray diffraction data. Hydrogen atoms and phenyl groups are omitted for clarity.

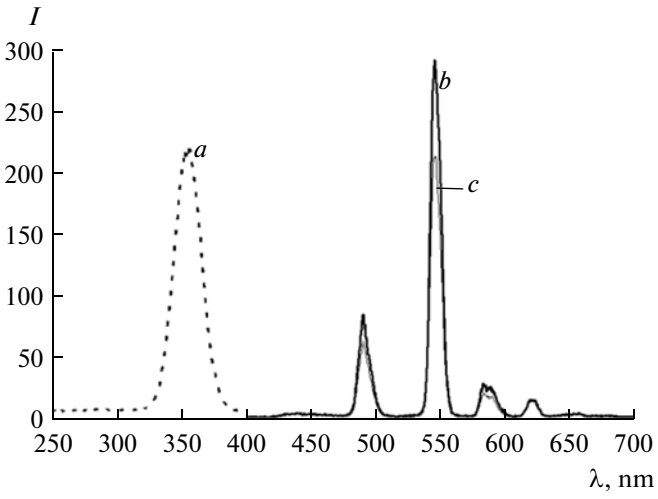


Fig. 2. Excitation spectra of $Tb(Q_{n\text{Pe}})_3(EtOH)(LP)$ (*a*) and the luminescence spectra of (*b*) $Tb(Q_{n\text{Pe}})_3(H_2O)_2$ and (*c*) $Tb(Q_{n\text{Pe}})_3(EtOH)(LP)$ ($c_{complex} = 10^{-3}$ mol/L, EtOH, $\lambda_{exc} = 356$ nm).

to study the addition products of a series of phosphorus-containing molecules with different substituents to acyl pyrazolonates of rare-earth metals to reveal the dependence of the luminescence properties on the character of these substituents, which is needed for the development of efficient sensor devices.

ACKNOWLEDGMENTS

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