Synthesis, structure, and luminescent properties of Pr^{III} complexes with pyrazole-derived 1,3-diketone and 1,10-phenanthroline*

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The interaction of $PrCl_3$ with 1,3-bis(1,3-dimethyl-1*H*-pyrazol-4-yl)-1,3-propanedione in aqueous ethanol in the presence of a base and 1,10-phenanthroline was studied. It was shown that the composition of the products was dependent on the reaction conditions. The solvate $[Pr(L)_3(Phen)] \cdot 3Pr^iOH$ crystallizes in a monoclinic crystal system ($P2_1/c$ space group, $a = 12.2239(12)$ Å, $b = 20.3403(19)$ Å, $c = 26.134(3)$ Å, $\beta = 102.380(2)°$ at 150 K). Absorption spectra of the complex in solution, as well as the spectra and the kinetic parameters of photoluminescence were investigated.

Key words: coordination compounds, praseodymium, 1,3-diketones, pyrazole, luminescence.

Lanthanide complexes with various organic ligands often possess interesting luminescent properties; this is related to the so-called antenna effect, the idea of which is in the absorption of the excitation radiation by the organic part of the molecule and the subsequent transfer of energy to the central ion.[1—3] Owing to this effect, it is possible to solve the problem of the small absorption cross-section of free Ln^{3+} ions and increase the luminescence intensity by several orders of magnitude.

Such complexes are widely used in modern techniques and technologies, in particular, as materials for organic photonics, electronics, fluorescent microscopy, and many other areas. The largest number of works in this area was carried out for Eu^{3+}, Tb^{3+}, and Sm^{3+} compounds, which possess the strongest luminescence in the visible region of spectrum.[4,5]

Derivatives of other lanthanides, in particular, Pr^{3+}, while being considerably less studied, are also interesting due to their emission properties in the visible and near-IR regions of the spectrum.

It is well known that for the design of complexes possessing good luminescent properties, the inclusion of hydroxyl-containing solvents in the inner sphere of a molecular complex should be avoided, in particular, this includes water or alcohols, because they can efficiently quench luminescence by multiphonon relaxation processes *via* OH-oscillators. One of the methods for removing such molecules involves the introduction of additional ligands, for example, bidentate tertiary amines (2,2-bipyridyl or 1,10-phenanthroline), in the complex structure. In addition, such supplementary ligands can also take the role of an antenna, increasing the efficiency of the transformation of energy.[6]

The goal of this work is the synthesis and the study of luminescent properties of Pr^{III} complex compounds with a new class of ligands, 1,3-diketones containing a pyrazole fragment, in particular, 1,3-bis(1,3-dimethyl-1*H*-pyrazol-4-yl)-1,3-propanedione. The obtained compounds can be interesting for the development of emissive and supporting layers in various optoelectronic devices.

Results and Discussion

The HL ligand (**1**) (Scheme 1) was synthesized by Claisen condensation of 1-(1,3-dimethyl-1*H*-pyrazol-4-yl)ethanone with methyl 1,3-dimethyl-1*H*-pyrazole-4-carboxylate in the presence of NaH according to the procedure described earlier.[7]

The reaction of $PrCl_3$ with ligand **1** and 1,10-phenanthroline (reactant molar ratio of 1 : 3 : 1) in aqueous ethanol at 40 °C in the presence of a stoichiometric amount of NaOH (reaction time of 0.5 h) gave a blue-green com-

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plex with a composition given by $[Pr(L)_3(H_2O)_2]$ (**2**) (according to elemental analysis). Such a result is not typical, since under these conditions, a complex of the expected composition is usually formed directly, and it does not contain the the inner-sphere water or ethanol molecules.[8]

Nonetheless, refluxing complex **2** in an ethanol solution in the presence of a 2.5-fold molar excess of 1,10-phenanthroline afforded the expected complex **3** with a composition given by $[Pr(L)_3(Phen)]$ in high yield.

In subsequent experiments, the reaction duration was increased to 3 h, and the temperature was increased to 80 °C (heating in a closed container), which resulted in the formation of compound **3** in one step (see Scheme 1).

Recrystallization of complex **3** from isopropanol made it possible to obtain crystals of unstable solvate $[Pr(L)_3(Phen)]\cdot 3Pr^iOH$ ($\mathbf{3}\cdot 3Pr^iOH$), the structure of which was determined by X-ray diffraction and was deposited with the Cambridge Crystallographic Data Center (CCDC 1450262). The light green transparent $\mathbf{3}\cdot 3Pr^iOH$ crystal at 150 K possesses a monoclinic structure, the space group is $P2_1/c$. The structure of the complex molecule **3** and the crystal packing are shown in Figs 1 and 2, respectively.

The coordination polyhedron $\{PrO_6N_2\}$ is a distorted square antiprism. The Pr—O bond lengths are somewhat different from each other. The average Pr—O bond length is 2.410 Å, which is virtually the same as the one found in the $[Pr(dbm)_3bipy]$ complex (2.409 Å). The Pr—N bond lengths are 2.684 and 2.687 Å.[9] The phenanthroline ring is practically flat (the angle between the planes is 2.21°), while the pyrazole moieties are rotated relative to the chelate ring plane by 9.22—26.96°. The phenyl groups in the dibenzoylmethane derivative act in a similar manner,

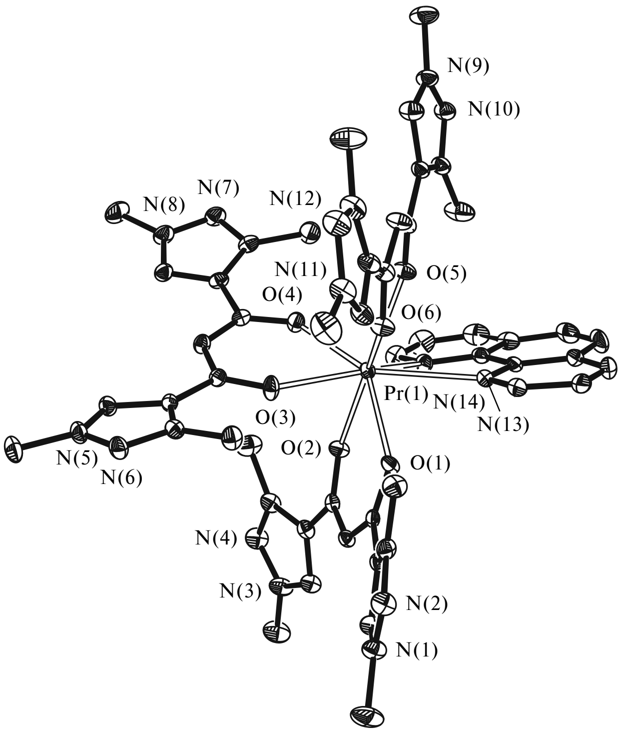
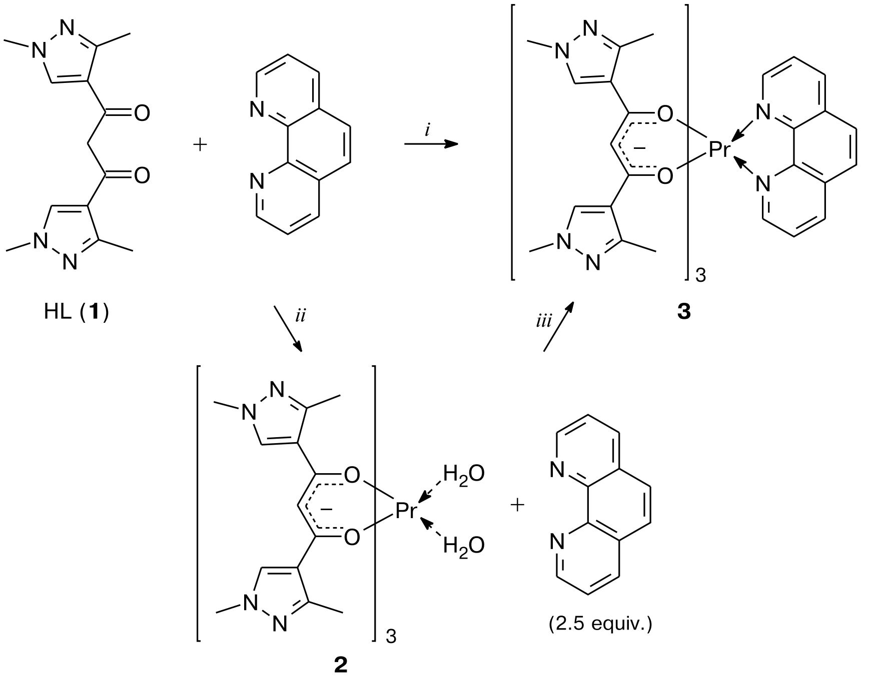


Fig. 1. Molecular structure of complex **3** (solvent molecules and hydrogen atoms are omitted, thermal ellipsoids are given with a 50% probability).

Scheme 1



Reaction conditions: *i.* $PrCl_3$, NaOH, H_2O/EtOH, 3 h, 80 °C; *ii.* $PrCl_3$, NaOH, H_2O/EtOH, 0.5 h, 40 °C; *iii.* EtOH, 2.5 h, 80 °C.

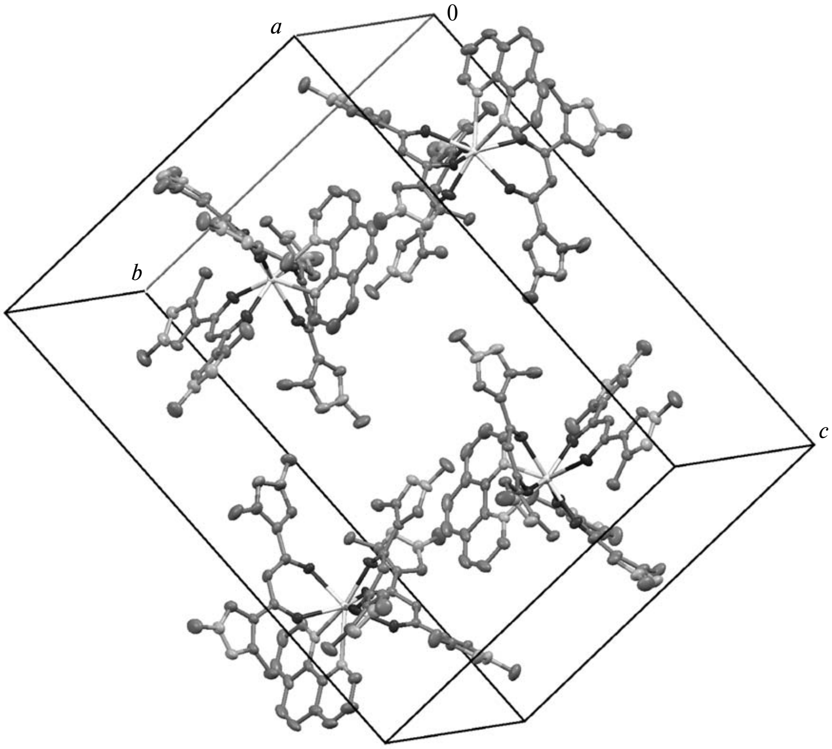


Fig. 2. Packing of complex **3**·3Pr^{i}OH in a crystal (solvent molecules and hydrogen atoms are omitted, thermal ellipsoids are given with a 50% probability).

with the rotation angles reaching 24.18°. The diketone moieties are flat, with the O—Pr—O angles changing insignificantly (from 70.02° to 72.02°), the N—Pr—N angle is equal to 60.99°. Some of the bond lengths and bond angles found in the molecular structure of complex **3** are given in Table 1.

Molecules in the crystal form chains, which are stabilized due to the numerous weak interactions CH...N and hydrogen bonds with solvent molecules.

The absorption spectra of solutions of complex **3** and free ligands in acetonitrile were recorded at room temperature in the wavelength region from 200 to 800 nm. The solution concentration was $5 \cdot 10^{-5}$ mol L^{-1}.

It should be noted that the chosen combination of ligands ensures a high optical absorption of complex **3** in the wavelength range of 200—387 nm with pronounced maxima at 250 and 350 nm (Fig. 3). Therefore, subsequently a laser with a wavelength of 355 nm was chosen for optical excitation of the complex for the purpose of measuring photoluminescence.

In the photoluminescence spectrum of complex **3** (Fig. 4, the following transitions are observed: $^1D_2 \rightarrow {}^3H_2$ (595 nm), $^1D_2 \rightarrow {}^3H_3$ (605 nm), $^1D_2 \rightarrow {}^3H_4$ (610 nm), $^1I_6 \rightarrow {}^3H_6$ (618 nm), $^3P_1 \rightarrow {}^3H_6$ (622 nm), $^3P_0 \rightarrow {}^3H_6$ (630 nm), $^3P_1 \rightarrow {}^3F_2$ (648 nm), and $^3P_0 \rightarrow {}^3F_2$ (651 nm). The complex **3** luminescence band with the strongest intensity is in the region of 605 nm, which corresponds to the energy transition $^1D_2 \rightarrow {}^3H_3$. The energy diagram and the transitions of the Pr^{3+} ion observed in the spectrum are shown in Fig. 5.[5,10]

The kinetic dependencies of the specified bands of the luminescence spectrum of the praseodymium(III) complex

Table 1. Selected bond lengths and bond angles in the complex **3** molecule

Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg
Pr(1)—O(1)	2.417(2)	Pr(1)—N(2)	2.684(3)	O(1)—Pr(1)—O(2)	71.27(9)
Pr(1)—O(2)	2.405(3)	C(1)—C(2)	1.475(5)	O(3)—Pr(1)—O(4)	71.02(9)
Pr(1)—O(3)	2.392(3)	C(2)—C(3)	1.401(6)	O(5)—Pr(1)—O(6)	70.02(9)
Pr(1)—O(4)	2.398(2)	C(3)—C(4)	1.397(6)	N(1)—Pr(1)—N(2)	60.01(9)
Pr(1)—O(5)	2.435(3)	C(4)—C(5)	1.483(5)	O(1)—C(2)—C(3)	124.74(9)
Pr(1)—O(6)	2.416(3)	O(1)—C(2)	1.273(5)	C(2)—C(3)—C(4)	124.54(4)
Pr(1)—N(1)	2.678(3)	O(2)—C(4)	1.267(5)	C(3)—C(4)—O(2)	124.91(4)

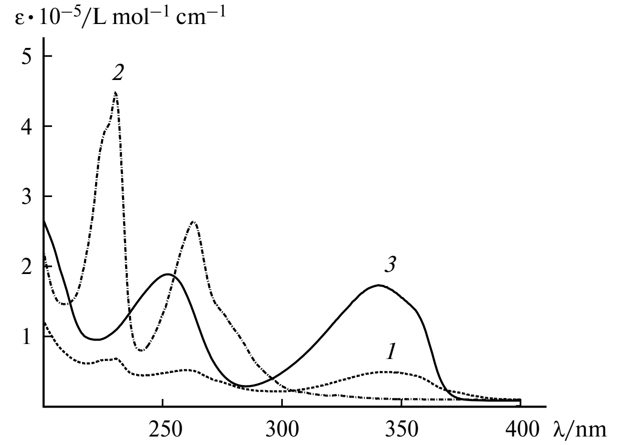


Fig. 3. Absorption spectra of ligand HL (*1*), 1,10-phenanthroline (*2*), and complex **3** (*3*) in solution.

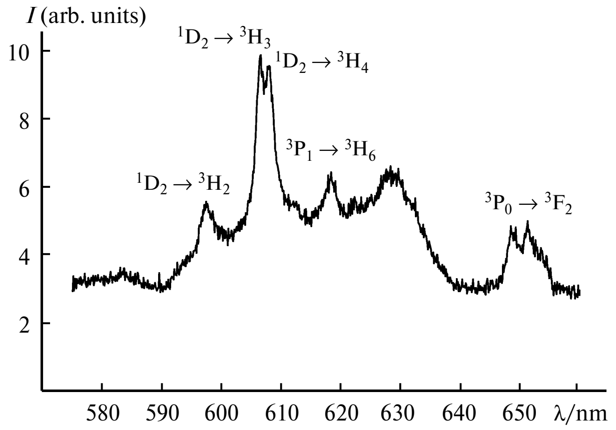


Fig. 4. Photoluminescence spectrum of complex **3** at $\lambda_{ex} = 355$ nm.

are shown in Fig. 6. The presence of several linear regions in the obtained dependencies in logarithmic scale indicates the contribution of several (two) elementary exponential processes. Deconvolution of the experimental data by the Levenberg—Marquardt algorithm made it possible to determine the lifetimes and the amplitudes of the contributions (A_1, A_2) of the elementary exponential processes to the general relaxation picture (Table 2). From the obtained data it follows that with a decrease of the photoluminescence registration wavelength from 610 to 510 nm, a decrease of the contribution of the component with a longer relaxation time and an increase of the contribution of the component with a shorter relaxation time are observed. The same behavior was observed when increasing the recorded wavelength of luminescence from 610 to 650 nm. In the region of 610 nm the component with a longer relaxation time makes the greatest contribution.

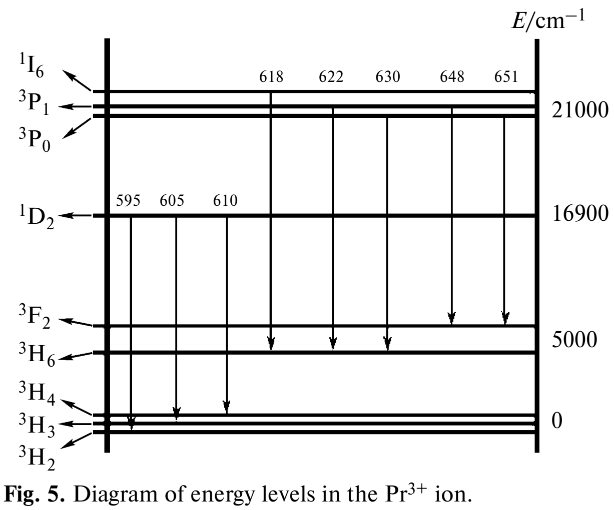


Fig. 5. Diagram of energy levels in the $\mathrm{Pr^{3+}}$ ion.

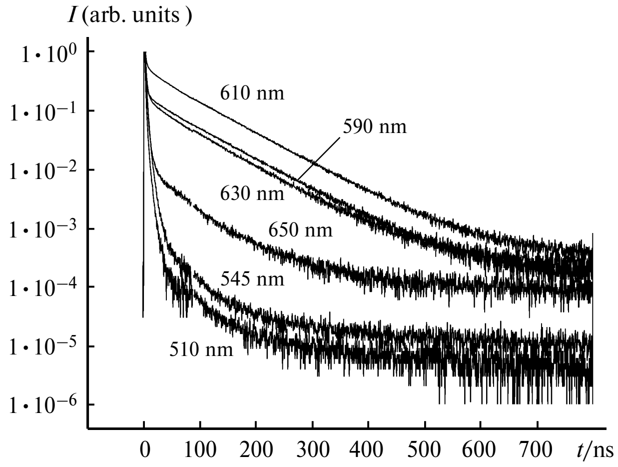


Fig. 6. Kinetic dependencies of photoluminescence of complex **3** in different spectral ranges at $\lambda_{ex} = 376$ nm.

A comparison of the obtained relaxation times with those found in literature[11] suggests that the component with the long decay time most probably corresponds to a radiative relaxation process from the resonance levels of the praseodymium(III) ion. The short decay time, apparently, corresponds to the electron excitation transfer from the ligand triplet level to the resonance levels of the central ion. Thus, due to the spectral separation it is possible to observe two processes, which are characterized by

Table 2. Amplitudes (A) and lifetimes (τ) of elementary exponential contributions in the photoluminescence relaxation process of complex **3** at $\lambda_{ex} = 376$ nm and registration in various spectral ranges

λ/nm	τ_1/ns	A_1	τ_2/ns	A_2
510	—	—	1.5	2.5
545	—	—	2.3	2.4
590	80.8	0.17	—	—
610	81.3	0.48	—	—
630	77.1	0.14	—	—
650	78.3	0.008	2.3	2.4

different lifetimes of the exited state, that is, the ligand fluorescence (spectral region of 510—545 nm) and the subsequent phosphorescence of the Pr^{3+} ion (the region of 590—650 nm).

Since the energy of the T_1 triplet level of ligand **1** was determined earlier[12] and is equal to 21300 cm^{-1}, the transfer of energy to the $^1D_2$ level of the Pr^{3+} ion (16900 cm^{-1}) is the most probable. The sensitization of the higher levels $^3P_0$ and $^1I_6$ (21000 cm^{-1}) is also possible, but is considerably less efficient. Such a picture corresponds to the observed distribution of intensity in the luminescence spectrum of complex **3**, where the band at 605—610 nm, corresponding to the $^1D_2 \to 3H_j$ transitions (j = 3.4), is the principal one. The triplet level T_1 of 1,10-phenanthroline (E = 22100 cm^{-1}) can take part in the sensitization of high-energy levels $^3P_0$ and $^1I_6$; however, as it follows from the analysis of the spectrum, the efficiency of such a process is small.

In conclusion, the interaction of the new ligand 1,3-bis(1,3-dimethyl-1*H*-pyrazol-4-yl)-1,3-propanedione, with $PrCl_3$ in aqueous ethanol in the presence of a base and an additional ligand (1,10-phenanthroline) proceeds in two steps and depends on the temperature and the reaction time. The hydrated complex $[Pr(L)_3(H_2O)_2]$ is formed easily and under mild conditions, while the substitution of 1,10-phenanthroline for water molecules in it requires more drastic conditions.

The study of the absorption spectra in a solution and photoluminescence in the solid state of complex $[Pr(L)_3(Phen)]$ showed that ligand HL (**1**) in combination with 1,10-phenanthroline quite efficiently sensitizes the Pr^{3+} ion photoluminescence. The lifetime of the excited state of complex **3** corresponds to the lifetimes of praseodymium(III) complexes with a similar structure found in literature.

Experimental

A solution of $PrCl_3$ (1 mol L^{-1}) was prepared by dissolution of an accurately weighed amount of $PrCl_3 \cdot 6H_2O$ (99.9%, Aldrich, USA) in distilled water. The concentration was additionally determinated by complexometric titration. A solution of NaOH (1 *M*) was prepared by dissolution of a weighed amount of solid alkali (reagent grade) in distilled water and the subsequent titration with a solution of HCl to determine the accurate concentration. The other reagents were purchased from Aldrich and used without additional purification.

Elemental analysis was performed on an Elementar Vario Micro cube analyzer (Elementar Analysensysteme GmbH, Germany). The content of praseodymium was determined by complexometry after decomposition of the sample with 70% nitric acid (high purity grade).

Absorption spectra of solutions were recorded on a Perkin Elmer Lambda 45 spectrophotometer in quartz cells with a 1-cm optical pathway. Acetonitrile purchased from HPLC SuperGradient (Panreac, Spain) was used as a solvent.

Photoluminescence spectra of the complex in the visible region of the spectrum were recorded at room temperature, using an SDL-1 double monochromator and a Hamamatsu H8259-01 PMT. A Lotis Tii LS-2134UTF solid-state pulsed laser with a radiation wavelength of 355 nm was used as a source of excitation, the pulse duration was 6 ns, the frequency was 15 Hz. A powdered sample was placed into quartz cylindrical cells 5 mm in diameter.

Kinetic dependencies of photoluminescence intensity upon pulsed optical excitation were measured by time-correlated single photon counting on a MicroTime 200 installation (PicoQuant, Germany), using a direct start-stop measurement scheme. The sample was placed on the microscope stage of an Olympus microscope incorporated in the installation. A 376-nm wavelength PDL 828 semiconductor laser was used as a source of excitation, the pulse duration was 50 ps, the frequency was 100 kHz. Using optical interference filters (Chroma, USA) with a half-width of the transmission band equal to 10 nm, the bands with the following wavelength were separated from the luminescence spectrum of the complex: 510, 545, 590, 610, 630, and 650 nm. The measurements with a picosecond time resolution were performed using an incorporated detector based on a τ-SPAD single-photon avalanche photodiode and a PicoHarp 300 module for time-correlated single photon counting.

Diaqua-tris[1,3-bis(1,3-dimethyl-1*H*-pyrazol-4-yl)-1,3-propanedionato]praseodymium(III) ($[Pr(L)_3(H_2O)_2]$, 2). 1,10-Phenanthroline (0.09 g, 0.5 mmol) and diketone (0.39 g, 1.5 mmol) were dissolved in ethanol (10 mL) with heating, followed by the addition of a solution of $PrCl_3$ (0.98 mol L^{-1}, 0.5 mL, 0.5 mmol). The resulting light green solution was heated to 40 °C, followed by a dropwise addition of a solution of NaOH (0.97 *M*, 1.5 mL) with vigorous stirring. The mixture was stirred for 30 min, concentrated to dryness, and extracted with CH_2Cl_2 (50 mL). The organic phase was washed with water (5 mL), dried with $MgSO_4$, and concentrated *in vacuo* to 5 mL, which was accompanied by the crystallization of the complex. The crystals were collected by filtration, washed with hexane (5 mL), and dried *in vacuo* (1 Torr) at 40 °C until the weight was constant. The yield was 0.365 g (76%), light green finely crystalline product. Found (%): C, 49.11; H, 5.10; N, 17.64; Pr, 14.79. $C_{39}H_{49}N_{12}O_8Pr$. Calculated (%): C, 49.06; H, 5.17; N, 17.60; Pr, 14.76.

Tris[1,3-bis(1,3-dimethyl-1*H*-pyrazol-4-yl)-1,3-propanedionato](1,10-phenanthroline)praseodymium(III) ($[Pr(L)_3(Phen)]$, 3). A mixture of complex **2** (0.19 g, 0.2 mmol) with a solution of 1,10-phenanthroline 0.09 g, 0.5 mmol) in anhydrous ethanol (10 mL) was heated in a sealed tube with stirring at 80 °C. After 1 h, a clear solution was formed, which after 1 h became opaque, indicating the crystallization of the complex. After another 30 min, the heating was removed, and the tube was slowly cooled down. The crystalline precipitate was separated, washed with cold ethanol (1 mL), and dried *in vacuo* (1 Torr) at 40 °C until the weight was constant. The yield of complex **3** was 0.195 g (89%). Found (%): C, 55.91; H, 4.93; N, 17.80; Pr, 12.99. $C_{51}H_{53}N_{14}O_6Pr$. Calculated (%): C, 55.74; H, 4.86; N, 17.84; Pr, 12.82.

The one-step synthesis was carried out similarly to that used for obtaining complex **2**. The reaction was carried out in a vessel for operation at elevated pressure. After addition of a solution of NaOH, the vessel was hermetically sealed and allowed to stand for 3 h at 80 °C. Then, it was slowly cooled down. The product was separated according to the method described above. The yield of complex **3** was 0.445 g (81%) (taken 1.5 mmol of the ligand). Found (%): C, 55.88; H, 5.01; N, 17.90; Pr, 12.96. $C_{51}H_{53}N_{14}O_6Pr$. Calculated (%): C, 55.74; H, 4.86; N, 17.84; Pr, 12.82.

Recrystallization of complex **3** from boiling isopropanol with subsequent slow cooling of the solution gave light green plate crystals of solvate $[Pr(L)_3(Phen)] \cdot 3Pr^iOH$ suitable for X-ray diffraction and rapidly decomposing in air.

X-ray diffraction study. X-ray diffraction study was performed according to the standard procedure on a Bruker SMART Apex II automated diffractometer equipped with a CCD-detector (λ_{Mo}, graphite monochromator, ω-scan technique). The structure was calculated using the SHELXTL PLUS (PC-version) software package. Refinement was performed using the SHELXTL-97 program.[13,14] For complex **3**: $C_{57}H_{69}N_{14}O_8Pr$, M = 1219.17, space group $P2_1/c$, a = 12.2239(12) Å, b = 20.3403(19) Å, c = 26.134(3) Å, β = 102.380(2)°, V = 6346.9(11) $Å^3$ (at 150(2) K), Z = 4, number of measured reflections 69007, of them 11174 reflections were independent (R(int) = 0.0839); ρ_{calc} = 1.276 g cm^{-3}, μ = 8.28 cm^{-1}, R_1 = 0.0572, wR_2 = 0.11439. The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Center (CCDC 1450262) (http://www.ccdc.cam.ac.uk/data_request/cif).

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