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Synthesis of Lanthanide Pyrazolonate Complexes by the Reactions of 1-Phenyl-3-Methyl-4-(2,2-Dimethylpropan-1-oyl)pyrazol-5-One with Metallic Lanthanides. Crystal Structures of $[Ln(Bu^t\text{-}PMP)_3]_2$ (Ln = Gd, Tb, and Tm)

A. V. Safronova, L. N. Bochkarev*, and E. V. Baranov

Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,
ul. Tropinina 49, Nizhni Novgorod, 603600 Russia
**e-mail: lnb@iomc.ras.ru*

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Abstract—Lanthanide pyrazolonate complexes $Ln(Bu^t\text{-}PMP)_3$ (Ln = Pr, Nd, Gd, Tb, Tm, and Lu) are synthesized by the reactions of 1-phenyl-3-methyl-4-(2,2-dimethylpropan-1-oyl)pyrazol-5-one (Bu^t-PMPH) with metallic lanthanides in the presence of catalytic amounts of the corresponding metal triiodides. The yields of the products are close to quantitative ones. The synthesized compounds can sublime in vacuo (10^{-3} Torr) in the temperature range from 235 to 270°C. X-ray diffraction analyses of the sublimed complexes show that they are dimers $[Ln(Bu^t\text{-}PMP)_3]_2$ (Ln = Gd, Tb, and Tm) in which metal atoms are linked by two bridging pyrazolonate fragments. The coordination environment of the lanthanide is a distorted one-capped trigonal prism.

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INTRODUCTION

It is known that metallic lanthanides react with diverse organic and organometallic substrates to form coordination or organometallic compounds of various types [1–5]. We have recently shown that the reactions of metallic lanthanides with 1-phenyl-3-methyl-4-isobutyrylpyrazol-5-one (*iso*-Pr-PMPH) in the presence of catalytic amounts of the corresponding metal triiodides afford the pyrazolonate complexes Ln(*iso*-Pr-PMP)$_3$ in high yields [6]. The lanthanide derivatives with various 4-acylpyrazolonate ligands are used as efficient emissive materials in organic light-emitting diodes [7–9]. The commonly used synthesis of these compounds includes the reactions of lanthanide chlorides or nitrates with pyrazolone in the presence of NaOH (KOH) in aqueous or alcoholic media [10]. The formed lanthanide complexes contain coordinated water or alcohol molecules, which noticeably decreases their luminescence characteristics [8]. Therefore, the development of new general methods for the synthesis of nonsolvated lanthanide pyrazolonate complexes is an urgent problem.

In this work, we found that the reactions of metallic lanthanides with pyrazolone (Bu^t-PMPH) proceeded similarly to the earlier studied reactions with *iso*-Pr-PMPH and can be used as a preparative method for the synthesis of the nonsolvated complexes $Ln(Bu^t\text{-}PMP)_3$. The structures of the synthesized compounds were determined by X-ray diffraction analysis.

EXPERIMENTAL

All reactions were carried out in vacuo or in argon using a standard Schlenk technique. The solvents used were thoroughly purified and degassed. Compounds Bu^t-PMPH [11] and $LnI_3(THF)_{3.5}$ [12] (THF is tetrahydrofuran) were synthesized according to described procedures.

IR spectra were recorded on an FSM 1201 FT-IR light-emitting diodes spectrometer. Samples of the compounds were prepared by pellet pressing (the substance to KBr ratio was 1 : 200). NMR spectra were measured on a Bruker DPX-200 spectrometer (^{1}H NMR: 200 MHz, ^{13}C NMR: 50 MHz). Tetramethylsilane was used as an internal standard. Differential scanning calorimetry (DSC) was carried out on a DSC 204 F1 Phoenix instrument (Netzsch) in a dry argon flow (flow rate 20 cm^3/min, heating rate 5°C/min).

Synthesis of $Pr(Bu^t\text{-}PMP)_3$ (I). (a) Iodine (I_2) (0.0063 g, 0.025 mmol) in THF (3 mL) was added to metallic praseodymium as filings (0.45 g, 3.19 mmol). The mixture was stirred for 5 min at 60°C until the solution decolorized. Then a solution of pyrazolone Bu^t-PMPH (0.26 g, 1.01 mmol) in THF (5 mL) was added to the reaction mixture, and the resulting mixture was stirred for 1.5 h at 70°C. The reaction solution was separated from a metal excess and the PrI_3 catalyst by centrifuging. After the solvent was removed, the residue was washed with hexane and dried in vacuo at ambient temperature. The elemental analysis data and the IR spectrum of the isolated product correspond to the formula $Pr(Bu^t\text{-}PMP)_3 \cdot THF$. An additional keeping of the compound in vacuo at 100°C for 3 h results in the formation of the nonsolvated complex $Pr(Bu^t\text{-}PMP)_3$ as a pale green amorphous (DSC) substance. The yield of compound **I** was 0.30 g (98%). The compound crystallizes upon sublimation in vacuo.

IR (KBr), ν, cm^{-1}: 3071, 1090, 1060, 1034, 999 ν; 851, 757 γ(C–H)$_{Ar}$; 2931 ν, 1386, 1310 β$_s$, 1174, 1155 β(C–H)$_{Alk}$; 1607 ν$_{as}$(C···O); 1590 ν, 1500 ν$_{as}$, 1474 ν, 1239 ν$_s$(C=C)$_{Ar}$; 1523, 1455, 1398 ν(pyrazole ring); 905, 878 ν(C–C); 692, 635 β, 605 ν(chelate ring); 514 ν(Ln–O).

(b) $PrI_3(THF)_{3.5}$ (0.0094 g, 0.01 mmol) was added to a mixture of metallic Pr (0.30 g, 2.13 mmol) and Bu^t-PMPH (0.16 g, 0.62 mmol) in THF (10 mL). The mixture was stirred for 1.5 h at 70°C. Complex **I** was isolated as described above. The yield of compound **I** was 0.18 g (95%).

Synthesis of $Nd(Bu^t\text{-}PMP)_3$ (II). The synthesis and isolation were carried out as described for complex **I**. The yield of compound **II** as a pale lilac amorphous substance was 0.32 g (93%).

IR (KBr), ν, cm^{-1}: 3071, 1098, 1057, 1030, 999 ν, 852, 757 γ(C–H)$_{Ar}$; 2931 ν, 1371, 1337 β$_s$, 1155, 1144 β(C–H)$_{Alk}$; 1610 ν$_{as}$(C···O); 1584 ν, 1500 ν$_{as}$, 1474 ν, 1239 ν$_s$(C=C)$_{Ar}$; 1527, 1451, 1398 ν(pyrazole ring); 908, 878 ν(C–C); 692, 639 β, 605 ν(chelate ring); 514 ν(Ln–O).

Synthesis of $Gd(Bu^t\text{-}PMP)_3$ (III). The synthesis and isolation were carried out as described for complex **I**. The yield of compound **III** as a colorless amorphous substance was 0.35 g (97%).

IR (KBr), ν, cm^{-1}: 3071, 1098, 1060, 1034, 999 ν, 852, 757 γ(C–H)$_{Ar}$; 2931 ν, 1386, 1310 β$_s$, 1174, 1155 β(C–H)$_{Alk}$; 1610 ν$_{as}$(C···O); 1591 ν, 1500 ν$_{as}$, 1474 ν, 1238 ν$_s$(C=C)$_{Ar}$; 1523, 1455, 1398 ν(pyrazole ring); 905, 878 ν(C–C); 692, 635 β, 605 ν(chelate ring); 514 ν(Ln–O).

Synthesis of $Tb(Bu^t\text{-}PMP)_3$ (IV). The synthesis and isolation were carried out as described for complex **I**. The yield of compound **IV** as a colorless amorphous substance was 0.29 g (97%).

IR (KBr), ν, cm^{-1}: 3071, 1090, 1060, 1034, 999 ν, 852 γ, 757 γ(C–H)$_{Ar}$; 2931 ν, 1386, 1310 β$_s$, 1174, 1155 β(C–H)$_{Alk}$; 1610 ν$_{as}$(C···O); 1595 ν, 1500 ν$_{as}$, 1478 ν, 1239 ν$_s$(C=C)$_{Ar}$; 1523, 1447, 1398 ν(pyrazole ring); 905, 878 ν(C–C); 692, 639 β, 605 ν(chelate ring); 514 ν(Ln–O).

Synthesis of $Tm(Bu^t\text{-}PMP)_3$ (V). The synthesis and isolation were carried out as described for complex **I**. The yield of compound **V** as a colorless amorphous substance was 0.27 g (96%).

IR (KBr), ν, cm^{-1}: 3071, 1098, 1060, 1034, 999 ν, 852, 757 γ(C–H)$_{Ar}$; 2931 ν, 1375, 1310 β$_s$, 1174, 1155 β(C–H)$_{Alk}$; 1610 ν$_{as}$(C···O); 1595 ν, 1500 ν$_{as}$, 1478 ν, 1239 ν$_s$(C=C)$_{Ar}$; 1527, 1451, 1398 ν(pyrazole ring); 905, 878 ν(C–C); 692, 639 β, 609 ν(chelate ring); 514 ν(Ln–O).

Synthesis of $Lu(Bu^t\text{-}PMP)_3$ (VI). The synthesis and isolation were carried out as described for complex **I**. The yield of compound **VI** as a colorless amorphous substance was 0.37 g (97%).

IR (KBr), ν, cm^{-1}: 3071, 1094, 1060, 1034, 999 ν, 852, 757 γ(C–H)$_{Ar}$; 2931 ν, 1375, 1310 β$_s$, 1174, 1155 β(C–H)$_{Alk}$; 1610 ν$_{as}$(C···O); 1595 ν, 1500 ν$_{as}$, 1474 ν, 1239 ν$_s$(C=C)$_{Ar}$; 1523, 1458, 1398 ν(pyrazole ring); 905, 878 ν(C–C); 692, 639 β, 609 ν(chelate ring); 514 ν(Ln–O).

^{1}H NMR ($CDCl_3$), δ, ppm: 1.25 s (27H, $C(CH_3)_3$), 2.53 s (9H, CH_3), 7.12 t (3H, *p*-H(Ph)), 7.26 t (6H, *m*-H(Ph)), 7.88 d (6H, *o*-H(Ph)).

^{13}C NMR ($CDCl_3$), δ, ppm: 19.4, 27.0, 28.7, 41.1, 76.2, 119.9, 124.1, 127.5, 137.7, 144.7, 200.8.

The elemental analysis data for complexes **I–VI** are given in Table 1.

X-ray diffraction analysis. Single crystals of compounds **III**, **IV**, and **V** for X-ray diffraction analysis were obtained by sublimation in high vacuum. The crystallographic data were obtained on Bruker AXS SMART APEX (for **III** and **IV**) and Oxford Xcalibur Eos (for **V**) automated diffractometers (graphite monochromator, MoK_α radiation, ω scan mode, $\lambda = 0.71073$ Å). Reflection intensities were processed using the SAINT [13] (**III**, **IV**) and CrysAlisPro [14] (**V**) programs. The SADABS [15] (**III**, **IV**) and SCALE3 ABSPACK [16] (**V**) programs were used for applying absorption corrections. The structures were solved by a direct method (SHELXTL) [17] and refined by the full-matrix least-squares method for F^2_{hkl} in the anisotropic approximation for all nonhydrogen atoms. Hydrogen atoms were placed in geometrically calculated positions and refined in the riding model. In the symmetrically independent part of complexes **III–V**, one of three pyrazolonate ligands contains the –N=C(Me)– moiety of the pyrazole fragment disordered over two positions. In two pyrazolonate ligands, several methyl groups of the Bu^t substituents are disordered over two positions. The main crystallographic characteristics and the X-ray diffraction experimental parameters for structures **III–V** are listed in Table 2. Selected bond lengths and bond

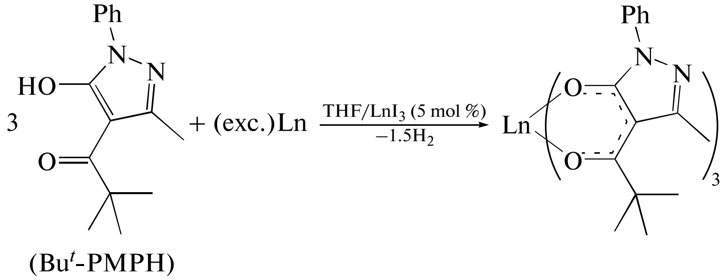
Table 1. Elemental analysis data, the sublimation temperatures, and the melting points of sublimed complexe **I–VI**

Complex	Content (calculated/found, %)			T_s, °C	T_m, °C
	C	H	Ln		
$[Pr(Bu^t\text{-}PMP)_3]_2$ (**I**)	59.21/59.16	5.63/5.70	15.44/15.86	255–260	271.5
$[Nd(Bu^t\text{-}PMP)_3]_2$ (**II**)	59.00/58.93	5.61/5.67	15.74/15.93	260–265	278.8
$[Gd(Bu^t\text{-}PMP)_3]_2$ (**III**)	58.17/58.11	5.53/5.58	16.92/17.35	265–270	249.6
$[Tb(Bu^t\text{-}PMP)_3]_2$ (**IV**)	58.07/58.01	5.52/5.58	17.07/17.13	260–265	293.7
$[Tm(Bu^t\text{-}PMP)_3]_2$ (**V**)	57.45/57.41	5.46/5.51	17.96/17.97	250–255	244.2
$[Lu(Bu^t\text{-}PMP)_3]_2$ (**VI**)	57.08/57.04	5.43/5.48	18.48/18.45	235–245	229.7

angles are given in Table 3. The crystallographic information for the compounds was deposited with the Cambridge Crystallographic Data Centre (nos. 910956 (**III**), 910957 (**IV**), and 910958 (**V**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Metallic lanthanides were found to react with pyrazolone Bu^t-PMPH in a THF solution in the presence of catalytic amounts of LnI_3 and form pyrazolonate complexes in yields close to quantitative ones.



Ln = Pr(I), Nd(II), Gd(III), Tb(IV), Tm(V), Lu(VI)

The interaction between the reactants is accompanied by hydrogen evolution and completes within 1.5–2 h at 70°C. The reaction time was controlled by the amount of the reacted metal. Under these conditions, in the absence of LnI_3, rare-earth metals are inactive towards pyrazolone Bu^t-PMPH. The LnI_3 catalyst can be prepared in situ by the interaction of the rare-earth metal with the corresponding amount of I_2 or can be introduced into the reaction mixture as the preliminarily prepared individual compound $LnI_3(THF)_{3.5}$. In both cases, the reactions proceed similarly. The removal of the solvent from the reaction solution at ambient temperature results in the isolation of pyrazolonate complexes, which, according to the IR spectroscopy data and elemental analysis to lanthanide, contain coordinatively bound THF. The composition of the compounds corresponds to the formula $Ln(Bu^t\text{-}PMP)_3 \cdot THF$. The heating of the products in vacuo at 100°C for 3–4 h results in the complete removal of the solvate solvent and formation of compounds with the composition $Ln(Bu^t\text{-}PMP)_3$. The nonsolvated lanthanide pyrazolonate complexes isolated in 93–98% yields are amorphous substances stable in air, insoluble in hexane, moderately soluble in CH_2Cl_2, and well soluble in THF. The compounds were characterized by elemental analysis and IR spectroscopy. The diamagnetic lutetium derivative was studied by the NMR method. The compounds can sublime in vacuo without decomposition (10^{-3} Torr) in the range from 235 to 270°C. The sublimed products are crystalline substances with distinct melting points (DSC), and their

Table 2. Main crystallographic data and the X-ray diffraction experimental and refinement parameters for compounds **III–V**

Parameter	Value		
	III	**IV**	**V**
Molecular fortmula	$C_{90}H_{102}N_{12}O_{12}Gd_2$	$C_{90}H_{102}N_{12}O_{12}Tb_2$	$C_{90}H_{102}N_{12}O_{12}Tm_2$
Molecular weight	1858.34	1861.68	1881.70
Temperature, K	100(2)	100(2)	100(2)
Crystal size, mm	0.15 × 0.07 × 0.03	0.42 × 0.15 × 0.09	0.30 × 0.30 × 0.10
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	14.0963(8)	14.1090(6)	13.9678(2)
b, Å	19.3710(11)	19.3582(8)	19.25612(17)
c, Å	16.8854(10)	16.8423(7)	16.9252(2)
β, deg	111.6480(10)	111.6450(10)	111.5915(17)
V, Å^3	4285.5(4)	4275.7(3)	4232.85(10)
Z	2	2	2
ρ_{calcd}, g/cm^3	1.440	1.446	1.476
μ, mm^{-1}	1.602	1.708	2.151
F(000)	1900	1904	1920
θ Scan range, deg	1.88–27.00	1.93–27.00	3.11–27.00
Ranges of indices	$-16 \le h \le 18$, $-23 \le k \le 24$, $-21 \le l \le 12$	$-18 \le h \le 17$, $-24 \le k \le 24$, $-21 \le l \le 21$	$-17 \le h \le 17$, $-24 \le k \le 24$, $-21 \le l \le 21$
Total number of reflections	27417	39087	71056
Number of independent reflections (R_{int})	9325 (0.0669)	9283 (0.0253)	9184 (0.0553)
Goodness-of-fit	1.038	1.051	1.023
R ($I > 2\sigma(I)$)	$R_1 = 0.0487$, $wR_2 = 0.0795$	$R_1 = 0.0304$, $wR_2 = 0.0737$	$R_1 = 0.0264$, $wR_2 = 0.0559$
R (all data)	$R_1 = 0.0864$, $wR_2 = 0.0865$	$R_1 = 0.0406$, $wR_2 = 0.0781$	$R_1 = 0.0391$, $wR_2 = 0.0591$
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	1.281/–0.819	1.313/–0.938	0.978/–0.661

Table 3. Selected bond lengths and bond angles in complexes **III–V**

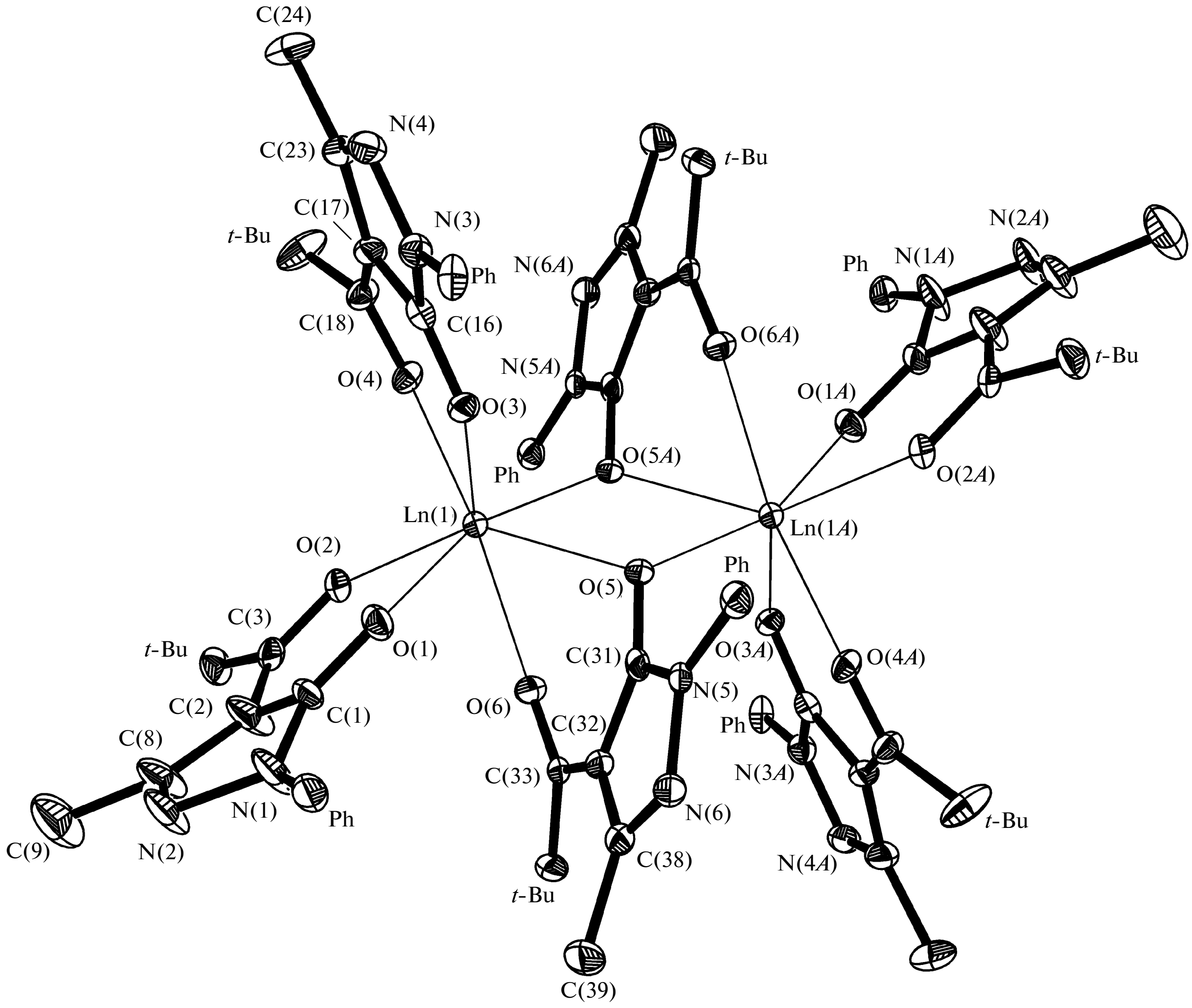
Bond	*d*, Å		
	III	**IV**	**V**
Ln(1)–O(1)	2.265(2)	2.255(1)	2.214(1)
Ln(1)–O(2)	2.301(2)	2.293(2)	2.251(1)
Ln(1)–O(3)	2.262(2)	2.257(2)	2.217(1)
Ln(1)–O(4)	2.285(2)	2.280(1)	2.240(1)
Ln(1)–O(5)	2.418(2)	2.408(1)	2.358(1)
Ln(1)–O(6)	2.389(2)	2.373(2)	2.327(1)
Ln(1)–O(5*A*)	2.373(2)	2.363(1)	2.314(1)
Ln(1)···Ln(1*A*)	3.8772(3)	3.8742(2)	3.7896(2)
O(1)–C(1)	1.265(4)	1.252(3)	1.256(3)
O(2)–C(3)	1.269(4)	1.261(2)	1.260(2)
O(3)–C(16)	1.283(4)	1.275(2)	1.271(2)
O(4)–C(18)	1.268(4)	1.255(3)	1.257(3)
O(5)–C(31)	1.316(3)	1.326(2)	1.322(2)
O(6)–C(33)	1.256(4)	1.251(2)	1.249(2)
N(1)–N(2)	1.415(6)	1.400(4)	1.402(4)
N(1)–C(1)	1.356(5)	1.357(3)	1.360(3)
N(2)–C(8)	1.316(4)	1.317(4)	1.324(4)
N(3)–N(4)	1.386(4)	1.387(3)	1.387(2)
N(3)–C(16)	1.365(4)	1.360(3)	1.363(3)
N(4)–C(23)	1.299(5)	1.306(3)	1.307(3)
N(5)–N(6)	1.402(3)	1.391(2)	1.387(2)
N(5)–C(31)	1.339(4)	1.329(3)	1.351(3)
N(6)–C(38)	1.328(5)	1.317(4)	1.320(3)
Angle	ω, deg		
O(1)Ln(1)O(2)	72.76(8)	73.12(6)	74.45(5)
O(3)Ln(1)O(4)	72.50(8)	72.77(5)	73.97(5)
O(5)Ln(1)O(6)	68.77(7)	69.19(5)	70.17(5)
O(5)Ln(1)O(5*A*)	71.94(8)	71.43(5)	71.58(5)
Ln(1)O(5)Ln(1*A*)	108.06(8)	108.56(5)	108.42(5)

compositions (Table 1) do not differ from those of the amorphous complexes before sublimation.

The X-ray diffraction analyses of the sublimed gadolinium (**III**), terbium (**IV**), and thulium (**V**) complexes show that the compounds are isostructural and represent the centrosymmetric dimeric complexes (figure, Table 3) similarly to the earlier studied derivatives [Ln(*iso*-Pr-PMP)$_3$]$_2$ [6]. The inversion center lies in the plane of the Ln(1)–O(5)–Ln(1*A*)–O(5*A*) fragment. The chelating Bu^t-PMP ligands with the O(1–4) and O(1*A*–4*A*) oxygen atoms are terminal and coordinate to the Ln(1) and Ln(1*A*) atoms, respectively. Similar ligands with the O(5,6) and O(5*A*,6*A*) atoms are bridging. The Ln(1) and Ln(1*A*) atoms are linked with each other by the O(5) and O(5*A*) atoms of the bridging Bu^t-PMP ligand. Thus, the coordination number of the lanthanide atoms in compounds **III– V** is 7. The coordination polyhedron is a distorted one-capped trigonal prism.

The Ln–O distances in complexes **III–V** are comparable with similar distances in the [Ln(*iso*-Pr-PMP)$_3$]$_2$ derivatives (Ln = Gd, Tb, and Tm). The Ln–O bonds of the bridging Bu^t-PMP ligands are elongated compared to Ln–O of the terminal Bu^t-PMP ligands. The Ln(1)···Ln(1*A*) distances in compounds **III–V** are 3.8772(3), 3.8742(2), and 3.7896(2) Å, respectively, which are noticeably shorter than similar distances in [Ln(*iso*-Pr-PMP)$_3$]$_2$: 3.9786(3) (Ln = Gd), 3.9528(2) (Ln = Tb), and 3.8397(3) Å (Ln = Tm). The shortening of the Ln···Ln distances in complexes **III–V** changes the angular characteristics in the planar Ln(1)–O(5)–Ln(1*A*)–O(5*A*) fragment. The O(5)Ln(1)O(5*A*) angles in compounds **III–V** (71.43(5)°–71.94(8)°) are noticeably larger than similar angles in the [Ln(*iso*-Pr-PMP)$_3$]$_2$ complexes (67.77(5)°–68.91(10)°), whereas Ln(1)O(5)Ln(1*A*) in complexes **III–V** have smaller values (108.06(8)°–108.56(5)°) compared to similar angles in [Ln(*iso*-Pr-PMP)$_3$]$_2$ (111.09(10)°–112.23(5)°). The Ln···Ln distances decreases in a series of complexes **III**, **IV**, and **V**, which is consistent with a decrease in the ionic radii of the lanthanide for the coordination number equal to 7: Gd^{3+} (1.012 Å), Tb^{3+} (0.998 Å), and Tm^{3+} (0.943 Å) [18].

In complexes **III–V**, the O(5) and O(6) atoms of the bridging Bu^t-PMP ligand have different coordination modes: μ_2 and μ_1, respectively. Due to this, the O(5)–C(31) and O(6)–C(33) distances differ: 1.316(3) and 1.256(4) Å in **III**, 1.326(2) and 1.251(2) Å in **IV**, and 1.322(2) and 1.249(2) Å in **V**. In the terminal Bu^t-PMP ligand, the O–C distances are similar: 1.265(4)–1.283(4) (**III**), 1.252(3)–1.275(2) (**IV**), and 1.256(3)–1.271(2) Å (**V**). The C–C distances in the chelate ring of the bridging Bu^t-PMP ligand differ noticeably: C(31)–C(32) and C(32)–C(33) are 1.416(5) and 1.444(5) (**III**), 1.411(3) and



Molecular structure of complexes **III–V** with 30% probability ellipsoids. The hydrogen atoms and methyl groups of the Bu^t substituents are omitted. The first carbon atoms of the phenyl substituents at the N(1,3,5) and N(1*A*,3*A*,5*A*) nitrogen atoms are designated as Ph.

1.452(3) (**IV**), and 1.405(3) and 1.453(3) Å (**V**), respectively. Similar C–C distances in the terminal Bu^t-PMP ligands differ insignificantly.

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Translated by E. Yablonskaya