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Synthesis, Structure, and Some Properties of 1-Phenyl-3-Methyl-4-(2,3,4,5,6-Pentafluorobenzoyl)pyrazol-5-one and Its Lanthanide Complexes

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Abstract—A new 4-acylpyrazolone—1-phenyl-3-methyl-4-(2,3,4,5,6-pentafluorobenzoyl)-1*H*-pyrazole-5(4*H*)-one (Pfb-PMPH)—was prepared in a high yield by the reaction of 1-phenyl-3-methylpyrazol-5-one with pentafluorobenzoyl chloride in the presence of calcium and barium hydroxides. On heating this compound in vacuum up to 170°C, elimination of HF takes place to give the intramolecular cyclization product, 1-phenyl-3-methyl-5,6,7,8-tetrafluorochromeno[2,3-c]pyrazol-4(1*H*)-one. The structures of Pfb-PMPH (HL^1) and the cyclization product (L^2) were determined by X-ray diffraction (CIF files CCDC nos. 1010331 (HL^1), 1010332 (L^2), 1010333 (**VI**), 1010334 (**VII**), 1010335 (**VIII**), 1010336 (**IX**), and 1010337 (**X**)). The reactions of Pfb-PMPH with lanthanide silylamides $[(Me_3Si)_2N]_3Ln$ in a THF solution give pyrazolonate complexes $(Pfb\text{-}PMP)_3Ln(THF)$ (Ln = Sm, Eu, Gd, Tb, Lu). The compounds react with Ph_3PO to give the derivatives $(Pfb\text{-}PMP)_3Ln(OPPh_3)_2 \cdot x$EtOH, which were studied by X-ray diffraction. The synthesized lanthanide complexes are luminescent at room temperature and exhibit ligand- and metal-centered emission.

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INTRODUCTION

Acylpyrazolones are heterocyclic analogs of β-diketones forming complexes with most of metals of the Periodic Table [1]. Numerous investigations demonstrated that the nature of the acyl moiety in 4-acylpyrazolones largely determines the properties of both the proper pyrazolonate ligands and the metal complexes based on them. The effect of the nature of the acyl moiety on the physicochemical and luminescence properties of metal complexes is especially pronounced in the lanthanide series [2]. For example, among terbium pyrazolonate complexes, the highest photo- and electroluminescence efficiency are characteristic of compounds containing alkyl substituents in the acyl group of the pyrazolonate ligand [3], whereas in the case of europium complexes, the highest luminescence efficiency was attained upon inclusion of a naphthyl substituent into the acyl group of the pyrazolonate ligand [4]. Lanthanide compounds containing perfluoroalkyl substituents in pyrazolonate ligands are known [5–8], but their luminescence behavior has been scarcely studied. Recently, preparation of 4-acylpyrazolones containing partly fluorinated phenyl substituents was reported [9, 10]. No data on lanthanide complexes with these ligands are available from the literature.

This communication describes the synthesis of a new 4-acylpyrazolone with a pentafluorophenyl substituent in the acyl group and preparation of samarium, europium, gadolinium, terbium, and lutetium complexes with this ligand. The structure and the photophysical properties of the obtained compounds are discussed.

EXPERIMENTAL

All operations with easily oxidizable and hydrolyzable compounds were carried out in vacuum or under argon using standard Schlenk techniques. The solvents used were thoroughly purified and degassed. 1-Phenyl-3-methylpyrazol-5-one, pentafluorobenzoyl chloride, and Ph_3PO (Aldrich) were used as received. The crystal hydrates of calcium and barium hydroxides were dried in vacuum at 120°C to a constant weight. The absence of crystallization water was checked by IR spectroscopy. $[(Me_3Si)_2N]_3Ln$ was synthesized as reported in the literature [11].

IR spectra were recorded on an FSM 1201 FT IR spectrometer. The samples were prepared as films from a $CHCl_3$ solution. The NMR spectra were recorded on a Bruker Avance III-400 spectrometer (^1H NMR: 400 MHz; ^{13}C NMR: 100 MHz; ^{19}F NMR: 376.5 MHz). The chemical shifts are given in ppm and referred to internal tetramethylsilane. The melting points were measured in evacuated sealed capillaries (and were not corrected). Volatile compounds were

chromatographed on a Tsvet 800 chromatograph with a heat conductivity detector using helium as the carrier gas. The mass spectra were run on a Polaris-Q mass spectrometer (Thermo Electron Corporation, USA) using ion trap as mass analyzer. The compound was rubbed into the internal surface of a standard glass cup of the sample injection system. Positive ion mass spectra in the range of mass numbers of 70–990 were recorded at an ionizing energy of 70 eV with sample heating from 50 to 450°C at a rate of 100°C min^{-1}. The UV/Vis spectra of compounds were recorded in CH_2Cl_2 on a PerkinElmer Lambda 25 spectrometer. The photoluminescence spectra were measured on a PerkinElmer LS 55 fluorescence spectrometer.

Synthesis of Pfb-PMPH (HL^1). A suspension of a mixture of $Ca(OH)_2$ (1.43 g, 19.3 mmol) and $Ba(OH)_2$ (0.82 g, 4.8 mmol) in THF (50 mL) was added to a solution of 1-phenyl-3-methylpyrazol-5-one (1.68 g, 9.6 mmol) in THF (50 mL). The reaction mixture was stirred at 70°C for 1 h and cooled to room temperature; then 2,3,4,5,6-pentafluorobenzoyl chloride (2.22 g, 9.6 mmol) was added over a period of 1 min. The mixture was stirred at 80°C for 3 h, cooled to room temperature, and treated with 3 M HCl (350 mL). The precipitate was filtered off, washed with water to neutral reaction, and crystallized from a $C_2H_5OH–H_2O–CHCl_3$ mixture (2 : 2 : 1). HL^1 was formed as colorless crystals in a yield of 3.02 g (85%).

For $C_{17}H_9F_5N_2O_2$		
anal calcd., %:	C, 55.43;	H, 2.44.
Found, %:	C, 55.36;	H, 2.55.

IR (ν, cm^{-1}): 3125 ν(N–H); 2720 ν(O–H···O); 3062, 1074, 1030, 994 $\nu(C_{Ar}–H)$, 822, 804, 754 $\gamma(C_{Ar}–H)$; 2918 ν, 1355, 1299 β_s, 1163 $\beta(C_{Alk}–H)$; 1633 $\nu_{as}(C=O)$; 1598, 1458 ν, 1497 $\nu_{as}(C=C_{Ar})$; 1556, 1444, 1405 ν(pyrazole ring); 900,875 ν(C–C); 689, 656 β, 591 ν(chelate ring); 1100 ν(C–F). ^1H NMR (δ, ppm): 2.04 (s, 3H, CH_3, ^1J_C = 128.97 Hz), 2.17 (s, 0.1H, N–*H*), 7.36 (t, 1H, *p*-H(Ph)), 7.49 (t, 2H, *m*-H(Ph)), 7.82 (d, 2H, *o*-H(Ph)), 9.12 (br., 0.9H, O–*H*). ^{13}C NMR (δ, ppm): 13.4, 104.9, 105.3, 121.3, 127.5, 129.3, 136.5, 139.0, 142.0, 144.5, 147.8, 159.3, 179.9. ^{19}F NMR (δ, ppm): −159.2, −149.7, −141.1. MS (*m/z*, %): 368 (M, 100), 348 (M − HF, 71), 347 (M^+ − HF, 48), 243 (22), 201 (44), 200 (82), 195 (37), 91 (31). T_{dec} = 165–170°C.

Synthesis of 1-phenyl-3-methyl-5,6,7,8-tetrafluorochromeno[2,3-c]pyrazol-4(1*H*)-one (L^2). Pfb-PMPH (0.20 g) was heated in a vacuum (10^{-3} Torr) in a sublimation setup at 170°C for 3 h. During sublimation, L^2 is formed as light yellow crystals (0.18 g, 95%).

For $C_{17}H_8F_4N_2O_2$		
anal calcd., %:	C, 58.63;	H, 2.32.
Found, %:	C, 58.58;	H, 2.29.

IR (ν, cm^{-1}): 1083, 1062, 1038, 970 $\nu(C_{Ar}–H)$, 840, 760 $\gamma(C_{Ar}–H)$; 2924 ν, 1340$_s$, 1331, 1320 β_s, 1183, 1157 $\beta(C_{Alk}–H)$; 1675 $\nu_{as}(C=O)$; 1571, 1541, 1518, 1503 ν, 1482 ν_{as}, 1216 $\nu_s(C=C_{Ar})$; 1598, 1447, 1423, 1115 ν(pyrazole ring); 914, 890 ν(C–C); 1260 ν(C–O–C); 1127 ν(C–F). ^1H NMR (δ, ppm): 2.67 (s, 3H, CH_3, ^1J_C = 129.60 Hz), 7.42 (t, 1H, *p*-H(Ph)), 7.56 (t, 2H, *m*-H(Ph)), 7.86 (d, 2H, *o*-H(Ph)). ^{13}C NMR (δ, ppm): 14.0, 104.9, 110.8, 121.0, 127.9, 129.6, 136.6, 140.0, 142.3, 145.0, 147.7, 148.5, 151.4, 170.0. ^{19}F NMR (δ, ppm): −159.5, −157.7, −146.9, −141.4. MS (*m/z*, %): 348 (M, 100), 347 (M^+, 48), 227 (17), 209 (22), 91 (21), 77 (30). mp = 172–174°C.

The lanthanide complexes $Ln(Pfb\text{-}PMP)_3(THF)$ (Ln = Sm, Eu, Gd, Tb, Lu) were synthesized by a typical procedure described below for the samarium compound.

Synthesis of $(Pfb\text{-}PMP)_3Sm(THF)$ (I). A solution of Pfb-PMPH (0.32 g, 0.8689 mmol) in THF (5 mL) was added to a solution of $[(Me_3Si)_2N]_3Sm$ (0.18 g, 0.2857 mmol) in THF (5 mL). The mixture was stirred at room temperature for 24 h. The solvent and volatile products were distilled off in vacuum. GLC analysis of the volatile products showed the presence of 0.13 g (95%) of $(Me_3Si)_2NH$. The residue was recrystallized from hexane and dried in vacuum for 3 h at 100°C. Complex **I** was obtained as a light yellow finely crystalline solid in a 0.38 g (97.4%) yield.

For $C_{55}H_{32}F_{15}N_6O_7Sm$			
anal calcd., %:	C, 49.89;	H, 2.44;	Sm, 11.35.
Found, %:	C, 49.96;	H, 2.49;	Sm, 11.05.

IR (ν, cm^{-1}): 3068, 1074, 1060, 1012, 991 $\nu(C_{Ar}–H)$, 813, 760 $\gamma(C_{Ar}–H)$; 2930 ν, 1423 β_{as}, 1379$_s$, 1308 β_s, 1160 $\beta(C_{Alk}–H)$; 1621 ν_{as}, 1360 $\nu_s(C\cdots O)$; 1595, 1460 ν, 1500 ν_{as}, 1215 $\nu_s(C=C_{Ar})$; 1533, 1440, 1405 ν(pyrazole ring); 908, 873 ν(C–C); 692, 645 β, 621 ν(chelate ring); 508 ν(Ln–O); 1030, 858 ν(coordinated THF); 1118 ν(C–F). $T_{dec.}$ > 150°C.

$(Pfb\text{-}PMP)_3Eu(THF)$ (II) was obtained as a light yellow finely crystalline solid. Yield 0.28 g (96.6%).

For $C_{55}H_{32}F_{15}N_6O_7Eu$			
anal calcd., %:	C, 49.83;	H, 2.43;	Eu, 11.46.
Found, %:	C, 49.86;	H, 2.49;	Eu, 11.57.

IR (ν, cm^{-1}): 3065, 1074, 1062, 1012, 988 $\nu(C_{Ar}–H)$, 813, 760 $\gamma(C_{Ar}–H)$; 2930 ν, 1420 β_{as}, 1375, 1307 β_s, 1160 $\beta(C_{Alk}–H)$; 1624 ν_{as}, 1358 $\nu_s(C\cdots O)$; 1595, 1460 ν, 1500 ν_{as}, 1215 $\nu_s(C=C_{Ar})$; 1533, 1438, 1405

ν(pyrazole ring); 908 ν, 875 ν(C–C); 690, 645 β, 618 ν(chelate ring); 509 ν(Ln–O), 1030, 858 ν(coordinated THF), 1118 ν(C–F). $T_{dec.} > 150°C$.

(Pfb-PMP)$_3$Gd(THF) (III) was obtained as a light yellow finely crystalline solid. Yield 0.23 g (99.8%).

For $C_{55}H_{32}F_{15}N_6O_7Gd$

anal calcd., %:	C, 49.63;	H, 2.42;	Gd, 11.81.
Found, %:	C, 49.68;	H, 2.46;	Gd, 11.25.

IR (ν, cm^{-1}): 3065, 1074, 1060, 1012, 988 ν(C_{Ar}–H), 813, 760 γ(C_{Ar}–H); 2925 ν, 1417 β_{as}, 1375, 1305 β_s, 1155 β(C_{Alk}–H); 1624 ν_{as}, 1358 ν_s(C···O); 1595, 1460 ν, 1500 ν_{as}, 1210 ν_s(C=C_{Ar}); 1533, 1440, 1405 ν(pyrazole ring); 908, 875 ν(C–C); 690, 645 β, 618 ν(chelate ring); 508 ν(Ln–O), 1030, 858 ν(coordinated THF), 1118 ν(C–F). $T_{dec.} > 145°C$.

(Pfb-PMP)$_3$Tb(THF) (IV) was obtained as a light yellow finely crystalline solid. Yield 0.30 g (96.8%).

For $C_{55}H_{32}F_{15}N_6O_7Tb$

anal calcd., %:	C, 49.57;	H, 2.42;	Tb, 11.92.
Found, %:	C, 49.51;	H, 2.39;	Tb, 11.41.

IR (ν, cm^{-1}): 3068, 1074, 1062, 1012, 988 ν(C_{Ar}–H), 813, 760 γ(C_{Ar}–H); 2929 ν, 1420 β_{as}, 1375, 1304 β_s, 1160 β(C_{Alk}–H); 1624 ν_{as}, 1358 ν_s(C···O); 1595, 1459 ν, 1500 ν_{as}, 1210 ν_s(C=C_{Ar}); 1533, 1438, 1400 ν(pyrazole ring); 908, 875 ν(C–C); 692, 645 β, 618 ν(chelate ring); 509 ν(Ln–O), 1030, 860 ν(coordinated THF), 1118 ν(C–F). $T_{dec.} > 150°C$.

(Pfb-PMP)$_3$Lu(THF) (V) was obtained as a light yellow finely crystalline solid. Yield 0.34 g (97.1%).

For $C_{55}H_{32}F_{15}N_6O_7Lu$

anal calcd., %:	C, 48.98;	H, 2.39;	Lu, 12.97.
Found, %:	C, 49.06;	H, 2.44;	Lu, 12.59.

IR (ν, cm^{-1}): 3068, 1074, 1060, 1012, 988 ν(C_{Ar}–H), 810, 760 γ(C_{Ar}–H); 2930 ν, 1420 β_{as}, 1375, 1305 β_s, 1156 β(C_{Alk}–H); 1624 ν_{as}, 1358 ν_s(C···O); 1595, 1458 ν, 1500 ν_{as}, 1210 ν_s(C=C_{Ar}); 1530, 1438, 1402 ν(pyrazole ring); 908, 875 ν(C–C); 689, 645 β, 618 ν(chelate ring); 508 ν(Ln–O); 1030, 858 ν(coordinated THF), 1118 ν(C–F). ^{1}H NMR (δ, ppm): 1.85 (s, 9H, CH_3, ^1J_C = 128.97 Hz), 3.49 (m, 4H, α-CH_2^{THF}), 3.70 (m, 4H, β-CH_2^{THF}), 7.18 (t, 3H, *p*-H(Ph)), 7.23 (t, 6H, *m*-H(Ph)), 7.83 (d, 6H, *o*-H(Ph)). $T_{dec.} > 155°C$.

The lanthanide complexes (Pfb-PMP)$_3$Ln(OPPh$_3$)$_2$ · *x*EtOH (Ln = Sm, Eu, Gd, Tb, Lu) were prepared by a general procedure described below for the samarium compound.

Synthesis of (Pfb-PMP)$_3$Sm(OPPh$_3$)$_2$ · EtOH (VI). A mixture of complex **I** (0.29 g, 0.22 mmol) and Ph_3PO (0.12 g, 0.44 mmol) in $CHCl_3$ (5 mL) was stirred for 20 h at room temperature. After removal of the solvent, the residue was recrystallized from ethanol. The yield of complex **VI** was 0.40 g (98.5%).

For $C_{89}H_{60}F_{15}N_6O_2P_2Sm$

anal calcd., %:	C, 57.64;	H, 3.26;	Sm, 8.11.
Found, %:	C, 57.70;	H, 3.29;	Sm, 8.02.

IR (ν, cm^{-1}): 3062, 1062, 1012, 988 ν(C_{Ar}–H), 810, 760 γ(C_{Ar}–H); 2924 ν, 1417 β_{as}, 1373 β_s, 1305 β_s, (C_{Alk}–H); 1633 ν_{as}, 1360 ν_s(C···O); 1595, 1458 ν, 1512 ν_{as}(C=C_{Ar}); 1530, 1438, 1402 ν(pyrazole ring); 905 ν(C–C); 692, 639 β, 618 ν(chelate ring); 508 ν(Ln–O); 1118 ν(C–F); 1497, 1195, 1175 ν(Ph_3PO); 3401 ν, 1259, 1308 δ, 1072 ν(C_2H_5OH). $T_{dec.} > 180°C$.

(Pfb-PMP)$_3$Eu(OPPh$_3$)$_2$ · 0.5EtOH (VII) was isolated as a light yellow crystalline solid. Yield 0.49 g (98.4%).

For $C_{88}H_{57}F_{15}N_6O_{8.5}P_2Eu$

anal calcd., %:	C, 57.65;	H, 3.13;	Eu, 8.29.
Found, %:	C, 57.67;	H, 3.30;	Eu, 8.19.

IR (ν, cm^{-1}): 3059, 1059, 1008, 988 ν(C_{Ar}–H), 810, 760 γ(C_{Ar}–H); 2924 ν, 1417 β_{as}, 1370, 1305 β_s(C_{Alk}–H); 1630 ν_{as}, 1355 ν_s(C···O); 1595, 1458 ν, 1512 ν_{as}(C=C_{Ar}); 1527, 1438, 1402 ν(pyrazole ring); 905 ν(C–C); 692, 642 β, 618 ν(chelate ring); 508 ν(Ln–O); 1118 ν(C–F); 1497, 1186, 1165 ν(Ph_3PO); 3415, 1067 ν, 1262, 1306 δ(C_2H_5OH). $T_{dec.} > 180°C$.

(Pfb-PMP)$_3$Gd(OPPh$_3$)$_2$ · 0.75EtOH (VIII) was isolated as a light yellow crystalline solid. Yield 0.12 g (95.3%).

For $C_{88.5}H_{58.5}F_{15}N_6O_{8.75}P_2Gd$

anal calcd., %:	C, 57.46;	H, 3.19;	Gd, 8.50.
Found, %:	C, 57.48;	H, 3.28;	Gd, 8.45.

IR (ν, cm^{-1}): 3062, 1062, 1012, 988 ν(C_{Ar}–H), 810, 760 γ(C_{Ar}–H); 2924 ν, 1417 β_{as}, 1373, 1305 β_s(C_{Alk}–H); 1633, 1360 ν_s(C···O); 1595, 1458 ν, 1512 ν_{as}(C=C_{Ar}); 1530, 1438, 1402 ν(pyrazole ring); 905 ν(C–C); 692, 639 β, 618 ν(chelate ring); 508 ν(Ln–O); 1118 ν(C–F); 1497, 1195, 1175 ν(Ph_3PO); 3446, 1071 ν, 1265, 1306 δ(C_2H_5OH). $T_{dec.} > 175°C$.

(Pfb-PMP)$_3$Tb(OPPh$_3$)$_2$ · 0.75EtOH (IX) was isolated as a light yellow crystalline solid. Yield 0.16 g (95.4%).

For $C_{88.5}H_{58.5}F_{15}N_6O_{8.75}P_2Tb$

anal calcd., %:	C, 57.40;	H, 3.18;	Tb, 8.58.
Found, %:	C, 57.37;	H, 3.25;	Tb, 8.53.

IR (ν, cm^{-1}): 3062, 1062, 1012, 988 ν(C_{Ar}–H), 810, 760 γ(C_{Ar}–H); 2924 ν, 1417 β_{as}, 1373, 1305

β_s(C$_{Alk}$–H); 1633 ν_{as}, 1360 ν_s(C···O); 1595, 1458 ν, 1512 ν_{as}(C=C$_{Ar}$); 1530, 1438, 1402 ν(pyrazole ring); 905 ν(C–C); 692, 639 β, 618 ν(chelate ring); 508 ν(Ln–O); 1118 ν(C–F); 1497, 1195, 1175 ν(Ph$_3$PO); 3415, 1071 ν, 1264, 1306 δ(C$_2$H$_5$OH). $T_{dec.}$ > 180°C.

Synthesis of (Pfb-PMP)$_3$Lu(OPPh$_3$)$_2$ · 0.1EtOH (X). The compound was isolated as a light yellow finely crystalline solid. Yield: 0.27 g (96.9%).

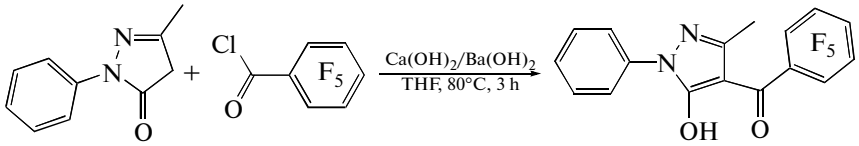
For $C_{87.2}H_{54.6}F_{15}N_6O_{8.1}P_2Lu$			
anal calcd., %:	C, 56.99;	H, 2.99;	Lu, 9.52.
Found, %:	C, 56.97;	H, 3.28;	Lu, 9.31.

IR (ν, cm^{-1}): 3062, 1062, 1012, 988 ν(C$_{Ar}$–H), 810, 760 γ(C$_{Ar}$–H); 2924 ν, 1417 β_{as}, 1373, 1305 β_s(C$_{Alk}$–H); 1633 ν_{as}, 1360 ν_s(C···O); 1595, 1458 ν, 1512 ν_{as}(C=C$_{Ar}$); 1530, 1438, 1402 ν(pyrazole ring); 905 ν(C–C); 692, 639 β, 618 ν(chelate ring); 508 ν(Ln–O); 1118 ν(C–F); 1497, 1195, 1175 ν(Ph$_3$PO); 3398 ν, 1265, 1308 δ, 1071 ν(C$_2$H$_5$OH). ^{1}H NMR (δ, ppm): 1.26 (t, 0.3H CH$_3$(C$_2$H$_5$OH)), 1.80 (s, 9H, CH$_3$), 2.69 (s, 0.1H, OH(C$_2$H$_5$OH)), 3.72 (m, 0.2H, CH$_3$(C$_2$H$_5$OH)), 7.12 (t, 3H, *p*-H(Ph)), 7.16 (t, 6H, *m*-H(Ph)), 7.28 (d, 12H, *o*-H(Ph$_3$P)), 7.52 (*m*, 18H, *m*,*p*-H(Ph$_3$P)), 7.85 (*d*, 6H, *o*-H(Ph)). $T_{dec.}$ > 185°C.

X-ray diffraction. The crystallographic data for compounds HL^1, L^2, and **VI**–**X** were collected on Bruker AXS SMART APEX (L^2), Bruker AXS D8 Quest Photon (**VI**, **VIII**, **IX**), and Oxford Xcalibur Eos (HL^1, **VII**, **X**) automated diffractometers (MoK_α radiation, ω-scan mode, λ = 0.71073 Å) at 100(2) K. The experimental sets of reflection intensities were integrated using SAINT [12 (L^2), 13 (**VI**, **VIII**, **IX**)] and CrysAlisPro [14] (HL^1, **VII**, **X**) software. The absorption corrections were applied using the SADABS [15 (L^2), 16 (**VI**, **VIII**, **IX**)] and SCALE3 ABSPACK [17] (HL^1, **VII**, **X**) program packages. The structures were solved by the direct method using the SHELXTL program package [18] and refined by the full-matrix least-squares method on F^2_{hkl} in the anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms were placed into geometrically calculated positions and refined in the riding model. The H(2*A*,*B*) atoms of HL^1 and the H(1*S*) atom of the OH group of the solvent ethanol molecule in **VI**–**X** were located from the difference electron density map and refined isotropically. In the crystal of complexes **VI**–**X**, the C$_2$H$_5$OH solvent molecule is located in the general position; in **VI**–**IX**, it is disordered over two positions. The molecules of complexes **VI**–**X** contain fluorophenyl, phenyl, and pyrazolone moieties disordered over two positions. The key crystal data and X-ray experiment details for HL^1, L^2, and **VI**–**X** are summarized in Table 1. The crystallographic information for the compounds is deposited at the Cambridge Crystallographic Data Centre (nos. 1010331 (HL^1), 1010332 (L^2), 1010333 (**VI**), 1010334 (**VII**), 1010335 (**VIII**), 1010336 (**IX**), and 1010337 (**X**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

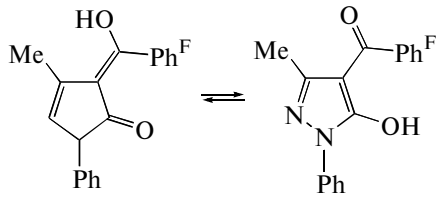
RESULTS AND DISCUSSION

Pyrazolone (Pfb-PMPH) (HL^1) was synthesized by a reported procedure [19] as follows:

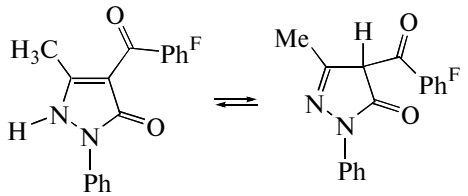


(HL^1)

Pyrazolone HL^1 was isolated as an air-stable colorless crystalline solid readily soluble in THF, dichloromethane, chloroform, and ethanol and virtually insoluble in hexane. 4-Acylpyrazolones are known to exist as several ketone and enol forms [1, 20]:



enol 1 enol 2



ketone 3 ketone 4

The ^{1}H NMR spectrum of HL^1 exhibits a broadened singlet at 9.12 ppm characteristic of the O–H···O group in the enol form and a singlet at 2.17 ppm corresponding to the N–H group of ketone 3. The integrated intensity ratio of these signals (9 : 1) indicates

Table 1. Key crystal data and X-ray experiment and structure refinement details for HL^1, L^2, and **VI**–**X**

Parameter	HL^1	L^2	**VI**	**VII**	**VIII**	**IX**	**X**
Molecular formula	$C_{17}H_9F_5N_2O_2$	$C_{17}H_8F_4N_2O_2$	$C_{89}H_{60}F_{15}N_6O_9P_2Sm$	$C_{88}H_{57}F_{15}N_6O_{8.5}P_2Eu$	$C_{88.5}H_{58.5}F_{15}N_6O_{8.75}P_2Gd$	$C_{88.5}H_{58.5}F_{15}N_6O_{8.75}P_2Tb$	$C_{87.2}H_{54.6}F_{15}N_6O_{8.1}P_2Lu$
M	368.26	348.25	1854.72	1833.29	1850.10	1851.77	1837.88
Crystal size, mm	0.60 × 0.20 × 0.10	0.10 × 0.09 × 0.08	0.20 × 0.18 × 0.15	0.40 × 0.20 × 0.05	0.30 × 0.25 × 0.20	0.30 × 0.25 × 0.20	0.40 × 0.40 × 0.10
System	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	10.0706(3)	7.1516(2)	12.9512(6)	12.9828(3)	12.9912(10)	12.9845(8)	12.88053(16)
b, Å	11.8207(5)	11.4758(3)	13.8322(7)	13.8465(3)	13.7818(11)	13.7165(9)	13.55178(18)
c, Å	14.3157(5)	17.3754(5)	25.3076(13)	25.5629(5)	25.4396(19)	25.3775(17)	25.4879(3)
α, deg	112.661(4)	82.778(1)	89.753(1)	90.0206(16)	79.157(2)	79.109(1)	78.9895(11)
β, deg	101.891(3)	85.824(1)	75.334(1)	75.3970(19)	75.277(2)	75.240(1)	75.6900(11)
γ, deg	90.162(3)	82.942(1)	67.728(1)	68.143(2)	68.055(2)	68.377(1)	69.7193(12)
V, Å^3	1532.47(10)	1401.59(7)	4037.4(3)	4104.47(17)	4063.9(5)	4040.3(5)	4016.49(10)
Z	4	4	2	2	2	2	2
ρ(calcd.), g/cm^{-3}	1.596	1.650	1.526	1.483	1.512	1.522	1.520
μ, mm^{-1}	0.147	0.146	0.865	0.898	0.952	1.012	1.365
F(000)	744	704	1870	1846	1861	1863	1841
Scanning range of θ, deg.	2.891–27.999	2.035–27.998	2.430–25.999	2.896–25.999	2.497–30.000	2.711–27.000	3.092–27.000
Range of indices	$-13 \le h \le 13$, $-15 \le k \le 15$, $-18 \le l \le 18$	$-9 \le h \le 9$, $-15 \le k \le 15$, $-22 \le l \le 22$	$-15 \le h \le 15$, $-17 \le k \le 17$, $-31 \le l \le 31$	$-15 \le h \le 16$, $-17 \le k \le 16$, $-31 \le l \le 31$	$-18 \le h \le 18$, $-19 \le k \le 19$, $-35 \le l \le 35$	$-16 \le h \le 16$, $-17 \le k \le 17$, $-32 \le l \le 32$	$-16 \le h \le 16$, $-17 \le k \le 17$, $-32 \le l \le 32$
Total number of reflections	27175	14144	41813	36511	56564	44494	67955
Number of independent reflections (R_{int})	7382 (0.0638)	6713 (0.0251)	15829 (0.0277)	16094 (0.0541)	23577 (0.0329)	17596 (0.0236)	17479 (0.0524)
Number of reflections with ($I > 2\sigma(I)$)	4680	4973	13637	12640	20546	16094	14552
GOOF	1.014	1.049	1.023	1.008	1.050	1.003	1.054
R ($I > 2\sigma(I)$)	$R_1 = 0.0476$, $wR_2 = 0.0745$	$R_1 = 0.0487$, $wR_2 = 0.1184$	$R_1 = 0.0370$, $wR_2 = 0.0898$	$R_1 = 0.0510$, $wR_2 = 0.1145$	$R_1 = 0.0405$, $wR_2 = 0.1007$	$R_1 = 0.0349$, $wR_2 = 0.0873$	$R_1 = 0.0461$, $wR_2 = 0.1038$
R (all data)	$R_1 = 0.0924$, $wR_2 = 0.0828$	$R_1 = 0.0689$, $wR_2 = 0.1276$	$R_1 = 0.0467$, $wR_2 = 0.0939$	$R_1 = 0.0714$, $wR_2 = 0.1227$	$R_1 = 0.0489$, $wR_2 = 0.1043$	$R_1 = 0.0392$, $wR_2 = 0.0893$	$R_1 = 0.0621$, $wR_2 = 0.1092$
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.263/−0.250	0.392/−0.280	1.673/−0.629	2.060/−2.029	1.942/−0.739	1.337/−0.493	3.305/−0.990

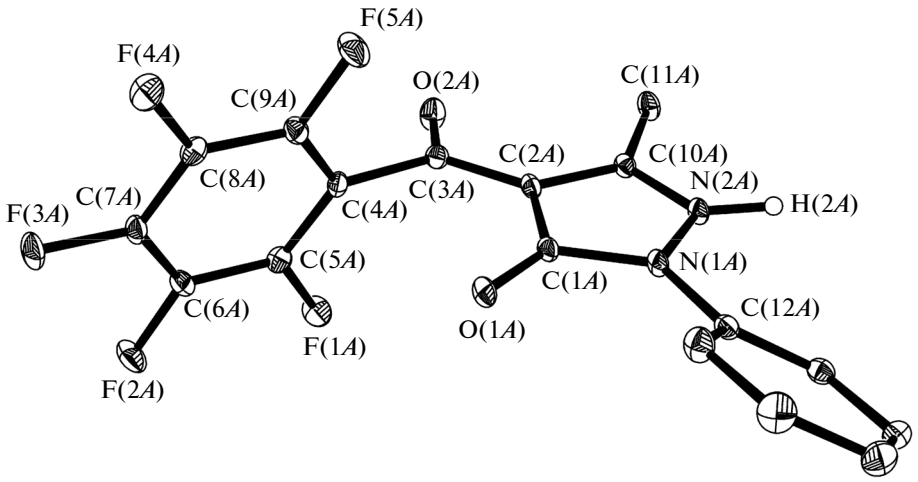


Fig. 1. Structure of molecule A of HL^1. The thermal ellipsoids are given with a 30% probability. The hydrogen atoms (except for H(2*A*)) are omitted. Key bond lengths and bond angles (here and below the second value is for molecule B): O(1)–C(1), 1.248(2); 1.248(2); O(2)–C(3), 1.226(2), 1.227(2); C(1)–C(2), 1.438(2), 1.441(2); C(2)–C(3), 1.441(2), 1.444(2); C(2)–C(10), 1.403(2), 1.395(2); C(3)–C(4), 1.519(2), 1.521(2); C(4)–C(5), 1.386(2), 1.387(2); N(1)–N(2), 1.385(2), 1.383(2); N(1)–C(1), 1.393(2), 1.391(2); N(1)–C(12), 1.424(2), 1.427(2); N(2)–C(10), 1.331(2), 1.334(2) Å; O(1)C(1)C(2), 132.30(14)°, 132.21(15)°; N(1)C(1)C(2), 105.31(13)°, 105.14(13)°; C(1)C(2)C(3), 127.52(14)°, 127.52(14)°; C(1)C(2)C(10), 107.49(13)°, 107.42(14)°; C(2)C(3)C(4), 118.44(13)°, 118.91(1)°; C(2)C(3)O(2), 123.73(15)°, 123.58(15)°; N(2)C(10)C(2), 108.31(13)°, 108.73(13)°; N(1)N(2)C(10), 110.20(13)°, 109.72(13)°; C(1)N(1)N(2), 108.66(12)°, 108.94(12)°; C(12)N(1)N(2), 120.78(12)°, 120.96(13)°; C(3)C(4)C(5), 120.76(14)°, 122.96(14)°.

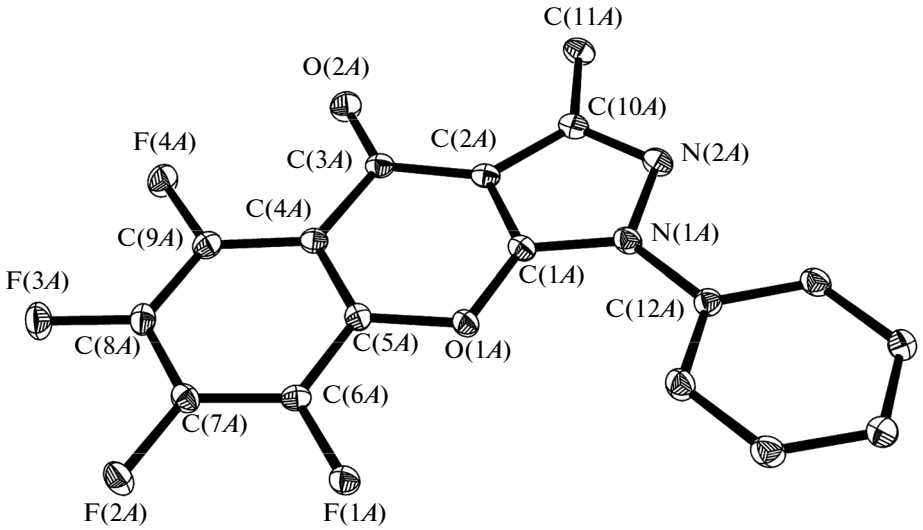


Fig. 2. Structure of molecule A of L^2. The thermal ellipsoids are given with a 30% probability. The hydrogen atoms are omitted. Key bond lengths and bond angles: O(1)–C(1), 1.347(2), 1.344(2); O(1)–C(5), 1.376(2), 1.383(2); O(2)–C(3), 1.226(2), 1.217(2); C(1)–C(2), 1.372(2), 1.368(2); C(2)–C(3), 1.439(2), 1.444(2); C(2)–C(10), 1.425(2), 1.425(2); C(3)–C(4), 1.498(2), 1.496(2); C(4)–C(5), 1.399(2), 1.399(2); N(1)–N(2), 1.396(2), 1.398(2); N(1)–C(1), 1.348(2), 1.353(2); N(1)–C(12), 1.433(2), 1.422(2); N(2)–C(10), 1.324(2), 1.316(2) Å; O(1)C(1)C(2), 127.51(12)°, 127.31(13)°; N(1)C(1)C(2), 110.01(12)°, 109.62(12)°; C(1)C(2)C(3), 121.10(13)°, 121.78(12)°; C(1)C(2)C(10), 103.74(12))°, 104.14(12))°; C(2)C(3)C(4), 112.10(12)°, 111.49(12)°; C(2)C(3)O(2), 125.35(13)°, 124.80(13)°; N(2)C(10)C(2), 111.21(1))°, 111.16(12)°; N(1)N(2)C(10), 106.21(11)°, 106.36(11)°; C(1)N(1)N(2), 108.83(11)°, 108.71(11)°; C(12)N(1)N(2), 119.90(11)°, 118.74(11)°; C(3)C(4)C(5), 120.54(12)°, 120.83(12)°; C(4)C(5)O(1), 124.34(12)°, 124.20(12)°; C(5)O(1)C(1), 114.30(11)°, 114.24(11)°.

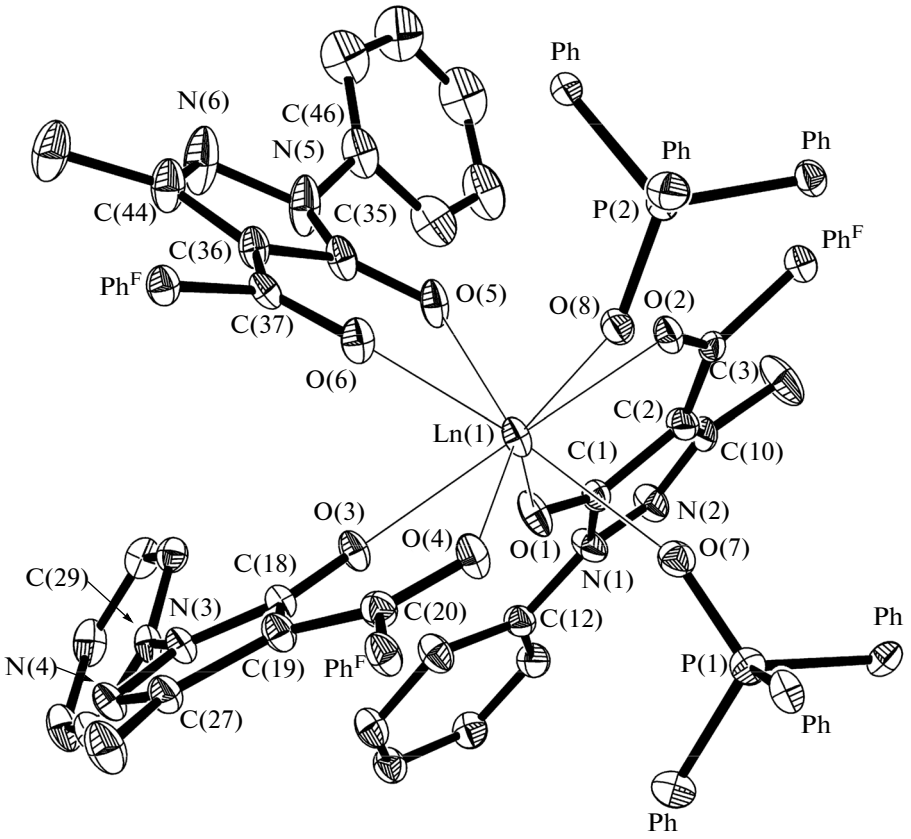


Fig. 3. Molecular structure of complexes **VI**–**X**. The thermal ellipsoids are given with a 30% probability. The hydrogen atoms are omitted. The phenyl and pentafluorophenyl groups are designated as Ph and Ph^F, respectively.

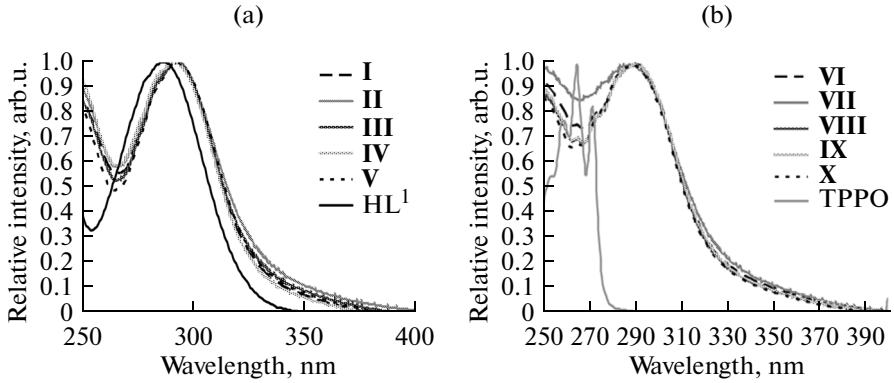


Fig. 4. Absorption spectra (CH_2Cl_2 solution) of complexes: (a) **I**–**V**, (b) **VI**–**X**.

that pyrazolone HL^1 in a $CDCl_3$ solution at room temperature occur mainly in the enol form.

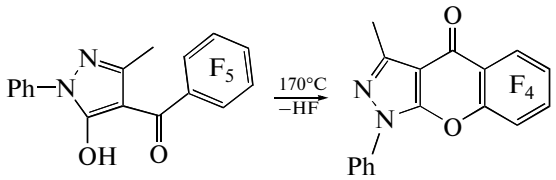
In the solid state, HL^1 also exists as a mixture of ketone and enol forms, which is confirmed by the presence of a broad band at 2720 cm^{-1} in the IR spectrum, characteristic of an intramolecular hydrogen bond and a narrow medium-intensity band at 3125 cm^{-1}, due to N–H stretching vibrations.

By crystallization of the compound from a mixture of ethanol, water, and chloroform, single crystals suitable for X-ray diffraction were obtained. According to X-ray diffraction data, the crystalline sample comprises only ketone tautomer 3 (Fig. 1).

The asymmetric part of the crystal unit cell of compound HL^1 was found to contain two molecules (A and B) with identical structure according to geometri-

cal characteristics. Figure 1 presents the structure of molecule A. Compound HL^1 is non-planar, the Ph^F and Ph substituents being rotated relative to the pyrazole plane by 79.2° (67.8°) and 29.7° (31.7°), respectively. The bond lengths in the N(1,2)O(1,2)C(1–4,10–12) fragment are similar to the bond lengths of the same type in related compounds Me–PMPH [21] and Ph–PMPH [22]. The O(1) and O(2) atoms are located on different sides of the line connecting the C(1) and C(3) atoms. The O(1)–C(1)–C(3)–O(2) torsion angle is 173.5° (175.0°), which is close to the corresponding value in Me–PMPH (175.6°). In compound Ph–PMPH, the O(1)–C(1–3)–O(2) moiety has the opposite conformation, the O(1)–C(1)–C(3)–O(2) torsion angle being 31.1°.

Attempted vacuum sublimation of HL^1 (10^{-3} Torr) resulted in hydrogen fluoride splitting off at 170°C to give the intramolecular cyclization product, namely, 1-phenyl-3-methyl-5,6,7,8-tetrafluorochromeno[2,3-c]pyrazol-4(1*H*)-one (L_2):



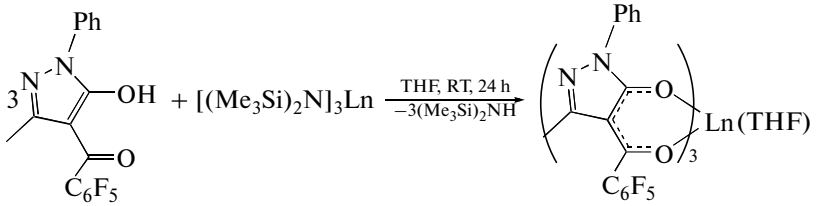
(HL^1) (L^2)

Note that the formation of analogous chromene derivatives has been observed previously in the reaction of fluorine-containing 4-acylpyrazolones with NaH in DMF or with K_2CO_3 in acetonitrile [9].

Compound L^2 is an air-stable light yellow crystalline solid, readily soluble in THF and chloroform and almost insoluble in ethanol and hexane. Elemental analysis and ^1H, ^{13}C, and ^{19}F NMR and IR spectroscopy data correspond to the presented formula. The structure of derivative L^2 was determined by X-ray diffraction (Fig. 2).

The crystal of L^2, analogous to HL^1 , was found to contain two crystallographically independent molecules (A and B) the geometric characteristics of which differ little. Figure 2 shows the structure of molecule A. Compound L^2 is almost planar; the average deviation of atoms of the benzopyranopyrazole moiety, N(1,2)O(1)C(1–10), from the plane is 0.024 Å. The Ph substituent at N(1) is located in the N(1,2)O(1)C(1–10) plane. The dihedral angle between their planes is 6.2°. The structural characteristics of L^2 are consistent with the published data for the related compound, 6,7,8-trifluoro-5-hydroxy-1,3-dimethylbenzopyrano[2,3-c]pyrazol-4(1*H*)-one [23] containing a similar benzopyranopyrazole ring.

It was found that pyrazolone HL^1 reacts with lanthanide silylamides to give the corresponding complexes in high yields:



(HL^1) Ln = Sm (**I**), Eu (**II**), Gd (**III**), Tb (**IV**), Lu (**V**)

The reactions were monitored by GLC considering the amount of hexamethyldisilazane formed. The reaction between the reactants is completed in 24 h at room temperature. Complexes **I**–**V** are air-stable light yellow finely crystalline solids. The compounds were characterized by elemental analysis and IR spectroscopy. The diamagnetic lutetium derivative was studied by NMR. It is of interest that when the compounds are kept in moist air, the coordinated THF is not replaced by water molecules. The exchange of neutral ligands occurs upon the reaction with triphenylphosphine oxide in a $CHCl_3$ solution. Recrystallization of the products from EtOH affords $(Pfb\text{-}PMP)_3Ln(OPPh_3)_2 \cdot x$EtOH (Ln = Sm (**VI**), Eu (**VII**), Gd (**VIII**), Tb (**IX**), Lu (**X**)), which contain two Ph_3PO molecules in the lanthanide coordination sphere and ethanol solvent molecules in the crystal cells.

According to X-ray diffraction, the crystals of compounds **VI**–**X** are isostructural. The general view of the molecular structure of complexes **VI**–**X** is shown in Fig. 3 (the molecules of crystallization EtOH are not shown). Selected bond lengths and bond angles are presented in Table 2. The lanthanide atom is coordinated by three bidentate pyrazolone ligands and two monodentate triphenylphosphine oxide ligands. The Ln coordination number is 8; the Ln coordination polyhedron is a distorted square antiprism. The O(2,5,6,8) and O(1,3,4,7) atoms are located in opposite bases of the antiprism.

Table 2. Selected bond lengths and bond angles in complexes **VI**–**X**

Bond	**VI** (Ln = Sm)	**VII** (Ln = Eu)	**VIII** (Ln = Gd)	**IX** (Ln = Tb)	**X** (Ln = Lu)
	d, Å				
Ln(1)–O(1)	2.352(1)	2.355(2)	2.337(1)	2.321(1)	2.274(2)
Ln(1)–O(2)	2.469(1)	2.476(2)	2.453(1)	2.436(1)	2.396(2)
Ln(1)–O(3)	2.386(1)	2.390(2)	2.367(1)	2.354(1)	2.302(2)
Ln(1)–O(4)	2.416(1)	2.427(2)	2.409(1)	2.390(1)	2.347(2)
Ln(1)–O(5)	2.333(2)	2.339(2)	2.320(1)	2.304(1)	2.247(2)
Ln(1)–O(6)	2.445(2)	2.453(2)	2.433(1)	2.419(2)	2.381(2)
Ln(1)–O(7)	2.328(2)	2.334(2)	2.314(1)	2.295(2)	2.237(2)
Ln(1)–O(8)	2.338(1)	2.342(2)	2.317(1)	2.303(1)	2.256(2)
O(1)–C(1)	1.234(2)	1.241(3)	1.243(2)	1.241(2)	1.246(4)
O(2)–C(3)	1.234(2)	1.243(3)	1.237(2)	1.236(2)	1.244(4)
O(3)–C(18)	1.254(2)	1.264(3)	1.254(2)	1.257(2)	1.260(3)
O(4)–C(20)	1.246(2)	1.243(3)	1.241(2)	1.244(2)	1.252(3)
O(5)–C(35)	1.243(3)	1.256(3)	1.248(2)	1.247(3)	1.244(4)
O(6)–C(37)	1.244(2)	1.260(3)	1.248(2)	1.245(2)	1.242(4)
O(7)–P(1)	1.487(2)	1.494(2)	1.490(1)	1.487(2)	1.489(2)
O(8)–P(2)	1.490(1)	1.499(2)	1.496(1)	1.491(1)	1.478(2)
C(1)–C(2)	1.423(2)	1.430(3)	1.431(2)	1.428(3)	1.434(4)
C(2)–C(3)	1.394(2)	1.417(3)	1.396(2)	1.394(3)	1.399(4)
C(2)–C(10)	1.463(3)	1.475(3)	1.471(3)	1.472(3)	1.461(3)
C(18)–C(19)	1.428(3)	1.431(3)	1.435(2)	1.428(3)	1.434(4)
C(19)–C(20)	1.389(2)	1.401(3)	1.397(2)	1.392(3)	1.401(4)
C(19)–C(27)	1.430(3)	1.439(3)	1.434(2)	1.433(3)	1.439(4)
C(35)–C(36)	1.420(3)	1.432(4)	1.430(3)	1.421(3)	1.434(5)
C(36)–C(37)	1.399(3)	1.396(4)	1.393(2)	1.402(3)	1.412(4)
C(36)–C(44)	1.422(3)	1.430(4)	1.428(3)	1.423(3)	1.425(5)
N(1)–N(2)	1.413(3)	1.413(3)	1.414(3)	1.416(3)	1.410(4)
N(1)–C(1)	1.359(2)	1.374(3)	1.371(2)	1.367(3)	1.377(4)
N(2)–C(10)	1.308(3)	1.315(3)	1.308(3)	1.309(3)	1.308(4)
N(3)–N(4)	1.395(2)	1.406(3)	1.399(2)	1.396(2)	1.407(3)
N(3)–C(18)	1.359(2)	1.374(3)	1.367(2)	1.363(2)	1.374(4)
N(4)–C(27)	1.295(2)	1.312(3)	1.302(2)	1.297(3)	1.304(4)
N(5)–N(6)	1.399(3)	1.399(4)	1.406(3)	1.404(3)	1.399(4)
N(5)–C(35)	1.352(3)	1.365(4)	1.363(2)	1.358(2)	1.369(4)
N(6)–C(44)	1.306(3)	1.307(4)	1.309(3)	1.308(3)	1.305(4)
Angle	ω, deg				
O(1)Ln(1)O(2)	73.12(4)	73.45(6)	73.82(4)	74.20(5)	76.00(7)
O(3)Ln(1)O(4)	72.56(4)	72.75(6)	73.06(4)	73.51(4)	74.61(7)
O(5)Ln(1)O(6)	71.86(5)	72.11(6)	72.41(4)	72.71(5)	74.02(7)
O(7)Ln(1)O(8)	81.84(5)	82.10(6)	82.09(4)	81.64(5)	81.98(8)

Table 3. Photophysical characteristics of compounds **I**–**X**

Compound	λ_{abs}, nm (log ε) (in CH_2Cl_2)	λ_{em}, nm in the solid state	CIE color coordinates (*x*/*y*)
I	293 (3.89)	424, 447, 461, 485, 530	0.16/0.19
II	293 (4.31)	400, 424, 447, 461, 485, 530	0.16/0.14
III	293 (4.24)	405, 424, 447, 461, 485, 530	0.17/0/23
IV	292 (3.89)	405, 424, 447, 461, 485, 530	0.16/0.18
V	293 (4.07)	408, 424, 448, 461, 485, 528	0.18/0.27
VI	266 (4.80), 275 (4.84), 293 sh (4.92)	404, 423, 447, 461, 485, 530, 564, 600, 644	0.18/0.17
VII	269 (4.83), 277 (4.85), 289 sh (4.89)	405, 424, 447, 461, 485, 530, 579, 592, 615	028/022
VIII	265 (4.49), 274 (4.53), 291 sh (4.64)	405, 423, 447, 460, 485, 528	0.17/0.20
IX	265 (4.77), 274 (4.81), 283 sh (4.90), 291 sh (4.92)	408, 423, 447, 460, 484, 530	0.16/0.17
X	266 (4.51), 274 (4.58), 283 sh (4.66), 290 sh (4.68)	408, 424, 448, 461, 485, 528	0.18/0.27
HL^1	287 (4.45)	405, 423, 447, 460, 484, 528	

In the samarium complex **VI**, the Sm–O distances of pyrazolone ligands vary in the range of 2.333(2)–2.469(1) Å. The Sm(1)–O(3,4) distances are equalized and differed by ~0.03 Å, whereas the Sm(1)–O(1,2) and Sm(1)–O(5,6) distances differ noticeably (by ~0.1 Å). A similar trend is followed for **VII**–**X**. The Sm–O(7,8) distances for neutral phosphine oxide ligands are 2.328(2) and 2.338(1) Å. In the series **VI**–**X**, the Ln–O distances regularly decrease on going from Sm to Lu (as the Ln ionic radius decreases [24]). The Eu complex (**VII**) somewhat deviates from this trend.

In complex **VI**, the chelate angles of pyrazolone ligands are 73.12(4)° (O(1)Sm(1)O(2)), 72.56(4)° (O(3)Sm(1)O(4)), and 71.86(5)° (O(5)Sm(1)O(6)). A similar descending trend can be followed for **VII**–**X**.

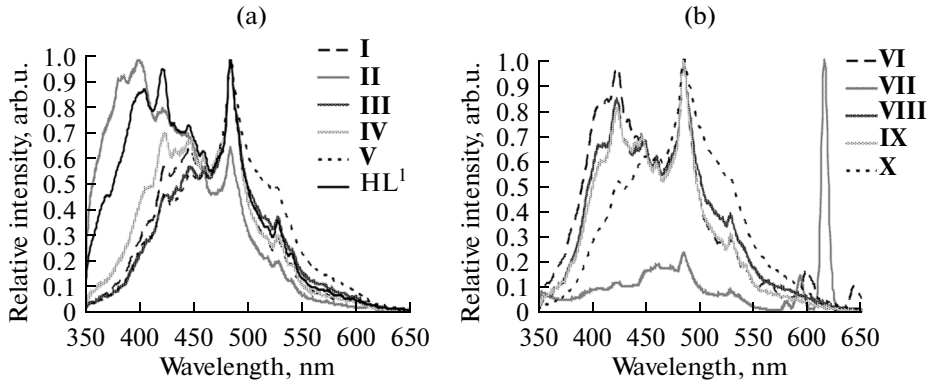


Fig. 5. Emission spectra (solid state) of complexes: (a) **I**–**V**, (b) **VI**–**X**.

In the series **VI**–**X**, the decrease in the Ln ionic radius from samarium to lutetium entails a systematic increase in the OLnO chelate angles. The O(7)Ln(1)O(8) angles between the phosphine oxide ligands in **VI**–**X** are in the narrow range of 81.64(5)°–82.10(6)°.

Study of the photophysical properties of lanthanide complexes indicated that the absorption spectra of compounds **I**–**V** (Fig. 4a, Table 3) are similar and contain broad bands with maxima at 290–293 nm corresponding to the $\pi \rightarrow \pi^*$ transitions in the aromatic systems of the pyrazolonate ligands.

The absorption maximum of **I**–**V** is shifted by 3–5 nm to shorter wavelength with respect to that of ligand HL^1, which is apparently due to more extended system of conjugation arising upon coordination of the pyrazolonate ligands to the lanthanide atom. A similar bathochromic shift was observed for europium complexes with various pyrazolonate ligands [25]. The absorption spectra of derivatives **VI**–**X** (Fig. 4b, Table 3), unlike complexes **I**–**V**, exhibit additional bands at 265–269 and 274–277 nm caused by the $\pi \rightarrow \pi^*$ transitions in the triphenylphosphine oxide benzene rings.

The photoluminescence spectra (PL) of solid complexes **I**–**V** show only the ligand-centered emission as a series of bands at 380–550 nm (Fig. 5a, Table 3). The emission color coordinates (Table 3) in the CIE (Commission Internationale de L'Eclairage) diagram correspond to blue.

In the samarium (**VI**) and europium (**VII**) complexes containing Ph_3PO ligands, the excitation energy is partially transferred from the coordination environment to the lanthanide ion; as a result, the PL spectra exhibit not only ligand emission but also bands at 579, 592, and 615 nm related to the $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, and $^5D_0 \rightarrow {}^7F_2$ transitions in the europium cations and bands at 564, 600, and 644 nm due to the $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^4G_{5/2} \rightarrow {}^6H_{7/2}$, and $^4G_{5/2} \rightarrow {}^6H_{9/2}$ in the samarium cations. Since the spectrum of complex **VII** shows bands for europium cation and ligand emission, the PL color coordinates are around white.

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