The complex Eu(phen)$L_3 \cdot 5CH_2Cl_2$ (HL is 1,3-bis(1,3-dimethyl-1*H*-pyrazol-4-yl)propane-1,3-dione): synthesis, crystal structure, and luminescent properties

I. V. Taydakov,[a*] *B. E. Zaitsev,*[b] *S. S. Krasnosel´skiy,*[b] *Z. A. Starikova,*[c] *and R. S. Borisov*[d]

[a]*G. S. Petrov Institute of Plastics,*
35 Perovskii proezd, 111024 Moscow, Russian Federation.
E-mail: taidakov@gmail.com
[b]*People´s Friendship University of Russia,*
6 ul. Miklukho-Maklaya, 117198 Moscow, Russian Federation
[c]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 119991 Moscow, Russian Federation
[d]*A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences,*
29 Leninsky prosp., 119991 Moscow, Russian Federation

A reaction of $Eu(NO_3)_3 \cdot 6H_2O$ with the novel heterocyclic ligand 1,3-bis(1,3-dimethyl-1*H*-pyrazol-4-yl)propane-1,3-dione and 1,10-phenanthroline in the presence of NaOH gave the complex Eu(phen)$L_3 \cdot 5CH_2Cl_2$. The crystal structure of the complex was determined by single-crystal X-ray diffraction. The coordination polyhedron $\{EuO_6N_2\}$ is a tetragonal antiprism. The complex shows bright orange-red luminescence in both the solid state and solution.

Key words: europium, complexes, pyrazole, 1,3-diketones, X-ray diffraction, luminescence.

Rare earth metal diketonates have been under intensive study in the last few decades because of their unique physicochemical properties. Possible applications of such complexes include separation and identification of lanthanides, preparation of finely divided powders and films by the CVD method, and the use as luminescent materials.[1]

Despite much research done in this field, rational design of lanthanide complexes with good luminescence is still problematic and, as a rule, is based on empirical selection of ligands.

It is known[2] that bright luminescence of such complexes can be attained by combination of several conditions: (1) considerable absorption of the excitation radiation by the ligand, (2) an optimum energy difference between the triplet level of the ligand and the corresponding resonance level of the rare earth metal ion (*e.g.*, for Eu^{3+}, the empirical optimum is 2000—2500 cm^{-1}), and (3) efficient shielding of the central ion by the ligand, which reduces the non-radiative energy transfer.

In particular, it has been demonstrated[3] that mixed complexes of diketones with such ligands as 2,2´-bipyridyl (bpy), 1,10-phenanthroline (phen), or triphenylphosphine oxide (TPPO) usually show more intense emission than do analogous hydrate and solvate complexes.

Earlier,[4] we have developed a general approach to the synthesis of novel heterocyclic ligands, namely, pyrazole-containing 1,3-diketones. In contrast to 4-acylpyrazolones,[5] such diketones virtually have not been examined hitherto. The only documented example is a complex of Be with a simpler diketone, *viz.*, (3,5-dimethyl-1*H*-pyrazol-4-yl)pentane-2,4-dione.[6]

As for electron-withdrawing properties, the pyrazole fragment can be likened, to some degree, to pyridine or (trifluoromethyl)benzene.[7] Since a sufficient number of europium(III) 1,3-diketonates with electron-withdrawing groups exhibit bright luminescence,[1] we found it interesting to obtain such a complex with a novel ligand, namely, 1,3-bis(1,3-dimethyl-1*H*-pyrazol-4-yl)propane-1,3-dione (**HL**). 1,10-Phenanthroline was added because the presence of this ligand usually enhances luminescence intensity.[8]

Complex **1** was obtained in one step according to a modified method[9] (Scheme 1).

The reaction was carried out in aqueous ethanol, which is a good solvent for both ligands and metal salts. After the reaction was completed, the solvent was removed and the target complex was extracted from the residue with CH_2Cl_2. Slow evaporation of the solvent at room temperature gave the complex Eu(phen)$L_3 \cdot 5CH_2Cl_2$ ($\mathbf{1} \cdot 5CH_2Cl_2$) as colorless crystals suitable for X-ray diffraction study.

We examined the behavior of complex **1** under the laser desorption-ionization (LDI-MS) conditions. In our case, organic matrices traditionally used to enhance the ionization conditions deteriorated the MS pattern showing many additional fragmentation peaks. The best-quali-

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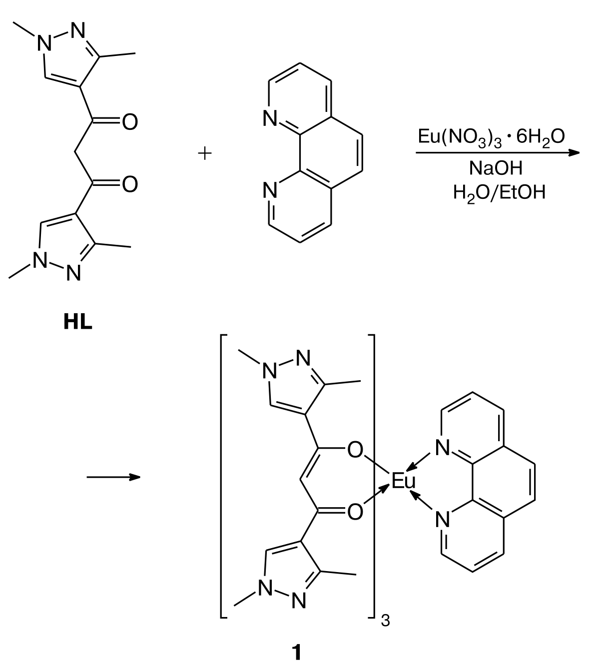
Scheme 1



ty spectra were obtained with no matrix at all; sodium acetate was employed as a neutral matrix (Fig. 1).

The signal at *m/z* 1133 (I = 1.6%) near the baseline level was assigned to the ion [M + Na]$^+$. The isotope distribution calculated for this cluster with the Isoform program agrees well with the experimental data. The formation of such clusters with alkali metal ions (in particular, Na$^+$) is quite characteristic of the LDI method.

The other clusters can be formulated as follows: *m/z* 671 [EuL$_2$ + H]$^+$, 852 [EuL$_2$Phen + H]$^+$, 954 [EuL$_3$Na + H]$^+$, 1082 [Eu$_2$L$_3$], 1042 [Eu$_2$L$_4$ + H]$^+$, and 1601 [Eu$_2$L$_5$]$^+$. However, special studies (MS/MS) are required to prove the above compositions.

X-ray diffraction data for complex **1** were used to visualize its structure in Figs 2 and 3.

The coordination number of the central Eu^{III} ion is eight; its coordination polyhedron is a square antiprism (Fig. 4).

The bases of the antiprism O(1)—O(2)—O(5)—O(6) (Pl^1) and O(3)—O(4)—N(1)—N(2) (Pl^2) are planar (the average deviations of the atoms from the mean planes are 0.04 and 0.10 Å, respectively) and parallel to each other; the Eu(1) atom is shifted toward Pl^2 (Eu(1)—Pl^1, 1.179 Å; Eu(1)—Pl^2, 1.455 Å).

The average Eu—O bond length (2.357 Å) is close to the bond lengths observed in similar complexes: [Eu(DBM)$_3$(phen)] (2.356 Å),[10] [Eu(DBM)$_3$(phen)]·CH$_3$COCH$_3$ (2.354 Å),[11] and [Eu(acac)$_3$(phen)] (2.359 Å).[12] The average Eu—N bond length (2.618 Å) is somewhat shorter than those in [Eu(DBM)$_3$(phen)] and [Eu(DBM)$_3$(phen)]·CH$_3$COCH$_3$ (2.641 and 2.642 Å, respectively).

The diketonate moieties (diket) are planar to within 0.03 Å. The pyrazole rings (pyr) are rotated about the C$_{pyr}$—C$_{diket}$ bonds so that the angles with the diket plane

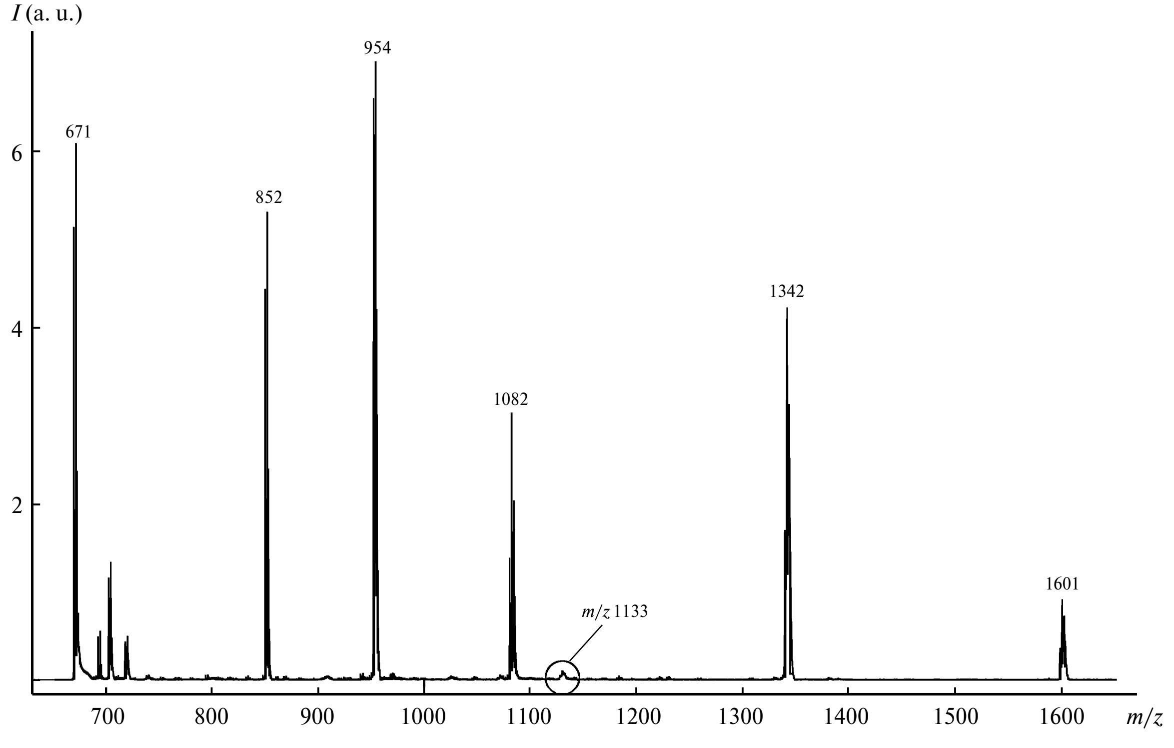


Fig. 1. LDI-MS spectrum of complex **1**.

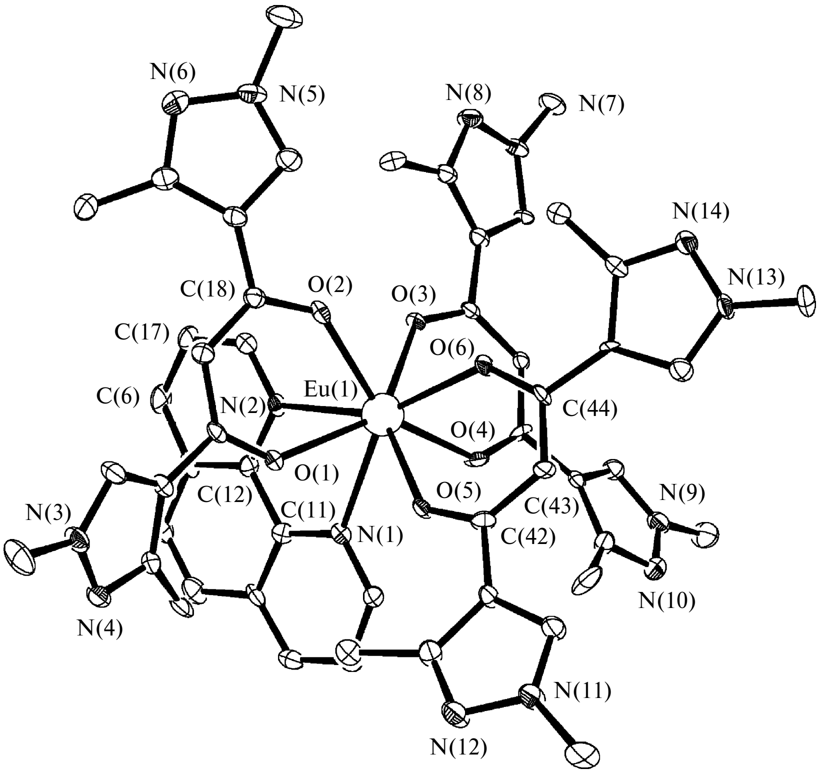


Fig. 2. Molecular structure of complex $\mathbf{1} \cdot 5CH_2Cl_2$ with atomic thermal displacement ellipsoids ($p = 50\%$); the solvent molecules and the hydrogen atoms are omitted.

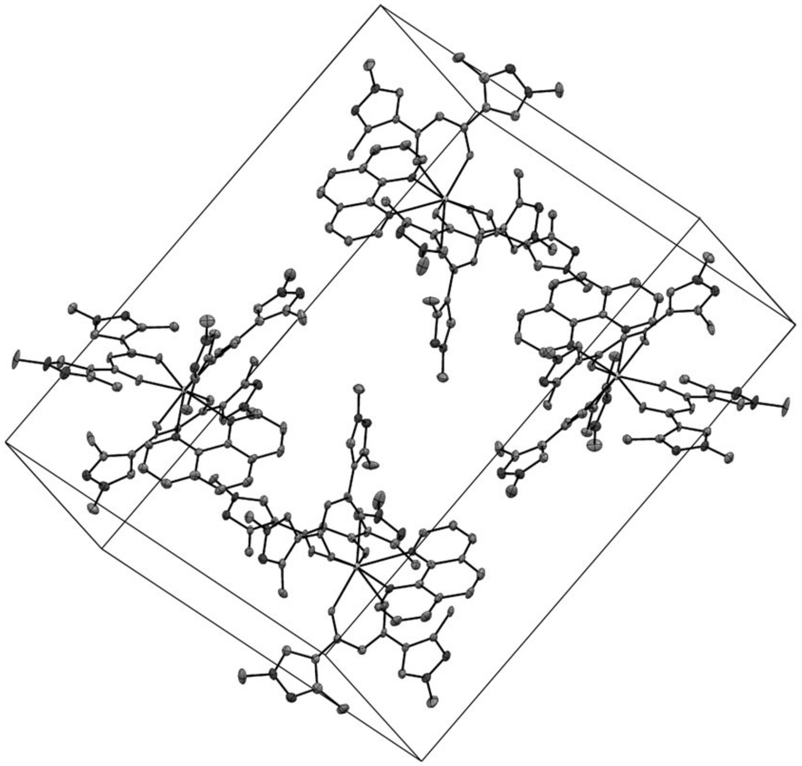


Fig. 3. Projection of the molecular packing of complex $\mathbf{1} \cdot 5CH_2Cl_2$ onto the plane *ab* with atomic thermal displacement ellipsoids ($p = 50\%$); the solvent molecules and the hydrogen atoms are omitted.

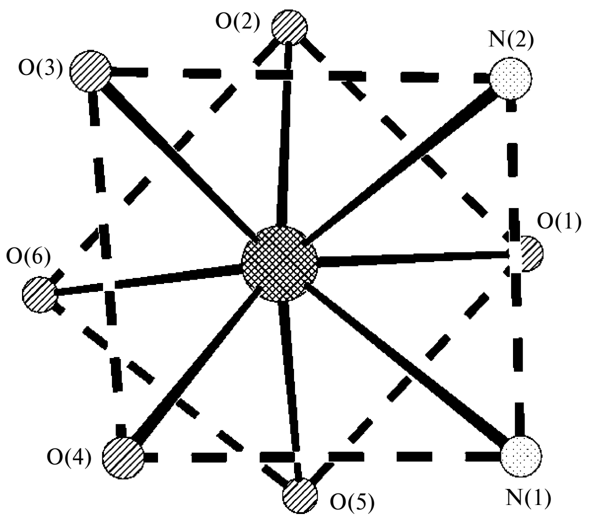


Fig. 4. Coordination polyhedron $\{EuO_6N_2\}$.

are 29.3° and 22.5° in the molecule containing the O(1) and O(2) atoms, 15.1° and 23.9° in the molecule containing the O(3) and O(4) atoms, and 11.2° and 11.4° in the molecule containing the O(5) and O(6) atoms.

The bright orange-red luminescence of complex **1** under UV light (365 nm) is visible to the naked eye. The emission and excitation spectra of the complex in the crystalline state are shown in Fig. 5. The highest emission intensity is observed upon the excitation at a wavelength of 380 nm. The emission spectrum is typical of Eu^{3+} complexes:^{2} the most intense peak at 615 nm corresponds to the transition $^5D_0 \rightarrow {}^7F_2$, while the less intense peaks at 653 and 708 nm, to the transitions $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_5$, respectively. In solution, the emission pattern remains qualitatively the same; however, the peak intensities are much lower.

To sum up, the reaction of $Eu(NO_3)_3 \cdot 6H_2O$ with 1,3-bis-(1,3-dimethyl-1*H*-pyrazol-4-yl)propane-1,3-dione and 1,10-phenanthroline in the presence of NaOH afforded the complex $Eu(phen)L_3$ (**1**). The structure of the complex (as an unstable solvate with five CH_2Cl_2 molecules) was examined by single-crystal X-ray diffraction. The composition of complex **1** was confirmed by elemental analysis and ^1H NMR spectroscopy. We also studied the behavior of this complex under laser desorption-ionization conditions and found that complex **1** undergoes fragmentation into a number of relatively stable clusters. When exposed to UV light ($\lambda_{max\ ex}$ = 380 nm), the complex exhibits luminescence with three main peaks at 615, 653, and 708 nm.

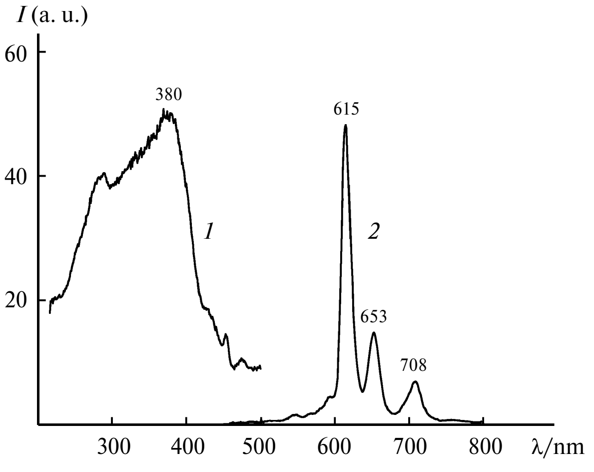


Fig. 5. Emission (*1*, λ_{em} = 615 nm) and excitation spectra (*2*, λ_{ex} = 380 nm) of complex **1**.

Experimental

The ligand was prepared according to a known procedure.^{4} The other reagents (Aldrich) were used as purchased.

^1H NMR spectra were recorded at 300 K on a Bruker AC-300 instrument (300 MHz) in $CDCl_3$ with $SiMe_4$ as the internal standard (δ 0.0).

Elemental analysis was carried out on an Elementar Vario Micro cube instrument (Elementar Analysensysteme GmbH, Germany).

Mass spectra (LDI-MS) were measured on a Bruker Autoflex II (TOF) instrument (reflectron mode, positive ion detection). A nitrogen laser (λ = 337 nm) was used as an excitation source. Measurements were performed for a mass range from 400 Da to 10 kDa; all signals below 400 Da were suppressed. A solution of complex **1** (2 mg mL^{-1}; prepared from its solid sample recrystallized and dried *in vacuo*) in THF was mixed with a solution of sodium acetate (5 mg mL^{-1}) in THF in a ratio of 1 : 1 (v/v); the resulting mixture was applied to the target. The data obtained were processed with the Bruker DataAnalysis for TOF 1.6g and Isoform program packages.

The excitation and emission spectra of complex **1** in the solid state and in $1 \cdot 10^{-3}$ *M* solutions in ethanol (quartz tube with a layer thickness of 10 mm) were recorded on a Fluorat Panorama instrument (LUMEX, Russia) equipped with a fiber-optic probe. A pulse xenon lamp was used as an excitation source.

Synthesis of tris[1,3-bis(1,3-dimethyl-1*H*-pyrazol-4-yl)-propane-1,3-dionato](1,10-phenanthroline)europium(III). 1,10-Phenanthroline (0.18 g, 1 mmol) and the diketone HL (0.781 g, 3 mmol) were dissolved with heating in ethanol (15 mL). Then 1 *M* aqueous NaOH (3 mL, 3 mmol) was added and the resulting mixture was centrifuged at 5000 rpm for 5 min and transferred to a beaker. Then a solution of $Eu(NO_3)_3 \cdot 6H_2O$ (0.446 g, 1 mmol) in water (5 mL) was added dropwise with vigorous stirring. The resulting solution was neutralized to pH 7 by adding several drops of acetic acid and kept in a thermostat at 40 °C for 2 h and at room temperature for 24 h. Then the solvent was completely removed *in vacuo* and CH_2Cl_2 (30 mL) was added to the solid residue. The solution was filtered, dried with anhydrous $MgSO_4$ (~0.5 g), and filtered again through a short column of Celite™ (Aldrich). The resulting transparent solution was left for slow evaporation at room temperature. The crystals that formed were filtered off, washed on the filter with a small amount of pentane, and dried *in vacuo*. The yield of complex **1** was 0.52 g (46%). Found (%): C, 54.43; H, 4.63; N, 17.76. $C_{51}H_{53}EuN_{14}O_6$. Calculated (%): C, 55.18; H, 4.81; N, 17.67.

Table 1. Crystallographic parameters and the data collection statistics for complex **1**

Parameter	Value
Molecular formula	$C_{56}H_{63}Cl_{10}EuN_{14}O_6$
Molecular weight	1534.66
T/K	100(2)
Wavelength	0.71073 Å (Mo-Kα)
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	12.3712(17)
b/Å	20.372(3)
c/Å	26.623(4)
α/deg	90
β/deg	95.618(3)
γ/deg	90
V/Å^3	6677.3(16)
Z	4
d_{calc}/g cm^{-3}	1.527
μ(Mo-Kα)/mm^{-1}	1.398
T_{min}/T_{max}	0.514/0.767
F(000)	3112
θ_{min}—θ_{max}/deg	1.26—26
Number of measured reflections	59854
Number of independent reflections	12969
Number of parameters refined	797
$R(F)$ ($I > 2\sigma(I)$)	0.0644
$R_w(F^2)$	0.0696
$\Delta\rho_{max}$, $\Delta\rho_{min}$/e Å^{-3}	2.495, −2.047

^{1}H NMR, δ: 11.1 (br.s, 2 H, CH); 10.8 (br.s, 4 H, CH); 10.4 (br.s, 5 H, CH); 8.9 (br.s, 6 H, CH); 3.7 (br.s, 18 H, N—Me); 2.1 (br.s, 18 H, Me).

Table 2. Selected bond lengths in structure **1**

Bond	d/Å	Bond	d/Å
Eu(1)—O(1)	2.383(4)	N(3)—C(22)	1.332(9)
Eu(1)—O(2)	2.332(4)	N(3)—C(23)	1.462(9)
Eu(1)—O(3)	2.375(4)	N(4)—C(14)	1.341(8)
Eu(1)—O(4)	2.363(4)	N(5)—N(6)	1.354(9)
Eu(1)—O(5)	2.351(4)	N(5)—C(24)	1.331(8)
Eu(1)—O(6)	2.338(4)	N(5)—C(25)	1.46(1)
Eu(1)—N(1)	2.610(5)	N(6)—C(20)	1.34(1)
Eu(1)—N(2)	2.627(4)	N(7)—N(8)	1.361(7)
O(1)—C(16)	1.264(7)	N(7)—C(35)	1.342(8)
O(2)—C(18)	1.285(7)	N(7)—C(36)	1.455(8)
O(2)—C(18)	1.285(7)	N(8)—C(27)	1.351(8)
O(3)—C(29)	1.275(7)	N(9)—N(10)	1.352(8)
O(4)—C(31)	1.248(6)	N(9)—C(37)	1.343(8)
O(5)—C(42)	1.273(7)	N(9)—C(38)	1.438(9)
O(6)—C(44)	1.276(7)	N(10)—C(33)	1.339(8)
N(1)—C(10)	1.322(8)	N(11)—N(12)	1.366(9)
N(1)—C(11)	1.349(9)	N(11)—C(48)	1.33(1)
N(2)—C(1)	1.315(8)	N(11)—C(49)	1.45(1)
N(2)—C(12)	1.368(8)	N(12)—C(40)	1.323(9)
N(3)—N(4)	1.350(7)	N(13)—N(14)	1.362(8)

Table 3. Selected bond angles in structure **1**

Angle	ω/deg	Angle	ω/deg
O(1)—Eu(1)—O(2)	72.1(1)	O(4)—Eu(1)—O(6)	80.9(1)
O(1)—Eu(1)—O(3)	139.2(1)	O(4)—Eu(1)—N(1)	70.3(2)
O(1)—Eu(1)—O(4)	138.8(1)	O(4)—Eu(1)—N(2)	101.5(1)
O(1)—Eu(1)—O(5)	73.0(1)	O(5)—Eu(1)—O(6)	73.2(1)
O(1)—Eu(1)—O(6)	122.2(1)	O(5)—Eu(1)—N(1)	77.3(2)
O(1)—Eu(1)—N(1)	71.5(2)	O(5)—Eu(1)—N(2)	134.0(1)
O(1)—Eu(1)—N(2)	73.6(1)	O(6)—Eu(1)—N(1)	140.5(2)
O(2)—Eu(1)—O(3)	78.8(1)	O(6)—Eu(1)—N(2)	152.7(2)
O(2)—Eu(1)—O(4)	148.8(1)	N(1)—Eu(1)—N(2)	62.6(2)
O(2)—Eu(1)—O(5)	116.6(1)	Eu(1)—O(1)—C(16)	136.6(4)
O(2)—Eu(1)—O(5)	116.6(1)	Eu(1)—O(2)—C(18)	137.0(4)
O(2)—Eu(1)—O(6)	83.2(1)	Eu(1)—O(3)—C(29)	134.2(4)
O(2)—Eu(1)—N(1)	134.3(2)	Eu(1)—O(4)—C(31)	136.6(4)
O(2)—Eu(1)—N(2)	81.3(1)	Eu(1)—O(5)—C(42)	134.6(4)
O(3)—Eu(1)—O(4)	72.2(1)	Eu(1)—O(6)—C(44)	133.5(4)
O(3)—Eu(1)—O(5)	147.2(1)	Eu(1)—N(1)—C(10)	121.1(4)
O(3)—Eu(1)—O(6)	80.8(1)	Eu(1)—N(1)—C(11)	120.7(4)
O(3)—Eu(1)—N(1)	113.8(2)	C(10)—N(1)—C(11)	117.9(5)
O(3)—Eu(1)—N(2)	74.3(1)	Eu(1)—N(2)—C(1)	122.0(4)
O(4)—Eu(1)—O(5)	84.1(1)	Eu(1)—N(2)—C(12)	119.5(4)

X-ray diffraction study was carried out for a light yellow plate-like crystal (0.55×0.40×0.20 mm) of [Eu(phen)L_3]•5CH_2Cl_2. An experimental X-ray diffraction data set of 59 854 reflections was collected at 100 K on a Bruker APEX II diffractometer equipped with a CCD detector (λMo-Kα radiation, $2\theta_{max}$ = 63.84°). After merging of equivalent reflections, 10 969 independent reflections (R_{int} = 0.0456) were used to solve and refine the structure. An absorption correction (μ = 1.398 mm^{-1}) was applied with the SADABS program.[13] The structure was solved by direct methods. All non-hydrogen atoms were located from difference electron-density maps and refined on F^2_{hkl} anisotropically. All hydrogen atoms were positioned geometrically and refined using a riding model with $U(H) = nU(C)$, where n = 1.2 for the methine groups and 1.5 for the Me groups (U(C) is the equivalent thermal parameter of the C atom to which the corresponding H atom is attached). In one CH_2Cl_2 molecule, the Cl atoms are disordered over two positions with occupancies of 0.9 and 0.1. All calculations were performed with the SHELXTL PLUS 5 program package.[14] The crystallographic parameters and the data collection statistics for complex **1** are summarized in Table 1. Selected geometrical parameters are given in Tables 2 and 3. The atomic coordinates, bond lengths, bond angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Center (CCDC No. 797532) and are available from www.ccdc.cam.uk/conts/retrieving.html (or CCDC, 12 Union Road, Cambridge CB2 1EZ; fax: +44 1223 335 033; or deposit@ccdc.cam.ac.uk).

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