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Binuclear Dysprosium(III) Complex with 2,6-Diformyl-4-*tert*-Butylphenol Bisphthalazinylhydrazone: Crystal Structure and Magnetic Properties

S. I. Levchenkov[a, *], **L. D. Popov**[b], **S. S. Beloborodov**[b], **I. N. Shcherbakov**[b], **G. G. Aleksandrov**[c], **Yu. P. Tupolova**[b], **V. V. Lukov**[b], **and V. A. Kogan**[b, †]

[a] *Southern Scientific Center, Russian Academy of Sciences, Rostov-on-Don, Russia*
[b] *Southern Federal University, Rostov-on-Don, 344104 Russia*
[c] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow, 119991 Russia*
**e-mail: s.levchenkov@gmail.com*

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Abstract—The Dy(III) binuclear complex with N_4O-donor 2,6-diformyl-4-*tert*-butylphenol bis-1'-phthalazinylhydrazone (H_3L) of the composition $[Dy_2(H_2L)_3](NO_3)_3 \cdot 3C_2H_5OH$ (CIF file CCDC 1048418) is synthesized and structurally characterized. In the complex cation $[Dy_2(H_2L)_3]^{3+}$, ligands H_2L^- form a three-blade helix around the Dy(III) ions. Both right-side (Δ configuration) and left-side (Λ) helicates are presented in crystal in an equimolar ratio. The magnetic properties of the complex are studied.

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INTRODUCTION

Bishydrazones of 2,6-diformyl-4-R-phenols are classical binucleating ligand systems, whose structure predetermines the formation of binuclear complexes with many transition metals [1–3]. Numerous studies of transition metal complexes with these ligands made it possible to formulate a series of regularities that are used for the prediction of the structures and magnetic properties of the complexes [4, 5]. The lanthanide complexes with 2,6-diformyl-4-R-phenol bishydrazones were studied to a significantly lower extent. Only several similar compounds were structurally studied [6–11], and the slow relaxation of magnetization was found for one of the binuclear dysprosium(III) complexes [9]. The magnetic properties of bi- and polynuclear lanthanide complexes attract attention of many researchers due to developments of new molecular magnetic materials [12–15].

The results of the X-ray diffraction and magnetochemical studies of the binuclear dysprosium(III) complex with 2,6-diformyl-4-*tert*-butylphenol bis-1'-phthalazinylhydrazone (H_3L) are presented in this report.

EXPERIMENTAL

Bishydrazone H_3L was synthesized using a described procedure [16].

Synthesis of $[Dy_2(H_2L)_3](NO_3)_3 \cdot 3C_2H_5OH$ (I). A hot solution of dysprosium(III) nitrate (1 mmol) in methanol (10 mL) was poured to a hot solution of H_3L (1 mmol) in methanol (30 mL). The reaction mixture was refluxed with a reflux condenser for 1 h and left to stay overnight. The precipitate was filtered off, washed with methanol, dried in vacuo, and recrystallized from ethanol. The yield was 30%.

For $C_{90}H_{93}N_{27}O_1Dy_2$

anal. calcd., %:	C, 51.04;	H, 4.43;	N, 17.86.
Found, %:	C, 50.54;	H, 4.29;	N, 17.51.

IR (ν, cm^{-1}): 3325 ν(NH), 1610, 1595 ν(C=N).

IR spectra were recorded on a Varian Scimitar 1000 FT-IR instrument in a range of 400–4000 cm^{-1} for samples as suspensions in Nujol.

The magnetic susceptibility of complex **I** in a temperature range of 300–2 K was determined on a Quantum Design SQUID magnetometer in a magnetic field of 5 kOe.

X-ray diffraction analysis of complex **I** was carried out on a Bruker APEX II diffractometer (MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator) at 120(2) K. The initial massif of measured intensities was processed using the SAINT [17] and SADABS programs [18]. The structure was solved by a direct method and refined by full-matrix least squares in the anisotropic approximation for non-hydrogen atoms for F^2_{hkl}. Hydrogen atoms were placed in the geometri-

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[†] Deceased.

Table 1. Crystallographic data and experimental and refinement characteristics for compound **I**

Parameter	Value
FW	2117.91
Crystal size, mm	0.32 × 0.22 × 0.11
Crystal system	Rhombohedral
Space group	R_3c
a, Å	16.4228(17)
c, Å	62.620(6)
γ, deg	120
V, Å^3	14626(2)
Z	6
ρ_{calcd}, g/cm^3	1.443
μ, mm^{-1}	1.596
F(000)	6444
Scan θ range, deg	1.57–29.44
Number of measured reflections	36861
Number of independent reflections	8851
Number of reflections with $I > 2\sigma(I)$	4955
Ranges of reflection indices	$-22 \le h \le 22$,
	$-17 \le k \le 22$,
	$-85 \le l \le 85$
Number of refined parameters	386
R_1 ($I > 2\sigma(I)$)	0.0593
wR_2 (all reflections)	0.2208
Goodness-of-fit (all reflections)	0.999
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	1.42/–1.59

cally calculated positions and refined by the riding model (U_{iso}(H) = nU_{iso}(C), n for the carbon atoms of the methyl groups, $n = 1.2$ for other C atoms). All calculations were performed using the SHELXTL program package [19]. The PLATON program was used for an analysis of the molecular and crystal structures [20]. The experimental characteristics and crystallographic data are presented in Table 1. Selected interatomic distances and bond angles are listed in Table 2. The coordinates of atoms and temperature factors were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC 1048418).

RESULTS AND DISCUSSION

The reaction of bishydrazone H_3L with dysprosium(III) nitrate in methanol followed by recrystallization from ethanol afforded complex **I**, whose structure was determined by X-ray diffraction analysis. The structure of the binuclear cation $[Dy_2(H_2L)_3]^{3+}$ is shown in Fig. 1. The binuclear cation of the complex has symmetry C_3 (the 3-fold axis passes through the dysprosium atom).

Each organic ligand H_2L^-, which exists in the monodeprotonated hydrazone tautomeric form, is coordinated by the phthalazine N(1) atom and azomethine N(4) atom to the Dy(1) atom and by the phthalazine N(7) atom and azomethine N(5) atom to the Dy(2) atom. The phenoxide O(1) atom performs the bridging function. Each Dy^{3+} ion has a coordination number of 9. The Dy(1)–Dy(2) distance is 3.5460(8) Å, and the Dy(1)O(1)Dy(2) bond angle is 108.2(3)°. The dysprosium ions lie exactly in the planes formed by the azomethine donor atoms N(4), N(4a), and N(4b) in the case of Dy(1) and N(5), N(5a), and N(5b) in the case of Dy(2).

The five-membered metallochelate rings Dy(1)N(1)C(8)N(3)N(4) and Dy(2)N(7)C(17)N(6)N(5) have an envelope conformation, and their valves are formed by the Dy atom shifting from the mean plane of other atoms of the cycle by 0.694 and 0.550 Å, respectively. The six-membered metallocycles Dy(1)O(1)C(15)C(10)C(9)N(4) and Dy(2)O(1)C(15)C(14)C(16)N(5) are strongly distorted: their conformation can be described as "twist" relatively to the Dy(1)–O(1) and Dy(2)–O(1) bonds, respectively.

The ligands in the complex are nonplanar. The phthalazine cycles N(1)N(2)C(1)C(2)C(3)C(4)C(5)C(6)C(7)C(8) and N(7)N(8)C(24)C(23)C(22)C(21)C(20)C(19)C(18)C(17) are unfolded relatively to the C(10)C(11)C(12)C(13)C(14)C(15) benzene ring along the N(3)–N(4) and N(5)–N(6) bonds to opposite sides. The dihedral angles between the corresponding mean planes of the cycles are 48.9° and 43.3°. As a result, in the complex cation $[Dy_2(H_2L)_3]^{3+}$, ligands H_2L^- form the right-side (Δ configuration) or left-side (Λ) three-blade helices (helicates) around two Dy^{3+} ions [9]. The general view of the right- and left-side helicates is shown in Fig. 2.

In a single crystal of complex **I**, the enantiomers are in the equimolar ratio. The complex cations in crystal are linked by a branched network of hydrogen bonds involving counterions and solvate molecules. However, since the positions of the nitrate ions and ethanol molecules are disordered and characterized by site occupancies lower than unity, it is impossible to deter-

Table 2. Selected interatomic distances and bond angles in the coordination polyhedra of the dysprosium atoms in a molecule of complex **I**

Bond	*d*, Å	Bond	*d*, Å
Dy(1)–O(1)	2.321(7)	Dy(2)–O(1)	2.316(6)
Dy(1)–N(1)	2.482(9)	Dy(2)–N(7)	2.532(8)
Dy(1)–N(4)	2.599(8)	Dy(2)–N(5)	2.614(8)
Angle	ω, deg	Angle	ω, deg
O(1)Dy(1)N(1)	125.1(2)	O(1)Dy(2)N(5)	65.5(2)
O(1)Dy(1)N(4)	64.4(2)	O(1)Dy(2)N(7)	124.5(3)
O(1)Dy(1)O(1a)	67.8(2)	O(1)Dy(2)O(1a)	68.0(2)
O(1)Dy(1)N(1a)	85.3(3)	O(1)Dy(2)N(5a)	128.9(2)
O(1)Dy(1)N(4a)	73.9(3)	O(1)Dy(2)N(7a)	144.1(3)
O(1)Dy(1)O(1b)	67.8(3)	O(1)Dy(2)O(1b)	68.0(3)
O(1)Dy(1)N(1b)	143.5(4)	O(1)Dy(2)N(5b)	76.2(3)
O(1)Dy(1)N(4b)	126.9(2)	O(1)Dy(2)N(7b)	85.3(3)
N(1)Dy(1)N(4)	62.5(3)	N(5)Dy(2)N(7)	61.2(3)
N(1)Dy(1)O(1a)	143.5(3)	N(5)Dy(2)O(1a)	76.2(3)
N(1)Dy(1)N(1a)	91.2(4)	N(5)Dy(2)N(5a)	120.0(3)
N(1)Dy(1)N(4a)	147.8(3)	N(5)Dy(2)N(7a)	145.8(3)
N(1)Dy(1)O(1b)	85.3(3)	N(5)Dy(2)O(1b)	128.9(3)
N(1)Dy(1)N(1b)	91.2(4)	N(5)Dy(2)N(5b)	120.0(3)
N(1)Dy(1)N(4b)	72.3(3)	N(5)Dy(2)N(7b)	71.0(3)
N(4)Dy(1)O(1a)	126.9(3)	N(7)Dy(2)O(1a)	85.3(3)
N(4)Dy(1)N(1a)	72.3(4)	N(7)Dy(2)N(5a)	71.0(3)
N(4)Dy(1)N(4a)	119.8(3)	N(7)Dy(2)N(7a)	91.2(3)
N(4)Dy(1)O(1b)	73.9(2)	N(7)Dy(2)O(1b)	144.1(2)
N(4)Dy(1)N(1b)	147.8(3)	N(7)Dy(2)N(5b)	145.8(3)
N(4)Dy(1)N(4b)	119.8(3)	N(7)Dy(2)N(7b)	91.2(3)

mine the parameters of hydrogen bonds. There is a weak stacking interaction between the phthalazine cycles of each complex ion and six adjacent ions (which are optical antipodes) in crystal (Fig. 3). The dihedral angle between the mean planes of the cycles is 3.83°, the distance between the centroids N(1)N(2)C(1)C(2)C(7)C(8) and C(18)C(19)C(20)C(21)C(22)C(23) is 3.668 Å, and that between the centroids C(2)C(3)C(4)C(5)C(6)C(7) and N(7)N(8)C(24)C(23)C(18)C(17) is 3.513 Å.

The effective magnetic moment (μ_{eff}) of complex **I** at 300 K (14.75 μ_B) is somewhat lower than the expected value for two noninteracting Dy^{3+} ions ($^6H_{15/2}$, $S = 5/2$, $L = 5$, $g = 4/3$). On cooling to 2 K, μ_{eff} decreases to 11.60 μ_B, which can be due to the antiferromagnetic exchange interaction between the Dy^{3+} ions, a thermal decrease in the occupancy of the Stark sublevels, or substantial magnetic anisotropy [21–24].

The field dependence of the magnetic moment of complex **I** at 2 K is well approximated by the Brillouin

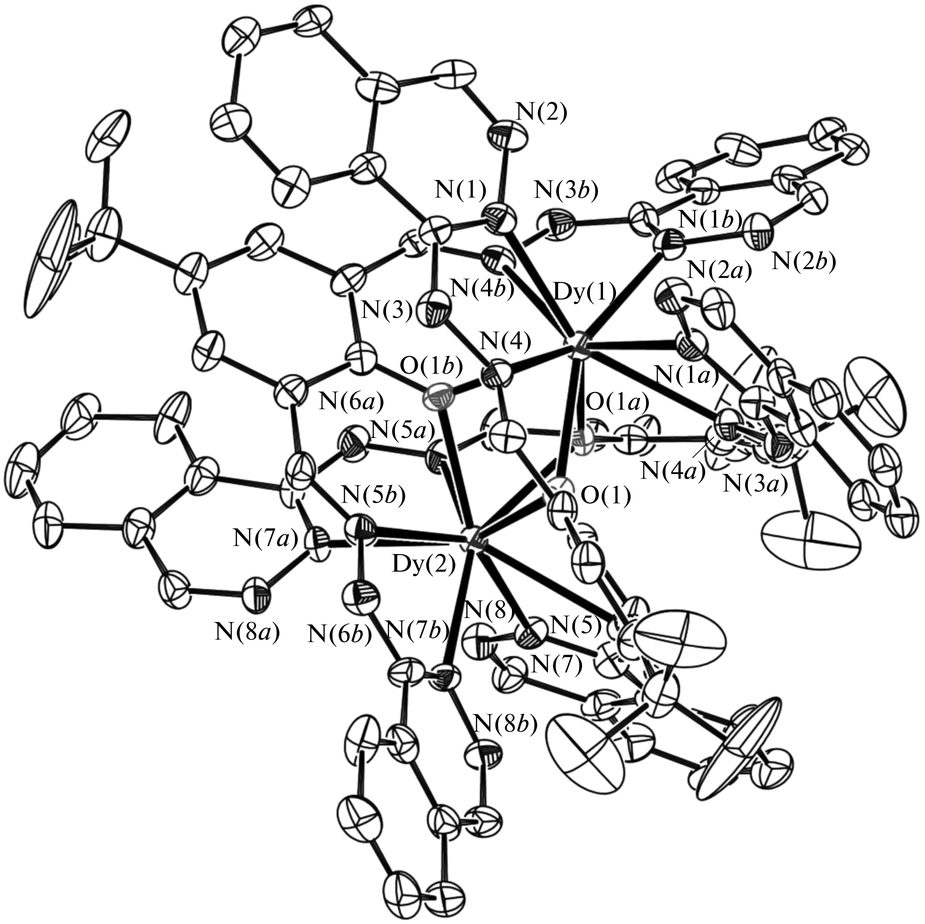

Fig. 1. Structure of the cation of complex **I** in the representation of atoms by ellipsoids of atomic shifts with 30% probability (hydrogen atoms are omitted).

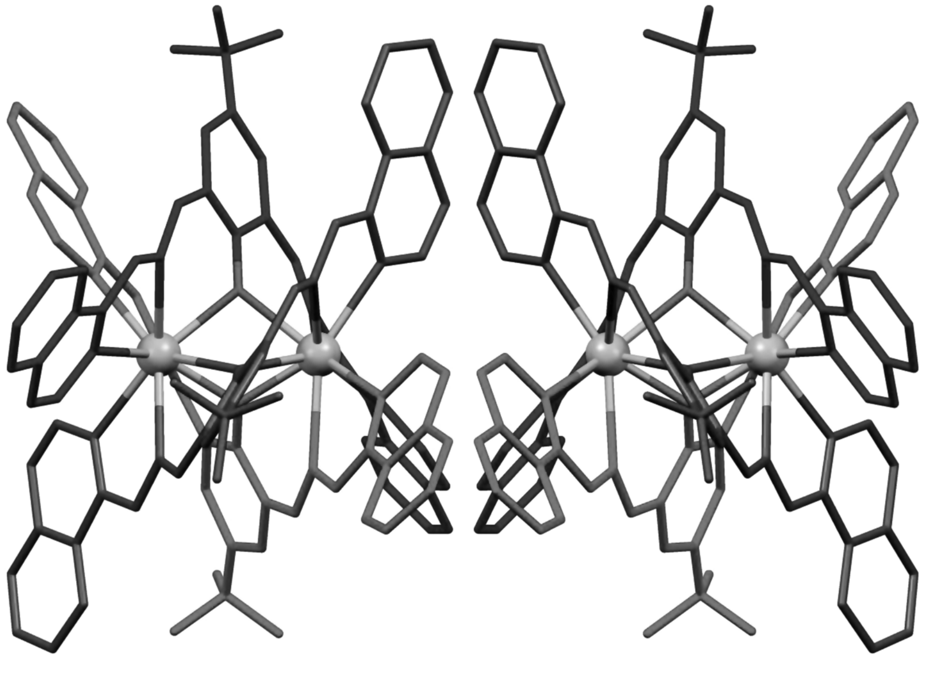

Fig. 2. (Δ, at the left) Right-side and (Λ, at the right) left-side configurations of the cations of complex **I** (hydrogen atoms are omitted).

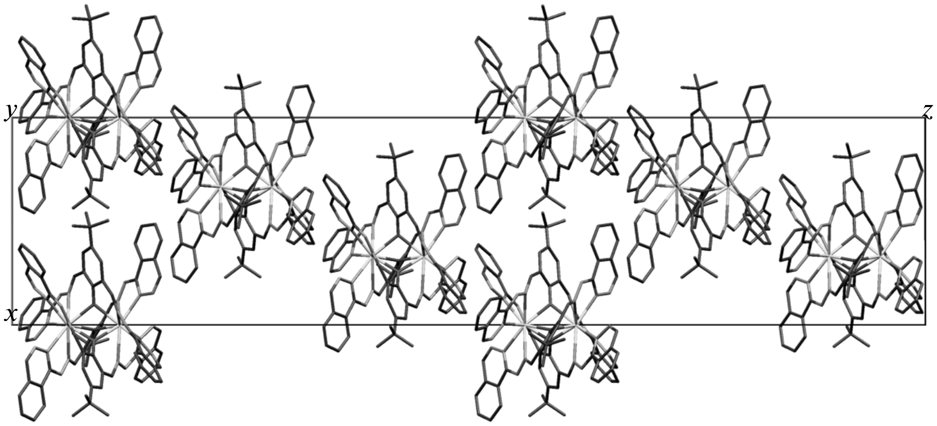

Fig. 3. Crystal packing of the cations of complex **I** (view along the crystallographic axis *y*).

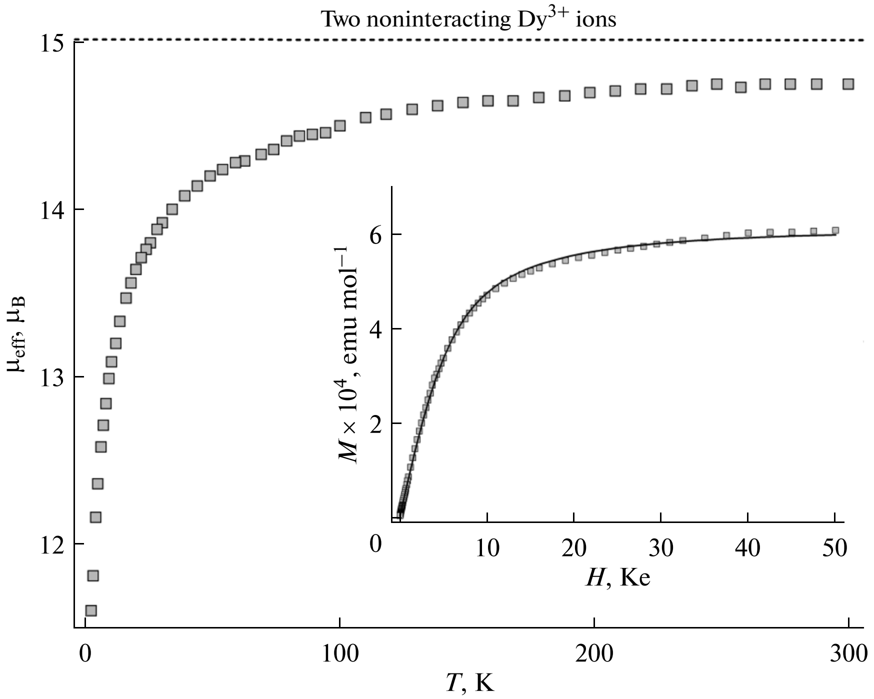

Fig. 4. Temperature dependence of μ_{eff} for complex **I**. Inset: the field dependence of the magnetic moment of complex **I** at 2 K (solid line is the approximation by the Brillouin function).

function (inset in Fig. 4; $J = 8.39 \pm 1.21$, $g = 1.29 \pm 0.16$). As in the case of the earlier described Dy(III) complexes with 2,6-diformyl-4-R-phenol bisacylhydrazones [11], this fact excludes the manifestation of the properties of a single-molecule magnet by complex **I**.

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