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Crystal structure and magnetic properties of binuclear Dy^{III} complexes with 4-substituted 2,6-diformylphenol bis(acylhydrazones)

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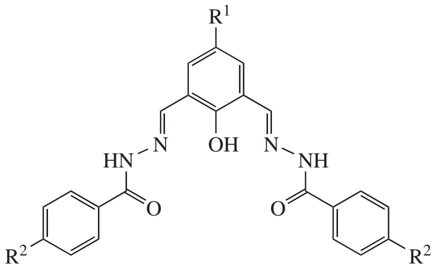
Two binuclear Dy^{III} complexes of the general formulas [$Dy_2(H_2L^1)_3$]·$3NO_3$·EtOH·H_2O and [$Dy_2(H_2L^2)_3$]·$3NO_3$·2EtOH·$4H_2O$ [H_3L^1 and H_3L^2 are 2,4-diformyl-4-fluorophenol bis(benzoylhydrazone) and 2,4-diformyl-4-metoxyphenol bis(4-methylbenzoylhydrazone), respectively] have been synthesized and characterized by X-ray diffraction analysis and low-temperature magnetic measurements.

4-Substituted 2,6-diformylphenol bis(hydrazones) are classical compartmental ligands (so-called Robson-type ligands).[1–6] Their structure predetermines the formation of binuclear complexes with a wide variety of transition metal ions. Generally, these complexes contain an exogenous bridging ligand like an anion used for complexation, a μ-hydroxy or μ-alkoxy moiety and the pyrazolate anion.[5–7] Studies of transition metal complexes with such ligands led to the formulation of general rules for predicting their structure and magnetic behaviour.[5–8]

Only a few lanthanide(III) complexes with 2,6-diformyl-4-R-phenol bis(hydrazone) ligands were described, and only five binuclear complexes were studied by X-ray diffraction analysis.[9–13] A binuclear Dy^{III} complex with 2,6-diformyl-4-methylphenol bis(benzoylhydrazone) exhibits slow magnetic relaxation resulting from a molecular-based blocking anisotropy.[12] The magnetism of bi- and polynuclear lanthanide complexes and the design of single molecule magnets (SMMs) are of considerable current interest[14–16] due to the large inherent anisotropy of lanthanide metal ions.

Here, we describe the molecular and crystal structures and the magnetic properties of two new binuclear Dy^{III} complexes based on 2,4-diformyl-4-fluorophenol bis(benzoylhydrazone) (H_3L^1) and 2,4-diformyl-4-methoxyphenol bis(4-methylbenzoylhydrazone) (H_3L^2).

The synthesis of these bis(hydrazones) has been reported earlier.[17,18] By reaction of bis(hydrazones) with Dy^{III} trinitrate pentahydrate in methanol solution the complexes of general formula [$Dy_2(H_2L)_3$]·$3NO_3$ have been obtained.† Single crystals for X-ray diffraction analysis were prepared by slow crystallization from ethanol solutions.‡



H_3L^1: $R^1 = F$, $R^2 = H$
H_3L^2: $R^1 = OMe$, $R^2 = Me$

The molecular structure of complex [$Dy_2(H_2L^1)_3$]·$3NO_3$·EtOH·H_2O **1** is shown in Figure 1. Three monodeprotonated 2,4-diformyl-4-fluorophenol bis(benzoylhydrazone) ligands are bonded to two Dy^{III} cations. The ligand strands twist along a pseudo-threefold axis defined by two Dy(1) and Dy(2) ions forming a triple-stranded helical structure.

Each organic ligand is linked to a Dy^{III} atom *via* one N atom and two O atoms. The coordination of hydrazone to Dy^{III} ions results in the formation of five-membered (DyOCNN) and six-membered (DyNCCCO) chelating rings. The two Dy^{III} centres have

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† *Synthetic procedure*. A hot solution of Dy^{III} trinitrate pentahydrate (1 mmol) in methanol (10 ml) was added to a hot suspension of bis(hydrazone) H_3L^1 or H_3L^2 (1 mmol) in methanol (10 ml) and the mixture was refluxed for 1 h. Precipitate formed was filtered off, washed with methanol, dried *in vacuo* at room temperature and recrystallized from ethanol.

For **1**: yield 30%, mp > 250 °C. IR (Nujol, ν/cm^{-1}): 3400 (ν_{OH}), 3215 (ν_{NH}), 1641($\nu_{C=O}$), 1620, 1582($\nu_{C=N}$). Found (%): C, 45.5; H, 3.29, N, 11.3. Calc. for $C_{70}H_{62}Dy_2F_3N_{15}O_{21}$ (%): C, 45.9; H, 3.41; N, 11.5.

For **2**: yield 25%, mp > 250 °C. IR (Nujol, ν/cm^{-1}): 3410 (ν_{OH}), 3207 (ν_{NH}), 1636 ($\nu_{C=O}$), 1615, 1585 ($\nu_{C=N}$). Found (%): C, 47.9; H, 4.61; N, 10.8. Calc. for $C_{79}H_{89}Dy_2N_{15}O_{27}$ (%): C, 47.3; H, 4.47; N, 10.5.

‡ *Crystal data for* **1**: yellow crystals, $C_{70}H_{62}Dy_2F_3N_{15}O_{21}$ ($M = 1831.35$), triclinic, space group $P\bar{1}$, at 150(2) K: $a = 12.8474(6)$, $b = 16.8422(8)$ and $c = 18.9658(9)$ Å, $\alpha = 89.9550(8)°$, $\beta = 88.6628(7)°$ and $\gamma = 71.4588(7)°$, $V = 3889.6(3)$ Å^3, $Z = 2$, $d_{calc} = 1.564$ g cm^{-3}, $F(000) = 1828$, $\mu = 1.994$ mm^{-1}, $R_{int} = 0.023$, $\theta_{max} = 26.7°$. Bruker Smart Apex II CCD diffractometer, 27717 reflections collected, 17263 independent reflections, 12491 observed reflections with $I > 2\sigma(I)$, $R_1 = 0.0428$ [$I > 2\sigma(I)$], $wR_2 = 0.1502$ (all reflections), 997 refined parameters, GOOF = 0.998 (all reflections).

Crystal data for **2**: yellow crystals, $C_{158}H_{178}Dy_4N_{30}O_{54}$ ($M = 4011.30$), monoclinic, space group $P2$, at 150(2) K: $a = 20.8291(10)$, $b = 19.1045(9)$ and $c = 22.0498(11)$ Å, $\beta = 91.0202(7)°$, $V = 8772.9(7)$ Å^3, $Z = 2$, $d_{calc} = 1.519$ g cm^{-3}, $F(000) = 4064$, $\mu = 1.775$ mm^{-1}, $R_{int} = 0.068$, $\theta_{max} = 29.6°$. Bruker Smart Apex II CCD diffractometer, 94844 reflections collected, 47977 independent reflections, 31772 observed reflections with $I > 2\sigma(I)$, $R_1 = 0.0811$ [$I > 2\sigma(I)$], $wR_2 = 0.2439$ (all reflections), 1015 refined parameters, GOOF = 1.018 (all reflections).

CCDC 967318 and 967319 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2014.

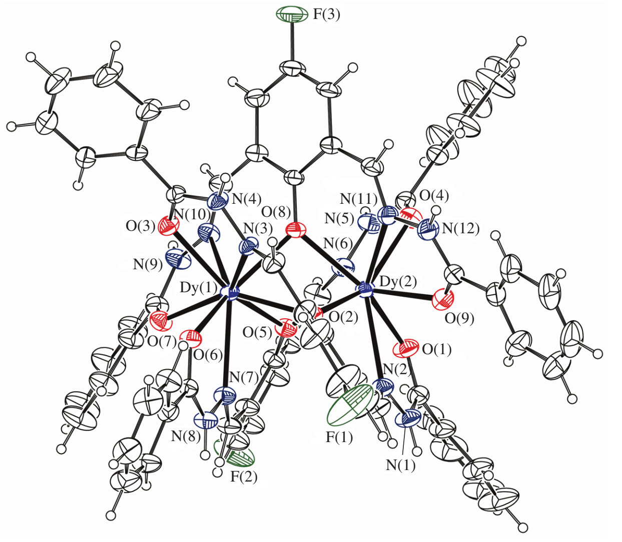
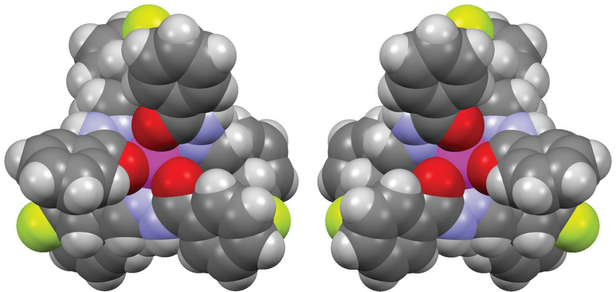


Figure 1 ORTEP view of the trication of complex **1** (the thermal ellipsoids are shown with a 30% probability; the nitrate ions and solvent molecules are omitted for clarity). Selected distances (Å): Dy(1)–O(5) 2.331(3), Dy(1)–O(8) 2.344(3), Dy(1)–O(2) 2.347(4), Dy(1)–O(7) 2.376(4), Dy(1)–O(3) 2.378(4), Dy(1)–O(6) 2.382(4), Dy(1)–N(3) 2.567(4), Dy(1)–N(10) 2.604(5), Dy(1)–N(7) 2.606(4), Dy(1)–Dy(2) 3.5153(4), Dy(2)–O(8) 2.323(3), Dy(2)–O(5) 2.330(4), Dy(2)–O(9) 2.336(4), Dy(2)–O(2) 2.347(4), Dy(2)–O(1) 2.357(4), Dy(2)–O(4) 2.358(4), Dy(2)–N(11) 2.610(5), Dy(2)–N(6) 2.616(5), Dy(2)–N(2) 2.630(5). Selected bond angles (°): Dy(2)–O(2)–Dy(1) 96.98(13), Dy(2)–O(5)–Dy(1) 97.92(13), Dy(2)–O(8)–Dy(1) 97.74(12).

the same coordination environment. Each Dy^{III} atom exhibiting a distorted tricapped trigonal-prismatic coordinated arrangement is bound by six O atoms and three N atoms of the ligand. The Dy^{III} ions are bridged by the three endogenous phenoxide oxygen atoms O(2), O(5) and O(8) of the three ligands with a Dy–Dy distance of 3.5153(4) Å. All of the Dy–O–Dy bond angles formed by the phenoxide bridging atoms do not differ notably (Figure 1). The Dy–O and Dy–N distances are 2.323–2.382 and 2.567–2.630 Å, respectively. The dysprosium ions are positioned on the planes formed by three nitrogen donor atoms, N(3), N(7) and N(10) for Dy(1) and N(2), N(6) and N(11) for Dy(2).

The three ligands in the cationic entity $[Dy_2L^1_3]^{3+}$ are twisted along the central N–N bonds. The dihedral angles between the two terminal phenyl rings of the ligand are 64.14, 13.17 and 34.73° for the moieties containing F(1), F(2) and F(3) atoms, respectively. The ligands strand wrap around a pseudo-threefold axis defined by two Dy ions. The configuration of two $[Dy_2L^1_3]^{3+}$ cations in the unit cell is a right-hand (Δ) and a left-hand (Λ) triple-stranded helicate, forming a mixture of both enantiomers in the single crystal of complex **1**. Figure 2 shows the relation between the two complex cations of Δ and Λ configurations along the Dy–Dy line.

In the crystal of compound **1**, there is extensive hydrogen bonding leading to a very complex motif. All the NH groups of the hydrazonic moieties of the ligand are hydrogen bonded to uncoordinated solvent molecules or to the oxygen atoms of the nitrate counter ions.



Δ Λ

Figure 2 Right- (Δ) and left-hand (Λ) configurations of the complex cation $[Dy_2L^1_3]^{3+}$ along the Dy–Dy line.

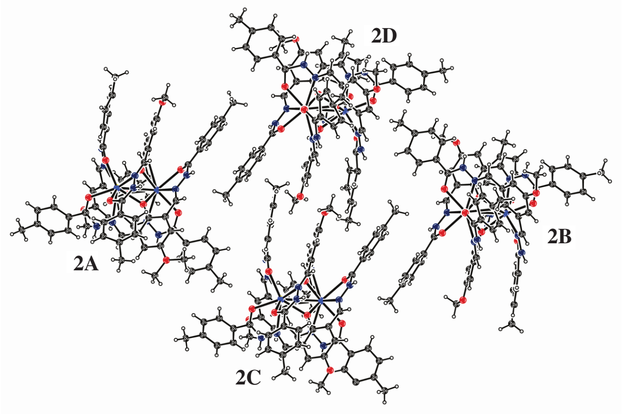


Figure 3 General view of four independent molecules in the crystal structure of **2** along the crystallographic axis *a* (the thermal ellipsoids are shown with a 30% probability; the nitrate ions and solvent molecules are not shown).

The crystal structure of complex $[Dy_2(H_2L^2)_3]\cdot 3\,NO_3\cdot 2EtOH\cdot 4\,H_2O$ **2** includes four independent molecules A–D (Figure 3) having the C_2 symmetry. The C_2 axis is defined by the phenoxide bridging atom and the oxygen atom of the methoxy group of an organic ligand; this axis is parallel to the crystallographic axis *b*.

The distances Dy(1)–Dy(1′), Dy(2)–Dy(2′), Dy(3)–Dy(3′) and Dy(4)–Dy(4′) are 3.4864(6), 3.491(1), 3.494(1) and 3.496(3) Å, respectively. The other molecular structure parameters of complex **2** are very similar to those of complex **1**. Note that the structural parameters of both of the complexes are similar to those of earlier described binuclear Dy^{III} complexes with other 2,4-diformyl-4-R-phenol bis(hydrazones).[10,12]

The crystal structure of compound **2** is significantly different from those of complex **1** and all of the previously described Ln^{III} complexes with 2,6-diformyl-4-R-phenol bis(hydrazones).[9–13] The unit cell in a single crystal of compound **2** is not characterized by an inversion centre. The configuration of two $[Dy_2L^2_3]^{3+}$ cations [**2A** and **2C**, including Dy(1) and Dy(1′), Dy(3) and Dy(3′) atoms, respectively] is close to right-hand (Δ) triple-stranded helicates. The configuration of other two complex cations [**2B** and **2D**, including Dy(2) and Dy(2′), Dy(4) and Dy(4′) atoms] is close to left-hand (Λ) helicates. Each of these helicates does not have a corresponding enantiomer in the single crystal of complex **2**.

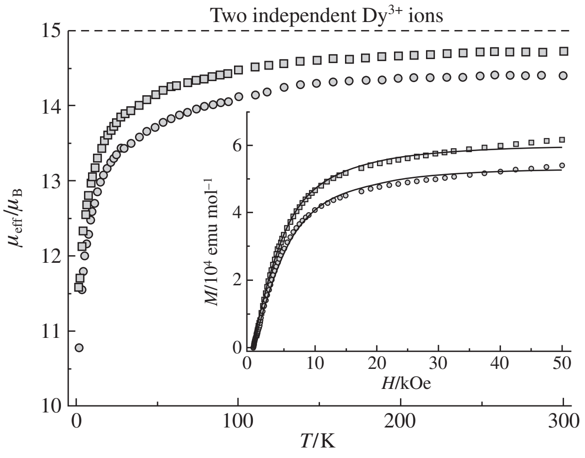


Figure 4 Temperature dependence of μ_{eff} per mol of (◎) **1** and (▣) **2**. Inset: the field dependence of the magnetic moments of (◎) **1** and (▣) **2** at 2 K (solid lines are the best fit by the Brillouin function; $J = 6.78702\pm1.4517$, $g = 1.4146\pm0.2875$ for complex **1** and $J = 8.3857\pm1.22597$, $g = 1.28932\pm0.18049$ for complex **2**).

Temperature-dependent magnetic susceptibility measurements for compounds **1** and **2** have been carried out with a Quantum Design MPMSXL SQUID magnetometer in an applied magnetic field of 1 kOe over a temperature range of 300–302 K (Figure 4).

The observed effective magnetic moment μ_{eff} values of $14.40\mu_{\mathrm{B}}$ for **1** and $14.72\mu_{\mathrm{B}}$ for **2** at 300 K are somewhat lower than the expected values for two uncoupled $\mathrm{Dy^{III}}$ ions ($^6\mathrm{H}_{15/2}$, $S = 5/2$, $L = 5$, $g = 4/3$). The values of μ_{eff} gradually decrease until temperature is down to 30 K and then further decrease to a minimum of $10.77\mu_{\mathrm{B}}$ for **1** or $11.58\mu_{\mathrm{B}}$ for **2** at 2 K. For such lanthanide ions with an unquenched orbital moment associated with a ligand field, the decrease in μ_{eff} can originate from the following possible contributions: (i) antiferromagnetic interactions between the $\mathrm{Dy^{III}}$ centres; (ii) the thermal depopulation of the Stark sublevels; and (iii) the presence of significant magnetic anisotropy.[19–21] The antiferromagnetic interactions seem unlikely due to a well-shielded character of $\mathrm{Dy^{III}}$ 4*f* magnetic orbitals. The field dependence of magnetic moments at 2 K for both complexes has been successfully approximated by the Brillouin function (Figure 4, inset) being ruled out their possible SMM behaviour at this temperature.

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