CHEMISTRY
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Accepted Article

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To be cited as: *Chem. Asian J.* 10.1002/asia.201801643

Link to VoR: http://dx.doi.org/10.1002/asia.201801643

A Journal of
ACES
Asian Chemical Editorial Society

A sister journal of **Angewandte Chemie** and **Chemistry – A European Journal**

WILEY-VCH

Synthesis, Structures and Single Molecule Magnet Properties of Three Dy_2 Complexes

Yu Ge,[a] Yuan Huang,[a] Jessenia Lisseth Becerra Montenegro,[c] Yanfeng Cui,[a] Wei Liu,[a] Yahong Li,*[a] and Bao-Lin Wang*[b]

Abstract: To explore the influences of the subtle structural variations of the ligand backbones on the single molecule magnet properties of dinuclear dysprosium(III) complexes, three ligands H_2L_1 (H_2L_1 = N_1,N_3-bis(salicylaldehyde)diethylenetriamine), H_2L_2 (H_2L_2 = N_1,N_3-bis(3-methoxysalicylidene)diethylenetriamine) and H_2L_3 (H_2L_3 = N_1,N_3−bis(5−chlorosalicyladehyde)diethylenetriamine) were synthesized and employed to prepare the expected dinuclear dysprosium(III) complexes. The three ligands differ in the substituents at the benzene rings of the salicylaldehyde moieties. The reactions of $Dy(NO_3)_3·6H_2O$, pivalic acid and the ligands H_2L_1, H_2L_2, and H_2L_3, respectively, generated complexes of formulae $[Dy_2(L_1)_2(piv)_2]$ (**1**), $[Dy_2(L_2)_2(piv)_2]$ (**2**) and $[Dy_2(L_3)_2(piv)_2]·2MeCN$ (**3**). The purposeful attachment of the functional groups with varied sizes at the benzene rings of the salicylaldehyde backbones resulted in the slight differences of Dy−O−Dy bond angles and Dy···Dy bond lengths in **1**−**3**; consequently, three complexes exhibited distinct magnetic properties. They all show slow magnetization relaxation with energy barriers of 40.32 K (**1**), 31.67 K (**2**), and 33.53 K (**3**). The CASSCF calculations were performed on **1**−**3** to rationalize the observed slight discrepancy in the magnetic behavior. The calculated results well explained the experimental outcomes.

Introduction

The study of single molecule magnets (SMMs) has received sustainable interest over the past decades due to their potential applications in the fields of memory storage, quantum computation, spintronic devices, and molecular refrigeration,[1-2] and so forth. Currently, the lanthanide-based SMMs are the focus of this research topic. The high anisotropic nature of 4*f* ions has certainly been advantageous for producing magnetic materials on a molecular level.[3-4] Particularly Dy^{III} ion is one of the best candidates for magnetic centers, because it possesses large magnetic moment and remarkable anisotropy, and may afford SMMs with higher energy barriers.[5-6] Among the dysprosium-based SMMs, Dy_2 SMMs have attracted intense attention of the chemists and physicists around the world.[7-8] There are many reasons for this, but the preliminary impetuses include the elucidation of the effects of the magnetic interactions on relaxation of magnetization, the interpretation of the possible orientation of anisotropy,[9] as well as the illustration of the relationships between single-ion relaxation and the relaxation of a molecular entity.[10]

Recent advances in this area reveal that Dy_2 SMMs can be achieved by employing a variety of ligands *e.g.* carboxylates,[11] diketones,[12] Schiff-bases,[13-14] *etc*. Whereas, there are few reports about the preparation of Dy_2 SMMs by the combination of salicylaldehyde Schiff-bases with carboxylic acids as the ligands.[15-17]

In this work, we have used salicylaldehyde Schiff-bases H_2L_1 (H_2L_1 = N_1,N_3-bis (salicylaldehyde)diethylenetriamine), H_2L_2 (H_2L_2 = N_1,N_3-bis(3-methoxysalicylidene)diethylenetriamine) and H_2L_3 (H_2L_3 = N_1,N_3-bis(5-chlorosalicyladehyde)diethylenetriamine) in combination with pivalic acid for the synthesis of Dy_2 SMMs. The three ligands differ in the substituents at the benzene rings of the salicylaldehyde backbones. Three complexes of compositions $[Dy_2(L_1)_2(piv)_2]$ (**1**), $[Dy_2(L_2)_2(piv)_2]$ (**2**) and $[Dy_2(L_3)_2(piv)_2]·2MeCN$ (**3**) were generated. They all exhibited SMM behavior. In this paper, the synthesis, structures and magnetic properties of **1**−**3** are reported.

Experimental

Materials and Physical Measurements

All solvents and reagents were obtained from commercial sources and used without further purification. Fourier Infrared (FTIR) spectra were acquired in the 4000−600 cm^{-1} range with a Bruker Tensor 27 FTIR spectrophotometer. The elemental analyses for C, H and N were performed on Perkin-Elmer 2400 analyzer. ^1H NMR spectra were recorded at ambient temperature on Bruker Avance-III 600 MHz NMR spectrometer, and ^1H NMR chemical shifts were referenced to the solvent signal in $CDCl_3$. Powder XRD patterns were obtained through a Rigaku D/Max-2500 diffractometer at 40 kV and 100 Ma with a Mo-target tube and a graphite monochromator. Magnetic susceptibility measurements were performed in the temperature range of 2−300 K, using a Quantum Design MPMS XL-7 SQUID magnetometer.

Synthesis of the Ligands

N_1,N_3-bis(salicylaldehyde)diethylenetriamine (H_2L_1)

The ligand H_2L_1 was synthesized by mixing salicylaldehyde (0.025 mol) with diethylenetriamine (0.0125 mol) in EtOH (40 mL). After the reaction mixture was stirred at room temperature for 5 hours, yellow precipitates were formed. The yellow precipitates were filtered, washed with *n*-hexane (3×10 mL) and collected as a yellow powder. Yield: 2.46 g (79%). Anal. calcd for $C_{17}H_{19}N_3O_2$: C 69.24, H 6.86, N 13.55; found: C 69.43, H 6.80, N 13.49. IR (KBr, cm^{-1}): 2842 (w), 1629 (s), 1580 (w), 1496 (m), 1460 (w), 1416 (w), 1337 (w), 1277 (s), 1210 (w), 1150 (m), 1116 (w), 1040 (w), 1021 (w), 973 (w), 894 (w), 852

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(w), 751 (s), 736 (s), 657 (w), 640 (w). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.29 (s, 2H), 7.18 (d, *J* = 7.4 Hz, 2H), 6.92 (d, *J* = 8.2 Hz, 2H), 6.82 (t, *J* = 7.4 Hz, 2H), 3.65 (t, *J* = 5.4 Hz, 4H), 3.06 – 2.83 (m, 4H).

N_1,N_3-bis(3-methoxysalicylidene)diethylenetriamine (H_2L_2) and N_1,N_3-bis(5-chlorosalicyladehyde)diethylenetriamine (H_2L_3)

The ligands H_2L_2 and H_2L_3 were obtained in the same way as that of H_2L_1 except replacing salicylaldehyde with *o*-vanillin and 5-chlorosalicyladehyde, respectively.

The yield of H_2L_2 is 3.69 g (82%). Anal. calcd for $C_{20}H_{25}N_3O_4$: C 64.58, H 6.94, N 11.34; found: C 63.67, H 6.78, N 11.31. IR (KBr, cm^{-1}): 2827 (w), 1627 (s), 1466 (w), 1440 (s), 1412 (w), 1376 (m), 1333 (w), 1300 (w), 1253 (w), 1167 (m), 1148 (s), 1127 (w), 1080 (w), 1024 (w), 991 (s), 980 (m), 964 (w), 903 (m), 863 (w), 838 (w), 776 (m), 759 (m), 733 (s), 641 (w), 633 (w), 615 (w), 608 (w). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.30 (s, 2H), 6.95 – 6.66 (m, 6H), 3.85 (s, 2H), 3.67 (s, 4H), 2.95 (s, 4H).

The yield of H_2L_3 is 3.80 g (81%). Anal. calcd for $C_{18}H_{21}N_3O_2Cl_2$: C 54.80, H 5.24, N 9.68; found: C 54.55, H 5.26, N 9.54. IR (KBr, cm^{-1}): 2802 (w), 1632 (s), 1574 (w), 1481 (m), 1393 (s), 1362 (w), 1301 (w), 1275 (s), 1208 (m), 1187 (m), 1137 (w), 1116 (w), 1086 (w), 1068 (w), 1045 (m), 1032 (w), 1007 (w), 965 (w), 954 (w), 920 (w), 904 (w), 890 (s), 878 (s), 827 (m), 777 (w), 718 (w), 685 (w), 645 (s). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.23 (d, 2H), 7.25 – 7.09 (m, 4H), 6.84 (d, *J* = 8.6 Hz, 2H), 3.68 (s, 4H), 2.96 (s, 4H).

Synthesis of 1−3

$[Dy_2(L_1)_2(piv)_2]$ (1)

A 10 mL Pyrex glass tube was loaded $Dy(NO_3)_3\cdot 6H_2O$ (46 mg, 0.1 mmol), H_2L_1 (45 mg, 0.1 mmol), pivalic acid (10 mg, 0.1 mmol), MeCN (1 mL), MeOH (1 mL) and triethylamine (14 mg, 0.1 mmol). The glass tube was sealed and heated in an oven to 70°C for 2 d, and then cooled to ambient temperature. Yellow block crystals of **1** were collected and washed with MeOH. Yield: 74 mg (65% yield based on Dy). Anal. calcd for $C_{46}H_{56}Dy_2N_6O_8$: C 48.22, H 5.22, N 7.33; found: C 48.21, H 4.93, N 7.33. IR (KBr, cm^{-1}): 2968 (w), 1626 (s), 1594 (w), 1531 (s), 1472 (s), 1443 (w), 1425 (w), 1352 (m), 1311 (w), 1276 (m), 1241 (w), 1226 (w), 1196 (m), 1160 (m), 1147 (w), 1124 (w), 1088 (w), 1043 (w), 991 (w), 931 (m), 910 (s), 895 (w), 856 (w), 792 (m), 759 (s), 745 (m), 637 (w), 608 (m).

Compounds **2** and **3** were prepared in the same method as that of **1** except that H_2L_1 was replaced by H_2L_2 and H_2L_3, respectively.

$[Dy_2(L_2)_2(piv)_2]$ (2)

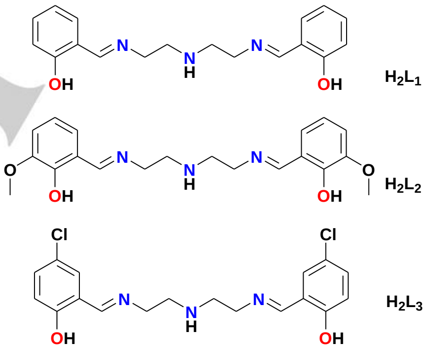
Yield: 86 mg (68% yield based on Dy). Anal. calcd for $C_{50}H_{64}Dy_2N_6O_{12}$: C 46.95, H 5.44, N 6.55; found: C 47.43, H 5.10, N 6.64. IR (KBr, cm^{-1}): 3218 (w), 2911 (w), 2190 (w), 1640 (s), 1621 (w), 1594 (s), 1537 (w), 1506 (m), 1484 (s), 1468 (m), 1445 (w), 1428 (w), 1418 (m), 1340 (m), 1388 (s), 1350 (s), 1332 (w), 1262 (w), 1241 (w), 1218 (w), 1166 (s), 1143 (s), 1120 (m), 1110 (w), 1093 (w), 1079 (w), 1039 (w), 1000 (w), 986 (w), 971 (m), 938 (m), 897 (w), 852 (w), 829 (m), 808 (w), 792 (w), 744 (m), 734 (s), 716 (m), 640 (w), 626 (w), 609 (w).

$[Dy_2(L_3)_2(piv)_2]\cdot 2MeCN$ (3)

Yellow block crystals of **3** were collected and washed with MeOH. Yield: 102 mg (75% yield based on Dy). Anal. calcd for $C_{50}H_{58}Cl_4Dy_2N_8O_8$: C 43.34, H 4.05, N 8.63; found: C 43.97, H 4.28, N 8.20. IR (KBr, cm^{-1}): 2914 (w), 2193 (s), 1540 (s), 1525 (w), 1484 (s), 1467 (s), 1431 (m), 1386 (w), 1225 (w), 1190 (m), 1175 (m), 1088 (w), 1069 (w), 983 (w), 932 (w), 877 (w), 867 (m), 835 (m), 800 (m), 745 (w), 700 (s), 647 (m), 608 (w).

X-Ray Data Collection and Structure Determination

Single-crystal X-ray diffraction data for **1−3** were collected on Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromated Mo-Kα (λ = 0.71073 Å) by using the Φ/ω scan technique. Absorption correction was based on symmetry equivalent reflections using the SADABS program. The crystal structures of **1−3** were solved by direct methods and refined on F^2 by full-matrix least-squares methods with the SHELXL program.[18] Crystal data parameters for **1−3** are summarized in Table 1. Selected bond lengths and angles for **1−3** were listed in Table S1. CCDC 1843525 (**1**), 1843524 (**2**), 1843523 (**3**) contain all supplementary crystallographic data of the three complexes for this paper.



Scheme 1. The structures of three ligands.

Results and Discussion

Synthetic and Spectral Aspects

To generate the dinuclear complexes with SMM properties and to evaluate the influences of the subtle structural variations on the magnetic properties, three salicylaldehyde Schiff-bases with rich coordination atoms were selected as flexible ligands and pivalic acid which possesses both steric hindrance and terminal coordination sites was chosen as an ancillary ligand.

The solvothermal reactions of $Dy(NO_3)_3\cdot 6H_2O$ with the salicylaldehyde Schiff-bases (Scheme 1) and pivalic acid at 1:1:1 molar ratio in acetonitrile and methanol at 70 ℃ afforded complexes **1−3**. They are air and moisture stable compounds. They were characterized by elemental analyses. The structures of these complexes were further confirmed by single crystal X-ray diffraction analysis.

Table 1. Crystallographic data for **1−3**

	1	**2**	**3**
Empirical formula	$C_{46}H_{56}Dy_2N_6O_8$	$C_{50}H_{64}Dy_2N_6O_{12}$	$C_{50}H_{58}Cl_4Dy_2N_8O_8$
Formula weight	1145.96	1266.07	1365.84
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a/Å	9.850(2)	10.922(2)	19.8837(16)
b/Å	10.935(2)	11.530(3)	13.0974(11)
c/Å	10.966(2)	12.385(3)	21.7140(18)
α/°	74.522(6)	68.405(7)	90
β/°	85.808(6)	76.038(7)	100.217(3)
γ/°	84.963(6)	62.728(6)	90
Volume/Å^3	1132.5(4)	1283.9(5)	5565.2(8)
Z	1	1	4
ρ_{calc}g/cm^3	1.680	1.637	1.630
μ/mm^{-1}	3.333	2.954	2.914
F(000)	570.0	634.0	2712.0
Crystal size/mm^3	0.4 × 0.18 × 0.15	0.6× 0.5 × 04	0.6 × 0.5 × 0.4
Θ range	3.38 to 55.016	4.552 to 55.326	4.92 to 55.108
Index ranges	$-12 \le h \le 12$ $-14 \le k \le 14$ $-14 \le l \le 14$	$-14 \le h \le 14$ $-15 \le k \le 14$ $-16 \le l \le 16$	$-24 \le h \le 25$, $-17 \le k \le 17$, $-28 \le l \le 27$
Reflections collected	27822	50932	108132
Independent reflections	5256 $R_{int} = 0.0645$	5923 $R_{int} = 0.0588$	12759 $R_{int} = 0.0801$
Data/restraints/ parameters	5256/0/283	5923/0/321	12759/0/657
Goodness-of-fit on F^2	1.172	1.110	1.020
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0389$, $wR_2 = 0.0975$	$R_1 = 0.0332$, $wR_2 = 0.0945$	$R_1 = 0.0401$, $wR_2 = 0.0878$
Final R indexes [all data]	$R_1 = 0.0389$, $wR_2 = 0.0975$	$R_1 = 0.0353$, $wR_2 = 0.0956$	$R_1 = 0.0556$, $wR_2 = 0.0945$
Largest diff. peak/hole / e Å^{-3}	1.88/-2.10	1.73/-2.00	1.21/-1.75

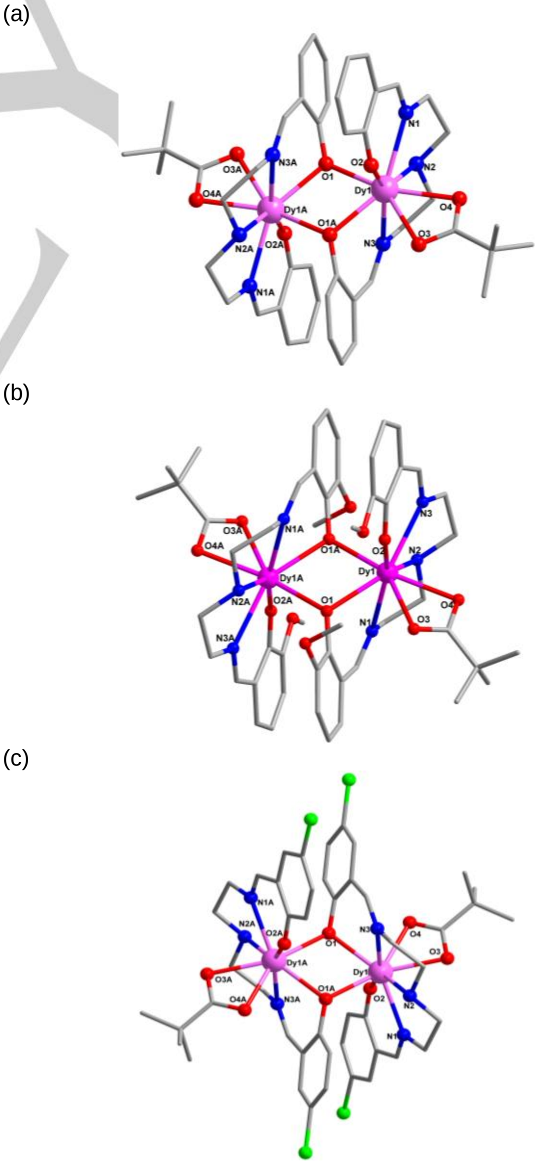
Crystal Structure Description

Crystal Structures of 1−3

The single-crystal X-ray diffraction studies showed that complexes **1**−**2** crystalize in the triclinic space group $P\bar{1}$ and compound **3** crystalizes in the monoclinic space group $P2_1/n$. Complexes **1**−**3** are isostructural, thus only the structure of **1** was described in detail. The molecule of **1** consists of two Dy^{III} ions, two L_1^{2-} ligands and two pivalate ions. The Dy1 atom is coordinated by two phenolate oxygen atoms and three amino nitrogen atoms from one L_1^{2-} ligand, two oxygen atoms from one pivalate ion and one oxygen atom from the other L_1^{2-} ligand. Each Dy^{III} ion exhibits triangular dodecahedron geometry. The two symmetry-related Dy^{III} ions are doubly bridged by the two phenolate oxygen atoms from two L_1^{2-} ligands. Each L_1^{2-} ligand chelates with two Dy^{III} ions in a $\mu^2:\eta^2:\eta^1:\eta^1:\eta^1:\eta^1$ mode. The Dy1⋯Dy1A distance is 3.789(3) Å and the Dy1−O1−Dy1A angle is 110.19(7)°. The Dy1−O1, Dy1−O1A, Dy1−O2, Dy1−O3 and Dy1−O4 bond lengths are 2.328(3), 2.368(3), 2.185(16), 2.411(3), and 2.429(3) Å, and the bonds lengths of Dy1−N are 2.542(4), 2.543(4) and 2.368(3) Å, respectively.

The coordination environments of Dy^{III} ions in **2** and **3** are identical with those of **1**; whereas the bond lengths and bond angles around Dy^{III} ions in **2** and **3** are slightly different, indicating that the attachment of the functional groups at the benzene rings of salicylaldehyde backbones results in the subtle structural variations. Considering the effects of the bond angles and the bond lengths of **1**−**3** on their magnetic properties, they are summarized in Table 2.

For lanthanides, the geometries of metal centers are strongly correlated to the local anisotropy of the paramagnetic ions. Thus, a systematic analysis of coordination geometry was carried out. The program SHAPE 2.0 was used to analyze the exact geometry of the eight-coordinated dysprosium.[19] The calculated results indicate triangular dodecahedron (D_{2h}) geometry for **1**−**2**, **3_a**, **3_b** with minimum CShM values of 1.736, 2.293, 1.913, and 2.262, respectively. The minimum CShM values reveal that the configurations of **1**−**3** are slightly different.



(d)

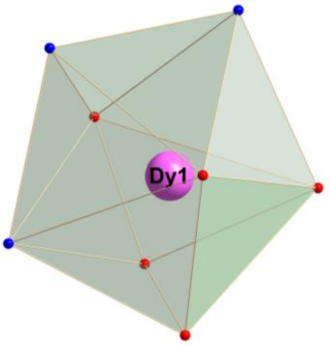


Figure 1. (a) The molecular structure of $[Dy_2(L_1)_2(piv)_2]$ (**1**); (b) The molecular structure of $[Dy_2(L_2)_2(piv)_2]$ (**2**); (c) The molecular structure of $[Dy_2(L_3)_2(piv)_2]\cdot 2MeCN$ (**3**); (d) Coordination polyhedron of the Dy^{III} ions in **1−3**. Color code: purple (Dy), red (O), blue (N), gray (C).

Table 2. Selected bond distances [Å] and angles [°] for **1**, **2**, **3_a**, **3_b**.

	1	**2**	**3_a**	**3_b**
Dy1-Dy1A	3.798 (4)	3.810(4)	3.8350(5)	3.8226(4)
Dy1-O1	2.328(3)	2.391(3)	2.355(3)	2.361(3)
Dy1-O2	2.202(3)	2.213(3)	2.202(3)	2.196(3)
Dy1-O3	2.415(3)	2.420(3)	2.415(3)	2.409(3)
Dy1-O4	2.388(3)	2.406(3)	2.388(3)	2.413(3)
Dy1-N1	2.559(3)	2.564(3)	2.559(3)	2.535(3)
Dy1-N2	2.551(3)	2.553(3)	2.551(3)	2.564(3)
Dy1-N3	2.557(3)	2.536(3)	2.557(3)	2.524(3)
O1-Dy1-O3	78.38(10)	78.38(10)	77.96(10)	77.68(9)
O1-Dy1-O4	130.71(10)	130.71(10)	127.38(10)	128.39(10)
O1-Dy1-N1	69.07(10)	69.07(10)	69.90(10)	70.29(10)
O1-Dy1-N2	129.30(10)	129.30(10)	129.13(10)	130.03(10)
O1-Dy1-N3	148.33(10)	148.33(10)	146.01(10)	145.65(10)
O2-Dy1-O1	88.37(10)	88.37(10)	86.91(10)	85.64(10)
O2-Dy1-O3	102.62(11)	102.62(11)	104.31(12)	102.62(11)
O2-Dy1-O4	82.95(11)	82.95(11)	82.17(11)	82.25(10)
O2-Dy1-N1	155.94(11)	155.94(11)	155.29(11)	153.48(11)
O2-Dy1-N2	138.15(10)	138.15(10)	138.53(11)	139.71(11)
O2-Dy1-N3	72.48(10)	72.48(10)	72.12(11)	73.29(11)
O3-Dy1-N1	84.60(11)	84.60(11)	84.68(11)	84.81(11)
O3-Dy1-N2	72.76(11)	72.76(11)	71.99(11)	71.65(11)
O3-Dy1-N3	84.85(11)	84.85(11)	84.52(11)	84.81(11)
O4-Dy1-O3	53.85(10)	53.85(10)	53.95(10)	53.94(10)
O4-Dy1-N1	83.08(11)	83.08(11)	84.32(11)	83.41(11)
O4-Dy1-N2	120.30(11)	120.30(11)	120.67(10)	119.05(11)
O4-Dy1-N3	125.58(11)	125.58(11)	123.37(11)	124.24(11)
N2-Dy1-N1	65.88(11)	65.88(11)	66.05(11)	66.47(11)
N2-Dy1-N3	65.70(11)	65.70(11)	66.41(11)	66.81(11)
N3-Dy1-N1	131.43(11)	131.43(11)	132.33(11)	133.19(11)
Dy1A-O1-Dy1	110.19(7)	106.74(1)	109.07(10)	108.38(10)

Magnetic Studies

The direct-current (*dc*) magnetic susceptibility measurements of **1−3** were performed on polycrystalline samples at a temperature range of 2−300 K under an applied magnetic field of 1000 Oe. The data are plotted as $\chi_M T$ versus T in Figure 2.

For complex **1**, the $\chi_M T$ value is 29.67 cm^3 mol^{-1} K at room temperature, which is approached to the two uncoupled Dy^{III} ($^6H_{15/2}$, $g = 4/3$) ions of 28.34 cm^3 mol^{-1} K. The $\chi_M T$ value of **1** is decreasing gradually in the range of 300−25 K, reaching to a minimum value of 3.94 cm^3 mol^{-1} K at 2 K.

The room-temperature $\chi_M T$ value of 26.70 cm^3 mol^{-1} K for **2** is close to the expected value of 28.34 cm^3 mol^{-1} K for two uncoupled Dy^{III} ($^6H_{15/2}$, $g = 4/3$) ions. By increasing temperature, $\chi_M T$ value of **2** exhibits a very slow decrease which accelerates upon lowering the temperature below 20 K, giving a minimum value of 5.14 cm^3 mol^{-1} K.

The $\chi_M T$ value of **3** is 28.91 cm^3 mol^{-1} K at 300 K, which is approached to the theoretical value of 28.34 cm^3 mol^{-1} K for two magnetically isolated Dy^{III} ($^6H_{15/2}$, $g = 4/3$) ions. With the decreasing of temperature, $\chi_M T$ value decreases gradually and then sharply to a value of 7.84 cm^3 mol^{-1} K.

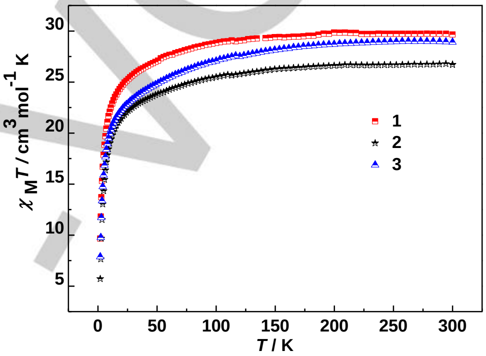
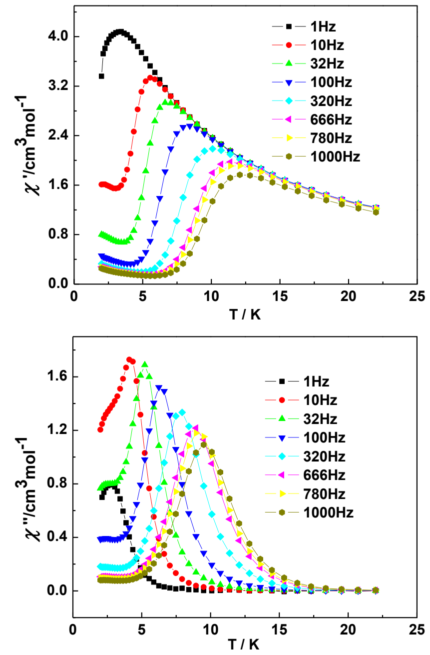


Figure 2. Temperature dependence of magnetic susceptibilities in the form of χT vs. T for **1−3** at 2-300 K with a *dc* applied field of 1000 Oe.

As the purpose of our research is to explore the effects of the structural variations on the magnetic properties, we studied the magnetization dynamics of **1−3**. The temperature dependence of alternating current (*ac*) magnetic susceptibilities for **1−3** were determined at the indicated frequencies of 1, 10, 32, 100, 320, 660, 780 and 1000 Hz under zero *dc* field (Figure 3). The *ac* magnetic susceptibilities of **1−3** all presented frequency dependent character in the in-of-phase (χ') and out-of-phase signal (χ'') at zero direct current (*dc*) field, indicating that they are SMMs.

(a)



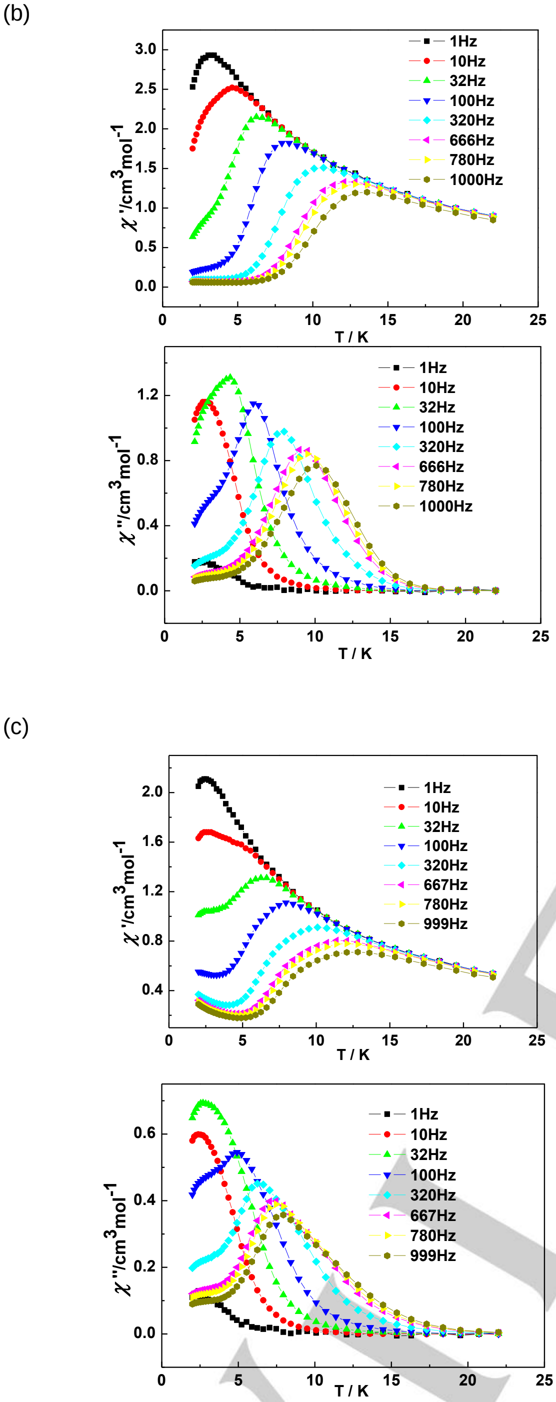


Figure 3. Temperature dependence of the in-phase (χ') and out-of-phase (χ'') susceptibilities for **1**(a), **2**(b) and **3**(c) in the range 2 to 22 K. The susceptibilities are determined at 1 Hz, 10 Hz, 32 Hz, 100 Hz, 20 Hz, 666 Hz, 780 Hz, 900 Hz, 1000 Hz frequencies under zero *dc* field.

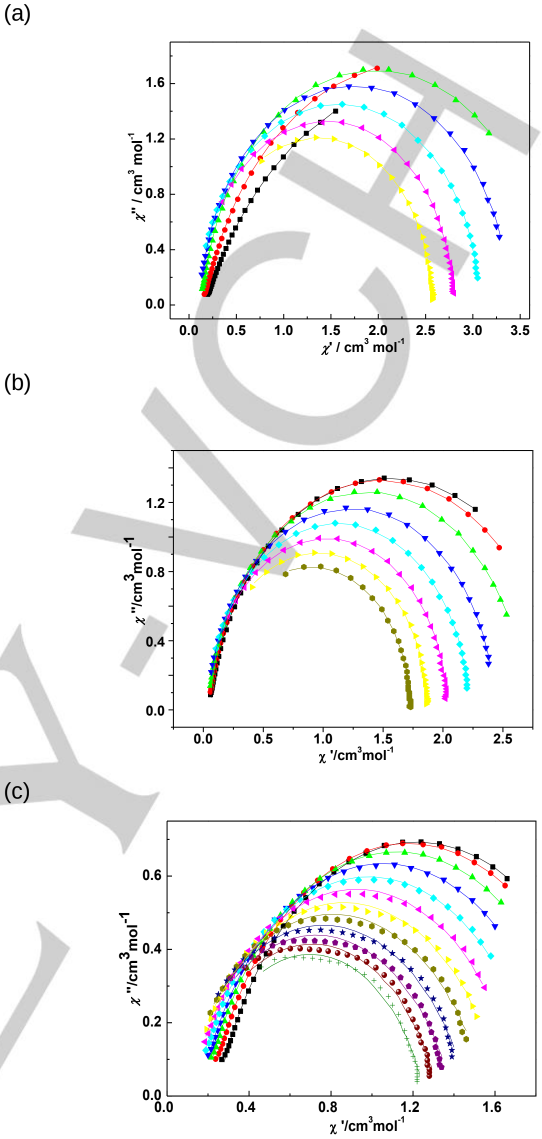


Figure 4. Cole-Cole plots of **1**−**3** measured from 2.5 to 8 K for **1**(a), 3 to 10 K for **2**(b), 3 to 9 K for **3**(c) under zero *dc* field. The solid lines are best fits to the experimental data.

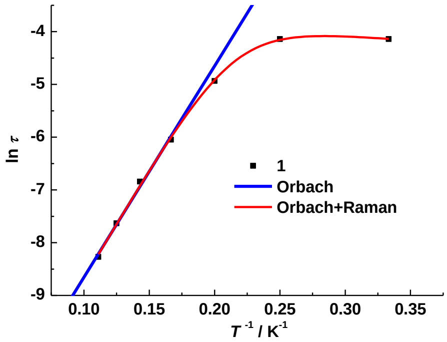
The Cole-Cole plots (Figure 4) have been fitted using a generalized Debye model. It implied that the thermally activated relaxation processes of **1**−**3** have wide distribution of relaxation times. The curvatures of lnτ versus 1/T plots at low temperature indicate other relaxation pathways may exist. For an Orbach-type relaxation, the relaxation time (τ_0) and barrier will follow the Arrhenius equation $\ln \tau = \ln \tau_0 + U_{\mathrm{eff}}/k_{\mathrm{B}}T$ (Equation 1), where U_{eff} is the effective spin-reversal barrier and k_{B} is the Boltzmann constant. The fit of the above-mentioned equation affords U_{eff} = 40.32 K, 31.67 K, 33.53 K and τ_0 = 3.06 × 10^{-6} s, 9.19 × 10^{-6} s, 2.17 × 10^{-6} s for **1**−**3**, respectively.

Other relaxation processes may exist at low temperature, thus the magnetic data of **1**−**3** are fitted by the equation (2): $1/\tau = CT^{n} + \tau_0^{-1}\exp(-U_{\mathrm{eff}}/k_BT)$, in which the spin-lattice relaxation of both the Orbach and Raman processes are considered (Figure 5).[20] The best fit of the equation (2) on the whole temperature range provides U_{eff} = 39.99 K, τ_0 = 1.9 × 10^{-6} s, C = 86.11 s^{-1} K$^{-0.27}$, n = 0.55 for **1**, U_{eff} = 36.78 K, τ_0 = 5.62 × 10^{-6} s, C = 63.36 s^{-1} K$^{-0.57}$, n = 0.57 for **2**, and U_{eff} = 41.68 K, τ_0 = 2.6 × 10^{-6} s, C = 118.36 s^{-1} K$^{-0.58}$, n = 0.58 for complex **3**.

Complexes **1−3** join a small family of Dy^{III} SMMs with pivalic acid as ancillary ligands (Table 3).[21] Pivalic acid is a particular compound, which could fulfill both the chelating and steric hindrance requirements, giving clusters with smaller nuclearities. Among the reported Dy^{III} SMMs utilizing pivalic acid as co-ligand, the energy barriers of **1−3** are relatively higher.

A comparison of the energy barriers among **1−3** indicates a correlation of energy barriers with their structures. The CShM values of **1**, **2**, **3_a** and **3_b** are 1.736, 2.293, 1.913 and 2.262, respectively, thus, the configuration of **1** is more close to a standard triangular dodecahedron (D_{2h}), leading to the higher energy barrier of **1** consequently. This result reveals that the attachment of functional groups at the benzene rings of salicylaldehyde motifs causes the subtle variations of the configurations of complexes, leading to the alteration of the magnetic properties.

(a)



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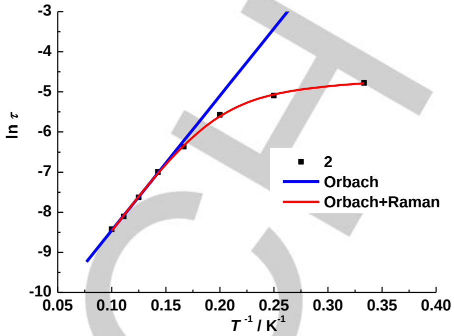

(c)

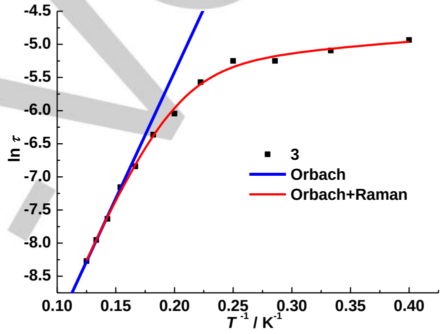

Figure 5. Temperature dependence of magnetic relaxation times under zero *dc* fields for **1** (a), **2** (b) and **3** (c). The blue solid lines represent data fits to the Equation (1) and the red solid lines represent data fits to Equation (2).

Table 3 Examples of U_{eff} in Dy_2 SMMs coordinated with pivalate ligand

Complexes	Magnetic behavior	Magnetic Field/ Oe	Energy barrier/ K	τ_0/ s
$[Dy_4(L_1H)_2(\mu_3\text{-}OH)_2(\eta_2\text{-}piv)_2(\mu_2\text{-}\eta^1\text{: }\eta^1Piv)_2]$[21a]	AF	zero	40.92	1.5×10^{-7}
$[Dy_2(L_2H)_2(\mu_2\text{-}piv\text{-}\kappa^2O,O')_2(NO_3\text{-}\kappa_2O,O')_2]$[21b]	AF	zero	40	6.5×10^{-5}
$[Dy_2(H_2L_3)_2\ (\mu\text{-}piv)_2(piv)_2]\cdot 2CHCl_3$[21c]	AF	zero	8.96/ 35.5	8.81×10^{-5}/ 1.48×10^{-6}
$[Dy_4(\mu_3\text{-}OH)_4(L_4)_4(\mu_2\text{-}piv)_4(MeOH)_4]$ [21d]	F	500	18.07	2.5×10^{-5}
$[Ln_4(\mu_3\text{-}OH)_2(ampdH_4)_2(piv)_{10}]\cdot 4CH_3CN$[21e]	AF	zero	5.4	1.1×10^{-5}
$[Dy_5(LH)_4(\eta^1\text{-}piv)(\eta_2\text{-}piv)_3(\mu^2\text{-}\eta^2\eta^1piv)_2(H_2O)]\cdot Cl\cdot 9.5H_2O\cdot 5MeOH$ [21f]	AF	3000	5.2	2.6×10^{-2}
$[Dy_{12}Na_3(\mu_3\text{-}OH)_2(hmmp)_6(piv)_{12}(CO_3)_6(MeOH)_6]OH\cdot 5MeOH$ [21g]	AF	zero	3.5	1.2×10^{-7}
$[[Dy_2(L_6H_2)_2(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}piv)]Cl\cdot 2MeOH\cdot H_2O$	F/AF	zero	no peak	/
$[Dy_4(L_6H)_2(\mu_3\text{-}OH)_2(piv)_4(MeOH)_2]\cdot 4MeOH\cdot 2H_2O$ [21h]	F/AF	zero	no peak	/
$[Dy_8(L_7H_2)_4(\mu\text{-}piv)_4(\eta_2\text{-}piv)_4(\mu\text{-}OMe)_4]\cdot 8CH_3OH$[21i]	AF	zero	not SMMs	/
$[Dy_2(L_8)_2(piv)_2]$ (**1**)[this work]	AF	zero	40.32	3.06×10^{-6},
$[Dy_2(L_9)_2(piv)_2]$ (**2**)[this work]	AF	zero	31.67	9.19×10^{-6},
$[Dy_2(L_{10})_2(piv)_2]\cdot 2MeCN$ (**3**) [this work]	AF	zero	33.53	2.17×10^{-6}

piv = pivalate; L_1H_2 = 2-{[6-(hydroxymethyl)pyridin-2-yl]methyleneamino}phenol); L_2H_2 = *N'*-(2-hydroxy-3-methoxybenzylidene)acetohydrazide; H_3L_3 = 2,2'-(2-hydroxy-3-methoxy-5-methylbenzylazanediyl)diethanol; L_4H = [1,3-bis(*o*-methoxyphenyl)-propane-1,3-dione]; $ampdH_4$ = 3-amino-3-methylpentane-1,5-diol; L_5H_3 = N'-(2-hydroxy-3-(hydroxymethyl)-5-methylbenzylidene)acetohydrazide; $hmmpH_2$ = 2-[(2-hydroxyethylimino)methyl]-6-methoxyphenl; L_6H_4 = 6-((bis(2-hydroxyethyl)amino)methyl)-N'-((8-hydroxyquinolin-2-yl)methylene)picolinohydrazide; L_7H_5 = (2E,N′E)-N′-(3-((bis(2-hydroxyethyl)amino)methyl)-2-hydroxy-5-methylbenzylidene)-2-(hydroxyimino)propanehydrazide; H_2L_8 = N_1,N_3-bis(salicyladehyde)diethylenetriamine; H_2L_9 = N_1,N_3-bis(3-methoxysalicylidene) diethylenetriamine; H_2L_{10}=N_1,N_3−bis(5−chlorosalicyladehyde)diethylenetriamine (this work). F = ferromagnetic, AF = antiferromagnetic.

Theoretical Calculation

Complete-active-space self-consistent field (CASSCF) calculations on individual Dy^{III} fragments for **1−3** on the basis of X-ray determined geometries have been carried out with MOLCAS 8.2[22] and Single_Aniso[23] programs (see Supporting Information for details). The lowest eight Kramers doublets (KDs) and the corresponding *g* tensors of complexes **1−3** are shown in Table S6, where the energy gaps between the lowest two KDs are similar for three complexes. The m_J components for the lowest two doublets of individual Dy^{III} fragments for **1−3** are shown in Table S7, where the ground states of three complexes are all mostly composed by m_J = 15/2 state. However, the first excited state of complex **3** is composed by several m_J states (m_J = 13/2, 1/2 and 3/2 have the similar weights). For the first excited state of **1** and **2**, the m_J = 13/2 state is predominant. The corresponding quantum tunneling gaps of individual Dy^{III} fragments for **1−3** are shown in Figure S18 where the gaps in the ground state of **1** and **3** are both about 10^{-2} μ_B, and therefore the QTM is suppressed at low temperature. But, that of **2** is about 10^{-1} μ_B, therefore allowing a fast QTM in its ground state. Although their magnetic anisotropies of **1−3** mainly come from individual Dy^{III} fragments, the Dy^{III}-Dy^{III} interactions have some influence on their slow magnetic relaxation processes.

From Table S6, the calculated ground g_z values of individual Dy^{III} fragments for **1−3** are all close to 20, and thus the Dy^{III}−Dy^{III} exchange interactions for complexes **1−3** were approximately regarded as the Ising type during the fitting. The program Poly_Aniso[23] (see Figure S18) was used to fit the magnetic susceptibilities of complexes **1−3** using the exchange parameters from Table 4. This indicated that the magnetic properties of **1−3** may have slight difference.

Table 4. Fitted exchange coupling constant J_{exch}, the calculated dipole-dipole interaction J_{dip} and the total J between Dy^{III} ions in complexes **1−3** (cm^{-1}). The intermolecular interactions zJ' of complexes **1−3** were fitted to −0.02 cm^{-1}, −0.11 cm^{-1} and −0.12 cm^{-1}, respectively.

	1	**2**	**3**
J_{exch}	−1.50	−1.75	−1.50
J_{dip}	−2.91	−2.98	−2.91
J_{total}	−4.41	−4.73	−4.41

All parameters from Table 4 were calculated with respect to the pseudospin $\tilde{S}$ = 1/2 of the Dy^{III} ions. For complexes **1−3**, the total coupling parameters J (dipolar and exchange) was included into fit the magnetic susceptibilities. The calculated and experimental $\chi_M T$ versus T plots of complexes **1−3** are shown in Figure S18 where the fit for **1** is close to the experimental data.[24a] However, the fits for complexes **2** and **3** have some deviation from the experiment. The Dy^{III}-Dy^{III} interactions in complexes **1−3** within Lines model[24b] are all antiferromagnetic. The main magnetic axes on Dy^{III} ions for complexes **1−3** were indicated in Figure S19, where the magnetic axes on Dy^{III} for complexes **1−3** are all antiparallel. Moreover, we gave the exchange energies and the main values of the g_z for the lowest two exchange doublets of **1−3** in Table S8 where the g_z value of the ground exchange state for complexes **1−3** are all 0.000, which confirms that the Dy^{III}−Dy^{III} couplings are all antiferromagnetic. These calculation results are well consistent with the experimental results.

Conclusion

In summary, solvothermal reactions of $Dy(NO_3)_3 \cdot 6H_2O$ with three salicylaldehyde Schiff-base ligands H_2L_1 (H_2L_1 = N_1,N_3-bis(salicylaldehyde)diethylenetriamine), H_2L_2 (H_2L_2 = N_1,N_3-bis(3-methoxysalicylidene)diethylenetriamine) and H_2L_3 (H_2L_3 = N_1,N_3−bis(5−chlorosalicyladehyde)diethylenetriamine), in the presence of pivalic acid as ancillary ligand, yielded eight-coordinated dinuclear complexes **1−3**. They all contain μ_2-phenoxyl oxygen atom bridged Dy_2O_2 cores. There are slight differences in the bond lengths of Dy−O1, and the bond angles of Dy−O−Dy in compounds **1−3,** which are caused by the alteration of the substituents at the benzene rings of the salicylaldehyde moieties. Complexes **1−3** exhibit SMM behaviors with slight difference in energy barriers. Theoretical calculations are consistent with the experiment results.

Acknowledgements

The authors appreciate the financial support from Natural Science Foundation of China (21272167 and 21772140), Natural Science Foundation of Jiangsu Province of China (BK20171213), a Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institution, and the project of scientific and technologic infrastructure of Suzhou (SZS201708).

Keywords: single molecule magnets •dysprosium ion • pivalate• Schiff−base • energy barrier

CCDC: 1843525 (**1**), 1843524 (**2**), 1843523 (**3**) respectively.

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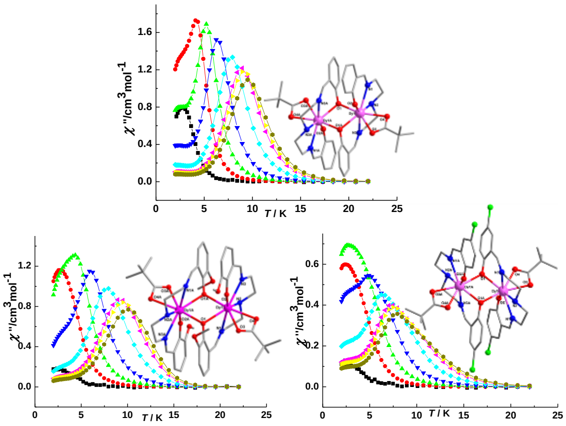

Three dinuclear complexes $[Dy_2(L_1)_2(piv)_2]$ (**1**), $[Dy_2(L_2)_2(piv)_2]$ (**2**), $[Dy_2(L_3)_2(piv)_2]\cdot 2MeCN$ (**3**) are synthesized and characterized. The subtle structural differences result in variations of the magnetic properties.

Yu Ge, Yuan Huang, Jessenia Lisseth Becerra Montenegro, Yanfeng Cui, Wei Liu, Yahong Li and Bao-Lin Wang**

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Synthesis, Structures and Single Molecule Magnet Properties of Three Dy_2 Complexes