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# Four polynuclear complexes based on a versatile salicylamide salen-like ligand: Synthesis, structural variations and magnetic properties



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# ABSTRACT

Four new polynuclear complexes based on a versatile asymmetric ligand,  $[Cu_2(H_2L)_2Cl_2]$  (1),  $[Cu_4(H_2L)_2(L)_2]$ ·4CH<sub>3</sub>OH (2),  $[MnL]_n$  (3),  $[Er_2(HL)_2(NO_3)_4]$ ·4CH<sub>3</sub>CN (4),  $H_3L = 2$ -hydroxy-N-(2-((2-hydroxybenzylidene)amino)ethyl)benzamide], were prepared and structurally characterized. The coordination behavior as well as deprotonation of the  $H_3L$  in the four complexes reveal considerable variations depending on the metal ions as well as counter anion. The hydroxyl-bridged dinuclear complex 1 with a Cu–O–Cu–O four-membered ring was obtained when copper chloride was used as metal source. The tetranuclear complex 2 with two Cu–O–Cu–O four-membered rings which bridged both through hydroxy and amide group was obtained using copper acetate instead. Reacting the ligand with manganese acetate yielded complex 3 which exhibits 1-D zig–zag chains only bridged through amide group. While complex 4 which holds a dinuclear one by aid of hydroxyl-bridge without nitrogen atom participating in coordination when erbium nitrate was introduced. The experimental magnetic susceptibilities indicate 1, 2 and 4 exhibit antiferromagnetic interactions through hydroxy bridge, while 3 exhibits dominant antiferromagnetic interactions with spin canting through the amido bridge.

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# 1. Introduction

Polynuclear metal complexes exhibit a fascinating variety of unusual symmetries and structural patterns [1]. The potentially important functions in magnetic behavior [2], optical materials [3], catalytic [4] and biological activities [5] add to their interest and significance. The possibility of obtaining multifunctional materials comes from the structure and flexibility for structural design of these compounds. However, the rational construction of desirable architectures remains a long-term challenge due to the wide range of factors which may influence structures of coordination compounds, including organic ligand, metal ion, solvent system, pH value of the solution, the metal-to-ligand ratio, counter anions, etc [6]. Among these, the organic ligand is an important factor undoubtedly. On the other hand, metal ions, especially their radii and coordination geometry, determine the extending directions important for the structure of the complexes. Therefore, much more work is required to establish proper synthetic strategies that can lead to the desired species with predictable structures and properties.

Multidentate organic ligands based on N- and O-donors have been witnessed to be excellent structural constructors due to their various coordination modes related to metal ions. Up to now, a number of polynuclear compounds with chelating-bridging organic ligands based on N- and O-donors have received considerable attention because they can incorporate virtues of different functional groups and it is easier to get architecture controlled by delicate modification [7–10]. In addition, salicylamide salen-like ligands are alterative excellent ligands because of their interesting features as follows: (a) they have multiple O- and N-coordination sites together with hydrogen-bond acceptors as well as hydrogen bond donors, which are good candidates for the assembly of novel 3d, 4f or 3d-4f architectures; (b) they have abstractable protons that allow various acidity dependant coordination modes, and as a result different structures can be constructed via changing only the pH values while using the same reagents; (c) This kind of ligands can be good choices to construct coordination compounds because the flexible nature of spacers between the amide and imine groups allow the ligands to bend and rotate to adapt somewhat to the changing size of the host metal ions. However, there are few reports on compounds base on salicylamide salen-like ligands. To date, some Mn(III) CPs with ligands incorporating salicylamide derivatives have been isolated [11,8a], and the previously results showed that substituted groups



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of this kind of ligands can impact the coordination structures as well as the magnetic properties effectively. This observation prompted us to extend the synthesis of this kind of ligands together with their complexes.

In the present work, two transition metal elements,  $Mn^{II}$  and  $Cu^{II}$ , and one lanthanide element,  $Er^{III}$ , are selected to investigate metal ion effects on the coordination ability of the ligand. As a result, four new complexes which were determined by single-crystal X-ray diffraction analyses and further characterized by elemental analysis, infrared spectra (IR), thermogravimetric analysis (TGA) and powder X-ray diffraction (PXRD) were obtained:  $[Cu_2(H_2L)_2Cl_2]$  (1),  $[Cu_4(H_2L)_2(L)_2]$ ·4CH<sub>3</sub>OH (2),  $[MnL]_n$  (3),  $[Er_2(HL)_2(NO_3)_4]$ ·4CH<sub>3</sub>OH (4). Their magnetic properties were investigated and the results indicate 1, 2 and 4 exhibit antiferromagnetic interactions through hydroxy bridge, while 3 exhibits dominant antiferromagnetic interactions with spin canting through the amido bridge.

# 2. Experimental

#### 2.1. Materials and instrumentation

All chemicals and solvents were obtained from commercial sources and used as received. N-(2-aminoethyl)-2-hydroxybenzamide was prepared according to the literature [12].

Carbon, nitrogen, and hydrogen analyses were performed using an EL elemental analyzer. Melting points were determined on a Kofler apparatus. Powder X-ray diffraction patterns (PXRD) were determined with Rigaku-D/Max-II X-ray diffractometer with graphite-monochromatized Cu Ka radiation. Thermogravimetric analyses were carried out on a SDT Q600 thermogravimetric analyzer from room temperature to 800 °C under N<sub>2</sub> atmosphere. A platinum pan was used for heating the sample with a heating rate of 10 °C/min. Infrared spectra (4000–400 cm<sup>-1</sup>) were obtained with KBr discs on a Nicolet FT-170SX instrument in the wavenumber range of  $4000 \sim 400 \text{ cm}^{-1}$  with an average of 128 scans and 4 cm<sup>-1</sup> of spectral resolution. <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> solution at room temperature on a Bruker 400 instrument operating at a frequency of 400 MHz and referenced to tetramethylsilane (0.00 ppm) as an internal standard. Chemical shift multiplicities are reported as s = singlet, d = doublet, t = triplet and m = multiplet. The magnetic measurements were carried out on polycrystalline samples using a Quantum Design MPMS SQUID magnetometer.

#### 2.2. Synthesis of the ligand

The synthetic route for 2-hydroxy-N-(2-((2-hydroxybenzylidene) amino)ethyl)benzamide (H<sub>3</sub>L) is shown in Scheme 1. 10 mmol (1.22 g) salicylaldehyde in 10 mL anhydrous ethanol was added dropwise in 10 min to a 10 mL ethanol solution of 10 mmol (1.80 g) N-(2-aminoethyl)-2-hydroxybenzamide. The resulted mixture was stirred and heated at reflux for 4 h. Then the mixture was allowed to stand overnight at room temperature. The crude product was separated by filtration and further recrystallized with ethanol to

give a yellow solid which was washed with diethyl ether and dried in air. H<sub>3</sub>L: 2.16 g, Yield 76.0%. m.p. 135–136 °C. *Anal.* Calc. for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>: C, 67.59; H, 5.67; N, 9.85. Found: C, 67.81, H, 5.65, N, 9.87%; IR (KBr, v, cm<sup>-1</sup>): 3381 (w), 1633 (s), 1594 (s), 1553 (s), 1490 (m), 1449 (m), 1360 (m), 1276 (m), 1230(m), 823 (m), 781 (m), 753 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ : 3.80 (m, 2H, CH<sub>2</sub>), 3.85 (m, 2H, CH<sub>2</sub>), 6.71 (s, 1H, ArH), 6.80 (m, 1H, ArH), 6.88 (m, 1H, ArH), 6.97 (m, 1H, ArH), 7.23(m, 1H, ArH), 7.35 (m, 3H, CH=N), 8.41 (t, 1H, NH, *J* = 4 Hz), 12.21(s, 2H, OH).

## 2.3. Synthesis of the complexes

To the acetonitrile solution of 0.1 mmol (0.028 g)  $H_3L$ , 0.1 mmol metal salt was added and the solution was stirred for another 4 h to obtain a suspension. To this turbid solution 5 mL methanol was add to obtain a clear solution. The mixture was filtered into a sealed 10–20 mL glass vial for crystallization at room temperature. After about two weeks single crystals suitable for crystal analysis were obtained.

 $[Cu_2(H_2L)_2Cl_2]$  (1) The empirical formula and the molecular weight is  $C_{32}H_{30}Cl_2Cu_2N_4O_6$  and 764.60 respectively. Yield: 22 mg, 58% based on CuCl\_2·2H\_2O). *Anal.* Calc. for C, 50.27; H, 3.95; N, 7.33. Found: C, 50.48; H, 3.96; N, 7.30%; IR (KBr, v, cm^{-1}): 3360(m), 1608 (s), 1533 (s), 1477(s), 1288 (s), 1209 (m), 1157 (m), 816 (w), 755 (s).

[ $Cu_4(H_2L)_2L_2$ ]·4CH<sub>3</sub>OH (**2**) The empirical formula and the molecular weight is  $C_{68}H_{72}Cu_4N_8O_{16}$  and 1511.50 respectively. Yield: 26 mg, 68% based on  $Cu(OAc)_2$ ·H<sub>2</sub>O). *Anal.* Calc. for C, 54.03; H, 4.80; N, 7.41. Found: C, 54.24; H, 4.78; N, 7.46; IR (KBr, v, cm<sup>-1</sup>): 3455 (w), 2932(w), 2854 (w), 1635(s), 1600(s), 1525 (s), 1485 (s), 1449(s), 1387(m), 1293(s), 1262(m) 1127(m) 1052 (m), 847 (w), 757 (s).

 $[MnL]_n$  (**3**) The empirical formula and the molecular weight is  $C_{16}H_{12}MnN_2O_3$  and 335.22 respectively. Yield: 24.8 mg, 74% based on Mn(OAc) 2·2H<sub>2</sub>O). *Anal.* Calc. for C, 57.33 H, 3.61; N, 8.36. Found: C, 57.40; H, 3.60; N, 8.38%; IR (KBr, v, cm<sup>-1</sup>): 3419(w), 3057(w), 2913(w), 1635(s), 1600(s), 1572(s), 1528(s), 1498 (s),1466(s), 1449(s), 1387(m), 1322(m), 1262(m), 1127(m), 901 (m), 854(m), 751(s), 621(s), 473(m).

 $[Er_2(HL)_2(NO_3)_4]$ ·4CH<sub>3</sub>CN (**4**) The empirical formula and the molecular weight is  $C_{40}H_{42}Er_2N_{12}O_{18}$  and 1313.38 respectively. Yield: 37 mg, 57% based on  $Er(NO_3)_3$ ·6H<sub>2</sub>O). *Anal.* Calc. for C, 36.58; H, 3.22; N, 12.80; Found: C, 36.49; H, 3.20; N, 12.84%; IR (KBr, v, cm<sup>-1</sup>): 3358(m), 2927 (m), 2854 (w), 1655 (s), 1608 (s), 1594 (s), 1563 (m), 1477(s), 1309 (s), 1238 (m), 1024 (m), 768 (s).

# 2.4. X-ray single-crystal diffraction analysis

Single crystals of dimensions  $0.26 \times 0.22 \times 0.16 \text{ mm}^3$  for **1**,  $0.32 \times 0.20 \times 0.10 \text{ mm}^3$  for **2**,  $0.32 \times 0.28 \times 0.26 \text{ mm}^3$  for **1** and  $0.16 \times 0.06 \times 0.04 \text{ mm}^3$  for **4** was mounted on a glass rod. The crystal data were collected with a Bruker SMART CCD diffractometer using monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 293 K. A hemisphere of data was collected in



Scheme 1. The synthetic route of the ligand.

#### Table 1

Crystal data and structure refinement parameters for 1, 2, 3 and 4.

Compound	1	2	3	4
Empirical formula	C <sub>16</sub> H <sub>15</sub> ClCuN <sub>2</sub> O <sub>3</sub>	C <sub>68</sub> H <sub>72</sub> Cu <sub>4</sub> N <sub>8</sub> O <sub>16</sub>	$C_{16}H_{12}MnN_2O_3$	C40H40Er2N12O18
T (K)	296(2)	298(2)	296(2)	293(2)
Μ	764.60	1511.50	335.22	1311.36
Crystal system, Space group	monoclinic, P2(1)/c	monoclinic, P2(1)/c	monoclinic, P2(1)/c	monoclinic, P2(1)/c
a (Å)	10.5771(4)	13.0600(11)	10.850(4)	13.9131(10)
b (Å)	16.609(2)	16.2379(14)	8.263(3)	17.3702(10)
<i>c</i> (Å)	9.8455(14)	16.6451(15)	15.645(6)	20.8947(15)
β(°)	116.963(2)	109.807(2)	91.995(4)	106.007(8)
V (Å <sup>3</sup> ), Z	1541.7(4), 2	3321.0(5), 2	1401.8(9), 4	4853.9(6), 4
Crystal size (mm)	$0.26 \times 0.22 \times 0.16$	$0.32 \times 0.20 \times 0.10$	$0.32\times0.28\times0.26$	$0.14 \times 0.06 \times 0.05$
$D_{\text{calcd}}$ (kg m <sup>-3</sup> )	1.647	1.512	1.588	1.794
$\mu ({\rm mm^{-1}})$	1.606	1.338	0.955	3.519
F(000)	780	1560	684	2576
$\theta$ range for data collection (°)	2.01-25.00	2.51-25.02	2.61-25.49	3.66-26.02
Completeness to theta = 25.02 (%)	99.9	99.8	99.8	99.7
index ranges, hkl	$-12 \leqslant h \leqslant 12$	$-15 \leqslant h \leqslant 15$	$-13 \leqslant h \leqslant 13$	$-15 \leqslant h \leqslant 17$
	$-19 \leqslant k \leqslant 19$	$-16 \leqslant k \leqslant 19$	$-9 \leqslant k \leqslant 10$	$-21 \leqslant k \leqslant 19$
	$-9 \leqslant l \leqslant 11$	$-19 \leqslant l \leqslant 16$	$-18 \leqslant l \leqslant 18$	$-22 \leqslant l \leqslant 25$
R <sub>int</sub>	0.0196	0.0594	0.0278	0.0634
Reflections collectedcted/unique	8259/2714	16546/5857	10279/2606	11274/4778
Data/restraints/parameters	2714/0/213	5857/0/433	2606/0/199	4778/0/331
Goodness-of-fit on F <sup>2</sup>	1.189	1.022	1.025	1.002
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0242, wR_2 = 0.0294$	$R_1 = 0.0461, wR_2 = 0.1104$	$R_1 = 0.0321$ , $wR_2 = 0.0411$	$R_1 = 0.0443, wR_2 = 0.0732$
R indices (all data)	$R_1 = 0.0719, wR_2 = 0.0871$	$R_1 = 0.0779, wR_2 = 0.1178$	$R_1 = 0.0837, wR_2 = 0.0891$	$R_1 = 0.0678, wR_2 = 0.0810$
Largest diff. peak and hole (e ${\rm \AA}^{-3})$	-0.262 and 0.682	-0.366 and 0.455	-0.258 and 0.669	–1.186 and 1.163

#### Table 2

Selected bond lengths (Å) for 1, 2, 3 and 4.

[Cu <sub>2</sub> (H <sub>2</sub> L) <sub>2</sub> Cl <sub>2</sub> ] (1) Cu1-N1 1.951(2) N1-Cu1-O2 168.76(8) O2-Cu1-Cl1 98.20(5) O2-Cu1-O1 98.19(7)	Cu1-O2 1.9551(17) N1-Cu1-O2 93.46(8) O2-Cu-Cl1 136.99(6)	Cu1-O2 1.9785(16) O2-Cu1-O2 77.40(7) N1-Cu1-O1 85.84(8)	Cu1-Cl1 2.2804(7) N1-Cu1-Cl1 92.94(7) O2-Cu1-O1 88.97(7)	Cu1-O1 2.3132(18)
$[Cu_4L_2(H_2L)_2] \cdot 4CH_3OH (2)$ Cu1-O3 1.908(3) Cu2-O2 1.996(3) O3-Cu1-N1 169.65(14) O2-Cu1-N2 177.45(15) N1-Cu1-O4 86.71(14) O1 <sup>#1</sup> -Cu2-N4 169.13(14) O6-Cu2-O3 111.04(13)	Cu1-O2 1.915(3) Cu2-O1 1.973(3) O3-Cu1-O2 84.74(12) N1-Cu1-N2 85.66(17) N2-Cu1-O4 91.69(16) O6-Cu2-O2 171.56(14) O1 <sup>#1</sup> -Cu2-O3 91.24(12)	Cu1-N1 1.916(4) Cu2-N4 1.980(4) O2-Cu1-N1 94.96(14) O3-Cu1-O4 103.63(12) O6-Cu2-O1 <sup>#1</sup> 83.73(14) O1 <sup>#1</sup> -Cu2-O2 88.90(12) N4-Cu2-O3 99.62(13)	Cu1-N2 1.926(4) Cu2-O2 1.996(3) O3-Cu1-N2 94.21(16) O2-Cu1-O4 90.81(12) O6-Cu2-N4 91.90(15) N4-Cu2-O2 94.62(14) O2-Cu2-O3 73.13(11)	Cu1-O4 2.485(4) Cu2-O3 2.309(3)
[ <i>MnL</i> ] <sub>n</sub> ( <b>3</b> ) Mn1-O3 1.8526(17) O3-Mn1-O1 92.69(7) O1-Mn1-N1 88.56(8) N2-Mn1-O2 96.09(9)	Mn1-O1 1.8974(17) O3-Mn1-N2 92.90(7) N2-Mn1-N1 83.23(8) N1-Mn1-O2 91.98(8)	Mn1-N2 1.941(2) O1-Mn1-N2 166.35(8) O3-Mn1-O2 100.88(7)	Mn1-N1 1.987(2) O3-Mn1-N1 166.90(8) O1-Mn1-O2 95.07(8)	Mn1-O2 2.1519(18)
$ \begin{array}{l} [Er_2(HL)_2(NO_3)_4] \cdot 4CH_3CN \ (\textbf{4}) \\ Er1-O3 \ 2.210(4) \\ Er1-O9 \ 2.396(5) \\ O3-Er1-O2 \ 74.66(15) \\ O2-Er1-O1 \ 140.44(15) \\ O1-Er1-O7 \ 149.39(16) \\ O1-Er1-O9 \ 157.10(16) \\ O2-Er1-O4 \ 76.30(16) \\ O9-Er1-O4 \ 106.9(2) \\ O1-Er1-O5A \ 83.6(3) \end{array} $	Er1-02 2.276(4) Er1-04 2.411(5) O3-Er1-01 99.54(15) O1-Er1-01 73.27(16) O1-Er1-07 137.29(16) O1-Er1-09 84.50(17) O1-Er1-04 81.38(19) O3-Er1-05A 153.3(3) O7-Er1-05A 84.4(4)	Er1-01 2.278(4) Er1-05A 2.419(13) O2-Er1-01 76.28(15) O3-Er1-07 86.64(17) O3-Er-09 84.02(19) O7-Er1-09 52.89(17) O1-Er1-04 122.38(17) O2-Er1-05A 127.023(3) O9-Er1-05A 70.115(4)	Er1-O1 2.312(4) O3-Er1-O1 86.05(15) O2-Er1-O7 76.58(17) O3-Er1-O9 126.10(17) O3-Er1-O4 149.79(17) O7-Er1-O4 78.7(2) O1-Er1-O5A 101.0(4) O4-Er1-O5A 51.5(3)	Er1-07 2.391(5)

the  $\theta$  range of 0.98–25.00° using a narrow-frame method with scan widths of 0.30° in  $\omega$  and an exposure time of 5 s/frame. The data were integrated using the Siemens SAINT program, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. Multiscan absorption corrections were applied. The structure was solved by the Direct Method of SHELXS-97 [13] and refined by full-matrix least-squares techniques using the SHELXL-97 program [14]. Nonhydrogen atoms of the compounds were refined with anisotropic temperature parameters. All H atoms

were placed in geometrically idealized positions (C–H = 0.96 Å for methyl groups, C–H = 0.97 Å for CH<sub>2</sub> groups, C–H = 0.93 Å for phenyl groups and O–H = 0.82 Å for hydroxyl groups) and constrained to ride on their parent atoms with Uiso(H) = 1.5 Ueq(C) for methyl groups, 1.2 Ueq(C) for aromatic and CH<sub>2</sub> groups, and 1.5 Ueq(O) for hydroxyl groups. The detailed crystallographic data and structure refinement parameters of compounds are summarized in Table 1. Selected bond distances for these compounds are listed in and Table 2. CCDC reference numbers: 1408852–1408855. Graphics were drawn with DIAMOND (Version 3.2) [15].

# 3. Results and discussion

# 3.1. Synthesis and physical measurement

 $H_{3}L$  was synthesized in good yield by condensation of N-(2-aminoethyl)-2-hydroxybenzamide with salicylaldehyde in 1:1 M ratios according to a literature procedure [12] with minor modification as depicted in Scheme 1. The four compounds which were found to be rather insoluble in most solvents other than methanol, acetonitrile, DMSO and DMF were obtained by solvent evaporation method with metal:ligand molar ratio of 1:1 in a methanol and acetonitrile mixture. The elemental analysis were consistent with their chemical formulas. The manganese oxidation states in compound **3** were established as +3 by bond-valence sum (BVS) calculations. It is well established that  $Mn^{II}$  can readily be oxidized by atmospheric oxygen to  $Mn^{III}$  and stabilized by complex formation on reacting with ligands involving imine group, as can be inferred from numerous reports in this field [16].

In the infrared spectra of H<sub>3</sub>L, the characteristic sharp NH stretching of the amide function are present at 3381 cm<sup>-1</sup> with the carbonyl(C=O) and imine(C=N) stretch appears at 1633 and 1594 cm<sup>-1</sup> as the strongest bands. Upon ligation to Cu<sup>II</sup>, the C=O group splits to two bands at 1632 and 1608 cm<sup>-1</sup>, and C=N group hypochromatic shift of  $60-70 \text{ cm}^{-1}$  with obvious difference above  $3000 \text{ cm}^{-1}$  compared to the free ligand, clearly indicating Cu<sup>II</sup> ion in complex 1 and 2 is coordinated to amide oxygen and imine nitrogen atom. While the absence of characteristic sharp NH band in the Mn<sup>III</sup> complex IR spectra indicates the deprotonation of the amide group. The appearance of a broad band at 3419 cm<sup>-1</sup>, the splitting of the C=O group to two bands at 1635 and 1600  $\text{cm}^{-1}$ , as well as 22 cm<sup>-1</sup> hypochromatic shift of C=N group of the Mn<sup>III</sup> complex compared to the free ligand, clearly indicates Mn<sup>III</sup> ion of the complex **3** is coordinated to the amido and imine nitrogens and the two phenoxo oxygen atoms as well as amide oxygen atom which are very similar to our previously reported Mn<sup>III</sup> complex [8a]. The imine C=N stretch remained at  $1594 \text{ cm}^{-1}$  in compound 4, suggesting that the C=N group does not take part in coordination when erbium was introduced to the reaction system. These IR spectra analysis were further validated by the structural analysis as follows.

PXRD experiments were also carried out for **1–4** to confirm whether the crystal structures are truly representative of the bulk materials (Figs. S1–S4). By comparison, the experimental patterns and the simulated ones are in good agreement with each other, which confirms the phase purity of the as-synthesized products.

# 3.2. Crystal structure descriptions

# 3.2.1. Crystal structure of $[Cu_2(H_2L)_2Cl_2]$ (1)

A single-crystal X-ray diffraction study reveals that compound 1 crystallizes in the monoclinic space group  $P2_1/c$  with a crystallographic inversion center, implying that the asymmetric unit contains half of a dinuclear molecule. The asymmetric unit is composed of one crystallographically unique Cu<sup>II</sup> ions, one chloride and one partly deprotonated  $H_2L^-$  ligand. It is worth noting that the ligand in compound 1 is tetradentate without coordination of both nitrogen atom from amide and phenolic oxygen atom from salicylamide. As shown in Fig. 1a, Cu<sup>II</sup> ion is five-coordinated to one carbonyl oxygen atom, two phenoxy oxygen atoms and one Schiff base nitrogen atom that come from two different one deprotonated ligands and one chloride anion. As depicted in Fig. 1b, Cu1 exhibits a slightly distorted trigonal bipyramidal configuration with phenoxy oxygen(O1), amide oxygen atom (O2) from the same monoanion ligand, chloride ion consisting of the equatorial plane and Schiff base nitrogen atom from the same monoanion ligand, phenoxy oxygen(O2) from another monoanion ligand occupying the axial site. The Cu<sup>II</sup> atom strays from the equatorial plane 0.045 Å. As illustrated in Table 2, The Cu–O bond distances in equatorial plane are 1.9551(2) and 1.9785(2) Å and Cu-Cl distances is 2.2804(7) Å that are comparable to those found in the basal plane [17]. The Cu atom is shifted by about 0.045 Å from the least-square basal planes toward the apical imine N atoms. The Addison  $\tau$ parameter for the Cu<sup>II</sup> centers is 0.20, highlighting a slight tbp (trigonal-bipyramid) distortion from ideal spy geometry [18]. Notably, the one deprotonated ligand anion  $H_2L^-$  in *cis*-configuration adopts tetradentate coordination modes with one phenolic oxygen atom and one Schiff base nitrogen atom and one amide oxygen atom chelating to one copper ion as well as one phenolic oxygen atom bridging another copper ion. As shown in Fig. 1c. two crystallographically equivalent Cu<sup>II</sup> ions are bridged by two  $\mu_2$ -O (O2) to give a dinuclear building block possessing a Cu-O-Cu-O four membered ring with Cu--Cu distance of 3.070 Å and Cu–O–Cu angle of 102.5°. Upon careful investigation of the structure, it can be seen that two neighboring dinuclear units are held together to a puckered two-dimensional(2D) supramolecular network via O–H···Cl hydrogen bonding with phenolic oxygen atom from salicylamide as donor and chloride from adjacent units as acceptor (Fig. 2). The  $O3 \cdots O1$  distance (3.110(2) Å), as well as O3-H3A...C1 angle (168°), are all within the ranges of those reported O-H···C1 hydrogen bonds [19].

# 3.2.2. Crystal structure of $[Cu_4(H_2L)_2(L)_2] \cdot 4CH_3OH(2)$

To investigate the influence of the counter anion on the structure of the Cu<sup>II</sup> complex, the acetate analogue was used to perform the same reaction. Owing to the weaker coordination ability of acetate compared to that of chloride ion, the coordination behavior of the ligand changed dramatically which acts both as a tridentate and pentadentate coordination mode. The X-ray diffraction study performed on **2** reveals that the asymmetric unit contains two crystallographically unique Cu<sup>II</sup> ion, one fully deprotonated ligand anion L<sup>3-</sup>, one partly deprotonated ligand anion H<sub>2</sub>L<sup>-</sup> and two lattice methanol molecules. As shown in Fig. 3a. Cu1 atom is coordinated by two phenoxy oxygen atoms (02, 03), two nitrogen atoms (N1 and N2) from one fully deprotonated ligand anion L<sup>3-</sup>, one oxygen atom of amide group (O4) from one partly deprotonated ligand anion H<sub>2</sub>L<sup>-</sup>. While the coordination of Cu2 is completed by one imine nitrogen atom(N4), one phenoxy oxygen atom (O6) from the partly deprotonated ligand anion H<sub>2</sub>L<sup>-</sup>, two phenoxy oxygen atoms (02, 03) and one oxygen atom of amide group (01) from the fully deprotonated ligand anion  $L^{3-}$ . As shown in Fig. 3b, both Cu1 and Cu2 exhibit slightly distorted square pyramid. The O2, O3, N1 and N2 atoms from the same ligand anion consist of the equatorial plane with O4 occupying the axial position and Cu1 atom straying from the equatorial plane 0.107 Å; while Cu2 atom strays from the equatorial plane consisted of O1, O2, O6 and N4 atoms 0.128 Å with the axial site occupied by O3 atom. As shown in Table 2, the Cu–N bond lengths vary from 1.916(4) Å to 1.980 (4) Å, and Cu-O bond lengths vary from 1.908(3) Å to 2.309(4) Å with the Cu-O<sub>carbonyl</sub> bond length of 2.485(4) Å which are longer due to the Jahn-Teller effect. The angles of N2-Cu1-O2, N1-Cu1-N3 N4-Cu2-O1 and O2-Cu2-O6 are 177.44(11)°, 169.64  $(11)^{\circ}$ ,  $171.56(11)^{\circ}$  and  $169.10(9)^{\circ}$ , respectively, which are deviated from the theoretical value of 180°. Therefore, the local coordination geometry around the Cu<sup>II</sup> center can be described as distorted square pyramids. Addison  $\tau$  parameter for the Cu<sup>II</sup> centers in **2** are 0.01 and 0.045, highlighting a slight distortion from ideal spy geometry. As shown in Fig. 3c, Cu1 and Cu2 are bridged by two phenolic  $\mu_2$ -O (O2 and O3) to give a dinuclear building block possessing a Cu-O-Cu-O four membered rings with Cu1...Cu2 separations of 3.126 Å and Cu–O–Cu angle of 95.2° and 106.1° respectively. On the other hand, the two crystallographically



**Fig. 1**. (a) Coordination environment of Cu<sup>II</sup> ion in compound **1** with 30% probability thermal ellipsoids, all hydrogen atoms are omitted for clarity. (b) Coordination polyhedron of Cu<sup>II</sup> in compound **1**. (c) View of the dinuclear structure of compound **1** with a Cu–O–Cu–O four-membered ring.



**Fig. 2.** The 2D supramolecular structure of compound 1 with  $O-H\cdots$ Cl hydrogen bond which are indicated with dashed lines (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).



**Fig. 3.** (a) Coordination environment of Cu<sup>II</sup> ion in compound **2** with 30% probability thermal ellipsoids (all hydrogen atoms as well as crystalline methanol molecules are omitted for clarity). (b) Coordination polyhedron of Cu1 and Cu2 in compound **2**. (c) View of the tetranuclear structure of compound **2** with two Cu–O–Cu–O four-membered rings.

equivalent dinuclear Cu<sup>II</sup> units are syn-syn amido bridged by two amide from the fully deprotonated ligand anion  $L^{3-}$  to give a tetranuclear parallelogram building block with separations of Cu1...Cu2 (5.222 Å) which is greatly longer than that between Cu1 and Cu2 bridged by two phenolic oxygen atoms.

Notably, significant intermolecular hydrogen bonding interactions exist between the tetranuclear units. Intermolecular

quintuple cooperative hydrogen bonds among two crystalline methanol molecules which acted both as hydrogen bonding donor and acceptor, oxygen atom of amide group of one fully deprotonated ligand anion  $L^{3-}$  (O1) and phenoxy oxygen atom (O6) from the partly deprotonated ligand anion  $H_2L^-$  which acted as hydrogen bonding acceptor, and CH groups of phenyl ring (H21 and H23) acted as hydrogen bonding donor, are formed among six



Fig. 4. The 2D supramolecular structure of compound 1 with quintuple O-H···O and C-H···O hydrogen bond which are indicated with dashed lines (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

neighbouring tetranuclear units. As a result, the supramolecular tetranuclear units are held together into a 2D puckered supramolecular architecture as shown in Fig. 4. The O···O distance (2.800(7)-2.856(5) Å), C··O distance (3.239(8)-3.404(7)) Å) and O-H···O angle  $(138-170^\circ)$ , C-H···O angle  $(151-160^\circ)$  are all within the ranges of those reported hydrogen bonds [20].

## 3.2.3. Crystal structure of $[MnL]_n$ (3)

The introduction of  $Mn^{II}$  during the synthesis results in quite a different product. In contrast to the tetradentate chelating-bridging coordination mode in compound **1** and both tridentate and pentadentate coordination mode in compound **2** observed for Cu<sup>II</sup> complexes, the ligand coordinates to  $Mn^{III}$  in a pentadentate chelating-bridging mode, A single-crystal X-ray diffraction study revealed that  $Mn^{III}$  complex of the ligand is a 1D polymeric chain crystallized in the monoclinic space group  $P2_1/c$  which is very similar to our previously reported [8a]. As shown in Fig. 5a. The asymmetric unit of Mn<sup>III</sup> complex contains one independent Mn<sup>III</sup> ions and one trianion  $L^{3-}$  with  $Mn^{III}$  ion unusually fivecoordinating to one carbonyl oxygen atom, two hydroxy oxygen atoms and two nitrogen atoms that come from two different fully deprotonated ligands. As shown in Fig. 5b, Mn1 exhibits a slightly distorted square pyramidal configuration with O1, O3, N1 and N2 atoms from the same ligand trianion consisting of the equatorial plane and an amide oxygen atom from another ligand trianion occupying the apical site. The Mn<sup>III</sup> atom strays from the equatorial plane of 0.205 Å. The axial position is occupied by O2 from another ligand anion with the longer bond length of 2.1519 (18) Å. The angles of O1-Mn1-N2, and O3-Mn1-N2 are 166.35 (8)° and 166.90(8)° respectively, which are deviated from the theoretical value of 180°. Therefore, the local coordination geometry around the Mn<sup>III</sup> center can be described as a slightly



**Fig. 5.** (a) View of the coordination environment of Mn1 centre with thermal ellipsoids at 30% probability with a labelling scheme for compound **3** (All hydrogen atoms are omitted for clarity). (b) The coordination polyhedron of Mn1. (c) 1D zig-zag Mn<sup>III</sup> coordination chain view along *c*-axis.

distorted square pyramid which is very rare for Mn<sup>III</sup>. As a whole, the ligand is distorted with two phenyl rings deviating from the N2O2 equatorial coordination plane of 2.51° and 21.58° respectively. Similar to our previous report, the fully deprotonated ligand anion  $L^{3-}$  in *cis*-configuration adopts pentadentate coordination modes with two phenolic oxygen atoms and two nitrogen atoms chelating to one manganese as well as one carbonyl oxygen atom of amide group bridging another manganese. As shown in Fig. 5c, the amido oxygen atoms are involved in the coordination process as well as the related nitrogen atom, allowing the amido function with a head to tail arrangement to actually bridge adjacent Mn<sup>III</sup> ions in a svn-anti mode, thus leading to a one-dimensional zig-zag chain running along the crystallographic *c*-axis. It is important to note that the adjacent MnN2O2 equatorial coordination planes in the chain are nearly perpendicular and the corresponding dihedral angle is 88.40°. larger than that of previously reported Mn<sup>III</sup> analogues [8a]. The amido oxygen atom coordinates to Mn<sup>III</sup> with the slight longer bond length of 2.1519 (18) Å than those previously reported [8a]. The amido-bridged Mn...Mn distance is 6.032(2) Å with the C-O-Mn bond angle is 165.7(2)° and the torsion of Mn-amide-Mn of 159.57°, which is slight longer than that of 1D Mn<sup>III</sup> coordination polymer previously reported [8b,11]. Quite different from the  $Cu^{II}$  analogue of the H<sub>3</sub>L and the Mn<sup>III</sup> coordination polymer of the similar ligand [8a], there is no intermolecular hydrogen bond between the neighbouring chains.

# 3.2.4. Crystal structure of [Er<sub>2</sub>(HL)<sub>2</sub>(NO<sub>3</sub>)<sub>4</sub>]·2CH<sub>3</sub>OH (4)

To study the influence of lanthanide element on the coordination behavior of the ligand, erbium nitrate was selected in place of transition element under similar synthetic conditions and a new dinuclear complex **4** was obtained. Single-crystal X-ray diffraction analysis reveals that compound **4** crystallizes in the monoclinic I2/c space group. A view of the molecular structure, together with its numbering scheme, is depicted in Fig. 6a. The erbium atom is in a distorted [NdO8] dodecahedron coordination geometry (Fig. 6b), of which the coordination sphere for Er<sup>III</sup> is defined by three oxygens (O1, O2, O3) from the same partly deprotonated HL<sup>2-</sup> ligand, one oxygen(O1) from another partly deprotonated HL<sup>2-</sup> ligand and the remaining four oxygen atoms from two bidentate nitrates (O4, O5A, O7, O9). Quite different from compound **1**, **2** and **3**, the ligand adopts tridentate coordination modes with two phenolic oxygen atoms and one amide oxygen atom chelating to one erbium ion as well as one phenolic oxygen atom bridging another erbium ion. As shown in Fig. 6c, two crystallographically equivalent  $Er^{III}$  ions are bridged by two  $\mu_2$ -O (01) to give a dinuclear building block with shorter separations of Er...Er of 3.644 Å, in which there is only one inversion center (i) without any crystallographically imposed symmetry for the ligands or the metal centers. Furthermore, two neighboring dinuclear units are held together to a one-dimensional (1D) supramolecular chain via C-H···O hydrogen bonding with methylene carbon atoms as donor and nitrate oxygen atoms of adjacent units as acceptor (Fig. 6d). The  $C9 \cdots O4$  distance (3.109(9) Å), as well as C9-H9B...O4 angle (131°), are all within the ranges of those reported C–H $\cdots$ O hydrogen bonds [21].

#### 3.3. Effect of the reaction system on structural diversity

As shown in Fig. 7, the coordination behavior and deprotonation of the ligand presented in the four compounds are significantly different and reveal a much stronger dependence on the nature of the metal ions as well as counter anion. The complexes **1–4** were obtained from the same starting materials and similar experimental method, however, four structural types were obtained as follows. The one deprotonated  $H_2L^-$  ligand adopts tridentate



**Fig. 6.** (a) Coordination environment of Er<sup>III</sup> ion in compound **4** with 30% probability thermal ellipsoids (All hydrogen atoms as well as crystalline acetonitrile molecules are omitted forclarity). (b) Coordination polyhedron of Er(III) in compound **4**. (c) View of the dinuclear structure of compound **4** with a Er–O–Er–O four-membered ring. (d) The 2D supramolecular structure of compound **4** with C–H···O hydrogen bond which are indicated with dashed lines (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).



Fig. 7. The coordination mode and conformation of the ligand presented in compound 1, 2, 3 and 4.

chelating-bridging coordination mode to obtain a dinuclear compound 1 exempting amide nitrogen atom and salicylamide phenolic oxygen atom from coordination to Cu<sup>2+</sup> ion on the condition that CuCl<sub>2</sub> was used to carry out the reaction (Type 3). When Cu  $(Ac)_2$  rather than CuCl<sub>2</sub> was introduced to the reaction system, obvious counter anion effect was observed. As a result, we obtained a novel tetranuclear compound 2, where the ligand adopts two kind of coordination mode, one is the fully deprotonated L<sup>3-</sup> anion acted as pentadentate ligand with all its three oxygen atoms and two nitrogen atom binding three Cu<sup>2+</sup> ions (Type 1), the other is the one deprotonated  $H_2L^-$  anion employing tridentate chelating-bridging coordination to bind to two Cu<sup>2+</sup> ions without amide nitrogen atom and salicylamide phenolic oxygen atom participating in coordination which is quite different from Type 3 (Type 2). While manganese acetate was adopted, 1D zigzag coordination polymer was obtained, where the fully deprotonated L<sup>3-</sup> anion take the role of pentadentate ligand chelating one manganese ion with its two phenol oxygen atoms and two nitrogen atoms from imine and amide group and bridging another manganese with amide oxygen atom (Type 4). However, upon erbium nitrate was incorporated to perform the reaction, the dinuclear rare earth complex was obtained, where the one deprotonated HL<sup>2-</sup> anion coordinated to erbium ion as tridentate ligand with all its three oxygen rather than nitrogen atom taking part in coordination (Type 5). During this work we realized not only that the metal ion was important but also that the counter anions used in the synthesis were not-innocent for the construction of diverse metal complexes of H<sub>3</sub>L.

# 3.4. Magnetic properties

The temperature-dependent molar magnetic susceptibilities of **1**, **2**, **3** and **4** were measured at 1 kOe in the temperature range 2–300 K. The  $\chi_{M}T$  and  $\chi_{M}$  versus *T* plots for **1** are shown in Fig. 8. On cooling, the  $\chi_{M}T$  value decreases gradually indicating an antiferromagnetic coupling between the Cu<sup>II</sup> ions. The room temperature effective magnetic moment of 0.751 cm<sup>3</sup> K mol<sup>-1</sup> per Cu<sub>2</sub> is close to the expected spin only value for spin *S* = 1/2 (0.750 cm<sup>3</sup> K mol<sup>-1</sup>). The plots of  $\chi_{M}$  versus *T* shows the typical signature for a strongly coupled binuclear Cu<sup>II</sup> complex: there is a maximum close to 98–100 K which then decreases to, theoretically, 0 cm<sup>3</sup> mol<sup>-1</sup>. However, at very low temperature there is an increasing, typical of these strongly coupled systems, that indicates the presence of small amount of paramagnetic impurities.

Considering the magneto-structural remarks, the magnetic properties of the compound can be analyzed in a first approximation with the same magnetic model including two identical S = 1/2

spin dimers with only one exchange parameter, denoted as *J*. The magnetic susceptibility has thus been calculated from the following isotropic spin Heisenberg–Hamiltonian:  $H = -2J\{S_{Cu,1}, S_{Cu,2}\}$  where  $S_i$  are the spin operators for each center with S = 1/2. Application of the van Vleck equation [22] allows the determination of the low-field analytical expression of the magnetic susceptibility [23] taking into account the presence of a residual extrinsic paramagnetic contribution:

$$\chi_{\mathrm{M}} = (1-\rho) \frac{2\mathrm{N}\mathrm{g}^{2}\beta^{2}}{\mathrm{k}\mathrm{T}} \times \frac{1}{3+e^{-2J/\mathrm{k}\mathrm{T}}} + \frac{\mathrm{N}\mathrm{g}^{2}\beta^{2}}{2\mathrm{k}\mathrm{T}}\rho$$

As shown in Fig. 8, the above expression of the magnetic susceptibility reproduces almost perfectly the experimental  $\chi_M T$  versus *T* data at 1 KOe. The best sets of parameters obtained are given as g = 2.00,  $J = -55.73 \text{ cm}^{-1}$ ,  $\rho = 3\%$ , with an agreement factor  $R = [\sum (\chi_M T)_{obsd} - (\chi_M T)_{calcd}]^2 / \sum [(\chi_M T)_{obsd}]^2$  of  $4.0 \times 10^{-4}$  (solid line in Fig. 8). The negative sign of the magnetic interaction implies that the Cu<sup>II</sup> dimer unit possess an  $S_T = 0$  spin ground state, i.e., a diamagnetic ground state. The  $\rho$  values indicate that a very small amount of residual paramagnetic contribution is present in the measured samples of **1**, as it is seen for materials displaying a diamagnetic ground state. Taking into account that the impurity possesses a Curie S = 1/2 paramagnetic behavior and the same molecular weight as the major complex, the amount is about 3% for **1**.

The  $\chi_{\rm M}$  and  $\chi_{\rm M}T$  versus T plots for **2** is shown in Fig. 9. On cooling, the  $\chi_{\rm M}T$  value decreases gradually indicating an antiferromagnetic coupling between the Cu<sup>II</sup> ions. The room temperature effective magnetic moment of 1.35 cm<sup>3</sup> K mol<sup>-1</sup> per Cu<sub>4</sub> unit is lower than expected for four uncoupled  $Cu^{II}$  ions (1.5 cm<sup>3</sup> K mol<sup>-1</sup>, S = 1/2, g = 2.0). Considering the magneto-structural remarks, the magnetic exchange in 2 can be modeled as depicted in Fig. S5 (Supporting Information). A appropriate fit can be obtained by the Hamiltonian derived from the parallelogram model  $Cu1(S_1)-J_1-Cu2(S_2)-J_2 Cu1A(S_3)-J_1-Cu2A(S_4)-J_2-Cu1(S_1)$ ,  $Cu1(S_1)-J_3-Cu1A(S_3)$  and Cu2 $(S_2)$ –J4–Cu2A $(S_4)$ . Considering these four different exchange parameters, the distance of Cu1···Cu2A, Cu1···Cu1A and Cu2···Cu2A are 5.031 Å, 5.222 Å and 6.985 Å, therefore the value of  $J_3$  and  $J_4$  are considered as negligible. Thus, the Hamiltonian can be performed using the following expression:  $H = -2J_1(S_1S_2 + S_3S_4) - 2J_2(S_2S_3 + S_4S_1)$ [24]. The Cu<sub>4</sub><sup>II</sup> expression of the magnetic susceptibility can be performed:  $\chi_{\rm M} = (\text{Ng}^2\beta^2/3\text{kT})$  [A/B], where A = [30exp(6J<sub>1</sub>/kT) + 6exp  $(4J_1/kT) + 6\exp(2J_1/kT) + 6\exp((2J_2 - 4J_1)/kT)]$  and B = [5exp (6J\_1/kT) +  $3\exp(4J_1/kT)$  +  $3\exp(2J_1/kT)$  +  $4\exp((2J_2 - 4J_1)/kT)$  + 1]. As shown in Fig. 9, the above expression of the magnetic susceptibility reproduces almost perfectly the experimental  $\chi_{M}T$  versus T data at 1 KOe. The best sets of parameters obtained are given as g = 2.11(2),



Fig. 8. The  $\chi_M T$  and  $\chi_M$  vs. T plot for 1 collected in an applied dc field of 0.1 T. The solid line shows the best fit to the magnetic model.



Fig. 9. The  $\chi_M T$  and  $\chi_M$  vs. T plot for 2 collected in an applied dc field of 0.1 T. The solid line shows the best fit to the magnetic model.

 $J_1 = -40.66(8) \text{ cm}^{-1}$  and  $J_2 = 0 \text{ cm}^{-1}$ , with an agreement factor  $R = \left[\sum (\chi_M T)_{obsd} - (\chi_M T)_{calcd}\right]^2 / \sum [(\chi_M T)_{obsd}]^2$  of  $1.93 \times 10^{-4}$  (solid line in Fig. 9).

It is well known that comparing the  $\mu$ -O bridge, three-atom bridges such as O–C–N play a negligible role in propagating the magnetic exchanges. According to the structure of compound **2**, the magnetic exchanges within the  $(Cu_2(\mu-O)_2)$  unit is dominant. Merz and Haase [25] found an almost linear correlation between the magnitude of the exchange interaction and the Cu–O–Cu bridging angle within the symmetric  $Cu_2O_2$  core of dimeric alkoxobridged copper(II) complexes. They concluded that when the Cu–O–Cu angle is greater than 95.8°, the overall magnetic behavior is antiferromagnetic. Otherwise ferromagnetic coupling is observed. In the case of compound **1** and **2**, the Cu(1)–O(2)–Cu (1), Cu(1)–O(2)–Cu(2) and Cu(1)–O(3)–Cu(2) bond angles are 102.16 106.1(2) and 95.2(4)°, respectively. Thus the exchange across the hydroxy group in the two complexes are antiferromagnetic.

For compound **3**, the room temperature magnetic moment per Mn  $(2.84 \text{ cm}^3 \text{ K mol}^{-1})$  is slight lower than the spin-only value expected for a high-spin  $Mn^{III}$  ions with S = 2 and g = 2 $(3.00 \text{ cm}^3 \text{ K mol}^{-1})$ . Upon cooling,  $\chi_M T$  decreases smoothly from  $2.84 \text{ cm}^3 \text{ K} \text{ mol}^{-1}$  at 300 K to a minimum of  $1.83 \text{ cm}^3 \text{ mol}^{-1}$  K at ca. 11 K, suggesting a dominant antiferromagnetic interaction. Below 11 K, a maximum of 17.13 cm<sup>3</sup> mol<sup>-1</sup> K is observed at 4.5 K which is much larger than its room-temperature value. Below 4.5 K, the  $\chi_{\rm M}T$  drops abruptly again and approaches to a value of 9.85 cm<sup>3</sup> mol<sup>-1</sup> K, indicating a magnetic phase transition (Fig. 10). The susceptibility data of the compound above 22 K follow the Curie–Weiss law, with C = 3.05 cm<sup>3</sup> K mol<sup>-1</sup> and  $\theta$  = -8.10 K indicating antiferromagnetic interactions predominate between Mn(III) ions at 22-300 K. The C value is close to the spinonly value of  $3.0 \text{ cm}^3 \text{ K mol}^{-1}$  expected from two high-spin  $d^4$ (S = 2) species. The nearest-neighbor interaction can be attributed to the through bond Mn<sup>3+</sup>-Mn<sup>3+</sup> coupling across the amidobridges. Fig. 11 shows the isothermal magnetization vs. field plot



**Fig. 10.** The plot of  $\chi_{\rm M}T$  and  $\chi_{\rm M}^{-1}$  vs. *T* (inset) for **3** collected in an applied dc field of 0.1 T.



Fig. 11. Magnetization-magnetic field strength (M–H) curves for polycrystalline of 3 measured at 2 K with sweep rates of 100 Oe/min from 0-80 KOe (inset: plot of the hysteresis loop at 2 K).

at 2 K. The magnetization at 80 kOe (1.78 N $\beta$ ) is far below the saturation value of 4.0 N $\beta$  expected for an *S* = 2 system, consistent with a canted antiferromagnetism. The magnetizations measured at 2 K show hysteresis loops. Extrapolating the linear part of the magnetization curve at high fields to *H* = 0 gives a magnetization value of 0.037 N $\beta$ . If we assume this to be the uncompensated magnetization, the canting angle is estimated to be 5.3° [26]. The coercive field (Hc) and the remnant magnetization (Mr) at 2 K are 24.4 Oe and 0.0028 N $\beta$ , respectively (Fig. 11, inset).

For **4**, the value of  $\chi_M T$  is 24.14 cm<sup>3</sup> K mol<sup>-1</sup> at 300 K as shown in Fig. 12, which is greater than the spin-only value of two uncoupled Er<sup>III</sup> ions (<sup>4</sup>I<sub>15/2</sub>, 11.48 cm<sup>3</sup> K mol<sup>-1</sup>, *S* = 3/2, *g* = 6/5). As the temperature is lowered,  $\chi_M T$  undergoes a gradual reduction and then a more abrupt decrease below 64 K. This behavior is due to the depopulation of the Stark sublevels and the probable weak magnetic interactions between the metal centers [27]. The latter contribution is not readily extracted from the magnetic data because of the orbital angular moment arising from  $\text{Er}^{III}$  ions. The data between 2 K and 300 K are fitted by the Curie–Weiss law and affords  $\theta = -6.78 \text{ cm}^3 \text{ K} \text{ mol}^{-1}$ , C = 24.48 K, the negative value of  $\theta$  confirms the presence of antiferromagnetic interaction between  $\text{Er}^{III}$  ions.

# 3.5. Thermogravimetric analyses

The thermal study, both Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC), was carried out for the four compounds to examine their thermal stabilities (Fig. 13).



**Fig. 12.** The plot of  $\chi_M T$  and  $\chi_M^{-1}$  vs. *T* (inset) for **4** collected in an applied dc field of 0.1 T.



Fig. 13. Weight loss (TG thermograms) and DSC thermograms at high temperature for compound 1–4. The observed and theoretical values of the weight loss and the estimated intermediate products are indicated.

There is no solvent molecule in compound **1**, and it began to lose weight above 191 °C with two endothermic peaks observed by DSC at 210 and 400 °C to producing a residue of CuO around 850 K. All uncoordinated solvent molecules in complexes 2 and 4 were lost at the first weight loss. For complex 2, the TG curve shows that the first weight loss of 8.55% (Calc. 8.48%) from 46 to 184 °C corresponds to the loss of four lattice methanol molecules. Increasing temperature led to the further decomposition of complex 2 at 254 °C. The final pyrolysis was completed at 674 °C, as indicated by a significant weight loss 73.4%, giving the powder of CuO (Calc. 73.7%). There is no solvent molecule in compound 3, and it began to lose weight above 345 °C, this shows that the thermal stability of compound **3** are much higher than that of compound 1 and 2. The curve exhibits that complex 3 began to lose weight from 345 °C with several endothermic peaks observed by DSC to produce a residue of MnO and the final pyrolysis was completed at 686 °C, as indicated by a significant weight loss 81.1% MnO (calcd. 81.5%) was obtained. In the case of compound 4, the thermal behavior presents two features: the acetonitrile loss and the final decomposition producing Er<sub>2</sub>O<sub>3</sub>. Loss of four crystalline acetonitrile molecules take place from 61 °C to 145 °C. Up to a temperature of around 333 °C, it starts to decompose with several exothermic peaks observed and the decomposition finishes at around 865 °C.

# 4. Conclusions

Four new metal complexes with diverse structures of a asymmetric amide-imine multidentate ligand were prepared and structurally characterized. This investigation demonstrates that the nature of the metal ion as well as counter anions have significant effects both on coordination behavior of the ligand as well as magnetic properties of the resulted complexes. The thermogravimetric analyses show that complexes **1–4** exhibit high thermal stability. The experimental magnetic susceptibilities indicate 1, 2 and 4 exhibit antiferromagnetic interactions through hydroxy bridge, while 3 exhibits dominant antiferromagnetic interactions with spin canting through the amido bridge. Our current studies of metal ions effects both on structures and magnetic properties are helpful in achieving further insights into the rational design and construction of functional complexes through the selection of the ligands and metal ions under corresponding conditions. We are currently working on variation of reaction system to induce the formation of hetero-polynuclear metallic complexes of this ligand.

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# Appendix A. Supplementary data

CCDC 1408852-1408855 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at http:// dx.doi.org/10.1016/j.ica.2015.09.022.

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