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# Tuning nuclearity of clusters by positional change of functional group: Synthesis of polynuclear clusters, crystal structures and magnetic properties



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## ABSTRACT

Four neutral polynuclear magnetic clusters,  $[Mn_{H}^{HI}Mn_{I}^{H}Na_{2}^{H}(N_{3})_{8}(\mu_{4}-O)_{2}(L^{1})_{6}(CH_{3}OH)_{2}]$  (1),  $[Mn_{H}^{HI}Na_{2}^{H}(N_{3})_{4}(\mu_{4}-O)_{2}(L^{2})_{4}(CH_{3}OO)_{4}]$  (2),  $[Ni_{5}^{H}(N_{3})_{4}(HL^{1})_{4}(HCOO)_{2}(CH_{3}OH)_{2}(H_{2}O)_{2}]$ -2CH<sub>3</sub>OH (3) and  $[Ni_{4}^{H}Na_{2}^{H}(N_{3})_{4}(HL^{2})_{6}]$ -2CH<sub>3</sub>OH (4) have been synthesized using tetradentate ligands  $H_{2}L^{1-2}$  along with azide as a co-ligand.  $H_{2}L^{1-2}$  are the products formed *in situ* upon condensation of 2-hydroxy-3-methoxybenzaldehyde with 1-aminopropan-2-ol and 1-aminopropan-3-ol, respectively. Single crystal X-ray diffraction and bond valence sum calculation showed that complex 1 is composed of both  $Mn^{III}$  and  $Mn^{II}$ . Complex 3 contains coordinated formate, which was formed upon *in situ* oxidation of methanol. The magnetic study over a wide range of temperatures of all the complexes (1–4) showed that 1 and 2 are antiferromagnetic whereas other two (3–4) are predominantly ferromagnetic. The estimated ground states of the complexes are  $S \approx 3(1)$ , S = 4(2), S = 5(3) and  $S \approx 4(4)$ , respectively.

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# 1. Introduction

Considerable efforts have been paid in recent time to design and synthesize polynuclear paramagnetic clusters because of their fascinating magnetic properties. The most appealing classes among them is single molecular magnet (SMM) [1], which can display nano-scale magnetic behavior [2] and can be used in high density information storage devices and in quantum information processing [3]. To show SMM behavior, the molecule must possess large ground-state spin (S) and a significant magneto-anisotropy (D) of the Ising (easy-axis) type so that it can give rise to high barrier  $(|DS^2|)$  to magnetization relaxation [1]. Several manganese and nickel clusters with high nuclearity are known and their magnetic behavior was studied widely because many of them have exceptionally high ground spin state along with negative uniaxial anisotropy [4]. It has been a challenge for the researchers to design molecules that have high ground spin state as well as high negative anisotropy, correspond to high energy barrier and thus can show a slow relaxation of magnetization and quantum tunneling of magnetization [5].

It is quite obvious that ligand is one of the key components for achieving polynuclear clusters with diverse structural topology. Polyhydroxy ligands have been well established as extremely effective chelating and bridging groups that have afforded a large number of polynuclear paramagnetic clusters [6]. On the other hand, the use of azide as bridging ligand may develop a wide variety of structural topologies with complex magnetic behavior due to its versatile bridging nature [7].

Several polydentate Schiff bases have been used to obtain polynuclear clusters with diverse magnetic behavior [8]. Variation in structural topology of metal clusters with the position of functional group in Schiff base ligands is less studied because of difficulty in controlling the nuclearity, which needs to rely on serendipity. In a recent communication, we have shown the use of a tridentate dihydroxy ligand in constructing heterometallic polyclusters featuring Mn(II) and Na(I) in unusual trigonal prismatic geometry [9]. Herein, we report the use of two different dihydroxy Schiff bases  $H_2L^1$ [2-(((2-hydroxypropyl))mino)methyl)-6-methoxyphenol] and H<sub>2</sub>L<sup>2</sup>[2-(((3-hydroxypropyl)imino)methyl)-6-methoxyphenol] for the synthesis of four new manganese and nickel clusters of different nuclearity  $[Mn_6^{II}Mn_2^{I}Na_2^{I}(N_3)_8(\mu_4-O)_2(L^1)_6(CH_3OH)_2]$  (1),  $[Mn_6^{III}Na_2^{I}]$  $(N_3)_4(\mu_4-O)_2(L^2)_4(CH_3COO)_4$ ] (2),  $[Ni_5^{II}(N_3)_4(HL^1)_4(HCOO)_2(CH_3OH)_2$  $(H_2O)_2$ ]·2CH<sub>3</sub>OH (**3**) and  $[Ni_4^{II}Na_2^{I}(N_3)_4(HL^2)_6]$ ·2CH<sub>3</sub>OH (**4**) including their structures and magnetic studies (Chart 1).  $H_2L^1$  and  $H_2L^2$  were obtained upon condensation of 2-hydroxy-3-methoxybenzaldehyde with 1-aminopropan-2-ol and 1-aminopropan-3-ol, respectively. Although a few other metal complexes with these ligands are known in the literature [10], they are mononuclear and magnetically less interesting. Herein, we demonstrate how a simple change in the







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**Chart 1.** Schiff bases  $H_2L^1$  and  $H_2L^2$  used to prepare polynuclear clusters **1–4**.

position of the hydroxy group in these Schiff bases can control the nuclearity of the magnetic clusters. Interestingly, in complex **3**, oxidation of methanol to formic acid occurs to satisfy the coordination of Ni<sup>II</sup> ions. Such kind of metal-ion induced methanol oxidation is known in the literature [11]. The detail cryomagnetic study revealed that complexes **1** and **2** are antiferromagnetic, while **3** and **4** are ferromagnetic in nature with magnetic anisotropy in all the cases.

#### 2. Experimental

## 2.1. Materials

 $Mn(ClO_4)_2 \cdot 6H_2O$ ,  $Mn(OAc)_2 \cdot 4H_2O$ ,  $NiCl_2 \cdot 6H_2O$ ,  $NaN_3$ , sodiummethoxide, triethylamine, 2-hydroxy-3-methoxybenzaldehyde, 1-aminopropan-2-ol, 1-aminopropan-3-ol and all solvents were obtained from commercial sources and used as received without further purification.

#### 2.2. Physical measurements

Elemental analyses of C. H. and N were performed using a Perkin Elmer 240C elemental analyzer. IR spectra were recorded on a Bruker ALPHA FT-IR spectrometer. Variable-temperature magnetic susceptibility measurements were carried out on a Quantum Design MPMS-XL5 SQUID magnetometer. Susceptibility data were collected under an external magnetic field of 2000 Oe for all complexes in the temperature range of 2-300 K. The saturation of magnetization is the state where with increasing the magnetic field the magnetization of the complex does not change. Since, saturation of magnetization, which is prominent at the low temperature regime, observed at higher external magnetic field. We have collected DC susceptibility data in the presence of lower external magnetic field 500 Oe (Supporting information, Fig. S7). However, we could not find any such difference in magnetization at those two different fields. The reduced magnetization of all complexes was recorded in the temperature range of 2-20 K. Alternating current (ac) susceptibility measurements for all the complexes were done in the presence of oscillating ac field of 4 Oe with the frequency range of 1–1000 Hz in the temperature range of 3–20 K. It is noted that there was no out-of-phase susceptibility signal observed for the complexes **1**, **2** and **4** (Supporting information). The experimental susceptibility data were corrected for diamagnetism (Pascal's tables) [12].

**Caution!** Although we did not experience any problems with the compounds reported in this work, perchlorate salts and azido complexes of metal ions in the presence of organic ligands are potentially explosives. Only a small amount of the materials should be prepared, and should be handled carefully.

# 2.3. Synthesis of complexes 1-4

# 2.3.1. Complex $[Mn_6^{II}Mn_2^{I}Na_2^{I}(N_3)_8(\mu_4-0)_2(L^1)_6(CH_3OH)_2]$ (1)

2-Hydroxy-3-methoxybenzaldehyd (0.5 mmol, 76 mg) was taken in 10 mL of acetonitrile. 1-Aminopropan-2-ol (0.5 mmol, 37.5 mg) was added with stirring to get the ligand  $H_2L^1$  in situ in solution. Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (1 mmol, 361.9 mg) was added to that solution and stirred for 15 min to yield a light brown solution. NaN<sub>3</sub> (1 mmol, 65 mg) was added to the resulting solution followed by dropwise addition of triethylamine (1 mmol, 0.140 mL). A yellow precipitate was appeared to form, which slowly dissolved upon addition of 5 mL methanol and the solution turned dark brown. The resulting mixture was stirred for another 15 min and filtered. Rectangular black crystals of **1** were obtained at 2 h from the filtrate. Isolated yield: 80%. *Anal.* Calc. for complex **1**, C<sub>68</sub>H<sub>86</sub>-N<sub>30</sub>O<sub>22</sub>Mn<sub>8</sub>Na<sub>2</sub>: C, 37.79; H, 4.01; N, 19.44. Found: C, 37.54.74; H, 4.12; N, 19.64%. IR ( $\nu$  cm<sup>-1</sup>): 3365 (w), 2969 (w), 2038 (s), 1624 (s), 1552 (m), 1439 (s), 1395 (w), 1297 (m), 1219 (m), 1076 (m), 1036 (m), 1003 (w), 966 (w), 857 (m), 786 (w), 736 (m), 658 (m), 559 (w).

## 2.3.2. Complex $[Mn_6^{III}Na_2^I(N_3)_4(\mu_4-0)_2(L^2)_4(CH_3COO)_4]$ (2)

2-Hydroxy-3-methoxybenzaldehyde (0.5 mmol, 76 mg) was taken in 1:1 mixture of 10 mL methanol and acetonitrile. To that 1-aminopropan-3-ol (0.5 mmol, 37.5 mg) was added with stirring to obtain ligand  $H_2L^2$  as a yellow product in solution. After 15 min stirring, Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (1 mmol, 245 mg) was added to that solution, which turned light brown solution immediately. NaN<sub>3</sub> (1 mmol, 65 mg) was added slowly to the mixture followed by addition of triethylamine (1 mmol, 0.140 mL). The reaction mixture was kept for stirring at room temperature for another 2 h. The dark brown reaction mixture was filtered and the filtrate was kept for slow evaporation. X-ray quality brown rectangular crystals were obtained after two days. Isolated yield: 73%. Anal. Calc. for complex **2**, C<sub>52</sub>H<sub>64</sub>N<sub>16</sub>O<sub>22</sub>Mn<sub>6</sub>Na<sub>2</sub>: C, 38.06; H, 3.93; N, 13.66. Found: C, 38.25; H, 4.23; N, 13.53%. IR (v cm<sup>-1</sup>): 2928 (w), 2848 (w), 2029 (s), 1610 (s), 1576 (s), 1547 (s), 1413 (s), 1302 (s), 1245 (m), 1218 (m), 1071 (s), 954 (w), 860 (m), 786 (w), 736 (m), 665 (w), 623 (w), 576 (s), 466 (w).

## 2.3.3. Complex $[Ni_{5}^{II}(N_{3})_{4}(HL^{1})_{4}(HCOO)_{2}(CH_{3}OH)_{2}(H_{2}O)_{2}]\cdot 2CH_{3}OH$ (**3**)

1-Aminopropan-2-ol (0.5 mmol, 37.5 mg) in 10 mL of methanol was added dropwise to 2-hydroxy-3-methoxybenzaldehyde (0.5 mmol, 76 mg) with constant stirring at room temperature over a period of 15 min. NiCl<sub>2</sub>·6H<sub>2</sub>O (1 mmol, 237.7 mg), NaN<sub>3</sub> (1 mmol, 65 mg) and NaOMe (1 mmol, 54 mg) were added to the above solution successively. The reaction mixture was stirred at room temperature for 2 h and subsequently refluxed for further 1 h. The mixture was cooled to room temperature and filtered. X-ray quality green single crystals were obtained upon diffusion of diethyl ether into the filtrate in 5 days. Isolated yield: 43%. *Anal.* Calc. for complex **3**, C<sub>49</sub>H<sub>74</sub>N<sub>16</sub>O<sub>21</sub>Ni<sub>5</sub>: C, 38.78; H, 5.08; N, 18.95. Found: C, 38.74; H, 5.04; N, 19.32%. IR ( $\nu$  cm<sup>-1</sup>): 2909 (w), 2059 (s), 1630 (s), 1630 (m), 1544 (w), 1463 (m), 1440 (s), 1406 (m), 1311 (s), 1209(s), 1127 (w), 1079 (m), 1038 (m), 970 (w), 929 (w), 851 (w), 781 (w), 736 (m), 640 (w), 553 (w), 481 (w), 429 (w).

## 2.3.4. Complex $[Ni_4^{ll}Na_2^{l}(N_3)_4(HL^2)_6]$ ·2CH<sub>3</sub>OH (**4**)

2-Hydroxy-3-methoxybenzaldehyde (0.5 mmol, 76 mg) was taken in 5 mL of methanol and 1-aminopropan-3-ol (0.5 mmol, 37.5 mg) was added to it with stirring to obtain yellow  $H_2L^2$  in solution. Triethylamine (0.5 mmol, 0.07 mL) was added to the above solution followed by addition of a 5 mL methanolic solution of NiCl<sub>2</sub>·6H<sub>2</sub>O (0.5 mmol, 118.8 mg) and NaN<sub>3</sub> (0.5 mmol, 32.5 mg) with continuous stirring. The reaction mixture was stirred for 1 h at room temperature and then refluxed for 6 h before it was cooled again to room temperature. Dark green X-ray quality single crystals were isolated upon slow evaporation of the filtrate in two days. Isolated yield: 67%. Anal. Calc. for complex **4**, C<sub>68</sub>H<sub>92</sub>N<sub>18</sub>O<sub>20</sub>Ni<sub>4</sub>Na<sub>2</sub>: C, 46.34; H, 5.26; N, 14.31. Found: C, 46.57; H, 5.64; N, 14.25%. IR ( $\nu$  cm<sup>-1</sup>): 3354 (w), 2937 (w), 2894 (w), 2041 (s), 1617 (s), 1545 (w),

1454 (s), 1405 (m), 1335 (m), 1303 (m), 1209 (s), 1068 (s), 967 (m), 854 (w), 789 (w), 736 (s), 623 (w), 548 (w), 442 (w).

# 2.4. X-ray crystallographic data collection and refinements

Single-crystal X-ray data for complexes **1–4** were collected on a Bruker SMART APEX CCD diffractometer using the SMART/SAINT software [13]. Graphite-monochromatized Mo-Ka radiation (0.71073 Å) was used to collect intensity data at 90 K. Direct methods were used to solve the structures by using the SHELX-97 [14] program implemented into WinGX [15]. Absorption corrections were done by empirical method applied with sadabs [16]. All non-hydrogen atoms were refined with anisotropic displacement coefficients.

# Table 1

The hydrogen atoms bonded to carbon were included in geometric positions and given the thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Crystallographic data and refinement parameters are given in Table 1, and important interatomic distances and angles are provided in Tables 2-5.

# 3. Results and discussion

## 3.1. Synthesis

In situ condensation of the 2-hydroxy-3-methoxybenzaldehyde and 1-aminopropan-2-ol in acetonitrile gives ligand  $H_2L^1$  as a yellow product in solution. The reaction of the  $H_2 L^1$  solution,

	Complex 1	Complex 2	Complex <b>3</b>	Complex <b>4</b>
Empirical formula	$C_{68}H_{86}N_{30}O_{22}Mn_8Na_2$	$C_{52}H_{64}N_{16}O_{22}Mn_6Na_2$	$C_{50}H_{78}N_{16}O_{22}Ni_5$	C <sub>68</sub> H <sub>92</sub> N <sub>18</sub> O <sub>20</sub> Ni <sub>4</sub> Na <sub>2</sub>
Formula weight	2161.08	1640.77	1548.72	1760.32
T (K)	90(2)	90(2)	90(2)	90(2)
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	$P2_1/c$	ΡĪ	ΡĪ
a (Å)	19.187(4)	14.3544(14)	12.0550(11)	12.0560(5)
b (Å)	11.741(2)	19.407(2)	12.0933(11)	12.6176(5)
c (Å)	19.806(4)	11.8377(13)	13.5730(13)	14.1007(6)
α (°)	90.00	90.00	66.683(5)	94.312(3)
β (°)	99.599(9)	107.998(5)	88.200(5)	95.841(4)
γ (°)	90.00	90.00	63.754(5)	116.149(4)
$V(Å^3)$	4399.3(15)	3136.4(6)	1604.8(3)	1898.04(14)
Ζ	2	2	1	1
$ ho_{ m calc}~( m g~cm^{-3})$	1.104	1.681	2.033	1.649
$\mu$ (Mo K $lpha$ ) (mm $^{-1}$ )	0.497	0.895	1.264	1.074
λ (Å)	0.71073	0.71073	0.71073	0.71073
F(000)	1494	1614	1024	975
Collected reflections	85695	64880	33179	16126
Unique reflections	13403	9620	9669	11856
R <sub>int</sub>	0.0899	0.0483	0.0453	0.0215
Goodness-of-fit (F <sup>2</sup> )	1.012	1.029	1.034	0.727
$R_1^{a}$	0.0503	0.0344	0.0492	0.0444
wR <sub>2</sub> <sup>b</sup>	0.1070	0.0695	0.0949	0.1220

<sup>a</sup>  $R_1 = (\sum ||F_0| - |F_c||) / \sum |F_0|.$ <sup>b</sup>  $wR_2 = [\sum w(F_0^2 - F_c^2) / \sum wF_0^4]^{1/2}.$ 

#### Table 2

Selected bond lengths (Å) and bond angles (°) of the complex 1.

$M_{\rm P}(1) O(6)$	1 202(2)	$M_{\rm P}(1) O(4)$	1 202(2)	$M_{\rm P}(1) = O(11)$	1.006(2)
N(1) = O(0)	1.092(2)	$M_{1}(1) = O(4)$	1.898(2)	VIII(1) = O(11)	1.900(2)
NIII(1) - N(15)	1.998(3)	VIII(1) - N(4)	2.295(3)	VIII(1) = N(10)	2.302(3)
Mn(2) - O(3)	1.912(2)	Mn(2) - O(1)	1.919(2)	Mn(2) - O(11)	1.921(2)
Mn(2) - N(13)	1.974(3)	Mn(2)-O(10)	2.240(2)	Mn(2)–N(7)	2.283(3)
Mn(3)-O(9)	1.896(2)	Mn(3)–O(7)	1.913(2)	Mn(3)–O(11)	1.940(2)
Mn(3)-N(14)	1.981(3)	Mn(3)–N(7)	2.290(3)	Mn(3)–N(10)	2.295(3)
Mn(4)-O(3)	2.109(2)	Mn(4)-O(6)	2.112(2)	Mn(4)-N(1)	2.118(3)
Mn(1)-Mn(3)	3.137(8)	Mn(2)-Mn(3)	3.107(9)	Mn(1)-Mn(2)	3.632(2)
Mn(1)-Mn(4)	3.322(5)	Mn(2)-Mn(4)	3.377(4)	Mn(3)-Mn(4)	3.417(7)
$Mn(4) - N(6)^{\#1}$	2.283(3)				
O(6)-Mn(1)-N(4)		89.31(10)	O(4)-Mn(1)-l	N(4)	89.43(10)
O(6)-Mn(1)-O(4)		174.46(8)	O(6)-Mn(1)-O(11)		92.87(8)
O(6) - Mn(1) - N(10)	h(1)-N(10) 88.87(10)		O(4)-Mn(1)-N(10)		92.49(10)
O(11)-Mn(1)-N(10)	0) 81.85(9)		N(15)-Mn(1)	-N(10)	92.34(11)
O(3)-Mn(2)-O(11)	n(2)-O(11) 91.19(9)		O(1)-Mn(2)-0	0(11)	95.19(8)
O(3)-Mn(2)-N(13)		83.11(10)	O(1)-Mn(2)-l	N(13)	90.65(10)
O(11)-Mn(2)-N(13)	11)-Mn(2)-N(13) 172.66(10)		O(3)-Mn(2)-0	O(10)	89.36(9)
O(1)-Mn(2)-O(10)		88.78(9)	O(11)-Mn(2)-	-O(10)	93.94(9)
O(9)-Mn(3)-N(7)		89.18(9)	O(7)-Mn(3)-I	N(7)	91.43(9)
O(11)-Mn(3)-N(10)		81.33(9)	N(14)-Mn(3)	-N(10)	100.54(11)
N(7)-Mn(3)-N(10)		163.54(10)	O(3) - Mn(4) - - Mn	O(6)	123.10(8)
O(3) - Mn(4) - N(1)		112.81(10)	O(6)-Mn(4)-I	N(1)	123.78(10)
O(3) - Mn(4) - O(9)		97.27(8)	O(6) - Mn(4) - -	0(9)	87.90(8)
$O(3)-Mn(4)-N(6)^{\#1}$	90.00(10)		$O(6) - Mn(4) - N(6)^{\#1}$		86.62(9)
$N(1)-Mn(4)-N(6)^{\#1}$		88.06(11)	O(9)-Mn(4)-l	N(6) <sup>#1</sup>	172.51(10)

Symmetry transformations used to generate equivalent atoms: #1 = -x + 1, -y, -z.

Table	3
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Selected bond lengths (Å) and bond angles (°) of the complex 2.

	5	0	,	I · ·		
Mn(1)-O(7)	1.885(1)	Mn(1)-O(3)	1.916(1)	Mn(1)-O(6)	1.917(1)	
Mn(1) - N(1)	2.015(2)	Mn(1) - O(9)	2.138(1)	Mn(1) - N(3)	2.344(2)	
Mn(1)-Mn(3)	2.841(4)	Mn(1)-Mn(2)	3.212(5)	Mn(1)-Na(1)	3.436(8)	
Mn(2) - O(5)	1.872(1)	Mn(2) - O(1)	1.904(1)	Mn(2)-O(6)	1.929(1)	
Mn(2) - N(2)	2.008(2)	Mn(2) - O(10)	2.229(1)	Mn(2) - N(3)	2.404(2)	
Mn(2)-Mn(3)	2.911(4)	Mn(2)-Na(1)	3.423(8)	Mn(3)-O(6)	1.902(1)	
Mn(3)-N(6)	1.956(2)	Mn(3)-O(11)	1.967(1)	Mn(3)-O(3)	1.975(1)	
Mn(3)-O(8)	2.155(1)	Mn(3)-O(5)	2.185(1)			
O(7)-Mn(1)-O	(3)	174.39(5)	O(7)-Mn(	1)-O(6)	90.86(5)	
O(3)-Mn(1)-O	(6)	83.54(5)	O(7)-Mn(	1)-N(1)	91.23(6)	
O(7)-Mn(1)-N	(3)	90.80(5)	O(3)-Mn(	1)-N(3)	88.71(5)	
O(5)-Mn(2)-O	(6)	87.11(5)	O(1)-Mn(	2)-0(6)	91.39(5)	
O(6)-Mn(2)-N	(2)	170.43(6)	O(5)-Mn(	2)-0(10)	83.48(5)	
O(1)-Mn(2)-O	(10)	93.10(5)	0(6)-Mn(	2)-0(10)	89.01(5)	
N(2)-Mn(2)-O	(10)	100.09(5)	O(5)-Mn(	2)-N(3)	88.09(5)	
O(1)-Mn(2)-N	(3)	94.99(5)	O(6)-Mn(	2)-N(3)	79.79(5)	
O(6)-Mn(3)-N	(6)	172.45(6)	O(6)-Mn(	3)-0(11)	93.84(5)	
O(6)-Mn(3)-O	(8)	92.63(5)	N(6)-Mn(	3)-0(8)	93.61(6)	
O(11)-Mn(3)-0	D(8)	89.42(5)	O(3)-Mn(	3)-O(8)	91.33(5)	
						2

Table 4

Selected bond lengths (Å) and bond angles (°) of the complex  $\boldsymbol{3}.$ 

Ni(1)-O(8)	2.051(2)	Ni(1)-N(3)	2.052(2)	Ni(1)-O(11)	2.078(2)
Ni(2) = O(2)	1.978(2)	NI(2) - N(1)	1.990(2)	Ni(2) = O(10)	2.065(2)
Ni(2) - N(6)	2.081(2)	Ni(2)–O(6)	2.090(2)	Ni(2) - O(7)	2.112(2)
Ni(3)–N(2)	1.985(2)	Ni(3)-O(3)	2.024(2)	Ni(3)–N(6)	2.074(2)
Ni(3)-N(3)	2.107(2)	Ni(3)-O(11)	2.116(2)	Ni(3)-O(5)	2.153(2)
Ni(1)-Ni(3)	3.231(2)	Ni(2)-Ni(3)	3.623(2)	Ni(1)-Ni(2)	5.586(2)
O(8)#1-Ni(1)-	-O(8)	180.00(1)	O(8)-Ni(1	)-N(3)	88.10(9)
N(3)-Ni(1)-N	(3)#1	180.00(0)	O(8)-Ni(1	)-O(11) <sup>#1</sup>	93.19(8)
O(8)-Ni(1)-O	(11)	86.81(8)	N(3)-Ni(1	)-0(11)	78.51(8)
O(2)-Ni(2)-N	(6)	91.91(9)	N(1)-Ni(2	)-N(6)	95.26(9)
N(1)-Ni(2)-O	(6)	81.82(9)	O(10)-Ni(2	2)-0(6)	93.83(8)
N(6)-Ni(2)-O	(6)	90.45(9)	O(2)-Ni(2	)–O(7)	90.00(9)
N(1)-Ni(2)-O	(7)	87.57(9)	O(10)-Ni(2	2)-0(7)	82.57(8)
N(6)-Ni(2)-O	(7)	176.49(9)	O(6)-Ni(2	)–O(7)	87.90(9)
N(2)-Ni(3)-O	(11)	169.97(9)	O(3)-Ni(3	)-O(11)	91.34(7)
N(6)-Ni(3)-O	(11)	93.06(8)	N(3)-Ni(3	)-0(11)	76.45(8)
N(6)-Ni(3)-O	(5)	85.82(9)	N(3)-Ni(3	)-O(5)	93.74(9)
Ni(1)-N(3)-N	i(3)	101.92(10)	Ni(1)-O(1	1)–Ni(3)	100.78(8)
Ni(3)-N(6)-N	i(2)	121.35(1)			

Symmetry transformations used to generate equivalent atoms: #1 - x, -y + 2, -z.

## Table 5

Specified hydrogen-bond parameters of complex 3.

D−H···A	D-H	$H{\cdot}{\cdot}{\cdot}A$	$D{\cdots}A$	∠DHA
08-H1···03	0.71(3)	1.98(3)	2.660(3)	161(4)
07–H7WB· · · 01 <sup>#1</sup>	0.82(4)	2.06(4)	2.832(3)	156(4)
O7–H7WB· · · O2 <sup>#1</sup>	0.82(4)	2.36(4)	2.984(3)	133(4)
07–H7WA·…010 <sup>#1</sup>	0.82(4)	2.08(4)	2.895(3)	171(4)
06-H204···09	0.76(3)	1.89(3)	2.649(3)	175(4)
05-H203···02	0.70(3)	2.08(3)	2.765(3)	167(4)

#1 -x - 1, -y + 2, -z.

Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and sodium azide in the presence of triethylamine in acetonitrile yielded a brown precipitate. Dropwise addition of methanol to the above heterogeneous mixture dissolved the precipitate. Complex **1** was obtained as dark brown crystals in 80% isolated yield after keeping the filtrate undisturbed for 2 h. However, continuous stirring of the above reaction mixture even after addition of methanol for longer periods (more than 2 h) yielded an uncharacterizable precipitate which was not soluble in excess methanol. The same reaction using Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O instead of Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O yielded a known {Mn<sub>4</sub>Na} complex [17]. Complex **2** was synthesized upon treatment of *in situ* generated  $H_2L^2$ solution with Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O, NaN<sub>3</sub> and triethylamine. X-ray quality dark brown crystals of complex **2** were obtained in 73% isolated yield from the reaction mixture in 2 days. The *in situ* oxidation of  $Mn^{II}$  precursor to  $Mn^{III}$  in both the complexes **1** and **2** took place in the presence of the atmospheric oxygen. This was confirmed by performing the same reactions in inert atmosphere. The same reaction in absence of oxygen did not show any color change (colorless to brown is the indication of transformation of  $Mn^{II}$  to  $Mn^{III}$ ). The above experiment also excludes the possibility of  $Mn^{II}$  oxidation *via* basic condition (Scheme 1).

$$\begin{split} &8Mn(ClO_4)_2 \cdot 6H_2O + 6H_2L^1 + 8NaN_3 + 10NEt_3 + 1.5O_2 + 2MeOH \\ &\rightarrow [Mn_6^{III}Mn_2^{II}Na_2^{I}(N_3)_8(\mu_4\text{-}O)_2(L^1)_6(MeOH)_2] + 10HNEt_3(ClO_4) \\ &\qquad + 6NaClO_4 + 49H_2O \quad (Complex \ \textbf{1}) \end{split}$$

$$\begin{split} & 6 Mn (CH_3 COO)_2 \cdot 4H_2 O + 4H_2 L^2 + 4NaN_3 + 6NEt_3 + 1.5O_2 \\ & \rightarrow [Mn_6^{III} Na_2^I (N_3)_4 (\mu_4 - O)_2 (L^2)_4 (CH_3 COO)_4] + 6HNEt_3 (CH_3 COO) \\ & + 2CH_3 COONa + 25H_2 O \quad (Complex \ \textbf{2}) \end{split}$$

Reaction of  $H_2L^1$ , NiCl<sub>2</sub>·6H<sub>2</sub>O, NaN<sub>3</sub> and NaOMe in a 0.5:1:1:1 M ratios in methanol afforded a dark green solution from which complex 3 was obtained as green crystals in 43% isolated yield after 5 days. During the course of reaction, unusual oxidation of methanol to formic acid was observed and it coordinated to Ni<sup>II</sup>. The absorption peaks at 2059 and 1630 cm<sup>-1</sup> in the IR spectrum of **3** are presumably due to the bridging azide and the formate moieties, respectively. Complex 4 was synthesized by refluxing a mixture of  $H_2L^2$ , NiCl<sub>2</sub>·6H<sub>2</sub>O, NaN<sub>3</sub> and triethylamine in 1:1:2:1 M ratios in methanol for 6 h. The coordinated Schiff base is present in this complex in monoanionic  $[HL^2]^-$  form even in the presence of two equivalents of triethylamine with respect to ligand  $H_2L^2$ . In infrared spectrum, the intense and broad absorption peaks at 2038 cm<sup>-1</sup> for **1**, 2029 cm<sup>-1</sup> for **2**, 2059 cm<sup>-1</sup> for **3** and 2041 cm<sup>-1</sup> for **4** are corresponding to the azido stretching vibrations which are consistent with the presence of various bonding modes of the azido ligands in the complexes.

$$\begin{split} &5NiCl_2 \cdot 6H_2O + 4H_2L^1 + 4NaN_3 + 6NaOCH_3 + 2O_2 \\ &\rightarrow [Ni_5^{II}(N_3)_4(HL^1)_4(HCOO)_2(CH_3OH)_2(H_2O)_2] \cdot 2CH_3OH \\ &\qquad + 10NaCl + 30H_2O \quad (Complex \ \textbf{3}) \end{split}$$

$$\begin{split} &4NiCl_2 \cdot 6H_2O + 6H_2L^2 + 4NaN_3 + 6NEt_3 + 2CH_3OH \\ &\rightarrow [Ni_4^{II}Na_2^{I}(N_3)_4(HL^2)_6] \cdot 2CH_3OH + 2NaCl \end{split}$$

 $+ 6HNEt_3Cl$  (Complex 4)

## 3.2. Description of crystal structure

#### 3.2.1. Complex 1

Complex 1 crystallizes in the centrosymmetric monoclinic space group  $P2_1/n$ , and the partially labeled structure is shown in Fig. 1. The selected crystallographic parameters and bond parameters are compiled in Tables 1 and 2, respectively. Due to the centrosymmetry, the octanuclear manganese cluster is composed of two equivalent [Mn<sub>4</sub>Na] units. Bond valence sum calculation (BVS) (Supporting information) on Mn atoms revealed that each [Mn<sub>4</sub>Na] unit is composed of three MnIII (Mn1, Mn2 and Mn3) and one MnII (Mn4) metal centers. These two [Mn<sub>4</sub>Na] units are linked together through two end-to-end (EE) azides (between Mn1 of one Mn4 unit and Mn4 of other Mn<sub>4</sub> unit) with torsional angle 143.26° (the angle between two planes originated by Mn1-N4-N6 and Mn4-N6-N4) to form novel [Mn<sub>6</sub><sup>III</sup>Mn<sub>2</sub><sup>II</sup>] octanuclear mixed valence manganese cluster. There are several other Mn clusters known in the literature involving Na ions (or other alkali metal ions) with diverse structural variation, which leads to interesting magnetic behavior [9,17,18].



Scheme 1. Observed coordination modes of ligands  $H_2L^1$  and  $H_2L^2$  and other co-ligands observed in the complexes 1-4.

Here, in each [Mn<sub>4</sub>Na] unit, four Mn centers are rearranged in tetrahedral fashion where three Mn<sup>III</sup> form a triangular plane with Mn1-Mn2, Mn1-Mn3 and Mn2-Mn3 distances of 3.632(2), 3.137(8) and 3.107(9) Å, respectively. These Mn<sup>III</sup> are connected to each other via one central  $\mu_4$ -O (O11). Mn1 and Mn2 are linked to Mn3 through one end-on (EO) azide (N10 and N7) each with angle  $\angle$ Mn1–N10–Mn3 = 86.07(10)° and  $\angle$ Mn2–N7–Mn3 = 85.60(8)°, respectively. However, there is no other bridge observed between Mn1 and Mn2. Each Mn<sub>4</sub> unit contains three Schiff-base ligands. The phenolic O of the each ligand coordinates to each of the Mn<sup>III</sup> atoms and provides another coordination site along with methoxy O to chelate sodium ion. There is a weak interaction between Na<sup>+</sup> and  $\mu_4$ -O (O11) with the distance of 2.828(2) Å and each Na<sup>+</sup> ion is considered as seven coordinated. Mn<sup>II</sup> is connected to three Mn<sup>III</sup> (Mn1-Mn4, Mn2-Mn4 and Mn3-Mn4 distances are 3.322(5), 3.377(4) and 3.417(7) Å, respectively) through ethanolic O from three Schiff base ligands to construct tetrahedral Mn<sub>4</sub> unit.

Interestingly, Mn4 is penta-coordinated with distorted trigonalbipyramidal geometry (degree of distortion ( $\tau$ ) = 0.81). The basal plane composed of two ethanolic O (O3 and O6) of two Schiff base ligands and N from (N1) of one non-bridging azide with the average bond length of 2.113 Å. Whereas, the axial positions are occupied by ethanolic O (O9) of another Schiff base and N (N6) of end-to-end bridged azide with average bond length 2.230 Å. The three-dimensional packing pattern of **1** showed that all the molecules arrange in the parallel fashion to each other with weak  $\pi$ - $\pi$  interaction (with a distance of 3.788 Å) (Fig. 2) to form a onedimensional chain.

#### 3.2.2. Complex 2

Complex **2** crystalizes in monoclinic space group  $P2_1/c$ . A labeled plot of the neutral centrosymmetric heterometallic molecular view of complex **2** is shown in Fig. 3. The [Mn<sub>6</sub>Na<sub>2</sub>] consists of two equivalent [Mn<sub>3</sub>Na] units, and simple charge balance calculation shows that all the Mn are in Mn<sup>III</sup> oxidation state. Mn<sup>III</sup> centers are six coordinated with considerable Jahn-Teller distortion as expected for high-spin Mn<sup>III</sup> in octahedral geometry. Each [Mn<sub>3</sub>Na] contains two dianionic Schiff base ligands, two acetate and two types of azide ligands. Three Mn<sup>III</sup> are connected through a  $\mu_3$ -O (O6), which has a weak interaction to Na<sup>+</sup> ion with a distance of 2.605(1) Å, with Mn1-Mn2, Mn1-Mn3 and Mn2-Mn3 distances of 3.212(5), 2.841(4) and 2.911(4) Å, respectively. Mn1 and Mn2 possess very similar coordination environment with four O and two N donors and bridged to each other through one end-on (EO) azide (N3) with an angle  $\angle Mn1-N3-Mn2 = 85.15(5)^{\circ}$  and oxo bridge with an angle  $\angle Mn1-06-Mn2 = 113.31(6)^\circ$ , whereas Mn3 has five O and one N around it. Apart from the  $\mu_3$ -O (O6), Mn3 linked to the Mn1 and Mn2 through ethanolic O of the two Schiff base ligands with angles of  $\angle$ Mn3–O3–Mn1 = 93.76(5)° and  $\angle$ Mn3–O5–Mn2 = 91.35(5)°, respectively. In addition, each of the two Schiff base ligands provides two different coordination environments from one phenolic O and one methoxy O to chelate



**Fig. 1.** (a) Molecular structure of complex **1** as obtained from single crystal X-ray diffraction. Two  $[Mn_4Na]$  clusters are connected by the two end-to-end azides forming  $[Mn_8Na_2]$  cluster. (b) Partial label plot of the complex **1** with polyhedral showing the tetrahedral nature of the each  $Mn_4$  unit. Color code: C, black; N, blue; O, red;  $Mn^{II}$ , purple;  $Mn^{II}$ , pink and Na, yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Na<sup>+</sup> ion. Other sites of Na<sup>+</sup> are coordinated by two acetate ligands, which are acting as a bridge between two [Mn<sub>3</sub>Na] clusters by connecting Na<sup>+</sup> of one unit and Mn3 of the other unit to form [Mn<sub>6</sub>Na<sub>2</sub>] cluster. The solid-state packing arrangement (Fig. 4) shows that each molecule is connected to the neighboring molecule through  $\pi$ - $\pi$  interaction of the aromatic ring (distance 3.66 Å) of the ligands forming a supramolecular chain along *a*-axis (Table 6).

### 3.2.3. Complex 3

Complex **3** crystalizes in triclinic space group  $P\overline{1}$ . The structure of centrosymmetric complex 3 is shown in the Fig. 5. It is composed of pentanuclear Ni<sup>II</sup> with Ni1 at the center. All the Ni<sup>II</sup> are in six coordinated and oriented in octahedral fashion. The Ni1 center is connected to Ni3 (Ni1-Ni3 distance is 3.231(2) Å) via an endon (EO) azide (N3) and one O of formate (O11) with the angle of  $\angle$ Ni1-N3-Ni3 = 101.92(10)° and  $\angle$ Ni1-O11-Ni3 = 100.78(8)°, respectively. Two axial positions of the Ni1 are occupied by two methanol with Ni1-O8 bond distance of 2.051(2) Å. Ni3, Ni2 and their symmetry generated equivalents Ni3', Ni2' contain one monoanionic ligand  $HL^1$  each in tridentate fashion. Ni2 is connected to Ni3 by an end-on azide (N6) and a formate in 1, 2-syn fashion with Ni2-Ni3 distance of 3.623(2) Å. However, the connection between Ni2 and Ni1 takes place by the same formate bridge in 1, 2-anti fashion with a Ni1-Ni2 distance of 5.586(2) Å. A water molecule satisfies the sixth coordination site of Ni(II) with Ni2-O7 bond distance of 2.112(2) Å. The Ni1, Ni3 and Ni3' are arranged in linear fashion whereas Ni2 and Ni2' are situated above and below of the line. The pentanuclear clusters are intermolecularly connected to each other through H-bonding to form a one-dimensional (1D) network (Table 5). H-bonds took place between water, coordinated to Ni2 of one molecule, and the O of formate and methoxy groups of another molecule. The H-bonded picture of complex 3 has been given in Fig. 6.

## 3.2.4. Complex 4

Complex **4** crystalizes in triclinic space group  $P\overline{1}$ . The molecular structure (Fig. 7) consists of two distinct [Ni<sub>2</sub>Na] units, which are

connected to each other via two ethanolic O atoms (O6) of two Schiff base ligands. Each [Ni<sub>2</sub>Na] unit consists of three monoanionic Schiff base and two azide (one EO and one EE) ligands with each Ni<sup>II</sup> center is in hexacoordinated octahedral geometry. Ni1 and Ni2 are connected (with Ni1-Ni2 distance of 3.207(2)Å) to each other via an end-on (EO) azide (N4) and a phenolic oxygen (O5) of Schiff base ligand with angles of  $\angle Ni1-N4-Ni2 = 96.51(9)^{\circ}$  and  $\angle$ Ni1–O5–Ni2 = 103.75(8)°, respectively. The coordination sphere of the Ni2 is composed of four N atoms (N4, N7 from azides and N1, N2 from two Schiff base ligands, respectively) with the bond distances in the range of 2.052(8)-2.192(10) Å. The Ni2 coordination environment composed of four O atoms and two N atoms. The O atoms are contributed from two phenolic O, one ethanolic O and one methoxy group of Schiff base ligands. However, two N are from bridging azide and Schiff base ligand. Solid state packing diagram of **4** showed that each molecule is connected by intermolecular H-bonding through non-coordinated methanol between two clusters to form a one-dimensional network (Fig. 8). The H-bonding parameters for complex **4** are given in Table 7.

#### 3.3. Magnetic behavior

#### 3.3.1. Complex 1

Variable temperature magnetization data of the crystalline samples (**1–4**) (the purity of the samples are confirmed by the PXRD) have been collected in the temperature range of 2–300 K under dc magnetic field of 2000 Oe. The  $1/\chi_m$  versus *T* plot (300–50 K) obeys the Curie–Weiss law with a negative Weiss constant of  $\theta = -26.49$  K (Supporting information, Fig. S2) indicates the antiferromagnetic nature of the cluster. The  $\chi_m$  versus *T* and  $\chi_m T$  versus *T* plots are shown in Fig. 9. The experimentally measured room temperature  $\chi_m T$  value of 21.20 cm<sup>3</sup> K mol<sup>-1</sup> for the [Mn<sub>6</sub><sup>III</sup>Mn<sub>2</sub><sup>II</sup>] cluster is lower than the calculated uncoupled spin only value 26.75 cm<sup>3</sup> K mol<sup>-1</sup>, which indicates the existence of considerable antiferromagnetic interaction even at room temperature. Upon cooling, the  $\chi_m T$  value gradually decreases in the low temperature region. Experimental susceptibility data could not be fitted with



**Fig. 2.** Solid state packing diagram of complex **1** as obtained from single crystal X-ray diffraction. Each cluster is connected by the  $\pi$ - $\pi$  interaction to form 1D chain showed by dotted pink line with the distance of 3.788 Å. Color code: C, black; N, blue; O, red; Mn, purple; and Na, yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

reliable parameters due to having many non-identical magnetic exchange pathways. The low temperature  $\chi_m T$  value (5.69 cm<sup>3</sup> K mol<sup>-1</sup>) indicates  $S \approx 3$  ground state. Each Mn<sub>4</sub> unit has residual spin state S = 7/2 with g = 2. The S = 7/2 of each Mn<sub>4</sub> unit is generated from the ferromagnetic interaction (the bridging angle between Mn<sup>III</sup> ions confirmed the ferromagnetic interaction) of the Mn<sup>III</sup> ions (S = 2) in the Mn<sub>3</sub><sup>III</sup> base resulted S = 6, which is further antiferromagnetically coupled to  $Mn^{II}$  ion (S = 5/2) giving final 7/2 spin state. However, each Mn<sub>4</sub> are interacting with each other through two end-to-end azides, which are generally acting as weak antiferromagnetic couplers. Thus, the weak antiferromagnetic interaction through end-to-end azide between two  $Mn_4$  gives final ground state  $S \approx 3$  at low temperature. The variable temperature magnetizations at different magnetic fields (Fig. 10) in the temperature range of 2-20 K at 5 T correspond to  $S \approx 3$  ground spin state with g = 2. Interestingly, the reduced magnetization data in different fields were not fitted by a single master curve, which is due to the presence of zero-field splitting. The magnetic anisotropy is mainly originated from axially elongated Mn<sup>III</sup> ions due to the Jahn-Teller effect.

## 3.3.2. Complex 2

Temperature dependent magnetic susceptibility measurements were performed under the same conditions as applied for **1**. The  $\chi_m$ versus *T* and  $\chi_m T$  versus *T* plots of complex **2** are shown in Fig. 12. The  $\chi_m T$  value at room temperature is 14.8 cm<sup>3</sup> K mol<sup>-1</sup>, which is considerably lower than the uncoupled spin only magnetic moment 18 cm<sup>3</sup> K mol<sup>-1</sup> of the six Mn<sup>III</sup> ions. The  $1/\chi_m$  versus T plot (300-75 K) obeys the Curie-Weiss law with a negative Weiss constant of  $\theta$  = -76.40 K (Supporting information, Fig. S2) indicated that presence of overall or predominant antiferromagnetic interaction among the Mn<sup>III</sup> ions.  $\chi_m T$  decreases upon cooling and reaches 5.03 cm<sup>3</sup> K mol<sup>-1</sup> at 2 K suggesting an overall antiferromagnetic interaction within the complex. The rapid fall of  $\chi_m T$  below 6 K attributed due to the presence of zero-field splitting at low temperature. In order to simulate the interactions among the Mn<sup>III</sup> ions, the interactions between Mn1···Mn3 and Mn2···Mn3 have been considered identical  $(I_2)$  for simplicity (bridging modes and bridging angles are close for these pathways). To calculate two different exchange parameters  $J_1$  and  $J_2$ , the  $\chi_m T$  versus T data were fitted



**Fig. 3.** Partial labeled molecular structure of complex **2** as obtained from single crystal X-ray diffraction. Two  $[Mn_3Na]$  clusters are connected by the four acetate ligands forming  $[Mn_6Na_2]$  cluster. Color code: C, black; N, blue; O, red;  $Mn^{III}$ , purple and Na, yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

based on the interaction pattern shown in the Fig. 11(b) using the following Hamiltonian,

$$\mathcal{H} = -J_1(S_1 \cdot S_2) - J_2(S_1 \cdot S_3 + S_2 \cdot S_3)$$

$$\chi_{\rm m}^{\rm inter \ dimer} = rac{\chi_{\rm m}}{1 - \left[rac{2zj}{Neta^2 g^2}
ight]\chi_{\rm m}}$$

Where,  $\chi_{\rm m}^{\rm inter \ dimer}$  is the magnetic susceptibility considering intercluster exchange parameter (*zj*), which is defined by the magnetic exchange interaction among adjacent clusters through weak interactions.

The best fit parameters obtained are  $J_1 = -37.49 \text{ cm}^{-1}$ ,  $J_2 = 2.88 \text{ cm}^{-1}$ ,  $zj = 0.10 \text{ cm}^{-1}$ , g = 1.99 and  $R = 5.6 \times 10^{-5}$ , where  $R = \sum [(\chi_m T)_{exp} - (\chi_m T)_{cal}]^2 / \sum (\chi_m T)_{exp}^2$ .

The antiferromagnetic interaction between Mn(1) and Mn(2) is consistent with their bridging interaction and angles with  $\angle$ Mn1–N3(EO azide)–Mn2 = 85.15(5)° and  $\angle$ Mn1–O6(oxo)–Mn2 = 113.31(6)°. It is well known in literature, the coupling constant changes considerably by varying the angle ( $\theta$ ) on an end-on (EO) azide bridging mode [19]. It has been found that for manganese complexes, a  $\angle$ Mn–N–Mn crossover angle from antiferro- to ferromagnetic was predicted in  $\theta \approx 98^\circ$ . However, for oxo-bridge the crossover angle is  $\theta \approx 98^\circ$  in the opposite manner, where angle below 98° allows ferromagnetic and above 98° mediates antiferromagnetic interactions, respectively. So, the expected magnetic

Table 6	
Selected bond lengths (Å) and bond angles	(°) of the complex 4.

$\begin{array}{c c c c c c c c c c c c c c c c c c c $						
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Ni(1)-O(8)	1.965(2)	Ni(1)-N(3)	2.005(3)	Ni(1)-O(5)	2.036(2)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ni(1)-O(9)	2.074(2)	Ni(1)–N(4)	2.108(2)	Ni(1) - O(4)	2.218(2)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Ni(1)-Na(1)	3.359(1)	Ni(2) - O(2)	2.015(2)	Ni(2)-O(5)	2.041(2)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Ni(2)-N(1)	2.058(2)	Ni(2)-N(2)	2.083(3)	Ni(2)-N(7)	2.163(3)
$\begin{array}{ccccc} 0(8)-Ni(1)-N(3) & 91.83(1) & 0(8)-Ni(1)-O(5) & 89.91(8) \\ N(3)-Ni(1)-O(5) & 178.05(1) & 0(8)-Ni(1)-O(9) & 168.56(9) \\ N(3)-Ni(1)-O(9) & 92.96(10) & 0(5)-Ni(1)-O(9) & 85.16(8) \\ 0(8)-Ni(1)-N(4) & 97.21(9) & N(3)-Ni(1)-N(4) & 100.48(1) \\ 0(5)-Ni(1)-N(4) & 80.16(8) & 0(9)-Ni(1)-N(4) & 92.13(9) \\ 0(8)-Ni(1)-O(4) & 85.60(9) & N(3)-Ni(1)-O(4) & 104.71(1) \\ 0(9)-Ni(1)-O(4) & 83.14(8) & N(4)-Ni(1)-O(4) & 154.57(9) \\ 0(2)-Ni(2)-O(5) & 84.77(8) & 0(2)-Ni(2)-N(1) & 90.24(9) \\ 0(5)-Ni(2)-N(1) & 171.43(9) & 0(2)-Ni(2)-N(2) & 97.30(9) \\ 0(5)-Ni(2)-N(1) & 174.66(9) & 0(5)-Ni(2)-N(7) & 90.69(9) \\ N(1)-Ni(2)-N(7) & 93.93(1) & N(2)-Ni(2)-N(7) & 85.37(1) \\ 0(2)-Ni(2)-N(4) & 89.96(9) & 0(5)-Ni(2)-N(4) & 78.14(8) \\ N(1)-Ni(2)-N(4) & 94.93(9) & N(2)-Ni(2)-N(4) & 164.22(1) \\ Ni(1)-N(4)-Ni(2) & 96.51(9) & Ni(1)-O(5)-Ni(2) & 103.75(8) \\ \end{array}$	Ni(2)-N(4)	2.190(2)	Ni(2)-Na(1)	3.532(1)	Ni(1)-Ni(2)	3.207(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	O(8)-Ni(1)-N(	3)	91.83(1)	O(8)-Ni(1	)-0(5)	89.91(8)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(3)-Ni(1)-O(	5)	178.05(1)	O(8)-Ni(1	)-0(9)	168.56(9)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(3)-Ni(1)-O(	9)	92.96(10)	O(5)-Ni(1	)-0(9)	85.16(8)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	O(8)-Ni(1)-N(	4)	97.21(9)	N(3)-Ni(1	)-N(4)	100.48(1)
$\begin{array}{c ccccc} O(8)-Ni(1)-O(4) & 85.60(9) & N(3)-Ni(1)-O(4) & 104.71(1) \\ O(9)-Ni(1)-O(4) & 83.14(8) & N(4)-Ni(1)-O(4) & 154.57(9) \\ O(2)-Ni(2)-O(5) & 84.77(8) & O(2)-Ni(2)-N(1) & 90.24(9) \\ O(5)-Ni(2)-N(1) & 171.43(9) & O(2)-Ni(2)-N(2) & 97.30(9) \\ O(5)-Ni(2)-N(2) & 88.55(9) & N(1)-Ni(2)-N(2) & 99.01(1) \\ O(2)-Ni(2)-N(7) & 174.66(9) & O(5)-Ni(2)-N(7) & 90.69(9) \\ N(1)-Ni(2)-N(7) & 93.93(1) & N(2)-Ni(2)-N(7) & 85.37(1) \\ O(2)-Ni(2)-N(4) & 89.96(9) & O(5)-Ni(2)-N(4) & 78.14(8) \\ N(1)-Ni(2)-N(4) & 94.93(9) & N(2)-Ni(2)-N(4) & 164.22(1) \\ Ni(1)-N(4)-Ni(2) & 96.51(9) & Ni(1)-O(5)-Ni(2) & 103.75(8) \\ \end{array}$	O(5)-Ni(1)-N(	4)	80.16(8)	O(9)-Ni(1	)-N(4)	92.13(9)
$\begin{array}{ccccc} 0(9)-Ni(1)-O(4) & 83.14(8) & N(4)-Ni(1)-O(4) & 154.57(9) \\ 0(2)-Ni(2)-O(5) & 84.77(8) & O(2)-Ni(2)-N(1) & 90.24(9) \\ 0(5)-Ni(2)-N(1) & 171.43(9) & O(2)-Ni(2)-N(2) & 97.30(9) \\ 0(5)-Ni(2)-N(2) & 88.55(9) & N(1)-Ni(2)-N(2) & 99.01(1) \\ 0(2)-Ni(2)-N(7) & 174.66(9) & O(5)-Ni(2)-N(7) & 90.69(9) \\ N(1)-Ni(2)-N(7) & 93.93(1) & N(2)-Ni(2)-N(7) & 85.37(1) \\ O(2)-Ni(2)-N(4) & 89.96(9) & O(5)-Ni(2)-N(4) & 78.14(8) \\ N(1)-Ni(2)-N(4) & 94.93(9) & N(2)-Ni(2)-N(4) & 164.22(1) \\ Ni(1)-N(4)-Ni(2) & 96.51(9) & Ni(1)-O(5)-Ni(2) & 103.75(8) \\ \end{array}$	O(8)-Ni(1)-O(	4)	85.60(9)	N(3)-Ni(1	)-0(4)	104.71(1)
$\begin{array}{c ccccc} O(2)-Ni(2)-O(5) & 84.77(8) & O(2)-Ni(2)-N(1) & 90.24(9) \\ O(5)-Ni(2)-N(1) & 171.43(9) & O(2)-Ni(2)-N(2) & 97.30(9) \\ O(5)-Ni(2)-N(2) & 88.55(9) & N(1)-Ni(2)-N(2) & 99.01(1) \\ O(2)-Ni(2)-N(7) & 174.66(9) & O(5)-Ni(2)-N(7) & 90.69(9) \\ N(1)-Ni(2)-N(7) & 93.93(1) & N(2)-Ni(2)-N(7) & 85.37(1) \\ O(2)-Ni(2)-N(4) & 89.96(9) & O(5)-Ni(2)-N(4) & 78.14(8) \\ N(1)-Ni(2)-N(4) & 94.93(9) & N(2)-Ni(2)-N(4) & 164.22(1) \\ Ni(1)-N(4)-Ni(2) & 96.51(9) & Ni(1)-O(5)-Ni(2) & 103.75(8) \\ \end{array}$	O(9)-Ni(1)-O(	4)	83.14(8)	N(4)-Ni(1	)-0(4)	154.57(9)
$\begin{array}{cccc} 0(5)-Ni(2)-N(1) & 171.43(9) & 0(2)-Ni(2)-N(2) & 97.30(9) \\ 0(5)-Ni(2)-N(2) & 88.55(9) & N(1)-Ni(2)-N(2) & 99.01(1) \\ 0(2)-Ni(2)-N(7) & 174.66(9) & 0(5)-Ni(2)-N(7) & 90.69(9) \\ N(1)-Ni(2)-N(7) & 93.93(1) & N(2)-Ni(2)-N(7) & 85.37(1) \\ 0(2)-Ni(2)-N(4) & 89.96(9) & 0(5)-Ni(2)-N(4) & 78.14(8) \\ N(1)-Ni(2)-N(4) & 94.93(9) & N(2)-Ni(2)-N(4) & 164.22(1) \\ Ni(1)-N(4)-Ni(2) & 96.51(9) & Ni(1)-O(5)-Ni(2) & 103.75(8) \\ \end{array}$	O(2)-Ni(2)-O(	5)	84.77(8)	O(2)-Ni(2	)-N(1)	90.24(9)
$\begin{array}{c ccccc} O(5)-Ni(2)-N(2) & 88.55(9) & N(1)-Ni(2)-N(2) & 99.01(1) \\ O(2)-Ni(2)-N(7) & 174.66(9) & O(5)-Ni(2)-N(7) & 90.69(9) \\ N(1)-Ni(2)-N(7) & 93.93(1) & N(2)-Ni(2)-N(7) & 85.37(1) \\ O(2)-Ni(2)-N(4) & 89.96(9) & O(5)-Ni(2)-N(4) & 78.14(8) \\ N(1)-Ni(2)-N(4) & 94.93(9) & N(2)-Ni(2)-N(4) & 164.22(1) \\ Ni(1)-N(4)-Ni(2) & 96.51(9) & Ni(1)-O(5)-Ni(2) & 103.75(8) \\ \end{array}$	O(5)-Ni(2)-N(	1)	171.43(9)	O(2)-Ni(2	)-N(2)	97.30(9)
$\begin{array}{cccc} O(2)-Ni(2)-N(7) & 174.66(9) & O(5)-Ni(2)-N(7) & 90.69(9) \\ N(1)-Ni(2)-N(7) & 93.93(1) & N(2)-Ni(2)-N(7) & 85.37(1) \\ O(2)-Ni(2)-N(4) & 89.96(9) & O(5)-Ni(2)-N(4) & 78.14(8) \\ N(1)-Ni(2)-N(4) & 94.93(9) & N(2)-Ni(2)-N(4) & 164.22(1) \\ Ni(1)-N(4)-Ni(2) & 96.51(9) & Ni(1)-O(5)-Ni(2) & 103.75(8) \end{array}$	O(5)-Ni(2)-N(	2)	88.55(9)	N(1)-Ni(2	)-N(2)	99.01(1)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	O(2)-Ni(2)-N(	7)	174.66(9)	O(5)-Ni(2	)-N(7)	90.69(9)
$\begin{array}{cccc} O(2)-Ni(2)-N(4) & 89.96(9) & O(5)-Ni(2)-N(4) & 78.14(8) \\ N(1)-Ni(2)-N(4) & 94.93(9) & N(2)-Ni(2)-N(4) & 164.22(1) \\ Ni(1)-N(4)-Ni(2) & 96.51(9) & Ni(1)-O(5)-Ni(2) & 103.75(8) \end{array}$	N(1)-Ni(2)-N(	7)	93.93(1)	N(2)-Ni(2	)-N(7)	85.37(1)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	O(2)-Ni(2)-N(	4)	89.96(9)	O(5)-Ni(2	)-N(4)	78.14(8)
Ni(1)-N(4)-Ni(2) 96.51(9) Ni(1)-O(5)-Ni(2) 103.75(8)	N(1)-Ni(2)-N(	4)	94.93(9)	N(2)-Ni(2	)-N(4)	164.22(1)
	Ni(1)-N(4)-Ni	(2)	96.51(9)	Ni(1)-O(5	)-Ni(2)	103.75(8)



**Fig. 5.** View of the molecular structure of complex **3** with atom numbering. The Ni1, Ni3 and symmetry generated Ni3' are arranged in linear fashion whereas Ni2 and Ni2' are situated above and below that line (left). Color code: C, navy blue; N, blue; O, red and Ni<sup>11</sup>, green. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

coupling between Mn1 and Mn2 is antiferromagnetic, which is also obtained from the fitting of the experimental  $\chi_m T$  versus T plot. The other coupling constant ( $J_2$ ) between Mn1–Mn3 and Mn2–Mn3 is +2.88 cm<sup>-1</sup> as expected from the bridging angles. The Mn1–Mn3 and Mn2–Mn3 are connected to each other through almost identical bridging ligands with two *oxo* bridges (O3 and O6 connecting Mn1–Mn3, O5 and O6 connecting Mn1–Mn3) and one carboxylate bridge. The  $\angle$ Mn1–O3–Mn3 = 93.76°



**Fig. 4.** Solid state packing diagram of the complex **2** as obtained from single crystal X-ray diffraction. Each cluster is forming a supramolecular chain along *a*-axis through  $\pi$ - $\pi$  interaction of the ligands with the distance of 3.66 Å. Color codes: C, black; N, blue; O, red; Mn<sup>III</sup>, purple and Na, orange. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 6.** Solid state packing diagram of complex **3** as obtained from single crystal X-ray diffraction. Each cluster is connected to each other through intermolecular H-bonding to form one dimensional network. Color code: C, navy blue; N, blue; O, red and Ni<sup>II</sup>, green. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 7.** (a) Molecular structure of complex **4** as obtained from single crystal X-ray diffraction. Two[Ni<sub>2</sub>Na] units are connected by two Na ions of each unit to give a [Ni<sub>4</sub>Na<sub>2</sub>] heterometallic cluster. (b) Partial labeled view of complex **4** showing only the coordinating atoms around each metal center. Color codes: C, navy blue; N, blue; O, red and Ni<sup>11</sup>, green and Na, yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and  $\angle$ Mn1–O3–Mn3 = 96.12° fall below the cutoff angle of ~98° for ferromagnetic interaction. The almost similar bridging angle was observed between Mn2 and Mn3 ( $\angle$ Mn2–O5–Mn3 = 91.35° and  $\angle$ Mn2–O6–Mn3 = 98.87°), which overcome the antiferromagnetic interaction through *syn–syn* carboxylate bridge, resulted overall ferromagnetic coupling constant ( $J_2$ ).

The inter-cluster coupling constant (*zj*) is the interaction between two  $Mn_{J}^{II}$  clusters through two  $Na^{I}$  ions and the calculated value from magnetic data fitting is *zj* = 0.10 cm<sup>-1</sup>. By analyzing all the coupling constants, an overall antiferromagnetic behavior of **2** is justified (*J*<sub>1</sub> > *J*<sub>2</sub>).

The ground state of the  $Mn_3^{II}$  building unit was calculated from the variation of spin state energy with the ratio of antiferromagnetic

and ferromagnetic coupling constants  $(|J_1/J_2|)$  (Fig. 13a). It predicts E  $|2,0\rangle$  corresponds to S = 2 (for Mn<sub>3</sub><sup>III</sup> unit) is the most stable state, which was also supported by the reduced magnetization data in the range of 2–20 K (Fig. 13b). The first excited state E  $|1,1\rangle$  is about 3.0 cm<sup>-1</sup> above the ground state, however, second excited state E  $|2,1\rangle$  is very closely placed to the first excited state by an energy of 0.6 cm<sup>-1</sup>. Reduced magnetization versus external field plot and the spin alignments of the Mn<sup>III</sup> in complex **2** are presented in Fig. 13b. The saturation magnetization value of ~8 for [Mn<sub>6</sub>Na<sub>2</sub>] at 5.0 T corresponds to S = 4 ground spin state with g = 2. The plot of reduced magnetization versus H/T implied the magnetic anisotropy, which is generated probably due to the Jahn–Teller distortion in the Mn<sup>III</sup> ions.

# 3.3.3. Complex 3

Experimentally obtained room temperature  $\chi_m T$  value  $(6.15 \text{ cm}^3 \text{ K mol}^{-1})$  is higher than the calculated value  $(5 \text{ cm}^3 -$ K mol<sup>-1</sup>, considering g = 2) for five uncoupled Ni<sup>II</sup> ions either may be due to the room temperature ferromagnetic interaction or  $g \approx 2.2$  when the room temperature  $\chi_m T$  value becomes closer to the calculated value 6.05 cm<sup>3</sup> K mol<sup>-1</sup>. The  $1/\chi_m$  versus T plot (300-50 K) obeys the Curie-Weiss law with positive Weiss constant of  $\theta$  = 6.67 K (Supporting information, Fig. S2). The  $\chi_m T$  value gradually increases upon cooling and reaches a maximum value  $(11.33 \text{ cm}^3 \text{ K mol}^{-1})$  at 19 K before it drops rapidly to 4.55 cm<sup>3</sup> -K mol<sup>-1</sup> at 2 K (Fig. 15a). Overall results are in support of the existence of dominant ferromagnetic nature of complex **3**. The rapid decrease in low temperature may be ascribed due to zero field splitting (ZFS) of the Ni<sup>II</sup> ions or/and intermolecular antiferromagnetic interaction. The magnetic data couldn't well fit even after using the MAGPACK software [20] due to high nuclearity (Ni<sub>5</sub>) complex system and the presence of the several non-identical interactions among the Ni<sup>II</sup> ions and zero field splitting parameter. Thus, the best possible fitting obtained up to 18 K after using the following Hamiltonian and the fitting results are  $J_1 = 3.95 \text{ cm}^{-1}$ and  $J_2 = 3.98 \text{ cm}^{-1}$  with  $R = 2.3 \times 10^{-3}$  (Fig. 15).

$$\mathcal{H} = -J_1(S_1 \cdot S_2 + S_1 \cdot S_3) - J_2(S_2 \cdot S_4 + S_3 \cdot S_5)$$

To determine the spin ground state of the cluster, magnetization data were collected in the ranges of 0.1–5 T and 2–20 K and plotted the reduced magnetization data versus *H*/*T* in Fig. 15b. The saturated magnetization ~10.0 at 5.0 T corresponds to *S* = 5 ground spin state with *g* = 2. The *S* = 5 for complex **3** arises from ferromagnetic coupling of five Ni<sup>II</sup> ions each with *S* = 1.



**Fig. 8.** Solid state packing diagram of complex **4** showing each cluster is connected to each other through H-bonding (dotted pink line). Non-coordinated methanol molecules between two clusters act as connectors to form one-dimensional network. Color codes: C, navy blue; N, blue; O, red and Ni<sup>II</sup>, green and Na, yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 7
Specified hydrogen-bond parameters of complex 4.

D−H···A	D-H	$H{\cdot}{\cdot}{\cdot}A$	$D{\cdots}A$	∠DHA
O(2S)−H(42)···N(6)	0.92(6)	2.12(6)	3.022(4)	169(5)
$O(6)-H(43)\cdots O(2S)^{\#1}$	0.84(5)	1.95(5)	2.778(4)	168(5)
$O(3)-H(14)\cdots N(7)$	0.92(5)	2.00(5)	2.918(4)	173(5)

#1 - x - 1, -y, -z + 1.

## 3.3.4. Complex 4

Experimental  $\chi_m T$  value (6.11 cm<sup>3</sup> K mol<sup>-1</sup>) at 300 K (Fig. 14) is much higher than the spin only value of four uncoupled Ni<sup>II</sup> ions (4 cm<sup>3</sup> K mol<sup>-1</sup>, considering g = 2) which is probably due to the room temperature ferromagnetic interaction. The  $1/\chi_m$  versus Tplot (300–50 K) obeys the Curie–Weiss law with a positive Weiss constant of  $\theta = 3.79$  K (Supporting information, Fig. S2). The  $\chi_m T$ value of **4** gradually increases from 300 K to a maximum at 14 K (6.90 cm<sup>3</sup> K mol<sup>-1</sup>) and then on further cooling, rapidly falls to 4.02 cm<sup>3</sup> K mol<sup>-1</sup> at 2 K (Fig. 16a). The initial increase from 300 K to 14 K indicates a considerable ferromagnetic exchange interaction between the Ni<sup>II</sup> ions, while the decrease at a lower



**Fig. 10.** Plots of reduced magnetization vs. H/T of complex **1** in the temperature range of 2–20 K at different external magnetic fields.



**Fig. 9.** (a) View of the core structure of complex 1 showing several magnetic interactions between the paramagnetic centers through bridging N and O atoms. (b) The  $\chi_m$  vs. *T* and  $\chi_m T$  vs. *T* (inset) plots of complex 1.



**Fig. 11.** (a) The magnetic interaction between two  $Mn_3^{III}$  units through two  $Na^1$  ions is defined by the *zj*, inter cluster magnetic coupling parameter. (b) The schematic representation of the magnetic coupling interactions among the paramagnetic centers in **2**.



**Fig. 12.** Plots of  $\chi_m$  vs. *T* and  $\chi_m T$  vs. *T* (inset) of complex **2.** Red line represents the best-fit curve of  $\chi_m T$  vs. *T* considering three different coupling parameters and using the Hamiltonian described in the text. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

temperature region (below 14 K) can be attributed due to the zero field splitting (ZFS) of the ground state or/and due to intermolecular antiferromagnetic interaction.

The  $Ni_{4}^{II}$  unit in complex **4** can be considered as a combination of two dimeric  $Ni^{II}$  units. The exchange interaction between two  $Ni^{II}$ 

ions is represented by *J*, whereas *zj* represents the interdimer interaction (Fig. 17). The  $\chi_m T$  versus *T* data were fitted using the Ginsberg's model, considering the isotropic spin-coupling Hamiltonian [21–22],

$$\mathcal{H} = -2JS_1 \cdot S_2 - D(S_{1z}^2 + S_{2z}^2) - g_i \mu_B H \cdot S_2$$

Where i = x, y or z. The term D represents the usual zero-field splitting parameter [23].

$$\chi_{\rm M}^{
m inter\ dimer} = rac{\chi_{\rm A}^{
m dimer}}{1 - rac{2zj}{g^2 N_{\rm A} eta^2} \chi_{\rm A}^{
m dimer}}$$

The susceptibility data were fitted using the following equation considering inter-dimer interaction.

The best-fit parameters obtained for 4 using the above expression are J = +3.62 cm<sup>-1</sup>, D = -0.55 cm<sup>-1</sup>, zj = -0.37 cm<sup>-1</sup>, g = 2.33and  $R = 4.7 \times 10^{-5}$  (Fig. 16a). The observed weak ferromagnetic interaction in the molecule can be easily ascribed due to the presence of two different bridging angles ∠Ni1-N3(azido)-Ni3 = 97.8(4)°, which is significantly below the cut off angle  $108^{\circ}$ above which end-on azido bridged Ni(II) complexes show antiferromagnetic interaction [24], whereas  $\angle Ni1-O8(phenoxo)$ -Ni3 =  $103.2(3)^{\circ}$  above the crossover angle ( $\approx 98$ ) (antiferromagnetic region) that's leads to overall weak ferromagnetic behavior. The weak inter-dimer interaction parameter ( $z_i = -0.37 \text{ cm}^{-1}$ ) is consistent with the structural link between two dimeric Ni<sup>II</sup> units. Notably, the low temperature  $\gamma_m T$  value (4 cm<sup>3</sup> K mol<sup>-1</sup>) is close to two effectively isolated  $Ni_2$  units with S = 2 in the ground state, suggesting a very weak antiferromagnetic interaction between the two units. Moreover, the field dependence of magnetization of 4 at different temperatures showed (Fig. 16b) that magnetization increases with increasing dc field and reaches almost saturation of magnetization  $\sim$ 8  $\mu_B$  at 5T and 3 K (Fig. 16b) which is again supported the ground state composed of two halves each with a spin of 2. The reduced magnetization plot (M versus H/T) of **4** at low temperature region (2–20 K) indicated that the magnetization data (Fig. 16b) are not completely superimposed on a single master-curve as expected for isotropic system, which suggests the presence of considerable magnetic anisotropy and/or low lying excited states [25].

## 3.4. Alternating current magnetic susceptibility measurements

The ac susceptibility measurements were performed on microcrystalline samples of **1–4** at 4 Oe ac magnetic field in the temperature range of 3–20 K at different oscillating frequencies



**Fig. 13.** (a) Variation of spin-state energy of the Mn<sub>3</sub><sup>III</sup> unit with |*J*<sub>1</sub>/*J*<sub>2</sub>|. (b) The plot of reduced magnetization vs. *H*/*T* of complex **2** in the temperature range of 2–20 K at different external magnetic fields.



Fig. 14. The possible magnetic interactions between Ni<sup>II</sup> ions with two different coupling constants  $J_1$  and  $J_2$ .



**Fig. 15.** (a) Plots of  $\chi_m$  vs. *T* and  $\chi_m T$  vs. *T* (inset) of complex **3**. The red line represents fitting of the  $\chi_m T$  vs. *T* data up to 18 K. (b) The plot of reduced magnetization vs. *H*/*T* of complex **3** in the range of 2–20 K at different magnetic fields. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

1–1000 Hz. The in-phase  $(\chi_m')$  and out-of-phase  $(\chi_m')$  ac signals of all the complexes are given in the Fig. S3–S6 (Supporting information). The  $\chi_m'$  value increases with lowering the temperature as suggested by the dc magnetic susceptibility measurements and does not show any frequency dependence of these complexes. Although, both complexes **1** and **2** contain Mn<sup>III</sup> ions, which are known to provide anisotropy through Jahn–Teller distortion, however, they do not show any considerable out-of-phase  $(\chi_m'')$ 



**Fig. 16.** (a) Plots of  $\chi_m$  vs. *T* and  $\chi_m T$  vs. *T* (inset) of complex **4**. Red line represents the best-fit curve of  $\chi_m T$  vs. *T* considering a dimeric model with single ion anisotropy parameter. (b) Plots of reduced magnetization vs. *H*/*T* of complex **4** in the range of 2–20 K at different external magnetic fields (0.1–5.0 T); and field vs. magnetization at different temperatures (inset). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 17.** The schematic presentation of the magnetic pathways in complex **4**. The magnetic interaction between two  $Ni_{2}^{II}$  units through two  $Na^{I}$  ions is defined by *zj* (intercluster magnetic coupling parameter).

signal down to 2 K may be because of the anisotropic axes are not parallel to each other resulting in the smaller anisotropy of the molecule. Moreover, the spin states (ground spin state is separated by a small energy gap with respect to first excited spin state) are closely situated and hence spins can relax faster. Generally, the Ni<sup>II</sup> based coordination compounds are less often exhibit slow relaxation of magnetization. The anisotropy in Ni<sup>II</sup> ion originates from second order perturbation, which is not favorable enough for complexes **3** and **4** to freeze the relaxation of magnetization even at low temperatures.

#### 4. Conclusions

Tuning the polynulcear metal-organic clusters has great importance for their diverse magnetic behavior. In this regards we have tried to investigate how the nuclearity of the clusters changes upon changing the position of the functional hydroxyl group of the organic ligands. We were able to isolate four new class of molecular clusters Mn<sub>6</sub><sup>III</sup>Mn<sub>2</sub><sup>II</sup>, Mn<sub>6</sub><sup>III</sup>, Ni<sub>5</sub><sup>II</sup> and Ni<sub>4</sub><sup>II</sup> using hydroxy rich Schiff base ligands  $H_2L^{1-2}$ . The importance of functional hydroxy group position in the structural diversity is discussed thoroughly. The complex **1** is a mixed valent Mn<sub>8</sub> cluster, which is the combination of two dimeric Mn<sub>4</sub> units connected through two end-to-end azide linker. Furthermore, dc magnetic susceptibility measurements exhibit 1 and 2 to be antiferromagnetic, whereas the other two are ferromagnetic in nature. The field dependent magnetization experiments suggested that the ground states of all the complexes are  $S \approx 3$ , S = 4, S = 5and  $S \approx 4$  for  $Mn_6^{III}Mn_2^{II}$  (1),  $Mn_6^{III}$  (2),  $Ni_5^{II}$  (3) and  $Ni_4^{II}$  (4) clusters, respectively. Although all the complexes showed the presence of considerable magnetic anisotropy, none of them show any considerable frequency dependence of magnetization either in in-phase  $(\chi_m)$ or out-of-phase  $(\chi''_m)$  ac signals.

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## Appendix A. Supplementary data

CCDC 912767-912770 contains the supplementary crystallographic data for complexes 1-4, respectively. 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.2014.02.017.

#### References

[1] (a) R. Sessoli, H.-L. Tsai, A.R. Schake, S.Y. Wang, J.B. Vincent, K. Folting, D. Gatteschi, G. Christou, D.N. Hendrickson, J. Am. Chem. Soc. 115 (1993) 1804; (b) R. Sessoli, D. Gatteschi, A. Caneschi, M.A. Novak, Nature 365 (1993) 141; (c) R. Bagai, G. Christou, Chem. Soc. Rev. 38 (2009) 1011;

(d) V. Chandrasekhar, B. Murugesapandian, Acc. Chem. Res. 42 (2009) 1047; (e) G.A. Timco, T.B. Faust, F. Tuna, R.E.P. Winpenny, Chem. Soc. Rev. 40 (2011) 3067;

(f) A. Das, K. Gieb, Y. Krupskaya, S. Demeshko, S. Dechert, R. Klingeler, V. Kataev, B. Büchner, P. Müller, F. Meyer, J. Am. Chem. Soc. 133 (2011) 3433; (g) V. Chandrasekhar, B. Murugesapandian, J.J. Vittal, Inorg. Chem. 48 (2009) 1148;

(h) R.E.P. Winpenny, Dalton Trans. (2002) 1;

(i) P. Jain, V. Ramachandran, R.J. Clark, H.D. Zhou, B.H. Toby, N.S. Dalal, H.W. Kroto, A.K. Cheetham, J. Am. Chem. Soc. 131 (2009) 13625;

(j) P. Jain, N.S. Dalal, B.H. Toby, H.W. Kroto, J. Am. Chem. Soc. 130 (2008) 10450. [2] (a) D. Gatteschi, R. Sessoli, Angew. Chem., Int. Ed. 42 (2003) 268;

(b) C.J. Milios, A. Vinslava, W. Wernsdorfer, S. Moggach, S. Parsons, S.P. Perlepes, G. Christou, E.K. Brechin, J. Am. Chem. Soc. 129 (2007) 2754; (c) A.L. Barra, L. Brunel, D. Gatteschi, L. Pardi, R. Sessoli, Acc. Chem. Res. 31 (1998) 460; (d) C.J. Milios, R. Inglis, A. Vinslava, R. Bagai, W. Wernsdorfer, S. Parsons, S.P.

Perlepes, G. Christou, E.K. Brechin, J. Am. Chem. Soc. 129 (2007) 12505; (e) T.C. Stamatatos, D. Foguet-Albiol, S.C. Lee, C.C. Stoumpos, C.P. Raptopoulou, A. Terzis, W. Wernsdorfer, S.O. Hill, S.P. Perlepes, G. Christou, J. Am. Chem. Soc.

129 (2007) 9484; (f) D. Gatteschi, R. Sessoli, A. Cornia, Chem. Commun. (2000) 725.

[3] (a) M. Mannini, F. Pineider, P. Sainctavit, C. Danieli, E. Otero, C. Sciancalepore, A.M. Talarico, M.-A. Arrio, A. Cornia, D. Gatteschi, R. Sessoli, Nat. Mater. 8 (2009) 194;

(b) M. Mannini, F. Pineider, C. Danieli, F. Totti, L. Sorace, Ph. Sainctavit, M.-A. Arrio, E. Otero, L. Joly, J.C. Cezar, A. Cornia, R. Sessoli, Nature 468 (2010) 417; (c) P.C.E. Stamp, A. Gaita-Arino, J. Mater. Chem. 19 (2009) 1718; (d) M. Dube, P.C.E. Stamp, Chem. Phys. 268 (2001) 257; (e) M.N. Leuenberger, D. Loss, Phys. Rev. B 61 (2000) 12200; (f) M. Cavallini, J. Gomez-Segura, D. Ruiz-Molina, M. Massi, C. Albonetti, C.

- Rovira, J. Veciana, F. Biscarini, Angew. Chem., Int. Ed. 44 (2005) 888.
- (a) S.M.J. Aubin, N.R. Dilley, M.W. Wemple, M.B. Maple, G. Christou, D.N. Hendrickson, J. Am. Chem. Soc. 120 (1998) 839;

(b) S.M.J. Aubin, N.R. Dilley, L. Pardi, J. Krzystek, M.W. Wemple, L.-C. Brunel, M.B. Maple, G. Christou, D.N. Hendrickson, J. Am. Chem. Soc. 120 (1998) 4991; (c) H. Oshio, M. Nihei, S. Koizumi, T. Shiga, H. Nojiri, H. Nakano, N. Shirakawa, M. Akatsu, J. Am. Chem. Soc. 127 (2005) 4568; (d) E.K. Brechin, Chem. Commun. (2005) 5141;

- (e) R. Shaw, I.S. Tidmarsh, R.H. Laye, B. Breeze, M. Helliwell, E.K. Brechin, S.L. Heath, M. Murrie, S. Ochsenbein, H.-U. Güdel, E.J.L. McInnes, Chem. Commun. (2004) 1418;
- (f) D. Foguet-Albiol, T.A. O'Brien, W. Wernsdorfer, B. Moulton, M.J. Zaworotko, K.A. Abboud, G. Christou, Angew. Chem., Int. Ed. 44 (2005) 897;
- (g) M. Murugesu, W. Wernsdorfer, K.A. Abboud, G. Christou, Angew. Chem., Int. Ed. 44 (2005) 892;
- (h) G. AromÍ, S. Parsons, W. Wernsdorfer, E.K. Brechin, E.J.L. McInnes, Chem. Commun. (2005) 5038;
- (i) C. Cadiou, M. Murrie, C. Paulsen, V. Villar, W. Wernsdorfer, R.E.P. Winpenny, Chem. Commun. (2001) 2666;
- (j) S.T. Ochsenbein, M. Murrie, C. Sekine, H. Stoeckli-Evans, E. Rusanov, H.-U. Güdel, Inorg. Chem. 41 (2002) 5133;

(k) A. Bell, G. Aromĺ, S.J. Teat, W. Wernsdorfer, R.E.P. Winpenny, Chem. Commun. (2005) 2808;

- (1) A. Canechi, D. Gatteschi, J. Laugier, P. Rey, R. Sessoli, C. Zanchini, J. Am. Chem. Soc. 110 (1988) 2795;
- (m) D.P. Goldberg, A. Caneschi, S.J. Lippard, J. Am. Chem. Soc. 115 (1993) 9299; (n) D.P. Goldberg, A. Caneschi, C.D. Delfs, R. Sessoli, S.J. Lippard, J. Am. Chem. Soc. 117 (1995) 5789.
- [5] (a) J.R. Friedman, M.P. Sarachik, J. Tejada, R. Ziolo, Phys. Rev. Lett. 76 (1996) 3830:

(b) E.K. Brechin, C. Boskovic, W. Wernsdorfer, J. Yoo, A. Yamaguchi, E.C. Sañudo, T.R. Concolino, A.L. Rheingold, H. Ishimoto, D.N. Hendrickson, G. Christou, J. Am. Chem. Soc. 124 (2002) 9710;

- (c) W. Wernsdorfer, N. Aliaga-Alcalde, D.N. Hendrickson, G. Christou, Nature 416 (2002) 406.
- [6] (a) N.C. Harden, M.A. Bolcar, W. Wernsdorfer, K.A. Abboud, W.E. Streib, G. Christou, Inorg. Chem. 42 (2003) 7067;

(b) C. Boskovic, E.K. Brechin, W.E. Streib, K. Folting, J.C. Bollinger, D.N. Hendrickson, G. Christou, J. Am. Chem. Soc. 124 (2002) 3725; (c) L. Lecren, O. Roubeau, C. Coulon, Y.-G. Li, X.F.L. Goff, W. Wernsdorfer, H.

Miyasaka, R. Clérac, J. Am. Chem. Soc. 127 (2005) 17353;

(d) L. Lecren, W. Wernsdorfer, Y.-G. Li, O. Roubeau, H. Miyasaka, R. Clérac, J. Am. Chem. Soc. 127 (2005) 11311; (e) C. Boskovic, W. Wernsdorfer, K. Folting, J.C. Huffman, D.N. Hendrickson, G.

Christou, Inorg. Chem. 41 (2002) 5107;

- (f) H. Miyasaka, K. Nakata, L. Lecren, C. Coulon, Y. Nakazawa, T. Fujisaki, K. Sugiura, M. Yamashita, R. Clérac, J. Am. Chem. Soc. 128 (2006) 3770;
- (g) C. Dendrinou-Samara, M. Alexiou, C.M. Zaleski, J.W. Kampf, M.L. Kirk, D.P. Kessissoglou, V.L. Pecoraro, Angew. Chem., Int. Ed. 42 (2003) 3763;
- (h) C.M. Zaleski, E.C. Depperman, C. Dendrinou-Samara, M. Alexiou, J.W. Kampf, D.P. Kessissoglou, M.L. Kirk, V.L. Pecoraro, J. Am. Chem. Soc. 127 (2005) 12862:

(i) K. Hegetschweiler, D. Gatteschi, A. Cornia, L. Hausherr-Primo, V. Gramlich, Inorg. Chem. 33 (1996) 4414;

(i) C. Boskovic, H.-U. Gudel, G. Labat, A. Neels, W. Wernsdorfer, B. Moubaraki, K.S. Murray, Inorg. Chem. 44 (2005) 3181;

(k) A. Cornia, A.C. Fabretti, P. Garrisi, C. Mortalo, D. Bonacchi, D. Gatteschi, R. Sessoli, L. Sorace, W. Wernsdorfer, A.L. Barra, Angew, Chem., Int. Ed. 43 (2004) 1136:

(1) A.M. Ako, I.J. Hewitt, V. Mereacre, R. Clérac, W. Wernsdorfer, C.E. Anson, A.K. Powell, Angew, Chem., Int. Ed. 45 (2006) 4926:

- (m) AJ. Tasiopoulos, S.P. Perlepes, Dalton Trans. (2008) 5537; (n) K.C. Mondal, M.G.B. Drew, P.S. Mukherjee, Inorg. Chem. 46 (2007) 5625; (o) K.C. Mondal, Y. Song, P.S. Mukherjee, Inorg. Chem. 46 (2007) 9736.
- [7] (a) S. Mukherjee, B. Gole, R. Chakrabarty, P.S. Mukherjee, Inorg. Chem. 48 (2009) 11325;
  - (b) S. Mukherjee, P.S. Mukherjee, Inorg. Chem. 49 (2010) 10658;
  - (c) M. Murugesu, S. Takahashi, A. Wilson, K.A. Abboud, W. Wernsdorfer, S. Hill,
  - G. Christou, Inorg. Chem. 47 (2008) 9459; (d) T.C. Stamatatos, K.M. Poole, K.A. Abboud, W. Wernsdorfer, T.A. O'Brien, G.
  - Christou, Inorg. Chem. 47 (2008) 5006; (e) T.C. Stamatatos, D. Foguet-Albiol, K.M. Poole, W. Wernsdorfer, K.A. Abboud,
  - T.A. O'Brien, G. Christou, Inorg. Chem. 48 (2009) 9831;
  - (f) T.C. Stamatatos, K.M. Poole, D. Foguet-Albiol, K.A. Abboud, T.A. O'Brien, G. Christou, Inorg. Chem. 47 (2008) 6593;

(g) T.C. Stamatatos, A. Escuer, K.A. Abboud, C.P. Raptopoulou, S.P. Perlepes, G. Christou, Inorg. Chem. 47 (2008) 11825:

(h) O. Waldmann, A.M. Ako, H.U. Güdel, A.K. Powell, Inorg. Chem. 47 (2008) 3486:

(i) G. Abbas, Y. Lan, V. Mereacre, W. Wernsdorfer, R. Clérac, G. Buth, M.T.

Sougrati, F. Grandjean, G.J. Long, C.E. Anson, A.K. Powell, Inorg. Chem. 48 (2009) 9345

(j) C. Papatriantafyllopoulou, T.C. Stamatatos, W. Wernsdorfer, S.J. Teat, A.J. Tasiopoulos, A. Escuer, S.P. Perlepes, Inorg. Chem. 49 (2010) 10486;

(k) S. Mukherjee, P.S. Mukherjee, Acc. Chem. Res. 46 (2013) 2556;

(1) P.S. Mukherjee, S. Dalai, T. Mallah, N. Ray Chaudhuri, Inorg. Chem. Commun. 5 (2002) 472. [8] (a) D. Liu, Q. Zhou, Y. Chen, F. Yang, Y. Yu, Z. Shi, S. Feng, Dalton Trans. 39

(2010) 5504;

(b) S. Nayak, H.P. Nayek, S. Dehnen, A.K. Powell, J. Reedijk, Dalton Trans. 40 (2011) 2699;

(c) P.P. Yang, X.Y. Song, R.N. Liu, L.C. Li, D.Z. Liao, Dalton Trans. 39 (2010) 6285; (d) C. Boskovic, R. Bircher, P.L.W. Tregenna-Piggott, H.-U. Güdel, C. Paulsen, W. Wernsdorfer, A.L. Barra, E. Khatsko, A. Neels, H. Stoeckli-Evans, J. Am. Chem. Soc. 125 (2003) 14046;

(e) H. Asada, K. Hayashi, S. Negoro, M. Fujiwara, T. Matsushita, Inorg. Chem. Commun. 6 (2003) 193;

(f) R. Bagai, K.A. Abboud, G. Christou, Dalton Trans. (2006) 3306;

(g) J.A. Hoshiko, G. Wang, J.W. Ziller, G.T. Yee, A.F. Heyduk, Dalton Trans. (2008) 5712;

(h) H.C. Yao, M.M. Li, L.M. Zheng, Z.J. Li, J. Coord. Chem. 61 (2008) 2814; (i) G. Wu, I.J. Hewitt, S. Mameri, Y. Lan, R. Clérac, C.E. Anson, S. Qiu, A.K. Powell, Inorg. Chem. 46 (2007) 7229;

(j) Y.Z. Zheng, Y. Lan, C.E. Anson, A.K. Powell, Inorg. Chem. 47 (2008) 10813; (k) D.I. Alexandropoulos, T.N. Nguyen, L. Cunha-Silva, T.F. Zafiropoulos, A. Escuer, G. Christou, T.C. Stamatatos, Inorg. Chem. 52 (2013) 1179.

- [9] S. Mukherjee, Y.P. Patil, P.S. Mukherjee, Inorg. Chem. 51 (2012) 4888.
- [10] (a) L. Yan, S. Ding, Y. Ji, Z. Liu, C. Liu, J. Coord. Chem. 64 (2011) 3531;
- (b) Y.-F. Ji, R. Wang, S. Ding, C.-F. Du, Z.-L. Liu, Inorg. Chem. Commun. 16 (2012) 47:

(c) Z. Lu, T. Fan, W. Guo, J. Lu, C. Fan, Inorg. Chim. Acta 400 (2013) 191;

(d) P. Bhowmik, N. Aliaga-Alcalde, V. Gómezc, M. Corbellac, S. Chattopadhyay, Polyhedron 49 (2013) 269;

(e) W.-H. Chen, H.-H. Wei, G.-H. Lee, Y. Wang, Polyhedron 20 (2001) 515.

- [11] (a) H. Bluhm, M. Hävecker, A. Knop-Gericke, E. Kleimenov, R. Schlo1gl, D. Teschner, V.I. Bukhtiyarov, D.F. Ogletree, M. Salmeron, J. Phys. Chem. B 108 (2004) 14340;
  - (b) L.J. Burcham, I.E. Wachs, Catalysis Today 49 (1999) 467.
- [12] (a) R.L. Dutta, A. Syamal, Elements of Magnetochemistry, second ed., East West Press, Manhattan Beach, CA, 1993;
- (b) O. Kahn, Molecular Magnetism, VCH Publishers, New York, 1993. [13] SMART/SAINT. Bruker AXS Inc., Madison, WI, 2004.
- [14] G.M. Sheldrick, SHEIX-97, University of Göttingen, Göttingen, Germany, 1998.
  [15] (a) L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837;
- (b) L.J. Farrugia, WinGX, Version 1.65.04, Department of Chemistry, University of Glasgow, Glasgow, Scotland, 2003.
- [16] G.M. Sheldrick, sadabs, University of Göttingen, Göttingen, Germany, 1999.
- [17] I.J. Hewitt, J.-K. Tang, N.T. Madhu, R. Clérac, G. Buth, C.E. Anson, A.K. Powell, Chem. Commun. (2006) 2650.
- [18] (a) M.U. Anwar, L.N. Dawe, M.S. Alam, L.K. Thompson, Inorg. Chem. 51 (2012) 11241;

(b) A. Saha, K.A. Abboud, G. Christou, Inorg. Chem. 50 (2011) 12774.

- [19] E. Ruiz, J. Cano, S. Alvarez, P. Alemany, J. Am. Chem. Soc. 120 (1998) 11122.
- [20] (a) J.J. Borras-Almenar, E. Coronado, S.M. Ostrovsky, A.V. Palii, B.S. Tsukerblat, Chem. Phys. 240 (1999) 149; (b) J.J. Borras-Almenar, J.M. Clemente-Juan, E. Coronado, B.S. Tsukerblat, J.
- Comput. Chem. 22 (2001) 985. [21] A.P. Ginsberg, R.W. Brookes, R.L. Martin, R.C. Sherwood, Inorg. Chem. 11 (1972) 2884.
- [22] K.O. Joung, C.J. O'Connor, E. Sinn, R.L. Carlin, Inorg. Chem. 18 (1979) 804.
- [23] D.E. Freedman, W.H. Harman, T.D. Harris, G.J. Long, C.J. Chang, J.R. Long, J. Am. Chem. Soc. 132 (2010) 1224.
- [24] J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortes, L. Lezama, T. Roji, Coord. Chem. Rev. 193 (1999) 1027.
- [25] C. Benelli, D. Gatteschi, Chem. Rev. 102 (2002) 2369.