



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, $[\text{Mn}_6^{\text{III}}\text{Mn}_2^{\text{II}}\text{Na}_2(\text{N}_3)_8(\mu_4\text{-O})_2(\text{L}^1)_6(\text{CH}_3\text{OH})_2]$ (**1**), $[\text{Mn}_6^{\text{III}}\text{Na}_2(\text{N}_3)_4(\mu_4\text{-O})_2(\text{L}^2)_4(\text{CH}_3\text{COO})_4]$ (**2**), $[\text{Ni}_5^{\text{II}}(\text{N}_3)_4(\text{HL}^1)_4(\text{HCOO})_2(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_2]\cdot 2\text{CH}_3\text{OH}$ (**3**) and $[\text{Ni}_4^{\text{II}}\text{Na}_2(\text{N}_3)_4(\text{HL}^2)_6]\cdot 2\text{CH}_3\text{OH}$ (**4**) have been synthesized using tetradentate ligands H_2L^{1-2} along with azide as a co-ligand. H_2L^{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 $\text{Mn}(\text{II})$ and $\text{Na}(\text{I})$ in unusual trigonal prismatic geometry [9]. Herein, we report the use of two different dihydroxy Schiff bases H_2L^1 [2-((2-hydroxypropyl)imino)methyl]-6-methoxyphenol] and H_2L^2 [2-((3-hydroxypropyl)imino)methyl]-6-methoxyphenol] for the synthesis of four new manganese and nickel clusters of different nuclearity $[\text{Mn}_6^{\text{III}}\text{Mn}_2^{\text{II}}\text{Na}_2(\text{N}_3)_8(\mu_4\text{-O})_2(\text{L}^1)_6(\text{CH}_3\text{OH})_2]$ (**1**), $[\text{Mn}_6^{\text{III}}\text{Na}_2(\text{N}_3)_4(\mu_4\text{-O})_2(\text{L}^2)_4(\text{CH}_3\text{COO})_4]$ (**2**), $[\text{Ni}_5^{\text{II}}(\text{N}_3)_4(\text{HL}^1)_4(\text{HCOO})_2(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_2]\cdot 2\text{CH}_3\text{OH}$ (**3**) and $[\text{Ni}_4^{\text{II}}\text{Na}_2(\text{N}_3)_4(\text{HL}^2)_6]\cdot 2\text{CH}_3\text{OH}$ (**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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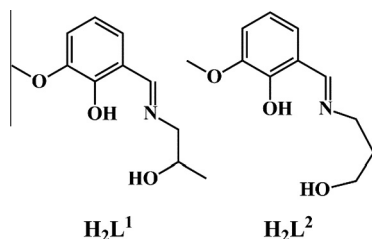


Chart 1. Schiff bases H_2L^1 and H_2L^2 used to prepare polynuclear clusters 1–4.

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^{II} 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 , sodium-methoxide, 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 $[Mn^{III}Mn^{II}Na_2(N_3)_8(\mu_4-O)_2(L^1)_6(CH_3OH)_2]$ (**1**)

2-Hydroxy-3-methoxybenzaldehyde (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 solution. $Mn(ClO_4)_2 \cdot 6H_2O$ (1 mmol, 361.9 mg) was added to that solution and stirred for 15 min to yield a light brown solution. NaN_3 (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**, $C_{68}H_{86}N_{30}O_{22}Mn_8Na_2$: C, 37.79; H, 4.01; N, 19.44. Found: C, 37.5474; H, 4.12; N, 19.64%. IR (ν cm^{-1}): 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 $[Mn^{III}Na_2(N_3)_4(\mu_4-O)_2(L^2)_4(CH_3COO)_4]$ (**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, $Mn(CH_3COO)_2 \cdot 4H_2O$ (1 mmol, 245 mg) was added to that solution, which turned light brown solution immediately. NaN_3 (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**, $C_{52}H_{64}N_{16}O_{22}Mn_6Na_2$: C, 38.06; H, 3.93; N, 13.66. Found: C, 38.25; H, 4.23; N, 13.53%. IR (ν cm^{-1}): 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 $[Ni^{II}(N_3)_4(HL^1)_4(HCOO)_2(CH_3OH)_2(H_2O)_2] \cdot 2CH_3OH$ (**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. $NiCl_2 \cdot 6H_2O$ (1 mmol, 237.7 mg), NaN_3 (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**, $C_{49}H_{74}N_{16}O_{21}Ni_5$: C, 38.78; H, 5.08; N, 18.95. Found: C, 38.74; H, 5.04; N, 19.32%. IR (ν cm^{-1}): 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 $[Ni^{II}Na_2(N_3)_4(HL^2)_6] \cdot 2CH_3OH$ (**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 $NiCl_2 \cdot 6H_2O$ (0.5 mmol, 118.8 mg) and NaN_3 (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**, $C_{68}H_{92}N_{18}O_{20}Ni_4Na_2$: C, 46.34; H, 5.26; N, 14.31. Found: C, 46.57; H, 5.64; N, 14.25%. IR (ν cm^{-1}): 3354 (w), 2937 (w), 2894 (w), 2041 (s), 1617 (s), 1545 (w),

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