Ligand induced diversification from tetranuclear to mononuclear compounds: Syntheses, structures and magnetic properties

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ABSTRACT

Using the solvothermal method, we present the comparative preparation of $[Ni(L^1)Cl(CH_3CN)]_4$ (**1**), $[Ni(L^2)Cl(C_2H_5OH)]_4$ (**2**) and $[Ni(HL^3)_2(CH_3COO)_2]\cdot 2DMF$ (**3**), where HL^1 is (1*H*-benzimidazol-2-yl)-methanol, HL^2 is (6-methyl-1*H*-benzoimidazol-2-yl)-methanol and HL^3 is 1-(1*H*-benzoimidazol-2-yl)-ethanol. All the compounds were characterized by elemental analysis, IR and X-ray single-crystal diffraction. Compounds **1** and **2** are tetranuclear clusters with a cubane topology, in which the metal ions and the oxygen atoms from the *L* ligands occupy alternate vertices of the cubane. However, compound **3** is a mononuclear nickel complex with the triclinic crystal system, $P\bar{1}$ space group, different from that of compounds **1** and **2**. These results show that the position and space steric hindrance of the substituents groups are essential in determining the final structures of the assemblies. The magnetic properties of **1** and **2** in the 2–300 K temperature range have also been discussed. The $\{Ni_4O_4\}$ core displays dominant ferromagnetic interactions.

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1. Introduction

In recent decades, much attention has been given to the synthesis of polymetallic clusters since the discovery of "single-molecule magnets" (SMMs) [1–4]. The search for key ligands to suit the respective needs is one of the most important processes to advance this research. An effective and facile approach for the synthesis of such complexes is still the appropriate choice of organic ligands as bridge or terminal groups, with metal ions or metal clusters as nodes. For instance, previous studies have shown that the (1*H*-benzimidazol-2-yl)-methanol (HL^1) ligand can form dinuclear structures, cubane-based structures or wheel-like heptanuclear clusters [5,6]. HL^1 possesses three coordination donor atoms, consisting of one oxygen atom of the methanol group and two nitrogen atoms of the benzimidazol group (Scheme 1). On the other hand, relatively small modifications in the bridging ligand may lead to significant changes in the overall structures of the assemblies [2b,5a,7]. Thus, two derivatives of HL^1, (6-methyl-1*H*-benzoimidazol-2-yl)-methanol (HL^2) and 1-(1*H*-benzoimidazol-2-yl)-ethanol (HL^3), were

considered to investigate such metal-assembly phenomenons and also to enrich the coordination chemistry of (1*H*-benzimidazol-2-yl)-methanol-like ligands.

In this work, we have investigated the coordination chemistry of Ni(II) complexes involving the above-mentioned (1*H*-benzimidazol-2-yl)-methanol-like ligands, HL^1–HL^3 (Scheme 2). Although the coordination modes of HL^2 and HL^3 are not well defined, the two ligands possess the same coordination atoms as HL^1. Thus, these two derivatives of HL^1, i.e. HL^2 and HL^3, may coordinate *via* an analogous mode as observed for HL^1, and lead to the formation of different clusters. Therefore, we can study the influence of the position and steric hindrances on the overall structures of the complexes formed.
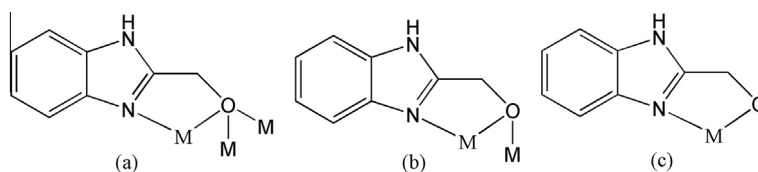
2. Experimental

### 2.1. Materials and instrumentation

All chemicals were commercially available and used as received without further purification. Elemental analyses (CHN) were performed using an Elemental Vario-EL CHN elemental analyzer. FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Bio-Rad FTS-7 spectrophotometer. The crystal

Scheme 1. Coordination modes of the ligands.
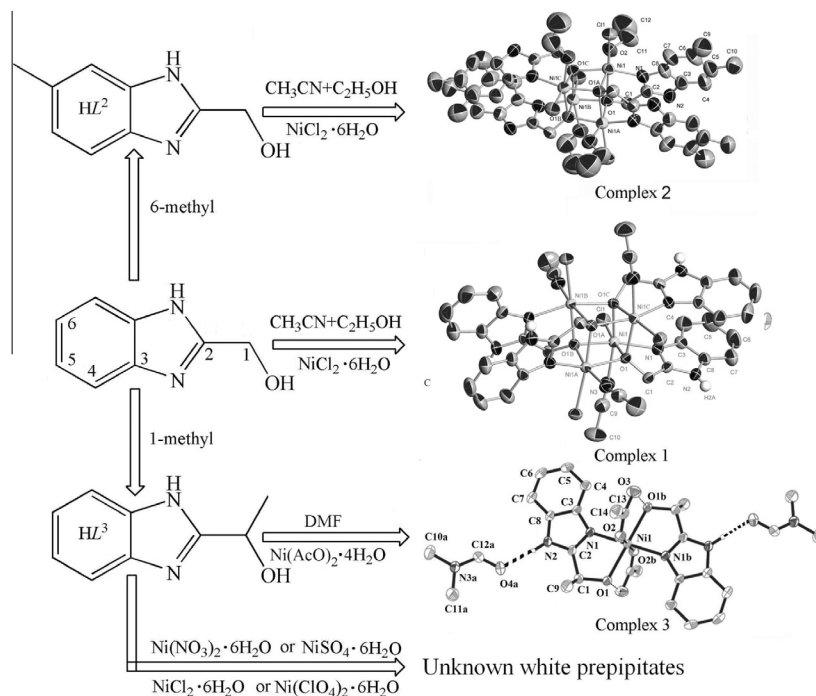
Scheme 2. Substitutional group bulk induced diversification from tetranuclear to mononuclear complexes in the (1H-benzimidazol)-methanol system.

structures were determined by single-crystal X-ray diffraction, using the SHELXL crystallographic software for molecular structures. Magnetization measurements were carried out with a Quantum Design MPMS-XL7 SQUID to 5 T for **1** and **2**.

2.2. Synthesis

Preparation of HL^1–HL^3: the ligand (1H-benzimidazol-2-yl)-methanol (HL^1) and its derivatives (HL^2 and HL^3) were prepared according to the literature procedures [5,6].

2.2.1. $[Ni(L^1)Cl(CH_3CN)]_4$ (**1**)

A mixture of $NiCl_2 \cdot 6H_2O$ (0.238 g, 1 mmol), HL^1 (0.074 g, 0.5 mmol), acetonitrile (4 mL) and ethanol (4 mL), with a pH adjusted to 7.5 by addition of triethylamine, was poured into a Teflon-lined autoclave (15 mL) and then heated at 160 °C for 3 days. Green crystals of **1** were collected by filtration, washed with ethanol and dried in air. Phase pure crystals of **1** were obtained by manual separation (yield: 89.5 mg, *ca.* 63.4% based on the HL^1 ligand). *Anal.* Calc. for **1**: $C_{40}H_{40}Cl_4N_{12}Ni_4O_4$ (M_r = 1129.40), Calc.: C, 42.54; H, 3.57; N, 14.88. Found: C, 42.51; H, 3.59; N, 14.91%. IR data for **1** (KBr, cm^{-1}): 3425 s, 1274 m, 1458 s, 1069 s, 1280 m, 600 m, 467 m.

2.2.2. $[Ni(L^2)Cl(C_2H_5OH)]_4$ (**2**)

Complex **2** can be prepared in a similar way to **1**, except that HL^1 was replaced by HL^2. Green crystals of **2** were collected by filtration, washed with ethanol and dried in air. Phase pure crystals

of **2** were obtained by manual separation (yield: 78.4 mg, *ca.* 52.2% based on the HL^2 ligand). *Anal.* Calc. for **2**: $C_{44}H_{60}Cl_4N_8Ni_4O_8$ (M_r = 1205.64), Calc.: C, 43.83; H, 5.02; N, 9.29. Found: C, 43.95; H, 4.72; N, 9.31%. IR data for **2** (KBr, cm^{-1}) 3251 s, 1641 w, 1463 s, 1393 s, 1292 s, 1059 s, 818 m, 643 m, 437m.

2.2.3. $[Ni(HL^3)_2(CH_3COO)_2] \cdot 2DMF$ (**3**)

Complex **3** can be prepared in a similar way to **1**, except that HL^1 was replaced by HL^3, $NiCl_2 \cdot 6H_2O$ by $Ni(AcO)_2 \cdot 4H_2O$, and the mixed solvent of acetonitrile and ethanol by DMF. Green crystals of **3** were collected by filtration, washed with ethanol and dried in air. Phase pure crystals of **3** were obtained by manual separation (yield: 140.5 mg, *ca.* 86.8% based on the HL^3 ligand). *Anal.* Calc. for **3**: $C_{28}H_{40}NiN_6O_8$ (M_r = 647.37), Calc.: C, 51.95; H, 6.23; N, 12.98; Found: C, 51.92; H, 6.24; N, 12.95%.

2.3. Crystal structure determination

The diffraction data were collected on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and using the ω-θ scan mode in the ranges $1.72° \leqslant \theta \leqslant 25.09°$ (**1**), $1.64° \leqslant \theta \leqslant 25.99°$ (**2**) and $2.27° \leqslant \theta \leqslant 25.10°$ (**3**). Raw frame data were integrated with the SAINT program. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares on F^2 using SHELXS-97 [8]. An empirical absorption correction was applied with the program SADABS [8]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were positioned geometrically and refined as