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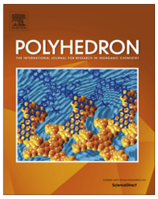

Homo and heterometallic rhomb-like Ni_4 and Mn_2Ni_2 complexes

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ABSTRACT

Two new polynuclear complexes with hydroxyl-rich Schiff base ligand 3-[(2-Hydroxy-benzylidene)-amino]-propane-1,2-diol (H_3L), namely $[Ni^{II}_2(HL)(H_2L)(SCN)]_2 \cdot DMF$ (**1**) and $[Mn^{III}_2Ni^{II}_2(HL)_2(L)_2]$ (**2**) have been synthesized and characterized by single crystal X-ray diffraction, elemental analyses, FTIR, UV–Vis spectroscopy and variable temperature magnetic susceptibility measurements. The X-ray refinements reveal that both compounds present defective rhomb-like dicubane central cores (Ni_4 in **1** and Mn_2Ni_2 in **2**). Magnetic susceptibility measurements indicate the presence of overall antiferromagnetic exchange interactions in **1** along the side connected by a N and O atoms ($J_1 = -43.6\ cm^{-1}$) and along the short diagonal of the rhomb ($J_3 = -3.9\ cm^{-1}$) and a weak ferromagnetic coupling ($J_2 = +5.8\ cm^{-1}$) along the side of the rhomb connected by a double O-bridge. In **2** the three exchange interactions are negative ($J_1 = J_2 = -0.3\ cm^{-1}$ and $J_3 = -0.7\ cm^{-1}$). A magneto-structural correlation with the ratio between the Ni–O–Mn bond angle and the Mn–O bond length is also discussed for double O-bridged Mn–Ni pairs.

1. Introduction

The design and synthesis of polynuclear transition-metal clusters has been an active area of study for the last couple of decades [1,2]. The presence of polynuclear transition-metal clusters in the active sites of many enzymes has stimulated scientists to explore this fascinating area of research [3]. Manganese and nickel are both very important metal ions present in biological systems [4,5]. Apart from the biological importance, a growing interest in polynuclear transition-metal clusters originates from the prospects of application in many other directions [6,7]. One of the most appealing ones is related to the presence of interesting magnetic properties in polynuclear transition-metal clusters as in molecule-based magnets, whose possible applications in different areas as data storage and magnetic refrigeration have encouraged an extensive research interest in new transition-metal clusters [1,8–13]. Thus, numerous research groups around the world are actively engaged in the development of new synthetic procedures for the preparation of high nuclearity transition metals clusters. Among the different strategies employed to reach this aim, the use of polyalkoxide ligands [14–17] has become one of the most efficient strategy to design and synthesize polynuclear transition-metal clusters. Although there is a large number of homometallic cubane-like Mn and Ni clusters [18–20] and there are also many coordination compounds containing heterometallic Mn-Ni cores [21–26], the number of mixed metal Mn–Ni rhomb-like cubane clusters is very limited [27]. Such clusters show interesting magnetic properties, including single-molecule magnets [24]. Inspired by these studies, research efforts have been made to synthesize homo- and heterometallic mixed-metal clusters, using Mn and Ni as paramagnetic units. In this context, we have chosen the hydroxyl-rich Schiff base ligand 3-[(2-Hydroxy-benzylidene)-amino]-propane-1,2-diol (H_3L) [28–30] that presents four potential donor sites (one imine nitrogen, one phenoxido oxygen and two alkoxido oxygen atoms) (Scheme 1). Gorden and co-workers utilized this ligand for the first time and reported the syntheses and structural characterization of four dinuclear uranyl complexes [28]. Recently the ligand has been explored to construct polynuclear complexes with various core structures, such as Cu_4, Ni_4, $Mn^{III}_3Mn^{II}Na$, $Gd_{12}Mo_4$ etc., [29–38]. Herein we describe the syntheses and characterization of two novel defective rhomb-like dicubane clusters of the type Ni_4 and Mn_2Ni_2:$[Ni^{II}_2(HL)(H_2L)(SCN)]_2$.DMF (**1**) and $[Mn^{III}_2Ni^{II}_2(HL)_2(L)_2]$ (**2**), prepared with the ligand H_3L.

2. Experimental

2.1. Physical measurements

Elemental (C, H and N) analyses were performed on a Perkin–Elmer 2400 II analyzer. IR spectra were recorded in the region 400–4000 $cm^{-1}$with a Bruker Optics Alpha-T spectrophotometer as KBr

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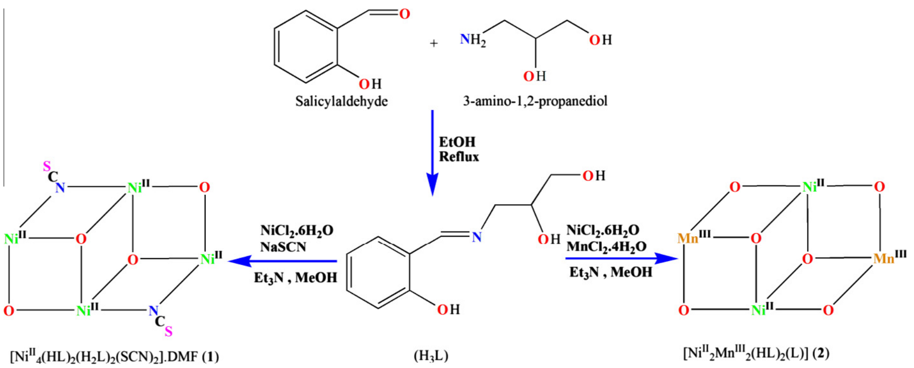

Scheme 1. Synthetic route of formation **1** and **2**.

pellets. NMR spectra were recorded with a Bruker AV 300 MHz Supercon NMR system Dual Probe. Magnetic susceptibility measurements were carried out in the temperature range 2-300 K with an applied magnetic field of 0.1 T on polycrystalline samples of compounds **1** and **2** (with masses of 29.97 and 42.30 mg, respectively) with a Quantum Design MPMS-XL-5 SQUID susceptometer. The susceptibility data were corrected for the sample holders previously measured using the same conditions and for the diamagnetic contributions of the salt as deduced by using Pascals constant tables ($\chi_{\text{dia}} = 662 \times 10^{-6}$ and 500×10^{-6} emu mol^{-1} for **1** and **2**, respectively) [39].

Phase purity of polycrystalline samples **1** and **2** was established by XRPD. Polycrystalline samples were lightly ground in an agate mortar and pestle and filled into 0.7 mm borosilicate capillaries. Data were collected at room temperature in the 2θ range 5–40° on a Empyrean PANalytical powder diffractometer, using Cu Kα radiation (λ = 1.54177 Å). In both cases, the powder diffraction pattern of the bulk sample was consistent with the pattern calculated from single-crystal data (see Figs. S1 and S2).

2.2. X-ray crystallographic data collection and refinement of the structures

The crystallographic data of the compounds are summarized in Table 1. Diffraction data were collected on a Nonius APEX-II diffractometer with CCD-area detector at 150 K using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Crystal structure was determined by direct methods and subsequent Fourier and difference Fourier syntheses, followed by full-matrix least-squares refinements on F^2 using SHELXL-97 [40]. Absorption correction was done by SADABS method. Hydrogen atoms were located and refined freely. The hydrogen atoms were refined isotropically, while the non hydrogen atoms were refined anisotropically. The contribution of the electron density associated with disordered solvent molecules was removed by the SQUEEZE subroutine in PLATON [41].

2.3. Synthesis

All the chemicals were purchased from Sigma–Aldrich. All chemicals were of reagent grade and were used as received.

2.3.1. Synthesis of the ligand3-[(2-Hydroxy-benzylidene)-amino]-propane-1,2-diol (H_3L)

The mono-condensed Schiff base (H_3L) was prepared by a standard method [28]: 10 mmol of salicylaldehyde(1.05 mL) were mixed with 10 mmol of 3-amino-1,2-propanediol (0.911 g) in 10 mLof absolute ethanol. The resulting mixture was refluxed for one hour, after removal of the solvent under reduced pressure; the crude product was washed with diethyl ether and dried under vacuum (Yield: 74%).

2.3.2. Synthesis of $[Ni^{II}_2(HL)(H_2L)(SCN)]_2.DMF$ (**1**)

A methanolic solution (5 mL) of NaSCN (0.160 g, 2 mmol) was added drop-wise to a methanolic solution (10 mL) of $NiCl_2{\cdot}6H_2O$ (0.951 g, 4 mmol). The resulting solution was stirred for one hour and then a methanolic solution (5 mL) of H_3L (0.780 g, 4 mmol) was added to the mixture followed by 0.606 g (6 mmol) of Et_3N. The resulting green solution was stirred for 2.5 h and was evaporated to dryness under reduced pressure. The resulting solid was dissolved in DMF. Crystals suitable for X-ray studies were obtained by slow diffusion of diethyl ether into this DMF solution.

Complex **1**: Yield: (~72%). *Anal.* Calc. for $C_{42}H_{46}N_6Ni_4O_{12}S_2$: C, 44.81; H, 4.12; N, 7.47. Found: C, 44.71; H, 4.09; N, 7.28%. Selected IR data (KBr, cm^{-1}) (Fig. S3): $\nu_{(OH)} = 3424$, $\nu_{(SCN)} = 2031$, $\nu_{(C{=}N)} = 1632$, $\nu_{(C\text{–}O,Phen)} = 1193$, $\nu_{(C\text{–}O,Alco)} = 1093$ cm^{-1}.

2.3.3. Synthesis of $[Ni^{II}_2Mn^{III}_2(HL)_2(L)_2]$ (**2**)

A solution of $NiCl_2.6H_2O$ (0.951 g, 2 mmol) in methanol (5 mL) was added to a solution of H_3L (0.901 g, 4 mmol) in methanol (10 mL) followed by the addition of a methanolic solution (5 mL) of $MnCl_2{\cdot}4H_2O$ (0.394 g, 2 mmol). To the resulting solution, Et_3N (0.404 g, 4 mmol) was added dropwise. The resulting mixture was stirred for 2 h and filtered to remove any insoluble material. The filtrate was left at room temperature overnight resulting in the precipitation of brown block shaped crystals of compound **2**.

Complex **2**: Yield: (~ 62%). *Anal.* Calc. for $C_{40}H_{42}Mn_2N_4Ni_2O_{12}$: C, 48.14; H, 4.24; N, 5.61. Found: C, 48.04; H, 4.10; N, 5.40%. Selected IR data (KBr, cm^{-1}) (Fig. S4): $\nu_{(O\text{–}H)} = 3407$, $\nu_{(C{=}N)} = 1612$, $\nu_{(C\text{–}O,Phen)} = 1208$, $\nu_{(C\text{–}O,Alco)} = 1095$ cm^{-1}.

3. Results and discussion

3.1. Syntheses and IR spectra of the complexes

The reaction of methanolic solution of NaSCN and $NiCl_2.6H_2O$ with H_3L in presence of Et_3N afforded the tetranuclear complex $[Ni^{II}_2(HL)(H_2L)(SCN)]_2.DMF$ (**1**) by slow diffusion of diethyl ether into DMF solution. When methanolic solutions of $NiCl_2{\cdot}6H_2O$ and $MnCl_2{\cdot}4H_2O$ are used with H_3L in presence of Et_3N, a $Ni^{II}_2Mn^{III}_2$ based tetranuclear complex, $[Ni^{II}_2Mn^{III}_2(HL)_2(L)_2]$ (**2**) is formed. The two complexes, **1** and **2** are characterized elemental microanalysis, infrared (IR) spectroscopy and single crystal X-ray crystallography (Scheme 1).

IR spectra provided valuable information about the coordination environment of the complexes. In the IR spectra of **1** and **2**, the strong peaks at 1632 and 1612 cm^{-1} may be ascribed to the presence of coordinated imine group. The spectrum of **1** reveals