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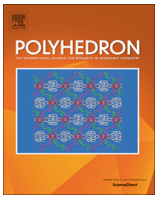

A ferromagnetic tetranuclear nickel(II) Schiff-base complex with an asymmetric Ni_4O_4 cubane core ☆

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ABSTRACT

The ferromagnetic tetranuclear nickel(II) complex $[Ni_4(L)_4(CH_3OH)_2]\cdot 2MeOH\cdot 8H_2O$ (**1**) has been synthesized by reacting nickel nitrate hexahydrate with the Schiff base ligand H_2L (H_2L = *N*-(2-hydroxyphenyl)-3-methoxy-salicylideneamine). Complex **1** was characterized by analytical, thermogravimetric, optical and magnetic techniques. The solid state structure of **1** was established by single crystal X-ray diffraction analysis. Crystal structure determination shows the formation of a distorted Ni_4O_4 cubane moiety encapsulated by four Schiff base ligands. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with $a = 12.7624(9)$ Å, $b = 15.0477(9)$ Å, $c = 16.8589(10)$ Å, $\alpha = 94.732(2)°$, $\beta = 94.308(2)°$, $\gamma = 99.136(2)°$ and $Z = 2$. The magnetic properties of complex **1** show a predominant ferromagnetic coupling inside the Ni_4 cluster with $g = 2.240$, $J_1 = +0.88\ cm^{-1}$, $J_2 = +0.84\ cm^{-1}$, $J_3 = -0.014\ cm^{-1}$, $J_4 = +1.22\ cm^{-1}$ and $D = 9.6\ cm^{-1}$.

1. Introduction

The design and synthesis of polynuclear metal complexes have attracted tremendous attention because of their structural diversity and potential applications in biology, catalysis, molecular recognition and magnetism [1,2]. In this context, tetranuclear cubane-like Ni_4O_4 complexes have been a very important class of molecules [3]. Most of these complexes have been synthesized by using a polydendate ligand which features nitrogen and oxygen donor atoms. Four nickel centers are linked by four μ_3-oxygens arising from hydroxido, alkoxido and methoxido moities [4–7]. A variety of ligands have been used ranging from simple aldehydes and pyridyl-alcohols to Schiff-base ligands derived from aldehyde and amino alcohols. For instance, 3,5-dichloro-2-hydroxy-benzaldehyde, 2-hydroxy-3-methoxy-benzaldehyde, 5-bromo-2-hydroxybenzaldehyde and 2-hydroxy-3-ethoxy-benzaldehyde have been employed to synthesize tetranuclear nickel complexes with a Ni_4O_4 core [8–10]. 2-Hydroxymethylpyridine, *gem*-diol form of di-2-pyridyl ketone, 8-quinolinol and its derivatives have also been used [11–15].

Moreover, several tetranuclear nickel complexes have been stabilized by several Schiff-base ligands [16–20]. In general, Ni_4O_4 cubane is highly symmetric and may present either ferromagnetic or antiferromagnetic interactions among the nickel ions. The symmetry of the cube can be modified with the coordinating ligands and the crystallization conditions such as solvent, temperature, guest molecules and pH. The lowering of the symmetry implies differences in the Ni–O–Ni angles that may lead to the presence of both ferro- and antiferromagnetic intra-molecular interactions. Interestingly, among the ca. 120 structures of Ni_4O_4 cubanes deposited in the CCDC database (updated Nov 2013) there are very few examples with no symmetry elements at all as in our compound [21].

Recently, we have started to develop new polynuclear metal complexes based on polydendate Schiff-base ligands in order to tune the magnetic properties of the synthesized complexes. Here we present the results obtained with the Schiff-base ligand *N*-(2-hydroxyphenyl)-3-methoxy-salicylideneamine (H_2L) [22] which can coordinate to one or two metal ions simultaneously (Scheme 1).

Reaction of H_2L with nickel(II) nitrate hexahydrate in presence of triethyl amine in methanol results in the formation of a tetranuclear Ni(II) complex, $[Ni_4(L)_4(MeOH)_2]\cdot 2MeOH\cdot 8H_2O$ (1) that contains a

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☆ This paper is dedicated to Prof. Dr. Werner Massa on the occasion of his 70th birthday.

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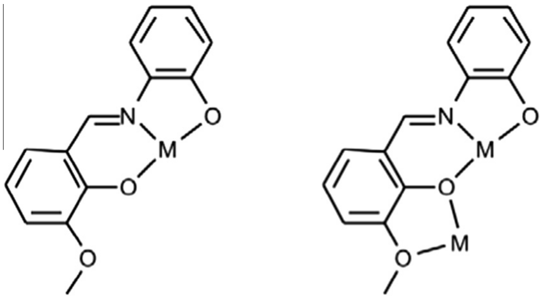

Scheme 1. Coordination modes of the deprotonated ligand (L^{2-}).

Ni_4O_4 cubane core. Variable temperature magnetic susceptibility measurements shows the presence of both ferro- and antiferromagnetic intramolecular interactions. Herein we describe the synthesis, solid-state structure, thermal stability, magnetic and optical properties of complex **1**.

2. Experimental

2.1. Materials

All chemicals and solvents used for the synthesis were of analytical grade. O-vanillin, 2-amino phenol and $Ni(NO_3)_2{\cdot}6H_2O$ were commercially available and used as received without further purification. Schiff base ligand *N*-(2-hydroxyphenyl)-3-methoxy-salicylideneamine (H_2L) was prepared by condensation of o-vanillin and 2-amino phenol according to the literature procedure [22].

2.2. Synthesis of 1

A methanolic solution (5 mL) of $Ni(NO_3)_2.6H_2O$ (0.087 g, 0.30 mmol) was added to 10 mL of a methanolic solution of the Schiff base ligand H_2L (0.048 g, 0.20 mmol). Et_3N (75 μL, 0.54 mmol) was addded to the resulting solution followed by a further addition of 5 mL of MeOH. The resulting brown solution was stirred for 5 min and kept at room temperature for slow evaporation. Brown colour crystals appeared after 7 days. yield 62.8 (%). *Anal.* Calc. for $C_{60}H_{76}N_4Ni_4O_{24}$ (%): C, 48.96; H, 5.20; N, 3.81. Found: C, 48.53; H, 5.16; N, 3.74%. IR (KBr pellet, cm^{-1}): 3426(br), 1601(s), 1477(s), 1241(s), 731(m), 522(m).

2.3. Physical measurements

Elemental analyses were performed on a VARIO MICRO cube analyser by Elemental analyser system GMBH. IR spectra in KBr (4500–500 cm^{-1}) were recorded using a Perkin–Elmer RXI FT-IR spectrometer. Variable temperature susceptibility measurements were carried out in the temperature range 2–300 K with an applied magnetic field of 0.1 T on a ground polycrystalline sample (21.29 mg) with a SQUID magnetometer (Quantum Design MPMS-XL-5). The susceptibility data were corrected for the diamagnetic contributions of the sample, as deduced using Pascal's constant tables ($\chi_{dia} = -779.4 \times 10^{-6}\ cm^3\ mol^{-1}$) [23]. The electronic spectrum in methanol was recorded with a Shimadzu UV-1800 spectrometer. Thermogravimetric analyses (TGA) were performed with a NETZSCH leading Thermal analysis STA449F3 Jupiter thermal analyser system in a dynamic atmosphere of N_2 at a heating rate of 10 °C/min.

2.4. X-ray crystallography

The data of **1** were collected on a Bruker D8 Quest diffractometer equipped with a Photon 100 CMOS area detector system, using Mo Kα radiation with graphite monochromator ($\lambda = 0.71073$ Å) at $T = 100(2)$ K. The structure was solved by direct methods (SIR92) [24] and refined on F^2 by full-matrix least-squares methods using SHELXL-2013 [25,26]. Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The oxygen atoms of lattice water molecules were highly disordered and refined isotropically and corresponding hydrogen atoms are included in the molecular formula of **1**. The function minimized was $[\sum w(F_o^2 - F_c^2)^2]$ ($w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$), where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics. The function R_1 and wR_2 were $(\sigma||F_o| - |F_c||)/\sigma|F_o|$ and $[\sigma w(F_o^2 - F_c^2)^2/\sigma(wF_o^4)]^{1/2}$, respectively.

3. Results and discussions

3.1. Synthesis

The synthesis of **1** was carried out by reacting H_2L with nickel nitrate hexahydrate in methanol in presence of triethylamine as base at ambient temperature. Detailed synthetic procedures are given in the experimental section. Complex **1** was characterized by standard analytical/spectroscopic techniques and the solid-state structure was established by single crystal X-ray diffraction analysis. The IR spectrum of the free ligand (H_2L) exhibits strong bands at 1617 and 3040 cm^{-1} attributed to the stretching vibrations of the azomethine [ν(C=N)] and [ν(OH)] groups, respectively [22]. In the spectrum of **1**, the azomethine ν(C=N) stretching frequency appears at 1606 cm^{-1}, below that of the free ligand, due to a decrease in the C=N bond order as a consequence of the coordination to the nickel ion. Several bands because of Ni-O and Ni-N bonds appear in the range of 472–576 cm^{-1}, further supporting the coordination of the ligand to Ni(II) ions. A broad band at 3426 cm^{-1} may be assigned to water molecules [12].

3.2. Description of the structure

Single crystal X-ray structure analysis reveals that complex **1** crystallizes in the triclinic space group $P\bar{1}$ with two formula units in the unit cell (crystal data and refinement parameters are provided in Table 1). The molecular structure of compound **1** is shown

Table 1
Single crystal data and structure refinement parameters for **1**.

Compound	1
Formula	$C_{60}H_{76}N_4Ni_4O_{24}$
Formula weight	1472.02
Temperature (K)	100(2)
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	12.7624(9)
b (Å)	15.0477(9)
c (Å)	16.8589(10)
α (°)	94.732(2)
β (°)	94.308(2)
γ (°)	99.136(2)
Z	2
D_{calc} (g cm^{-3})	1.541
μ (mm^{-1})	1.253
$F(000)$	1536
Total reflections	30407
Unique reflections	11794
Observed data [$I > 2\sigma(I)$]	7226
No. of parameters	865
R_{int}	0.0654
$R_1[I > 2\sigma(I)]$	0.0539
R_1, wR_2 (all data)	0.1189, 0.1069
Goodness-of-fit (all data)	1.014
Maximum peak/hole	0.483/−0.423