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Synthesis, Characterization, and Structure of a New Ferromagnetically Coupled Tetranuclear Nickel Cubane Complex[1]

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Abstract—A new nickel complexes $[Ni(L)_4(OCH_3)_4(CH_3OH)_4]$ (**I**) (HL = salicylaldehyde) was synthesized and structurally characterized by elemental analyses and single-crystal X-ray diffraction (CIF file CCDC no. 1410887). The complex crystallizes in monoclinic $P2_1/c$ space group and consists of one crystallographically independent molecule which contains a distorted tetranuclear cubane core with alternating nickel and oxygen atoms of the four on the corners. The magnetic properties reveal the presence of ferromagnetic interactions between the nickel(II) centers in the cubic cluster with two different exchange pathways.

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INTRODUCTION

The rational design and construction of coordination compounds have received a considerable attention in recent decades, because of their intriguing structural diversitiesand potential applications as functional materials [1, 2]. With a large single ion zero field splitting and an S = 1, the distorted octahedral Ni(II) is good candidate for the generation of molecular magnetic materials [3]. To date, plenty of polynuclear nickel(II) assemblies with different ground spin state are found in documents [4]. Especially, the cubane-like Ni_4 tetranuclear compounds have received intense interest since such molecules may exhibit single-molecule magnets behavior [5–7]. For instance, Yang used 2-hydroxymethylpyridine as the ligand to prepare a series of Ni_4 cubane complexes with different symmetries, which show single-molecule magnets behavior [8]. Song obtained an unexpected cubane-like Ni_4 complex bridged by the anion of 2-hydroxymethylbenzimidazole [9]. Although many ligands have been used to synthesize tetranuclear nickel compounds, to our best of knowledge, there is no example constructed with the common ligand of salicylaldehyde. Herein, we reported the synthesis, crystal structure and magnetic property of a new cubane-like Ni_4 tetranuclear compound with salicylaldehyde ligand (HL), $[Ni(L)_4(OCH_3)_4(CH_3OH)_4]$ (**I**).

EXPERIMENTAL

Materials and methods. All chemicals used during the course of this work were of reagent grade and used as received from commercial sources without further purification.

Synthesis of complex I. Solid of $NiCl_2 \cdot 6H_2O$ (237.6 mg, 1 mmol) was added to 50 mL of a methanolic solution dissolved HL (122.4 mg, 2 mmol) with stirring for 10 min. Then excess triethylaminewas added slowly to the above mixture. After refluxed for 2 h, the resulting solution was filtered when it was still hot. The filtrate was left at room temperature, and green crystals suitable for X-ray single-crystal diffraction analysis appeared after 3 days. They were collected by filtration, washed with methanol (the yield was 62% based on Ni).

For $C_{36}H_{48}O_{16}Ni_4$

anal. calcd., %:	C, 44.51;	H, 4.98.
Found, %:	C, 44.47;	H, 5.02.

X-ray crystallography. Crystallographic data of complex **I** was collected using a Bruker SMART APEXII CCD diffractometer operating at room temperature. Intensities were collected with graphite monochromatized MoK_α radiation (λ = 0.71073 Å), using the φ and ω scan technique. Data reduction was made with the Bruker SAINT package [10]. Absorption correction was performed using the SADABS program. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares using SHELXL-2000 with anisotropic displacement parameters for all non-hydrogen atoms [11]. H atoms were introduced in calculations using the riding model. All computations were carried out using the SHELXTL-2000 program package [12]. X-ray crystallographic

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Table 1. Crystallographic data and structural refinement details of complex **I**

Parameter	Value
Formula weight	971.58
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	14.418(11)
b, Å	14.441(11)
c, Å	21.569(13)
β, deg	116.29(4)
V, Å^3	4026(5)
Z	4
ρ_{calcd}, g/cm^3	1.603
μ, mm^{-1}	1.912
F(000)	2016
Reflections collected/unique	38809/7340
R_{int}	0.1060
Limiting indices	$-17 \leqslant h \leqslant 17, -17 \leqslant k \leqslant 17,$ $-25 \leqslant l \leqslant 25$
Refinement parameters	521
GOOF (all reflections)	0.957
R_1, wR_2 ($I > 2\sigma(I)$)	0.0414, 0.0818
R_1, wR_2 (all data)	0.0589, 0.0886
Largest diff. peak/hole, e Å^{-3}	0.801/–0.970

Table 2. Selected bond lengths (Å) and bond angles (deg) for complexes **I**

Bond	d, Å	Bond	d, Å
		I	
Ni(1)–O(1)	2.007(2)	Ni(1)–O(9)	2.066(2)
Ni(1)–O(2)	2.046(2)	Ni(1)–O(12)	2.041(2)
Ni(1)–O(3)	2.054(2)	Ni(1)–O(13)	2.079(2)
Ni(2)–O(3)	2.046(2)	Ni(2)–O(10)	2.055(2)
Ni(2)–O(6)	2.047(2)	Ni(2)–O(11)	2.010(2)
Ni(2)–O(9)	2.050(2)	Ni(2)–O(14)	2.082(2)
Ni(3)–O(3)	2.036(2)	Ni(3)–O(6)	2.077(2)
Ni(3)–O(4)	2.036(2)	Ni(3)–O(12)	2.048(2)
Ni(3)–O(5)	1.999(2)	Ni(3)–O(15)	2.112(3)
Ni(4)–O(6)	2.057(2)	Ni(4)–O(9)	2.034(2)
Ni(4)–O(7)	2.062(2)	Ni(4)–O(12)	2.045(2)
Ni(4)–O(8)	2.010(2)	Ni(4)–O(16)	2.101(2)
Angle	ω, deg	Angle	ω, deg
		I	
Ni(3)O(3)Ni(2)	96.31(9)	Ni(3)O(3)Ni(1)	99.32(10)
Ni(2)O(3)Ni(1)	95.68(11)	Ni(2)O(6)Ni(4)	99.46(10)
Ni(2)O(6)Ni(3)	95.03(9)	Ni(4)O(6)Ni(3)	95.46(10)
Ni(4)O(9)Ni(2)	100.13(10)	Ni(4)O(9)Ni(1)	95.32(10)
Ni(2)O(9)Ni(1)	95.19(10)	Ni(1)O(12)Ni(4)	95.73(10)
Ni(1)O(12)Ni(3)	99.37(9)	Ni(4)O(12)Ni(3)	96.72(10)

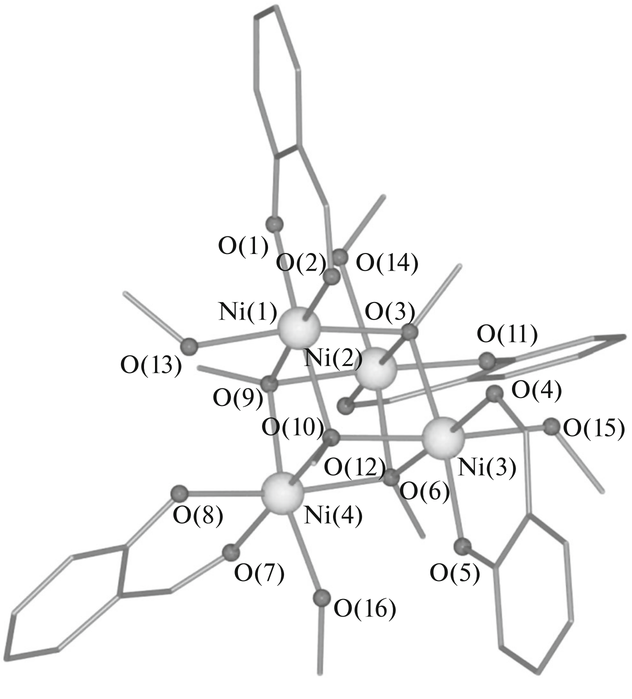

Fig. 1. Molecular structures of **I**. All hydrogen atoms are been omitted for clarity.

data and refinement details are summarized in Table 1. The selected bond lengths and angles for the complex are given in Table 2.

Crystallographic data for the structure has been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1410887; www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The single crystal X-ray structural analysis reveals that complex **I** comprises one crystallographically independent molecule which contains a distorted Tetranuclear cubane core with alternating nickel and oxygen atoms of the four on the corners. As presented in Fig. 1, the asymmetric unit contains four Ni^{2+} ions, four L$^-$ ligands, four CH$_3$O$^-$ anions and four coordinated methanol molecules. Each Ni(II) atom is chelated by two oxygen atoms from the salicylaldehyde ligand and by the μ$_3$-OCH$_3$ oxygen atom. The coordination sphere of Ni is completed with one methanol molecule and making six-coordinate with a distorted octahedral geometry. The Ni–O bond lengths are in the range of 1.999(2)–2.112(3) Å, consistent with the normal ranges for a NiO$_6$ group [13]. Each μ$_3$-OCH$_3$

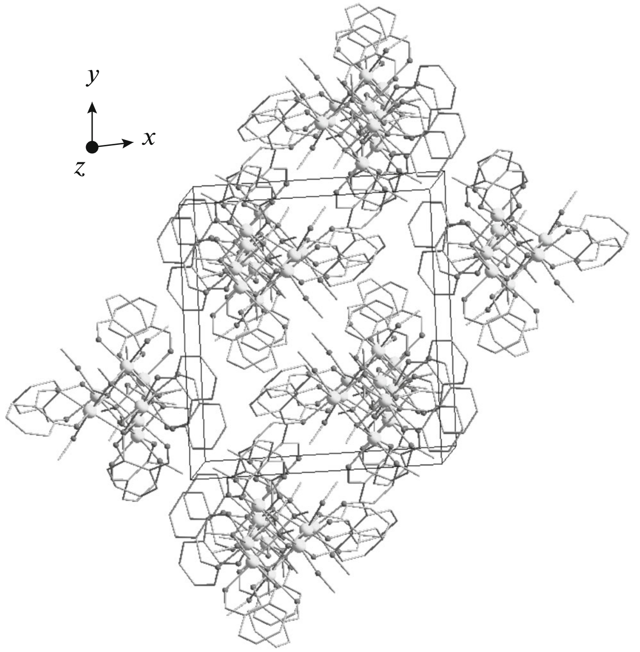

Fig. 2. 3D supramolecular architecture of **I**.

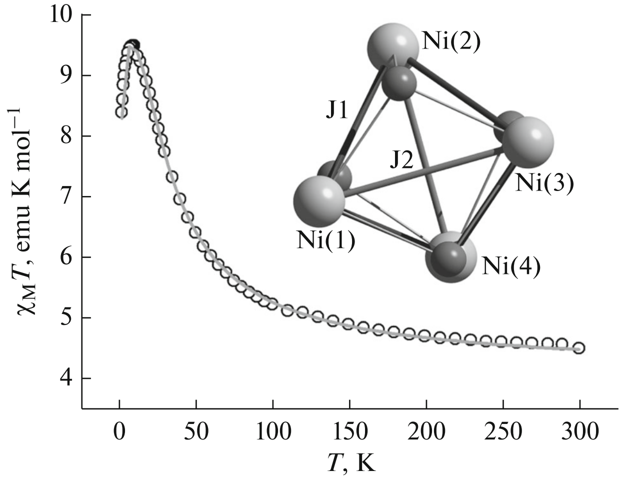

Fig. 3. Temperature dependence of $\chi_M T$ versus T of **I**. The solid line represents the bestfitting of the data; inset: coupling scheme.

oxygen bridges three nickel centers leading to form a Ni_4O_4 core which is similar to the cubane structures have been reported previously [14]. The Ni–Ni distances on different cubic faces are different, vary from 3.030 to 3.131 Å. The molecular packing of the Ni(II) complex is presented in Fig. 2, viewed along the z axis.

The magnetic susceptibility measurements of the crystalline sample of **I** were carried out at an applied field of 1 kOe on a MPMS-XL7 SQUID magnetometer in the temperature range of 2–300 K. The results are depicted in the form of $\chi_M T$ product versus T in Fig. 3. The $\chi_M T$ value of I is 4.58 emu K mol^{-1} at room temperature, larger than the spin-only value of 4.00 emu K mol^{-1} for four Ni^{2+} ions ($S = 1$ and $g = 2.0$), suggesting that ferromagnetic couplings dominate [15]. Upon cooling, $\chi_M T$ increases progressively to a maximum of 9.49 emu K mol^{-1} at 9 K, and then decreases to 8.39 emu K mol^{-1} at 2 K. This overall behavior is characteristic of a system with predominant ferromagnetic interactions between the metal ions. The drop of $\chi_M T$ value below 9 K can be associated with zero-field splitting effects originated from the ground state of the Ni^{2+} ions and/or antiferromagnetic interactions between the Ni_4 units.

In order to further investigate the nature of coupling interactions between the Ni^{2+} ions, the model (Fig. 3 inset) constructed by using a full-diagonalization treatment based on the interaction pattern and the corresponding Hamiltonian $H = -2J_1(S_{Ni1}S_{Ni2} + S_{Ni2}S_{Ni3} + S_{Ni3}S_{Ni4} + S_{Ni4}S_{Ni1}) - 2J_2(S_{Ni1}S_{Ni3} + S_{Ni2}S_{Ni4})$ [16]. In addition, to take into account the zero-field splitting, the best fit was obtained with $J_1 = 9.1(1)$ cm^{-1}, $J_2 = 2.47(3)$ cm^{-1}, $D = -0.050(1)$ cm^{-1}, $g = 2.003(2)$. The values of the coupling constants (J_1 and J_2) are ferromagnetic and fall in the normal range observed in this kind of cubane Ni_4O_4 complex [17]. Furthermore, the Ni–O–Ni bond angles are in the range of 95.03(9)°–100.13(10)°, which are coincided with the normal range where ferromagnetic interactions are expected in previous magneto-structural correlations for nickel(II) complexes with double oxido-bridges [18].

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