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Double azido-bridged and mixed-bridged binuclear copper(II) and nickel(II) compounds with N,N,O-donor Schiff bases: Synthesis, structure, magnetic and DFT study

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ABSTRACT

Two dinuclear complexes $\mu_{1,1}$-azido bridged $[Cu(L1)(N_3)]_2$ (**1**) and μ-phenoxo, $\mu_{1,1}$-azido bridged $[Ni_2(L2)_2(\mu_{1,1}\text{-}N_3)(N_3)\ H_2O]$ (**2**) bearing HL1 and HL2 as a blocking co-ligands produced by the 1:1 condensation of N-benzyl ethylenediamine with *ortho*-hydroxy acetophenone and N-methyl propanediamine with 3-methoxy salicylaldehyde respectively, have been synthesized and successfully characterized by elemental analyses, IR and electronic spectroscopy, single-crystal X-ray diffraction, variable temperature magnetic study and DFT studies. X-ray crystal structures of **1** reveal that the Cu(II) ion displays a five-coordinate square pyramidal coordination with a centro-symmetric $\mu_{1,1}$-azido bridging and forming a dimeric structure. The complex **2** compose of octahedrally coordinated dimeric nickel(II) complex with μ-phenoxo, $\mu_{1,1}$-azido bridging. Variable-temperature magnetic study (between 4.5 and 300 K) indicates a very weak and a moderate ferromagnetic intramolecular interaction are mediating through the metal centers for both of the complexes. The magnetic results have also been supported by the theoretical interpretations for both complexes.

1. Introduction

A variety of ligands containing N or O as donor atoms have been employed for preparation of polynuclear coordination complexes, aiming at understanding the structural and chemical factors that govern the exchange coupling between paramagnetic centers [1–9]. Among the bridging groups, the azido ligand is suitable bridging ligand due to its versatile binding abilities and its capacity to mediate different types of magnetic exchange interactions [1–9]. This versatility makes the azide bridged complexes as one of the most fascinating subjects for studying the superexchange pathways for magnetic interactions [1–9,10–14]. For example, it has been established that when the azido ligand bridges two Cu(II) ions in an end-on manner, the nature of the exchange coupling changes from ferromagnetic to antiferromagnetic when the Cu–N–Cu angle is around 108° [15]. The interaction is ferromagnetic for lower angle values and antiferromagnetic for higher angle values. This correlation, in principle, is valid only for basal–basal coordination, although sometimes has also been applied in basal–apical coordination mode, leading to the confusion [6,9]. In the basal–apical type of complexes, usually the coupling is very small as the magnetic orbital describing the single electron is mainly of an $x^2 - y^2$ type lying in the basal plane of the copper atoms and has only a small contribution on the axis perpendicular to the basal plane. Moreover, supra-molecular networks due to the formation of strong H-bonding created between the azido ligand and OH or NH_2 of the blocking ligands play an important role to decide the magnetic interaction among these type of Cu(II) systems [16–18].

On the other hand, the discoveries of nickel containing enzymes and activities of nickel in biological systems have led to the increasing interest in the coordination chemistry of nickel(II) [19–23]. In addition, the dinuclear Ni(II) complexes also possess

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interesting magnetic properties. The exchange interactions of such complexes changes dramatically in the presence of exogenous bridging group, e.g., chloro and azido ions, in their close proximity as these groups show diverse magnetic properties depending on their orientation with respect to the magnetic center [24–29]. Therefore, these systems still remain interesting for further investigations.

Here, we extend the examples of two dinuclear complexes $\mu_{1,1}$-azido bridged $[Cu(L1)(N_3)]_2$ (**1**) and μ-phenoxo, $\mu_{1,1}$-azido bridged $[Ni_2(L2)_2(\mu_{1,1}\text{-}N_3)(N_3)\ H_2O]$ (**2**) bearing HL1 and HL2 as a blocking co-ligands produced by the 1:1 condensation of N-benzyl ethylenediamine with *o*-hydroxy acetophenone and N-methyl propanediamine with 3-methoxy salicylaldehyde respectively, reporting the synthesis, X-ray crystal structures, magnetic study and the theoretical interpretation of the exchange pathway between the paramagnetic centers.

2. Experimental

2.1. Materials and physical measurements

All reagents and solvents for the synthesis and analysis were commercially available and used as received without further purification. IR spectra were recorded as KBr pellets within the range 4000–400 cm^{-1}on a Perkin–Elmer Spectrum 65 FTIR Spectrometer. The UV visible spectra were obtained using an Agilent 8453 diode array spectrophotometer. Elemental analyses were carried out using a Heraeus CHN-O-Rapid elemental analyzer. Variable-temperature magnetic susceptibility measurements over the range 4.5–300 K were carried out using Quantum Design MPMS SQUID magnetometer by taking microcrystalline powder samples and the magnetic susceptibility data were collected by applying a magnetic field of 0.1 Tesla. Diamagnetic corrections for the complexes were estimated from Pascal's constants and were corrected accordingly along with sample holder correction.

2.2. Syntheses

2.2.1. Synthesis of the complex 1

Caution! *Since the metal azide and perchlorate are potentially explosive, only small amount of the material should be prepared and it should be handled with care.*

To a solution of *ortho*-hydroxy acetophenone (0.136 g, 1 mmol) in 20 mL of methanol was added N-benzyl ethylenediamine (0.150 g, 1 mmol), and the resulting mixture was refluxed under stream bath for 4 h. After cooling to room temperature, a methanolic solution (10 mL) of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.370 g, 1 mmol) was slowly added to it and then the reaction mixture was refluxed again for 2 h. An aqueous solution of NaN_3 (0.26 g, 4 mmol) was then added to it and stirred at about 2 h. The resulting solution was then filtered. After about two weeks black block shaped crystals of **1** were formed with a 70% yield. *Anal.* Calc. for $C_{34}H_{38}Cu_2N_{10}O_2$: C, 54.8; H, 5.1; N, 18.8. Found: C, 55.0; H, 4.9; N, 19.1%.

2.2.2. Synthesis of the complex 2

A solution of 3-methoxy salicylaldehyde (0.152 g, 1 mmol) in 20 mL of methanol was added to N-methyl 1,3-propanediamine (0.088 g, 1 mmol) and the resulting mixture was refluxed under water bath for 4 h. Then a methanolic solution (10 mL) of $Ni(ClO_4)_2{\cdot}6H_2O$ (0.366 g, 1 mmol) was added to it and again refluxed for 2 h. Then 2 mL of aqueous solution of NaN_3 (0.26 g, 4 mmol) was then added to it and stirred at about 1.5 h. The resulting solution was then filtered and kept in desiccator. After about two weeks green block shaped crystals of **2** were formed with a 70% yield. *Anal.* Calc. for $C_{24}H_{36}Ni_2N_{10}O_5$: C, 43.5; H, 5.4; N, 21.1. Found: C, 43.9; H, 4.9; N, 21.6%.

2.3. Crystal structure determinations of 1 and 2

Crystal data for the complexes **1** and **2** are given in Table 1. The bond distances and bond angles for the compounds **1** and **2** are given in Table 2. Total independent datas-4032 and 6906 for compounds **1** and **2** respectively, were collected on a STOE IPDS2T diffractometer equipped with a graphite monochromator Mo K_α radiation ($\lambda = 0.71073$ Å). The structures of the complexes were solved by SIR 97 [30]. The structure refinements were also performed by full-matrix least squares based on F^2 with SHELXL-97 [31]. All non-hydrogen atoms were refined anisotropically. The C-bound H atoms were constrained to ideal geometry and were included in the refinement in the riding model approximation. Data for molecular geometry, intermolecular interactions and pictures were produced using PLATON-2009 [32] and ORTEP3.2 [33] programs.

2.4. DFT study and computational methodology

The magnetic properties of the complexes **1** and **2** are analyzed according the phenomenological Heisenberg Hamiltonian $\widehat{H} = -2J\widehat{S_1}.\widehat{S_2}$, where S_1 & S_2 are the local spin on centres 1 & 2 respectively and J is the coupling constant between them.

According to Yamaguchi and co-workers [34,35] the magnetic coupling constant (J) between two metallic centre 1 & 2 over the full range from the weak to strong coupling limits can be estimated from the equation as shown bellow.

$$J = -\frac{E_{HS} - E_{BS}}{{}^{HS}\langle S^2\rangle - {}^{BS}\langle S^2\rangle}$$

Here, *HS* and *BS* denote high-spin and broken-symmetry and the terms beneath are the expectation values of S^2 are evaluated for high-spin and broken-symmetry Kohn–Sham determinants.

The broken-symmetry state is constructed by permitting the system to localize antiparallel, unpaired spins separately on the

Table 1
Crystallographic data for **1** and **2**.

Crystal data	Complex **1**	Complex **2**
Empirical formula	$C_{34}H_{38}Cu_2N_{10}O_2$	$C_{24}H_{36}N_{10}Ni_2O_5$
Formula weight	745.82	662.05
Crystal dimension (mm)	0.56 × 0.25 × 0.13	0.35 × 0.27 × 0.15
Crystal system	monoclinic	triclinic
Space group	$P21/n$	$P\bar{1}$
a (Å)	9.4579(19)	8.0840(4)
b (Å)	12.271(2)	10.2822(4)
c (Å)	15.149(3)	18.4348(8)
α (°)	90.00	82.8862(11)
β (°)	105.459(6)	85.8224(11)
γ (°)	90.00	70.3692(10)
V ($Å^3$)	1694.5(6)	1431.35(11)
Z	2	2
Temperature (K)	173(2)	173(2)
D_{calc} ($g\ cm^{-3}$)	1.462	1.536
μ (mm^{-1})	1.302	1.369
$F(000)$	772	692
θ (°)	2.2–27.8	2.11–27.99
Total data	4032	6906
Unique data	3142	5604
R	0.0795	0.0551
R_w	0.1510	0.0796
Goodness-of-fit (GOF) on F^2, S	1.060	1.134
R_{int}	0.0615	0.0399
$\Delta\rho_{max}$ ($e\ Å^{-3}$)	0.7456	0.7456
$\Delta\rho_{min}$ ($e\ Å^{-3}$)	0.3482	0.6485