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A 3D hydrogen bonding framework of trinuclear Ni(II) complex in mixed ligands system: Structural and magnetic studies

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ABSTRACT

Employing *N*-benzoyl-salicylhydrazide (H_3bzshz) and imidazole (Himdz) as mixed ligands, a novel linear trinuclear Ni(II) complex $[Ni_3(bzshz)_2(Himdz)_2(H_2O)_2]\cdot 2DMF$ (**1**) has been synthesized and characterized. The three nickel atoms in **1** arrange in a strictly linear structure. The complex exhibits a novel 3D hydrogen bonding framework through the intermolecular O–H···O and N–H···O hydrogen bonding interactions. The magnetic property of **1** has been investigated by variable temperature magnetic susceptibility measurement.

In recent years, self-assemblies of coordination compounds to form polynuclear structures and supramolecular networks (1D, 2D or 3D) have gained importance due to their intriguing molecular architecture and magnetic properties [1]. The confidence to accomplish this goal is based upon the sophisticated selection and utilization of suitable metal ions, multifunctional organic ligands with certain features, such as versatile coordination modes, configurations and the ability to form hydrogen bonding [2].

By now, due to their inherent coordination functionalities the trianionic pentadentate *N*-acyl-salicylhydrazide ligands with flexible N–N single bonds have been utilized in the system of self-assembly in metallacrowns with different ring-sizes and nuclearities based on trivalent 3d metal ions such as Fe^{3+}, Gd^{3+}, Co^{3+} and Mn^{3+}[3,4], and a few trinuclear complexes based on bivalent 3d metal ions such as Ni^{2+}, Cu^{2+} and Zn^{2+} [5,6]. Some of these complexes have potential application in chemically modified electrodes, anion-selective separation agents, magnetic materials and biological activities. However, among these trinuclear complexes reported, the supramolecular coordination chemistry of *N*-acyl-salicylhydrazide ligands with hydrogen-bonding donor/acceptor functionalities has been less well explored. As far as we know, only $[Ni_3(acbshz)_2(DMA)_2(H_2O)_2]\cdot 2DMF$ [5c] with 2D infinite structure constructed by hydrogen bonding and $[Zn_3(p\text{-nbzshz})_2(py)_4]$ [6d] with 1D extended chain constructed by bridging deprotonated phenol groups are reported. Meanwhile, few of them contain auxiliary ligands.

In this study, we select *N*-benzoyl-salicylhydrazide as a common ligand to form the polynuclear cluster. And *N*-donor heterocyclic imidazole has also been introduced as the ancillary ligand, not only because it can bind to metal ion, but also because it can act as hydrogen bond donor to form hydrogen bonds. Herein, we wish to report the synthesis, structure and magnetic property of a novel linear trinuclear compound, $[Ni_3(bzshz)_2(Himdz)_2(H_2O)_2]\cdot 2DMF$ with mixed ligands. To the best of our knowledge, it represents the first trinuclear nickel complex of these kinds of pentadentate ligands which exhibits a novel 3D hydrogen bonding framework.

The red prismatic crystals of **1** were obtained *via* a solution synthetic method [7] and structurally characterized by single crystal X-ray diffraction analysis [8].

Single crystal X-ray diffraction analysis revealed that the main fragment in complex **1** is a trinuclear nickel complex (Fig. 1) comprising two μ_2-bridged $bzshz^{3-}$ ligands bound to three nickel centers in a linear array, with all ligand donor sites involved in coordination. The three nickel atoms are directly linked together by two *trans* diazine (N–N) bridges, with the Ni1···Ni2···Ni1a (symmetry code: (a) $-x+1, -y+1, -z+1$) angle of 180.0° and the Ni1–N1–N2–Ni2 torsion angle of 172.01(1)°.

The central Ni2 atom is located on the crystallographic inversion center with either of the other two terminal nickel atoms located 4.641 (7) Å away. The Ni2 atom is six-coordinated by two coordinated water oxygen atoms (Ni2–O4 = 2.155(4) Å) in axial positions, and the two carbonyl oxygen atoms and the two hydrazine nitrogen atoms (Ni2–O2 = 2.027(3) Å and Ni2–N2 = 2.106(4) Å) from the two $bzshz^{3-}$ groups in the equatorial plane, conferring an elongated octahedral geometry. The basal plane is ideally planar and the Ni2 atom completely lies in the equatorial plane. The terminal Ni1 atom is

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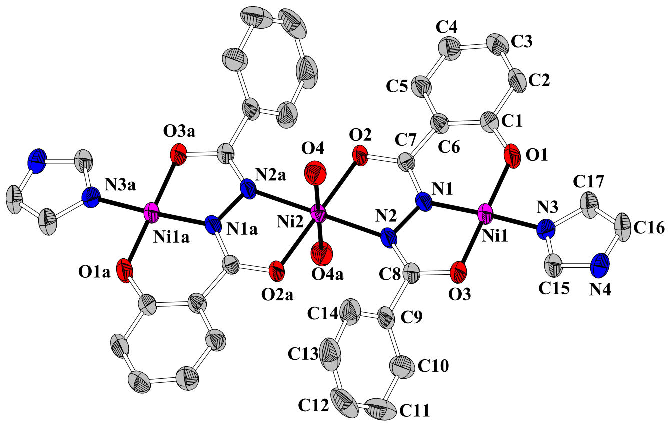

Fig. 1. The molecular structure of complex **1** with 30% thermal ellipsoids, solvent molecules and all hydrogen atoms have been omitted for clarity.

coordinated in a square-planar configuration composed of the other hydrazine nitrogen (Ni1–N1 = 1.823(4) Å), carbonyl oxygen (Ni1–O3 = 1.830(3) Å) and phenolic oxygen (Ni1–O1 = 1.817(3) Å) of one bzshz^{3-} ligand, as well as one coordinated Himdz nitrogen (Ni1–N3 = 1.903(4) Å). There is no deviation of the Ni1 center from the N_2O_2 square-plane, with the maximum and minimum deviations from the mean plane constituted by O1, O3, N1, N3 and Ni1 being 0.045(2) and 0.028(1) Å, respectively. Therefore, each bzshz^{3-} ligand is κ^2(O, N)-chelated to Ni2 and κ^3(O, N, O)-chelated to Ni1. And all non-H atoms of each ligand are non-coplanar, confirmed by the dihedral angle of 65.6(1)° between the two benzene rings of the ligand. The distances in the coordination planes around Ni1 and Ni2 shown above and the bond lengths in the ligand moieties are comparable with the related Ni(II) complexes [6a].

There are many different hydrogen bonds in complex **1**, playing an important role in the supramolecular assembly process. Firstly, each $[Ni_3(bzshz)_2(Himdz)_2(H_2O)_2]$ molecule is connected to four non-coordinated DMF molecules *via* $O-H(H_2O)\cdots O(DMF)$ hydrogen bonds ($O\cdots H = 2.111(43)$ Å, $O-H\cdots O = 154.0°$; $O\cdots H = 2.023(70)$ Å, $O-H\cdots O = 139.4°$), resulting in an extended one-dimensional chain along the *a* axis (Fig. 2). In this uniform chain-like arrangement, two Ni2 atoms are bridged by a 8-membered ring, with the Ni2···Ni2 distance being 8.12(1) Å.

At the same time, each $[Ni_3(bzshz)_2(Himdz)_2(H_2O)_2]$ molecule is linked to four adjacent trinuclear nickel complex molecules by two pairs of intermolecular $N-H(Himdz)\cdots O(carbonyl)$ hydrogen bonds ($O\cdots H = 2.103(4)$ Å, $N-H\cdots O = 166.9°$) to form an extended two-dimensional layer parallel to *bc* plane. These layers and chains are linked to construct a novel three-dimensional hydrogen bonding framework (Fig. 3). To the best of our knowledge, this type of three-dimensional framework has not been found in the similar trinuclear nickel complexes so far.

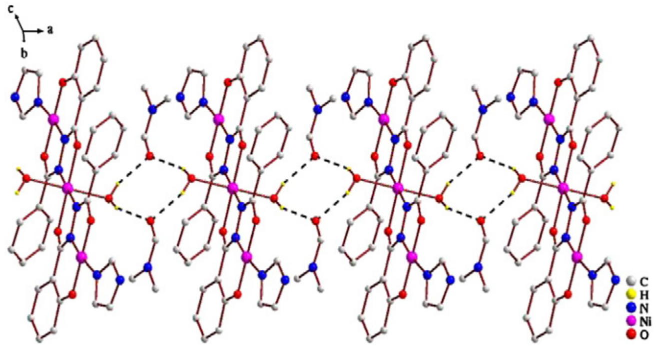

Fig. 2. 1D chain structure of complex **1** along *a* axis by intermolecular hydrogen bonding interactions.

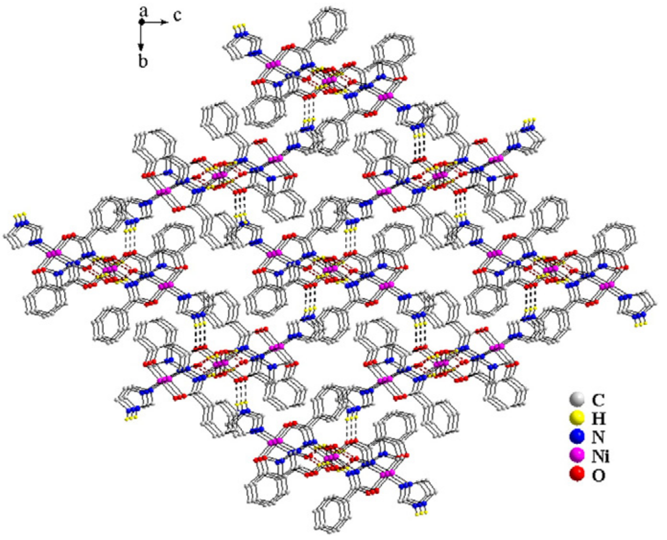

Fig. 3. A view of the 3D hydrogen bonding framework of complex **1**.

To study the thermal stability of the complex, the thermogravimetric analysis was carried out under an air atmosphere with a heating rate of 5 °C min^{-1} (Fig. S1). The TGA curve of **1** exhibits a first weight loss of 15.0% over the temperature range 76–204 °C corresponding to the removal of two unligated DMF molecules and one coordinated water molecule (calcd. value 16.41%). The second weight loss of 15.0% over the temperature range 204–370 °C corresponds to the removal of one coordinated water molecule and two coordinated imidazole ligands (calcd. value 15.40%). The third weight loss of 7.9% over the temperature range 370–451 °C may be attributed to the loss of one benzyl group of the ligand (calcd. value 7.70%). A further decomposition occurred over 451 °C, with a mass remnant of 21.7% at 563 °C, corresponding to the deposition of NiO (calcd. value 22.39%).

The magnetic property of **1** has been investigated by variable temperature magnetic susceptibility measurement in the solid state. Complex **1** has two four-coordinated, square-planar Ni(II) ions that are treated as low spin and diamagnetic. Additionally, there is one six-coordinated Ni(II) ion that is paramagnetic [9]. The magnetic properties of **1** in the form of $\chi_M T$ vs. T plots are shown in Fig. 4. At

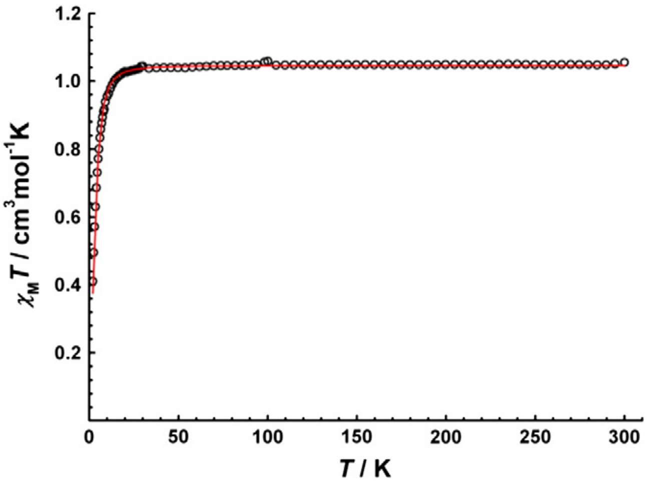

Fig. 4. $\chi M T$ *vs.* T plot of complex **1**. The red solid line is fit to the experimental data (see text).

room temperature, the $\chi_M T$ value is 1.1 $cm^3\ mol^{-1}$ K which is a typical value for an isolated Ni(II) ion with $g > 2.00$. $\chi_M T$ is practically constant to about 30 K and then decreases to 0.4 $cm^{-3}\ mol^{-1}$ K at 2 K. This feature indicates typical paramagnetic behavior for a Ni(II) ion in which the *D* parameter and/or intermolecular interactions (usually antiferromagnetic) are active at low temperature [10]. In an attempt to calculate the *D* value, we have fitted the experimental $\chi_M T$ value to the formula given by Kahn for a mononuclear Ni(II) ion considering the zero field split (*ZFS*) of the S = 1 ground state [10]. The best fit value are $|D| = 7.7\ cm^{-1}$ and *g* (average) = 2.05. The *D* value is consistent with that typical for Ni(II) ions (close to 5–8 cm^{-1}).

In summary, a novel linear trinuclear nickel(II) complex, $[Ni_3(bzshz)_2(Himdz)_2(H_2O)_2]\cdot 2DMF$ was synthesized by the mixed ligands *N*-benzoyl-salicylhydrazide and imidazole. This is the first nickel (II) complex based on *N*-acyl-salicylhydrazide ligands to form a 3D hydrogen bonding framework. The magnetic determination shows that both the terminal Ni(II) ions are diamagnetic and the central Ni (II) shows typical paramagnetic behavior.

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Appendix A. Supplementary material

CCDC 773488 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, or from the Cambridge Crystallographic Data Center, 12 Union Road Cambridge CB2 1EZ, UK.

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.02.008.

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[7] Syntheses: The ligand N-benzoylsalicylhydrazidate (H_3bzshz) was prepared according to the reported procedure [6b]. Synthesis of $[Ni_3(bzshz)_2(Himdz)_2(H_2O)_2]\cdot 2DMF$ 1: To a mixture solution of MetOH (15 mL) and DMF (6 mL) of H_3bzshz (25.6 mg, 0.1 mmol) and Himdz (13.6 mg, 0.2 mmol), a methanol solution (10 mL) of $Ni(CH_3COO)_2\cdot 4H_2O$ (24.8 mg, 0.1 mmol) was added gradually with stirring. The resulting red solution was further stirred for 1 h and filtered. The red crystals separated after several days were collected in 30% yield based on Ni. Anal. Calcd for $C_{40}H_{44}N_{10}O_{10}Ni_3$ (%): C, 48.00; H, 4.43; N, 14.00. Found: C, 48.15; H, 4.31; N, 14.12. IR (KBr pellet, cm^{-1}): 3425 (w); 3136 (vs); 2924(vs); 2855 (vs); 1657 (s); 1601 (vs); 1569 (s); 1523 (s); 1448 (s); 1410 (s); 1384 (s); 1357 (s); 1259 (s); 1151 (s); 1067 (s); 757 (s); 659 (s); 574 (s).
[8] Intensity data were collected at a Rigaku RAPID Weissengberg IP diffractometer at 293 K using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71\,073$ Å) and the ω scan mode. Crystallographic data for 1: $C_{40}H_{44}N_{10}O_{10}Ni_{33}$, $M_r = 1000.98$, Monoclinic, space group $P2_1/c$, a = 8.117(12) Å, b = 14.548(16) Å, c = 19.20(3) Å, $\beta = 114.92(7)°$, V = 2056(3)$Å^3$, Z = 2, Dc = 1.617 g cm^{-3}, $\mu = 1.432\ mm^{-1}$, 3952 unique data, 2895 observed $[I > 2\sigma(I)]$, 290 variables, $R_{int} = 0.0757$, $R_1 = 0.0477$, $wR_2 = 0.0936$, S = 1.068. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms of water molecules were located from the difference Fourier maps and the other hydrogen atoms were placed in their calculated positions.
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