Inorg. Chem. **2007**, *46*, 8448–8450

Inorganic Chemistry

Communication

One-Pot Synthesis of Schiff-Base-Containing Ni_8 Clusters: Solvothermal Synthesis, Structure, and Magnetic Properties

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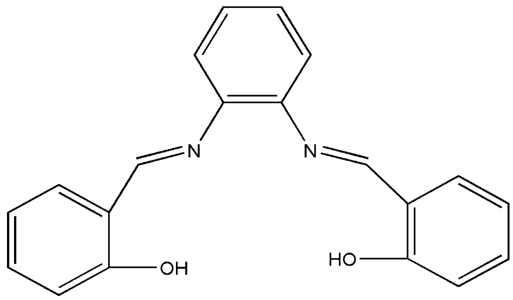
Received May 25, 2007

Solvothermal in situ generation of a Schiff-base ligand (L) in the presence $NiCl_2$ and trimesic acid (H_3BTC) in ethanol resulted in clusters, $Ni_8(L)_4Cl_8 \cdot (H_2O)_{0.5}$, consisting of three different coordination geometries, four paramagnetic and four diamagnetic Ni(II), exhibiting both ferromagnetic and antiferromagnetic exchange interactions.

Recently, a number of studies have revealed the hydrothermal synthesis at low temperatures (100−200 °C) to be an effective method for the in situ ligand synthesis. Such a strategy not only affords the opportunity to generate organic ligands that are difficult to synthesize by general methods but also provides a one-pot synthesis for the construction of metal−organic coordinated complexes through crystal engineering.[1] Until now, a variety of in situ ligand syntheses under hydrothermal conditions have been reported, including hydrolysis of −CN and −COOR groups,[2] reduction of $-COO^-$,[3] hydroxylation,[4] C−C bond formation by reductive or oxidative coupling,[5] cleavage and formation of disulfide bonds,[6] etc.

Here, we report the in situ preparation of Schiff-base-containing Ni_8 clusters. Usually, in order to prepare the L-based (L = Schiff-base, *N,N′-o*-phenylenebis(salicylideneimine), see Scheme 1), coordination polymer, the L ligands should be synthesized first. To the best of our knowledge, the in situ preparation of L-containing compounds is never explored. Via mild solvothermal synthesis (120 °C), the self-assembly of salicylaldehyde, 1,2-phenylenediamine, $NiCl_2$, and H_3BTC generated the cluster $Ni_8(L)_4Cl_8 \cdot (H_2O)_{0.5}$ (**1**).[7] In this reaction, the L ligands were formed in situ from salicylaldehyde and 1,2-phenylenediamine, and in the resultant products, the H_3BTC component is excluded. Additional experiments suggest that the presence of H_3BTC ligands provide a suitable environment for the formation of **1**, in other words, the H_3BTC cannot be excluded and displaced by other multi-carboxylate ligands (such as 1,2,4,5-benzenetetracarboxylic acid, 1,4-benzene dicarboxylate acid, 1,3-benzene dicarboxylate acid, and 1,2-benzene dicarboxylate acid).

Scheme 1



The single-crystal X-ray diffraction found that **1** crystallizes in the triclinic $P\bar{1}$ space group.[8] In the asymmetric unit, there are four independent nickel atoms: Ni1 and Ni3 adopt a square-planar NiO_2N_2 geometry within one ligand; Ni2 is

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(7) **Synthesis of 1.** $Ni_8(L)_4Cl_8 \cdot (H_2O)_{0.5}$. A C_2H_5OH (10 mL) solution of H_3BTC, $NiCl_2$, salicyl aldehyde, and 1,2-phenylenediamine in a ratio of 1:2:2:1 was sealed in a Teflon reactor and heated at 120 °C for 1 day and then cooled to room temperature at 3 °C h^{-1}. Subsequently, red crystals were obtained in 61% yield based on Ni. Anal. Calcd (%) for **1**: C, 47.58; H, 2.84; N, 5.55. Found: C, 47.56; H, 2.86; N, 5.56.

(8) Data collections were performed with Mo Kα radiation (0.71073 Å) on a Rigaku r-axis rapid IP area detector, the structures were solved by direct methods, and all non-hydrogen atoms were subjected to anisotropic refinement by full matrix least-squares on F^2 using the SHELXTL program. Crystal data for **1**: triclinic, space group $P\bar{1}$, $a = 12.543(3)$ Å, $b = 12.896(3)$ Å, $c = 13.782(3)$ Å, $\alpha = 97.06(3)°$, $\beta = 105.64(3)°$, $\gamma = 115.01(3)°$, $V = 1872.4(7)$ Å^3, $Z = 1$, GOF = 1.042, final R1 = 0.0688, wR2 = 0.1813. CCDC No. 642847(**1**).

10.1021/ic7010259 CCC: $37.00

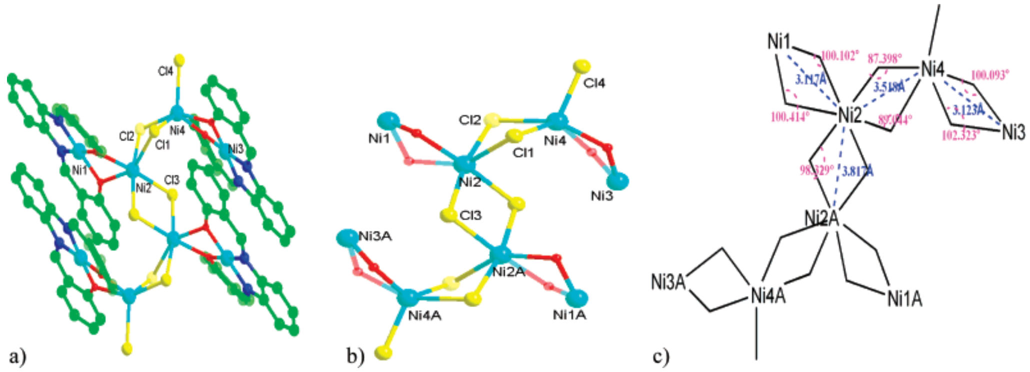

Figure 1. (a) Butterflylike Ni_8 cluster: Ni/cyan, Cl/yellow, C/green, N/blue, O/red, all hydrogen atoms are omitted for clarity. (b) The ball/sticks of description of the butterflylike Ni_8 cluster. (c) Schematic description of the butterflylike Ni_8 cluster.

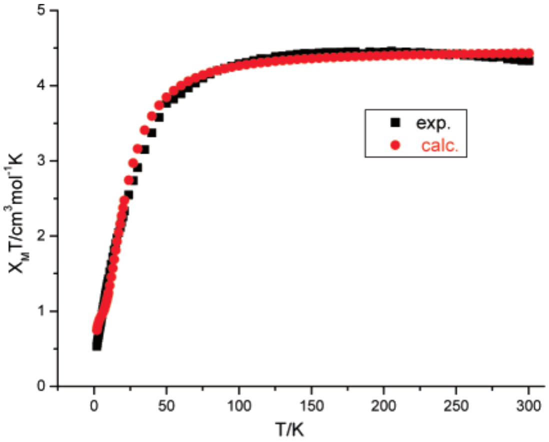

Figure 2. Experimental and simulated $\chi_M T$ vs T plots.

six-coordinated by two L oxygen atoms and four μ_2-Cl^- ions to form the distorted octahedral configuration; Ni4 displays the NiO_2Cl_3 distorted square pyramidal geometry with $\tau = 0.35$.[12] The Ni−O/N bond lengths vary from 1.84 to 2.214 Å, whereas the Ni−Cl bond lengths are in the range of 2.214−2.606 Å. The phenyl groups of L are not coplanar, and adopt the μ_2:η^1:η^1:η^2:η^2 coordinated mode.

As shown in Figure 1, Ni1, Ni2 and Ni3 and Ni4 are bridged by two L μ_2-O atoms to give the Ni_2 fragments; furthermore, these dimers are connected by the μ_2-Cl bridges, resulting in the butterflylike Ni_8 cluster. Within this Ni_8 cluster, the closest Ni−Ni distance is 3.117 Å for Ni1−Ni2, 3.518 Å for Ni2−Ni4, 3.123 Å for Ni4−Ni3, and 3.817 Å for Ni2−Ni2A, and the Ni−μ_2-O/Cl−Ni angles vary from 87.4° to 102.3°. To the best of our knowledge, this particular arrangement within the cluster is unprecedented. Upon careful inspection of the structure of **1**, we find that there are several significant H-bonds observed between free water molecules and Ni_8 clusters (O_{water}···Cl, 3.241 Å, O_{water}···C30, 2.423 Å, O_{water}···C37, 3.410 Å), which extended the discrete Ni_8 clusters into the 2D supramolecular frameworks.

The magnetic measurements of **1** were carried out with a Quantum Design (SQUID) magnetometer MPMS-XL-5 in a field of 500Oe (Figure 2). At 300 K, the diamagnetism-corrected $\chi_M T$ value of 4.55 $cm^3 mol^{-1}$ K is slightly bigger than the expected value calculated for four isolated Ni(II) moment carriers(ca. 4.0 cm^3 mol^{-1} K, $g = 2.0$). Upon the temperature cooling, it increases gradually up to 4.45 $cm^3 mol^{-1}$ K at 175 K, suggesting somewhat ferromagnetic interactions between Ni(II) ions. Below this temperature, the decrease of the $\chi_M T$ value upon the temperature cooling is due to antiferromagnetic exchange and/or other factors, such as ZFS (zero field splitting) and intermolecular interaction. Meanwhile, $1/\chi_M$ vs T is not linear and the Curie constant and Weiss temperature are dependent on the chosen temperature range used in the Curie−Weiss fitting. As mentioned above, within this Ni_8 cluster, Ni1 and Ni3 are diamagnetic carriers. Thereafter, a 'two J' mode is employed to analyze the left Ni_4 cluster (Ni−J1−Ni−J2−Ni−J1−Ni).[9] A least-squares fit to the data leads to $g = 2.11$, $J1 = 34.01$ cm^{-1}, $J2 = -15.83$ cm^{-1}, TIP = 19×10^{-6} cm^3 mol^{-1}, $\rho = 0.01$ cm^3 mol^{-1} K, $\theta = -1$ K: J is the magnetic coupling parameter between Ni(II) ions, g the Zeeman factor, TIP the temperature-independent paramagnetism, ρ the paramagnetic impurities, and θ the other factors. In addition, the experimental and simulated results are also consistent with the Kanamori-Goodenough rule:[10] as discussed above, the Ni−μ_2-Cl−Ni angles between Ni2−Ni4 and symmetry-related Ni2A−Ni4A are close to 90°, which usually shows ferromagnetic coupling according to the Kanamori-Goodenough rule, while the other exchange pathways between nickel atoms (Ni2−Ni2A) are antiferromagnetic with Ni−μ_2-Cl−Ni angles larger than 98°. Hence, in this compound, both antiferromagnetic and ferromagnetic couplings between Ni(II) ions coexist.

In summary, the in situ preparation of the Schiff-base ligand has resulted in an unusual coordination cluster consisting of three different coordination geometries for nickel(II), viz, square-planar, square-pyramid, and octahedral, where the magnetic susceptibility is consistent with diamagnetic square-planar Ni and paramagnetic penta- and octacoordinated Ni. Both ferromagnetic and antiferromagnetic exchanges exist between nearest-neighbor nickel atoms, but no blocking of the moments was experience in the temperature range studied. The present Ni_8 cluster has the highest degree of metal aggregation in the field of Schiff-base-based coordination polymer. To some extent, this research opens

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(9) MAGMUN has been developed by Dr Zhiqiang Xu and OW01.exe by Dr. O. Waldmann.

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up a promising pathway to design and preparation of Schiff-base-based polynuclear polymer.

Acknowledgment. This work was supported by the Nation Natural Science Foundation of China under Project No. 50572040 and CNRS-France.

Supporting Information Available: X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC7010259