

## Crystal Structures and Magnetic Properties of Two New Schiff Base Complexes

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**Abstract:** Two new Schiff base complexes,  $[\text{NiL}]\text{ClO}_4$  **1** and  $[\text{CuL}]\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$  **2**, were synthesized and characterized, where L is the 1:1 condensation product of salicylaldehyde and diethylenetriamine. Their crystal structures and magnetic properties were determined and investigated. The H-bonding interactions concern just in neighbor cation and anion, do not extend into network for both **1** and **2**. The temperature dependence of the magnetic susceptibilities (2-300K) showed that **1** is diamagnetism and **2** is paramagnetism with weak antiferromagnetic exchange interactions between adjacent spin carriers, no magnetic ordering taking place in these two complexes.

**Keywords:** Schiff base complex, crystal structure, H-bonding interaction, magnetic property.

Recently, continuing efforts have been taken to explore molecule-based ferromagnets both experimentally and theoretically<sup>1</sup>, while the critical temperatures of these materials are normally very low so far<sup>2</sup>. In order to obtain high critical temperature ( $T_c$ ) molecule-based magnets, it is important to enhance cooperating interactions between molecules, thus the better approach is to construct the coordination polymers by assembling transition metal ions with organic ligands<sup>3</sup>. In our research project, we have paid attention to design and synthesize molecule-based magnets assembled by H-bonding interactions, and found that the  $T_c$  value was significant higher when the dimensions of the H-bonding interactions increased<sup>4</sup>. Herein we report the crystal structures and magnetic properties of two new Schiff base complexes with H-bonding interactions.

Complexes **1** and **2** were prepared by refluxing equivalent molar ratios of salicylaldehyde, diethylenetriamine and corresponding  $\text{M}(\text{ClO}_4)_2$  ( $\text{M} = \text{Cu}^{2+}, \text{Ni}^{2+}$ ) using ethanol as solvent. Their chemical structures and purities were determined and checked by spectra and elemental analysis<sup>5</sup>. Single crystals of both **1** and **2** suitable for X-ray structure analysis were grown by diffusing diethyl ether into the ethanol solution of these complexes, and the dimensions of crystals selected are  $0.20 \times 0.10 \times 0.10 \text{ mm}^3$  for **1** and  $0.20 \times 0.15 \times 0.10 \text{ mm}^3$  for **2**, respectively<sup>6</sup>. Single crystals of **1** and **2** were put on an Enraf-Nonius CAD-4 diffractometer. Intensity data were collected at room temperature using graphite monochromatic Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structure was

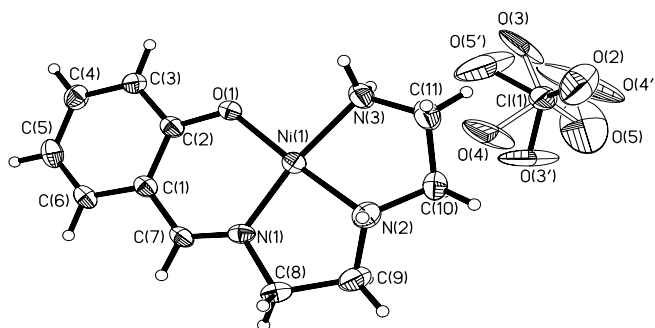
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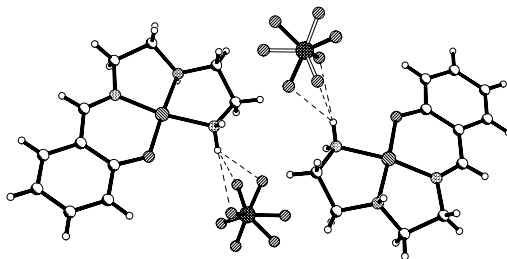
solved by direct method and refined on  $F^2$  by full-matrix least-square method using SHELXTL<sup>7</sup>. All the nonhydrogen atoms were refined anisotropically, hydrogen atoms were placed in their calculated positions and refined following the riding model, but the hydrogen atoms in solvent H<sub>2</sub>O for complex **2** were not added.

The Ni atom is bonded by one O atom and three N atoms of Schiff base ligand L<sup>-</sup> in a [NiL]<sup>+</sup> cation, the Ni-N bond lengths are in the range of 1.843(5)-1.936(6) Å, Ni-O bond length is 1.830(4) Å, and the bond angles of O(1)-Ni(1)-N(1), N(1)-Ni(1)-N(2),

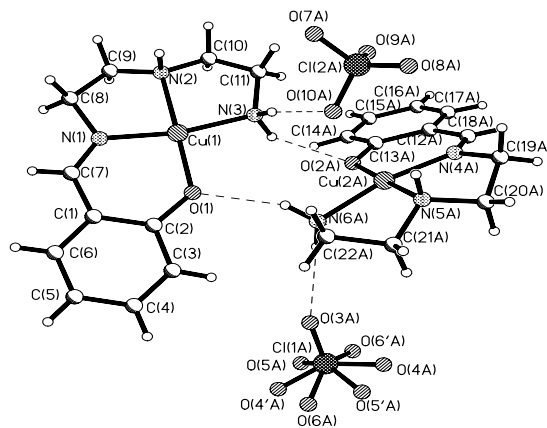
**Figure 1** ORTEP draw with 30% thermal possibility for **1**



**Figure 2** The H-bond interactions between anion and cation for **1**



**Figure 3** The dimer connected through H-bond interactions for **2**



N(2)-Ni(1)-N(3) and N(3)-Ni(1)-O(1) are 96.8(2), 86.5(3), 86.5(3) and 90.3(2)°, respectively, thus the Ni atom exhibits a square coordination geometry, and the derivation from the least-square plane of N(1)N(2)N(3)O(1) is just 0.0385(23) Å (Figure 1). The dihedral angle between the coordination plane and the benzene ring is only 5.77(35)°, which are almost parallel to each other. The [ClO<sub>4</sub>]<sup>-</sup> anion is disorder, the H-bonding interactions concern just in neighbor cations and anions, do not extend into network (Figure 2), the corresponding geometric parameters about H-bond interactions are listed in the Table 1.

The complex 2 is isostructural with the complex 1, but there are two cations of [CuL]<sup>+</sup>, two anions of [ClO<sub>4</sub>]<sup>-</sup> and a solvent H<sub>2</sub>O molecule in an asymmetric unit. One of the two anions is disorder to like the complex 1, the solvent H<sub>2</sub>O molecule is near by the Cu(2) atom, and the distance between O(w1) and Cu(2) is 2.755(4)Å. The Cu-N bond lengths are in the range of 1.898(12)-2.029(12) Å in the Cu(1) moiety *versus* 1.928(15)-2.034(11) Å in the Cu(2) moiety, Cu-O bond length is 1.894(9) Å in the Cu(1) moiety (1.882(9) Å in the Cu(2) moiety). In part of [Cu(1)L]<sup>+</sup>, the bond angles of O(1)-Cu(1)-N(1), N(1)-Cu(1)-N(2), N(2)-Cu(1)-N(3) and N(3)-Cu(1)-O(1) are 95.0(5), 84.2(6), 85.0(6) and 95.9(4)°, respectively. The correspondence bond angles in part of [Cu(2)L]<sup>+</sup> compare with that in part of [Cu(1)L]<sup>+</sup>. The two Cu atoms of both [Cu(1)L]<sup>+</sup> and [Cu(2)L]<sup>+</sup> moieties exhibit approximate square-planar N<sub>3</sub>O coordination sphere, which are similar to the Ni atom in the complex 1. The [Cu(1)L]<sup>+</sup> cations and the neighbor [Cu(2)L]<sup>+</sup> cations form dimer though H-bond interactions of N(6)<sup>i</sup>-H(6A)<sup>i</sup>... O(1) and N(3)-H(3B)...O(2)<sup>i</sup> (symmetric code i = x+1, y, z) as shown in Figure 3, the parameters of H-bond interaction are summarized in Table 1.

The temperature dependence magnetic susceptibilities for polycrystalline samples of 1 and 2 were measured on a MagLab system 2000 magnetometer (2-300 K). The complex 1 is diamagnetism in the temperature range of 2-300 K, this result is in agreement with the square-planar molecular structure of [NiL]<sup>+</sup> (Ni<sup>2+</sup>, 3d<sup>8</sup> and s = 0). The plots of  $\chi_m \cdot T$  and  $\chi_m T \cdot T$  of 2 are displayed in Figure 4. Based on the crystal structure, the dimer with s = 1/2 magnetic exchange model was selected to fit the magnetic susceptibility data, and the magnetic susceptibility as the temperature function is expressed as follows (spin Hamiltonian is  $H = -2J s_1 s_2$ ):

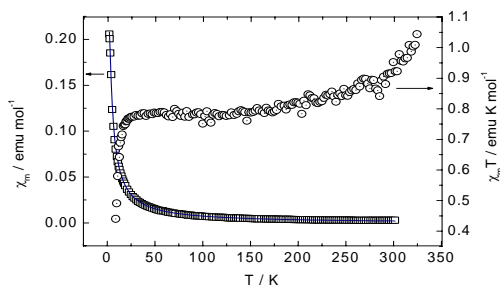
$$\chi_m = \frac{2Ng^2\mu_B^2}{k_B T} \frac{1}{(3 + \exp(-2J/k_B T))} + \chi_0 \quad (1)$$

where the symbol  $N$ ,  $g$ ,  $\mu_B$ ,  $k_B$  and  $J$  have normal meaning, and  $\chi_0$  represents the diamagnetic contribution of core. The best fitting gives the parameter -1.55 K of  $J$ , 2.08 of  $g$ -factor,  $-5.8 \times 10^{-4}$  emu mol<sup>-1</sup> of  $\chi_0$ , and the agreement factor  $R = 1.2 \times 10^{-6}$  ( $R$  defined as  $\sum_i [(\chi_m)_{obs}(i) - (\chi_m)_{calc}(i)]^2 / \sum_i [(\chi_m)_{obs}(i)]^2$ ). These results reflect there exist very weak antiferromagnetic interactions between the Cu<sup>2+</sup> ions in a dimer, so the ground state is singlet.

Summarily, the main goal of this work was to design molecular magnetic materials with larger dimensionality based on H-bonding interactions as mentioned in the introduction, but it was not achieved. So our presently research work, in which both intermolecular H-bond interactions and coordination polymerizations will be taken into account, are in progress.

**Table 1** The parameters of H-bonding interactions for **1** and **2**

	D-H	H...A	$\angle(\text{D-H}\dots\text{A})^\circ$	$d(\text{D-H}\dots\text{A})/\text{\AA}$
Complex <b>1</b>	N(3)-H(3B)	H(3B)...O(2) <sup>i</sup>	161.9	3.202(9)
	N(3)-H(3B)	H(3B)...O(3) <sup>i</sup>	139.9	3.310(12)
	N(3)-H(3B)	H(3B)...O(5') <sup>i</sup>	134.3	3.316(11)
Symmetry code $i = 1-x, 1-y, 1-z$				
Complex <b>2</b>	N(3)-H(3A)	O(10) <sup>i</sup>	165.7	3.021(19)
	N(3)-H(3B)	O(2) <sup>i</sup>	137.2	2.900(15)
	N(6)-H(6A)	O(1) <sup>j</sup>	158.6	3.127(14)
	N(6)-H(6B)	O(3) <sup>k</sup>	147.6	2.995(13)
Symmetry code $i = x+1, y, z; j = x-1, y, z; k = -x, -1/2+y, 3/2-z$				

**Figure 4**  $\chi_m$  ( $\square$ ),  $\chi_m T$  ( $\circ$ ) as the functions of temperature and solid line representing theoretic calculation result for **2**

### Acknowledgments

The work was supported by the National Natural Science Foundation (No.20171001), the Natural Science Foundation of Anhui Province (No.01012038) and the Natural Science Foundation of Anhui Province Education Commission (No. 2003kj253, 2003jq153)

### References and Notes

- L. Ding, D. Q. Zhang, B. Zhang, D. B. Zhu, *Chin. Chem. Lett.*, **2000**, *11*, 749; J. S. Miller, A. J. Epstein, *Angew. Chem. Int. Ed.*, **1994**, *33*, 385.
- D. Gatteschi, P. Carretta, A. Lascialfari, *Physica B*, **2000**, *289-290*, 94.
- S. M. Holmes, G. S. Girolami, *J. Am. Chem. Soc.*, **1999**, *121*, 5593; T. Mallah, M. Thiebaut, M. Verdagner, P. Veillet, *Science*, **1993**, *262*, 1554.
- X. M. Ren, Y. C. Chen, C. He, S. Gao, *J. Chem. Soc., Dalton Trans.*, **2002**, 3915; Y. C. Chen, G. X. Liu, H. Xu, H. Zhou, X. M. Ren, *Russ. J. Coord. Chem.*, **2003**, *29*, 251.
- Complex **1**: Blue crystal; FT-IR(KBr,  $\text{cm}^{-1}$ ): 1089(Cl-O), 1626(C=N), 3423(N-H); Anal. Calcd. for  $\text{C}_{11}\text{H}_{16}\text{ClN}_3\text{NiO}_5$ : C 36.25, H 4.43, N 11.53; Found C 35.89, H 4.56, N 11.29. Complex **2**: Blue violet crystal; FT-IR(KBr,  $\text{cm}^{-1}$ ): 1120(Cl-O), 1642(C=N), 3433(N-H); Anal. Calcd. for  $\text{C}_{22}\text{H}_{34}\text{Cl}_2\text{N}_6\text{Cu}_2\text{O}_{11}$ : C 34.93, H 4.53, N 11.11; Found C 35.07, H 4.64, N 11.02.
- The crystal data are as follows: monoclinic, P2(1)/c,  $a = 8.9120(18)\text{\AA}$ ,  $b = 13.353(3)\text{\AA}$ ,  $c = 11.920(2)\text{\AA}$ ,  $\beta = 98.29(3)^\circ$ ,  $V = 1403.7(5)\text{\AA}^3$ ,  $Z = 4$ ,  $R1 = 0.0629$ ,  $wR = 0.1672$  for **1**; P2(1)/c,  $a = 12.053(2)\text{\AA}$ ,  $b = 13.060(3)\text{\AA}$ ,  $c = 19.073(4)\text{\AA}$ ,  $\beta = 97.90(3)^\circ$ ,  $V = 3005.0(10)\text{\AA}^3$ ,  $Z = 4$ ,  $R1 = 0.0880$ ,  $wR = 0.1745$  for **2**.
- G. M. Sheldrick, *SHELXTL, Structure Determination Software Programs, Version 5.10*. Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA, **1997**.

Received 28 July, 2003