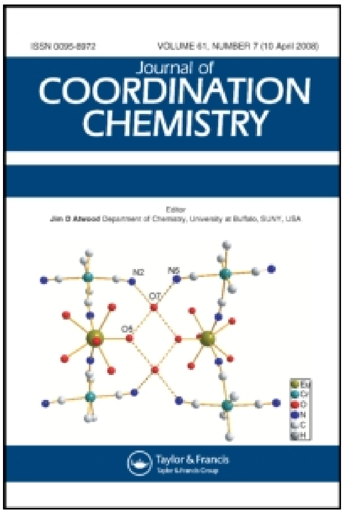

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Synthesis, characterization, crystal structures, and magnetic properties of two new dissymmetrical Schiff-base metal complexes

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Two dissymmetrical Schiff-base metal complexes, $[CuL1]_2$ (**1**) (L1 = N-3-carboxylsalicylidene-N-5-bromosalicylaldehyde-1,3-diaminopentane) and $[NiL2]\cdot H_2O$ (**2**) (L2 = N-5-bromosalicylaldehyde-1,3-diaminopentane), have been synthesized and characterized by IR, elemental analyses, magnetic studies, and the crystal structures. The crystal structure of **1** contains one binuclear molecule in which each central Cu has N_2O_3 coordination. The magnetism of **1** has been determined in the temperature range of 5–300 K. Results indicate that interaction between the two Cu ions is weak antiferromagnetic. The crystal structure of **2** shows mononuclear structure with similar structural features. Through intermolecular hydrogen-bonding interactions, **2** gives an infinite chain structure.

Keywords: Dissymmetrical; Double Schiff base; Crystal structure; Magnetic properties

1. Introduction

Schiff-base complexes of transition metals have been widely employed in the development of heterogeneous catalysis [1], gas sorption [2], molecular electronics [3], single molecule-based magnetism [4], photochemistry [5], and medicine [6]. Their physical, optical, magnetic, and electronic properties have been explored in different coordination environments with organic chelators, blockers, and suitable bridging units. A large number of complexes with Schiff bases, from dimers to 3-D networks, have been structurally characterized. These complexes are of interest as models for the active sites of enzymes [7]. Much effort has been spent on the synthesis of mono-, bi-, and multi-nuclear copper complexes as functional and structural models of multicopper enzymes [8]. Dissymmetrical Schiff-base complexes attract special attention in biochemistry since the active center of enzymes is often dissymmetrical.

Owing to synthetic difficulties, only a few dissymmetrical double Schiff-base complexes have been both structurally and magnetically characterized. Template reaction is one of the most important strategies to synthesize the dissymmetrical double

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Schiff-base ligands. In this article, we report the crystal structures and properties of two complexes, $[CuL1]_2$ (**1**) and $[NiL2] \cdot H_2O$ (**2**), based on new dissymmetrical Schiff-base ligands H_3L1 (H_3L1 = N-3-carboxylsalicylidene-N′-5-bromosalicylaldehyde-1, 3-diaminopentane) and HL2 (HL2 = N-5-bromosalicylaldehyde-1,3-diaminopentane).

2. Experimental

2.1. *Materials*

3-Carboxylsalicylidene was synthesized by a literature procedure [9]. Other reagents and solvents were of reagent grade and used without purification.

2.2. *Synthesis of Cu(II) precursor [CuL2OH]•2H$_2$O*

Cu(II) precursor was prepared according to the literature method [10]. Twenty millilitres water solution of 5 mmol (1.5 g) $Cu(ClO_4)_2 \cdot 6H_2O$ and 0.6 mmol (0.024 g) NaOH were added into 10 mL ethanol solution of 5 mmol (1.005 g) 5-bromosalicylaldehyde, then 10 mL ethanol solution of 5 mmol (0.52 mL) 1,3-diaminopentane was added dropwise for 4 h in an ice bath under stirring. Removing solvent in vacuum gives a deep blue solid. The blue solid was washed with a little ethanol and diethyl ether and dried in vacuum. Yield 1.32 g (70%). IR (KBr, cm^{-1}): ν_{NH2} 3306, 3240(s); $\nu_{C=N}$ 1627(s).

2.3. *Synthesis of mononuclear complex HCuL1*

After 10 mL ethanol solution of 5 mmol (0.83 g) 3-carboxylsalicylidene was added to 10 mL ethanol solution of 3 mmol (0.61 g) Cu(II) precursor, the mixture was heated for 2 h in a water bath. After cooling, green precipitate obtained was washed with ethanol and diethyl ether and dried. Yield 1.32 g (85%) HCuL1. Anal. Calcd for $C_{20}H_{19}BrCuN_2O_4$ (%): C, 48.50; H, 3.84; N, 5.66; Cu, 12.93. Found: C, 48.65; H, 3.72; N, 5.71; Cu, 13.15. IR (KBr, cm^{-1}): $\nu_{C=N}$ 1601(s), ν_{COOH} 1682(s).

2.4. *Preparation of [CuL1]$_2$ (1)*

Addition of 2 mmol (0.74 g) $Cu(ClO_4)_2 \cdot 6H_2O$ to a solution of 2 mmol (0.98 g) HCuL1 in 15 mL methanol gave a green suspension that was stirred and heated for 30 min and filtered. Evaporation of the filtrate gave a few green diamond crystals suitable for X-ray study. Yield 0.41 g (42%). Anal. Calcd for $C_{40}H_{38}Br_2Cu_2N_4O_8$ (%): C, 48.50; H, 3.84; N, 5.66; Cu, 12.93. Found: C, 48.52; H, 3.92; N, 5.70; Cu, 12.69. IR (KBr, cm^{-1}): $\nu_{C=N}$ 1617(s); ν_{COOH} 1684(s).

2.5. *Preparation of [NiL2]•H$_2$O (2)*

With the substitution of $Ni(ClO_4)_2 \cdot 6H_2O$ for $Cu(ClO_4)_2 \cdot 6H_2O$, we prepared and purified complex **2** by the analogous method described for **1** in Sections 2.2, 2.3, and 2.4.

Red-brown crystals were obtained. Unexpectedly, mononuclear Ni(II) crystal was obtained through the ligand decomposing synchronously. Yield 34%. Anal. Calcd for $C_{24}H_{34}Br_2N_4NiO_3$ (%): C, 44.65; H, 5.27; N, 8.68; Ni, 9.10. Found: C, 44.62; H, 5.29; N, 8.66; Ni, 9.04. IR (KBr, cm^{-1}): ν_{NH2} 3262, 3181(s); $\nu_{C=N}$ 1614(s).

2.6. *Physical measurements*

Elemental analyses for C, H, and N were carried out on a Perkin-Elmer elemental analyzer, model 2400II. Metal contents were determined by EDTA titration. Infrared spectra were recorded on an Avater-360 spectrometer using KBr pellets from 400–4000 cm^{-1}. Thermogravimetric analysis was carried out with a METTLER TOLEDO TG/SDTA 851^e type analyzer in a nitrogen atmosphere and the complexes were heated to 1000°C at a heating rate of 10°C min^{-1}. Magnetic measurements were carried out on polycrystalline samples with a MPMS-7SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all atoms.

2.7. *X-ray analysis*

Single crystals used for data collection of the two compounds were selected and mounted on a Bruker APEX diffractometer with a IICCD detector using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Lorentz and polarization factors were made for the intensity data and absorption corrections were performed using SADABS [11]. The crystal structures were solved using SHELXTL and refined using full-matrix least-squares [12]. The positions of hydrogen atoms were calculated and included in the final cycles of refinement in a riding model along with attached carbon atoms. Crystal data collection and refinement parameters are given in table 1.

Table 1. Crystal data and structure refinement for 1 and 2.

	1	2
Formula	$C_{40}H_{38}Br_2Cu_2N_4O_8$	$C_{24}H_{34}Br_2N_4NiO_3$
Formula weight	989.64	645.08
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	*P*P_21/n	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	10.877(2)	10.9492(7)
b	11.819(2)	11.3743(8)
c	15.203(3)	12.2766(8)
α	90	104.4790(10)
β	91.396(2)	90.7160(10)
γ	90	103.8780(10)
V (Å^3)	1953.9(6)	1432.87(17)
Z	2	2
D_{calcd} (g cm^{-3})	1.682	1.495
μ (mm^{-1})	3.192	3.496
Crystal size (mm^3)	0.21 × 0.14 × 0.08	0.25 × 0.17 × 0.14
θ range (°)	2.18–25.00	1.72–25.00
Independent reflns	3427 ($R_{int} = 0.1064$)	5044 ($R_{int} = 0.0286$)
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0478$, $wR_2 = 0.1118$	$R_1 = 0.0557$, $wR_2 = 0.1931$
R indices (all data)	$R_1 = 0.1243$, $wR_2 = 0.1302$	$R_1 = 0.0807$, $wR_2 = 0.2056$

3. Results and discussion

3.1. *IR spectra and UV-Vis*

In the IR spectra, there are sharp bands at 3306 and 3240 cm^{-1} for Cu(II) precursor and 3262 and 3181 cm^{-1} for **2** ([NiL2] · H_2O), which are characteristic of the –NH_2 group in the Schiff-base ligands [13]. Complexes HCuL1 and $[CuL1]_2$ contain no significant peaks in the region 3100–3300 cm^{-1} since there is no NH_2 group. Bands corresponding to the azomethine (C = N) group occur at 1617 and 1614 cm^{-1} for **1** and **2**, respectively. The data of **1** show –COOH stretches at 1684 cm^{-1}, which is undissociated –COOH in agreement with the result of X-ray analysis. The medium strong peak at 1316 cm^{-1}, 1314–1350 cm^{-1} [14] is assigned to the phenoxy group coordinated to Cu(II) and Ni(II) in **1** and **2**, respectively.

UV-Vis absorption of **1** in methanol solution shows a wide and weak absorption at *ca* 577 nm, due to the d–d transition of Cu(II) ion in square pyramidal coordination.

3.2. *Thermal properties*

There are two decomposition stages (Supplementary material) for **1** in the temperature range 280–780°C. The first stage, in the range 280–318°C, had mass loss 18.3% corresponding to loss of one 5-bromosalicylaldehyde (calculated value 18.4%); the second step in the range 318–880°C, with slow decomposition of 78.2%, corresponds to losing the ligands with the total loss of 96.5%.

Thermogravimetric analysis for **2** shows that it lost 2.9% (expected, 2.7%) at 25–79°C corresponding to the loss of one water. Compound **2** decomposed continuously in the 79–1000°C range, indicating that **2** is not thermally more stable than **1**.

3.3. *Description of the structure*

The crystal structure of $[CuL1]_2$ (**1**) contains one binuclear molecule. The phenoxo oxygen is responsible for the dimerization, yielding pentacoordinate copper. An ORTEP view of one molecule is shown in figure 1. Selected bond distances and angles are shown in table 2. Two coppers are connected by an asymmetric single bridge involving the phenoxo oxygen from 5-bromosalicylaldehyde. Each Cu1 is a 4 + 1 distorted square-pyramid; the basal plane of the copper involves the four donor atoms (N1, N2, O3, O4), with a displacement of the Cu1 atom of 0.103 Å from the mean plane. O4# from the neighboring ligand occupies its apex to complete the configuration, the distance of Cu1–O4# is 2.57 Å (34). Cu1–N1 bond length (1.982(5) Å) is slightly longer than Cu1–N2 (1.981(5) Å); Cu1–O3 (1.938(4) Å) is longer than Cu1–O4 (1.925(33) Å). The bond angle between Cu1#–O4#–Cu1 is 95.10(138)°; the distance between two Cu ions is 3.35(11) Å.

The crystal structure of [NiL2] · H_2O (**2**) contains two crystallographically independent mononuclear molecules having similar structural features. An ORTEP view is shown in figure 2. Selected bond distances and angles are collected in table 3. The coordination environment of the Ni(II) center may be described as elongated octahedral. The equatorial plane is formed by two phenoxo–oxygen and two

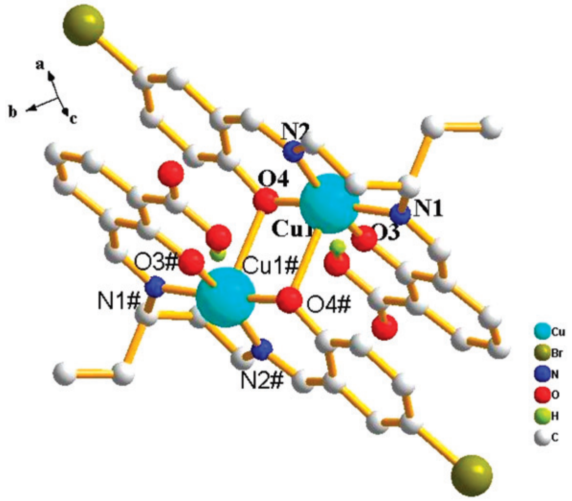

Figure 1. $[CuL1]_2$ (**1**) at 30% probability level, with hydrogen atoms omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Cu1–O4	1.924(4)	N1–Cu1–N2	96.1(2)
Cu1–O3	1.938(4)	O4–Cu1–O3	81.73(18)
Cu1–N1	1.982(5)	O4–Cu1–N1	171.44(2)
Cu1–N2	1.981(5)	O3–Cu1–N1	89.88 (2)
		O4–Cu1–N2	92.02(19)
		O3–Cu1–N2	165.58(2)

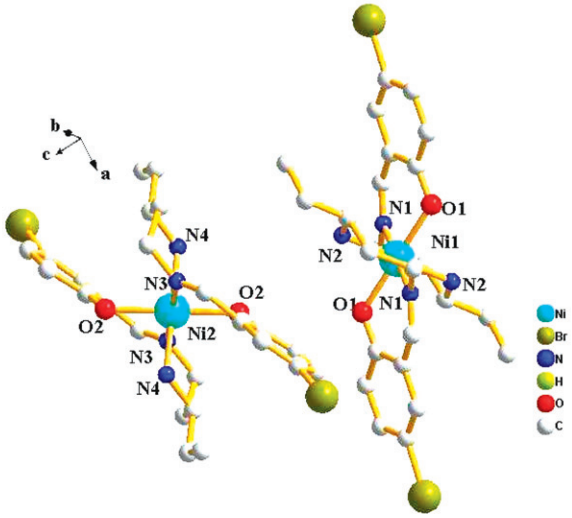

Figure 2. $[NiL2] \cdot H_2O$ (**2**) at 30% probability level. Hydrogens and solvent molecules have been omitted for clarity. #(1) $-x+1$, $-y$, $-z+1$; #(2) $-x+1$, $-y+1$, $-z+2$.

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Ni1–N1	2.041(4)	O1^{i}–Ni1–N2^{i}	90.26(16)
Ni1–N1^{i}	2.041(4)	O1–Ni1–N2^{i}	89.74(15)
Ni1–O1^{i}	2.060(3)	N2–Ni1–N2^{i}	180.0(2)
Ni1–O1	2.060(3)	N3–Ni2–N3^{ii}	180.000(1)
Ni1–N2	2.129(4)	N3–Ni2–O2^{ii}	95.20(18)
Ni1–N2^{i}	2.129(4)	N3^{ii}–Ni2–O2^{ii}	84.80(18)
Ni2–N3	2.058(5)	N3–Ni2–O2	84.80(18)
Ni2–N3^{ii}	2.058(5)	N3^{ii}–Ni2–O2	95.20(18)
Ni2–O2^{ii}	2.068(4)	O2^{ii}–Ni2–O2	180.000(1)
Ni2–O2	2.068(4)	N3–Ni2–N4	85.7(2)
Ni2–N4	2.130(5)	N3^{ii}–Ni2–N4	94.3(2)
Ni2–N4^{ii}	2.130(5)	O2^{ii}–Ni2–N4	92.48(17)
N1–Ni1–N1^{i}	180.0(3)	O2–Ni2–N4	87.52(17)
N1–Ni1–O1^{i}	93.53(16)	N3–Ni2–N4^{ii}	94.3(2)
N1^{i}–Ni1–O1^{i}	86.47(16)	N3^{ii}–Ni2–N4^{ii}	85.7(2)
N1–Ni1–O1	86.47(16)	O2^{ii}–Ni2–N4^{ii}	87.52(17)
N1^{i}–Ni1–O1	93.53(16)	O2–Ni2–N4^{ii}	92.48(17)
O1^{i}–Ni1–O1	180.000(1)	N4–Ni2–N4^{ii}	180.000(1)
N1–Ni1–N2	84.99(17)	N1–Ni1–N2^{i}	95.01(17)
N1^{i}–Ni1–N2	95.01(17)	N1^{i}–Ni1–N2^{i}	84.99(17)
O1^{i}–Ni1–N2	89.74(15)	C10–N2–Ni1	119.3(3)
O1–Ni1–N2	90.26(16)	Ni1–N2–H2A	107.500
N1–Ni1–N2^{i}	95.01(17)	Ni1–N2–H2B	107.500

Symmetry transformations used to generate equivalent atoms: i: $-x+1$, $-y$, $-z+1$; ii: $-x+1$, $-y+1$, $-z$.

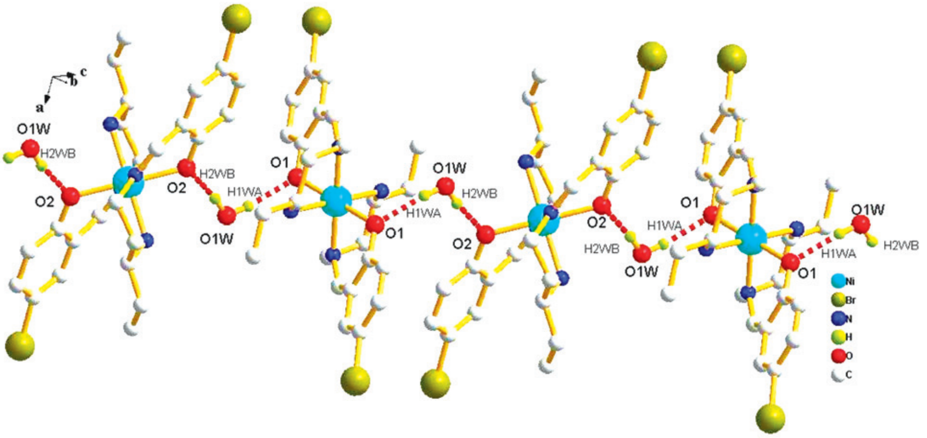

Figure 3. View of the crystal packing of **2**, showing 1D chain of hydrogen-bound molecules. Hydrogens not involved in H-bond are omitted for clarity. (A) $-x+1$, $-y$, $-z+1$; (B) $-x+1$, $-y+1$, $-z+2$.

amide–nitrogen donors from L2, while the axial positions are occupied by two nitrogens of the half-unit ligand with longer bond distances (2.13 Å).

The intramolecular bond distances [Ni1–N1 2.041(4) Å; Ni2–N3 2.058(5) Å] and angles [N1–Ni1–O1 86.47(16)° and N3–Ni2–O2 84.80(18)°] define the core of the two crystallographically independent molecules.

Through hydrogen-bonding interactions between O1 and O2, **2** presents an infinite chain along the *b*-axis (figure 3).

3.4. *Magnetic properties*

The magnetic behavior of **1** is shown in figure 4. At room temperature, the μ_{eff} value for **1** is $2.68\mu_{\text{B}}$, close to the spin-only value of $2.45\mu_{\text{B}}$ expected for two uncoupled Cu(II) ($S = 1/2$) spin systems. As the temperature is lowered, the μ_{eff} value slightly decreases and then rapidly decreases and reaches a value of $2.04\mu_{\text{B}}$ at 2K. The magnetic susceptibility χ_{M} increases from $0.004\,\text{cm}^3\,\text{mol}^{-1}$ at 300 K to broad maximum of $0.26\,\text{cm}^3\,\text{mol}^{-1}$ at 2K. Such magnetic behavior is characteristic of a weak antiferromagnetic exchange interaction. There is only one magnetic interaction, Cu(II)–Cu(II) through the phenoxo oxygen. The experimental magnetic interaction data can be analyzed on the basis of the spin Hamiltonian $\hat{H} = -2J\hat{S}_{\text{Cu1}}\hat{S}_{\text{Cu2}}$,

$$\chi_M = \frac{2Ng^2\beta^2}{KT}\left[\frac{1}{3+\exp(-2J/KT)}\right] + N_\alpha$$

where $N_\alpha = 120 \times 10^{-6}\,\text{cm}^3\,\text{mol}^{-1}$, J is the exchange integral between Cu(II) atoms and N_α is the paramagnetism irrespective to temperature.

The best-fit parameters were $g = 2.17$, $J = -1.02\,\text{cm}^{-1}$, and an agreement factor R $(= \sum(\chi_{\text{obsd}} - \chi_{\text{Calcd}})^2/\sum\chi_{\text{obsd}}{}^2)$ of 1.01×10^{-3}. $J = -1.02\,\text{cm}^{-1}$ indicates a very weak antiferromagnetic exchange interaction between Cu(II) ions. From a magnetic viewpoint, with the unpaired electron of each Cu(II) ion lying in $d(x^2-y^2)$, the magnetic orbitals of both Cu(II) ions extend towards N1, N2, O3, O4, and N1#, N2#, O3#, O4#, respectively, are approximately parallel [15, 16], and a very weak antiferromagnetic interaction should be observed [17].

The magnetic data obtained for **2** are shown in figure 5. At 300 K, the μ_{eff} is $3.09\mu_{\text{B}}$, corresponding to the value expected for an isolated Ni(II) ion ($3.11\mu_{\text{B}}$). It decreases very slowly, then decreases rapidly and reaches $2.15\mu_{\text{B}}$ at 2K. The molecular structure of **2** shows that the metal centers are linked by hydrogen bonds, and such interactions can transmit magnetic interactions [18, 19]. The simpler analytical

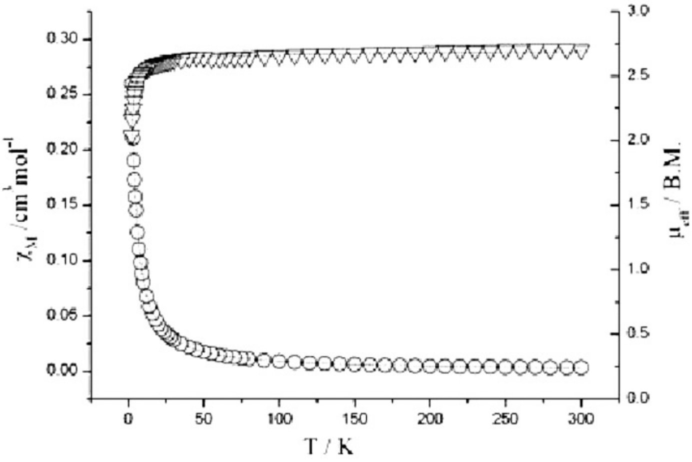

Figure 4. χ_{M} *vs.* T and μ_{eff} *vs.* T plots for **1**.

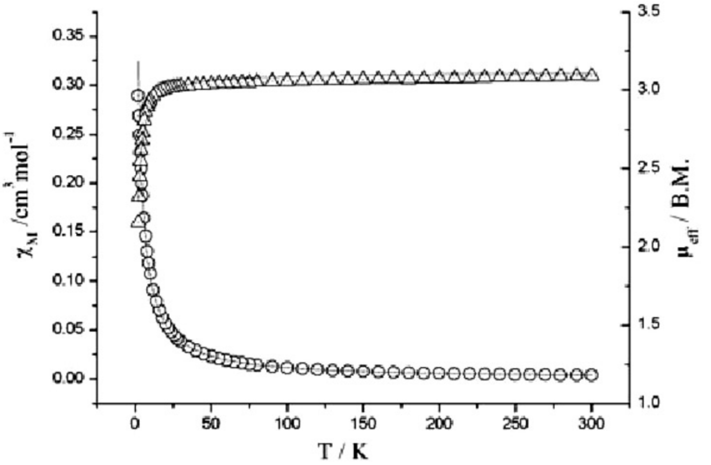

Figure 5. χ_M *vs.* T and μ_{eff} *vs.* T plots for **2**.

expression that may be used to fit the experimental data derives from the following expression:

$$\chi_{\square} = \frac{2Ng_{\square}^2\beta^2}{KT}\frac{\exp(-D/kT)}{1+2\exp(-D/kT)}$$

$$\chi_{\perp} = \frac{2Ng_{\perp}^2\beta^2}{D}\frac{1-\exp(-D/kT)}{1+2\exp(-D/kT)}$$

$$\chi_M = \frac{2\chi_{\perp}+\chi_{\square}}{3}$$

At the same time, the magnetic interactions between the different mononuclear Ni(II) units are disposed by molecular field approximation (zj'), $\chi'_M = \frac{\chi_M}{1-(2zj'/Ng^2\beta^2)\chi_M}$, the best agreement between experimental and calculated data from 300 to 2K corresponds to $zJ' = -0.57\,\text{cm}^{-1}$, $g_{\perp} = 2.20$, $g_{||} = 2.17$, $D = -5.6\,\text{cm}^{-1}$ with an agreement factor $R = (\sum(\chi_{\text{obsd}} - \chi_{\text{Calcd}})^2/\sum\chi_{\text{obsd}}{}^2)$ of 1.85×10^{-3}.

4. Conclusion

In this article, dianionic asymmetrical ligands with imines and carboxyl functions have been synthesized by template reaction. The Cu(II) precursor complex plays an important role during construction of the asymmetrical Schiff-base ligand. Binuclear Cu(II) complex has been obtained through self-assembly of mononuclear HCuL1. Only the mononuclear Ni(II) complex of half-unit ligand has been obtained in the same way. The magnetic properties of both complexes have been discussed in connection with their structures.

Supplementary material

Crystallographic data (excluding structure factors) for the structure analysis have been deposited with the Cambridge Crystallographic Data Center as supplementary publication Nos. 715992 for **1** and 715991 for **2**. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

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