

# Exchange Interaction of a Novel Heterospin Polynuclear Complex Containing Transition Metals and Imino Nitroxide Radicals: $\{[(\text{CuL})\text{Ni}(\text{IM-2Py})_2](\text{ClO}_4)_2\}_2 \cdot 2\text{H}_2\text{O}$

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A novel heterospin complex  $\{[(\text{CuL})\text{Ni}(\text{IM-2Py})_2](\text{ClO}_4)_2\}_2 \cdot 2\text{H}_2\text{O}$  (L = 2, 3-dioxo-5, 6:14, 15-dibenzo-1, 4, 8, 12-tetraazacyclopentadeca-7, 12-diene, IM-2Py = 2-(2'-pyridyl)-4, 4, 5, 5-tetramethyl-4, 5-dihydro-1H-imidazoline-1-oxyl) has been synthesized and its crystal structure was determined by X-ray diffraction analysis. In order to interpret the exchange interaction of this asymmetric heterospin system, a theoretical model has been established. Using this theoretical model the magnetic susceptibility data have been fitted and lead to coupling constant values equal to  $1.4 \text{ cm}^{-1}$  (Ni-Rad) and  $-38.0 \text{ cm}^{-1}$  (Ni-Cu), respectively.

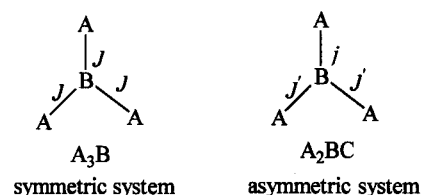
**Keywords** crystal structure, imino nitroxide radical, heterospin complex, exchange interaction

## Introduction

The major research aims in the field of molecular magnetism are on the one hand the design of molecular assemblies that exhibit a spontaneous magnetization and on the other hand the rationalization of magnetostructural correlation.<sup>1</sup> Polynuclear macrocyclic complexes and nitroxide radical metallic complexes are two active fields of research for designing and synthesizing new magnetic materials.<sup>2-6</sup>

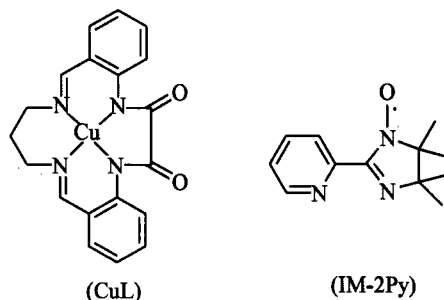
Polynuclear macrocyclic complexes containing multiatomic bridge such as phenolate oxygen, oxamido and oximato groups have been considerably investigated in structural and magnetic characterizations.<sup>7-9</sup> Meanwhile, important results have been obtained for compounds including stable organic nitroxide radicals coordinated to paramagnetic metal ions.<sup>10,11</sup> Therefore, to combine the two synthetic approaches, namely, assembling complexes by nitroxide radical ligands and macrocyclic complexes containing oxamido bridge group will open one of the best strategies to design heterospin systems. And, from a magnetic point of view, some symmetric systems such as  $A_3B$  type (Scheme 1) have been studied much more,<sup>12</sup> but asymmetric system such as  $A_2BC$  model has not been studied so far.

Scheme 1



Herein, we report a novel heterospin polynuclear complex containing different paramagnetic metal ions and imino nitroxide radicals:  $\{[(\text{CuL})\text{Ni}(\text{IM-2Py})_2](\text{ClO}_4)_2\}_2 \cdot 2\text{H}_2\text{O}$  derived from the precursor CuL and IM-2Py radical [Ligand L is 2, 3-dioxo-5, 6:14, 15-dibenzo-1, 4, 8, 12-tetraazacyclopentadeca-7, 12-diene, and radical IM-2Py stands for 2-(2'-pyridyl)-4, 4, 5, 5-tetramethyl-4, 5-dihydro-1H-imidazoline-1-oxyl (Scheme 2)]. We will successively describe the synthesis, crystal structure and magnetic properties of this complex. It is shown that  $\text{CuNiR}_2$  has a mixed spin state arising from the interaction between Ni(II) and Cu(II). The results of this preliminary investigation have prompted us to develop a new method to learn about the fundamental spin-coupling behaviors of heterospin-magnetic system.

Scheme 2



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## Experimental

### Synthesis

**Synthesis of the CuL precursors and IM-2Py** The diformyloxanilide was prepared according to the reported methods.<sup>12,13</sup> The CuL was prepared by refluxing and stirring diformyloxanilide (0.294 g, 1 mmol), 1, 3-propanediamine (0.16 mL, 2 mmol) and Cu(Ac)<sub>2</sub>·H<sub>2</sub>O (0.2 g, 1 mmol) for 2 h in 20 mL of MeOH with the presence of 2 drops of 2 mol/L NaOH. After cooling and filtering, the precipitate was thus obtained. This precipitate was then washed with water, methanol and diethyl ether successively, and dried under vacuum. Yield 52%; IR (KBr)  $\nu_{C=O}$  1640;  $\nu_{C=N}$  1610, 1590 cm<sup>-1</sup>. Anal. calcd for C<sub>19</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub>Cu: C 57.64, H 4.07, N 14.15; found C 57.32, H 4.04, N 14.21.

2-(2'-Pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-1-oxyl was prepared by the reported method.<sup>14</sup>

**Preparation of the title complex**  $\{[(CuL)Ni(IM-2Py)_2](ClO_4)_2\}_2 \cdot 2H_2O$  A solution of 10 mL of MeOH containing Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (37.0 mg, 0.1 mmol) and IM-2Py

(44 mg, 0.2 mmol) was added to CuL precursor (39.5 mg, 0.1 mmol) in 30 mL of MeOH under stirring and slightly heating. The mixture was further stirred for 30 min and filtered. Dark-red crystals were obtained from the filtrate after some days. Anal. calcd for C<sub>86</sub>H<sub>100</sub>Cl<sub>4</sub>Cu<sub>2</sub>N<sub>20</sub>Ni<sub>2</sub>O<sub>26</sub>: C 46.57, H 4.51, N 12.64; found C 46.58, H 4.58, N 12.94.

### X-Ray analysis and structure determination

A dark-red single crystal (0.35 mm × 0.30 mm × 0.20 mm) of the title complex was selected and mounted on a BRUKER SMART 1000 diffractometer equipped with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.071073$  nm). The crystallographic data are given in Table 1. The structure was solved with direct method using the SHELXS-97 program.<sup>15</sup> The H atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints. A full-matrix least-squares refinement on  $F^2$  was carried out using the SHELXL-97 package of program.<sup>16</sup>

**Table 1** Crystal data and structural refinements of the complex

Compound	$\{[(CuL)Ni(IM-2Py)_2](ClO_4)_2\}_2 \cdot 2H_2O$
Empirical formula	C <sub>86</sub> H <sub>100</sub> Cl <sub>4</sub> Cu <sub>2</sub> N <sub>20</sub> Ni <sub>2</sub> O <sub>26</sub>
Color	Dark red
Crystal size (mm)	0.30 × 0.30 × 0.20
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit-cell dimensions	$a = 2.2856(11)$ nm, $b = 2.4498(11)$ nm, $c = 1.8614(8)$ nm, $\beta = 75.768(6)^\circ$
Volume (nm <sup>3</sup> )	10.106(8)
Z	4
Formula weight	2216.16
Density (calcd) (Mg·m <sup>-3</sup> )	1.457
Absorption coefficient (mm <sup>-1</sup> )	0.970
$F(000)$	4584
Diffractometer used	BRUKER SMART 1000
Temperature (K)	293(2)
Radiation	Mo K $\alpha$ ( $\lambda = 0.071073$ nm)
Monochromator	Graphite
$\theta$ range (°)	2.22 to 25.03
Scan type	$\omega$ -2 $\theta$
Index ranges	$-27 \leq h \leq 25$ , $-29 \leq k \leq 23$ , $-22 \leq l \leq 20$
Reflections collected	40002
Independent reflections	17614 ( $R_{int} = 0.4694$ )
Reflections used in refinement	4586
Absorption correction	Semi-empirical from equivalents
$(\Delta/\rho)_{max}$	0.070
Max. and min. transmission	0.8297 and 0.7596
Solution	Direct method
Refinement method	Full-matrix least-squares on $F^2$
Goodness-of-fit on $F^2$	0.952
Final R [ $I > 2\sigma(I)$ ]	$R_1 = 0.1020$ , $wR_2 = 0.2292$
Largest diff. peak and hole	751 and -775 e <sup>-</sup> nm <sup>-3</sup>

$$R = \sum(|F_o| - |F_c|) / \sum |F_o|, \quad wR = (\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w |F_o|^2)^{1/2}$$

## Physical measurements

Elemental analyses for carbon, hydrogen and nitrogen were carried out on a Perkin-Elmer elemental analyzer, model 240. The infrared spectrum was taken on a Nicolet 5DX FT-IR spectrophotometer using KBr pellets. Variable-temperature magnetic susceptibility measurement was carried out in the temperature range of 2–300 K on a Maglab system2000 magnetometer at a field strength of 1 T. Data were corrected for the magnetization of the sample holder and for diamagnetism of the constituent atoms (Pascal table).

## Results and discussion

## Structure

The title compound crystallizes in the monoclinic crystal system, space group  $P2_1/c$ . The cell parameters are  $a = 2.2856(11)$  nm,  $b = 2.4498(11)$  nm,  $c = 1.8614(8)$  nm,  $\beta = 75.768(6)^\circ$ ,  $V = 10.106(8)$  nm<sup>3</sup>,  $Z = 4$ . The selected bond lengths and angles are given in Table 2.

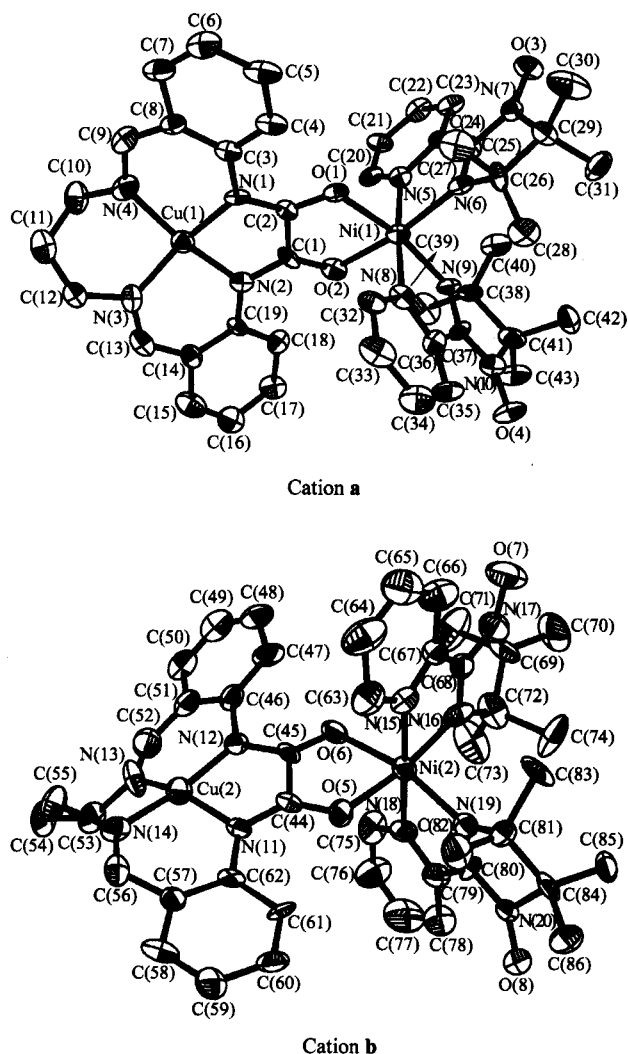
Table 2 Selected bond lengths (nm) and bond angles ( $^\circ$ ) of the complex

Ni(1)—O(2)	0.2003(10)	Ni(1)—O(1)	0.2036(10)	Ni(1)—N(8)	0.2042(13)
Ni(1)—N(9)	0.2049(13)	Ni(1)—N(6)	0.2057(12)	Ni(1)—N(5)	0.2067(13)
Cu(1)—N(1)	0.1891(11)	Cu(1)—N(3)	0.1900(14)	Cu(1)—N(4)	0.1912(15)
Cu(1)—N(2)	0.1936(12)	O(1)—C(2)	0.1289(15)	O(2)—C(1)	0.1270(17)
O(3)—N(7)	0.1311(14)	O(4)—N(10)	0.1274(16)	N(1)—C(2)	0.1287(17)
N(1)—C(3)	0.1370(17)	N(2)—C(1)	0.1342(16)	N(2)—C(19)	0.1398(16)
N(3)—C(13)	0.129(2)	N(3)—C(12)	0.148(2)	N(4)—C(9)	0.1300(19)
N(4)—C(10)	0.152(2)	N(5)—C(20)	0.1321(17)	N(5)—C(24)	0.1403(16)
N(6)—C(25)	0.1286(17)	N(6)—C(26)	0.1503(18)	N(7)—C(25)	0.1356(16)
N(7)—C(29)	0.1470(18)	N(8)—C(32)	0.1323(18)	N(8)—C(36)	0.1373(19)
N(9)—C(37)	0.1319(18)	N(9)—C(38)	0.1527(18)	N(10)—C(37)	0.1374(19)
N(10)—C(41)	0.152(2)	C(1)—C(2)	0.1526(19)	C(8)—C(9)	0.148(2)
Ni(2)—N(16)	0.2006(16)	Ni(2)—O(5)	0.2016(11)	Ni(2)—N(19)	0.2041(16)
Ni(2)—O(6)	0.2048(12)	Ni(2)—N(15)	0.2083(15)	Ni(2)—N(18)	0.2085(14)
Cu(2)—N(12)	0.1856(13)	Cu(2)—N(14)	0.1896(15)	Cu(2)—N(13)	0.1945(17)
Cu(2)—N(11)	0.1946(13)	O(5)—C(44)	0.129(2)	O(6)—C(45)	0.1235(17)
O(7)—N(17)	0.1291(19)	O(8)—N(20)	0.1293(16)	N(11)—C(44)	0.1291(19)
N(11)—C(62)	0.1445(19)	N(12)—C(45)	0.1346(19)	N(12)—C(46)	0.150(2)
N(13)—C(52)	0.134(2)	N(13)—C(53)	0.148(2)	N(14)—C(56)	0.129(2)
N(14)—C(55)	0.156(2)	N(15)—C(63)	0.137(2)	N(15)—C(67)	0.137(2)
N(16)—C(68)	0.128(2)	N(16)—C(72)	0.149(2)	N(17)—C(68)	0.138(2)
N(17)—C(69)	0.148(2)	N(18)—C(79)	0.134(2)	N(18)—C(75)	0.140(2)
N(20)—C(84)	0.154(2)	C(44)—C(45)	0.158(2)		
O(2)—Ni(1)—O(1)	79.8(4)	O(2)—Ni(1)—N(8)	88.7(4)	O(1)—Ni(1)—N(8)	93.8(5)
O(2)—Ni(1)—N(9)	92.1(4)	O(1)—Ni(1)—N(9)	168.7(4)	N(8)—Ni(1)—N(9)	78.1(5)
O(2)—Ni(1)—N(6)	171.3(5)	O(1)—Ni(1)—N(6)	94.5(4)	N(8)—Ni(1)—N(6)	98.2(5)
N(9)—Ni(1)—N(6)	94.5(4)	O(2)—Ni(1)—N(5)	93.5(5)	O(1)—Ni(1)—N(5)	90.8(4)
N(8)—Ni(1)—N(5)	175.2(5)	N(9)—Ni(1)—N(5)	97.6(5)	N(6)—Ni(1)—N(5)	80.0(5)
N(1)—Cu(1)—N(3)	159.0(5)	N(1)—Cu(1)—N(4)	93.6(6)	N(3)—Cu(1)—N(4)	92.6(7)
N(1)—Cu(1)—N(2)	86.8(5)	N(3)—Cu(1)—N(2)	93.4(6)	N(4)—Cu(1)—N(2)	162.0(5)
C(2)—O(1)—Ni(1)	115.5(9)	N(16)—Ni(2)—O(5)	170.2(6)	N(16)—Ni(2)—N(19)	96.8(6)
O(5)—Ni(2)—N(19)	89.4(5)	N(16)—Ni(2)—O(6)	94.8(5)	O(5)—Ni(2)—O(6)	80.4(5)
N(19)—Ni(2)—O(6)	165.7(5)	N(16)—Ni(2)—N(15)	78.3(7)	O(5)—Ni(2)—N(15)	92.9(6)
N(19)—Ni(2)—N(15)	102.8(6)	O(6)—Ni(2)—N(15)	87.7(5)	N(16)—Ni(2)—N(18)	101.6(6)
O(5)—Ni(2)—N(18)	87.3(5)	N(19)—Ni(2)—N(18)	77.5(7)	O(6)—Ni(2)—N(18)	92.0(6)
N(15)—Ni(2)—N(18)	179.6(7)	N(12)—Cu(2)—N(14)	167.8(6)	N(12)—Cu(2)—N(13)	94.1(6)
N(14)—Cu(2)—N(13)	90.3(6)	N(12)—Cu(2)—N(11)	86.0(6)	N(14)—Cu(2)—N(11)	94.3(6)
N(13)—Cu(2)—N(11)	157.2(6)				

The title complex consists of two cations which have the same constitution but different in some bond lengths, bond angles and dihedrals (Table 3), four  $\text{ClO}_4^-$  and two waters. An ORTEP drawing of the complex cation  $[(\text{CuL})\text{Ni}(\text{IM-2Py})_2]^{2+}$  is shown in Fig. 1.

**Table 3** Dihedral angles ( $^\circ$ ) of some important least-square planes

Least-square planes		Dihedral angles ( $^\circ$ )
Ni(1)N(5)C(24)C(25)N(6)	(P1)	P1-P2 87.6
Ni(1)N(8)C(36)C(37)N(9)	(P2)	P1'-P2' 82.1
Ni(1)O(2)C(1)C(2)O(1)	(P3)	P1-P3 93.0
Cu(1)N(1)C(2)C(1)N(2)	(P4)	P1'-P3' 93.6
Ni(2)N(15)C(67)C(68)N(16)	(P1')	P2-P3 94.7
Ni(2)N(18)C(79)C(80)N(19)	(P2')	P2'-P3' 83.8
Ni(2)O(5)C(44)C(45)N(6)	(P3')	P3-P4 173.8
Cu(2)N(11)C(44)C(45)N(12)	(P4')	P3'-P4' 175.3



**Fig. 1** ORTEP views of the cations **a** and **b**. Thermal ellipsoids are drawn at the 30% probability level.

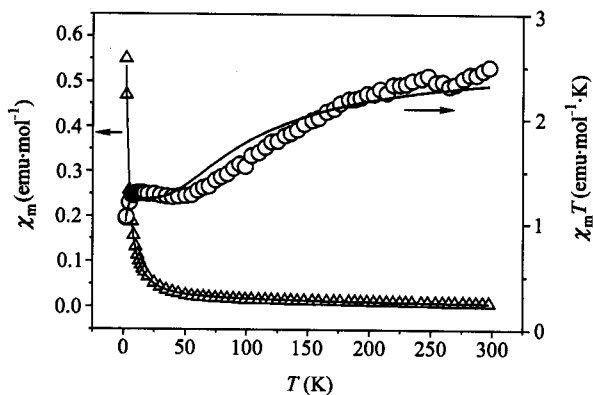
Within each cation of the complex the Cu(II) ion displays the square planar coordination with the  $\text{N}_4$  donor set

from the respective macrocyclic ligand L. The square plane in each case suffers a small tetrahedral distortion as indicated by deviations of the relevant atoms from the mean plane of the  $\text{N}_4$  atoms. In cation **a**, deviation of Cu(1) from the least-square plane through N(1), N(2), N(3) and N(4) is 0.00223 nm; in cation **b**, deviation of Cu(2) from the least-square plane through N(11), N(12), N(13) and N(14) is -0.00923 nm.

The coordination environments around Ni(II) are similar in cation **a** and **b**. Ni(II) ion is hexacoordinated by four nitrogen atoms of two different IM-2Py ligands and by two oxygen atoms of an oxamido macrocyclic ligand, the coordination octahedron is severely distorted. The Cu(II) atom is connected to the Ni(II) via the *exo-cis* oxygen atoms of the oxamido macrocyclic ligands with the  $\text{Ni}\cdots\text{Cu}$  separations of 0.5281 and 0.5296 nm for **a** and **b**, respectively. In cation **a**, the dihedral angle between the planes which share the C(1)—C(2) bond of oxamido is  $173.8^\circ$ ; and in cation **b**, the dihedral angle between the planes which share the C(44)—C(45) bond of oxamido is  $175.3^\circ$ . Some important dihedral angles are shown in Table 3 and these dihedral angles reflect the main difference between cation **a** and cation **b**.

#### Magnetic behavior

The variable temperature magnetic susceptibility of the complex was investigated in the range of 2–300 K at a magnetic field of 1 T and the results are shown in Fig. 2 as a plot of  $\chi_m T$  (and  $\chi_m$ ) vs.  $T$ . The  $\chi_m T$  value per molecule is equal to  $2.61 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$  at 300 K, which is lower than the spin-only value expected for one  $S = 1$  [Ni(II)], one  $S = 1/2$  [Cu(II)] and two  $S = 1/2$  (radical) uncorrelated spins ( $4.25 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$ ), indicating the presence of antiferromagnetic interactions between the spin carriers.

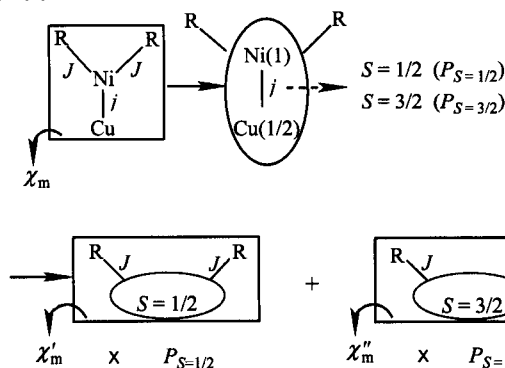


**Fig. 2** Plots of  $\chi_m$  and  $\chi_m T$  versus  $T$  for the title complex with the solid line showing the fitting values.

For present complex, the four-spin system is asymmetric from a magnetic point of view. The spin Hamiltonian that fully describes the situation of this system can be given as  $\hat{H} = -2J_{\text{NiR}}\hat{S}_{\text{Ni}}(\hat{S}_{\text{R1}} + \hat{S}_{\text{R2}}) - 2j_{\text{NiCu}}\hat{S}_{\text{Ni}}\hat{S}_{\text{Cu}}$ , where  $J_{\text{NiR}}$  and  $j_{\text{NiCu}}$  characterize the Ni—R and Ni—Cu exchange interac-

tions, respectively. In order to define accurately the energy level of the system, a  $24 \times 24$  matrix should be diagonalized, and the solution to this question is quite complicated. However, the nature of the experimental data allows us to make some simplifications to the above question and still interpret the magnetic data in a meaningful fashion. Being enlightened by Miller,<sup>17</sup> a simple model can be established to evaluate quantitatively the magnitude of the spin exchange interactions in the four-spin asymmetric system (Scheme 3).

Scheme 3



In this model, first, we consider Ni-Cu as a fragment having coupling states of  $S = 1/2$  and  $S = 3/2$ . The populations of each state at various temperatures can be derived:<sup>18</sup>

$$P_{S=1/2} = \frac{2\exp(-3j/KT)}{4 + 2\exp(-3j/KT)} \quad (1)$$

$$P_{S=3/2} = \frac{4}{4 + 2\exp(-3j/KT)} \quad (2)$$

where the  $j$  presents the Ni—Cu interaction. Second, we can evaluate the interactions of each state of the fragment with the two radicals using spin Hamiltonian  $\hat{H}' = -2J(\hat{S}_{(1/2)}\hat{S}_{R1} + \hat{S}_{(1/2)}\hat{S}_{R2})$  and  $\hat{H}'' = -2J(\hat{S}_{(3/2)}\hat{S}_{R1} + \hat{S}_{(3/2)}\hat{S}_{R2})$ , where  $\hat{S}_{(1/2)}$  and  $\hat{S}_{(3/2)}$  present spin operator of coupling states of fragment ( $S = 1/2$  and  $S = 3/2$ ). The coupling constant  $J$  is the average of the interaction between the radical and different coupling states. Assuming  $g_{Ni} = g_{Cu} = g_R = g$  to simplify the question and using the Van Vleck equation results in Eq. (3) and Eq. (4) for magnetic susceptibilities of each coupling state and two radicals, respectively:

$$\chi'_m = \frac{Ng^2\beta^2}{4KT} \left[ \frac{1 + \exp(-2J/KT) + 10\exp(-J/KT)}{1 + \exp(-2J/KT) + 2\exp(-J/KT)} \right] \quad (3)$$

$$\chi''_m = \frac{Ng^2\beta^2}{4KT} \times \left[ \frac{10 + \exp(-5J/KT) + 10\exp(-2J/KT) + 35\exp(3J/KT)}{2 + \exp(-5J/KT) + 2\exp(-2J/KT) + 2\exp(3J/KT)} \right] \quad (4)$$

where  $J$  is exchange interaction between fragment ( $S = 1/2$  or  $S = 3/2$ ) and radical. Last, the total magnetic susceptibility  $\chi_m$  is

$$\chi_m = \chi'_m \times P_{S=1/2} + \chi''_m \times P_{S=3/2} \quad (5)$$

The least-squares analysis of magnetic susceptibility data led to  $J = 1.4 \text{ cm}^{-1}$ ,  $j = -38.0 \text{ cm}^{-1}$  and  $g = 2.09$ ; agreement factor  $R = \sum[(\chi_m)_{\text{obs}} - (\chi_m)_{\text{calcd}}]^2 / \sum[(\chi_m)_{\text{obs}}]^2 = 8.05 \times 10^{-4}$ .

The small positive  $J$  value implies a weak ferromagnetic magnetic interaction between Ni(II) and radical. This agrees with reported Ni(II)-imino nitroxide complexes exhibiting ferromagnetic exchange couplings between Ni(II) and radical.<sup>19,20</sup> The ferromagnetic exchange coupling is mainly because of the orbital orthogonality between the  $\pi^*$  molecular orbital of the IM-2Py and the metal  $d_{x^2-y^2}$ . Due to the lower overlap density of IM-2Py radical and nickel(II) ion resulting from high electronegativity of oxygen, the ferromagnetic coupling is accordingly small.<sup>21</sup> According to Kahn,<sup>22</sup> the antiferromagnetic interaction between Cu(II) and Ni(II) arises from the non-zero overlap between the  $d_x^2$  or  $d_{x^2-y^2}$  magnetic orbitals centered on the two metal ions and delocalized towards ligands. The larger the overlap, the stronger the antiferromagnetic interaction. This may be explained on the basis of structural distortion, and in this regard, one of the relevant factors is the value of the dihedral angle ( $\gamma$ ) between the mean equatorial plane of the metal ion and the oxiamido plane;<sup>23,24</sup> the greater the value of  $\gamma$ , the stronger the antiferromagnetic coupling. The greater  $\gamma$  value ( $\sim 174^\circ$ ) of this complex results in relatively strong antiferromagnetic coupling between Cu(II) and Ni(II). When the sample is cooled,  $\chi_m T$  decreases, then reaches a plateau with  $\chi_m T = 1.37 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$  corresponding to the temperature range (4–70 K) where only the ground state ( $S = 3/2$ ) is thermally populated. Below 4 K, zero splitting effect of Ni(II) and intermolecular antiferromagnetic interaction result in  $\chi_m T$  decreasing sharply.

## Conclusion

Our results suggest that the introducing of radicals into polynuclear complexes explored a new route for designing heterospin complexes. Meanwhile, in order to interpret the exchange interaction of this heterospin system, a theoretical model has been established. Using this theoretical model the magnetic susceptibility data have been fitted and lead to coupling constant values equal to  $1.4 \text{ cm}^{-1}$  (Ni-Rad) and  $-38.0 \text{ cm}^{-1}$  (Ni-Cu), respectively. The fitting results indicate that the theoretical model is suitable to evaluate this heterospin system.

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