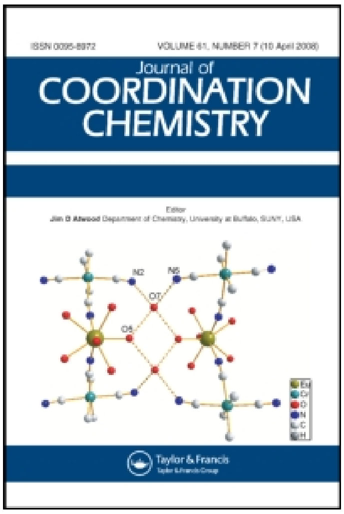

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# Synthesis, structure, and properties of a 1-D copper(II) complex with nitronyl nitroxide radicals

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A 1-D chain complex $[Cu(NIT4Py)(IDA)]_\infty$ (NIT4Py = 2-(4′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide and IDA = iminodiacetate) has been prepared and characterized by single-crystal X-ray diffraction, IR, TGA, and magnetic analysis. Each Cu(II) is five-coordinate with distorted square pyramidal geometry. Each IDA bridges two Cu(II) ions via one carboxylate which occupies the axial site of Cu(II), leading to a chain structure composed of Cu(II)-radical cations and IDA anions. In the complex, there exist three magnetic exchange pathways, (i) interaction between units of (Cu(II)-NIT4Py) through IDA, (ii) Cu(II)-NIT4Py interaction, and (iii) NIT4Py-NIT4Py interaction through space. Compared with the first two magnetic interactions, the last magnetic exchange interaction should be too weak to be counted because of the large distance of the neighboring NIT4Py molecules (4.993 Å). Analysis of the magnetic properties was performed using the Bleany–Bowers (dimer) model, showing that the complex exhibited both weak antiferromagnetic interaction between the Cu(II) and NIT4Py, and between the units of (Cu(II)-NIT4Py) through IDA with exchange coupling parameters $J = -7.28\,\text{cm}^{-1}$ and $zJ' = -0.40\,\text{cm}^{-1}$.

*Keywords*: Crystal structure; Nitronyl nitroxide; Copper complex; Magnetic property

## 1. Introduction

The design of molecular materials with interesting magnetic properties has been one of the major challenges during the past two decades. Research focuses on the chemical design of molecule assemblies that exhibit spontaneous magnetization and also on rationalization of magnetostructural correlations [1, 2].

Metal complexes based on nitronyl nitroxides have the ability to coordinate with metal ions and act as magnetic couplers, leading to new functional materials with a variety of structural topologies [3–12]. Iminodiacetic acid (IDA) plays both chelating and bridging roles [13–18], the latter giving polymeric chain compound which extends parallel to the *a*-axis in the crystal of $[Cu(IDA)(H_2O)_2]_\infty$ [15]. If 2-(4′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (NIT4Py) coordinates with Cu(II) substituting

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for $H_2O$, a new 1-D coordination compound with IDA and radical would be created. The 1-D coordination compound $[Cu(NIT4Py)(IDA)]_\infty$ was synthesized. Here we report the crystal structure and properties of the new complex.

## 2. Experimental

### 2.1. *Materials and equipment*

All reagents and solvents were purchased commercially and used without purification. Elemental analyses for carbon, hydrogen, and nitrogen were carried out on a Model 240 Perkin–Elmer elemental analyzer. The infrared spectrum was taken on a Shimadzu IR spectrophotometer Model 408 in the 4000–600 $cm^{-1}$ region using KBr pellets. Temperature dependence of magnetic susceptibilities was measured on a MPMS-7 SQUID magnetometer from 2.0 to 300 K. Diamagnetic corrections were made with Pascal's constants for all constituent atoms. Thermal stability (TG-DTA) studies were carried out on a Dupont thermal analyzer from room temperature to 800°C.

### 2.2. *Synthesis of $[Cu(NIT4Py)(IDA)]_\infty$*

2-(4′-Pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide was prepared by the literature method [19, 20]. Dipotassium iminodiacetate was prepared by addition of KOH (0.112 g, 2.0 mmol) to aqueous solution of iminodiacetic acid (0.132 g, 1.0 mmol). The mixture was stirred for 20 min, water was removed by desiccation under vacuum, and white powder was obtained (yield: 78%).

The complex $[Cu(NIT4Py)(IDA)]_\infty$ was synthesized by addition of an aqueous solution (5 mL) of dipotassium iminodiacetate (0.063 g, 0.6 mmol) to a MeOH solution (30 mL) which contained $Cu(ClO_4)_2 \cdot 6H_2O$ (0.111 g, 0.3 mmol) and NIT4Py (0.144 g, 0.6 mmol). The mixture was stirred for 40 min and then filtered; the blue filtrate was allowed to stand at room temperature for 1 week. Blue crystals were obtained. Anal. Calcd Found: (Anal. calcd for $C_{16}H_{21}N_4O_6Cu$): C, 44.76(44.80); H, 4.90(4.94); N, 12.98(13.06)%.

**Caution!** Perchlorate salts are potentially explosive. Be careful when $Cu(ClO_4)_2 \cdot 6H_2O$ is used.

### 2.3. *X-ray crystallography*

A blue single crystal ($0.30 \times 0.25 \times 0.20\,mm^3$) of the title complex was selected and mounted on a Bruker Smart 1000 diffractometer equipped with graphite-monchromated Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å). Data were collected at room temperature by $\phi - \omega$ scan technique in the range $2.22° \le \theta \le 25.02°$. The collected data were reduced by SAINT [21] and empirical absorption correction was done using the SADABS program [22]. The structure was solved with direct methods using SHELXS-97 [23]. The H atoms were assigned with common isotropic displacement factors and included in the final refinement with geometrical restraints. A full-matrix least-squares refinement on $F^2$ was carried out using SHELXL-97 [24].

Table 1. Crystallographic data and processing parameters for $[Cu(NIT4Py)(IDA)]_\infty$.

| | |
|---|---|
| Empirical formula | $C_{16}H_{21}CuN_4O_6$ |
| Formula weight | 428.91 |
| Temperature (K) | 293(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Monoclinic |
| Space group | $P2(1)/c$ |
| Unit cell dimensions (Å, °) | |
| $a$ | 9.221(6) |
| $b$ | 7.804(5), |
| $c$ | 24.941(17) |
| $\beta$ | 96.848(12) |
| Volume (Å$^3$) | 1782(2) |
| $Z$ | 4 |
| $D_{Calcd}$(g cm$^{-3}$) | 1.599 |
| Absorption coefficient (mm$^{-1}$) | 1.268 |
| $F$(000) | 888 |
| Crystal size (mm$^3$) | 0.30 × 0.25 × 0.20 |
| $\theta$ Range for data collection (°) | 2.22–25.02 |
| Limiting indices | $-7 \le h \le 10$, $-9 \le k \le 8$, $-29 \le l \le 27$ |
| Reflections collected | 5881 |
| Independent reflection | 2659 [$R$(int) = 0.0370] |
| Completeness to $\theta = 25.02$ | 84.5% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7855 and 0.7022 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 2659/0/244 |
| Goodness-of-fit on $F^2$ | 1.044 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0682$, $wR_2 = 0.1380$ |
| $R$ indices (all data) | $R_1 = 0.0764$, $wR_2 = 0.1417$ |
| Largest different peak and hole (e Å$^{-3}$) | 0.982 and −1.193 |

All non-hydrogen atoms were readily located and refined with anisotropic thermal parameters; $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $wR_2 = (\sum|(F_o{}^2| - |F_c|^2)^2/(\sum w|F_o|^2)^2$, respectively, with the weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0193P)^2 + 17.51P]$, where $P = (F_o^2 + 2F_c^2)/3$. A summary of the crystallographic data is given in table 1. Selected bond distances and angles are given in table 2.

## 3. Results and discussion

### 3.1. *Crystal structure and determination*

An ORTEP drawing of the title complex is shown in figure 1. Each Cu(II) exhibits a distorted square pyramidal coordination (type 4 + 1). Each tridentate IDA ligand coordinates to the Cu(II) occupying three basal plane positions; the other basal plane position is occupied by pyridyl nitrogen from the NIT4Py. Each IDA ligand is a $\mu_2$-bridge linking two Cu(II) via one carboxylate, occupying the apical position of the coordination sphere with bond length of 2.314(5) Å. Thus, the 1-D chain structure is formed by Cu(II)-radical cations and IDA anions. The distortion of this square pyramidal stereochemistry towards a hypothetical trigonal one as obtained from the angles $\theta$ = N4–Cu1–N3 and $\rho$ = O3–Cu1–O5 is $\tau = (\theta - \rho)/60 = 0.027$

Table 2. Selected bond lengths (Å) and angles (°) for $[\mathrm{Cu(NIT4Py)(IDA)}]_\infty$[a].

| | | | |
|---|---|---|---|
| Cu(1)–O(3) | 1.952(4) | N(2)–O(2) | 1.273(7) |
| Cu(1)–O(5) | 1.957(4) | N(2)–C(7) | 1.350(8) |
| Cu(1)–N(4) | 1.968(5) | N(2)–C(2) | 1.502(8) |
| Cu(1)–N(3) | 1.983(5) | N(3)–C(10) | 1.324(8) |
| Cu(1)–O(6)#1 | 2.314(5) | N(3)–C(12) | 1.357(8) |
| N(1)–O(1) | 1.265(7) | O(3)–C(13) | 1.284(8) |
| N(1)–C(7) | 1.368(8) | O(4)–C(13) | 1.224(7) |
| N(1)–C(1) | 1.509(8) | O(5)–C(16) | 1.286(8) |
| | | O(6)–C(16) | 1.230(8) |
| O(3)–Cu(1)–O(5) | 166.4(2) | O(1)–N(1)–C(1) | 121.1(5) |
| O(3)–Cu(1)–N(4) | 83.6(2) | C(7)–N(1)–C(1) | 110.9(5) |
| O(5)–Cu(1)–N(4) | 83.88(19) | O(2)–N(2)–C(7) | 126.5(5) |
| O(3)–Cu(1)–N(3) | 96.6(2) | O(2)–N(2)–C(2) | 121.5(5) |
| O(5)–Cu(1)–N(3) | 94.5(2) | C(10)–N(3)–Cu(1) | 123.5(4) |
| N(4)–Cu(1)–N(3) | 168.0(2) | C(12)–N(3)–Cu(1) | 119.1(4) |
| O(3)–Cu(1)–O(6)#1 | 90.2(2) | C(13)–O(3)–Cu(1) | 113.9(4) |
| O(5)–Cu(1)–O(6)#1 | 95.7(2) | C(16)–O(5)–Cu(1) | 113.0(4) |
| N(4)–Cu(1)–O(6)#1 | 92.3(2) | C(16)–O(6)–Cu(1)#2 | 132.2(5) |
| N(3)–Cu(1)–O(6)#1 | 99.7(2) | C(7)–N(2)–C(2) | 111.8(5) |
| O(1)–N(1)–C(7) | 127.3(5) | C(10)–N(3)–C(12) | 117.1(5) |
| C(14)–N(4)–Cu(1) | 106.4(4) | C(15)–N(4)–Cu(1) | 107.1(4) |

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x+2$, $y+1/2$, $-z+1/2$; #2: $-x+2$, $y-1/2$, $-z+1/2$.

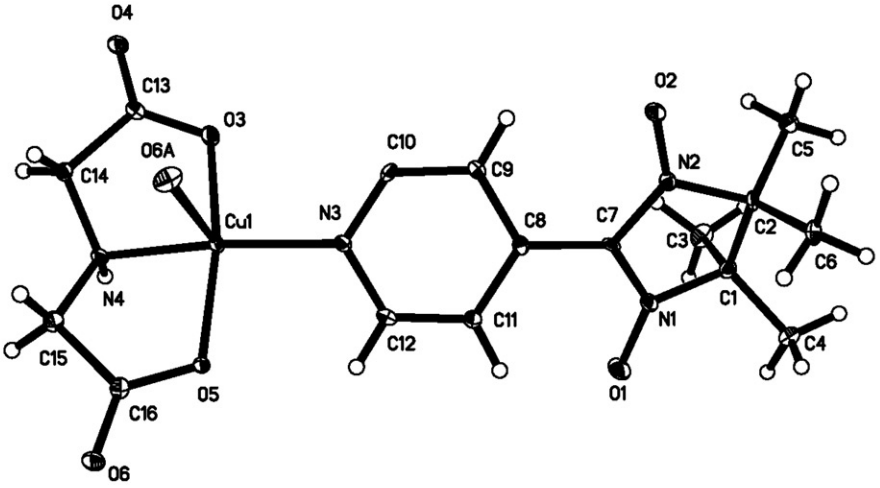


Figure 1. ORTEP of $[\mathrm{Cu(NIT4Py)(IDA)}]_\infty$ (A: $-x+2, y+1/2, -z+1/2$). Thermal ellipsoids are scaled to enclose 15% probability.

suggests that the complex is a near ideal square pyramid [25, 26]. The O1–N1–C7–N2–O2 moieties are coplanar as expected, forming a dihedral angle of 22.2° with the pyridyl ring. Within the chain, the distance between successive Cu(II) ions is 5.878 Å.

The 1-D chain is created by the linkage of IDA molecule. A sketch of the 1-D complex is shown in figure 2.

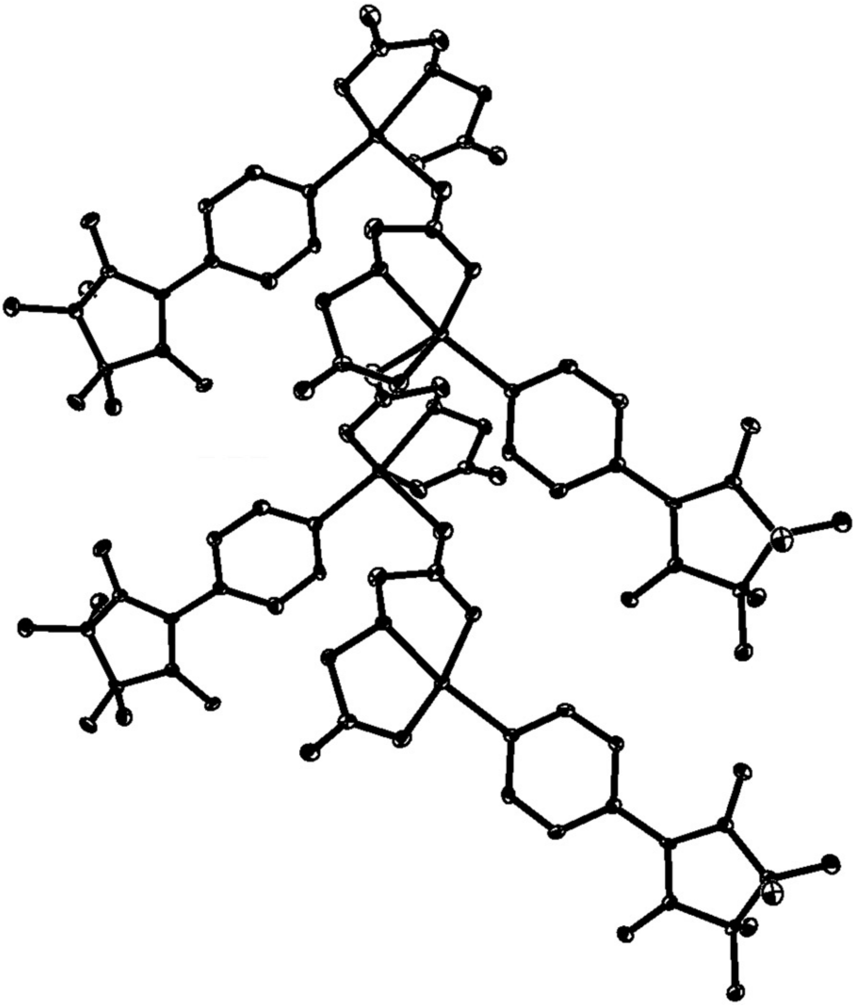


Figure 2. A sketch of $[Cu(NIT4Py)(IDA)]_{\infty}$ along *b* direction.

In the crystal packing of the complex, hydrogen bonds of N–H···O type have been observed between hydrogen from the amido group of the IDA molecule and oxygen from the carboxylate group of the other IDA. The geometric data for such hydrogen bonds are as follows: bond length of 2.813 Å for N(4)–O(4) $(-x, y+1/2, -z+1/2)$, bond angle of 108.4° for N(4)–H(4)···O(4). Every nitrogen and uncoordinated oxygen of IDA take part in such hydrogen bonds connecting adjacent units of [Cu(NIT4Py)(IDA)] into 2-D structures.

### 3.2. *Infrared spectrum*

The IR spectrum shows a strong broad band at $1610\,cm^{-1}$, characteristic $\nu(COO^{-1})$ band. The other strong absorption at $1366\,cm^{-1}$ is due to the $\nu$(C–O) vibration. The absence of a characteristic band at $1250\,cm^{-1}$ indicates deprotonation of carboxylate in

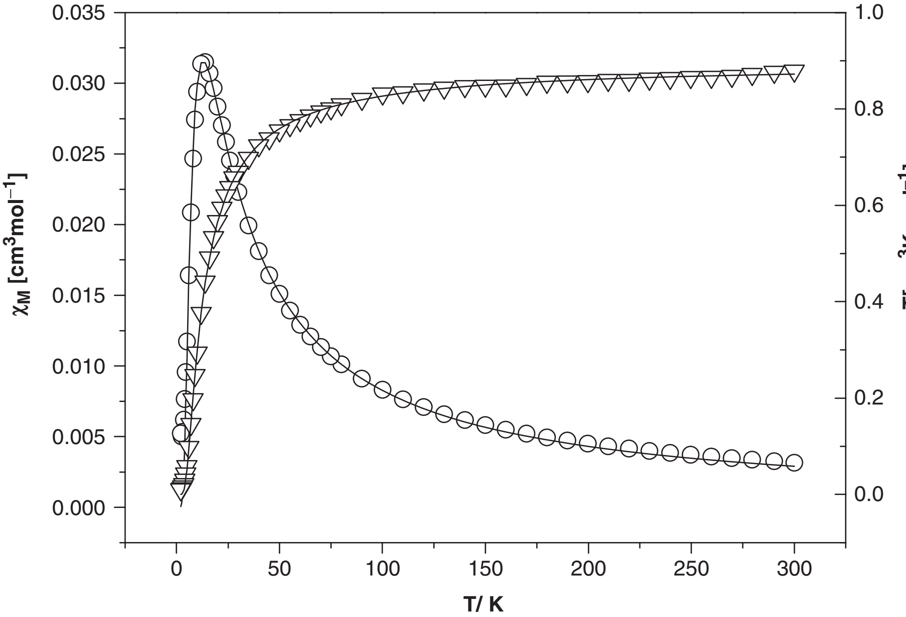


Figure 3. Temperature dependence of $\chi_M T(\Delta)$ and $\chi_M(\circ)$ for $[Cu(NIT4Py)(IDA)]_\infty$ and their corresponding theoretical curves (solid lines).

IDA and coordination to the metal. The strong band observed at $1340\,cm^{-1}$ is the $\nu$(N–O) band.

### 3.3. *Thermal gravimetric analysis*

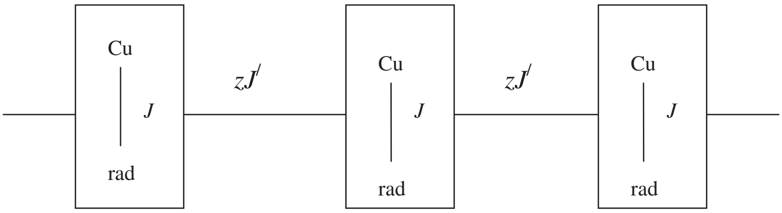
The TGA diagram shows two steps of weight loss. From 215 to 236°C, one NIT4Py is lost (Anal. Calcd: 54.6%, exp: 54.3%). From 236 to 800°C, one IDA molecule is lost (Anal. Calcd: 30.8%, exp: 27.0%), indicating complete decomposition of the complex. The final residue is CuO.

### 3.4. *Magnetic properties*

The magnetic susceptibilities, $\chi_M$, of the title complex were measured in the range 2.0–300 K at a magnetic field of 1000 G, and plots of $\chi_M$ and $\chi_M T$ *versus* $T$ are shown in figure 3. The $\chi_M T$ value per molecule at room temperature is $0.879\,cm^3\,K\,mol^{-1}$. When the temperature is decreased to 30 K, the $\chi_M T$ decreases gradually and then rapidly decreases, reaching $0.011\,cm^3\,K\,mol^{-1}$ at 2 K. The magnetic behavior indicates that weak antiferromagnetic interactions are predominant in the complex.

To quantify the exchange coupling constants, the complex was treated as a 1-D chain of Cu(II)-NIT4Py binuclear units (scheme 1).

The magnetic data were fitted on the isotropic model $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$, where $J$ is the interaction parameter between two paramagnetic centers. For Cu(II)–NIT4Py



Scheme 1. The model of magnetic interaction in the complex.

Table 3. Selected magnetic parameters for Cu and NIT4Py compounds.

| Complex | $J$ (cm$^{-1}$) | $g$ | Reference |
|---|---|---|---|
| $Cu(NITpPy)_2(NO_3)_2$ | $-14.1 \pm 0.1$ | 2.022 | [31] |
| $Cu(NITpPy)_2(CH_3COO)_2$ | $-16.7 \pm 0.6$ | 2.033 | [31] |
| $Cu(NITpPy)_2[N(CN)_2]_2 \cdot (H_2O)_2$ | $-17.0 \pm 0.2$ | 2.070 | [31] |
| $Cu(NITpPy)_2[N(CN)_2]_2 \cdot n CH_3CN$ needle crystals | $-18.2 \pm 0.6$ | 2.046 | [31] |
| $Cu(NITpPy)_2[N(CN)_2]_2 \cdot n CH_3CN$ Plate crystals | $-16.3 \pm 0.5$ | 2.05 | [31] |
| $[Cu_2\ (\mu\text{-}ClCH_2CO_2)_2(ClCH_2CO_2)_2(NITpPy)_2(H_2O)_2]CH_3OH$ | $-170$ | 2.0 | [32] |
| $[Cu(Cl_2CHCO_2)_2(NITpPy)_2(H_2O)]$ | $-11.5$ | 1.98 | [32] |
| $[Cu(Cl_3CCO_2)_2(NITpPy)_2(H_2O)]$ | $-13$ | 1.97 | [32] |
| $[Cu(NIT4Py)(IDA)]_\infty$ | $-7.28$ | 2.14 | This work |

complexes, the analysis of the magnetic properties is performed using the Bleany–Bowers (dimer) model [27]. The theoretical expression of the magnetic susceptibility is

$$\chi_{\text{bi}} = \frac{2Ng^2\beta^2}{kT}[3 + \exp(-2J/kT)]^{-1} \tag{1}$$

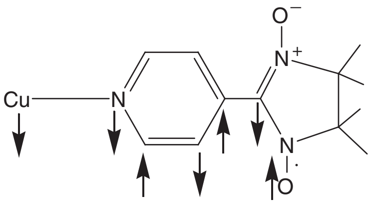
An additional coupling parameter, $zJ'$, was added in equation (2) (a mean field correction) to take into account the magnetic behavior between the Cu(NIT4Py) units [28–30]. The theoretical expression of the molar magnetic susceptibility is

$$\chi_{\text{M}} = \frac{\chi_{\text{bi}}}{1 - (2zJ'N\beta^2g^2)\chi_{\text{bi}}} \tag{2}$$

where $J$ represents the Cu(II)-NIT4Py interacting through the pyridyl ring of NIT4Py and $zJ'$ represents the units of (Cu(II)-NIT4Py) interacting through the IDA molecules.

The best-fit parameters are $J = -7.28\,\text{cm}^{-1}$, $zJ' = -0.40\,\text{cm}^{-1}$, $g = 2.14$ with $R = 7.63 \times 10^{-3}$, where $R$ is defined as $R = \sum[(\chi_{\text{M}})_{\text{obs}} - (\chi_{\text{M}})_{\text{calcd}}]^2 / \sum(\chi_{\text{M}})^2_{\text{obs}}$. The negative $J$ and $zJ'$ imply weak antiferromagnetic interaction between Cu(II) and NIT4Py, and also between Cu(II)-NIT4Py through IDA.

The possible reason for the weak magnetic exchange interaction is the long distance between Cu(II) ion and the N–O group of NIT4Py (the pyridyl nitrogen from the NIT4Py coordinates to Cu(II)) and poor overlap between the metal and radical centered magnetic orbitals (22.2°) [31, 32]. The relevant magnetic data of some complexes are listed in table 3. When the magnetic exchange interaction



Scheme 2. The model of spin polarization in the complex.

between Cu(II) and the N–O group of NIT4Py dominates, the weak magnetic exchange interaction is obtained in the compound. However, when the magnetic exchange interaction between Cu(II) and Cu(II) dominates, the difference between the strong and the weak magnetic exchange interaction is due to the coordination mode of carboxylate.

Weak interaction between copper(II) ions has been previously observed for carboxylate-bridged complexes in which the carboxylate group bridges from the basal to the axial position with a long Cu–O distance. Generally, magnetic coupling for out-of-plane carboxylate-bridged compounds is relatively weak because of the near-orthogonality of magnetic orbitals. The value of $J$ is small as expected for this kind of compound exhibiting an out-of-plane bridging framework. Meanwhile, magnetic coupling for in-plane carboxylate-bridged compounds is relatively strong [33–35]. In this compound, the relatively long Cu–O axial distance (Cu1–O6A: 2.314 Å), out-of-plane exchange pathway (Cu1–O6A–Cu1A: 83.2°) dominating magnetic exchange interaction between Cu(II) ion and the N–O group of NIT4Py and the large dihedral angle of 22.2° between nitroxide and the pyridyl ring are favorable to weak magnetic interactions. Thus, the compound has the smallest $J$ value in table 3. The approximation used to obtain the Hamiltonian to calculate the $J$ value is somewhat simplified, which can explain the $g$ value being somewhat large in comparison with other copper-radical compounds in table 3.

The weak antiferromagnetic interaction between the Cu(II) and NIT4Py in this compound can be explained by McConnell's mechanism [36]. According to this model, a spin distribution would induce the contrary spin on the adjacent atom due to the spin polarization. In the radical ligand, the spin distribution arising from intramolecule spin polarization of the adjacent atoms leads to alternating positive and negative spin density on the carbon backbone of the radical ligand. Large positive spin density is located on the NO groups, while large negative spin density is located on the $sp^2$ carbon bridging two NO groups and the alternative delocalization takes place over the pyridyl ring due to the spin polarization. This in turn induces the negative spin density on the pyridyl nitrogen atom of NIT4Py (scheme 2).

The magnetic orbital $d_{x^2-y^2}$ of Cu(II) has $\sigma$-character and cannot participate in $\pi$-conjugation. The orthogonal geometry between the 2p$\pi$ orbital of the nitrogen of the pyridyl ring and the $d_{x^2-y^2}$ orbital of Cu(II) leads to the same spin sign of the nitrogen atom in the pyridyl ring with the Cu(II). In phenyl nitroxide derivatives, the negative spin densities are at the *para* nitrogen of the pyridyl ring and the Cu(II) is negatively spin polarized [37, 38]. Thus, it is an antiferromagnetic relation between the Cu(II) spin and the main spin of NIT4Py because of the spin antiparallel.

## 4. Conclusion

We have demonstrated a 1-D metal-nitronyl nitroxide radical complex, $[Cu(NIT4Py)(IDA)]_\infty$. Magnetic coupling between Cu(II) and NIT4Py and between units of Cu(II)-NIT4Py are both weak antiferromagnetic interactions. Although a compound with weak antiferromagnetism was obtained, our effort is in pursuit of 1-D metal-nitronyl nitroxide radical coordination magnets (single-molecule magnets). To realize the purpose, new radicals (thiazyl, verdazyl) will be used [39].

## Acknowledgments

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