A Ladder-like One-dimensional Chain Based on a New Biradical and Cu^{II}: Crystal Structure and Magnetic Properties[†]

Wang, Chao(王超) Ma, Yue(马越) Yang, Xi(杨曦) Yan, Shiping(阎世平) Liao, Daizheng*(廖代正)

Department of Chemistry, Nankai University, Tianjin 300071, China

A new biradical di(4-(1'-oxyl-3'-oxido-4',4',5',5'-tetramethyl-4',5'-dihydro-1'*H*-imidazol-2'-yl)phenyl) ether (**1**) and its copper complex **2** were synthesized and characterized structurally. The X-ray structure determination revealed that, the complex is in the triclinic *P*-1 space group and displays a ladder-like structure. Each copper atom is surrounded by four oxygen atoms from hexafluoroacetylacetone and two oxygen atoms from biradical. The magnetic measurements show that biradical **1** exhibits a weak intramolecular nitroxide-nitroxide antiferromagnetic coupling and copper complex **2** possesses weak ferromagnetic coupling (J=5.09 cm^{-1}) between Cu^{II} and radical, which attributed to interaction between copper spin and the axially coordinated nitronyl nitroxide spin.

Keywords copper, biradical, magnetic properties, crystal structures

Introduction

Some of stable radicals,[1] especially the Ullman's type, and their complexes[2] exhibit unusual magnetic properties due to their unpaired electron and versatile coordination mode. In this Ullman's radical, the coordination of the two oxygens (O-N-C-N-O) with metals can be used to form low dimensional structures.[3-5] These low dimensional radical-metal complexes show a wide variation of magnetic properties.[6-29,46-48] On the other hand, biradicals[35-45] themselves have two unpaired electrons and these electrons can interact with each other, then metal complexes containing biradicals are expected to show more manifold magnetic properties than mono-radicals. However, the use of biradicals as ligands has been somewhat limited due to the difficulty in synthesis. Therefore, to explore further the research area based on radicals, it seemed interesting to us to design and synthesize new biradicals. With this aim, in this paper, we first present the main structural features and magnetic properties of a new biradical, di(4-(1'-xyl-3'-oxido-4',4',5',5'-tetramethyl-4',5'-dihydro-1'*H*-imidazol-2'-yl)phenyl) ether (**1**) ($C_{26}H_{32}N_4O_5$). We then report its copper(II) complex **2** ($C_{47}H_{38}Cl_2Cu_2F_{24}N_4O_{13}$), in which the radical oxygen only acts as monodentate ligand and each biradical molecule links four copper atoms to form a ladder-like framework.

Experimental

Material and general methods

All the commercial chemicals were used as received without further purification. The solvents were purified by standard methods. 4-(4-Formylphenoxy)benzaldehyde and 2,3-bis(hydroxylamino)-2,3-dimethylbutane were synthesized by the procedure described by Dann[30] and Ullman,[34] respectively. Elemental analyses for C, H and N were carried out on Perkin-Elmer elemental analyzer (Model 240). Variable temperature magnetic susceptibilities were measured on SQUID MPMS XL-7 magnetometer in the temperature range of 2.0 and 300 K at a magnetic field of 0.5 T using polycrystalline samples. Diamagnetic corrections were estimated from Pascal's constants for all constituent atoms.

Single-crystal structure determination

The data were collected at 113(2) K on a Rigaku MM-007 single-crystal diffractometer equipped with CCD area detector with graphite-monochromatized Mo Kα (λ=0.71070 Å). A summary of crystallographic data is given in Table 1. The empirical absorption corrections by semi-empirical from equivalents were carried out. The structure was solved with the SHELX program,[33] and refined by full-matrix least square methods based on F^2, with anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms

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* E-mail: liaodz@nankai.edu.cn

Received July 12, 2010; revised August 16, 2010; accepted August 20, 2010.

Project supported by the National Natural Science Foundation of China (Nos. 20631030 and 90922032), the National Basic Research Program of China (973 Program, 2007CB815305), and Natural Science Foundation of Tianjin (No. 09JCYBJC05500).

[†] Dedicated to the 60th Anniversary of Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

were located theoretically and refined isotropically. The selected bond lengths and bond angles are listed in Table 3.

Synthesis of 1

2,3-Bis(hydroxylamino)-2,3-dimethylbutane (2.96 g, 20.0 mmol) and 4-(4-formylphenoxy)benzaldehyde (2.26 g, 10.0 mmol) were dissolved in a minimum amount of methanol. After stirring at room temperature for 48 h, this slurry was filtered and washed with 5 mL cold methanol twice. This off-white powder was suspended in 150 mL CH_2Cl_2, and then 30 g (0.125 mol) PbO_2 was added to this suspension. The resulting mixture was stirred vigorously for 30 min at room temperature and filtered, and then the dark blue solution was obtained, dried over anhydrous $MgSO_4$ overnight. After filtration to remove any inorganic salts, the CH_2Cl_2 solution was evaporated to a small amount under reduced pressure. The residue was purified by column chromatography on silica gel [*V*(hexane)∶*V*(actone)＝3∶1 as eluent]. The last violet blue fraction was collected, evaporated to dryness, and recrystallized using *V*(hexane)∶*V*(actone)＝5∶1. The obtained precipitate was filtered off, washed with cold hexane and dried in air. Single-crystal suitable for X-ray analysis was obtained by slow evaporation of a heptane-dichloromethane solution. Yield 820 mg (17.1%). M.p. 189—192 ℃. Elemental analysis calculated for $C_{26}H_{32}N_4O_5$ (480.56): C 64.92, H 6.71, N 11.66; found C 65.11, H 6.62, N 11.80.

Preparation of the copper complex (2)

51.4 mg (0.1 mmol) of $Cu(hfac)_2 \cdot 2H_2O$ was dissolved in 20 mL of boiling *n*-heptane and this light blue-green transparent solution was refluxed for 2 h. When the solution was cooled to about 60 ℃, 24.0 mg (0.05 mmol) of **1** was added under stirring and followed by 10 mL of CH_2Cl_2. After stirred for an additional 1 h, the final dark green solution was allowed to cool, filtered and was kept at 4 ℃ for 3 d to give dark green crystals suitable for X-ray analysis. Yield: 19 mg (25%). Elemental analysis calculated for $C_{47}H_{38}Cl_2Cu_2F_{24}N_4O_{13}$(1520.81): C 37.12, H 2.52, N 3.68; found C 36.89, H 2.66, N 3.81.

Results and discussion

Crystal structure

Summary of crystallographic data is listed in Table 1. Selected bond lengths and angles of **1** and **2** are summarized in Tables 2 and 3. As shown in Figures 1 and 2, this compound is a typical biradical with the N—O bond length in the range of 1.2836—1.2862 Å. The molecule of **1** is not a centrosymmetric compound due to the angle of C(11)-O(3)-C(14) to be 119.81°. The shortest distance between two oxygen atoms from the adjacent molecules is 4.089 Å, while the shortest distance between two oxygen atoms within the molecule is 9.231 Å.

Table 1 Summary of crystallographic data for **1** and **2**

	1	**2**
Empirical formula	$C_{26}H_{32}N_4O_5$	$C_{47}H_{38}Cl_2Cu_2F_{24}N_4O_{13}$
Formula weight	480.56	2242.36
Temperature	113(2) K	113(2) K
Wavelength	0.71070 Å	0.71070 Å
Crystal system	Monoclinic	Triclinic
Space group	*P*2(1)/*c*	*P*-1
Unit cell dimensions		
a	10.202(2) Å	10.550(6) Å
b	22.707(5) Å	16.045(11) Å
c	11.601(2) Å	18.554(13) Å
α	90°	107.492(13)°
β	109.20(3)°	92.251(9)°
γ	90°	90.234(11)°
Volume	2538.1(9) $Å^3$	2993(3) $Å^3$
Z	4	2
Calculated density	1.258 Mg/m^3	1.688 Mg/m^3
Absorption coefficient	0.088 mm^{-1}	0.937 mm^{-1}
F(000)	1024	1520
Crystal size	0.30 mm×0.24 mm×0.10 mm	0.80 mm×0.74 mm×0.56 mm

Continued

	1	**2**
θ range for data collection	1.859° to 27.857°	1.475° to 27.104°
Limiting indices	$-12\leqslant h\leqslant 12$	$-12\leqslant h\leqslant 12$
	$-21\leqslant k\leqslant 27$	$-18\leqslant k\leqslant 19$
	$-13\leqslant l\leqslant 13$	$-22\leqslant l\leqslant 21$
Reflections collected/unique	14532/4464 [R(int) = 0.0609]	22549/10574 [R(int) = 0.0758]
Completeness to theta	99.7%	99.2%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max and min transmission	0.9912 and 0.9740	0.5768 and 0.3157
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4464/0/325	10574/0/856
Goodness-of-fit on F^2	1.052	0.957
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0470$, $wR_2 = 0.1151$	$R_1 = 0.0729$, $wR_2 = 0.1715$
R indices (all data)	$R_1 = 0.0598$, $wR_2 = 0.1234$	$R_1 = 0.1041$, $wR_2 = 0.1880$

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

Bond length			
O(1)—N(1)	1.2858(18)	O(2)—N(2)	1.2862(19)
O(4)—N(3)	1.2836(18)	O(5)—N(4)	1.2857(18)
N(1)—C(1)	1.357(2)	N(1)—C(2)	1.503(2)
N(2)—C(1)	1.360(2)	N(2)—C(5)	1.500(2)
N(3)—C(20)	1.355(2)	N(3)—C(21)	1.504(2)
N(4)—C(20)	1.356(2)	N(4)—C(24)	1.504(2)
Bond angle			
C(11)-O(3)-C(14)	119.81(13)	O(1)-N(1)-C(1)	127.22(14)
O(1)-N(1)-C(2)	120.07(13)	C(1)-N(1)-C(2)	112.20(14)
O(2)-N(2)-C(1)	127.16(15)	O(2)-N(2)-C(5)	120.19(14)
C(1)-N(2)-C(5)	112.02(14)	O(4)-N(3)-C(20)	126.75(14)
O(4)-N(3)-C(21)	121.08(13)	C(20)-N(3)-C(21)	111.86(13)
O(5)-N(4)-C(20)	126.94(15)	O(5)-N(4)-C(24)	120.80(13)
C(20)-N(4)-C(24)	111.95(13)	N(1)-C(1)-N(2)	106.95(15)
N(3)-C(20)-N(4)	107.65(15)		

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

Bond length			
Cu(1)—O(4)	1.938(4)	Cu(1)—O(1)	1.939(4)
Cu(1)—O(2)	1.947(4)	Cu(1)—O(3)	1.950(4)
Cu(1)—O(10)	2.321(4)	Cu(1)—O(11)	2.501(4)
Cu(2)—O(8)	1.950(4)	Cu(2)—O(6)	1.953(5)
Cu(2)—O(5)	1.957(4)	Cu(2)—O(7)	1.959(5)
Cu(2)—O(12)	2.331(4)	Cu(2)—O(9)	2.457(4)
N(1)—O(9)	1.275(6)	N(2)—O(10)	1.290(6)
N(3)—O(11)	1.285(6)	N(4)—O(12)	1.291(6)
Bond angle			
C(21)-O(13)-C(34)	120.2(5)	O(4)-Cu(1)-O(1)	178.06(16)
O(4)-Cu(1)-O(2)	88.69(18)	O(1)-Cu(1)-O(2)	91.88(18)
O(4)-Cu(1)-O(3)	93.42(17)	O(1)-Cu(1)-O(3)	86.51(17)
O(2)-Cu(1)-O(3)	165.01(17)	O(4)-Cu(1)-O(10)	84.89(15)

Continued

O(1)-Cu(1)-O(10)	93.19(16)	O(2)-Cu(1)-O(10)	98.10(16)
O(3)-Cu(1)-O(10)	96.87(16)	O(4)-Cu(1)-O(11)	77.10(16)
O(1)-Cu(1)-O(11)	104.83(16)	O(2)-Cu(1)-O(11)	78.51(16)
O(3)-Cu(1)-O(11)	87.49(16)	O(10)-Cu(1)-O(11)	161.70(15)
O(8)-Cu(2)-O(6)	87.19(19)	O(8)-Cu(2)-O(5)	176.58(15)
O(6)-Cu(2)-O(5)	92.31(19)	O(8)-Cu(2)-O(7)	93.73(19)
O(6)-Cu(2)-O(7)	163.35(16)	O(5-)Cu(2)-O(7)	87.71(19)
O(8)-Cu(2)-O(12)	84.89(16)	O(6)-Cu(2)-O(12)	103.83(16)
O(5)-Cu(2)-O(12)	91.94(16)	O(7)-Cu(2)-O(12)	92.81(16)
O(8)-Cu(2)-O(9)	81.91(16)	O(6)-Cu(2)-O(9)	80.93(16)
O(5)-Cu(2)-O(9)	101.36(16)	O(7)-Cu(2)-O(9)	82.75(16)
O(12)-Cu(2)-O(9)	165.75(15)		

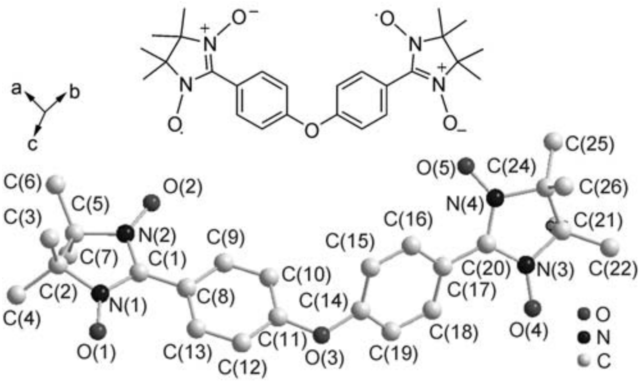

Figure 1 Chemical structure of biradical (**1**).

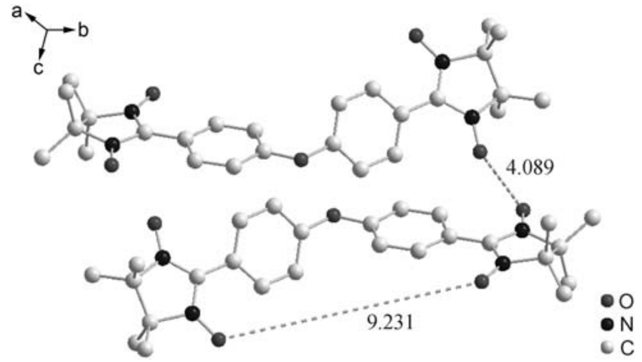

Figure 2 View of the molecular structure showing the distance of the oxygen atoms.

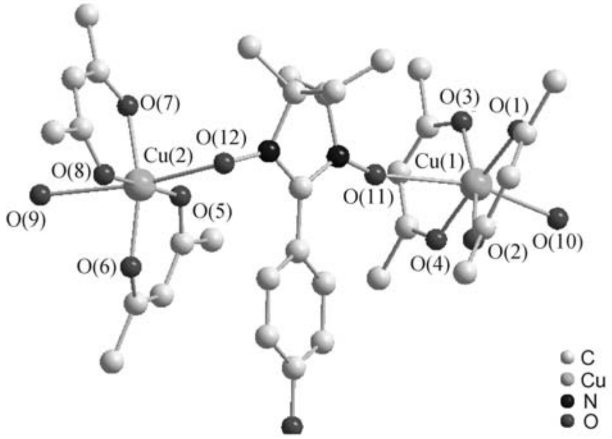

Figure 3 The coordination environments of two nonequivalent copper atoms in **2**.

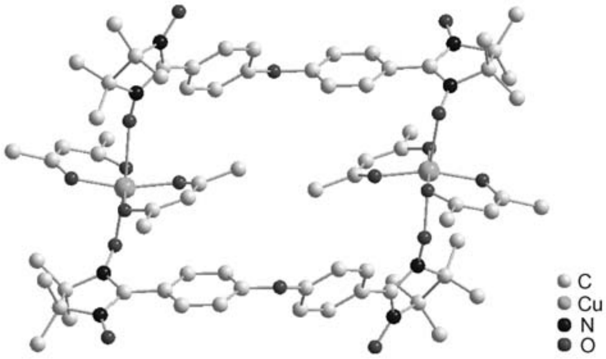

Figure 4 The rectangle unit of ladder-like framework. The fluorine atoms, hydrogen atoms and the disordered dichloromethane are omitted for clarity.

Single-crystal X-ray analysis revealed triclinic *P*-1 space group for **2**. This complex is formed by infinite chains, in which the [Cu(hfac)$_2$] fragments are connected via the O-N-C-N-O atom groups from nitronyl nitroxide units. Figures 3 and 4 show a part of a one dimensional chain structure of **2**, in this complex, the copper atoms are all in severely distorted coordination environments and coordinated by four oxygen atoms coming from two hfacs occupying the equatorial positions and two oxygen atoms from two different nitronyl nitroxide units in the axial positions. As shown in Figure 3, the coordination environments of two copper atoms [Cu(1) and Cu(2)] are not completely equivalent but exceedingly similar. In the octahedral coordination environment of Cu(1) center, the two radical oxygen atoms [O(11) and O(12)] have different bond lengths with Cu(1) [Cu(1)—O(11) of 2.501 Å, Cu(1)—O(10) of 2.321 Å]. Both of them are much longer than the equatorial ones (1.938—1.950 Å). The bond angles of

Cu(1)-O(10)-N(2) and Cu(1)-O(11)-N(3) are 118.59° and 150.93°, respectively. This bond angles are in good agreements with the previously reported.[6,9,17,26,32]

Because one biradical has two radical unit, and the four coordination sites of this biradical are all employed to construct this one-dimensional chain, thus, not a simple one dimensional chain but a ladder-like structure (Figure 5) consisting of two parallel alternating Cu-R-Cu-R chains is formed with the adjacent stairs distance of 8.023 Å. The shortest interchain Cu—Cu distance is 8.286 Å, while the Cu—Cu distance of two parallel alternating chains is 11.552 Å, which is longer than 7.864 Å, the shortest intra-chain Cu—Cu distance along the Cu-R-Cu-R chains.

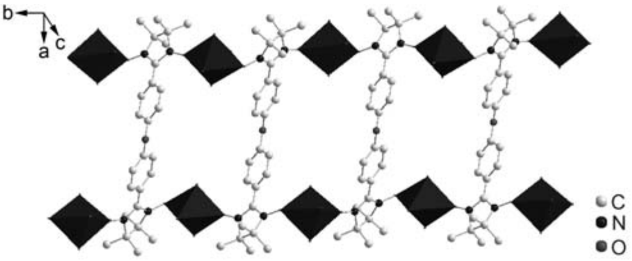

Figure 5 The ladder-like chain structure of the complex **2**. The copper atoms are displayed as octahedrons, hexfluoroacetylacetone, hydrogen atoms and the disordered dichloromethane are omitted for clarity.

Magnetic properties

The magnetic behavior of the biradical is shown in Figure 6. The data of variable temperature magnetic susceptibility were collected in the range of 2.0—300 K at 5000 Oe field. The $\chi_M T$ value at room temperature is 0.765 $cm^3•K•mol^{-1}$, which is slightly higher than the expected value for uncoupled system of two radicals (0.750 $cm^3•K•mol^{-1}$) with g value of 2.00. The $\chi_M T$ value decreases gradually on cooling. Below 20 K, the $\chi_M T$ value decreases sharply reaching 0.323 $cm^3•K•mol^{-1}$ at 2.0 K, suggesting that there are antiferromagnetic interactions between the biradical molecules. These antiferromagnetic interactions are further demonstrated by negative θ value ($T=-3.03$ K) when the Curie-Weiss law is used to simulate the $\chi_M{}^{-1}$—T linear, while a rational $C=0.778$ $emu•K•mol^{-1}$ is obtained. To evaluate the exchange coupling constants within this biradical at the temperature range of 5—300 K, Eq. (1) derived from the spin Hamiltonian $\hat{H}=-2J\hat{S}_R\hat{S}_{R'}$ is applied.

$$\chi_M=\frac{Ng^2\beta^2}{KT}\left(\frac{2}{3+\exp(\frac{-2J}{KT})}\right) \tag{1}$$

where J corresponds to the magnetic interactions between the two radical unit within one molecule. The best fitting parameters were obtained as, $g=2.01$, $J=-2.12$ cm^{-1}. Below 5 K, these theoretical analysis did not give us a satisfactory fit with the experimental data, possibly due to the complicated intermolecular interactions.

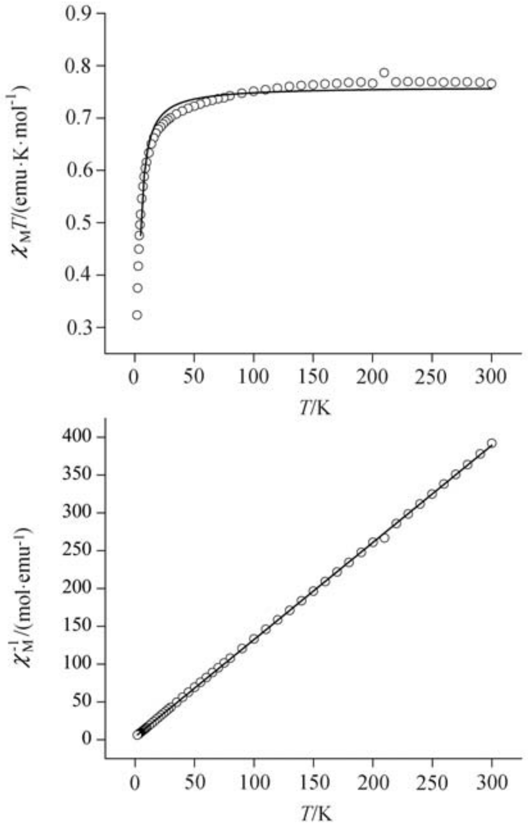

Figure 6 The magnetic behavior of the biradical. The solid line of the later figure is the simulation by Curie-Weiss law with the parameters: $T=-3.03$ K, $C=0.778$ $emu•K•mol^{-1}$.

The magnetic properties of **2** in the form of $\chi_M T$ versus T plots are presented in Figure 7. At room temperature, the $\chi_M T$ is 0.870 $cm^3•mol^{-1}•K$, which is slightly higher than the expected value (0.750 $cm^3•mol^{-1}•K$) for an uncoupled system with one Cu(II) ion ($S=1/2$, $\chi_M T=0.375$ $cm^3•mol^{-1}•K$) and one radical unit ($S=1/2$, $\chi_M T=0.375$ $cm^3•mol^{-1}•K$). As the temperature decreases, $\chi_M T$ value increases gradually below 80 K, then increases sharply on cooling and reaches a peak of 2.025 $cm^3•mol^{-1}•K$ at 3.5 K. Finally, $\chi_M T$ decreases slowly as the temperature descended. The magnetic behavior suggests ferromagnetic interaction is dominant within **2**. The decrease of $\chi_M T$ values in the low temperature region is most likely due to very weak inter-chain interaction.

The experimental data of **2** were analyzed by using an $S=1/2$ ferromagnetic chain model[31] with the Hamiltonian $H=-2J\Sigma S_i•S_{i+1}$, where all symbols have their usual meaning (Eq. 2).

$$\chi_{chain}=\frac{Ng^2\beta^2}{2KT}\left(\frac{1+5.7979916Y+16.902653Y^2+29.376885Y^3+29.832959Y^4+14.036918Y^5}{1+2.7979916Y+7.0086780Y^2+8.6538644Y^3+4.5743114Y^4}\right)^{\frac{2}{3}} \tag{2}$$

where $Y = J/KT$.

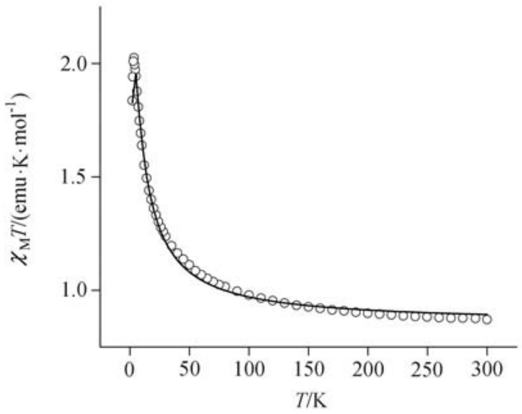

Figure 7 Plots of $\chi_M T$ versus T of complex **2**. The solid line represents the best theoretical fitting with the parameter: $g = 2.13$, $J = 5.09$ cm^{-1} and $zJ' = -0.38$ cm^{-1}.

A molecular field correction has been taken into account in the mean-field approximation with the parameter zJ' (Eq. 3) as the magnetic interaction between chains.[49]

$$\chi_M = \frac{\chi_{\text{chain}}}{1 - \left(\frac{2zJ'}{Ng^2\beta^2}\right)\chi_{\text{chain}}} \tag{3}$$

The best fit parameters for the data are $g = 2.13$, $J = 5.09$ cm^{-1} and $zJ' = -0.38$ cm^{-1}. This obtained parameter value are comparatively close to the previously reported for a similar compound with different substituents attached to the radical ring, and these parameters are listed in the Table 4. This ferromagnetic coupling between the radical and the Cu(hfac)$_2$ probably attribute to that the π* orbital of the radical oxygen and nitrogen is nearly orthogonal to the magnetic $3d_{x^2-y^2}$ orbital of the copper atom.[17]

Table 4 One dimensional ferromagnetic chain compounds with different substituents

R	g factor	J/cm^{-1}	zJ'/cm^{-1}	Hamiltonian
Me (low temperature)[6]	2.08	−30.8	0.046	$J_{ij}\sum_{ij}S_iS_j$
i-Pr (low temperature)[9]	2.13	−24.5	−0.002	$J_{ij}\sum_{ij}S_iS_j$
n-Pr[32]	2.10	−32.1	0.038	$J_{ij}\sum_{ij}S_iS_j$
Ph-C≡C-SiMe$_3$-p[17]	2.1	6	N/A	$-2J_{ij}\sum_{ij}S_iS_j$
Ph-C≡N-p[26]	2.03	6.7	−0.72	$-2J_{ij}\sum_{ij}S_iS_j$
This work	2.13	5.09	−0.38	$-2J_{ij}\sum_{ij}S_iS_j$

Conclusion

In conclusion, we have characterized a new biradical **1** and its copper complex **2** structurally and magnetically. The complex **2** is in the triclinic *P*-1 space group and displays a ladder-like structure. The magnetic measurements show that biradical **1** exhibits a weak intramolecular nitroxide-nitroxide antiferromagnetic coupling and copper complex **2** exhibits a weak ferromagnetic coupling between Cu$^{\text{II}}$ and radical.

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(E1007124 Ding, W.)