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Synthesis and magnetic properties of an iminonitroxide-substituted phenolate–Cu complex

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Abstract

A new spin-chelate, iminonitroxide-substituted phenolate–copper complex (**1**), was designed and prepared. The structure of the complex **1** was considerably deviated from a square-planar geometry. The dihedral angle between the two planes defined by a set of copper, oxygen and nitrogen atoms was about 41° . The complex was found to have a relatively strong ferromagnetic interaction and a weaker antiferromagnetic interaction: $J/k_B = +250$ K and $\theta = -17$ K using a three-spin model. The ferromagnetic interaction was assigned to the intramolecular interaction between the copper atom and the iminonitroxide. The antiferromagnetic interaction was assigned as an intermolecular interaction. These assignments were supported by susceptibility measurements for the diluted sample in polyvinyl chloride (PVC) film. The antiferromagnetic interaction was tentatively assigned due to the observed short intermolecular contacts between the C5 and O1 atoms or between the H5 and O1 atoms.

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1. Introduction

Recently, much attention has been focused on magnetic properties of organic, inorganic and their composite materials [1]. In this field, radical-based approaches utilizing stable nitroxides as ligands to magnetic metal ions have been successfully developed by Gatteschi's group (nitronyl nitroxides) [2] and Iwamura's (*t*-butyl nitroxides) group [3]. These approaches enable tight magnetic interactions between the coordinating radical center and the magnetic metal ions, although the method requires the rather specific hexafluoroacetylacetonate (hfac)-coordinated metal ions. There are several data on these complexes whose magnetic interactions and structures have been clarified. For the Cu(II)–nitroxide or Cu(II)–nitronyl nitroxide complexes, the axial coordination of the nitroxide group generally gives ferromagnetic interactions ($J/k_B = +7$ –

50 K) with the Cu–O bond length of 2.3–2.4 Å [4], whereas the equatorial coordination tends to be antiferromagnetic [4].

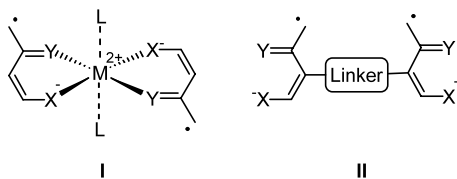
Much stronger magnetic interactions have been observed by Gatteschi and coworkers. They prepared a $\text{Cu}(\text{hfac})_2$ –2-pyridyl(iminonitroxide)₂, where a large magnetic interaction close to $J/k_B \sim +200$ K or more was attained [5a]. The large magnetic interaction is mainly due to the short Cu–N equatorial coordination bond length (typically 2.0 Å). Although the iminonitroxide structure possesses excellent properties as a spin-building block, this ligand failed to form a long chain structure because of the weak coordination of the nitroxide to the magnetic metals [5a].

We have been interested in developing an anionic spin-chelating ligand that forms a neutral metal-chelate shown in general formula **I**. In principle, this method can be extended to an aggregate system using a bis(spinnelating ligand) bridged by a suitable π -conjugated linker shown in **II**. This spin-chelate approach has the following advantages: (1) the anionic center X facilitates the coordination of Y, (2) the chelate structure can control the coordination geometry [6] and (3) the neutral

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nature of the metal complexes allows dissolution in organic solvents. In the case of $M = \text{Cu(II)}$, the expected square-planar geometry would result in an orthogonal relation between the radical p-orbital and the Cu(II) magnetic orbital, leading to the ferromagnetic interaction. We report herein the structure and magnetic properties of a spin-chelate copper(II) bis{2-[(4,4,5,5-tetramethylimidazoline-1-oxyl)-2-yl]phenolate} (**1**).



2. Experimental

2.1. General method

Chemicals were used as received without further purification. Melting points were measured on a Yanako MP-J3 apparatus and are uncorrected. ^1H NMR spectra were recorded on JEOL JNM-LA300 (300 MHz). The chemical shifts were described as values in ppm relative to tetramethylsilane. MS spectra were obtained using a JEOL JMS-700T mass spectrometer. ESR spectra were recorded on a JEOL JFS-FE2XG. X-ray data were collected with Rigaku/MSC Mercury CCD system using graphite monochromated Mo $K\alpha$ radiation. The magnetic susceptibility measurements were achieved on a Quantum Design SQUID magnetometer MPMS-XL with an applied field of 0.1 T.

2.2. Syntheses of **1** and **3**

2.2.1. Synthesis of 2-[(3-hydroxy-4,4,5,5-tetramethylimidazoline)-2-yl]phenol (**3**)

2-[(4,4,5,5-Tetramethylimidazoline-1-oxyl-3-oxide)-2-yl]phenol (**2**) (1.45 g, 5.82 mmol) [7] was dissolved in DMF (15 ml) and cooled to 0°C . Sodium nitrate (1.25 g, 18.1 mmol) in a minimal amount of water was added to the DMF solution. Then, an aqueous hydrochloric acid solution (6 M, 4 ml) was added dropwise to the DMF solution at 0°C and the mixture was stirred for 30 min at 0°C . During the addition, the original blue color turned to orange. To the orange solution was added zinc dust (3.5 g, 54 mmol) in portions at 0°C . The color of the solution faded after 30 min stirring at 0°C . The mixture was filtered through a celite and the zinc residue was washed with methylene chloride. The methylene chloride-rich filtrate was washed with water to remove DMF and dried over sodium sulfate. After evaporation of the solvent, the residue was subjected to silica gel

chromatography. The desired product was obtained as a fraction of $R_f = 0.4$ (eluent: benzene–ethyl acetate, 1:3 (v/v)). Recrystallization from methanol–water (1:1, v/v) gave **3** in 77% yield (1.05 g). **3**: m.p. 140°C ; pale yellow needles (water–methanol). MS (FAB), m/z : 235 ($M+H$). ^1H NMR (300 MHz, CDCl_3): δ 1.33 (s, 6H), 1.38 (s, 6H), 6.78 (t, $J = 8.2$ Hz, 1H), 6.97 (d, $J = 8.2$ Hz, 1H), 7.26 (dd, $J = 8.2, 1.5$ Hz, 1H), 7.40 (td, $J = 8.2, 1.5$ Hz, 1H). IR (KBr disk): ν 2980, 2748, 1610, 1578, 1446, 1394, 1371, 1313, 1256, 1122, 1134, 752, 665, 507 cm^{-1} . Anal. Calc. for $\text{C}_{13}\text{H}_{18}\text{N}_2\text{O}_2$: C, 66.64; H, 7.74; N, 11.96. Found: C, 66.68; H, 7.77; N, 11.91%.

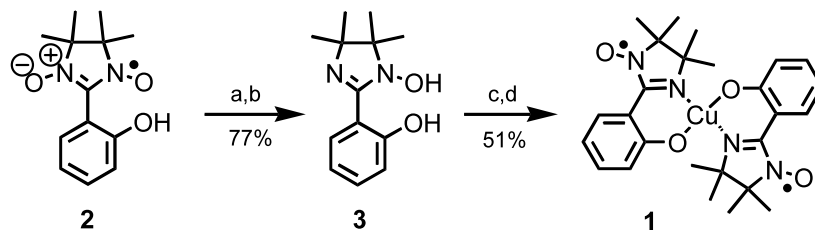
2.2.2. Synthesis of copper(II) bis{2-[(4,4,5,5-tetramethylimidazoline-1-oxyl)-2-yl]phenolate} (**1**)

Copper(II) acetate (0.163 g, 0.898 mmol) was dissolved in a mixture of methanol (2.25 ml), aqueous ammonia (0.75 ml) and water (1.5 ml). To this solution was added a solution of **3** (0.208 g, 0.888 mmol) in 50% aqueous methanol (2.5 ml). The mixture was heated at 80°C for 30 min under aerated conditions and cooled down to room temperature. The solvent was concentrated under reduced pressure to about one-half, giving a mixture of precipitates (0.173 g) including dark green crystals and a green powder. The filtered precipitates were dissolved in 20 ml of methylene chloride. Lead(IV) oxide (0.896 g, 3.75 mmol) was added to the methylene chloride solution and the resulted suspension was stirred for 30 min at room temperature. The mixture was filtered through a celite. Evaporation of the filtrate gave a dark powder. Recrystallization from a mixture of methylene chloride–hexane gave dark green crystals (0.120 g, 51%). **1**: m.p. $194\text{--}196^\circ\text{C}$ (decomposition); dark green plates (from dichloromethane–hexane). MS (FAB) m/z : 529 ($M+2H$). IR (KBr disk): ν 2986, 1601, 1553, 1526, 1466, 1429, 1344, 1248, 1215, 1161, 1134, 880, 766, 548 cm^{-1} . Anal. Calc. for $\text{C}_{26}\text{H}_{32}\text{N}_4\text{O}_4\text{Cu}$: C, 59.13; H, 6.11; N, 10.61. Found: C, 58.91; H, 6.06; N, 10.42%. ESR (powder) $g = 2.126$.

3. Results and discussion

3.1. Synthesis and structure of **1**

The synthesis of **1** is outlined in Scheme 1. The starting 2-[(4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide)-2-yl]phenol (**2**) was synthesized according to the literature procedure [7]. The deoxygenation of **2** was carried out by reaction with nitrous acid. The produced iminonitroxide radical was unstable under aerated conditions at room temperature and the isolation of the iminonitroxide radical was difficult. In situ treatment of the deoxygenated mixture with an excess amount of zinc gave the reduced 2-[(3-hydroxy-4,4,5,5-tetramethylimidazoline)-2-yl]phenol (**3**) as a stable com-



Scheme 1. (a) $\text{NaNO}_2\text{-HCl/DMF}$ at 0°C , (b) Zn at 0°C , (c) $\text{Cu(OAc)}_2/\text{methanol-aqueous NH}_3$ and (d) $\text{Pb(IV)O}_2/\text{CH}_2\text{Cl}_2$.

pound. Compound **3** was treated with Cu(II) acetate (2 equiv.) at 80°C in a mixture of methanol and aqueous ammonia, giving a mixture of precipitates of the partially oxidized Cu(II) complexes. The oxidation of the mixture in methylene chloride with lead(IV) oxide gave the desired Cu(II) complex **1**. The copper (II) complex **1** was soluble in various organic solvents. Recrystallization from a mixture of methylene chloride–hexane in a freezer gave dark green crystals suitable for X-ray structure analysis. The copper complex **1** was fairly stable under aerated conditions.

The crystallographic data for **1** are shown in Table 1. Two structurally similar but crystallographically independent molecules, **A** and **B**, were observed in a unit cell. One of them is shown in Fig. 1 (upper). The structure of the Cu complex was considerably deviated from a square-planar geometry and the dihedral angles between the two planes defined by a set of copper and the coordinating oxygen and nitrogen atoms were $41 \pm 5^\circ$ (Table 2). This distortion comes from the congestion of the coordinating ligands around the metal center. Table 2 also lists the bond lengths including the copper atom. The bond length of the Cu-N bond was approximately 2.0 \AA that was a typical equatorial bond length between the copper atom and the sp^2 nitrogen atoms [8].

Interestingly, two short intermolecular contacts were observed between the two independent molecules **A** and **B**: 3.14 \AA contact between the C5 carbon atom of the molecule **A** and the phenolate oxygen atom (O1) of the molecule **B** and 2.34 \AA contact between the H5 (calculated atom) attached to the C5 carbon (**A**) and the O1 atom (**B**) (Fig. 1, lower). Both contacts are shorter than the sum of van der Waals values (3.29 \AA in a total of the aromatic carbon atom (1.77 \AA) and the oxygen atom (1.52 \AA), and 2.53 \AA in a total of the hydrogen atom (1.01 \AA) and the oxygen atom (1.52 \AA)) [9]. Other intermolecular contacts were not observed within 3.3 \AA .

3.2. Magnetism of **1**

Fig. 2 shows temperature dependence of $\chi_p T$ for **1**. The $\chi_p T$ value at room temperature was $1.70 \text{ emu K mol}^{-1}$. The value was larger than that for three $S = 1/2$ spins ($\chi_p T = 1.27 \text{ emu K mol}^{-1}$ with $g = 2.126$ from EPR) but smaller than that for an $S = 3/2$ spin ($\chi_p T =$

Table 1
Crystallographic data of **1**

Formula	$\text{C}_{26}\text{H}_{32}\text{N}_4\text{O}_4\text{Cu}$
Formula weight	528.11
Crystal system	triclinic
Space group	$P\bar{1}$ (No. 1)
Unit cell dimensions	
a (\AA)	10.167(3)
b (\AA)	10.377(3)
c (\AA)	13.337(3)
α ($^\circ$)	70.46(2)
β ($^\circ$)	70.96(2)
γ ($^\circ$)	86.74(2)
V (\AA^3)	1251.4(6)
Z	2
Crystal size (mm)	$0.40 \times 0.30 \times 0.02$
T (K)	298
D_{calc} (g cm^{-3})	1.401
$F(000)$	554.00
μ (cm^{-1})	9.12 ($\text{Mo K}\alpha$)
Unique reflections	5462
Observation [$I > 3.000\sigma(I)$]	2078
R_1 [$I > 3\sigma(I)$] ^a	0.051
R_w ^b	0.107
Goodness-of-fit	1.14
Largest shift	2.28

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b R_w = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

$2.12 \text{ emu K mol}^{-1}$). On cooling the temperature, the $\chi_p T$ value gradually increased up to $1.76 \text{ emu K mol}^{-1}$ at about 130 K and decreased below 100 K . The increase in the $\chi_p T$ values suggests the occurrence of considerably large ferromagnetic interaction in this three-spin system and is assignable to the ferromagnetic interaction between the Cu(II) and the iminonitroxide radical. The decrease in the $\chi_p T$ values below 100 K is assigned as an intermolecular magnetic interaction.

In order to obtain further insight, we carried out magnetic measurement for a diluted sample of **1** in a polyvinyl chloride (PVC) film. The magnetic susceptibility of **1** diluted (6.9 wt.%) in the PVC film is shown in Fig. 2. The $\chi_p T$ value at room temperature was a little larger than that of the neat powder sample as expected. The values gradually increased to reach a plateau on cooling the temperature ($\chi_p T = 2.00 \text{ emu K mol}^{-1}$ at

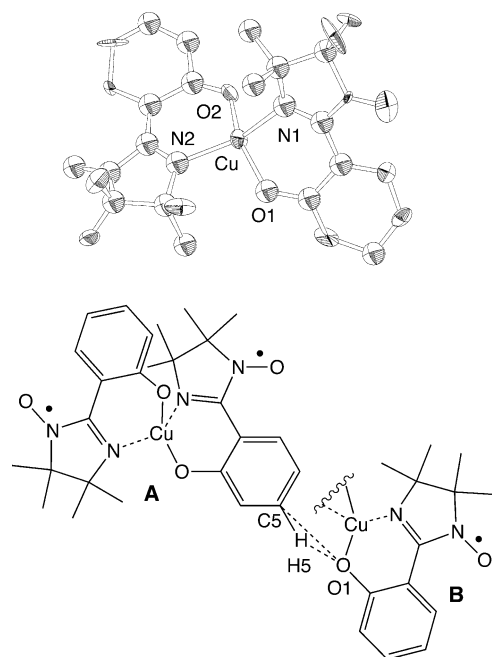


Fig. 1. Molecular structure with 50% thermal ellipsoids (upper) and a schematic presentation for the intermolecular contacts (lower) for **1**.

Table 2
Bond lengths around Cu(II) and dihedral angles^a for **1**

Bond or dihedral angle	Bond length (Å) or dihedral angle (°)	
	Fragment A	Fragment B
Cu–O1	1.85(2)	1.92(2)
Cu–O2	1.82(2)	1.92(2)
Cu–N1	1.92(2)	1.94(2)
Cu–N2	2.01(2)	2.03(3)
Dihedral angle ^a	36.9	45.5

^a Dihedral angles between the two planes defined by Cu, O1, N1 and Cu, O2, N2 atoms.

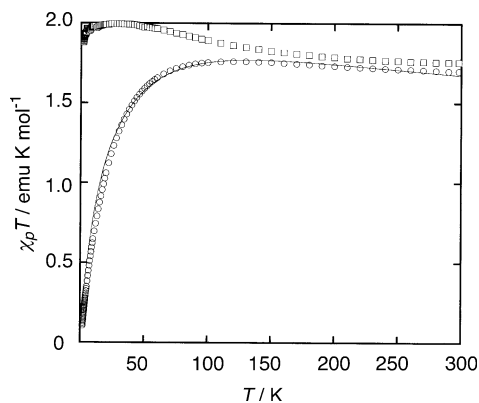


Fig. 2. $\chi_p T$ – T plot for the powder **1** (circle) and the simulation curve (line); the upper plot (square) shows the magnetic data for the diluted sample of **1** in the PVC film.

about 50–10 K). The plateau value was a little lower than the expected $\chi_p T$ value for $S = 3/2$ (2.12 emu K mol^{−1}). The lower value would be ascribed to small decomposition of **1** in the PVC film, which may occur during the film-preparation step that required slow evaporation of the methylene chloride solvent over 2 days. The decrease in $\chi_p T$ value below about 5 K can be due to small amounts of aggregations that still exist in the diluted sample in the PVC film. Thus, the intramolecular ferromagnetic interaction was confirmed by the susceptibility measurement on the diluted sample.

The temperature dependence of magnetic susceptibility χ_p for the complex **1** was analyzed using a three-spin (trimer) model

$$H = -2J(S_{R1} \cdot S_{Cu} + S_{Cu} \cdot S_{R2}) \quad (1)$$

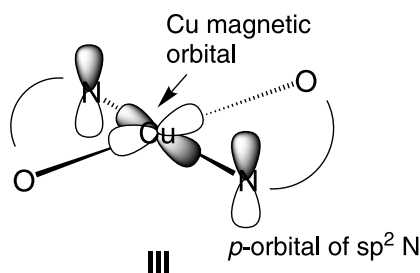
where the three $S = 1/2$ operators, S_{R1} and S_{R2} on the radicals and S_{Cu} on the Cu(II) ion, were coupled by the exchange interaction J . The possible difference in the exchange interactions, $J(R1-Cu) \neq J(R2-Cu)$, in the fragments **A** and **B** was disregarded in order to avoid overparametrization; four adjustable parameters were hard to determine simultaneously from the observed $\chi_p T$ values. The parameter J in Eq. (1) is regarded as an averaged one. The trimer model affords one quartet ($S = 3/2$) and two doublet ($S = 1/2$) states. The thermal equilibrium between these states gives the temperature dependence of susceptibility as

$$\chi_p = \frac{N_a g^2 \mu_B^2}{3k_B(T - \theta)} \frac{15 + (3/2) e^{-J/kT} + (3/2) e^{-3J/kT}}{4 + 2 e^{-J/kT} + 2 e^{-3J/kT}} \quad (2)$$

where θ represents the intermolecular interaction in the mean-field approximation. The observed temperature dependence of $\chi_p T$ is reproduced by Eq. (2) with the parameters $J/k_B = +250$ K and $\theta = -17$ K, as depicted by the solid line in Fig. 2.

The obtained J value is considerably larger than the value of ferromagnetic interaction ($J/k_B = +7$ – 50 K) between the copper (II) and the nitroxides [4]. The reason for the larger interaction in this imino-coordinating complex is mainly due to the short equatorial bond length compared to the longer axial bond (2.3–2.4 Å) for the copper–nitronyl nitroxide complexes [4]. The present J/k_B value is close to that for the distorted octahedral 2-pyridyl(iminonitroxide)–Cu(hfac)₂ complexes ($J/k_B \sim +220$ K) [5a] and smaller than those for recently reported square-planar [phenyl(iminonitroxide)]₂–Cu(tfac)₂ complexes ($J/k_B > +360$ K) [5b]. Ferromagnetic coupling of the ideal square-planar Cu–iminonitroxide complex is clearly visualized in schematic model **III**, where the orthogonal relation between the copper magnetic orbital ($d_{x^2-y^2}$) and the

iminonitrogen *p*-orbital is tightly held. Generally speaking, the effect of geometrical change of the coordination center on the magnetic interaction should be important; for instance, a square-pyramidal nitronyl nitroxide–Cu(hfac)₂ complex has been reported to have a stronger ferromagnetic interaction than square-planar complexes [4d]. To the best of our knowledge, however, tetrahedral-type Cu(II)–radical systems have not been reported. The present ferromagnetic coupling that falls into the value between the distorted octahedral and the square-planar geometries may suggest that the distortion from planar to tetrahedral geometry may little suppress the ferromagnetic interaction on Cu(II)–radical spin systems.



According to the X-ray structure, two intermolecular short contacts were observed between the C5 aromatic carbon atom and the O1 phenolate oxygen atom and between the H5 hydrogen and the O1 atom (see Section 3.1). The C5 atom is in *para* position of the electron-withdrawing iminonitroxide substituent. The H5 atom is attached on the C5 atom. Both atoms would be positively charged. Furthermore, the O1 oxygen atom is an anionic center. For this reason, the observed short contacts may have a Coulombic nature in origin. Since there are no other contacts less than 3.3 Å, these contacts were tentatively assigned as an origin of the antiferromagnetic interaction.

In sum, we have synthesized a novel Cu spin-chelate **1** whose structure and magnetic properties were clarified. The temperature dependence of $\chi_p T$ showed the presence of a large ferromagnetic interaction and a weaker antiferromagnetic interaction, $J/k_B = +250$ K and $\theta = -17$ K, respectively, based on the trimer model. The ferromagnetic interaction was assigned as the intramolecular interaction between the Cu(II) and the coordinating iminonitroxide. The antiferromagnetic interaction was assigned as an intermolecular interaction. The susceptibility measurement of the sample diluted in the PVC film strongly supported these assignments. The intermolecular contacts (C5–O1 and/or H5–O1) observed in the crystal structure were tentatively assigned as an origin of the antiferromagnetic interaction of the complex **1**. Work on the

synthesis of **1**-based bidentate ligands and their metal complexes is in progress.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 194727 for complex **1**. Copies of this information may be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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