New Cuprous Iodide Coordination Compounds with Four Nitronyl Nitroxides as Paramagnetic Ligands

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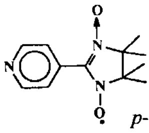
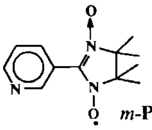
Two new cuprous iodide coordination compounds $[Cu_2I_2(p\text{-PYNN})_4]$ (**1**) and $[Cu_4I_4(m\text{-PYNN})_4]$ (**2**) containing four nitronyl nitroxides were synthesized, and their crystal structures as well as magnetic properties were investigated.

In recent years, molecules with multi-nitronyl nitroxides/nitroxides have received great attention.[1] Most of them were obtained by multi-step organic syntheses, and in some cases the separation and purification in the work-up stage were tedious. Another strategy for constructing molecular systems containing multiple spins was based on the coordination chemistry.[2] Our approach to molecules with multi-nitronyl nitroxides was based on this strategy. It was found that cuprous iodide with ligands such as pyridine could form different kinds of clusters.[3] We want to take advantage of these reactions, employing 4-(nitronyl nitroxide) pyridine (*p*-PYNN) and 3-(nitronyl nitroxide) pyridine (*m*-PYNN), instead of pyridine, to construct molecules containing multi-nitronyl nitroxides. In this communication, we wish to describe the syntheses, crystal structures and magnetic properties of two new iodo cuprous coordination compounds, $[Cu_2I_2(p\text{-PYNN})_4]$ (**1**) and $[Cu_4I_4(m\text{-PYNN})_4]$ (**2**), with four nitronyl nitroxides.



p-PYNN



m-**PYNN**

Complexes **1** and **2** were synthesized from cuprous iodide and *p*-PYNN / *m*-PYNN with the modified procedure according to the literature[3a]. Interestingly, under the same conditions only complex **1** with a Cu_2I_2 rhombus was obtained starting from *p*-PYNN, while from *m*-PYNN a cubane like cluster **2** was yielded, although there were only minor differences in terms of chemical structures between *p*-PYNN and *m*-PYNN. Complexes **1** and **2** were characterized by spectroscopic methods and elemental analysis.[4]

Crystal structures of **1** and **2** were determined.[5] Compound **1** is centrosymmetric as shown in Figure 1 (up). Two *p*-PYNN ligands are coordinated to each cuprous ion, and thus it incorporates four nitronyl nitroxides in a single $Cu_2I_2(4\text{-PYNN})_4$ molecule. As for the free *p*-PYNN, the imidazoline and pyridine rings are not coplanar, and the pyridine planes form dihedral angles of 28.2° and 24.3° with the linked imidazoline ones. The bond lengths of Cu(1)–N(1) and Cu(1)–N(4) are 2.054(3) and 2.059(3) Å, respectively, being comparable to those of cuprous iodide–pyridine complexes. Short interatomic contacts (2.39–2.48 Å) were found between the oxygen and hydrogen atoms of methyl groups in neighboring nitronyl nitroxide units. Furthermore, such intermolecular interactions were extended along molecular stacking direction as clearly manifested in Figure 1 (down). Previous results[6] indicated that for nitronyl nitroxide derivatives the oxygen and nitrogen atoms possess positive spin densities, while the hydrogen atoms of methyl groups contain small negative spin densities. According to McConnell principle,[7] such interactions will lead to intermolecular spin–spin ferromagnetic coupling. Hence, one dimensional ferromagnetic chain was formed for **1**, which corresponds well with the result of magnetic property of **1** as discussed below.

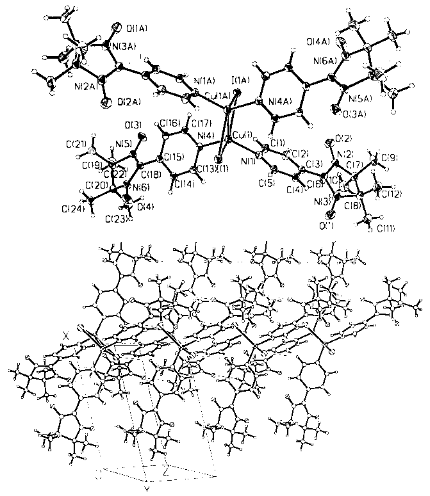


Figure 1. Molecular structure of **1** (up); Intermolecular arrangements in the crystal of **1** (down).

As shown in Figure 2, the molecular structure of $Cu_4I_4(m\text{-PYNN})_4$ contains a Cu_4I_4 unit, which can also be referred to as "cubane-like". The copper atoms are on the four vertexes of a tetrahedron. Each copper atom is bridged by three iodine atoms and further coordinated by one *m*-PYNN ligand. Thus, one $Cu_4I_4(m\text{-PYNN})_4$ molecule contains four nitronyl nitroxides. The Cu–N bond lengths are varied from 2.035 Å to 2.060 Å. Similarly, the imidazoline and corresponding pyridine rings are not coplanar, and the formed dihedral angles are in the range of 12.4–21.1°. In the crystal lattice, on one hand, short interatomic contacts were found between the oxygen atoms of nitronyl nitroxide and the hydrogen atoms of methyl groups and these hydrogen atoms (H_{meta}) attached to the carbon atoms being *meta* to nitrogen atoms of pyridine rings (~ 2.47–2.49 Å). As discussed for **1**, hydrogen atoms of methyl groups possess small negative spin densities, and according to the spin polarization mechanism the H_{meta} atoms also have small negative spin densities. Thus, such intermolecular interactions will lead to ferromagnetic property. On the other hand, short interatomic distances were also found between the oxygen, nitrogen and carbon atoms of neighboring

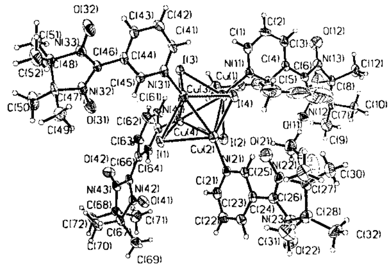


Figure 2. Molecular structure of **2** together with three CH_3CN molecules

molecules: O11–O41^{i} 3.735 Å (symmetry: –x+1, y, –z+2), O12–O32^{i} 3.485 Å (symmetry: –x, –y, –z+1), O32–N13^{i} 3.182 Å (symmetry: –x, –y, –z+1), O41–N12^{i} 2.969 Å (symmetry: –x+1, –y, –z+2), O11–C22^{i} 3.294 Å (symmetry: –x+1, –y, –z+2), O22–C2^{i} 3.396 Å (symmetry: x+1, y, z), C62–O12^{i} 3.187 Å (symmetry: –x, –y, –z+2). As stated before, oxygen and nitrogen atoms of nitronyl nitroxide units possess positive spin densities, and the atoms C2, C22 and C62 also have small positive spin densities according to the spin polarization mechanism. Hence, such intermolecular interactions will favor the intermolecular spin–spin antiferromagnetic coupling. Therefore, the magnetic property of **2** in the solid state will depend on the competition of these kinds of intermolecular interactions. The antiferromagnetic property of **2** inferred from experimental results (see below) implies that antiferromagnetic interactions are dominant over ferromagnetic ones for **2**.

Figure 3 (up) shows the temperature dependence of molar magnetic susceptibility for **1**, which can be interpreted in terms of a 1D ferromagnetic chain,[8] using the following equation:

$$\chi_p = (C/T)\,[(1 + 5.7979916K + 16.902653K^2 + 29.376885K^3 + 29.832959K^4 + 14.036981K^5) / (1 + 2.7979916K + 7.0086780K^2 + 8.6538644K^3 + 4.5743114K^4)]^{2/3},$$

where $K = J / 2k_bT$, and symbols have the usual meanings. The theoretical best fit is obtained with C = 1.494 emu·K·mol^{-1}, J / k_b = 0.2 K. Positive J means ferromagnetic spin–spin interactions for **1** in the solid state. The inset of Figure 3 (up) displays the plot of the product of molar magnetic susceptibility with temperature ($\chi \cdot T$) versus temperature. At 300 K, the value of $\chi \cdot T$ is 1.49 emu·mol^{-1}·K, which is very close to the theoretical value (1.5 emu·mol^{-1}·K) for four independent S = 1/2 spins. Above 70 K, $\chi \cdot T$ almost keeps constant. Below 70 K, however, $\chi \cdot T$ increases gradually with decreasing temperature, reaching 1.71 emu·mol^{-1}·K at 5 K. This property again indicates that **1** in the solid state possesses ferromagnetic property. The field dependence of magnetization was measured for **1** at 5 K. The magnetization was almost linearly increased with the external field, and it showed no saturation tendency.

Figure 3 (down) shows the temperature dependences of the product of molar magnetic susceptibility with temperature ($\chi \cdot T$) and the reciprocal molar magnetic susceptibility ($1/\chi$) for **2**. At 300 K, the value of $\chi \cdot T$ is 1.46 emu·mol^{-1}·K, deviating a little from the theoretical value (1.5 emu·mol^{-1}·K) for four independent S = 1/2 spins. The value of $\chi \cdot T$ decreases slowly with decreasing temperature from 300 K to 50 K, but the variance is quite little. Below 50 K, however, the value of $\chi \cdot T$ is reduced sharply with decreasing temperature further. In the whole measuring temperature range the molar magnetic susceptibility of **2** follows the Curie–Weiss law quite well as indicated by the good linear relationship between the reciprocal molar magnetic susceptibility and temperature. The fitted values for C and θ are 1.5 emu·mol^{-1}·K and –3.0 K, respectively.

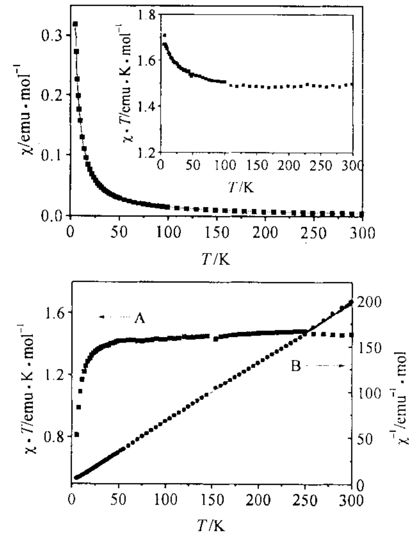


Figure 3. Temperature dependence of molar magnetic susceptibility of **1** (up) and **2** (down): A, $\chi \cdot T$ versus T; B, $1/\chi$ versus T.

In summary, new compounds **1** and **2** with four nitronyl nitroxides were prepared by a simple procedure. Their crystal structures were determined by X-ray diffraction analysis. Magnetic studies indicated that **1** displayed ferromagnetic property, while **2** showed antiferromagnetic behavior in their solid states.

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References and Notes

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4 **1**: mp 216–217 °C; IR, 1374, 1137 cm^{-1}; ESR (solid, 293 K, strong single peak): g = 2.0086; Anal.Calcd. for $C_{48}H_{64}Cu_2I_2N_{12}O_8$: C, 43.74; H, 4.89; N, 12.75%. Found; C, 43.71; H, 4.95; N, 12.77%. **2**: mp.195–196 °C; IR, 1371, 1136 cm^{-1}; ESR (solid, 293 K, strong single peak): g =2.0075; Anal.Calcd. for $C_{48}H_{64}Cu_4I_4N_{12}O_8$: C, 33.94; H, 3.80; N, 9.89%. Found: C, 33.94; H, 3.63; N, 10.29%.

5 Crysta data: **1**, $C_{48}H_{64}Cu_2I_2N_{12}O_8$, MW = 1318.01, triclinic, P1(No.2), a = 13.668(3)Å, b = 14.280(3) Å, c = 7.273 (1) Å, α = 90.18(3)°, β = 101.86(3)°, γ = 91.09(3)°, V = 1388.9 (5) Å^3, Z = 1, D_c = 1.576 g·cm^{-3}. 4217 observed reflections [$I > 2\sigma(I)$] and 334 variable parameters and converged to R = 0.0310 and wR = 0.0805; **2**, $C_{48}H_{64}Cu_4I_4N_{12}O_8$.3$CH_3CN$, MW = 1822.03, triclinic, P1(No. 2), a =15.569(9) Å, b =16.247(7) Å, c =15.103(9) Å, α = 94.48(5)°, β =116.15(5) °, γ =83.07(5) °, V =3402.9(32) Å^3, Z = 2, D_c = 1.778 g·cm^{-3}. 8311 observed reflections [$I > 2\sigma(I)$] and 785 variable parameters and converged to R = 0.0686 and wR = 0.1933.

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