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Syntheses, Crystal Structures and Magnetic Properties of Copper(I) Iodide Complexes with Nitronyl Nitroxide-Substituted Pyridine

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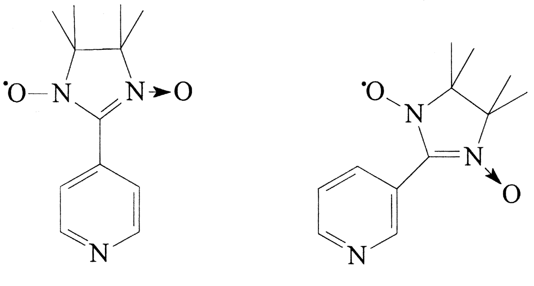
(Received April 5, 2001)

Two new copper(I) iodide coordination compounds $[Cu_2I_2(p\text{-PYNN})_4]$ (**1**) and $[Cu_4I_4(m\text{-PYNN})_4]$ (**2**), where *p*-PYNN and *m*-PYNN are 4,4,5,5-tetramethyl-2-(4-pyridyl)-4,5-dihydro-1*H*-imidazol-1-oxy-3-oxide and 4,4,5,5-tetramethyl-2-(3-pyridyl)-4,5-dihydro-1*H*-imidazol-1-oxyl-3-oxide, respectively, were synthesized and characterized. They both were found to be fluorescent. Their crystal structures were determined: **1**, triclinic, space group $P\bar{1}$, 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)°, Z = 1, R = 0.0310 (R_w = 0.0805) for 4217 observed reflections with $I \geq 2\sigma(I)$; **2**, triclinic, space group $P\bar{1}$, 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)°, Z = 2, R = 0.0686 (R_w = 0.1933) for 8311 observed reflections with $I \geq 2\sigma(I)$. Magnetic studies indicated that **1** showed ferromagnetic behavior, while **2** displayed antiferromagnetic properties. Discussions about the relationship between their crystal structures and magnetic properties are also presented.

Since the discovery of the first purely organic ferromagnet in 1991,[1] nitronyl nitroxide and related stable radicals were extensively studied and indeed more than ten organic ferromagnets were obtained.[2] But, ferromagnetic transition temperatures of these ferromagnets are rather low, with the highest being 1.48 K.[3] In recent years, molecules with multi-nitronyl nitroxides/nitroxides have received great attention due to the fact that they may result in the enhancement of intermolecular spin–spin interaction and the dimensionality of the magnetic materials.[4] Furthermore, nitronyl nitroxide/nitroxides of these molecules can form coordination bonds with suitable metal ions, which will also sterengthen the intermolecular spin–spin coupling and increase the dimensionality of the resulting magnets.[5] In fact, several new molecular magnets with significantly high *Tc* values were obtained by these approaches.[6]

Most of the molecules with multi-nitronyl nitroxides/nitroxides 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. In this strategy, we employed molecules with two prospective ligating centers, one of which carries little spin density and the other of which bears high spin density, and only the former ligating center, not the latter one, was bound to the metal ions.[7] Our approach to molecules featuring multi-nitronyl nitroxides was based on this strategy. Such molecules containing multi-nitronyl nitroxides prepared with the principle of coordination chemistry may exhibit altered intermolecular arrangements of organic radical units, which would affect the intermolecular spin–spin interactions. Like the analogous organic molecules with multi-nitronyl nitroxide units, these molecules can be used as new building blocks for the creation of novel magnetic materials through the coordination of nitronyl nitroxide units with paramagnetic ions.

It was found that copper(I) iodide with ligands such as pyridine could form different kinds of clusters.[8] We want to take advantage of these reactions, employing 4,4,5,5-tetramethyl-2-(4-pyridyl)-4,5-dihydro-1*H*-imidazol-1-oxyl-3-oxide (*p*-PYNN) and 4,4,5,5-tetramethyl-2-(3-pyridyl)-4,5-dihydro-1*H*-imidazol-1-oxyl-3-oxide (*m*-PYNN) (Scheme 1), instead of pyridine, to construct molecules containing multi-nitronyl nitroxides. In this paper, we will describe the syntheses, crystal structures and magnetic properties as well as the fluorescence spectra of two new iodide copper(I) coordination compounds $[Cu_2I_2(p\text{-PYNN})_4]$ (**1**) $\{Cu_4I_4(m\text{-PYNN})_4]$ (**2**) with four nitronyl nitroxides. A preliminary communication of this work has



***p*-PYNN** ***m*-PYNN**

Scheme 1. Chemical structures of *p*-PYNN and *m*-PYNN.

been published.[9]

Experimental

General. Melting points, XT_4-100_X, uncorrected; IR, Pekin-Elmer 2000 (KBr platelets); ESR, Varian E-109 spectrometer (in CH_2Cl_2, $\sim 10^{-5}$ M); Fluorescence, F-4500 (in CH_2Cl_2, $\sim 10^{-5}$ M); Elemental analysis, Heraeus Chn-Rapid.

X-ray Crystal Structural Analysis. The intensity data were collected at 293 K, on a Rigaku AFC6S diffractometer with a graphite monochromator for the Mo-$K\alpha$ ($\lambda = 0.71073$ Å) radiation. Absorption was corrected with Psi scan type. Cell constants were determined from a least-squares fit of the setting angles for the 25 selected reflections with $5 < \theta < 10°$ for both **1** and **2**. Data reduction, structure solution and refinement were performed using SHELXS97 package. Non-hydrogen atom sites were directly solved, and refined with full least-squares method. Hydrogen atoms were theoretically added and included in the final refinement. Because single crystals of $[Cu_4I_4(m\text{-PYNN})_4]$ contained acetonitrile molecules which escaped readily, during data collection the chosen single crystal was sealed in a glass tube under acetonitrile atmosphere. Consequently, the intensities of all reflections were weakened, resulting in relatively large standard derivations for the reported bond lengths and angles. The crystallographic and refinement data are summarized in Table 1. The details of structures have been deposited as Document No. 74052 at Office of the Editor of Bull. Chem. Soc. Jpn.

Magnetic Susceptibility Measurement. The magnetic susceptibility was measured on the bulk material in the temperature range of 5–300 K for each compound with a SQUID magnetometer (MMPS-7, Quantum Design). The data were corrected for magnetization of the sample holder and the diamagnetism of the constituent atoms using Pascal constants.

Table 1. Crystallographic and Refinement Data of Compound **1** and **2**

	1	**2**
Chemical formula	$C_{48}H_{64}Cu_2I_2N_{12}O_8$	$C_{54}H_{73}Cu_4I_4N_{15}O_8$
Formula weight	1318.0	1822.03
T/K	293(2)	293(2)
λ/Å	0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	13.668(3)	15.569(9)
b/Å	14.280(3)	16.247(7)
c/Å	7.273(1)	15.103(9)
α/°	90.18(3)	94.48(5)
β/°	101.86(3)	116.15(5)
γ/°	91.09(3)	83.07(5)
V/Å^3	1388.9(5)	3402.9(32)
$F(000)$	664	1788
D_{calc}/g cm^{-3}	1.576	1.778
Z	1	2
μ/mm^{-1}	1.937	3.107
Reflns collected	51.3	12348
Reflns unique	4879	11904
Reflns observed $[I \geq 2\sigma(I)]$	4217	8311
R_1[a)]	0.0310	0.0686
wR_2[b)]	0.0805	0.1933

a) $R_1 = \dfrac{\sum[|F_o| - |F_c|]}{\sum|F_o|}$. b) $wR_2 = \left\{\dfrac{\sum[w(F_o{}^2 - F_c{}^2)]}{\sum[w(F_o{}^2)]}\right\}^{1/2}$

Preparation of Materials. The two ligands p-PYNN and m-PYNN were prepared according to the general procedure reported in the literature.[10] They were strictly purified by column chromatography and recrystallization from ethyl acetate before being used for the following reactions.

$[Cu_2I_2(p\text{-PYNN})_4]$. Copper(I) iodide (0.294 g, 1.5 mmol) and p-PYNN (0.362 g, 1.5 mmol) were dissolved in 40 mL of acetonitrile, and the mixture was stirred at 80 °C for 3 h. Then the solution was allowed to cool naturally to room temperature. Crystals were precipitated from the solution and separated by filtration; among the precipitated crystals dark single ones suitable for X-ray structural analysis were selected. Another sample of crystals was obtained by standing the above filtrate in the refrigerator for 24 h. Yield, 0.386 g (78%). Mp 216–217 °C. IR 1374, 1137 cm^{-1} (typical absorption peaks for nitronyl nitroxides). ESR (solid, 293 K, single line) $g = 2.0086$. Anal. Found: C, 43.71; H, 4.95; N, 12.77%. Calcd for $C_{48}H_{64}Cu_2I_2N_{12}O_8$: C, 43.74; H, 4.89; N, 12.57%. Fluorescence (soled, $\lambda^{ex} = 420$ nm), $\lambda_{max} = 627$ nm (298 K), 628 nm (77 K).

$[Cu_4I_4(m\text{-PYNN})_4]$. It was prepared in a similar way using m-PYNN in place of p-PYNN, except that its single crystals could only be obtained by standing the solution in the refrigerator. In addition, its single crystals should always be kept at low temperature, since they were prone to decompose. Yield 70%. Mp 195 °C. IR 1371, 1136 cm^{-1}. ESR (solid, 293 K, single line) $g = 2.0075$. Anal. Found: C, 33.94; H, 3.63; N, 10.29%. Calcd for $C_{48}H_{64}Cu_4I_4N_{12}O_8$: C, 33.94; H, 3.80; N, 9.89%. Fluorescence (solid, $\lambda^{ex} = 420$ nm), $\lambda_{max} = 626$ nm (298 K), 626 nm (77 K).

Results and Discussion

Preparation and Characterization. Complexes **1** and **2** were synthesized from copper(I) iodide and p-PYNN/m-PYNN with a modified procedure according to Ref. 8b. Under the same conditions, complex **1** with rhombohedron structure was obtained starting from p-PYNN, while from m-PYNN a cubane-like cluster **2** was yielded. Complexes **1** and **2** were characterized by FT-IR, fluorescence, EPR, elemental analysis and X-ray diffraction analysis (see below). Typical absorption bands around 1370 cm^{-1} were found in the IR spectra of **1** and **2**. Only one approximately symmetrical peak was observed for both **1** and **2** in their EPR spectra measured in their solid states.

The acetonitrile molecules captured in the lattice of crystals of **2** were liable to escape, and such an effect significantly reduced the crystal quality. Thus, the X-ray structural analysis of **2** has to be performed under acetonitrile atmosphere. Also, because of such properties of the crystal of **2**, correct elemental analysis could not be obtained for the fresh sample of **2**. After the material was kept in vacuum at room temperature for 3 h, the acetonitrile molecules in the lattice of crystal **2** were completely removed, as indicated by the result of elemental analysis (see experimental).

Copper(I) iodide cluster complexes were studied for their interesting fluorescent properties.[8] Figures 1 and 2 show the fluorescent spectra of **1** and **2** excited at 420 nm in the solid state at room temperature and 77 K. Both compounds display broad and featureless emission bands centered at 627 and 628 nm, respectively. According to previous studies of copper(I)

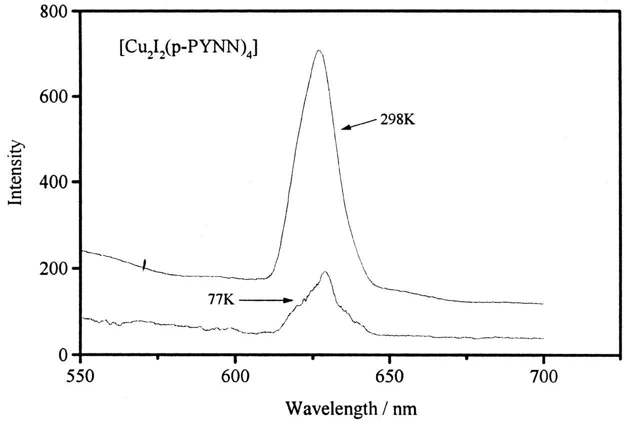


Fig. 1. Fluorescence spectrum of **1** in the solid state (λ^{ex} = 420 nm).

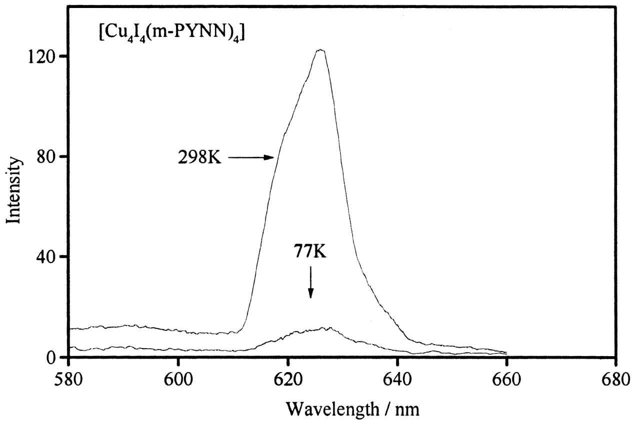


Fig. 2. Fluorescence spectrum of **2** in the solid state (λ^{ex} = 420 nm).

iodide complexes,[8d,8e] these observed emissions of **1** and **2** should be due to the copper(I)–iodide cluster centered excited state, for which the Cu–Cu distances should be less than 2.8 Å.[8e] In the cases of **1** and **2**, short Cu–Cu separation was found (see the section of crystal structure). As compared to those of $[Cu_2I_2Py_4]$ and $[Cu_4I_4Py_4]$,[8d] the emission bands of **1** and **2** show smaller line width and their band maxima are red-shifted. When the temperature was decreased from 298 K to 77 K, the emission band maxima varied very little, but their intensities were largely reduced. This may be owing to the fact that the process for the formation of copper(I)–iodide cluster centered excited state is retarded from the initially generated excited state at low temperature. A emission band at short wavelength, which was detected for $Cu_4I_4(Py)_4$ ($\lambda_{\max}$ = 438 nm) in the solid state at 77 K,[8d,8e] was not observed for Cu_4I_4(*m*-PYNN)$_4$. Indeed, for $Cu_4I_4(Py)_4$ the intensity of the emission band at short wavelength was increased, and that of emission band at long wavelength was decreased by lowering the temperature from 293 K to 77 K.[8d] Measurements were also performed under excitations at 320 nm, 350 nm, and 360 nm, but in these cases the fluorescence intensities of both **1** and **2** were very weak. More detailed investigations are in progress.

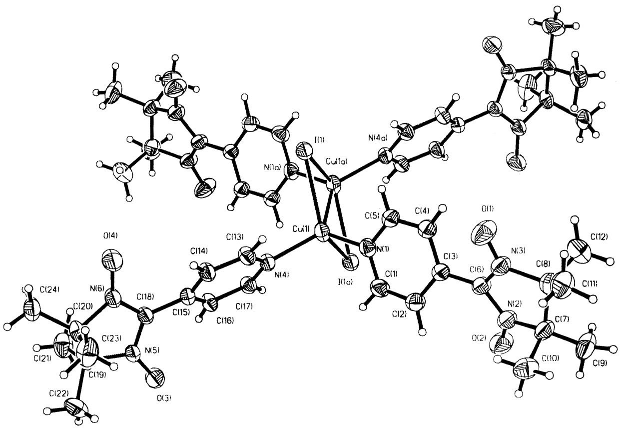


Fig. 3. Molecular Structure of **1**.

Table 2. Selected Bond Lengths (Å) and Angles (°) for **1**

I(1)–Cu(1)	2.6436(9)	N(5)–C(18)	1.346(4)
I(1)–Cu(1)#1	2.6505(8)	N(6)–C(18)	1.343(4)
Cu(1)–N(4)	2.054(3)	N(4)–Cu(1)–N(1)	109.81(11)
Cu(1)–N(1)	2.059(3)	N(4)–Cu(1)–I(1)	105.41(8)
Cu(1)–Cu(1)#1	2.617(1)	Cu(1)#1–Cu(1)–I(1)	60.50(3)
O(1)–N(3)	1.280(4)	I(1)–Cu(1)–I(1)#1	120.74(3)
O(2)–N(2)	1.277(4)	N(2)–C(6)–N(3)	108.7(3)
O(3)–N(5)	1.271(4)	N(2)–C(6)–C(3)	125.1(3)
O(4)–N(6)	1.268(4)	N(3)–C(6)–C(3)	126.3(3)
N(2)–C(6)	1.341(4)	N(6)–C(18)–N(5)	109.7(3)
N(3)–C(6)	1.352(4)	N(6)–C(18)–C(15)	124.7(3)
		N(5)–C(18)–C(15)	125.4(3)

Symmetry transformations used to generate equivalent atoms: #1 −x, −y+1, −z+1.

Crystal Structures. $[Cu_2I_2$(*p*-PYNN)$_4]$ is centrosymmetric, as shown in Fig. 3, and selected bond lengths and angles are included in Table 2. Each copper(I) ion coordinates with two aromatic nitrogen atoms of the pyridine rings, and thus it incorporates four nitronyl nitroxides in a single $[Cu_2I_2$(*p*-PYNN)$_4]$ molecule. Like 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 copper(I) iodide-pyridine complexes. The two copper atoms Cu(1) and Cu(1a) form a weak bond with a bond length of 2.617(1) Å. Other bond lengths and angles are in normal range.

Figure 4 represents molecular stacking pattern in the crystal lattice of $[Cu_2I_2$(*p*-PYNN)$_4]$. 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 Fig. 4. Previous theoretical and experimental results[11] 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 the McConnell principle,[12] such interaction will lead to intermolecular spin–spin ferromagnetic coupling. The importance of this kind of interaction has been already emphasized.[13] Hence, a one-dimensional ferromagnetic chain was formed for **1**, which corresponds well with the results of the

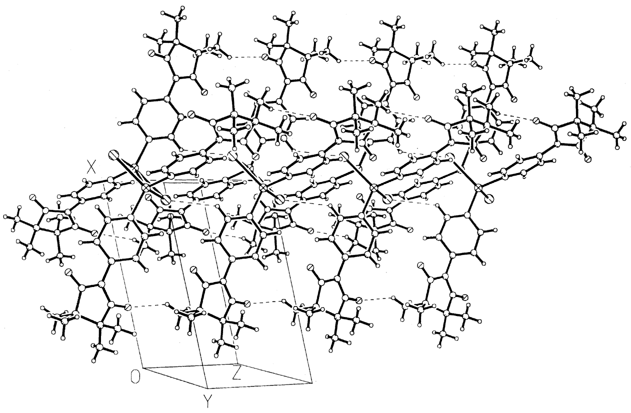


Fig. 4. Molecular packing patterns of **1** in the crystal lattice.

Table 3. Selected Bond Lengths (Å) and Angles (°) for **2**

I(1)–Cu(3)	2.648(2)	O(21)–N(22)	1.240(11)
I(1)–Cu(4)	2.650(1)	O(22)–N(23)	1.258(12)
I(1)–Cu(2)	2.780(2)	O(31)–N(32)	1.245(12)
I(2)–Cu(1)	2.641(2)	O(32)–N(33)	1.298(12)
I(2)–Cu(2)	2.686(2)	O(41)–N(42)	1.272(11)
I(2)–Cu(4)	2.670(2)	O(42)–N(43)	1.270(11)
I(3)–Cu(4)	2.694(2)	Cu(1)–I(2)–Cu(2)	59.59(5)
I(3)–Cu(1)	2.706(2)	N(11)–Cu(1)–I(2)	111.3(5)
I(3)–Cu(3)	2.782(2)	I(1)–Cu(1)–I(3)	113.08(6)
I(4)–Cu(2)	2.664(2)	I(2)–Cu(1)–I(4)	114.91(6)
I(4)–Cu(3)	2.694(2)	I(3)–Cu(1)–I(4)	110.38(6)
I(4)–Cu(1)	2.726(2)	I(2)–Cu(1)–Cu(3)	107.44(6)
Cu(1)–N(11)	2.044(8)	Cu(2)–Cu(1)–Cu(4)	63.58(5)
Cu(1)–Cu(2)	2.647(2)	I(4)–Cu(2)–I(2)	115.51(6)
Cu(1)–Cu(3)	2.728(2)	I(4)–Cu(2)–I(1)	113.78(7)
Cu(1)–Cu(4)	2.749(2)	I(2)–Cu(2)–I(1)	106.96(6)
Cu(2)–N(21)	2.035(8)	I(1)–Cu(3)–I(4)	117.24(6)
Cu(2)–Cu(3)	2.640(2)	I(1)–Cu(3)–I(3)	112.28(5)
Cu(2)–Cu(4)	2.844(2)	I(4)–Cu(3)–I(3)	110.71(5)
Cu(3)–N(31)	2.043(8)	I(1)–Cu(4)–I(3)	113.27(6)
Cu(3)–Cu(4)	2.709(2)	N(12)–C(6)–N(13)	109.4(8)
Cu(4)–N(41)	2.060(8)	N(23)–C(26)–N(22)	108.9(8)
O(11)–N(12)	1.279(10)	N(33)–C(46)–N(32)	108.1(8)
O(12)–N(13)	1.284(13)	N(43)–C(66)–N(42)	106.7(9)

magnetic property of **1**, as discussed below.

Selected bond lengths and angles of **2** are presented in Table 3. As shown in Fig. 5, the molecular structure of [Cu_4I_4(*m*-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, and each copper atom is bridged by three iodine atoms. The nitrogen atoms of pyridine rings are directed outward from the copper atoms. Thus, one [Cu_4I_4(*m*-PYNN)$_4$] molecule contains four nitronyl nitroxides. There are no crystallographically imposed symmetry elements on the Cu_4I_4 cluster, and small variations are found among Cu–I and Cu–Cu bond lengths (from 2.64 to 2.72 Å, from 2.64 to 2.84 Å, respectively). The Cu–Cu distances are all longer than those of [Cu_2I_2(*p*-PYNN)$_4$], indicating even weaker metal-metal bonding. The Cu–N bond lengths also 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°.

Figure 6 demonstrates the molecular arrangements in the crystal of **2**. 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, based on the McConnell principle, such intermolecular interactions will lead to ferromagnetic behavior. On the other hand, short interatomic distances were also found between the oxygen, nitrogen and carbon atoms of neighboring 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:

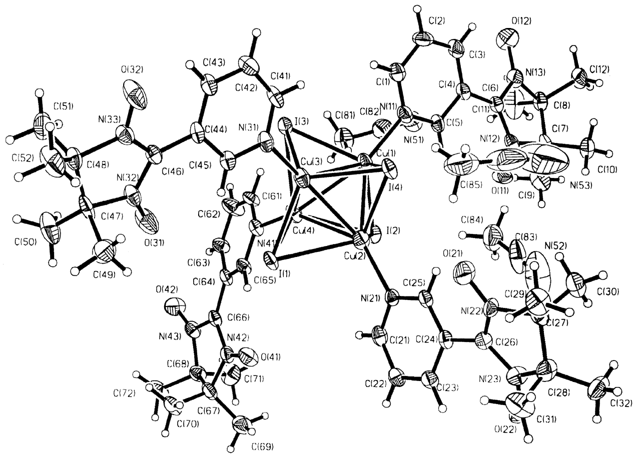


Fig. 5. Molecular structure of **2**.

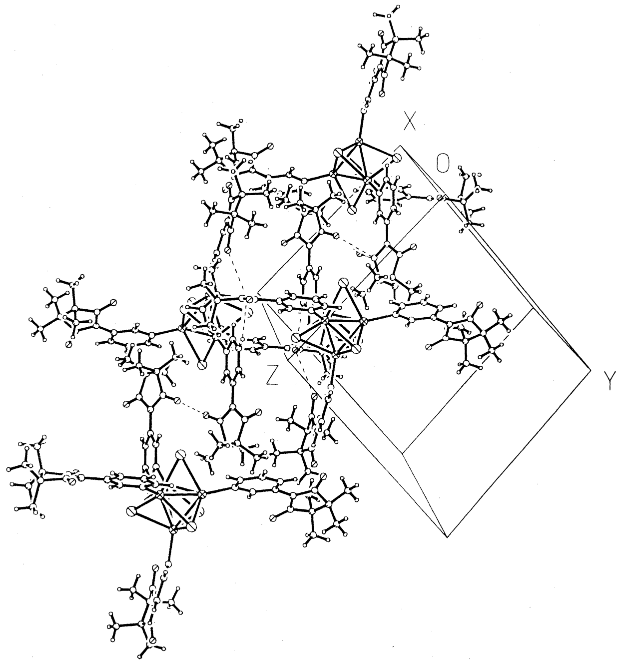


Fig. 6. Molecular arrangements in the crystal of **2**.

−x+1, −y, −z+2), O11–C22$^{\mathrm{i}}$ 3.294 Å (symmetry: −x+1, −y, −z+2), O22–C2$^{\mathrm{i}}$ 3.396 Å (symmetry: x+1, y, z), O62–O12$^{\mathrm{i}}$ 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) inplies that the antiferromagnetic interactions outweigh the ferromagnetic ones for **2**.

Previous results[11] confirm that, for nitronyl nitroxide derivatives, most of the spin densities are distributed in the imidazoline part; the rest of the atoms of the molecule possess only small spin densities. Furthermore, the copper atoms in complexes **1** and **2** have the configuration of d,^{10} being diamagnetic. Thus, as compared to the complexes formed between the pyridine-featuring nitroxides and paramagnetic ions, where strong intramolecular spin–spin interaction was reported,[7] intramolecular (through bond) spin–spin interaction for **1** should be rather weak. For **2**, due to the fact that neighboring nitronyl nitroxide units are separated by longer distances, the intramolecular (through-bond) spin–spin interaction should even be negligible. Therefore, the magnetic behaviors of **1** and **2** in their solid states should be mainly ascribed to the (through-space) interactions of *p*-PYNN and *m*-PYNN moieties.

Magnetic Studies. Figure 7 shows the temperature dependence of the molar susceptibility for **1**, which can be interpreted in terms of a 1D ferromagnetic chain,[15] using the following equation:

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

where $K = J/2k_{\mathrm{b}}T$, and symbols have the usual meanings. The theoretical best fit is obtained with $C = 1.494$ emu·K·mol^{-1}, $J/k_{\mathrm{b}} = 0.2$ K. Positive J means the intrachain spin–spin interactions are of ferromagnetic type. The inset of Fig. 7 displays the plot of the product of molar magnetic susceptibility with temperature (χ·T) *versus temperature.* At 300 K, the value of χ·T is 1.49 emu·mol^{-1}·K, which is very close to the theoretical values (1.5 emu·mol^{-1}·K) for four independent $S = 1/2$ spins. Above 70 K, χ·T almost keeps constant. Below 70K, however, χ·T increases gradually with decreasing temperature, reaching 1.71 emu·mol^{-1}·K at 5 K. This property again indicates that Cu_2I_2(*p*-PYNN)$_4$ in the solid state possesses ferromagnetic properties. The field dependence of magnetization was measured for **1** at 5 K. The magnetization increased almost linearly with the external field up to 6 T, and it shows no saturation tendency. This can be explained by the magnetic anisotropy related to the one-dimensional ferromagnetic chain structure of **1**.

The magnetic measurements for **2** were conducted under the following two conditions: 1) crystals of **2** suspended in the acetonitrile were rapidly filtered and left on the dry filter paper in open air for 5 min in order to remove the residual acetonitrile molecules adsorbed on the crystal surfaces. Then, these crystals were weighed as quickly as possible, placed in the capsule which was loaded to the sample holder and measured with the SQUID magnetometer which had been cooled to 5 K. All the procedures were finished within 10 min. The measurement was performed with increasing temperature from 5 K; 2) The crystals of **2** were dried in vacuum as indicated before, and measurements proceeded routinely. Figure 8 shows the temperature dependence of the product of molar magnetic susceptibility with temperature (χ·T) and the reciprocal molar magnetic susceptibility (1/χ) based on the data measured under the first condition. At 300 K, the value of χ·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 χ·T decreases slowly with decreasing temperature from 300 K to 50 K, but the variance is quite little. Below 50 K, however, the value plunged promptly with further decreasing temperature. Over the entire 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. Similar results were obtained from the measurement under the second condition as indicated in Fig. 9, where the temperature dependence of the product of molar magnetic susceptibility with temperature (χ·T) and the reciprocal molar magnetic susceptibility (1/χ) are presented. From 300 K to 50 K the product χ·T decreases slightly, and it decreases sharply below 50 K, being typical for antiferromagnetic interactions. Again, the temperature dependence of molar magnetic susceptibility can be well fitted with the Curie–Weiss law with $C = 1.48$ emu·mol^{-1}·K and $\theta = -8.0$ K. These two measurements give similar results, and both indicated that **2** shows antiferromagnetic properties in the solid state. Thus, it turns out that acetonitrile molecules trapped in its crystal lattice have no impact on the magnetic behavior of **2** in the solid state. Consequently, one may be allowed to correlate the magnetic property with its crystal structure as presented above (see the section of crystal structures).

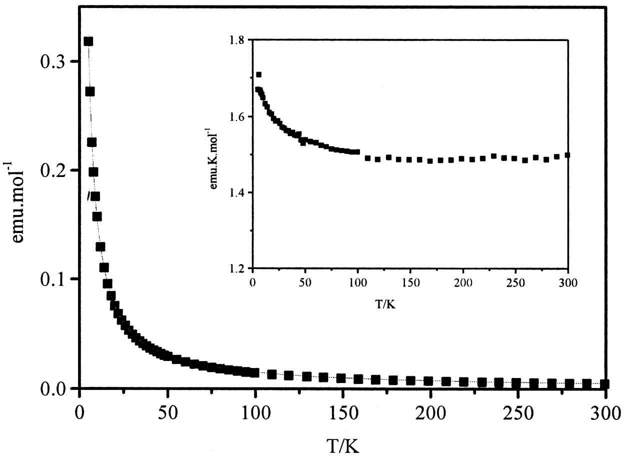


Fig. 7. Temperature dependence of molar susceptibility of **1** (the solid line represents the best fit to the one dimensional ferromagnetic model); Inset, plot of χ·T versus temperature.

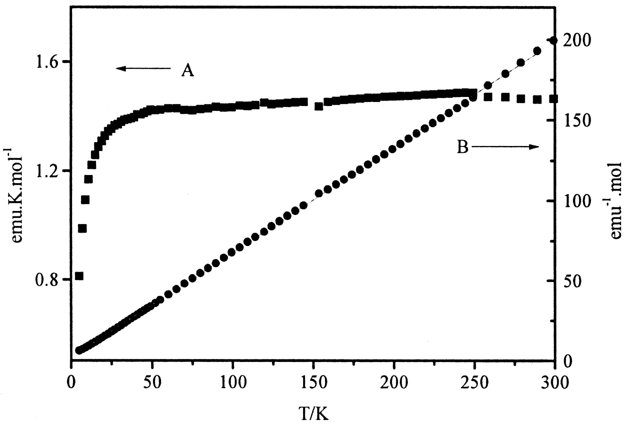


Fig. 8. Temperature dependence of molar susceptibility of **2** measured under first condition (see text): A) $\chi\cdot T$ versus temperature; B) $1/\chi$ versus temperature (the solid line represents the best fit to Curie–Weiss Law).

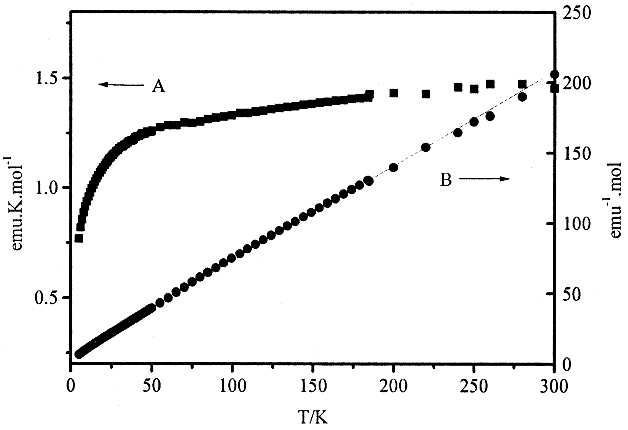


Fig. 9. Temperature dependence of molar susceptibility of **2** measured under second condition (see text): A) $\chi\cdot T$ versus temperature; B) $1/\chi$ versus temperature (the solid line represents the best fit to Curie–Weiss Law).

Summary

Crystal structures and magnetic studies of two new copper(I) iodide coordination compounds each with four nitronyl nitroxides are described. The ligating nitronyl nitroxides *p*-PYNN and *m*-PYNN vary little in chemical structure; in addition, though our preparation methods for the two coordination compounds are the same, still different crystal and molecular structures are obtained: one with rhombohedron geometry, and the other with “cubane-like” structure. Magnetic studies indicate that **1** shows ferromagnetic property, while **2** displays antiferromagnetic behavior in their solid states. Besides, we can conclude that the acetonitrile molecules captured in the lattice of **2** have no significant effect on its magnetic property. Some possible spin–spin interaction mechanisms are proposed based on the crystal structures of **1** and **2**. Taking advantage of the coordination capabilities of four nitronyl nitroxides, we plan to prepare more complicated coordination compounds with interesting magnetic materials of high dimensionality with complexes **1** and **2** as new building blocks.

The present research work was supported by NSFC (29972044), Chinese Academy of Sciences and the Major State Basic Research Development Program (G2000077500).

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