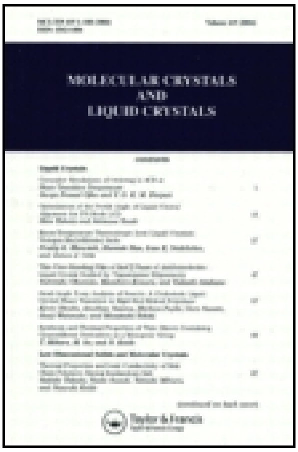

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MAGNETISM OF IMINONITROXIDE NETWORK LINKED BY COPPER(I) HALIDES

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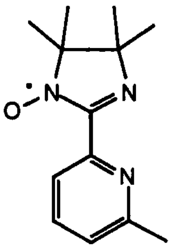
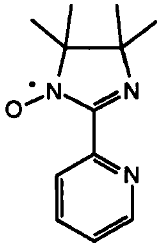
Abstract Reaction of CuI or CuBr with some iminonitroxides (impy or immepy) in methanol gave halogen bridged dinuclear Cu(I) complexes $[Cu(\mu\text{-}I)(impy)]_2$ (**1**), $[Cu(\mu\text{-}I)(immepy)]_2$ (**2**), and $[Cu(\mu\text{-}Br)(immepy)]_2$ (**3**), respectively. Complexes **1** - **3** have dimeric structures where two copper ions are doubly bridged by halide ions in a μ_2 fashion and each copper ion is tetrahedral with a bidentate iminonitroxide and two halide ions. Ligand iminonitroxides in **1** - **3** form one-dimensional radical chains and the chains are linked with halocuprate dimer units. Structural and magnetic susceptibility data support that **1** is the ferromagnetic S = 1/2 Heisenberg chains (J_F = 5.8(2) cm^{-1} and zJ' = -4.45 cm^{-1}), while **2** and **3** are the antiferromagnetic S=1/2 Heisenberg chains (J_{AF} = -0.68(2) and -1.12(2) cm^{-1}, respectively). These magnetic behaviors are discussed in connection with the stacking modes of the radicals.

INTRODUCTION

There have been increasing interest in molecular assemblies which have macroscopic properties like ferromagnetism. A key point to have such macroscopic properties in solids is to have strong intermolecular interactions. Diamagnetic metal ions have been believed not to mediate magnetic interactions. Some diamagnetic metal complexes with organic radicals as a ligand, however, have shown that ferromagnetic interactions were operative through the diamagnetic metal ions. In Ti^{IV}-[1] and Ga^{III}-semiquinone complexes,[2] for example, the semiquinone ligands show ferromagnetic interaction (J = -56 cm^{-1} ; $H = JS_1 \cdot S_2$ and 7.8 cm^{-1}; $H = -2\Sigma S_i \cdot S_j$, respectively). We have also shown that a copper(I) ion in $[Cu^I(immepy)_2](PF_6)$ (immepy = bidentate iminonitroxide) mediates rather strong intramolecular ferromagnetic coupling ($2J$ = 102 cm^{-1}; $H = -2JS_1 \cdot S_2$) between the coordinating radicals.[3] If the certain conditions are fulfilled, these diamagnetic metal ions are considered to be particularly suitable for linking organic radicals. On the other hand, copper(I) halocuplates have wide variety in structures. These molecules form discrete geometries of varying nuclearity or polymeric extended systems.[4] If organic radicals are introduced into the halocuprate cluster or network, interesting magnetic materials might be obtained. We report here the syntheses, crystal structures, and magnetic properties of halogen bridged dinuclear copper(I) complexes with iminonitroxides, $[Cu^{I}(\mu\text{-}X)(L)]_2$ (X = I or Br and L = impy or immepy).



immepy



impy

EXPERIMENTAL

Synthesis

Chemicals used were of reagent grade quality and were used without further purification. All procedures were carried out under N_2 atmosphere by using Schlenk technique. Ligand iminonitroxides were prepared by the literature method.[5]

$[Cu(\mu\text{-}I)(impy)]_2$ (**1**). To a suspension of 0.19 g (1 mmol) of CuI in 10 ml of methanol was slowly added 0.22 g of impy (1 mmol) with stirring and solution turned to dark red. Upon standing at ambient temperature for 2 days, the mixture deposited dark-red tablets. These were filtered off and air-dried and one of these was subjected to the X-ray analysis.

$[Cu(\mu\text{-}I)(immepy)]_2$ (**2**). **2** was obtained similarly to **1** with immepy (0.23 g: 0.1 mmol) instead of impy used. Dark red crystals were obtained. One of the dark red tablets was subjected to the X-ray analysis.

$[Cu(\mu\text{-}Br)(immepy)]_2$ (**3**). To a methanol solution (10 ml) of 0.18 g (0.5 mmol) of $[Cu(CH_3CN)_4](PF_6)$[6] was added 0.05 g (1 mmol) of NaBr. To this suspension of 0.07 g (0.5 mmol) of CuBr was slowly added methanol solution (10 ml) of immepy (0.12 g, 0.5 mmol). The suspension was stirred at room temperature for 1 h, yielding a dark red solution. After standing for over night, dark red tablets separated from the solution.

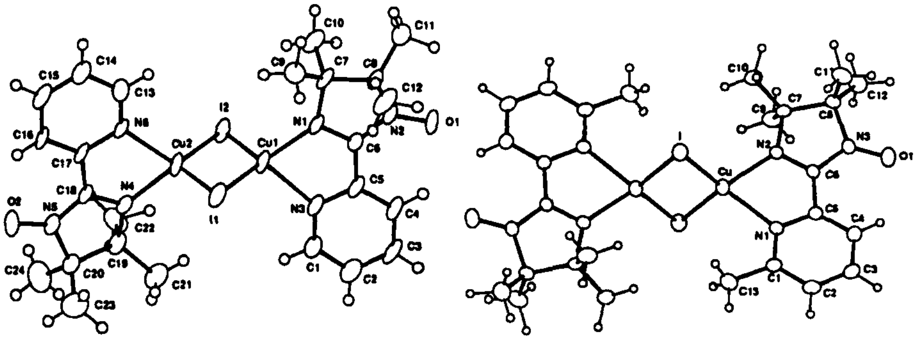
Magnetic measurement

Magnetic susceptibility data were collected in the temperature range 2.0 - 300 K and in applied 10 K Gauss with the use of a Quantum Design Model MPMS SQUID magnetometer. Powdered samples were contained in the small half of a gelatin capsule and a phenolic guide (clear soda straw) was used to house the sample holder and was fixed to the end of the magnetometer drive rod. $[Cr(NH_3)_6](NO_3)_3$ was employed as duel magnetometer calibrants. Pascal's constants were used to determinate the constituent atom diamagnetism.[7]

RESULTS

Description of the structure

$[Cu(\mu\text{-}I)(impy)]_2$ (**1**). The structure is noncentrosymmetric. An ORTEP drawing of the molecule is depicted in Figure 1(a).



(a) (b)

FIGURE 1 ORTEP diagrams of (a) $[Cu(\mu\text{-}I)(impy)]_2$ (**1**) and $[Cu(\mu\text{-}I)(immepy)]_2$ (**2**).

The structure of the complex molecule consists of discrete dimers. In the dimer, two copper(I) ions are bridged by two iodide ions, where the bond angles between two copper and bridging iodide ions are close to 60°, and the metal centers are separated by 2.592(2) Å. Coordination geometry about the copper ion is a distorted tetrahedron with two nitrogen atoms of the impy and two iodide ions. Coordinating ligands in the adjacent molecules are stacked to form one dimensional chain along the [101] direction and the chains are linked by CuI_2Cu units (Figure 2).

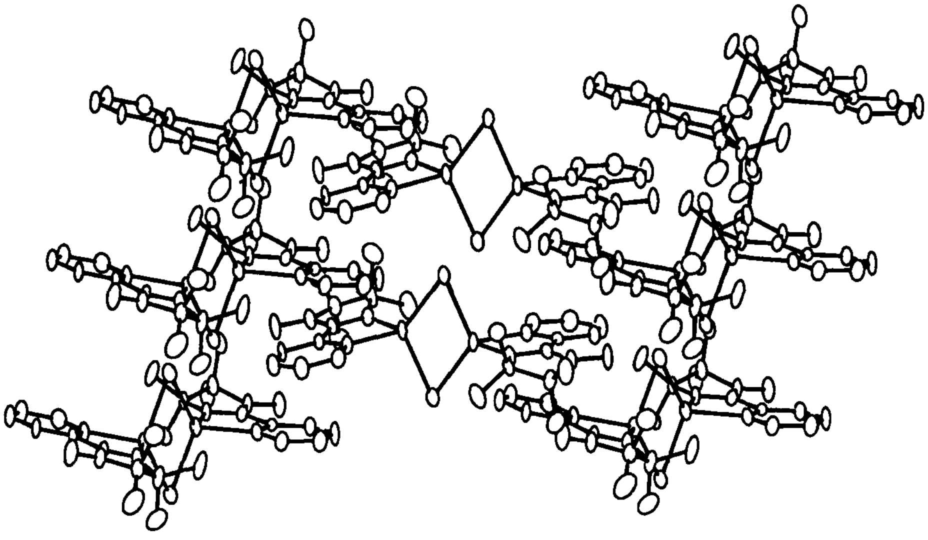


FIGURE 2 Stacking diagram of $[Cu(\mu\text{-}I)(impy)]_2$ (**1**).

Within the stack the adjacent radical ligands are related by a (1/2+x,1/2-y,1-z) and the N-O groups are close each other (O1···N4' = 3.52(1) Å). It should be noted that the closest intermolecular distance is observed between the oxygen atom (O1) of the nitroxide and the sp^2 carbon atom of the next iminonitroxide moiety (O1···C18' = 3.33(1) Å). The conjugated imino-nitroxyl fragments of the two adjacent molecules (O1-N2-C6-N1 and O2'-N5'-C18'-N4') make an angle of 22.0(8)°.

$[Cu(\mu\text{-}I)(immepy)]_2$ (**2**). An ORTEP drawing of **2** is depicted in Figure 1(b). Complex **2** crystallizes in the monoclinic space group $P2_1/a$. The complex molecule has a halogen bridged dinuclear form and is positioned on a crystallographic inversion center. Copper ions in each asymmetric unit are bridged by the two iodide ions and the two copper ions in the molecule are separated by 2.6869(8) Å. Coordination geometry about the copper ion is a pseudo tetrahedron and the four coordination sites are completed by the two nitrogen atoms from immepy and two bridging iodide ions. Bond distances about the copper ion are similar to those of **1**. The Cu-N(iminonitroxide) bond is shorter (2.030(3) Å) than the Cu-N(pyridine) bond (2.173(3) Å) and the Cu-I bond distances are 2.5978(7) - 2.6041(7) Å. Complex molecules are aligned in [101] direction and the radicals are stacked with close inter-radical distances (O1···N3' = 3.968(7) Å and O1···C6' = 3.751(8) Å) (Figure 4b). The dihedral angle formed by the conjugated imino-nitroxyl fragments of two adjacent molecules (O1-N3-C6-N2 and O1'-N3'-C6'-N2') is only 6.8(4)°.

$[Cu(\mu\text{-}Br)(immepy)]_2$ (**3**). Crystals of **3** and **2** are isomorphous. The structure consist of discrete dimer and in this dimeric entity, two copper ions are bridged by two bromide ions. Owing to the geometrical configuration, there is a inversion center in the middle of the Cu-Cu vector. Coordination geometry of the copper ion is a distorted tetrahedron. The Cu-N(pyridine) and Cu-N(iminonitroxide) distances are 2.164(3) and 1.996(2) Å, respectively, and the two of the Cu-Br distance are 2.443(1) and 2.444(2)Å. The two copper and one bridging bromide ions make a distorted equilateral triangle with the Cu···Cu distance of 2.736 Å. The radicals immepy are stacked by the same manner as **2**, where the intermolecular O1···N3' and O1···C6' distances within the stacks are 3.774(7) and 3.588(7) Å, respectively. The dihedral angle between the conjugated imino-nitroxyl fragments of two adjacent molecules (O1-N3-C6-N2 and O1'-N3'-C6'-N2') is 8.3(4)°.

Magnetic Properties

Temperature dependent magnetic susceptibilities for **1** - **3** have been measured down to 2.0 K and $\chi_m T$ values vs. temperature are plotted in Figure 3, where χ_m is molar magnetic susceptibility.

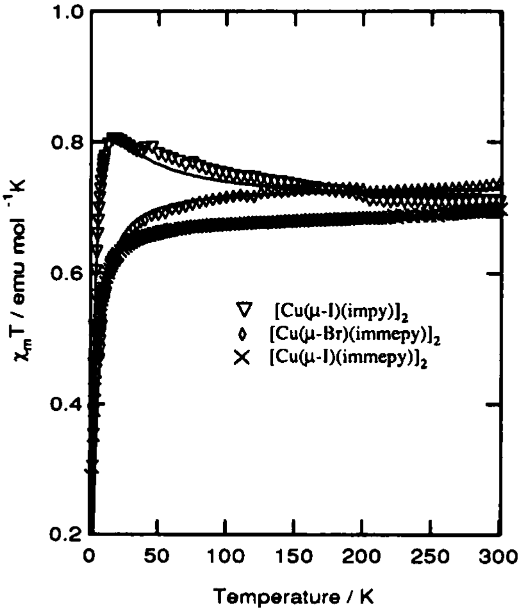


FIGURE 3 Experimental and calculated (——) $\chi_m T$ versus T plots for $[Cu(\mu\text{-}I)(impy)]_2$ (**1**) ( ), $[Cu(\mu\text{-}I)(immepy)]_2$ (**2**) ( ), and $[Cu(\mu\text{-}Br)(immepy)]_2$ (**3**) ( ).

For **1** - **3**, the $\chi_m T$ values (0.70 - 0.73 emu mol^{-1} K) at 300 K are smaller than the value expected for uncorrelated spins (0.75 emu mol^{-1} K), which is due to the small diamagnetic impurities like copper(I) halides. On lowering the temperature, $\chi_m T$ for **1** increases and exhibits a maximum at 16 K ($\chi_m T$ = 0.80 emu mol^{-1} K) and then decreases, while constant decreases down to 2 K are observed in **2**, and **3**. These magnetic behaviors suggest that in **1** some ferromagnetic interaction is predominant at intermediate temperatures and then a weaker antiferromagnetic coupling is involved at lower temperature, while in **2** and **3** radicals are antiferromagnetically coupled.

The structural analysis of **1** shows that the radical ligands are stacked to form a chain with the short contact (O1···N4' = 3.52(1) and O1···C18' = 3.33(1) Å), while the Cu-I_2-Cu unit separates the coordinating radicals by 6.33(1) Å (= N1···N4). Therefore, the magnetic interaction in **1** can be interpreted by a ferromagnetic intrachain interaction with a weak interchain (intramolecular) antiferromagnetic interaction. Assuming isotropic Heisenberg interaction, the hamiltonian is expressed as

$$H = -2J\sum S_i \cdot S_{i+1} \qquad (1)$$

where J is the intrachain-exchange coupling constant and the summation is over all members of the chain. The magnetic susceptibility for the Heisenberg ferromagnetic chain can be express as[8]

$$\chi_m = Ng^2\mu_B^2\left[\frac{1+a_1K+a_2K^2+a_3K^3+a_4K^4+a_5K^5}{1+b_1K+b_2K^2+b_3K^3+b_4K^4}\right] \qquad (2)$$

where $K = J_F/2k_BT$ and a_i and b_i are expansion coefficients and other symbols have their usual meaning. The total magnetic susceptibility is

$$\chi_m' = \frac{\chi_m}{\left[1-2zJ'\chi_m / Ng^2\mu_B^2\right]} \qquad (3)$$

where J' and z are the interchain interaction and the number of neighboring chains, respectively. The least square fitting of the experimental data with the eq. (3) led to J_F = 5.8(2) cm^{-1}, zJ' = -4.45(5) cm^{-1}, and g = 1.940(3) for **1**.

The magnetic behaviors of **2** and **3** are different from that of **1** in spite of the fact that the radicals are aligned in the chain structure. In **2** and **3** gradual decreases in $\chi_m T$ values down to 2.0 K suggest that both intra- and interchain antiferromagnetic interactions are operative. Therefore, the magnetic data for **2** and **3** can be interpreted by the alternating antiferromagnetic Heisenberg model. The appropriate spin hamiltonian is eq. (4),

$$H = -2J\sum_{i=1}^{n/2}\left[S_{2i}\cdot S_{2i-1} + \alpha S_{2i}\cdot S_{2i+1}\right] \qquad (4)$$

where J and αJ are exchange integral couplings of a spin with its nearest neighbor and its other neighbor, respectively, with $|\alpha|<1$. This leads to numerical results that can be fitted by the empirical expressions given in eq. (5),

$$\chi_m = \frac{Ng^2\mu_B^2}{k_BT}\left[\frac{A + Bx + Cx^2}{1 + Dx + Ex^2 + Fx^3}\right] \qquad (5)$$

where $x = -J_{AF}/k_BT$ and constants A - F are power series in terms of α.[9] Total magnetic susceptibility can be expressed as eq. (3) which includes interchain interaction. The best fits to the data were obtained with J_{AF} = -0.68(2) cm^{-1}, zJ' = -0.79(4) cm^{-1} and g = 1.910(1) for **2**, J_{AF} = -1.12(2) cm^{-1}, zJ' = -0.49(5) cm^{-1} and g = 1.999(1) for **3**. In these calculation, the α values were fixed to 1 because the radicals are stacked with equidistance.

DISCUSSION

Nitronylnitroxides and iminonitroxides have been reported to have a variety of intermolecular magnetic couplings. Intermolecular ferromagnetic interactions have been observed in a series of nitroxides[10] and some of them exhibit spontaneous magnetization at very low temperature (0.6 K).[11] In contrast to the ferromagnetic couplings, a large number of intermolecular antiferromagnetic couplings have been reported. The sign and magnitude of the intermolecular magnetic interactions depend strongly on a relative arrangement of adjacent N-O groups, and the correlation between the magnetic interactions and geometrical parameters have been discussed.[12]

The magnetic interaction between two unpaired electrons are generally antiferromagnetic. On the other hand, the ferromagnetic interactions require that peculiar conditions are fulfilled. This situation has been well rationalized by Kahn et al,[13] and Miller and Epstein.[14] i) Orthogonality of magnetic orbitals. The magnetic interaction J can be expressed as the sum of K (exchange integral) and $2\beta S$ (β: transfer integral and S: overlap integral) which favor the ferromagnetic and antiferromagnetic interaction, respectively. If the magnetic orbitals are (accidentally) orthogonal each other, the ferromagnetic interaction is obtained. (ii) Spin polarization (McConnell mechanism[15]). Spin polarization induces positive or negative spin density on a molecule. If molecules overlap with opposite sign of the spin density, an intermolecular ferromagnetic interaction would be expected.[16] iii) Ferromagnetic interaction involving charge transfer interactions (a configurational mixing interaction between ground and excited high-spin configurations).[17]

Complex **1** shows intermolecular ferromagnetic coupling, while complexes **2** and **3** show intermolecular antiferromagnetic interactions. Subtle differences in stacking modes must be responsible for the magnetic behaviors in **1** - **3**. The spin density distributions in some nitronylnitroxides have been determined by the polarized neutron diffraction study and MO calculation.[18] The positive spins are populated over the N-O groups, while the large negative spin density appears on the sp^2 carbon atom bridging two N-O groups. This indicates large spin-polarization effect on the nitronylnitroxide. The electronic structures of pyridyl-iminonitroxides is considered to be very similar to the nitronylnitroxide. The positive spin density locates on both imino-nitrogen atom and N-O group, while the negative spin on the carbon atom. Structural analysis reveals that a short intermolecular contact in **1** involves the oxygen atom of the N-O group and the sp^2 carbon atom of the adjacent molecule (O1···C18' = 3.33(1) Å). The corresponding intermolecular contacts (O1···C6') in **2** and **3** are 3.751(8) and 3.588(7) Å, respectively. These two atoms carry the opposite sign of the spin which alternate along the stack and this matches the McConnell's criteria. The observed contact distances in **1** - **3** suggest that the spin polarization leading to the intermolecular ferromagnetic interaction is more effective for **1** than for **2** and **3**.

Different intrachain magnetic behaviors of **1** from **2** and **3** can be understood by the stacking mode of the radicals (Figure 4). In **2** and **3** the conjugated imino-nitroxyl fragments of two adjacent molecules stack with a parallel alignment, where dihedral angles between the two imino-nitroxyl planes are 6.8(4) and 8.3(4)°, respectively. In **1**, on the other hand, two imino-nitroxyl planes tilt toward each other with an angle of 22.0(8)°. Gatteschi and Rey have pointed out that a σ-type overlap (SOMO-SOMO overlap) of the nitronylnitroxide π^* orbital leads to the antiferromagnetic interaction and this will be maximum when the adjacent N-O groups are parallel.[19] The resulting overlaps in **2** and **3** favor the antiferromagnetic interaction, while the tilted stacking in **1** diminishes the antiferromagnetic contribution. As the result, in spite of the fact that the intermolecular short contacts in **1** - **3** contribute to the stabilization of the intermolecular ferromagnetic interaction due to the spin-polarization, the intrachain magnetic interaction for **1** is ferromagnetic and those for **2** and **3** are antiferromagnetic.

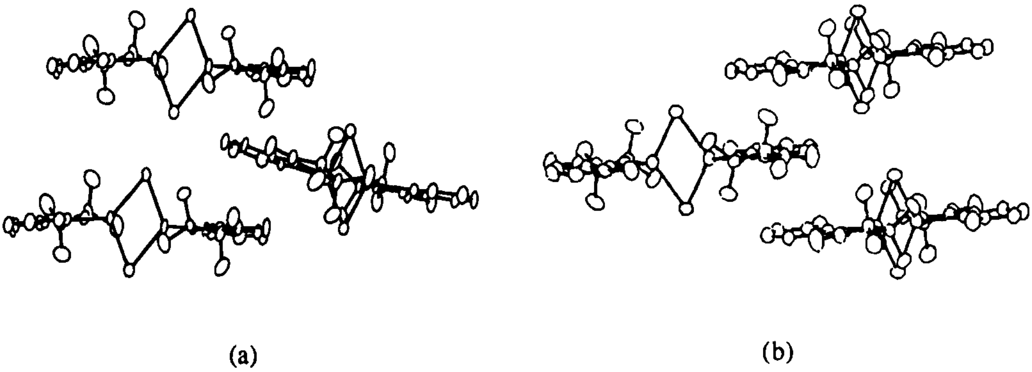

(a) (b)

FIGURE 4 Packing diagram in a view parallel iminonitroxides of (a) [Cu(μ-I)(impy)]$_2$ (**1**) and (b) [Cu(μ-I)(immepy)]$_2$ (**2**).

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