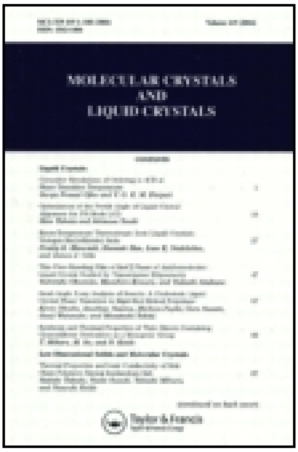

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MAGNETIC INTERACTIONS IN Cu(I) AND Ag(I) IMINONITROXIDES

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Abstract Orthogonal arrangement of iminonitroxides in [Cu^{I}(immepy)$_2$](PF$_6$) (**1**) and [Ag^{I}(impy)$_2$](PF$_6$) (**2**) results in propagation on intramolecular ferromagnetic interaction between coordinating iminonitroxides through these diamagnetic ion. In **1**, iminonitroxides coordinate to the Cu^{I} ion in a tetrahedral fashion, the dihedral angle between coordinating iminonitroxides being 88.7 °. Magnetic susceptibility and epr measurements for **1** show the typical ferromagneic behavior with large zero field splitting ($2J = 91(1)$ cm^{-1} ($H = -2JS_1 \cdot S_2$); $D = 3.62$ cm^{-1}). In **2**, the four coordination sites of Ag^{I} ion were completed with two iminonitroxides and the dihedral angle between the iminonitroxides is 79.2 °. Temperature dependence of teh epr spectra for frozen ethanol solution of **2** shows that the intramolecular mangetic interaction between radicals is ferromagnetic ($\theta = 4$ K).

INTRODUCTION

Magnetic interactions within or between molecules are typically antiferromagnetic, which is well understood by the molecular orbital considerations. If two magnetic orbitals, each having one electron, are sufficiently close to interact, they can overlap to form antibonding and bonding orbitals. Both electrons localize on the bonding orbital with anti-parallel spin alignment. This situation can be regarded as a very weak chemical bond. However, ferromagnetic interaction can arise in several ways.[1] (i) Orthogonal arrangement of the magnetic orbitals can lead to stabilization of the high-spin state, such situation being obseved for metal complexes and metal-radical complexes.[2] (ii) Spin polarization, a strategy originally proposed by McConnell,[3] and documented for intermolecular stacks having complementaly spin alignment can lead to ferromagnetic interaction.[4] (iii) Topological symmetry of π-electron network was applied to design high-spin organic molecules using poly carbenes.[5] (iv) Certain configurational mixing of a ground high-spin ground state with high-spin charge transfer configurations stabilizes the high-spin ground state.[6] It should be noted that the easiest way to achieve ferromagnetic interactions is the approach based on the orthogonality of magnetic orbitals. In addition to orthogonality, the existence of direct or indirect charge transfer interactions between paramagnetic centers can generate or enhance ferromagnetic interactions, such effects being most conveniently treated with a valence bond-like approach.

Recently, metal semiquinones such as $[M^{III}(3,6\text{-DBSQ})_3]$[7] (M = Al and Ga) and $[Ga^{III}(3,5\text{-dtbsq})_3]$,[8] which have orthogonal coordinations of semiquinones, have been reported to show weak ferromagnetic interactions (J = 6.2, 8.6, and 7.8 cm^{-1} where $H = -2J\Sigma S_i \cdot S_j$). On the other hand, $[M^{IV}(\text{Cat-N-SQ})_2]$ (M = Ti, Ge, an Sn) (Cat-N-SQ = tridentate Schiff base biquinone)[9] were characterized by triplet ground state with the exchange coupling constants of J = -56, -27, and -23 cm^{-1} ($H = J\Sigma S_1 \cdot S_2$), respectively. It should be noted that the magnitude of magnetic interactions through the diamagnetic ion depends strongly on energy of the dπ orbitals of metal ions.

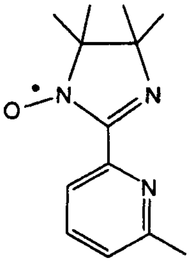
Which diamagnetic metal complexes provide the appropriate symmetry and orbital energy to propagate ferromagnetic interaction? Ab initio molecular orbital calculations of the divalent metal oxides have proven that among the first low transition metal ions d-orbital energy of the copper ion is the closest to the oxygen p-orbitals among the first row transition metal ions.[10] Furthermore, XPS study of $[2,5\text{-DM-DCNQI}]_2Cu$ (2,5-DM-DCNQI = 2, 5-dimethyl-N, N'-dicyanoquinonediimine),[11] which shows conducting properties, has revealed that the copper ion is in the mixed valence state.[12] It is, therefore, expected that the copper ion has an appropriate d-orbital energy to interact with the organic π-orbitals. In addition, Cu^I ions are known to favor a tetrahedral coordination geometry[13] which is suitable for the orthogonal arrangement for bidentate ligands. Thus, it is anticipated that coordination of two bidentate radical ligands to copper(I) ion would lead to a ferromagnetic interaction between radicals. In this report, we synthesized copper(I) and silver(I) complexes of general formula $[M(L)_2](PF_6)$ where L is the bidentate iminonitroxide (immepy and impy) and their magnetic properties are discussed. A preliminary communication of the structure and magnetic property of the copper(I) complex has already been published.[14]

EXPERIMENTAL

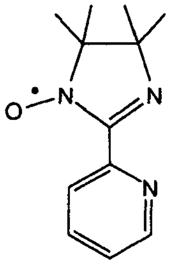
Syntheses.

$[Cu^{I}(immepy)_2](PF_6)$ (**1**). All procedure has been carried out under nitrogen atmosphere. A solution of immepy[15] (0.23 g, 1.0 mmol) in ethanol (10 mL) was added to a solution of $[Cu^{I}(CH_3CN)_4](PF_6)$ (0.19 g, 0.5 mmol) in ethanol (15 mL). After the solution was left standing overnight, dark red tablets were filtered by suction and one of them was subjected to the X-ray analysis.

$[Ag^{I}(imepy)_2](PF_6)$ (**2**). $Ag^{I}(PF_6)$ (0.25 g, 0.1 mmol) dissolved in methanol (30 mL), was added to a solution of impy (0.44 g, 0.2 mmol) in methanol (10 mL). The resulting red crystalline solids were filtered, recrystallized from hot ethanol to produce red needlelike crystals and one of them was subjected to the X-ray analysis.



immepy



impy

RESULTS AND DISCUSSION

Description of the Structure.

Structures of $[Cu^{I}(immepy)_2]^+$ (**1**) and $[Ag^{I}(impy)_2]^+$ (**2**) are shown in Figure 1. In **1**, copper ion, which locates on two fold axis, is coordinated by the crystallographically equivalent immepy ligands acting as bidentate ligands. The coordination geometry about copper ion can be express as a pseudotetrahedron and four coordination sites of the copper ion are completed by four nitrogen atoms. The Cu-N(iminonitroxide) bond is slightly shorter (1.953(5) Å) than the Cu-N(pyridine) bond (2.081(6) Å). It should be noted that two radical planes (magnetic orbitals) coordinating to copper ion are perpendicular to each other with the dihedral angle of 88.7 °.

In **2**, four nitrogen atoms from two of impy coordinate to silver ion in distorted tetrahedral fashion. The average bond lengths between silver ion and coordinating nitrogen atoms are 2.375 and 2.228 Å for Ag-N(pyridine) and Ag-N(iminonitroxide), respectively. Dihedral angle between two radical planes is 79.2°.

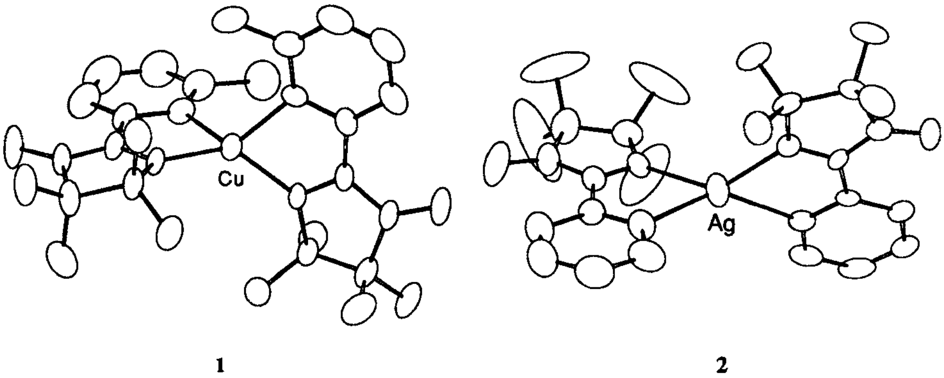


FIGURE 1. Crystal structures of $[Cu^I(immepy)_2]^+$ **1** and $[Ag^I(impy)_2]^+$ **2**.

Magnetic Properties

Temperature dependence of magnetic susceptibilities in the temperature range of 2.0 to 300 K were measured and depicted in Figure 2 in the form of χ_mT versus T plot.

$[Cu^I(immepy)_2](PF_6)$ (**1**). χ_mT values for **1** show a gradual increase as the temperature decreases, reaching a plateau (0.96 emu mol^{-1}) and χ_mT values decrease suddenly below 20 K. There are two iminonitroxides coordinating to diamagnetic copper ion, hence, a magnetic exchange interaction makes singlet and triplet states. Temperature dependence of the χ_mT above 20 K is quite characteristic of ferromagnetically coupled biradical. Sudden decrease of χ_mT values below 20 K is due to either intermolecular antiferromagnetic interaction or zero-field splitting of the triplet state. We have measured X-band epr spectrum (Figure 4(a)) of a dilute frozen ethanol solution at 5 K in order to eliminate the effect of intermolecular antiferromagnetic interactions. This spectrum represents an intense signal at 11800 G in addition to a sharp feature at 3300 G most likely due to radical impurity. We analysed the esr spectrum, using the method reported by Kottis and Lefebvre,[16] and obtained $g = 2.0$, $|D| = 3.6$ cm^{-1}, and $|E| = 0$. The spectrum also shows a poorly resolved feature around 1300 and 5400 G, the origin of which is not understood yet. It should be noted that Q band epr spectrum for frozen ethanol solution at 5K shows no signal except for radical impurity.

Temperature dependence of the magnetic susceptibility for **1** can be explicitly expressed by the intramolecular exchange J and zero field splitting parameters. If no

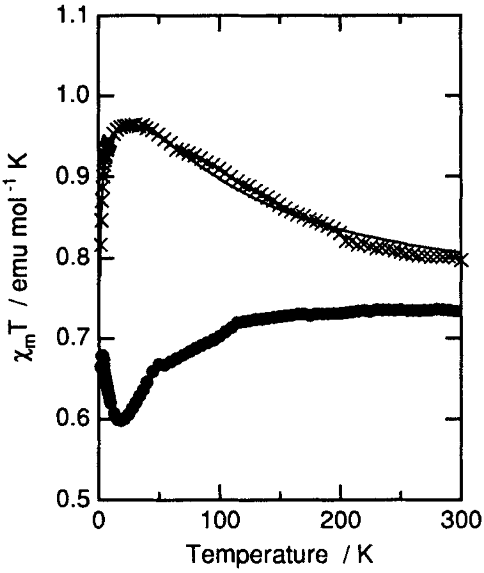


FIGURE 2. $\chi_m T$ versus T plots for (x) [Cu^I(immepy)$_2$](PF$_6$) (**1**) and (●) [Ag^I(impy)$_2$](PF$_6$) (**2**)

hyperfine interaction and an isotropic g-tensor are assumed and the magnetic field is parallel to the z axis, the spin Hamiltonian is given by equation 1.

$$H = -2JS_1 \cdot S_2 + g\beta HS_z + D\left\{S_z^2 - \frac{1}{3}S(S+1)\right\} + \frac{E}{2}(S_+^2 + S_-^2) \qquad (1)$$

The molar susceptibility is given by the Van Vleck equation and the resulting magnetic susceptibility equation has been used to fit the magnetic data. The least squares fitting of the data lead to $2J$ = 91(1) cm^{-1} and g=1.978(3), θ = 0.2(1) K, where D and E were fixed to -3.62 and 0 cm^{-1}, respectively.

[Ag^I(impy)$_2$](PF$_6$) (**2**). Figure 2 shows plots of $\chi_m T$ versus T for **2**. The high-temperature $\chi_m T$ value (0.73 emu K mol^{-1}) is lower than expected for uncorrelated two spins (0.75 emu K mol^{-1}). The $\chi_m T$ values steadily decrease as the temperature lowered and reached to the minimum value of 0.60 emu K mol^{-1} at 19 K. In the high-temperature region of 19 - 300K, inflection points are observed at 50 and 120 K. Below 19 K, a very abrupt rise in $\chi_m T$ is observed ($\chi_m T$ = 0.678 emu K mol^{-1} at 2.5 K). The interpretation

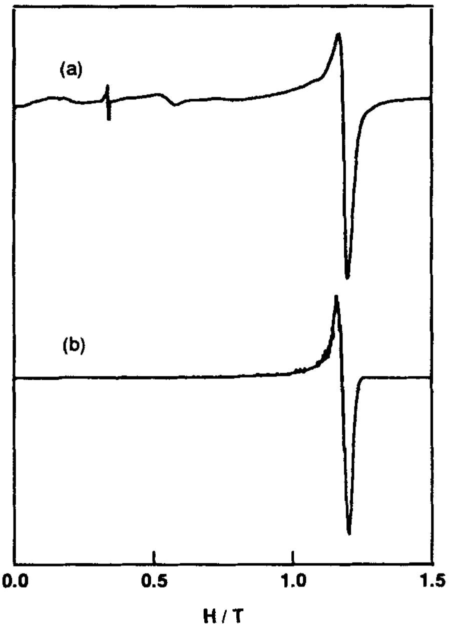


FIGURE 3. X-band epr spectra of $[Cu^{I}(immepy)_2](PF_6)$:
(a) experimental spectrum in frozen ethanol solution at 5K;
(b) theoretical spectrum for a randomly oriented triplet system for given values of $|D|$ and $|E|$ in the text.

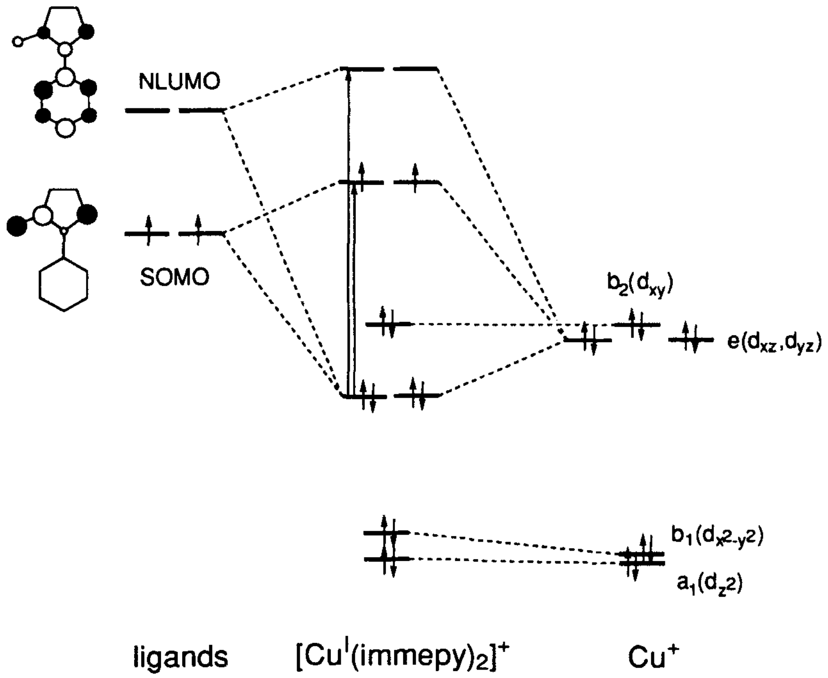
of the magnetic data requires the consideration of the intramolecular coupling of the two spins as well as the intermolecular coupling. The unusual abrupt rise in $\chi_m T$ below 19 K is due to either intramolecular ferromagnetic or weakened antiferromagnetic interactions accompanied with phase transition.

In order to get insight about the intramolecular magnetic interaction of **2**, we measured X-band epr spectrum of frozen ethanol solution at 5 K. It presents an intense feature at 3370 G with weak signals at 2910 and 3830 G and well resolved half-field signal at 1607 G. To interpret this spectrum quantitatively, we calculated the zero-field splitting parameters using the method described in epr study for **1**. |D| and |E| values obtained are 0.043 and 0.014 cm^{-1}, respectively. It should be noted that the relative intensity of the signal at 3370 G in the observed spectrum is larger than that for the simulated one, however, the origin of which is not understood yet. We have measured temperature dependence of the signal intensity for $\Delta m=2$ transition in the temperature range 10 to 80 K. The Curie plot gives a positive Weiss constant $\theta = 4$ K. It should be noted that the intramolecular magnetic interaction is ferromagnetic. Gradual decrease of the $\chi_m T$ values in high-temperature region is due to the intermolecular antiferromagnetic interaction.

Electronic Spectra.

UV-visible spectra of **1**, **2**, and immepy were measured in acetonitrile. $[Cu(immepy)_2]^+$ shows intense absorption bands at 460 nm (ε = 6300 mol dm^{-3}) with a shoulder band at 510 nm and 764 nm (ε = 5000), while these absorption bands were not observed both in the spectra of immepy and $[Ag(impy)_2]^+$. If we asume pseudotetrahedral symmetry (D_{2d}) for **1**, t_2 orbitals of the copper ion in T_d symmetry split into $e(d_{xz},d_{yz})$ and $b_2(d_{xy})$ orbitals. Under the D_{2d} symmetry, a combination of ligand π^* orbitals have e, a_2, and b_1 representations, of which e has the same symmetry as two of the copper d orbitals. PM3 molecular orbital calculation of the ligand immepy, where iminonitroxide moiety and pyridine ring are coplanar, shows that singly occupied molecular orbital (SOMO) consists mainly with iminonitroxide moiety, while the next lowest unoccupied orbital (NLUMO) delocalizes onto the whole π system. Both SOMO and NLUMO have the same symmetry

Scheme I.



as e(d_{xz},d_{yz}), which allows to overlap with d_{xz} and d_{yz} orbitals. Hence, the lower energy band (764 nm) corresponds to a e(d_{xz},d_{yz}) → SOMO transition, the higher energy band (460 nm: 2.70 eV) to e(d_{xz},d_{yz}) → NLUMO, and shoulder at 510 nm (2.43 eV) to b_2(d_{xy}) → NLUMO (Schem I). It should be noted that the lack of such metal to ligand charge transfer bands in silver complex **2** is supposed to be due to the large energy separation between metal d and ligand π* orbitals.

CONCLUSION

The results reported here show that (pseudo)tetrahedral coordination of copper(I) and silver(I) ions offer the orthogonal coordination of two iminonitroxides and this leads to ferromagnetic interactions. Especially, $[Cu^I(immepy)_2](PF_6)$ (**1**) showed the fairly strong ferromagnetic interaction with a large zero-filed splitting ($|D| = 3.62$ cm^{-1}). The large zero-filed splitting can be interpreted by the charge transfer interaction. Complex **1** showed a strong absorption band at 764 nm which corresponds to the electron transfer from the e(d_{xz},d_{yz}) orbital to the SOMO (radical). The π-back donation, which mixes the e(d_{xz},d_{yz}) orbital and SOMO, induces a large spin delocalization onto cooper(I) ion and the closer spins results in the large zero-filed splitting.

The mechanism, which determines the relative energy (J) of the triplet and singlet states, has been often discussed by Heitler-London interaction and valence bond configuration interaction between ground and charge transfer configurations.[17] J depends primarily on Heitler-London type interaction within the ground state and the triplet singlet energy gap is expressed as:

$$J_{GS} = 2K_{\pi^*\pi^*} + 4\beta_{\pi^*\pi^*}S_{\pi^*\pi^*}$$

where $K_{\pi^*\pi^*}$, $\beta_{\pi^*\pi^*}$ and $S_{\pi^*\pi^*}$ represent the two electron exchange, transfer, and overlap integrals between radical SOMOs, respectively. In **1**, the coordinating two radicals are orthogonally arranged. As a result, $S_{\pi^*\pi^*}$ is zero and the strong ferromagnetic coupling in **1** primarily arises from two-electron exchange integral $2K_{\pi^*\pi^*}$. Compound **1**, however, showed the fairly strong charge transfer band which corresponds to the π-back donation to the radical SOMO. It might be necessary to consider a valence bond configuration interaction to interpret the ferromagnetic interaction.

In this paper we showed that coordination geometry characteristic of d^{10} metal ion provides an orthogonal arrangement of iminonitroxides and this leads to ferromagnetic interaction. In design of magnetic material, metal ions have been regarded and used as a source of spins. The strong ferromagnetic interaction observed in the copper(I) iminonitroxides indicates that the copper(I) ion is undoubtedly useful for being used as joints of radical networks. We are currently attempting to design multi-dentate radical ligands, which are able to bridge two copper(I) ion.

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