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The Metal-Dependent Regiospecificity in the Exchange Coupling of Manganese(II), Copper(II), and Chromium (III) Ions with the Aminoxyl Radical Attached as a Substituent on the Aromatic Base Ligands

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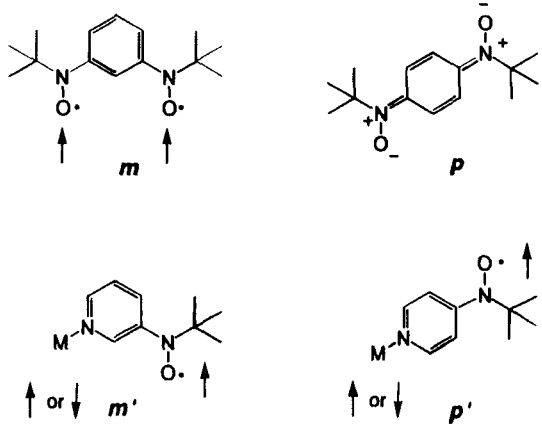
[Mn(II)(hfac)$_2$] and **[Cu(II)(hfac)$_2$]** formed 1:2 and 1:1 complexes with 3- and 4-(*tert*-butyloxyamino)pyridine (3- and **4NOPy**) and 1-{3- and 4-(*tert*-butyloxyamino)phenyl}imidazole (3- and **4NOIm**). The molecular and crystal structures for seven of them were investigated by X-ray analyses to show that the 1:2 complexes of **Mn(II)** and **Cu(II)** with 3-and **4NOPy** have hexacoordinated structures in *trans* geometry and 1:1 complexes of Mn(II) with 4NOPy, 3-, and 4NOIm have cyclic dimer structures in *cis* coordination. Magnetic properties of the obtained fourteen complexes including *meso*-tetraarylporpyrinatochromium(III)Cl derivatives were investigated by magneto/susceptometry. Temperature dependence of the molar paramagnetic susceptibilities revealed that the coupling between the metal ion and the aminoxyl radicals through the aromatic rings in the complex ligated with **4NOPy** were antiferromagnetic for Mn(II) and Cr(III) and ferromagnetic for Cu(II) complexes. The magnetic couplings opposite in sign to those of 4NOPy were obtained in the Cu(II) complex with 3NOIm and Cr(III)TPP complexes with 3NOPy.

Keywords: free radicals; aminoxyl radicals; manganese(II) complexes; copper(II) complexes; exchange coupling; hybrid spin systems

INTRODUCTION

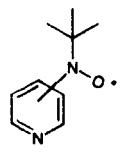
Whereas *o*- and *p*-quinodimethanes and their analogs, e.g., the Thiele hydrocarbon, have closed-shell electronic structures, *m*-quinodimethane and the Schlenk hydrocarbon have triplet ground states.[1] The same is true for the corresponding dicarbenes; whereas the *p*-phenylenebis(phenylcarbene) has a low-spin ground state,[2a] the *m*-isomer is a high-spin quintet species in the ground state.[2,3] In heteroatom-centered diradicals, *p*-benzoquinonediimine *N*, *N'*-dioxide (***p***)[4a] and *m*-phenylenebis(*N*-*tert*-butylaminoxyl) (***m***) are obtained as stable solids with singlet and triplet ground states, respectively.[4] This regiospecificity in the exchange interaction between the two radical centers at the benzylic positions is derived from differences in the phase of the spin polarization of the π-electrons on the benzene ring and has served as an important guiding principle for designing super-high-spin organic molecules as prototypes for purely organic ferromagnets.[4,5] Connection of *n* carbene units through the *m*-phenylene, 1,3,5-benzenetriyl, and other ferromagnetic coupling units gives rise to various polycarbenes with $S = n$ ground states[3] in which the highest record of the series reported so far is $S = 9$.[6]

Scheme 1

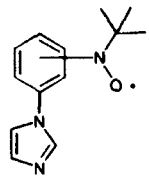


Efforts to increase numbers of the aligned spins have been hampered by the development of antiferromagnetic intra- and/or interchain interactions between the carbene centers assembled in high local concentration; chemical bonds appear to be formed in the extreme.[7]

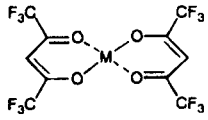
Since metal ions serve as connectors for high dimensional molecular architecture by bridging the lower dimensional organic ligand molecules used as building blocks,[8] construction of heterospin systems[9] from organic free radicals and metal ions by self-assembly appears to be one of the most promising design strategies for real molecular-based magnets.[10] Recently we reported successful synthesis of ferri/ferromagnets by using bis- and tris(*tert*-butylaminoxyl) radical units ligated to bis(hexafluoroacetylacetonato)-manganese [Mn(hfac)$_2$].[11] In order to obtain further insight into the sign and magnitude of the exchange coupling between the magnetic metal ions and the radical centers, it is of particular interest to see if the regiospecificity found in organic π-diradicals like quinodimethanes (*p* vs *m*) is also applicable to the interaction between free radical centers and coordinated magnetic metal ions (M) that are separated by π-conjugated ligands (*p* ′ vs. *m* ′ in Scheme 1). For this purpose, M(hfac)$_2$; M = Mn(II) and Cu(II), and pyridine (NOPy) and *N*-phenylimidazole (NOIm) derivatives as base ligands having the *tert*-butyl-aminoxyl radical at 3- or 4-positions of the aromatic ring were selected. Possible structures of 1:2 and 1:1 complexes are shown in Scheme 2. Since the ligands NOPy and NOIm are bis(monodentate) and capable of ligation at the aminoxyl radical, there are a number of structural possibilities for 1:1



3- position : 3NOPy
4- position : 4NOPy

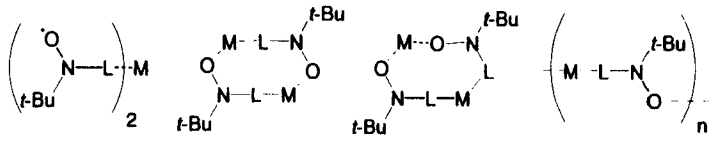


3- position : 3NOIm
4- position : 4NOIm



M(hfac)$_2$
M = Cu(II) and Mn(II)

Scheme 2



complexes in addition to 1:2 complex (a). Cyclodimerization (b) would give two macrocycles in which both M ions are ligated to one N and one O with a formal center of symmetry or one M ion is attached to two Ns and the other to two O's with a formal plane of symmetry (c). Polymerization of these should lead in principle to head-to-tail (d), head-to-head/tail-to-tail, or irregular polymers. There are a number of other possibilities for oligomerization. The sign and magnitude of the exchange interaction between the two components in these metal-radical heterospin systems are expected to depend not only on the periodicity of the ligand π orbitals, but also strongly on the magnetic d orbitals of the metal ion. For example, Mn(II) ions have unpaired electrons in the π magnetic orbitals which can overlap with the 2p orbital at the nitrogen atom in which the spin is polarized due to the substituent aminoxyl radical. On the contrary, the Cu(II) ion in the octahedral ligand field has one unpaired electron in the $d_{x^2-y^2}$ orbital that has a σ character,[12,13] and therefore its complexes are expected to show different magnetic behavior from that of Mn(II) ion.[13]

Furthermore, the exchange coupling between chromium(III) ion and aminoxyl radical was investigated by employing *meso*-tetraphenylporphyrinato- and tetraanisylporphyrinatochromium(III) complexes, [Cr(III)TPPCl] and [Cr(III)TAPCl] with 3- and 4NOPy.

RESULTS AND DISCUSSION

1. Preparation and X-ray Structure Analyses of Metal Complexes

1:2 Complexes [M(hfac)$_2$(3- and 4NOPy)$_2$] and 1:1 complexes [M(hfac)$_2$-(4NOPy)]$_2$ where M = Mn(II)[14] and Cu(II)[12] were prepared by mixing [M(hfac)$_2$] in *n*-heptane solution and free ligands NOPy in CH_2Cl_2 solution in molar ratios of one to two and one to one, respectively. The resulting precipitates were recrystallized from appropriate solvents to afford 1:2 and 1:1 complexes as greenish and orange crystals for Cu(II) and Mn(II) complexes, respectively. Two kinds of 1:1 complexes of Mn(II) ligated with 4NOPy were obtained (complex **a** and **b**). Similarly, complexes [M(hfac)$_2$-(NOIm)]$_2$ were prepared. The solvent was slowly evaporated under a stream of nitrogen gas to give dark brown crystals. Elemental analysis showed that they were unexpected 1:1 complexes of [Mn(hfac)$_2$] with NOIm,[15] and 1:2 complexes of [Cu(hfac)$_2$] with NOIm. In the former, the composition did not change even when they were mixed in a 1:8 molar ratio. The 1:1 complexes [CrTPP(4NOPy)Cl] and [CrTAP(4NOPy)Cl] were obtained as powders by reprecipitation from CH_2Cl_2-*n*-hexane.[14]

Seven metal complexes, [Mn(hfac)$_2$(4NOPy)$_2$], [Mn(hfac)$_2$(4NOPy)]$_2$, [Mn(hfac)$_2$(3- and 4NOIm)]$_2$, [Cu(hfac)$_2$(3- and 4NOPy)$_2$], and [Cu(hfac)$_2$-(4NOPy)]$_2$ gave single crystals amenable to X-ray crystal structure analysis. ORTEP drawings of the representative molecular structures are shown in FIGURE 1.

1.1 The Manganese Complexes

(A) [Mn(hfac)$_2$(4NOPy)$_2$]. As shown in the ORTEP drawing in FIGURE 1a, two pyridyl nitrogen atoms are ligated to a manganese(II) ion in the *trans* configuration. The bond distances Mn-N and Mn-O are 2.27 and 2.16 Å, respectively, and the coordination geometry is an elongated, distorted octahedron. The angle between the planes of the *tert*-butyl aminoxyl moiety and the pyridine ring is only 1.7 °, a value considerably smaller than those of *N*-phenyl *N*-*tert*-butyl aminoxyls. The observed near coplanarity suggests that the electron spin of the aminoxyl radical center would be effectively delocal-

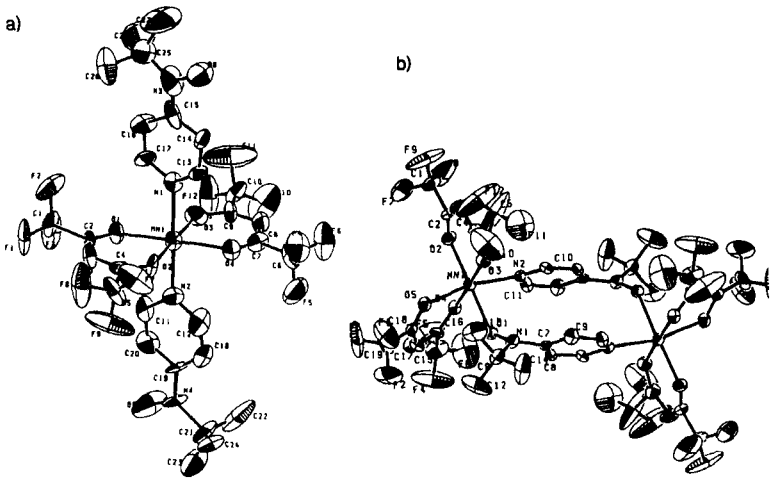


FIGURE 1. 14] ORTEP drawings of the molecular structure for a) [Mn(hfac)2(4NOPy)2] and b) [Mn(hfac)2(4NOPy)]2. The fluorine atoms have been omitted for the sake of clarity.

ized onto the pyridine ring. In the crystal structure of [Mn(hfac)2(4NOPy)2], the oxygen atom of one aminoxyl has short contacts of 3.31 and 3.46 Å from pyridine ring belonging to the adjacent complex molecule. A possible intermolecular magnetic interaction due to these short distances will be taken into account by a Weiss field for the interpretation of the magnetic properties.

(B) [Mn(hfac)2(4NOPy)]2. The 1:1 complex **a** has a cyclic dimer structure in which the oxygen of the aminoxyl and the pyridyl nitrogen of one bis-(monodentate) ligand are coordinated to different manganese ions in a *cis* configuration. As shown in Figure 1b, the molecular structure has a center of symmetry corresponding to (b) in Scheme 2. The dihedral angle between the pyridine ring and the aminoxyl moiety is about 33.5 ° and the distance between the two manganese ions in the dimer molecule is 8.498(4) Å. The

$Mn(hfac)_2(4NOPy)$ units are considered to be well separated from each other through space in the cyclic dimer molecules (> 6.7 Å).

(C) $[Mn(hfac)_2(3\text{- and }4NOIm)]_2$. Both complexes take similar cyclic dimer structures in which the oxygen of the aminoxyl group and the imidazole nitrogen of one NOIm molecule are ligated to two different Mn(II) ions in *cis* coordination. The molecules have center of symmetry as observed in $[Mn(hfac)_2(4NOPy)]_2$ of FIGURE 1b. In the molecular structure of the Mn(II) complex with 4NOIm, the distance between the Mn(II) ions and the dihedral angles between the phenyl and imidazolyl rings and between the phenyl ring and the aminoxyl group are 10.99 Å, 13°, and 27°, respectively. The corresponding distance and angles are 10.65 Å, 28°, and 24° in $[Mn(hfac)_2(3NOIm)]_2$. In the crystal structures of both the complexes, the shortest Mn • • • • Mn separations between the nearest dimers are 8.21 and 7.54 Å for $[Mn(hfac)_2(4\text{- and }3NOIm)]_2$, respectively.[15]

1.2 The Copper Complexes

(A) $[Cu(hfac)_2(4NOPy)_2]$. The molecular structure of complex $[Cu(hfac)_2(4NOPy)_2]$ is similar to that of $[Mn(hfac)_2(4NOPy)_2]$; two pyridyl nitrogen atoms are coordinated to the copper(II) ion in the *trans* configuration. The copper(II) ion resides in the center of symmetry of a distorted octahedron in which bond lengths are Cu-O(1) = 2.294 Å, Cu-O(2) = 2.036(7) and Cu-N(1) = 2.045(9) Å and the bond angles between Cu-O(1) and the other ligands are nearly 90°. The elongation axis lying through O(1)-Cu-O(1') indicates that the lobes of the magnetic orbital $d_{x^2-y^2}$, which is orthogonal to the d_z orbital of Cu(II) ion, are directed toward the O(2)s of the hfac units and the N(1)s of the pyridine ligands. The dihedral angle between the planes of the *N-tert*-butylaminoxyl moiety and the pyridine ring is 10°. The average distance between the radical centers of the neighboring molecules is 5.85 Å in the crystal structure of $[Cu(hfac)_2(4NOPy)_2]$.

(B) $[Cu(hfac)_2(3NOPy)_2]$. The molecular structure of $[Cu(hfac)_2(3NOPy)_2]$ is very similar to that of the corresponding 4NOPy complex: two

pyridine units are coordinated to the Cu(II) ion in a *trans* configuration. As the bond lengths of Cu(II) with the six ligating atoms are 2.019(8), 2.327(10) and 2.07(1) Å for Cu-O(1), Cu-O(2) and Cu-N(1), respectively, the coordination geometry is a distorted octahedron with the O(2)s of hfac units as apical ligands. The dihedral angle between the planes of *N-tert*-butylaminoxyl moiety and the pyridine ring is 39°. Both aminoxyl groups in $[Cu(hfac)_2(3NOPy)_2]$ pack in close proximity to those of the neighboring molecules with a remarkably short distance (the average distance between the two radical centers is only 2.45 Å). This leads to the formation of a magnetically linear chain along the *b* axis. The N-O π-orbitals of the adjacent aminoxyl radicals overlap with each other almost perfectly in a head-to-tail configuration.

(C) $[Cu(hfac)_2(4NOPy)]$. The complex has a discrete five-coordinated structure and the coordination geometry is intermediate between a square pyramid and a trigonal bipyramid. The obtained bond angles indicate that the coordination geometry is closer to a square pyramid than to a trigonal bipyramid. As the longest bond length between Cu(II) and the five ligating atoms is 2.198 (7) Å for Cu-O(2), the axial ligand of the square pyramid is considered to be O(2) of the hfac unit. Furthermore, this Cu(II) ion interacts with an additional oxygen atom from the aminoxyl group of the neighboring complex. This Cu-O(5') interaction at a distance of 2.79 Å leads to a pseudo-head-to-tail dimer structure in which the two pyridine planes lie in a face-to-face configuration at a distance of 3.76 - 3.83 Å. The dihedral angle between the planes of *tert*-butylaminoxyl moiety and the pyridine ring is 26°.[12]

2. Magnetic Properties of Metal Complexes

The magnetic susceptibilities for microcrystalline samples of the 1:2 and 1:1 complexes were measured by SQUID magneto/susceptometry. The temperature dependence of molar paramagnetic susceptibilities (χ_{mol}) were obtained in the range 2-300 K at a constant field in the range 50-500 mT. The $\chi_{mol}T$-T plots of eight complexes are shown in FIGURE 2.

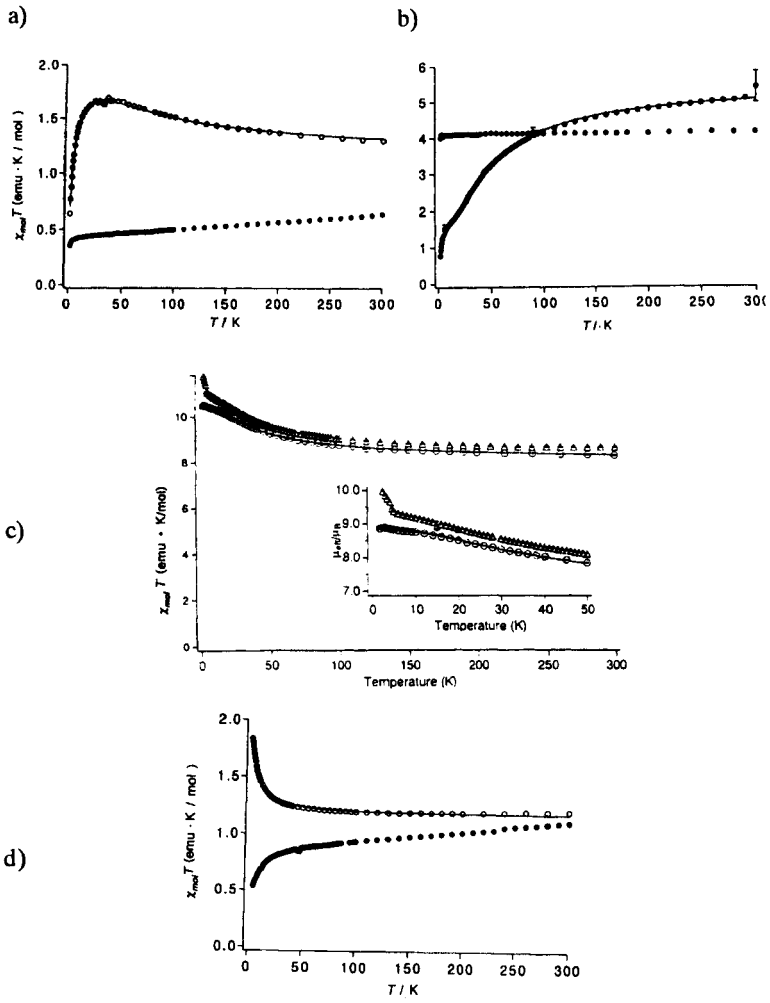


FIGURE 2. $\chi_{mol}T$-T plots for crystalline samples of a) [Mn(hfac)$_2$-(3NOPy)$_2$] (●) and [Mn(hfac)$_2$(4NOPy)$_2$] (○), b) [Cu(hfac)$_2$-(3NOPy)$_2$] (●) and [Cu(hfac)$_2$(4NOPy)$_2$] (○), c) complexes **a** (△) and **b** (□) of [Mn(hfac)$_2$(4NOPy)]$_2$ and d) [Cu(hfac)$_2$-(3NOIm)$_2$] (●) and [Cu(hfac)$_2$(4NOIm)$_2$] (○). Solid curves are the best-fit theoretical ones.

2.1 The Manganese(II) Complexes

(A) $[Mn(hfac)_2(3NOPy)_2]$ and $[Mn(hfac)_2(4NOPy)_2]$. The $\chi_{mol}T$ values of $[Mn(hfac)_2(3NOPy)_2]$ and $[Mn(hfac)_2(4NOPy)_2]$ at 290 K were 4.12 and 5.04 emu· K· mol^{-1}, respectively. The latter value is slightly smaller than but nearly equal to a theoretical spin-only value of 5.12 for a degenerate state among four S = 3/2, 5/2, 5/2, and 7/2 spins with g = 2. As the temperature was lowered, the $\chi_{mol}T$ values of the 4NOPy complex (open circles in FIGURE 2a) decreased gradually, reached an S-shaped plateau at ca 20 K, and then decreased steeply below 10 K. A $\chi_{mol}T$ value approaching 1.90 emu· K· mol^{-1} at ca. 10-20 K is qualitatively interpreted in terms of the spin-only value for S = 3/2. In order to analyze the temperature dependence of the observed $\chi_{mol}T$ values quantitatively, a linear three-spin model suggested by the X-ray crystal and molecular structure was assumed. Its spin Hamiltonian is written as $:H = -2J (S_1S_M + S_MS_2)$. A theoretical equation derived from the eigenvalues was fitted to the experimental data by means of a least-squares method. The Weiss constant θ represented the intermolecular interaction expected from the short contact of 3.31 Å in the crystal packing of the complex. The best-fit parameters were J/k_B = -12.4 ± 0.1 K, θ = -2.58 ± 0.05 K, and g = 2.059. The theoretical curve is included in FIGURE 2a. On the other hand, the temperature dependence of the χ_{mol} values of $[Mn(hfac)_2$-$(3NOPy)_2]$ (filled circles in FIGURE 2a) is quite different from that of the 4NOPy complex analyzed above. A $\chi_{mol}T$ value of 4.12 at 300 K is close to 4.06 emu· K· mol^{-1} for $[Mn(hfac)_2Py_2]$ obtained under similar conditions, and remained constant in the temperature range 300 - 2 K. Although a bit smaller than a theoretical $\chi_{mol}T$ value of 4.38, it suggests S = 5/2. It appears as if the two 3NOPy ligands did not carry any spin; cancellation of the spins between the two 3NOPy's is suggested as in $[Cu(hfac)_2(3NOPy)_2]$.

(B) 1:1 Complexes **a** and **b** of $[Mn(hfac)_2(4NOPy)]_2$. A $\chi_{mol}T$ value of 6.15 emu· K· mol^{-1} at 300 K is in good agreement with the theoretical spin-only value of 6.00 emu· K· mol^{-1} for two degenerate S = 4/2 (= 5/2 - 1/2) species with g = 2. As the temperature was decreased to 2 K, the $\chi_{mol}T$ value

began to increase gradually and approached to a theoretical value of 9.98 for $S = 4$ at 2 K. According to the molecular structure revealed by X-ray analysis, the cyclic dimer structure should be interpreted in terms of a cyclic array of four spins 5/2, 1/2, 5/2 and 1/2. The $\chi_{mol}T$ values at 300 and 2 K seem to suggest that, since the exchange interaction between the Mn(II) ion and the directly attached aminoxyl radical is considerably stronger and antiferromagnetic ($J/k_B = -100 \sim -200$ K), the system may be regarded with good approximation as composed of two $S = 4/2$ spins coupled weakly (by J) through two non-magnetic head-to-tail couplers. Fitting of such a theoretical equation to the observed $\chi_{mol}T$ vs. T plot of the dimeric Mn(II) complex by means of a least-squares method gave $J/k_B = + 4.35 \pm 0.05$ K and $g = 1.970$. The calculated temperature dependence of $\chi_{mol}T$ is shown in FIGURE 2c as a solid curve. The magnetic susceptibility for complex **b** measured under similar conditions showed a temperature dependent behavior similar to complex **a**. The observed $\chi_{mol}T = 6.69$ emu· K· mol^{-1} at 300 K was slightly higher than the one for complex **a**. As the temperature was lowered from 300 to 4.5 K, the $\chi_{mol}T$ value increased gradually in a manner similar to complex **a** and then steeply below 4.5 K. The value at 17 K surpassed a theoretical value of $\chi_{mol}T = 9.98$ emu· K· mol^{-1} for the cyclic dimer structure with $S = 8/2$ such as complex **a**. In order to determine the effective spin quantum number in the low temperature region, the magnetization (M) for complex **b** was measured at 1.8 K on a Faraday balance. The saturation magnetization value Ms of 36 emu· G· g^{-1} is in good agreement with the MS = 35.2 emu· G· g^{-1} calculated for a 1:1 complex for $S = 4/2$. The M values obtained in the magnetic field range 0 - 5 T were fitted to the Brillouin function with $J = S = 4.8$. The value is clearly higher than a ferromagnetically coupled dimer of two $S = 4/2$'s, suggesting the operation of a ferromagnetic interaction between the one-to-one units.

Although no direct structural information is available for complex **b**, the temperature dependence of the $\chi_{mol}T$ at temperatures below 4.5 K and the

magnetization experiment strongly suggest that a part of complex **b** does not have a dimer structure such as complex **a** but exist as a higher oligomer as shown by (c) in Scheme 2.

(C) $[Mn(hfac)_2(3\text{- and }4NOIm)]_2$. Values of $\chi_{mol}T$ were 6.10 and 6.21 emu· K· mol^{-1} at 300 K for $[Mn(hfac)_2(3\text{- and }4\text{-}NOIm)]$, respectively, and are in good agreement with $\chi_{mol}T = 6.00$ which is a theoretical spin-only value for two degenerate $S = 4/2$ (= 5/2 - 1/2) species with $g = 2$. The $\chi_{mol}T$ values were nearly constant at 300 - 100 K. As the temperature was decreased below 100 K, the values for the 3NOIm complex began to decrease gradually, while those for the 4NOIm complex increased gradually and approached a theoretical value of $\chi_{mol}T = 9.98$ emu· K· mol^{-1} for $S = 4$ at 2 K. The observed temperature dependences of the $\chi_{mol}T$ values obviously suggest that, while the short-range magnetic coupling between the Mn(II) ion and the ligated aminoxyl radical is strongly antiferromagnetic, the long-range exchange interaction between the resultant spin 4/2's through the 1-imidazolylphenyl units are ferro- and antiferromagnetic for the 4- and 3NOIm complexes, respectively. On the basis of such a model, we obtained an equation for the Boltzmann distribution of the spins among the five spin states derived from the spin Hamiltonian $H = -2JS_a \cdot S_b$ and $S_a = S_b = 4/2$. Fitting of the theoretical equation to the observed $\chi_{mol}T$ vs. T plots for the two Mn(II) complexes by means of a least-squares method gave $J/k_B = +0.59 \pm 0.29$ K and $f = 1.03$ for $[Mn(hfac)_2(4NOIm)]_2$ and $J/k_B = -0.22 \pm 0.002$ K and $f = 1.001$ for $[Mn(hfac)_2(3NOIm)]_2$.

2.2 The Copper(II) Complexes

(A) $[Cu(hfac)_2(4\text{- and }3NOPy)_2]$. A $\chi_{mol}T$ value of 1.29 emu· K· mol^{-1} obtained for $[Cu(hfac)_2(4NOPy)_2]$ at 300 K is close to a theoretical one (1.13 emu· K· mol^{-1}) calculated for three isolated $S = 1/2$ spins in terms of the spin only equation. As the temperature was decreased, the $\chi_{mol}T$ value gradually increased, reached a maximum at 36 K, and rapidly decreased below 10 K (FIGURE 2b). A maximum $\chi_{mol}T$ value of 1.69 emu· K· mol^{-1} that was ob-

served is slightly smaller than the theoretical one (1.87) calculated for S = 3/2. The obtained $\chi_{mol}T$ - T curve for [Cu(hfac)$_2$(4NOPy)$_2$] was analyzed quantitatively on the basis of a linear three spin model {S_1--S_M--S_2 ; H = -2J (S_1S_M + S_MS_2)} that was deemed to be appropriate from X-ray molecular and crystal structure analysis. Equation for three spins with S_1 = S_2 = S_M = 1/2 was applied and fitted to the observed $\chi_{mol}T$ - T plot for [Cu(hfac)$_2$-(4NOPy)$_2$] by means of a least-squares method. The parameters of a best fit are 60.4 ± 3.3 K, 2.048 ± 0.0091, -3.58 ± 0.09 K for J/k_B, g, and θ, respectively, and the theoretical curve is presented by a solid line in FIGURE 2b.

A $\chi_{mol}T$ - T plot for the isomeric complex [Cu(hfac)$_2$(3NOPy)$_2$] showed a quite different temperature dependence behavior. The $\chi_{mol}T$ value was ca. 0.6 emu· K· mol^{-1} at 300 K and gradually decreased to 0.43 at 10 K, as the temperature was lowered from 300 K. Since the theoretical $\chi_{mol}T$ values calculated for spin only situations with S = 1/2, 3/2, and with degenerate two doublet and one quartet states are 0.37, 1.88, and 1.13 emu· K· mol^{-1}, respectively, the observed values at 10 and at even 300 K are close to a theoretical one calculated for S = 1/2. Taking the crystal and molecular structure of [Cu(hfac)$_2$(3NOPy)$_2$] revealed by X-ray analysis into account, it is possible to explain the observed $\chi_{mol}T$ - T plot that the two spins of the aminoxyl radicals canceled each other out by a strong antiferromagnetic interaction. The relatively large dihedral angle (39°) between the plane of *N-tert*-butylaminoxyl moiety and the pyridine ring is considered to weaken the interaction between the aminoxyl and the copper ion whereas the short distance of 2.45 Å between one aminoxyl group and another one belonging to its nearest neighbor molecule strengthens the through-space antiferromagnetic interaction between the two aminoxyl groups. Taking the dihedral angle of 39 °, the relative geometry of the π-orbitals, and the distance of 2.45 Å into account, $-J_{inter}$ should be smaller than - 239 K. ($-J_{intra}$ >> $-J_{inter}$). Therefore,

in the $\chi_{mol}T$ - T plot it appears as if the copper complex has no aminoxyl radical units.

(B) [Cu(hfac)$_2$(4NOPy)]. When the temperature was decreased from 300 to 2 K, the $\chi_{mol}T$ values (1.96 emu· K· mol^{-1} at 300 K) increased gradually, and reached a maximum (3.20 emu· K· mol^{-1} at 9 K), and then decreased. For quantitative analysis of the observed $\chi_{mol}T$ - T plot, a rectangular four-spin model suggested by the X-ray crystal and molecular structure analysis was assumed. The spin Hamiltonian for such a system is given by $H = -2J(S_1S_{M1} + S_{M2}S_2) - 2\alpha J(S_1S_{M2} + S_{M1}S_2)$, where J and αJ are intra- and intermolecular exchange coupling parameters, respectively. Fitting of the theoretical equation to the observed values was refined by means of a least-squares method. The best-fit parameters, J, α, g, and θ are 58.5 K, 1.001, 2.113, and -0.33 K, respectively. The α value is almost 1, indicating that the magnitude of the exchange interactions of the aminoxyl radical and the copper ion through the pyridine ring and through space is accidentally equal. Although the dihedral angle between the radical plane and pyridine ring is slightly larger (26°), the J/k_B value (58 K) is close to the value of 62 K obtained in [Cu(hfac)$_2$(4NOPy)$_2$] under similar conditions and which is due to the interaction through the pyridine ring .

(C) [Cu(hfac)$_2$(3- and 4NOIm)$_2$]. The obtained $\chi_{mol}T$ values at 300 K for both isomeric copper complexes are close to each other; 1.21 and 1.12 emu· K· mol^{-1} for [Cu(hfac)$_2$(3NOIm and 4NOIm)$_2$], respectively, and in good agreement with the theoretical one ($\chi_{mol}T$ = 1.13 emu· K· mol^{-1}) for an isolated three spins system with S = 1/2. However, their $\chi_{mol}T$ - T plots (FIGURE 2d) contrast sharply, especially in the low temperature region below 30 K. As the temperature was decreased, the $\chi_{mol}T$ value for [Cu(hfac)$_2$-(4NOIm)$_2$] remained nearly constant until 30 K and then increased below this temperature, while the $\chi_{mol}T$ value for [Cu(hfac)$_2$(3NOIm)$_2$] decreased gradually below 30 K. Although structural information by X-ray analysis for both complexes are missing, a linear three-spin model was assumed and the

observed $\chi_{mol}T$ - T plots were fitted to the theoretical equation. The best fit parameters were J/k_B = 4.26 ± 0.08 K, θ = -0.024 ± 0.008 K, and g = 2.043 ± 0.002 for [Cu(hfac)$_2$(4NOIm)$_2$]. These values show that a weak ferromagnetic interaction is operating between the copper ion and aminoxyl radical in the 4NOIm complex. An antiferromagnetic interaction appears to take place between these centers in the 3NOIm complex (J/k_B = - 2.7 K).

2.3 Chromium(III) Complexes

(A) Porphyrinatochromium(III) Complexes with 3- and 4NOPy.

Epr spectra of frozen toluene solutions of [Cr(TPP)Cl] in the presence of a slight excess of 3- and 4NOPy were measured at 10 K. Other than signals at g = 2 due to the free aminoxyl radicals present in excess, the obtained spectra are characteristically different from each other and also quite different from those of [Cr(TPP)Cl] ligated with pyridine itself under similar conditions, indicating that the magnetic interaction between the chromium(III) and the aminoxyl radicals by coordination with the pyridyl nitrogen of NOPy is significant. A careful analysis of the temperature dependence of the spectra revealed that quintet and triplet ground states might be produced by ferro- and antiferromagnetic interaction between Cr(III) (S = 3/2) as the central metal of [Cr(TPP)Cl] and the aminoxyl radical (S = 1/2) on the sixth ligand in 3- and 4NOPy, respectively. New signals observed for [Cr(TPP)(4NOPy)Cl] above 75 K were assigned to thermally populated quintet species. From the temperature of 75 K, the energy difference ($\Delta E_{Q\text{-}T} = 4J$) between the quintet and triplet states was estimated to be greater than 70 K. There was no significant difference in the overall EPR spectral behavior under similar conditions when [Cr(TAP)Cl] was used in place of [Cr(TPP)Cl].

To understand the magnetic interaction in more detail, the magnetic susceptibilities of the powder samples were measured in the temperature range 5 - 300 K at a constant magnetic field of 0.2 T. The $\chi_{mol}T$-T plots of [Cr(TPP)-(3- and 4NOPy)Cl] together with [Cr(TPP)(Py)Cl] as a reference and are

shown in FIGURE 3. The $\chi_{mol}T$ values at 300 K were 1.95 and 1.45 emu· K· mol^{-1} for [Cr(TPP)(3- and 4NOPy)Cl], respectively. As the temperature was decreased, the $\chi_{mol}T$ value for the 3NOPy complex increased gradually and reached a maximum of $\chi_{mol}T$ = 2.35 emu· K· mol^{-1} at 24 K, while that of the 4NOPy complex decreased monotonically from 300 to 70 K and became nearly constant at 70 to 13 K. The $\chi_{mol}T$ values for [Cr(TPP)(Py)Cl] were almost constant in all the temperature range studied. Sharp decreases of the $\chi_{mol}T$ values below 24 and 13 K for [Cr(TPP)(3- and 4NOPy)Cl], respectively, suggest the operation of an intermolecular antiferromagnetic interaction.

The observed temperature dependencies were analyzed in terms of a model in which quintet and triplet states in equilibrium are separated by $4J$. The intermolecular interaction was taken into account by a Weiss field. From the best fit theoretical curves to experimental ones, parameters J/k_B ($\Delta E_{T\text{-}Q} = 4J$), θ, and g were evaluated to be 12.3 ± 0.3 K, -3.4 K, and 1.93 for [Cr(TPP)-(3NOPy)Cl] and -77 ±0.8 K, -1.1 K, and 1.89 for [Cr(TPP)(4NOPy)Cl], respectively. Isomeric [Cr(TAP)(NOPy)Cl]'s showed similar temperature

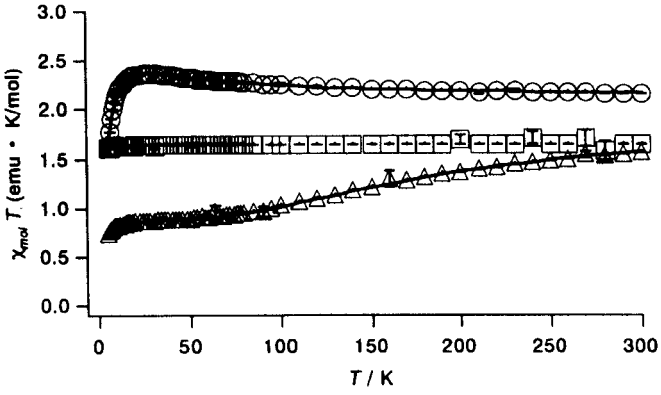


FIGURE 3. $\chi_{mol}T$-T plots for powder samples of [Cr(TPP)(3NOPy)-Cl] (○), [Cr(TPP)(4NOPy)Cl] (△), and [Cr(TPP)PyCl] (□). Solid curves are the best-fit theoretical ones.

dependence of $\chi_{mol}T$ although intermolecular antiferromagnetic interactions at low temperature were somewhat weakened. Parameters J/k_B, θ, and g were found to be 16 ± 0.3 K, -0.3 K, and 1.82 for [Cr(TAP)(3NOPy)Cl] and -86 ± 1.5 K, -0.23 K, and 1.86 for [Cr(TAP)(4NOPy)Cl], respectively.

3. The Exchange Interaction between Aminoxyl Radical and Metal Ion in the Mn(II), Cu(II), and Cr(III) Complexes

Exchange coupling parameters for all the 1:2 and 1:1 metal complexes obtained from the temperature dependence of χ_{mol} are summarized in Table I. Thus the magnetic interaction between the metal ions and the aminoxyl radical centers showed metal-dependent regiospecificity. In the metal complexes with 4NOPy and 4NOIm, the magnetic metal ions and organic radical centers interact ferromagnetically in the copper(II) complexes and antiferromagnetically in the manganese(II) and chromium(III) complexes.

On the other hand, in the metal complexes with 3NOPy and 3NOIm, similar interactions are dominated by strong antiferromagnetic intermolecular interactions and are difficult to determine. However, they are clearly negative for the Cu(II) complexes and positive for the Cr(III) complexes. The observed metal-dependent regiospecificity of the exchange coupling is explained by the relative geometries between the π-orbital at the nitrogen atom of

TABLE I. Exchange coupling parameters J/k_B (K) for various complexes

M		4NOPy	3NOPy	4NOIm	3NOIm
Mn(II)(hfac)$_2$	(1:2)	-12.4	?	----	----
	(1:1)	-11.3 [a]		+0.6	-0.2
Cu(II)(hfac)$_2$	(1:2)	+60.4	<0	+4.3	-2.7
	(1:1)	+58.6 [b]			
CrTPPCl		-77	+12.3	----	----
CrTAPCl		-86	+16.0	----	----

[a] for the cyclic dimer[16]

[b] for the pseudo cyclic dimer

pyridine and the magnetic d orbitals occupied by the unpaired electrons in the metal ions; d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ and d_{z^2} for Mn(II) and $d_{x^2-y^2}$ for Cu(II) ions.[17] The relative geometry between the magnetic orbitals and the π orbital on the pyridine ring as revealed by X-ray molecular structure analyses is illustrated in FIGURE 4. The coordination geometry of the $[Mn(hfac)_2(4NOPy)_2]$ complex is a slightly elongated octahedron in which the axial ligands are the nitrogen atoms of pyridine groups. Since the magnetic orbitals for Mn(II) contain π-charactered d_{xy}, d_{yz}, and d_{xz}, the overlap with the π orbital at the pyridyl nitrogen to which the spin is polarized due to the presence of the aminoxyl radical center in the *p*-position is possible for any direction of the coordination (FIGURE 4a and 4b). The observed antiferromagnetic exchange coupling in the chromium(III) complex is understood similarly

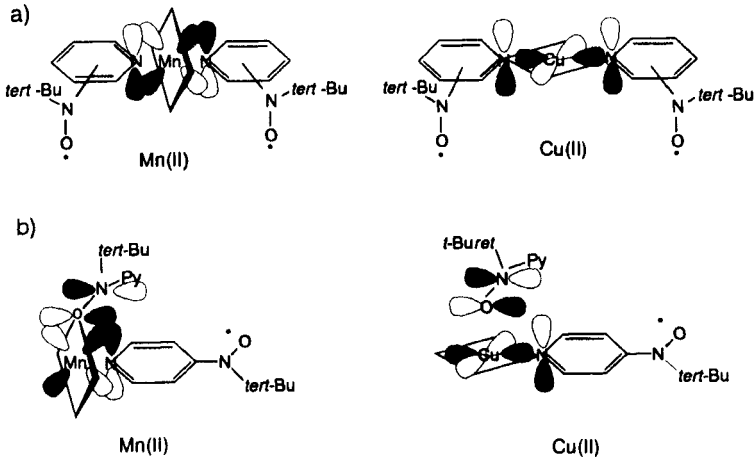


FIGURE 4. Scheme illustrating the interaction of the magnetic orbital of the Mn(II) and Cu(II) ions with (a) two π-orbitals at the nitrogens of the pyridine rings in the 1:2 complex, and (b) one π-orbital of the pyridyl nitrogen and that of the aminoxyl radical from a second ligand molecule in the 1:1 dimer complex.

since the magnetic orbitals for d3 chromium(III) are d_{xy}, d_{yz}, and d_{xz}. The magnetic orbital $d_{x^2-y^2}$ orthogonal to the elongated axis of octahedral Cu(II) is directed to the two nitrogen atoms of the pyridine groups and the oxygen atoms of the two hfac ligands in the 1:2 complexes (FIGURE 4b). On the other hand, the magnetic orbital $d_{x^2-y^2}$ of Cu(II) on the basal plane of the square pyramid is directed to one pyridyl nitrogen atom and three of the oxygen atoms of the hfac units in the 1:1 complex. Furthermore, the oxygen atom of the aminoxyl radical in the other molecule of the dimer is situated at the axial position of the pentacoordinated structure (FIGURE 4b). As seen clearly in Figure 4, both the magnetic $d_{x^2-y^2}$ orbital of Cu(II) and the π-orbital at the nitrogen atom of the pyridine unit or the oxygen atom in the aminoxyl radical unit have no significant overlap and the relative geometry between them should be orthogonal. This orthogonality of the singly occupied d orbital and the nitrogen 2p orbital to which the spin is polarized via the π-electrons on the pyridine ring from the aminoxyl radical center is responsible for the ferromagnetic interaction.

The magnetic interactions between copper(II) and *N*-(4-pyridyl)-*N*-*tert*-butylaminoxyl radical found in this work are unique in that they are ferromagnetic and considerably strong: J/k_B = 60.4 and 58.5 K for the 1:2 and 1:1 complexes, respectively. The couplings of the copper ions attached directly to the aminoxyl radicals via their oxygen atoms are well documented and typically antiferromagnetic due to the overlap of the singly occupied orbitals of the metal ion and the free radical. Only when the oxygen atom of an aminoxyl radical is axially bound to a tetragonal copper (II) ion, a weak ferromagnetic coupling (~20 K) develops.

Conclusion

The metal-dependent regiospecificity in the exchange coupling of Mn(II),

Cu(II) and Cr(III) with the aminoxyl radical attached as a substituent on the pyridine and *N*-phenylimidazole ligands has been found and rationalized in terms not only of the topology of the free radical ligands but also of the overlap vs orthogonality of the magnetic d orbital on the metal ions and the π-orbital at the ligating nitrogen atom to which the spin is polarized by the aminoxyl radical attached as a substituent on the aromatic base ligands. This knowledge will be of use as an important design principle for constructing metal-radical complexes having higher dimensional extended structure and interesting magnetic properties.

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