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Proximate Nitroxide Ligands in the Coordination Spheres of Manganese(II) and Nickel(II) Ions. Precursors for High-Dimensional Molecular Magnetic Materials

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The chelating nitroxide ligands 2-(2-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-3-oxide-1-oxy (NITPy, **1**), 2-(2-imidazolyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-3-oxide-1-oxy (NITImH, **2**), and 2-(2-benzimidazolyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-3-oxide-1-oxy (NITBzImH, **3**) and some of their transition metal complexes (Mn(II), Ni(II), Zn(II)) have been prepared and characterized by X-ray diffraction techniques and magnetic susceptibility measurements. All complexes are four- (or three-) spin systems where the metal coordination sphere is free of ancillary ligands because of the chelate effect which enforces the coordination of the oxyl group. The *fac* or *mer* nature of these species depends on the metal ions and on the steric demand of the ligand. It has been found that crystal packing is an important driving force toward the *fac* modification when steric requirements are not important. Crystal packing is probably also the cause of the noncentrosymmetric space group observed for the derivatives of NITPy. For the Zn(II) complex of NITImH, a moderate inter-nitroxide interaction within the metal coordination sphere of -14 cm^{-1} is estimated. However, due to the modification of the spin distribution upon complexation, this interaction does not play a major role in the other complexes, where strong antiferromagnetic metal−nitroxide interactions ($H = -2J\mathbf{S}_i\cdot\mathbf{S}_j$, $-111 < J < -53$ cm^{-1}) are operative. The derivatives of NITImH are precursors of extended species which would be obtained by deprotonation of the ligand.

Exceptional stability,[1,2] ease of chemical modification,[3−6] and versatility in their coordination properties[6−8] have made nitroxide free radicals one of the most attractive spin carriers for the design of molecular magnetic materials. In nitroxide−metal complexes, exchange interactions ranging from strongly ferro- to strongly antiferromagnetic have been characterized.[8] However, the donor properties of the nitroxyl group are poor[9] and this is a strong limitation for obtaining structures of high dimensionality since coordination of the nitroxyl group occurs only to crowded metal centers carrying electron-withdrawing groups.

A strategy aimed at overcoming this limitation was recently described which uses polynitroxides possessing a high-spin ground state and metal hexafluoroacetylacetonates.[10] However, we thought that metal centers free of ancillary ligands would bring more versatility to the design of all types of molecular magnetic materials, not only of multidimensional exchange-coupled species.

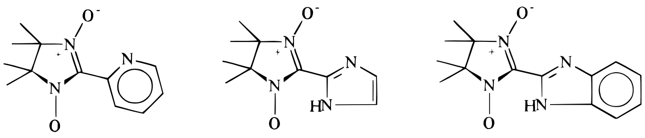

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Figure 1. Chemical structures of the ligands NITPy (**1**), NITImH (**2**), and NITBzImH (**3**).

In a first attempt along this line, we prepared and studied complexes of nitroxide ligands where the coordination of the spin density rich oxyl group is enforced by the chelate effect. These studies involved 2-(2-pyridyl)-substituted nitronyl nitroxide (NITPy, **1**; Figure 1) and metal chlorides.[11] It was found that this strategy is indeed efficient in giving strongly coupled nitroxide−metal complexes with poorly acidic metal centers, but in these trans complexes, two sites of coordination were still occupied by the coordinating chloride anions.

We have now investigated the coordination properties of the same nitroxide ligand and those of the closely related chelating nitroxides 2-(2-imidazolyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-3-oxide-1-oxy (NITImH, **2**) and 2-(2-benzimidazolyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-3-oxide-1-oxy (NITBzImH, **3**) with the perchlorates of the same metal ions. In this case, the weakly coordinating anion allows us to

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characterize complexes where the metal coordination sphere is fully occupied by three chelating nitroxide ligands. Interest in these complexes relies on three features: (i) The X_3Y_3 donor set in these octahedral species gives rise to stereo- and enantioisomerism. Thus, structural and magnetic properties may be compared in related compounds. (ii) Complexes of the three ligands are three- or four-spin systems in which three nitroxide ligands are located in close proximity. Depending on the sign and magnitude of the different possible interactions, one can obtain a large variety of magnetic behaviors. (iii) Finally, some of these systems are precursors of more extended structures which might be obtained by deprotonation of the ligand.

We report the structural and magnetic properties of five complexes of ligands **1**−**3** with nickel(II) and manganese(II) along with a complex of zinc(II) specially prepared to obtain insight into the inter-nitroxide interactions within the coordination sphere of the metal. Most of the complexes have been characterized as the *OC*-6-21 (*mer)* modifications; in one case, however, both isomers, *OC*-6-21 and *OC*-6-22 (*fac*), of related ligands have been characterized. In addition, two of these compounds crystallize in a noncentrosymmetric space group and exhibit the interesting properties of being pure enantiomers. Finally, ionization of the imidazole fragment in ligand **2** affording a bis-chelating spin carrier will be discussed in connection with the synthesis of extended structures.

Experimental Section

Syntheses of the Ligands. The nitroxide ligands **1**−**3** were prepared as previously described.[12,13]

Syntheses of the Complexes. All complexes were obtained using the same procedure: A 5×10^{-4} mol (≈100 mg) sample of ligand and 1.5×10^{-4} mol of the appropriate metal perchlorate were dissolved in 10 mL of methanol. The solution was kept in the dark at room temperature. After 4 days, the crystalline material was filtered off and dried under vacuum. The yield of tris(2-midazolyl-κN^3-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy-κ*O*-3-oxide)metal(II) perchlorate was generally close to 50% (≈60 mg). Anal. Calcd (found) for $\mathrm{Mn(NITImH)_3(ClO_4)_2}$-*fac*, **4**, $\mathrm{C_{30}H_{45}Cl_2N_{12}O_{14}Mn}$: C, 39.01 (39.23); H, 4.91(4.82); Cl, 7.58 (7.79); N, 18.22 (18.12); Mn, 5.96 (6.11). Calcd (found) for $\mathrm{Mn(NITBzImH)_3(ClO_4)_2(EtOH)}$-*mer*, **5**, $\mathrm{C_{44}H_{57}Cl_2N_{12}O_{15}Mn}$: C, 47.22 (46.98); H, 5.14 (5.21); Cl, 6.25 (6.38); N, 15.03 (14.91); Mn, 4.91 (5.02). Calcd (found) for $\mathrm{Mn(NITPy)_3(ClO_4)_2}$-*mer*, **6**, $\mathrm{C_{36}H_{48}Cl_2N_9O_{14}Mn}$: C, 45.23 (45.28); H, 5.06 (4.92); Cl, 7.32 (7.56); N, 13.19 (12.97); Mn, 5.75 (5.88). Calcd (found) for $\mathrm{Ni(NITImH)_3(ClO_4)_2}$-*mer*, **7**, $\mathrm{C_{30}H_{45}Cl_2N_{12}O_{14}Ni}$: C, 38.91 (38.75); H, 4.90 (4.97); Cl, 7.56 (7.32); N, 18.16 (18.11); Ni, 6.26 (6.37). Calcd (found) for $\mathrm{Ni(NITPy)_3(ClO_4)_2}$-*mer*, **8**, $\mathrm{C_{36}H_{48}Cl_2N_9O_{14}Ni}$: C, 45.08 (45.21); H, 5.05 (4.97); Cl, 7.30 (7.52); N, 13.15 (13.02); Ni, 6.05 (6.27). Calcd (found) for $\mathrm{Zn(NITImH)_3(ClO_4)_2}$-*fac*, **9**, $\mathrm{C_{30}H_{45}Cl_2N_{12}O_{14}Zn}$: C,38.66 (38.77); H, 4.87 (4.68); Cl, 7.51 (7.83); N, 18.05 (17.89); Zn, 6.87 (6.64). In an alternative procedure, the same quantity of ligand was mixed with $^1/_3$ equiv of M(II) (Mn or Ni) acetate in 10 mL of methanol. Then, $^1/_3$ equiv of $\mathrm{M(ClO_4)_2{\cdot}6H_2O}$ was added and the solution kept in the dark. Using ligand **1**, both procedures gave identical compounds, while for ligands **2** and **3**, 1D complexes (described in the following paper) were obtained. However, in one experiment, the manganese(II) complex $\mathrm{Mn(NITImH)_3(ClO_4)_2}$ was isolated (≈1%) by hand-picking and identified as the *mer* modification. Crystals suitable for X-ray diffraction studies were found in all preparations. For compound **5**, satisfactory crystals were obtained only using ethanol as solvent which is included as solvate.

X-ray Diffraction Studies. Crystals of approximate dimensions 0.2 × 0.1 × 0.1 mm^3 were mounted on an Enraf-Nonius CAD-4 four-circle diffractometer equipped with graphite-monochromatized Mo Kα radiation. The unit cell parameters were obtained by a least-squares fit of the automatically centered settings from 25 reflections; they are reported in Table 1, along with pertinent details regarding the structure determination. Intensity data were corrected for Lorentz and polarization effects but not for absorption.

Structure determinations were performed using the heavy-atom method included in the SHELXTL package, and the absolute structure of the crystal used was established as described by Flack.[14] The non-hydrogen atoms were located in subsequent Fourier difference maps and refined anisotropically. In the last refinement model, hydrogen atoms were included in fixed and calculated positions with isotropic thermal parameters proportional to those of the connected carbon atoms.

Selected bond lengths and angles are found in Table 2. Summaries of the crystal data and experimental parameters, atomic positional parameters, complete bond lengths and angles, and anisotropic thermal parameters for compounds **4**−**9** are deposited as Supporting Information.

Magnetic Measurements. Magnetic measurements were performed on samples checked for stereoisomeric purity by powder X-ray patterns. Magnetic susceptibility data were collected by use of a Quantum Design SQUID susceptometer working at a 0.5 T field strength in the 2−300 K temperature range. The SQUID outputs were corrected for the contribution of the sample holder, and the magnetic susceptibilities were corrected for the diamagnetic contribution of the constituent atoms by use of Pascal constants.

Results and Discussion

Synthesis. As already observed,[11] the use of nitroxide chelating ligands affords complexes where the nitroxyl oxygen is coordinated. From the synthetic point of view, the only special feature stems from the possibility of obtaining the different stereoisomeric modifications, *OC*-6-21 (*mer*) and *OC*-6-22 (*fac*), which are possible for an $\mathrm{MX_3Y_3}$ coordination pattern. Worthy of note is the fact that two modifications of the same complex have only been obtained for $\mathrm{Mn(NITImH)_3(ClO_4)_2}$ and one of them, the *mer* isomer, was obtained as a side product in one experiment when the synthesis was conducted using a procedure aimed at designing 1D species. Unfortunately, only a few crystals of this compound could be characterized and its magnetic properties were not studied. For all other ligands and metal ions, only one modification was structurally characterized. Therefore, using the procedure described in the Experimental Section, the complexes were obtained in a pure stereoisomeric form which depends on the nature of the nitroxide ligand and of the metal ion.

Structural Studies. Among the six compounds, both *fac* modifications of NITImH (Mn(II), **4**; Zn(II), **9**) crystallize in the $P2_1/n$ space group and both *mer* modifications of NITBzImH (Mn(II), **5**) and of NITImH (Ni(II), **7**) crystallize in the $C2/c$ space group, while, for both NITPy derivatives (Mn(II), **6**; Ni(II), **8**), the $P2_1$ space group is observed.

The molecular structures of the three different types of complexes are displayed in Figures 2−4 for $\mathrm{[Mn(NITImH)_3]^{2+}}$-*fac* ($\mathbf{4}^{2+}$), $\mathrm{[Mn(NITBzImH)_3]^{2+}}$-*mer* ($\mathbf{5}^{2+}$), and $\mathrm{[Mn(NITPy)_3]^{2+}}$-*mer* ($\mathbf{6}^{2+}$), respectively.

Although for all compounds the bond distances are within the expected range, the octahedral coordination sphere of the Mn(II) ions is highly distorted. Angles far from the ideal values of 180 and 90° such as N3B−Mn−N3C = 157.0(2)° and N3A−Mn−N3C = 106.5(2)° are found in **5**. These distortions must be considered as upper limits because of the presence of the sterically demanding ligand NITBzImH, but the data concerning the Ni(II) and Zn(II) compounds also show significant distor-

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Table 1. Crystallographic Data for Compounds **4**−**9**

	4	**5**	**6**
chem formula	$C_{30}H_{45}Cl_2N_{12}O_{14}Mn$	$C_{44}H_{57}Cl_2N_{12}O_{15}Mn$	$C_{36}H_{48}Cl_2N_9O_{14}Mn$
fw	923.6	1119.9	956.7
cryst system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$C2/c$	$P2_1$
T (K)	293	293	293
λ (Å)	0.710 73	0.710 73	0.710 73
ρ_{calcd} (g cm^{-3})	1.503	1.421	1.458
ρ_{obsd} (g cm^{-3})	1.48(3)	1.43(3)	1.47(3)
μ (cm^{-1})	5.1	4.3	5.0
a (Å)	15.832(3)	40.415(4)	10.587(2)
b (Å)	10.346(3)	12.875(2)	14.766(3)
c (Å)	26.029(4)	25.917(1)	14.603(3)
β (deg)	106.78(1)	129.09(1)	107.31(3)
V (Å^3)	4082	10 468	2179
Z	4	8	2
$R(F_o)^a$	0.051	0.062	0.052
$R_w(F^2)^b$	0.133	0.187	0.136

	7	**8**	**9**
chem formula	$C_{30}H_{45}Cl_2N_{12}O_{14}Ni$	$C_{36}H_{48}Cl_2N_9O_{14}Ni$	$C_{30}H_{45}Cl_2N_{12}O_{14}Zn$
fw	927.4	960.4	934.1
cryst system	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$P2_1$	$P2_1/n$
T (K)	293	293	293
λ (Å)	0.710 73	0.710 73	0.710 73
ρ_{calcd} (g cm^{-3})	1.386	1.486	1.524
ρ_{obsd} (g cm^{-3})	1.36(3)	1.50(3)	1.54(3)
μ (cm^{-1})	6.3	6.5	7.1
a (Å)	23.773(2)	10.523(2)	15.788(2)
b (Å)	11.391(2)	14.679(3)	10.364(2)
c (Å)	33.356(3)	14.528(3)	26.013(4)
β (deg)	100.14(3)	107.00(3)	106.98(3)
V (Å^3)	8891.7	2146.0	4070.6
Z	8	2	4
$R(F_o)^a$	0.085	0.046	0.090
$R_w(F^2)^b$	0.239	0.127	0.161

[a] $R(F_o) = \sum[|F_o| - |F_c|]/\sum|F_o|$. [b] $R_w(F^2) = \{\sum[w(F_o^2 - F_c^2)]/\sum[w(F_o)^2]\}^{1/2}$.

tions. Within the series, complexes of NITImH are less distorted than those of NITPy. In all complexes, the three nitroxide ligands show the expected structural characteristics such as a slight elongation ($\approx$0.1 Å) of the N−O bond of the coordinated nitroxyl group[8] and significant differences of the angle between the two rings (Table 3). This twist angle seems to be independent of the isomeric modification of the complex but is much weaker in the NITImH derivatives than in the NITPy ones, and in **5**, the ligand is almost planar. This fact is not consistent with steric crowding of the coordination sphere since the more bulky ligand is the less twisted; it seems to be related to the more delocalized nature of the ligand NITBzImH.

Steric crowding, however, is expected to play an important role in stereoselectivity. Among the six complexes, only two (**4** and **9**) exhibit the *fac* configuration and both are derivatives of NITImH, the less sterically demanding ligand. However, the third derivative of NITImH, the nickel(II) complex, **7**, is found as the *mer* modification; the shorter bond lengths expected and observed for Ni(II) compared to Mn(II) are probably at the origin of steric congestion, which results in a preferred *mer* arrangement. Such an influence of the size of the ligand is illustrated by complex **5**, in which three bulky NITBzImH ligands could not be accommodated around the metal ion in a *fac* configuration. The same considerations hold for the derivatives of NITPy, a ligand which is fairly bulkier than NITImH. Following this line of arguments, however, the *mer* modification of complex **4** should be highly probable, while it has been only obtained in poor yield and in special circumstances. Another driving force for stereoselectivity is found in crystal packing. Considering the *fac* modification, it is seen that this more symmetrical molecule (local C_{3v} symmetry) packs more compactly than the *mer* molecule. This is illustrated by the higher density values (>1.5) observed for the crystals of **4** and **9**. Therefore, the *mer* or *fac* nature of a complex depends on steric crowding related to the nature of the metal ion and the nature the ligand; it also depends on intermolecular interactions which drive the compound toward the modification which packs more compactly.

From the magnetic point of view, bonding interactions are of importance, but in such crowded coordination spheres, it is worthwhile to consider also the intramolecular contacts between nonbonded spin carriers since, in all complexes, distances between nitroxyl oxygen atoms as small as 2.95 Å are observed. In addition, intermolecular interactions may be important for understanding the magnetic behavior, at least at low temperature.

Although not isometric, the two complexes exhibiting a *fac* arrangement, **4** and **9**, are isomorphous and show several intermolecular short contacts resulting from a peculiar crystal packing as shown in Figure 5. The perchlorate anions connect the molecules through a net of hydrogen bonds involving the amino group of the imidazole fragments, which results in chains running along the *b* axis. In addition, two molecules belonging to neighboring chains and related by the inversion center are close enough to bring one oxyl group (O2C) into contact (3.1(1) Å) with another one (O1A). Finally, in this pair of molecules, stacking of two imidazole fragments is observed with a short distance of 3.24(5) Å. A similar arrangement is also observed in **5**, but π-stacking involves phenyl groups at distances of 3.48(6) Å. In addition, the molecule of ethanol is hydrogen-bound to an oxyl oxygen and an imidazole NH group belonging

Table 2. Selected Bond Lengths (Å) and Angles (deg)

	4	5	6
M−O1A	2.180(3)	2.181(3)	2.111(5)
M−O1B	2.134(3)	2.199(4)	2.107(5)
M−O1C	2.175(3)	2.142(4)	2.114(4)
M−N3A	2.209(4)	2.206(4)	2.231(5)
M−N3B	2.212(4)	2.257(4)	2.283(5)
M−N3C	2.227(4)	2.214(4)	2.255(5)
N1A−O1A	1.305(4)	1.291(5)	1.281(7)
N1B−O1B	1.290(4)	1.294(5)	1.296(6)
N1C−O1C	1.287(4)	1.305(5)	1.297(6)
N2A−O2A	1.275(5)	1.272(5)	1.274(8)
N2B−O2B	1.269(5)	1.270(5)	1.273(7)
N2C−O2C	1.271(5)	1.23(5)	1.262(7)
O1A−M−O1C		175.2(1)	167.5(2)
O1A−M−N3B	169.1(2)		
O1C−M−N3B		171.9(1)	173.3(2)
O1B−M−N3C	169.5(2)		
N3B−M−N3C		157.0(2)	160.6(2)
O1C−M−N3A	172.3(2)		

	7	8	9
M−O1A	2.109(6)	2.012(4)	2.17(1)
M−O1B	2.049(7)	2.047(4)	2.12(1)
M−O1C	2.120(6)	2.059(4)	2.17(1)
M−N3A	2.074(8)	2.060(4)	2.07(1)
M−N3B	2.096(8)	2.106(4)	2.08(1)
M−N3C	2.052(8)	2.103(4)	2.11(1)
N1A−O1A	1.285(9)	1.292(6)	1.30(1)
N1B−O1B	1.252(10)	1.283(6)	1.28(1)
N1C−O1C	1.288(9)	1.287(5)	1.28(1)
N2A−O2A	1.276(10)	1.268(7)	1.27(1)
N2B−O2B	1.268(11)	1.251(6)	1.28(1)
N2C−O2C	1.264(11)	1.265(6)	1.32(1)
O1A−M−O1C	177.6(3)	176.8(2)	
O1A−M−N3B			166.1(5)
O1B−M−N3A	176.1(3)	177.9(2)	
O1B−M−N3C			166.3(5)
N3B−M−N3A	174.0(3)	165.8(2)	
O1C−M−N3A			175.0(6)

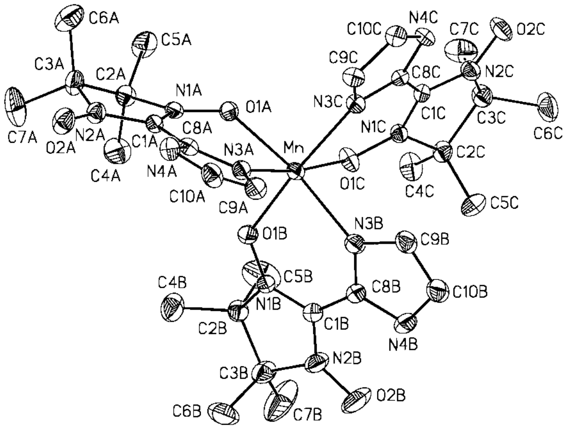

Figure 2. Molecular structure of [Mn(NITImH)$_3$]$^{2+}$ (**4**$^{2+}$) showing the numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

to the same molecule; these contacts are not expected to have significant influence on the magnetic properties. As mentioned before, the crystal packing is less effective in all other complexes, **6**−**8**, which exist as the *mer* modification. Therefore, much larger intermolecular distances are observed in these species so that, from the magnetic point of view, they will be considered as isolated four-spin systems.

All other structural features need no further comments except for the presence of chiral selectivity in the complexes of NITPy, which is probably related to crystal packing and intermolecular interactions. Close examination of the structural parameters for **6** and **8** provides no a clear understanding of this selectivity.

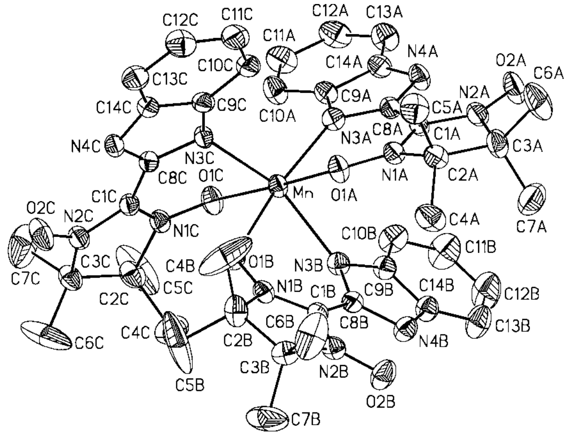

Figure 3. Molecular structure of [Mn(NITBzImH)$_3$]$^{2+}$ (**5**$^{2+}$) showing the numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

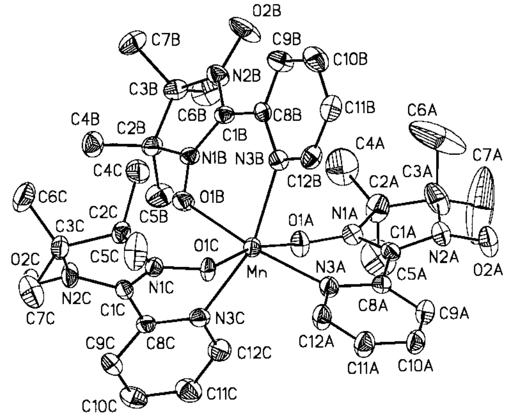

Figure 4. Molecular structure of [Mn(NITPy)$_3$]$^{2+}$ (**6**$^{2+}$) showing the numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

Magnetic Studies. At first sight, these systems are simple, and interpretation of their magnetic properties is expected to be straightforward. However, several interactions have to be considered: large direct coupling between metal(II) ions and organic radicals[8] (except for **9**) and through-space direct intramolecular interactions within the metal coordination spheres between the nitroxide ligands (O1A−O1B = 2.95(4) Å, in **4**) which are difficult to quantify but can be rather large.[15,16] Both interactions are expected to be antiferromagnetic.

An overall antiferromagnetic behavior is indeed observed, as shown for complex **4** in Figure 6. At 300 K, the value of χT is much weaker than that expected for independent spins and, upon a decrease in temperature, reaches a plateau whose value ($\chi T = 1.02$ cm^3 K mol^{-1}) corresponds to an $S = 1$ ground spin state. Such a ground state of low-spin multiplicity and antiferromagnetic metal−radical interactions are confirmed by the magnetization which saturates in a field weaker than 5 T at 2 K to a value of 11 200 cm^3 G mol^{-1}(2.01 μ_B). A similar qualitative magnetic behavior is observed for complexes **4**−**6** and **8**; in the last however, the ground spin state is a doublet corresponding to a high-spin nickel(II) ion antiferromagnetically coupled to three nitroxide groups. For the three other com-

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Table 3. Structural Parameters Relevant to the Understanding of the Magnetic Properties (for Ligands A−C)

	α^a (deg)			M−O−N (deg)			β^b (deg)		
compd	A	B	C	A	B	C	A	B	C
4	7.4(2)	12.1(3)	14.6(3)	125.4(2)	128.1(3)	129.1(3)	9.6(2)	31.3(4)	18.9(4)
5	2.9(1)	5.5(2)	10.5(3)	125.1(3)	122.6(3)	117.3(3)	23.9(2)	35.6(3)	40.6(3)
6	27.9(4)	24.2(4)	18.9(5)	123.7(5)	121.3(4)	114.4(3)	46.4(5)	44.3(4)	35.2(3)
7	15.6(2)	11.7(2)	7.7(3)	124.0(5)	124.4(6)	126.1(5)	24.1(3)	24.3(4)	11.9(4)
8	45.3(5)	16.2(3)	33.8(5)	121.3(3)	117.5(3)	114.6(3)	25.5(5)	43.8(6)	45.2(5)
9	16.4(7)	11.4(5)	3.8(2)	123.1(9)	123.4(9)	127.3(9)	18.2(6)	9.7(5)	13.7(7)

[a] Angle between the imidazole and the imidazoline rings in the nitroxide ligands. [b] Angle between the M−O−N plane and the imidazoline plane for each ligand.

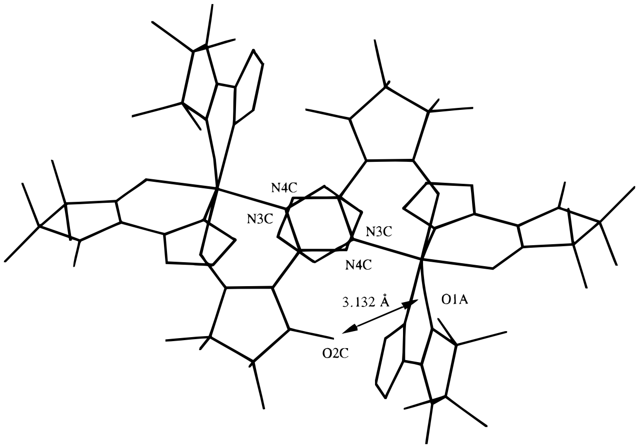

Figure 5. Scheme displaying the closest intermolecular contact in the *fac* complexes **4** and **9**.

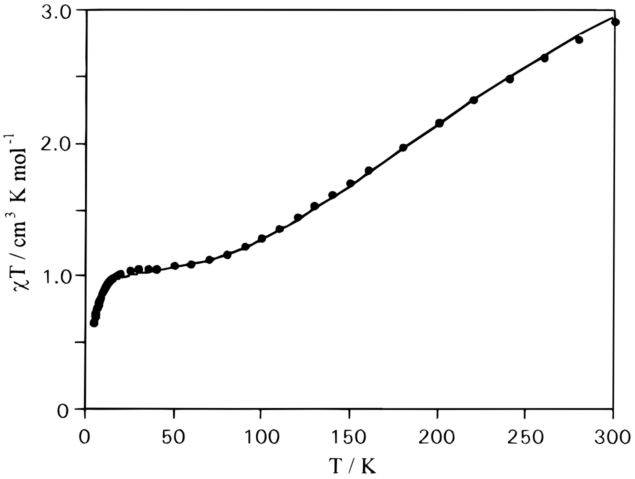

Figure 6. Temperature dependence of χT for complex **4**.

plexes, no such clear qualitative description of the ground state is available. For Ni(NITImH)$_3$(ClO$_4$)$_2$, **7**, the value of χT below 50 K depends on the rate of cooling, and measurements are not reproducible. The compound is probably subject to crystallographic modifications inducing changes of the bonding parameters within the coordination sphere and changes of the coupling interactions. No attempts have been made to determine a coupling constant from these data.

In contrast, for complex **9**, whose magnetic behavior is shown in Figure 7, the measurements are reproducible. This compound is very interesting since the three nitroxide ligands are coordinated to a diamagnetic metal ion and one could expect to determine the coupling between neighbor radicals within the metal coordination sphere. Obviously, if this three-spin system could be considered as isolated molecules in the solid, the ground spin state would be a doublet and the corresponding χT value would be 0.375 cm^3 K mol^{-1}. In contrast, χT approaches zero as T reaches 2 K. The crystal structure shows several intermolecular short contacts (vide infra). Hydrogen bonding through perchlorate anions is not expected to mediate any strong magnetic interaction; in contrast, close inter-nitroxyl contacts within the metal coordination sphere could be more efficient, but since the nitroxyl groups involved in these contacts are almost orthogonal, the resulting interaction is expected to be rather weak.[17] The last intermolecular coupling pathways would involve neighboring molecules related by the inversion center: π-stacking of imidazole groups and contacts between uncoordinated NO groups. In this pair of molecules, the imidazole groups are oriented in such a way that sites of positive spin density are in close contact with sites of negative spin density.[18] Polarized neutron diffraction experiments have shown that delocalization of spin density on an aromatic substituent in nitronyl nitroxide is weak, and therefore, the resulting magnetic coupling should also be weak.[19] More significant could be the interactions between uncoordinated NO groups, but on examining the structural parameters, one does not expect a large coupling. In a first attempt, the magnetic behavior was fit by considering one intramolecular coupling constant between the three nitroxide ligands and intermolecular interactions were modeled in the molecular field approximation.[20] A nitroxyl−nitroxyl interaction of $J = -17(3)$ cm^{-1} and an unrealistic intermolecular interaction of $zJ' = -11(2)$ cm^{-1} were obtained. This result and the monotonic temperature dependence of χT

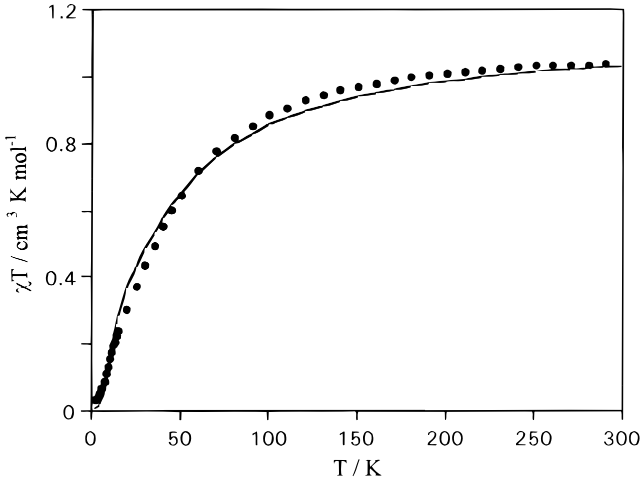

Figure 7. Temperature dependence of χT for complex **9**.

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suggest that the inter-nitroxide interactions within the coordination sphere are not dominant and that, as suggested by the crystal structure, a model including two molecules should be considered. Such a model of two exchange-coupled three-spin systems afforded an intramolecular nitroxyl−nitroxyl interaction of $J = -14(3)$ cm^{-1} and an intermolecular interaction of $J'' = -24(4)$ cm^{-1}. Notably, the quality of the fit ($R = \sum(\chi_{obsd} - \chi_{calcd})^2/\sum(\chi_{obsd})^2 = 5.2 \times 10^{-5}$) was much better.

For the manganese(II) analogue, **4**, which is isomorphic (although not isometric) with **9**, the same model including an additional Mn−nitroxyl interaction was not considered since our program[21] cannot handle so many magnetic centers. However, for a four-spin system, a metal−nitroxide interaction of $J = -53(2)$ cm^{-1} and $zJ' = -1.4(3)$ cm^{-1} were obtained by fixing the intramolecular inter-nitroxide interaction to zero. Interestingly, the quality of the fit and the value of J were almost independent of the value of the inter-nitroxide interaction. The latter fact and the weak intermolecular interaction can be understood by considering the $S = 1$ total ground state where, compared to that of the uncoupled spin carriers, the spin distribution is strongly modified because the manganese−nitroxide interaction is dominant. Indeed, straightforward calculations show that the contribution of each nitroxide ligand to the magnetic moment of the ground spin state is only $-^1/_4$ while that of the manganese ion is $+^7/_4$. Thus, although the intra- and intermolecular nitroxide−nitroxide interactions are expected to be of the same order of magnitude, their values are probably much weaker than those observed for **9**. Therefore, in compounds **4**−**8**, where the metal ion is paramagnetic, the magnitude of the antiferromagnetic metal−nitroxide interaction minimizes the role of inter-nitroxide coupling. The following metal−nitroxide coupling constants were determined: **4**, −53(2) cm^{-1}; **5**, −79(5) cm^{-1}; **6**, −88(5) cm^{-1}; **7**, undetermined; **8**, −111(7) cm^{-1}. The function minimized, $R = \sum(\chi_{obsd} - \chi_{calcd})^2/\sum(\chi_{obsd})^2$, was in the range 3.6×10^{-4}−2.4×10^{-5}, and intermolecular interactions (zJ') were weaker than 1.6 cm^{-1}.

For both manganese(II) and nickel(II) complexes, the coupling constants compare well with those observed for the derivatives of NITPy with the corresponding metal chlorides, −79(5) and −110 (11) cm^{-1}, respectively.[11] In contrast, they are much weaker than those observed for other species involving metal hexafluoroacetylacetonates and nitronyl nitroxide ligands that are bound only by the nitroxyl oxygen atoms.[22,23] Indeed, exchange interactions 50% larger ($|J| \approx 150$ cm^{-1}) have been reported in the latter case which suggest that binding of the imidazole or pyridyl groups in a chelating mode substantially lessens the magnitude of the exchange coupling. From the magnetic point of view, such a chelating mode is characterized by the presence of another coupling pathway through the chelating nitrogen atom which could be the cause of the observed weakening. However, as stated before, polarized neutron data have shown that, in the phenyl-substituted nitroxide, delocalization of the spin density on an aromatic substituent is rather weak, suggesting that the new pathway is not highly efficient. A consequence of such a chelating mode, however, is reflected in structural parameters around the bound nitroxyl oxygen atom. Indeed, if one considers that the antiferromagnetic interaction results primarily from the overlap of the nitroxide π^* magnetic orbital and the metal orbital pointing toward this ligand, the formation of a chelate ring results in a low value of the M−O−N angle and a value of the angle between the MON plane and the imidazoline ring far from 90 °. While the first feature would increase the overlap between the metal and ligand orbitals, the second feature is expected to result in a large weakening of the overlap and of the exchange value. Another consideration supports a weaker metal−radical exchange interaction. Compared to the previous examples, in compounds **4**−**6** and **8** the metal center does not carry electron-withdrawing groups. Therefore, the d metal orbitals involved in the coordination of the nitroxyl oxygen is destabilized and the binding is weaker. Thus, the exchange constant is expected to decrease.

Conclusion. Complexes **4**−**9** show that, using chelating ligands, it is possible to obtain metal−nitroxide species where the coordination sphere is free of ancillary electron-withdrawing groups. In these four-spin systems, the metal−nitroxide coupling constant is weaker than that observed in derivatives of metal hexafluoroacetylacetonates but still rather large.

The complexes of the imidazole-substituted nitroxide deserve special mention since ionization of the imidazole substituent will result in another chelating site; such an imidazolato-substituted bridging ligand is expected to allow the preparation of extended species where metal ions and nitroxide ligands alternate regularly.

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Supporting Information Available: Listings of crystallographic data, atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters for **4**−**9** (55 pages). Ordering information is given on any current masthead page.

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