contain a further wealth of information related to the dihedral angle between the Fe–S–C and S–C–H planes and between interproton distances in both oxidized and reduced species. This information is being investigated also through comparison of the spectra of HiPIPs from different organisms.

Acknowledgment. We thank J.-J. Girerd for a long and stimulating discussion about the subtle interplay between the *J* and *B* parameters. We also thank L. Noodleman for clarifying to us the formalism used in eqs 7 and 9. Early suggestions by A. Bencini about the possibility of using only *J* values as parameters are also acknowledged.

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N-Bonded Copper(II)–Imino Nitroxide Complexes Exhibiting Large Ferromagnetic Interactions

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Abstract: The magnetic interactions between copper(II) and imino nitroxide free radicals have been investigated in two novel adducts of copper(II)–bis(hexafluoroacetylacetonato): bis(μ-1,3-(2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy))hexakis(hexafluoroacetylacetonato)tricopper(II) (**1**) and (2-(2-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy)bis(hexafluoroacetylacetonato)copper(II) (**2**). The crystal and molecular structures of both compounds have been determined. In **1**, the three metal ions are linked by two μ-1,3 bridging nitroxide ligands, the two external copper ions are in trigonal-bipyramidal environments with the imino nitroxide nitrogen atom coordinated in the basal plane, while the central metal ion is axially coordinated by the two nitroxide oxygen atoms. In **2**, the imino nitroxide and the imino pyridyl nitrogen atoms are both equatorially bound to the octahedral copper ion; in addition, the molecules interact in pairs in the crystal lattice. In both cases, the high-temperature magnetic behavior is governed by a large ferromagnetic interaction, $J > 300$ cm^{-1} ($H = -JS_iS_j$), which develops within the imino coordinated metal ion and the free radical. By contrast, the low-temperature magnetic properties strongly depend on weak additional interactions corresponding to the binding of the nitroxide oxygen to the central metal ion in **1**, and to the intermolecular short contact between the uncoordinated NO groups in **2**. The ferromagnetic coupling of spins is rationalized as arising from the exchange interaction of unpaired electrons in orthogonal magnetic orbitals. This situation is the consequence of the binding geometry of the imino nitroxide nitrogen atom to the copper(II) ion. Crystal data. **1**: a = 12.740 (4) Å, b = 16.269 (5) Å, c = 19.470 (6) Å, α = 78.89 (1)°, β = 78.30 (1)°, γ = 81.00 (1)°, triclinic, $P\bar{1}$. **2**: a = 9.317 (4) Å, b = 12.922 (5) Å, c = 13.525 (6) Å, α = 95.24 (1)°, β = 109.71 (1)°, γ = 110.92 (1)°, triclinic, $P\bar{1}$. This study shows that large ferromagnetic interactions between metal ions and nitroxide free radicals are possible; it opens new perspectives for the design of molecular high-spin species.

Among the strategies that have been developed for designing molecular ferromagnets,[2-6] the metal–radical approach[6] has led to promising results. This strategy is based on the building of chains of alternating antiferromagnetically coupled metal and organic spins of different magnitude leading to ferrimagnetic one-dimensional compounds. The solid-state properties of these materials depend on the interchain coupling, which is generally not a controlled process. However, using nitronyl nitroxides[7] (Figure 1) and manganese(II) ions we were able to prepare such ferrimagnetic chains, which were coupled in the solid state, leading to low-temperature ferromagnets.[8,9] The low transition temperatures in these materials may be accounted for by the bulkiness of the ligands surrounding the metal ion and the absence of exchange pathways between the chains. This results from the fact that bulky electron-withdrawing hexafluoroacetylacetonato groups are needed to induce the nitroxide bonding to the metal.

In spite of this limitation, the metal–radical approach is one of the most versatile strategies for preparing high-spin species by different coupling schemes. Although large antiferromagnetic interactions and ferrimagnetic extended derivatives are the rule in metal–nitroxide magnetochemistry, chains of ferromagnetically coupled copper ions and nitroxides have also been prepared.[10,11] Indeed, when a free radical is axially bound by its oxygen atom to a tetragonal copper(II) ion, a weak ferromagnetic interaction develops. This is the only case where such a coupling is observed. The magnitude of the interaction has been qualitatively studied by empirical theoretical methods;[12] it depends on the binding of the nitroxide, mainly the bonding distance, which is always large in this geometry. Therefore, it is now generally accepted that strong metal–nitroxide ferromagnetic interactions cannot be obtained by using nitronyl nitroxides.

Previous investigations of the magnetic properties of metal organic free radical complexes such as semiquinonates[13,14] and

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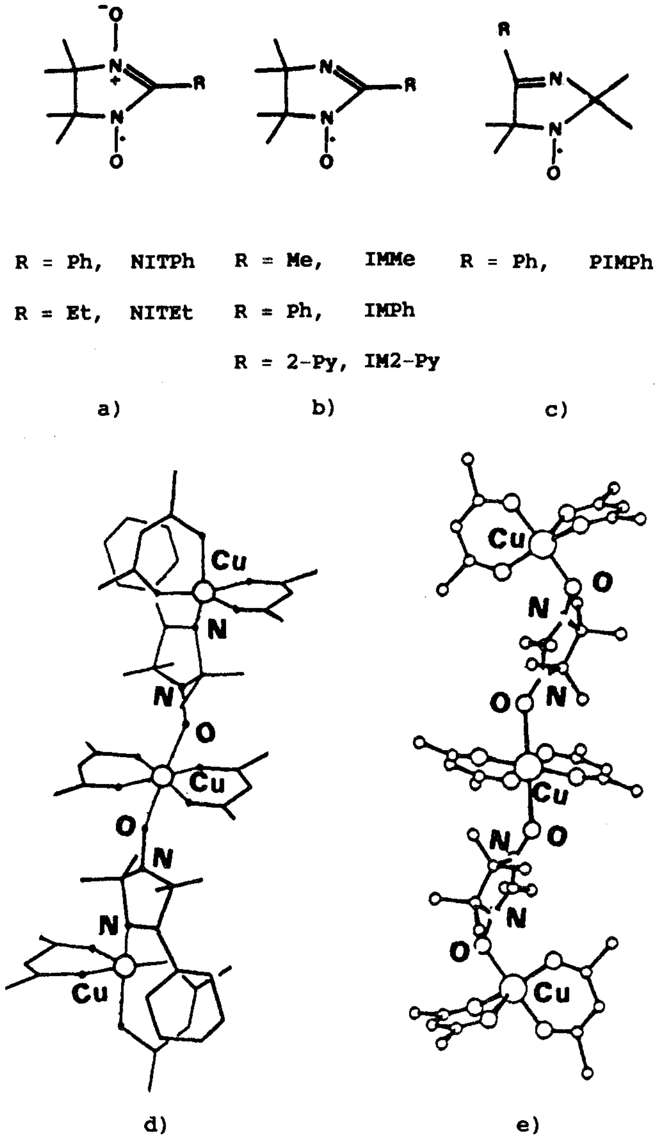

Figure 1. Chemical structure of the nitroxide free radicals (a) nitronyl nitroxides (NITR), (b) imino nitroxides (IMR), (c) proxylimino nitroxides (PIMR), and of the previously reported trinuclear copper(II) complexes (d) $(Cu(hfac)_2)_3(PIMPh)_2$ (**3**) and (e) $(Cu(hfac(_2)_3(NITEt)_2$ (**4**).

Table I. Crystallographic Data

compd	1	2
chem formula	$C_{56}H_{40}F_{36}N_3O_{14}Cu_3$	$C_{22}H_{18}F_{12}N_3O_5Cu$
a, Å	12.740 (4)	9.317 (4)
b, Å	16.269 (5)	12.922 (5)
c, Å	19.470 (6)	13.525 (6)
α, deg	78.89 (1)	95.24 (1)
β, deg	78.30 (1)	109.71 (1)
γ, deg	81.00 (1)	110.92 (1)
V, Å^3	3848.55	1389.74
Z	2	2
fw	1867.04	695.73
space group	$P\bar{1}$	$P\bar{1}$
T, °C	20	20
ρ_{calcd}, g/cm^3	1.612	1.663
μ, cm^{-1}	0.1	0.1
R	0.063	0.053
R_w	0.067	0.058

porphyrin radical cations[15,16] have shown that large ferromagnetic couplings can be observed when the magnetic orbitals of the metal and the ligand are orthgonal and the bonding distances are short. Examination of the structures of these complexes showed that the ligands have strong donor properties and peculiar bonding geometries. Similar features are found in the imino nitroxides,[17] IMR, (Figure 1): the imino nitrogen atom has a pronounced basic character and some preliminary investigations showed that the magnetic behavior of these free radicals is markedly different from that of the nitronyl nitroxides and related to different binding geometries. Indeed, in some dirhodium(II) tetrakis(trifluoroacetato) complexes of IMMe,[18] it was found that the coupling between the radicals is either weakly antiferro- or ferromagnetic, while in the NITR analogues, the nitronyl nitroxides are strongly paired.

Another interesting feature of these paramagnetic ligands is the presence of two different donor sites, one of which has strong binding properties. Therefore, it can be expected that less acidic and less crowded metal centers may be used as building blocks and, in principle, heteropolymetallic chains might be designed. In these compounds, if the interactions of the nitroxide with the two neighboring metal ions have different signs, new coupling schemes and magnetic properties are anticipated. Thus, our metal-radical approach would become more versatile.

For these reasons we began studying the coordination chemistry of the imino nitroxides with the aim of comparing the magnetic properties of closely related derivatives of the nitronyl and imino nitroxides and, in a first step, to get magnetostructural correlations for the metal–N-bonded imino nitroxide complexes. We report herein the structural and magnetic characterization of two copper(II) complexes with imino nitroxide ligands, $(Cu(hfac)_2)_3(IMPh)_2$ (**1**) and $Cu(hfac)_2IM2\text{-}Py$ (**2**), which exhibit the largest metal–nitroxide ferromagnetic interactions yet observed. Actually, these interactions have the same magnitude but the opposite sign as those observed in most of the O-bonded copper(II)–nitroxide adducts.

Experimental Section

Syntheses. Copper(II)–bis(hexafluoroacetylacetonato),[19] $(Cu(hfac)_2)$, IMPh,[17] and IM2-Py[20] (see Figure 1) were prepared by reported procedures.

Bis(μ-1,3-(2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy)hexakis(hexafluoroacetylacetonato)tricopper(II) ($(Cu(hfac)_2)_3(IMPh)_2$, **1**). A 360-mg sample of $Cu(hfac)_2$ (0.75 mmol) and 110 mg (0.5 mmol) of IMPh were dissolved in 10 mL of warm pentane. The solution was evaporated to a volume of 5 mL, rapidly filtered, and allowed to cool to room temperature. After a couple of hours large dark green crystals formed, which analyzed satisfactorily for $(Cu(hfac)_2)_3(IMPh)_2$ (228 mg, 48%, mp 101 °C). Anal. Calcd for $C_{56}H_{40}F_{36}N_4O_{14}Cu_3$: C, 35.99; H, 2.16; F, 36.64; N, 3.00; O, 12.00; Cu, 10.21. Found: C, 35.93; H, 2.06; N, 3.02; F, 35.98; Cu, 10.36.

2-(2-Pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy-bis(hexafluoroacetylacetonato)copper(II) ($Cu(hfac)_2IM2\text{-}Py$, **2**). A 478-mg sample of $Cu(hfac)_2$ (1 mmol) and 218 mg (1 mmol) of IM2-Py were dissolved in 5 mL of diethyl ether. After the mixture was stirred a few minutes, 5 mL of heptane was added and the solution was left to evaporate at room temperature in the dark. The adduct precipitated in 12 h in the form of well-shaped orange crystals (403 mg, 58%, mp 197 °C). Anal. Calcd for $C_{22}H_{18}F_{12}N_3O_5Cu$: C, 37.94; H, 2.61; F, 32.77; N, 6.04; O, 11.50; Cu, 9.13. Found: C, 38.06; H, 2.88; N, 5.97; F, 32.31; Cu, 9.02.

The crystals of both compounds were suitable for X-ray diffraction study.

X-ray Data Collection and Structure Determination. Preliminary Weissenberg photographs showed the triclinic system for both com-

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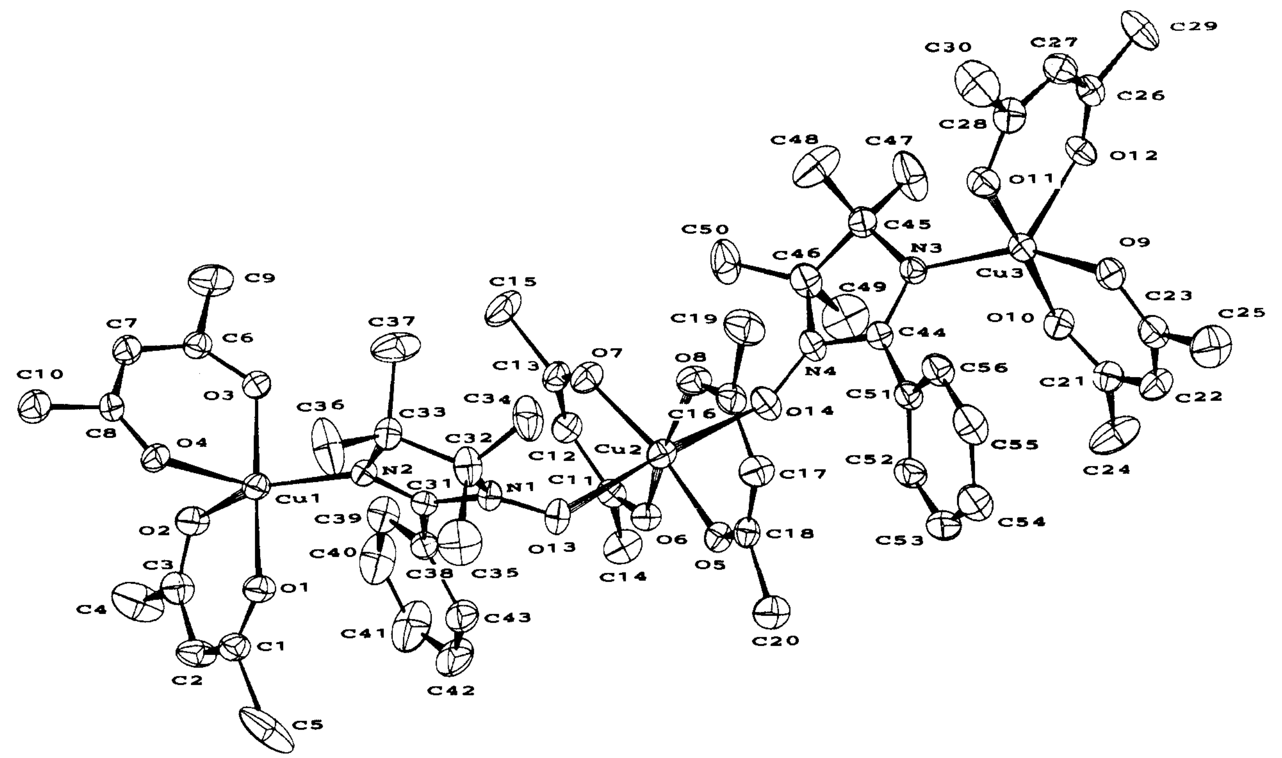

Figure 2. View of $(Cu(hfac)_2)_3(IMPh)_2$ (**1**) showing 30% probability ellipsids and the atom numbering scheme. Fluorine atoms have been omitted for clarity.

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

		$(Cu(hfac)_2)_3(IMPh)_2$ (**1**)			
Cu(1)–O(1)	1.934 (4)	Cu(1)–O(2)	2.116 (4)	Cu(1)–O(3)	1.913 (5)
Cu(1)–O(4)	2.011 (4)	Cu(1)–N(2)	1.990 (5)	Cu(2)–O(5)	1.933 (3)
Cu(2)–O(6)	1.926 (4)	Cu(2)–O(7)	1.932 (4)	Cu(2)–O(8)	1.914 (4)
Cu(2)–O(13)	2.497 (5)	Cu(2)–O(14)	2.515 (5)	Cu(3)–O(9)	1.995 (5)
Cu(3)–O(10)	1.929 (5)	Cu(3)–O(11)	1.908 (5)	Cu(3)–O(12)	2.120 (5)
Cu(3)–N(3)	2.006 (5)	O(13)–N(1)	1.256 (6)	O(14)–N(4)	1.269 (8)
O(1)–Cu(1)–O(3)	176.7 (2)	O(2)–Cu(1)–O(4)	91.5 (2)		
O(2)–Cu(1)–N(2)	124.1 (2)	O(4)–Cu(1)–N(2)	144.4 (2)		
Cu(1)–N(2)–C(31)	124.0 (5)	Cu(1)–N(2)–C(33)	126.8 (4)		
O(6)–Cu(2)–O(13)	95.2 (2)	O(6)–Cu(2)–O(14)	78.6 (2)		
O(13)–Cu(2)–O(14)	173.4 (2)	O(10)–Cu(3)–O(11)	173.6 (2)		
O(9)–Cu(3)–N(3)	148.4 (2)	O(10)–Cu(3)–N(3)	87.5 (2)		
O(12)–Cu(3)–N(3)	117.7 (2)	O(9)–Cu(3)–O(12)	94.0 (2)		
Cu(3)–N(3)–C(44)	122.0 (4)	Cu(3)–N(3)–C(45)	128.4 (5)		
		$Cu(hfac)_2IM2$-Py (**2**)			
Cu–O(1)	2.283 (4)	Cu–O(2)	1.967 (3)	Cu–O(3)	1.956 (4)
Cu–O(4)	2.293 (4)	Cu–N(1)	2.003 (4)	Cu–N(3)	2.021 (4)
O(5)–N(2)	1.262 (8)				
O(1)–Cu–N(1)	93.8 (2)	O(4)–Cu–N(1)	95.2 (2)		
O(1)–Cu–N(3)	92.1 (2)	O(2)–Cu–N(1)	171.4 (2)		
O(3)–Cu–N(3)	176.9 (2)	O(2)–Cu–N(3)	90.9 (2)		
N(1)–Cu–N(3)	80.5 (2)	O(4)–Cu–N(3)	98.1 (2)		
O(1)–Cu–O(4)	167.4 (2)	O(2)–Cu–O(3)	90.6 (2)		
Cu–N(1)–C(11)	112.7 (3)	Cu–N(1)–C(12)	136.7 (4)		
Cu–N(3)–C(18)	115.1 (3)	Cu–N(3)–C(22)	126.2 (4)		

pounds. Crystals of approximate dimensions: 0.2 × 0.2 × 0.2 mm were mounted on an Enraf-Nonius four-circle diffractometer using Mo Kα radiation and a graphite monochromator. Accurate cell constants were derived from least-squares refinement of the setting angles of 25 reflections and are reported in Table I with other experimental parameters. The data were corrected for decay, Lorentz, and polarization effects but not for absorption.

Both crystal structures were solved by the conventional Patterson method using the SHELX76[21] package, which led to the location of the copper atoms. Then, assuming the $P\bar{1}$ space group, successive difference Fourier maps allowed for the location of all the other non-hydrogen atoms. The hydrogen atoms were included in the final refinement model in calculated and fixed positions with isotropic thermal parameters. The final R values are reported in Table I.

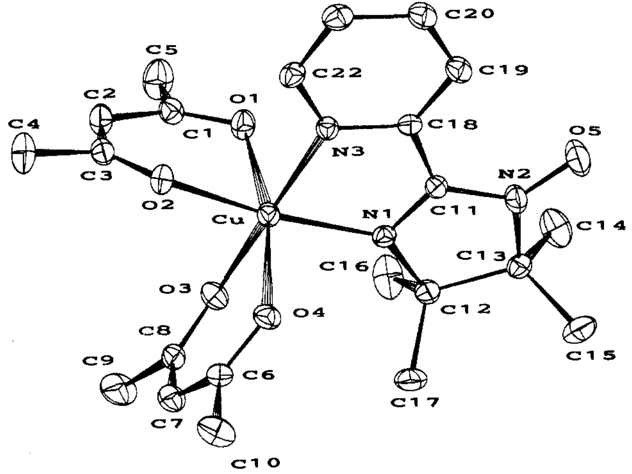

Figure 3. View of $Cu(hfac)_2IM2$-Py (**2**) showing 30% probability ellipsoids and the atom numbering scheme. Fluorine atoms have been omitted for clarity.

Selected bond lengths and angles are found in Table II. Summary of crystal data and experimental parameters (Table SI), atomic positional parameters (Tables SII and SIII for **1** and **2**, respectively), compete listing of bond lengths (Tables SIV and SV), bond angles (Tables SVI and VII), anisotropic thermal parameters (Tables SVIII and IX), and observed and calculated structure factors (Tables SX and XI) are deposited as supplementary materials.

Magnetic Susceptibility Measurements. The magnetic susceptibilities of the two adducts were measured in the 2–300 K temperature range with a Quantum Design MPMS superconducting SQUID magnetometer operating at field strength of 0.5 T. The data were corrected for the magnetization of the sample holder and the magnetic susceptibilities were corrected for the diamagnetism of the constituent atoms by using Pascal constants.

Results

Description of the Structures. Views of the structures of the two adducts are shown in Figures 2 (**1**) and 3 (**2**).

The unit cell comprises two formula units of **1**. The molecule is formed by three copper atoms linked by two μ-1,3 bridging imino nitroxides. The coordination geometry around the two "external"

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[21] Sheldrick, G. *SHELX76 System of Computing Programs*; University of Cambridge; Cambridge, England, 1976.

copper ions, Cu(1) and Cu(3), is trigonal bipyramidal with the nitroxide bound in the basal plane by the imino nitrogen atom while the central copper is in a distorted octahedral environment, the apical positions being occupied by the oxygen atoms of the two bridging nitroxides. There are severe distortions from this idealized bonding pattern, in particular in the basal plane of the five-coordinate coppers where the angles involving the imino nitrogens are far from 120° (O(4)–Cu(1)–N(2) = 144.4 (2)° and O(9)–Cu(3)–N(3) = 148.4 (2)°). It is worth noting that the molecule is not centrosymmetric. Although the distances and angles within the coordination spheres of the two pentacoordinated metal ions, Cu(1) and Cu(3), are similar, the directions of the axes of the pyramids make an angle of 108.8°; in addition, the angles defining the two Cu(2)–O(nitroxyl) bonds around the central copper ion are significantly different: O(6)–Cu(2)–O(13) = 95.2 (2)° and O(6)–Cu(2)–O(14) = 78.6 (2)°. The coordination pattern of the hexafluoroacetylacetonato fragments is very close to that previously described in related examples[22-24] and needs no further comment.

The two imino nitroxide moieties are very similar and have the same structural characteristics as those reported for IMMe in some rhodium complexes.[18] The nitroxide oxygen atoms are only very loosely bonded to the metal (Cu(2)) and the N–O bond lengths (O(13)–N(1) = 1.256 (6) Å and O(14)–N(4) = 1.269 (8) Å) have essentially the same values as those observed in uncoordinated nitroxides[25,26] or in complexes where the NO group is axially bound to copper(II) ions.[22,24] In both nitroxide ligands, the phenyl ring makes an angle of 45.2° with the mean plane of the radical and is arranged so that its plane is parallel to a Cu(2) acetylacetonato mean plane (4.1 and 4.3°) at distances of 3.58 and 3.98 Å, respectively.

Whereas the oxygen binding of a nitronyl nitroxide to a copper ion is well documented, the coordination of an imino nitroxide by the imino nitrogen atom to this metal has never been described before. Since the geometrical parameters of the binding of the imino nitroxide to the metal are of great importance for the understanding of the magnetic properties, they will be discussed in some detail. For each "external" copper ion the imino nitrogen binding of the nitroxide occurs in such a way that the plane of the π system, N(1)–N(2)–C(31)–O(13) or N(3)–N(4)–C(44)–O(14), of the radical is almost perpendicular to the main axis of the trigonal bipyramid (83.6 and 84.3°). In other words, in both the Cu(1) and the Cu(3) fragments, this π system is almost coplanar with the basal plane of the pyramid. The two binding distances are short, CU(1)–N(2) = 1.990 (5) Å and Cu(3)–N(3) = 2.006 (5) Å, and the Cu–N bond nearly bisects the C–N–C angle of the nitroxide.

Finally, each molecule in the cell is well shielded from its neighbors and no intermolecular contact that could be of any importance in the discussion of the magnetic properties is observed. The shortest intermolecular metal–metal or metal–radical distance is 7.2 Å.

The triclinic cell of compound **2** contains two molecules of the complex. The copper ions are in a slightly distorted octahedral environment, the axial positions being occupied by acetylacetonato oxygen atoms. The free radical is coordinated to the metal by its two imino nitrogen atoms, which are located in the basal plane at similar distances of 2.003 (4) and 2.021 (4) Å for the nitroxyl and the pyridyl nitrogen, respectively. Noteworthy is the arrangement of the two closed fragments of the ligand: the pyridyl ring and the five-membered ring are exactly coplanar, the copper ion being also located in this plane. Surprisingly, the five-membered ring of the radical is rigorously planar and the methyl groups are eclipsed. Within the cell, the two molecules related by a center of symmetry are placed in such a way that the main intermolecular contacts are found between the methyl groups of the nitroxyl ligands. However, from one cell to the other, it can be seen (Figure 4) that contacts between the uncoordinated NO groups of two molecules are short enough (3.88 (1) Å) to play a role in determining the magnetic properties of the compound, at least at low temperature.

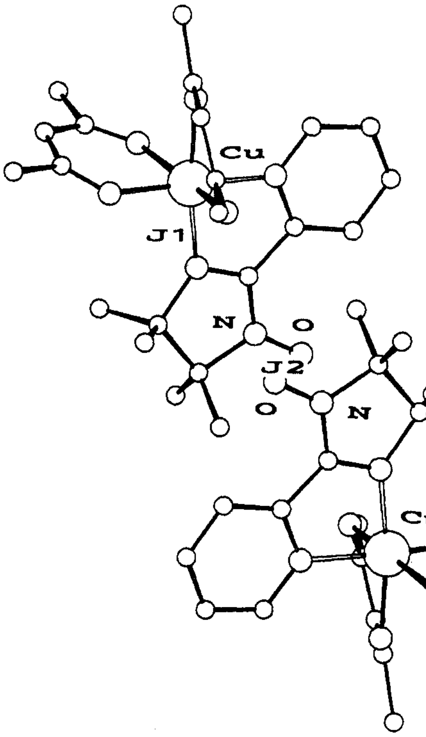

Figure 4. Scheme showing the NO–NO intermolecular contacts in Cu(hfac)$_2$IM2-Py (**2**).

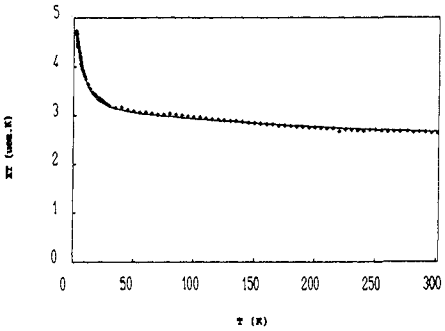

Figure 5. Magnetic data for (Cu(hfac)$_2$)$_3$(IMPh)$_2$ (**1**) in the form of XT vs T. The solid line is calculated with the parameters reported in Table III.

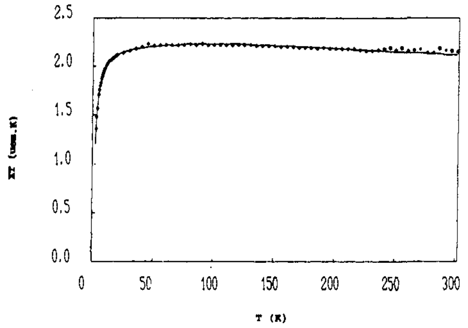

Figure 6. Magnetic data for the dimer of **2**, (Cu(hfac)$_2$IM2-Py)$_2$, in the form of XT vs T. The solid line is calculated with the parameters reported in Table III.

Magnetic Properties. Magnetic data are shown in Figures 5 and 6 for **1** and **2**, respectively, in the form of XT vs T. As the

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temperature decreases from 300 to 2 K, the XT product increases smoothly from 2.73 to 4.69 emu·K for **1**, while for **2**, it has an almost constant value of 1.07 emu·K down to 30 K but then decreases sharply to 0.5 emu·K at 2 K.

In **1**, the low-temperature value of XT (4.69 emu·K) is close to, but higher than, that expected for an $S = {}^5/_2$ ground state (4.375 emu·K if $g = 2$), suggesting a ferromagnetically coupled system of five $S = {}^1/_2$ spins. In that case, owing to the shielding of the molecules in the crystal, a finite value of XT is expected but not observed because 2 K was the lowest temperature we could reach. On the other hand, the room-temperature value of the XT product is much larger than that expected for independent spins, 1.875 emu·K, if $g = 2$. Since the low-temperature data point to a system where only ferromagnetic interactions are operative, this high room-temperature value of the XT product may be accounted for by considering that one of these interactions is strong enough to show up in this temperature range. Indeed, the two following qualitative models lead to XT values close to that observed at room temperature: (i) the two N-bonded copper–radical pairs are considered as two $S = 1$ spins, the value expected for the complex being 2.375 emu·K; (ii) the central copper(II) ion and the two nitroxyl ligands are taken as an $S = {}^3/_2$ spin leading to a XT value of 2.625 emu·K for the five-spin system. A similar question is raised by the room-temperature data for compound **2**. Indeed, the observed value is higher than that expected for two independent $S = {}^1/_2$ spins (0.75 emu·K) and corresponds exactly to that of a triplet state, suggesting a strong ferromagnetic interaction within the copper–nitroxide pair. However, since in the solid state we must consider a four-spin system, an acceptable value of the XT product is also obtained if the two uncoordinated NO groups are strongly ferromagnetically coupled, the g factor being larger than 2. Hence, the magnetic behavior of the two compounds may be, qualitatively, accounted for by predominantly ferromagnetic interactions between the constituent spins. However, the sharp decrease observed at low temperature for **2** is the signature of some weak antiferromagnetic coupling.

Neither compound shows any EPR signal at room temperature except for a weak feature attributable to some monomeric copper(II) impurity. In both cases, the spectra recorded at 4.2 K show many broad features, which do not allow for any interpretation, but which strongly suggest that, at this temperature, spin states larger than ${}^1/_2$ are thermally populated. In line with these findings, solutions of compound **2** have been found EPR silent at room temperature.[27] This behavior is probably related to unfavorable electron spin relaxation at room temperature; in solution, however, it is likely that the failure to observe an EPR spectrum is due to incompletely averaged large anisotropic interactions.

The X-ray results suggest models for interpreting the magnetic data. Since for **1** the molecules are well shielded, a linear five $S = {}^1/_2$ spin model was considered. Assuming a centrosymmetric structure, we considered only two coupling constants: J_1 within the two "external" metal–nitroxide pairs and J_2 related to the interaction between the central metal ion and the radicals; all other possible interactions between nonneighbor magnetic centers were neglected. This assumption seemed reasonable since the environments of both the pentacoordinated copper ions are rather similar; for the same reason, only one coupling constant was used to describe the magnetic behavior of the central copper ion. We considered also that a larger number of coupling constants would have overparametrized the problem and led to differences in J values of doubtful significance. For compound **2**, it is obvious that some antiferromagnetic intermolecular interactions are operative at low temperature and the simplest model that could be built up was that of a crystallographically defined centrosymmetric dimer (Figure 4) with an intramolecular copper(II)–radical (J_1) and an intermolecular nitroxide–nitroxide (J_2) interaction.

Table III. Fitting Parameters of the Magnetic Data

compd	g	TIP (10^{-6})	J_1,[a] cm^{-1}	J_2 cm^{-1}	R[b] (10^5)	ref
(Cu(hfac)$_2$)$_3$(IMPh)$_2$ (**1**)	2.09	182	400	10.2	2.04	*c* *d*
	2.11	197	17.2	387	11.4	
(Cu(hfac)$_2$IM2-Py)$_2$ (**2**)	2.12	139	292	−4.8	0.21	*c* *d*
	2.17	88	−3.2	283	2.6	
(Cu(hfac)$_2$)$_3$(PIMPh)$_2$ (**3**)	2.11		0	24		30
(Cu(hfac)$_2$)$_3$(NITEt)$_2$ (**4**)	2.22		<−500			31

[a] The Hamiltonian used was in the form $H = -JS_iS_j$. [b] The function minimized in the fitting process was $R = \sum(X^{\text{obsd}} - X^{\text{calcd}})^2/\sum(X^{\text{obsd}})^2$. [c] Parameters used for calculating the curves shown in Figures 5 and 6. [d] This work.

Although analytical expressions of the magnetic susceptibility might have been derived for these models, in fitting the data, we avoided tedious calculations using a homemade program[28] coupled to the Minuit minimization routine, which diagonalizes numerically the isotropic exchange Hamiltonian of a cluster. For both compounds, in a first attempt, the g values and the temperature-independent contribution of the copper ions (TIP) were fixed to 2.0 and 60 × 10^{-6} emu per ion, respectively; large J_1 and weak J_2 starting values were used. This procedure gave a first set of J values. In a second step, the J values were fixed and the g and TIP parameters allowed to vary one after another. This procedure was repeated three times until the function minimized showed no significant variation. In both cases, large positive J_1 values were obtained. The results of these best least-squares fitting processes are summarized in Table III, which also includes examples of copper–nitroxide derivatives possessing similar structures. It must be noted that acceptable results were also obtained for other sets of parameters. In particular, including 1% of an uncoupled impurity having $g = 2$ in the fitting scheme, J_1 and J_2 values differing by up to 10% from those reported in Table III were obtained. Acceptable agreements were also obtained fixing the J_1 parameters at values 30% higher than those reported; on the other hand, fixing these parameters at 30% lower values gave poor results. Therefore, the values reported in Table III must be considered as a lower limit of the J_1 coupling constants. The discrepancy between the different fitting schemes may be accounted for by the difficulty of determining ferromagnetic interactions, as already reported.[29]

Since, for both compounds, a qualitative model corresponding to large J_2 values would also account for the room-temperature data, we investigated this possibility by including large starting positive values of J_2 in the fitting processes. In both cases, another set of J parameters where J_2 is large and positive was obtained, which reproduces the magnetic data in the all-temperature range with acceptable agreement factors. Although these new sets of coupling constants are meaningless (see Discussion), they are included in Table III.

In summary, the quantitative treatment of the magnetic data of **1** and **2** gave, in each case, two sets of coupling constants, which correspond to the two qualitative models outlined before to account for the high-temperature data. The four sets of parameters all show that surprisingly large ferromagnetic interactions are operative in these complexes.

Discussion

Trinuclear derivatives are rather common in coordination chemistry of bidentate nitroxides with Cu(hfac)$_2$. Thus, clusters similar to **1** have been described for PIMPh, (Cu(hfac)$_2$)$_3$(PIMPh)$_2$ (**3**),[30] and NITEt, (Cu(hfac)$_2$)$_3$(NITEt)$_2$ (**4**)[31] (see Figure 1). These structures are probably determined by a delicate balance between steric and electronic factors, as observed for adducts of nitroxides with most metal ions.[32] In the case of copper,

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it is worth noting that the steric factors are of great importance because the Cu–O or the Cu–N bonds are short. It is therefore expected that part of the steric hindrance will be overcome if a lower number of ligands is accommodated around the metal ion leading to pentacoordinated species and discrete clusters. This is the case for phenyl-substituted nitroxides such as IMPh or PIMPh, in which the substituent is sterically demanding. Moreover, phenyl groups have been shown to interact with acetylacetonato rings and to stabilize unpredictable structural arrangements.[33] As mentioned in under Results, it is indeed found that the phenyl rings of the two IMPh fragments are almost parallel to one Cu(2) acetylacetonato mean plane at such a distance that they may have an important role in determining the structure of the complex. The reaction of equimolar quantities of Cu(hfac)$_2$ and IMPh does not afford an extended chain compound. This result, also observed for NITPh,[24,34] illustrates the reluctance of phenyl-substituted radicals to bridge two copper ions in an octahedral environment due to steric constraints.

The second ligand used in this study bears an imino pyridyl nitrogen atom possessing strong donor properties. It has been especially designed in order to enforce the ligation of the paramagnetic center to weak electrophilic metal centers by the chelate effect. The observed coordination of such a ligand possessing two strong donor atoms with the strong acceptor Cu(hfac)$_2$ was, therefore, not a surprise. In designing this ligand, we also expected that, in the resulting adduct, the imino(nitroxide) nitrogen atom would be *equatorially* bound to an octahedral copper(II) ion, as indeed observed. The NO group of the ligand is not coordinated and, as observed in several cases,[24,34,35] it is engaged in intermolecular NO–NO contacts, as shown in Figure 4. We never succeeded, starting from the appropriate ratio of the reactants, in obtaining a structure similar to that found in **1**, i.e., the coordination of these NO groups to a central bridging copper ion. Such a structure, in which the radical bridges two octahedral copper ions, is not likely for the same reasons as those considered in the case of IMPh, as phenyl and pyridyl groups have comparable steric requirements. Owing to these intermolecular NO–NO contacts, this compound must be regarded, from the magnetic point of view, as a four-spin system.

The most striking feature of the magnetic behavior of these two adducts is the large ferromagnetic interaction that shows up in the XT product even at room temperature. On the other hand, the low-temperature magnetic behavior, in both compounds, is mainly governed by weak additional interactions.

Owing to the diverse coordination polyhedra that are found in copper(II) chemistry, the magnetic interactions in the corresponding oxygen-bonded metal–nitroxide complexes are spread over a large range of energy.[6] Most of the available data come from recent studies of Tempo,[36-38] Proxyl,[23,39] and nitronyl nitroxide[6] adducts for which a large number of examples has allowed rather precise magnetostructural correlations to be drawn. Thus, it is now accepted with confidence that the axial ligation (Figure 7a) of a nitroxide through the oxygen atom to a square-planar copper(II) ion results in the formation of a high-spin ground state. In this case, the two magnetic orbitals ($d_{x^2-y^2}$ on copper and π^* on the NO group) are quasi orthogonal, and the antiferromagnetic contribution to the coupling constant cancels out. On the other hand, the same simple molecular orbital considerations are consistent with a strongly stabilized ground state of low-spin multiplicity when the nitroxide is equatorially bound to a square-planar or trigonal-bipyramidal copper ion (Figure 7b,c). Also generally accepted is the antiferromagnetic nature of the interaction between two uncoordinated NO groups; although it has been theoretically predicted that the reverse situation could occur,[40] it has never been experimentally observed.

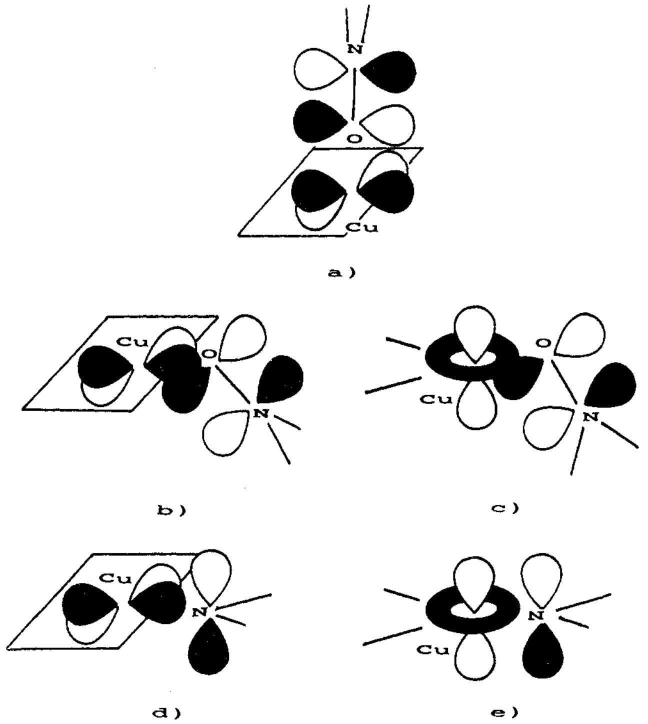

Figure 7. Scheme depicting the interaction of the magnetic orbitals in copper nitroxide complexes. (a) Axial binding of NITR to an octahedral Cu(II) ion; (b) equatorial binding of NITR to an octahedral Cu(II) ion; (c) equatorial binding of NITR to a trigonal-bipyramidal Cu(II) ion; (d) equatorial binding of IMR to an octahedral Cu(II) ion; (e) equatorial binding of IMR to a trigonal-bipyramidal Cu(II) ion.

The latter considerations bring a strong support to the assignment, the sign, and the magnitude of the weak additional interactions in compounds **1** and **2**. The extent of the coupling of the two NO groups in **2** (Figure 4) depends on their separation and the relative orientation of the π^* orbitals. In the present case, these orbitals are not disposed favorably for strong overlap because the shortest inter NO group distance is rather large (3.88 (1) Å) and the angle between the plane defined by the two NO groups and the plane of the π system of the nitroxides is 110°. These geometrical parameters are consistent with a weak antiferromagnetic coupling constant of $J_2 = -4.8$ cm^{-1}. On the other hand, a large ferromagnetic interaction between these two NO groups, as suggested by the second set of parameters, would have required that the π^* orbitals were orthogonal; the centrosymmetric arrangement of the four-spin system excludes this possibility. Therefore, in complex **2**, the weak antiferromagnetic coupling constant is unambiguously assigned to the interaction between the uncoordinated NO groups while the large ferromagnetic coupling describes the magnetic behavior of the N-bonded metal–nitroxide pair. This result strongly suggests that, in **1**, the ferromagnetic coupling constant also corresponds to the interaction of the N-bonded trigonal-bipyramidal copper ions with the nitroxide ligands. Indeed, on considering previous studies, the assignment of the large ferromagnetic coupling constant to the interaction between the central metal ion and the radical ligands is totally unrealistic. Although a J value of 78 cm^{-1} has been observed in one example, most of the copper–nitroxide complexes where the radical is axially bound through the oxygen atom exhibit

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exchange interactions weaker than 30 cm^{-1};[6,10,11,24,38] in the present case, the large metal–oxygen distance (~2.5 Å) precludes any interaction to be large. These expectations are confirmed by compounds **3** and **4**, which have similar binding geometries, and do exhibit weak interactions between the central copper ion and the radical ligands. It is therefore concluded that the ligation of an imino nitroxide to a copper ion by the imino nitrogen atoms gives rise to a large metal–radical ferromagnetic interaction.

Although the experimental determination of ferromagnetic coupling constants is generally not very precise,[29] it can be safely stated that interactions of the order of $J_1 = 300$ cm^{-1} are unusually large for metal–nitroxide complexes. This result is even more surprising if one notes that for both compounds this coupling arises in situations that show strong antiferromagnetic behavior in the O-bonded nitronyl nitroxide analogues, i.e., the equatorial coordination of the free radical to a trigonal-bipyramidal or a tetragonal copper(II) ion. Since the imino and nitronyl nitroxides have closely related electronic structures,[18] the origin of the reversal of the sign of the interaction has to be found in structural differences. Indeed, in the nitronyl nitroxide adducts, the Cu–O–N angle is close to 120° and the Cu–O–N plane is perpendicular to the O–N–C–N–O plane. This geometry strongly favors the overlap of the magnetic orbitals (the π^* orbital of the radical and the appropriate d orbital of the metal), leading to large antiferromagnetic couplings (Figure 7b,c). On the other hand, in the two complexes studied here, the coordination of the imino nitroxide by the nitrogen atom occurs in such a way that the magnetic orbitals are now rigorously orthogonal. Indeed, in both compounds, the mean plane of the radical is coplanar with the basal plane of the metal, and since the π^* orbital of the nitroxide is perpendicular to this plane, the interactions between the magnetic orbitals may be depicted as shown in Figure 7d,e for **2** and **1**, respectively. Assuming an ideal local C_{2v} symmetry for each copper–nitroxide fragment under consideration, the π^* orbital belongs to the B_2 representation while the copper magnetic orbital belongs to the A_1 representation, and in both compounds, the overlap is symmetry forbidden. However, owing to the short binding distances (≃2 Å) the overlap density is probably large and a strong ferromagnetic interaction is observed. This simple description does not take into account a probable participation of the pyridyl nitrogen to the coupling mechanism in compound **2**. We are aware that a precise understanding of the magnetic properties of the metal complexes of this pyridyl-substituted nitroxide might rely on a complete description of the spin population on the coordinated atoms. However, in the complex under consideration, since the basal plane of the metal, the pyridyl ring, and the π system of the nitroxide are perfectly coplanar, any delocalized unpaired spin population on the pyridyl nitrogen would be located in a π orbital belonging to the B_2 representation. Therefore, in this case, the contributions of the two coordinated nitrogen atoms would concur with the same result.

Comparison of the structures and the magnetic properties of the three compounds, so far reported, containing three copper(II) ions and two nitroxide radicals, **1**, **3**, and **4**, affords an illustrative summary of the dependence of the magnetic interactions on both the nature of the nitroxide ligand and the coordination geometry of the copper(II) ion in copper–nitroxide complexes. Despite their similar structures, these molecules illustrate all kinds and magnitudes of interactions that can be encountered in copper(II)–nitroxide chemistry. In **3**, PIMPh[30] is not a conjugated nitroxide, as shown by EPR solution spectra in which only the NO nitrogen hyperfine splitting is observed. The absence of spin population on the imino nitrogen atom precludes development of any strong interaction between the nitroxides and the terminal copper ions. This situation is similar to that observed in Cu(hfac)$_2$Tempol,[22,38] in which the interaction between the NO group and the hydroxyl coordinated copper ion has been measured at 0.08 cm^{-1}.[41] On the other hand, the localization of all the spin density on the NO group favors an interaction of medium magnitude with the central metal ion. Indeed, the reported value of $J_2 = 24$ cm^{-1} compares well with those observed in Tempo derivatives of related binding geometry.[22,36,38] Compound **4**[31] is representative of an equatorially oxygen bonded nitroxide in which the unpaired electron is delocalized over two identical coordination sites. In that case, the interaction of the radical with the external metal centers is so strongly antiferromagnetic that each pair behaves as a diamagnetic fragment. The compound exhibits the magnetic properties of an isolated $^1/_2$ spin just as if the central copper ion were coordinated by two diamagnetic ligands. In contrast, compound **1** exhibits a strong ferromagnetic coupling within the same pairs. In addition, the two free radicals are weakly coupled to the central metal ion, leading to a $S = {}^5/_2$ ground state.

In summary, strong metal–nitroxide ferromagnetic interactions are observed in copper–imino nitroxide complexes. It is clear that in these compounds, both the sign and the magnitude of the magnetic interaction are the consequence of the imino nitrogen binding geometry to the metal. Such a bonding geometry has been observed for most of the imino nitrogen coordinated metal complexes. Therefore, ferromagnetic interactions are expected to occur not only in copper derivatives but in adducts of other metal ions as well. Indeed, preliminary results show that nickel–imino nitroxide derivatives do exhibit large ferromagnetic couplings. Such strong ferromagnetic interactions have been reported for other metal–organic free-radical complexes such as copper(II)[13] and nickel(II)[14] semiquinonates and iron(II)[16] and copper(II)[15] porphyrin cation radicals. The understanding of the magnetic properties of these compounds has relied on the same molecular orbital considerations as those presently used for the imino nitroxide derivatives.

These results allow the design of new high-spin species. Indeed, in the imino nitroxides, the unpaired electron is delocalized on two inequivalent coordination sites, one of which has strong donor properties. This chemical structure gives, in principle, the opportunity to use metal centers possessing poor acceptor strength and would allow the design of heteropolymetallic chains in which the sign of the interactions alternates regularly.

Supplementary Material Available: Summary of crystal data and experimental parameters (Table SI), positional parameters for **1** and **2** (Tables SII and SIII, respectively), complete listing of the bond lengths (Tables IV and V), complete listing of the bond angles (Tables SVI and VII), and anisotropic thermal parameters (Tables SVIII, IX) (23 pages); observed and calculated structure factors (Tables SX and XI) (50 pages). Ordering information is given on any current masthead page.

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