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Crystal Structure and Magnetic Properties of Two Nitronyl Nitroxide Biradicals and of Their Copper(II) Complexes

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The crystal structures and the magnetic properties of two nitronyl nitroxide biradicals, NITPh(4-NIT) = 1,4-bis(1′-oxyl-3′-oxido-4′,4′,5′,5′-tetramethyl-4,5-dihydro-1*H*-imidazol-2′-yl)benzene (I) and NITPh(3-NIT) = 1,3-bis(1′-oxyl-3′-oxido-4′,4′,5′,5′-tetramethyl-4,5-dihydro-1*H*-imidazol-2-yl)benzene (II), and of two novel adducts with Cu(hfac)$_2$, [Cu(hfac)$_2$]$_4$NITPh(4-NIT) (III) and [Cu(hfac)$_2$]$_3$NITPh(3-NIT) (IV), where hfac = hexafluoroacetylacetonate, are reported. All the compounds crystallize in monoclinic space groups: I, $P2_1/c$ with $a = 6.266(1)$ Å, $b = 11.790(3)$ Å, $c = 13.781(4)$ Å, $\beta = 93.14(3)°$, and $Z = 2$; II, $P2_1/n$ with $a = 7.318(2)$ Å, $b = 25.368(3)$ Å, $c = 11.669(2)$ Å, $\beta = 104.72(2)°$, and $Z = 4$; III, $C2/c$ with $a = 22.892(5)$ Å, $b = 27.151(6)$ Å, $c = 13.611(7)$ Å, $\beta = 98.66(4)°$, and $Z = 4$; IV, $P2/n$ with $a = 13.942(3)$ Å, $b = 16.422(4)$ Å, $c = 16.473(3)$ Å, $\beta = 97.93(2)°$, and $Z = 2$. The magnetic susceptibilities and the room-temperature EPR spectra of the free biradicals indicate that the two spins in I are antiferromagnetically coupled with $J = 72.3$ cm^{-1}, while they are essentially not coupled in II. In the complexes, all the NO groups of the biradical molecules are used to bind Cu(hfac)$_2$ moieties. In III, the Cu(II) ions are pentacoordinated and the tetranuclear molecules are well separated from each other. In IV, one Cu(II) ion is hexacoordinated, while the other two are pentacoordinated, and an extended chain structure is originated. The temperature dependences of the magnetic susceptibilities of III and IV have been measured. In III, the six spins are coupled through one antiferromagnetic interaction between the biradical spins ($J = 54.0$ cm^{-1}) and four ferromagnetic interactions between Cu(II) and radical spins ($J' \approx 13.0$ cm^{-1}), yielding an $S = 0$ ground state. In IV, a sudden variation of $\chi_m T$ is observed at $T \cong 30$ K and related to a structural phase transition involving the pentacoordinated Cu(II) spins. A simple justification of the observed difference in the exchange coupling constants between the two spins in the biradicals is proposed.

Introduction

Several approaches are followed to synthesize magnetic molecular materials,[1] which can be classed as inorganic,[2] organic–inorganic,[3] organic,[4] and organic–organometallic[5] according to the chemical nature of the magnetic centers. So far, we have used nitronyl nitroxides 2-R-4′,4′,5′,5′-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1′-oxyl 3′-oxide, NITR, as paramagnetic ligands on transition metal and lanthanide ions[6,7] and obtained a large number of different types of molecular-based magnetic materials. In particular, it has been shown that the complexes M(hfac)$_2$NITR (M = Mn^{II}, Ni^{II}; hfac = hexafluoroacetylacetonate) behave as one-dimensional ferrimagnets, ordering ferromagnetically at temperatures in the range of 10 K.[3]

In order to increase the critical temperatures, we are currently trying several approaches, either by changing the ancillary ligands around the metal ions, i.e. the bulk hfac with carboxylates,[8,9] or by using more complex radicals, which can cross-link the chains,[10] forming two- and ideally three-dimensional structures.

We have now decided to characterize structurally and magnetically two previously reported nitronyl nitroxide biradicals,[11] 1,4-bis(1′-oxyl-3′-oxido-4′,4′,5′,5′-tetramethyl-4,5-dihydro-1*H*-imidazol-2′-yl)benzene, NITPh(4-NIT) (I), and 1,3-bis(1′-oxyl-3′-oxido-4′,4′,5′,5′-tetramethyl-4,5-dihydro-1*H*-imidazol-2-yl)benzene, NITPh(3-NIT) (II), and to investigate their ability to act as ligands toward Cu(hfac)$_2$. We report here the crystal structures and magnetic properties of the two radicals and their complexes with copper(II).

Experimental Section

Synthesis. NITPh(4-NIT) and NITPh(3-NIT) were prepared as previously reported,[11] with minor modifications.

The complexes were obtained from either NITPh(4-NIT) or NITPh(3-NIT) and Cu(hfac)$_2$, prepared as previously reported.[12] Two 1-mmol samples of Cu(hfac)$_2$ were dissolved separately in hot *n*-heptane, the

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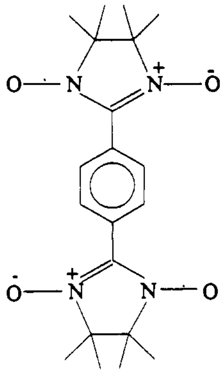

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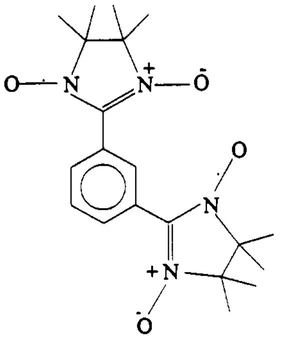

II

Table I. Crystallographic Data and Experimental Parameters for NITPh(4-NIT) (I) and NITPh(3-NIT) (II)

	I	II
formula	$C_{20}H_{28}N_4O_4$	$C_{20}H_{28}N_4O_4$
mol wt	388.5	388.5
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a, Å	6.266(3)	7.318(2)
b, Å	11.790(3)	25.368(3)
c, Å	13.781(4)	11.669(2)
β, deg	93.14(3)	104.72(2)
V, Å^3	1016.6	2095.2
Z	2	4
density (calcd), g/cm^3	1.269	1.231
μ, cm^{-1}	0.839	0.814
temp, K	298	298
λ, Å	0.7107	0.7107
R	0.0637	0.091
R_w	0.0706	0.106

Table II. Crystallographic Data and Experimental Parameters for $[Cu(hfac)_2]_4$NITPh(4-NIT) (III) and $[Cu(hfac)_2]_3$NITPh(3-NIT) (IV)

	III	IV
formula	$Cu_4C_{60}H_{36}N_4O_{20}F_{48}$	$Cu_3C_{50}H_{34}N_4O_{16}F_{36}$
mol wt	2299.1	1821.4
crystal system	monoclinic	monoclinic
space group	$C2/c$	$P2/n$
a, Å	22.892(5)	13.942(3)
b, Å	27.151(6)	16.422(4)
c, Å	13.611(7)	16.473(3)
β, deg	98.66(4)	97.93(2)
V, Å^3	8363.3	3735.5
Z	4	2
density (calcd), g/cm^3	1.826	1.618
μ, cm^{-1}	20.7	9.31
temp, K	298	298
λ, Å	1.5418	0.7107
R	0.0759	0.0809
R_w	0.0924	0.0899

Table III. Atomic Positional Parameters (×10^4) and Isotropic Thermal Factors (Å^2 × 10^3) for NITPh(4-NIT) (I)

	x/a	*y/b*	*z/c*	U_{iso}^{a}
C1	8475(5)	1907(2)	8880(2)	39(2)
C2	9280(5)	929(3)	9449(2)	38(2)
C3	11372(5)	883(3)	9817(2)	43(2)
C4	12092(5)	−43(3)	10365(2)	41(2)
C7	6599(6)	2995(3)	7675(2)	48(2)
C9	7766(8)	2839(4)	6725(3)	81(3)
C8	7779(5)	3800(3)	8410(2)	46(2)
C10	4273(8)	3217(4)	7465(4)	70(3)
C11	9059(7)	4745(3)	7981(4)	69(3)
C12	6335(7)	4297(3)	9152(3)	67(3)
N1	6879(4)	1879(2)	8203(2)	45(2)
N2	9230(4)	2982(2)	8960(2)	44(2)
O1	5777(5)	1023(2)	7927(2)	72(2)
O2	10748(4)	3321(2)	9538(2)	67(2)

^{a} $U_{iso} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\cdot\mathbf{a}_j$.

solutions were cooled to about 75 °C, and chloroform solutions containing 0.5-mmol samples of the biradicals were added. The mixtures were filtered, and the filtrates were stored at room temperature for a few days; in both cases, dark-brown crystals were collected which analyzed well for $[Cu(hfac)_2]_4$NITPh(4-NIT) and $[Cu(hfac)_2]_3$NITPh(3-NIT), respectively. Anal. Calcd for $Cu_4C_{60}N_4O_{20}H_{36}F_{48}$: C, 31.35; H, 1.58; N, 2.44; Cu, 11.05. Found: C, 31.45; H, 1.56; N, 2.43; Cu, 11.05. Calcd for $Cu_3C_{50}N_4O_{16}H_{34}F_{36}$: C, 32.97; H, 1.88; N, 3.08; Cu, 10.47. Found: C, 32.90; H, 1.86; N, 3.01; Cu, 10.54.

X-ray Structure Determination. X-ray data were collected on an Enraf-Nonius CAD-4 four-circle diffractometer, using Mo Kα radiation for NITPh(4-NIT) (I), NITPh(3-NIT) (II), and $[Cu(hfac)_2]_3$NIT(3-NIT) (IV) but Cu Kα for $[Cu(hfac)_2]_4$NIT(4-NIT) (III).

Unit cell parameters were derived from least-squares refinements of the setting angles of 25 reflections (9° ≤ *θ* ≤ 18° for I, 9° ≤ *θ* ≤ 15° for II, 18° ≤ *θ* ≤ 28° for III, and 10° ≤ *θ* ≤ 15° for IV) and are reported in Tables I and II with other experimental parameters. Data for all the compounds were corrected for Lorentz and polarization effects and for III also for the absorption.[13] The systematic extinctions revealed that I, II, and IV crystallize in the monoclinic space groups $P2_1/c$, $P2_1/n$, and $P2/n$ respectively, while for III the $C2/c$ and Cc space groups were possible. Refinement procedures indicated that for III the correct space group is $C2/c$.

The crystal structures of I and II were solved by direct methods using the program SIR[14] and by Fourier methods with the SHELX-76 package.[15] The direct methods enabled us to locate carbon, nitrogen, and oxygen atoms. The positions of the hydrogen atoms of the benzene rings were found by successive Fourier and difference Fourier syntheses. Due to disorder, in II, the best refinement was obtained by considering some atoms to occupy two different positions. The initial occupation factors were set to 0.5. Anisotropic thermal parameters were introduced for the carbon, nitrogen, and oxygen atoms. Isotropic thermal parameters were introduced for the hydrogen atoms of the benzene rings, and for the atoms C16 and C16B in II. The other hydrogen atoms were introduced in fixed and idealized positions with thermal factors about 10% greater than those of the respective carbon atoms. The refinements were made with 1208 reflections and $F_o \geq 6\sigma(F_o)$ for I and with 2474 reflections and $F_o \geq 4\sigma(F_o)$ for II.

For III and IV, the positions of the copper atoms were located from the Patterson map. Successive Fourier and difference Fourier syntheses with the SHELX-76 package enabled us to find the positions of the other non-hydrogen atoms. For IV, the positions of two hydrogens of the benzene ring were found too. Because of disorder or thermal motion of a $C(CH_3)_2$ group at one end of the biradical in III, the best refinement was obtained by considering the three carbon atoms involved to occupy two different positions. An initial value of 0.5 was chosen for their occupation factors. Anisotropic thermal parameters were introduced for the copper, oxygen, and fluorine atoms. Anisotropic thermal parameters were introduced also for the atom C10 and for the carbons of the CH_3 and CF_3 groups of III and for the nitrogen and methylic carbon atoms of IV. Isotropic thermal parameters were introduced for the other located atoms. The hydrogen atoms not found with the Fourier and difference Fourier syntheses were localized in fixed and idealized positions. The hydrogens of the benzene ring of III and of hfac groups were introduced with thermal factors equal to their respective carbon atoms. The thermal parameters for the methylic hydrogens were set 10% greater than those for their respective carbon atoms. The refinements were made with 3942 and 3268 reflections for III and IV, respectively, and with $F_o \geq 4\sigma(F_o)$.

The final atomic positional parameters and isotropic thermal factors for I–IV are listed in Tables III–VI, respectively.

Magnetic and EPR Measurements. The magnetic susceptibility of I was measured in a field of 1.35 T by using an Aztec DMS 5 Faraday balance magnetometer equipped with a Bruker B-E15 electromagnet and an Oxford Instruments CF1200S continuous-flow cryostat. Magnetic susceptibilities of the other compounds were measured in the temperature range 2.4–300 K in a field of 2 T by using a Métronique Ingéniérie MS03 SQUID magnetometer. Diamagnetic corrections were estimated from

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Table IV. Atomic Positional Parameters (×10^4) and Isotropic Thermal Factors (Å^2 × 10^3) for NITPh(3-NIT) (II)

	x/a	*y/b*	*z/c*	U_{iso}
C1	2775(5)	4106(2)	4936(3)	40(2)
C2	4075(5)	3809(1)	5755(3)	41(2)
C3	3605(5)	3605(2)	6748(4)	45(2)
C4	1796(6)	3712(2)	6908(4)	56(2)
C5	514(6)	3995(2)	6083(4)	56(3)
C6	972(5)	4195(2)	5094(4)	47(2)
C7	3262(5)	4307(1)	3876(3)	39(2)
C8	5088(5)	4525(2)	2552(3)	43(2)
C9	2941(5)	4636(2)	1952(3)	48(2)
C10	5778(6)	4002(2)	2199(5)	60(3)
C11	6402(6)	4965(2)	2434(4)	60(3)
C12	2203(7)	4411(2)	714(4)	71(3)
C13	2395(7)	5206(2)	2014(5)	67(3)
C14	4927(6)	3277(2)	7598(4)	52(2)
C15	7273(7)	2652(2)	8439(4)	67(3)
C16	5944(11)	2712(3)	9294(7)	54(3)
C16B	6967(14)	2965(4)	9377(9)	55(3)
C17	7866(25)	2147(6)	8172(13)	105(10)
C17B	9159(23)	2452(7)	8345(12)	82(10)
C18	9109(17)	3025(8)	8894(20)	134(14)
C18B	5940(26)	2105(5)	8227(14)	93(10)
C19	6670(10)	2754(3)	10539(5)	103(5)
C20	4627(16)	2235(5)	9127(12)	95(8)
C20B	8770(18)	3345(6)	9753(16)	85(9)
N1	4995(4)	4462(1)	3810(3)	39(2)
N2	2060(4)	4351(1)	2795(3)	46(2)
N3	6199(5)	2947(2)	7357(3)	56(2)
N4	4802(22)	3157(5)	8772(15)	57(7)
N4B	5324(29)	3328(6)	8728(19)	56(8)
O1	6473(3)	4502(1)	4681(2)	54(2)
O2	324(4)	4201(2)	2485(3)	66(2)
O3	6485(6)	2862(2)	6326(3)	89(3)
O4	3685(18)	3407(6)	9300(10)	91(8)
O4B	4560(20)	3621(7)	9345(13)	83(8)

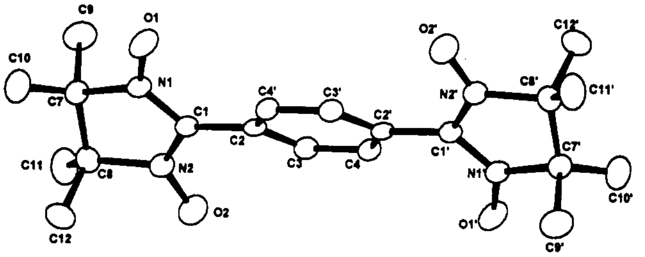

Figure 1. ORTEP view of NITPh(4-NIT).

Pascal's constants. Single-crystal EPR spectra were obtained with a Varian E9 spectrometer at X-band frequency; low-temperature spectra were recorded by using an Oxford Instruments ESR9 liquid-helium continuous-flow cryostat. Single crystals were oriented with the CAD4 diffractometer mentioned above.

Results and Discussion

(A) NITPh(4-NIT) (I) and [Cu(hfac)$_2$]$_4$NITPh(4-NIT) (III). Crystal Structures. The asymmetric unit of I contains half the atoms corresponding to the molecular formula $C_{20}H_{28}N_4O_4$ because a symmetry center is present in the middle of the benzene ring. The whole molecule is shown in Figure 1.

The O1–N1–C1–N2–O2 atoms are coplanar as expected due to orbital conjugation, while the five-membered heterocyclic ring is not planar, the tetramethylethylene moiety being twisted out of the plane by 0.157(4) and 0.259(4) Å. The methyl groups are staggered one relative to the other in order to relieve steric repulsion. The plane of the benzene ring makes an angle of 28.0(3)° with the radical conjugation planes, and this value is similar to that reported for the nitronyl nitroxide radical NITPh.[16] Also the bond lengths and angles agree with those observed for free nitronyl nitroxide radicals.[16,17] The shortest intermolecular distances between the NO groups are 4.670(5) Å, between the N1 and O2 atoms of molecules reported by translation in the *a* direction.

Table V. Atomic Positional Parameters (×10^4) and Isotropic Thermal Factors (Å^3 × 10^3) for [Cu(hfac)$_2$]$_4$NITPh(4-NIT) (III)

	x/a	*y/b*	*z/c*	U_{iso}
Cu1	1504(1)	1046(1)	4509(1)	72(1)
Cu2	1394(1)	3239(1)	292(1)	72(1)
O1	1008(2)	772(2)	2996(3)	60(3)
O2	554(2)	3154(2)	1214(4)	90(4)
O3	2237(2)	982(2)	4019(4)	83(3)
O4	1583(2)	399(2)	5126(4)	80(3)
O5	1594(2)	1751(2)	4346(4)	78(3)
O6	766(2)	1134(2)	5003(4)	76(3)
O7	1159(2)	3881(2)	−203(3)	76(3)
O8	1077(2)	2935(2)	−971(4)	79(3)
O9	1926(2)	3552(2)	1337(4)	81(3)
O10	1654(2)	2593(2)	718(4)	82(3)
N1	482(2)	626(2)	2733(3)	51(1)
N2	279(2)	3308(2)	1914(4)	67(1)
C1	0	920(3)	2500	49(2)
C2	0	1458(3)	2500	47(2)
C3	469(3)	1712(2)	2209(4)	53(1)
C4	466(3)	2219(2)	2183(4)	56(2)
C5	0	2483(3)	2500	53(2)
C6	0	3019(3)	2500	55(2)
C7	296(6)	98(5)	2875(14)	52(4)
C7P	330(6)	95(5)	2443(15)	55(4)
C8	731(12)	−276(11)	2605(17)	70(12)
C8P	777(15)	−217(11)	3116(25)	95(18)
C9	213(7)	23(5)	3943(9)	62(9)
C9P	431(8)	31(6)	1366(13)	92(13)
C10	187(4)	3843(2)	2092(6)	88(5)
C11	760(6)	4081(5)	2289(16)	285(20)
C12	−170(10)	4026(5)	1103(10)	266(20)
C13	2561(4)	623(3)	4103(6)	86(2)
C14	2458(4)	172(3)	4575(6)	96(2)
C15	2001(4)	102(3)	5070(6)	82(2)
C16	3124(4)	673(4)	3676(8)	123(8)
C17	1939(4)	−376(4)	5622(8)	116(7)
C18	1246(3)	2079(3)	4568(5)	68(2)
C19	716(3)	2016(2)	4919(5)	63(2)
C20	523(3)	1543(2)	5115(5)	62(2)
C21	1475(3)	2593(3)	4444(6)	82(5)
C22	−59(4)	1496(3)	5515(6)	82(5)
C23	947(3)	3978(3)	−1093(5)	69(2)
C24	831(3)	3665(3)	−1860(6)	79(2)
C25	916(3)	3157(3)	−1758(5)	71(2)
C26	806(4)	4527(3)	−1238(6)	93(6)
C27	825(3)	2848(4)	−2678(7)	93(6)
C28	2325(4)	3333(3)	1890(6)	84(2)
C29	2434(4)	2830(3)	1923(6)	93(2)
C30	2093(3)	2498(3)	1347(5)	75(2)
C31	2719(5)	3667(5)	2574(8)	130(9)
C32	2214(3)	1953(3)	1419(8)	104(6)
F1	3059(3)	877(3)	2811(5)	155(6)
F2	3395(4)	263(4)	3555(10)	274(12)
F3	3512(3)	916(6)	4215(8)	271(12)
F4	2000(4)	−288(3)	6593(5)	168(6)
F5	2388(3)	−681(2)	5574(6)	166(6)
F6	1456(4)	−585(3)	5392(8)	225(9)
F7	1893(2)	2706(2)	5164(4)	115(4)
F8	1053(2)	2935(2)	4488(5)	120(4)
F9	1662(3)	2658(2)	3617(4)	150(5)
F10	−367(2)	1905(2)	5476(5)	122(4)
F11	−405(2)	1160(2)	5035(4)	108(4)
F12	38(3)	1349(2)	6455(4)	123(4)
F13	1246(4)	4791(2)	−929(7)	195(7)
F14	664(3)	4646(2)	−2165(5)	136(5)
F15	382(5)	4660(3)	−813(8)	249(9)
F16	402(2)	2991(3)	−3360(4)	133(5)
F17	1299(2)	2803(3)	−3065(5)	151(5)
F18	684(4)	2383(3)	−2474(5)	168(6)
F19	2882(6)	4037(4)	2218(8)	251(11)
F20	3132(5)	3474(4)	3125(9)	244(10)
F21	2433(6)	3850(6)	3246(9)	276(14)
F22	1786(2)	1690(2)	1463(8)	165(6)
F23	2520(4)	1808(2)	803(10)	239(10)
F24	2585(6)	1843(3)	2234(10)	237(10)

The asymmetric unit of III consists in a Cu(hfac)$_2$[NITPh(4-NIT)]$_{1/2}$ group. Figure 2 shows two asymmetric units related

Table VI. Atomic Positional Parameters ($\times 10^4$) and Isotropic Thermal Factors ($Å^2 \times 10^3$) for $[Cu(hfac)_2]_3NITPh(3\text{-}NIT)$ (IV)

	x/*a*	*y*/*b*	*z*/*c*	U_{iso}
Cu1	0	0	0	49(1)
Cu2	3743(1)	-3785(1)	1123(1)	87(1)
O1	448(5)	-1355(3)	573(4)	71(4)
O2	-1323(4)	-369(3)	-177(3)	62(4)
O3	-74(4)	304(3)	1123(3)	61(4)
O4	2246(4)	-3654(3)	1349(3)	58(3)
O5	4636(4)	-3160(4)	1895(4)	74(4)
O6	3601(6)	-2904(5)	354(5)	120(6)
O7	3563(5)	-4542(4)	190(4)	90(5)
O8	3916(6)	-4656(4)	1897(4)	100(5)
N1	794(5)	-2065(4)	590(4)	53(4)
N2	1628(5)	-3162(4)	971(4)	51(4)
C1	1522(5)	-2367(5)	1142(4)	45(2)
C2	2035(5)	-1919(4)	1826(4)	43(2)
C3	2042(7)	-1072(5)	1821(6)	69(3)
C4	2500	-663(11)	2500	80(5)
C5	2500	-2328(7)	2500	41(3)
C6	446(7)	-2668(5)	-81(5)	63(2)
C7	-629(8)	-2596(7)	-345(10)	97(10)
C8	988(11)	-2457(7)	-787(6)	95(9)
C9	827(6)	-3478(5)	358(5)	60(2)
C10	1190(10)	-4097(7)	-171(7)	93(9)
C11	80(9)	-3845(8)	848(8)	101(9)
C12	-1852(7)	-425(6)	388(6)	66(3)
C13	-1647(8)	-187(6)	1182(6)	76(3)
C14	-804(7)	159(6)	1474(5)	64(2)
C15	-2845(11)	-808(10)	86(9)	110(4)
C16	-631(11)	436(9)	2378(9)	101(4)
C17	5019(7)	-2518(6)	1719(6)	74(3)
C18	4808(9)	-2034(7)	1030(7)	90(3)
C19	4121(8)	-2274(7)	416(7)	90(3)
C20	5818(12)	-2227(10)	2367(10)	120(5)
C21	3948(18)	-1712(14)	-386(14)	162(7)
C22	3545(8)	-5291(7)	248(7)	90(3)
C23	3666(9)	-5758(9)	939(8)	111(4)
C24	3872(9)	-5371(8)	1702(9)	108(4)
C25	3391(16)	-5730(12)	-566(12)	135(6)
C26	4051(19)	-5981(16)	2450(16)	177(8)
F1	-3213(6)	-539(9)	-612(6)	207(10)
F2	-2775(6)	-1556(6)	29(10)	241(13)
F3	-3500(5)	-657(6)	553(6)	159(7)
F4	84(8)	48(8)	2786(5)	196(10)
F5	-1320(7)	282(8)	2781(5)	196(9)
F6	-367(12)	1142(6)	2471(5)	239(12)
F7	6408(6)	-1702(6)	2123(5)	176(8)
F8	5501(8)	-1972(8)	3006(6)	209(11)
F9	6386(7)	-2839(7)	2660(6)	178(9)
F10	4507(8)	-1140(7)	-373(8)	239(12)
F11	3881(17)	-2134(8)	-999(7)	310(18)
F12	3076(10)	-1381(8)	-315(12)	278(16)
F13	2571(8)	-5623(9)	-935(7)	240(13)
F14	3484(17)	-6496(7)	-520(8)	309(17)
F15	3945(11)	-5552(10)	-1032(8)	260(15)
F16	3836(14)	-6695(6)	2310(7)	306(16)
F17	3672(15)	-5715(6)	3050(7)	249(15)
F18	4956(14)	-5920(9)	2723(10)	274(17)

by the C_2 symmetry axis: the carbon atoms C1, C2, C5, and C6 lie on this axis. In the asymmetric unit, there are two copper atoms, slightly different from each other, even though they both have a coordination geometry that can be approximated to a distorted square pyramid. The distortion is larger for Cu1. The axial positions of the square pyramids around the copper atoms are occupied by oxygen atoms of NO groups at larger distances (2.319(4)–2.461(6) Å) than those of the equatorial oxygen atoms of the hfac anions (1.905(5)–1.946(5) Å). Stacking interactions exist between the benzene ring and the plane of hfac defined by the atoms Cu1–O5–C18–C19–C20–O6: the average planes form an angle of ca. 3.2(2)° and the shortest contacts are about 3.6 Å. Similar stacking interactions were previously observed in M(hfac)$_2$NITR complexes.[18,19] One of the five-membered heterocyclic rings is disordered with the C7, C8, and C9 atoms occupying two different positions with occupation factors 0.49(2) and 0.51(2), respectively. In Figure 2, only one set of C7, C8, and C9 atoms is shown for the sake of clarity.

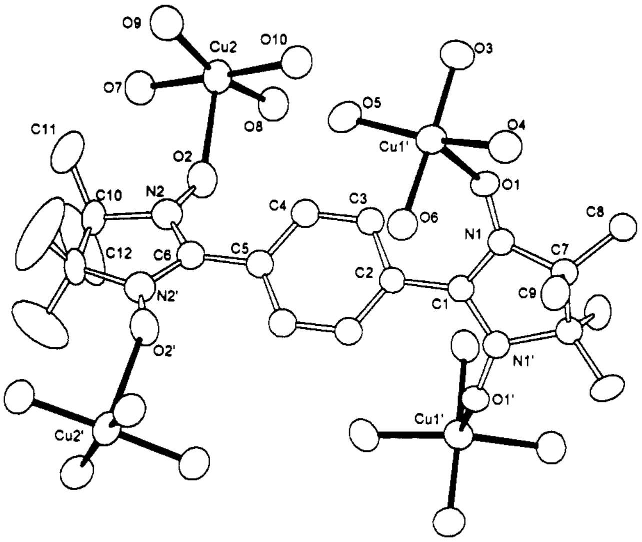

Figure 2. ORTEP view of $[Cu(hfac)_2]_4NITPh(4\text{-}NIT)$. Carbon and fluorine atoms of the hfac groups are not shown for the sake of clarity.

Table VII. Selected Bond Lengths (Å) and Angles (deg) for NITPh(4-NIT) (I) and $[Cu(hfac)_2]_4NITPh(4\text{-}NIT)$ (III)

	Biradical I		
C1–N1	1.331(4)	C1–N2	1.356(5)
N1–O1	1.270(4)	N2–O2	1.271(4)
N1–C1–N2	109.0(3)	C2–C1–N1	125.3(4)
C1–N1–C7	112.3(3)	C1–N1–O1	127.3(4)
C1–N2–C8	111.1(3)	C1–N2–O2	126.2(4)
	Complex III		
Cu1–O1	2.319(4)	Cu1–O3	1.906(5)
Cu1–O4	1.944(5)	Cu1–O5	1.941(5)
Cu1–O6	1.925(5)	Cu2–O2	2.461(6)
Cu2–O7	1.915(5)	Cu2–O8	1.946(5)
Cu2–O9	1.925(5)	Cu2–O10	1.914(5)
O1–N1	1.267(6)	O2–N2	1.288(8)
N1–C1	1.360(7)	N2–C6	1.347(8)
O5–Cu1–O6	91.8(2)	O4–Cu1–O6	89.4(2)
O4–Cu1–O5	159.4(2)	O3–Cu1–O6	178.1(2)
O3–Cu1–O5	86.4(2)	O3–Cu1–O4	92.2(2)
O1–Cu1–O6	90.7(2)	O1–Cu1–O5	105.1(2)
O1–Cu1–O4	95.5(2)	O1–Cu1–O3	89.9(2)
O9–Cu2–O10	92.6(2)	O8–Cu2–O10	86.4(2)
O8–Cu2–O9	161.8(3)	O7–Cu2–O10	176.5(2)
O7–Cu2–O9	88.4(2)	O7–Cu2–O8	91.6(2)
O2–Cu2–O10	89.4(2)	O2–Cu2–O9	96.9(2)
O2–Cu2–O8	101.2(2)	O2–Cu2–O7	93.7(2)
Cu1–O1–N1	131.9(4)	Cu2–O2–N2	148.5(4)

The bond distances and angles in the biradical agree with those measured in other metal ion β-diketonate adducts with nitronyl nitroxides.[6] In the biradical, the conjugation planes O1–N1–C1–N1′–O1′ and O2–N2–C6–N2′–O2′ and the benzene planes are not coplanar, forming dihedral angles of 36.7(1) and 28.2(1)°, respectively. The five-membered heterocyclic rings N1–C1–N1′–C7′–C7 and N1–C1–N1′–C7P′–C7P are not planar, with the tetramethylethylene moiety twisted out of the conjugation plane. The other five-membered heterocyclic ring (N2–C6–N2′–C10′–C10) is nearly planar, C10 and C10′ being displaced about

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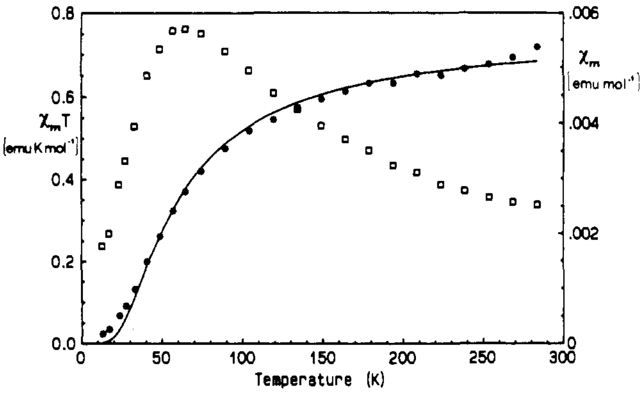


Figure 3. Temperature dependence of χ_m (□) and χ_mT (✱) for NITPh-(4-NIT). The solid line represents the calculated values with the best fit parameters.

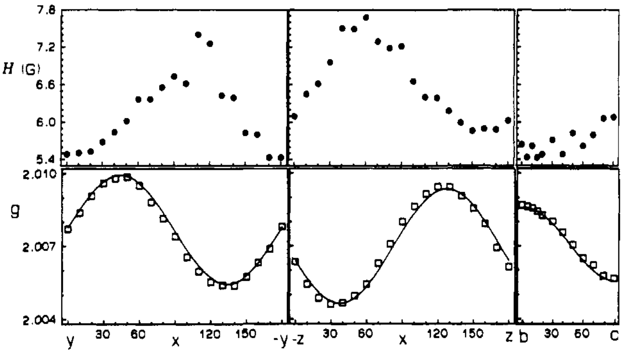


Figure 4. Angular dependence of the observed g (□) and line width (●) values for NITPh(4-NIT) in the room-temperature rotations around the z, y, and x axes defined in the text. The solid lines represent the best fit calculated values (see text).

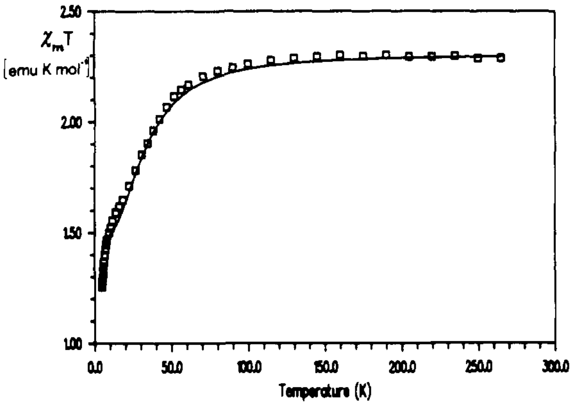


Figure 5. Temperature dependence of χ_mT for unit formula of $[Cu(hfac)_2]_4$NITPh(4-NIT). The solid line represents the best fit calculated values.

0.013(9) Å, but the very high thermal parameters shown by the methyl carbon atoms bonded to C10 indicate a thermal motion of the corresponding methyl group.

Selected bond distances and angles for compounds I and III are given in Table VII.

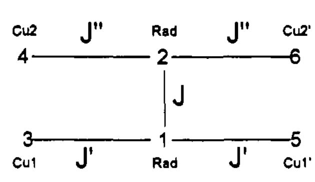
Magnetic and EPR Data. Figure 3 shows plots of χ_m and χ_mT vs T for the biradical. The high-temperature χ_mT value (≅0.7 emu K mol^{-1} at 270 K) is lower than expected for two $S = {}^1/_2$ uncorrelated spins ($\chi_mT = 0.75$ emu K mol^{-1}). The χ_mT curve decreases steadily with temperature and tends to zero at low temperature. The susceptibility goes through a maximum at $T \approx 65$ K. This behavior can be easily reproduced by considering that the two $S = {}^1/_2$ spins of the biradical are antiferromagnetically coupled. The J value ($H = J\mathbf{S}_1\cdot\mathbf{S}_2$) can be derived from the relation $J/k_BT_{max} = 8/5$.[20] The value so obtained is $J = 72.3$ cm^{-1}, in good agreement with the value derived from the fitting of the experimental χ_mT vs T data, $J = 72.0$ cm^{-1}, with $g = 2.01$ and $R = 3.3 \times 10^{-2}$.[21]

Room-temperature single-crystal EPR spectra of NITPh(4-NIT), recorded at X-band frequency by rotating the crystal around the three perpendicular x, y, and z axes, where $x = a$ and $y = [011]$, show a single exchange-narrowed Lorentzian line. The angular dependences of g and of the line width are reported in Figure 4. The components of the g tensor were obtained with a standard fitting procedure.[22] The results $g_1 = 2.003$, $g_2 = 2.008$, and $g_3 = 2.010$ are in good agreement with the data reported for nitroxide[23] and nitronyl nitroxide radicals.[24-26]

The observed values are *crystal* values; i.e., they correspond to the average response of the magnetically nonequivalent biradicals present in the monoclinic unit cell. It is well-known that in nitroxides the lowest g value is observed perpendicular to the conjugation plane;[23] therefore we considered these directions for the various magnetically nonequivalent NO groups present in the unit cell and averaged them. The result is that g_1 is expected to lie in the ac plane, along a direction which is in agreement with the one found within experimental error.

The observed line widths are in the range 5.4–7.8 G. Since the lines are exchange narrowed it is possible to relate the peak-to-peak line widths ΔH_{pp} to the second moment M_2 and to the exchange interactions.[27] In principle, there are three factors which can influence the second moment, namely the dipolar interaction, the unresolved hyperfine splitting, and the g anisotropy. We calculated estimates of these three contributions to the second moment of the line. The dipolar contribution to M_2, due to the interaction between two spins of magnetically nonequivalent biradicals, was dominant over the other broadening mechanisms. The observed ΔH_{pp} can be reproduced with the usual formula for exchange-coupled systems, $\Delta H_{pp} \cong M_2/J'$,[27] with the interadical exchange coupling constant, J', of about 0.4 cm^{-1}. This small value found for the intermolecular coupling constant J', compared to the intramolecular coupling constant J, confirms the goodness of the magnetic data fitting for NITPh(4-NIT), neglecting the intermolecular spin interactions.

The χ_mT vs T plot of $[Cu(hfac)_2]_4$NITPh(4-NIT) is shown in Figure 5. The high-temperature value ($\chi_mT = 2.29$ emu K mol^{-1} at 265 K) is expected for six $S = {}^1/_2$ uncorrelated spins. χ_mT is practically constant down to about $T = 100$ K, below which it decreases, displaying an inflection point at about 15 K, and reaches the value $\chi_mT = 1.25$ emu K mol^{-1} at $T = 4.59$ K. The different coordination geometries of the two pentacoordinated copper ions are expected to influence the couplings between the metal ions and the biradical spins. An appropriate scheme of the magnetic coupling in $[Cu(hfac)_2]_4$NITPh(4-NIT) is the following:



The corresponding spin Hamiltonian is

$$H = J\mathbf{S}_1\cdot\mathbf{S}_2 + J'(\mathbf{S}_1\cdot\mathbf{S}_3 + \mathbf{S}_1\cdot\mathbf{S}_5) + J''(\mathbf{S}_2\cdot\mathbf{S}_4 + \mathbf{S}_2\cdot\mathbf{S}_6)$$

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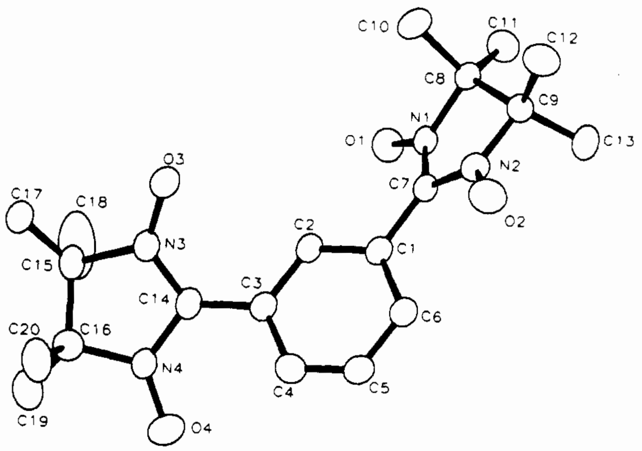
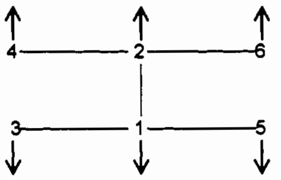


Figure 6. ORTEP view of NITPh(3-NIT).

A comparison of the coordination of the radical to copper(II) with previously reported data suggests that in both cases the coupling is weakly ferromagnetic[6] and the fit is expected to be sensitive to the average of J' and J''. Therefore we used $J' = J''$ for the sake of simplicity. The parameter values which best reproduce the χT vs T curve are $J = 54.0$ cm^{-1} and $J' = -12.8$ cm^{-1}, with $g = 2.025$, giving $R = 2.9 \times 10^{-2}$. The calculated $\chi_m T$ curve is shown in Figure 5. The $S = 0$ ground state can be schematized as follows:



The J value for the complex $[Cu(hfac)_2]_4$NITPh(4-NIT) is smaller than the value for the free biradical NITPh(4-NIT). This difference may be attributed either to the difference in the dihedral angle between the two nitronyl nitroxide conjugation planes in the biradical molecule in the two compounds, 64.9 and 0°, respectively, or to delocalization effects associated with the coordination to the metal ions.

(B) NITPh(3-NIT) (II) and $[Cu(hfac)_2]_3$NITPh(3-NIT) (IV). Crystal Structures. The structure of II is characterized by the disorder existing in one of the five-membered heterocyclic rings, some atoms occupying two different positions. The atoms reported in Table IV with label B have final occupation factors of 0.45(1), while the others have complementary occupation factors of 0.55(1). However, the carbon atom C19 has an occupation factor of 1 because it is at the same time the equatorial methyl carbon atom of the C19–C16–C20 and C19–C16B–C20B groups. The differences in bond lengths and angles between homologous atoms are presumably due to disorder. The other bond lengths and angles are similar to those reported for other free nitronyl nitroxide radicals.[16,17]

Figure 6 shows the asymmetric unit, where only the atoms without label B are shown. The fragment O1–N1–C7–N2–O2 is nearly planar; the maximum deviation from the least-squares plane defined by these atoms is 0.038(4) Å. The fragments O3–N3–C14–N4–O4 and O3–N3–C14–N4B–O4B show larger deviations from planarity with deviations of 0.20(1) and 0.25(1) Å. However, the bonds around the nitrogen atoms N3, N4, and N4B are coplanar, as shown by the sum of the bond angles. The five-membered heterocyclic rings are not planar, since the tetramethylethylene moieties are twisted out of the respective conjugation planes. The plane of the benzene ring makes angles of about 35° with the O1–N1–C7–N2–O2 plane, 31° with the O3–N3–C14–N4–O4 plane, and 36° with the O3–N3–C14–N4B–O4B plane. The shortest intermolecular contacts between NO groups involve nitronyl nitroxides related by the inversion center. The distances N1–O1′ and O1–N1′ are 3.480(5) Å, while N1–N1′ and O1–O1′ are 3.892(5) and 3.518(5) Å, respectively; the distance O1–N2′ and the symmetric one N2–O1′ are not much longer (4.087(5) Å). Contacts between NO groups of molecules related by a translation along the a axis, are slightly longer (O1–O2″ = 4.331(5) Å and N1–O2″ = 4.589(5) Å).

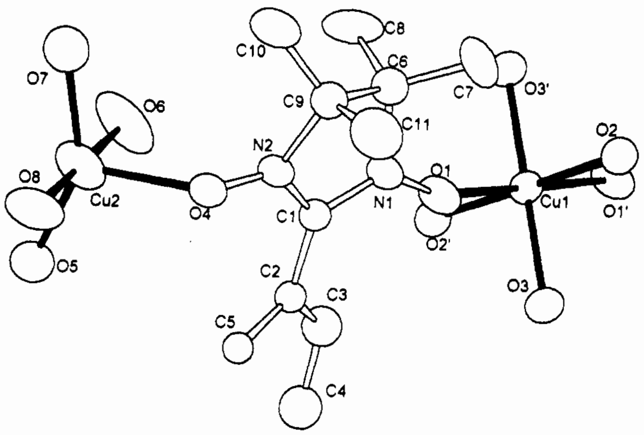


Figure 7. ORTEP view of the asymmetric unit of $[Cu(hfac)_2]_3$NITPh(3-NIT). Carbon and fluorine atoms of the hfac groups are not shown for the sake of clarity.

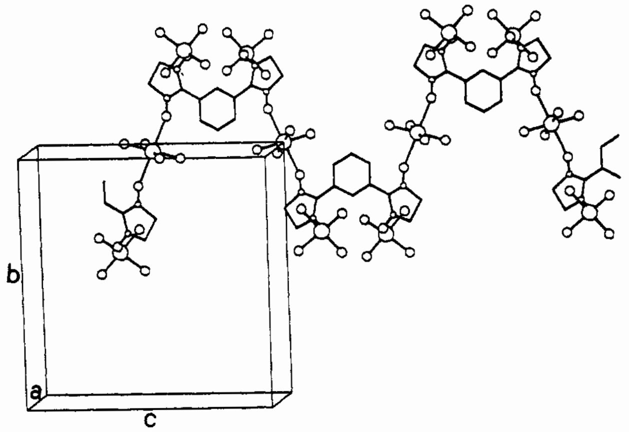


Figure 8. View of the chain structure of $[Cu(hfac)_2]_3$NITPh(3-NIT).

The asymmetric unit of IV consists of a $[Cu(hfac)_2]_{3/2}$NITPh(3-NIT)$_{1/2}$ group, which is shown in Figure 7. A C_2 axis passes through the C4, C5, H4, and H5 atoms. In the asymmetric unit, there are two different copper atoms. The copper atom Cu1 is located at the inversion center and has a distorted octahedral environment, four oxygen atoms of two hfac ligands (O2, O3; O2′, O3′) occupying the equatorial positions and two oxygen atoms of two biradicals (O1; O1′) in the axial ones. The axial bonds are much longer than the equatorial ones, 2.464(6) Å vs an average value of 1.928(5) Å. The copper atom Cu2 is pentacoordinated by two hfac ligands and one oxygen atom of NITPh(3-NIT). The coordination geometry is intermediate between square pyramidal and trigonal bipyramidal, and the high thermal parameters of the group O6–Cu2–O8 indicate thermal motion. The two NO groups in the nitronyl nitroxide moiety in the biradical are bound to the copper atoms Cu1 and Cu2. The combination of the inversion center and the C_2 axis results in zigzag chains along the diagonal of the a and c axes, as shown in Figure 8. $Cu(hfac)_2$ molecules, where the copper atoms are of Cu2 type, make up pendants located alternatively above and below the average plane containing the chain.

The bond distances and angles in the biradical molecule in IV agree with those previously reported.[6] In the biradical, the conjugation plane O1–N1–C1–N2–O4 and the benzene plane form a dihedral angle of 21.0(4)°. The five-membered hetero-

Table VIII. Selected Bond Lengths (Å) and Angles (deg) for NITPh(3-NIT) (II) and $[Cu(hfac)_2]_3$NITPh(3-NIT) (IV)

	Biradical II		
C7–N1	1.355(5)	C7–N2	1.343(4)
C14–N3	1.333(6)	C14–N4	1.411(18)
C14–N4B	1.301(21)	N1–O1	1.284(4)
N2–O2	1.292(4)	N3–O3	1.286(6)
N4–O4	1.309(23)	N4B–O4B	1.266(27)
N1–C7–N2	108.7(4)	N3–C14–N4	107.5(7)
N3–C14–N4B	105.9(9)	C7–N1–O1	126.2(4)
C7–N2–O2	127.1(4)	C14–N3–O3	126.1(4)
C14–N4–O4	125.2(4)	C14–N4B–O4B	125.9(18)
C16B–N4B–O4B	120.4(7)		
	Complex IV		
Cu1–O1	2.464(6)	Cu1–O2	1.924(5)
Cu1–O3	1.933(5)	Cu2–O4	2.180(6)
Cu2–O5	1.944(6)	Cu2–O6	1.915(8)
Cu2–O7	1.966(7)	Cu2–O8	1.910(6)
O1–N1	1.259(9)	O4–N2	1.278(8)
N1–C1	1.358(9)	N2–C1	1.348(10)
O1–Cu1–O3	84.9(2)	O1–Cu1–O2	87.7(2)
O2–Cu1–O3	92.8(2)	O7–Cu2–O8	92.2(3)
O6–Cu2–O8	178.7(4)	O6–Cu2–O7	88.3(3)
O5–Cu2–O8	87.0(3)	O5–Cu2–O7	147.8(3)
O5–Cu2–O6	91.9(3)	O4–Cu2–O8	89.7(3)
O4–Cu2–O7	100.1(3)	O4–Cu2–O6	91.4(3)
O4–Cu2–O5	112.1(2)	Cu1–O1–N1	156.9(5)
Cu2–O4–N2	125.1(5)		

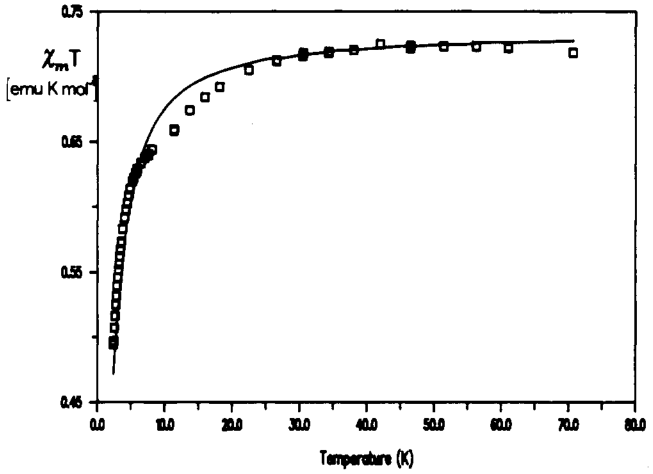


Figure 9. Temperature dependence of $\chi_m T$ for NITPh(3-NIT). The solid line represents the calculated values with the parameters $J = 0.0$ cm^{-1}, $J' = 4.0$ cm^{-1}, and $g = 1.98$ (see text).

cyclic ring N1–C1–N2–C9–C6 is not planar, with the tetramethylethylene moiety twisted out of the conjugation plane.

Selected bond distances and angles for compounds II and IV are given in Table VIII.

Magnetic and EPR Data. Figure 9 shows the observed $\chi_m T$ vs T plot per unit formula of NITPh(3-NIT) in the temperature range 2.4–80 K. $\chi_m T$ is approximately constant, with a value of 0.72 emu K mol^{-1}, down to about 35 K, while below this temperature it decreases with a slope which dramatically increases at about $T = 7$ K and it reaches the value of 0.495 emu K mol^{-1} at $T = 2.40$ K, indicating the presence of dominating antiferromagnetic coupling. No maximum is observed in the χ_m vs T plot.

Room-temperature single-crystal EPR spectra of NITPh(3-NIT) were recorded at X-band frequency by rotating the crystal around the b, c, and $a^* = b \times c$ axes. At every orientation of the crystal in the external magnetic field, a single exchange-narrowed Lorentzian line was observed. Figure 10 shows the angular dependences of **g** and of the line width. The calculated **g** tensor components are $g_1 = 2.005$, $g_2 = 2.009$, and $g_3 = 2.010$.

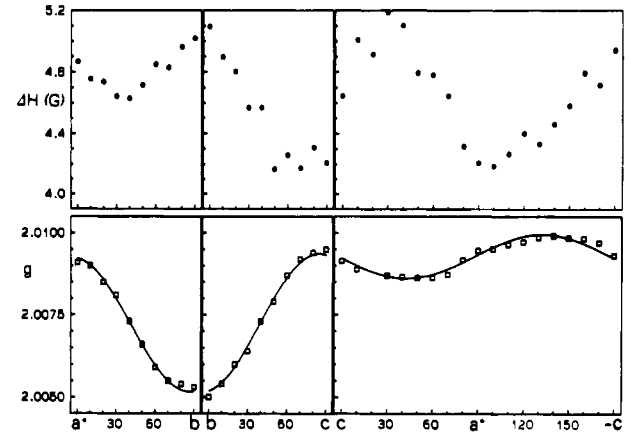
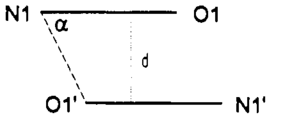


Figure 10. Angular dependence of the observed g (□) and line width (●) values for NITPh(3-NIT) in the room-temperature rotations around the c, a^*, and b axes. The solid lines represent the best fit calculated values (see text).

Also in this case, the **g** tensor is the result of a crystal averaging. By the same procedure outlined for I, we found that g_1 is expected to be parallel to b, in agreement within error with the experimental result.

The interpretation of the magnetic data requires the consideration of the coupling between the two spins within the biradical as well as that between the two NO groups related by the inversion center, represented by the coupling constants J and J', respectively. In fact, it has been shown that the extent of the coupling between neighboring NO groups can be related to the geometric parameters α and d as follows:



It can also be related to β, the angle between the normal lines to the conjugation planes and the plane containing the four atoms.[6] In III, we found $d = 3.48$ Å, $\alpha = 98.9°$, and $\beta = 67.0°$. The comparison with previously reported cases[6] suggests an antiferromagnetic coupling constant J' of about 5 cm^{-1}. Other intermolecular interactions, leading to an extended magnetic structure, are expected to be of minor extent and will be neglected in a first approach.

In view of these considerations, the system can be considered as a system of four $S = {}^1/_2$ spins with the following spin Hamiltonian:

$$H = J(\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_3 \cdot \mathbf{S}_4) + J' \mathbf{S}_2 \cdot \mathbf{S}_3$$

where (S_1, S_2) and (S_3, S_4) are pairs of interacting spins within each biradical. The fitting procedure does not give unique results because several sets of the three parameters g, J, and J' reproduce equally well the experimental $\chi_m T$ vs T data. Two limiting cases have been considered, in which either J or J' is set to zero. The two fits yielded respectively (i) $J = 0.0$ cm^{-1}, $J' = 4.0$ cm^{-1}, $g = 1.980$, and $R = 1.8 \times 10^{-2}$ or (ii) $J = 1.8$ cm^{-1}, $J' = 0.0$ cm^{-1}, $g = 1.975$, and $R = 2.5 \times 10^{-2}$.

Additional information on the values of the coupling constants can be derived from the analysis of the EPR line widths, which are in the range 4.2–5.2 G. The second moment M_2 of the line must be due to the dipolar interaction, the other broadening mechanisms being at least 200 times smaller. The observed line widths can be reproduced by assuming the interradical J' coupling constant of about 3 cm^{-1}. This agrees more closely with fit i of the magnetic data given above.

Magnetic data for $[Cu(hfac)_2]_3$NITPh(3-NIT) are given in Figure 11. The room-temperature value per unit formula is $\chi_m T$

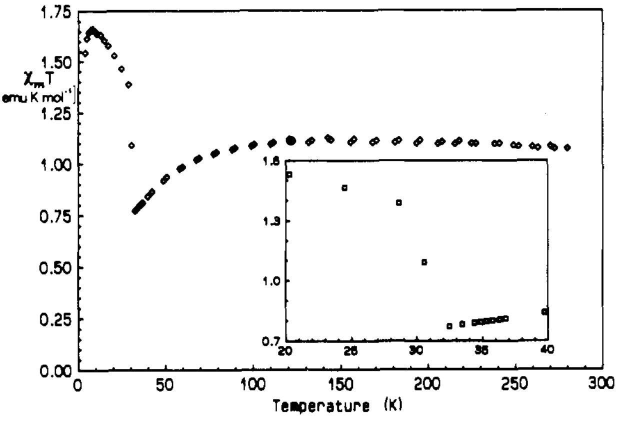
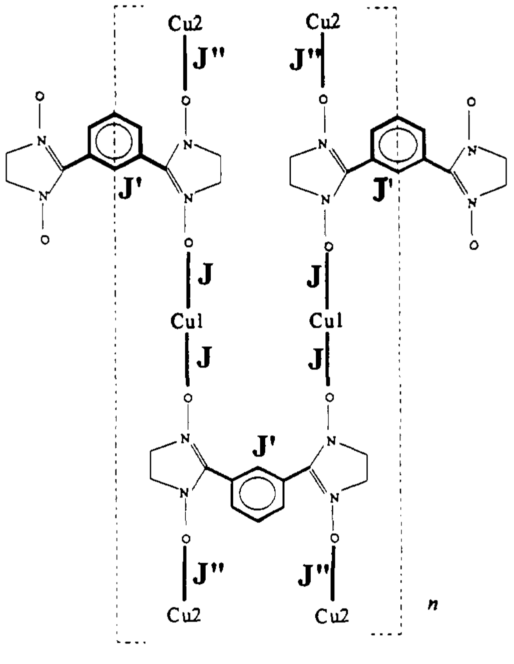


Figure 11. Temperature dependence of $\chi_m T$ for the unit formula of $[Cu(hfac)_2]_3NITPh(3\text{-}NIT)$. The insert better shows the variation of $\chi_m T$ in the region of the drop.

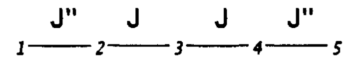
$\cong$ 1.075 emu K mol^{-1}. $\chi_m T$ increases slightly with decreasing temperature, displaying a very broad maximum at $T \approx 140$ K with $\chi_m T \cong 1.12$ emu K mol^{-1}. It then decreases to $\chi_m T \cong 0.77$ emu K mol^{-1} at $T = 32.5$ K. Below this temperature, a very abrupt rise in $\chi_m T$ is observed ($\chi T \cong 1.39$ emu K mol^{-1} at $T = 28.7$ K). $\chi_m T$ keeps increasing down to $T = 8$ K ($\chi_m T \cong 1.66$ emu K mol^{-1}), where it reaches a maximum. $\chi_m T$ then decreases to 1.543 emu K mol^{-1} at the lowest temperature reached, $T = 3.8$ K. This behavior of the $\chi_m T$ curve was observed during either cooling or heating.

The unusual abrupt rise in $\chi_m T$ at $T \approx 30$ K suggests a phase transition. No magnetic phase transition can be responsible for such a feature, and we attribute it to a structural phase transition. This hypothesis is also in qualitative agreement with the explosion of the single crystals at low temperature.

We could not work out any simple model for the interpretation of the magnetic data of $[Cu(hfac)_2]_3NITPh(3\text{-}NIT)$. In fact, it corresponds to a spin chain which is formed by the repetition of a complex building block. Within this block we must consider two interactions with alike coupling constants J between Cu1 and nitronyl nitroxide spins and one interaction J' between the two spins of the biradical. Further we must include the interaction J'' between Cu2 and nitronyl nitroxide spins. The complete coupling scheme is therefore the following:



The analysis of the magnetic properties of the free biradical suggest that J' is small, although the geometry of the biradical is slightly different in the complex (the dihedral angles between the conjugation planes of the nitronyl nitroxide groups and benzene in the complex and in the free biradical are 21.0 and ca. 33°, respectively). On the other hand, the comparison with previously reported Cu(II)–nitronyl nitroxide radical complexes suggests that J is ferromagnetic, $J \approx -20/-60$ cm^{-1}, and that J'' is strong and antiferromagnetic.[6] Therefore a possible simplified scheme for the high-temperature data might be an $S = {}^1/_2$ five-spin cluster represented as follows:



with a spin Hamiltonian

$$H = J(S_2 \cdot S_3 + S_3 \cdot S_4) + J''(S_1 \cdot S_2 + S_4 \cdot S_5)$$

The room-temperature value $\chi_m T \cong 1.075$ emu K mol^{-1} is much smaller than expected for five uncorrelated $S = {}^1/_2$ spins ($\chi_m T \cong 1.875$ emu K mol^{-1}), so that some antiferromagnetic coupling must be operative. If J'' were as large as usually observed in copper(II) complexes equatorially bonded to nitronyl nitroxides,[6] $\chi_m T$ should reach the value of ca. 0.375 emu K mol^{-1}, corresponding to one $S = {}^1/_2$ spin, at relatively high temperature. However the $\chi_m T$ vs T plot in the 100–300 K temperature range does not agree with this model. According to this fact, to the abnormally large thermal ellipsoids of the atoms in the group O8–Cu2–O6, and to the presence of a structural phase transition at about 30 K, we postulate that a thermally activated interconversion between square pyramidal and trigonal bipyramidal coordination geometries of the Cu2 atom occurs, leading to a J'' value which is intermediate between those associated with the limiting geometries. This J'' value will vary with temperature, depending on the energies of these limiting cases relative to one another, and will not allow the fitting of the magnetic data through the usual temperature-independent exchange coupling constants. We suggest that the structural phase transition at $T \cong 30$ K is the result of freezing the coordination geometry of Cu2 atoms. EPR spectra recorded on single crystal at $T = 4.2$ and 12 K showed signals from multiplets with zero-field splitting and two signals with $g \cong g_{Cu}$, indicating an interruption of the magnetic exchange in the chain and a decrease of the symmetry of the crystals.

(C) Considerations on the Intraradical Exchange. The analysis of the magnetic interactions confirms the fundamental importance of topology in determining the values of the exchange coupling constants J. In fact, when the two nitronyl nitroxide moieties are in the para position of the benzene ring, as in NITPh(4-NIT), the coupling constants are antiferromagnetic ($J = 72.3$ and 54.0 cm^{-1}, respectively, in I and in III), while in the case of the meta geometry of NITPh(3-NIT) spins are essentially not interacting ($J \approx 0$ cm^{-1} in II). A simple way to rationalize this behavior is to use the extended Hückel approach in order to evaluate the interaction between the SOMO's of the two NITR moieties of the radicals. With an extension of the treatment used for weakly coupled dinuclear metal complexes, the observed coupling constant may be associated with the splitting of the two interacting SOMO's.[28] However, sample calculations showed an exceedingly small splitting in both cases, which might indicate ferromagnetic coupling.

It is known that spin-polarization effects are not negligible in organic radicals,[29,30] making the required treatment more elaborate. In the case of the monoradical NITPh, both NMR measurements and INDO calculations showed the presence of a

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large negative spin density on the ortho and para carbons of the benzene and of a smaller positive spin density on the meta carbons.[31,32]

We can imagine the biradical molecules NITPh(4-NIT) and NITPh(3-NIT) built up from the monoradical NITPh by substituting one hydrogen atom of the benzene ring with a second NIT group. The second NIT group, entering para to the first, would require a spin polarization at each position within the ring which is opposite to that induced by the first one, while entering meta it would give the same pattern. Therefore, for the para case, the two conflicting polarization patterns can agree if the two spins are antiferromagnetically coupled. On the other hand, for the meta biradical, spin polarization tends to keep the second radical with the spin parallel to the first, thus inducing a ferromagnetic coupling. This extremely simplified scheme requires that the NIT and benzene planes all be parallel to each other. It is not unlikely that the angles of these planes with respect each other may influence the extent of the coupling. However, it is remarkable that the observed coupling is antiferromagnetic in I and II and very weak in III.

Conclusions

One of the purposes of this paper was to verify the possible use of the nitronyl nitroxide biradicals NITPh(4-NIT) and NITPh(3-NIT) as building blocks in the synthesis of molecular-based magnetic materials. The NITPh(4-NIT) biradical does not appear to be suitable for this purpose, since the large antiferromagnetic exchange coupling between the biradical spins, found either in the free molecule or in the Cu(II) complex III, would eventually give a nonmagnetic ground state.

More appealing possibilities seem to be available for the NITPh(3-NIT) biradical, whose spins are only weakly coupled, and it can be hoped that minor geometric variations may even induce a ferromagnetic coupling between them. An important feature is that all four NO groups of the biradical are bound to metal ions. Therefore, we feel that it could be of interest to synthesize magnetic materials by reacting the biradical NITPh(3-NIT) with metal ions having a spin larger than $^1/_2$, such as Mn(II) and Ni(II). In this way we hope to obtain extended structures in which the biradical molecules cross-link two chains. We are currently working in this direction.

Note Added in Proof

A paper describing the crystal structure and the magnetic properties of NITPh(3-NIT) was published: Shiomi, D.; Tamura, M.; Sawa, H.; Kato, R.; Kinoshita, M. *J. Phys. Soc. Jpn.* **1993**, *62*, 289. Their experimental results are consistent with ours.

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Supplementary Material Available: Tables SI–SVI, listing experimental and crystallographic data, anisotropic thermal factors, hydrogen atom coordinates, and bond lengths and angles for compounds I–IV, and Figure SI, showing the part of the molecule of II displaying disorder (24 pages). Ordering information is given on any current masthead page.

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(31) Davis, M. S.; Morokuma, K.; Kreilick, R. W. *J. Am. Chem. Soc.* **1972**, *94*, 5588.

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