

Metal Complexes with Nitronyl Nitroxide Substituted Phenolate Ligands Providing New Magnetic Exchange Interaction Pathways – Synthesis, Structures, Magnetic Dilution Studies, and Ab Initio Calculations

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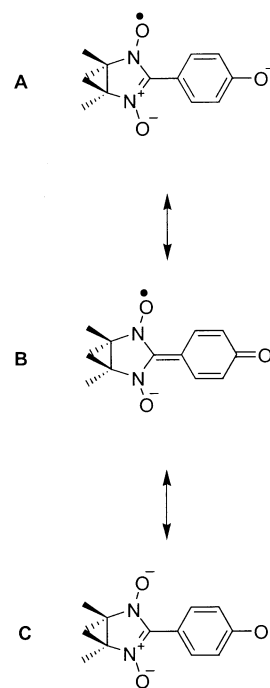
The synthesis and magnetic properties of seven new nitronyl nitroxide substituted phenolates with chelating amine groups are reported. Copper(II) and nickel(II) complexes prepared with these ligands are structurally and magnetically characterized, showing exchange interactions between the metal and the radical ligands through the phenolate oxygen. Magnetically diluted samples are prepared by embedding

the compounds in a poly(vinyl chloride) film to suppress intermolecular exchange interactions. This method is used for the first time in a quantitative way to separate intra- and intermolecular exchange interactions in radical-metal systems. The experimentally determined ground states are further confirmed by DFT calculations.

Introduction

In the preparation of molecular magnetic materials, transition metal complexes with organic radical ligands have found widespread interest in recent years. Research has focused on the nitronyl nitroxide family of radicals^[1] since they are stable and easy to functionalize. A wide variety of transition metal complexes have been prepared with these ligands, most of them involving metal coordination to the NO groups. Since nitronyl nitroxide radicals are poor electron-donor ligands, the use of strongly electron-withdrawing coligands at the metal, like hexafluoroacetylacetonate, is required. The steric demand of these coligands restricts the dimensionality of the resulting metal-radical compounds. A large number of ring systems and infinite chain compounds have been prepared by this strategy,^[2–4] but few showed ferromagnetic ordering at low temperatures due to small interchain interactions.^[5–8] Only in the very last years has work been published in which the sterically demanding coligands are avoided. Functionalized nitronyl nitroxide radicals with electron-donating substituents like 2-pyridine, 2,2'-bipyridine, imidazole, benzimidazole, or 1,2,4-triazole were prepared.^[9–22] In all cases the nitronyl nitroxide is in an *ortho* position to the aromatic nitrogen atom of the substituent and one NO group coordinates to the transition metal ion to form a chelate ring. This usually leads to small, discrete molecules, although some 1D- and 2D-systems were reported with imidazole-substituted nitronyl nitroxide ligands.^[15,18] As we are interested in the magnetochemistry of spin systems of higher dimensionality, we were surprised that very few compounds are published in which the nitronyl nitroxide radicals are bound to transition

metal ions by additional functional groups in the *para* position of the aromatic ring.^[23–30] Even less work has been published in which a remarkable spin-exchange interaction between the unpaired electron of the nitronyl nitroxide and an open-shell transition metal ion, mediated by the functional group, is reported.^[23,26,30] In order to try and work out a synthetic strategy to build up higher dimensional networks of radicals and transition metal ions in which the NO moiety and the functional group bind to different metal ions, we were prompted to use the phenolate group as a promising substituent. Although some nitronyl nitroxide



Scheme 1. Mesomeric structures of nitronyl nitroxide substituted phenolates indicating possible delocalization of the unpaired electron from the NO groups to the phenolic oxygen

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substituted phenols have been prepared in an approach to form purely organic ferromagnets,^[31–37] their use as ligands for transition metals has not been explored. Since phenolates are fairly basic, a strong coordination towards metal ions is possible. Moreover, a delocalization pathway of the unpaired electron from the nitronyl nitroxide moiety onto the phenolic oxygen atom can be formulated (Scheme 1), leading to a spin-exchange interaction between the radical and a coordinated metal center.

We have synthesized a family of substituted nitronyl nitroxides with a phenolate group in the *para* position of the phenyl ring and an amine substituent in the *meta* position as an additional anchoring group (Scheme 2). This eliminates the need for coligands and leaves both the NO groups, as well as unoccupied coordination sites on the metal center, free for interconnection through bridging metal centers M' or coligands L (Scheme 3a and 3b). In addition, oxidation of the phenolate group to a phenoxyl radical might lead to triplet radical ligands allowing the preparation of metal complexes in higher spin states (Scheme 3c). In this contribution, the synthesis and magnetic properties of seven new nitronyl nitroxide radicals are described. Copper(II) and nickel(II) compounds were prepared with these ligands. Their structural, magnetic, and electrochemical properties are reported here together with the results of density functional calculations. A method for the magnetic dilution of organic radicals as well as nitronyl nitroxide-metal complexes is quantified and applied to magnetic susceptibility measurements and EPR spectroscopy.

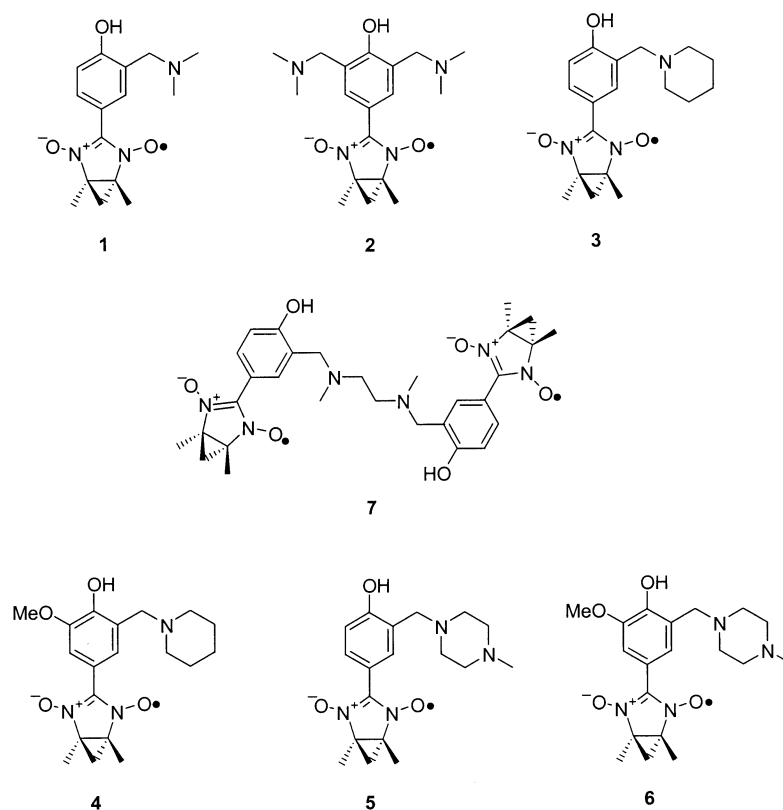
Results and Discussion

Synthesis

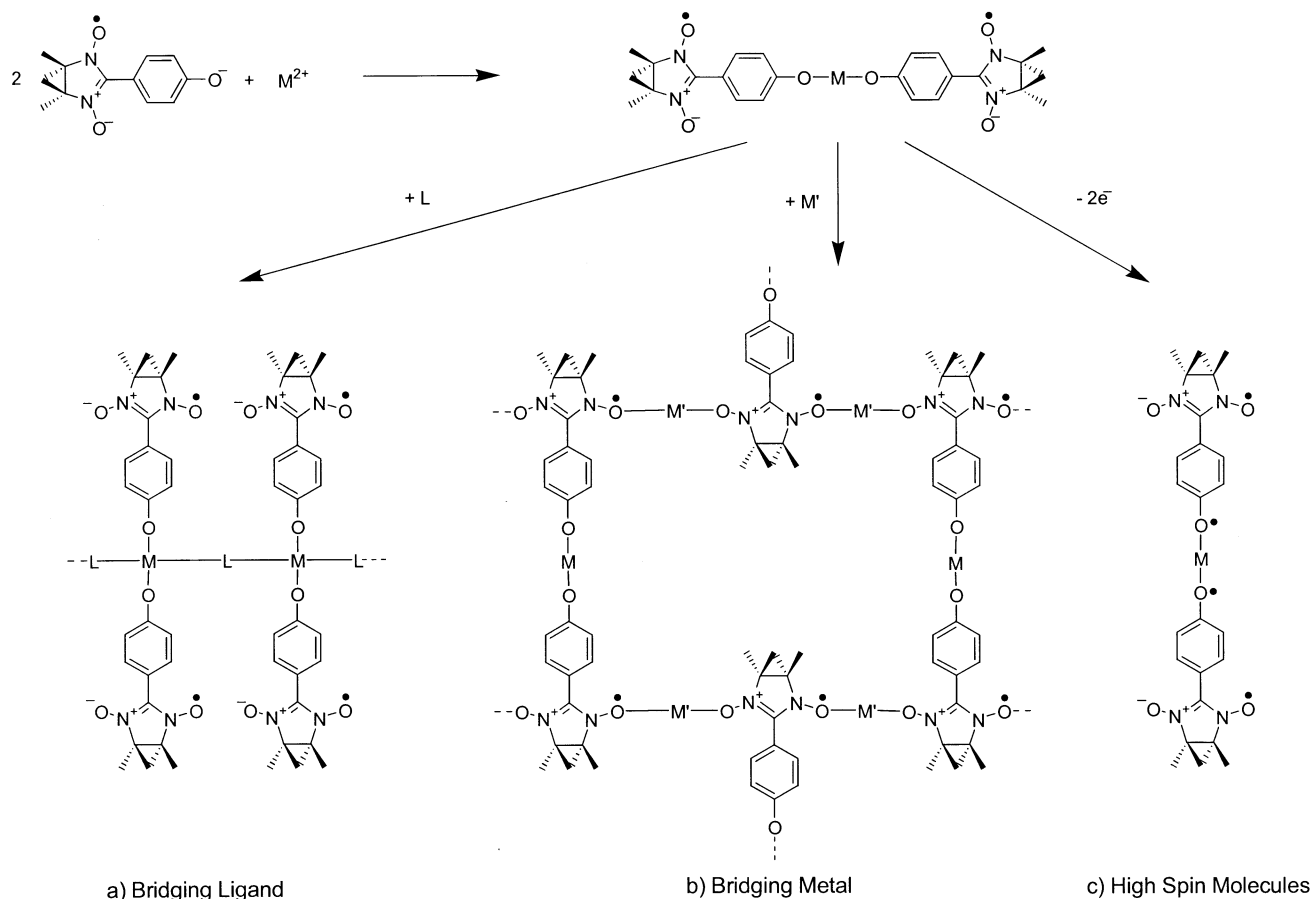
The nitronyl nitroxides **1–6** (see Scheme 2) were prepared by an aromatic Mannich reaction from 4-hydroxybenzaldehyde or vaniline, formaldehyde, and a secondary amine, followed by coupling of the resulting aldehyde with 2,3-bis(hydroxylamino)-2,3-dimethylbutane and oxidation, as described by Ullman et al.^[38] In the cases of the piperidine- and piperazine-substituted compounds **3–6** the yields of the Mannich reaction were higher when the intermediate *N*-(alkoxymethyl)amines were prepared and purified separately. For the bis-nitronyl nitroxide ligand **7**, a different approach utilizing the reaction between 3-chloromethyl-4-hydroxybenzaldehyde and a secondary amine was employed to prevent the formation of polymeric by-products. This synthetic strategy allows the introduction of a wide variety of chelating amine substituents to accommodate different metal-binding preferences. The copper(II) and nickel(II) complexes **8–10** prepared with the nitronyl nitroxide ligands **1** and **3** precipitated upon the addition of anhydrous metal chlorides to a solution of the deprotonated ligand in dry methanol and can be separated from cocrystallized sodium chloride by simple recrystallization.

Magnetism and Crystal Structure of the Ligands

The magnetic properties of purely organic nitronyl nitroxide radicals are interesting in their own right, since the



Scheme 2. Prepared nitronyl nitroxide ligands **1** to **7**



Scheme 3. Substituted nitronyl nitroxides as building blocks for high-dimensional metal-radical assemblies by: a) bridging ligands, b) bridging metals, and c) high-spin molecules

β -phase of 4-nitrophenyl nitronyl nitroxide was the first organic ferromagnet reported.^[39] Therefore, we measured the temperature dependence of the magnetic moment for compounds **1–7**. The susceptibility follows the Curie–Weiss law over the whole temperature range from room temperature down to 4 K with θ -Weiss constants of -0.56 , -0.54 , -2.00 , -0.84 , -0.96 , and $+0.58$ K for **1**, **2**, **3**, **5**, **6**, and **7**, respectively. An exception is found for compound **4**, where the temperature dependence of the magnetic susceptibility clearly indicates a fairly strong overall antiferromagnetic exchange interaction of the radicals. As shown in Figure 1, the $\chi_M T$ product decreases from $0.34 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ at room temperature, steadily with decreasing temperature, to $0.02 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ at 4 K. To elucidate the intermolecular exchange interaction pathways operating in this system, and for uses as a reference guide for structural changes induced in the ligands when coordinated to transition metals, we determined the crystal structures of **1**, **3**, **4**, and **7**. The crystallographic data and details of the refinement procedures are collected in Table 1. All intramolecular bond lengths and angles of the five-membered rings are as expected and comparable to other substituted nitronyl nitroxides (see Tables S1 and S2 in the supporting information). The NO bond lengths of $1.275(5)$ – $1.288(5)$ Å indicate delocalization of the unpaired electron over both NO groups. The molecular structure of **4** is depicted in Figure 2. As shown in Fig-

ure 3, the molecules are arranged in alternating chains along the x axes with remarkably short intermolecular contacts involving both NO groups of the nitronyl nitroxide. The distance $\text{O4} \cdots \text{O4A}$ is shortest (3.46 Å), although $\text{O1} \cdots \text{O1A}$ and $\text{N1} \cdots \text{O1A}$ are only slightly longer (3.69 Å

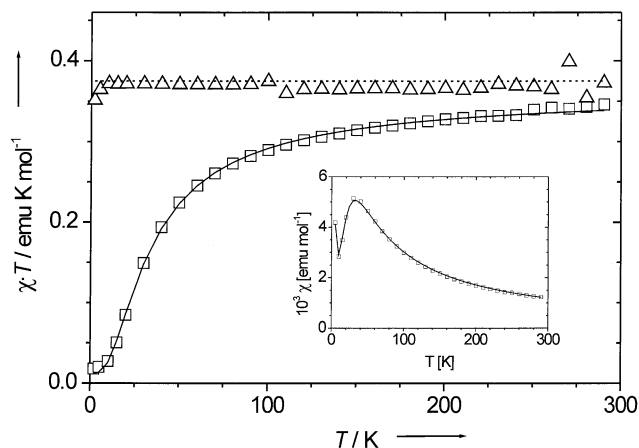


Figure 1. Temperature dependence of the magnetic susceptibility for **4** in the form of the $\chi_M T$ product versus T curve for the polycrystalline powder ($\square$), polymer embedded sample (Δ) and theoretical curve for the dimer model (—); inset: temperature dependence of the magnetic susceptibility of **4** ($\square$) and theoretical curve for the Heisenberg alternating linear chain model (—)

Table 1. Summary of the crystal structure data collection and refinement for **1**, **3**, **3a**, **4** and **7**

	1	3	3a	4	7
Chem formula	C ₁₆ H ₂₄ N ₃ O ₃	C ₁₉ H ₂₈ N ₃ O ₃	C ₁₉ H ₂₈ N ₃ O ₃	C ₂₀ H ₃₀ N ₃ O ₄	C ₃₂ H ₄₆ N ₆ O ₆
Fw	306.38	346.44	346.44	376.47	610.75
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>Pbca</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	7.167(3)	11.3931(9)	10.1839(8)	10.0751(8)	17.580(4)
<i>b</i> , Å	11.142(5)	12.1913(11)	11.4709(8)	10.6168(10)	9.974(2)
<i>c</i> , Å	20.610(9)	14.206(2)	31.870(2)	10.7897(10)	9.385(2)
α , deg	90	81.47(2)	90	88.019(12)	90
β , deg	94.49(3)	83.35(2)	90	65.673(12)	101.47(3)
γ , deg	90	71.82(2)	90	72.943(12)	90
<i>V</i> , Å ³	1640.8(12)	1848.8(3)	3723.0(5)	1000.4(2)	1612.7(14)
<i>Z</i>	4	4	8	2	4
<i>T</i> , K	100(2)	100(2)	100(2)	100(2)	100(2)
ρ calcd, g cm ⁻³	1.240	1.245	1.236	1.250	1.258
μ (Mo- <i>K</i> α), cm ⁻¹	0.87	0.85	0.84	0.87	0.90
Diffractionmeter used	Nonius Kappa-CCD	Siemens SMART	Nonius Kappa-CCD	Siemens SMART	Siemens SMART
Refl. Collected	6120	17868	38347	10169	16137
Unique refl. [<i>I</i> > 2 σ (<i>I</i>)]	2123/1552	9761/5718	4221/3144	5689/3712	1725/1246
No. parameters	200	461	234	250	200
2 θ _{max} , deg	44.98	60.00	54.80	62.00	42.00
<i>R</i> 1 ^[a] [<i>I</i> > 2 σ (<i>I</i>)]	0.0750	0.0490	0.0431	0.0494	0.1501
<i>wR</i> 2 ^[b] [<i>I</i> > 2 σ (<i>I</i>)]	0.1715	0.0928	0.1046	0.1080	0.4481

^[a] $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. – ^[b] $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ where $w = 1/(\sigma^2(F_o^2) + (aP)^2 + bP)$, $P = (F_o^2 + 2F_c^2)/3$.

and 3.53 Å, respectively). The N1O1 groups are aligned antiparallel with angles N1–O1–N1A and O1–N1–O1A close to 90°, the two NO vectors thus forming a rectangle. The spin-carrying π^* -orbitals are located in this plane with a distance between the NO vectors of 3.42 Å. A large overlap is therefore possible,^[40,41] resulting in the observed strong antiferromagnetic exchange interaction.

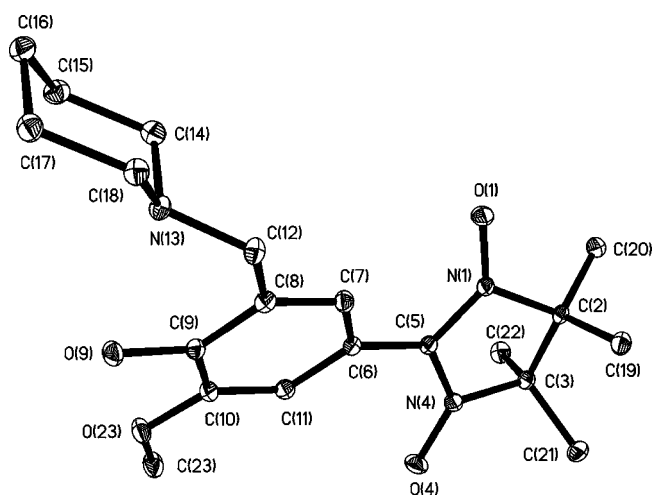


Figure 2. Molecular structure of **4**; ellipsoids are drawn at the 50% probability level

The magnetic susceptibility data can be interpreted in terms of two different models. First, assuming a dimer model with next-nearest neighbor interactions, the experimental data could be simulated applying the Heisenberg–Dirac–Van Vleck Hamiltonian [Equation (1)].

$$\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2 \quad (1)$$

The expression of magnetic susceptibility is given by Equation (2):

$$\chi_M = \frac{2N\beta^2 g^2}{3k(T - \Theta)} \left(1 + \frac{1}{3 \exp(-2J/kT)} \right) (1 - \rho) + \left(\frac{N\beta^2 g^2}{2kT} \right) \rho \quad (2)$$

where *N*, *g*, β , *k*, *T*, Θ and ρ have their usual meanings. A least-squares fit to the magnetic susceptibility data gives the values *g* = 2.00 (fixed), *J* = −21.47 cm^{−1}, Θ = −4.42 K, and ρ = 0.066 with *R* = 1.14·10^{−4} (Figure 1).

Alternatively, it was possible to fit the data according to the Heisenberg alternating chain model, with the appropriate Hamiltonian shown in Equation (3):

$$\hat{H} = -2J \sum_{i=1}^{n/2} [\hat{S}_{2i} \cdot \hat{S}_{2i-1} + \alpha \hat{S}_{2i} \cdot \hat{S}_{2i+1}] \quad (3)$$

where *J* and αJ are the two interaction parameters and α is the alternation parameter. The parameters *A*–*F* in the expression for the magnetic susceptibility were calculated according to Hatfield et al. [Equation (4)]:^[42]

$$\chi_m = \frac{N\beta^2 g^2}{kT} \frac{A + Bx + Cx^2}{1 + Dx + Ex^2 + Fx^3} (1 - \rho) + \left(\frac{N\beta^2 g^2}{2kT} \right) \rho \quad (4)$$

with $x = |J|/(kT)$. The fit to data (inset in Figure 1) gave the parameters *g* = 2.00 (fixed), $|J|$ = 19.91 cm^{−1}, α = 0.3, and ρ = 0.031 with *R* = 2.65·10^{−4}, which are in fairly good

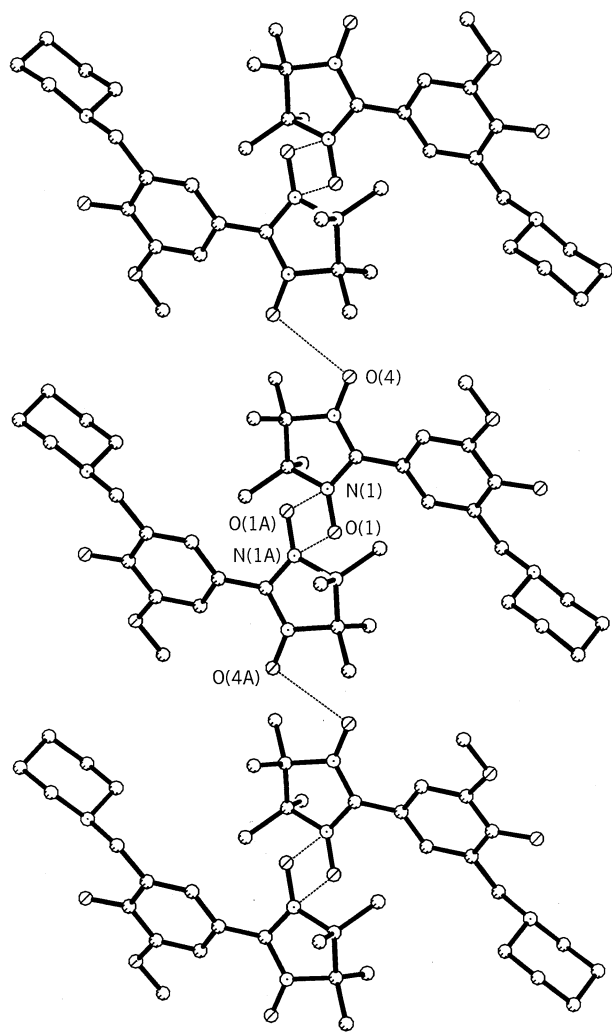


Figure 3. Molecular packing of **4** showing the intermolecular contacts between adjacent nitronyl nitroxide radicals

agreement with the parameters obtained with the previous model.

Magnetic Dilution

Since all the interactions are intermolecular in nature, compound **4** is an ideal candidate to improve a method of magnetic dilution in order to separate inter- and intramolecular exchange interactions. This experiment is essential in order to be able to analyze the transition metal complexes, in which intramolecular exchange interactions are small and have to be separated from intermolecular ones. For a pure organic radical like compound **4**, one expects to end up with an overall temperature dependence of the magnetic susceptibility of a simple paramagnet if it is possible to eliminate all intermolecular interactions. Compound **4** was therefore embedded in a poly(vinyl chloride) matrix of precisely determined weight. No chemical modification occurs during this process as proved by IR and UV/Vis spectroscopic measurements on the polymer films. The spectra obtained were identical for both the KBr disc and solution,

except for additional IR bands resulting from vibrations of the polymer matrix. The diamagnetic correction for the poly(vinyl chloride) film was determined in a separate run of susceptibility measurement and subtracted from the χ_V probe measurement. The result for compound **4** is shown in Figure 1. As expected, the $\chi_M T$ product was found to be close to the theoretical value of $0.375 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ over the whole temperature range. The method can also be applied to EPR spectroscopy. The low temperature EPR spectrum of **4** embedded in a poly(vinyl chloride) film is depicted in Figure 4 and was found to be identical to that measured on a frozen solution. It shows the typical signal of a nitronyl nitroxide in a solid matrix^[43] and was simulated with $g_1 = 2.0105$, $g_2 = 2.0120$, $g_3 = 2.0030$, $A_{11} = A_{22} = -4.5 \text{ G}$, $A_{33} = 19.5 \text{ G}$, and a line-width of 6 G . The anisotropy of the low temperature spectrum is in accordance with theory. Defining the local coordinates of the molecule so that the z axis is perpendicular to the O–N–C–N–O plane, we observe the smallest deviation from the Landé factor for the g value in the z direction. Contributions from the admixing of excited states into the ground state through spin-orbit coupling are negligible since the energy of the $\sigma \rightarrow \sigma^*$ excitation is far too high in energy. In the xy plane, however, $\sigma \rightarrow \pi$ and $\pi \rightarrow \pi^*$ excitations are more favorable which, as a result, lead to deviations from g_e for g_x and g_y . For the anisotropic hyperfine coupling constant we observe the largest value for the A_z tensor, since the spin density is highest in the p_z orbitals and the interaction of the nuclear spin with the magnetic field is most pronounced.

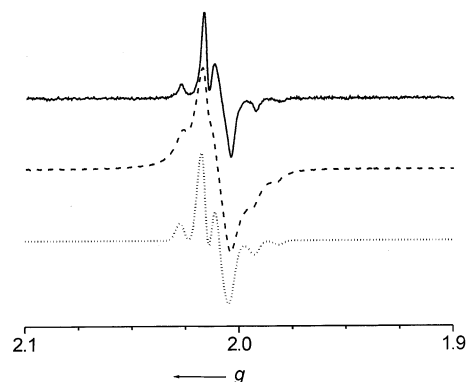


Figure 4. X-band EPR spectrum of **4** at 10 K of: a) a frozen methanol solution (microwave frequency 9.4371 GHz ; power 196.7 nW ; modulation amplitude 3.1 G ; solid line), b) a polymer embedded sample (microwave frequency 9.443 GHz ; power $1.0 \text{ }\mu\text{W}$; modulation amplitude 5.0 G ; dashed line), and c) the simulated spectrum (dotted line, see text for parameters)

Crystal Structures of the Coordination Compounds **8**, **9**, and **11**

Crystals suitable for an X-ray structure determination could be grown from acetonitrile or dichloromethane for compounds **8**, **9**, and **11**. The crystallographic data and details of the refinement procedures are collected in Table 2. Important bond lengths and angles are given in Tables 3 and 4. The molecules show the desired coordination of the

Table 2. Summary of the crystal structure data collection and refinement for **8**, **9**, and **11**

	8	9	11
Chem formula	C ₃₈ H ₅₄ CuN ₆ O ₆	C ₃₂ H ₄₆ CuN ₆ O ₆ ·H ₂ O·2CH ₃ CN	C ₃₂ H ₄₆ N ₆ NiO ₆
Fw	754.41	774.41	669.46
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>Pbca</i>
<i>a</i> , Å	10.7647(8)	25.725(2)	12.7575(8)
<i>b</i> , Å	12.3029(9)	8.9606(4)	9.1507(12)
<i>c</i> , Å	28.715(2)	16.9301(8)	27.293(3)
α , deg	90	90	90
β , deg	90	97.60(1)	90
γ , deg	90	90	90
<i>V</i> , Å ³	3802.9(5)	3868.3(4)	3186.2(6)
<i>Z</i>	4	4	4
<i>T</i> , K	100(2)	100(2)	100(2)
ρ calcd, g cm ^{−3}	1.318	1.330	1.396
μ (Mo- <i>K</i> α), mm ^{−1}	0.627	0.622	0.663
Diffractometer used	Siemens SMART	Nonius Kappa-CCD	Nonius Kappa-CCD
Refl. Collected	34570	36467	30911
Unique refl./[<i>I</i> > 2 σ (<i>I</i>)	8933/6601	8761/6165	6031/3748
No. parameters	468	489	211
2 Θ _{max} , deg	56.0	54.96	66.28
<i>R</i> 1 ^[a] [<i>I</i> > 2 σ (<i>I</i>)]	0.0486	0.0442	0.0422
<i>wR</i> 2 ^[b] [<i>I</i> > 2 σ (<i>I</i>)]	0.0885	0.1097	0.0973

^[a] $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, ^[b] $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ where $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, $P = (F_o^2 + 2F_c^2)/3$.

metal through the peripheral N,O donor set of the ligand without the participation of the nitronyl nitroxide groups. The coordination geometry at the metal and the supramolecular arrangement of the molecules is mainly affected by the steric demand of the ligand.

Bis[2-(piperidin-1-ylmethyl)-4-NIT-phenolato]copper(II) (**8**)

In this compound, the bulky piperidine side-arm forces the copper(II) into a tetragonally compressed tetrahedral coordination (Figure 5). Although the complex possesses no center of symmetry, the Cu–O bond lengths are almost identical [1.905(2) and 1.900(2) Å] as are the Cu–N distances, [2.041(2) and 2.039(2) Å]. The N–Cu–N and O–Cu–O angles of 157.06(9)° and 149.92(10)°, respectively, show a strong distortion of the tetrahedron towards a square-planar environment. The O–Cu–N angles are all close to 90° ranging from 91.16(9)–96.45(10)°. The phenolate rings show a small deviation from a benzoic to a quinoidal structure, with the two *ortho-meta* bonds [1.371(4)–1.386(4) Å] slightly shorter than the other four C–C bonds [1.405(4)–1.417(4) Å]. This is attributable to a contribution of the quinoidal form **B** to the electronic structure of the ligands (Scheme 1). A similar distortion was also found in a manganese complex with a bridging, nitronyl nitroxide substituted benzoic acid.^[29] The nitronyl nitroxide groups exhibit the usual characteristics with NO bond lengths of 1.285(3)–1.295(3) Å, indicating the delocalization of the unpaired electron over both NO groups. The torsion angles between the phenolate rings and the ONCNO planes are rather small at 3.8° and 17.4°. The C9–O9–Cu1 and C39–O39–Cu1 angles α are 123.0° and 124.6°, respectively, as expected for an sp²-hybridized oxygen atom. The planes of the phenolate rings and the coordination mean plane of the copper are twisted, enclosing

torsion angles β of 34.9° and 43.5°, respectively. The piperidine groups are in a chair conformation and oriented almost perpendicular to the coordination mean plane of the copper. There are no intermolecular contacts involving the NO groups below 4.7 Å. The shortest intermolecular distances are found between O1 and C2A as well as C3A at 3.88 and 3.94 Å ($x - 0.5, 0.5 - y, 1 - z$), respectively. The shortest Cu...Cu distance is 6.43 Å ($1 - x, y - 0.5, 1.5 - z$) between copper atoms forming a zigzag chain along the *y*-axis.

Aqua[bis(2-dimethylaminomethyl-4-NIT-phenolato)]-copper(II) (**9**)

The copper(II) complex **9** with the smaller dimethylamino ligand forms a distorted square-pyramidal complex with an additional water molecule in the apical position (Figure 6). The base plane of the pyramid is formed by an N₂O₂ donor set with Cu–N distances of 2.073(2) and 2.080(2) Å, and Cu–O distances of 1.930(2) and 1.902(2) Å. The N–Cu–N angle is 176.02(7)°, while the O9–Cu1–O29 angle is more bent [156.25(7)°]. The N–Cu–O angles at the base of the pyramid are in the range 85.13(7)–93.27(7)°, with the copper lying 0.223 Å above the base plane. The distance of the apical oxygen O10 to Cu1 is longer [2.293(2) Å], and the O10–Cu–N/O angles are 91.35(7)–105.31(7)°. As in compounds **8** and **11**, the phenolate rings are slightly distorted towards a quinoidal structure with the *ortho-meta* bonds slightly shorter [1.368(3) to 1.390(3) Å] than the other four C–C bonds [1.403(3) to 1.415(3) Å]. The bond lengths and angles within the nitronyl nitroxide groups are in the normal range, with N–O distances of 1.280(2)–1.296(2) Å. The torsion angles between the ONCNO planes and the phenolate rings are 19.0° and 19.4°. The

Table 3. Selected bond lengths (Å) for **8**, **9** and **11**

[(3) ₂ Cu] ⁰ 8		[(1) ₂ (H ₂ O)Cu] ⁰ 9		[(1) ₂ Ni] ⁰ 11	
Cu(1)–O(39)	1.900(2)	Cu(1)–O(29)	1.902(2)	Ni(1)–O(9)	1.8600(10)
Cu(1)–O(9)	1.905(2)	Cu(1)–O(9)	1.930(2)	Ni(1)N(13)	1.9783(13)
Cu(1)–N(43)	2.039(2)	Cu(1)–N(13)	2.073(2)	N(1)–O(1)	1.283(2)
Cu(1)–N(13)	2.041(2)	Cu(1)–N(33)	2.080(2)	N(4)–O(4)	1.2871(14)
O(1)–N(1)	1.295(3)	Cu(1)–O(10)	2.293(2)	N(1)–C(5)	1.364(2)
O(4)–N(4)	1.285(3)	O(1)–N(1)	1.294(2)	N(4)–C(5)	1.357(2)
N(1)–C(5)	1.358(4)	O(4)–N(4)	1.280(2)	N(1)–C(2)	1.498(2)
N(4)–C(5)	1.356(4)	N(1)–C(5)	1.346(2)	N(4)–C(3)	1.508(2)
N(1)–C(2)	1.505(4)	N(4)–C(5)	1.366(3)	C(2)–C(3)	1.548(2)
N(4)–C(3)	1.500(4)	N(1)–C(2)	1.501(3)	C(5)–C(6)	1.456(2)
C(2)–C(3)	1.546(5)	N(4)–C(3)	1.505(3)	C(6)–C(7)	1.408(2)
C(5)–C(6)	1.451(4)	C(2)–C(3)	1.550(3)	C(7)–C(8)	1.381(2)
C(6)–C(7)	1.408(4)	C(5)–C(6)	1.457(3)	C(8)–C(9)	1.410(2)
C(7)–C(8)	1.386(4)	C(6)–C(7)	1.406(3)	C(9)–C(10)	1.408(2)
C(8)–C(9)	1.417(4)	C(7)–C(8)	1.382(3)	C(10)–C(11)	1.381(2)
C(9)–C(10)	1.420(4)	C(8)–C(9)	1.419(3)	C(11)–C(6)	1.405(2)
C(10)–C(11)	1.371(4)	C(9)–C(10)	1.415(3)	C(9)–O(9)	1.326(2)
C(11)–C(6)	1.405(4)	C(10)–C(11)	1.381(3)		
C(9)–O(9)	1.315(4)	C(11)–C(6)	1.415(3)		
N(31)–O(31)	1.291(3)	C(9)–O(9)	1.317(3)		
N(34)–O(34)	1.285(4)	O(21)–N(21)	1.296(2)		
N(31)–C(35)	1.355(4)	O(24)–N(24)	1.281(2)		
N(34)–C(35)	1.353(4)	N(21)–C(25)	1.344(3)		
N(31)–C(32)	1.502(4)	N(24)–C(25)	1.367(3)		
N(34)–C(33)	1.489(4)	N(21)–C(22)	1.504(3)		
C(32)–C(33)	1.551(4)	N(24)–C(23)	1.506(3)		
C(35)–C(36)	1.453(5)	C(22)–C(23)	1.547(3)		
C(36)–C(37)	1.407(4)	C(25)–C(26)	1.458(3)		
C(37)–C(38)	1.380(5)	C(26)–C(27)	1.403(3)		
C(38)–C(39)	1.408(4)	C(27)–C(28)	1.390(3)		
C(39)–C(40)	1.410(5)	C(28)–C(29)	1.414(3)		
C(40)–C(41)	1.379(5)	C(29)–C(30)	1.406(3)		
C(41)–C(36)	1.410(5)	C(30)–C(31)	1.368(3)		
C(39)–O(39)	1.325(4)	C(31)–C(26)	1.407(3)		
		C(29)–O(29)	1.320(3)		

Table 4. Selected bond and dihedral angles (°) for **8**, **9**, and **11**

[(3) ₂ Cu] ⁰ 8		[(1) ₂ (H ₂ O)Cu] ⁰ 9		[(1) ₂ Ni] ⁰ 11	
O(39)Cu(1)O(9)	149.92(10)	O(29)Cu(1)O(9)	156.25(7)	O(9)Ni(1)N(13)	93.57(5)
O(39)Cu(1)N(43)	96.45(10)	O(29)Cu(1)N(13)	85.13(7)	C(9)O(9)Ni(1)	125.91(10)
O(9)Cu(1)N(43)	91.86(10)	O(9)Cu(1)N(13)	93.27	C(2)N(1)C(5)	111.65(11)
C(9)O(9)Cu(1)	123.0(2)	N(13)Cu(1)N(33)	176.02(7)	C(3)N(4)C(5)	112.21(11)
C(39)O(39)Cu(1)	124.6(2)	O(29)Cu(1)O(10)	105.31(7)	N(1)C(5)N(4)	107.38(12)
N(43)Cu(1)N(13)	157.06(9)	O(9)Cu(1)O(10)	98.42(6)		
C(2)N(1)C(5)	112.7(3)	N(13)Cu(1)O(10)	91.63(7)		
C(3)N(4)C(5)	112.4(2)	N(33)Cu(1)O(10)	91.35(7)		
N(1)C(5)N(4)	107.0(3)	C(9)O(9)Cu(1)	125.43(14)		
C(32)N(31)C(35)	112.6(3)	C(29)O(29)Cu(1)	131.8(2)		
C(33)N(34)C(35)	113.7(3)	C(2)N(1)C(5)	112.8(2)		
N(31)C(35)N(34)	106.6(3)	C(3)N(4)C(5)	111.9(2)		
		N(1)C(5)N(4)	107.4(2)		
		C(22)N(21)C(25)	112.4(2)		
		C(23)N(24)C(25)	111.6(2)		
		N(21)C(25)N(24)	107.3(2)		
N(1)C(5)N(4)–	3.8	N(1)C(5)N(4)–	19.0	N(1)C(5)N(4)–C(7)C(8)C(10)C(11)	18.6
C(7)C(8)C(10)C(11)		C(7)C(8)C(10)C(11)			
N(31)C(35)N(34)–	17.4	N(21)C(25)N(24)–	19.4		
C(37)C(38)C(40)C(41)		C(27)C(28)C(30)C(31)			
C(7)C(8)C(10)C(11)–	34.9	C(7)C(8)C(10)C(11)–	40.1	C(7)C(8)C(10)C(11)–(9)N(13)O(9)'N(13)	30.2
O(9)N(13)O(39)N(43)		O(9)N(13)O(29)N(33)			
C(37)C(38)C(40)C(41)–	43.5	C(27)C(28)C(30)C(31)–	22.6		
O(9)N(13)O(39)N(43)		O(9)N(13)O(29)N(33)			

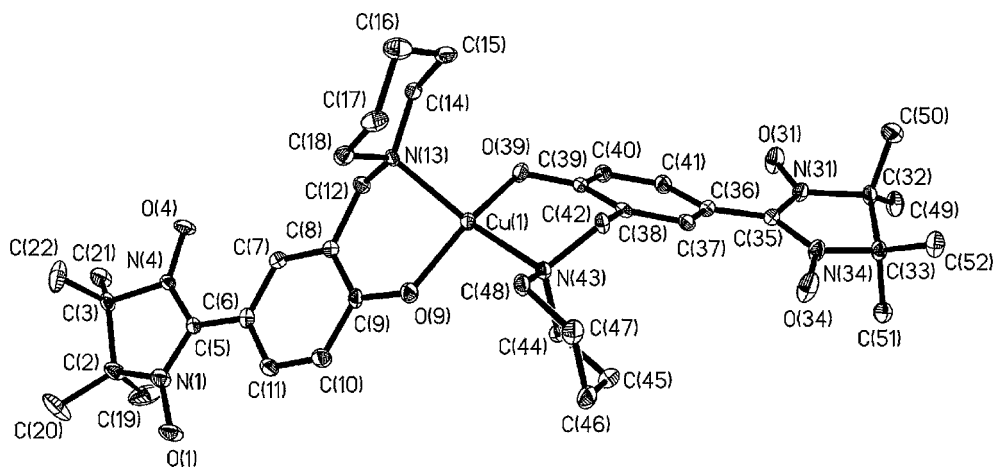


Figure 5. Molecular structure of **8**; ellipsoids are drawn at the 50% probability level

C(phenolate)–O–Cu angles α are 131.8° and 125.4° , while the torsion angles β between the coordination plane of the copper and the phenolate rings are 40.1° and 22.6° , the latter being significantly smaller than in complexes **8** and **11**. The apical water molecule is connected through hydrogen bonds to the nitronyl nitroxide groups of two adjacent molecules. The first hydrogen bond links O10 and O1A with a distance of 2.76 Å, forming a chain along the y axis (Figure 7). The second hydrogen bond links O10 with O21B over a distance of 2.72 Å, forming a zigzag chain along the z axis; these two hydrogen bonding interactions together result in a 2D network in the yz plane. There are additional short intermolecular contacts between adjacent nitronyl nitroxide groups, one between O24 and O24C ($-x, 3 - y, -1 - z$) of two nitronyl nitroxides in a tail-to-tail arrangement, with a distance of 3.89 Å, and another one between O21 and O1D with a distance of 3.64 Å ($x, 2.5 - y, 0.5 + z$), forming another zigzag chain in the z direction.

Bis(2-dimethylaminomethyl-4-NIT-phenolato)nickel(II) (**11**)

With the smaller dimethylamino-ligand and nickel(II) one obtains a square-planar complex (Figure 8). The metal

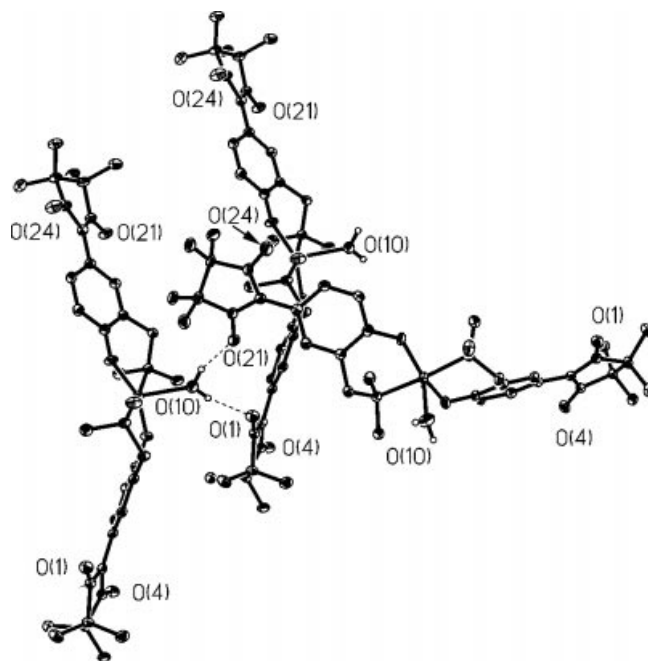


Figure 7. Crystal structure of **9**, showing the hydrogen bonds between the apical water molecule and the adjacent NO groups

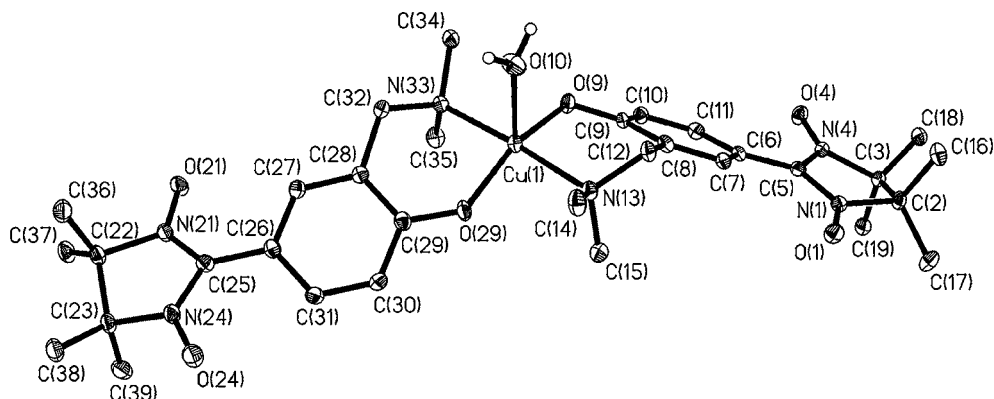


Figure 6. Molecular structure of **9**; ellipsoids are drawn at the 50% probability level

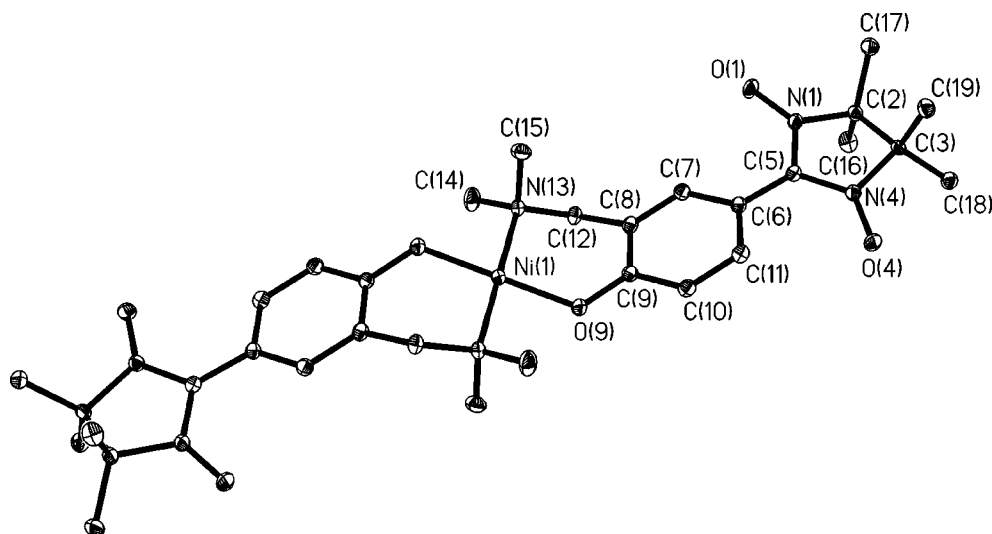


Figure 8. Molecular structure of **11**; ellipsoids are drawn at the 50% probability level

ion is located on an inversion center. The Ni–O distance is 1.86(1) Å and the Ni–N distance is 1.978(1) Å with an O–Ni–N angle of 93.57(3)°. The phenolate ring shows the same deviation from the benzoid structure as in the copper complexes **8** and **9** with both *ortho*–*meta* bond lengths at 1.381(2) Å, while the other carbon–carbon bond lengths are in the range 1.405(2)–1.410(2) Å. The bond lengths and angles within the nitronyl nitroxide group are in the expected range with N–O distances of 1.283(2) and 1.2871(14) Å. The torsion angle between the ONCNO plane and the phenolate ring is 18.6°. The angle α at the phenolate oxygen (C–O–Ni) is 125.9° — similar to that of the copper compound **8** — while the torsion angle β between the coordination mean plane of the nickel and the phenolate is 30.2°. Compound **11** forms an interesting 1D chain structure. Each oxygen atom O1 of the nitronyl nitroxide group points towards a nickel center of a neighboring complex with an O1...Ni1A distance of 4.33 Å, which is in turn connected in the same way, through O1A, to the Ni1 of the first complex, forming a molecular rectangle with the nickel atoms sitting in the two opposite corners. The diagonal distance between the Ni centers is 9.15 Å. Each rectangle shares the corners with its two neighbors, forming a chain of rectangles along the *y* axis (Figure 9). The chains are isolated from each other, with the shortest interchain distance being 4.19 Å between an O4 and the C3B of neighboring nitronyl nitroxide groups ($-x, y - 0.5, 0.5 - z$).

Magnetic Properties of the Coordination Compounds

The temperature dependence of the molar magnetic susceptibility χ_M was measured in the 2–290 K range on polycrystalline samples of complexes **8**–**11**. Since nitronyl nitroxides often show considerable intermolecular exchange interactions due to close contacts between adjacent spin-carrying NO groups, it was crucial to this study to be able to differentiate between intra- and intermolecular exchange

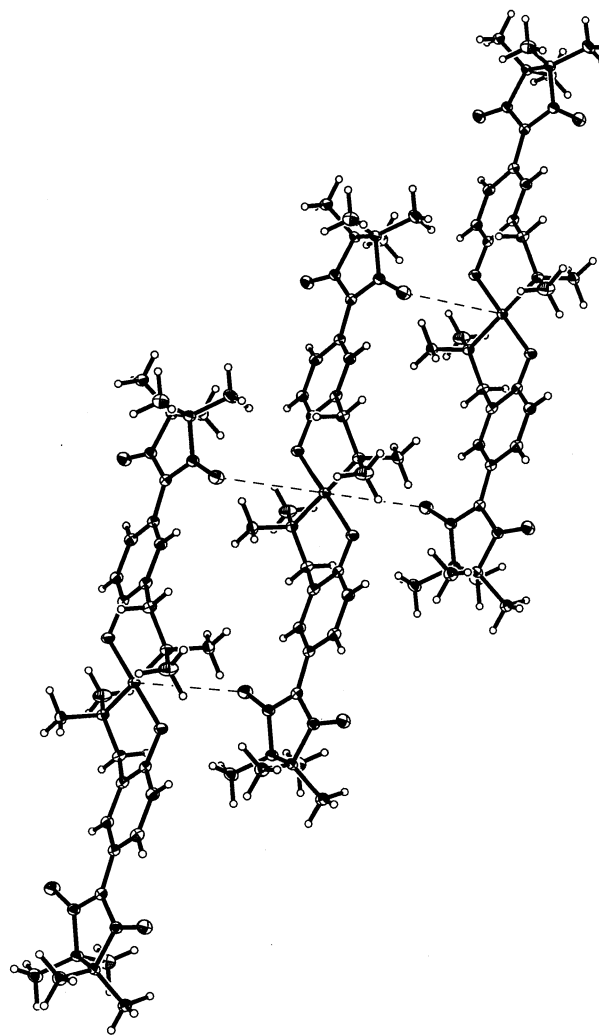


Figure 9. Crystal structure of **11**; dashed lines indicate the Ni1...O1A distances of 4.33 Å

interaction pathways. With the purely organic radical **4**, we were able to show that embedding the substance in a poly(vinyl chloride) film is a very efficient method of preparing magnetically diluted samples. No chemical modification occurs during this process. We could also apply this method to the transition metal complexes.

Bis[2-(piperidin-1-ylmethyl)-4-NIT-phenolato]copper(II) (**8**)

At room temperature, the value of the $\chi_M T$ product for the polycrystalline sample is $1.17 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$, which corresponds to that calculated for copper(II) and two nitronyl nitroxide radicals ($1.125 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$). With decreasing temperature, $\chi_M T$ decreases continuously, reaching $0.40 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$ at 2 K, close to the value of $0.375 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$ expected for an isolated unpaired electron (Figure 10).

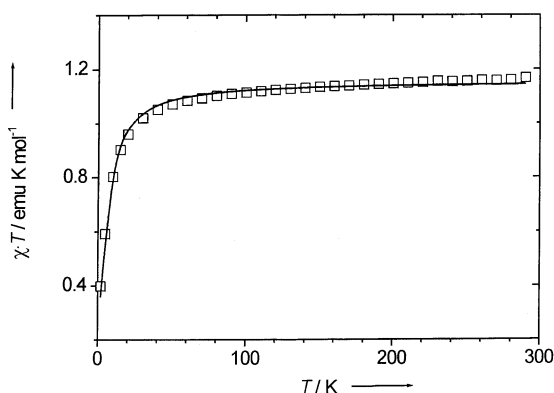


Figure 10. Temperature dependence of the product of the molar magnetic susceptibility with temperature ($\chi_M T$) for **8**; the solid line represents the best fit calculated data (see text for parameters)

The susceptibility was fitted to the Heisenberg–Dirac–Van Vleck Hamiltonian [Equation (5)]:

$$\hat{H} = -2J(\hat{S}_{\text{NIT}1}\hat{S}_M + \hat{S}_{\text{NIT}2}\hat{S}_M) \quad (5)$$

assuming the coupling between the two nitronyl nitroxides to be zero because of the large distance. The best result was obtained with the parameters $J = -2.90 \text{ cm}^{-1}$, $g_{\text{NIT}} = 2.00$ (fixed), $g_{\text{Cu}} = 2.05$, and $R = 2.15 \times 10^{-4}$. In accordance with the presence of isolated molecules as seen in the solid state structure, measurements on polymer-embedded samples also showed antiferromagnetic coupling.

Aqua[bis(2-dimethylaminomethyl-4-NIT-phenolato)]copper(II) (**9**)

At room temperature, $\chi_M T$ has a value of $1.16 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$, which is close to that expected for three uncoupled $S = 1/2$ spins ($1.125 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$). The $\chi_M T$ product decreases to $0.21 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$ at 2 K (Figure 11). We fitted the magnetic data to the HDVV Hamiltonian [Equation (5)]. The best result was obtained with $J = -2.88 \text{ cm}^{-1}$, $g_{\text{NIT}} = 2.00$ (fixed), $g_{\text{Cu}} = 2.11$ and $R = 6.11 \times 10^{-4}$. Compound **9** has a 2D network structure with several possible intra- and intermolecular exchange interaction

pathways. To gain insight into the intramolecular exchange interactions in operation, we performed additional magnetic measurements on a magnetically diluted sample of **9** embedded in a poly(vinyl chloride) matrix. Here the compound shows an entirely different behavior. The room temperature value of $\chi_M T$ is $1.09 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$, slightly lower than expected for three uncoupled $S = 1/2$ spins ($1.125 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$). Decreasing the temperature causes $\chi_M T$ to increase, reaching a maximum of $1.33 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$ at 10 K. On further lowering of the temperature, the $\chi_M T$ value decreases to reach $1.13 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$ at the lowest attainable temperature of 2 K (Figure 11). We could simulate the data down to very low temperature values satisfactorily with the values $J = +2.65 \text{ cm}^{-1}$, $g_{\text{NIT}} = 2.00$ (fixed), $g_{\text{Cu}} = 2.07$, and $R = 7.24 \times 10^{-3}$. This shows that in the case of **9**, intramolecular ferromagnetic interactions are operative which are masked by the intermolecular interactions in the polycrystalline sample.

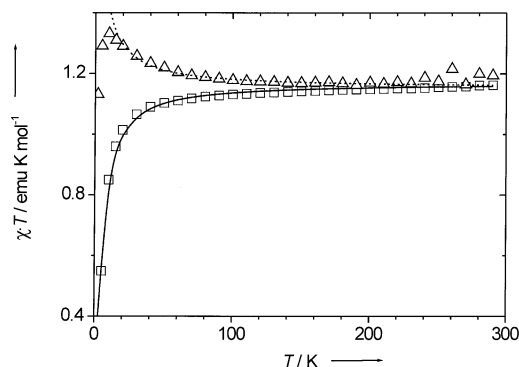


Figure 11. Temperature dependence of $\chi_M T$ for **9** as a powdered sample ($\square$) and embedded in a poly(vinyl chloride) film (Δ); the solid and dashed lines represent the best fit calculated data (see text)

Bis(methanol)bis(2-dimethylaminomethyl-4-NIT-phenolato)nickel(II) (**10**)

The value of $\chi_M T$ at 290 K ($1.83 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$) is as expected for an $S = 1$ of Ni^{II} in octahedral coordination with $g > 2$ and two nitronyl nitroxide radical ligands. When lowering the temperature, $\chi_M T$ decreases steadily to $0.81 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$ at 2 K (Figure 12). The data were fitted to

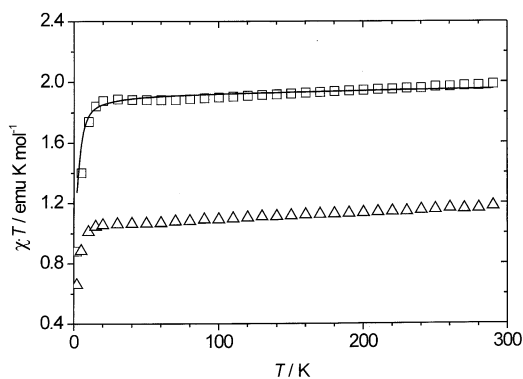


Figure 12. Temperature dependence of $\chi_M T$ for **10** ($\square$) and **11** (Δ); the solid line represents the best fit calculated data (see text for parameters)

Equation (5) yielding $J = -0.40 \text{ cm}^{-1}$, $g_{\text{NIT}} = 2.00$ (fixed), $g_{\text{Ni}} = 2.16$ and $R = 1.99 \times 10^{-3}$. A polymer-embedded sample shows similar behavior, suggesting the presence of isolated molecules in the powdered samples.

Bis(2-dimethylaminomethyl-4-NIT-phenolato)nickel(II) (11)

The $\chi_{\text{M}}T$ product has a value of $1.18 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ at room temperature and decreases to $1.06 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ with decreasing temperature (Figure 12). This value is much higher than the value of $0.75 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ expected for two uncoupled nitronyl nitroxide ligands and an $S = 0$ for Ni^{II} in square-planar coordination, and significantly lower than the value calculated for an $S = 1$ plus two $S = 1/2$ radical spins as in **10**. However, it is very close to the value of $1.00 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ for an $S = 1$ state arising from a ferromagnetic coupling between the two nitronyl nitroxide ligands. Given the large distance between the two radical moieties of $13.81 \text{ \AA}$ (taken between C5 and C5' related to each other by an inversion center), this is a surprising result, but was further confirmed by EPR spectroscopy and *ab initio* calculations.

Structural Correlation

In the structurally characterized copper complexes **8** and **9**, the sign of the exchange coupling constant can be related to the C(phenolate)–O–M angle α (with $\alpha = 180^\circ$ denoting a linear arrangement) and the torsion angle β between the coordination mean plane at the metal center and the plane of the phenolate ligand, with $\beta = 0^\circ$ if the two planes are coplanar. In a tetrahedral environment of the copper(II) ion, its magnetic d_{xy} orbital is orthogonal to the spin-carrying p_z of the phenolate oxygen for $\beta = 0^\circ$, irrespective of the size of α . However, with twisted planes and $\beta > 0^\circ$, decreasing α from 180° enlarges the overlap, resulting in antiferromagnetic coupling (Figure 13). Only in the case of both $\alpha \rightarrow 90^\circ$ and $\beta \rightarrow 90^\circ$, the coupling becomes ferromagnetic again. In square-pyramidal coordination geometry at the copper(II), the magnetic $d_{x^2-y^2}$ orbital is also orthogonal to p_z for $\beta = 0^\circ$, irrespective of α . In contrast to the d_{xy} orbital, the coupling stays antiferromagnetic when decreasing α for β values greater than 0° . At the intermediate values of $\alpha = 123.0^\circ$ to 131.8° observed in compounds

8 and **9**, the sign of the coupling is therefore determined by the torsion angle β for both magnetic d_{xy} and $d_{x^2-y^2}$ orbitals. A ferromagnetic interaction should be observed for small angles, switching to antiferromagnetic upon increasing β . These simple considerations agree well with the experimental findings. Compound **8** with larger β angles (34.9° and 43.5°) shows an antiferromagnetic coupling, while compound **9**, in accordance with its one small value for β of 22.6° , exhibits an intramolecular ferromagnetic interaction between the metal and the nitronyl nitroxide radical ligands.

EPR Spectroscopy

The X-band EPR spectra of **8–11** were measured as powders and in frozen solution at low temperature. Powdered samples of **8** show a broad isotropic signal at $g = 2.02$ with a line-width of 240 G . The spectra in frozen acetonitrile or chloroform solutions are dominated by the anisotropic signal of the nitronyl nitroxide group^[43] at $g = 2.00$ with an additional broad tail between $g = 2.03$ to 2.20 , better visible in the integrated spectrum. No signal clearly assignable to a copper(II) ion is observed. This is in accordance with an antiferromagnetic coupling between the copper(II) and the radical ligands, as determined from the susceptibility measurement. The spectrum measured on a polymer-embedded sample of **8** is identical to that obtained in frozen solution. The copper complex **9** in the powder has an isotropic signal centered at $g = 2.04$ with a line-width of 90 G . In frozen solution, the signal of the strongly coupled system shown in Figure 14a is observed. A quantitative evaluation of the signal intensity is not hampered by saturation, and comparison with a Cu^{II} standard shows that it accounts exactly for three electrons. In accordance with the intramolecular ferromagnetic coupling between the nitronyl nitroxide radicals and the copper(II) as seen in the susceptibility measurement on magnetically diluted samples, one observes a half-field signal at $g = 4.15$ (inset in Figure 14a). The spectrum obtained on a polymer-embedded sample of **9** is identical to that of the frozen solution. The EPR of **10**, in powder and frozen solution, is identical to that of the free protonated ligand and no signal indicative of a Ni^{II} ion is observed. The powder EPR of the nickel(II) complex **11** is shown in Figure 15. In addition to the small, intense signal at $g = 2.01$ with a line-width of only 20 G , two additional features occur that belong to an $S = 1$ system and that could be simulated assuming a zero-field splitting of $D = 0.0098 \text{ cm}^{-1}$, confirming the ferromagnetic coupling between the two radical ligands, although no half-field signal was observed.

Electrochemical Properties

We investigated the electrochemistry of the coordinated nitronyl nitroxide substituted phenolates by cyclic voltammetry, square-wave voltammetry, and spectro-electrochemistry to see if the coordinated ligands can be oxidized to singlet or triplet nitronyl nitroxide-phenoxy diradicals, possibly leading to molecules in higher spin states (Scheme 2c).

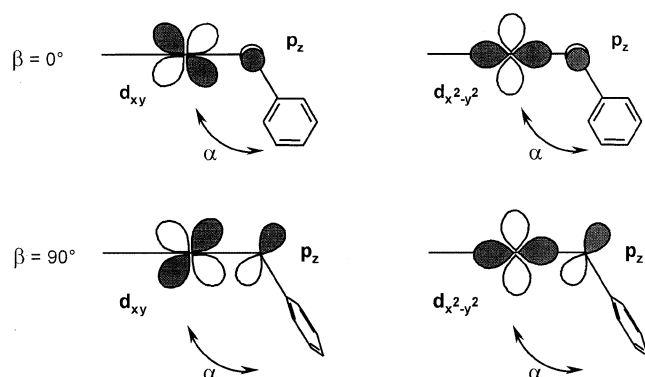


Figure 13. Depiction of the spatial arrangement of the orbitals relevant to the magnetic exchange interaction

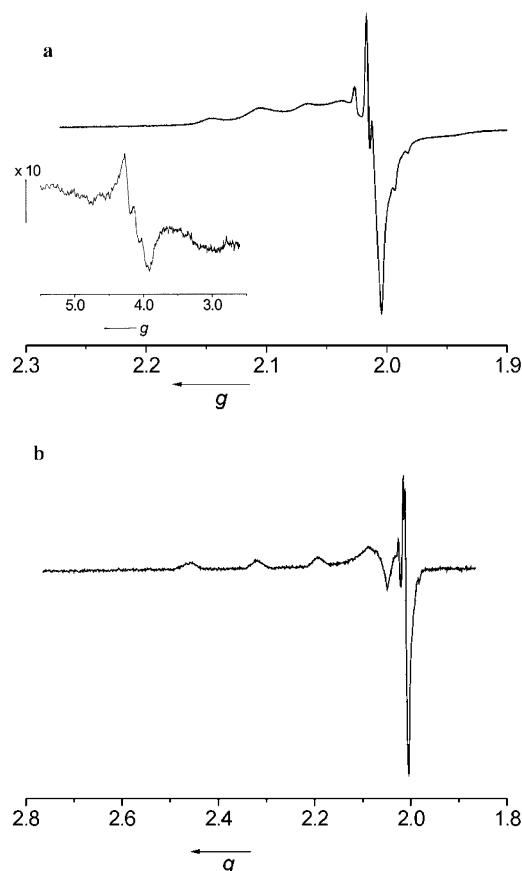


Figure 14. X-Band EPR of **9** at 60 K: a) before oxidation, with the inset showing the half-field signal, and b) after oxidation by two electrons

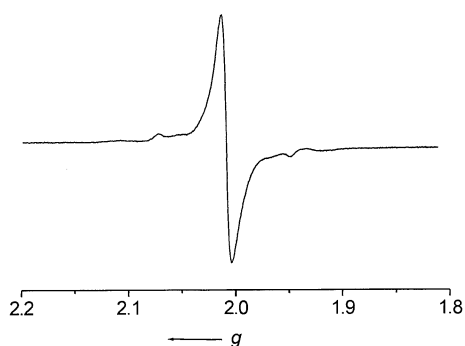


Figure 15. X-Band EPR of a powdered sample of **11** at 10 K

Compounds **8–10** undergo at least two oxidations in the range of 100–300 mV vs. ferrocenium/ferrocene (Fc^+/Fc), accompanied by an additional oxidative step depending on ligand, metal, and coordination geometry. The relevant data is collected in Table 5.

Compound **8** is simultaneously oxidized by three electrons at +228 mV vs. Fc^+/Fc . The most evident spectral change is the disappearance of the phenolate $n \rightarrow \pi^*$ band at 298 nm and the simultaneous appearance of a new intense band at 412 nm, whose maximum shifts to a lower wavelength during the course of the oxidation (Figure 16a); after the complete removal of three electrons it appears at

Table 5. Half-wave potentials for **8–10** in mV vs. Fc^+/Fc at 100 mV/s, measured in acetonitrile solution (2×10^{-4} mol/L) containing 0.1 mol/L TBAPF₆

Compound	$E^{0,0/+1}$	ΔE_p
$[(3)_2\text{Cu}]^0$ 8	+228	89
$[(1)_2(\text{H}_2\text{O})\text{Cu}]^0$ 9	+178	76
$[(1)_2\text{Ni}]^0$ 10	+103	[a]
	+202	[a]
	+249	[a]
	+290	[a]

[a] Not resolved in CV.

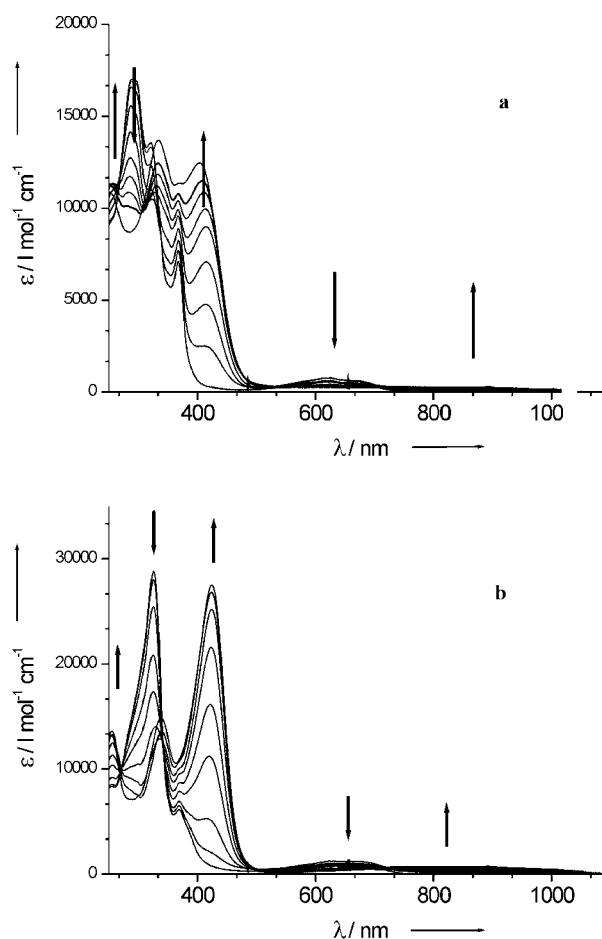
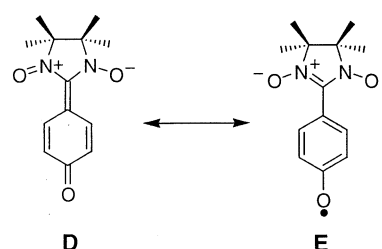


Figure 16. Spectral changes upon oxidation of: a) **8** and b) **9** in acetonitrile solution at +597 mV vs. Fc^+/Fc at -25°C

404 nm. In addition, the $n \rightarrow \pi^*$ band of the nitronyl nitroxide group at 615 nm decreases in intensity. In the EPR spectrum of the oxidized form, the overall signal intensity decreases without the appearance of new features. A quantitative evaluation is not possible due to signal saturation even at the lowest microwave power in the concentration range required for coulometry. These results can be interpreted as a concerted oxidation of both nitronyl nitroxide groups to diamagnetic nitrosonium cations plus the oxidation of one phenolate to a phenoxyl radical. Phenoxyl rad-

icals show similar spectral patterns and are known to be strongly coupled to coordinated copper ions.^[44,45] The copper compound **9** is reversibly oxidized by two electrons at +178 mV vs. Fc⁺/Fc. In the UV/Vis spectrum, this is accompanied by the appearance of a very strong band at 424 nm with isosbestic points at 270, 340, 500, and 714 nm. The phenolate $n \rightarrow \pi^*$ band at 326 nm as well as the $n \rightarrow \pi^*$ absorption of the nitronyl nitroxide group at 633 nm vanish, as in **8** (Figure 16b). The EPR of the oxidized species is dominated by the axial signal typical of a copper(II) atom in a square-planar coordination environment, as depicted in Figure 14b, with $g_{\perp} = 2.04$, $g_{\parallel} = 2.255$, $A_{\perp} = 40$ G, and $A_{\parallel} = 180$ G. Its intensity accounts for exactly one electron. No signals attributable to triplet radical ligands were observed. To gain further insight into the electronic structure of the oxidized product, resonance Raman (RR) spectroscopic measurements were performed on this compound. To prevent decomposition of the oxidized species, which is unstable at room temperature, the spectra were measured at 138 K on frozen solutions using an excitation wavelength of 413 nm coincident with the strong absorption of the oxidized product. Three prominent bands were observed at 1435, 1515, and 1602 cm^{-1} , respectively (Figure 17). The latter two occur at positions similar to those reported for phenoxyl-metal compounds.^[46,47] According to the literature, they are assigned to ν_{7a} and ν_{8a} modes having C–O stretching and C_{ortho} – C_{meta} double bond character, arising from a quinoidal mesomeric structure. The strong band at 1435 cm^{-1} is absent in the RR spectra of reported phenoxyl-metal complexes and is thought to originate from modes of the nitronyl nitroxide group. To gain evidence for this assumption, the vibrational spectrum of NIT-H was calculated by DFT (see Exp. Sect. for details on the computational procedures used). The simplest nitronyl nitroxide was chosen as a model since the whole ligand is too large to be treated theoretically and we assumed the modes of the phenolate and nitronyl nitroxide groups to be only weakly coupled. The calculated frequency of the symmetric stretching mode involving both NO groups is 1448 cm^{-1} when

employing an appropriate scaling factor,^[46] close to the band at 1435 cm^{-1} in the experimental spectrum. The theoretically determined frequency of the asymmetric stretching mode of the NO groups is 1484 cm^{-1} . A weak vibration is observed close to this value at 1467 cm^{-1} . These results indicate that two mesomeric structures – **D** with a nitrosonium-quinone formulation, and **E** with a nitronyl nitroxide-phenoxyl structure (Scheme 4) – contribute equally to the electronic structure of the coordinated, oxidized ligands. Although a triplet ground state was reported for a free nitronyl nitroxide-phenoxyl diradical,^[48–50] which we could also confirm by theoretical calculations, no evidence for triplet or sextet signals was found here in the EPR spectrum. The quinoidal structure **D** is probably stabilized upon coordination, leading to an $S = 0$ ground state for the oxidized ligand.



Scheme 4. Mesomeric structures of an oxidized nitronyl nitroxide radical

Density Functional Calculations

Density functional methods have recently been shown to give a good description of the electronic structure of nitronyl nitroxide radicals and at least a semi-quantitative picture of the spin-density distribution when compared with neutron diffraction data.^[51–53] Combined with the broken symmetry approach as proposed by Noodleman,^[54] they allow the theoretical determination of the exchange coupling constant in a wide variety of bimetallic compounds and diradicals to a good degree of accuracy.^[55–60] To get a first idea of the exchange interaction pathways operative in our nitronyl nitroxide-metal complexes, we calculated the spin density distribution of the deprotonated nitronyl nitroxide **1** with the geometry taken from the crystal structure (see Exp. Sect. for details on computational procedures used). The HOMO ($\alpha 83$) is delocalized over both the five- and six-membered rings, with contributions from the phenolic oxygen and the lone pair of the amine nitrogen (Figure 18a), although the SOMO ($\alpha 80$) was found to be entirely localized on the ONCNO group (Figure 18b). This is also reflected in the spin density map (Figure 18c and Table 6), which shows only a minor contribution at the phenolic oxygen atom resulting from configuration interaction, and is in accordance with very recent calculations of the spin-density distribution in a large variety of structurally characterized substituted nitronyl nitroxides, which also showed localization of the unpaired electron on the ONCNO group.^[61] The electronic structure of **1** is therefore

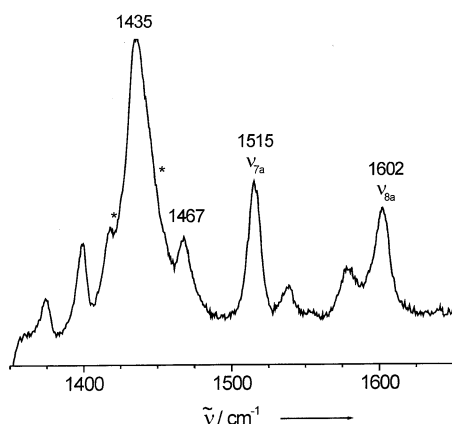


Figure 17. Resonance Raman spectrum of **9** oxidized by two electrons in frozen acetonitrile solution at 138 K (excitation wavelength 413 nm); the stars denote peaks attributed to solvent and/or supporting electrolyte

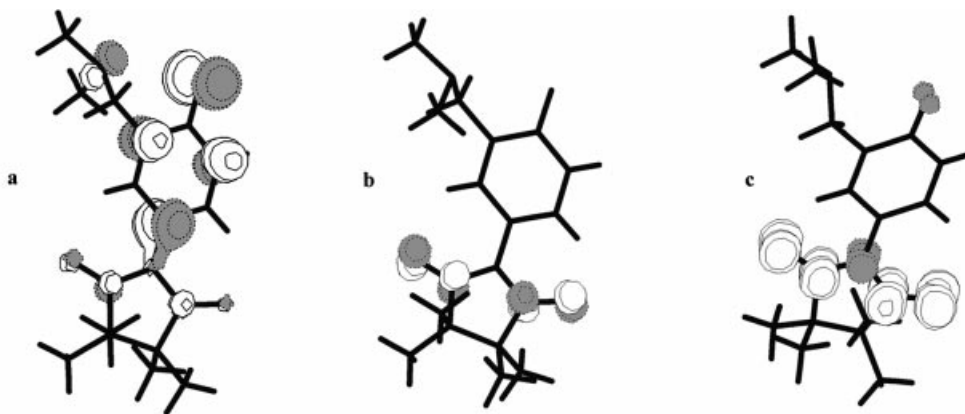


Figure 18. a) HOMO ($\alpha 83$) of deprotonated **1**, showing the contribution from the p_z of the phenolic oxygen, b) SOMO ($\alpha 80$) of deprotonated **1**, and c) spin density distribution

Table 6. Atomic spin densities of deprotonated **1** calculated at the B3LYP level; the numbering scheme is analogous to that used in Figure 2

N(1)	0.281	C(8)	−0.010
O(1)	0.365	C(9)	−0.002
C(2)	−0.017	O(9)	−0.042
C(3)	−0.013	C(10)	−0.009
N(4)	0.247	C(11)	−0.012
O(4)	0.321	C(19)	0.003
C(5)	−0.145	C(20)	0.000
C(6)	0.012	C(21)	0.018
C(7)	−0.013	C(22)	0.002

best described by the mesomeric structure **A** with little contribution from the phenoxyl form **C** (Scheme 1). This is in accordance with the observed weaker exchange interaction in the nitronyl nitroxide-metal complexes reported here, relative to published phenoxyl-metal complexes, which show a substantial spin density at the phenoxyl oxygen and in which the metal is therefore strongly coupled to the radical.^[62,63]

To further substantiate the electronic ground states as determined by EPR and magnetic susceptibility measurements, we carried out broken symmetry DFT calculations at the B3LYP level on models of the copper complexes **8** and **9**, in which one of the nitronyl nitroxide groups was replaced by a hydrogen atom, to determine the energies of the triplet and singlet states. Since it has been shown that contamination from higher spin states is not significant in density functionals,^[64–67] no spin projection was used and the exchange coupling parameter J was directly calculated from Equation (6):

$$J = E_{BS} - E_T \quad (6)$$

For copper models **8'** and **8''**, referring to the different torsion angles of 3° and 17° between the five- and six-membered rings, a singlet ground state was found in accordance with the experimental data, with J calculated to be -13.0

cm^{-1} and -5.6 cm^{-1} , respectively. The triplet state was found to be lower in energy in model compound **9'** with J calculated as $+9.8 \text{ cm}^{-1}$, thus confirming the intramolecular ferromagnetic coupling as observed in the magnetically diluted sample of this compound (just one calculation was done since the torsion angles on both ligands are almost equal in **9**).

For the nickel complex **11**, the calculation yielded a triplet ground state with $J = +64.0 \text{ cm}^{-1}$ in accordance with the EPR and susceptibility measurements. This large ferromagnetic coupling is rather surprising given the distance of $13.81 \text{ \AA}$ between the two radicals. It is thought to be mediated by the empty $d_{x^2-y^2}$ orbital of the Ni^{II} in a square-planar coordination. To gain further insight into the mechanism in operation, the corresponding zinc compound (**1**)₂Zn, which could not be obtained in pure form and characterized, was geometry optimized and the exchange-coupling constant calculated. With a completely filled 3d-shell, J was found to be zero within the accuracy of the calculation, thereby confirming the contribution of the empty metal $d_{x^2-y^2}$ orbital to the exchange-coupling pathway in **11**.

Conclusion

Nitronyl nitroxide substituted phenolate ligands with an additional chelating amine group were synthesized and provided the expected tight binding of transition metal ions at the periphery of the ligand without the participation of the NO groups. Four metal complexes of these ligands with copper(II) and nickel(II) were isolated and characterized. Their coordination geometry and supramolecular arrangement is controlled by the steric demand of the ligand, the preference of the metal ion for a certain geometry and the presence of coligands. The bulky piperidine group of ligand **3** forces copper(II) into a distorted tetrahedral coordination. No nickel(II) complexes could be obtained with this ligand. In addition, the large extent of the piperidine substituent prevented close intermolecular contacts between the molecular units, resulting in discrete molecules. The

smaller ligand **1** resulted in a planar arrangement of the N_2O_2 donor set of the two ligands in both its copper(II) and nickel(II) complexes, with coligands completing the preferred coordination number of the metal. With the smaller dimethylamino group, the molecular units are interconnected, forming 1D- and 2D-arrangements. The unpaired spin on the nitronyl nitroxide groups is coupled to the metal through the phenolic oxygen, as shown by susceptibility measurements and EPR spectroscopy. The intermolecular exchange interactions could be suppressed by embedding the compounds in a poly(vinyl chloride) film. The method was first tested and quantified on the free organic radical **4**, which shows strong intermolecular exchange interactions, and then successfully applied to the transition metal complexes. Both EPR and magnetic susceptibility measurements could be performed on magnetically diluted samples prepared this way, introducing it as a suitable method to investigate systems in which intra- and intermolecular exchange interactions of equal magnitude are operative. A structural relationship was found between the sign of the exchange coupling and the degree of torsion between the coordination mean plane of the metal center and the plane of the phenolate ligands. Density functional theory calculations further confirmed the experimentally determined electronic ground states. The obtained complexes will be used as synthons for supramolecular assemblies by both interconnection of the NO groups with Lewis acidic metal ions or replacement of the solvent molecules by bridging coligands.

Experimental Section

General: All reagents were purchased from commercial sources and used as received. Solvents were purified and dried by standard methods. Reactions were carried out under an atmosphere of argon where necessary. Elemental analyses were carried out by H. Kolbe, Mikroanalytisches Laboratorium, Mülheim an der Ruhr. Infrared spectra were recorded on a Perkin–Elmer FT-IR 2000. UV/Vis spectra were recorded on a Perkin–Elmer Lambda 19 spectrometer or a Hewlett Packard 8452A diode array spectrometer. EI mass spectra were measured on a Finnigan MAT 8200 instrument, and ESI mass spectra on a Finnigan MAT 95 instrument. Susceptibility measurements were performed on polycrystalline powders or polymer films on a Quantum Design MPMS SQUID magnetometer in the temperature range 2–295 K. Magnetically diluted samples were prepared by slowly evaporating a solution of poly(vinyl chloride) containing 5 wt. % of the compound under investigation in dichloromethane. The diamagnetic contribution of the polymer was determined in a separate run. EPR spectra were recorded as polycrystalline powders, in frozen solution, or on the polymer films used in the magnetic susceptibility measurements with a Bruker ESP 300 spectrometer with a Bruker ER041 XK-D microwave bridge and an Oxford Instruments cryostat model 910. Cyclic voltammograms and square-wave voltammograms were obtained with a three-electrode cell and an EG&G Princeton Applied Research 273A potentiostat. An Ag/AgNO₃ (0.01 mM) reference electrode, a glassy carbon disc working electrode and a Pt wire counter electrode were used. Acetonitrile solutions (10^{-4} M) contained 0.1 mol/L (*n*Bu)₄NPF₆ as supporting electrolyte. Ferrocene was added as an

internal standard after each measurement, its ΔE being +100 mV under these conditions. The coulometric measurements were performed at –25 °C with the same setup, and the spectral changes during oxidation were followed with a Hewlett Packard 8452A diode array spectrometer. EPR spectroscopic measurements on the oxidized species were performed on samples removed with a syringe under argon and immediately frozen in liquid nitrogen. RR spectra were obtained with the 413 nm excitation of a krypton ion laser (Coherent Innova 302) using a spectrograph (ISA U1000) equipped with a liquid nitrogen cooled CCD detector (Jobin Yvon). The spectral slit width was 5.6 cm^{–1}, and the wavenumber increment was 0.53 cm^{–1}. The sample holder was placed in a cryostat (Cryovac) at 138 K to prevent sample degradation and the scattered light collected in a 135° scattering geometry.

Preparation of the Nitronyl Nitroxide Radicals: The nitronyl nitroxide radicals were prepared from their aldehyde precursors (see Supporting Information) according to a literature procedure.^[38] For **1**, **2**, **4**, **5**, and **6**, benzene was used as solvent for the coupling of the aldehyde with 2,3-bis(hydroxylamino)-2,3-dimethylbutane. Chloroform was used as solvent for **3** and tetrahydrofuran for **7**. Oxidation to the radical was carried out with lead(IV) oxide for **1**–**3** and with sodium periodate for **4**–**7**. All radicals were purified by preparative HPLC on a Phenomenex Luna-5-PhenylHexyl column with methanol/aqueous ammonium acetate as the eluent. After extraction from the buffer with chloroform, they were obtained as blue solids by crystallization from toluene for **1**, **2**, **5**–**7** and from diethyl ether for **3** and **4**.

3-Dimethylaminomethyl-4-hydroxyphenyl-NIT (1): Yield (after HPLC): 1.09 g (55%). – IR (KBr disc): $\tilde{\nu}$ = 2990, 2957, 2831, 2784, 1654, 1598, 1483, 1416, 1384, 1364, 1350, 1298, 1282, 1218, 1141, 1111, 1019, 826, 542 cm^{–1}. – EI-MS: m/z = 306 [M⁺], 261, 176, 84, 69, 58, 44. – UV/Vis (MeOH): λ_{max} (ϵ) = 287 (12413), 317 (7926), 365 (4247), 615 nm (672 L·mol^{–1}·cm^{–1}). – EPR (solid, 60 K, 9.4391 GHz): g_{iso} = 2.0095. – EPR (CHCl₃, 80 K, 9.4374 GHz): g_x = 2.0105, g_y = 2.0130, g_z = 2.0040, A_{xx} = A_{yy} = –4.5 G, A_{zz} = 19.5 G. – C₁₆H₂₄N₃O₃ (306.38): calcd. C 62.72, H 7.90, N 13.71; found C 62.65, H 7.88, N 13.92.

3,5-Bis(dimethylaminomethyl)-4-hydroxyphenyl-NIT (2): Yield (after HPLC): 1.71 g (37%). – IR (KBr disc): $\tilde{\nu}$ = 2989, 2947, 2851, 2829, 2811, 2753, 1603, 1459, 1413, 1386, 1369, 1349, 1296, 1121, 1045, 1032, 844, 813, 541, 449 cm^{–1}. – EI-MS: m/z = 363 [M⁺], 346, 318, 301, 275, 187, 147, 84, 69, 44. – UV/Vis (CHCl₃): λ_{max} (ϵ) = 290 (15304), 372 (5789), 621 (952), 663 nm (783 L·mol^{–1}·cm^{–1}). – EPR (CHCl₃, 80 K, 9.4382 GHz): g_x = 2.0105, g_y = 2.0130, g_z = 2.0040; A_{xx} = A_{yy} = –4.5 G, A_{zz} = 19.5 G. – C₁₉H₃₁N₄O₃ (363.48): calcd. C 62.78, H 8.60, N 15.41; found C 63.10, H 8.55, N 15.25.

4-Hydroxy-3-(piperidin-1-ylmethyl)phenyl-NIT (3): Yield (after HPLC): 1.22 g (47%). – IR (KBr disc): $\tilde{\nu}$ = 3449, 2989, 2938, 2855, 2814, 1483, 1452, 1384, 1352, 1281, 1113, 827, 755, 540 cm^{–1}. – EI-MS: m/z = 346 [M⁺], 329, 261, 216, 84, 69, 56, 41. – UV/Vis (CHCl₃): λ_{max} (ϵ) = 371 (5604), 623 nm (742 L·mol^{–1}·cm^{–1}). – EPR (CHCl₃, 9.646 GHz, 295 K): Quintet, g_{iso} = 2.0085, A_N = 7.60 G. – EPR (CHCl₃, 9.646 GHz, 10 K): g_x = 2.0120, g_y = 2.0105, g_z = 2.0030, A_{xx} = A_{yy} = –4.5 G, A_{zz} = 19.5 G. – EPR (CHCl₃, 33.916 GHz, 293 K): g_x = 2.0062, g_y = 2.0062, g_z = 2.0010. – C₁₉H₂₈N₃O₃ (346.45): calcd. C 65.87, H 8.15, N 12.12; found C 65.96, H 8.11, N 12.06.

4-Hydroxy-3-methoxy-5-(piperidin-1-ylmethyl)phenyl-NIT (4): Yield (after HPLC): 0.33 g (8%). – IR (KBr disc): $\tilde{\nu}$ = 3440, 2938, 1478, 1413, 1385, 1356, 1308, 1129, 1089, 1038, 858, 714, 543 cm^{–1}. –

EI-MS: m/z = 376 [M^+], 291, 246, 162, 84, 69, 41. – UV/Vis ($CHCl_3$): λ_{max} (ϵ) = 298 (15976), 370sh (4704), 629 nm ($948 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). – EPR ($CHCl_3$, 9.464 GHz, 10 K): g_x = 2.012, g_y = 2.0105, g_z = 2.004, A_{xx} = A_{yy} = -4.5 G , A_{zz} = 19.5 G . – $C_{20}H_{30}N_3O_4$ (376.48): calcd. C 63.81, H 8.03, N 11.16; found C 63.69, H 8.10, N 11.04.

4-Hydroxy-3-(4-methylpiperazin-1-ylmethyl)phenyl-NIT (5): Yield (after HPLC): 0.13 g (28%). – IR (KBr disc): $\tilde{\nu}$ = 3481, 2956, 2795, 1446, 1350, 1291, 1260, 1137, 1111, 803, 540 cm^{-1} . – EI-MS: m/z = 361 [M^+], 344, 261, 231, 99, 84, 56, 44. – UV/Vis ($CHCl_3$): λ_{max} (ϵ) = 288 (16719), 326 (6087), 372 (8156), 620 nm ($968 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). – EPR ($CHCl_3$, 9.438 GHz, 10 K): g_x = 2.0120, g_y = 2.0110, g_z = 2.0040, A_{xx} = A_{yy} = -4.50 G , A_{zz} = 19.5 G . – $C_{19}H_{29}N_4O_3\cdot 1.5 \text{ H}_2O$ (388.49): calcd. C 58.74, H 8.30, N 14.42; found C 59.25, H 8.51, N 13.81.

4-Hydroxy-5-methoxy-3-(4-methylpiperazin-1-ylmethyl)phenyl-NIT (6): Yield (after HPLC): 0.68 g (51%). – IR (KBr disc): $\tilde{\nu}$ = 3449, 2984, 2941, 2825, 1458, 1388, 1359, 1303, 1122, 1082, 1009, 782 cm^{-1} . – EI-MS: m/z = 391 [M^+], 374, 357, 291, 261, 190, 162, 99, 84, 69, 58, 43. – UV/Vis ($CHCl_3$): λ_{max} (ϵ) = 296 (17360), 339 (9103), 368 (5647), 627 nm ($1061 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). – EPR ($CHCl_3$, 9.437 GHz, 10 K): g_x = 2.0120, g_y = 2.0110, g_z = 2.0040, A_{xx} = A_{yy} = -4.50 G , A_{zz} = 19.5 G . – $C_{20}H_{31}N_4O_4$ (391.49): calcd. C 61.36, H 7.98, N 14.31; found C 61.48, H 7.85, N 14.39.

***N,N'*-Bis(2-hydroxy-5-NIT-benzyl)-*N,N'*-dimethylethan-1,2-diamine (7):** Yield (after HPLC): 0.08 g (5%). – IR (KBr disc): $\tilde{\nu}$ = 2988, 1607, 1484, 1411, 1383, 1349, 1274, 1107, 1025, 831, 620, 541, 448 cm^{-1} . – ESI⁺MS (CH_2Cl_2): m/z = 596 [$M - 15 + H$], 611 [$M + H$], 633 [$M + Na$], 1191 [$2M + H$]. – UV/Vis ($CHCl_3$): λ_{max} (ϵ) = 287 (75877), 371 (17879), 619 nm ($971 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). – EPR ($CHCl_3$, 80 K, 9.4372 GHz): g_x = 2.0105, g_y = 2.0130, g_z = 2.0045, A_{xx} = A_{yy} = -4.5 G , A_{zz} = 19.5 G . – $C_{32}H_{46}N_6O_6$ (610.76): calcd. C 62.93, H 7.59, N 13.76; found C 63.11, H 7.68, N 13.58.

Preparation of Metal Complexes 8–11: The ligand (1.3 mmol) was dissolved in dry methanol (8 mL) under argon and deprotonated by addition of a fresh 1.2 M solution of sodium methanolate (1.6 mL; prepared by addition of a calculated quantity of sodium metal to dry methanol), resulting in a color change from deep blue to deep green. The anhydrous metal chloride (0.7 mmol) was then dissolved in dry methanol (8 mL) under argon and added dropwise to the solution of the deprotonated ligand over a period of 30 min. A crystalline precipitate began to form almost immediately. After complete addition this was collected by suction, washed with dry methanol, ether, and pentane before being dried in air. Recrystallization from the indicated solvents yielded the complexes in analytically pure form. Single crystals were grown from acetonitrile for **8** and **9**, while **11** was obtained in crystalline form by slow evaporation of a dichloromethane solution layered with ether.

Bis[2-(piperidin-1-ylmethyl)-4-NIT-phenolato]copper(II) (8): Yield: 0.60 g (99%). – IR (KBr disc): $\tilde{\nu}$ = 2922, 2854, 1599, 1470, 1408, 1382, 1357, 1309, 1260, 1117, 829, 636, 453 cm^{-1} . – ESI⁺MS (MeOH): m/z = 754 [$M + H$], 776 [$M + Na$]. – UV/Vis ($CHCl_3$): λ_{max} (ϵ) = 298 (26500), 329 (25400), 372 (10280), 634 nm ($2410 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). – $C_{38}H_{54}CuN_6O_6$ (754.43): calcd. C 60.50, H 7.21, N 11.14, Cu 8.42; found C 59.88, H 7.14, N 11.12, Cu 8.32.

Aqua[bis(2-dimethylaminomethyl-4-NIT-phenolato)]copper(II) (9): Yield: 0.39 g (73%). – IR (KBr disc): $\tilde{\nu}$ = 3416, 2983, 2923, 1599, 1473, 1408, 1381, 1348, 1323, 1301, 1117, 999, 823, 633, 541, 454 cm^{-1} . – ESI⁺MS (MeCN): m/z = 674 [$M - H_2O + H$], 696

[$M - H_2O + Na$]. – UV/Vis ($CHCl_3$): λ_{max} (ϵ) = 329 (54620), 375 (10180), 633 (2550), 678 nm ($2550 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). – $C_{32}H_{48}CuN_6O_7$ (692.32): calcd. C 55.52, H 6.99, N 12.14, Cu 9.18; found C 54.04, H 6.84, N 11.77, Cu 9.23.

Bis(methanol)bis(2-dimethylaminomethyl-4-NIT-phenolato)-nickel(II) (10): Yield: 0.32 g (87%). – IR (KBr disc): $\tilde{\nu}$ = 1595, 1484, 1471, 1410, 1376, 1333, 1297, 1118, 829, 628, 445, 453 cm^{-1} . – ESI⁺MS (MeOH): m/z = 669 [$M + H$], 691 [$M + Na$]. – UV/Vis ($CHCl_3$): λ_{max} (ϵ) = 299 (23140), 371 (9200), 628 nm ($1570 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). – $C_{34}H_{54}NiN_6O_8$ (733.53): calcd. C 55.67, H 7.42, N 11.46, Ni 8.00; found C 54.80, H 6.83, N 11.45, Ni 7.46.

Computational Details: The hybrid B3LYP method, as implemented in Gaussian 98,^[68] was used in the calculation of the spin-density distribution and the energies, mixing the exact Hartree–Fock exchange with Becke’s expression for the exchange^[69] and the Lee–Yang–Parr correlation functional.^[70,71] A double- ζ quality basis set (Lanl2DZ) was employed throughout.^[72–75] Because of the small energy differences, a tight convergence criterion with the limit set to 10^{-8} and the ultrafine grid were used. The vibrational spectrum of NIT-H was calculated with a cc-pVDZ basis set^[76–78] and the BP86-functional.^[79,80]

X-ray Crystallographic Collection and Refinement of the Structures:

Dark blue single crystals of **1**, **3**, **3a**, **4**, **7**, **8**, **9**, and **11** were coated with perfluoropolyether, picked up with a glass fiber, and mounted on a diffractometer equipped with a nitrogen cold stream operating at 100 K. Graphite monochromated Mo- K_α radiation (λ = 0.71073 Å) was used throughout. The crystallographic data of the compounds and the diffractometer types used are listed in Tables 1 and 2. Cell constants were obtained from a least-squares fit of the diffraction angles of several thousand strong reflections. Intensity data were corrected for Lorentz and polarization effects. The crystal faces of **4** were determined and the face-indexed correction routine embedded in SHELXTL^[81] was used to correct for absorption. The intensity data of **8** were collected on a Siemens Smart CCD diffractometer system and the program SADABS^[82] was used to correct for absorption. An absorption correction was carried out for the data set of **9**, for which the program MulScanAbs^[83] was used. The Siemens SHELXTL^[81] software package was used for solution, refinement, and artwork of the structures, and the neutral-atom scattering factors of the program were used. All structures were solved and refined by direct methods and difference Fourier techniques. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at their calculated positions and refined as riding atoms with isotropic displacement parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-149525, -149526, -149527, -149528, -157121, -157122, and -157123 for structures **1**, **3**, **3a**, **4**, **8**, **9**, and **11**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax: (internat.) +44–1223/336–033; E-mail: deposit@ccdc.cam.ac.uk].

Supporting Information (see footnote on page 1): Synthetic procedures for preparation of the nitronyl nitroxide precursors and figures showing the molecular structure and crystal packing of compounds **1**, **3**, **3a**, and **7** (13 pages).

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