New Chelating Nitroxide Free Radical Ligands For Heterospin-Magnetic Engineering

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Polychelating nitroxide ligands derived from *N*-methylethylenediamine and piperazine have been prepared by reactions of 2-bromomethyl nitronyl nitroxide with the corresponding polyamines. Two of these ligands have been structurally and magnetically characterized, along with some of their transition metal complexes, the magnetic properties of which are compared to those of previously reported related species. In particular, the properties of a nickel(II) derivative of a pentadentate tris(nitroxide), the ground spin-state of which is a quadruplet, are discussed in detail.

The popularity of nitroxide free radicals stems from their high stability and the well-studied, sophisticated organic chemistry.[1−3] Thus, ease of chemical modification allows the synthesis of nitroxides specially designed for use in fields as different as spin labelling[4][5] and materials chemistry.[6−9] In recent years, there has been increasing interest in the incorporation of nitroxide spin carriers into large homo-[9−11] and heterospin assemblies[6−8,12−15] of exchange-coupled species.

Coordination compounds incorporating nitroxide ligands are especially attractive since ligation through the nitroxyl oxygen atom ensures significant magnetic interactions. Moreover, overlap of magnetic orbitals of different types, d and p, may result in special situations where these orbitals are orthogonal and the interaction is ferromagnetic.[6][7] Among the various types of nitroxides, nitronyl nitroxides[16][17] have attracted special interest because of their delocalized electronic structures and their bridging properties, which have been exploited in the construction of extended structures made up of interacting organic and metallic spin carriers. The coordination chemistry of nitroxide free radicals is, however, highly dependent on the weakly basic character of ligands of this type, which precludes coordination to metal ions other than those bearing electron-withdrawing groups.[18−21] Enhancement of the Lewis acid properties of the metal center may easily be achieved, but most of the coordination sites would then be occupied by ancillary ligands and structures of high dimensionality would not be accessible, other than for high-spin polyradicals.[8] Consequently, most of the extended species described to date are one-dimensional alternating arrays of metal ions and nitroxide ligands which are ordered at low temperature.[22−24] In an attempt to circumvent this difficulty, we have investigated the coordination properties of a few nitronyl nitroxides in which the substituent bears a donor such as a nitrogen atom, which enforces the coordination of the nitroxyl oxygen atom through the chelate effect.[12,14,25] The results of these preliminary investigations have prompted us to develop a more general method, which should allow the design of paramagnetic ligands suitable for developing the field of molecular nitroxide-based magnetic coordination compounds.

We report herein on the preparation of a reactive nitroxide synthon, **1** (Figure 1), which couples with *N*-methylethylenediamine to afford tri- (**2**) and tetranitroxide (**3**) ligands, and with piperazine to give a biradical (**4**). The magnetic properties of these polychelating ligands have been investigated and two of them (**3**, **4**) have been structurally characterized. In a preliminary step, and for comparison with previously reported species, complexes of metal hexafluoroacetylacetonates **6** {**4**[$Mn(hfac)_2]_2$}, **7** {**4**[$Co(hfac)_2]_2$}, and **8** {**4**[$Ni(hfac)_2]_2$} have been prepared and their structural and magnetic properties have been investigated. Finally, we report the synthesis and magnetic behavior of a pentacoordinate nickel(II) complex, **5** {**2**[$Ni(ClO_4)_2] \cdot H_2O$}, which illustrates the potential of ligands of this type in the design of new molecular magnetic materials.

Results and Discussion

Although the yield of **1** was rather low (ca. 30%), the one-pot synthesis from the readily available 2,3-dimethyl-2,3-dinitrobutane described here affords samples of the compound from which the amino derivatives can conveniently be prepared. Synthesis of a similar synthon, the chloro compound analogous to **1**, has been described previously.[26] This chloro compound was used in the preparation of 2-(phenyloxymethyl)imidazoline-*N,N′*-dioxyl derivatives, but it is unreactive toward amines.

The synthesis of metal complexes did not present any problems; the chelating nature of these ligands ensures coordination of the nitroxyl groups to the metal center, as

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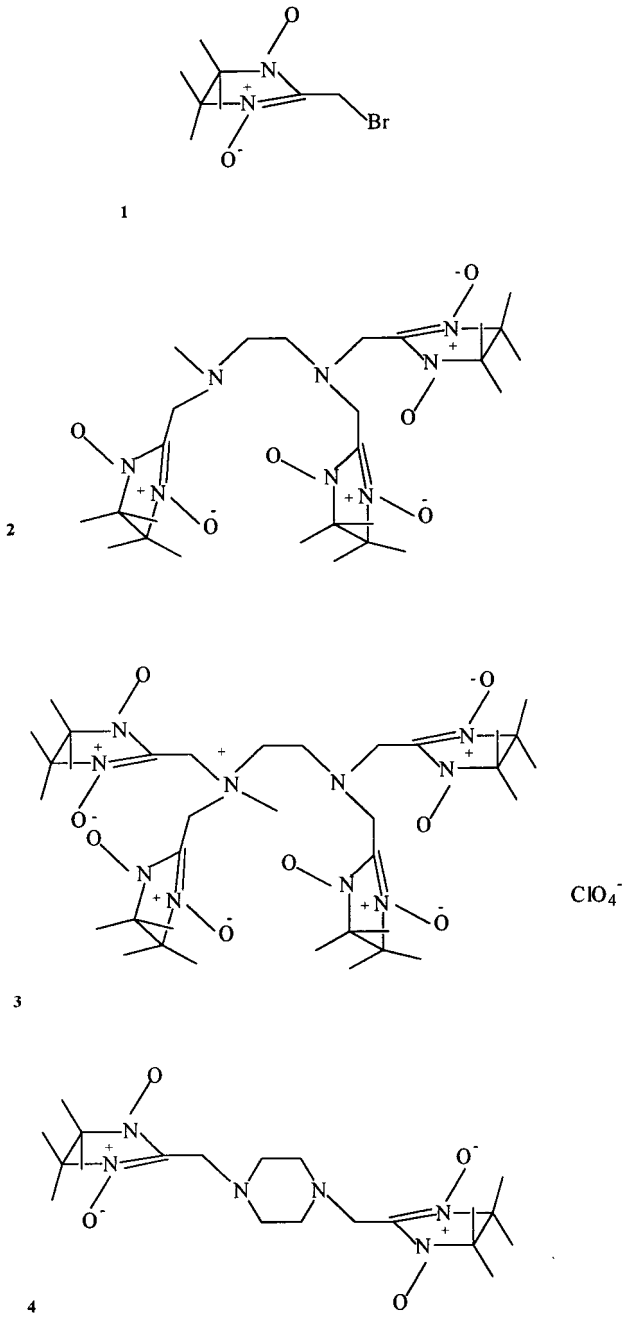

Figure 1. Chemical structure of the nitroxide synthon **1** and of the polychelating ligands **2**−**4**

observed for the Mn^{II} (**6**), Co^{II} (**7**), and Ni^{II} (**8**) derivatives of **4**, the X-ray structures of which have been determined.

Structural Studies

Since only one structure of a 2-aminomethyl derivative of a nitronyl nitroxide has been reported previously,[26] it seemed worthwhile to structurally characterize a few of these ligands.

Views of the molecular structures of $\mathbf{3}^+$ and **4** are depicted in Figures 2 and 3, respectively. In both compounds, the imidazoline *N*-oxide *N*′-oxyl fragments exhibit struc-

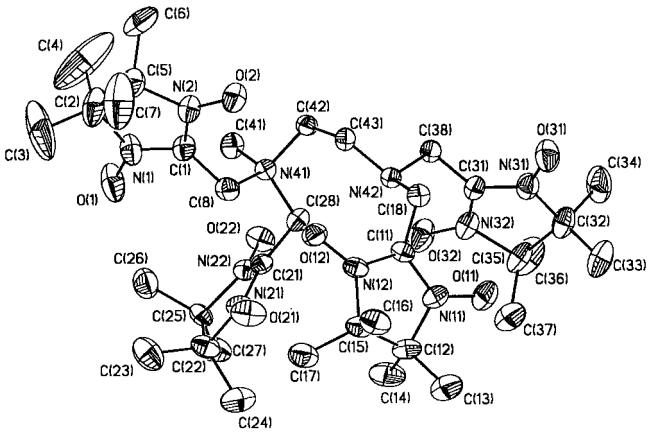

Figure 2. Molecular structure of ligand $\mathbf{3}^+$ showing the atom numbering scheme; thermal ellipsoids are drawn at a 30% probability level; selected bond lengths [Å] and angles [°]: Oi−Ni (av.) = 1.281(6), Ci1−Ci8 (av.) = 1.470(6), C8−N41 = 1.514(4), C28−N41 = 1.530(6), C18−N42 = 1.490(5), C38−N42 = 1.470(4); C1−C8−N41 = 114.3(4), C11−C18−N42 = 112.4(3), C21−C28−C41 = 112.9(3), C31−C38−N42 = 114.6(4)

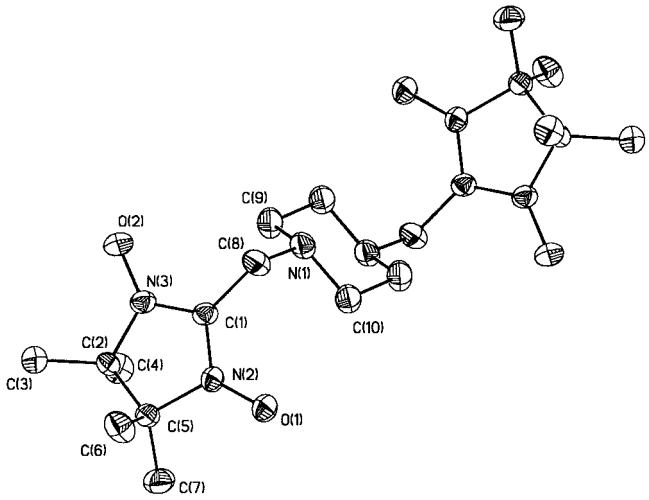

Figure 3. Molecular structure of ligand **4** showing the atom numbering scheme; thermal ellipsoids are drawn at a 30% probability level; selected bond lengths [Å] and angles [°]: N2−O1 = 1.272(4), N3−O2 = 1.285(4), C1−C8 = 1.489(5), C8−N1 = 1.461(5); C1−C8−N1 = 117.0(3)

tural features characteristic of nitronyl nitroxides,[6] such as NO bond lengths in the range 1.26−1.29 Å. Regarding the 2-aminomethyl moiety, one observes the following structural features: (i) In both ligands, the imidazoline ring is almost perpendicular to the plane defined by the sp^2-hybridized carbon atom (C1; Figure 2) and the aminomethyl group (84.6−93.5°). This can be rationalized by considering the steric requirements, since in this arrangement the oxyl groups are far removed from the organic fragment bearing the amino function. (ii) In **3**, the relative arrangement of the four imidazoline-*N*,*N*′-dioxyl groups is such that two of them are almost parallel [12.4(4)°] and each group within this pair is almost perpendicular (83−87°) to the other two. (iii) In **4**, the C1−C8−N1 plane is roughly orthogonal to

both the imidazole ring and the mean plane of the piperazine fragment. Finally, the ethylenediamino group in **3** is in a gauche conformation, while in the centrosymmetric compound **4** the six-membered piperazine ring adopts a chair form. Numerous weak intermolecular interactions involving the oxyl groups are observed, with distances larger than 5 Å.

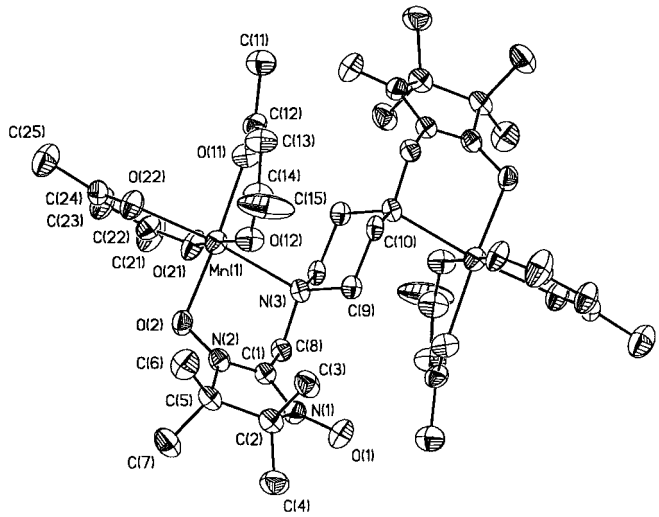

Figure 4. Molecular structure of complex **6** showing the atom numbering scheme; thermal ellipsoids are drawn at a 30% probability level; selected bond lengths [Å] and angles [°]: N1−O1 = 1.266(7), O2−N2 = 1.309(7), Mn−O2 = 2.158(5), Mn−N3 = 2.463(5); O2−Mn−N3 = 88.7(2), O2−Mn−O11 = 163.3(2), N3−Mn−O22 = 163.3(2), C1−C8−N3 = 112.0(5)

Although complex **6** {**4**[Mn(hfac)$_2$]$_2$} on the one hand, and the isostructural complexes **7** {**4**[Co(hfac)$_2$]$_2$} and **8** {**4**[Ni(hfac)$_2$]$_2$} on the other, do not crystallize in the same space group (*P*1 and *P*21/*n*, respectively), their molecular structures (Figure 4) are very similar. They are centrosymmetric species incorporating a piperazine ring in a chair conformation. The metal coordination spheres are octahedral, with that of the manganese ion being more distorted than those of the cobalt and nickel ions. It is worth noting that each metal center is chiral, but since the molecular structures are centrosymmetric the complexes exist in inactive forms. In both molecular structures, the chelate ring involving the nitroxide oxygen atom adopts a boat conformation, and the N−O distance in the coordinated nitroxyl group is larger than that in the uncoordinated one by as much as 0.03 Å. This latter feature is diagnostic of significant metal−nitroxide magnetic coupling. Furthermore, the chelate ring is distorted because, due to steric factors, the metal−nitrogen(piperazine) distance is much larger than usual [2.463(5) Å in **6** and 3.300(6) Å in **7**]. Finally, the smallest intermolecular distances are observed between symmetry-related uncoordinated oxyl groups, with distances as small as 3.41 Å in **6**. Therefore, the magnetic behavior of these metal complexes may depend not only on intramolecular metal−nitroxide couplings, but also on intermolecular nitroxide−nitroxide interactions.

Magnetic Studies

Ligands **2**−**4** exhibit similar magnetic behavior characterized by obeyance of the Curie law down to ca. 40 K, followed by a decrease of the product of the magnetic susceptibility and the temperature, indicative of antiferromagnetic interactions. In biradical **4**, the saturated piperazine moiety is not expected to mediate sizeable intramolecular interactions between the two nitroxide spin carriers. Indeed, the Bleaney−Bowers expression[27] was not able to reproduce the experimental data. However, fairly good results were obtained by considering independent spins interacting with neighboring molecules[28] [^{z}J = −2.4(3) cm^{-1}, R = 6.2·10^{-4}].[29] As mentioned above, in tetraradical **3** intra- and intermolecular contacts are of the same order of magnitude. Consequently, good agreements were obtained either by considering a four-spin system with identical intramolecular interactions being operative between the nitroxide fragments [J = −2.1(2) cm^{-1}, R = 2.4·10^{-4}] or an S = 1/2 spin interacting with an unknown number (z) of neighbors [^{z}J = −6.8(2) cm^{-1}, R = 1.7·10^{-4}]. This latter model could also be successfully applied to triradical **2** [^{z}J = −5.9(3) cm^{-1}, R = 3.5·10^{-4}], for which structural information is not available. Although the magnetic behavior of the ligands is somewhat unremarkable, the small magnitudes of the coupling constants suggest that analysis of the magnetic properties of the complexes could be performed neglecting inter-nitroxide coupling within the metal coordination sphere.

Curie behavior is observed for complex **6**. The almost constant value of χT from room temperature (6.06 cm^3·K·mol^{-1}) down to 5 K (5.97 cm^3·K·mol^{-1}) precludes any quantitative analysis of the coupling constant. This value of $\chi T \approx 6$ cm^3·K·mol^{-1} is consistent with the presence of two independent S = 2 spins, resulting from a large metal−nitroxide antiferromagnetic interaction at both complexing sites of the molecule. Indeed, the value at room temperature indicates that the magnitude of the coupling constant should be as large as −100 cm^{-1}, and that intermolecular interactions should be negligible. Such large Mn^{II}−nitroxide interactions have been reported previously, but it has been suggested that geometric constraints imposed by the chelation usually lessen the extent of magnetic interaction.[25] Indeed, if one considers that the interaction primarily originates from overlap of the π* orbital of the nitroxyl group with the metal orbital directed towards the oxyl oxygen atom, chelation would result in unfavorable local structural parameters for overlap and strong coupling. In **6**, these parameters (M−O−N angle 116.5°; angle between the M−O−N and N−C−N planes 51.4°) are similar to those observed in the related complex Mn(hfac)$_2$NIT · 2 Py (120° and 42°),[25] where the chelating donor atom is a pyridyl nitrogen atom and the Mn^{II}−nitroxide interaction has a magnitude of just −65 cm^{-1}.

Similarly, antiferromagnetic behavior is shown by the analogous nickel(II) complex **8**, for which the value of χT decreases from 2.04 to 0.91 cm^3·K·mol^{-1} over the 300−2 K temperature range and the ground spin-state is the sum of

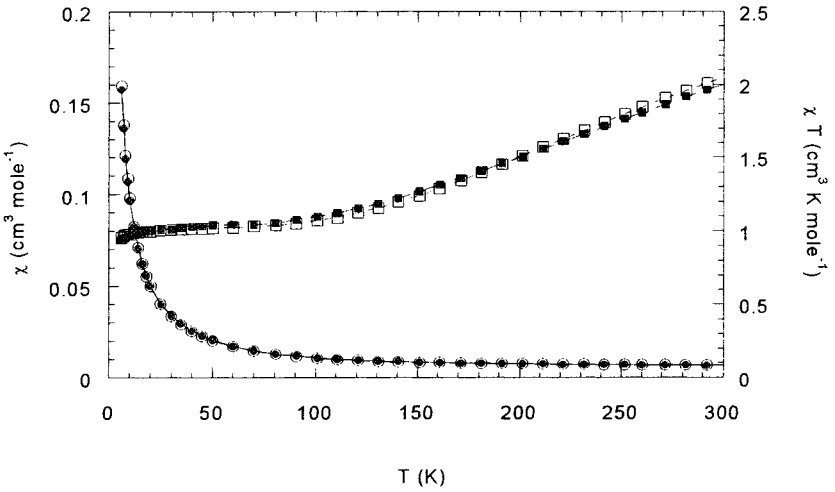

Figure 5. Magnetic behavior of complex **8** displayed as χ (full circle: experimental; open circle: calculated; see text) and χT (full square: experimental; open square: calculated)

two doublets. However, in this case the variation of χT is sufficiently large (Figure 5) to allow calculation of a reliable value of $J_{Ni-nitroxide} = -131(4)$ cm^{-1} [$g = 2.11(1)$, $R = 3.4 \cdot 10^{-4}$], which is smaller than that found for the Ni^{II} complex of the pyridyl-substituted radical (-161 cm^{-1}).[25] Structural parameters relating to magnetic orbital overlap in these two compounds are also similar. Therefore, these two examples illustrate how slight structural modifications within the metal coordination sphere can have a significant influence on the magnitude of the metal−radical magnetic interaction.

In the case of complex **7** {**4**[Co(hfac)$_2$]$_2$}, one observes a decrease in χT, which is probably the result of antiferromagnetic metal−nitroxide interactions. Owing to the significant orbital contribution to the magnetic behavior of octahedral Co^{II} species, no attempts have been made to determine a coupling constant.

The magnetic behavior of complex **5** is depicted in Figure 6. On decreasing the temperature, χT increases from 2.31 emu·K·mol^{-1} (independent spins) to 2.53 emu·K·mol^{-1} at 38 K, and then decreases to ca. 1.0 emu·K·mol^{-1} at 2 K. The presence of dominant ferromagnetic interactions is confirmed by a positive θ value of 8.6 K, as shown by the temperature dependence of $1/\chi$. Although Ni^{II}−nitroxide interactions are usually antiferromagnetic, recent reports have documented special situations where ferromagnetic couplings can be attributed to specific structural features of the coordination sphere.[30] In the present case, structural information is not available but, as shown in Figure 7, the complex may exist in two isomeric forms, namely OC-6-25 (*mer*) and OC-6-35 (*fac*). Of these, the *mer* configuration is probably more stable due to steric factors, as has been observed previously for related nickel(II) complexes of other chelating nitroxide ligands.[13]

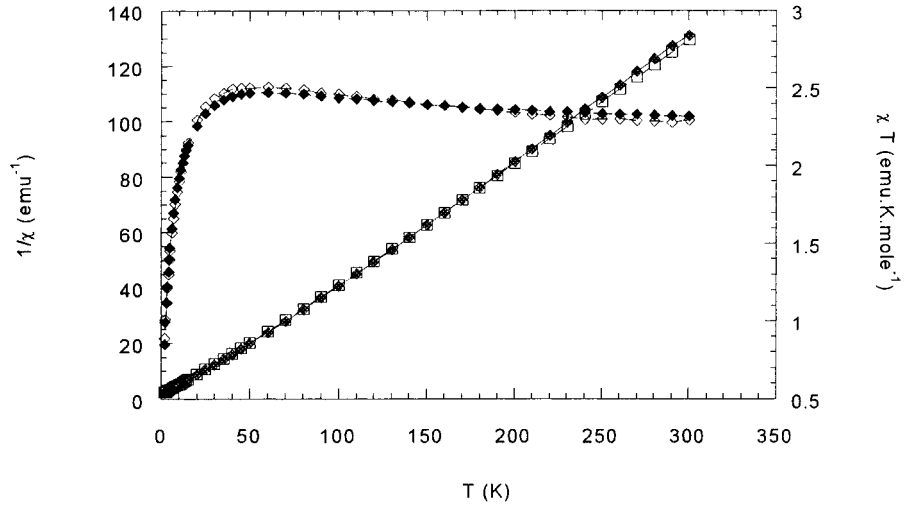

Figure 6. Temperature dependence of χT (full circle: experimental; open circle: calculated) and $1/T$ (full square: experimental; open square: calculated) for complex **5**

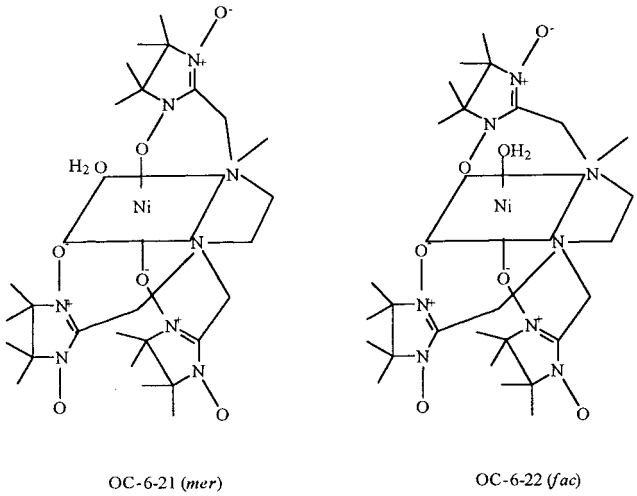

Figure 7. Sketch of the possible isomeric modifications of complex **5**; enantiomeric modifications are not represented

From a magnetic point of view, there are two different sets (axial and equatorial) of coordinated nitroxide ligands, irrespective of the configuration. Accordingly, a model including two different Ni−nitroxide coupling constants was considered, which led to the following parameters: $J_{Ni-C} = -5.3(6)$ cm^{-1}, $J_{Ni-A} = J_{Ni-B} = +12(3)$ cm^{-1}, $g = 2.13(2)$, and furthermore indicated a weak intermolecular interaction of 0.45(2) cm^{-1} ($R = 8.2 \cdot 10^{-4}$). This coupling scheme suggests that the ground spin-state of the "isolated" complex is a quadruplet. Figure 8 shows plots of the theoretical Brillouin function for $S = 3/2$ ($g = 2.13$) and the magnetization data of the complex collected at $T = 2$ K. These two curves have been extrapolated to high field using a sum of exponential functions for the experimental data. Although at low field the data deviate markedly from the calculations, one observes that at high field the experimental magnetization extrapolates to a value close to that of a quadruplet state. The discrepancy observed at low field is most likely attributable to zero-field effects, which split the ground state into two Kramer doublets.

Concluding Remarks

We have presented a general strategy for the incorporation of donor atoms in chelating positions to the oxyl group in nitronyl nitroxides. The method allows the preparation of metal−nitroxide exchange-coupled species with weakly acidic metal centers. The variety of amino-functionalized organic fragments that can be used as precursors for designing nitroxide ligands makes this strategy very attractive for magnetochemists. For example, complex **5**, which has a spin quadruplet ground state and a free coordinating position, can be used to build up high-spin clusters. Work along these lines using this $S = 3/2$ complex as a terminal building block for metal hexacyanates is currently in progress.

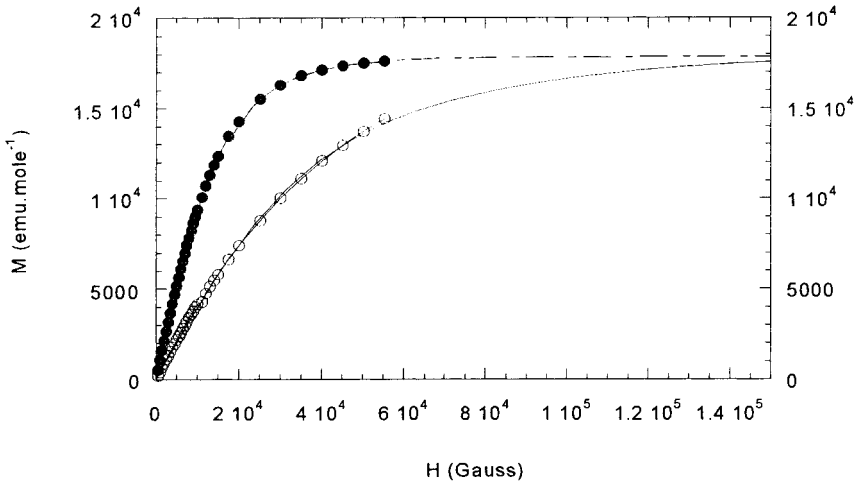

Figure 8. Field dependence of the magnetization for complex **5** (full circle: theoretical Brillouin curve for $S = 3/2$ and $g = 2.13$; open circle: experimental data)

Experimental Section

Synthesis of 2-Bromomethyl-4,5-dihydro-4,4,5,5-tetramethyl-1-oxy-1*H*-imidazolyl 3-Oxide (1): This compound was synthesized directly from 2,3-dimethyl-2,3-dinitrobutane.[31] The precursor (10 g, 57 mmol) and ammonium chloride (5 g) were dissolved in a mixture of water (20 mL) and THF (80 mL). Subsequent reduction to the bis(hydroxylamino) derivative was performed by adding zinc powder (13 g) over a period of 1 h at 10°C. The resulting slurry was stirred for 5 h at room temperature and then filtered. The filtrate was acidified to pH = 1 with HCl and the THF was evaporated in vacuo. The remaining aqueous solution was treated with 8 mL of 2-bromoacetaldehyde dimethylacetal and the resulting mixture was stirred at 10°C for 2 d. The solution was subsequently extracted with diethyl ether and the aqueous phase was neutralized to pH = 7 with $NaHCO_3$. Then, 200 mL of dichloromethane was added, the mixture was cooled to 5°C, and oxidation was carried out by adding 7 g of sodium periodate in 50 mL of water over a period of 1 h. The organic phase was subsequently dried and concentrated in vacuo and the crude deep-red compound was chromatographed (SiO_2; diethyl ether) to afford 2.6 g (18%); m.p. 126°C (dec.). The product was found to be stable for months at −28°C, but only for a few hours at room temperature. Thus, it had to be used promptly in the subsequent reactions.

Synthesis of *N*-Methylethylenediamine Derivatives: Celite (5 g) and *N*-methylethylenediamine (100 mg, 1.35 mmol) were mixed in 30 mL of acetonitrile. A solution of 1.0 g (4.0 mmol) of bromomethyl nitronyl nitroxide in 20 mL of MeCN was then added dropwise at room temperature and stirring was continued for a further 2 h. Filtration and evaporation of the solvent from the filtrate afforded a crude mixture, which was chromatographed on alumina (Woelm, activity grade V). Compounds **2** and **3** were successively eluted. − **2**: With dichloromethane/acetonitrile, 60:40; 423 mg (72%); m.p. 145°C (dec.); $C_{27}H_{52}N_8O_6$ (585): calcd. C 55.46, H 8.96, N 19.16; found C 55.58, H 8.72, N 18.97. − Bromide **3:** With acetonitrile. **3** was dissolved in a mixture of methanol/water (1:1) containing one equiv. of sodium perchlorate. After allowing the mixture to stand for 2 d, the crystals deposited were collected by filtration; yield 158 mg (17%); m.p. 189°C (dec.); $C_{35}H_{71}ClN_{10}O_{12} \cdot 4\,H_2O$: calcd. C 45.37, H 8.05, N 15.12, Cl 3.83; found C 45.18, H 8.12, N 15.26, Cl 4.08. Crystals of this compound proved suitable for an X-ray diffraction study.

Synthesis of a Piperazine Derivative: Using the same procedure as above, starting from 1.0 g (4.0 mmol) of **1** and 172 mg of piperazine (2.0 mmol), chromatography on alumina (Woelm activity grade V, CH_2Cl_2/CH_3CN, 70:30) afforded 428 mg (50%) of **4**; m.p. 156°C; $C_{20}H_{36}N_6O_4$ (424.5): calcd. C 56.58, H 8.55, N 19.80; found C 56.78, H 8.53, N 19.92. Crystals suitable for an X-ray diffraction study were obtained by slow evaporation of the solvents from acetone/hexane solutions. Other compounds were present in small quantities, which were not characterized.

Metal Complexes

Nickel(II) 5: Ligand **2** (100 mg, 0.17 mmol) was dissolved in 8 mL of methanol. To this solution, a solution of Ni(ClO4)2·6H2O (70 mg, 0.2 mmol) in 5 mL of MeOH was added portionwise. A red powder (128 mg, 95%) was immediately precipitated, which, after drying in vacuo, gave a satisfactory analysis for $C_{27}H_{51}Cl_2N_8NiO_{15}$ (786.4): calcd. C 37.83, H 6.00, N 13.07, Ni 6.85; found C 37.59, H 5.93, N 13.12, Ni 6.94. All attempts to grow single crystals from solutions in various solvents were unsuccessful.

Manganese(II) Complex 6: Manganese(II) hexafluoroacetylacetonate dihydrate (250 mg, 0.5 mmol) was dissolved in 30 mL of boiling heptane and reflux was continued in order to obtain an anhydrous solution of the metal salt. A solution of ligand **4** (100 mg, 0.23 mmol) in 5 mL of dichloromethane was added to the solution at ca. 50°C. Precipitation occurred on cooling and acetone was added until the solid redissolved. Subsequent slow evaporation of the solvent led to well-formed crystals of complex **6** (223 mg, 33%; m.p. 188°C); $C_{40}H_{40}F_{24}Mn_2N_6O_{12}$ (1362.6): calcd. C 35.26, H 2.96, Mn 8.06, N 6.17; found C 34.98, H 3.11, Mn 7.97, N 6.04.

Cobalt(II) Complex 7 and Nickel(II) Complex 8: Crystals suitable for X-ray diffraction experiments were obtained starting from the appropriate metal salt and following the same procedure as above.

Crystal Structure Determinations: All crystals (**3**, **4**, **6**, **7**) were analyzed using a Siemens SMART CCD area detector three-circle diffractometer (Mo-K_α radiation, graphite monochromator, λ = 0.71073 Å). The cell parameters were determined from intensities detected in three batches of 15 frames with a 10-s exposure time for each. For three settings of Φ and 2Θ, 1200 narrow data frames were collected for successive increments in ω of 0.3°. A full hemisphere of data was collected for each complex. At the end of collection, the first 50 data frames were re-examined in order to check for decay during the data collection. Unique intensities with $I > 10\sigma(I)$ selected from all the data frames using the SAINT program were used to refine the cell parameters. The substantial degree of redundancy in the data allowed empirical absorption corrections to be applied using multiple measurements of equivalent reflections with the SADABS program. Space groups were derived from systematic absences and were later confirmed by the successful solutions of the structures.[32] The structures were solved by direct methods as implemented in the SHELXTL 5.05 package and all atoms were located on difference Fourier maps. Non-hydrogen atoms were refined anisotropically on F^2, while hydrogen atoms, located by calculation, were refined isotropically. For compound **4**, use of the data collected at 20°C led to a structural scheme in which the perchlorate anion was highly disordered. Attempts to collect the data at low temperature were unsuccessful owing to disintegration of the crystals. Therefore, the anion was tentatively modelled on two different chlorine locations with equal occupancies and the oxygen atoms were distributed over a sphere. Although this disorder has a significant effect on the *R* factor values, it does not hamper the chemical interpretation of the cationic part of the molecule. The nickel(II) complex **8** was found to be isostructural with the cobalt(II) analogue **7**.

Magnetic Susceptibility Measurements: Magnetic susceptibility data were collected using a Quantum Design MPMSR2 magnetometer working at a 0.5-T field strength over the 2−300 K temperature range. Squid outputs were corrected for the contribution of the sample holder and susceptibility data were corrected for the diamagnetic contribution of the constituent atoms using Pascal constants.

Acknowledgments

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