Synthesis, Structure, and Magnetic Properties of Transition Metal Complexes of the Nitroxide 2,5-Dihydro-4,5,5-trimethyl-2,2-bis(2-pyridyl)imidazole-1-oxyl

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With the radical 2,5-dihydro-4,5,5-trimethyl-2,2-bis(2-pyridyl)imidazole-1-oxyl (**L**) a series of transition metal complexes have been prepared: $[\mathbf{ML}_2](\mathrm{SbF}_6)_2$ with $\mathrm{M}^{2+} = \mathrm{Mn}^{2+}$ (**1**), Fe^{2+} (**2**), Co^{2+} (**3**), Ni^{2+} (**4**), Cu^{2+} (**5**), and Zn^{2+} (**6**), Cu(**L**)$(\mathrm{Cl})_2$(MeOH) (**7**), and Cu(**L**)$\mathrm{SO}_4\cdot\mathrm{H}_2\mathrm{O}$ (**8**). The structures of **1**, **3**, and **6** were determined by X-ray structural analyses. In these compounds the tridendate **L** is coordinated to the metal ion by the two pyridine nitrogen donors and by the oxygen atom of the nitroxide group. The N−O bond distances are 1.25(2) Å (**1**), 1.267(13) Å (**3**), and 1.260(11) Å (**6**). The M−O−N angles are 117.0(10)° (**1**), 114.5(8)° (**3**), and 114.2(7)° (**6**). Crystal data: space group $P2_1/n$, for **1**, **3**, and **6**; compound **1**, $a = 10.806(3)$ Å, $b = 14.101(6)$ Å, $c = 14.253(4)$ Å, $\beta = 108.82(2)°$, $V = 2055.7(12)$ Å^3, $Z = 2$, $R_1 = 0.0677$, w$R_2 = 0.1512$. Compound **3**, $a = 10.761(4)$ Å, $b = 14.253(6)$ Å, $c = 14.108(5)$ Å, $\beta = 111.16(3)°$, $V = 2017.9(13)$ Å^3, $Z = 2$, $R_1 = 0.0702$, w$R_2 = 0.1460$; compound **6**, $a = 10.788(2)$ Å, $b = 14.147(3)$ Å, $c = 14.196(3)$ Å, $\beta = 109.93(3)°$, $V = 2036.8(7)$ Å^3, $Z = 2$, $R_1 = 0.0573$, w$R_2 = 0.1194$. Magnetic measurements of **1**, **2**, **5**, and **8** show strong antiferromagnetic interaction between the spin of the metal ion and the spin of the radical which increases at lower temperatures. For **6** the magnetic moment corresponds to two noninteracting spins in the temperature range 60−300 K.

Introduction

During the last two decades, development of molecular magnetic materials has become a challenging field of research. Different approaches were made[3] to realize three-dimensional ferro- or ferrimagnetic behavior. Miller et al. employed metallocenium and porphyrinium salts of TCNE and TCNQ and explained the ferromagnetic state with the McConnel II mechanism.[4] Kahn et al. used the antiferromagnetic coupling of $\mathrm{Mn}^{2+}/\mathrm{Cu}^{2+}$ pairs to realize one-dimensional ferrimagnetic chains which gave in some cases a three-dimensional ferromagnetic state.[5] A similar strategy was followed by Gatteschi and Rey et al., who synthesized alternating chains of nitronyl nitroxide radicals of 2-imidazoline and metal hexafluoroacetylacetonate units.[6] Due to the antiferromagnetic coupling between the radical spins and the metal spins, ferrimagnetic states were realized.

Our Munich group was one of the first to prepare transition metal complexes with nitroxides.[7] Up to now, a large number of transition metal complexes of nitroxide radicals have been prepared.[6,8] The coordination chemistry of 2,5-dihydroimidazole nitroxide radicals was investigated by Ovcharenko et al.[8c−e,9] They succeeded in generating ferromagnetic interactions between the radicals and transition metal ions.[10]

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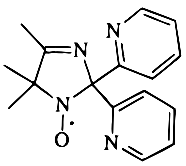
Recently we described the preparation of the radical 2,5-dihydro-4,5,5-trimethyl-2,2-bis(2-pyridyl)imidazole-1-oxyl (**L**),[11a]



L

and a disilver complex of this ligand was structurally characterized.[11b] We herein report the synthesis, the structures, and the magnetic properties a series of transition metal complexes with this nitroxide.

Experimental Section

Starting Materials. The 2,5-dihydro-4,5,5-trimethyl-2,2-bis(2-pyridyl)imidazole-1-oxyl-radical **L** was prepared as published.[11] All other reagents and solvents were purchased from commercial sources and used as supplied. The products were dried in vacuo (0.1 Torr) for 4−8 h. Elemental analyses were carried out with a Heraeus VT. EPR spectra (X-band) were recorded on a Varian E-Line spectrometer with a Varian E-101 microwave bridge. Magnetic measurements were carried out with 8−15 mg samples in the temperature range 60−300 K with a Faraday balance at the Institut für Physikalische Chemie der Universität München. One additional measurement was made at 4.2 K. IR spectra were obtained with a Nicolet 520 FT-IR spectrometer. Melting and decomposition points were measured on the apparatus of Dr. Tottoli, Büchi, Germany.

Synthesis of the Hexafluorantimonate Salt of Bis(2,5-dihydro-4,5,5-trimethyl-2,2-bis(2-pyridyl)imidazole-1-oxyl)manganese(II) (1). To a solution of $MnCl_2$ (13.8 mg, 0.110 mmol) in methanol (7 mL) was added a solution of $AgSbF_6$ (75.6 mg, 0.220 mmol) in 7 mL of methanol. The mixture was boiled for 1 min, evaporated to dryness, and extracted with methanol (10 mL). AgCl was centrifuged off and the solution of $Mn(SbF_6)_2$ was dropped into a solution of 2,5-dihydro-4,5,5-trimethyl-2,2-bis(2-pyridyl)imidazole-1-oxyl (62.8 mg, 0.220 mmol) in methanol (10 mL). After 2 d, the yellow-brown crystals were separated from the mother liquor, washed with a small amount of methanol, and dried in vacuo: yield 39 mg (33%); dec >240 °C. Anal. Calcd for $C_{32}H_{34}N_8O_2MnSb_2F_{12}$: C, 35.29; H, 3.15; N, 10.29. Found: C, 35.29; H, 3.25; N, 10.23. IR (KBr): 1647 vs (C=N), 1600 vs (py), 1579 m, 1479 s, 1467 vs, 1444 vs, 1383 s, 1158 s, 1057 s, 1019 vs, 787 s, 774 vs, 760 s, 402 s, 289 vs cm^{-1}. EPR (CH_3CN): $g = 2.0064$, $a_N = 13.6$ G.

Synthesis of the Hexafluorantimonate Salt of Bis(2,5-dihydro-4,5,5-trimethyl-2,2-bis(2-pyridyl)imidazole-1-oxyl)iron(II) (2). The same procedure as for **1** was followed, using $FeCl_2$. After 3 d, the product was isolated as a dark green powder: yield 125 mg (67%); dec >255 °C. Anal. Calcd for $C_{32}H_{34}N_8O_2FeSb_2F_{12}$: C, 35.26; H, 3.14; N, 10.28. Found: C, 35.15; H, 3.14; N, 10.08.

Synthesis of the Hexafluorantimonate Salt of Bis(2,5-dihydro-4,5,5-trimethyl-2,2-bis(2-pyridyl)imidazole-1-oxyl)cobalt(II) (3). The same procedure as for **1** was followed, using $CoCl_2$ and acetonitrile as solvent. Diethyl ether was added to the mixture of $Co(SbF_6)_2$ and the radical. After 4 weeks dark-brown crystals were isolated: yield 37 mg (66%); mp 323.5 °C. Anal. Calcd for $C_{32}H_{34}N_8O_2CoSb_2F_{12}$: C, 35.16; H, 3.14; N, 10.25. Found: C, 35.02; H, 3.16; N, 10.16. EPR (CH_3CN): $g = 2.0056$, $a_N = 13.1$ G.

Synthesis of the Hexafluorantimonate Salt of Bis(2,5-dihydro-4,5,5-trimethyl-2,2-bis(2-pyridyl)imidazole-1-oxyl)nickel(II) (4). The same procedure as for **1** was followed, using $NiCl_2$. After 3 weeks, the product was isolated as a red-brown powder: yield 133 mg (59%); dec >310 °C. Anal. Calcd for $C_{32}H_{34}N_8O_2NiSb_2F_{12}$: C, 35.17; H, 3.14; N, 10.25. Found: C, 35.03; H, 3.16; N, 10.11. EPR (CH_3CN): $g = 2.0077$, $a_N = 13.4$ G.

Synthesis of the Hexafluorantimonate Salt of Bis(2,5-dihydro-4,5,5-trimethyl-2,2-bis(2-pyridyl)imidazole-1-oxyl)copper(II) (5). The same procedure as for **4** was followed, using $CuCl_2$. After 1 week the product was isolated as a red-brown powder: yield 34 mg (32%); dec >250 °C. Anal. Calcd for $C_{32}H_{34}N_8O_2CuSb_2F_{12}$: C, 35.01; H, 3.12; N, 10.21. Found: C, 34.55; H, 3.15; N, 10.07. EPR (CH_3CN): $g = 2.0067$, $a_N = 13.9$ G.

Synthesis of the Hexafluorantimonate Salt of Bis(2,5-dihydro-4,5,5-trimethyl-2,2-bis(2-pyridyl)imidazole-1-oxyl)zinc (6). Same procedure as for **4** was followed, using $ZnCl_2$. After 2 weeks, the product was isolated as bright yellow crystals: yield 47 mg (32%); dec >275 °C. Anal. Calcd for $C_{32}H_{34}N_8O_2ZnSb_2F_{12}$: C, 34.96; H, 3.12; N, 10.19. Found: C, 34.59; H, 3.16; N, 9.77. EPR (CH_3CN): $g = 2.0066$, $a_N = 13.5$ G.

Synthesis of (2,5-Dihydro-4,5,5-Trimethyl-2,2-Bis(2-pyridyl)imidazole-1-oxyl)dichlorocopper (7). $CuCl_2$ (22.9 mg, 0.170 mmol) dissolved in methanol (10 mL) was treated with a solution of **L** (96.1 mg, 0.342 mmol) in methanol (5 mL). The mixture was stirred for 2 h and layered with diethyl ether. After 4 d, bright green plates and dark green crystals had precipitated. Both showed identical IR spectra and elemental analyses. Yield 48 mg (64%); mp 159−159.5 °C dec. Anal. Calcd for $C_{16}H_{17}N_4OCuCl_2{\cdot}CH_3OH$: C, 45.59; H, 4.72; N, 12.51. Found: C, 45.56; H, 4.52; N, 12.83. IR (KBr): 3448 m (OH), br, 1637 vs (C=N), 1599 s (py), 1463 vs, 1442 s, 1383 s, 1161 s, 1057 s, 1032 s, 1025 s, 778 s, 770 s, 762 s, 680 s, 675 s, 648 s, 612 s, 308 s, 288 s (Cu−Cl) cm^{-1}.

Synthesis of (Sulfato)(2,5-dihydro-4,5,5-trimethyl-2,2-bis(2-pyridyl)imidazole-1-oxyl)copper(II) Hemihydrate (8). A solution of **L** (104 mg, 0.370 mmol) in methanol (4 mL) was added to a solution of $CuSO_4{\cdot}5H_2O$ (92.4 mg, 0.370 mmol) in methanol (5 mL). The mixture was stirred for 1 d, methanol was removed in vacuo, and the residue was treated with boiling acetonitrile. A yellow-green precipitate was separated from the dark green solution. Small dark green crystals formed from the solution within 1 d and were collected, washed with a small amount of acetonitrile, and dried in vacuo: yield 68 mg (41%). Anal. Calcd for $C_{16}H_{17}N_4OCuSO_4{\cdot}{}^1/_2H_2O$: C, 42.71; H, 4.03; N, 12.45. Found: C, 42.64; H, 3.92; N, 12.27. IR (KBr): 3524 m, 3480 m, 3405 m (OH), 1641 s (C=N), 1602 s (py), 1217 s, 1147 vs, 1129 vs, 1122 vs, 1055 s, 1032 s, 977 s (SO_4), 779 s, 676 s, 618 s, 284 s, 275 s cm^{-1}.

Crystal Structure Determinations. The crystal structures were determined using a SYNTEX R3 diffractometer, using MoKα radiation and a graphite monochromator. The structures were solved with SHELXS 86 by the Patterson method and refined with SHELXL 93-PC on a Compaq PC with a 486 processor on a 66 MHz/8 MB RAM. This program uses full-matrix least-squares refinement on F^2, leading to R values (wR_2) different from those from the conventional refinement on F (R_1). All atoms except hydrogen were refined anisotropically, while the hydrogen atoms were refined isotropically with a temperature factor calculated by multiplication of the U_{eq} value of the corresponding carbon atom with a factor between 1.2 and 1.5 and with a fixed geometry using a riding model.

The three compounds all crystallize in space group $P2_1/n$, with the metal atoms residing on the inversion center at (0, 0, 0.5). The SbF_6^- anions always show substantial disorder. This was modeled by introducing the restraint of assuming a regular octahedron, keeping as well all Sb−F and all F−F cis distances within certain limits, and refining the site occupation factors, which turned out to be not far from 0.50.

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Table 1. Crystal Data and Structure Refinement

	1	**3**	**6**
empirical formula	$C_{32}H_{34}F_{12}Mn$-$N_8O_2Sb_2$	$C_{32}H_{34}CoF_{12}$-$N_8O_2Sb_2$	$C_{32}H_{34}F_{12}$-$N_8O_2Sb_2Zn$
fw	1089.11	1093.10	1099.54
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	10.806(3)	10.761(4)	10.788(2)
b, Å	14.101(6)	14.253(6)	14.147(3)
c, Å	14.253(4)	14.108(5)	14.196(3)
β, deg	108.82(2)	2017.9(13)	2036.8(7)
V, Å^3	2055.7(12)	2017.9(13)	2036.8(7)
Z	2	2	2
d(calc), g cm^{-3}	1.760	1.799	1.793
abs coeff, mm^{-1}	1.702	1.831	1.996
final *R* indices[a] $[I > 2\sigma(I)]$	$R_1 = 0.0677$ $wR_2 = 0.1512$	$R_1 = 0.0702$, $wR_2 = 0.1460$	$R_1 = 0.0573$ $wR_2 = 0.1194$

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, with $w = 1/\sigma^2(F_o^2) + (0.0600P)^2 + 0.15P$, where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$.

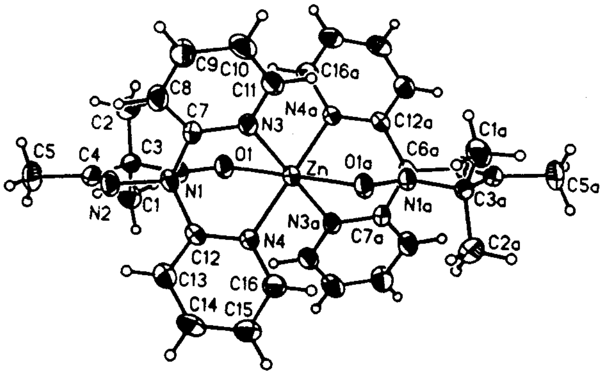

Figure 1. Molecular structure of **6**. The structures of **1** and **3** are practically identical with that of **6**.

Results and Discussion

The reactions of in situ prepared solutions of hexafluoroantimonate salts (from MCl_2 and $AgSbF_6$) of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) with the nitroxide radical **L** in methanol or acetonitrile gave the complexes **1**−**6**:

$$M(SbF_6)_2 + 2L \rightarrow [ML_2]^{2+}[SbF_6^-]_2$$

M	Mn	Fe	Co	Ni	Cu	Zn
	1	**2**	**3**	**4**	**5**	**6**

From $CuCl_2$ or $CuSO_4$ and the nitroxide **L** the complexes **7** and **8** were obtained:

$$\underset{\mathbf{7}}{Cu(\mathbf{L})(Cl)_2{\cdot}CH_3OH} \qquad \underset{\mathbf{8}}{Cu(L)SO_4{\cdot}{}^1/_2H_2O}$$

Structures (Figure 1). The X-ray structural determinations of **1**, **3**, and **6** show that two tridendate nitroxide ligands **L** are coordinated through the two pyridine N atoms and the oxygen atom of the nitroxide group. This coordination gives less strained six-membered chelate rings compared to five-membered rings, which would arise by coordination of the imidazoline N atom. The two O donors of both nitroxide groups are in *trans* positions.

Six-membered chelate complexes with coordination of the nitroxide O atom and the pyridine N atom of 2-pyridyl-substituted nitronyl nitroxides have been previously reported by Gatteschi[12] and Luneau et al.[13]

The pyridine N atom−metal distances decrease in the order Mn(II) > Zn(II) > Co(II), which corresponds to the change of the ionic radii.[14] The O−metal bond lengths vary to a much lesser extent, which may be due to the weak donor strength of the nitroxide group.[15] In accordance with this finding, the N−O distances of the coordinated nitroxide group (1.25−1.27 Å) do not differ remarkably from that of free nitroxides.[16]

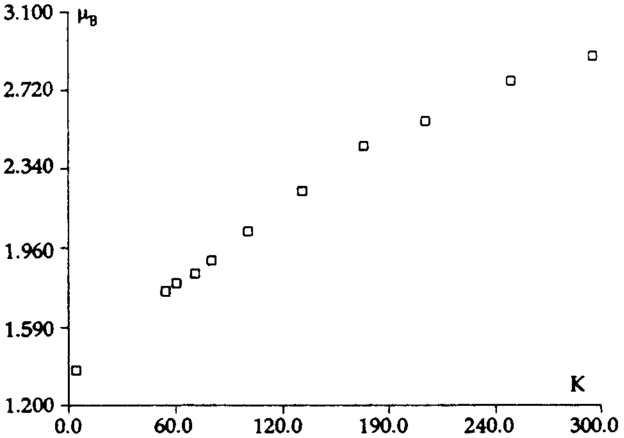

Figure 2. Magnetic moment of **5** vs temperature.

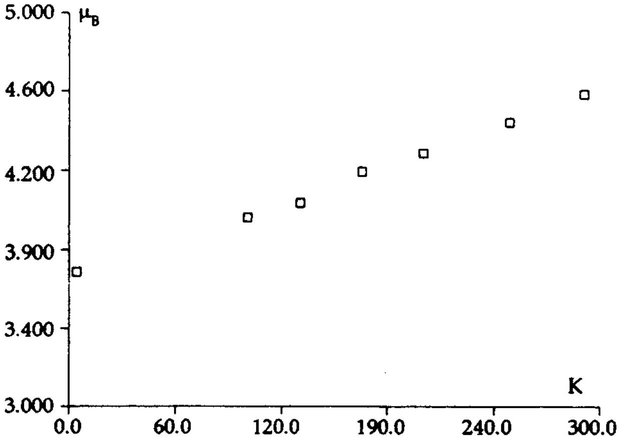

Figure 3. Magnetic moment of **1** vs temperature.

Table 2. Selected Bond Lengths (Å) for **1**, **3**, and **6**

	1	**3**	**6**
N1−O1	1.25(2)	1.267(13)	1.260(11)
N1−C3	1.50(2)	1.47(2)	1.467(14)
N1−C6	1.46(2)	1.48(2)	1.483(14)
M−O1	2.149(11)	2.104(10)	2.152(8)
M−N3	2.226(14)	2.091(11)	2.141(9)
M−N4	2.207(14)	2.056(12)	2.101(9)
N2−C4	1.24(2)	1.26(2)	1.26(2)

The angles around the N atom of the nitroxide group correspond to a sp^2 N atom. This and the N−O bond lengths show that the R_2N−O ligand is not a hydroxylaminate (expected N−O bond length ∼1.39 Å). Therefore, the formal oxidation state of the metal is +II. The O−M distance of 2.10−2.15 Å and the angle of ∼115° are found also in other nitroxide metal complexes.[17] The imidazoline ring in **1**, **3**, and **6** is nearly

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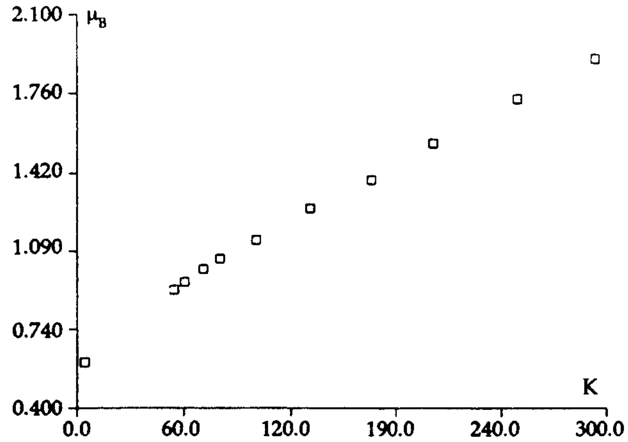

Figure 4. Magnetic moment of **2** vs temperature.

Table 3. Selected Bond Angles (deg) of **1**, **3**, and **6**

	1	3	6
C6−N1−O1	125.5(13)	124.3(11)	124.9(9)
C3−N1−O1	123(2)	123.6(12)	123.8(11)
C3−N1−C6	110.5(14)	111.2(11)	110.6(10)
N1−O1−M	117.0(10)	114.5(8)	114.2(7)
C7−N3−M	121.2(11)	119.2(10)	119.6(8)
C12−N4−M	120.1(12)	120.4(10)	120.0(8)
O1−M−N3	83.2(5)	86.6(4)	85.4(4)
O1−M−N4	83.9(5)	88.0(4)	86.6(4)
N3−M−N4	81.5(5)	84.9(5)	84.9(4)

planar. The C═N bond lengths are shortened to 1.24 and 1.26 Å in comparison to those of free 2,5-dihydroimidazole-1-oxyls.[11]

In the range 3000−700 cm^{-1} the IR spectra of **1**−**6** are identical; the same structure can be assumed for all these complexes.

Magnetic Properties. The zinc(II) complex **6** exhibits in the 60−300 K temperature range a magnetic moment $\mu = 2.44 \pm 0.03\ \mu_B$, which is expected for two noninteracting spins (2.45 μ_B).[3c] Obviously there is no exchange between the radicals through the orbitals of the d^{10} ion. At 4.2 K, a magnetic moment of 2.08 μ_B is observed for **6**, indicating small exchange among the nitroxide radicals. In contrast to the case of monomeric **6**, Gatteschi et al. reported a one-dimensional polymeric Zn(II) complex of a nitronyl nitroxide with antiferromagnetically coupled radicals at 5 K and an effective magnetic moment of 0.63 μ_B.[18]

The magnetic moment (Figure 2) of the copper(II) complex **5** at room temperature is 2.89 μ_B; this is a little lower than expected for three noninteracting spins (3.00 μ_B). At lower temperature, the magnetic moment of **5** decreases (60 K: 1.8 μ_B) due to antiferromagnetic coupling between the spins of the radicals and the Cu(II) d^9 ion. At 4 K ($\mu = 1.37\ \mu_B$), intermolecular interactions may occur. Whether the interaction of a nitroxide radical with a Cu^{2+} ion is antiferro- or ferromagnetic depends on the structure of the complex.[19]

For the manganese(II) complex **1**, $\mu = 4.59\ \mu_B$ at 291 K and 3.69 μ_B at 4 K (Figure 3). The expected spin-only values are 6.40 μ_B (high-spin d^5 Mn(II) and independent spins $S = {}^{5}/_{2} + 2{}^{1}/_{2}$) and 3.87 μ_B (spin coupling $S = {}^{3}/_{2}$). The observed values show strong antiferromagnetic interaction between Mn(II) and the radicals even at room temperature, which is observed with all known manganese(II) complexes of nitroxides.[6−9]

Only a few iron complexes with nitroxide radicals are known.[9,20] The iron complex **2** gave a magnetic moment $\mu = 1.81\ \mu_B$ at 293 K, which decreases to 1.0 μ_B at 60 K (Figure 4). We assume that iron has the oxidation state +II and is low spin d^6 ($S = 0$). Due to the orbital symmetry, there could be significant overlap between the π^* orbitals of the nitroxides in which the unpaired electron resides with the empty $d_{x^2-y^2}$ orbital of Fe^{2+}. The latter could function as a pathway for coupling of the spins.

The Cu(II) complexes **7** and **8** of unknown structure show at room temperature a magnetic moment of 2.54 μ_B (**7**) and 2.41 μ_B (**8**) which corresponds to two noninteracting spins (theoretical 2.45 μ_B). Below 60 K (**7**) and 190 K (**8**), respectively, strong antiferromagnetic coupling is observed (**7**, 4 K, 1.35 μ_B; **8**, 4 K, 0.4 μ_B). For **8**, the SO$_4$ absorptions in the IR spectra indicate that the sulfate ion is coordinated to the metal[21] (see Experimental Section).

EPR Spectra. The EPR spectra of **1**, **3**, **4**, and **5** in CH$_3$CN show a triplet which has to be attributed to the uncomplexed radical.[11] The EPR spectra of **2** and **6** show a triplet with two additional lines in very diluted CH$_3$CN solutions, while in more concentrated solutions five lines are observed. A possible explanation is that the coordinated nitroxide group is partially substituted by CH$_3$CN and the EPR pattern appears as a superposition of signals for free and coordinated ligands.

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Supporting Information Available: Complete tables of positional parameters, bond lengths and angles, and thermal parameters for **1**, **3**, and **6** (21 pages). Ordering information is given on any current masthead page.

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