Contribution from the Department of Chemistry, University of Florence, Florence, Italy, and Laboratoire de Chimie (UA CNRS 1194), Department de Recherche Fondamentale, Centre d'Etudes Nucleaires, F 38041 Grenoble, France

Structure and Magnetic Properties of Chains of Diamonds of Four Spins Formed by Metal(II) Hexafluoroacetylacetonates (Metal = Cobalt, Nickel) and the Nitronyl Nitroxide Radical 4,4,5,5-Tetramethyl-2-ethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-Oxide

A. Caneschi,[†] D. Gatteschi,*[†] J. Laugier,[‡] P. Rey,*[‡] and R. Sessoli[†]

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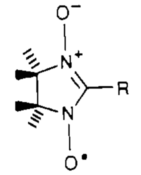
Metal hexafluoroacetylacetonates, $M(hfac)_2$ (M = Co, Ni), react with the nitronyl nitroxide radical 4,4,5,5-tetramethyl-2-ethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide, NITEt, yielding adducts of formula $[M(hfac)_2NITEt]_2$. The X-ray crystal structure of the cobalt derivative has shown that the compound crystallizes in the monoclinic system, space group $P\bar{1}$, with a = 10.996 (3) Å, b = 11.479 (4) Å, c = 13.311 Å, α = 60.97 (2)°, β = 65.28 (2)°, γ = 81.67 (2)°, and Z = 1. The structure consists of dinuclear $[Co(hfac)_2NITEt]_2$ centrosymmetric units, with the nitronyl nitroxide radical bridging two different metal ions through one of its oxygen atoms. Weak interactions between different $[M(hfac)_2NITEt]_2$ groups cause the magnetic properties to be those of chains rather than of discrete clusters. The intermolecular coupling constant of $[Ni(hfac)_2NITEt]_2$ has been calculated from the low-temperature magnetic data as $J' = 2\ cm^{-1}$ by applying the equation for $S = 1$ chains, while the intramolecular coupling constant has been estimated to be 300 cm^{-1} from the high-temperature data.

Introduction

Nitronyl nitroxides have been shown to be extremely efficient ligands toward transition-metal ions in yielding low-dimensional magnetic materials.[1-3] The ones we have employed have the general formula

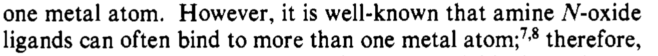


They are generally indicated as NITR, R being methyl (NITMe), ethyl (NITEt), and phenyl (NITPh).

The two oxygen atoms are equivalent; therefore, they are particularly well-suited to form chains by binding to two different moieties. They can bind to two different metal ions, yielding a sequence of the type

This has been experimentally observed, and ferromagnetic alternating-spin chains have been obtained with M = copper,[4] while ferrimagnetic chains have been obtained with M = manganese, the radical being NITMe.[5]

Chains can be formed also when one oxygen of NITR binds to a metal ion, while the second interacts with the oxygen atom of another radical. This behavior has already been observed[6] in $CuCl_2(NITPh)_2$, where the chains can be schematized as



In all these compounds the oxygen atom of a radical binds to one metal atom. However, it is well-known that amine *N*-oxide ligands can often bind to more than one metal atom;[7,8] therefore, it is conceivable that NITR radicals can yield also spin arrangements more complicated than those outlined above.

We have now found that the radical NITEt can bind in such a way that one of its oxygen atoms bridges two different metal ions (M = Co, Ni) in a μ-1,1 fashion while the other oxygen atom is involved in a weak interaction with the NO group of another NITEt molecule. Structurally this corresponds to a chain of $[M(hfac)_2(NITEt)]_2$ dimers (hfac = hexafluoroacetylacetonate) and magnetically to a chain of clusters of four spins, two from the metals and two from the radicals. We wish to report here the X-ray crystal structure of $Co(hfac)_2NITEt$ and the magnetic properties of $Co(hfac)_2NITEt$ and $Ni(hfac)_2NITEt$.

Table I. Crystallographic Data and Experimental Parameters

formula	$Co_2C_{38}F_{24}H_{38}N_4O_{12}$
mol wt	1316.6
cryst syst	triclinic
space group	$P\bar{1}$
cell params	a = 10.996 (3) Å, b = 11.479 (4) Å, c = 13.311 (4) Å, α = 60.97 (2)°, β = 65.28 (2)°, γ = 81.67 (2)°, Z = 1, V = 1330.9 Å^3
density	1.64 (calcd)
linear abs	$\mu = 0.8\ mm^{-1}$
cryst size	0.30 × 0.25 × 0.10 mm
temp	20 °C
radiation	takeoff angle 6°, wavelength 0.7107 Å (Mo Kα), graphite monochromator
bragg angle	$1 < \theta < 30°$
scan mode	ω
scan range	$0.8 + 0.35 \tan \theta$
scan speed	0.6–4°/min
detector window	height 4 mm, width $2.40 + 3.0 \tan \theta$
test rflns	(134), 0,–3,3)
hkl range	$-15 \leq h \leq 15, -16 \leq k \leq 16, 0 \leq l \leq 18$
total no. of rflns	8055
no. of rflns with $F < 3\sigma(F)$	3335
refinement	$R = 0.054$, $R_w = 0.053$, $w = 1/\sigma^2$

Experimental Section

Syntheses of the Complexes. The $Co(hfac)_2$ and $Ni(hfac)_2$ salts were prepared by mixing a water solution of $M(CH_3COO)_2 \cdot nH_2O$ with the stoichiometric amount of hfac; immediately a precipitate appeared, which was filtered, washed with cold water, and dried under vacuum on silica gel. The NITEt radical was prepared according to the literature.[9,10] One millimole of $M(hfac)_2$ was dissolved in 80 mL of hot dry *n*-heptane, then 1 mmol of the NITEt radical was added, and the solution was stirred for a few minutes and filtered. Good red-brown crystals were obtained after 10–12 h at room temperature.

The cobalt compound gave a satisfactory analysis for $Co(hfac)_2NITEt$. Anal. Calcd for $CoC_{19}F_{12}H_{19}N_2O_6$: C, 34.65; H, 2.89;

[†] University of Florence.

[‡] Centre d'Etudes Nucleaires.

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Table II. Positional Parameters ($\times 10^4$)[a]

	x	y	z	B_{eq}, Å^2
Co	800 (1)	312 (1)	3510 (1)	2.57
O1	2088 (4)	1854 (4)	1898 (4)	4.41
O2	−695 (4)	1364 (4)	3010 (4)	3.10
O3	919 (4)	−621 (4)	2485 (4)	3.10
O4	2386 (4)	−699 (4)	3790 (4)	2.65
O5	623 (3)	1044 (3)	4742 (3)	2.05
O6	1197 (5)	5446 (5)	3690 (5)	4.11
N1	1187 (4)	2170 (5)	4456 (4)	2.10
N2	1478 (5)	4237 (5)	3934 (5)	2.91
F1	4032 (6)	2436 (6)	−368 (5)	17.85
F2	2925 (6)	3823 (7)	−1288 (5)	14.93
F3	3594 (6)	4163 (7)	−207 (6)	9.45
F4	−2476 (6)	1420 (6)	1949 (7)	4.16
F5	−1763 (5)	3361 (6)	629 (5)	10.04
F6	−2705 (5)	2856 (6)	2521 (5)	7.93
F7	2063 (8)	−177 (6)	−40 (5)	7.17
F8	790 (7)	−1834 (6)	1247 (6)	3.84
F9	2818 (7)	−2036 (8)	604 (7)	8.76
F10	5244 (5)	−2247 (7)	2850 (7)	7.52
F11	4136 (6)	−2446 (9)	4561 (7)	16.43
F12	5135 (6)	−694 (7)	3183 (9)	4.67
C1	1848 (7)	2504 (6)	932 (6)	5.06
C2	603 (7)	2685 (7)	846 (6)	5.14
C3	−562 (6)	2131 (6)	1901 (6)	3.12
C4	3098 (9)	3210 (10)	−290 (9)	8.29
C5	−1873 (8)	2461 (8)	1744 (8)	4.39
C6	1954 (7)	−1070 (6)	1966 (6)	3.07
C7	3106 (7)	−1359 (7)	2210 (7)	3.46
C8	3194 (6)	−1171 (6)	3123 (6)	2.96
C9	1937 (10)	−1291 (10)	933 (9)	4.36
C10	4450 (8)	−1624 (10)	3388 (10)	4.13
C11	630 (5)	3314 (5)	4151 (5)	2.40
C12	2769 (7)	3708 (8)	3947 (10)	4.24
C13	2505 (7)	2254 (6)	4536 (7)	2.43
C14	3589 (9)	4414 (8)	4092 (11)	2.62
C15	3637 (10)	4067 (12)	2424 (10)	10.50
C16	1974 (9)	1960 (12)	6020 (9)	7.30
C17	3382 (7)	1364 (10)	4316 (13)	3.59
C18	−676 (6)	3609 (6)	4041 (6)	3.02
C19	−558 (9)	4679 (7)	2737 (7)	4.51

[a] Standard deviations in the last significant digits are in parentheses.

Table III. Bond Lengths (Å)[a]

Co–Co	3.334 (2)	C7–C8	1.375 (14)
Co–O1	2.060 (3)	C8–C10	1.524 (12)
Co–O2	2.041 (4)	C11–C18	1.479 (9)
Co–O3	2.063 (6)	C12–C13	1.471 (10)
Co–O4	2.016 (4)	C12–C14	1.420 (19)
Co–O5	2.105 (2)	C12–C15	1.696 (16)
O5–N1	1.326 (7)	C13–C16	1.674 (15)
O6–N2	1.284 (7)	C13–C17	1.352 (12)
O1–C1	1.255 (9)	C18–C19	1.525 (9)
O2–C3	1.253 (7)	C1–C4	1.261 (11)
O3–C6	1.247 (7)	F2–C4	1.250 (13)
O4–C8	1.240 (8)	F3–C4	1.359 (17)
N1–C11	1.312 (7)	F4–C5	1.305 (13)
N1–C13	1.517 (10)	F5–C5	1.297 (9)
N2–C11	1.356 (9)	F6–C5	1.287 (11)
N2–C12	1.464 (9)	F7–C9	1.276 (9)
C–C2	1.399 (11)	F8–C9	1.299 (14)
C1–C4	1.539 (9)	F9–C9	1.277 (13)
C2–C3	1.373 (7)	F10–C10	1.257 (14)
C3–C5	1.511 (12)	F11–C10	1.289 (12)
C6–C7	1.392 (12)	F12–C10	1.249 (15)
C6–C9	1.522 (17)		

[a] Standard deviations in the last significant digits are in parentheses.

Table IV. Bond Angles (deg)[a]

O1–Co–O2	85.7 (1)	F6–C5–C3	112.1 (9)
O1–Co–O3	89.4 (2)	O3–C6–C7	127.5 (8)
O1–Co–O4	89.9 (1)	O3–C6–C9	114.9 (7)
O1–Co–O5	171.1 (2)	C7–C6–C9	117.6 (7)
O2–Co–O3	88.3 (2)	C6–C7–C8	120.6 (7)
O2–Co–O4	173.0 (2)	O4–C8–C7	129.6 (7)
O2–Co–O5	90.7 (1)	O4–C8–C10	114.0 (8)
O3–Co–O4	86.2 (2)	C7–C8–C10	116.4 (7)
O3Co–O5	98.7 (1)	F7–C9–F8	104.0 (10)
O4–Co–O5	94.4 (1)	F7–C9–F9	108.4 (8)
O5–Co–O5	75.5 (1)	F7–C9–C6	110.6 (10)
Co–O5–N1	127.6 (3)	F8–C9–F9	105.5 (11)
Co′–O5–N1	127.7 (3)	F8–C9–C6	112.0 (7)
O5–N1–C11	123.9 (5)	F9–C9–C6	115.6 (10)
O5–N1–C13	123.5 (4)	F10–C10–F11	103.2 (8)
C11–N1–C13	112.5 (5)	F10–C10–F12	106.8 (7)
O6–N2–C11	123.7 (5)	F10–C10–C8	117.7 (12)
O6–N2–C12	124.4 (6)	F11–C10–F12	103.8 (12)
C11–N2–C12	111.9 (6)	F11–C10–C8	110.8 (6)
O1–C1–C2	128.2 (5)	F12–C10–C8	113.2 (8)
O1–C1–C4	114.4 (7)	N1–C11–N2	107.8 (5)
C2–C1–C4	117.4 (6)	N1–C11–C18	128.3 (6)
C1–C2–C3	120.8 (6)	N2–C11–C18	123.9 (5)
O2–C3–C2	128.2 (6)	N2–C12–C13	103.8 (6)
O2–C3–C5	114.1 (4)	N2–C12–C14	117.2 (8)
C2–C3–C5	117.7 (6)	N2–C12–C15	101.0 (8)
F1–C4–F2	111.5 (9)	C13–C12–C14	128.2 (9)
F1–C4–F3	103.8 (9)	C13–C12–C15	100.3 (9)
F1–C4–C1	111.4 (6)	C14–C12–C15	101.4 (7)
F2–C4–F3	104.8 (7)	N1–C13–C12	101.4 (6)
F2–C4–C1	117.1 (8)	N1–C13–C16	101.3 (5)
F3–C4–C1	107.0 (9)	N1–C13–C17	115.0 (9)
F4–C5–F5	104.3 (10)	C12–C13–C16	96.5 (8)
F4–C5–F6	106.2 (6)	C12–C13–C17	127.3 (6)
F4–C5–C3	111.5 (6)	C16–C13–C17	111.3 (9)
F5–C5–F6	107.2 (6)	C11–C18–C19	113.4 (5)
F5–C5–C3	114.9 (5)		

[a] Standard deviations in the last significant digits are in parentheses.

N, 4.25; Co, 8.97. Found: C, 34.78; H, 2.87; N, 4.21; Co, 8.75.

The nickel compound gave a satisfactory analysis for Ni(hfac)$_2$NITEt. Anal. Calcd for $NiC_{19}F_{12}H_{19}N_2O_6$: C, 34.65; H, 2.89; N, 4.25; Ni, 8.92. Found: C, 34.61; H, 2.93; N, 4.07; Ni, 8.65.

X-ray Data Collection and Reduction. Weissenberg photographs taken for a regularly shaped crystal of the cobalt compound (0.30 × 0.25 × 0.10 mm) revealed Laue symmetry and exhibited systematic absences that were only consistent with the triclinic space group $P\bar{1}$. The same crystal was mounted on a Enraf-Nonius CAD-4 four-circle diffractometer with monochromatized Mo Kα radiation. Accurate cell constants were derived from least-squares refinement on the setting angle of 25 indexed reflections in the $25° < 2\theta < 30°$ range and are reported in Table I with other crystal data. The intensities of 8055 independent reflections were collected. Two standard reflections were periodically checked and showed no significant discrepancy. The data were corrected for the Lorentz-polarization factor but not for absorption or extinction. For the independent reflections collected 3335 had $F_o > 3\sigma(F_o)$ and were used to refine the structural parameters.

Structure Solution and Refinement. The position of the cobalt atom was identified by means of sharpened Patterson functions. The structure was then developed, assuming the space group $P\bar{1}$, by iterating least-squares refinements and Fourier syntheses.[11] The hydrogen atoms were included in fixed and idealized positions. Final refinement using anisotropic temperature factors for all non-hydrogen atoms converged to the R value of 0.054.

The final atomic positional parameters are listed in Table II and bond lengths and angles in Tables III and IV, respectively.

Magnetic Susceptibility Measurements. Magnetic susceptibilities were measured between 5 and 300 K by using an SHE superconducting SQUID susceptometer at a field strength of 0.5 T. Data were corrected for the magnetization of the sample holder and for diamagnetic contributions, which were estimated from Pascal's constants.

Electronic Reflectance Spectra. The electronic reflectance spectra were recorded at room temperature in the range 5000–35 000 cm^{-1} with a Perkin-Elmer Lambda 9 spectrophotometer.

Results

Crystal Structure. In Figure 1 are shown the asymmetric unit and the labeling of the atoms. The crystal structure of [Co(hfac)$_2$NITEt]$_2$ consists of centrosymmetric dimers, as shown in Figure 2. Bond distances and angles are shown in Tables III and

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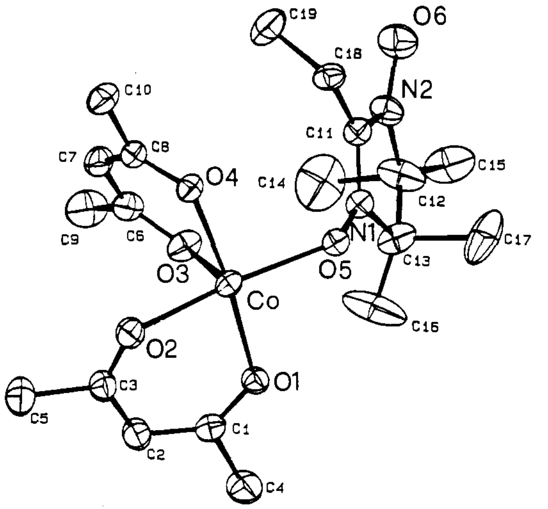


Figure 1. ORTEP view of the Co(hfac)$_2$NITEt asymmetric unit.

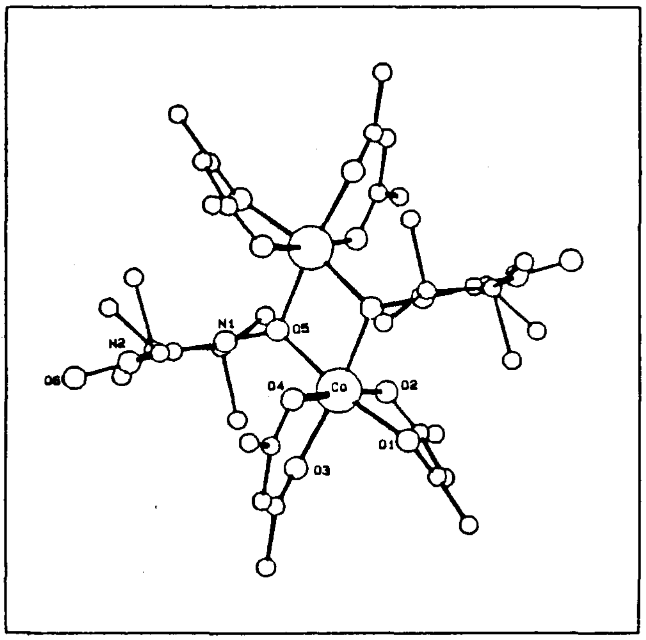


Figure 2. Sketch of the [Co(hfac)$_2$NITEt]$_2$ dimer.

IV, respectively. Each cobalt(II) ion is hexacoordinated by two hfac molecules and two oxygen atoms of two different NITEt radicals. This is the first example of a nitroxyl group functioning as a bridging ligand in a μ-1,1 fashion. The metal–hfac oxygen distances are fairly similar to each other, ranging from 2.016 (4) to 2.063 (6) Å, while the cobalt–NITEt oxygen distances are longer, 2.105 (2) and 2.111 (2) Å. The cobalt–cobalt distance is 3.334 (2) Å, and the Co–O5–Co angle is 104.5 (1)°. This can be compared with values larger than 108° reported for bis(μ-pyridine *N*-oxide) copper(II) complexes.[12-15] The other O–Co–O angles are close to 90° as expected.

The nitronyl nitroxide fragment has its usual shape.[4,6,16] However, the five-membered ring (N1–C11–C12–C13–N2) is planar, in contrast to the case for several known examples of the 2-phenyl derivative, in which the twisting of carbon atoms C12 and C13 is believed to release steric hindrance in the *gem*-dimethyl groups. These methyl groups are, however, arranged in order to minimize steric interactions. Two of them, C15 and C16, bound respectively to C12 and C13, are positioned such that the C12–C15 and C13–C16 bonds are almost perpendicular to the ring plane.

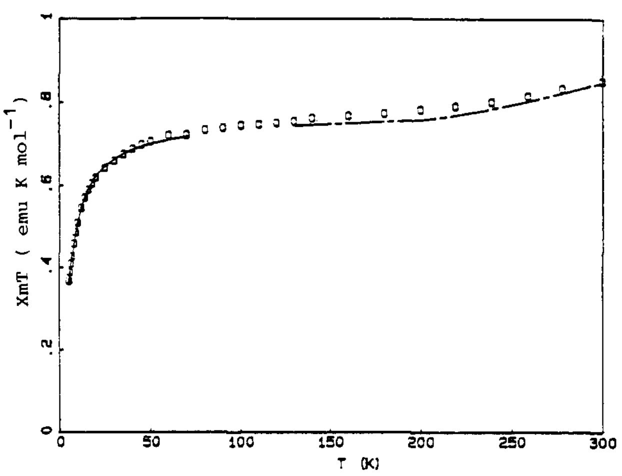
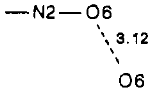


Figure 3. Temperature dependence of $\chi_M T$ for Ni(hfac)$_2$NITEt: (solid line) values calculated for a chain of spin $S = 1$; (broken line) values calculated for a cluster of four spins.

At the same time the other methyl groups C14 and C17 are very close to the mean ring plane so that the main interactions occur with the C–N bonds. It is very likely that, owing to the lower steric requirement of the nitrogen atom, this arrangement is the conformation of lowest energy. As shown in Table II, the two axial methyl groups have very long bond lengths of ca. 1.60 Å while the two equatorial ones have short bond lengths of ca. 1.40 Å. Difference Fourier maps did not give evidence for any alternative internally consistent set of methyl groups and showed that the refined position accounted for the expected electron density associated with the carbon atoms. Although some similar bond lengthening and shortening has been observed for dimethyl groups, this effect remains unexplained.

The system O5–N1–C11–N2–O6, which contains the unpaired electron, is perfectly planar and is perpendicular (87.2°) to the four-membered ring containing the metal atoms. The methyl group of the 2-ethyl substituent is oriented in such a way that the C11–C18–C19 plane is parallel (1.3°) to the mean plane of the nearest hfac ligand.

The only relevant interdimer contacts are found between the uncoordinated oxygen atoms of the nitronyl nitroxide:



The planes of the corresponding nitroxides are parallel to each other because they are related by the inversion center, and they form an angle of 65.6° with the plane defined by the two N–O groups.

If we consider this interaction as significant, we may describe the structure as a chain of [Co(hfac)$_2$NITEt]$_2$ moieties along the *b* axis. A confirmation for this comes from the analysis of the magnetic data (see below).

We did not obtain crystals of the nickel derivative suitable for an X-ray structure determination, but the powder spectrum was satisfactorily reproduced by the cell parameters of [Co(hfac)$_2$NITEt)]$_2$.

Magnetic Properties. The temperature dependence of the magnetic susceptibility of Ni(hfac)$_2$NITEt, in the form χT vs T, is shown in Figure 3: the susceptibility is in reference to the formula unit Ni(hfac)$_2$NITEt. In the whole temperature range 5–300 K χT decreases smoothly; however, the rate of decrease is smaller at higher temperatures, and it becomes much steeper below ca. 80 K. The room-temperature value, 0.850 emu K mol^{-1}, is lower than the high-temperature limit, 1.375 emu K mol^{-1}, expected for $g = 2$, suggesting an antiferromagnetic interaction between the spins. This is confirmed by the low-temperature value, 0.367 emu K mol^{-1}, lower than that expected for one unpaired electron.

The temperature dependence of the magnetic susceptibility of Co(hfac)$_2$NITEt, in the form χT vs T, is shown in Figure 4. χT

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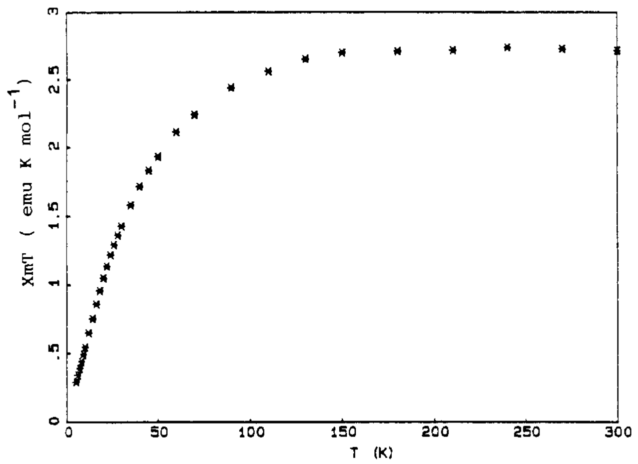

Figure 4. Temperature dependence of $\chi_M T$ for Co(hfac)$_2$NITEt.

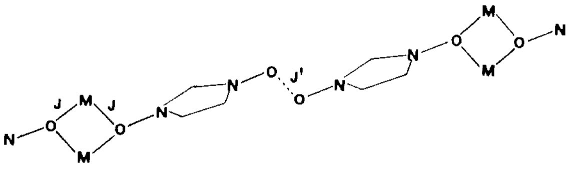

Figure 5. Schematic view of chains of diamonds of four spins.

is substantially constant in the range 300–120 K, with a value of ca. 2.7 emu K mol^{-1}, and below 120 K it decreases smoothly, reaching a value of 0.292 emu K mol^{-1} at 5 K.

Electronic Spectra. The electronic reflectance spectra of Co(hfac)$_2$NITEt in the solid state reveal two peaks, near 8500 and 16 000 cm^{-1}, comparable to the $^4T_{2g}$ (8470 cm^{-1}) and $^4A_{2g}$ (15 700 cm^{-1}) transitions[17,18] observed in Co(MeOH)$_6^{2+}$, while in the electronic spectra of Ni(hfac)$_2$NITEt two peaks are observed, near 8950 and 13 700 cm^{-1}, comparable to the $^3T_{2g}$ (8500 cm^{-1}) and $^3T_{1g}$ (13 800) transitions[17] of Ni(H$_2$O)$_6^{2+}$. In the two spectra the main peak of the radical is also present, corresponding to the n–π^* transition, at the same value of the free radical absorption[10] (18 500 cm^{-1}).

Discussion

The magnetic properties of both Ni(hfac)$_2$NITEt and Co(hfac)$_2$NITEt can be best understood as chains of diamonds of four spins, as indicated in Figure 5. At the simplest level of approximation the four M–O coupling constants J are taken as equal, the non-nearest-neighbor interactions are neglected, and the additional constant J' is associated with the intermolecular coupling between the NO groups of two radicals. As noted in the description of the structure, the O–O distances are such that a small direct overlap between the π^* orbitals is possible. The analysis of the magnetic properties of such a chain, with J and J' having any relative value, is certainly difficult; however, many simplifications are possible if $J > J'$, because in this case the clusters of four spins must all be in the ground S state before the effect of J' is noticeable and the magnetic data at low temperature can be interpreted as for chains of spin S, while at high temperature the clusters can be treated as if they were isolated.

That this can indeed be the case is shown by the rather flat curves of χT at high temperature; therefore, we will attempt an interpretation of the magnetic properties of Ni(hfac)$_2$NITEt and Co(hfac)$_2$NITEt following these lines.

Rings of four spins, $S_1S_2S_1S_2$, with $S_1 = {}^1/_2$ and S_2 variable, have been often considered with the purpose of extrapolating the magnetic properties of chains.[19,20] With only nearest-neighbor interactions included, the ground state for the ring is $S = 2(S_2 - S_1)$ for an antiferromagnetic and $S = 2(S_2 + S_1)$ for a ferromagnetic interaction. The limit χT values, calculated for one pair are

$$T = g_s^2\frac{S(S+1)}{16}$$

The g_s values are expected to be given by

$$g_s = c_1g_1 + c_2g_2$$

where $c_1 = [S(S+1) + S_1(S_1+1) - S_2(S_2+1)]/2S(S+1)$ and $c_2 = [S(S+1) + S_2(S_2+1) - S_1(S_1+1)]/2S(S+1)$.

In the case of nickel, for which $S_2 = 1$, S can be either 1 for antiferromagnetic or 2 for ferromagnetic coupling. The g value is not known, but since for hexaaquo ions it has been reported[21–23] in the range 2.25–2.30, and the electronic spectra of Ni(hfac)$_2$NITEt indicate that the average Dq value is similar to that of water, we may use $g_{Ni} = 2.30$ to obtain[24] $g = 2.40$ for $S = 1$ and 2.20 for $S = 2$. Consequently, the limit values for χT are 0.720 emu K mol^{-1} for $S = 1$ and 2.160 emu K mol^{-1} for $S = 2$. Since the room-temperature value is 0.850 emu K mol^{-1}, the latter value must be discarded. As a consequence the ground state for the (NiNITEt)$_2$ cluster must be $S = 1$. A confirmation for this comes from the χT value at 80 K, 0.734 emu K mol^{-1}, in substantial agreement with the value calculated above. The fact that χT increases on increasing temperature above 80 K shows that J is large but not infinite. The high-temperature data (130–300 K) can be calculated with the following formula for the magnetic susceptibility:

$$\chi = \frac{N\mu\beta^2g^2\sum_i S_i(S_i+1)(2S_i+1)\exp(-E_i/kT)}{6kT\sum_i(2S_i+1)\exp(-E_ikT)}$$

where S_i is the total spin state of the clusters of four spins. The curve shown in Figure 3 was calculated for $g = 2.45$ and $J = 300$ cm^{-1}. We did not attempt to arrive at a best fit because the number of significant points, i.e. experimental points significantly different from the plateau value, is rather limited and the calculated curve is not very sensitive to the J value in this range of temperature. However, the calculated curve satisfactorily reproduces the experimental points and clearly shows that the intracluster antiferromagnetic coupling is strong.

The low-temperature data can be fit with the formulas that are valid[25–27] for chains of $S = 1$. Using Weng's procedure[26] as modified by Meyer et al.,[27] we find the best fit reported in Figure 2 with $J' = 2.006$ (3) cm^{-1}, $g = 2.47$ (1), and $R^{28} = 1.668 \times 10^{-4}$. Essentially identical results were obtained with the Fischer model of classical spins.[29] In our procedure we have neglected zero-field splitting effects and complications that might originate from the Haldane conjecture.[30,31] The value of J' observed here may be compared with $J = 15$ cm^{-1} reported for Cu(NITPh)$_2$Cl$_2$. The treatment of the magnetic data of Co(hfac)$_2$NITEt is complicated by the fact that octahedral cobalt(II) has a ground $^4T_{1g}$ state,

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which can yield large anisotropy components in the spin Hamiltonian. However, we may assume that at high temperature it is possible to treat the spin state of cobalt(II) with an effective $S = {}^3/_2$ and a g value sensibly different from 2. In this scheme the total spin states for the $(\mathrm{CoNITEt})_2$ clusters are $S = 2$ for antiferromagnetic and $S = 4$ for ferromagnetic coupling. The latter can be immediately discarded, because, even with a spin-only formalism, which clearly underestimates the cobalt contribution, it requires $\chi T = 5$ emu K mol^{-1}, much larger than the experimental value. Therefore, it can be reasonably assumed that also in $\mathrm{Co(hfac)_2NITEt}$ the intracluster coupling is antiferromagnetic. In fact, for $S = 2$ the limit χT value can be reproduced by using for the cluster $g = 2.68$. This value, in turn, can be used to calculate the individual g value for cobalt, $g_{\mathrm{Co}} = 2.54$, which yields a simple ion χT value of 3.03 emu K mol^{-1}, in excellent agreement with values ranging from 2.82 to 3.30 emu K mol^{-1} found in a series of adducts of cobalt(II) complexes of β-diketonates. The fact that the χT curve is essentially flat at high temperature shows that the ground $S = 2$ level of the cluster is the only one to be populated even at room temperature. It seems further that J must be at least as in the nickel derivative.

The low-temperature magnetic behavior is more difficult to analyze, because the single-ion cobalt(II) energy levels become largely depopulated, until eventually a single Kramers doublet is occupied. In this limit antiferromagnetic coupling within the cluster yields a nonmagnetic ground state. Therefore, the low χT value observed at 5 K may be justified by both intra- and intermolecular effects. However, by analogy with the nickel derivative, it can be assumed that intermolecular effects play a significant role.

The extent of the coupling between both metal ions and radicals is fairly large. This is easily understood on the basis of exchange pathways involving the $x^2 - y^2$ and z^2 orbitals of the metals and the π^* orbitals of the radicals. Indeed, the structure shows that the latter lie practically in the $\mathrm{Co_2O_2}$ plane, thus maximizing the overlap with the $x^2 - y^2$ and z^2 orbitals. It must be recalled here that copper(II) complexes in which the nitroxide is equatorially bound all show very strong antiferromagnetic coupling.[32-35]

Conclusions. The present investigation has shown the versatility of the nitronyl nitroxide radicals in yielding complex architectures of magnetic structures with transition-metal ions. It is confirmed that, although the magnetic orbital can overlap with appropriate magnetic orbitals on the metals, the spin pairing is incomplete, and finite coupling constants can be observed.

Registry No. $\mathrm{Co(hfac)_2NITEt}$, 113218-91-0; $\mathrm{Ni(hfac)_2NITEt}$, 113218-92-1; $\mathrm{Co(hfac)_2}$, 19648-83-0; $\mathrm{Ni(hfac)_2}$, 14949-69-0.

Supplementary Material Available: Tables SI and SIII (anisotropic thermal parameters and derived hydrogen positions for $[\mathrm{Co(hfac)_2NITEt}]_2$, respectively) and Tables SIV and SV (observed values of the χT product for the cobalt and nickel derivatives, respectively) (5 pages); Table SII (calculated and observed structural factors for the cobalt derivative) (17 pages). Ordering information is given on any current masthead page.

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Contribution from the Fachbereich Chemie, Universität Oldenburg, D-2900 Oldenburg, FRG,
and Department of Chemistry, Gorlaeus Laboratories, Leiden University, 2300 RA Leiden, The Netherlands

Synthetic and Structural Studies on the Novel Nitrogen Ligand 2,5,8,10,13,16-Hexaazapentacyclo[8.6.1.$1^{2,5}$.$0^{9,18}$.$0^{13,17}$]octadecane and Its Reaction Products with Methanolic Cadmium Halogenide Solutions: C_i-$\mathrm{C_{12}H_{22}N_6}$, $[\mathrm{CdX_2}(C_2\text{-}\mathrm{C_{12}H_{22}N_6})]$ (X = Cl, Br, I), and $[\mathrm{CdI_2(C_{12}H_{23}N_6OCH_3)}]$

Henry Strasdeit,*[1a] Wolfgang Saak,[1a] Siegfried Pohl,[1a] Willem L. Driessen,[1b] and Jan Reedijk[1b]

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Ethanolic solutions of diethylenetriamine and aqueous glyoxal react to give the novel 2:2 condensation product C_i-$\mathrm{C_{12}H_{22}N_6}$ (**1**). In methanol equimolar amounts of **1** and $\mathrm{CdX_2}$ (X = Cl, Br, I) yield $[\mathrm{CdCl_2}(C_2\text{-}\mathrm{C_{12}H_{22}N_6})]$ (**2**), $[\mathrm{CdBr_2}(C_2\text{-}\mathrm{C_{12}H_{22}N_6})]\cdot 2\mathrm{MeOH}$ (**3**), and $[\mathrm{CdI_2}(C_2\text{-}\mathrm{C_{12}H_{22}N_6})]\cdot 2\mathrm{MeOH}$ (**4**), respectively. On small variations in the $\mathrm{CdI_2}$/**1**/MeOH system the compound $[\mathrm{CdI_2(C_{12}H_{23}N_6OCH_3)}]\cdot\mathrm{MeOH}$ (**5**) crystallizes instead of **4**. All five products have been structurally characterized by single-crystal X-ray diffraction (space group; unit cell parameters; Z; R, R_w (%)). **1**: $P2_1/c$; $a = 7.415$ (1) Å, $b = 5.780$ (1) Å, $c = 14.196$ (1) Å, $\beta = 98.32$ (1)°; 2; 3.5, 3.9. **2**: $Pbcn$; $a = 15.840$ (1) Å, $b = 7.968$ (1) Å, $c = 12.868$ (1) Å; 4; 2.2, 2.4. **3**: $C2/c$; $a = 21.795$ (2) Å, $b = 7.885$ (1) Å, $c = 18.023$ (1) Å, $\beta = 137.77$ (1)°; 4; 2.8, 3.0. **4**: $Pccn$; $a = 9.232$ (1) Å, $b = 14.571$ (1) Å, $c = 16.465$ (1) Å; 4; 3.0, 3.1. **5**: $P2_1/c$; $a = 15.986$ (1) Å, $b = 9.142$ (1) Å, $c = 15.289$ (1) Å, $\beta = 97.17$ (1)°; 4; 3.9, 3.8. The centrosymmetric hexaamine (or "tetraaminal") molecules in solid **1** are pentacyclic with three $\mathrm{C_4N_2}$ and two $\mathrm{C_3N_2}$ rings. In methanolic $\mathrm{CdX_2}$ solutions they undergo a configurational change to the axially symmetric "C_2" form. C_2-$\mathrm{C_{12}H_{22}N_6}$ acts as a tetradentate ligand in the six-coordinate $[\mathrm{CdX_2(C_{12}H_{22}N_6)}]$ complexes, which are situated on crystallographic twofold axes in **2**–**4**. Two of the Cd–N bonds are "normal" (2.369 (2) (**2**), 2.336 (3) (**3**), 2.372 (4) Å (**4**)), while the other two are "secondary" bonds (2.625 (2) (**2**), 2.736 (3) (**3**), 2.739 (4) Å (**4**)). The coordination polyhedra are derived from distorted $\mathrm{N_2X_2}$ tetrahedra by insertion of the two weakly bonded N atoms near the N···N tetrahedral edge. Geometrical changes with increasing softness of the halogenide and the comparison of calculated and experimental (2.468 (1) (**2**), 2.586 (1) (**3**), 2.774 (1) Å (**4**)) Cd–X bond lengths suggest a high electron density at the metal atom in the iodo complex. This is consistent with the observed lowering of the Cd coordination number from 6 to 5 by formation of $[\mathrm{CdI_2(C_{12}H_{23}N_6OCH_3)}]$. The tridentate $\mathrm{C_{12}H_{23}N_6OCH_3}$ ligand in **5** is derived from C_i-$\mathrm{C_{12}H_{22}N_6}$ by covalent addition of methanol. Addition and elimination of methanol is a plausible pathway for the observed $C_i \rightarrow C_2$ transformation of $\mathrm{C_{12}H_{22}N_6}$ on coordination. The Cd atom in **5** has a distorted-square-pyramidal $\mathrm{N_3I_2}$ environment (Cd–N: 2.325 (7), 2.393 (5), 2.506 (5) Å; Cd–I: 2.775 (1) (apical), 2.812 (1) Å (basal)). In all five compounds hydrogen bonding is present (N–H···N (**1**); O–H···N, N–H···O (**3**, **4**)) or at least possible (N–H···Cl (**2**), O–H···N (**5**)).

Introduction

The mobilization and immobilization of cadmium in the environment, in organisms, and in some technical processes can depend significantly on the complexation by chelating organic molecules, especially by those containing nitrogen or sulfur donor atoms. For example, anthropogenic chelators released into the environment, humic acids, and several types of chelators produced by microorganisms contribute to the transfer of cadmium between solid and aqueous phases.[2]

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(1) (a) Universität Oldenburg. (b) Leiden University.

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