3230 *Inorg. Chem.* **1989**, *28*, 3230-3234

in other IR studies.[7,8] The radiolabeling experiments, if correct, would preclude the appearance of any significant amount of label into the axial position in the time of the IR experiment. It is therefore reasonable to conclude that the earlier radiochemical exchange results are incorrect.

In summary, our applications of the principles of microscopic reversibility and of detailed balancing to the understanding of the exchange reactions of M(CO)$_5$X compounds are in agreement with Jackson's positions. I regard his discussion of the fluxionality of the five-coordinate intermediate, to the extent that it depends on the assumption of the correctness of early radiochemical carbon exchange work, as incorrect. In this connection, Davy and Hall have recently completed extensive calculations of the barriers to CO loss in Mn(CO)$_5$Cl.[11] Their results support the concept of a strong cis-labilizing influence for Cl as heteroligand. Their calculations also predict a high barrier for conversion of the intermediate resulting from radial CO loss to the intermediate resulting from axial CO loss. Thus, the *direct* interconversion between these two intermediates would not, according to these calculations, provide a means for scrambling of the CO groups in the Mn(CO)$_4$X intermediate. However, their calculations show that an indirect process, proposed by Lichtenberger and Brown,[12] permits exchange in the five-coordinate intermediate via a low-energy pathway.

---

(11) Davy, R. D.; Hall, M. B. *Inorg. Chem.*, in press.

(12) Lichtenberger, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 366.

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

One-Dimensional Magnetism of a Linear Chain Compound Containing Yttrium(III) and a Nitronyl Nitroxide Radical

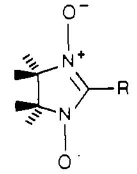
Cristiano Benelli, Andrea Caneschi, Dante Gatteschi,* Luca Pardi, and Paul Rey

Received February 16, 1989

Y(hfac)$_3$NITEt (hfac = hexafluoroacetylacetonate; NITEt = 2-ethyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy 3-oxide) crystallizes in the monoclinic space group $P2_1/n$ with cell parameters a = 11.245 (1) Å, b = 17.257 (7) Å, c = 18.357 (3) Å, β = 98.39 (1)°, V = 3524.13 Å^3, and Z = 4. The crystal structure determination converged with R = 0.132. The molecular structure consists of linear chains made by Y(hfac)$_3$ moieties bridged by nitronyl nitroxide radicals. Single-crystal EPR spectra and magnetic susceptibility data measured in the 300–4.2 K temperature range are discussed.

Introduction

Nitronyl nitroxides, 4,4,5,5-tetramethyl-2-R-4,5-dihydro-1*H*-imidazolyl-1-oxy 3-oxide, NITR, of the general formula shown below have proved to be versatile ligands towards transition metal and lanthanide ions.[1-3]



They can bind through the oxygen atoms to paramagnetic metal ions, giving rise to exchange interactions that can be either ferromagnetic or antiferromagnetic depending on the overlap between the magnetic orbitals. The nitronyl nitroxides[4,5] and the nitroxides in general[6,7] have also been found to interact with each other, in general in an antiferromagnetic fashion even at relatively long distances. In particular, it has been observed that two NITR radicals bound to one lanthanide ion are antiferromagnetically coupled[8-10] with constants J of ca. 10 cm^{-1}. This result is rather surprising, because the distance between the radicals is too long to justify the observed coupling on the basis of the direct exchange, and the involvement of the metal orbitals in a superexchange pathway has been suggested[10] as a possible origin of the interaction. However, the exact determination of the extent of the coupling between the radicals in these compounds is hampered by the fact that gadolinium(III) is magnetic, and so is europium(III) at high temperature. In order to understand how relevant are the metal orbitals in transmitting the exchange interaction between the nitronyl nitroxides, we synthesized Y(hfac)$_3$NITEt (hfac = hexafluoroacetylacetonate), in which the metal ion is nonmagnetic and any deviation from Curie law must be attributed to interactions between the radicals. We wish to report here the magnetic properties and the EPR spectra of Y(hfac)$_3$NITEt, which behaves as a one-dimensional antiferromagnet.

Table I. Crystallographic Data for Y(hfac)$_3$NITEt

formula: $YC_{24}H_{20}F_{18}N_2O_8$	space group: $P2_1/n$ (No. 14)
formula weight: 895.31	T = 18 °C
a = 11.245 (1) Å	λ = 0.71069 Å (Mo Kα)
b = 17.257 (7) Å	ρ_{calcd} = 1.69 g cm^{-3}
c = 18.357 (3) Å	μ = 17.04 cm^{-1}
β = 98.39 (1)°	$R(F_o)$ = 0.132
V = 3524.13 Å^3	$R_w(F_o)$ = 0.132
Z = 4	

Experimental Section

Synthesis. The NITEt radical was prepared as previously described[11,12] and identified by melting point and EPR spectra. Y(hfac)$_3$·3H$_2$O was prepared according to the literature method[13] and

---

*To whom correspondence should be addressed at the University of Florence.

(1) Benelli, C.; Caneschi, A.; Gatteschi, D.; Rey, P. In *Organic and Inorganic Low Dimensional Materials*; Delhaes, P., Drillon, M., Eds.; Plenum Press: New York, 1987; p 109.

(2) Benelli, C.; Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P. In *Organic and Inorganic Low Dimensional Materials*; Delhaes, P., Drillon, M., Eds.; Plenum Press: New York, 1987; p 385.

(3) Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P.; Sessoli, R.; Zanchini, C. In *Organic and Inorganic Low Dimensional Materials*; Delhaes, P., Drillon, M., Eds.; Plenum Press: New York, 1987; p 381.

(4) Laugier, J.; Rey, P.; Benelli, C.; Gatteschi, D.; Zanchini, C. *J. Am. Chem. Soc.* **1986**, *108*, 6931.

(5) Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P.; Sessoli, R. *Inorg. Chem.* **1988**, *27*, 1553.

(6) Blaise, A.; Lemarie, H.; Pilon, J.; Veyret, C. *C. R. Acad. Sci., Ser. 2* **1972**, *274*, 157.

(7) Capiomont, A.; Chion, B.; Lajzerowicz, J.; *Acta Crystallogr.* **1971**, *B27*, 32.

(8) Benelli, C.; Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P. *Angew. Chem., Int. Ed. Engl.* **1987**, *27*, 913.

(9) Benelli, C.; Caneschi, A.; Gatteschi, D.; Pardi, L.; Rey, P.; Shum, D. P.; Carlin, R. L. *Inorg. Chem.* **1989**, *28*, 272.

(10) Benelli, C.; Caneschi, A.; Gatteschi, D.; Pardi, L.; Rey, P. *Inorg. Chem.* **1989**, *28*, 275.

(11) Lanchen, M.; Wittag, T. W. *J. Chem. Soc. C* **1966**, 2300.

(12) Ullman, E. F.; Osieki, J. H.; Boocock, D. G. B.; Darcy, R. *J. Am. Chem. Soc.* **1972**, *94*, 7049.

0020-1669/89/1328-3230$01.50/0

Table II. Positional Parameters ($\times 10^4$) and Isotropic Thermal Factors ($Å^2 \times 10^3$) for $Y(hfac)_3NITEt$[a]

	x	y	z	U_{iso}
Y	1982 (3)	1347 (2)	2601 (2)	44 (1)
O1	2038 (17)	1653 (11)	3822 (11)	58 (4)
O2	575 (17)	3333 (12)	2687 (11)	62 (4)
O3	4018 (16)	1519 (11)	3055 (10)	56 (4)
O4	3058 (18)	958 (11)	1672 (11)	54 (4)
O5	437 (20)	629 (13)	3006 (12)	78 (5)
O6	604 (19)	1137 (11)	1587 (11)	66 (5)
O7	2646 (19)	2466 (13)	2088 (12)	73 (5)
O8	2805 (19)	108 (13)	2912 (12)	77 (5)
N1	2358 (20)	3181 (14)	1854 (13)	50 (5)
N2	2772 (22)	−600 (16)	3155 (15)	66 (5)
C1	1322 (27)	1977 (18)	4231 (17)	60 (5)
C2	442 (29)	2481 (19)	3958 (19)	74 (5)
C3	143 (29)	2622 (19)	3255 (20)	74 (5)
C4	4927 (23)	1490 (17)	2762 (15)	50 (5)
C5	5093 (27)	1235 (19)	2059 (18)	73 (5)
C6	4110 (26)	962 (17)	1578 (16)	52 (5)
C7	−645 (30)	463 (20)	2682 (20)	77 (6)
C8	−1129 (29)	549 (19)	1977 (20)	75 (6)
C9	−523 (32)	874 (22)	1516 (21)	90 (6)
C10	1768 (41)	1865 (31)	5060 (29)	146 (6)
C11	−954 (37)	3183 (28)	2911 (27)	123 (6)
C12	6139 (33)	1703 (24)	3344 (23)	98 (6)
C13	4403 (39)	782 (27)	811 (26)	125 (6)
C14	−1337 (39)	−18 (29)	3280 (28)	132 (6)
C15	−1197 (50)	831 (41)	639 (41)	242 (6)
C16	2472 (23)	−1209 (18)	2713 (15)	53 (5)
C17	3211 (29)	−794 (20)	3921 (20)	78 (6)
C18	2067 (26)	3346 (17)	1028 (17)	56 (5)
C19	4565 (37)	−608 (27)	3969 (25)	141 (6)
C20	2797 (34)	−256 (24)	4464 (23)	119 (6)
C21	3265 (35)	3194 (26)	693 (24)	127 (6)
C22	1058 (31)	2800 (22)	706 (21)	98 (6)
C23	2135 (30)	−1183 (22)	1917 (19)	91 (6)
C24	831 (32)	−1162 (23)	1712 (21)	104 (6)
F1	2736 (26)	1762 (18)	5288 (17)	169 (6)
F2	1177 (28)	1153 (20)	5149 (18)	196 (6)
F3	1087 (22)	2309 (16)	5427 (14)	138 (5)
F4	−1489 (22)	3419 (15)	3447 (15)	139 (5)
F5	−1563 (24)	3040 (16)	2363 (16)	152 (5)
F6	−321 (23)	3867 (16)	2808 (15)	150 (5)
F7	6247 (23)	1184 (16)	3878 (16)	147 (5)
F8	6010 (24)	2353 (17)	3617 (15)	154 (5)
F9	7078 (21)	1670 (14)	3008 (13)	128 (5)
F10	5479 (27)	505 (18)	806 (17)	181 (6)
F11	3951 (23)	8 (16)	715 (14)	147 (5)
F12	3855 (28)	1045 (18)	301 (19)	190 (6)
F13	−1167 (22)	250 (15)	3882 (16)	136 (5)
F14	−2477 (24)	−104 (16)	2951 (14)	145 (5)
F15	−879 (24)	−741 (18)	3224 (16)	160 (6)
F16	−654 (27)	1348 (20)	267 (18)	193 (6)
F17	−1173 (35)	282 (26)	349 (25)	278 (6)
F18	−2128 (34)	1083 (24)	628 (23)	260 (6)

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

satisfactorily analyzed for C, H, N.

First, 0.5 mmol of $Y(hfac)_3{\cdot}3H_2O$ was dissolved in 100 mL of hot *n*-heptane, then 0.5 mmol of NITEt was added and the solution was allowed to cool down to room temperature and stored at 4 °C for 1 day. Orange elongated crystals were collected and were found to analyze well for $Y(hfac)_3NITEt$. Anal. Calcd for $YC_{24}H_{20}F_{18}N_2O_8$: C, 32.54; H, 2.26; N, 3.16. Found: C, 32.58; H, 2.30; N, 3.11.

X-ray Structure Determination. A crystal of dimensions 0.6 × 0.3 × 0.2 mm was mounted on the goniometer head of an Enraf-Nonius CAD4 diffractometer equipped with a Mo Kα X-ray tube and a graphite monochromator. Cell parameters were obtained from 24 machine-centered reflections in the range $7.1 \leq \theta \leq 15.2°$. Details of crystal and experimental data are reported in Table I. Data collection was performed in the $\omega - 2\theta$ scan mode, measuring the intensity of three test reflections every 160 min.

Corrections for Lorentz and polarization effects were made. Absorption correction was made by using the DIFABS program.[14] Systematic absences ($h0l$, $h + k = 2n + 1$) were only compatible with the monoclinic space group $P2_1/n$.

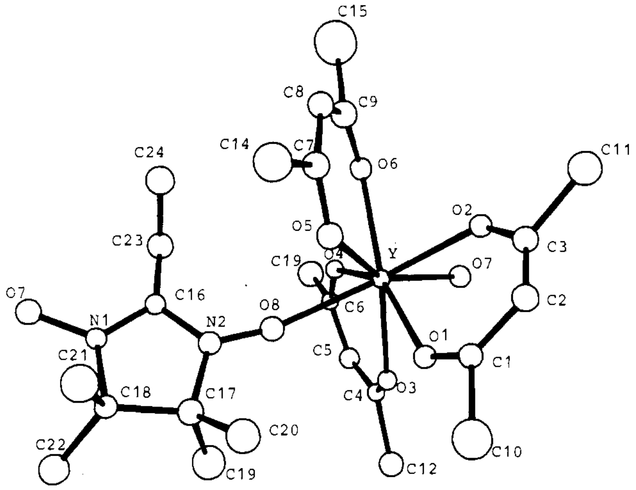


Figure 1. ORTEP view of the asymmetric unit for $Y(hfac)_3NITEt$.

Table III. Selected Bond Distances (Å) and Angles (deg) for $Y(hfac)_3NITEt$[a]

	Distances		
Y–O1	2.29 (2)	Y–O2	2.34 (2)
Y–O3	2.34 (2)	Y–O4	2.33 (2)
Y–O5	2.34 (2)	Y–O6	2.27 (2)
Y–O7	2.32 (2)	Y–O8	2.37 (2)
O1–C1	1.30 (4)	O2–C3	1.31 (4)
O3–C4	1.22 (3)	O4–C6	1.22 (4)
O5–C7	1.30 (4)	O6–C9	1.33 (4)
O7–N1	1.33 (3)	O8–N2	1.30 (4)
	Angles		
O7–Y–O8	135.4 (8)	O6–Y–O8	104.6 (8)
O6–Y–O7	91.1 (7)	O5–Y–O8	74.1 (8)
O5–Y–O7	150.2 (8)	O5–Y–O6	74.2 (8)
O4–Y–O8	72.0 (7)	O4–Y–O7	73.1 (7)
O4–Y–O6	73.8 (7)	O4–Y–O5	124.7 (7)
O3–Y–O8	72.5 (7)	O3–Y–O7	71.6 (7)
O3–Y–O6	145.9 (7)	O3–Y–O5	133.3 (7)
O3–Y–O4	73.2 (7)	O2–Y–O8	152.1 (7)
O2–Y–O7	71.5 (8)	O2–Y–O6	77.4 (7)
O2–Y–O5	79.9 (8)	O2–Y–O4	133.2 (7)
O2–Y–O3	121.4 (7)	O1–Y–O8	90.8 (7)
O1–Y–O7	104.1 (7)	O1–Y–O6	139.1 (7)
O1–Y–O5	74.1 (7)	O1–Y–O4	146.9 (7)
O1–Y–O3	74.8 (7)	O1–Y–O2	72.1 (7)
Y–O1–C1	138 (2)	Y–O2–C3	131 (2)
Y–O3–C4	132 (2)	Y–O4–C6	136 (2)
Y–O5–C7	131 (2)	Y–O6–C9	131 (2)
Y–O7–N1	146 (2)	Y–O8–N2	154 (2)
O7–N1–C18	120 (2)	O8–N2–C17	122 (2)
O8–N2–C16	123 (2)	C16–N2–C17	115 (3)

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

The yttrium atom was localized from the Patterson map. The positions of the other non-hydrogen atoms were found by successive Fourier and difference Fourier syntheses. The least-squares refinement converged with $R = 0.132$. We kept isotropic temperature factors and ignored hydrogen atoms because of the small number of reflections. We attribute the poor quality of the diffraction data to disorder present in the CF_3 group of the hexafluoroacetylacetonate ligands as frequently observed in reported structures.[10] The computer programs used in the present work are reported in ref 15.

Results and Discussion

Crystal Structure. The structure of $Y(hfac)_3NITEt$ consists of linear chains made up on nitronyl nitroxide radicals bridging

---

(13) Richardson, M. F.; Wagner, D. F.; Sands, D. E. *J. Inorg. Nucl. Chem.* **1968**, *30*, 1275.

(14) Walker, N.; Stuart, D. *Acta. Crystallogr.* **1983**, *A39*, 158.

(15) (a) Sheldrick, G. "SHELX-76 System of Computing Programs", University of Cambridge, England, 1976. (b) Johnson, C. K. "ORTEP"; Report ORNL 3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965. (c) Rizzoli, C.; Sangermano, V.; Calestani, G.; Andreetti, G. D. "CRYSRULER PACKAGE", Universitá degli Studi di Parma, 1986.

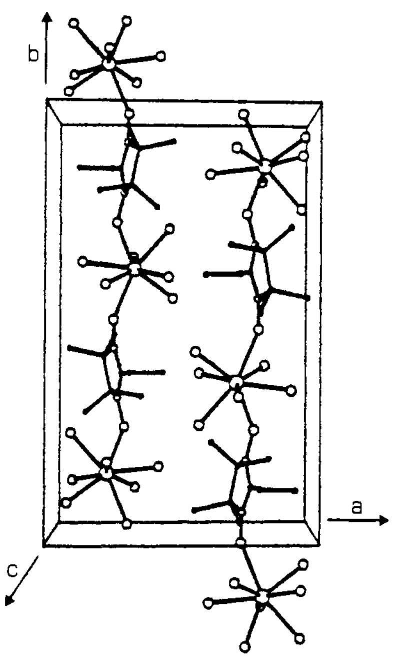


Figure 2. Unit cell view of Y(hfac)$_3$NITEt showing the chain structure of the system. For the sake of simplicity carbon and fluorine atoms of the hexafluoroacetylacetonate ligands have been omitted.

Table IV. Radical–Radical Coupling Constant Values in Rare-Earth-Metal Complexes with Nitronyl Nitroxides

compds	J, cm^{-1}	ref
Gd(hfac)$_3$NITEt	10.2	10
Eu(hfac)$_3$NITEt	≈12	10
Gd(hfac)$_3$NITPh$_2$	5.1	9
Gd(hfac)$_3$NITEt$_2$	4.3	9
Eu(hfac)$_3$NITPh$_2$	17.6	9
Eu(hfac)$_3$NITEt$_2$	16.3	9

two different Y(hfac)$_3$ units. The chains grow along the crystallographic b direction parallel to the binary screw axis. The chain structure is shown in Figure 2, while in Figure 1 is reported the ORTEP plot of the asymmetric unit.

Tables II and III contain positional parameters of non-hydrogen atoms and relevant bond angles and distances respectively.

The Y–O(hfac) distances are in the range 2.27–2.35 Å and compare well with those of the reported Y(hfac)$_3$(H$_2$O)$_2$ structure.[16,17] The two nitroxides are coordinated to the yttrium ion in a rather symmetric way, the two Y–O(NITEt) distances being 2.33 and 2.35 Å and the two N–O–Y angles being 146.3 (1) and 155.0 (1)°.

The least-squares planes of the two nitroxide molecules coordinated to the same yttrium ion, calculated by using only the O7–N1–C16–N2–O8 unit for each radical, form an angle of 10 (1)° with each other, while the relative N–O directions form an angle of 15.9 (2)°. The shortest interchain contacts are 8.08 (3) Å for the N2 atom and the same atom reported by the symmetry operation $-x + 1$, $-y$, $-z + 1$.

Magnetic Properties. The magnetic susceptibility of Y(hfac)$_3$NITEt, shown in Figure 3, goes through a maximum at ca. 6 K, indicating an antiferromagnetic coupling between the radicals. The experimental data can be fit with the expression valid for Heisenberg $S = {}^1/_2$ chains,[18,19] yielding the following parameter values: $g = 2.01$, $J = 4.51$ cm^{-1}, and an agreement factor $R = 4 \times 10^{-2}$. R is defined as $R = \sum_i[(\chi_i^{\text{obsd}} - \chi_i^{\text{calcd}})]^2/\sum_i[\chi_i^{\text{obsd}}]^2$. The value of the coupling constant is compared to those previously observed for lanthanide derivatives in Table IV. The present value is smaller than the values observed in europium(III) derivatives and very close to the value observed for gadolinium(III).

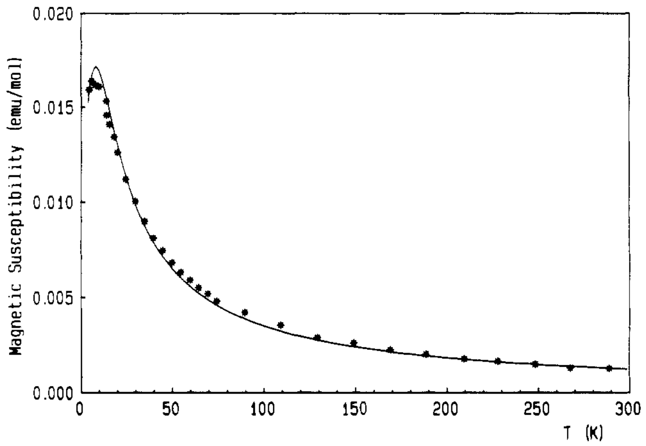


Figure 3. Variation of the magnetic susceptibility with temperature in the range 300–4.2 K for Y(hfac)$_3$NITEt. The solid line represents the best fit to data (see text).

The mechanism of exchange between the nitronyl nitroxides can be in principle of three different types: (i) direct overlap between the magnetic orbitals of the radicals; (ii) superexchange through the metal orbitals; (iii) superexchange through the orbitals of the hfac ligands. Possibility i does not seem to be relevant here, because the shortest radical–radical contact is ca. 4.5 Å, and it does not allow a significant direct overlap between the radical orbitals.

Superexchange through the metal orbitals is allowed through the empty 5s and 4d orbitals. Sample extended Hückel calculations show that indeed the energies of the π^* nitroxides are split by a weak interaction with the yttrium(III) 5s orbitals. Analogous calculations including an acetylacetonate molecule do not show any significant interaction between the π^* radical orbitals. Therefore, we conclude that the main origin of the exchange interaction is superexchange through the empty metal orbitals. Presumably an analogous mechanism is responsible of the interaction mediated by rare-earth-metal ions.

This result is extremely important in order to justify the ferromagnetic coupling observed in gadolinium(III) nitroxide complexes[8,10] and also in complexes containing copper(II) ions coupled to gadolinium(III) for which up to now no orbital interpretation had been attempted.[20,21] In fact, if we assume that also in these cases the magnetic orbitals of the radicals (or of the copper ion) overlap to the empty 5s orbitals, determining the transfer of a fraction of unpaired electron in these orbitals, then the electrons of gadolinium are forced to be parallel to that of the paramagnetic ligand by Hund's rule. In other terms the ferromagnetic exchange is determined by the third rule of Goodenough and Kanamori.[22,23] Similar mechanisms were advocated for instance to justify the observed coupling in chromium(II) halide derivatives.[24,25] This mechanism might easily justify even long-range ferromagnetic exchange mediated by extended bridges, and we are currently looking for experimental confirmations.

EPR Spectra. Single-crystal EPR spectra of Y(hfac)$_3$NITEt were recorded at room temperature by rotating the crystal around the $a(X)$, $b(Y)$, and c^* (Z) axes. The spectra revealed only one signal for every crystal orientation, with a small g anisotropy and a much more marked line-width anisotropy. The principal g values are $g_1 = 2.004$, $g_2 = 2.008$, and $g_3 = 2.010$. g_3 is parallel to b, while g_1 is in the ac plane, making an angle of ca. 30° with c^*.

---

(16) Cunningham, J. A.; Sands, D. E.; Wagner, W. F. *Inorg. Chem.* **1967**, *6*, 499.

(17) Burns, J. M.; Danford, M. D. *Inorg. Chem.* **1969**, *8*, 1781.

(18) Bonner, J. C.; Fisher, M. E. *Phys. Rev.* **1964**, *A135*, 646.

(19) Hatfield, W. E. *Inorg. Chem.* **1983**, *22*, 883.

(20) Bencini, S.; Benelli, C.; Caneschi, A.; Carlin, R. L.; Dei, A.; Gatteschi, D. *J. Am. Chem. Soc.* **1985**, *107*, 8128.

(21) Bencini, S.; Benelli, C.; Caneschi, A.; Dei, A.; Gatteschi, D. *Inorg. Chem.* **1986**, *25*, 572.

(22) Goodenough, J. B. *J. Phys. Chem. Solids* **1958**, *6*, 287.

(23) Kanamori, J. *J. Phys. Chem. Solids* **1959**, *10*, 87.

(24) Bellitto, C.; Filaci, P.; Patrizio, S. *Inorg. Chem.* **1987**, *26*, 2750.

(25) Bellitto, C.; Day, P. *J. Chem. Soc., Dalton Trans.* **1978**, 1207.

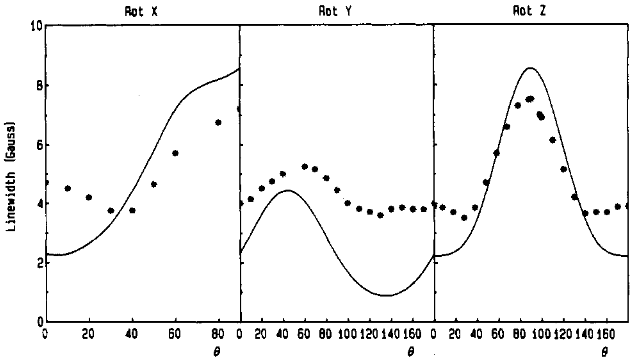
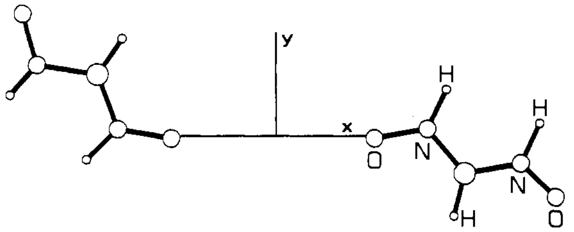


Figure 4. Angular dependence of the EPR line width for Y(hfac)$_3$NITEt. The solid curve represents the best fit to data (see text).

Chart I



The values compare well with those reported for nitroxide radicals,[26] and the lowest g value is observed close to the direction corresponding to the perpendicular to the ONCNO planes as expected.

The angular dependence of the line width, shown in Figure 4, is reminiscent of that of typical one-dimensional magnetic materials,[27,28] with a maximum along the crystal b axis, the chain direction, and a minimum close to the magic angle, i.e. at $\theta = \cos^{-1}(1/\sqrt{3})$. The rotation around b shows a less marked anisotropy. The line shape is Lorentzian at all angular settings.

The EPR line shape is given by the Fourier transform of the spin relaxation function, which for one-dimensional magnets can be written[29] as

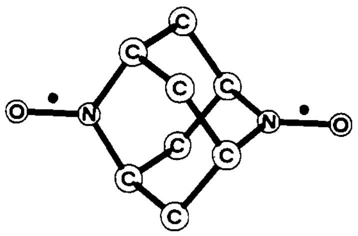
$$\varphi(t) = \exp(-[(\gamma t)^{3/2} + \eta t]) \qquad (1)$$

where γ and η depend on the degree of one-dimensionality of the material and on the nature of the interaction that broadens the line. In the present case, both dipolar interactions and electron-nuclear hyperfine interactions can concur. In order to assess the relative strengths of the two, it is possible to use the method of moments,[30] which requires a knowledge of $A_\parallel$ and $A_\perp$ for the hyperfine interaction and $\mathbf{D}_{jk}$ for the dipolar interaction. $A_\parallel$ and $A_\perp$ can be estimated by independent measurements on free nitronyl nitroxides[31] as 15 and 3 G, respectively. $\mathbf{D}_{jk}$ is the parameter relative to the dipolar interaction between the two centers j and k, defined through the spin Hamiltonian

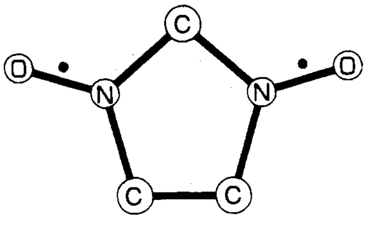
$$H = \mathbf{S}_j\mathbf{D}_{jk}\mathbf{S}_k \qquad (2)$$

In nitronyl nitroxides the unpaired electron is not localized on any particular atom, but rather it is spread out essentially on the two nitrogen and two oxygen atoms, so that the use of the point-dipolar approximation to calculate the extent of the through-space interaction is at least dubious. Therefore, we used a MO formalism, with a computer program developed by Keijzers and Gribnau.[32,33]

As a preliminary test of the validity of our approach, we used two nitroxide biradicals, I and II. The EPR spectra of both have been reported;[34,35] D has been found to be 0.02 cm^{-1} for I and 0.0715 cm^{-1} for II. Correspondingly the N–N distance has been estimated to be 320 pm for I and 222 pm for II from X-ray crystal structure data.[35]



I



II

The extended Hückel calculations for both yielded a very good agreement with the experimental data, D being 0.0214 cm^{-1} for I and 0.0780 cm^{-1} for II. It is interesting to note that the value calculated with the simple point-dipolar approximation, setting the centers of the dipoles halfway between nitrogen and oxygen atoms, compared well with the value calculated with the MO scheme and with experiment (0.0240 and 0.0715 cm^{-1} for I and II respectively).

The nitronyl nitroxides to our knowledge do not provide an opportunity to make independent tests because no well-characterized system is available with reported dipolar interactions; therefore, we addressed Y(hfac)$_3$NITET directly. We used the model molecules shown in Chart I.

We took pairs of molecules held at distances and in relative orientations analogous to those observed in the experimental structure. The result of the calculation is an axial **D** tensor, with the direction corresponding to the largest component practically parallel to X. The value of $\mathbf{D}_{jk}$ is 126 × 10^{-4} cm^{-1}. It is instructive to compare this value with the one which can be calculated within a point-dipolar formalism, for instance setting half an electron halfway between nitrogen and oxygen in either NO group. The calculated value in this case is 114 × 10^{-4} cm^{-1}, the principle direction being again parallel to X.

For a typical one-dimensional system[28] $\gamma = (4/3)^{2/3}M_{20}^{2/3}\tau_c^{1/3}$, where M_{20} is the secular second moment given by

$$M_{20} = {}^1/_{12}S(S+1)\textstyle\sum_j \mathbf{D}_{jk}^2(3\cos^2\theta_{jk} - 1)^2 \qquad (3)$$

The sum is over all the paramagnetic centers j connected to a central one k, and θ_{jk} is the angle of the direction connecting j and k with the direction of the external magnetic field. In well-behaved one-dimensional materials, only intrachain interactions are important and θ_{jk} is the same for all the pairs. Under these conditions the ηt component of $\varphi(t)$ is negligible, except at the magic angle. The line shape is intermediate between Lorentzian and Gaussian, and the line width follows a $(3\cos^2\theta - 1)^{4/3}$ dependence.[29]

In the present case, the line shape is Lorentzian, like in a normal exchange narrowing regime, while the angular dependence of the

---

(26) Berliner, L. J. *Spin Labeling*; Academic Press: New York, 1976; p 565.

(27) Drumheller, J. E. *Magn. Reson. Rev.* **1982**, *7*, 123.

(28) Bencini, A.; Gatteschi, D. *EPR of Exchange Coupled Systems*; Springer Verlag: Berlin, in press.

(29) Richards, P. M. In *Local Properties at Phase Transitions*; Rigamonti, A., Muller, A. K., Eds.; Editrice Compositori: Bologna, Italy, 1975; p 539.

(30) van Vleck, J. H. *Phys. Rev.* **1948**, *74*, 1168.

(31) Osiecki, J. H.; Ullman, E. F. *J. Am. Chem. Soc.* **1968**, *90*, 1678.

(32) Hefui, M. A.; McConnell, N. M.; Rietmeijer, F. J.; Gribnau, M. C. M.; Keijzers, C. P. *Mol. Phys.* **1986**, *57*, 1283.

(33) Gribnau, M. C. M. Ph.D. Thesis, University of Nijmegen, 1988.

(34) Dupeyre, R. M.; Rassat, A.; Ronzaud, J. *J. Am. Chem. Soc.* **1974**, *96*, 6559.

(35) Keana, J. F. W.; Norton, R. S.; Morello, M.; van Engen, D.; Clardy, J. *J. Am. Chem. Soc.* **1978**, *100*, 935.

line width is much closer to the behavior expected for one-dimensional systems. In fact, it is known that the line shape is much more sensitive than the line width in recording deviations from ideal one-dimensional behavior, which can be determined either by interchain exchange, which effectively increases the magnetic dimensionality of the system, or by noncollinear dipolar interactions as in the present case.[29,36]

The line width in this case is difficult to express on first principles, because both the $(\gamma t)^{3/2}$ and ηt components must be taken into account. A simplified version was suggested by Mc Gregor et al.[37] according to which the peak-to-peak width ΔB_{pp} can be expressed as

$$\Delta B_{pp} = 1.09[M_2 + \rho M_{20}]/J \qquad (4)$$

where M_2 is the total second moment. If ρ is zero, the behavior is that of a normal exchange narrowed system, while if ρ is large the material goes closer to the one-dimensional limit.

Using this approach, the value of $\mathbf{D}_{jk}$ computed above, extending the sum only to nearest neighbors, and the coupling constant obtained from the fit of the magnetic susceptibility, we calculate the angular dependence of the line width as shown in Figure 4 with only ρ as an adjustable parameter. Given the simplification of the model the agreement with experiment can be considered as satisfactory. The very large value of $\rho = 70$, which is needed to fit the data, shows that the secular enhancement is indeed very large.

Conclusion

Y(hfac)$_3$NITEt is a one-dimensional magnetic material in which the exchange interaction between the radicals is transmitted through a superexchange interaction with the metal orbitals. The EPR spectra show that indeed the material is highly one-dimensional even if marked deviations from ideal behavior are observed, essentially due to the zigzag nature of the chain.

Acknowledgment. Thanks are expressed to the Italian Ministry of Public Education and the CNR for financing the research. L.P. thanks Europa Metalli-LMI SpA for a research grant.

Supplementary Material Available: Table SI, containing experimental and crystallographic data, and Table SII, containing a complete listing of bond distances and angles (7 pages); Table SIII, listing observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

---

[36] Hennessy, M. J.; McElwee, C. D. *Phys. Rev.* **1973**, *B7*, 930.
[37] McGregor, K. T.; Soos, Z. G. *J. Chem. Phys.* **1976**, *64*, 2506.

Contribution from the Laboratorium für chemische und mineralogische Kristallographie, Universität Bern, CH-3012 Bern, Switzerland, and Research School of Chemistry, The Australian National University, G.P.O. Box 4, Canberra, ACT 2601, Australia

Crystal and Molecular Structures of Encapsulated Ruthenium(II) and Ruthenium(III) Ions with Virtually Identical Geometries

Paul Bernhard,*,[1a,b] Hans-Beat Bürgi,*,[1a] Andrea Raselli,[1a] and Alan M. Sargeson*,[1c]

Received January 20, 1989

Single-crystal X-ray structure determinations at 130 K are reported for two encapsulated Ru compounds, [Ru^{II}(Mesar)](CF$_3$SO$_3$)$_2$ (II) and [Ru^{III}(sar)](CF$_3$SO$_3$)$_3$ (III) (Figure 1; sar = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane; Mesar = 1-methyl derivative of sar). Compound II crystallizes in the orthorhombic space group *Pnma* with unit cell parameters $a = 21.941$ (4) Å, $b = 8.967$ (2) Å, $c = 13.078$ (2) Å (130 K), and $Z = 4$. For compound III the space group is $P\bar{3}c1$ (trigonal) with $a = b = 12.544$ (3) Å, $c = 22.638$ (5) Å, $\gamma = 120°$ (130 K), and $Z = 4$. The structure of II was refined to $R(F) = 0.038$ ($R_w(F) = 0.044$) for 2138 unique reflections with $F_o > 6\sigma(F_o)$. The structure of III was refined with use of a twin model to $R(F^2) = 0.073$ ($R_w(F^2) = 0.116$) for 2138 unique reflections with $F^2_o > 3\sigma(F^2_o)$. The two ions Ru(Mesar)$^{2+}$ and Ru(sar)$^{3+}$ exhibit virtually indistinguishable *lel*$_3$ geometries as illustrated by relevant structural parameters: $d(\text{Ru–N})_{av} = 2.105$ (10) Å (II) and 2.097 (8) Å (III); $\alpha(\text{Ru–en(bite)})_{av} = 83.6$ (9)° (II) and 83.6 (2)° (III); trigonal twist = 49.7 (5)° (II) and 48.8 (2)° (III). By implication the activation free energy for structural reorganization of Ru(sar)$^{n+}$ (ΔG_{in}^*) in the electron-exchange reaction is negligible. Therefore, the rate constant ($k_{ex} = 1.2 \times 10^5$ M^{-1} s^{-1}, $T = 25$ °C, $\mu = 0.1$ M)[2] in this instance represents an upper limit imposed by the frequency factor, work term, and solvent reorganization. The value, in turn, can be used to calculate ΔG_{in}^* for other M(sar)$^{3+/2+}$ couples, i.e. $\Delta G_{in}^*(\text{M}) = RT \ln (k_{ex}(\text{Ru})/k_{ex}(\text{M}))$. Results are (in kJ mol^{-1}) 22 (Mn), 5 (Fe), 38 (Co), and 10 (Ni), which correlate qualitatively with the structural differences between the M(II) and M(III) complexes. Possible relations between the structures and the low pK_a value for Ru(sar)$^{3+}$ (6.2–6.4)[3] and the regiospecific amine dehydrogenation in the cage cap are discussed.

Introduction

Electron-transfer reactions between Ru(II) and Ru(III) amine complexes are fast because only minor changes in coordination geometry occur upon oxidation or reduction of the metal. Where crystal structures are available for both oxidation states, Ru–N bond length changes are generally found to be ≤0.04 Å for aliphatic and ≤0.13 for aromatic amines (Table I). The fast self-exchange rate for the Ru(sar)$^{3+/2+}$ couple ($k_{ex} = 1.2 \times 10^5$ M^{-1} s^{-1}; sar = 3,6,10,13,16,19-hexaazabicyclo[6,6,6]eicosane, Figure 1)[2] was, therefore, not surprising and pointed to very similar structures of the ions. In order to obtain a quantitative measure of the similarity and differences between the two complexes with respect to bond lengths, angles, and ligand conformation, we carried out single-crystal X-ray structure determinations for the compounds [Ru^{II}(Mesar)](CF$_3$SO$_3$)$_2$ and [Ru^{III}(sar)](CF$_3$SO$_3$)$_3$ at low temperature (Mesar = 1-methyl derivative of sar). The methyl-substituted ligand was chosen because of serious disorder problems with several salts of the nonmethylated Ru(sar)$^{2+}$ cation. Further points of interest concern relationships between the structure of Ru(sar)$^{3+}$ and the acidity of the amine groups[3] as well as the selectivity of amine dehydrogenation, which is confined to the cage cap.[4]

---

[1] (a) Universität Bern. (b) Present address: Ciba-Geigy AG, CH-1701 Fribourg, Switzerland. (c) The Australian National University.
[2] Bernhard, P.; Sargeson, A. M. *Inorg. Chem.* **1987**, *26*, 4122.
[3] Bernhard, P.; Sargeson, A. M.; Anson, F. C. *Inorg. Chem.* **1988**, *27*, 2754.
[4] Bernhard, P.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1985**, 1516; *J. Am. Chem. Soc.* **1989**, *111*, 597.
[5] Stynes, H. C.; Ibers, J. A. *Inorg. Chem.* **1971**, *10*, 2304.
[6] Trehoux, J.; Nowogrocki, G.; Thomas, D. *C.R. Séances Acad. Sci., Ser. C* **1972**, *274*, 1384.
[7] Smolenaers, P. J.; Beattie, J. K.; Hutchinson, N. D. *Inorg. Chem.* **1981**, *20*, 2202.
[8] Peresie, H. J.; Stanko, J. A. *J. Chem. Soc. D* **1970**, 1674.
[9] Gress, M. E.; Creutz, C.; Quicksall, C. O. *Inorg. Chem.* **1981**, *20*, 1522.
[10] Wishart, J. F.; Bino, A.; Taube, H. *Inorg. Chem.* **1986**, *25*, 3318.

0020-1669/89/1328-3234$01.50/0 © 1989 American Chemical Society