pm yielded $J = 2\ \mathrm{cm}^{-1}$ only.[16] In Eu(hfac)$_3$(NITR)$_2$ the distance between the NO groups bonded to the metal ion must be close to 436 pm, the value observed in the gadolinium derivative.[23] Again this distance seems to be too long to justify the coupling through the direct overlap of the π^* orbitals. Therefore, a mechanism must be operative through either the metal orbitals or the hfac ligands.

The involvement of the hfac orbitals may be suspected for the moiety containing the O1 and O2 oxygen atoms (Figure 4), whose plane is almost orthogonal to the planes of the two nitroxides. The distances of the oxygen atoms of the nitroxides from the atoms of this hfac molecule range from 273 to 374 pm so that some overlap, leading to antiferromagnetic coupling, may be anticipated. If this mechanism were the only one operative, the observed coupling should be very similar in both the europium and gadolinium derivatives. The values we calculate for Gd(hfac)$_3$(NITR)$_2$ are smaller than those of Eu(hfac)$_3$(NITR)$_2$, but the relative uncertainty in the determination of the parameters for the former does not allow us to reach any firm conclusion about the involvement of the metal orbitals.

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Registry No. Eu(hfac)$_3$(NITEt)$_2$, 117800-31-4; Gd(hfac)$_3$(NITPh)$_2$, 11015-58-0; Gd(hfac)$_3$(NITEt)$_2$, 117800-32-5; Eu(hfac)$_3$(NITPh)$_2$, 117800-33-6.

Contribution from the Department of Chemistry, University of Florence, Florence, Italy, and Department de Recherche Fondamentale, Centre d'Etudes Nucleaires, Grenoble, France

Structure and Magnetic Properties of Linear-Chain Complexes of Rare-Earth Ions (Gadolinium, Europium) with Nitronyl Nitroxides

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Gd(hfac)$_3$NITEt (hfac = hexafluoroacetylacetonate, NITEt = 2-ethyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide) crystallizes in the monoclinic space group $P2_1/n$ with cell parameters $a = 2006.4$ (4) pm, $b = 1706.4$ (4) pm, $c = 2267.3$ (2) pm, $\beta = 113.82$ (1)°, $V = 7101.3 \times 10^6$ pm^3, $Z = 4$, and $R_w = 0.076$. The crystal structure consists of linear chains made by Gd(hfac)$_3$ moieties linked by bridging nitroxide radicals. The magnetic behavior shows the presence of an antiferromagnetic coupling. Several models for interpreting the magnetic structure are proposed and discussed.

Low-dimensional magnetic materials have been the focus of very active research in the last years, because their properties are in principle much easier to treat theoretically than three-dimensional systems.[2] The combined efforts of physicists and chemists have produced a large number of new classes of materials, such as ferromagnetic chains,[3,4] ferrimagnetic chains,[5,6] alternating chains,[7,8] two-dimensional ferromagnets and antiferromagnets, etc. Most of these materials are formed by transition-metal ions, both in ionic and in molecular lattices, but also organic radicals are well represented.

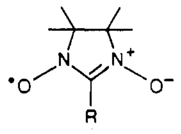
Low-dimensional materials containing lanthanide ions on the other hand are practically nonexistent, as reported in a popular textbook on magnetochemistry:[9] "there appear to be no low dimensional rare earth compounds". This result is rather unfortunate because the large anisotropy effects associated with the unquenched orbital angular momenta of the lanthanides might in principle yield interesting magnetic phenomena.

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

$Gd_2C_{48}H_{40}F_{36}N_4O_{16}$	fw = 1927.30
$a = 20.064$ (4) Å	space group: $P2_1/n$
$b = 17.064$ (4) Å	$T = 21.4$ °C
$c = 22.673$ (2) Å	$\lambda = 0.7107$ (Mo Kα)
$\beta = 113.82$ (1)°	$\rho = 1.80$ g cm^{-1}
$V = 7101.3$ Å	$\mu = 19.71$ cm^{-1}
$Z = 4$	$R(F_o) = 0.0854$
	$R_w(F_o) = 0.0763$

Very recently the new ceramic high-T_c superconductors have somewhat modified the negative picture because it has been suggested that when yttrium is substituted by magnetic rare-earth ions these form a two-dimensional magnet.[10,11]

We have recently reported that nitronyl nitroxides, NITR, stable organic radicals that have the general formula



R = C$_6$H$_5$, CH$_3$, CH$_2$CH$_3$

can form with transition metal ion linear-chain compounds[3,5] and two-dimensional materials.[12]

Trying to synthesize analogous compounds with the rare-earth ions appeared therefore to be a natural extension. We wish to

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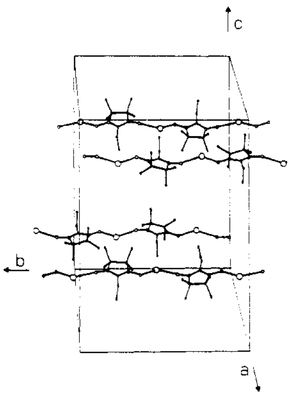

Figure 1. Schematic view of the unit cell of Gd(hfac)$_3$NITEt. For the sake of simplicity, only the gadolinium ions and the radical molecules are shown.

report here the crystal and molecular structure of Gd(hfac)$_3$NITEt (hfac = hexafluoroacetylacetonate, NITEt = 2-ethyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide) and the magnetic properties of M(hfac)$_3$NITEt (M = Gd, Eu), which to our knowledge are the first magnetic linear-chain compounds of lanthanides.

Experimental Section

Synthesis. M(hfac)$_3$·2H$_2$O (M = Gd, Eu) were prepared according to literature methods.[13] The NITEt radical was prepared as previously described.[14,15] To 1 mmol of M(hfac)$_3$·2H$_2$O dissolved in 60 mL of hot *n*-heptane was added 1 mmol of NITEt; the solution turned light orange. It was allowed to stay at room temperature for 12 h and then stored at 2 °C for 1 week. Well-shaped elongated orange crystals suitable for X-ray structure determination were obtained, which gave satisfactory analysis for M(hfac)$_3$NITEt. (Anal. Calcd for $C_{24}H_{20}N_2O_8F_{18}Eu$: C, 30.06; H, 2.09; N, 2.92. Found: C, 29.93; H, 2.04; N, 2.80. Calcd for $C_{24}H_{20}N_2O_8F_{18}Gd$: C, 29.91; H, 2.08; N, 2.91. Found: C, 29.84; H, 2.04; N, 2.77.)

X-ray Data Collection and Reduction. X-ray data for Gd(hfac)$_3$NITEt were collected by mounting a crystal of approximate dimensions 0.8 × 0.3 × 0.15 mm on an Enraf-Nonius CAD4 diffractometer equipped with a Mo Kα X-ray tube and a graphite monochromator. Crystal and experimental data are given in Table I. Cell parameters and the orientation matrix were determined by 16 machine-centered reflections, with $8° \leq \theta \leq 13°$. Four reflections were used as intensity and orientation standards and measured every 100 min during the data collection. Data were corrected for Lorentz and polarization effects but not for absorption.

Cell parameters of Eu(hfac)$_3$NITEt were determined by using 21 machine-centered reflections in the range θ between 8 and 12°. They were found to be a = 2006.3 (4) pm; b = 1702.1 (6) pm; c = 2270.6 (2) pm; β = 113.75 (1)°.

Structure Solution and Refinement. The structure was solved by conventional methods using the SHELX-76 package.[16] The systematic absences ($h0l$, $h + l = 2n$; $0k0$, $k = 2n$; $h00$, $h = 2n$; $00l$, $l = 2n$) are only compatible with the $P2_1/n$ space group.

A Patterson map enabled us to localize the two gadolinium atoms in the asymmetric unit. The positions of the other non-hydrogen atoms were found by successive Fourier and difference Fourier synthesis. Some difficulties were met in the refinement procedure due to disorder present in the CF$_3$ groups of the hexafluoroacetylacetonate moieties. Several attempts were made to find a model for these disordered groups. Fractional site occupation factors were attributed to the several spots present in the difference Fourier map, in positions suitable for F atoms. The least-squares procedure converged in that case with an R value of 0.071, resulting, however, in a quite distorted structure in which several unrealistic C–C distances between 160 and 170 pm were present. Other attempts were made to refine the CF$_3$ groups as well as the methyl groups of the nitronyl nitroxide molecules as rigid groups. In this case the least-squares procedure converged with a conventional R value of 0.087. In the final cycle all the hydrogen atoms were included in fixed and idealized positions. In the final stage of refinement peaks of intensity less than 1.0 e Å^{-3} appeared in the Fourier difference map.

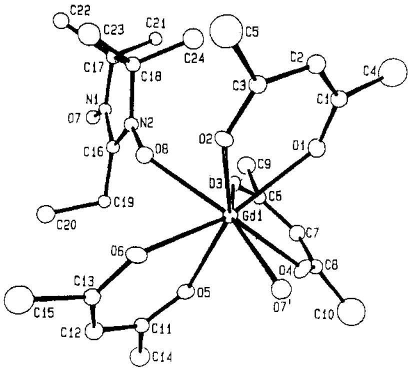

Figure 2. View of the first Gd(hfac)$_3$NITEt moiety contained in the asymmetric unit.

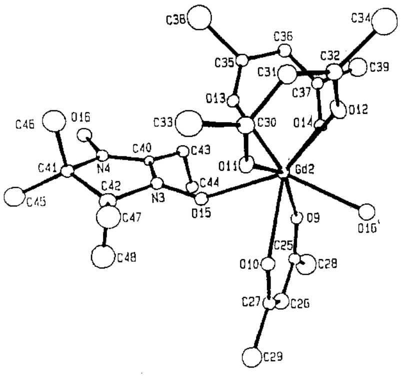

Figure 3. View of the second Gd(hfac)$_3$NITEt moiety contained in the asymmetric unit.

Magnetic Susceptibility Measurements. Magnetic susceptibilities were measured in the range 4.2–300 K with a SHE superconducting SQUID susceptometer at 0.5 T. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from Pascal constants.

Results

Crystal Structure. The structure of Gd(hfac)$_3$NITEt consists of linear chains built up by Gd(hfac)$_3$ units bridged by nitronyl nitroxide radicals. The view of the unit cell (Figure 1) shows that the chains grow in the crystallographic b direction. Positional parameters and isotropic thermal factors of Gd(hfac)$_3$NITEt are listed in Table II. Selected bond lengths and angles are given in Table III.

The asymmetric unit consists of two Gd(hfac)$_3$NITEt moieities, having a slightly different coordination geometry around the metal ion and belonging to different chains so that two slightly different chains are present in the structure. ORTEP views of the two Gd(hfac)$_3$NITEt moieities are given in Figures 2 and 3. In both cases the coordination number is 8 and the coordination polyhedron is best approximated by a distorted dodecahedron.[17] The set of Gd–O(hfac) distances is in the range 241–233 pm, in good agreement with those in other reported tris(β-diketonate) eight-coordinate lanthanide complexes.[18,19] The average of Gd–O(NITEt) bond distance of 238 pm is longer compared with that reported for Gd(hfac)$_3$(NITPh)$_2$[20] but is in the range of the lanthanide–oxygen bond lengths observed in rare-earth complexes with monodentate ligands.[21,22] The two bridging nitronyl nitr-

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Table II. Positional Parameters ($\times 10^4$) and Isotropic Thermal Factors ($Å^2 \times 10^3$) for Non-Hydrogen Atoms of Gd(hfac)$_3$NITEt[a]

	x	y	z	U_{eq}/U_{iso}
Gd1	2288 (1)	−320 (1)	7582 (1)	46
Gd2	2180 (1)	−2564 (1)	2235 (1)	47
O1	2484 (9)	−52 (11)	8680 (9)	73
O2	3460 (7)	281 (9)	8150 (6)	58
O3	1959 (8)	−1491 (9)	7939 (7)	63
O4	1099 (8)	−124 (9)	7520 (8)	75
O5	1468 (8)	−821 (9)	6595 (8)	67
O6	2744 (8)	−94 (9)	6779 (7)	64
O7	1974 (8)	1015 (10)	7254 (8)	75 (5)
O8	3141 (9)	−1313 (10)	7652 (8)	76 (5)
O9	2943 (8)	2593 (9)	1780 (7)	59
O10	1714 (8)	1964 (9)	1943 (7)	61
O11	2083 (8)	2190 (9)	3326 (7)	62
O12	3518 (8)	1798 (9)	3744 (7)	79
O13	3153 (8)	3495 (9)	3495 (7)	66
O14	4060 (8)	2737 (9)	3016 (7)	61
O15	2036 (8)	3517 (9)	2234 (9)	63 (5)
O16	3018 (8)	1155 (9)	2513 (8)	87 (5)
N1	1750 (10)	1703 (11)	7097 (9)	52 (5)
N2	3293 (10)	−2057 (12)	7877 (9)	58 (6)
N3	1830 (11)	4202 (12)	2339 (9)	58 (6)
N4	3218 (10)	415 (12)	2577 (9)	57 (5)
C1	2976 (12)	185 (14)	9175 (8)	63 (7)
C2	3646 (12)	481 (14)	9204 (12)	67 (7)
C3	3832 (8)	471 (13)	8708 (11)	57 (7)
C4	2807 (8)	141 (10)	9785 (6)	191 (18)
C5	4592 (7)	817 (10)	8818 (8)	150 (14)
C6	1374 (13)	−1747 (9)	7992 (11)	64 (7)
C7	746 (15)	−1315 (18)	7867 (14)	92 (9)
C8	645 (8)	−552 (14)	7622 (11)	64 (7)
C9	1487 (7)	−2572 (6)	8307 (6)	131 (13)
C10	−145 (7)	−231 (10)	7389 (8)	253 (24)
C11	1427 (10)	−887 (13)	6017 (10)	62 (7)
C12	1949 (14)	−639 (15)	5803 (13)	78 (9)
C13	2562 (10)	−264 (14)	6195 (10)	59 (7)
C14	729 (7)	−1332 (10)	5570 (7)	120 (12)
C15	3146 (9)	−92 (11)	5927 (9)	140 (14)
C16	2947 (13)	−2657 (14)	7545 (12)	57 (7)
C17	1134 (12)	1835 (14)	6499 (11)	63 (7)
C18	3903 (13)	−2216 (14)	8475 (12)	62 (7)
C19	2324 (12)	−2680 (14)	6899 (11)	54 (7)
C20	2648 (18)	−2747 (17)	6408 (16)	96 (10)
C21	1328 (14)	1542 (14)	5944 (11)	62 (7)
C22	432 (12)	1440 (14)	6472 (16)	77 (8)
C23	4594 (14)	−1886 (22)	8424 (17)	118 (12)
C24	3864 (19)	−1849 (20)	9081 (14)	116 (12)
C25	2558 (12)	2472 (14)	1199 (9)	59 (7)
C26	1822 (16)	2153 (17)	955 (17)	100 (10)
C27	1479 (8)	1936 (13)	1323 (11)	57 (7)
C28	2913 (9)	2667 (11)	722 (8)	204 (20)
C29	697 (6)	1589 (8)	1060 (7)	117 (12)
C30	2173 (11)	2067 (15)	3887 (12)	75 (8)
C31	2824 (15)	1860 (16)	4385 (15)	84 (9)
C32	3474 (8)	1714 (9)	4281 (9)	73 (14)
C33	1532 (8)	2151 (11)	4105 (9)	137 (14)
C34	4146 (7)	1350 (8)	4831 (7)	164 (12)
C35	3750 (8)	3784 (9)	3881 (9)	59 (13)
C36	4456 (14)	3582 (15)	3917 (13)	71 (8)
C37	4542 (11)	3094 (9)	3483 (9)	58 (9)
C38	3653 (7)	4327 (8)	4394 (9)	196 (13)
C39	5341 (8)	2879 (9)	3597 (8)	155 (11)
C40	2197 (11)	4868 (12)	2351 (9)	41 (6)
C41	3885 (11)	182 (12)	2489 (9)	56 (6)
C42	1092 (17)	4328 (18)	2316 (15)	93 (10)
C43	2857 (13)	4927 (16)	2244 (12)	69 (8)
C44	2718 (15)	4900 (18)	1568 (12)	76 (9)
C45	4582 (16)	673 (20)	2828 (18)	135 (13)
C46	3649 (22)	194 (26)	1747 (11)	150 (14)
C47	752 (21)	3635 (22)	2537 (24)	156 (14)
C48	584 (25)	4276 (32)	1585 (16)	187 (19)
F1	2846 (8)	−596 (10)	9943 (6)	201 (10)
F2	2155 (8)	401 (10)	9663 (6)	162 (8)
F3	3280 (8)	538 (10)	10258 (6)	208 (10)
F4	4918 (7)	1058 (10)	9410 (8)	200 (10)
F5	4972 (7)	259 (10)	8713 (8)	231 (12)
F6	4529 (7)	1396 (10)	8427 (8)	211 (12)
F7	1937 (7)	−2512 (6)	8908 (6)	151 (7)
F8	1744 (7)	−3068 (6)	8016 (6)	140 (7)
F9	859 (7)	−2819 (6)	8273 (6)	161 (7)
F10	−609 (7)	−707 (10)	7467 (8)	193 (10)
F11	−378 (7)	−31 (10)	6786 (8)	205 (10)
F12	−74 (7)	391 (10)	7741 (8)	253 (13)
F13	597 (7)	−1964 (10)	5824 (7)	234 (12)
F14	195 (7)	−840 (10)	5447 (7)	201 (10)
F15	794 (7)	−1509 (10)	5038 (7)	239 (13)
F16	3558 (9)	495 (11)	6223 (9)	236 (14)
F17	2817 (9)	67 (11)	5315 (9)	244 (12)
F18	3544 (9)	−716 (11)	6004 (9)	314 (17)
F19	3103 (9)	3401 (11)	806 (8)	268 (15)
F20	3485 (9)	2236 (11)	830 (8)	197 (10)
F21	2443 (9)	2560 (11)	132 (8)	226 (11)
F22	480 (6)	1577 (8)	436 (7)	159 (9)
F23	265 (6)	2033 (8)	1213 (7)	176 (9)
F24	685 (6)	881 (8)	1268 (7)	164 (9)
F25	931 (8)	2172 (11)	3587 (9)	160 (8)
F26	1525 (8)	1544 (11)	4449 (9)	287 (16)
F27	1586 (8)	2785 (11)	4439 (9)	319 (18)
F28	4726 (7)	1615 (9)	4776 (6)	192 (10)
F29	4132 (7)	590 (9)	4787 (6)	186 (9)
F30	4159 (7)	1555 (9)	5387 (6)	174 (9)
F31	4271 (7)	4633 (7)	4773 (6)	138 (7)
F32	3203 (7)	4881 (7)	4085 (6)	156 (8)
F33	3382 (7)	3931 (7)	4736 (6)	193 (9)
F34	5406 (6)	2825 (9)	3051 (7)	169 (9)
F35	5781 (6)	3416 (9)	3951 (7)	168 (9)
F36	5502 (6)	2210 (9)	3895 (7)	214 (11)

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

oxides form an O7–Gd1–O8 angle of 142.1 (6)° in the first unit and an O15–Gd2–O16 angle of 162 (2)° in the second one. The Gd–O–N angles are fairly different from each other, namely Gd1–O7–N1 = 173.6 (1.6)°, Gd1–O8–N2 = 137.8 (1.5)° and Gd2–O15–N3 = 142.5 (1.4)°, Gd–O16–N4 = 161.2 (1.4)°. The nitronyl nitroxide molecule has the conformation, already observed in other metal–nitroxide complexes,[3,5,23–33] in which the O–N–

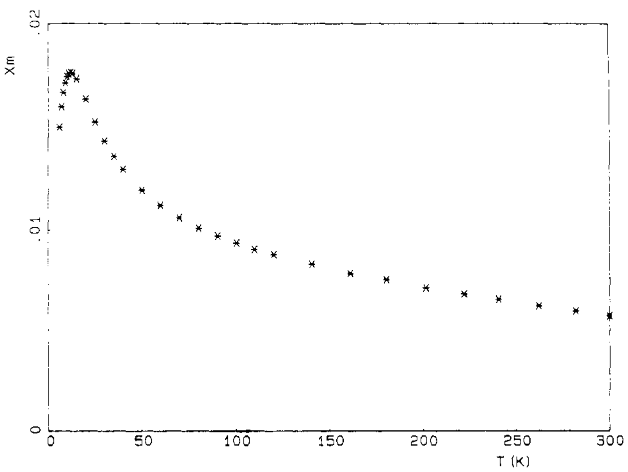

Figure 4. Temperature dependence of the observed magnetic susceptibility of Eu(hfac)$_3$NITEt in the 5–300 K range.

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Table III. Selected Bond Distances (pm) and Angles (deg)[a]

	Distances		
Gd1-O1	240 (2)	Gd1-O2	241 (1)
Gd1-O3	235 (2)	Gd1-O4	235 (2)
Gd1-O5	234 (1)	Gd1-O6	238 (2)
Gd1-O7	240 (2)	Gd1-O8	237 (2)
Gd2-O9	236 (2)	Gd2-O10	238 (1)
Gd2-O11	234 (2)	Gd2-O12	236 (1)
Gd2-O13	236 (2)	Gd2-O14	237 (2)
Gd2-O15	241 (2)	Gd2-O16	233 (2)
O7-N1	126 (2)	O8-N2	136 (3)
O15-N3	129 (3)	O16-N4	131 (2)
	Angles		
O7-Gd1-O8	142.31 (0.63)	O6-Gd1-O8	71.06 (0.59)
O6-Gd1-O7	75.04 (0.56)	O5-Gd1-O8	90.70 (0.58)
O5-Gd1-O7	93.19 (0.56)	O5-Gd1-O6	70.48 (0.55)
O4-Gd1-O8	142.45 (0.58)	O4-Gd1-O7	73.44 (0.57)
O4-Gd1-O6	128.71 (0.55)	O4-Gd1-O5	72.03 (0.59)
O3-Gd1-O8	70.40 (0.59)	O3-Gd1-O7	147.12 (0.60)
O3-Gd1-O6	130.62 (0.54)	O3-Gd1-O5	80.32 (0.54)
O3-Gd1-O4	73.90 (0.59)	O2-Gd1-O8	75.24 (0.59)
O2-Gd1-O7	80.69 (0.55)	O2-Gd1-O6	75.24 (0.52)
O2-Gd1-O5	145.59 (0.54)	O2-Gd1-O4	135.90 (0.53)
O2-Gd1-O3	121.86 (0.50)	O1-Gd1-O8	104.80 (0.62)
O1-Gd1-O7	93.06 (0.61)	O1-Gd1-O6	144.10 (0.62)
O1-Gd1-O5	145.01 (0.65)	O1-Gd1-O4	76.90 (0.63)
O1-Gd1-O3	75.90 (0.59)	O1-Gd1-O2	69.40 (0.57)
Gd1-O1-C1	138.36 (1.72)	Gd1-O2-C3	136.27 (1.36)
Gd1-O3-C6	134.97 (1.28)	Gd1-O4-C8	134.19 (1.48)
Gd1-O5-C11	137.62 (1.48)	Gd1-O6-C13	137.01 (1.50)
Gd1-O7′-N′	173.61 (1.57)	Gd1-O8-N2	137.83 (1.50)
O15-Gd2-O16	137.44 (0.58)	O14-Gd2-O16	89.79 (0.63)
O14-Gd2-O15	111.31 (0.59)	O13-Gd2-O16	149.55 (0.60)
O13-Gd2-O15	72.92 (0.59)	O13-Gd2-O14	72.20 (0.60)
O12-Gd2-O16	72.72 (0.59)	O12-Gd2-O15	147.57 (0.59)
O12-Gd2-O14	73.03 (0.60)	O12-Gd2-O13	78.51 (0.58)
O11-Gd2-O16	99.89 (0.61)	O11-Gd2-O15	88.88 (0.62)
O11-Gd2-O14	137.62 (0.58)	O11-Gd2-O13	79.50 (0.59)
O11-Gd2-O12	70.86 (0.59)	O10-Gd2-O16	71.90 (0.59)
O10-Gd2-O15	69.80 (0.59)	O10-Gd2-O14	144.41 (0.59)
O10-Gd2-O13	135.75 (0.61)	O10-Gd2-O12	126.18 (0.59)
O10-Gd2-O11	76.83 (0.60)	O9-Gd2-O16	77.38 (0.60)
O9-Gd2-O15	74.73 (0.58)	O9-Gd2-O14	72.64 (0.60)
O9-Gd2-O13	118.02 (0.60)	O9-Gd2-O12	133.94 (0.61)
O9-Gd2-O11	149.72 (0.60)	O9-Gd2-O10	73.67 (0.58)
Gd2-O9-C25	136.40 (1.63)	Gd2-O10-C27	132.71 (1.41)
Gd2-O11-C30	136.96 (1.70)	Gd2-O12-C32	135.43 (1.35)
Gd2-O13-C35	134.84 (1.51)	Gd2-O14-C37	132.63 (1.49)
Gd2-O15-N3	142.47 (1.37)	Gd2-O16′-N4′	161.22 (1.38)

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

C–N–O units lie approximately on a plane, while the two remaining carbon atoms of the pentaatomic cycle are out of that plane. In this case the deviation of C17, C18, C41, and C42 from the O–N–C–N–O least-squares planes in the range 10–20 pm. The shortest interchain Gd–Gd contact is 864.0 (3) pm.

Magnetic Data. The temperature dependence of the magnetic susceptibility of Eu(hfac)$_3$NITEt is shown in Figure 4. The curve goes through a maximum at ca. 12 K.

The magnetic data of Gd(hfac)$_3$NITEt are shown in Figure 5 in the χT vs T fashion. At room temperature the χT value is lower than expected for uncoupled $S = {}^7/_2$ and $S = {}^1/_2$ spins (8.20 vs 8.25 emu mol^{-1} K). When the temperature is lowered, χT remains quite constant until ca. 120 K and then decreases to 2.55 emu mol^{-1} K at 5.99 K.

Discussion

Europium(III) has a $^7F_0$ ground state, with the first excited state $^7F_1$ at ca. 350 cm^{-1} and $^7F_2$ at ca. 1000 cm^{-1}. At low temperature only the nonmagnetic ground level is occupied and the susceptibility of the isolated ion becomes temperature-independent due to field-determined admixing of the excited states into $^7F_0$.[34] Therefore, the low-temperature magnetic behavior of Eu(hfac)$_3$NITEt must be determined by the exchange interaction between the radicals. The maximum observed in the χ vs T curve at ca. 12 K indicates that an antiferromagnetic exchange interaction is operative. As the crystals of the europium derivative were found to be isomorphous with those of the gadolinium derivative, we assume a similar structure for both complexes. Therefore, the magnetic susceptibility at low temperature can be described as the sum of a temperature-independent contribution from europium(III) and that of an antiferromagnetic chain of spin $^1/_2$. The maximum in the χ vs T curve for such a type of chain is expected to occur at $T_{\max} \simeq 0.8$ J/K so that the coupling constant between the radicals can be estimated to be ca. 12 cm^{-1}. This value is close to that observed in mononuclear Eu(hfac)$_3$(NITR)$_2$, which is 16.3 cm^{-1}.[20]

The gadolinium(III) ion is a $^8S_{7/2}$ ion; therefore, it has no orbital angular momentum contribution and any exchange interaction should be essentially isotropic. Indeed, we have found that the magnetic properties of simple gadolinium complexes in which the metal ion is close to a nitronyl nitroxide or to a paramagnetic copper complex can be interpreted with a weak ferromagnetic isotropic coupling.[20,35-39]

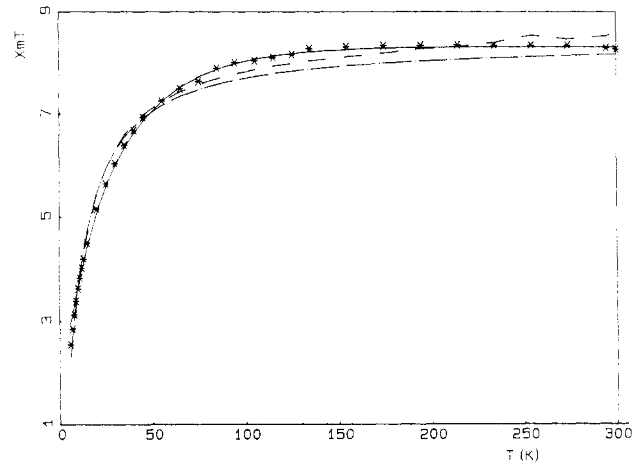

Figure 5. Temperature dependence of the observed χT product of Gd(hfac)$_3$NITEt in the 5–300 K range (*). The curves are the fitting to the experimental data with the Seiden model (- - -), the alternating-spin–alternating-chain model (—), and the interpenetrating lattice model (–•–) (see text).

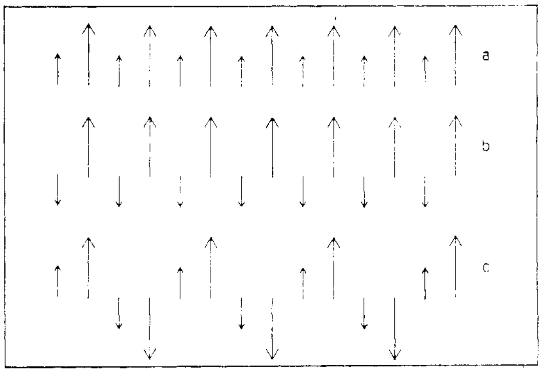

Figure 6. Proposed spin arrangements: (a) ferromagnetic chain; (b) ferrimagnetic chain; (c) alternating-spin–alternating-chain model.

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The magnetic properties of Gd(hfac)$_3$NITEt do correspond neither to a system with uncoupled spins, because in this case χT should remain constant throughout the whole temperature range at 8.25 emu mol^{-1} K, nor to a simple magnetic chain, because in this case χT should increase at low temperature, for both ferro- and antiferromagnetic coupling. In fact, in a ferromagnetic chain all the spins are parallel to each other at 0 K, and χ diverges. A similar result is expected as well for an antiferrimagnetic chain, i.e. in an one-dimensional system in which the nearest-neighbor spins are coupled antiparallel to each other.[2,40]

The origin of the observed decrease of χT on decreasing the temperature may be either intra- or interchain in nature. In Figure 6 we show three possible spin arrangements that can qualitatively justify the decrease of χT on decreasing the temperature. In parts a and b of Figure 6 we have depicted the case of ferro- and ferrimagnetic chains antiferromagnetically coupled, while Figure 6c shows a possible arrangement of the spins within the chains that yields a nonmagnetic ground state.

The quantitative treatment is rather difficult in both cases, unless some drastic simplifications are made. For the intermolecular hypothesis a possibility is that of using the reported formulas for regular alternating-spin chains[41] and adding a molecular field correction. For the chain the expression given by Seiden is appropriate: the gadolinium spins are treated as classical spins, while the radical spins are considered as quantum spins, and only nearest-neighbor interactions are included. The expression for the magnetic susceptibility is

$$\chi = \frac{N\beta\mu_2{}^2}{3}\left[g_S{}^2S^2\left(\frac{S+1}{S} - 2\frac{\delta}{1-\delta}\right) - 4g_Sg_s\Lambda sS\frac{1}{1-\delta} + g_s{}^2\left(s(s+1) + 2\Lambda^2s^2\frac{1}{1-\delta}\right)\right]$$

where S and g_S refer to the classical spin and s and g_s to the quantum spin, $\beta = 1/kT$, $\delta = A_0/3A_1$, and

$$\Lambda = 2\left[\frac{B_1}{3A_0} + \frac{B_0}{A_0}\right]$$

$$A_0 = 4[\gamma^{-1}\sinh\gamma - \gamma^{-2}\cosh\gamma + \gamma^{-2}]$$

$$A_1 = 12[(\gamma^{-1} + 12\gamma^{-3})\sinh\gamma - (5\gamma^{-2} + 12\gamma^{-4})\cosh\gamma - \gamma^{-2} + 12\gamma^{-4}]$$

$$B_0 = \gamma^{-1}(\cosh\gamma - 1)$$

$$B_1 = 3[(\gamma^{-1} + 4\gamma^{-3})\cosh\gamma - 4\gamma^{-2}\sinh\gamma + \gamma^{-1} - 4\gamma^{-3}]$$

$$\gamma = \beta JS$$

The molecular field correction is taken in the form[41]

$$\chi = \frac{\chi_{\text{chain}}}{1 - (nZJ'/Ng^2\mu_B)\chi_{\text{chain}}}$$

From this expression the experimental data are fitted as shown in Figure 4 and the fitting parameters are $g_s = 2.004$, $g_S = 2.059$, $J = 7.82$ cm^{-1}, and $nZJ' = -2.48$ cm^{-1}. The agreement can be considered as fairly good, but the parameters are not very satisfactory. Indeed, the nZJ' constant appears to be much larger than anticipated on the basis of the large distances between the chains and the lack of any effective exchange pathway[43,44] observed in the structure.

In order to obtain the spin arrangement of Figure 6c, a model including only the nearest neighbors demands that the coupling of a gadolinium is ferromagnetic with one radical and antiferromagnetic with the other. A rationale for this may come from the marked difference between the coordination of the two oxygen atoms of the two different radicals bound to the metal ion. In fact, in the first center of the asymmetric unit the two Gd–O(NITEt) distances are 240 (2) and 237 (2) pm and in the second one they are 241 (2) and 233 (2) pm, respectively; further, the Gd–O–N angles, which are known[30,31] to affect the metal–nitroxide coupling in the complexes of another S ion such as Mn^{2+}, are 173.6 (2) and 137.8 (2)° for Gd1 and 161.2 (1) and 142.5 (1)°, respectively, for Gd2.

The quantitative treatment of the susceptibility is possible due to a recent extension of the model of Seiden to the alternating-spin–alternating-exchange chain.[45] In the treatment there is no particular assumption bound to the sign of the coupling constant; therefore, it can be used also for the case of alternating ferromagnetic–antiferromagnetic exchange. The spin Hamiltonian is

$$\mathcal{H} = \sum_i JS_1{}^i[(1+\alpha)S_2{}^i + (1-\alpha)S_2{}^{i+1}]$$

The correct expression for the susceptibility is

$$\chi = \frac{N\mu_B{}^2}{3kT}\{g_1{}^2[S_1(S_1+1)(1-P) + 2RQ] + 4g_1g_2S_1S_2(R + Q) + g_2{}^2S_2{}^2[(S_2+1)(1-P)/S_2 + 2P]\}/(1-P)$$

where g_1 and S_1 are relative to the spin $^1/_2$, while g_2 and S_2 are relative to the spin $^7/_2$, $\beta = 1/kT$:

$$P = A_1/A_0$$

$$Q = \beta JS_2[(1+\alpha)B_0 + (1-\alpha)B_1]/A_0$$

$$R = \beta JS_2[(1-\alpha)B_0 + (1+\alpha)B_1]/A_0$$

$$Z = (1-\alpha^2)\beta^2J^2S_2{}^2$$

$$A_0 = \frac{1}{Z}\sum_{\sigma=-S_1}^{S_1}\sum_{\epsilon=\pm1}\frac{\epsilon\exp(\sigma\lambda_\epsilon)}{\sigma^2}(\sigma\lambda_\epsilon - 1)$$

$$B_0 = \frac{1}{Z}\sum_{\sigma=-S_1}^{S_1}\sum_{\epsilon=\pm1}\epsilon\exp(\sigma\lambda_\epsilon)$$

$$A_1 = \frac{1}{2Z^2}\sum_{\sigma=-S_1}^{S_1}\frac{\exp(\sigma\lambda_+)}{\sigma^4}\left[\frac{(1-\alpha^2)(\sigma\lambda_+)^3}{2} + \frac{(\alpha^2-5)(\sigma\lambda_+)^2}{2} + 6(\sigma\lambda_+ - 1)\right] - \frac{\exp(\sigma\lambda_-)}{\sigma^4}\left[(\sigma\lambda_-)^3 - 3(\sigma\lambda_-)^2 + 6\sigma\lambda_- - 6 - \frac{(\sigma\lambda_- - 1)(1+\alpha)^2(\sigma\lambda_+)^2}{2}\right]$$

$$B_1 = \frac{1}{2Z^2}\sum_{\sigma=-S_1}^{S_1}\frac{\exp(\sigma\lambda_+)}{\sigma^2}\left[\frac{(1-\alpha^2)(\sigma\lambda_+)^2}{2} - 2\sigma\lambda_+ + 2\right] - \left[(\sigma\lambda_-)^2 - 2\sigma\lambda_- + 2 - \frac{(\sigma\lambda_+)^2(1-\alpha^2)}{2}\right]$$

$$\lambda_+ = -2\beta J \qquad \lambda_- = \alpha\lambda_+$$

The fit of the experimental data is shown in Figure 4. The parameters are $g_1 = 1.992$, $g_2 = 1.982$, $J = 11.12$ cm^{-1}, and $\alpha = 2.03$, corresponding to a ferromagnetic coupling constant of -11.45 cm^{-1} and an antiferromagnetic one of 33.69 cm^{-1}. Although the fit appears to be rather satisfactory, the values of the parameters are much less so, because they both appear to be much larger than anticipated for gadolinium–radical interactions.

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One possible explanation for this might be that the assumption of only nearest-neighbor interaction is incorrect. In fact, in the analysis of the temperature dependence of the magnetic susceptibility of the simple complexes $M(hfac)_3(NITEt)_2$ ($M = Gd, Eu$) a fairly strong antiferromagnetic coupling between the radicals ought to be included,[39] and also the present europium chains show evidence of antiferromagnetic coupling between the radicals as large as 12 cm^{-1}. Therefore, it can be suspected that the large values of the parameters obtained from the fit of the magnetic susceptibility of $Gd(hfac)_3NITEt$ are actually artifacts, due to the neglect of the next-nearest-neighbor interactions. We are not aware of any kind of interaction that is suitable for our present compound; therefore, we tried to use a very simplified treatment in order to check the feasibility of the above hypothesis.

We simply reduced the chain to the contribution of two interpenetrating one-dimensional lattices, one formed by radicals and one by metal ions. We considered isotropic coupling within each lattice but not between lattices. In particular we used the Bonner–Fisher model[46] for $S = {}^1/_2$ antiferromagnetic Heisenberg chains and the Fisher expression[47] for classical Heisenberg chains with $S = {}^7/_2$. The experimental data could be fit reasonably well, given the roughness of the model, as shown in Figure 5. The values required for the fit need the antiferromagnetic coupling $J = 10.2$ cm^{-1} for the radicals and 0.28 cm^{-1} for the gadolinium ions. We do not attach any particular meaning to this fit, except that it gives some support to the hypothesis of next-nearest-neighbor coupling.

Registry No. $Eu(hfac)_3NITEt$, 117800-51-8; $Gd(hfac)_3NITEt$, 117800-52-9; $Eu(hfac)_3 \cdot 2H_2O$, 20558-33-2; $Gd(hfac)_3 \cdot 2H_2O$, 20558-32-1.

Supplementary Material Available: Table SI (complete crystallographic and experimental parameters), Table SII (distances and bond angles), and Table SIII (anisotropic thermal parameters) (10 pages); Table SIV (structure factors for $Gd(hfac)_3NITEt$) (25 pages). Ordering information is given on any current masthead page.

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Vibrational and X-ray Photoelectron Spectroscopy for $MoWCl_4(PMe_3)_4$

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Far-IR and Raman vibrational spectra and X-ray photoelectron spectra (XPS) have been obtained on the heteronuclear complex $MoWCl_4(PMe_3)_4$. A band at 326 cm^{-1} in the far-IR spectrum and at 322 cm^{-1} in the Raman spectrum has been attributed to the Mo–W stretching mode. The force constant for the heteronuclear M–M stretching mode is significantly larger compared to those of its homonuclear analogues. The XPS results for the heteronuclear complex indicate a partial shift in electron density from tungsten to molybdenum.

Introduction

Recently the structures and spectroscopic properties of the homologous series of quadruply bonded $M_2Cl_4(PMe_3)_4$ complexes, where $M_2 = Mo_2$, W_2, and MoW, have been reported in detail.[2] The structures indicate that the heteronuclear complex has M–M bonding characteristics intermediate between those of its homonuclear analogues. The M–M bond distances increase in the order Mo_2 (2.130 (0) Å)[3] < MoW (2.2092 (7) Å)[2] < W_2 (2.262 (1) Å).[3] The electronic spectra, electrochemical, and photoelectron results are consistent with this view.[2,4] We would like to report vibrational spectra and metal core-electron binding energies that provide additional information regarding this homologous series and that show apparent anomalous behavior for the heteronuclear complex.

Experimental Section

Materials. PMe_3 (Alfa Products) and $ClSiMe_3$ (Fisher Scientific Chemical Co.) were stored under vacuum and were freshly distilled under vacuum for each preparation. $BrSiMe_3$ (Aldrich Chemical Co.) was used as obtained. $Mo_2(O_2CCH_3)_4$,[5] $Mo_2(O_2CCMe_3)_4$,[5] $MoW(O_2CCMe_3)_4$,[6] and $W_2Cl_4(PMe_3)_4$[7] were synthesized according to literature procedures.

$MoWCl_4(PMe_3)_4$. The heteronuclear complex was prepared by a method developed in our laboratory.[8,9] $MoW(O_2CCMe_3)_4$ (0.45 g, 0.7 mmol) and excess PMe_3 (0.5 g, 5.0 mmol) were refluxed in ca. 15 mL of $ClSiMe_3$ for 2.5 days. After cooling, the mixture was filtered to give a green filtrate and a small quantity of a green solid. Excess $ClSiMe_3$ and PMe_3 were removed under vacuum leaving a blue-green, tarry residue. The green solid and filtrate were combined and were purified by heating under vacuum at 100 °C to expel any silyl ester resulting from reaction of $ClSiMe_3$ with the pivalate ligands. Subsequent extraction with cyclohexane yielded well-formed crystals. The heteronuclear complex was shown to be free of mononuclear impurities by ^{31}P NMR analysis.[2,8]

Table I. Far-IR Spectra of $Mo_2X_4(PR_3)_4$ Complexes[a]

complex	C–P–C bends		M–X str		ref
	assignments and wavenumbers, cm^{-1}				
$Mo_2Cl_4(PMe_3)_4$	351 s	329 s	329 s	285 s	this work
$Mo_2Br_4(PMe_3)_4$	345 s	330 m	263 s	226 s	this work
$Mo_2Cl_4(PBu_3)_4$			326 m	278 m	11
$Mo_2Br_4(PBu_3)_4$			260 m		11
$Mo_2Cl_4(PEt_3)_4$			332 s	282 m	this work

[a] Relative intensities are given as follows: s, strong; m, medium.

$Mo_2Cl_4(PMe_3)_4$. This homonuclear complex was prepared by using the same procedure as that used for the heteronuclear complex above except the homonuclear carboxylate $Mo_2(O_2CCMe_3)_4$ was used for the starting material.

$Mo_2Br_4(PMe_3)_4$. This complex was prepared from reaction of $Mo_2(O_2CCH_3)_4$ with $BrSiMe_3$ according to a described procedure using excess PMe_3.[9]

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