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Structure and Magnetic Properties of Ferromagnetic Alternating Spin Chains

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A novel compound formed by copper(II) and a nitronyl nitroxide stable radical of formula $Cu(hfac)_2NITiPr$ (hfac = hexafluoroacetylacetonate; NITiPr = 2-isopropyl-4,4,5,5-tetramethyl-4,5-dihydro-$1H$-imidazolyl-1-oxyl 3-oxide) has been synthesized. It crystallizes in the monoclinic system, space group $P2_1/c$ with a = 13.807 (7) Å, b = 10.966 (2) Å, c = 19.037 (8) Å, β = 102.42 (4)°, and Z = 4. The structure consists of chains in which the copper ions are bridged by the nitronyl nitroxides, which coordinate to two different metal ions by the two equivalent oxygen atoms. The magnetic susceptibility was measured in the temperature range 1–300 K, and the value of χT diverges on lowering the temperature. This behavior is typical of an infinite array of spins ferromagnetically coupled, and the coupling constant has been estimated to be J = –21.6 cm^{-1}. The single-crystal EPR spectra have shown a behavior typical of one-dimensional magnetic systems with line widths that follow a $((3 \cos^2 \theta) - 1)^n$ angular dependence. Also g shifts have been observed at low temperature. The low-temperature magnetic data have suggested the presence of a very weak 3-D ferromagnetic interaction. We report for comparison also the magnetic data of the analogous $Cu(hfac)_2NITMe$ compound (NITMe = 2,4,4,5,5-pentamethyl-4,5-dihydro-$1H$-imidazolyl-1-oxyl 3-oxide) in the range 1–4 K, which have shown the presence of a stronger 3-D antiferromagnetic interaction. The difference in the low-temperature behavior of these two compounds with that of already reported ferrimagnetic chains containing manganese(II) and nickel(II) has been rationalized by using a simple model that takes into account only the dipolar interaction between chains.

Introduction

One-dimensional magnetic materials have been the focus of very active research, because their thermodynamic properties are relatively easy to interpret[2,3] and also spin dynamics effects show up quite neatly in this class of compounds.[4–6] The original impetus in this area came from the interest of physicists toward simple systems on which to test statistical mechanics theories, but recently many new types of one-dimensional materials were synthesized, and the chemists largely contributed to the enlargement of the variety of magnetic systems. At the beginning linear chains were formed by identical spins, and simple ferro- or antiferromagnetic chains were reported.[7–9] The structures however became more complicated, with alternating chains[10–12] (i.e. systems in which one spin is coupled with two different coupling constants to its two nearest neighbors along the chain), ladder type structures,[13] etc.

A particularly relevant step forward was represented by the synthesis of ordered bimetallic chains, which provided a large number of new materials. In these compounds two different spins alternate regularly along the chains, and many one-dimensional ferrimagnets were thus reported.[14–22] It is interesting to note that

Table I. Crystallographic Data and Experimental Parameters for $Cu(hfac)_2NITiPr$

formula	$CuC_{20}F_{12}H_{21}N_2O_6$	fw	676.2
crys syst	monoclinic	space group	$P2_1/c$
a	13.805 (7) Å	b	10.966 (2) Å
c	19.037 (8) Å	β	102.42 (4)°
V	2814.5 Å^3	Z	4
ρ_{calcd}	1.597 g/cm^3	μ	6.78 cm^{-1}
temp	20 °C	λ	0.7107 Å
R	0.0629	R_w	0.0715

"different" in this case may indicate also otherwise identical spins, characterized by some anisotropy, which have different orientations in the chain.[23,24]

Another new class of materials is formed by systems in which metal ions alternate regularly in space with stable organic radicals.[25–31] These compounds, from a magnetic point of view, are

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similar to the ordered bimetallic chains. A comprehensive name for all these materials might be alternating spin chains. In particular we have reported alternating-exchange–alternating-spin chains, in which a copper ion is coupled ferromagnetically to one neighboring radical and antiferromagnetically to the other,[32] ferrimagnetic chains,[29-31] and ferromagnetic chains.[28] In particular we found that Cu(hfac)$_2$NITMe (hfac = hexafluoroacetylacetonate; NITMe = 2,4,4,5,5-pentamethyl-4,5-dihydro-1H-imidazolyl-1-oxyl 3-oxide) is a ferromagnetic chain, with $J = -25.7$ cm^{-1},[28] where the Hamiltonian is defined as $H = JS_1 \cdot S_2$ and that its EPR spectra are typical of one-dimensional magnetic materials.[33]

Given the current large interest in the study of molecular magnets,[34-36] it appeared of interest to us to synthesize other ferromagnetic chains and to determine their capacity to order as bulk ferromagnets.

We wish to report here the synthesis, the crystal structure, the magnetic properties in the range 1–300 K, and the EPR spectra of Cu(hfac)$_2$NITiPr (I) together with the magnetic properties of Cu(hfac)$_2$NITMe (II) in the range 1–4 K. Both compounds behave as one-dimensional ferromagnets, but no transition to three-dimensional magnetic order was observed.

Experimental Section

Synthesis of the Complexes. The synthesis of Cu(hfac)$_2$NITMe has already been reported.[28]

The NITiPr radical was synthesized according to literature reports.[37]

Cu(hfac)$_2$NITiPr was prepared by dissolving 0.5 mmol of anhydrous Cu(hfac)$_2$ in boiling n-heptane and adding 0.5 mmol of NITiPr radical. The solution was allowed to stay at room temperature for 12 h and then stored at −10 °C for 1 day. Red-brown crystals suitable for X-ray crystal structure determination were collected and well analyzed for Cu(hfac)$_2$NITiPr. Anal. Calcd for CuC$_{20}$F$_{12}$H$_{21}$N$_2$O$_6$: C, 35.49; H, 3.19; N, 4.14. Found: C, 35.69; H, 3.22; N, 4.19.

X-ray Structure Determination. Diffraction data of I were collected at room temperature with an Enraf-Nonius CAD4 four-circle diffractometer equipped with Mo Kα radiation and a graphite crystal monochromator.

Unit cell parameters were derived by least-squares refinement of the setting angles of 24 reflections with $8° \leq \theta \leq 16°$. The systematic extinctions revealed that the compound crystallizes in the monoclinic system, space group $P2_1/c$.

Data were corrected for Lorentz and polarization effects but not for absorption. No intensity decay was observed on three standard reflections collected every 120 reflections.

The asymmetric unit has two copper atoms occupying two independent special positions of coordinates (0, $^1/_2$, $^1/_2$) and ($^1/_2$, 0, $^1/_2$). The other atoms were found by successive Fourier syntheses performed by using the standard SHELX76 package.[38]

Due to the special positions of the copper atoms, which contribute only to half of the structure factors, and to the thermal motion and/or disorder present in the CF$_3$ groups, a relevant percentage of the reflections were too weak to be used in the refinement. In order not to overparametrize the least-squares procedure, only the copper, oxygen, fluorine, and 10 carbon atoms were refined anisotropically. The final refinement including the contribution of hydrogen atoms in calculated positions converged to $R = 0.0629$. The highest peaks in the last Fourier difference were less than 0.5 e/Å^3 and were located in the proximity of the CF$_3$ groups of C4 and C9.

More details are given in Table SI (supplementary material) of which Table I is a condensed form. Final atomic coordinates are given in Table II.

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Table II. Positional Parameters (×10^4) and Isotopic Thermal Factors (Å × 10^3) for Cu(hfac)$_2$NITiPr^a

	x/a	y/b	z/c	U_{iso}
Cu1	0	5000	5000	61
Cu2	−5000	10000	5000	63
O1	−248 (4)	4721 (5)	5949 (3)	62
O2	338 (4)	6698 (5)	5205 (3)	64
O3	−4595 (4)	11046 (5)	4298 (3)	63
O4	−3890 (4)	10486 (5)	5755 (3)	73
O5	−1734 (4)	5419 (6)	4550 (3)	83
O6	−4211 (6)	8115 (7)	4725 (4)	115
N1	−2374 (5)	6274 (7)	4386 (4)	62 (2)
N2	−3564 (6)	7548 (7)	4465 (4)	77 (2)
C1	−109 (6)	5488 (8)	6441 (4)	55 (2)
C2	236 (6)	6658 (8)	6433 (5)	62 (2)
C3	408 (6)	7175 (8)	5808 (5)	60 (2)
C4	−359 (8)	5027 (12)	7142 (4)	73
C5	685 (11)	8536 (10)	5822 (6)	89
C6	−3903 (7)	11792 (9)	4427 (5)	68 (3)
C7	−3237 (7)	11968 (9)	5077 (5)	79 (3)
C8	−3290 (8)	11306 (10)	5680 (5)	76 (3)
C9	−3776 (12)	12541 (11)	3782 (8)	103
C10	−2525 (15)	11545 (18)	6363 (9)	135
C11	−2908 (7)	6724 (8)	4823 (5)	69 (3)
C12	−2556 (7)	6924 (9)	3685 (5)	72 (3)
C13	−3552 (8)	7542 (10)	3675 (6)	82 (3)
C14	−2825 (9)	6358 (11)	5583 (6)	96 (3)
C15	−3673 (10)	5596 (12)	5662 (6)	143
C16	−2608 (10)	7386 (12)	6098 (6)	134
C17	−2545 (10)	6027 (11)	3087 (5)	122
C18	−1696 (9)	7829 (11)	3749 (7)	132
C19	−4436 (8)	6708 (13)	3346 (6)	130
C20	−3720 (11)	8789 (10)	3360 (6)	144
F1	69 (7)	4006 (7)	7348 (3)	149
F2	−1315 (5)	4820 (7)	7049 (3)	124
F3	−145 (6)	5790 (6)	7674 (3)	125
F4	−110 (7)	9205 (6)	5770 (5)	157
F5	1246 (7)	8870 (6)	6441 (4)	140
F6	1099 (6)	8859 (6)	5318 (4)	134
F7	−4545 (8)	13156 (9)	3517 (5)	195
F8	−3676 (7)	11860 (8)	3254 (4)	152
F9	−3029 (8)	13241 (9)	3892 (4)	211
F10	−1801 (8)	12194 (12)	6311 (5)	217
F11	−2156 (9)	10630 (12)	6685 (7)	251
F12	−2894 (9)	12067 (20)	6826 (7)	310

^{a} Standard deviations in the last significant digit are in parentheses.

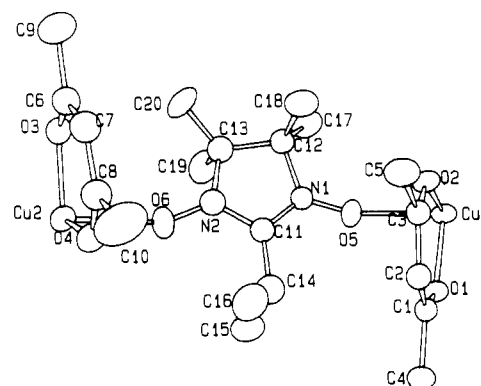**Figure 1.** ORTEP view of the asymmetric unit of Cu(hfac)$_2$NITiPr. The Fluorine atoms were omitted for the sake of clarity.

EPR and Magnetic Measurements. Polycrystalline powder and single-crystal EPR spectra of I were recorded with a Varian E9 spectrometer equipped with X- and Q-band facilities.

Variable temperature spectra in the range 4.2–300 K were recorded at X-band frequency by using an Oxford Instruments ESR9 liquid-helium continuous-flow cryostat.

A single crystal of Cu(hfac)$_2$NITiPr (I) was oriented with the same diffractometer used for the structure determination and was found to have the shape of a platelet with the faces (0,0,±1) largely developed and bounded by the (1,−1,0), (−1,1,0), (−1,−1,0), and (1,1,0) faces.

Magnetic susceptibility in the temperature range 5–300 K was measured for I by an SHE SQUID susceptometer at a field strength of 10

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

Distances			
Cu1–O1	1.933 (6)	Cu1–O2	1.938 (5)
Cu1–O5	2.407 (6)	Cu2–O3	1.933 (6)
Cu2–O4	1.936 (5)	Cu2–O6	2.446 (8)
O5–N1	1.279 (9)	O6–N2	1.272 (12)
N1–C11	1.320 (13)	N2–C11	1.354 (12)

Angles			
O1–Cu1–O5	90.0 (2)	O2–Cu1–O5	93.8 (2)
O1–Cu1–O2	92.7 (2)	O4–Cu2–O6	94.2 (3)
O3–Cu2–O6	98.4 (3)	O3–Cu2–O4	92.8 (2)
Cu1–O5–N1	143.9 (5)	Cu2–O6–N2	151.5 (6)

[a] Standard deviations in the last significant digit are in parentheses.
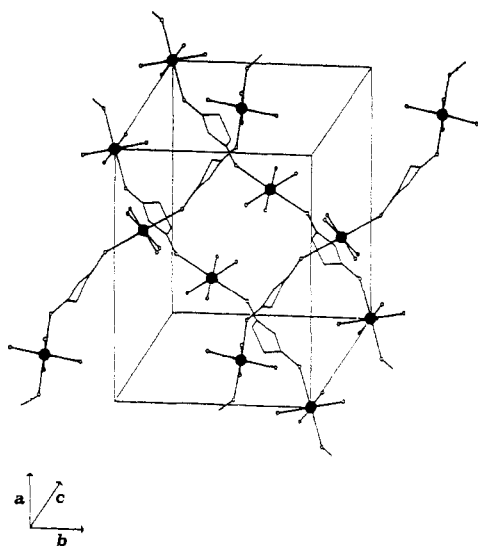
Figure 2. Schematic view of the contents of the unit cell of Cu-(hfac)₂NITiPr (I).

Figure 3. Schematic view of the contents of the unit cell of Cu-(hfac)₂NITMe (II).

Figure 4. Temperature dependence of the magnetic susceptibility for I. The solid line represents the calculated values with the best fit parameters (see text).

mT. Data were corrected for the magnetization of the sample holder and for the diamagnetic contributions, which were estimated from Pascal's constants.

The magnetic susceptibilities of I and II in the range 1.15–4.2 K were measured by an AC mutual-inductance technique at nearly zero field. The sample was immersed in liquid helium, and the temperature was measured by means of a germanium resistor thermometer calibrated against the vapor pressure of helium.

Results and Discussion

Crystal Structure. The molecular structure of Cu(hfac)₂NITiPr (I) is substantially similar to that of the methyl derivative II already reported.[28] A view of the asymmetric unit is shown in Figure 1. The copper atoms are located on an inversion center and are octahedrally coordinated by four oxygens of two hfac ligands occupying the equatorial positions and two oxygens of two different radicals in the axial positions. Selected bond distances and angles are given in Table III, while all the bond lengths and angles are available in Tables SV and SVI (supplementary material). The radical bridges the two nonequivalent copper ions thus originating an infinite array structure. The octahedra of both copper centers are severely distorted with the axial Cu–O bond much longer than the equatorial ones, 2.407 (6) and 2.445 (8) Å vs 1.93 Å. The geometrical parameters relevant to the exchange interaction are similar for the two copper ions: the Cu–O bond lengths are 2.407 (6) and 2.446 (8) Å, the N–O lengths are 1.279 (9) and 1.272 (12) Å, and the Cu–O–N angles are 143.9 (5) and 151.5 (6)° for Cu1 and Cu2, respectively. The distances and angles within the radical compare well with those previously reported.[28-31,39,40] The five-membered ring deviates significantly from planarity with C12 0.14 Å below and C13 0.16 Å above the
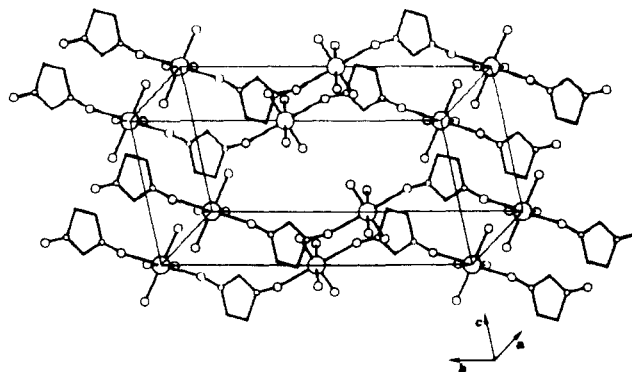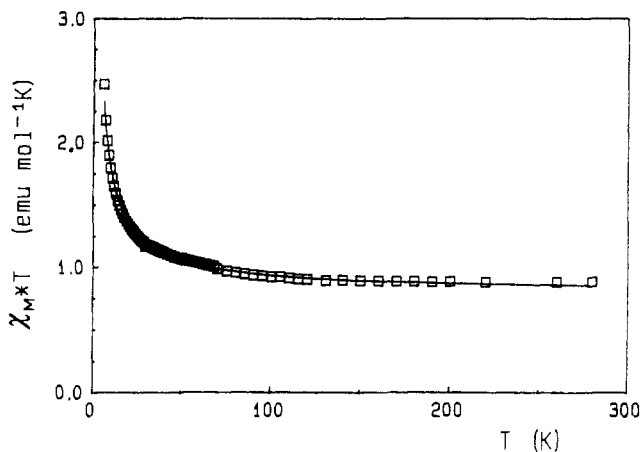
average plane, in agreement with previous findings.[28-31,39,40]

The main differences between I and II are observed in the orientation of the chains in the unit cells and are related to the different space groups, $P2_1/c$ and $P\bar{1}$, respectively. In the case of I in fact the glide plane and screw axes generate two sets of chains perpendicular to each other (see Figure 2), while in II the chains are parallel to each other, as shown in Figure 3. In II the shortest distance between magnetic centers belonging to different chains is 8.955 Å, the unit translation along the a axis, while each chain of I is surrounded by two other parallel chains at shorter distance. The shortest contacts are found between the radicals, and in particular, O5–O6 is 7.182 Å and N1–O6 is 7.190 Å. Each chain is also surrounded by four perpendicular chains, but in this case the shortest distance is 8.994 Å.

Magnetic Properties. The temperature dependence of χT for I is shown in Figure 4. The room temperature value is 0.85 emu mol⁻¹ K and increases steadily on lowering the temperature to a value of 2.47 emu mol⁻¹ K at 6 K. The behavior of II, previously reported, is similar to that of I, but the starting value is higher (0.954 emu mol⁻¹ K). The divergence of χT at low temperature is typical of an infinite array of spins ferromagnetically coupled. The quantitative analysis of the magnetic susceptibility was performed by using a formula based on the Padé approximants reported by Baker et al.[41] The best fit parameters for the data of I recorded above liquid-helium temperature are $J = -21.6$ (8) cm⁻¹, $g = 2.07$ (1), and $r = 3.73 \times 10^{-4}$ ($r = \sum_i (\chi T_{obs}{}^i - \chi T_{calc}{}^i)^2 / \sum_i (\chi T_{obs}{}^i)^2$), where the negative sign of the coupling constant indicates ferromagnetic interaction. Similar results were obtained for II: $J = -25.7$ cm⁻¹ and $g = 2.20$.

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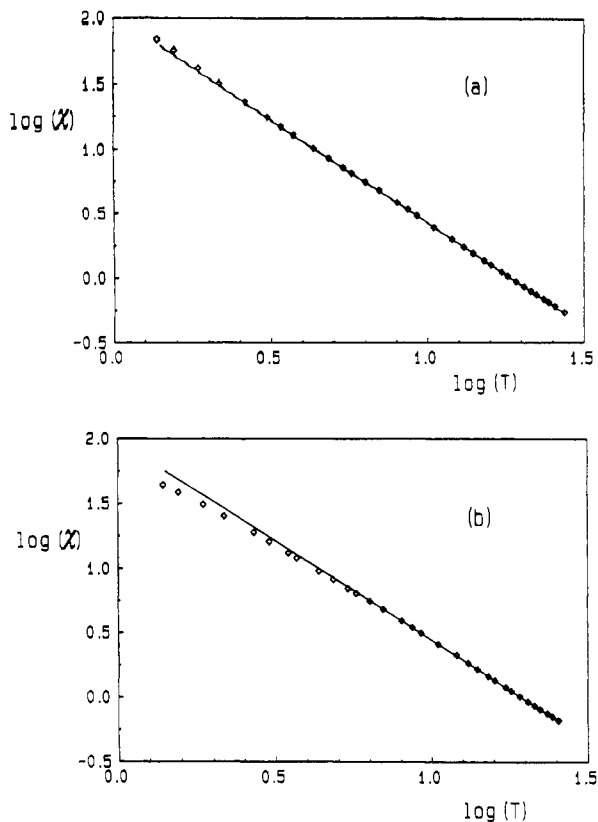(43) Bonner, J. C.; Fisher, M. E. *Phys. Rev.* **1964**, *135*, A640.

Figure 5. Temperature dependence of the magnetic susceptibility below 4.2 K in the form log χ vs log T for $Cu(hfac)_2NITiPr$ (a) and $Cu(hfac)_2NITMe$ (b). The solid line is the best fit to an exponential divergence of the susceptibility (see text).

Below 4.2 K the χT product steadily increases on decreasing temperature, for both I and II. In order to make evident the deviations from the one-dimensional behavior expected at low temperature in real systems, it is useful to plot the logarithm of the susceptibility vs the logarithm of the temperature. In fact when $kT \ll |J|$, the susceptibility of an ideal 1-D ferromagnet can be approximated to an exponential divergence:

$$\chi \propto T^{-\beta}$$

The parameter β has been calculated with different models and varies from 1.5 to 2.0 depending on the quantic or classical nature of the spins.[41-44] In the present case the experimental values are $\beta = 1.599$ for I and $\beta = 1.542$ for II, in good agreement with the values 1.5–1.67 calculated for quantic $S = \frac{1}{2}$ chains.[41,42] Figure 5 shows that compounds I and II behave differently. In the case of I (Figure 5a) the experimental susceptibility at the lowest temperatures is above the straight line of the exponential divergence, while for II the data lie below. These deviations of the magnetic susceptibility from the ideal 1-D behavior are due to weak interchain interactions, which are of ferromagnetic nature in I and antiferromagnetic nature in II. These interchain interactions can be taken into account by correcting the susceptibility calculated with the Baker model for the presence of a molecular field.[45] The susceptibility becomes

$$\chi = \frac{\chi_{chn}}{1 + (zJ'/c)\chi_{chn}}$$

where $c = N\mu_B^2 g^2$, χ_{chn} is the susceptibility calculated for the chain, and z is the number of nearest neighbors. The best fit parameters are $J = -24.5$ (1) cm^{-1}, $zJ' = -0.002$ (1) cm^{-1}, and $g = 2.13$ (2) for I and $J = -30.8$ (1) cm^{-1}, $zJ' = +0.046$ (1) cm^{-1}, and $g = 2.08$ (2) for II. The slight difference between the J and g values calculated for the low- and high-temperature data can be con-
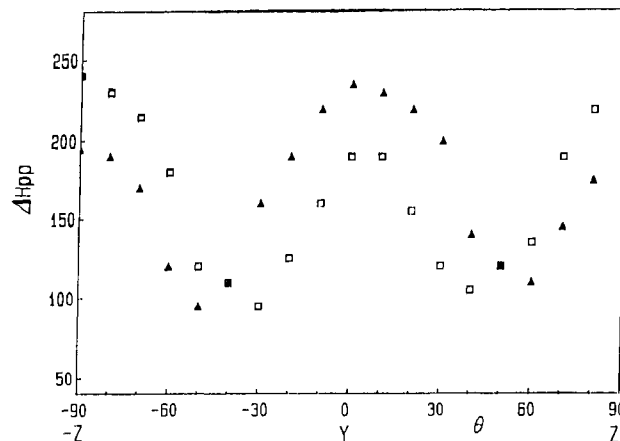

Figure 6. Angular dependence of the line width in $Cu(hfac)_2NITiPr$ at room temperature and 35.5 GHz, observed rotating along the x axis. The different symbols refer to the two signals of the two magnetically nonequivalent chains.

sidered as acceptable, considering the intrinsic low precision with which the J values are determined for ferromagnetic interactions.[46] The interchain coupling is ferromagnetic for I, and antiferromagnetic for II, but in every case is very small, in agreement with the one-dimensional nature of I and II. Although we used Heisenberg exchange for the sake of simplicity, the calculated values of the interaction are close to the limit expected for dipolar interaction, in agreement with the model already used for interpreting the nature of the magnetic phase transition in Mn-$(hfac)_2NITR$.[31,47] The difference in the sign of J' for I and II must depend on the different orientations of the nearest-neighbor chains in the two compounds.

EPR Spectra. The polycrystalline powder EPR spectrum of I at Q-band frequency is typical of an axial copper with $g_\perp = 2.05$ and $g_\parallel = 2.15$.[48] The single-crystal spectra were recorded at room temperature, with rotation around the orthogonal axes x, y, z, where $x = a \times b$ and z is the $(1\bar{1}0)$ direction. In general two signals were observed at each angular setting in the external magnetic field, due to the presence of two magnetically nonequivalent chains in the monoclinic cell.[49] The two chains develop parallel to y and z, respectively, so that in the rotation along x the magnetic field moves from parallel to perpendicular to both the chain directions. In particular when the field is parallel to z, it is parallel to chain 1 and perpendicular to chain 2, and vice versa when it is parallel to y.

The angular dependence of the EPR line width in the yz plane is shown in Figure 6, while the g factors are reported in Figure 7. The line width for signal 1 has a maximum (240 G) along z and goes through a minimum (95 G) about 55° from the maximum. A second maximum is observed along y (190 G). The same behavior is observed for signal 2, except that the y and z directions are reversed. The signal that has the largest line width along the z axis has also the largest g value, 2.15, approximately along this direction and the smallest g, 2.03, along y. Similar considerations apply to the other signal. The rotations along the other two axes show that one signal is essentially isotropic, because the field is in the plane orthogonal to the chain, while the other shows a behavior similar to that observed by rotation along the x axis. When the field is parallel to x, only one signal is observed with $g = 2.04$ and the peak-to-peak line width $\Delta H_{pp} = 290$ G.

The complete analysis of the angular dependence[50] of the g factors provided the principal directions and values reported in Table IV. The direction corresponding to the highest g value is very close to the bisector of the perpendiculars to the equatorial

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Table IV. Principal Values and Directions of the g Tensors at Room Temperature Compared with the Directions of the Two Magnetically Nonequivalent Chains[a,b]

	chain 1		chain 2
$g_1 = 2.15$	−0.088 0	$g_1 = 2.15$	0.089 32
	0.104 08		−0.948 08
	0.990 66		−0.305 24
$g_2 = 2.05$	−0.724 13	$g_2 = 2.06$	0.695 60
	0.676 24		0.278 73
	−0.135 40		−0.662 16
$g_3 = 2.03$	−0.684 02	$g_3 = 2.02$	−0.712 86
	−0.729 29		0.153 18
	0.015 83		−0.684 37
direction of chain 1	0.079 19	direction of chain 2	−0.079 19
	−0.058 36		−0.961 88
	0.996 17		−0.261 77

[a] The direction cosines of the indicated g_i values are referred to the orthogonal frame xyz defined in the text. [b] As the direction of the chain, we consider the bisector of the perpendiculars to the equatorial coordination planes of the two inequivalent copper sites in the chain.

coordination planes of the two inequivalent copper sites in the chain. Similar results were previously observed for II.[33] The actual g values must be considered as the average of the corresponding values of the copper ion and of the radical, as previously reported.[33] Assuming that g for the radical is isotropic and equal to 2, the principal g values of copper are calculated as $g_1 = 2.30$, $g_2 = 2.10$, and $g_3 = 2.06$ in agreement with an elongated octahedral coordination around copper.[48]

The angular dependence of the line width of the EPR spectra at room temperature conforms nicely to that expected for a one-dimensional ferromagnet.[51,52] In fact the maximum line width is observed parallel to the chain direction, as must be expected for dominant dipolar broadening. Similar conclusions are reached if the effect of anisotropic exchange is included, because theory predicts[53] that its largest component corresponds to that of the largest g value, as observed. The line width goes through a minimum at $\theta = 55°$, θ being the angle between the chain axis and the external magnetic field, in agreement with a $((3 \cos^2 \theta) - 1)^n$ dependence expected for large spin diffusion effects.[51,52] The magic angle behavior is indeed the signature of the one-dimensional nature of the compounds. No analysis of the line shape, which also in principle contains useful information on the nature of the material, could be attempted, because the signals of the two chains largely overlap each other.

On decreasing temperature the lines broaden, and the analysis of the spectra is complicated by the availability of only a X-band spectrometer in the liquid-helium region, which does not allow the resolution of two signals. However, there is some evidence that the resonance fields shift as a consequence of short-range order. In fact at low temperature the spins are correlated in relatively long segments of the chain due to the magnetic coupling, and as a consequence, internal fields are built up, which add or subtract to the external magnetic field.[54,55] In a one-dimensional ferromagnet, with dipolar intrachain interaction, the spins are expected to orient preferentially parallel to the chain direction. In this orientation therefore the internal field adds to the external field in such a way that the resonance shifts to lower fields at low temperature. This is what is experimentally observed with the g_1 value increasing from 2.15 at room temperature to 2.18 at 5 K.

Conclusions. The study of the magnetic properties of I and II down to 1 K has shown that the one-dimensional model is a good approximation for these materials. The small deviation observed at low temperature seems to indicate that either ferro- or anti-
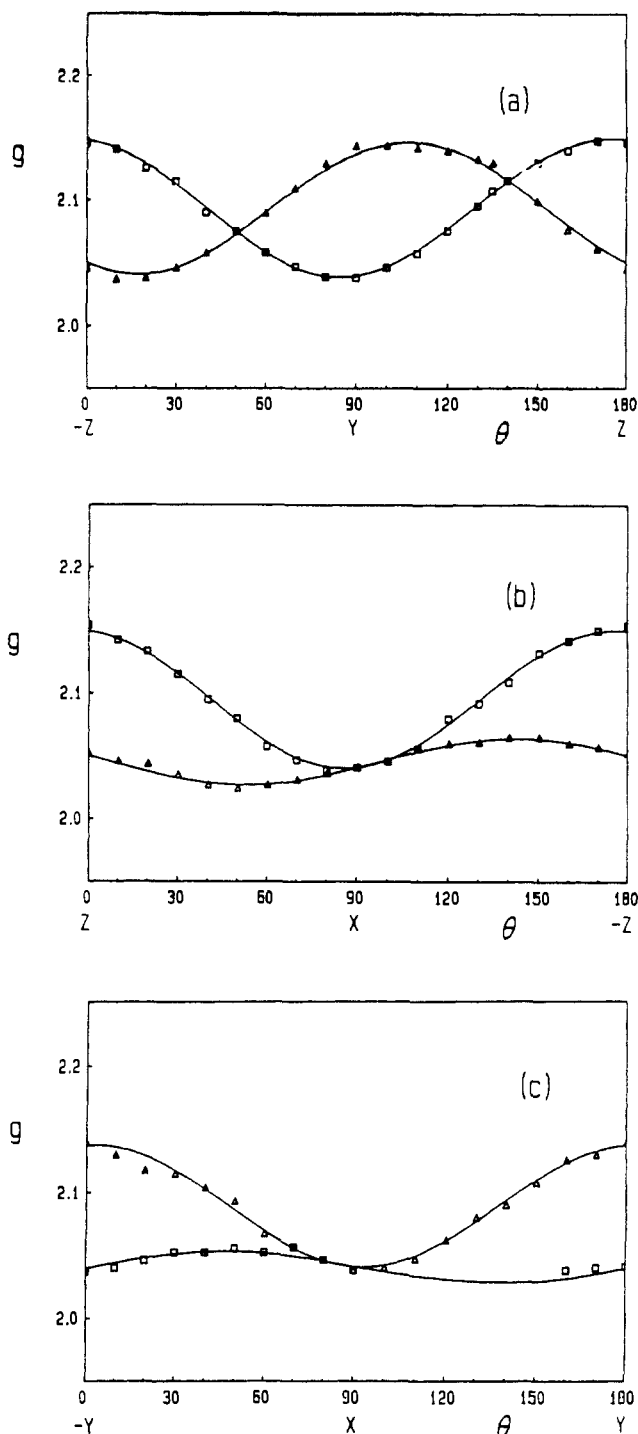
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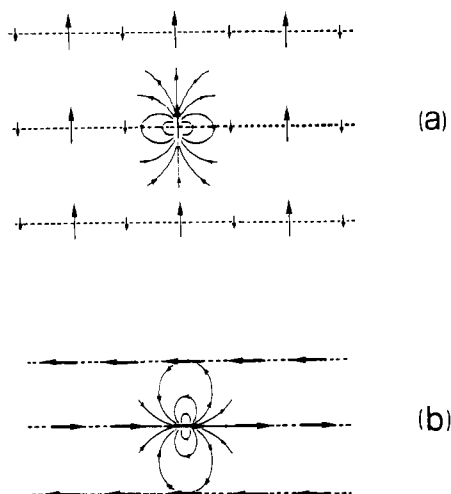(55) Karasudani, T.; Okamoto, H. *J. Phys. Soc. Jpn.* **1976**, *43*, 1131.

Figure 7. Observed and calculated g factors at room temperature and 35.5 GHz observed for the two signals of $Cu(hfac)_2NITiPr$, rotating along x (a), y (b), and z axes (c).

ferromagnetic interactions between the chains can be operative in these lattices but that in any way the extent of coupling is small, close to the dipolar limit.

It is instructive to compare the ferromagnetic $Cu(hfac)_2NITR$ with the ferrimagnetic $Ni(hfac)_2NITMe^{30}$ and $Mn(hfac)_2NITR$ chains.[29,31,47] In the latter compounds the interchain coupling constants are 1 order of magnitude larger than those reported in the present work for the copper derivatives and they undergo a phase transition to 3-D magnetic ordered state.[30,31,53] The transitions have been extensively investigated and have been revealed to be induced by the dipolar interaction. The ferromagnetic nature of the phase transition of these compounds can be intuitively understood by keeping in mind only classical considerations on the interaction between magnetic dipoles. In fact we have previously observed that in Heisenberg ferrimagnetic chains the

Figure 8. Schematic view of the dipolar field and preferred spin orientation in ideal 1-D ferrimagnets (a) and 1-D ferromagnets (b).

preferred spin orientation is orthogonal to the chain direction.[31,47] The dipolar field generated by a magnetic moment interacts with the moments of the neighboring parallel chains and orients the spins parallel to each other, as depicted in Figure 8a. On the other hand, if the coupling is ferromagnetic, the preferred spin orientation is parallel to the chain direction. In this case the dipolar interaction between parallel chains tends to keep the magnetic moments antiparallel to each other, as shown in Figure 8b.

Both $Cu(hfac)_2NITR$ compounds have shown a significant positive g shift along the chain, indicating this as the favorite spin orientation.[33] In the NITMe derivative II the chains are related by the unit translations and are parallel to each other and we

observe a 3-D antiferromagnetic interaction, as predicted by our simple model. In the case of the compound I each chain is surrounded by four orthogonal chains, so complicating the pattern of interchain dipolar interactions. Our simple model, based on the symmetry of translations, cannot apply in this case, and detailed calculations would be needed. On the other hand, these cannot be performed unless more information on the ordered phase is available.

Due to the long distances between chains the interchain dipolar energy is fairly small in all these products. However, in the case of the manganese and nickel derivatives the magnetic correlation along the chain originates at low temperature large effective moments that enhance the effects of the weak dipolar interaction. The observed transition temperatures are in fact 8 and 5 K for the manganese[31,47] and nickel[30] compounds, respectively, while the copper compounds, which have much smaller magnetic correlation within the chains, remain paramagnetic down to 1 K.

As a conclusion, even if it is possible to obtain both antiferro- and ferromagnetic 3-D interactions by starting from ferromagnetic chains, the ferrimagnetic chains seem to be the most suitable building blocks in order to obtain bulk magnetic materials with desired properties.

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Synthesis of CF3SSI, Vibrational Analyses for CF3SSX (X = F, Cl, Br, I, and H), and Gas-Phase Structures of CF3SSF and CF3SSH[1]

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CF_3SSI has been synthesized by reacting CF_3SSH with *N*-iodosuccinimide at −120 °C. The compound decomposes at −100 °C. It was characterized by its Raman spectrum recorded at −196 °C and by ^{19}F NMR and UV/vis spectroscopy. For comparison Raman spectra of solid and IR spectra of gaseous or matrix-isolated samples were also recorded for the homologues CF_3SSX with X = F, Cl, Br, and H. Valence force fields for these (trifluoromethyl)disulfanes were derived from the spectral data. The S–S force constant for X = Cl, Br, and I (2.50×10^2 N m^{-1}) is equal to that in S_8; it is larger for X = F (2.59×10^2 N m^{-1}) and smaller for X = H (2.32×10^2 N m^{-1}). The S–X force constants decrease steadily with increasing size of the halogen from 3.49 $\times 10^2$ N m^{-1} for S–F to 1.74×10^2 N m^{-1} for S–I. Furthermore, the gas-phase structures of CF_3SSF and CF_3SSH were determined by electron diffraction. The S–S bond lengthens from 197.0 (3) pm in CF_3SSF to 203.8 (5) pm in CF_3SSH (r_g values; error limits are 3σ values and include a possible scale error of 0.1%). The CSSF dihedral angle is 91 (3)°.

Introduction

Until now, only a few iodosulfanes RSI with R = aryl or alkyl have been synthesized and fully characterized,[3–7] even though the S–I moiety is of considerable biochemical interest.[8] Despite the

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thermal instability, we were recently successful in determining the crystal structure of $(C_6H_5)_3CSI$.[9] The experimental S–I distance in this compound (240.6 (4) pm) is close to the sum of the covalent radii (237 pm). It is longer than the distances in the S_7I^+ cation and its derivatives (S–I between 231.8 (8) and 234.2 (3) pm[10,11]), where iodine is bonded to three-coordinate sulfur.

An alternative synthetic route to iodosulfanes such as CF_3SI[3] and $CF_3C(O)SI$[6] is iodination of thiols with *N*-iodosuccinimide. In continuation of these experiments, we report here on CF_3SSI. Because of its low stability, it is not possible to determine a

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