Table I

	ΔG, kcal/mol	ΔH, kcal/mol	ΔS, cal/K·mol
2a $\rightleftharpoons$ **2b**	2.6	0.8	-6.2
3a $\rightleftharpoons$ **3b**	1.6	-0.5	-6.7
4a $\rightleftharpoons$ **4b**	-0.4	-3.6	-10.2
5a $\rightleftharpoons$ **5b**	1.7	-0.6	-7.5
6a $\rightleftharpoons$ **6b**	2.4	1.8	-2.0
7a $\rightleftharpoons$ **7b**	2.0	-0.6	-8.4

Monitoring the absorbance for the open, zwitterionic forms **2b**–**7b** (λ_{max} at 560 nm) of **2a** $\rightleftharpoons$ **2b**, **3a** $\rightleftharpoons$ **3b**, **4a** $\rightleftharpoons$ **4b**, **5a** $\rightleftharpoons$ **5b**, **6a** $\rightleftharpoons$ **6b**, **7a** $\rightleftharpoons$ **7b** (3×10^{-5} M in dimethyl sulfoxide at 25 °C) as the systems reach thermal equilibrium leads to the spectra shown in Figure 1.[8] Under conditions (25 °C in dimethyl sulfoxide) where **2**, **3**, **5**, **6**, and **7** exist predominantly in the closed form, i.e., very little absorbance at 560 nm is observed, there is a considerable absorbance at 560 nm for **4**.

The equilibrium constant and therefore ΔG for the **1a** $\rightleftharpoons$ **1b** equilibrium for each system can be determined,[9] and these values are shown in Table I. For the parent compound, **2**, the equilibrium constant is 1.2×10^{-2}, which corresponds to a ΔG between **2a** and **2b** (only the closed spiro[pyranindoline] forms of **2**–**7** are shown in Chart I) of 2.6 kcal/mol. Under these conditions, 99% of the mixture remains in the closed spiro pyran form, **2a**. In a similar manner, the ΔG for **3** is ca. 1.5 kcal/mol, so that this compound also exists predominantly in the closed form (**3a**). In dramatic contrast to the thermal behavior of **2** and **3**, we have found that **4** exists predominantly (65%) in the *open* form, **4b** (not shown), with a thermal equilibrium constant of 1.8, representing a ΔG of -0.4 kcal/mol between **4a** and **4b**. The free energy difference between the open and closed forms of the spiro[pyranindoline] systems **2a** $\rightleftharpoons$ **2b** and **4a** $\rightleftharpoons$ **4b** is ca. 3.0 kcal/mol. The effect of the macrocycle in this system is to increase the concentration of the zwitterionic form of the spiro[pyranindoline] $\rightleftharpoons$ merocyanine equilibrium *by a factor of 54*, from 1.2% (**2a** $\rightleftharpoons$ **2b**) to 65% (**4a** $\rightleftharpoons$ **4b**). We predicted that the effect of the macrocycle on the **1** $\rightleftharpoons$ **2** equilibrium would diminish on increasing ring size, and that is indeed observed. The thermal behavior of **6** and **7** closely parallels that of the parent nonmacrocyclic compounds **2** and **3** (Figure 1). The equilibrium constants for **6a** $\rightleftharpoons$ **6b** and **7a** $\rightleftharpoons$ **7b** are 1.8×10^{-2} and 3.5×10^{-2}, respectively, at 25 °C in dimethyl sulfoxide, corresponding to a free energy difference of 2.4 and 2.0 kcal/mol, so that once again >96% of the spiro[pyranindoline] exists in the closed form. However, the 18-membered ring appears to be a necessary but not sufficient condition for this remarkable thermochromic behavior. The thermal behavior of **5**, in which the lactone of **4** is replaced by an ether linkage, exists predominantly in the closed form, **5a** ($K_{eq} = 5.6 \times 10^{-2}$).

The relative contributions of enthalpy and entropy to the 3 kcal/mol $\Delta\Delta G$ between **2a** $\rightleftharpoons$ **2b** and **4a** $\rightleftharpoons$ **4b** were determined by plotting ln K_{eq} against $1/T$. The results are summarized in Table I. Only the opening of the smaller macrocycle, **4a** $\rightleftharpoons$ **4b**, is significantly (>1 kcal/mol) exothermic. The relative differences between ΔS values are much smaller, so that enthalpy is the primary source of the difference in ΔG between **4** and the other spiro[pyranindoline]s. We attribute this difference in large part to ring strain in the unusually constrained 18-membered ring of **4**. A critical role, however, must be ascribed to the conformation of the lactone, since **5**, in which the lactone is replaced by an ether linkage, no longer exhibits this unusual thermal behavior. While reports on the qualitative effects of metals on the **1a** $\rightleftharpoons$ **1b** equilibrium have appeared,[6m,n] we are not aware of any studies that have quantitatively demonstrated a change of this magnitude in the **1a** $\rightleftharpoons$ **1b** equilibrium. The further effect of added ligands on this equilibrium and the incorporation of the spiro[pyranindoline] into macrocycles that are capable of inclusion complex formation are currently being pursued in our laboratory.

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(7) Compounds **4**, **6**, and **7** were prepared from the corresponding hydroxy acids by macrolactonization using the method of Mukaiyama (cf.: Mukaiyama, T.; Usui, M.; Saigo, K. *Chem. Lett.* **1976**, 49), and NMR, IR, and FAB-MS data were compatible with the assigned structures. The hydroxy acids were in turn prepared by condensation of the appropriate indolines and salicylaldehydes. Compound **5** was prepared by intramolecular displacement of the corresponding chloromethyl spiro[pyranindoline] alcohol (potassium *tert*-butoxide, tetrahydrofuran, 45 °C), and **2** and **3** are described in ref 5.

(8) For a similar treatment, see ref 6k.

(9) The determination of the equilibrium constant requires a knowledge of ϵ, which we have calculated for the open form of the spiro[pyranindoline] from the equilibrium constant for **4a** $\rightleftharpoons$ **4b** that can be obtained by NMR. Integration of the peak heights of the singlet at δ 1.7 for the methyl protons of **4b** (six protons) and the signal (AB quartet) at δ 4.8 for the benzylic protons of **4a** gives a K_{eq} of 1.8, from which ϵ = 51 000 can be obtained from the equation

$$K_{eq} = \frac{A/\epsilon}{[S_T] - (A/\epsilon)}$$

where A = absorbance, ϵ = extinction coefficient, and S_T = starting concentration of the closed spiro[pyranindoline], **4a**.

Ferromagnetic Alternating Spin Chains

Andrea Caneschi,[†] Dante Gatteschi,*[†] Jean Laugier,[‡] and Paul Rey*[‡]

Department of Chemistry
University of Florence, Florence, Italy
Equipe Chimie de Coordination, Laboratoires de Chimie
Department de Recherche Fondamentale
Centre d'Etudes Nucleaires de Grenoble 85X
Grenoble, France

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The study of the magnetic properties of heteronuclear species has shown that ferromagnetic coupling is much more common than it was suspected before,[1,2] because by using different metal ions, or in general different spins, it is much easier to bring into interaction orthogonal magnetic orbitals. These results have been very stimulating, because they have suggested possible strategies to assemble ferromagnetic materials starting from pairs of different spins. The interest for such materials is bound both to the wish to make what has been called the magnetic zoo[3] as complete as possible and also to the possibility of determining which are the conditions under which molecular ferromagnets can be obtained.

The design of low dimensional materials is relatively simple using molecular building blocks, and chains are the systems for which more examples are available.[4,5] As regards the magnetic properties, either antiferro-, ferro-, or ferrimagnetic behavior has been reported. In particular, recently there have been reports in the literature concerning structurally ordered bimetallic chains in which a sequence of the type -M-M′-M-M′- has been obtained.[6-8] The coupling in these chains has been found to be antiferromagnetic in nature, but since different spins are coupled,

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[†] University of Florence.

[‡] Centre d'Etudes Nucleaires de Grenoble.

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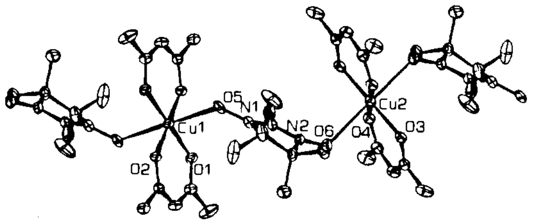


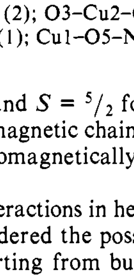
Figure 1. View of Cu(hfac)$_2$(NIT-Me). Bond distances (Å) and angles (deg): Cu1-O1, 1.956 (3); Cu1-O2, 1.936 (4); Cu1-O5, 2.341 (6); O5-N1, 1.284 (6); N2-O6, 1.278 (6); Cu2-O6, 2.431 (5); Cu2-O3, 1.927 (4); Cu2-O4, 1.939 (5); O1-Cu1-O2, 92.3 (1); O1--Cu1-O5, 85.2 (1); O2-Cu1-O5, 88.4 (2); O3-Cu2-O4, 91.5 (2); O3-Cu2-O6, 83.8 (1); O4-Cu2-O6, 98.3 (1); Cu1-O5-N1, 157.5 (3); Cu2-O6-N2, 123.7 (3).

e.g., $S = {}^1/_2$ for Cu(II) and $S = {}^5/_2$ for Mn(II), the magnetic behavior is that of a ferrimagnetic chain. These chains have also been found to order ferromagnetically at relatively high temperature.[9]

Since ferromagnetic interactions in heterodinuclear species can be fairly strong, we considered the possibility of obtaining new ferromagnetic chains starting from building blocks containing different spins. In particular we considered the possibility of using as repeat units moieties containing a metal ion coordinated to a stable organic radical in a geometry which is known to yield ferromagnetic coupling.

Indeed linear chains of this type were obtained[10] by using Cu(hfac)$_2$ (hfac = hexafluoroacetyl acetonate) and TEMPOL (TEMPOL = 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxy), a stable nitroxide containing two ligating functions, namely, N–O and O–H. The coupling between copper and N–O is ferromagnetic,[11] but the interaction between N–O and the further copper ion is antiferromagnetic, yielding the first example of an alternate ferromagnetic–antiferromagnetic chain[12] and not a pure ferromagnetic chain.

In order to overcome this problem, we addressed ourselves to nitronyl nitroxides of the following formula: which, being sym-



metric, with two equivalent N–O groups, might in principle form chains binding to two different metal ions and coupling in a similar fashion to both of them. With R = phenyl, NIT-Ph, and copper(II) we did not succeed, although an interesting magnetic behavior was evidenced[13] but with R = methyl and NIT-Me, we have now obtained the first example of a ferromagnetic alternating spin chain.

By reaction of Cu(hfac)$_2$ with NIT-Me (NIT-Me = 2,4,4,5,5-pentamethyl-1-oxyimidazoline-3-oxide) in hot dry heptane, single crystals which analyzed satisfactorily for the formula Cu(hfac)$_2$(NIT-Me) were obtained.

The structure[14] consists of chains in which one copper(II) ion is octahedrally coordinated by four oxygens of two hexafluoroacetyl acetonate ligands in a plane and two axial oxygen atoms of two different NIT-Me molecules, as shown in Figure 1. In the asymmetric unit there are two different copper ions: although the two coordination environments are very similar, slight differences do exist in the copper–axial oxygen distances (2.346 (8) Å vs. 2.433 (7) Å). The chains are reasonably well shielded, because the shortest contacts between paramagnetic centers belonging to different chains are 8.955 (2) Å.

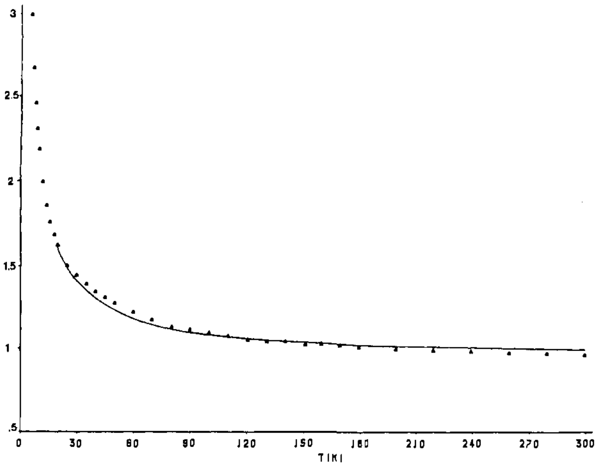


Figure 2. Temperature dependence of the χT product for Cu(hfac)$_2$-(NIT-Me) in the range 6–300 K. Experimental points are shown as triangles. The curve was calculated as discussed in the text.

The magnetic properties of Cu(hfac)$_2$(NIT-Me) are plotted in Figure 2 in the χT vs. T form. The room temperature value of χT is slightly higher than that expected for two noninteracting free spins with $S = {}^1/_2$ (0.954 emu mol^{-1} K vs. 0.75 emu mol^{-1} K). On a lowering of the temperature, χT increases up to 3 emu mol^{-1} K at 6 K, the lowest temperature we could reach. This value is much higher than expected for a triplet state (1 emu mol^{-1} K) and is indicative of a ferromagnetic coupling within the chain. A satisfactory fit of the experimental data was made by using the formula reported for ferromagnetic chains[15] of spin ${}^1/_2$ with the hamiltonian in the form $H = \sum_{i,j} J_{ij} S_i \cdot S_j$. The best fit parameters are $g = 2.208$ (1) and $J = -25.7$ (1) cm^{-1} with an agreement factor $R = 9.293 \times 10^{-3}$. The calculated J value compares well with those reported for other similar copper hexafluoroacetyl acetonate adducts with nitroxides.[10,16] Polycrystalline powder EPR spectra at room temperature are axial, with $g_{\parallel} = 2.18$ and $g_{\perp} = 2.07$.

As a conclusion, we want to state that by use of stable radicals as ligands toward transition-metal ions, it is possible to obtain alternating spin chains. In particular, fairly strong ferromagnetic interactions can be obtained with copper ions. Further studies are in progress in the low-temperature range, below 4 K, to determine if three-dimensional order, either ferro- or antiferromagnetic, sets in. We are now synthesizing similar complexes with different metal ions and different radicals. Preliminary data suggest that also the cobalt(II) and the nickel(II) analogues of Cu(hfac)$_2$(NIT-Me) yield ferromagnetic alternating spin chains, thus opening a new class of magnetic compounds.

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Registry No. Cu(hfac)$_2$NIT-Me, 106865-84-3.

Supplementary Material Available: Listing of atomic positional parameters and thermal parameters (2 pages). Ordering information is given on any current masthead page.

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(14) Crystal data: space group $P\bar{1}$, $a = 8.955$ (6) Å, $b = 15.915$ (7) Å, $c = 10.29$ (4) Å, $\alpha = 71.20$ (3)°, $\beta = 68.24$ (2)°, $\gamma = 76.44$ (3)°, $\rho_{\text{calcd}} = 1.636$ g cm^{-3}, $Z = 2$, 3445 unique reflections with $|F| > 3\sigma|F_o|$ were collected with an Enraf-Nonius four-circle diffractometer with use of Mo Kα radiation. The structure was solved by heavy-atom methods (with anisotropic thermal parameters for all non-hydrogen atoms). Refinement converged to $R = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.079$ and $R_w = |\sum w(|F_o| - |F_c|)^2/\sum wF_o^2|^{1/2} = 0.083$. Tables of positional and thermal parameters are available as supplementary material.

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