(50 MHz, $CDCl_3$): $\delta = 24.7, 26.4, 28.7, 37.4, 82.7, 171.5$. IR: (nujol) 1615, 1320, 1285, 1265, 1245, 1220, 1140, 1105, 1010, 985, 965, 890, 855, 670 cm^{-1}; MS: *m*/*z* (%): 350 ([M^++2], 0.2), 349 ([M^++1], 2), 348 ([M^+], 8), 347 ([$M^+ - 1$], 4), 333 ([$M^+ -$ Me], 8), 291 (100); elemental analysis calcd for $C_{19}H_{34}B_2O_4$ (%): C 65.56, H 9.84; found: C 65.31, H 10.03.

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Nitroxide Radicals as Templating Agents in the Synthesis of Magnets Based on Three-Dimensional Oxalato-Bridged Heterodimetallic Networks**

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Building an extended compound with a particular crystal structure from molecular precursors in solution is still a challenge in many areas of chemistry.[1] Coordination chemistry provides a useful algorithm for this purpose (lattice engineering) because coordination geometries are well defined by strong and highly directional bonds. This concept is especially relevant in the synthesis of molecular magnetic materials since metal complexes provide the spin carriers (metal ions) and ligands through which magnetic interactions can occur.[2]

The ability of the oxalate (ox) ion, $C_2O_4^{2-}$, to transmit efficiently magnetic interactions through its bridging mode has been well documented since the pioneering work on dinuclear copper(II) complexes.[3] Later, the use of the homoleptic species $[M(ox)_3]^{3-}$ ($M = Cr^{III}$, Fe^{III}) provided an easy access to systems of higher dimensionality.[4] Only two families of high-dimensional oxalato complexes displaying magnetic order have been described: a) two-dimensional (2D) heterodimetallic compounds of formula $A[M^{II}M^{III}(ox)_3]$ (A = quaternary onium cation, M = metal) with a honeycomb-layered structure[5] and b) three-dimensional (3D) homometallic compounds of formula $A[M_2^{II}(ox)_3]$ or $A[M^{II}M^{III}(ox)_3](ClO_4)$ ($A = [M(bpy)_3]^{2+}$) with a cubic chiral packing.[6] The resulting dimensionality depends on the type of A^{m+} ion used, so that these cations can be considered as *templating agents* for the overall structure.[7] There is a fine interplay between molecular recognition and chirality in this kind of system: 2D structures are achiral but, within each layer, all the M^{III} sites have the same chirality while all the M^{II} sites have the opposite one; in the 3D systems, both sites adopt the same configuration. In all cases, the enantioselective synthesis of the optically active stereoisomers using chiral building blocks is possible.[8] Besides their role as structure-directing agents, the A^{m+} ions can also introduce physical properties of interest to the magnetic system, leading to multiproperty materials. Along this line, we have synthesized a family of 2D compounds where the "innocent" quaternary onium cation has been replaced by redox-active species of the decamethylmetallocenium type[9] or organic donors such as BEDT-TTF (2,2′-bis(5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]di-

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[**] This work was supported by the European Union (TMR ERB 4061 PL97-0197) and the Ministerio de Ciencia y Tecnología (MCT) (Project no. MAT98-0880). C.G. and F.M.R. wish to thank the MCT for a research contract (Contrato de Reincorporación).

thiin)). The latter provided the first example of the coexistence of ferromagnetism and metal-like behavior in a molecular solid.[10]

Nitronyl-nitroxides have been widely used in the preparation of molecular magnetic materials, either by themselves (*all-organic approach*)[11] or as ligands in transition metal complexes (*metal-radical approach*).[12] The preparation of cationic nitronyl–nitroxide radicals of the *N*-alkylpyridinium type introduced by Awaga and co-workers[13] allowed the combination of these entities with simple paramagnetic anions.[14] Kahn realized that it was possible to bridge heterodimetallic ordered chains using these cations and prepared the first molecule-based magnets containing three different spin carriers.[15] To date, this is the only family of materials having this particularity.

This prompted us to investigate the synthesis of extended dimetallic oxalato complexes of the type rad[$M^{II}Cr(ox)_3$] (rad^+ = 2-(1-methylpyridinium-4-yl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide). They can be obtained by reaction of $(rad)_3[Cr(ox)_3]$ with the appropriate divalent metal salt. One such compound, rad[$Mn(H_2O)Cr(ox)_3$]$\cdot 2H_2O$ (**1**), is based on a cationic nitronyl–nitroxide free radical (rad^+) that acts as a templating agent in the formation of a 3D dimetallic oxalato network. Compound **1** crystallizes in the monoclinic C_c space group. The molecular structure of rad^+ (Figure 1a) is very similar to that found in the previously reported salts. Figure 2 shows the packing of the radicals in the bc plane. Note the formation of zigzag chains running along the *z*-axis. The shortest contact between proximate radicals within the chain is O2···C10(x, $1-y$, $z-½$): 4.312(5) Å. The N–O functions are well isolated from each other: the minimum O···O intermolecular distance also corresponds to two adjacent radicals in the chain (O1···O2 (x, $1-y$, $z-½$): 6.891(5) Å). This is in contrast with the situation found in most crystals of nitroxide radicals, where O···O contacts of about 3.5 Å are observed.

The oxalato network is also shown in Figure 2 to stress the role of the free radicals as structural directors. The zigzag chains of radicals find their replica in the inorganic lattice. Indeed, the packing of the 3D dimetallic network can be viewed, in a first step, as zigzag alternating Mn–Cr chains oriented in the same direction (continuous bonds). A detailed picture of this one-dimensional fragment is shown in Figure 3, where the linkage between adjacent metal ions by bisbidentate μ-oxalate bridges is clearly seen. Noteworthy is that the chirality of the metal centers follows the sequence $\cdots\Delta\Delta\Lambda\Lambda\Delta\Delta\cdots$ along the chain. This implies the existence of two distinct bisbidentate bridges: one connecting metal centers of the same chirality (Mn1···Cr1: 5.421(3) Å) and a second one connecting centers of opposite chirality (Mn1···Cr1 (x, $2-y$, $z+½$): 5.3927(16) Å).

The chains are linked between them through a new type of oxalate bridge (see Figure 1b) that is simultaneously bidentate (towards chromium) and monodentate (towards manganese). A water molecule occupies the vacant position in the coordination sphere of the Mn^{2+} center. References in the literature concerning this unusual bridging mode are very scarce.[16, 17] In our complex, the linkage (dashed bonds in Figure 2) takes place between a $Cr(ox)_3$ building block and a

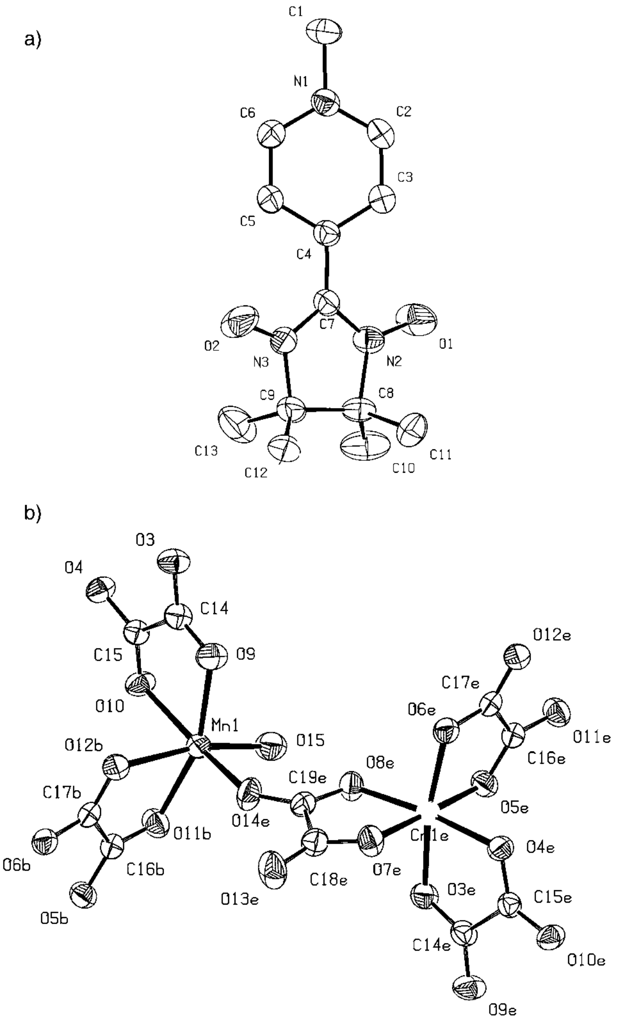

Figure 1. Molecular structure of a) rad^+ and b) $[Mn(H_2O)Cr(ox)_3]^-$ (ellipsoids are set at the 50% probability levels; all H atoms have been omitted for clarity). Selected distances [Å] and angles [°]: a) N2-O1 1.271(3), N3-O2 1.271(3); C3-C4-C7-N2 26.6(4); b) Mn1-O15 2.138(2), Mn1···Cr1e ($x+½$, $³⁄₂-y$, $z+½$): 5.5977(14).

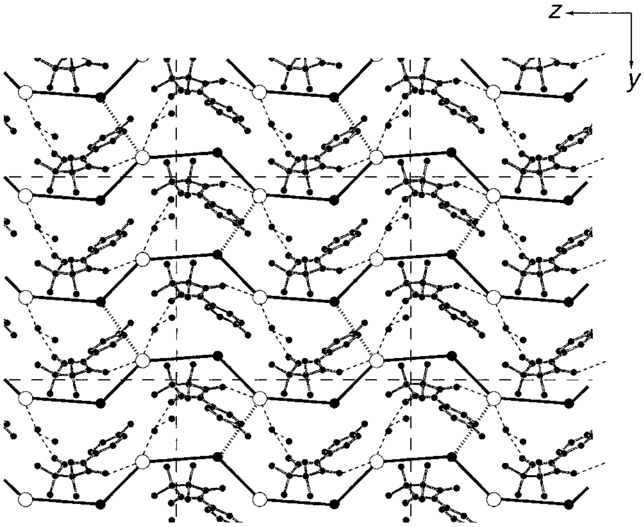

Figure 2. Projection of the crystal structure of **1** onto the bc plane (oxalate anions have been omitted for clarity). Thick bonds replace oxalate bridges: bisbidentate (continuous bonds) and bidentate/monodentate, whereas dashed lines (----) represent hydrogen bonds, broken lines (–––) the unit cell grid, ○ = Mn, ● = Cr.

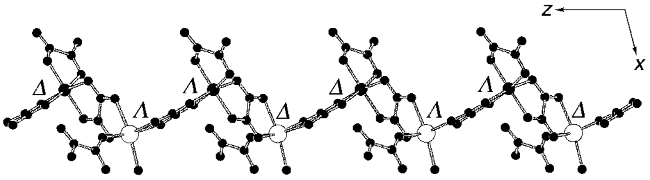

Figure 3. View along the b axis of the oxalato-bridged Mn–Cr ferromagnetic chains. The absolute configuration of the building blocks is also shown.

$Mn(ox)_3(H_2O)$ unit of opposite chirality. This results in the formation of an *achiral* 3-connected 10-gon network. Out of this plane, the decagonal units are arranged in such a way that hellical hexagonal channels are formed. Since the resulting network is achiral, both types of helix are found in the structure (Figure 4).

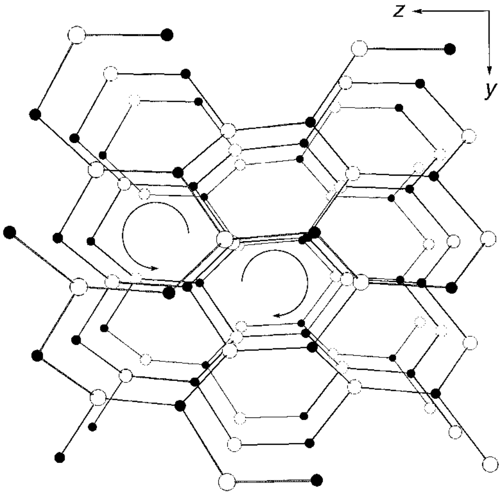

Figure 4. Perspective view along the a axis of the heterometallic lattice of **1** showing the metal connectivity and the hellical channels formed; ○ = Mn, ● = Cr.

The water molecules of crystallization are linked to each other (O17···O16 ($x+1$, y, z): 2.762(4) Å) and hydrogen bonded to the coordinated water molecule (Mn1-O15···O17: 2.674(4) Å). Short hydrogen bonds (Figure 2) are also found between the nitroxide oxygen atoms and the coordinated water molecules (Mn1-O15···O2-N3 ($x+½$, $³⁄₂-y$, $z+½$): 2.733(4) Å; O17···O1-N2: 2.800(3) Å. Thus, the radicals are tightly bound to the inorganic lattice by means of an extended hydrogen-bonded network.

Magnetic susceptibility (χ) measurements have been made on **1**. Figure 5 shows the thermal dependence of χT (the product of molar magnetic susceptibility with temperature) and χ. The χT has a constant value from room temperature down to 100 K ($\chi T = 6.55$ emu K mol^{-1}). Below this temperature, χT increases on cooling and reaches a maximum at 18 K, where it equals 7.15 emu K mol^{-1}. Then, χT drops abruptly and has a value of 1.5 emu K mol^{-1} at 2 K. The temperature dependence of χ shows a sharp maximum at 6 K with a typical Curie tail at lower temperatures.

At room temperature, the observed value of χT is approximately equal to the sum ($\chi T = 6.625$ emu K mol^{-1}) of the expected contributions corresponding to the three isolated spin carriers (nitroxide radical ($S = ½$), Mn^{2+} ($S = ⁵⁄₂$), and Cr^{3+} ($S = ³⁄₂$) cations). The sharp maximum observed in the χ versus T curve is characteristic of a long-range antiferromagnetic ordering. At temperatures above the transition, the magnetic behavior points to the presence of a low-dimensional system with dominant ferromagnetic interactions. Taking into account these considerations, the thermal variation of the χT product has been analyzed in terms of a regular AB chain model[18] with classical spins $S_A = ⁵⁄₂$ and $S_B = ³⁄₂$. The best-fit value for the exchange coupling constant (H_{ex}) is $J/k = +0.8$ K ($H_{ex} = -J\Sigma S_{Ai}S_{Bi}$). All previous studies indicate that the Mn^{II}–Cr^{III} exchange coupling through bisbidentate oxalate is ferromagnetic and, according to its structural features, the spin topology of **1** is best described in terms of ferromagnetic chains. An antiferromagnetic interaction between the chains should be present to account for the antiferromagnetic ordering observed at low temperatures. This interaction is certainly transmitted through the bidentate/monodentate oxalate anion. The lower symmetry of this bridge decreases the efficiency of the ferromagnetic pathway (as compared to the bisbidentate ligand) and the antiferromagnetic interaction becomes dominant, as has been shown recently in a chromium–manganese tetramer.[17] Note that the presence of a Curie tail at very low temperatures can been explained by considering the paramagnetism of an isolated nitroxide radical ($S = ½$). This indicates that the free radicals are not coupled to the metal centers, so that in the present example an antiferromagnetically ordered network coexists with a paramagnetic one. This is observed despite the fact that the nitroxide oxygen atom is hydrogen-bonded to the coordinated water molecule and, consequently, close to the manganese center (Mn1···O2 ($x+½$, $³⁄₂-y$, $z+½$): 3.8510(27) Å). It seems that the exchange interaction through this bridge is too weak to be appreciated in the temperature range of the experiment. An example of oxalato-based dimetallic magnets incorporating other uncoupled paramagnetic species, such as the decamethylferricinium cation, is known in the 2D family.[9]

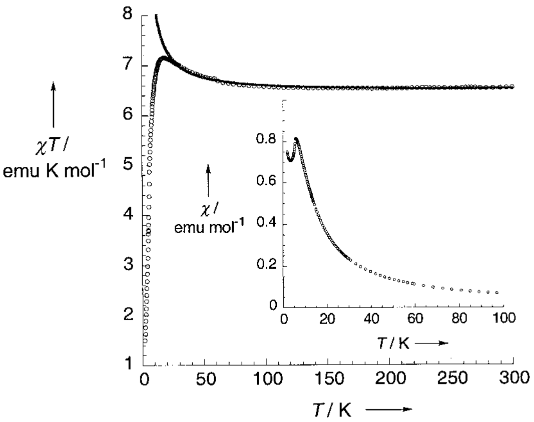

Figure 5. Thermal variation of the χT product (open circles) for **1**. The solid line represents the best-fit calculated data. Inset: Temperature dependence of χ.

The synthesis of molecular-based ferromagnets of this family can be anticipated by simply replacing Mn^{II} by Ni^{II}.

Owing to simple orbital symmetry considerations, this change should strengthen the ferromagnetic contribution from the bidentate/monodentate oxalate anion. In fact, our preliminary results on the analogous rad[NiCr(ox)$_3$] species shows that this compound is a ferromagnet with a critical temperature $T_c = 16$ K and a coercive field of 4000 Oe.

To summarize, the present report introduces the use of free radicals as counterions of an extended lattice. This is an efficient strategy for the synthesis of hybrid two-network magnetic materials based on organic free radicals and polymeric transition metal complexes. In the present case, nitroxide radicals act as templating agents in the formation of a unique three-dimensional oxalato-bridged heterometallic network. New molecular-based magnets with three different spin carriers have been obtained. This opens new synthetic pathways for novel and more complicated magnetic lattices.

Experimental Section

The cationic free radical prepared[13] as an iodide salt (100 mg, 0.26 mmol) was added to a suspension of $Ag_3[Cr(ox)_3]$ in EtOH (5 mL). After 30 min stirring, AgI was removed by filtration and a solution of $Mn(ClO_4)_2 \cdot 6H_2O$ (32 mg, 0.088 mmol) in the minimum amount of water was added to the filtrate. The resulting green suspension became clear after addition of H_2O (2 mL) and the mixture was left undisturbed in the dark. Green single crystals of **1** suitable for X-Ray structure analysis[19–21] grew within a few hours. IR(KBr): $\tilde{\nu} \sim 1376$ (N-O), 1140 cm^{-1} (N-O).

Received: September 14, 2000 [Z15805]

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[19] Crystal data for **1**: $C_{19}H_{25}CrMnN_3O_{17}$, $M = 674.36$, crystal dimensions: $0.61 \times 0.19 \times 0.12$ mm, monoclinic, C_c, $a = 11.343(2)$, $b = 14.311(2)$, $c = 16.928(10)$ Å, $\beta = 104.14(3)^\circ$, $V = 2665(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.681$ Mg m^{-3}. Data were collected on a Siemens SMART diffractometer equipped with a CCD detector by the ϕ-scan method ($4.68^\circ < 2\theta < 61.24^\circ$), $\lambda(Mo_{K\alpha}) = 0.71069$ Å, $T = 293(2)$ K. Of 11092 measured reflections, 6821 were independent ($R_{int} = 0.0245$) and used to refine 402 parameters (2 restraints). Absorption corrections were performed using the SADABS program[20a] ($\mu = 0.968$ mm^{-1}, min./max. transmission: 0.5899 and 0.8927). The structure was solved by direct methods (SIR97)[20b] and refined by full-matrix least-squares procedures on F^2 (SHELXL-97)[20c]. Hydrogen atoms were located in ideal positions and refined with a riding model. $R1$ ($F > 2\sigma(F)) = 0.0309$, $wR2 = 0.0642$ (all data) with $R1 = \Sigma||F_o| - |F_c||/ = \Sigma|F_o|$ and $wR2 = (\Sigma w(F_o - F_c^2)2/\Sigma w(F_o^2)^2)^{0.5}$. Max./min. residual peaks in the final difference map $0.253/-0.345$ e Å^{-3}. The absolute crystal structure was determined by the Flack method[21] (Flack number = 0.167(11)). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-149375. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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