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[16] The sample of [Nd(AlMe$_4$)$_3$] used in this study was transported from California to New York in a Dewar filled with dry ice.

[17] Full details (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC-100847. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033, e-mail: deposit@ccdc.cam.ac.uk).

[18] The principal distances and angles in **1** are similar to those reported earlier in the X-ray study.[8] From the present neutron study, the six Nd–C distances range from 2.58(2) to 2.64(2) Å, and the Al–C distances range from 1.97(3) to 2.12(3). The angles involving the nonbridging methyl groups, C3-Al1-C4, C7-Al2-C8, and C11-Al3-C12 (119.2(15), 116.8(13), and 119.0(13)°, respectively), are considerably larger than the other C-Al-C angles.

[19] The bridging Nd–H distance can be estimated from the difference between Nd–C (2.77 Å)[20] and Th–C (2.83 Å)[21] bond lengths in various Nd and Th cyclopentadienyl complexes, combined with the bridging Th–H distance (2.29 Å) in [{ThH$_2$Cp$^*_2$}$_2$].[21] This yields a value for Nd–H bond distance of 2.23 Å. Alternatively, if the difference between the ionic radii[22] of Nd^{III} (1.16 Å, nine-coordinate) and Th^{IV} (1.09 Å) is used, an estimated Nd–H distance of 2.36 Å is obtained.

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Two-Dimensional Nitroxide-Based Molecular Magnetic Materials**

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The temperature at which molecular solids exhibit macroscopic magnetic properties is strongly dependent on the dimensionality of the structure and on the magnitude of the exchange interactions between the spin carriers.[1] Only a few species meet the criteria at room temperature, namely, hexacyanometalates[2, 3] and an adduct of vanadium and tetracyanoethylene;[4] they exhibit ferro- or ferrimagnetic ordering. In these compounds a three-dimensional structure and a fairly strong exchange coupling are probably the cause of high-temperature magnetic ordering.

Most strategies for designing molecular magnetic materials involve antiferromagnetically coupled alternating metal ions with different spins that do not compensate one another. These ferrimagnetic structures are assembled with polydentate bridging ligands such as oxalato, oxamato, oxamido, oximato, and dithiooxalato groups.[5] The use of these ligands has been fruitful, and several structures of high dimensionality have been reported. These include a few three-dimensional structures in which control over the chirality of the coordination sphere of the metal was achieved.[6–8] However, the Curie temperatures of these materials are low because the compounds contain either diamagnetic bridging ligands, which are poor mediators of the magnetic interactions, or diamagnetic metal ions.

In contrast, the metal-radical approach[9, 10] exploits the direct coordination of a ligand atom of high spin density to the

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metal center, which ensures large exchange interactions. In addition, the ease of modification of the radical ligand allows versatility in the design of multidimensional structures. However, most of the reported metal-radical complexes with an extended structure are one-dimensional,[11–13] because the nitroxyl groups are so weakly basic that they bind only to sterically congested metal centers that bear electron-withdrawing groups. This limitation was overcome by using trinitroxide ligands with a quartet ground spin state. Their complexes with manganese(II) hexafluoroacetylacetonate are two- or three-dimensional and exhibit ferrimagnetic behavior.[14, 15] In all other known high-dimensionality compounds involving nitroxides, the role of the organic spin carrier was not optimized, and the magnetic behavior was still dependent on diamagnetic bridging groups.[16, 17]

Here we report another successful strategy based on bischelating nitronyl–nitroxide ligands (Figure 1). Their manganese(II) complexes are two-dimensional species in which the metal coordination sphere is free of electron-withdrawing groups and is occupied exclusively by paramagnetic bridging ligands. The complexes were obtained by mixing two equivalents of manganese(II) acetate, three equivalents of 2-(2-imidazolyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-3-oxide-1-oxy (NITImH) or 2-(2-benzimidazolyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-3-oxide-1-oxy (NITBzImH), and one equivalent of a sodium salt in methanol. The complex $[Mn_2(NITIm)_3]ClO_4$ (**1**) was characterized by X-ray structure analysis.

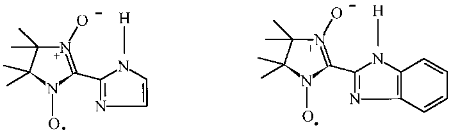
NITImH NITBzImH

Figure 1. Formulas of the nitroxide ligands.

Despite the small size of the crystals (0.12 × 0.14 × 0.005 mm), the quality of the reflections collected at 313 and 193 K was sufficiently high to allow a precise structure determination and an unambiguous description of the chemical features of the compound. These results were used as a guide to interpreting the magnetic properties of other compounds in this series. The molecular structure of the complex is shown in Figure 2. The asymmetric unit comprises two metal ions, three radical ligands, and one perchlorate anion. In the space group $P2_1$, this unit develops along the *bc* plane into a honeycomb structure in which the shortest and longest distances between metal centers are 6.3(2) and 13.2(2) Å. Therefore, the solid may be viewed as a lamellar material composed of $[Mn_2(NITIm)_3]_\infty$ layers that are roughly perpendicular to the *a* axis and separated by 10.32(1) Å. The interlayer space is occupied by the perchlorate anions. Both metal coordination spheres are highly distorted octahedra with angles far from the ideal values of 180 and 90° (N3B-Mn1-N3C 159(1), N3B-Mn1-N3A 102(2)°), but the Mn–O and Mn–N bond lengths are within the range observed in most manganese(II) complexes. A detailed description of the coordination sphere of both manganese ions must take into account the possible isomers resulting from an octahedral arrangement of the MX_3Y_3 type. In this planar complex, only an *OC*-6-21 (*mer*) arrangement is present. Further isomers could result from the chelating nature of the ligand, which can lead to Δ or Λ enantiomerism. Indeed, within a sheet, Δ and Λ configurations alternate regularly, and each crystallographically independent metal center has a specific chirality. Therefore, since the layers are related by a translation along the *a* axis, the crystal as a whole has a definite chirality that corresponds to one of the four diastereoisomers that can be formed from alternating Δ and Λ building blocks. It is also noteworthy that, as is commonly accepted, only the ΔΛ and ΛΔ configurations result in a planar structure;[6, 7] the two other possibilities involve metal centers of the same chirality and would lead to a three-dimensional network.[8]

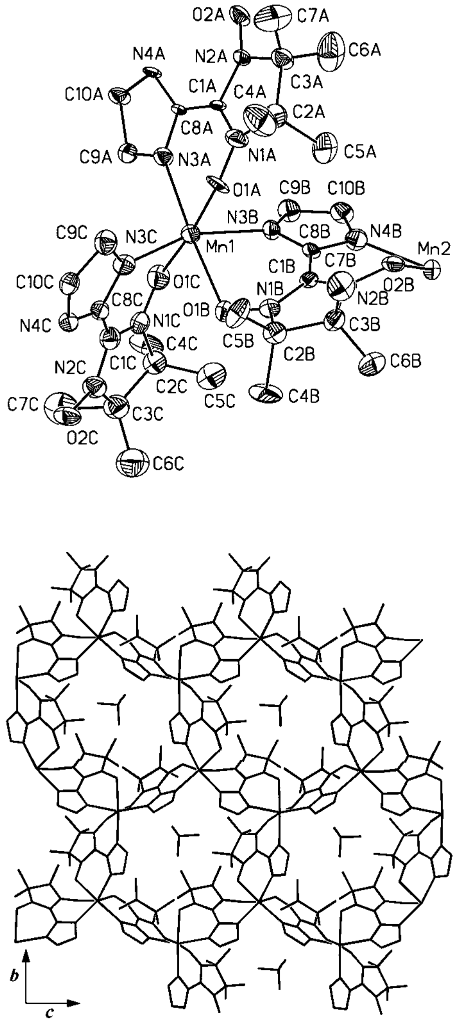

Figure 2. View of the asymmetric unit (top) and section of the honeycomblike structure (bottom) of **1**. Selected bond lengths [Å] and angles [°]: Mn1–O1A 2.18(2), Mn1–O1B 2.29(2), Mn1–O1C 2.16(2), Mn1–N3A 2.22(2), Mn1–N3B 2.26(2), Mn1–N3C 2.11(3), Mn2–O2A 2.19(2), Mn2–O2B 2.20(2), Mn2–O2C 2.23(2), Mn2–N4A 2.17(2), Mn2–N4B 2.17(3), Mn2–N4C 2.20(2); O1C-Mn1-O1A 174.7(8), N3B-Mn1-N3C 159.9(9), O1B-Mn1-N3A 176.0(8), O2B-Mn2-O2C 170.9(8), N4B-Mn2-N4A 161.6(9), O2A-Mn2-N4C 171.5(9).

At room temperature the magnetic susceptibility χ of **1** of $1.92 \times 10^{-2}\,cm^3\,mol^{-1}$ is lower than that expected for independent spins (2.46×10^{-2} cm^{3}mole^{-1}), and this indicates fairly large antiferromagnetic interactions between the manganese ions and the nitroxide radicals. With decreasing temperature, χ increases slightly to 2.87×10^{-2} cm^{3}mol^{-1} at 300.2 K and then decreases to reach a broad minimum (2.53×10^{-2} cm^{3}mol^{-1}) at 260 K. On further lowering the temperature, a sharp increase is observed, which gradually reaches a limiting value at low temperature. This limiting value is dependent on the applied field strength. The magnetic behavior is better described by the $1/\chi$ versus T curve, which shows two Curie – Weiss regimes with θ values of 101 and 23 K at high- and low temperature, repectively. In the series, only **1** exhibits such behavior. The closely related compounds $[Mn_2(NITBzIm)_3]ClO_4$ (**2**) and $[Mn_2(NITIm)_3]BPh_4$ (**3**) both exhibit only simple Curie – Weiss behavior with θ values of 105 and 71 K, respectively, which correspond fairly well to that of the high-temperature region of **1**. Compounds **1**, **2**, and **3** have Curie constants C of 6.8(2), 7.3(2), and 6.9(2) cm^{3}K mol^{-1}, respectively. These values are lower than that of 7.8 cm^{3}K mol^{-1} expected for two Mn^{II} ions that are antiferromagnetically coupled to three nitroxide radicals. However, the presence of ferrimagnetic coupling within the layers is confirmed by the magnetization values M, which for all compounds exhibit saturation values close to the theoretical value of 7 μ_B (6.7(1), 7.1(1), and 6.9(1) μ_B for **1**, **2**, and **3**, respectively).

Since the interlayer distance is large, one can assume that the Curie – Weiss behavior approximately reflects the properties of magnetically isolated layers. To understand the presence of two different Curie – Weiss regions in **1** the crystal structure was also determined at 193 K. No clear evidence for a phase transition was obtained, since the space group did not change, and the variation in the cell volume was smaller than 3%. However, on comparing the structures at both temperatures, one observes slight structural differences, which may result in a variation of the magnitude of the intralayer exchange interactions. Unfortunately, numerous possibilities exist for coupling in a layer: 1) Direct coupling between manganese(II) ions and organic radicals is expected to be large and antiferromagnetic.[18, 19] 2) A competing interaction between manganese ions by a superexchange pathway through the imidazole fragment is expected to be weaker.[20] 3) Finally, direct through-space intramolecular interactions between the nitroxide ligands within the metal coordination spheres (O1A – O1B 3.29(4) Å) are difficult to quantify but can be rather large.[21, 22] Therefore, no unambiguous correlation can be found between exchange interactions and structural parameters, but comparison of the high- and low-temperature structures suggests that at lower temperature slight structural changes lessen the average coupling constant within the layers. Nevertheless, the low magnetic susceptibility at 400 K and the low magnetization at 5 K indicate that ferrimagnetic coupling occurs in both Curie – Wiess regions of **1** and that such a coupling scheme holds for the other compounds in the series.

Preliminary measurements of the magnetization of **1** and **2** at low temperature are shown in Figure 3. On examining the zero-field magnetization and field-magnetization curves one observes the onset of remanence below 1.4 K in **1**. The presence of magnetic ordering below 1.4 K is confirmed by the field dependence of the magnetization at 85 mK. The curve exhibits a weak hysteresis loop with a coercive field of 270 Oe and a remnant magnetization of 0.22 μ_B. Similar behavior is observed for **2** and **3** for which remanence appears below 40 and 3.6 K, respectively. No hysteresis loop could be detected for **2** at 4.5 K. These results clearly indicate the presence of a weak ferromagnetic ground state, the full characterization of which is in progress.

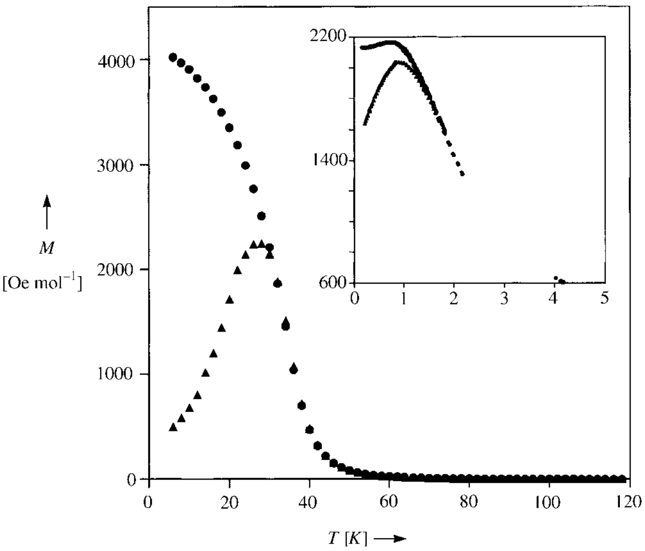

Figure 3. Magnetization – temperature curves of **1** (inset) and **2** in the low-temperature region in a field of 0.5 G. The zero-field magnetization is represented by triangles, and the field magnetization by solid circles.

Three-dimensional ordering in these compounds clearly depends not only on intralayer exchange coupling, but also on the interlayer interaction. For **1**, examination of the low- and high-temperature structures reveals a change in the three-dimensional arrangement. On lowering the temperature the lattice constants b and c become smaller, but surprisingly the lattice constant a increases by 0.363 Å. Since the layers are related by a translation along the a axis, the interlayer interaction is probably weakened. Therefore, the low-temperature properties of **1** are not only the consequence of a weaker intralayer interaction, but also of a modification of the coupling pathway between the layers. For **3**, the large θ value suggests a stronger intralayer interaction, but the bulkiness of the BPh_4 group is probably responsible for a weaker interlayer interaction. Finally, **2** deserves special mention. Its high-temperature magnetic behavior also follows a Curie – Weiss law, and the θ value of 105 K is almost equal to that of **1** in the high-temperature region; this suggests that a strong intralayer interaction associated with the small perchlorate anion is responsible for the high ordering temperature of 40 K. In this respect, the behavior of these compounds closely resembles that of recently described heteropolymetallic layered compounds, in which slight changes in the chemical nature of the counterion has strong effect on the low-temperature magnetic properties.[23, 24]

The results obtained with the planar compounds **1** – **3** provide support for the metal-radical strategy towards molecular magnetic materials and represent important progress in the design of multidimensional structures. Although two-dimensional systems with a honeycomblike layered structure have been described,[23–26] the derivatives of tetradentate bis-chelating nitroxides are unique because exchange coupling within the layers is large. This work can probably be extended to the field of intercalation compounds. The synthesis of similar compounds with other transition metal ions, counteranions, and/or chiral nitroxides is in progress.

Experimental Section

NITImH:[27] 2-imidazolecarboxaldehyde (1.3 g) and 2,3-bis(hydroxylamino)-2,3-dimethylbutane (2 g) were dissolved in methanol (40 mL). The solution was stirred for 36 h at room temperature. The solvent was then removed under vacuum, the crude product dissolved in CH_2Cl_2 (200 mL), and the resulting solution oxidized at 0°C for 30 min with $NaIO_4$ (5 g) in water (60 mL). After work up, the nitroxide was purified by chromatography on neutral alumina (type III, ethyl acetate eluent) to give pure NITImH (1.92 g, 64 %); m.p. 152°C.

NITBzImH: 2-hydroxymethylbenzimidazole was prepared as previously described.[28] This compound (5 g) was oxidized with MnO_2 (6 equiv) in dioxane for 60 h at room temperature. The mixture was filtered, the filtrate discarded, and the precipitate extracted continuously for 5 h with methanol to give 3.8 g of 2-benzimidazolcarbaldehyde (76 %, m.p. 166°C). A suspension of 2 g of this aldehyde and 2,3-bis(hydroxylamino)-2,3-dimethylbutane (2 g) in methanol (60 mL) was heated to reflux for 30 min and then stirred for 48 h at room temperature. The methanol was then evaporated off, and the residue dissolved in dichloromethane (200 mL). The solution was cooled in a ice bath, and $NaIO_4$ (4.5 g) in water (50 mL) was added slowly over a period of 15 min. Evaporation of the organic solvent and chromatography on alumina (type III, ethyl acetate eluent) afforded 2.3 g (61 %, m.p. 260°C decomp) of NITBzImH.

Preparation of the complexes: To a solution of the nitronylnitroxide (3 mmol) in methanol (50 mL) was added manganese(II) acetate tetrahydrate (2 mmol). To the resulting green solution was added a solution of a sodium salt (1 mmol; counterions: ClO_4^-, $B(C_6H_5)_4^-$). In most cases precipitation occurred immediately, except for the perchlorate salt of the imidazolyl derivative **1**, which was obtained as tiny crystals. Satisfactory elemental analyses. X-Ray powder diffraction spectra did not show the presence of Mn_3O_4. All complexes decompose before melting.

Crystal structure determination of **1**: $M_r = 879.09$, Siemens SMART system, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, graphite monochromator. Data collection, solution and refinement: monoclinic, space group $P2_1$; $T = 313$ K, $a = 10.325(1)$, $b = 17.870(6)$, $c = 11.063(1)$ Å, $\beta = 93.43(4)°$, $V = 2037(1)$ Å^3, $\rho_{calcd} = 1.428$ g cm^{-3}; 2958 unique reflections, 1020 with $I > 2\sigma(I)$, 496 parameters refined, $R(F) = 0.090$, $Rw(F^2) = 0.153$; $T = 193$ K, $a = 10.688(3)$, $b = 17.165(5)$, $c = 10.761(4)$ Å, $\beta = 90.648(6)°$, $V = 1974(1)$ Å^3, 2678 unique reflections, 962 with $I > 2\sigma(I)$, $R(F) = 0.102$, $Rw(F^2) = 0.189$. The data were processed with the SAINT[29] program package, and the structure was solved with the SHELXTL[30] program package. The absolute structure was determined by the method described by Flack.[31] 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-100351. 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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