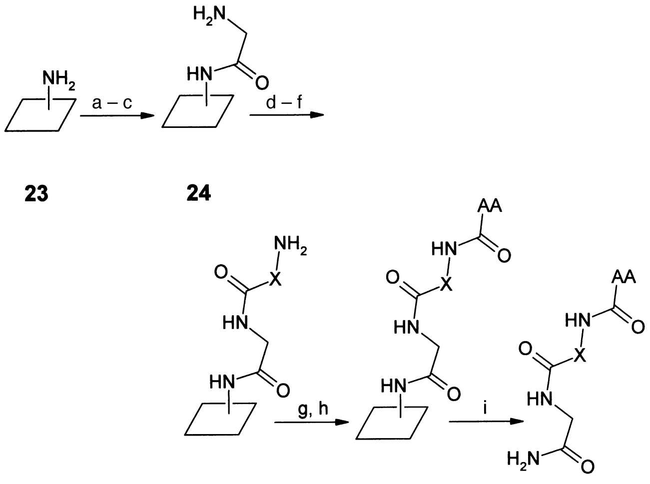

23 **24** **25 a-g** **26 a-g** **27-29**

Scheme 5. Reagents and conditions: a) N^{α}-Fmoc-Gly-OPfp (0.6 M in NMP), RT, 2 × 15 min; b) 10% Ac_2O, MeOH, RT, 1 h; c) 20% piperidine, DMF, RT, 2 × 10 min; d) coupling of sugar building blocks: 1) if activated with Pfp, 0.6 M solution of the sugar in NMP, RT, 2 × 15 min; 2) if free of acid functionality, 0.6 M solution of the sugar in NMP, PfpOH, DIC, RT, 2 × 15 min; e) 10% Ac_2O, MeOH, RT, 1 h; f) 20% piperidine, DMF, RT, 2 × 10 min; g) N^{α}-Fmoc-AA-OPfp (0.6 M in NMP), RT, 2 × 15 min; h) TFA, CH_2Cl_2, RT, 2.5h; i) UV light at 365 nm, 2 h. X = sugar building blocks 11, 13, 16–20, AA = different amino acids: N^{α}-Fmoc-Glu-(OH) **27 a–g**, N^{α}-Fmoc-Thr-(OH) **28 a–g**, N^{α}-Fmoc-Tyr-(OH) **29 a–g**.

Table 2. ESI MS data.

Compound	m/z [M^+]	Compound	m/z [M^+]	Compound	m/z [M^+]
27a	743.1	**28a**	715.1	**29a**	777.1
27b	702.0	**28b**	674.1	**29b**	736.1
27c	841.1	**28c**	786.1	**29c**	848.1
27d	773.0	**28d**	745.0	**29d**	807.0
27e	773.0	**28e**	745.0	**29e**	807.0
27f	773.0	**28f**	745.0	**29f**	807.0
27g	935.1	**28g**	907.1	**29g**	969.1

Received: November 4, 1999 [Z14224]

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Can a Homometallic Chain Be Ferrimagnetic?[**]

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Dedicated to Professor Harald Krischner
on the occasion of his 70th birthday

One-dimensional homometallic magnetic systems can behave either as antiferromagnetic (AF) or as ferromagnetic (F) chains depending on the sign of the nearest-neighbor exchange interactions.[1] The recent synthesis of molecular materials, however, has extended the range of magnetic behaviors that can be observed. For instance, regular alternating AF/F chains have been reported that show an overall AF behavior.[2] However, ferrimagnetic behavior has not been reported for homometallic chains because, in this case, the condition for the noncompensation of the individual spin moments is difficult to achieve. We have now found that the versatility of the azide ligand affords chains with Mn^{II} in which ferrimagnetic behavior is clearly observed.

From methanolic solutions of manganese(II) nitrate and the appropriate pyridine derivative, *trans*-$[\{Mn(N_3)_2(3\text{-Mepy})_2\}_n]$ **1** and *trans*-$[\{Mn(N_3)_2(Menic)_2\}_n]$ **2** were obtained upon addition of aqueous solutions of sodium azide (3-Mepy = 3-methylpyridine, Menic = methylnicotinate). Compounds **1** and **2** consist of one-dimensional systems[3] in which each manganese atom is coordinated by two *trans*-oriented pyridinic ligands and four azido ligands. Two azido bridges, oriented either end-to-end (EE) or end-on (EO), between neighboring manganese atoms build the one-dimensional system. Compound **1** shows azido bridges in the sequence (-EE-EE-EO-)$_n$ but compound **2** shows the sequence (-EE-EO-EO-EO-EO-)$_n$ (Figure 1). Bond lengths and angles in the bridging region lie in the range of values reported for conventional EE or EO bridges.[2, 4, 5] For the Mn^{II}-azido system, double EE azido bridges give AF interactions with

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[**] This research was supported by CICYT (Grant PB96/0163) and OENB (Grants 6630 and 7967). F.A.M. thanks Prof. C. Kratky and Dr. F. Belaj (Universität Graz) for the use of experimental equipment. A.E. and R.V. thanks Prof. Dante Gatteschi (University degli Studi di Firenze) for helpful discussions.

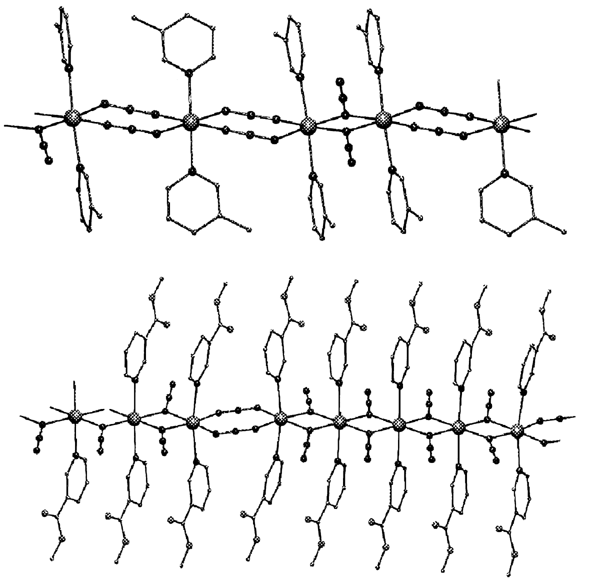


Figure 1. A view of chain structures of *trans*-[{Mn(N$_3$)$_2$(3-Mepy)$_2$}$_n$] **1** and *trans*-[{Mn(N$_3$)$_2$(Menic)$_2$}$_n$] **2**.

reported J values ranging between $J = -7$ to $J = -13$ cm^{-1} as a function of the bond parameters,[2, 4] whereas double EO azido bridges give F interactions with reported values of $J \leq 2$ cm^{-1}.[5] For compounds **1** and **2** the expected interaction pattern should be the (-AF-AF-F-)$_n$ and (-AF-F-F-F-F-)$_n$ sequences, respectively, and $J_{AF} \gg J_F$ may be assumed.

Compound **1** shows the typical features of ferrimagnetic behavior: on cooling $\chi_M T$ decreases from 3.63 cm^3 K mol^{-1} at room temperature to a minimum of 2.01 cm^3 K mol^{-1} at 40 K then an increase to 13.1 cm^3 K mol^{-1} at 2 K (Figure 2).

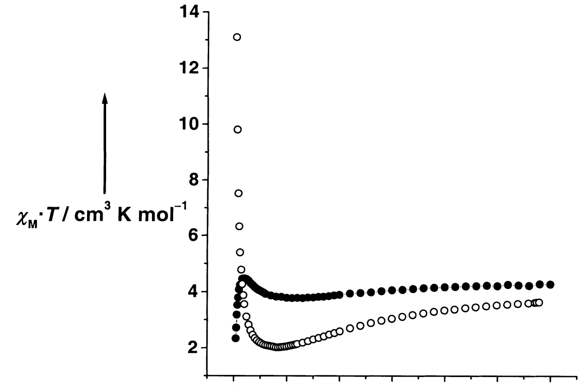


Figure 2. The product $\chi_M T$ versus T plot for **1** (○) and **2** (●).

Magnetization measurements indicate a saturation value of $S = 5/6$ per Mn^{II} atom (5/2 for each Mn$_3$ unit; Figure 3). These results are consistent with the expected ground state derived from the (-AF-AF-F-)$_n$ interaction sequence, which at very low temperature may be envisaged as a ferrimagnetic system with $S_A = 5/2$ and $S_B = 10/2$ (Scheme 1).

Compound **2** shows an unprecedented behavior: on cooling $\chi_M T$ slowly decreases from 4.26 cm^3 K mol^{-1} at room temperature to 3.77 cm^3 K mol^{-1} at 65 K. Below this broad minimum, $\chi_M T$ increases to a maximum of 4.47 cm^3 K mol^{-1} at 10 K and then falls to 2.34 cm^3 K mol^{-1} at 2 K (Figure 2). The shape of the $\chi_M T$ curve indicates ferrimagnetic-like behavior between 300–10 K, immediately followed by a strong decay of the magnetic moment. Magnetization measurements show a saturation value close to $S = 3/2$ per manganese atom (Figure 3). This value is striking as the ground state of this chain should be $S = 0$ (Scheme 2). The $\chi_M T$ decay observed below 10 K clearly corresponds to the population of the ground state but the shape of the plot and the magnetization results need further study to understand their unprecedented behavior. Formally, this ground state is the result of AF interactions between units of $S = 25/2$ that correspond to ferromagnetic coupling of each five-Mn^{II}-center unit.

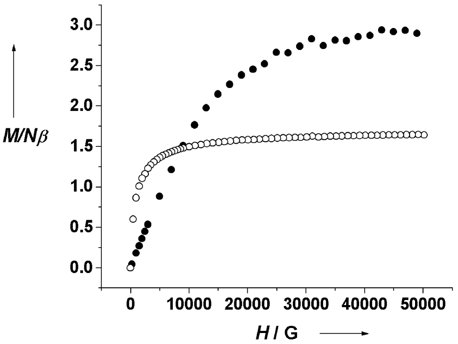
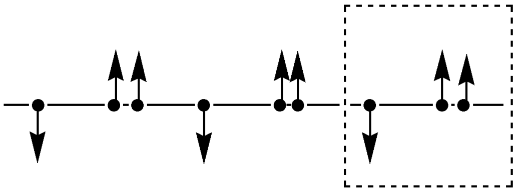
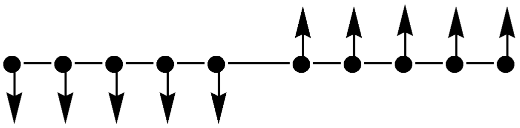


Figure 3. Molar magnetization (at 2 K) for **1** (○) and **2** (●).



Scheme 1. Ground state of an (-AF-AF-F-)$_n$ interaction sequence. $S_T = n\,5/6$ (5e per Mn$_3$ unit).



Scheme 2. Ground state of an (-AF-F-F-F-F-)$_n$ interaction sequence. $S_T = 0$.

The magnetic properties of compounds **1** and **2** indicate that some current definitions of magnetic systems are too narrow to include increasingly complex systems. Compound **1** shows a ferrimagnetic response although the system is homometallic; the interactions are either F or AF, and the ground state is equal to one S_A for each basic three-Mn^{II}-center unit. Compound **2** is an antiferromagnetic, homometallic system with a ground state $S = 0$ but not all the interactions are AF. The ferrimagnetic behavior down to 10 K and the magnetization response are far from those of a conventional antiferromagnet or even a regular alternating system. These systems show that complicated topologies with complicated alternating sequences of F/AF interactions are an unexplored tool to design materials with new magnetic properties.

Further study of the magnetic properties of these irregular alternating systems are planned but a general law may be easily envisaged for homometallic systems with sequences of more than one F/AF interaction. Ferromagnetism emerges, as observed for **2**, if $2n+1$ AF interactions are followed by one or more F interactions; the ground state here is always $S = 0$. An alternative possibility consists of an even number of AF interactions ($2n$) followed by one or more (m) F interactions, as observed for **1**, which induces net ferrimagnetic behavior with ground state $S_T = mS$ for each ($2n+m$) local S spin carrier.

Received: November 16, 1999 [Z14284]

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[3] Crystal data for **1** ($C_{12}H_{14}MnN_8$) and **2** ($C_{14}H_{14}MnN_8O_4$; in square brackets), monoclinic, $P2_1/n$ [$P2_1/a$], $a = 11.201(3)$, $b = 14.499(4)$, $c = 14.308(4)$ Å [$a = 15.556(2)$, $b = 16.831(2)$, $c = 17.595(2)$ Å], $\beta = 106.05(2)°$[$110.80(1)°$], $V = 2233.1(11)$ Å^3 [$4306.6(9)$ Å^3], $Z = 6$ [10], $\rho_{\text{calc}} = 1.451\ \text{g cm}^{-3}$ [$1.593\ \text{g cm}^{-3}$], crystal size $0.15 \times 0.28 \times 0.50$ mm [$0.30 \times 0.60 \times 1.0$ mm], $\mu = 0.893\ \text{mm}^{-1}$ [$0.807\ \text{mm}^{-1}$]. Of 4887 [17574] reflections collected, 3164 [6593] were observed with $I > 2\sigma(I)$; 289 [612] parameters. $R(F) = 0.0363$ [0.0641], $wR(F^2) = 0.0943$ [0.1861], min./max. residual electon density $\rho = -0.22/0.21\ \text{e Å}^{-3}$ [$-1.94/1.80\ \text{e Å}^{-3}$]. The data were collected on a modified STOE [IPDS] diffractometer with $\text{Mo}_{K\alpha}$ irradiation 0.71069 Å [0.71073 Å] at room temperature. Lorentz polarization effects, intensity decay, and absorption (DIFABS) [Lorentz polarization effects and numerical absorption (X-SHAPE, min./max. transmission 0.604/0.803)] corrections were made. Both structures were solved by direct methods and refined by full-matrix least-squares method on F^2 values. Refinement used the SHELXTL/PC package [SHELXL-97 for **2**, which was a twinned crystal; twin ratio 0.244/0.756(1)]. Nonhydrogen atoms were refined anisotropically; hydrogen atoms were included by a riding model. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-136997 and -136998. 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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Stereoselectivity in the Formation of a Cyclic Trinuclear *cis*-Dioxomolybdenum(VI) Complex of a Chiral Siderophore Analogue[**]

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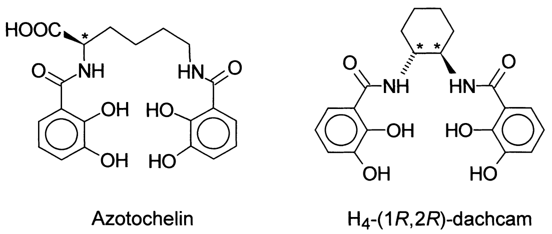
The stereoselective synthesis of coordination compounds can be achieved by using enantiomerically pure ligands, which, on metal binding, transfer their chiral information to the metal center.[1] Siderophores, high-affinity chelators synthesized by microorganisms to solubilize iron(III) for uptake into the cell, represent a biologically important example of this ligand type.[2] Most siderophores are enantiomerically pure amino acid derivatives, and the chirality of the molecules can play an important role in their biological activity. This is well documented for enterobactin, the native siderophore of *Escherichia coli*: Only the naturally occurring complex, having an L-seryl ligand backbone and a Δ configuration at the metal center, is able to supply iron to the cells.[3, 4] Interestingly, the N_2-fixing cells of *Azotobacter vinelandii* secrete azotochelin (Scheme 1), a tetradentate iron siderophore which also binds molybdenum.[5, 6] The structures of relevant model complexes have been reported.[7, 8] Molybdenum, as well as iron, is a component of the conventional nitrogenase, and in *A. vinelandii* the siderophore production depends not only on the amount of iron in the environment but also on the concentration of molybdenum.[5b, 6b] We report here that the L-lysine derivative azotochelin shows a high diastereoselectivity in forming the two possible Δ and Λ *cis*-dioxomolybdenum complexes. Use of the azotochelin analogue H_4-(1*R*,2*R*)-dachcam (Scheme 1) allowed us to investigate the chiral induction on molybdenum binding in the solid state and to compare the CD spectra of the model complex



Scheme 1.

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[**] This work was supported by the Fonds der Chemischen Industrie. We thank Dr. T. A. Dransfield, York, for the ES mass spectrum and Dr. T. Vogel and B. Beermann, Münster, for recording the CD spectra.