Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101228. 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).

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[{Mn(salen)CN}$_n$]: The First One-Dimensional Chain with Alternating High-Spin and Low-Spin Mn^{III} Centers Exhibits Metamagnetism**

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Of the few low-spin manganese(III) complexes,[1–3] the majority contain five or six cyano ligands.[1] Manganese(III) complexes with one or two cyano ligands are generally high spin:[4] monocyano manganese(III) porphyrins,[4a] discrete five-coordinate manganese species with L-Mn-CN coordination[4b] (L = tetradentate salen-type ligand; H_2salen = bis(salicylidene)ethylenediamine), and heterometallic species with Fe-CN-Mn(L)-NC repeat units.[4c, d] However, low-spin Mn^{III} is present in dicyanomanganese(III) porphyrins.[2] Finally, [Mn(trp)][5] (trp = tris[1-(2-azolyl)-2-azabuten-4-yl]amine) is the only manganese(III) complex known to exhibit a thermally induced $S = 1 \leftrightarrow S = 2$ spin crossover. In this complex, the ligand field generated by the three pyrrole and three imine N centers of trp is sufficiently strong to yield a Δ parameter close to the spin-pairing energy. The strong ligand field which stabilizes low-spin Mn^{III} in dicyanomanganese(III) porphyrins is probably provided by C-bonded cyano ligands in addition to the four pyrrole N donors. In this context, the question of whether the presence of two C-bonded cyanide ligands is sufficient to stabilize low-spin Mn^{III} in an octahedral coordination environment is of utmost interest. This will determine whether molecular magnetic materials can be built from a single Mn^{III} paramagnetic component.

The simplest way to obtain an NC-Mn-CN pattern is to induce CN^- bridging of $[Mn^{III}L]^+$ cations (L = planar tetradentate ligand). The reaction of an aqueous solution of NaCN with a methanolic solution of $[Mn(salen)(H_2O)]ClO_4$ yields red-brown microcrystals of [{Mn(salen)CN}$_n$] (**1**), a new type of one-dimensional coordination polymer which contains alternating $S = 1$ and $S = 2$ Mn^{III} spin states and exhibits

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metamagnetism. Compound **1** is structurally reminiscent of the one-dimensional "shish kebab" coordination polymers with porphyrins or phthalocyanines as equatorial ligands and diverse polyatomic axial bridges.[6]

The asymmetric unit of **1**[7] (Figure 1) contains two $\mathrm{Mn^{III}}$ ions with similar $\mathrm{N_2O_2}$ equatorial coordination environments provided by salen ligands. However, all four distances between MnA and the donor atoms of salen A are larger than the corresponding distances between MnB and salen B (av $\mathrm{MnA{-}L^A}$ 1.93 Å; av $\mathrm{MnB{-}L^B}$ 1.90 Å). The cyanide nitrogen atoms N3B and N3A′ are the axial ligands of MnA, while the cyanide carbon atoms C17A and C17B are axially coordinated to MnB. The MnA–N3B (2.25(3) Å) and MnA–N3A′ distances (2.34(3) Å) are close to those reported for bonds between high-spin $\mathrm{Mn^{III}}$ and cyanide ligands (2.290(5)–2.415(5) Å).[4c–e] The MnB–C17A (2.06(3) Å) and MnB–C17B distances (2.13(3) Å) are similar to those of low-spin $\mathrm{Mn^{III}}$ to cyanide bonds (1.940(15)–2.056(27) Å)[1] and shorter than the only known distance between high-spin $\mathrm{Mn^{III}}$ and cyanide (2.190(3) Å).[4b] Comparison of the MnA-N3B-C17B (147(3)°) and MnA-N3A′-C17A′ angles (143(2)°) with MnB-C17A-N3A (170(3)°) and MnB-C17B-N3B (165(3)°) also reveals different ligand environments of MnA and MnB and clearly indicates the high- and low-spin nature of their respective $\mathrm{d^4}$ systems. The MnA–MnB distance is 5.115(6) Å.

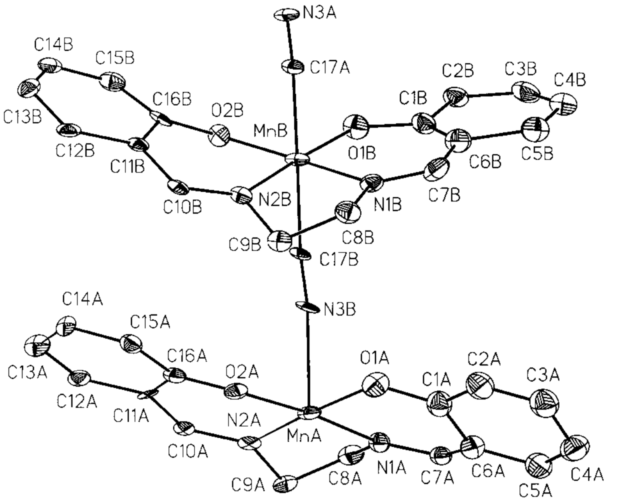

Figure 1. Perspective view of complex **1** (hydrogen atoms are omitted for clarity). Selected bond distances [Å] and angles [°]: MnA–O1A 1.92(2), MnA–O2A 1.89(2), MnA–N1A 1.94(2), MnA–N2A 1.97(2), MnA–N3B 2.25(3), MnA–N3A′ 2.34(3), MnB–O1B 1.90(2), MnB–O2B 1.86(2), MnB–N1B 1.92(2), MnB–N2B 1.91(2), MnB–C17A 2.06(3), MnB–C17B 2.13(3); MnA-N3A′-C17A′ 143(2), MnA-N3B-C17B 147(3), MnB-C17A-N3A 170(3), MnB-C17B-N3B 165(3) (the prime indicates atoms that are related by x, $y-1$, z symmetry.

The asymmetric units are linked together through $\mathrm{CN^-}$ bridges into infinite one-dimensional chains with alternating high- and low-spin $[\mathrm{Mn^{III}salen}]^+$ complex cations along the b axis (Figure 2). The closest contacts (3.18(6) Å) between adjacent chains involve the aromatic C3A atoms, which are related by the $1-x$, $-1-y$, $-z$ symmetry. The shortest distance between Mn ions of adjacent chains (7.215(8) Å) involves MnA and MnB ($1-x$, $-1/2+y$, $1/2-z$). No π-stacking interactions between aromatic rings of adjacent 1D chains are evident.

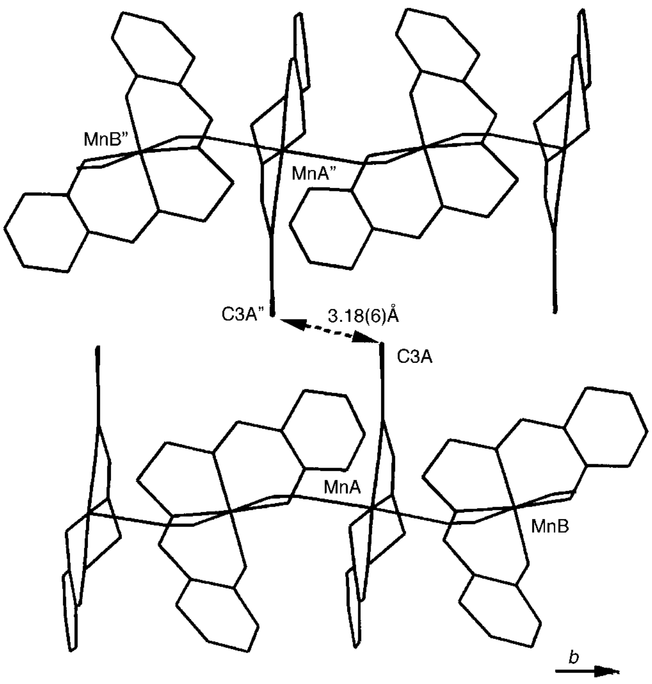

Figure 2. Perspective view of **1** emphasizing the closest contacts between aromatic C3A carbon atoms of adjacent chains, which are related by $1-x$, $-1-y$, $-z$ symmetry.

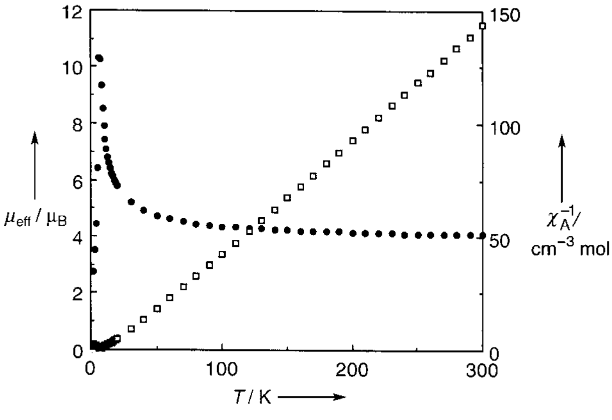

Figure 3. Plots of effective magnetic moment μ_{eff} and the reciprocal magnetic susceptibility χ_A^{-1} of **1** as a function of temperature T.

The magnetic susceptibility of **1** was measured in the temperature range of 2–300 K with a SQUID susceptometer in an applied magnetic field of 500 Oe. The plots of the effective magnetic moment μ_{eff} versus temperature T and of the reciprocal magnetic susceptibility χ_A^{-1} versus T are shown in Figure 3. The μ_{eff} value of 4.09 μ_B at room temperature is consistent neither with the spin-only value for high-spin $\mathrm{Mn^{III}}$ (4.89 μ_B for $S=2$) nor with the spin-only value for low-spin $\mathrm{Mn^{III}}$ (2.83 μ_B for $S=1$). On lowering the temperature, μ_{eff} increases over the whole temperature range 300–6 K, smoothly from 300 to 25 K, and then sharply reaching a maximum value of 10.3 μ_B at 6 K. Finally, μ_{eff} decreases to 2.75 μ_B at 2 K. The χ_A^{-1} versus T plot obeys a Curie–Weiss law with a positive θ constant of 5.6 K. The positive Weiss constant and the increase in μ_{eff} over the entire range 300–6 K is typical of a ferromagnetic coupling between adjacent $\mathrm{Mn^{III}}$ ions along the chains.[8] The abrupt increase in μ_{eff} between 25 and 6 K suggests the onset of magnetic ordering in the chains, and the decrease below 6 K suggests the operation of long-range weak antiferromagnetic interactions through interchain contacts between the salen ligands and/or the zero-field splitting (ZFS) of the anisotropic high-spin $\mathrm{Mn^{III}}$ ion. The field-dependent magnetization was measured up to 50 kOe at 2 and 6 K with a SQUID susceptometer, and up to 120 kOe at 4.2 K with a flux magnetometer by using conventional pulse techniques (Figure 4). The curve at 2 K (below the Néel temperature) has the sigmoidal shape expected for a metamagnet: The magnetization first increases slowly with increasing H due to antiferromagnetic interchain interactions, then increases abruptly for a phase transition to a ferromagnetic state, and finally reaches a saturation magnetization plateau of 2.83–2.91 $N\beta$ at 85–120 kOe. The large magnetic field required to reach saturation may be due to the ZFS of high-spin $\mathrm{Mn^{III}}$. The saturation magnetization value of about $3N\beta$ implies that the compound has an average of three unpaired electrons per Mn center. This unusual magnetic behavior can be rationalized on the basis of the molecular structure: 1) The complex is a mixed-spin system consisting of uniformly distributed high-spin ($S=2$) and low-spin ($S=1$) $\mathrm{Mn^{III}}$ ions; indeed, the μ_{eff} value of 4.09 μ_B at room temperature agrees with the spin-only value of 4.0 μ_B derived by assuming a magnetically dilute system with high- and low-spin $\mathrm{Mn^{III}}$ species ($g=2$) in a 1:1 ratio. 2) The saturation magnetization for such a system is expected to be $M_S = N\beta g(S_1 + S_2)/2 = 3N\beta$ per Mn center. 3) The ferromagnetic interactions operate between high-spin and low-spin $\mathrm{Mn^{III}}$ species through CN bridges within the chains, and the antiferromagnetic interactions operate between $\mathrm{Mn^{III}}$ ions of adjacent chains, probably by means of electrostatic interactions between the salen ligands; the result is a metamagnetic character.

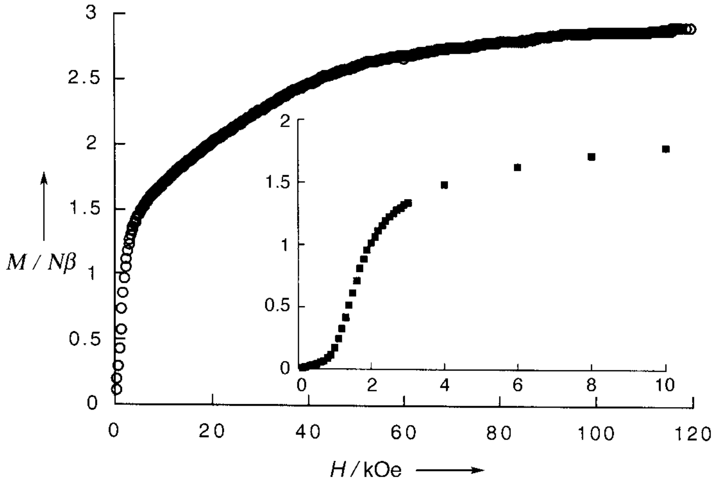

Figure 4. Plot of magnetization M of **1** as a function of the applied magnetic field H at 4.2 K (○) up to 120 kOe, and at 2 K (■) up to 10 kOe (inset).

Experimental Section

1: $[\mathrm{Mn(salen)(H_2O)}]\mathrm{ClO_4}$ was prepared by reaction of $\mathrm{Mn^{III}(OAc)_3 \cdot 2H_2O}$ with salen$\mathrm{H_2}$ and $\mathrm{NaClO_4}$ in methanol (1:1:1 molar ratio, 0.5 mmol in 20 mL). Reaction of an aqueous solution of NaCN (0.5 mmol in 5 mL) with a methanolic solution of $[\mathrm{Mn(salen)(H_2O)}]\mathrm{ClO_4}$ (0.5 mmol in 20 mL) at room temperature for 10 min yielded **1** as red-brown microcrystals, which were collected by suction filtration. Complex **1** is insoluble in common organic solvents. Slow interdiffusion of a solution of $[\mathrm{Mn(salen)(H_2O)}]\mathrm{ClO_4}$ in DMF/MeOH (1/1) and an aqueous solution of NaCN yielded single crystals of **1** in the form of very thin red-brown platelets. Elemental analysis calcd for $\mathrm{C_{17}H_{14}N_3O_2Mn}$: C 58.80, H 4.06, N 12.10; found: C 58.66, H 4.10, N 12.11; IR (KBr): $\tilde{\nu}_{\mathrm{CN}} = 2110\ \mathrm{cm^{-1}}$.

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[7] Crystal data for **1** ($\mathrm{C_{34}H_{28}N_6O_4Mn_2}$): $M_r = 694.50$, red-brown platelet ($0.05 \times 0.05 \times 0.01$ mm), monoclinic, space group $P2_1/c$, $a = 11.2454(8)$, $b = 10.2320(7)$, $c = 26.850(2)$ Å, $\beta = 98.138(2)^{\circ}$, $V = 3058.4(4)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.508\ \mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo_{K\alpha}}) = 8.76\ \mathrm{cm^{-1}}$. Data were collected at 193 K on a Siemens SMART CCD area detector system equipped with a normal focus molybdenum-target X-ray tube operated at 2 kW. A total of 1321 data frames were obtained with a narrow-frame method with 0.3° scan width, 60 s exposure time per frame, and a 5.922 cm crystal-to-detector distance. The data were processed with the SAINT reduction and SADABS absorption programs[9] to give a total of 8742 reflections ($3.06 \leq 2\theta \leq 40.0^{\circ}$), of which 2850 were independent ($R_{\mathrm{int}} = 0.0916$, $R(\sigma) = 0.1202$) and 1631 with $I > 2\sigma(I)$ were used to solve the structure with SHELXTL.[9] Crystals of **1** were very thin, weakly diffracting, and gave low-resolution data, and the refinement on F^2 converged to relatively high final R values: $R1 = 0.1063$, $wR2 = 0.3572$ (all data), GOF = 1.280. 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-101380. 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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