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Synthesis and Self-Assembly of Spin-Labile and Redox-Active Manganese(III) Complexes

Claudio Gandolfi, Tatiana Cotting, Paulo N. Martinho, Olha Sereda, Antonia Neels, Grace G. Morgan and Martin Albrecht*abc

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New amphiphilic and spin-labile MnIII complexes based on dianionic N2O2-hexadentate sal-trien or sal-bapen ligands were prepared that contain OC3H13, OC12H25, or OC18H37 alkoxy substituents at different positions of the salicylidene unit (H2sal-trien = N,N′′-bis(salicylidene)-1,4,7,10-tetraazadecane, H2sal-bapen = N,N′′-bis(salicylidene)-1,5,8,12-tetraazadodecane). According to electrochemical measurements, these complexes undergo two (quasi) reversible redox processes. Temperature-dependent magnetic measurements revealed a high-spin configuration for all sal-trien complexes (S = 2) and gradual spin crossover for sal-bapen complexes from high to low spin (S = 1). The chain length strongly influences the spin crossover, as C18-functionalization stabilizes the low spin state at much higher temperature than shorter alkyl chains. Moreover, long alkyl chains allow for spontaneous self-assembly of the molecules, which was investigated in single crystals and in Langmuir-films at the air-water interface. Long alkyl chains (C12 or C14) as well as a mutual syn-orientation of these molecular recognition sites were required for the Langmuir monolayers to be stable.

Introduction

Interest in complexes that undergo spin crossover (SCO) has been growing considerably during recent years because SCO-active materials show great potential for application as memory storage and processing devices. Ideally, the spin change is abrupt and displays hysteresis features to entail bistability over a given temperature range. Such behavior is related to high cooperativity of the spin-labile metal centers, induced for example by intermolecular interactions like hydrogen bonding, π–π stacking, and electrostatic interactions. Hence supramolecular principles may be particularly efficient for engineering and optimizing cooperativity. A few (self-)assembly approaches have been explored thus far for organizing spin-labile centers either in the solid state, in nanoparticles, in gels, and recently even in solution.

While most of these studies have involved spin-labile iron or cobalt centers, only little is known about engineering manganese(III) complexes for self-assembly. This is remarkable, especially when considering the significant potential of manganese(III) centers as active sites of switches, due to their high degree of electronic and magnetic variability. Manganese(III) centers undergo facile one-electron oxidations and reductions at relatively low potential costs, and the metal d4 electronic configuration presets such complexes for spin crossover. However, only a few SCO-active manganese(III) systems are known. A possible reason for the limited accessibility of SCO-active manganese complexes may be the difficulty associated with preparing configurationally stable low-spin complexes. In the few complexes that exhibit SCO activity, the manganese center is often ligated by a multidentate ligand. For example, complex I comprising a dianionic hexadentate N2O2 ligand framework was reported to undergo a thermally induced spin transition from S = 2 to S = 1 (Fig. 1). Based on our previous achievements in self-assembling iron(III) and cobalt(III) complexes comprising a related N2O2 ligand system, the functionalization of complexes related to I with aliphatic chains therefore constitutes an obvious approach for synthesizing amphiphilic species that may show both, (electro)magnetically activity and high propensity to (self-)assemble. These two properties, functionality and assembly, are key factors for the development of new functional devices.

Fig. 1 a) SCO-active Mn(3-MeO-sal-bapen) complex I; b) ligand frameworks used in this work, including generalized carbon labeling scheme for introducing substituents R at the phenolic ring

Here we report on new SCO active manganese(III) complexes and on the implications of aliphatic ligand functionalization. Specific attention has been directed towards the influence of the hydrophilic-lipophilic ratio on the chemical properties (SCO and redox activity) and on the propensity of the complexes to self-assemble. Variation of the
hydrophilic-lipophilic balance has been performed by modifying the skeleton of the hexadentate N₆O₂ ligand and by introducing alkyl chains of different length. Distinct trends have emerged from these studies that may serve as guidelines for further device fabrications using related SCO-active manganese(III) complexes.

Results and discussion

Synthesis of manganese(III) complexes

The amphiphilic manganese(III) complexes 3 comprising a sal₃trien ligand framework functionalized with two alkyl chains were prepared according to modified literature procedures. Thus, condensation of the known alkoxysubstituted salicylaldehydes 1 with triethylenetetramine (trien) followed by in situ metallation with manganese(II) nitrate in the presence of NaOMe afforded, after standing in air, the oxidized green manganese(III) complexes 3 (Scheme 1). A related protocol using N,N′'-bis(3-aminopropyl) ethylenediamine (bapen) instead of trien yielded the alkyl-tailed purple complexes 4 and 5. All products were purified by flash chromatography and, if required, by repetitive precipitation. The complexes containing the sal₃bapen ligand scaffold (complexes 4 and 5) consistently showed better solubility in organic solvents than their sal₃trien analogs 3, indicating a distinct influence of the alkyl linker between the amine and imine coordination sites.

Different spectroscopic analyses allowed the influence of ligand modifications to be examined. Infrared spectroscopy on complexes 3–5 revealed only slightly reduced energies of the strong νC=N absorption bands around 1600 cm⁻¹ (CHCl₃ solution) as compared to the analogous non-alkylated complexes. Similarly, the bands between 1524–1595 cm⁻¹, assigned to aromatic C=C vibrations, remain essentially unaltered. A characteristic shift of the νC=N band towards higher energy was noted upon expanding the ligand skeleton from sal₃trien to sal₃bapen (average νC=N 1591 cm⁻¹ in complexes 3 vs. 1605 cm⁻¹ in 4 and 1615 cm⁻¹ in 5), indicating that the C=N bond is influenced by both, the trans coordinated ligand (cf. 3 and 4) and the aromatic substitution pattern (cf. 4 and 5).

The UV-vis spectra of all complexes display strong charge transfer and intraligand π-π* transitions below 400 nm. In addition, the sal₃trien complexes 3 feature a shoulder at 480 nm (ε = 1700 M⁻¹cm⁻¹) originating from phenolate-to-manganese LMCT transitions, and a very broad and weak d-d absorption band around 640 nm (ε = 330 M⁻¹cm⁻¹). These general features do not vary significantly upon changing the alkyl chain length (3a–3c) and they are strongly related to those of analogues lacking alkoxyl groups. The absorption maxima of the sal₃bapen complexes 4–5 are shifted to lower energy as compared to 3. The LMCT band appears at around 510 nm (ε = 780 and 1100 M⁻¹cm⁻¹ for 4 and 5, respectively) and a very weak shoulder is observed around 660 nm (ε = 210 M⁻¹cm⁻¹).

Electrochemistry

Cyclic voltammetry (CV) measurements of complexes 3–5 (CH₂Cl₂ solutions) in the −1.2 V to +1.2 V potential range
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The magnetic properties of selected complexes have been investigated over a temperature range of 300–50 K. Akin to related complexes, crystalline samples of 3a × 1.75 H₂O and 3c displayed a temperature-independent magnetic moment (μ_eff = 4.85 and 4.56 μ_B, respectively). This value is in agreement with the expected spin-only magnetic moment calculated for a high spin complex with four unpaired electrons (S = 2, μ_eff = 4.90 μ_B). The hexyloxy bapen complexes 4a and 5a both exhibit a spin transition. Complex 4a shows a gentle and incomplete SCO between 150 and 50 K with T_1/2 around 100 K. The low temperature μ_eff = 4.33 μ_B corresponds to an approximate 1/3 distribution of low spin/high spin manganese centers.

The transition for crystalline 5a × H₂O is more pronounced, falling from almost 100% high spin at RT (μ_eff = 4.65 μ_B) to μ_eff = 3.32 μ_B at 120 K (Fig. 3b, T_1/2 ca. 150 K). The measured
low spin magnetic moment is higher than that expected for two unpaired electrons ($\mu_{\text{eff}} = 2.82 \mu_B$ for $S = 1$), suggesting that about 2/3 of the molecules have changed configuration. No distinct color change has been noted upon SCO.

The magnetic moments of the OC$_{18}$-functionalized complexes 3a and 5c are lower at RT ($\mu_{\text{eff}} = 3.74 \mu_B$ and 3.65 $\mu_B$, respectively; Fig. 3b). They decrease gradually upon cooling and reach a plateau at $\mu_{\text{eff}} = 2.85 \mu_B$ and 2.98 $\mu_B$, respectively, consistent with the $S = 1$ state.$^{22}$ Complex 4c adopts a low spin configuration only below 60 K, whereas 5c is low spin up to 220 K. The relatively low magnetic moment of these complexes at room temperature suggests a mixture of high and low spin centers at this temperature.$^{23}$ Upon heating a sample of 5c to 350 K the $\mu_{\text{eff}}$ indeed increases to $\mu_{\text{eff}} = 4.24 \mu_B$, indicating a predominantly $S = 2$ configuration. Accordingly, the spin transition is centered just around 295 K which would be very attractive for further processing. After heating, however, only a small fraction converted to the low spin state ($\mu_{\text{eff}} = 3.49 \mu_B$ at 100 K). Warming of complex 5c hence disables SCO, perhaps because of a modified packing of the complexes due to the presence of long alkyl chains.$^{24}$ Such a hypothesis is supported by the similar behavior of the warmed sample and an amorphous sample of 5c.$^{25}$ Nevertheless, we observe that long alkyl chains tend to stabilize the less common $S = 1$ configuration of manganese(III) centers.$^{26}$

### Solid state molecular structures

Single crystals of complexes 3a, 4a, and 5a were subjected to an X-ray diffraction analysis. The global structures (Fig. 4) are consistent with previous studies on related complexes.$^{14,16,19,20}$ Complex 3a features cis-positioned phenolato oxygens, whereas in complexes 4a and 5a, the oxygen atoms are in mutual trans arrangement. Generally a significant distortion from an ideally octahedral geometry is noted in all complexes, which may be reflected by the significant distortion parameter \(\Sigma\) (Table 2).$^{27}$

The asymmetric unit of 3a is composed of two unique complex cations, which each show a Jahn-Teller elongation along one of the amine nitrogens and one of the phenolato oxygens (Table 2). Generally, bond lengths and angles are consistent with a high spin configuration at the Mn$^{III}$ center as deduced from magnetic measurements ($vide supra$).$^{21}$ The alkyl chains are fully stretched and in a mutually cisoid arrangement. The dihedral angle \(\alpha\) between the two phenolato rings in each complex is about 117°. Values of \(\alpha\) above 90° have been suggested to preclude SCO activity in Fe(salen)trien complexes.$^{28}$ This criterion might be less relevant for the manganese series, since the equally spin-stable methoxy-substituted analog of 3a has \(\alpha\) = 87.8.$^{12}$

![Fig. 4 ORTEP representations of the Mn$^{III}$ complex cations 3a and 4a (a and b, respectively, 30% probability ellipsoids, only one of the two independent residues shown), and 5a (c, 50% probability ellipsoids). All hydrogen atoms, cocrystallized solvent molecules, and non-coordinating anions are omitted for clarity.](image)

The unit cell of 4a comprises two independent complexes that are nearly identical. Each has more regular geometry than that in 3a. The shorter Mn–O distances and the longer Mn–N bonds compared to 3a reflect the predominantly HS state with population of the d$_{x^2-y^2}$ orbital producing an axial compression.

Upon displacing the alkoxy chain to the imine ortho position (5a, Fig. 4c) the M–N$_{amine}$ distance decreases...
considerably (2.14 Å vs. > 2.20 Å in 4a), in line with the lower population of HS sites for 5a at 173 K. Otherwise, only little changes were observed for the M–O and M–N\textsubscript{amine} bond lengths. While most of the bond lengths in 5a at 173 K are similar to those in the methoxy-functionalized complex I at RT, which is known to be in high spin configuration, partial spin crossover may be supported by the short M–N\textsubscript{amine} bonds in 5a. In addition, the angular distortion parameter (Σ = 54.5) is between the parameters calculated for the high and the low spin states of complex I (70.7 and 45.0, respectively), and suggests neither a clear HS nor LS configuration (cf magnetic data above).

Crystal packing

In all measured crystals, a hydrogen bonding motif was detected that involves one or both of the ligand N-H bonds. For example in crystals of 3a, each unique complex cation forms a hydrogen bond via the amine hydrogen to a nitrate oxygen, which presumably also acts as acceptor for a co-crystallized water molecule (hydrogen atoms could not be located). This water molecule in turn is ideally placed for acting as hydrogen bond acceptor from another N–H unit, thus resulting in a dimeric structure that is interlinked via a N–H…O\textsubscript{nitrate}–H…O\textsubscript{water}–H–N motif. The two inequivalent complex cations of 4a also form a dimeric structure due to N–H…O\textsubscript{ON(O)O}–H–N interactions of the amine-bound hydrogens to two oxygen atoms of the nitrate counterion. Complexes of 5a are linked together by a similar hydrogen bonding motif as 3a, involving a NO\textsubscript{3}– counterion and a co-crystallized H\textsubscript{2}O molecule. Hence, hydrogen bond formation between the ligand N-H group and the NO\textsubscript{3}– anion seems to constitute a general feature that may also become useful for crystal engineering. In contrast to the previously discussed structures, the hydrogen bonding in 5a includes both N–H bonds of the cationic complex and hence results in the formation of a polymeric 1D-chain rather than dimeric structures as in 3a and 4a.

In addition to the hydrogen bonding, crystal packing analysis of 3a also revealed a highly anisotropic arrangement of the complex cations. Alignment of the alkyl chains along the crystallographic c-axis produces alternating apolar and polar layers within the crystallographic ab-plane (Fig. 5a). The layers are assembled in head-to-head and tail-to-tail arrangement, thus resulting in the formation of a well-defined 3-dimensional assembly comprising hydrophilic and hydrophobic lamellar domains that are about 9.1 and 14.9 Å thick, respectively. The alkyl chains are densely packed and are separated by about 4 Å. Hence, lipophilic interactions may further stabilize the molecular packing in 3a. In contrast, cations of 4a are arranged in perpendicular orientation and do not feature any specific alignment of the alkyl chains nor distinct hydrophilic and hydrophobic domains (Fig. 5b).

The packing of 5a shows, similar to 3a, a layered structure (Fig. 5c). As a consequence of the nearly orthogonal alignment of the alkyl chains within each complex, the aliphatic tails of adjacent layers are strongly interdigitated. Hence double layer formation is much less pronounced and the interplanar distance is only 12.4 Å and hence considerably smaller than in crystals of 3a.

![Fig. 5 Crystal packing of the complexes: (a) projection of 3a along the b-axis; (b) projection of 4a along the a-axis; (c) projection of 5a along the c-axis.](image-url)
a-axis (nitrate and water residue omitted for clarity); color code: carbon (grey), nitrogen (blue), oxygen (red), manganese (purple).

**Fig. 6** Chain length dependence of the isotherm plots of Langmuir monolayers of complexes 3 (a), 4 (b), and 5 (c), different alkoxy substituents are represented by dashed (OC$_{6}$H$_{13}$), solid (OC$_{12}$H$_{25}$), or bold lines (OC$_{18}$H$_{37}$); (d) film stability over time of monolayers composed of 3c (green), 4c (blue), and 5c (red).

Evaluation of the shortest metal-metal distance indicates that this parameter is not decisive for inducing SCO. In spin-labile 5a, the manganese(III) centers are separated by 9.153 Å within one layer. This distance is significantly larger than the closest intermetallic contact in crystals of complex 1 (8.914 Å in HS state and 8.411 Å in LS). The Mn···Mn separation in spin-stable complexes 3a and 4a is even smaller, 7.443 Å and 8.189 Å, respectively. Tentatively, the SCO activity of 5a may thus be attributed to the ordered interdigitation of the alkyl chains and the consequentially short layer separation, perhaps in combination with the hydrogen bonded 1D network, which interconnects complexes of different layers.

**Self-assembly at interfaces**

Langmuir-Blodgett (LB) film fabrication provides an elegant tool for arranging molecules at the supramolecular level and offers the possibility to sequentially deposit molecular monolayers with high precision and reproducibility. The assembly of amphiphilic molecules with a specific function can thus afford mono- and multilayered films, and hence offers an attractive methodology for device fabrication. These attractive features prompted us to investigate the potential of complexes 3–5 to form Langmuir films at the air-water interface. Representative pressure-area isotherms revealed that complexes with C$_{12}$ and C$_{18}$ alkyl tails self-assemble into densely packed Langmuir monolayers, which collapse typically at a surface area slightly below 70 Å$^2$/molecule (Fig. 6). The molecular area in the densely packed film is in good agreement with models based on crystal structure analyses suggesting a surface area of approximately 65(±5) Å$^2$ for the polar heads of 3–5. When using long chain C$_{18}$-functionalized complexes, intermolecular contacts establish at an earlier stage of compression than with C$_{12}$-functionalized complexes. Also the molecular area in compressed C$_{18}$-functionalized monolayers is larger than with shorter C$_{12}$ tails. Such behavior has been previously observed.
with analogous iron complexes,\textsuperscript{13} and may be due to the increased probability of long chains to backfold. In contrast, the complexes containing hexyloxy substituents did not form monolayers. The apolar section of these molecules is probably too small and thus favors diffusion into the subphase due to partial water solubility or due to micelle formation.

Interestingly, the isotherm of \textit{3c} shows two separated phase transitions at 92 and 72 Å\textsuperscript{2}/molecule, which may point to distinct transitions from liquid expanded to liquid condensed and then to the solid phase. Films built from sal\textsubscript{3}trien-type complexes \textit{3} seem to be the most robust in the series measured here, as high surface pressures can be reached (45–60 mN/m vs. ca. 35 mN/m for the sal\textsubscript{3}bapen-derived species \textit{4} and \textit{5}). In this regime, little changes in the specific area resulted in a marked pressure enhancement, indicating that a solid phase was reached. In contrast, the relative molecular area of monolayers composed of complexes \textit{4b–c} or \textit{5b–c} continuously shrunk upon compression, pointing to a liquid condensed phase. This specific behavior may be a consequence of the reduced hydrophilicity of the sal\textsubscript{3}bapen ligand as compared to the sal\textsubscript{3}trien system in \textit{3}.

When considering the transoid arrangement of the alkyl tails in complexes \textit{4} and its low tendency to pack into polar and apolar domains (cf. Fig. 5), it seems surprising that Langmuir monolayer formation with this complex is not significantly different from that of \textit{5} bearing cisoid alkyl chains.\textsuperscript{34} Notably, the films composed of complexes \textit{4} are highly unstable (Fig. 6d).\textsuperscript{21} In contrast, monolayers composed of \textit{3} and \textit{5} are reasonably stable over extended periods of time ($>$ 80 min) and may thus be used for transfer experiments.

Even though it is generally difficult to extrapolate molecular design to supramolecular organization,\textsuperscript{35} especially when using only weak molecular recognition tools such as London forces,\textsuperscript{36} complexes \textit{3–5} demonstrate a strong correlation between molecular design, crystal packing, and self-assembling properties. For example, appending the alkoxy tails in a different position on the aromatic ring of sal\textsubscript{3}bapen ligands reduces the intramolecular O\textsubscript{alkoxy}–O\textsubscript{alkoxy} distance from 11.8 Å in \textit{4a} to 6.7 Å in \textit{5a} (cf. X-ray structures) and simultaneously modifies the shape of the complex from a linear system (transoid alkyl chains in \textit{4a}) to a U-shaped geometry due to the cisoid arrangement of the alkyl chains. This modification separates the hydrophobic and lipophilic parts sufficiently well to entail the formation of stable films at the air-water interface.\textsuperscript{37}

Transfer of the Langmuir films onto supports was of limited success. Only partial transfer was observed due to significant desorption of material during downstrokes, resulting in ill-defined multilayered structures.\textsuperscript{37} This drawback may perhaps be resolved by introducing different types of molecular recognition sites for self-assembly and studies along these lines are currently in progress.

Conclusions

Amphiphilic manganese(III) complexes comprising different ligand skeletons were obtained using a simple alkoxy-functionalization approach that allows for adjustment of the hydrophilic-lipophilic balance. The aliphatic chains do not affect the electrochemical properties and allow for accessing three different oxidation states under mild conditions. However, they strongly influence the magnetic behavior of the complexes. Notably, octadecyloxy substituents attached to the sal\textsubscript{3}bapen ligand induce $S = 2$ to $S = 1$ spin transitions. Long aliphatic chains stabilize the low spin configuration at much higher temperature ($>$150 K) as compared to shorter hexyloxy groups. The observation of SCO in the isomeric complexes \textit{4c} and \textit{5e} — the latter with a transition centered around room temperature and hence very attractive for device fabrication—suggests that the inductive character of the alkoxy group is more relevant than mesomeric or steric effects.

Due to the amphiphilic character, the complexes have a high propensity to form distinct hydrophilic and hydrophobic domains upon self-assembly, both in the solid state (crystals) as well as at the air-water interface (Langmuir films). A clear separation between hydrophobic and hydrophilic moieties within the molecular building blocks is essential for the formation of a stable Langmuir monolayer. Since the sal\textsubscript{3}bapen framework is considerably less hydrophilic than the sal\textsubscript{3}trien analog, the length and the position of the aliphatic chains plays a critical role for inducing self-assembly.

Complex \textit{5e} represents an optimized building block, combining SCO lability and redox activity with acceptable Langmuir film stability.

Experimental section

General remarks

The syntheses of the 4-alkoxy-functionalized salicylaldehydes \textit{1,15} the 6-alkoxyfunctionalized salicylaldehydes \textit{2,31} and the Schiff base, which has been isolated for the preparation of \textit{3c,13} were reported elsewhere. THF was dried by passage through a solvent purification column, all other reagents were commercially available and used as received. Flash chromatography was performed using silica gel 60 (63-200 mesh) or basic alox (0.05–1.0 mm, pH 9.5). Melting points were determined using an OptiMelt apparatus (Stanford Research Systems) or a Mettler Toledo TGA/SDTA 851 analyzer and are uncorrected. UV-vis measurements were performed on a Perkin Elmer Lambda 40 instrument in CHCl\textsubscript{3} solution (0.2 mM). IR spectra were recorded on a Mattson 5000 FTIR instrument in CHCl\textsubscript{3} solution. UV-vis spectra of LB-films were recorded on a Perkin Elmer Lambda 900 instrument in transmission mode. High resolution mass spectra were measured by electrospray ionization (ESI-MS) on a Bruker 4.7 T BioAPEX II or on a Water Corp. USA Micromass LCT. Elemental analyses were performed at the ETH Zurich (Switzerland) or at the Micronanalytical Laboratory of UCD (Ireland). Electrochemical studies were carried out using an EG&G Princeton Applied Research Potentiostat Model 273A employing a gastight three-electrode cell under an argon atmosphere. A saturated calomel electrode (SCE) was used as reference; a Pt disk (3.14 mm\textsuperscript{2}) and a Pt wire were used as the working and counter electrode, respectively. The redox potentials were measured in dry CHCl\textsubscript{3} ($<$ 1 mM) with $n$-BuNPF\textsubscript{6} (0.1 M) as electrolyte and ferrocene ($E_{1/2} = 0.46$ V vs. SCE)\textsuperscript{38} or [Ru(bpy)$_3$][$PF_6$\textsubscript{2}] ($E_{1/2} =$...
1.39 V vs. SCE) as internal standard. Temperature-dependent magnetization of solid samples was studied using a Quantum Design PPMS system in a temperature range between 300 and 50 K (unless stated otherwise) using an applied field of 0.1 T (3c, 4) or 0.5 T (3a, 5). Susceptibility data were corrected for the diamagnetic contribution calculated from Pascal constants.

Langmuir-Blodgett Films

Pressure-area isotherms and time stability were measured at 25 °C on a KSV MiniMicro Langmuir-Blodgett trough (KSV, Finland) with a surface area between 1700 and 8700 mm². Water was purified with a Barnstead Nanopure system (Thermo Scientific), and its resistivity was measured to be higher than 18 MΩ cm. Chloroform (puriss. p.a. ≥ 99.8% Fluka) was used as spreading solvent. Typically drops of the solution were spread on the water subphase. After letting the solvent evaporate for 30 min, the barriers were compressed at 6 mm min⁻¹ (3 cm min⁻¹) and the surface pressure was monitored using a platinum Willhemy plate. Each isotherm has been measured three times with good reproducibility.

Synthesis of complex 3a

Triethylenetetramine (146 mg, 1.0 mmol) was dissolved in EtOH (5 mL) and treated with a solution of 1a (446 mg, 2.0 mmol) in THF (5 mL). After 5 min, NaOMe (108 mg, 2.0 mmol) was added as a solid and Mn(NO₃)₂·4H₂O (251 mg, 1.0 mmol) in EtOH (5 mL) was added dropwise to the yellow solution. The greenish brown suspension was heated to 60 °C for 30 min open to air and filtered over a bed of silica. The product was eluted with THF (60 mL) and evaporated under reduced pressure. The residue was dissolved in CHCl₃ (5 mL) and purified on a short pad of Al₂O₃ (12 cm) by consecutive elution with CHCl₃ (60 mL) and EtOH/THF 2:1 (150 mL). After evaporation of the EtOH/THF fraction, the product was redissolved in CHCl₃ (5 mL) and filtered over Celite. The supernatant was evaporated under reduced pressure to give 3c as a green solid (130 mg, 25%). Analytically pure material was obtained by dissolving 3c in CH₂Cl₂ (10 mL) and precipitation with Et₂O (70 mL) under stirring. M.p. 198 °C (decomp.). IR (CHCl₃): 1586 (νC=N), 1524 cm⁻¹ (νC–C). UV-vis (CH₂Cl₂): λmax (ε) = 252 nm (32800 M⁻¹ cm⁻¹), 286 nm (27400 M⁻¹ cm⁻¹), 321 nm (18800 M⁻¹ cm⁻¹), 380 nm (10800 M⁻¹ cm⁻¹), 481 nm (1750 M⁻¹ cm⁻¹), 606 nm (290 M⁻¹ cm⁻¹). HR-MS (ESI): Calcd. for C₆H₆MnN₃O₄ [M–NO₃]⁺ m/z = 775.4928, found m/z = 775.4917. Anal. found (calcd) for C₆H₆MnN₃O₄·H₂O (838.02): C 63.12 (63.06); H 8.69 (8.66); N 9.85 (10.39).

Synthesis of complex 3c

Solid NaOMe (54 mg, 1 mmol) was added to the Schiff base (446 mg, 0.5 mmol) in warm THF (20 mL). After 2 min stirring, a solution of Mn(NO₃)₂·4H₂O (248 mg, 0.61 mmol) in EtOH (5 mL) was added dropwise. The greenish brown suspension was stirred for 30 min at reflux and filtered over a bed of silica (1.5 cm height). The product was eluted with EtOH/THF 2:1 (100 mL) and dried under reduced pressure. The residue was taken into CHCl₃ (5 mL) and purified on a short pad of Al₂O₃ (12 cm) by consecutive elution with CHCl₃ (60 mL) and EtOH/THF 2:1 (150 mL). After evaporation of the EtOH/THF fraction, the product was redissolved in CHCl₃ (5 mL) and filtered over Celite. The supernatant was evaporated under reduced pressure to give 3e as a green solid (130 mg, 25%). Analytically pure material was obtained by dissolving 3e in CH₂Cl₂ (10 mL) and precipitation with Et₂O (70 mL) under stirring. M.p. 198 °C (decomp.). IR (CHCl₃): 1586 (νC=N), 1524 cm⁻¹ (νC–C). UV-vis (CH₂Cl₂): λmax (ε) = 252 nm (32800 M⁻¹ cm⁻¹), 286 nm (27400 M⁻¹ cm⁻¹), 321 nm (18800 M⁻¹ cm⁻¹), 380 nm (10800 M⁻¹ cm⁻¹), 481 nm (1750 M⁻¹ cm⁻¹), 606 nm (290 M⁻¹ cm⁻¹). HR-MS (ESI): Calcd. for C₆H₆MnN₃O₄·H₂O [M–NO₃]⁺ m/z = 943.6812, found m/z = 943.6821. Anal. found (calcd) for C₆H₆MnN₃O₄·H₂O (1006.35): C 66.97 (66.84); H 9.61 (9.61); N 6.74 (6.96).

Synthesis of complex 4a

This complex was synthesized according to the method described for 3a, starting from N,N′,N″,N‴-bis(3-amino-phenyl)ethylenediamine (278 mg, 1.5 mmol) dissolved in EtOH (8 mL), a solution of 1a (667 mg, 3.0 mmol) in THF (8 mL), NaOMe (162 mg, 3.0 mmol), and Mn(NO₃)₂·4H₂O (274 mg, 1.5 mmol) in EtOH (5 mL), thus yielding 4a as a purple solid (0.44 g, 42%). Crystals for single crystal structure analysis were grown by slow evaporation of an acetone/water mixture containing 4a. M.p. 185 °C (decomp.). IR (CHCl₃): 1604 (νC=N), 1538 cm⁻¹ (νC–C). UV-vis (CH₂Cl₂): λmax (ε) = 251 nm (30400 M⁻¹ cm⁻¹), 289 nm (36700 M⁻¹ cm⁻¹), 514 nm (790 M⁻¹ cm⁻¹), 663 nm (227 M⁻¹ cm⁻¹). HR-MS (ESI): Calcd. for C₁₃H₁₂MnN₄O₄·H₂O [M–NO₃]⁺ m/z = 365.3369, found m/z = 365.3362. Anal. found (calcd) for C₁₃H₁₂MnN₄O₄·H₂O (669.70): C 58.25 (58.53); H 7.45 (7.51); N 9.85 (10.04).

Synthesis of complex 4b

According to procedure used for 4a, the crude title product was obtained from N,N′,N″,N‴-bis(3-amino-phenyl)ethylenediamine (185 mg, 1.0 mmol) in EtOH (5 mL), 1b (613 mg, 2.0 mmol) in THF (5 mL), NaOMe (108 mg, 2.0 mmol), and Mn(NO₃)₂·4H₂O (183 mg, 1.0 mmol) in EtOH (5 mL), thus giving 4b as a purple solid (0.44 g, 51%). M.p. 177 °C (decomp.). IR

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(CHCl$_2$): 1604 ($\nu$C=O), 1537 cm$^{-1}$ ($\nu$C=C). UV-vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ ($\epsilon$) = 251 nm (29200 M$^{-1}$·cm$^{-1}$), 289 nm (36500 M$^{-1}$·cm$^{-1}$), 514 nm (800 M$^{-1}$·cm$^{-1}$), 663 nm (230 M$^{-1}$·cm$^{-1}$). HR-MS (ESI): Calcd. for Ca$_{45}$H$_{84}$N$_{80}$O$_{12}$ [M–NO$_2$]$^+$ m/z = 803.5247, found m/z = 803.5215. Anal. found (calcd) for Ca$_{45}$H$_{84}$N$_{80}$O$_{12}$ (866.08): C 63.49 (63.79); H 7.86 (8.85); N 7.85 (8.09).

**Synthesis of complex 4C**

According to procedure 4a the crude title product was obtained from N,N'-bis(3-aminopropyl)ethylenediamine (185 mg, 1.0 mmol) in EtOH (5 mL), 1c (613 mg, 2.0 mmol) in warm THF (50 mL), NaOMe (108 mg, 2.0 mmol) and Mn(NO$_3$)$_2$·xH$_2$O (183 mg, 1.0 mmol) in EtOH (5 mL). Purification was performed on a short pad of Al$_2$O$_3$ (13 cm) by consecutive elution with CHCl$_3$ (30 mL) and THF (60 mL).

After evaporation of the THF fraction, the product was redissolved in CHCl$_3$ (20 mL) and filtered over Celite. After evaporation of the filtrate under reduced pressure, the residue was recrystallized from warm acetone to give 4c as a purple solid (0.31 g, 30%). M.p. 187 °C (decomp.). IR (CHCl$_3$): 1607 ($\nu$C=O), 1532 cm$^{-1}$ ($\nu$C=C). UV-vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ ($\epsilon$) = 251 nm (28000 M$^{-1}$·cm$^{-1}$), 289 nm (36700 M$^{-1}$·cm$^{-1}$), 512 nm (740 M$^{-1}$·cm$^{-1}$), 663 nm (217 M$^{-1}$·cm$^{-1}$). HR–MS (ESI): Calcd. for C$_{59}$H$_{104}$N$_{80}$O$_{12}$ [M–NO$_2$]$^+$ m/z = 971.7120, found m/z = 971.7110. Anal. found (calcd) for C$_{59}$H$_{104}$N$_{80}$O$_{12}$ (1034.40): C 67.75 (67.35); H 9.81 (9.74); N 6.44 (6.77).

**Synthesis of complex 5a**

The procedure used for the synthesis of 3a was used, starting from N,N'-bis(3-aminopropyl)ethylenediamine (195 mg, 1.05 mmol) in EtOH (5 mL), 2a (113 mg, 2.10 mmol) in THF (5 mL), NaOMe (113 mg, 2.10 mmol) and Mn(NO$_3$)$_2$·xH$_2$O (269 mg, 1.05 mmol) in EtOH (5 mL). The dark purple suspension was stirred for 30 min at RT open to air and filtered over a bed of silica. The product was eluted with THF (40 mL) and evaporated under reduced pressure. The residue was dissolved in CHCl$_3$ (10 mL) and purified on a short pad of Al$_2$O$_3$ (5 cm) by first washing with CHCl$_3$, THF, and finally with EtOH/THF fraction 2:1 (50 mL). After evaporating the EtOH/THF fraction, the residue was repetitively redissolved in CHCl$_3$ (2 mL) and precipitated with pentane (80 mL) and EtO$_2$(O) (3 × 80 mL). The residue collected by centrifugation was dissolved in CHCl$_3$ and filtered over Celite. The filtrate was evaporated in vacuo to give 5a as a purple solid (0.34 g, 46%). Crystals for single crystal analysis were grown by slow evaporation of an acetone/water mixture containing 5a. M.p. 167 °C. IR (CHCl$_3$): 1615 ($\nu$C=N), 1595 ($\nu$C=C). UV-vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ ($\epsilon$) = 285 nm (19400 M$^{-1}$·cm$^{-1}$), 320 nm (13500 M$^{-1}$·cm$^{-1}$), 372 nm (5660 M$^{-1}$·cm$^{-1}$), 505 nm (1090 M$^{-1}$·cm$^{-1}$), 666 nm (210 M$^{-1}$·cm$^{-1}$). HR–MS (ESI): Calcd. for C$_{59}$H$_{104}$N$_{80}$O$_{12}$ [M–NO$_2$]$^+$ m/z = 971.7121, found m/z = 971.7120. Anal. found (calcd) for C$_{59}$H$_{104}$N$_{80}$O$_{12}$ (1034.40): C 69.70 (69.61); H 9.72 (9.78); N 6.47 (6.60).

**Crystal Structure Determinations**

Suitable single crystals were mounted on a Stoe Mark II Imaging Plate Diffractometer System equipped with a graphite monochromator. Data collection was performed at −100 °C using Mo-K$_α$ radiation ($\lambda = 0.71073 \AA$) with a nominal crystal to detector distance of 135 mm. All structures were solved by direct methods using the program SHELXS-97 and refined by full matrix least squares on F$^2$ with SHELXL-97. The hydrogen atoms were included in calculated positions and treated as riding atoms using the program SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically. A semi-empirical absorption correction was applied for structures 4a and 5a using MULABS (PLATON03). Compound 3a crystallized with two independent molecules and seven water molecules per asymmetric unit. The absolute structure was determined by refinement of the Flack parameter (0.08(5)). One nitrate anion is disordered and was refined isotropically; the oxygen atoms were split over two positions (occupancies 0.5/0.5). Complex 4a crystallized with two independent molecules per asymmetric unit. A region of disordered electron density was assumed to be co-crystallized solvent molecules. The absolute structure could be derived...
with a Flack parameter $x = 0.03(3)$. The SQUEEZE option in PLATON was used to calculate the potential solvent accessible volume in the unit cell: $810 \text{ Å}^3$ was calculated containing about 202 electrons, equated to six acetone molecules ($6 \times 32$ electrons) per unit cell. One nitrate anion is disordered over two positions (occupancies 0.70/0.3). The alkyl chains in 3a and 4a suffer from thermal disorder. In the final cycles of refinement their anisotropic displacement parameters were made identical, using the EADP instruction in SHELXL, and the C–C bonds were refined with distance restraints of 1.54(2) Å. Complex 5a crystallizes with one water molecule per asymmetric unit. Further details on data collection and refinement parameters are collected in the supporting information (Table S-2). Crystallographic data (excluding structure factors) for the structures 3a, 4a, and 5a have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 782475–782477. Copies of the data can be obtained free of charge on application to CCDS, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (int.) +44-1223-336-033; E-mail: deposit@ccds.cam.ac.uk].

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Notes and references

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4. Electronic Supplementary Information (ESI) available: Synthesis of compounds 2a–c, magnetic measurements of 3a and 3c, Langmuir studies (Langmuir plots and multilayering into LB films), and crystallographic details for complexes 3a, 4a, and 5a in CIF format. See DOI: 10.1039/b000000x
8. We are not aware of studies on the self-assembly of SCO-active manganese complexes other than Prussian blue analogues (e.g. Rb[MnFe(CN)₆]), in which the spin transition is associated with a metal-to-metal electron transfer, see for examples: (a) S. Cobo, R. Fernandez, L. Salmon, G. Molnar and A. Bousseksou, Eur. J. Inorg. Chem., 2007, 1549; (b) S. Ohkoshi, H. Tokoro and K. Hashimoto, Coord. Chem. Rev., 2005, 249, 1830. A study on single molecular spin transition, which obviously cannot be cooperative, has appeared recently: (c) E. A. Osorio, K. Moth-Poulsen, H. S. J. van der Zant, J. Paskie, P. Hedges, K. Flensberg, J. Bendix and T. Bjornholm, Nano Lett., 2010, 10, 105.
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M. Marchivie, P. Guionneau, J. Ksenofontov, Y. Galyametdinov, J. Kusz and P. Gütlich,
Magnetic measurements on complexes 4 and 5 in solution using Evans’ method indicated \(\mu_{\text{BS}}\) values between 4.74 and 4.82 \(\mu_B\) at RT, thus pointing to the presence of high-spin complexes only. Therefore, spectroscopic properties have been assigned to specific complexes rather than to a spin-equilibrated mixture.

Under identical conditions, the unfunctionalized complex [Mn(sal)bpen]NO displays \(E_{1/2} = +0.77\). This expected slightly higher potential in the absence of alkoxy substituents together with calculations on the unfunctionalized complex, which predict that the HOMO is largely metal-centered,\(^1\) may support the notion that the oxidation observed here is indeed metal-centered.

See the electronic supporting information for further details.
Further cooling of complex 5c to 3 K revealed an abrupt drop to 1.54 \(\mu_B\), indicating antiferromagnetism below 20 K. Since the inverse susceptibility \(\chi^{-1}\) is not linear over the measured temperature range, data fitting to the Curie-Weiss law was precluded.
The magnetic moment for complex 1 is \(\mu_{\text{BS}} = 4.4 \mu_B\) at 300 K.
Sample annealing may be another process to account for the different magnetic behavior of warmed 5c. Gradual desolvation in this temperature range has been ruled out by thermogravimetric analyses, which do not show any weight loss up to 80 °C.


The shortest distance is for 3a is slightly less than the closest Mn--Mn distance in the spin-stable trien analog of complex I, viz. [Mn(3-Ome-sal-trien)]NO, which is 7.814 Å and hence also considerably shorter than in 5a.


A possible rationale for this behavior may rely on the severe distortion of the octahedral coordination geometry around the manganese center, which imposes a certain coordinative flexibility. Upon compression, the rearrangement may be less rigid and may allow for interdigitation of alkyl chains of neighboring complexes. Such interdigitation may build up considerable tension, which is in agreement with the low stability of the formed films.
Determined using the ferrocenium/ferrocene (Fc+/Fc) couple.

Identical plots were obtained for 5c irrespective of whether the measurement was performed under an applied field of 0.1 T or 1 T.

Synthesis and Self-Assembly of Spin-Labile and Redox-Active Manganese(III) Complexes

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Amphiphilic functionalization of manganese(III) complexes induces spin crossover and promotes self-assembly in the solid state and at the air-water interface.