<table>
<thead>
<tr>
<th><strong>Title</strong></th>
<th>Synthesis and self-assembly of spin-labile and redox-active manganese(III) complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Author(s)</strong></td>
<td>Gandolfi, Claudio; Cotting, Tatiana; Martinho, Paulo N.; Morgan, Grace G.; Albrecht, Martin; et al.</td>
</tr>
<tr>
<td><strong>Publication date</strong></td>
<td>2011-03-07</td>
</tr>
<tr>
<td><strong>Publication information</strong></td>
<td>Dalton Transactions, 40 (9): 1855-1865</td>
</tr>
<tr>
<td><strong>Publisher</strong></td>
<td>Royal Society of Chemistry</td>
</tr>
<tr>
<td><strong>Item record/more information</strong></td>
<td><a href="http://hdl.handle.net/10197/6819">http://hdl.handle.net/10197/6819</a></td>
</tr>
<tr>
<td><strong>Publisher's version (DOI)</strong></td>
<td><a href="http://dx.doi.org/10.1039/c0dt01222j">http://dx.doi.org/10.1039/c0dt01222j</a></td>
</tr>
</tbody>
</table>
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

First published on the web Xth XXXXXXXXX 200X
DOI: 10.1039/b000000x

New amphiphilic and spin-labile Mn\textsuperscript{III} complexes based on dianionic N\textsubscript{2}O\textsubscript{2}-hexadentate sal-trien or sal-bapen ligands were prepared that contain O\textsubscript{18}H\textsubscript{33}, O\textsubscript{19}H\textsubscript{25}, or O\textsubscript{18}H\textsubscript{17} alkoxy substituents at different positions of the salicylidene unit (H\textsubscript{2}sal-trien = N,N\textsuperscript{37}37-bis(salicylidene)-1,4,7,10-tetraazadecane, H\textsubscript{2}sal-bapen = N,N\textsuperscript{13}13-bis(salicylidene)-1,5,8,12-tetraazadodecane). According to electrochemical measurements, these complexes underwent 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 C\textsubscript{14}-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 (C\textsubscript{12} or C\textsubscript{14}) 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.\textsuperscript{1} Ideally, the spin change is abrupt and displays hysteretic features to entail bistability over a given temperature range.\textsuperscript{2} 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\textsuperscript{3} 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,\textsuperscript{4} in nanoparticles,\textsuperscript{5} in gels,\textsuperscript{6} and recently even in solution.\textsuperscript{7}

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.\textsuperscript{8} 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 d\textsuperscript{4} electronic configuration presets such complexes for spin crossover. However, only a few SCO-active manganese(III) systems are known.\textsuperscript{9} A possible reason for the limited accessibility of SCO-active manganese complexes may be the difficulty associated with preparing configurationally stable low-spin complexes.\textsuperscript{10} In the few complexes that exhibit SCO activity, the manganese center is often ligated by a multidentate ligand.\textsuperscript{11} For example, complex I comprising a dianionic hexadentate N\textsubscript{2}O\textsubscript{2} ligand framework was reported to undergo a thermally induced spin transition from S = 2 to S = 1 (Fig. 1).\textsuperscript{12} Based on our previous achievements in self-assembling iron(III) and cobalt(III) complexes comprising a related N\textsubscript{2}O\textsubscript{2} ligand system,\textsuperscript{13} 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

This journal is © The Royal Society of Chemistry [year]
hydrophilic-lipophilic balance has been performed by modifying the skeleton of the hexadentate \( \text{N}_6 \text{O}_2 \) 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 sal\( \text{trien} \) ligand framework functionalized with two alkyl chains were prepared according to modified literature procedures.\(^{14} \) Thus, condensation of the known\(^{15} \) alkoxysubstituted salicylaldehydes 1 with triethylentetramine (trien) followed by \textit{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 \( \text{N}_2\text{N}'''\text{N}'''\text{bis(3-aminopropyl)} \) ethylenediamine (bapen) instead of trien yielded the alkylated purple complexes 4 and 5. All products were purified by flash chromatography and, if required, by repetitive precipitation. The complexes containing the sal\( \text{trien} \) ligand scaffold (complexes 4 and 5) consistently showed better solubility in organic solvents than their sal\( \text{trien} \) 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 \( \nu_{\text{C=O}} \) absorption bands around 1600 cm\(^{-1} \) (CHCl\(_3 \) solution) as compared to the analogous non-alkylated complexes.\(^{16} \) Similarly, the bands between 1524–1595 cm\(^{-1} \), assigned to aromatic \( \pi-\pi^* \) transitions,\(^{16a} \) remain essentially unaltered. A characteristic shift of the \( \nu_{\text{C=N}} \) band towards higher energy was noted upon expanding the ligand skeleton from sal\( \text{trien} \) to sal\( \text{trien} \)bapen (average \( \nu_{\text{C=N}} \) 1591 cm\(^{-1} \) in complexes 3 vs. 1605 cm\(^{-1} \) in 4 and 1615 cm\(^{-1} \) in 5), indicating that the C=\( \text{N} \) 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 \( \pi-\pi^* \) transitions below 400 nm. In addition, the sal\( \text{trien} \) complexes 3 feature a shoulder at 480 nm (\( \epsilon = 1700 \text{ M}^{-1} \text{ cm}^{-1} \)) originating from phenolate-to-manganese LMCT transitions, and a very broad and weak d-d absorption band around 640 nm (\( \epsilon = 330 \text{ M}^{-1} \text{ cm}^{-1} \)). 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.\(^{16c} \) The absorption maxima of the sal\( \text{trien} \)bapen complexes 4–5 are shifted to lower energy as compared to 3. The LMCT band appears at around 510 nm (\( \epsilon = 870 \text{ M}^{-1} \text{ cm}^{-1} \)) for 4 and 5, respectively and a very weak shoulder is observed around 660 nm (\( \epsilon = 210 \text{ M}^{-1} \text{ cm}^{-1} \)).

#### Electrochemistry

Cyclic voltammetry (CV) measurements of complexes 3–5 (CH\(_2\text{Cl}_2 \) solutions) in the −1.2 V to +1.2 V potential range...
This journal is © The Royal Society of Chemistry [year]

Fig. 2 Representative cyclic voltammogram (second cycle) showing the Mn$^{3+}$/Mn$^{2+}$ reduction and the Mn$^{4+}$/Mn$^{3+}$ oxidation of complexes 3a (grey) and 5a (black).

Table 1 Electrochemical Data of Manganese(III) Complexes$^a$

<table>
<thead>
<tr>
<th>Complex</th>
<th>Mn$^{4+}$/Mn$^{3+}$</th>
<th>Mn$^{5+}$/Mn$^{4+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E$_{pa}$/V $\Delta E$/mV</td>
<td>E$<em>{pa}$/V E$</em>{oc}$/V E$_{pa}$/V $\Delta E$/mV</td>
</tr>
<tr>
<td>3a</td>
<td>+0.59 197</td>
<td>-0.25 -0.02 -0.14 216</td>
</tr>
<tr>
<td>3b</td>
<td>+0.63 207</td>
<td>-0.23 -0.02 -0.13 212</td>
</tr>
<tr>
<td>3c</td>
<td>+0.58 202</td>
<td>-0.25 -0.02 -0.14 226</td>
</tr>
<tr>
<td>4a</td>
<td>+0.64 160</td>
<td>-0.48 -0.05 --- 438</td>
</tr>
<tr>
<td>4b</td>
<td>+0.66 169</td>
<td>-0.53 -0.01 --- 517</td>
</tr>
<tr>
<td>4c</td>
<td>+0.66 226</td>
<td>-0.54 -0.05 --- 494</td>
</tr>
<tr>
<td>5a</td>
<td>+0.69 160</td>
<td>-0.45 -0.25 -0.35 207</td>
</tr>
<tr>
<td>5b</td>
<td>+0.68 174</td>
<td>-0.46 -0.24 -0.35 221</td>
</tr>
<tr>
<td>5c</td>
<td>+0.70 117</td>
<td>-0.44 -0.26 -0.35 179</td>
</tr>
</tbody>
</table>

$^a$CH$_2$Cl$_2$ solution, 0.1 M n-Bu$_4$PF$_6$ as supporting electrolyte; E$_{pa}$ vs SCE, Pt working electrode, scan rate 100 mV s$^{-1}$; Fe$^{3+}$/Fe ($E_{pa} = +0.46$ V) or [Ru(bpy)$_3$]$_2^3+$/[Ru(bpy)$_3$]$_2^2+$ ($E_{pa} = +1.39$ V) as internal standard.

Indicated that reduction as well as oxidation of the complexes is accessible at moderate potential (Table 1). Quasi-reversible oxidation occurred for all complexes in a narrow potential window. The oxidation potentials suggest a small yet distinct modulation of the donor properties of the N$_2$O$_2$ ligand set, decreasing in the sequence 3 ($E_{pa}$ 0.60) > 4 ($E_{pa}$ 0.65) > 5 ($E_{pa}$ 0.69). These differences may be a consequence of the size of the metallacycle and of the alkoxide substitution pattern. No specific effect of the alkyl chain length on the oxidation potential was noted. Stronger disparities were observed for the Mn$^{3+}$ to Mn$^{2+}$ reduction in the three types of complexes. The reduction potentials for the sal-bapen complexes 4 and 5 are about 200 mV more negative than those of complexes 3. Hence, both the Mn$^{3+}$ and the Mn$^{2+}$ state are more easily accessible for complex 3 as compared to the sal-bapen complexes 4 and 5 (Fig. 2). Different reduction behavior may originate from modulation of the strain imposed by the ligand framework (five- vs six-membered metallacycles), or from modification of the donor group arrangement (cis- vs trans-positioned oxygens). Moreover, the relatively high anodic peak potential $E_{pa}$ in complex 4 paired with the low maximum peak current $i_{pa}$ indicate a more complex process than simple re-oxidation of electrochemically generated Mn$^{2+}$ to Mn$^{3+}$. Although Mn$^{3+}$ reduction was previously reported to be reversible, our results provide further support that the electrochemically generated Mn$^{3+}$ species is not stable.

Magnetism

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 H$_2$O and 3c displayed a temperature-independent magnetic moment ($\mu_{eff} = 4.85$ and 4.56 $\mu_B$, respectively). This value is in agreement with the expected spin-only magnetic moment calculated for a high spin complex with four unpaired electrons ($S = 2$, $\mu_{eff} = 4.90 \mu_B$). 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 $\mu_{eff} = 4.33 \mu_B$ corresponds to an approximate 1:3 distribution of low spin/high spin manganese centers.

The transition for crystalline 5a × H$_2$O is more pronounced, falling from almost 100% high spin at RT ($\mu_{eff} = 4.65 \mu_B$) to $\mu_{eff} = 3.32 \mu_B$ at 120 K (Fig. 3b, $T_{1/2}$ ca. 150 K). The measured...
complexes. hr have been suggested in the dihedral angle of alkyl chains are fully stretched and in a mutually cisoid arrangement. The dihedral angle characterizes the geometry of these complexes.

Table 2 Selected bond lengths (Å) for complexes 3a, 4a, and 5a at 173 K

<table>
<thead>
<tr>
<th></th>
<th>Bond Length</th>
<th>Bond Length</th>
<th>Bond Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn-O</td>
<td>2.062(10)</td>
<td>2.106(11)</td>
<td>2.004(12)</td>
</tr>
<tr>
<td>Mn-O</td>
<td>1.909(11)</td>
<td>1.914(11)</td>
<td>2.118(11)</td>
</tr>
<tr>
<td>Mn-N</td>
<td>2.296(11)</td>
<td>2.245(13)</td>
<td>2.118(11)</td>
</tr>
<tr>
<td>Mn-N</td>
<td>2.118(11)</td>
<td>2.176(12)</td>
<td>1.939(16)</td>
</tr>
</tbody>
</table>

* angular distortion parameter Σ calculated according to ref. 24.

The asymmetric unit of 3a comprises two unique complex cations, which each show a Jahn-Teller elongation along one of the amine nitrogens and one of the phenolate oxygens (Table 2). Generally, bond lengths and angles are consistent with a high spin configuration at the MnIII center. Nevertheless, a significant distortion from an ideally octahedral geometry is noted in all complexes, which may be reflected by the significant distortion parameter Σ (Table 2). 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 phenolate oxygens (Table 2). Generally, bond lengths and angles are consistent with a high spin configuration at the MnIII center as deduced from magnetic measurements (vide supra). The alkyl chains are fully stretched and in a mutually cisoid arrangement. The dihedral angle α between the two phenolate rings in each complex is about 117°. Values of α above 90° have been suggested to preclude SCO activity in Fe(salen)3trien complexes. This criterion might be less relevant for the manganese series, since the equally spin-stable methoxy-substituted analog of 3a has α = 87.8°.

Table 2 Selected bond lengths (Å) for complexes 3a, 4a, and 5a at 173 K

<table>
<thead>
<tr>
<th></th>
<th>Bond Length</th>
<th>Bond Length</th>
<th>Bond Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn-O</td>
<td>2.062(10)</td>
<td>2.106(11)</td>
<td>2.004(12)</td>
</tr>
<tr>
<td>Mn-O</td>
<td>1.909(11)</td>
<td>1.914(11)</td>
<td>2.118(11)</td>
</tr>
<tr>
<td>Mn-N</td>
<td>2.296(11)</td>
<td>2.245(13)</td>
<td>2.118(11)</td>
</tr>
<tr>
<td>Mn-N</td>
<td>2.118(11)</td>
<td>2.176(12)</td>
<td>1.939(16)</td>
</tr>
</tbody>
</table>

* angular distortion parameter Σ calculated according to ref. 24.

The magnetic moments of the OC18-functionalized complexes 4c and 5c are lower at RT (μeff = 3.74 μB and 3.65 μB, respectively; Fig. 3b). They decrease gradually upon cooling and reach a plateau at μeff = 2.85 μB and 2.98 μB, respectively, consistent with the S = 1 state. 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. Upon heating a sample of 5c to 350 K the μeff indeed increases to μeff = 4.24 μB, 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 (μeff = 3.49 μB 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. Such a hypothesis is supported by the similar behavior of the warmed sample and an amorphous sample of 5c. Nevertheless, we observe that long alkyl chains tend to stabilize the less common S = 1 configuration of manganese(III) centers.

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. Complex 3a features cis-positioned phenolate 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 Σ (Table 2).

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 M–N bonds compared to 3a reflect the predominantly HS state with population of the d2z2 orbital producing an axial compression. Upon displacing the alkoxy chain to the imine ortho position (5a, Fig. 4c) the M–Namine 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<sub>amine</sub> bond lengths. While most of the bond lengths in 5a at 173 K are similar to those in the methoxy-functionalized complex 1 at RT, which is known to be in high spin configuration, partial spin crossover may be supported by the short M–N<sub>amine</sub> 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 1 (70.7 and 45.0, respectively),<sup>12</sup> 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<sub>nitrate</sub>···H–O<sub>water</sub>···H–N motif.<sup>21</sup> The two inequivalent complex cations of 4a also form a dimeric structure due to N–H···O<sub>N</sub>(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<sub>3</sub> anion and a co-crystallized H<sub>2</sub>O molecule. Hence, hydrogen bond formation between the ligand N-H group and the NO<sub>3</sub> 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.<sup>29</sup> 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...
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<sub>6</sub>H<sub>13</sub>), solid (OC<sub>12</sub>H<sub>25</sub>), or bold lines (OC<sub>18</sub>H<sub>37</sub>); (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 I (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 consequently 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<sub>12</sub> and C<sub>18</sub> alkyl tails self-assemble into densely packed Langmuir monolayers, which collapse typically at a surface area slightly below 70 Å<sup>2</sup>/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<sup>2</sup>/molecule (Fig. 6). When using long chain C<sub>18</sub>-functionalized complexes, intermolecular contacts establish at an earlier stage of compression than with C<sub>12</sub>-functionalized complexes. Also the molecular area in compressed C<sub>18</sub>-functionalized monolayers is larger than with shorter C<sub>12</sub> tails. Such behavior has been previously observed...
with analogous iron complexes, and may be due to the increased probability of long chains to backfold. In contrast, the complexes containing hexaalkoxy 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 3e shows two separated phase transitions at 92 and 72 Å²/molecule, which may point to distinct transitions from liquid expanded to liquid condensed and then to the solid phase. Films built from saltrien-type complexes 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 sal2bapen-derived species 4 and 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 4b–c or 5b–c continuously shrunken upon compression, pointing to a liquid condensed phase. This specific behavior may be a consequence of the reduced hydrophilicity of the sal2bapen ligand as compared to the sal-trien system in 3.

When considering the transoid arrangement of the alkyl tails in complexes 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 5 bearing cisoid alkyl chains. Notably, the films composed of complexes 4 are hardly unstable (Fig. 6d). In contrast, monolayers composed of 3 and 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, especially when using only weak molecular recognition tools such as London forces, complexes 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 sal2bapen ligands reduces the intramolecular Oalkoxy...Oalkoxy distance from 11.8 Å in 4a to 6.7 Å in 5a (cf. X-ray structures) and simultaneously modifies the shape of the complex from a linear system (transoid alkyl chains in 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.

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. 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 sal2bapen 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 4c and 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 sal2bapen framework is considerably less hydrophilic than the saltrien analog, the length and the position of the aliphatic chains plays a critical role for inducing self-assembly. Complex 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 1, the 6-alkoxyfunctionalized salicylaldehydes 2, and the Schiff base, which has been isolated for the preparation of 3e, 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 (0.05–0.15 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 CHCl3 solution (0.2 mM). IR spectra were recorded on a Mattson 5000 FTIR instrument in CHCl3 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 mm2) and a Pt wire were used as the working and counter electrode, respectively. The redox potentials were measured in dry CHCl3 (-1 mM) with n-Bu4NPF6 (0.1 M) as electrolyte and ferrocene (E1/2 = 0.46 V vs. SCE) or [Ru(bpy)3]2+[PF6]2- (E1/2 =...
obtained from triethylenetetramine (146 mg, 1.0 mmol) in EtOH (5 mL), NaOMe (108 mg, 2.0 mmol) and Mn(NO$_3$)$_2$ x H$_2$O (275 mg, 1.0 mmol) in EtOH (5 mL) was evaporated for 30 min, the barriers were compressed at 6 mm Hg, and dried in vacuo. The precipitate was dissolved in CHCl$_3$ (12 cm) by washing first with CH$_2$Cl$_2$ (8 cm) and precipitation with EtOH (5 mL) under stirring. M.p. 198 °C (decomp.). IR (CHCl$_3$): 1856 (v$_{C-N}$), 1524 cm$^{-1}$ (v$_{C=C}$), 1286 nm (28400 M$^{-1}$ cm$^{-1}$), 286 nm (27400 M$^{-1}$ cm$^{-1}$), 321 nm (18800 M$^{-1}$ cm$^{-1}$), 380 nm (18000 M$^{-1}$ cm$^{-1}$), 481 nm (1750 M$^{-1}$ cm$^{-1}$), 606 nm (290 M$^{-1}$ cm$^{-1}$). HR-MS (ESI): Calculated for C$_{14}$H$_{22}$MnNO$_4$ [M–NO$_3$]$^+$ m/z = 607.3051, found m/z = 607.3058. Anal. found (calcd) for C$_{14}$H$_{22}$MnNO$_4$: C 47.67 (47.39); H 7.14 (7.22); N 10.36 (10.46).

Synthesis of complex 3a

According to the procedure used for 3a, complex 3b was obtained from triethylenetetramine (146 mg, 1.0 mmol) in EtOH (5 mL), NaOMe (108 mg, 2.0 mmol) and Mn(NO$_3$)$_2$ x 4H$_2$O (251 mg, 1.0 mmol) in EtOH (5 mL) as a green solid (0.34 g, 41%). M.p. 176 °C (decomp.). IR (CHCl$_3$): 1593 (v$_{C-N}$), 1523 cm$^{-1}$ (v$_{C=C}$). UV-vis (CH$_2$Cl$_2$): $\lambda_{max}$ (e) = 252 nm (33700 M$^{-1}$ cm$^{-1}$), 286 nm (27900 M$^{-1}$ cm$^{-1}$), 321 nm (19200 M$^{-1}$ cm$^{-1}$), 380 nm (15800 M$^{-1}$ cm$^{-1}$), 479 nm (1637 M$^{-1}$ cm$^{-1}$), 606 nm (378 M$^{-1}$ cm$^{-1}$). HR-MS (ESI): Calculated for C$_{14}$H$_{22}$MnNO$_4$ [M–NO$_3$]$^+$ m/z = 775.4928, found m/z = 775.4917. Anal. found (calcd) for C$_{14}$H$_{22}$MnNO$_4$: C 63.12 (63.06); H 8.69 (8.66); N 8.19 (8.36).

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(NO$_3$)$_2$ x H$_2$O (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 CHCl$_3$ (5 mL) and purified on a short pad of Al$_2$O$_3$ (12 cm) by consecutive elution with CHCl$_3$ (60 mL) and EtOH/THF 2:1 (150 mL). After evaporation of the EtOH/THF fraction, the product was redissolved in CHCl$_3$ (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 CH$_2$Cl$_2$ (10 mL) and precipitation with Et$_2$O (70 mL) under stirring. M.p. 198 °C (decomp.). IR (CHCl$_3$): 1856 (v$_{C-N}$), 1524 cm$^{-1}$ (v$_{C=C}$), UV-vis (CH$_2$Cl$_2$): $\lambda_{max}$ (e) = 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): Calculated for C$_{14}$H$_{22}$MnNO$_4$ [M–NO$_3$]$^+$ m/z = 635.6812, found m/z = 635.6821. Anal. found (calcd) for C$_{14}$H$_{22}$MnNO$_4$: 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$_2$N’-bis(3-aminopropyl)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(NO$_3$)$_2$ x H$_2$O (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 (CHCl$_3$): 1604 (v$_{C-N}$), 1538 cm$^{-1}$ (v$_{C=C}$), UV-vis (CH$_2$Cl$_2$): $\lambda_{max}$ (e) = 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): Calculated for C$_{15}$H$_{24}$MnNO$_4$ [M–NO$_3$]$^+$ m/z = 635.3369, found m/z = 635.3362. Anal. found (calcd) for C$_{15}$H$_{24}$MnNO$_4$: 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$_2$N’-bis(3-aminopropyl)ethylenediamine (185 mg, 1.0 mmol) in EtOH (5 mL), NaOMe (108 mg, 2.0 mmol), and Mn(NO$_3$)$_2$ x H$_2$O (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
Synthesis of complex 4c

According to procedure 4a the crude title product was obtained from \( N, N'-\text{bis}(3\text{-aminopropyl})\text{ethyl} \)enediamine (185 mg, 1.0 mmol) in EtOH (5 mL) and filtered over Celite. The filtrate was evaporated under reduced pressure, the residue was recrystallized from warm acetone to give 4c as a purple solid (30.13 g, 30%). M.p. 187 °C (decomp.). IR (CHCl3): 1607 \( \nu(C\equiv C) \times \text{cm}^{-1} \) (968, c); 1522 \( \nu(C\equiv C) \times \text{cm}^{-1} \) (1554, c); 1299 \( \nu(C\equiv C) \times \text{cm}^{-1} \) (289, m); 1129 \( \nu(C\equiv C) \times \text{cm}^{-1} \) (803.5215). Anal. found (calcd) for \( C_{67.75}H_{9.81}N_{6.44} \): C 67.35 (67.3); H 9.74 (9.7); N 6.77 (6.8). The hydrogen atoms were included in the calculations.

Synthesis of complex 5a

The procedure used for the synthesis of 3a was used, starting from \( N, N'-\text{bis}(3\text{-aminopropyl})\text{ethyl} \)enediamine (195 mg, 1.05 mmol) in EtOH (5 mL), 2a (113 mg, 2.10 mmol) in THF (5 mL), NaOMe (108 mg, 2.0 mmol) and Mn(NO3)2 \times H2O (183 mg, 1.0 mmol) in EtOH (5 mL). Purification was performed on a short pad of Al2O3 (13 cm) by consecutive elution with CHCl3 (30 mL) and THF (60 mL).

After evaporation of the THF fraction, the product was redissolved in CHCl3 (20 mL) and filtered over Celite. After evaporation of the filtrate under reduced pressure, the residue was obtained from Al2O3 (5 cm) by washing with CHCl3, THF, and finally with EtOH/THF 2:1 (50 mL). After evaporating the EtOH/THF fraction, the residue was repeatedly redissolved in CHCl3 (2 mL) and precipitated with pentane (80 mL) and EtO (3 \times 80 mL). The residue collected by centrifugation was dissolved in CHCl3 and filtered over Celite. The filtrate was evaporated in vacuo to give 5a as a purple solid (293 mg, 61%). Pure samples for magnetic measurements were prepared by slow evaporation of an acetone solution of 5c. M.p. 145 °C. IR (CHCl3): 1615 \( \nu(C\equiv C) \times \text{cm}^{-1} \) (1554, c); 1299 \( \nu(C\equiv C) \times \text{cm}^{-1} \) (285, m); 1129 \( \nu(C\equiv C) \times \text{cm}^{-1} \) (803.5242). Anal. found (calcd) for \( C_{67.75}H_{9.81}N_{6.44} \): C 67.35 (67.3); H 9.74 (9.7); N 6.77 (6.8).

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-Kα radiation (\( \lambda = 0.71073 \) Å) 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 F2 with SHELXL-97. The hydrogen atoms were included in calculated positions and treated as riding atoms using 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 (PLATON0352).

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 from N,N'-bis(3-aminopropyl)ethylenediamine (113 mg, 0.61 mmol) in EtOH (3 mL), 2b (372 mg, 1.21 mmol) in THF (5 mL), NaOMe (66 mg, 1.21 mmol) and Mn(NO3)2 \times 4H2O (155 mg, 0.61 mmol) in EtOH (3 mL). Purification was performed on a short pad of Al2O3 (7 cm) by consecutive elution with CHCl3 (100 mL) and THF (50 mL). After evaporation of the THF fraction, the residue was redissolved in acetone (2 mL), and precipitated with pentane (3 \times 80 mL). The residue was collected by centrifugation was dissolved in CH2Cl2 and filtered over Celite. The filtrate was evaporated in vacuo to give 5b as a purple solid (164 mg, 31%). M.p. 157 °C. IR (CHCl3): 1615 \( \nu(C\equiv C) \times \text{cm}^{-1} \) (1554, c); 1299 \( \nu(C\equiv C) \times \text{cm}^{-1} \) (285, m); 1129 \( \nu(C\equiv C) \times \text{cm}^{-1} \) (803.5242). Anal. found (calcd) for \( C_{67.75}H_{9.81}N_{6.44} \): C 67.35 (67.3); H 9.74 (9.7); N 6.77 (6.8).
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 Å³ was calculated containing about 202 electrons, equated to six acetone molecules (6 × 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].

Acknowledgments

We thank V. Malik and C. Bernhard (Univ Fribourg) for performing magnetic measurements. This research was supported by ERA-net Chemistry, the Swiss National Science Foundation, and the Alfred Werner Foundation.

Notes and references

1 Department of Chemistry, University of Fribourg, Chemin du Musée 9, CH-1700 Fribourg, Switzerland.
2 School of Chemistry & Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland. Fax: +353 1716 2501; Tel: +353 1716 2504; E-mail: martin.albrecht@ucd.ie.
3 XRD Application Lab, CSEM, Rue Jaquet-Droz 1, CH-2002 Neuchâtel, Switzerland.
4 Electronic Supplementary Information (ESI) available: Synthesis of compounds 2a–c, magnetic measurements of 3a and 3c. Langmuir studies (stability plots and multilayering into LB films), and crystallographic details for complexes 3a, 4a, and 5a in CIF format. See DOI: 10.1039/b000000x/


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 \( \mu_{eff} = 4.4 \mu_B \) at 300 K. Y. Bodenthin, G. Schwarz, Z. Tornkowicz, T. Geue, W. Haase, U. Pietsch and D. G. Kurth, *J. Am. Chem. Soc.*, 2009, 131, 2934.

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 1, viz. [Mn3(3-Ome-sal-trien)]NO3, which do not show any weight loss up to 80 °C.


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 should 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

C. Gandolfi, T. Cotting, P. N. Martinho, O. Sereda, A. Neels, G. G. Morgan, M. Albrecht*

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