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FULL PAPER

A Facile Synthetic Route to a Family of Mn(III) Monomers and their Structural, Magnetic and Spectroscopic Studies


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Abstract: We report a rapid and facile synthetic route to the synthesis of a family of Mn(III) monomers of general formula \([\text{Mn(III)F}_2(\text{H}_2\text{O})(\text{L}_x))\cdot \text{xH}_2\text{O} \cdot y\text{MeOH} (\text{where } \text{L}_x = 2,2'\text{-Bipyridyl, } x = 2,\ y = 0 (1); \text{L}_y = 1,10'\text{-Phenanthroline, } x = y = 0 (2); \text{L}_z = 6\text{-Methyl-2,2'-dipyridyl, } x = y = 0 (3); \text{L}_u = 4,4\text{-Dimethyl-2,2'-dipyridyl, } x = 2,\ y = 0 (4); \text{L}_v = 5,5'\text{-Dimethyl-2,2'-dipyridyl, } x = 0,\ y = 0.5 (5) \text{ and } \text{L}_w = 5\text{-Chloro-1,10-phenanthroline, } x = y = 0 (6).)\) Magnetic susceptibility and magnetisation experiments have been employed to elucidate the anisotropic \(\Omega\) tensor for each family member (ranging from \(-3.01\) cm\(^{-1}\) to \(-4.02\) cm\(^{-1}\)) in 5), while multi-frequency / high-field EPR spectroscopic measurements and subsequent simulations gave similar values for complexes 1\(^{'}\) (\(-4.25\) cm\(^{-1}\)), 2\(^{'}\) (\(-4.03\) cm\(^{-1}\)), 4 (\(-3.90\) cm\(^{-1}\)) and 5 (\(-4.04\) cm\(^{-1}\)). The terminal Mn-F vibrational stretches in 1\(^{'}\)-6 have been probed using Raman spectroscopy.

Introduction

Commercially available sources of the Mn(III) ion are relatively scarce and this has connotations for synthetic chemists working in many facets of research.[5] For instance, Mn(III) species are common catalytic reagents[2] in various organic transformations centred on oxidative radical cyclizations[5] while manganese complexes have been extensively studied as model compounds displaying slow relaxation of the magnetisation and magnetic bistability.[5] Synthetic chemists in this field predominantly rely on the redox manipulation of Mn(II), Mn(IV) and Mn(VII) precursors to produce Mn(III) rich polymetallic cages.[9] An alternative, and rather attractive, strategy would be to synthesise new monometallic Mn(III) complexes.

The strategic incorporation of F-bridges within paramagnetic 3d cations also holds significance in the fields of molecular magnetism and is perhaps best highlighted by the extensive work of Wippen and co-workers who have developed high yielding synthetic routes to numerous F- bridged Cr(III) complexes, including elegant, extended families of homo- (i.e. [CrF\(_4\)][10] [CrF\(_3\)][11] and [CrF\(_2\)][12]) and heterometallic ([Cr(III)-M\(_{1}\); M = Ni(II), Co(II), Fe(II), Mn(II), Cd(II)])[13] wheels and horseshoes.[14] Examples of F-bridged 3d-4f assemblies were recently presented by Bendix and co-workers when discussing the targeted formation of a family of [Gd(III)\(_2\)M(III)\(_3\)] molecular magnetic refrigerants (where M = Cr, Fe, Ga from CrF\(_3\), FeF\(_3\) and GaF\(_3\); 3H\(_2\)O precursors, respectively).[15] With these thoughts in mind, two such examples in the literature caught our eye in the form of the monometallic complexes [Mn(III)F\(_2\)(H\(_2\)O)(L)] \cdot xH\(_2\)O (L\(_x\) = 2,2'-Bipyridine, x = 0 (1) or L\(_z\) = 1,10'-Phenanthroline, x = 1 (2)). These molecules were first synthesised as powders by Chaudhuri et al.[16] and subsequently characterised crystallographically by the Nägele[17] (1) and Rajasekharan[18] (2) groups, respectively. Synthesis of these complexes involved the careful handling of toxic 48% HF solutions, requiring manipulation in well-ventilated areas. Drawing on our previous experience using anhydrous MnF\(_3\) as a precursor to larger polymeric architectures,[19] we herein report its utilisation in the synthesis of 1\(^{'}\)\(2\text{H}_2\text{O} (\text{the hydrated analogue of 1) and } 2\text{'} \text{ (the dehydrated analogue of 2), using a facile reaction route which may be performed in just 5 minutes (Fig. 1). We also demonstrate the robust nature of this synthetic route by describing the formation of their siblings: [MnF\(_3\)(H\(_2\)O)(L)] (3), [MnF\(_3\)(H\(_2\)O)(L)]\cdot 2\text{H}_2\text{O} (4), [MnF\(_3\)(H\(_2\)O)(L)]\cdot 0.5\text{MeOH} (5) and
Results and Discussion

The monometallic complexes shown in Figures 1 and 2 were synthesised by heating a methanolic solution of Mn(III)F₂ and the appropriate 1,2-diimine ligand (Lₓ) at 50°C until a dark red / black colour had formed. Such heating is required to break down and dissolve the extended network structure of MnF₃. Red / orange crystalline solids of 1'-6 subsequently precipitated slowly from the mother liquor, although slow Et₂O diffusion also facilitates X-ray diffraction quality single crystal growth of all complexes. The structures of 1'-6 each comprise a single Jahn-Teller elongated distorted octahedral Mn(III) centre, chelated by a single heterocyclic 1,2-dilime ligand ‘Lₓ’, while three terminal F⁻ ions and a H₂O ligand complete their coordination geometries. The axial distortions in these systems are consistently observed in the form of elongated Mn₁-N₁ and Mn₁-O₁ bonds with distances ranging between 2.146 and 2.309 Å, while the shorter terminal Mn-F bonds range from 1.805 to 1.884 Å (Table 1). The remaining Mn₁-N₂ bond distances range from 2.060 (in 3) to 2.129 Å (in 4). Full crystallographic data on all complexes can be found in Tables 2 and 3.

![Crystal structures of complexes 3-6 (a-d), respectively.](image)

The discrete moieties in 1'-3 each pack within their unit cells in a similar manner (Figure 3). The [MnF₃(H₂O)(Lₓ)] units in each case arrange in superimposable stacks along the b direction of their cells. These individual columns of monomeric units arrange along their ac planes in an interdigitated fashion with respect to their adjacent rows, forming close contacts primarily in the form of strong H-bonding interactions between the terminal F⁻ ligands and protons of juxtaposed terminal H₂O ligands (e.g. F₁-H₁₂(O1') = 1.832 Å in 1'; F₁-H₁'B(O1') = 1.878 Å in 2').

![Packing arrays observed in 1' (a), 2' (b) and 3 (c) as viewed along the a direction of their unit cells. All hydrogen atoms and solvents of crystallisation in 1' have been omitted for clarity. Colour code as used elsewhere in manuscript.](image)

The {Mn} moieties in 4 are linked via multiple hydrogen bonding interactions concerning metal bound F⁻ ligands with nearby H₂O solvents of crystallisation (as in 1) and not with ligated H₂O moieties as observed in 2' and 3 (see Table S1 for details). Offset Tegondoid·Tegondoid arrangements are also forged along the a direction of the unit cell in 4 and are separated at a distance of 3.678 Å ([C1'-N1']-[C7'-N2']) (Fig. S1). The packing arrangements in 5 and 6 share similarities in that they both comprise superimposable columns of {Mn} units along the b and a cell directions, respectively. More specifically these monomers arrange in brickwork sheets (propagating along the ab planes in 5 and ac plane in 6) which are held in place by interdigitated offset Tegondoid·Tegondoid close contacts at distances of 3.886 Å in 5 ([C7'-N2']-[C7'-N2']) and 3.681 Å in 6 ([C1'-N1']-[C1'-N1']). These 2D sheets align in parallel motifs across the ac plane in 5 and along the bc plane in 6 and are held in position via numerous H-
bonding interactions between terminal $F^-$ ions and ligated water protons of juxtaposed monomers (e.g. $F_1^-$:H$^+$O(1) = 1.758 Å in 5 and $F_1^-$:H$^+$A(1) = 1.766 Å in 6). Moreover, Cl–F dipole-dipole interactions also influence the overall packing in 6 (F3 ̅–Cl1 = 2.874 Å) and leads to the slight packing differences observed between the two complexes (Fig. S1).

Table 1. Angles and distances concerning the J–T elongation axes in 1–6.

<table>
<thead>
<tr>
<th>Complex</th>
<th>J-T elongation distance (Å) (Mn-N and Mn-OH)</th>
<th>J-T elongation angle (°) (Mn-N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[MnF$_3$(H$_2$O)(L)$_3$]·2H$_2$O (1)</td>
<td>2.220(2); 2.176(2)</td>
<td>168.95</td>
</tr>
<tr>
<td>[MnF$_3$(H$_2$O)(L)$_2$] (2)</td>
<td>2.261(2); 2.166(2)</td>
<td>166.99</td>
</tr>
<tr>
<td>[MnF$_3$(H$_2$O)(L)$_3$] (3)</td>
<td>2.309(2); 2.194(2)</td>
<td>164.92</td>
</tr>
<tr>
<td>[MnF$_3$(H$_2$O)(L)$_3$]·2H$_2$O (4)</td>
<td>2.216(8); 2.146(7)</td>
<td>166.67</td>
</tr>
<tr>
<td>[MnF$_3$(H$_2$O)(L)$_3$]·0.5MeOH (5)</td>
<td>2.246(3); 2.171(3)</td>
<td>168.60</td>
</tr>
<tr>
<td>[MnF$_3$(H$_2$O)(L)$_4$] (6)</td>
<td>2.260(7); 2.153(7)</td>
<td>172.65</td>
</tr>
</tbody>
</table>

Table 2 X-ray crystallographic data obtained from complexes 1'–4.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Formula</th>
<th>Mn$_x$</th>
<th>Crystal System</th>
<th>Space group</th>
<th>a Å</th>
<th>b Å</th>
<th>c Å</th>
<th>α°</th>
<th>β°</th>
<th>γ°</th>
<th>Volume (Å$^3$)</th>
<th>Z</th>
<th>T/K</th>
<th>χ$^2$/A$^2$</th>
<th>Meas./indep.</th>
<th>Crystallographic data obtained from complexes 5 and 6.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1'2H$_2$O</td>
<td>C$<em>{12}$H$</em>{14}$N$_2$O$_5$F$_2$Mn$_1$</td>
<td>322.17</td>
<td>Monoclinic</td>
<td>Pbca</td>
<td>9.0453(2)</td>
<td>8.3759(17)</td>
<td>8.3482(4)</td>
<td>6.8782(5)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>73.723(15)</td>
<td>1.548</td>
<td>1.822</td>
<td>1.5</td>
<td>2573/2226 (0.03233)</td>
</tr>
<tr>
<td>2'</td>
<td>C$<em>{12}$H$</em>{14}$N$_2$O$_5$F$_2$Mn$_1$</td>
<td>310.16</td>
<td>Monoclinic</td>
<td>Pbca</td>
<td>7.4042(3)</td>
<td>7.2941(15)</td>
<td>7.4997(3)</td>
<td>10.3111(14)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>73.723(15)</td>
<td>1.548</td>
<td>1.822</td>
<td>1.5</td>
<td>2573/2226 (0.03233)</td>
</tr>
<tr>
<td>3'</td>
<td>C$<em>{12}$H$</em>{14}$N$_2$O$_5$F$_2$Mn$_1$</td>
<td>300.17</td>
<td>Triclinic</td>
<td>P1</td>
<td>19.4455(4)</td>
<td>19.268(4)</td>
<td>18.7579(10)</td>
<td>10.6165(19)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>85.570(9)</td>
<td>0.969</td>
<td>1.295</td>
<td>0.5</td>
<td>2297/1224 (0.2124)</td>
</tr>
<tr>
<td>4'2H$_2$O</td>
<td>C$<em>{12}$H$</em>{14}$N$_2$O$_5$F$_2$Mn$_1$</td>
<td>346.19</td>
<td>Monoclinic</td>
<td>Pbca</td>
<td>9.0453(2)</td>
<td>8.3759(17)</td>
<td>8.3482(4)</td>
<td>6.8782(5)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>73.723(15)</td>
<td>1.548</td>
<td>1.822</td>
<td>1.5</td>
<td>2573/2226 (0.03233)</td>
</tr>
</tbody>
</table>

Table 3. X-ray crystallographic data obtained from complexes 5 and 6.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Formula</th>
<th>Mn$_x$</th>
<th>Crystal System</th>
<th>Space group</th>
<th>a Å</th>
<th>b Å</th>
<th>c Å</th>
<th>α°</th>
<th>β°</th>
<th>γ°</th>
<th>Volume (Å$^3$)</th>
<th>Z</th>
<th>T/K</th>
<th>χ$^2$/A$^2$</th>
<th>Meas./indep.</th>
<th>Crystallographic data obtained from complexes 5 and 6.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5'[0.5MeOH</td>
<td>C$<em>{12}$H$</em>{14}$N$_2$O$_5$F$_2$Mn$_1$</td>
<td>328.70</td>
<td>Monoclinic</td>
<td>Pbca</td>
<td>16.429(7)</td>
<td>7.315(5)</td>
<td>7.6236(4)</td>
<td>16.5375(14)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>1.548</td>
<td>1.822</td>
<td>1.5</td>
<td>2297/1224 (0.2124)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>C$<em>{12}$H$</em>{14}$N$_2$O$_5$F$_2$Mn$_1$</td>
<td>344.60</td>
<td>Orthorhombic</td>
<td>Pbca</td>
<td>23.0374(14)</td>
<td>20.773(2)</td>
<td>0.71073</td>
<td>0.71073</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>73.723(15)</td>
<td>1.548</td>
<td>1.822</td>
<td>1.5</td>
<td>2297/1224 (0.2124)</td>
</tr>
</tbody>
</table>

Magnetic susceptibility measurements

Dc magnetic susceptibility measurements were performed on powdered microcrystalline samples of 1–6 in an applied magnetic field of 0.1 T and in the temperature range 300 to 5 K. The results are plotted as the χM/T products versus T in the...
insets of Figure 4 and Figures S3 and S4. The high temperature $\chi_M T$ values obtained range from 2.84 (in 2') to 3.29 (in 3) cm$^3$ K mol$^{-1}$ and are very close to that expected (3.00 cm$^3$ K mol$^{-1}$ for $g = 2.00$) for a single, high-spin, $d^4$ Mn(III) ion. The values decrease gradually before dropping more rapidly at lower temperatures ($\sim$10 K). This behaviour can be assigned to the combination of extensive [and rather complicated] intermolecular interactions observed in the crystal structures of 1'-6 and zero-field splitting effects. The $T = 5$ K $\chi_M T$ products all lie in the range 1.94 (2') to 2.57 (5) cm$^3$ K mol$^{-1}$, somewhat lower than that expected from an isolated, isotropic $S = 2$ ion (3.00 cm$^3$ K mol$^{-1}$, $g = 2.00$). In order to determine the single-ion axial anisotropy parameter for the Mn(III) centres in 1'-6 variable-temperature-variable-field dc magnetisation ($M$) experiments were performed in the 2.0–7.0 K temperature and magnetic field ranges. The experimental data are presented in Figures 4, S3 and S4. The data were numerically fitted by use of the simplex algorithm[200] to the spin-Hamiltonian below, by numerical diagonalisation of the full spin-Hamiltonian matrix.

$$
\hat{H} = \sum_{i=1}^{2} \{ \mu_B \vec{B} \cdot \vec{S}_i + D [ \vec{S}_{z,i}^2 - \frac{1}{2} S_i (S_i + 1) / 3 ] \}
$$

Here, $D$ is the uniaxial anisotropy and $S_{\text{Mn(III)}} = 2$ the total spin of the Mn(III) ion. The best fit $D_{\text{Mn(III)}}$ parameters were (-3.97 (1'), -3.01 (2'), -3.10 (3), -3.90 (4), -4.02 (5) and -3.97 (6) (Table 3). These ZFS parameters were then employed to fit the corresponding magnetic susceptibility data, which also required use of a mean field term ($x \mu_B$) affording values of -0.55 K (1'), -1.33 K (2'), -1.00 K (3), -0.25 K (4), +0.07 K (5), -1.11 K (6).

Figure 4. Plots of magnetisation ($M / \mu_B$) versus Field ($H / G$) and (insets) magnetic susceptibility ($\chi_M T / \text{cm}^3 \text{K} \text{mol}^{-1}$) versus temperature ($T / K$) obtained from polycrystalline samples of 1' (top) and 2' (bottom). The solid lines represent the best-fit to the data. See main text and Table 4 for details.

**MF / HF-EPR Spectroscopy**

The magnitude of the $D$ tensor obtained for 1'-6 each lie on the upper limit of standard W-band spectrometers and so multi-frequency / high field EPR was employed here. Powdered and pelleted samples of 1', 2', 4 and 5 were measured at several frequencies ranging from 220 GHz to 575 GHz and at both 15 and 5 K (Figures 5-7 and S5-S8). In all spectra, a signal at $g = 2$ (7.9 T for 220.8 GHz and 11.8 T at 331.2 GHz) is observed with an increasing intensity as the temperature is increased and is tentatively assigned to a Mn(II) impurity. For all frequencies, several signals are recorded whose intensities change markedly with temperature. All spectra exhibit complicated fine structure, as expected for complexes with uniaxial anisotropies of several wavenumbers, which forbid any simple preliminary analysis. Satisfactory simulations of the spectra were obtained for all four complexes giving rise to the following sets of parameters: $D = -4.25(3)$ cm$^{-1}$, $E = 0.49(3)$ cm$^{-1}$, $g_x = g_y = 1.99(6)$ and $g_z = 2.00(5)$ (1'); $D = -4.03(5)$ cm$^{-1}$, $E = 0.18(2)$ cm$^{-1}$, $g_x = g_y = 1.96(5)$ and $g_z = 1.98(4)$ (2'); $D = -3.90(3)$ cm$^{-1}$, $E = 1.20(2)$ cm$^{-1}$, $g_x = g_y = 1.98(6)$ and $g_z = 2.00(5)$ (4) and $D = -4.04(6)$ cm$^{-1}$, $E = 0.22(3)$ cm$^{-1}$, $g_x = g_y = 2.00(7)$ and $g_z = 2.00(6)$ (5); which are comparable to those obtained from magnetisation measurements (Table 4). It should be noted here that accuracy in ascertaining $g$-values is severely hampered due to the masking effect of the large $|D|$ terms associated with each complex. As shown in Figures 5-7 (and S5-S8), the resonance positions in the experimental spectra are rather well reproduced in comparison to their corresponding simulated spectra, however their relative intensities within each spectrum are less satisfactorily reproduced. This less than ideal intensity reproduction is likely attributed to commonly observed torqueing effects; that are minimised (although not eradicated) through sample pelletisation, as is the case in this work.
For all complexes, the z component of their $M = -2 \rightarrow -1$ transition are observed in the spectra recorded at the highest frequencies; corresponding to an intense feature close to 3.5 T (at 460 GHz) and 7.5 T (at 575 GHz) at 5 K, whose intensity decreases when the temperature is increased. Similarly, at 220.8 GHz, the x and y components of the $M = -2 \rightarrow -1$ transition are clearly observed in the high field part of the spectra, with the same temperature behaviour. More specifically, the y component appears close to 13.5 T for complexes 1', 2' and 5 (Fig. 5 and S7) and at 9.3 T for the more rhombic complex 4 (Fig. 7). The x component is observed only for complexes 2' and 5 at 15.5 and 15.3 T respectively. For complexes 1' and 4 this resonance is expected at fields lying outside the range of our superconducting magnet (> 16 T). For all complexes except 2' (where the S/N does not allow confident assignment), signals associated with the $M = -1 \rightarrow 0$ transition are also observed, especially in the spectra recorded at 331.2 GHz. The z component is found at 8.7 T (1' and 5) or 9.2 T (4), while the x component resonated close to 12 T for both 1' and 5 and at 14.6 T for 4. The corresponding y component signals are observed at 9.3 T (1'), 8.8 T (4) and 10.4 T (5). The other recurrent features associated with allowed transitions are the x and y components of the $M = 0 \rightarrow +1$ transition. For instance at 460 GHz, the x component is found at 13.0 T (1'), 13.7 T (2'), 12.6 T (4) and 13.2 T (5), whereas the y component is found at 13.6 T (1' and 5), 13.9 T (2') and 14.1 T (4). As shown in Figures 6, 7 and S7, the close to zero field signal observed in the 331.2 GHz spectra of 1', 2' and 5 are assigned to the z component of the 'forbidden' transition $M_{ZFS} = +2 \rightarrow -1$ (using the ZFS labelling of the energy levels). Such a signal is absent for complex 4, where a quasi-rhombic (|$E/D$| ~ 0.31) energy diagram holds.
### Table 4. Anisotropic magnetic parameters obtained from 1-6 using magnetisation versus field (M vs H) and MF / HF-EPR measurements.

*Key:* - = not measured.

<table>
<thead>
<tr>
<th>Complex</th>
<th>g-value</th>
<th>D (cm⁻¹)</th>
<th>gₓ</th>
<th>gᵧ</th>
<th>gₜ</th>
<th>D (cm⁻¹)</th>
<th>E (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[MnF₃(H₂O)(L₁)]·2H₂O (1')</td>
<td>2.0</td>
<td>-3.97</td>
<td>1.99(6)</td>
<td>1.99(6)</td>
<td>2.00(5)</td>
<td>-4.25(3)</td>
<td>0.49(3)</td>
</tr>
<tr>
<td>[MnF₃(H₂O)(L₂)] (2')</td>
<td>2.0</td>
<td>-3.01</td>
<td>1.96(5)</td>
<td>1.96(5)</td>
<td>1.98(4)</td>
<td>-4.03(5)</td>
<td>0.18(2)</td>
</tr>
<tr>
<td>[MnF₃(H₂O)(L₃)] (3)</td>
<td>2.0</td>
<td>-3.10</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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<tr>
<td>[MnF₃(H₂O)(L₄)]·2H₂O (4)</td>
<td>2.0</td>
<td>-3.90</td>
<td>1.98(6)</td>
<td>1.98(6)</td>
<td>2.00(5)</td>
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<td>[MnF₃(H₂O)(L₅)]·0.5MeOH (5)</td>
<td>2.0</td>
<td>-4.02</td>
<td>2.00(7)</td>
<td>2.00(7)</td>
<td>2.00(6)</td>
<td>-4.04(6)</td>
<td>0.22(3)</td>
</tr>
<tr>
<td>[MnF₃(H₂O)(L₆)] (6)</td>
<td>2.0</td>
<td>-3.97</td>
<td>-</td>
<td>-</td>
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</tbody>
</table>
Complexes 1–6 add to a 600+ long list of reported monomeric Mn(III) complexes although only a small percentage (~5%) of these publications come with significant magnetic elucidation. For convenience, these complexes along with their various spin Hamiltonian parameters (i.e. g, D and E tensors) are given in Table S6. The spin Hamiltonian data extracted here are comparable to literature values, including the structurally related complex [Mn(III)F3(terpy)] (D = -3.82 cm⁻¹, E = 0.75 cm⁻¹, g₁ = 1.97(2), g₂ = 2.04(1) and g₃ = 1.96(1)); where terpy = 2,2'-6',2''-terpyridine (see Table S6 for more information). The simulation of complex 4 requires a significantly larger rhombohedral term (E = 1.20(2) cm⁻¹) when compared to its siblings (ranging from 0.18(2) cm⁻¹ (in 2') to 0.49(3) in 1) and may be attributed to its lower symmetry highlighted by its less pronounced axial elongation, with distances of Mn1-N1 (2.216(8)) and Mn1-O1 (2.146(7)) when compared to 1' (Mn1-N1 = 2.220(2), Mn1-O1 = 2.176(2)), 2' ((Mn1-N1 = 2.261(2), Mn1-O1 = 2.166(2)) and 5 (Mn1-N1 = 2.246(3), Mn1-O1 = 2.171(3)) (see Table 1). Another contributing factor may be the lower symmetry crystallisation of 4 (triclinic, P-1) when compared to complexes 1' and 2' (monoclinic P2₁/n and P2₁/c respectively), although it should be noted that complex 5 also crystallises in a monoclinic space group (P2₁/a).

Raman Studies

Solid state Raman spectra were obtained from 1.5% w/w dispersions in KBr solid matrixes of complexes 1–6, ligands L₁, L₄ and MnF₃ as purchased (see experimental section for details), while FT-IR spectra were also obtained from polycrystalline samples of 1–6. All data were normalised and baseline corrected using standard methods unless otherwise stated. The experimental Raman spectrum of MnF₃ deviates from the published literature values (283, 513 and 651 cm⁻¹ in ref. [22] and 530, 619 and 655 cm⁻¹ in ref. [23]). The peaks at 655 (and 651 cm⁻¹) and at 619 and 530 cm⁻¹ were tentatively attributed to Mn-F and Mn-F-Mn bridge stretching modes, respectively. When the MnF₃ / KBr matrix was prepared in this work the spectrum obtained exhibits prominent peaks at 262 (broad), 420-491 (a set of six bands), a strong peak at 574 with a shoulder at 595(sh) and a peak at 625 cm⁻¹ (Fig. S10). We attribute these differences to the hygroscopic nature of the MnF₃ starting material, leading to the formation of the MnF₃·3H₂O hydrate (of which there are two polymorphs). Indeed, peaks in the 300-400 cm⁻¹ region of our MnF₃ spectrum correspond to Mn-OH₂ stretches as observed in the literature.

The weak band at 625 cm⁻¹ is attributed to MnF₃, however since it is ~1/3⁻¹ as intense as the 574 cm⁻¹ band (which can be attributed to the terminal Mn-F stretching of the various octahedral Mn(III) species), it means that it is present in low concentration. The 491 cm⁻¹ band is assigned to the Mn-F-Mn bridge stretching mode. The Raman spectra of 1–6 corroborate these findings with each sample exhibiting peaks in these regions (i.e. 244, 481 and 582 cm⁻¹ in 1' and 276, 482, 574 cm⁻¹ in 2') (Figures 8, 9, S10 and S14). Since rigorous moisture control was not implemented during storage of the anhydrous MnF₃, we cannot be certain which octahedral species are present in the MnF₃ starting material. Acquisition of the Raman spectra of pure anhydrous MnF₃ by this KBr disc method would have required a much more arduous procedure, which was not necessary here. It was more important to look at the starting material as used during the synthesis of 1–6. Moreover, the KBr method was necessary for these darkly coloured complexes as many were burnt due to excessive absorption of excitation light; a common problem with coloured compounds during Raman analysis.

Figure 8. Raman spectra in the 320-700 cm⁻¹ region obtained from a crystalline sample of [Mn(III)F₂(H₂O)(L₁)₂·2H₂O (1') (red line), 2,2'-bipyridyl (green line) and a MnF₃·3H₂O / KBr mixture (black line).

Similarities between the Raman spectra of 1' and 2,2'-Bipyridyl (L₁) can be seen in Figures 8, S9 and S12 and pertinent bands are also tabulated in Tables S2 and S3. Castellucci and co-workers made reliable assignments of the internal Raman modes of 2,2'-bipyridyl and designated peaks at 616, 1056 and 1308 cm⁻¹ to an in-plane ring deformation, ring-ring stretching and a C-H deformation respectively, while other research groups have described similar results. These figures compare well with our experimental figures of 614, 1046 and 1301 cm⁻¹ for 2,2'-bipyridyl. Related peaks are present in the spectrum of complex 1' at 626, 1059 and 1311 cm⁻¹. Likewise, Figure 9 highlights the similarities between the Raman spectra of 2' and 1,10'-phenanthroline (L₂). More specifically, peaks at 410, 710, 1035, 1295, 1406 and 1445 cm⁻¹ are the most intense bands observed in the Raman spectrum of L₂, which correlate with literature values as shown in Table S4. These bands are due to in-plane modes (Aᵥ) and (Eᵥ).
All reagents and solvents were purchased commercially and used as supplied. Take caution when handling MnF₃ and heating solvent solutions. All manipulations were carried out in a fumehood and protective clothing was used throughout.

**General synthesis of [Mn(III)F₃(H₂O)(L₁₄)]**

Mn(III)F₃ (0.5 g, 4.46 mmol) and one equivalent of ligand ‘L’ were dissolved in 25 cm³ MeOH. The subsequent methanolic solution was warmed (with rapid stirring) on a heating mantle until the solution was simmering (~50°C). The solution was removed from the heat source using forceps as soon as a dark red colour was obtained. The resulting solution was then filtered upon cooling and X-ray quality crystals of 1'-6 were obtained upon slow evaporation of their mother liquors. Full details are available in the ESI.

**Single crystal X-ray structure determination**

The structures of 1'-6 were collected on an Xcalibur S single crystal diffractometer (Oxford Diffraction) using an enhanced Mo source. Each data reduction was carried out on the CrysAlisPro software package. The structures were solved by direct methods (SHELXS-97)[31] and refined by full matrix least squares using SHELXL-97.[32] SHELX operations were automated using the OSCAIL software package.[33] All non-hydrogen atoms were refined as anisotropic. The hydrogen atoms belonging to the bound water molecules in 1'-6 were located in the difference map. All other hydrogens were placed in calculated positions. The two waters of crystallisation in 4 were refined as anisotropic. The MeOH (labelled C13[489265] and heating C13[489270]) solvent molecule in 5 was modelled as disordered over two sites with 50:50 occupancy, while its associated proton (H2) was placed in a calculated position lying along an appropriate direction at a distance of 1.849 Å from F3. CCDC numbers: 1489265 (1') – 1489270 (6).

**MF / HF-EPR spectroscopy**

MF / HF-EPR measurements were performed on a multi-frequency spectrometer[34] operating in a double-pass configuration. A 110 GHz frequency source (Virginia Diodes Inc.) is multiplied by a doubler or a tripler to obtain 221 or 331 GHz, respectively. The 460 and 575 GHz spectra were obtained using a 115 GHz Gunn oscillator (Radiometer Physics GmbH) together with a quadrupler or a quintupler. The detection is performed with a hot electron InSb bolometer (QMC Instruments). The exciting light is propagated with a Quasi-Optical set-up (Thomas Keating) outside the cryostat and with the help of a corrugated waveguide inside it. The main magnetic field is supplied by a 16 T superconducting magnet associated to a VTI (Cryogenic). The measurements were done on...
powdered samples pressed into pellets in order to limit torqueing effects. Calculated spectra were obtained with the SIM program\textsuperscript{36} from H. Weihe (Univ. of Copenhagen).

Other measurements

Elemental analyses were carried out at the School of Chemistry, NUI Galway. Magnetic susceptibility measurements were obtained using a Quantum Design SQUID magnetometer in an applied field of 1000 G. Diamagnetic corrections were estimated from Pascal’s constants. All measured complexes were in eicosane to avoid torqueing of the crystallites. All magnetic samples were collected as single-crystalline products and analysed using microanalysis and IR measurements prior to their magnetic assessment. If necessary, phase purity between cross-batches were validated using unit cell checks and IR measurements.

Infra-red spectra were recorded on a Perkin Elmer FT-IR Spectrum One spectrometer equipped with a Universal ATR Sampling accessory. Raman measurements were recorded at room temperature using a Raman WORKSTATION\textsuperscript{\textregistered} Analyzer with PhAT imaging probe (Kaiser Optical Systems, Inc.) with 785 nm excitation. An exposure time of 10 × 8 seconds was used and spectra were collected from 250 to 4000 cm\textsuperscript{-1} (at a resolution of 5 cm\textsuperscript{-1}). Raman spectra of the coloured complexes 1\textsuperscript{\texttextdegree} - 6 were collected from a solid dispersion (approximately 1.5% weight of complex) in dry KBr which was pressed into a disk using a hydraulic press and a 13 mm die set. This was done to minimise sample burning due to excessive absorption of excitation light. All data were normalised to the peak of maximum intensity and baseline corrected using standard methods.

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Keywords: Molecular Magnetism • Electron Paramagnetic Resonance • Zero-field splitting • Mn(III)F\textsubscript{3} • D-tensor.

[1] Commercially available salts include Mn(acac)\textsubscript{3} (where acac = acetylacetonate), Mn\textsubscript{2}O\textsubscript{3} and Mn(OAc)\textsubscript{2}•2H\textsubscript{2}O (although in reality the latter has the trinuclear formula [MnIII]\textsubscript{3}O(OAc)\textsubscript{6}(solvent))3(OAc)\textsubscript{3}.


We report a rapid and facile synthetic route to the synthesis of a family of Mn(III) monomers of general formula \([\text{Mn(III)}\text{F}_3\text{(H}_2\text{O})(\text{L}_{1-6})]\). Magnetic susceptibility and magnetisation experiments along with multi-frequency / high-field EPR were employed to elucidate anisotropic \(D\) tensors. The terminal Mn-F vibrational stretches have been probed using Raman spectroscopy.

**Full Paper**

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A Facile Synthetic Route to a Family of Mn(III) Monomers and their Structural, Magnetic and Spectroscopic Studies