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Double-stranded, [4 + 4] helicates of Fe(II) and Mn(II) supported by an extended dipyrrolide ligand†

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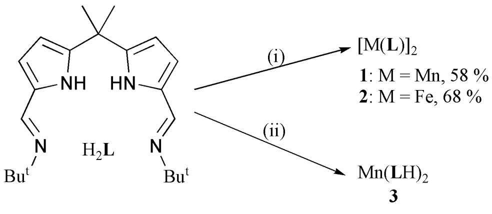
Transamination reactions between Mn and Fe amides and the diiminodipyrromethane H_2L result in the spontaneous formation of volatile, double-stranded helicates that exhibit distinct major and minor grooves.

With obvious parallels to the structure of DNA, metal complexes that spontaneously adopt helical structures have a long held fascination.[1,2] Helicates based on imine ligands are particularly prevalent, the ligands themselves being synthetically versatile and inexpensive,[3] and many supramolecular principles in helicate formation have been elucidated by studying these compounds. We are interested in the controlled formation of bi- and multimetallic compounds, and have shown that Group 1 complexes of donor-elaborated dipyrromethanes (*e.g.* H_2**L**) adopt intricate structures in which pyrrole–imine chelation is preferred over pyrrole–pyrrole chelation due to ligand twisting at the *meso*-carbon.[4] It was therefore clear that H_2**L** can potentially act as a dinucleating ligand for transition metals, and that the *meso*-twist may encourage helicate formation. Significantly, linked-dipyrro*methenes*[5] and also iminopyrroles[6] have been shown to promote helicate formation. Furthermore, diiminodipyrroles derived from chelating diamines form bimetallic helicates that can structurally reorganise in order to activate O_2.[7] Here, we report the synthesis and structures of Mn and Fe complexes of **L** and provide insight into a possible mechanism of their formation.

Reaction between H_2**L** and equimolar quantities of the diamides $M(THF)_n[N(SiMe_3)_2]_2$ (M = Mn, Fe) in toluene results in the spontaneous formation of the moderately air stable, 1 : 1 complexes $[M(\mathbf{L})]_2$ in good yields with concurrent elimination of $HN(SiMe_3)_2$ (Scheme 1).† In the case of M = Mn, elevated temperatures were required to ensure complete reaction (see later). While combustion analyses are consistent with 1 : 1 empirical formulae, mass spectrometry indicates that these compounds are dimeric in the solid state, and that surprisingly little fragmentation occurs under electron impact conditions; the molecular ion of **2** appears at 788 amu and 100% intensity. Furthermore, the dinuclear complexes were found to sublime without degradation at *ca.* 210 °C/10^{-2} mbar, and crystalline samples of both **1** and **2** suitable for X-ray diffraction studies were grown by vacuum sublimation in sealed tubes. Compounds **1** and **2** were found to be isomorphous (space group $P\bar{1}$), and the bimetallic nature of these compounds was confirmed. In **1** (Fig. 1),‡ each manganese is 4-coordinate and adopts a distorted tetrahedral geometry in which the N2–Mn1–N6 angle is considerably more obtuse than expected. Similarly expanded 'tetrahedral' angles have been observed in 4-coordinate Mn and Fe complexes, and generally result from the use of constraining chelating ligands.[8] The two metals and ligands are juxtaposed in a ΛΛ configuration, so forming a double stranded, [4 + 4] helicate; both *P*- and *M*-isomers (resulting from a ΔΔ configuration) are observed in the unit cell and therefore it is likely that **1** exists as a racemic mixture in the bulk material.



Scheme 1 Synthesis of Mn and Fe dipyrrolide complexes: (i) $M(THF)_n[N(SiMe_3)_2]_2$, toluene, M = Mn, 80 °C; M = Fe, 25 °C; (ii) <0.5 eq. $Mn(THF)_2[N(SiMe_3)_2]_2$, 25 °C.

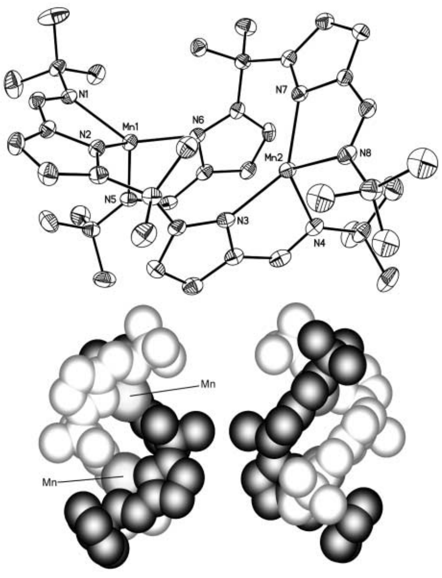


Fig. 1 Solid state structure of the double helicate, **1** (50% ellipsoids, hydrogens removed for clarity), with space-filling representations showing the major (left) and minor (right, rotated through 180°) grooves of the *P* enantiomer. Bond lengths (Å) and angles (°): Mn1–N1 2.162(2), Mn1–N2 2.086(2), Mn1–N5 2.169(2), Mn1–N6 2.086(2), Mn1 ··· Mn2 4.751, N1–Mn1–N2 81.11(9), N5–Mn1–N6 81.37(9), N2–Mn1–N6 136.59(9), N1–Mn1–N5 110.30(9).

Usually, [4 + 4] helicates have a symmetrical ligand disposition,[2] but in the case of **1**, face-to-face π-stacking between opposing iminopyrrole fragments results in the formation of distinct major and minor grooves (Fig. 1). Such control over groove formation occurs rarely in helicate synthesis,[9] and the presence of this motif may be a contributing factor towards the observed thermal stability and inertness towards O_2 of **1** and **2**.

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† Electronic supplementary information (ESI) available: full experimental for **1**, **2**, and **3**, magnetic data for **1** and **2** and crystallographic details for **2** and H_2[**L**]. See http://www.rsc.org/suppdata/dt/b3/b311093a/

Surprisingly, and in contrast to what has been previously reported for other iron helicates, **2** was also found to be inert towards CO in solution.[10] As the space filling representation of **1** shows (Fig. 1), the minor groove sterically obstructs one Mn_2 face towards potential reactive substrates, while access to the Mn_2 unit *via* the more open major groove is inhibited by the impinging *meso*-methyl groups; the interlocked Bu^t-groups also provide steric protection to the metal centres. To investigate the prospective redox reactivity of **1** and **2**, cyclic voltametry (CH_2Cl_2, Bu^n_4NCl) was carried out between −2 and +2 V, but no well defined reversible or irreversible redox behaviour was exhibited. Lack of oxidation is particularly surprising for Fe^{II}, and suggests that the necessary geometric reorganisation from tetrahedral Fe^{II} to square planar/octahedral Fe^{III} is arrested by the helical ligand arrangement.[7]

The potential of dinuclear complexes of paramagnetic metals to undergo magnetic exchange and lead to finite 1D magnetic chains[11] led us to investigate the magnetism of the helicates **1** and **2**; dc-magnetic susceptibility measurements were carried out between 5 and 300 K (1000 Oe) on powdered samples.† The observed moment for **1** of 8.22 μ_B at 300 K in the solid state is consistent with two magnetically independent, tetra-coordinate Mn^{II} centres, *i.e.* a $2 \times S = 5/2$ spin state ($\mu_{calc} = 8.37\ \mu_B$, $g = 2$). Upon cooling, antiferromagnetic coupling following Curie law behaviour is observed. Curie law behaviour is also seen for **2** between 5 and 300 K, with a $2 \times S = 2$ spin state observed at 300 K ($\mu_{exp} = 7.01$, $\mu_{calc} = 6.93\ \mu_B$). Satisfactory fits for both χ and μ were obtained using magnetic susceptibility equations for binuclear complexes, and confirm that no significant intracluster magnetic exchange occurs for either **1** ($g = 1.95$, $J = -0.23\ cm^{-1}$) or **2** ($g = 1.95$, $J = -0.26\ cm^{-1}$). This is expected, as both the long intrametal distances ($Mn \cdots Mn = 4.751$, $Fe \cdots Fe = 4.689$ Å) and the sp^3-hybridised *meso*-carbons preclude obvious superexchange pathways.

If the stoichiometry between H_2**L** and $Mn[N(SiMe_3)_2]_2$ is mismatched (6 : 1) and the reaction is conducted at 25 °C, the new, monometallic product Mn(**L**H)$_2$ **3** is formed in preference to bimetallic **1**. Yellow–brown crystals of **3** that were suitable for X-ray crystallography were grown from a cold hexane–THF mixture and were separated by hand from colourless crystals of H_2**L**;† the similarity of solubility between **3** and H_2**L** has so far precluded the satisfactory isolation of **3** in bulk. The solid state structure of **3** (Fig. 2) ‡ shows that Mn1 is symmetrically ligated by two diiminodipyrrolide ligands *via* two pyrrolic and one imino nitrogen of each ligand, so forming a distorted octahedral geometry at the metal with Δ-configuration (both Δ and Λ enantiomers are seen in the unit cell, and implies that **3** exists as a racemic mixture).

This coordination mode to Mn^{II} requires each ligand to be monodeprotonated, and as such has promoted a pyrrole–imine to azafulvalene–amine tautomerisation (Fig. 2); the hydrogen on N4 was located from the difference Fourier map. This is in direct contrast to the structure of H_2[**L**] in which the acidic hydrogens are located on the pyrrole nitrogens.† Thus, **3** represents a possible intermediate to the double helicate **1** *via* further transamination of amino N4 with a second equivalent of $Mn[N(SiMe_3)_2]_2$.

We have shown that the donor-elaborated dipyrrolide **L** can support divalent, dinuclear Mn and Fe, and that these complexes adopt double-stranded, helical structures with distinct molecular clefts. The mononuclear Mn complex **3** provides a route to the formation of dinuclear **1** *via* an eneamine tautomerisation mechanism, and represents a basis to mixed-metal helicates. We are at present investigating the reactivity of **1** and **2** towards small molecules and the synthesis of enantiomerically pure helicates by the incorporation of a chiral imine. We thank the Royal Society (JBL, University Research Fellowship), the University of Nottingham and the EPSRC for their support.

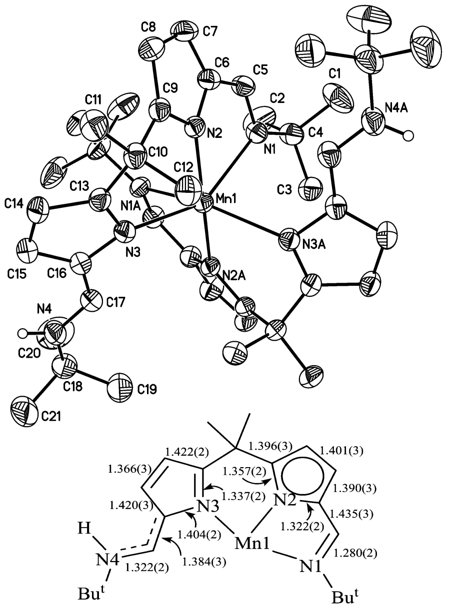

Fig. 2 Solid state structure of the bis(dipyrrolide)Mn complex, **3** (Δ enantiomer shown), and a pictorial representation of the iminopyrrolide bonding. Bond lengths (Å) and angles (°): Mn1–N1 2.4863(15), Mn1–N2 2.1390(15), Mn1–N3 2.3659(15), N1–Mn1–N2 72.46(5), N2–Mn1–N3 82.28(5), N2–Mn1–N2A 172.44(8).

Notes and references

‡ *Crystal data*: **1**: $C_{42}H_{60}Mn_2N_8$, triclinic, $a = 11.099(2)$, $b = 13.738(2)$, $c = 14.997(2)$ Å, $\alpha = 74.705(2)$, $\beta = 79.934(2)$, $\gamma = 71.465(2)$ °, $U = 2081.1(6)$ Å^3, $T = 150(2)$ K, space group $P\bar{1}$, $Z = 2$, μ(Mo-Kα) = 0.646 mm^{-1}, 17924 reflections measured, 9604 unique ($R_{int} = 0.048$) which were used in all calculations. The final $wR(F^2)$ was 0.1360 (all data). **3**: $C_{50}H_{78}MnN_8O_2$, monoclinic, $a = 17.635(2)$, $b = 14.208(2)$, $c = 21.382(2)$ Å, $\alpha = 90$, $\beta = 110.152(2)$, $\gamma = 90°$, $U = 5029.5(10)$ Å^3, $T = 150(2)$ K, space group $C2/c$, $Z = 4$, μ(Mo-Kα) = 0.307 mm^{-1}, 17490 reflections measured, 5926 unique ($R_{int} = 0.0024$) which were used in all calculations. The final $wR(F^2)$ was 0.1341 (all data). CCDC reference numbers 219487–219490. See http://www.rsc.org/suppdata/dt/b3/b311093a/ for crystallographic data in CIF or other electronic format.

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