Bioinspired manganese(II) complexes with a clickable ligand for immobilisation on a solid support†

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Clickable ligands like N,N'-bis((pyridin-2-yl)methyl)prop-2-yn-1-amine (L1) and N-((1-methyl-1H-imidazol-2-yl)methyl)-N-((pyridin-2-ylmethyl)prop-2-yn-1-amine (L2) have been used to synthesise a series of manganese(II) complexes for grafting onto appropriate solid supports. These ligands mimic the 2-His-1-carboxylate facial chelation present in the active site of the manganese-dependent dioxygenase (MndD), while the alkyne side function allows grafting of the ligand onto an azido-functionalised support using “click chemistry” methodologies. Such synthetic analogues of the MndD crystallise in the solid state as double halide or pseudohalide-bridged dinuclear manganese(II) complexes of the general formula [Mn2(µ-X)2X2L2] [L = L1 with X = Cl (1), Br (2), and N3 (3); L = L2 with X = N3 (4)]. Complexes 1–4 are characterised by a weak magnetic exchange interaction between the two high-spin MnII ions through the two X− bridges (J in the range of −0.059 to +5.30 cm−1, H = −JS>Mn1S>Mn2 with S>Mn1 = S>Mn2 = 5/2). A new magneto-structural correlation of superexchange bis(µ1,1-azido)diamanganese(II) complexes has been proposed using both structural parameters, the Mn−N−Mn bridging angle and the Mn−Nazido distance. In MeOH−EtOH solution the dimeric species are present together with few percents of mononuclear manganese(II) complexes as evidenced by electron paramagnetic resonance (EPR) spectroscopy. Grafting the complexes onto mesoporous silica of MCM-41 type stabilises both dimers and monomers in the nanopores of the solid.

Introduction

A natural evolution of bioinspired coordination chemistry is the immobilisation of metal complexes on solid supports where confinement can be created in metalloproteins.1–3 Fixation on a support allows not only achieving site isolation but also controlling site nuclearity. Indeed, for monomeric sites, oligomerisation and degradation are often observed in solution with molecular bioinspired complexes. Therefore, it is important to develop new ligands with side functions allowing reactions that are orthogonal to complexation for fixation on a solid support. One possibility is to use the Huisgen azide–alkyne [2 + 3] cycloaddition reaction referred to as “click chemistry” by Sharpless and co-workers.4 Indeed, this efficient and versatile strategy, developed mainly for the synthesis of elaborated organic molecules (such as inhibitors for pharmaceutical applications), removes constraining considerations of protection/deprotection and cross-reactivity.5,6 This synthetic strategy has been applied to graft molecules onto various substrates such as organic polymers, carbon nanotubes, oxides and metals for the design of hybrid nanocomposite materials.7–9 In the case of silica-based supports, either azide or alkyne functions are grafted onto the solid support using the suitable organosiloxane molecules before carrying out the Huisgen cycloaddition reaction. In the case of immobilisation of a metal complex, it is preferred to have the alkyne function in the ligand and the azide in the tether to avoid complexation of azide to the metal ion. This modular approach has been used for example in the grafting of Co and V complexes with Schiff base ligands, or Pt and Pd organometallic complexes to develop heterogeneous catalysts.10,11

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Electronic supplementary information (ESI) available: Crystallographic details of the complexes, crystal packing figures of 1–4, EPR simulation of 1 and N2 sorption isotherms of the porous materials. CCDC 905065, 911104–911106 for 1–4. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt53636j

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Among metalloproteins, iron and manganese oxygenases are particularly attractive because they can perform oxidation of organic substrates by activating molecular oxygen. In particular, catechol dioxygenases are ring-cleaving enzymes that oxidise catechol derivatives with a concomitant ring opening, which is a critical step in the aerobic degradation of aromatic compounds by bacteria. Therefore, these systems can be used as models to develop new materials for the degradation of aromatic chemicals. For instance, manganese-dependent dioxygenase (MndD) is known to catalyse the extradiol cleavage of catechol derivatives. The active site of this metalloprotein contains a mononuclear manganese centre coordinated to two histidines (His) and one glutamate (Glu) or one aspartate (Asp) in the facial position. This motif, called the 2-His-1-carboxylate facial triad, is observed in catechol dioxygenases as well as in other metalloproteins.

In this work a new series of manganese complexes with two different biomimetic clickable ligands $N,N'$-bis[(pyridin-2-yl)methyl]prop-2-yn-1-amine (L1) and $N$-[1-methyl-1H-imidazol-2-yl]methyl-$N'$-(pyridin-2-ylmethyl)prop-2-yn-1-amine (L2) is presented (Scheme 1). Both ligands can mimic the facial triad present in the active site of the MndD and possess an alkynie side function that allows for a efficient grafting onto a solid support using click chemistry.

We report herein the crystal structures and the magnetic properties of four novel manganese(n) complexes of formulæ $\left[\text{Mn}_2(L^1)_2\text{Cl}_2(\mu-\text{Cl})_2\right]$ (1), $\left[\text{Mn}(L^1)\text{Br}_2(\mu-\text{Br})_2\right]$ (2), $\left[\text{Mn}_2(L^2)_2(\text{N}_3)_2\right]$ (3), and $\left[\text{Mn}_2(L^2)_2(\text{N}_3)_2(\mu_1,\mu_1'-\text{N}_3)\right]$ (4). The grafting is exemplified by the reaction of 1 with mesoporous silica (MCM-41 type) modified with azide functions.

**Results and discussion**

**Synthesis of the ligands**

The ligands L1 and L2 were synthesised according to the procedures reported in the literature. In the case of L1, two different synthetic methods were explored. The first one is a two-step protocol starting with the reduction with NaBH4 of the Schiff base resulting from the condensation of 2-picolylamine with 2-pyridinecarboxaldehyde which is followed by an electrophilic substitution with propargyl bromide to obtain the desired L1 ligand.

The yield of the first step was 96% with a simple work-up whereas the purification by column chromatography on silica in the second step only yielded 11% of the product likely due to the less affinity of amino-pyrindinic sub-

**Synthesis of the Mn[n] complexes**

Complexes 1–4 were synthesized in MeOH using a stoichiometric amount of the ligand and metal salt (Scheme 3). For compounds 1 and 2 involving chloride and bromide counter-anions, respectively, the corresponding manganese salt was available and directly used for the reaction. In the case of 3 and 4, involving azide anions, manganese nitrate was reacted with the ligand and 4 equivalents of sodium azide were added to exchange the nitrate anion by the azide one. Except for 2, each compound precipitated as light brown powder in MeOH within 30 min. Those powders were then redissolved in a minimum amount of MeOH, while the solution containing 2 was used as it is. The crystals were grown using the same technique in all the cases, i.e., slow diffusion of diethyl ether in a methanolic solution of the compound to afford crystals within strates to the acidic nature of the silica. Yet this latter should not be taken as a standard reaction yield as results found in the literature show average yields around 90%.

The second method is a straightforward one-step protocol consisting of a double electrophilic substitution involving propargylamine and 2-picolyl chloride. The reaction time of 12 h was prolonged up to 5 days allowing us to retrieve L1 in a 90 to 96% yield, compared to a 32% yield for 12 h. Therefore this one-step protocol was the appropriate synthetic route to the L1 ligand (Scheme 2a).

L2 is an original ligand that has been synthesized using an adapted version of the first method, i.e., condensation of an amine and an aldehyde, namely 2-picolylamine and 1-methyl-2-imidazolecarboxaldehyde, respectively, followed by a reduction and an electrophilic substitution by propargyl bromide (Scheme 2b). The first step provided the secondary amine in 96% yield. It is interesting to note the absence of undesired by-products in the second step, in contrast to the synthesis of L1 that required purification by column chromatography. In fact, re-dissolution in CH2Cl2 and filtration through KBr provided the pure ligand L2 in 80% yield.
a couple of days. Apart from 3, all the crystals were stable in air at room temperature. Molecules of MeOH found in the structure of 3 were lost when left at room temperature, damaging the crystallinity of the solid.

**Description of the structures**

Complexes 1–4 are double halide or pseudohalide-bridged neutral dimers of Mn(II) and exhibit the same structural layout (Fig. 1). They differ in the nature of the donor groups from the organic ligand counterpart, i.e., amine and pyridines from L¹ (1–3), or amine, pyridine and imidazole from L² (4), as well as the coordinating anion composing the double bridge between the metal ions and completing the metal environment, i.e., chloride (1), bromide (2), or azide (3 and 4). Selected bond distances and angles for 1–4 are compiled in Table 1.

Within all complexes, the Mn(II) ions are located in a distorted N₃X₃ [X = Cl (1), Br (2) and N (3 and 4)] octahedral environment. In all the complexes, the Mn–N bond lengths from the tridentate ligands are similar and in good agreement with similar complexes involving a double bridge with double chloride,\(^{30-32}\) bromide\(^ {33}\) and end-on azide\(^ {34-37}\) bridges. It is important to note that the Mn–N bond length involving the central amine nitrogen atom of the ligand is usually ~0.1 Å longer than the two external ones involving the pyridine and/or imidazole nitrogen atoms. In the case of 4, involving L², one of the Mn–N bond lengths (N2) or the external nitrogen atoms of the ligand is shorter (~0.1) and the Mn–N bond length for the central (N3) one is longer (~0.1 Å) than those observed for complexes 1–3 involving L¹. The environment of the metal ions is completed by three X atoms with two of them involved in the double bridge between the two Mn(II) ions. As expected, Mn–Cl bond lengths are shorter than the Mn–Br ones. Moreover, Mn–X bond lengths within the double bridge (X = Cl1, Br1) are longer (~0.1 Å) than the terminal ones (X = Cl3, Br3).

The distortion of the octahedral environment of the metal ion is also exemplified by the distribution, far from the ideal values of 90 and 180°, of the X-Mn-X angles (X = N, Br and Cl) ranging from 69.72(5)° to 104.193(16)° and from 158.24(3)° to 163.59(4)° for 1, from 71.45(8)° to 101.689(15)° and from 159.85(5)° to 165.10(6)° for 2, from 72.86(5)° to 105.08(6)° and from 154.43(6)° to 163.57(6)° for 3, and from 69.79(4)° to 103.22(7)° and from 154.83(6)° to 161.98(5)° for 4.

In the crystal lattice of 1 and 2, structural packing is built by weak hydrogen bonding H⋯X (X = Cl and Br, respectively) interactions leading to a dense 3D network. In the case of 3, the co-crystallized methanol molecule, through the hydrogen atom of the alcoholic group, forms hydrogen bonds with the terminal nitrogen atom of the double end-on azido-bridge. Finally, for 3 and 4, the crystal packing, in both cases, is assumed to be formed by weak interactions as van der Waals interactions for example.
Magnetic properties

Fig. 2 shows the magnetic properties of 1–4 in the form of $\chi M T$ versus $T$ plots and $M$ versus $H$ plots, $\chi M$ and $M$ being the magnetic susceptibility and the magnetization per two Mn(II) ions respectively, while $T$ and $H$ are the absolute temperature and the applied magnetic field, respectively.

At room temperature, $\chi M T$ for 1 and 2 is ca. 8.75 cm$^3$ mol$^{-1}$ K. Whereas this value is expected for two magnetically isolated high-spin Mn$^{2+}$ ions ($S_{\text{Mn}} = 5/2$), the corresponding values for 3 and 4 are somewhat greater (ca. 9.5 cm$^3$ mol$^{-1}$ K). Upon cooling, $\chi M T$ for 1 remains constant until 25.0 K and it further decreases to 7.70 cm$^3$ mol$^{-1}$ K at 2.0 K, suggesting the occurrence of a very weak antiferromagnetic interaction. In contrast, $\chi M T$ for 2–4 continuously increases with the decrease of the temperature to reach maxima at 5.5 K (ca. 11.3 cm$^3$ mol$^{-1}$ K) for 2 and at 10 K (ca. 14.8 cm$^3$ mol$^{-1}$ K) for 3 and 4. After these maxima, $\chi M T$ decreases to 7.5 (2), 13.7 (3) and 13.9 cm$^3$ mol$^{-1}$ K (4) at 2.0 K. The increase of $\chi M T$ in the high temperature region for 2–4 is indicative of the occurrence of a ferromagnetic interaction between the paramagnetic Mn(II) ions, whereas the decrease at low temperatures can be attributed to weak intermolecular antiferromagnetic interactions and/or zero-field splitting of the $S = 5$ ground spin state. However, because of the large isotropic character of the six-coordinate high-spin Mn(II) ion, the zero-field splitting effects are expected to be negligible.

Table 1 Selected bond distances (Å) and angles (°)

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(1)–N(1)</td>
<td>2.280(4)</td>
<td>2.264(2)</td>
<td>2.255(2)</td>
<td>2.296(1)</td>
</tr>
<tr>
<td>Mn(1)–N(2)</td>
<td>2.272(3)</td>
<td>2.269(2)</td>
<td>2.265(2)</td>
<td>2.192(2)</td>
</tr>
<tr>
<td>Mn(1)–N(3)</td>
<td>2.388(3)</td>
<td>2.389(2)</td>
<td>2.384(2)</td>
<td>2.466(2)</td>
</tr>
<tr>
<td>Mn(1)–X(1)</td>
<td>2.515(2)</td>
<td>2.6641(5)</td>
<td>2.225(2)</td>
<td>2.231(1)</td>
</tr>
<tr>
<td>Mn(1)–X(2)</td>
<td>2.423(1)</td>
<td>2.5740(5)</td>
<td>2.153(2)</td>
<td>2.131(2)</td>
</tr>
<tr>
<td>Mn(1)–X(3)</td>
<td>2.574(1)</td>
<td>2.7333(5)</td>
<td>2.244(2)</td>
<td>2.209(1)</td>
</tr>
<tr>
<td>Mn–X(1)–Mn</td>
<td>97.52(4)</td>
<td>95.88(1)</td>
<td>104.50(6)</td>
<td>103.47(6)</td>
</tr>
</tbody>
</table>

$^a$ 1: X = Cl; 2: X = Br; 3 and 4: X = N3.
The expression of the magnetic susceptibility for a dimanganese(II) unit derived from the Van Vleck’s equation (the spin Hamiltonian being defined as \( H = -J S_{\text{Mn1}} S_{\text{Mn2}} \)) is given by eqn (1),

\[
\chi_M = \frac{2N g^2 \beta^2}{k(T - \theta)} (e^x + 5e^{3x} + 14e^{6x} + 30e^{10x} + 55e^{15x})
\]

where \( x = J/kT \) and \( \theta \) is the Weiss constant defined as \( \theta = z f^2 S(S + 1)/3k \) with \( z f \) accounting for the magnetic interaction between the \( z \) nearest dinuclear units. The other parameters have their usual meaning. The best-fit parameters obtained are listed in Table 2.

As indicated above, the decrease of \( \chi_M T \) at low temperatures for 2–4 could be alternatively interpreted by the presence of a zero-field splitting (\( D \)). Having this possibility in mind, the magnetic data for 2–4 were also analysed through the Hamiltonian of eqn (2) using VPMAG.

\[
H = -J S_{\text{Mn1}} S_{\text{Mn2}} + D(S_{\text{Mn1}}^2 + S_{\text{Mn2}}^2 + 35/6)
\]

The least-squares fit of the experimental data to eqn (2) gave values for the \( g \) and \( J \) parameters similar to those obtained through eqn (1) (Table 2), but the values for the \( D \) parameter [4.9 (2), 1.4 (3) and 1.1 cm\(^{-1}\) (4)] are too high to be considered real and they are meaningless. In fact, the reported \( D \) values for the high-spin d\(^5\) Mn\(^{II}\) ion in an octahedral environment are lower than 1 cm\(^{-1}\).\(^{40}\) So, the decrease of the \( \chi_M T \) values has to be mainly attributed to intermolecular antiferromagnetic interactions.

Field dependence magnetisation plots of 1–4 at 2.0 K are shown in the inset of the corresponding plot (Fig. 2). The isothermal magnetisation data for 1 are well below the Brillouin curve for two magnetically isolated \( S = 5/2 \) Mn(II) ions (with no ZFS), while they are well above for 2–4, in agreement with the occurrence of antiferro- (1) or ferromagnetic (2–4) interactions between the Mn(II) ions.

The main magneto-structural parameters for a series of [Mn\(^{II}\)(\( \mu-X \))\(_2\)Mn\(^{II}\)] \( (X = \text{Cl or Br}) \) dinuclear complexes which were the subject of previous studies are listed in Table 3. As far as we know, no theoretical magneto-structural correlation has been reported for this family of compounds. As one can see therein, no correlation seems to exist between the structural parameters (angles or distances) and the magnetic coupling parameter (\( J \)), this circumstance being most likely due to the low number of compounds, the small variation of the structural parameters and the experimental errors. However, there must exist a correlation between the nature and the magnitude of the magnetic exchange and the structural parameters, the value of the Mn–X–Mn angle being the most determinant one, as is known for other metal ions and bridging ligands.\(^{41} \)

In fact, the experimental data from Table 3 predict a change from ferro- to antiferromagnetic behaviour at an angle of ca. 97° for the bridgehead chloro atom. The value of this crossover Mn–Cl–Mn angle is very close to that observed for the bis(\( \mu \)-hydroxo)dicopper(II) complexes (ca. 97.5°).\(^{42} \)

Concerning the bis(\( \mu \)-azido)dimanganese(II) complexes (3 and 4), an experimental relationship between the magnetic coupling constant (\( J \)) and the Mn–N–Mn bridging angle (\( \theta \)), \( J \) (cm\(^{-1}\)) = 0.552\( \theta \) (deg) = 53.8, was proposed.\(^{36,43} \)

Table 4 shows the magneto-structural parameters for double end-on azido-bridged Mn(II) complexes. 3 and 4 follow roughly the above relationship and they are in good agreement with the fact that the value of the exchange coupling constant increases with the Mn–N–Mn bridging angle, which is consistent with theoretical predictions.\(^{41} \)

A careful inspection of the data listed in Table 4 shows that the values of the coupling parameter, \( J \), generally increase with an increase in the difference between the two Mn–N(bridging azide) bond distances (\( \Delta d \) in Table 4),\(^{36,43} \) which is an increase in the asymmetry of the azido bridging. In this sense, a better magneto-structural correlation is observed when we use both structural parameters (\( \theta \) and \( \Delta d \)).

Fig. 3 shows the values of \( J \) versus the corresponding values of \( \theta + 10\Delta d \) from Table 4. The best linear fit gives the equation \( J \) (cm\(^{-1}\)) = 0.553\( \theta \) (deg) + 10\( \Delta d \) (Å) = 54.111, which is slightly better than \( J \) (cm\(^{-1}\)) = 0.576\( \theta \) (deg) – 54.040, where the influence of \( \Delta d \) has been neglected.

### Table 2: Best-fit parameters for 1–4 (see the text)

<table>
<thead>
<tr>
<th>Compound</th>
<th>( g )</th>
<th>( J/\text{cm}^{-1} )</th>
<th>( zf/\text{cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.99(1)</td>
<td>-0.059(1)</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>1.99(1)</td>
<td>+1.04(2)</td>
<td>-0.20(1)</td>
</tr>
<tr>
<td>3</td>
<td>2.01(1)</td>
<td>+5.30(4)</td>
<td>-0.060(2)</td>
</tr>
<tr>
<td>4</td>
<td>2.02(1)</td>
<td>+4.99(3)</td>
<td>-0.052(2)</td>
</tr>
</tbody>
</table>

### Table 3: Selected magneto-structural parameters for bis(\( \mu-X \))dimanganese(II) complexes (\( X = \text{Cl or Br} \))

<table>
<thead>
<tr>
<th>Compound*</th>
<th>( d_{\text{Mn-Mn}}/\text{Å} )</th>
<th>( d_{\text{Mn-Cl}}/\text{Å} )</th>
<th>Mn–X–Mn(^{10})</th>
<th>( J/\text{cm}^{-1} )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mn(_2)(biz)(( \mu-\text{Cl} ))(_2)](_2)Cl(_2)</td>
<td>3.74</td>
<td>2.57</td>
<td>93.5</td>
<td>+0.66</td>
<td>32</td>
</tr>
<tr>
<td>[Mn(_2)(bpea)(_2)](( \mu-\text{Cl} ))(_2)</td>
<td>3.79</td>
<td>2.48</td>
<td>95.7</td>
<td>+0.68</td>
<td>30</td>
</tr>
<tr>
<td>[Mn(_2)(mpba)(_2)](( \mu-\text{Cl} ))(_2)</td>
<td>3.9</td>
<td>2.50</td>
<td>96.4</td>
<td>+1.1</td>
<td>31</td>
</tr>
<tr>
<td>1</td>
<td>3.82</td>
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<td>97.5</td>
<td>-0.06</td>
<td>t.w.</td>
</tr>
<tr>
<td>2</td>
<td>4.00</td>
<td>2.69</td>
<td>95.9</td>
<td>+1.04</td>
<td>t.w.</td>
</tr>
</tbody>
</table>

* Abbreviations: biz = 2,2′-biimidazolone; bpea = N,N′-bis(2-pyridylmethyl) ethylenamine; mpba = N-(3-methoxypropyl)-N,N′-bis(pyridin-2-ylmethyl) amine; L\(^1\) = see text; t.w. = this work.
EPR characterization of the complex in solution

The molecular complex 1 is conveniently dissolved in MeOH–EtOH solution. Such a solution exhibits at room temperature a 6 line EPR signal centered at $g = 2.001 \pm 0.001$, typical of Mn(II). It is assigned to the hyperfine coupling between the electronic spin ($I = 5/2$) and the nuclear manganese spin ($J = 7/2$) for the allowed transitions ($\Delta m_S = \pm 1, \Delta m_I = 0$). Upon simulation, the hyperfine coupling constant $A$ is $97 \pm 1$ G (Fig. S5†). At low temperatures, a pair of forbidden lines due to cross terms in the spin Hamiltonian lie between each of the main hyperfine lines (Fig. 4).† A quantitative study was performed with complex 1 at room temperature in order to determine the proportion of monomeric and dimeric species present in the solution. The spin concentration was measured using manganese(II) perchlorate in methanolic solution at various concentrations for calibration. Accordingly, only 1–1.5% of this dimeric complex yields EPR active monomeric species in solution at room temperature.

Grafting onto silica

The above solution was used to graft the manganese complex in the nanopores of a mesoporous silica. 2D hexagonal LUS silica (MCM-41 type) prepared using cetyltrimethylammonium tosylate as the surfactant was chosen as a support.50,51 It possesses a narrow pore size distribution of $3.8 \pm 0.1$ nm and a large mesopore volume of $0.78 \pm 0.01$ cm$^3$ g$^{-1}$. Then azide-functionalised $N_3$–(CH$_2$)$_3$–Si$\equiv$ groups were introduced into the

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### Table 4  
Selected magneto-structural parameters for bis($\mu_1$-azido)dimanganese(II) complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta d$/Å</th>
<th>$\theta$ (°)</th>
<th>$\theta + 10\Delta d$</th>
<th>$J$/cm$^{-1}$</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>[Mn$_2$(tpy)$_2$(μ$_1$-N$_3$)$_2$(N$_3$)$_2$]</td>
<td>0.236</td>
<td>103.45</td>
<td>105.81</td>
<td>4.92</td>
<td>36</td>
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<tr>
<td>[Mn$_2$(tpy)$_2$(μ$_1$-N$_3$)$_2$(N$_3$)$_2$]</td>
<td>0.252</td>
<td>103.13</td>
<td>105.65</td>
<td>4.50</td>
<td>36</td>
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<tr>
<td>[Mn$_2$(tpy)$_2$(μ$_1$-N$_3$)$_2$(N$_3$)$_2$]</td>
<td>0.150</td>
<td>105.29</td>
<td>106.79</td>
<td>3.84</td>
<td>36</td>
</tr>
<tr>
<td>[Mn$_2$(tpy)$_2$(μ$_1$-N$_3$)$_2$(N$_3$)$_2$]</td>
<td>0.090</td>
<td>104.60</td>
<td>105.50</td>
<td>4.86</td>
<td>44</td>
</tr>
</tbody>
</table>

† Average values. $\Delta d = d(Mn-N_{azido}) - d(Mn-N'_{azido})$. tp = 4'-p-Tolyl-2,2':6',2''-terpyridine, tpy-N$_3$ = 4'-p-azidomethylphenyl-2,2':6',2''-terpyridine, $L^A$ = [N,N-bis(pyridine-2-yl)benzylidene]ethane-1,2-diamine, $L^B$ = [N,N-bis(pyridine-2-yl)benzylidene]propane-1,3-diamine, $L^C$ = [N,N-bis(pyridine-2-yl)benzylidene]butane-1,4-diamine, bpbb$^+$ = 1,2-bis(pyridine-2-carboxamido)benzene, 2,2'dpa = 2,2'dipicolylamine, tptz = 2,4,6-tris(2-pyridyl)-1,3,5-triazine, pyz = pyrazine, 2-bzpy = 2-benzoylpyridine, $L^{19}$ = 2-(benzimidazol-2-yl)-N(1-pyridin-2-ylmethyl)ethanamine.
solid support using a molecular stencil patterning technique that allows an homogeneous distribution of the desired functions, which are separated by hydrophobic (CH$_3$)$_3$Si-groups. The manganese complex I was covalently grafted by using click chemistry. As an illustrative example, the azide-functionalized silica (N$_3$@SiO$_2$) was reacted with I in a MeOH–MeCN mixture in the presence of the tris-(triphenylphosphine) copper(i) bromide catalyst to obtain the hybrid material MnL$_1$@SiO$_2$, with 2.5 wt% manganese. This complex loading corresponds to ~80% yield for the click reaction. Note that the use of such a Cu(i) complex avoids the displacement of Mn(n) from the L$^1$ ligand by Cu(i) during the grafting of the complex. Indeed, there are no traces of Cu(n) that would form under aerobic conditions, according to the EPR spectrum (Fig. 4). On the other hand, the signal reveals the presence of Mn(n) as in solution. Indeed, the proportion of EPR active species remains similar to that in solution, consistent with most of the species being still dimeric. In addition, the signal is broader than in solution both at room temperature and at 116 K. Therefore, this broadening is not due to dynamic effects but due to distribution of species on the surface. This gives evidence of the heterogeneity of the environment around the grafted species as usually observed in such hybrid materials.

The hexagonal array of the internal pores of the material was unaltered all through the different steps of the synthesis, as shown from the X-ray diffraction patterns (Fig. 5). The decrease of pore volume from 0.78 cm$^3$ g$^{-1}$ down to 0.48 cm$^3$ g$^{-1}$ after grafting confirmed the presence of the metal complex inside the pores (ESI, Fig. S6†). Concomitantly, the specific surface area underwent a diminution from 990 m$^2$ g$^{-1}$ to 340 m$^2$ g$^{-1}$. This is consistent with partial pore filling due to internal molecular functionalization of the silica.

Conclusions

A series of dinuclear manganese(n) complexes with two $\mu$-X bridges (X = Cl, Br or N$_3$) has been synthesised using two different clickable ligands. These ligands allow both coordination to a metal ion and also grafting onto an azide-functionalized support using the Huisgen alkyne–azide cycloaddition reaction. Within this series we present the first $\mu$-Br bridged Mn(n) dinuclear complex for which a complete magnetic property study has been performed. It turned to be weakly ferromagnetic compared to the $\mu$-Cl analogue, which is weakly antiferromagnetic. It is also noteworthy that a better magnetostructural correlation is observed when both structural parameters ($\theta$ and $\Delta d$) are considered for the bis($\mu_1$-$\text{azido}$)dimanganese(n) complexes. Successful stabilisation of the complex mainly in its dimeric form has been achieved by grafting onto mesoporous silica. This kind of hybrid nanocomposite material, where confinement is at stake, could help by comparison to better understand the catalytic mechanism of MnD$^{16,23,56}$. The study of the catalytic properties of these silica-supported manganese(n) complexes is under progress. Alternatively, the alkyne function present in the ligand opens up other opportunities such as using these complexes as building blocks for the synthesis of metal–organic frameworks (MOFs).

Experimental

Synthesis of the ligands

$N,N'$-Bis((pyridin-2-yl)methyl)prop-2-yn-1-amine ligand (L$^1$). The synthesis was based on a published protocol. A mixture of propargylamine (1.50 g, 27.3 mmol) and potassium carbonate (22.8 g, 163.8 mmol) was stirred in 140 mL of acetonitrile for 5 min. Then 2-picolyl chloride hydrochloride (9.84 g, 60.0 mmol) dissolved in 140 mL of acetonitrile was added dropwise to a solution of 1-methyl-2-imidazolecarboxaldehyde (2.45 g, 22.7 mmol) in 25 mL of methanol. The resulting solution was stirred at reflux for 5 days. The solution was filtered and the filtrate was evaporated under reduced pressure. The resulting brown oil was dissolved in 100 mL of distilled water and extracted thrice with dichloromethane. The organic phases were gathered and dried over sodium sulphate. The solvent was finally evaporated to afford L$^1$ in 94% yield. 1H NMR (CDCl$_3$, 300 MHz): δ (ppm) 8.55 (dd, $J$ = 4.80, 1.80 Hz, 2H), 7.64 (td, $J$ = 7.50, 1.80 Hz, 2H), 7.50 (d, $J$ = 7.80 Hz, 2H), 7.15 (dd, $J$ = 7.50, 4.80 Hz, 2H), 3.91 (s, 4H), 3.41 (d, $J$ = 2.40 Hz, 2H), 2.29 (t, $J$ = 2.40 Hz, 1H). 13C NMR (300 MHz, CDCl$_3$): δ (ppm) 158.76, 149.26, 136.47, 123.14, 122.10, 78.32, 73.62, 59.44, 42.54. IR (KBr): 3294 (w), 3162 (w), 3011 (w), 2921 (w), 2839 (w), 2095 (m, C=O) cm$^{-1}$.

$N'-(1$-Methyl-1H-imidazol-2-yl)methyl)-$N-(pyridin-2-ylmethyl)-prop-2-yn-1-amine (L$^2$). This ligand was synthesized in two steps.

$N'-(1$-Methyl-1H-imidazol-2-yl)methyl)-pyrid-2-ylmethylene. To a solution of 1-methyl-2-imidazolocarboxaldehyde (2.5 g, 22.7 mmol) in 50 mL of methanol was added dropwise 2-Picolylamine (2.45 g, 22.7 mmol) in 25 mL of methanol.

Fig. 5 X-ray diffraction patterns (powder) of LUS (mesoporous SiO$_2$ support), N$_3$@SiO$_2$ and MnL$_1$@SiO$_2$ materials.
hydride (0.86 g, 22.7 mmol) was added portionwise and the solution was further stirred for two more hours at room temperature. The solvent was evaporated under reduced pressure and the orange oil thus obtained was redissolved in a mixture of water–methanol (25 mL/50 mL) before being extracted thrice with 50 mL of dichloromethane. The combined organic phases were washed with 50 mL of water and dried over sodium sulphate. The solvent was finally removed to obtain the product as an orange oil in 96% yield. 

\[\text{H}^1\text{NMR (CDCl}_3, \text{500 MHz): } \delta (\text{ppm}) \text{ } 8.51 (\text{t}, J = 7.80, 1H), 7.32 (\text{d}, J = 7.80, 1H), 7.12 (\text{ddd}, J = 7.50, 4.80, 1.20 Hz, 1H), 6.88 (\text{d}, J = 1.20 Hz, 1H), 6.76 (\text{d}, J = 1.20 Hz, 1H), 3.80 (s, 2H), 3.79 (s, 2H), 3.58 (s, 3H), 3.32 (\text{d}, J = 2.40 Hz, 2H), 2.27 (t, J = 2.40 Hz, 1H).\]

Synthesis of the manganese(II) complexes

The solution was stirred for 30 min, and then a solution of sodium azide (0.4 mmol) in 3 mL of methanol was added. The mixture was further stirred for 1 h, and the solid thus formed was filtered and washed with methanol. The solid was redissolved in methanol, and slow diffusion of diethyl ether into that solution provided crystals suitable for X-ray diffraction.

\[\text{[Mn}_2(\text{L}_1)_2(\text{N}_3)_2(\mu-\text{N}_3)](4)\]

The synthesis is similar to the synthesis of 3, the only difference being that L2 (24 mg, 0.1 mmol) was used instead of L1. Suitable crystals for X-ray diffraction were obtained following the same diffusion protocol.

Synthesis of MnL1@SiO2

The manganese complex was grafted onto LUS mesoporous silica where azide functions were previously incorporated using the so-called molecular stencil patterning technique described elsewhere.53

Mesoporous silica LUS. A solution of cetyltrimethylammonium tosylate (CTATos) (1.96 g, 4.3 mmol) in distilled water (71 mL) was stirred at 60 °C for 1 h. In the meantime, a sodium silicate solution (49 mL) was also stirred at 60 °C for 1 h. The silicate solution was added to the surfactant one by pouring it slowly on the edge of the recipient. After a vigorous shaking by hand, the resulting white mixture was placed in two autoclaves and heated in a microwave oven for 10 min at 180 °C. The autoclaves were cooled in an ice bath for 10 min before filtration and washing with distilled water (about 100 mL). The white solid obtained was dried at 80 °C to obtain 3.1 to 3.4 g of LUS. Elemental analyses: Si (23.63%), C (30.91%), H (6.31%), N (1.72%), S (0.20%).

N3@SiO2. LUS silica was functionalized with trimethylsilyl functions (TMS) using a reported protocol to afford TMS@SiO2.53 Then, TMS@LUS (500 mg) was pre-treated at 130 °C under argon for 2 h, and at 130 °C under vacuum for 2 more hours. After cooling under argon down to room temperature, a solution of 3-azidopropyl triethoxysilane (371 mg, 1.5 mmol) dissolved in 5 mL of dry toluene was added. The suspension was stirred for 1 h, 10 mL of toluene was added, and the mixture was stirred at 80 °C for 18 h. After filtration and washing with 20 mL of toluene, 20 mL of EtOH 70% and 20 mL of acetone, the solid was finally dried overnight at 80 °C. Elemental analysis (wt%): C: 5.18%, H: 1.80%, N: 2.06%.

MnL1@SiO2. N3@SiO2 (300 mg) was added to the mixture MeOH–MeCN (60 mL/20 mL) and stirred. After 10 min, complex 1 (176 mg, 0.5 mmol) was added and the suspension was stirred for 1 h, before addition of CuBr(PPh3)3 (93 mg, 0.10 mmol). Then the mixture was stirred at 60 °C for 6 days before filtration. The pale brown solid was washed with 200 mL of MeOH to eliminate any catalyst and unreacted species left, and dried overnight at 80 °C. Elemental analysis (wt%): C: 6.42%, H: 1.75%, N: 1.44%, Mn: 2.43%, Cl: 0.74%.

Crystal structure determination and refinement

Single crystal X-ray diffraction data for 2–3 were collected at 293(2) K on a Bruker APEX II diffractometer using graphite-monochromated Mo-Kα radiation while data for 1 and 4 were collected and treated on a Gemini Oxford Diffractometer at 150 K and the related analysis software.58 Data reduction for 2–3 were performed with the SMART and SAINT software.59
The structures were solved by direct methods using the SHELXS-97 program,\textsuperscript{60} and refined on \textit{F}²'s by full-matrix least-squares with the SHELXL-97 program included in the WINGX software package.\textsuperscript{60,61} Absorption correction was applied using SADABS.\textsuperscript{62} For complexes 1 and 4, an absorption correction based on the crystal faces was applied to the datasets (analytical).\textsuperscript{63} Structures of 1 and 4 were solved by direct methods combined with Fourier difference syntheses and refined against \textit{F} using reflections with \(||\alpha|/|\beta| > 3|\) using the CRYSTALS program.\textsuperscript{64} All non-hydrogen atoms were refined using anisotropic terms. The hydrogen atoms were placed at the calculated positions and refined with isotropic parameters as riding atoms. The hydrogen atoms for the co-crystallized methanol molecules were located from difference maps for complex 3. The final geometrical calculations and the graphical manipulations were carried out with PARST95,\textsuperscript{65} PLATON,\textsuperscript{66} (for complexes 2–4) and DIAMOND\textsuperscript{67} programs.

Crystal data, refinement results, atomic coordinates, selected bond lengths and bond angles for 1–4 are summarized in Tables S1–S12.\textsuperscript{†}

**Physical characterization**

Infrared spectra were recorded on KBr pellets using a Mattson 3000 IRTF spectrometer. Nitrogen sorption isotherms at 77 K were determined with a volume device Belsorp Max on solids that were dried at 80 °C under vacuum overnight. Low angle X-ray powder diffraction (XRD) experiments were carried out using a Brucker (Siemens) D5005 diffractometer with Cu Kα monochromatic radiation. Variable-temperature magnetic susceptibility measurements were made using a Quantum Design SQUID susceptometer, using an applied field of 1000 G. Diamagnetic corrections of the constituent atoms were estimated from Pascal constants. EPR spectra were recorded using a Bruker Elexys e500 X-band (9.4 GHz) spectrometer with a standard cavity. The EPR calibration was performed using manganese(II) perchlorate as the spin reference in the same range of concentrations as for the samples. The spin quantification was performed by double integration of the signal. The simulated spectra were calculated using the EasySpin toolbox from Matlab.

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**Notes and references**


