Towards a better understanding of magnetic exchange mediated by hydrogen bonds in Mn(III)/Fe(III) salen-type supramolecular dimers†

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A thorough study of structural and magnetic properties was performed on a series of trinuclear and dinuclear Mn(III)/Fe(III) complexes consisting of \([M(L4)(\text{Solv})]^+\) and \([\text{Fe(CN)}_5(\text{NO})]^2−\) moieties (\(M = \text{Fe(III)}\) or Mn(III), \(\text{Solv} = \text{H}_2\text{O} \text{ or CH}_3\text{OH}, L_4 = \text{tetradentate salen-type ligands}\), in which dominant magnetic exchange is mediated by \(O_s−H…O_m\) hydrogen bonds in \([M(L4)(\text{Solv})]^+−[M(L4)(\text{Solv})]^+\) supramolecular dimers. As deduced from magnetic analysis involving the determination of zero-field splitting (ZFS) parameters for Mn(III) and Fe(III) ions, as well as from comprehensive DFT calculations and modelling, it may be concluded that the strength of the magnetic exchange is correlated with the number of hydrogen bonds and with the \(O_m…O_s\) distance between the phenolic oxygen atom of the salen-type ligand (\(O_m\)) and the oxygen atom of the solvent molecule coordinated to the adjacent metal atom (\(O_s\)).

Introduction

In recent years, a significant amount of research has been devoted to the study of molecular magnetic materials due to their potential applications as molecular switches or high-density memory materials.\(^2\) There is a continuous effort to correlate the magnetic properties of such materials with their structures, in order to establish rational design methods for the preparation of molecule based magnetic materials. Most of the correlations reported thus far dealt with either the strength of the isotropic magnetic interactions, mediated through the covalent bonds between two paramagnetic metal atoms,\(^3\) or with the magnetic anisotropy defined by the zero-field splitting (ZFS) parameters – the prerequisite for observation of slow-relaxation of magnetisation. However, magnetic exchange mediated by non-covalent interactions such as hydrogen bonding or \(\pi−\pi\) stacking of aromatic rings is emerging as another magnetic exchange coupling phenomenon, especially in the study of organic-based molecular magnets. This kind of exchange might also play an important role in coordination compounds with interesting magnetic properties, e.g. in mediating intrachain exchange interactions, thus giving rise to single-chain magnets,\(^3\) in magnetic sponges,\(^4\) or in the occurrence of slow-magnetic relaxation in polynuclear compounds\(^5\) or in simple paramagnetic compounds.\(^6\)

Of particular importance amongst the magnetically interesting coordination compounds are the cyanido-bridged complexes (Prussian blue analogues and related compounds),\(^7,8\) which are of interest due to their structural and magnetic properties\(^9\) and their potential use as optical devices and catalysts.\(^10\) A wide variety of cyanido complexes can be used as bridging units and these can be generally divided into two subgroups: (a) homoleptic cyanido complexes with the general formula \([M(CN)_x]^+(x−m)^−\) (\(M = \text{transition metal, } x = \text{number of cyanido ligands, } m = \text{charge of } M\)) and (b) heteroleptic cyanido complexes \([M(L)]^+(x−l)^−\) (\(L = \text{organic ligand different from } CN\), \(l = \text{charge of } L\)). Such cyanidometallates can react with coordinatively unsaturated complexes (or labile complexes from a kinetic point of view) to form compounds which vary widely in their structures and magnetic properties.

The objective of the work reported herein was to prepare and characterize a series of trinuclear nitroprusside-bridged Mn(III)/Fe(III) complexes containing Schiff base ligands,\(^11\) or more specifically, salen-type ligands \((L_4^{2−} = \text{salen}^{2−} = N_{2}N′-\text{ethane-bis(salicylideneiminate)})\) dianion; other abbreviations of the ligands used or mentioned in this work can be found in ref. 12), and therefore, such polynuclear salen-type compounds bridged by metallocyanates are briefly discussed below.

The cationic part in the presented complexes consists of the tetradaentate salen-like dianionic ligand \((L_4^{2−})\) coordinated to the transition metal, thus creating the \([M(L_4)]^{(m−2)^−}\) moiety, where the \(L_4\) ligand occupies the equatorial plane of the complex. Two axial positions are potentially available for...
coordination and therefore the $[\text{M}(\text{L}4)]^{(m-2)-}$ moiety can be considered as a perfect building block for the preparation of low dimensional coordination compounds, and coordination polymers of various dimensions (1D, 2D or 3D) can also be prepared. In general, three basic structural types can be distinguished, where the $[\text{M}(\text{L}4)]^{(m-2)-}$ moiety is coordinated by:

(A) One N-cyanido ligand from the cyanidometallate, and a solvent molecule (most usually water or methanol) in the second axial position. The structure of the resulting complex is low-dimensional and polymeric due to the terminal function of the solvent ligand (further abbreviated as Solv). However, the Solv molecules often extend the dimensionality of the crystal structure (usually to 1D arrays) by forming hydrogen bonding interactions with suitable acceptor atoms from neighbouring molecules (Scheme 1A, vide infra).

(B) Two N-cyanido ligands, each from different adjacent cyanidometallate molecules, and therefore the structure of the resulting complex is polymeric in most cases (Scheme 1B, vide infra).

(C) One N-cyanido ligand from the cyanidometallate, and a phenolic oxygen atom from the adjacent $[\text{M}(\text{L}4)]^{(m-2)-}$ molecule in the second axial position, thus forming a dimeric unit. It must be stressed that this kind of dimer is not unique for Mn$^{III}$ complexes and can also be found in other transition metal complexes (Co$^{II/III}$,13 Fe$^{III}$,14 Ru$^{III}$,15 Ti$^{III}$,16 Zn$^{II}$,17 Cu$^{II}$ (ref. 18) and Ni$^{II}$,19 Scheme 1C).

In our previous work we have reported coordination compounds built from various $[\text{Mn}^{III}(\text{L}4)]^{n-}$ moieties bridged by $[\text{Pt}^{II}(\text{SCN})_4]^2-$ or $[\text{Pt}^{II}(\text{SCN})_6]^2-$ complex anions.20,21 Almost all of the prepared compounds were trinuclear with the general formula $[\text{Mn}(\text{L}4)(\text{Solv})]_3[\mu_2-\mu_\text{Pt}(\text{SCN})_2]$, where $x = 4$ or 6, and they thus belong to group (A). For those compounds it was shown that the exchange interactions mediated by the diamagnetic bridging anion are negligible and it was proven that the dominant magnetic exchange pathway occurs via non-covalent interactions, i.e. hydrogen bonding within the supramolecular dimer $[\text{Mn}(\text{L}4)(\text{Solv})]_2[\mu_2-\mu_\text{Pt}(\text{SCN})_2]$. Therefore, this kind of supramolecular system represents an ideal object of study for investigation of the magnetic exchange mediation through hydrogen bonding. Furthermore, it was observed that there is a significant difference in the strength of the magnetic exchange, depending on the type of Solv molecule bonded to the Mn$^{III}$ atom. In order to explore this phenomenon thoroughly we have studied another system with a diamagnetic bridging cyanidometallate, i.e. nitroprusside $[\text{Fe}(\text{CN})_5(\text{NO})]^2-$, and furthermore, we have focused our attention not only on its Mn$^{III}$ complexes, but also on its Fe$^{III}$ ones.

From a literature survey on the above mentioned compounds it is apparent that the nitroprusside-$[\text{Mn}^{III}(\text{L}4)]^{n-}$ compounds ($\text{M}^{III} = \text{Fe}^{III}, \text{Mn}^{III}$) which belong to group (A) (Scheme 1A) only include Mn$^{III}$ complexes (explanations of the following ligand abbreviations can be found in Scheme 2): $[\text{Mn}(\text{L}4)(\text{H}_2\text{O})]_2[\mu_\text{Fe}(\text{CN})_5(\text{NO})]$ (7a),22 $[\text{Mn}(\text{L}4b)(\text{H}_2\text{O})]_2[\mu_\text{Fe}(\text{CN})_5(\text{NO})]2\text{CH}_3\text{OH}$ (7b), $[\text{Mn}(\text{L}4m)(\text{CH}_3\text{OH})]_2[\mu_\text{Fe}(\text{CN})_5(\text{NO})]$ (7c),24 $[\text{Mn}(\text{L}4k)-(\text{H}_2\text{O})]_2[\mu_\text{Fe}(\text{CN})_5(\text{NO})]2\text{H}_2\text{O}$ (7d)24 and $[\text{Mn}(\text{L}4l)(\text{H}_2\text{O})]_2[\mu_\text{Fe}(\text{CN})_5(\text{NO})]$ (7e).25

The compounds which belong to group (B) are polymeric with two-dimensional crystal structures (Scheme 1B). In all reported cases the nitroprusside anion acts as a moiety which bridges four $[\text{M}^{III}(\text{L}4)]^{n-}$ entities, and thus creates grid-like sheets built from $[\text{M}(\text{L}4)]_2[\mu_4-\text{Fe}(\text{CN})_5(\text{NO})]_3$ units. This group contains six coordination polymers: $[\text{Mn}(\text{L}4j)]_2[\mu_4-\text{Fe}(\text{CN})_5(\text{NO})]$ (7f),24 $[\text{Mn}(\text{L}4f)]_2[\mu_4-\text{Fe}(\text{CN})_5(\text{NO})]$ (7g),24 $[\text{Fe}(\text{L}4f)]_2[\mu_4-\text{Fe}(\text{CN})_5(\text{NO})]_4$ (7h),27 $[\text{Fe}(\text{L}4g)]_2[\mu_4-\text{Fe}(\text{CN})_5(\text{NO})]$ (7i),28 $[\text{Mn}(\text{L}4f)]_2$...
Table 1  Selected structural parameters for nitroprusside complexes.

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<tr>
<th>M−N_m</th>
<th>M−O_P</th>
<th>M−N_C</th>
<th>M−O_s</th>
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**a** Average values calculated from two bond length values.  
**b** Distortion parameter defined as sum of deviations from 90° of the twelve cis angles in the coordination sphere.

Table 2  Crystallographic data and structure refinement details for complexes 3a, 4a, 4b, 5a and 6b

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<th>Formula</th>
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<td>150(2)</td>
<td>150(2)</td>
<td>150(2)</td>
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<td>σ(Å)</td>
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<td>b(Å)</td>
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<td>0.993</td>
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<td>F(000)</td>
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<td>Goodness-of-fit (GOF) on F²</td>
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<tr>
<td>R₁, wR₂ (F &gt; 2σ(F))</td>
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Results and discussion

Crystal structures of trinuclear complexes 3a, 4a, 4b and 5a

The selected bond lengths for herein and previously reported salen-type complexes are summarized in Table 1. The crystal data and structure refinements for compounds reported in this article are given in Table 2.
The molecular structures of these complexes are very similar, consisting of trinuclear \([\text{[M}^{\text{III}}(\text{L}4)(\text{H}2\text{O})]_2(\mu-\text{Fe}(\text{CN})_5(\text{NO}))}\) moieties (\(\text{M}^{\text{III}} = \text{Fe}^{\text{III}}\) or \(\text{Mn}^{\text{III}}\), Fig. S1–S4 in ESI†) which have slightly bent \(\{\text{H}2\text{O}−\text{M}^{\text{III}}−\text{NC}−\text{Fe−CN−M}^{\text{III}}−\text{H}2\text{O}\}\) arrangements (Fig. 1–3). The \(\text{M}^{\text{III}}⋯\text{M}^{\text{III}}\) separations within the trinuclear complexes are very similar (in Å): 10.1621(6) in 3a, 10.1532(5) in 4a, 10.225(4) in 4b and 10.173(4) in 5a. The coordination polyhedra of the \([\text{M}(\text{L}4)(\text{H}2\text{O})]+\) subunits can be described as axially elongated octahedrons, and the distortion is more obvious for the \(\text{Mn}^{\text{III}}\) derivatives due to the Jahn–Teller effect. In general, based on herein and previously reported salen-type complexes, it can be concluded that the \(\text{Mn}^{\text{III}}\) compounds show significantly longer axial (usually \(\text{M}−\text{NCN}\) and \(\text{M}−\text{OS}\) bonds; \(\text{NCN}\) stands for the nitrogen atom of the nitroprusside cyanido group, \(\text{OS}\) stands for the oxygen atom from the coordinated solvent molecule) bond lengths in comparison with the \(\text{Fe}^{\text{III}}\) compounds (\(\text{ca.}\); \(d(\text{Mn−NCN}) = 2.30\ \text Å\), \(d(\text{Fe−NCN}) = 2.17\ \text Å\), \(d(\text{Mn−OS}) = 2.27\ \text Å\), \(d(\text{Fe−OS}) = 2.10\ \text Å\), Table 1). On the contrary, the \(\text{M−N}^{\text{im}}\) bond lengths are longer in the case of the \(\text{Fe}^{\text{III}}\) complexes (\(\text{ca.}\); \(d(\text{Mn−N}^{\text{im}}) = 1.99\ \text Å\), \(d(\text{Fe−N}^{\text{im}}) = 2.11\ \text Å\); \(\text{N}^{\text{im}}\) stands for the nitrogen atom from the imino group of \(\text{L}4\)). The length of the \(\text{M−OPh}\) bonds is roughly the same for both central ions (Table 1; \(\text{O}^{\text{Ph}}\) stands for the phenolate oxygen atoms). The angular distortions from the ideal octahedron \(\Sigma^{10}\) are obviously smaller for the \(\text{Mn}^{\text{III}}\) compounds (Table 1).

As mentioned in the introduction, these trinuclear complexes belong to group (A), in which non-covalent connections between polynuclear species are provided by hydrogen bonding between coordinated \(\text{Solv}\) molecules and phenolate oxygen atoms and thus, roughly linear arrays of centro-symmetric and supramolecular \([\text{Mn}(\text{L}4)(\text{Solv})]+⋯[\text{Mn}(\text{L}4)(\text{Solv})]^+\) dimers connected by nitroprusside anions are formed. In the crystal structures of compounds 3a, 4a, 4b and 5a, the \(\text{Solv}\) molecules (\(\text{Solv} = \text{H}2\text{O}\)) form two basic types of interactions: (i) a simple \(\text{O}^{\text{Solv}}\text{H}⋯\text{O}^{\text{Solv}}\) hydrogen bond (in 3a) and (ii) a bifurcated hydrogen bond where two \(\text{H}\)-atoms from the water molecule interact with four oxygen atom acceptors (two alkoxy (\(\text{OA}\)) and two phenolate oxygen atoms, in 4a, 4b and 5a). The bifurcated hydrogen bonding prolongs the donor⋯acceptor lengths; in
the case of O₅⋯O₈ contacts (in Å): \(d(\text{O}_5\cdots\text{O}_8) = 2.690(3)\) in 3a vs. 2.792(2) and 2.927(2) in 4a, 2.851(3) and 2.934(3) in 4b, and 2.814(2) and 2.866(2) in 5a. The \(\text{O}_5\cdots\text{O}_8\) hydrogen bonds are longer in general, however, in the crystal structure of 4b we observe one relatively short contact (in Å): \(d(\text{O}_5\cdots\text{O}_8) = 3.024(2)\) and 3.248(2) in 4a, 2.866(3) and 3.115(4) in 4b, and 3.064(2) and 3.279(2) in 5a.

The M\(\text{III}\)⋯M\(\text{III}\) separations in the supramolecular dimers are within a relatively narrow range (in Å): 4.8728(5) in 3a, 4.5608(4) in 4a, 4.7132(9) in 4b and 4.594(2) in 5a. The crystal structure of 3a differs significantly from the structures of 4a, 4b and 5a due to the presence of a co-crystallized molecule of methanol. This extends the structural dimensionality of the compound to 2D by linking supramolecular chains \([\text{Fe(L4b)}(\text{H}_2\text{O})]_2[\mu-\text{Fe(CN)}_3\text{NO}]_n\) together through hydrogen bonding between a coordinated water molecule and a methanol molecule which in turn is hydrogen bonded to a non-coordinated nitrogen atom from the nitroprusside bridge of a neighbouring complex (Fig. 2).

Crystal structure of complex 6b

The crystal structure of 6b is depicted in Fig. 3. It consists of the dimer \([\text{Mn(L4e)}(\text{H}_2\text{O})]\)[\(\mu-\text{Fe(CN)}_3\text{NO}\)] (6b mol1) and \([\text{Mn(L4e)}(\text{H}_2\text{O})(\text{CH}_3\text{OH})]\) (6b mol2) moieties, in which both manganese atoms are hexacoordinated with four donor atoms (N₂O₂) coming from the L4e⁻ ligand. In 6b mol1 the remaining coordination sites (axial positions) are occupied by two oxygen atoms, coming from the coordinated water and methanol molecules. On the other hand, the axial positions in 6b mol2 are occupied by the oxygen atom from the water molecule and by the nitrogen atom from the bridging cyanido group of the nitroprusside. The average bond lengths are (mol1, mol2; in Å): \(d(\text{Mn}–\text{N}_\text{im}) = 1.961, 1.953\); \(d(\text{Mn}–\text{O}_\text{im}) = 1.882, 1.868\). The axial bond lengths differ due to the different solvent molecules coordinated to the Mn(III) atoms (in Å): \(d(\text{Mn}–\text{O}_\text{H}_2\text{O}) = 2.292(3)\) (H₂O) in mol1 and 2.256(3) (CH₃OH) and 2.309(3) (H₂O) in mol2. It must be noted that the crystal structure of 6b exhibits substitutional disorder on mol2, where the methanol molecule (the main part, with occupation factor of 0.68) is partially substituted by a water molecule which is further hydrogen bonded to another disordered water molecule (Fig. S5 in ESI†).

Both complexes create 2D networks of hydrogen bonds owing to the co-crystallized water and methanol molecules (Fig. 3). The \([\text{Mn(L4e)}(\text{H}_2\text{O})][\mu-\text{Fe(CN)}_3\text{NO}][\text{Mn(L4e)}(\text{H}_2\text{O})(\text{CH}_3\text{OH})]\) assembly (mol1⋯mol2), in which the interconnection between mol1 and mol2 is provided by hydrogen bonding between coordinated water molecules and complementary phenolate oxygen atoms, similarly to in compounds 3a–5a, can be considered as the main building block of the crystal structure.

The mol1⋯mol2 assembly is further propagated to a linear 1D chain by a series of hydrogen bonds; the coordinated methanol molecule from mol2 forms a hydrogen bond with a co-crystallized water molecule, which in turn hydrogen bonds to a co-crystallized methanol molecule which is in close contact with the adjacent cyanido group (the trans position with respect to the cyanido group coordinating the Mn atom) from the neighbouring mol1⋯mol2 assembly. Linear supramolecular chains are interconnected via hydrogen bonding between the coordinated water molecule from mol1 and the neighbouring cyanido group (the cis position with respect to the cyanido group coordinating the Mn atom), and between the co-crystallized water molecule and the cyanido group from the neighbouring mol1 moiety.

Infrared spectroscopy

The presence of the Schiff base in each of the complexes was indicated by FT-IR spectra measured in the range 400–4000 cm⁻¹. The spectra of each of the compounds exhibit two weak intensity bands at 3115–3132 and 3025–3037 cm⁻¹ corresponding to asymmetric and symmetric stretching vibrations of the aromatic C–H groups. The characteristic bands assignable to the C≡N and (C–C)ₐr vibrations were observed in the 1613–1625 cm⁻¹ and 1437–1595 cm⁻¹ regions,
respectively, for all complexes. Formation of the cyanido-bridges in all the nitroprusside complexes are evidenced by the C≡N stretching vibration bands in the 2000–2200 cm⁻¹ region. The maximum at 2143 cm⁻¹ in sodium nitroprusside dihydrate may be assigned to the vibration of the cyanido group, while the maxima associated with the same vibration in complexes 2a–6b were observed in the range 2138–2163 cm⁻¹.31 The strong peaks in the region 1906–1922 cm⁻¹ are assignable to the N=O stretching vibrations, which are at lower wavenumbers than that found for the same vibration in the complex Na₃[Fe(CN)₆NO]·2H₂O (1936 cm⁻¹).

**Magnetic properties**

In all the presented compounds, we can observe the formation of quasi-dimers amongst [(MnIII(L4)(H₂O))]⁺ or [(FeIII(L4)-(H₂O))]⁻ subunits, held together by hydrogen bonds between coordinated solvent molecules and phenolic oxygen atoms. Within these quasi-dimers, the Mn⋯Mn and Fe⋯Fe separations vary between 4.71–5.06 Å, and 4.59–4.87 Å, respectively, in contrast to their large interatomic separations (more than 10 Å) through covalent bonds formed by diamagnetic nitroprusside bridges.

These structural aspects strongly suggest that the superexchange mechanism is mainly active through hydrogen bonds. The nature of the magnetic exchange can be estimated by inspecting the temperature dependence of susceptibility and the effective magnetic moment of these compounds. The presence of the maximum of the susceptibility (T < 10 K) is a fingerprint of the antiferromagnetically coupled homospin dimer. This results in a decrease in μ_eff/μ_B on cooling. Moreover, the interplay of the zero-field splitting on the magnetic properties cannot be neglected, especially for Mn(III) atoms.

Therefore the following spin Hamiltonian was postulated

\[ \hat{H} = -J \sum_{i=1}^{2} (\hat{S}_{i \perp}^2 - \hat{S}_{i \perp}^2/3) + \mu_B B g_i \hat{S}_{i \perp} - J \sum_{i,j} \hat{S}_{i \parallel} \hat{S}_{j \parallel} \]  

(1)

where the first term stands for the isotropic exchange (J), the second part is due to the zero-field splitting (D – an axial single-ion ZFS parameter), the third part is the Zeeman term and the last expression represented with the \( \hat{S}_{i \perp} \) variable is the common molecular-field correction parameter, which is due to small intra/inter-chain molecular interactions. The \( \langle \hat{S}_{i \perp} \rangle \) is a thermal average of the molecular spin projection in the a direction of the magnetic field defined as \( B_a = B \sin \theta \cos \phi \), \( \sin \theta \sin \phi \). With the help of polar coordinates, then, the molar magnetization in the a direction of the magnetic field can be numerically calculated as

\[ M_a = -N_A \sum_i \left( \sum_j \sum_k C_{jk} (Z_i)_{jk} C_{ij} \right) \exp(-\epsilon_{a,i}/kT) \]  

(2)

where \( Z_i \) is the matrix element of the Zeeman term for the a direction of the magnetic field and C are the eigenvectors resulting from the diagonalization of the complete spin Hamiltonian matrix. Then, the averaged molar magnetization of the powder sample was calculated as integral (orientational) average

\[ M_{mol} = \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi M_a \sin \theta \, d\theta \, d\phi. \]  

(3)

With the aim to bring more insight into the general properties of the antiferromagnetically coupled dimer with ZFS, the shift in temperature of the maximum of the susceptibility (\( T_{max} \)) was inspected for varying ratios of \( DJ/|J| \), for either \( S_1 = S_2 = 2 \) or \( S_1 = S_2 = 5/2 \) (Fig. 4). There is a simple formula which interconnects the strength of the antiferromagnetic exchange with \( T_{max} \) but it is available only for the isotropic case: \( |J|/kT_{max} = 0.462 \) for \( S_1 = S_2 = 2 \) and \( |J|/kT_{max} = 0.347 \) for \( S_1 = S_2 = 5/2 \). In both cases, introducing the non-zero zero-field splitting results in an increase in \( T_{max} \) and this change is more emphasized for \( D < 0 \) (Fig. 4).

As both antiferromagnetic exchange and ZFS have similar effects on magnetic properties, the decrease in \( \mu_{eff}/\mu_B \) both the temperature and field dependent magnetization data were experimentally acquired and concurrently used in finding the best-fit parameters of the above introduced spin Hamiltonian (eqn (1)). Furthermore, the standard deviations of the varied parameters were calculated with 95% probability confidence limits.32
**Dinuclear complex 6b**

The unique molecular and crystal structure of 6b results in the formation of quasi linear and discrete trimers of type Mn(III)⋯Mn(III)⋯Fe(II) in which paramagnetic manganese atoms are connected through hydrogen bonds (d(Mn⋯Mn) = 5.0575(7) Å) and the diamagnetic nitroprusside anion serves as a terminal entity. This gives us an opportunity to study the magnetic exchange of the MnIII⋯MnIII type mediated by water-hydrogen bonds, unaffected by bridging through nitroprusside as found in the remaining reported complexes. The experimental magnetic data are presented in Fig. 5. The room temperature effective magnetic moment of 6b is 7.1 μB, which is very close to the theoretical value of 6.93 μB for two paramagnetic non-interacting centres with S = 2 (g = 2.0). The susceptibility is increasing on cooling and is reaching its maximum at 6.5 K, which is also accompanied by a decrease in μeff below 50 K down to 2.1 μB at 1.9 K. The isothermal magnetization at 2 K is not saturated even at B = 7 T and has a value of Mtot/NμB = 6.2, which is below the saturation limit of Mtot/NμB = 8 (2 × S = 2 and g = 2.0). By applying eqn (1)-(3) to both temperature and field dependent magnetic data, we obtained J = −0.72(1) cm⁻¹, g = 2.048(1), D = −3.65(9) cm⁻¹ and zJ = −0.06(1) cm⁻¹ (Fig. 5). The negative and large value of the D-parameter is in agreement with the elongated octahedrons of the Mn(III) centres due to the Jahn–Teller effect. However, the coordination chromophores of the respective Mn(III) centres differ in one apical position – {MnO₄N₂} for Mn1 and {MnO₅N} for Mn2 (Fig. 3), and therefore the calculated D-value serves as an average value of both distinct Mn(III) centers. The most important outcome is that considerably large magnetic exchange is mediated by hydrogen bonds between Mn(III) centers.

**Trinuclear [{Mn(L₄)(H₂O)}₂{μ-Fe(CN)₅(NO)}]·xCH₃OH complexes 4b and 2b**

Compound 4b shows very similar magnetic properties to compound 6b (Fig. 5), which justifies the presumption that dominant magnetic exchange is mediated through hydrogen bonds (d(Mn⋯Mn) = 4.7132(9) Å) and not through the diamagnetic nitroprusside anion (d(Mn⋯Mn) = 10.225(2) Å). Thus, the magnetic data of 4b were treated using the same procedure as for 6b under the condition that D₁ = D₂, because there is only one Mn atom in the asymmetric unit. The resulting parameters are J = −0.79(1) cm⁻¹, g = 1.981(2), D = −3.7(1) cm⁻¹ and zJ = +0.12(2) cm⁻¹ (Fig. 5). The last reported Mn(III) compound is complex 2b, which exhibits comparable properties to compounds 4b and 6b (Fig. 5). Thus, we used the same model despite the absence of its X-ray crystal structure. The best fit was obtained with the following parameters: J = −0.55(1) cm⁻¹, g = 1.987(2), D = −3.5(2) cm⁻¹ and zJ = −0.10(2) cm⁻¹ (Fig. 5).

**Trinuclear [{Fe(L₄)(H₂O)}₂{μ-Fe(CN)₅(NO)}]·xCH₃OH complexes 2a, 3a, 4a and 5a**

The magnetic behaviours of the trinuclear Fe(III)-nitroprusside complexes 2a, 3a, 4a and 5a were found to be very similar to one another (Fig. 6). The room temperature values of the effective magnetic moment are in the range 8.42–8.57 μB, which is very close to the theoretical value of 8.37 μB for two paramagnetic non-interacting centres with S = 5/2 (g = 2.0). Upon cooling, the μeff/μB dependencies are almost constant.

---
down to 50 K and then they start to decrease to values of 3.33, 3.46, 2.68 and 2.73 at $T = 1.9$ K for $2a$, $3a$, $4a$, and $5a$, respectively.

Furthermore, the maxima of the molar magnetization (or mean molar susceptibility) ranged from 3.5 to 6.5 K. This fact indicates the presence of antiferromagnetic exchange between Fe(III) centres, mediated by hydrogen bonds and/or the zero-field splitting of the Fe(III) centers. Moreover, the isothermal magnetization measurements at liquid helium temperatures (2.0 and 4.6 K) support this presumption, because the experimental values of $M_{\text{mol}}/N_{\text{eff}}$ are below the theoretical saturation value $M_{\text{mol}}/N_{\text{eff}} = gS^2/2 = 10$ ($g = 2.0$, $S = 5/2$) (Fig. 6). Therefore, the same spin Hamiltonian was used as in eqn (1), but in this case $S_1 = S_2 = 5/2$ holds. It must be stressed that including the ZFS term has been essential to reliably fit all experimental data together. We have found that slightly better fits could be obtained for positive rather than negative $D$-parameter values and both sets of values are tabulated for each of the presented compounds in Table 3 (see also Fig. 6 and Fig. S9–12, ESI†). Evidently, weak antiferromagnetic exchange was found in the range $-0.52$ to $-1.05$ cm$^{-1}$. In the case of positive $D$-parameters, the $|D/J|$ ratios vary between 1.70 and 2.45, but in the case of negative $D$-parameters, the $|D/J|$ ratios vary between 0.50 and 1.15. To summarize, the values of the antiferromagnetic exchange in Mn(III) and Fe(III) compounds $2a$–$6b$ were found to vary in a narrow range between $-0.52$ cm$^{-1}$ and $-1.05$ cm$^{-1}$, but the ZFS is much larger for the Mn(III) complexes. This is an expected feature for Mn(III) atoms due to the Jahn–Teller effect and larger distortion of the coordination polyhedra.3-11

Furthermore, we strived to find clear magneto-structural correlations either for isotropic exchange ($J$) or magnetic anisotropy ($D$) in the reported series of compounds by taking into account various structural parameters. However, the $D$-parameter does not simply correlate with geometric deformation of the coordination chromophore ($\Sigma$), which can be explained by the complexity and variedness of the donor atoms. Conversely, there are some remarks concerning the isotropic exchange which must be taken into account: our previous results20 predicted weaker exchange interactions within the supramolecular dimer $[\text{M(L4)}(\text{Solv})]^-$–$[\text{M(L4)}(\text{Solv})]^-$ when Solv = CH$_3$OH and stronger ones when Solv = H$_2$O. As can be seen from Table 3, this prediction holds true; the compounds containing $[\text{M(L4)}(\text{CH}_3\text{OH})]^-$ fragments possess weaker exchange interactions with $J$ values ranging from $-0.3$ to $-0.6$ cm$^{-1}$, while the compounds containing $[\text{M(L4)}(\text{H}_2\text{O})]^-$ fragments have lower $J$ values ranging from $-0.7$ to $-1.3$ cm$^{-1}$ (when not including most probably overestimated $J$ values, due

Fig. 6 Magnetic properties of $2a$, $3a$, $4a$ and $5a$. Each plot shows the temperature dependence of the effective magnetic moment (calculated from the temperature dependence of magnetization at $B = 0.1$ T; inset) and the isothermal magnetizations measured at $T = 2.0$ (□) and 4.6 K (◊). Empty symbols – experimental data, full lines – the best fit calculated with: $J = -0.64(2)$ cm$^{-1}$, $g = 2.031(2)$, $D = +1.12$ cm$^{-1}$ and $zj = -0.09(2)$ cm$^{-1}$ for $2a$, $J = -0.53(2)$ cm$^{-1}$, $g = 2.042(3)$, $D = +1.3(2)$ cm$^{-1}$ and $zj = -0.24(3)$ cm$^{-1}$ for $3a$, $J = -1.01(4)$ cm$^{-1}$, $g = 2.064(3)$, $D = +1.9(3)$ cm$^{-1}$ and $zj = +0.03(3)$ cm$^{-1}$ for $4a$ and $J = -0.94(2)$ cm$^{-1}$, $g = 2.035(1)$, $D = +1.6(2)$ cm$^{-1}$ and $zj = -0.026(4)$ cm$^{-1}$ for $5a$. This journal is © The Royal Society of Chemistry 2014

Dalton Trans., 2014, 43, 15602–15616 | 15609

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Table 3  Summary of structural details, results from magnetic analysis and DFT calculations for iron(III) and manganese(III) nitroprusside/polythiocyanadoplating-bridged complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Selected structural data&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Magnetic analysis data&lt;sup&gt;b&lt;/sup&gt;</th>
<th>DFT calculated data&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M⋯M* (Å)</td>
<td>M⋯M (Å)</td>
<td>OPh⋯OPh* (Å)</td>
</tr>
<tr>
<td>2a</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>3a</td>
<td>4.8728(5)</td>
<td>10.1621(6)</td>
<td>3.682(2)</td>
</tr>
<tr>
<td>4a</td>
<td>4.5608(4)</td>
<td>10.1532(5)</td>
<td>3.263(2)</td>
</tr>
<tr>
<td>5a</td>
<td>4.593(2)</td>
<td>10.173(4)</td>
<td>3.338(2)</td>
</tr>
<tr>
<td>7a</td>
<td>4.690(2)</td>
<td>10.358(3)</td>
<td>3.339(5)</td>
</tr>
<tr>
<td>7b</td>
<td>5.152(3)</td>
<td>10.288(3)</td>
<td>3.803(5)</td>
</tr>
<tr>
<td>7d</td>
<td>5.067(2)</td>
<td>10.400(2)</td>
<td>3.496(6)</td>
</tr>
<tr>
<td>7e</td>
<td>5.694(1)</td>
<td>10.388(3)</td>
<td>3.303(2)</td>
</tr>
<tr>
<td>8</td>
<td>4.7007(9)</td>
<td>12.5840(8)</td>
<td>3.242(4)</td>
</tr>
<tr>
<td>9</td>
<td>4.858(2)</td>
<td>12.017(2)</td>
<td>3.365(8)</td>
</tr>
<tr>
<td>10</td>
<td>5.004(2)</td>
<td>12.044(2)</td>
<td>3.469(3)</td>
</tr>
<tr>
<td>11</td>
<td>5.0682(2)</td>
<td>11.749(3)</td>
<td>3.764(2)</td>
</tr>
</tbody>
</table>

<sup>a</sup> M⋯M* is the shortest distance between metal atoms bridged through water mediated hydrogen bonds; M⋯M is the shortest distance between metal atoms bridged by nitroprusside or polythiocyanadoplating; OPh⋯OPh* and OPh⋯OPh† are distances between the oxygen atoms of two phenol groups, or the oxygen atom of a phenol group and the oxygen atom of a water/methanol molecule, attached to different metal atoms M and M*.<sup>b</sup>f-values reported in the literature were scaled according to the spin Hamiltonian in eqn (1).<sup>c</sup>Ref. 22.<sup>d</sup>Ref. 23.<sup>e</sup>Ref. 24, comment: f-value is most probably overestimated due to omitting the ZFS term.<sup>f</sup>Results based on DFT calculations performed on molecular fragments, in which hydrogen atoms were optimized with BP86/def2-TZVP(f).

DFT calculations

In order to support our conclusions from magnetochemical analyses of the experimental data, we performed isotropic exchange parameter calculations using the DFT method for H-bond bridged dinuclear molecular fragments [M(III)(L4)(H2O)(NC)2] (M = Fe, Mn) for compounds reported herein, 3a-
and also for similar compounds reported in literature, 7a–7e. Moreover, we also investigated the role of the diamagnetic nitroprusside anion in mediation of magnetic exchange for compound 4a using the \([\text{Fe}^{III}(L4c)[\text{H}_2\text{O}])_2(\mu-\text{Fe}^{III}(\text{CN})_2(\text{NO}))\] molecular fragment.

All the calculations were based on experimental X-ray geometries except for 7a, where some hydrogen atoms were missing in the CSD deposited data (CCDC IGAKEG) and their atomic positions were optimized with the BP86 functional and a def2-TZVP(-f) basis set.

As this work extends from our research on magnetic exchange in transition metal complexes containing diamagnetic bridging polythiocyanidoplutinate,14,15 the same hybrid functional B3LYP together with a def2-TZVP basis set and the scalar relativistic second-order Douglas–Kroll–Hess Hamiltonian were used.

Therefore, the results of relevant hydrogen bond bridged compounds, \([\text{Mn}(L4o)[\text{H}_2\text{O}])_2(\mu-\text{Pt}(\text{SCN}))\] [8], \([\text{Mn}(L4n)[\text{H}_2\text{O}])_2(\mu-\text{Pt}(\text{SCN}))\] [9], \([\text{Mn}(L4b)[\text{CH}_3\text{OH}])_2(\mu-\text{Pt}(\text{SCN}))\] [10] and \([\text{Mn}(L4p)[\text{CH}_3\text{OH}])_2(\mu-\text{Pt}(\text{SCN}))\] [11], where \(L_{4n} = N,N\)-benzene-bis(4-aminodiethylenesalicylideneiminate) dianion, \(L_{4o} = N,N\)-3-methylbenzene-bis(3-ethoxysalicylideneiminate) dianion and \(L_{4p} = N,N\)-ethylene-bis(naphthyldenedibenzoimidideneiminate) dianion, were also included in Table 3.

The isotropic exchange analysis was based on the following Heisenberg spin Hamiltonian

\[ \hat{H} = -J(\vec{S}_1 \cdot \vec{S}_2) \]  

and evaluation of energy differences between high-spin (HS) and broken-symmetry (BS) spin states, \(\Delta = E_{\text{BS}} - E_{\text{HS}}\), using quantum-chemical computational software ORCA. The final \(J\)-values were calculated by Ruiz’s

\[ J^{\text{Ruiz}} = \frac{\Delta}{2S_1S_2 + S_1} \]  

and Yamaguchi’s

\[ J^{\text{Yam}} = 2\Delta/\left(S^2_{\text{HS}} + S^2_{\text{BS}}\right) \]  

approaches and are tabulated for \([\text{Fe}^{III}(L4)[\text{H}_2\text{O}])_2\) fragments in Table 3. HS spin states had small spin contaminations, manifested by the calculated \(S^2_{\text{HS}}\) values that are close to the theoretical values \(S^2_{\text{HS}} = S(S + 1)\) where \(S = 5\) for \(M = \text{Fe}\) and \(S = 4\) for \(M = \text{Mn}\) (\(S_{\text{HS}}\) is the total spin value for the HS state), while the values of the BS spin states \(S^2_{\text{BS}}\) are close to \(M^2_{\text{BS}} + S^2_{\text{HS}}\) (\(M_s\) is the spin projection of the BS spin state).

First, the DFT calculation for the \([\text{Fe}^{III}(L4c)[\text{H}_2\text{O}])_2(\mu-\text{Fe}^{III}(\text{CN})_2(\text{NO}))\) molecular fragment of 4a resulted in insignificant magnetic exchange, \(J^{\text{Yam}} = +0.031\ \text{cm}^{-1}\) \(J^{\text{Ruiz}} = +0.026\ \text{cm}^{-1}\), thus supporting our presumption that this superexchange path is very inefficient in promoting magnetic exchange.

Next, the calculation performed for H-bonded dimers \([\text{Mn}^{III}(L4)[\text{H}_2\text{O}])_2]\ (\(M = \text{Fe}, \text{Mn}\)) resulted in the \(J\)-values tabulated in Table 3. The \(J^{\text{Yam}}\) values were found to be in the range from \(-0.54\) to \(-0.60\ \text{cm}^{-1}\) for \([\text{Fe}^{III}(L4)[\text{H}_2\text{O}])_2]\ (3a, 4a and 5a), and in the range from \(-0.56\) to \(-0.94\ \text{cm}^{-1}\) for \([\text{Mn}^{III}(L4)[\text{H}_2\text{O}](\text{NC}))_2\) and \([\text{Mn}^{III}(L4)[\text{H}_2\text{O}](\text{NCS}))_2\] (2b–6b and 7b–11). Good agreement between \(J\)-values derived from magnetochemical analysis of the experimental data and DFT calculations was obtained for compounds 3a, 4b, 6b and 7b, when taking into account the \(J^{\text{Yam}}\) values. However, larger discrepancies were observed for the remaining compounds, e.g. in the case of 4a, magnetic analyses resulted in \(J^{\text{Rhiz}} \approx -1.0\ \text{cm}^{-1}\), which is in contrast to the values of \(J^{\text{Yam}} = -0.48\ \text{cm}^{-1}\) or \(J^{\text{Yam}} = -0.57\ \text{cm}^{-1}\) (Table 3). The question then arises: why does the same DFT method result in such unequal results upon comparison with the magnetic analysis? We can speculate that these discrepancies are due to small changes in the crystal structures, which may occur at a lower temperature than that used for X-ray analysis. To test this possibility, we performed a constrained geometry optimization for the \([\text{Fe}^{III}(L4c)[\text{H}_2\text{O}])_2\) molecular fragment of 4a, where the \(\text{Fe} \cdots \text{Fe}\) distance was varied between 4.4 and 4.9 Å. The geometry was optimized using the BP86 functional with a def2-TZVP(-f) basis set together with a conductor-like screening model (COSMO), van der Waals corrections (VDW10) and the relativistic effects with the scalar relativistic second-order Douglas–Kroll–Hess Hamiltonian (DKH2). Afterwards, the \(J\)-values were calculated at the B3LYP + DKH2/def2-TZVP level of theory for each of the optimized molecular structures to ensure the same condition as that used for the molecular fragments of 3a–11 based on their X-ray structures.

This resulted in the magneto-structural correlation depicted in Fig. 8, from which we can conclude that the antiferromagnetic exchange is increasing with decreasing Fe–Fe separation. However, the change of \(\Delta J_{(\text{DFT})}/\Delta d_{\text{Fe-Fe}} \approx 0.5–1.0\ \text{cm}^{-1}/\text{Å}\) cannot explain the large discrepancies between

\[ \text{Fig. 8 The calculated isotropic exchange } J^{\text{Ruiz}} \text{ (circles)} \text{ and } J^{\text{Yam}} \text{ (squares) as a function of the Fe–Fe distance (left) and the O_{Ph}–O_{S} distance (right) in the } ([\text{Fe}(L4c)[\text{H}_2\text{O}](\text{NC}))_2 \text{ molecular fragment of 4a calculated using B3LYP + DKH2/def2-TZVP, while the molecular geometries were optimized using BP86 + COSMO + VDW10 + DKH2/def2-TZVP(-f)).} \]
$J_{\text{DFT}}$ and $J_{\text{mag}}$ in terms of possible small changes in the crystal structures induced by cooling to a very low temperature.

Thus, we also tested another hypothesis relating to the positions of the hydrogen atoms in the molecular/crystal structure. It is well known that determination of the hydrogen atom positions from X-ray analysis can be potentially inaccurate, especially when the hydrogen atoms are bonded to atoms with high electronegativities such as oxygen or nitrogen atoms. This was also pointed out in several DFT studies devoted to magnetic exchange mediated by hydrogen bonds in other transition metal complexes. Due to these reasons we have to find out how the positions of hydrogen atoms influence the magnetic exchange interactions. Therefore, the positions of hydrogen atoms involved in magnetic exchange pathways (in H-bond bridged dinuclear molecular fragments $[[\text{M}^{\text{III}}(L4)(H2O)(NC)]_2]_2$ ($\text{M} = \text{Fe, Mn}$) (4a, 5a, 4b, 7a, and 7e) and also for $[[\text{Mn}(L4)\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\·
substances were washed with diethyl ether and dried in a vacuum; yields were higher than 97%.

**Synthesis of the precursors** [Fe(L4a)Cl] (1a) [Mn(L4a)Cl] (1b), [Fe(L4b)Cl] (1c), [Fe(L4c)Cl] (1d), [Mn(L4c)Cl] (1e), [Fe(L4d)Cl] (1f) and [Mn(L4e)Cl] (1g)

A solution of 10 mmol of FeCl3·6H2O or MnCl2·4H2O in 10 mL of methanol was added to a solution of 10 mmol of H2L4a–H2L4e in 20 mL of ethanol. The mixture was stirred for 10 min, and then 20 mmol of triethylamine in ethanol (10 mL) was added. The resulting solution was refluxed for 2 h, then after cooling, diethyl ether was added, which resulted in precipitation of a black or a brown powder. The solid was filtered off, washed with diethyl ether and dried in a vacuum; yields were higher than 90%.

**Synthesis of the complexes** 2a–6b

The dark-brown crystals or dark powders of complexes 2a–6b were obtained from a methanol solution (40 mL) of complexes 1a–1g (0.2 mmol) combined with a methanol–water mixture (1:1) of Na2[Fe(CN)5(NO)]·2H2O (0.1 mmol). The solutions were stirred at room temperature for 4 h. Slow evaporation of the resulting solutions at room temperature afforded the complexes as black single crystals suitable for X-ray diffraction after a week. Black crystals were filtered off, washed twice with water and diethyl ether and dried in a vacuum.

$$\text{[Fe(L4a)(H}_2\text{O)}_2\text{][Fe(CN)}_5\text{NO)}\text{]·CH}_3\text{OH (2a). Yield: 76\%}}$$

Analyzed for C45H48N10O11Mn2Fe1; C, 50.48; H, 4.51; N, 13.08.

**General methods**

FT-IR (Nujol, cm$^{-1}$): 518m; 489m; 452m; 493m; 3514m; 3037m (C–H)ar; 2982w (C–H)alip; 2939w (C–H)alip; 2152w (C≡N); 1917m (ν=N=O); 1625s (ν=C=N); 1595m; 1541m; 1472m (ν=C≡C); 1452s (ν=C≡C); 1357w; 1274w; 1222w; 1193w; 1157w; 1114w; 1100w; 1039w; 1018w; 945w; 858w; 752m.

**FT-IR spectroscopy**

FT-IR (KBr, cm$^{-1}$): 1618vs $\nu$(C=O); 1614vs $\nu$(C=O); 1594s (ν=N=O; 1543m (ν=C≡C); 1463m (ν=C≡C); 1443m (ν=C≡C); 1395; 1345w; 1322w; 1250m; 1218m; 1180m; 1100w; 1076w; 1037w; 1014w; 895w; 850w; 769w; 763w; 732m; 690w; 603m.

**TG/DTA analyses**

TG/DTA (KBr, cm$^{-1}$): 3132w; 3074w (C≡N); 2912m; 2859w; 2163m (C≡N); 1922m (ν=N=O); 1618s (ν=C≡N); 1593m; 1544m; 1463m (ν=C≡C); 1443m (ν=C≡C); 1395; 1307w; 1268w; 1233w; 1196w; 1148w; 1052w; 1006w; 995w; 907w; 851w; 753m; 677w.

**Found**

C, 50.52; H, 4.64; N, 13.07. **Calcd** for C45H48N10O11Mn2Fe1: C, 50.39; H, 4.67; N, 13.06. Found: C, 50.55; H, 4.64; N, 13.27%. **Calcd** for C45H48N10O11Fe3: C, 50.39; H, 4.67; N, 13.06. Found: C, 50.52; H, 4.69; N, 13.33%.

**Elemental analyses**

Elemental analysis (CHNS) was performed on a FLASH 2000 CHNS Analyzer (ThermoFisher Scientific). Infrared spectra of the complexes were recorded on a ThermoNicolet NEXUS 670 FT-IR spectrometer using the KBr technique on a diamond plate in the range 400–4000 cm$^{-1}$ and Nujol techniques in the range 150–600 cm$^{-1}$. Thermogravimetric (TG) and differential thermal analyses (DTA) were measured on an Exstar TG/DTA 6200 thermal analyzer (Seiko Instruments Inc.). TG/DTA studies were performed in ceramic pans from room temperature to 850 °C with a 2.5 °C min$^{-1}$ temperature gradient in a dynamic air atmosphere (100 mL min$^{-1}$).
Single-crystal X-ray analysis details

X-ray measurements on the selected crystals of 3a–6b were performed on an Oxford Diffraction Xcalibur™ equipped with a Sapphire2 CCD detector using Mo-Kα radiation at 100 K. The CrysAlis program package (version 1.171.33.52, Oxford Diffraction) was used for data collection and reduction. The molecular structures were solved by direct methods SHELX-97 and all non-hydrogen atoms were refined anisotropically on F² using full-matrix least-squares procedure SHELXS-97. All the hydrogen atoms were found in differential Fourier maps and their parameters were refined using a riding model with Uiso(H) = 1.2 (CH, CH2, OH) or 1.5 (CH3) Ueq. Non-routine aspects of the structure refinements are as follows: in compounds 3a, 4a, 5a and 6b the Fe atom of the nitroprusside lies at the inversion center with disorder of the nitrosyl and cyanido groups in two trans positions. Occupation factors for both disordered parts were set to 0.5.

DFT calculations

The theoretical calculations were done with the ORCA 2.9.1 computational package. The magnetic exchange (J) was calculated using the hybrid B3LYP functional. The broken-symmetry (BS) spin state was generated by the “Flip-Spin” feature of the ORCA program and the isotropic exchange constants J were calculated both by Ruiz’s formula and the Yamaguchi approach. The polarized triple-ξ quality basis set (def2-TZVP) proposed by Ahlrichs and co-workers was used for all atoms. The relativistic effects were dealt with using the scalar relativistic second-order Douglas–Kroll–Hess Hamiltonian (DKH2) together with a relativistically recomputed version of the def2-TZVP basis set. The calculations utilized the RI approximation with the decontracted auxiliary def2-TZVP/J Coulomb fitting basis set and the chain-of-spheres (RIJCOSX) approximation to exact exchange as implemented in ORCA. Increased integration grids (Grid5 and Gridx5 in ORCA convention) and tight SCF convergence criteria were used in all calculations. The geometry optimization of molecular fragment [Fe(L4)2(H2O)(NC)]2− (4a) was done using the BP86 functional with the def2-TZVP(f) basis set together with the conductor-like screening model (COSMO), van der Waals corrections (VDW10) and DHK2. The positions of hydrogen atoms in H-bond bridged dinuclear molecular fragments [MIII(L4)(H2O)(NC)]2− [M = Fe, Mn] (4a, 5a, 4b, 7a and 7e) and also for [Mn(L4)2(H2O)(NCS)]2− (8 and 9) were calculated again with BP86/de2-TZVP(f).

Conclusions

We have reported the synthesis of trinuclear iron(II) and manganese(II) (2a–5a) and dinuclear manganese(II) (6b) Schiff base complexes utilizing the nitroprusside anion, [FeII(CN)5NO]2−, as a building block. The compounds were characterized by various physical methods (elemental analysis, FT-IR, TG/DTA, single-crystal X-ray analysis), which clearly confirmed their compositions and molecular/crystal structures. It was observed that coordinated water molecules are responsible for the formation of supramolecular 1D chains (3a–5a) or supramolecular dimers (6b) through O–H⋯O hydrogen bonds. Thorough magnetic analysis, which consisted of the concurrent fitting of temperature and field dependent powder magnetic data, played an important role in properly identifying values of the isotropic exchange J-parameters and zero-field splitting D-parameters.

This enabled us, in harmony with DFT calculations of J-parameters, to confirm weak antiferromagnetic exchange (J ≈ −0.5 to −1.3 cm⁻¹) between metal atoms mediated by O–H⋯O hydrogen bonds, while the super-exchange path through the diamagnetic nitroprusside anion was found to be negligible. Moreover, a detailed DFT study was performed to explain some discrepancies between J-values derived from magnetic analysis and DFT calculations themselves. We demonstrated that such DFT calculations are very sensitive to the position of the hydrogen atoms within the O–H⋯O hydrogen bond forming a super-exchange pathway. To summarize, the strength of the magnetic exchange in this class of complexes is controlled by the number of O–H⋯O(H) hydrogen bonds between metal atoms and by the O–O⋯O distance between the phenolic oxygen atom of the salen-type ligand (O₈) and the oxygen atom of solvent (water, methanol) molecules coordinated to the neighbouring metal atom (O₉). These results help to understand magnetic exchange interactions through hydrogen bonding within supramolecular [MIII(L4)(Solv)]−⋯[MIII(L4)(Solv)]⁺ dimers and they might be useful for estimating the strength of such interactions in more magnetically complicated systems (e.g. systems with paramagnetic bridging complexes or systems possessing magnetic ordering or slow-relaxation of magnetization).

Acknowledgements

We acknowledge the financial support from the Czech Science Foundation (GAČR P207/11/0841), the Operational Program Research and Development for Innovations – European Regional Development Fund (CZ.1.05/2.1.00/03.0058) of the Ministry of Education, Youth and Sports of the Czech Republic, and Palacký University (PrF_2013_015 a 2014009). The authors would like to thank Dr Radka Křížková for infrared spectroscopy measurements.

Notes and references

2 (a) V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson and W. E. Hatfield, Inorg. Chem., 1976, 15, 2107; (b) J. Glerup, D. J. Hodgson and E. Pedersen, Acta Chem. Scand., 1983, 37, 161; (c) S. M. Gorun and


32 The standard deviations were calculated as $σ_i = (P_{ii}^{-1} S(N - k))^{1/2}$, where $P_{ij} = \sum (δμ_i/δn_i)(δμ_j/δn_j)$ and $S = \sum (μ_n - μ_n^{\exp})^2$ with $n = 1$ to $N$; $a_i$ and $a_j$ are fitted parameters, $N$ is number of experimental points (sum of temperature and field dependent data), $μ_n$ and $μ_n^{\exp}$ are the calculated and experimental effective magnetic moments for a given temperature and magnetic field. The $σ_i$ was then multiplied by Student’s $t_{95%}$ to provide confidence limits with 95% probabilities listed in text.


