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A self-assembled octanuclear complex bearing the uncommon close-packed $\{Fe_4Mn_4(\mu_4\text{-}O)_4(\mu\text{-}O)_4\}$ molecular core†

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A one-pot open-air reaction of manganese powder with iron(II) chloride in DMF solution of the Schiff base (H_2L) formed *in situ* from salicylaldehyde and hydroxylamine hydrochloride yields the heterometallic complex $[Fe_4(\mu_4\text{-}O)_4Mn_4(L)_8(DMF)_4]\cdot 2DMF$ (**1**). Single crystal X-ray analysis shows that its molecular structure is based on the octanuclear core $\{Fe_4Mn_4(\mu_4\text{-}O)_4(\mu\text{-}O)_4\}$ with a quite rare molecular structure type $\{M_8(\mu_4\text{-}X)_4(\mu\text{-}X)_4\}$, where the central cube-like iron motif is modified with four terminal manganese fragments, the whole core being presented as the $\{Fe_4(\mu_4\text{-}O)_4\}$ + $4\{Mn(\mu\text{-}O)\}$ combination. Using the data from the Cambridge Structural Database (CSD), an analysis of the octanuclear structures with similar central $\{M_4(\mu_4\text{-}X)_4\}$ fragments was performed. The hierarchical order of molecular structure types with the general formula M_8X_n for such compounds was proposed and the topological features as well as the factors that influence the molecular type formation are discussed. Variable-temperature (1.8–300 K) magnetic susceptibility measurements reveal an antiferromagnetic coupling among the magnetic centres in **1**.

Introduction

Sophisticated topologies and intriguing physico-chemical properties are the relevant factors which determine a continued interest in high nuclear coordination compounds. High symmetry complexes possessing close-packed metal cores are within the most interesting objects in this field.[1] Moreover, by introducing few different metals into one molecule, it is possible not only to affect the complexity and structural diversity of the resulting heterometallic assembly but also to influence its spin ground states, magnetic anisotropy, exchange interactions and other magnetic properties.[1c,2] Besides, a combination of different metal centres within one complex can lead to uncommon physico-chemical properties.[3] This provides a background for building novel structure–property correlations.

The majority of high nuclear complexes with close-packed cores have been prepared *via* the spontaneous self-assembly of metal ions and relatively simple ligands.[1,4] This approach can lead to sophisticated coordination assemblies using non-laborious one-step protocol. However, in spite of the synthetic simplicity of such a method, it shows quite a low efficiency (yield of successful syntheses within the range of screened conditions) on account of considerable unpredictability. Although a huge number of high nuclear complexes has already been obtained, the exact structure and composition of the final product are hardly or, most commonly, completely not predictable before their isolation. Furthermore, the synthesis of heterometallic high nuclear complexes by spontaneous self-assembly is an even more complicated task, because the increasing number of initial reagents leads to a greater variety of their possible combinations. Therefore, there is a need for the study of synthesis–structure correlations in the self-assembly of poly- and high-nuclear species, as well as for the establishment of clear and definite classifications of their coordination cores.

In pursuit of our interest on the synthesis and investigation of high nuclear coordination compounds, we have expanded the classical spontaneous self-assembly approach and successfully applied the "direct synthesis of coordination compounds" method for the preparation of novel complexes.[4] The relevant features of this strategy are simplicity and "straightforward" formation of a complex high nuclear structure "directly" (upon

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one experimental stage) from metal powder(s). Using such conditions we have already obtained a series of uncommon heterometallic high nuclear $Cu^{II}_2Fe^{III}_2$,[5] $Co^{III}_2Fe^{III}_2$,[6] $Co^{III}_4Fe^{III}_4$,[6] and $Co^{III}_4Fe^{III}_2$[7] compounds with Schiff base aminoalcohol ligands[5–7] and determined the main factors responsible for the molecular structure type formation. Furthermore, we have shown that the synthesized complexes reveal an exceptionally high catalytic activity in the oxidation of cyclohexane with hydrogen peroxide under mild conditions, as well as an interesting magnetic behaviour.[5,7] In the current work, we have investigated the interaction of manganese powder and iron(II) chloride with an *in situ* formed Schiff base O,O,N-ligand that afforded the novel octanuclear $[Fe_4(\mu_4\text{-}O)_4Mn_4(L)_8(DMF)_4]\cdot 2DMF$ (**1**) coordination compound with an extremely rare type of molecular core, now observed for the first time for a heterometallic transition metal complex. The synthesis and magnetic investigation of **1**, as well as a discussion concerning its molecular structure type formation and analysis of octanuclear crystal structures having M_8X_n cores with the general $\{M_4(\mu_4\text{-}X)_4\}$ fragment are also reported.

Results and discussion

Synthesis and spectroscopic analysis

The condensation of salicylaldehyde and hydroxylamine hydrochloride in a basic (triethylamine) medium in DMF afforded the *in situ* formation of the Schiff base H_2L (Scheme 1). The manganese powder and iron(II) chloride were added to the solution of H_2L in the same reaction vessel and the reaction was brought to completion by heating and stirring until the total dissolution of manganese was observed (approximately 1 h). Dark-red microcrystals of **1** that showed analytical data consistent with the Fe(III) : Mn(III) = 1 : 1 stoichiometry were formed within six months after the addition of ^iPrOH and Et_2O into the resulting solution. Complex **1** was the unique product obtained from the reaction mixture. Reactions performed in DMSO or CH_3CN (typical solvents for the direct synthesis conditions[4]) did not afford any isolated product. When CH_3OH was employed as a solvent, a homometallic compound of manganese was the only product. Single crystal X-ray analysis disclosed its trinuclear structure with the formula $[Mn_3OCl_2(L_3)(CH_3OH)_2(H_2O)_2]\cdot H_2O$.[8] The general reaction of formation of **1** can be written as follows:

$$4Mn^0 + 4Fe^{II}Cl_2\cdot 4H_2O + 8H_2L\cdot HCl + 16Et_3N + 4O_2 + 6DMF \rightarrow [Fe^{III}_4(\mu_4\text{-}O)_4Mn^{III}_4(L)_8(DMF)_4]\cdot 2DMF + 16Et_3N\cdot HCl + 20H_2O$$

Single crystal X-ray analysis (see below) shows that the molecular core of **1** $\{Fe_4Mn_4(\mu_4\text{-}O)_4(\mu\text{-}O)_4\}$ can be viewed as a central cube-like iron motif $\{Fe_4(\mu_4\text{-}O)_4\}$ supplemented with four manganese fragments $\{Mn(\mu\text{-}O)\}$. According to the Cambridge Structural Database (CSD),[9] cube-like $\{M_4(\mu_4\text{-}X)_4\}$ (M = metal atom, X = bridging atom) is the most widespread molecular structure type for tetranuclear coordination compounds. Among them there are a lot of complexes of iron with Schiff base ligands.[10] Therefore, one could assume that the formation of the core of **1** starts from the assembling of the iron cube-like structure formed prior to the dissolution of the manganese powder:

$$4FeCl_2 + 4H_2L + 4DMF \rightarrow [Fe_4(L)_4(DMF)_4] + 8HCl$$

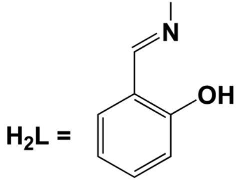
Such reactions are known to proceed with high yield under mild conditions with the Schiff bases formed from salicylaldehyde and simple aliphatic aminoalcohols, such as ethanolamine.[10c] However, the behaviour of H_2L is known to be considerably different due to the absence of the $-CH_2CH_2OH$ arm, which allows the formation of stable chelates. The known products of the interaction of iron salts with H_2L are tetranuclear cores with a distorted geometry, where the oxime group serves as a bridge (M–N–O–M):[11]

$$4Fe^{II}Cl_2 + 8H_2L + O_2 \rightarrow [Fe^{III}_4(L)_4(HL)_4] + 8HCl + 2H_2O$$

The tetranuclear compound with such a structure is a presumable intermediate in the formation of **1**. It should be noted that further growth of the nuclearity towards the octanuclear iron core $[Fe_8(L)_8]$, similar to that in **1**, can be supposed as an unfavourable process, which requires harsh (solvothermal) or specific (microwave synthesis) conditions.[12] Due to gradual oxidation of Mn^0 powder, the equilibrium concentration of "free" manganese ions in the reaction mixture should be quite low: Mn^{II} and Mn^{III} ions are very labile and easily participate in substitution coordination reactions. Thus, all the manganese ions should readily react with excess of the ligand and iron intermediate to form complex **1**:

$$Mn^0 + H_2L + [Fe^{III}_4(L)_4(HL)_4] + O_2 \rightarrow \mathbf{1}$$

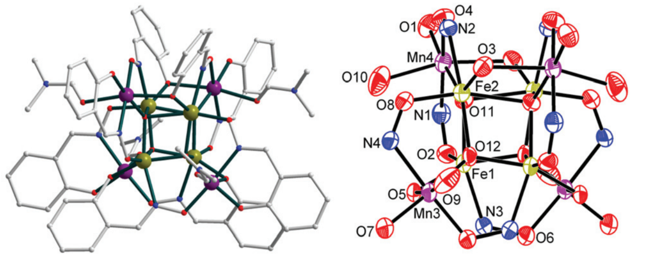
The IR spectrum of **1** in the 4000–400 cm^{-1} range shows a very strong band at 1598 cm^{-1} which is assigned to $\nu(C{=}N)$ of the Schiff base ligand. The strong peak at 1647 cm^{-1} and the shoulder at 1668 cm^{-1} are attributed to $\nu(C{=}O)$ the vibrations of coordinated and solvate molecules of DMF, respectively.



Scheme 1

Crystal structures

The single crystal X-ray analysis reveals that **1** (Fig. 1) features the octanuclear core $\{Fe_4Mn_4(\mu_4\text{-}O)_4(\mu\text{-}O)_4\}$, belonging to the $\{M_8(\mu_4\text{-}X)_4(\mu\text{-}X)_4\}$ (M = metal atom, X = bridging atom) molecular structure type (MST). This MST is obtained excluding all

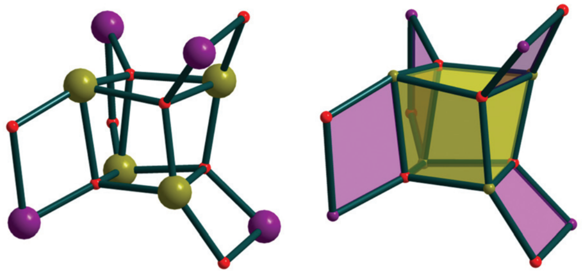


(a) (b)

Fig. 1 Molecular structure of **1** in the ball-and-stick representation (a) and the central part of **1** with atom numbering (b) where non-hydrogen atoms are shown as 40% ellipsoids. The hydrogen atoms and carbon atoms in (b) are omitted for clarity. Colour scheme: Fe, olive; Mn, violet; O, red; N, blue; C, light grey.

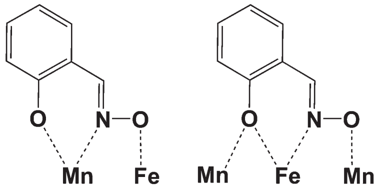
non-bridging non-metal atoms of the coordination core of the complex. The whole core $\{Fe_4Mn_4(\mu_4\text{-}O)_4(\mu\text{-}O)_4\}$ can be described as a cube-like iron structure modified with four terminal manganese fragments $\{Fe_4(\mu_4\text{-}O)_4\}$ + $4\{Mn(\mu\text{-}O)\}$ (Fig. 2).

All Schiff bases H_2L in the structure are doubly deprotonated and show tridentate coordination (N,O,O) in two different modes (Scheme 2), thus being responsible both for the molecular structure type formation and for the metal ion charge compensation. Compound **1** contains two crystallographically independent iron(III) metal ions, Fe(1) and Fe(2), and two independent manganese(III) atoms, Mn(3) and Mn(4), each having a distorted octahedral environment with an O_5N donor set. In contrast to the iron(III) atoms, the coordination spheres of the manganese(III) ones also involve the oxygen atoms from coordinated DMF molecules. The Fe–O(N) bond lengths range from 1.921(5) to 2.265(5) Å, while the Mn–O(N) distances vary from 1.865(4) to 2.279(5) Å (Table S1†). The O(N)–M–O(N)$_{trans}$ angles lie in the range of 149.15(18) to 162.1(2)° for iron(III) and 165.4(2) to 176.4(2)° for manganese(III).



(a) (b)

Fig. 2 The ball-and-stick (a) and polyhedral (b) representations of the octanuclear $\{Fe_4Mn_4(\mu_4\text{-}O)_4(\mu\text{-}O)_4\}$ core in **1**. Color scheme: Fe, olive; Mn, violet; O, red.



Scheme 2

A huge variety of high nuclear coordination compounds has been reported and their number continues to grow.[13] In this broad field of coordination chemistry, the comparison and classification of the newly prepared compounds can be a complicated task. Often, identical compounds from the topological point of view are drastically different from the chemical one. An even more difficult task is to predetermine and predict the final structure of the high nuclear assembly. The idea that the majority of the crystal structures of high nuclear complexes can be covered by the limited number of molecular structure types, where the MST is seen as a set of topologically identical M_aX_b combination (M = metal atom, X = bridging atom),[4,14] can be not only helpful in the classification of such compounds but also can result in an impressive progress in their targeted synthesis. Bearing these ideas in mind, we continued to investigate the properties of molecular structure types of newly obtained high nuclear complexes and compared our data with the statistical ones obtained from the CSD.

The MST $\{M_8(\mu_4\text{-}X)_4(\mu\text{-}X)_4\}$ observed in **1** is found to be rather rare, according to the CSD. The CSD contains *ca.* 600 records of the octanuclear complexes and, among them, only 4 structures with the same MST as in **1** are found.[15] Moreover, compound **1** represents the first example of a heterometallic transition metal complex possessing such a MST.

Trying to find a topological place of **1** in the group of octanuclear compounds, we chose complexes similar to **1** with a cube-like central fragment $\{M_4(\mu_4\text{-}X)_4\}$ modified with terminal metal-containing groups. Analysis of CSD data shows that only 57 hits of such a type are found. The carbonyl (M–C–O) and the organometallic (M–C–C) compounds, as well as coordination polymers and polyoxometalates, were excluded according to the search conditions. We succeeded in building a hierarchical order of these complexes, which includes 4 different MSTs, distinguished from each other by the number of μ-X bridging atoms (Fig. 3).

The first and simplest member of this row is the MST $\{M_8(\mu_4\text{-}X)_4\}$ (a), where four terminal metal atoms are coordinated by each bridging atom of the cube fragment (Fig. 3). This type of compound is the most abundant and includes complexes of two categories – unsupported, where terminal metal atoms do not have any additional coordination (20 hits in CSD), and supported, where terminal metal atoms are connected with metal atoms from the cube through the bridges M–X–X⋯–M (22 hits, the search includes hits with 2, 3 and 4 bridging X atoms in the terminal fragments) (Fig. 4). In the majority of the second type crystal structures, the supporting bridges are carboxylate and pyrazole-containing ligands. The presence of such additional bridges is essential for the com-

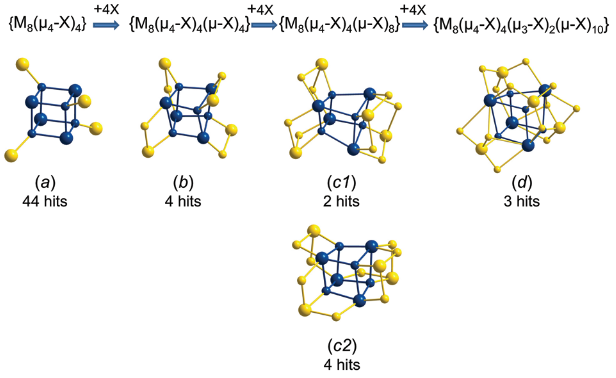


Fig. 3 Hierarchical order of MSTs M_8X_n for octanuclear complexes with the similar cube-like central fragment $\{M_4(\mu_4\text{-}X)_4\}$, modified with terminal metal-containing groups and distribution of known complexes according to CSD.

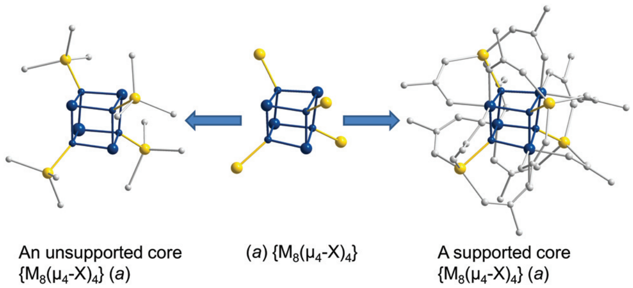


Fig. 4 Examples of complexes belonging to unsupported (exemplified by $[\mathrm{Me_3SnOZnMe}]_4)^{16}$ and supported (exemplified by $[\mathrm{Co^{II}_4Co^{III}_4}(\mu_4\text{-}\mathrm{O})_4(\mu\text{-}\mathrm{O_2CPh})_{12}(\mathrm{C_2H_5OH})_4]\cdot 3\mathrm{C_3H_6O}\cdot\mathrm{C_2H_6O})^{17}$ types of the of MST $\{M_8(\mu_4\text{-}X)_4\}$ (a).

pounds of transition metals which allow a wide range of geometries and coordination numbers, while the unsupported $\{M_8(\mu_4\text{-}X)_4\}$ type is common for complexes of p-metals.

The addition of four bridging atoms to MST $\{M_8(\mu_4\text{-}X)_4\}$ (a) (Fig. 3) affords the MST $\{M_8(\mu_4\text{-}X)_4(\mu\text{-}X)_4\}$ (b), found in complex **1** and in some reported O-bridged Mn_8,[15a,c] Fe_8 [15b] and Se-bridged $\mathrm{Mn_4Li_4}$ [15d] clusters. It should be noted that all known octanuclear compounds with this MST show the same geometrical configuration (b1) (Fig. 5), although one of them could reveal the existence of the other topology (b2), which has no examples in the CSD yet. Obviously, the formation of complexes with the same MST but with a different geometrical configuration, at the least (b2), is also possible. One can suggest that for the construction of such compounds, rigid and bulky ligands could be used simultaneously, which are successfully employed in the synthesis of complexes with MST (c) with a similar type (c2) of structural configuration.

The next MST $\{M_8(\mu_4\text{-}X)_4(\mu\text{-}X)_8\}$ (c) (Fig. 3) can be formed by the addition of four more bridging atoms to the MST (b). According to CSD, this MST includes examples of two predicted geometrical configuration (c1 and c2). The first type (c1) contains two pairs of terminal groups fasted to the two opposite faces of a cube-like central fragment. Such configurations are observed in two bismuth complexes, in which crystal structures display dimeric units formed by two tetrametalated calixarenes.[18] In the second type (c2), four terminal groups sequentially coordinate to four neighbouring faces. This type of geometrical configuration is reported for $[(\mathrm{CaO})_4\cdot 4(\mathrm{THF})_3\mathrm{CaI_2}]$,[19] $[\mathrm{MgTaO(OBu}\text{-}n)_5(n\text{-}\mathrm{BuOH})]_4$,[20] $[\{\mathrm{FeCl}(\mathrm{H_2L})\}_4\mathrm{Fe_4}(\mu_4\text{-}\mathrm{O})_4\mathrm{Cl_4}]$ ($\mathrm{H_4L}$ = $\mathrm{N[(CH_2CH_2NH_2)(CH_2CH_2OH)(CH_2CH_2CH_2OH)]}$)[21] and $[\mathrm{V_8O_{20}}(4,4'\text{-}{}^t\mathrm{Bubpy})_4]$[22] octanuclear complexes.

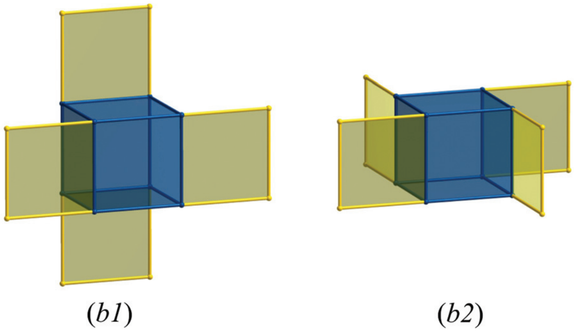


Fig. 5 The polygonal representation of known (b1) and the suggested (b2) structure configurations of the MST $\{M_8(\mu_4\text{-}X)_4(\mu\text{-}X)_4\}$ (b) (see the text).

The MST $\{M_8(\mu_4\text{-}X)_4(\mu_3\text{-}X)_2(\mu\text{-}X)_{10}\}$ (d) (Fig. 3) is observed only in three $\mathrm{Ti_4Ba_4}$ crystal structures[23–25] and it is the most complex one since it is formed using 16 bridging atoms. A determining role in the formation of such structures conceivably is the ability of Ti and Ba to show high coordination numbers, supported by the small size of coordinated isopropanol ligands.

Looking at the hierarchical order of the octanuclear MSTs a–d (Fig. 3), observed from the CSD, one may notice that bridging atoms X are always added "four-by-four": from the simplest M_8X_4 (a) to the most complex M_8X_{16} (d). Therefore, the general formula of the MSTs of this series can be written as M_8X_{4n} (n = 1–4). These MSTs possess the highest possible symmetry for each case, from cubic type a (T_d) to monoclinic d (C_2) (Fig. 3). The elimination of even one X atom from the $4n$ complete set of bridging X atoms (non-M_8X_{4n} MST) would result in a lower symmetry, in general. No structures belonging to non-M_8X_{4n} MSTs have been found in the CSD, although there are no obvious geometrical or topological restrictions for their existence. These observations, as well as previous statistical studies[1e,4,7,14b] on the CSD, point to the assumption that poly- and high-nuclear species tend to form symmetrical cores (MSTs).

Magnetic properties

Four Fe(III) and four Mn(III) high-spin centres in the molecule of **1** result in a limiting value of the dimensionless product function

$$\chi T/C_0(HT) = 4g_{\mathrm{Fe}}{}^2 s_{\mathrm{Fe}}(s_{\mathrm{Fe}}+1)/3 + 4g_{\mathrm{Mn}}{}^2 s_{\mathrm{Mn}}(s_{\mathrm{Mn}}+1)/3 \quad (1)$$

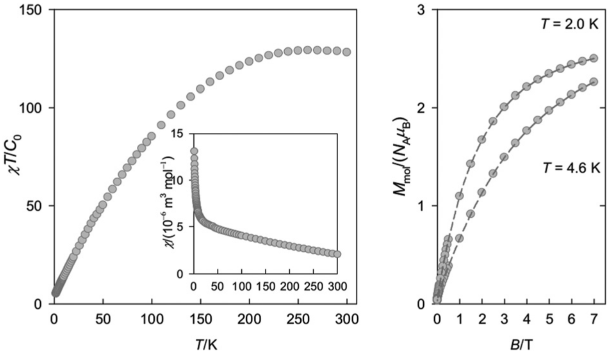


Fig. 6 Magnetic functions for **1**. Left – product function, right – magnetization per formula unit, inset – molar magnetic susceptibility (SI units, χ(SI) = χ(cgs emu) ($4\pi \times 10^{-6}$).

which amounts to 78.7 when $s_{Fe} = 5/2$, $s_{Mn} = 2$, and all g = 2.0 ($C_0 = N_A\mu_0\mu_B{}^2/k_B$ contains universal physical constants in their usual meaning). On cooling, the product function gradually decreases from its room temperature value of $\chi T/C_0$ = 128 to the value of 5.3 at T = 1.9 K (Fig. 6) and down to 2.0 K; the molar magnetic susceptibility only increases showing no maximum. This feature indicates a dominating antiferromagnetic coupling among the magnetic centres through a delicate balance with several coupling constants that could reveal that the state of the highest spin is not the highest in energy and also the state with S = 0 may not be the lowest in energy. The abnormal room-temperature value of the χT product may arise due to several reasons: increased g-factors, high temperature-independent (para)magnetism, spin delocalization in the $d^4d^4d^4d^4d^5d^5d^5d^5$ system, and a local Jahn–Teller effect on Mn (III) centres. Also a non-isotropic exchange interaction (the asymmetric and antisymmetric exchange) can be applied and in such a case the spin is not a good quantum number any longer.

The molar magnetization per formula unit possesses the saturation limit $M_1 = M_{mol}/N_A\mu_B = 4g_{Fe}s_{Fe} + 4g_{Mn}s_{Mn}$ which yields M_1 = 36 for S_{max} = 18. The measured magnetization adopts a value of only M_1 = 2.5 at T = 2.0 K and B = 7 T. This reduction is a fingerprint of the antiferromagnetic exchange, eventually combined with the single-ion anisotropy. The Fe(III) centres could be considered as isotropic ($g_{Fe} \sim 2.0$, $D_{Fe} \sim 0$), while the Mn(III) ones are slightly anisotropic ($g_{Mn} < 2.0$, $|D_{Mn}| > 0$).

The number of magnetic energy levels in complex **1** is $N = 6^4 \times 5^4$ = 810 000; the number of spin states at zero magnetic field with M_S = 0 is N_{zf} = 71 346. The numbers of states for S_{min} = 0 until S_{max} = 18 are 1650, 4735, 7221, 8844, 9500, 9250, 8290, 6890, 5326, 3829, 2555, 1576, 892, 458, 210, 84, 28, 7, and 1. These numbers represent the dimensions of blocks for which the eigenvalues need to be evaluated. The complication arises from the fact that the Zeeman term mixes the states of different spins. This complexity prevents a fitting of the magnetic data for **1** at present.

Conclusions

We have successfully applied the direct synthesis approach for the preparation of the novel octanuclear $Fe^{III}Mn^{III}$ Schiff base complex **1**. Its crystal structure reveals the uncommon $\{M_8(\mu_4\text{-}X)_4(\mu\text{-}X)_4\}$ type of molecular core, the formation of which is discussed and the analysis of octanuclear structures with the similar central $\{M_4(\mu_4\text{-}X)_4\}$ fragment is performed. It has been demonstrated, by means of the search *via* the Cambridge Structural Database, that the molecular structure type of **1** belongs to a family of M_8X_{4n} MSTs, (where n = 1–4), which differ one from another by four bridging X atoms. The topological study reveals the presence of one more possible molecular structure type of this series (a topological isomer of the MST of **1**), which still has no examples in the CSD. The obtained data lead to the assumption that the more symmetrical coordination cores (MSTs) are favoured over the less symmetrical types, at least within the studied row of complexes. This assumption is important in terms of developing a concept of a predictable self-assembly synthesis of high-nuclear complexes, especially those with close-packed molecular cores. The magnetic investigations of **1** disclose an antiferromagnetic coupling between the paramagnetic centres.

Experimental section

General

General: All chemicals were of reagent grade and used as received. All experiments were carried out in air. Infrared spectra (4000 – 400 cm^{-1}) were recorded on a BX-FT IR "Perkin Elmer" instrument in KBr pellets.

Synthesis of $[Fe_4(\mu_4\text{-}O)_4Mn_4(L)_8(DMF)_4]\cdot 2DMF$ (1). Salicylaldehyde (0.27 cm^3, 2.5 mmol), hydroxylamine hydrochloride (0.174 g, 2.5 mmol) and triethylamine (0.7 ml, 5 mmol) were dissolved in DMF (25 cm^3) in this order, forming a yellow solution which was magnetically stirred at 50–60 °C (10 min). Then, manganese powder (0.069 g, 1.25 mmol) and $FeCl_2\cdot 4H_2O$ (0.249 g, 1.25 mmol) were added to the hot yellow solution of the ligand and the system was magnetically stirred until the total dissolution of manganese powder was observed (1 h). A dark-red solution was obtained at the end of the reaction. X-ray suitable microcrystals of **1** were formed within six months after the addition of ^iPrOH and Et_2O into the resulting solution. Yield: 0.1 g, 16%. Anal. calc. for $C_{74}H_{82}Fe_4Mn_4N_{14}O_{26}$ (M = 2026.70): C, 43.86; H, 4.08; N, 9.68; Fe, 11.02; Mn, 10.84%. Found: C, 43.4; H, 4.0; N, 9.3; Fe, 11.8; Mn, 11.1%.

Crystallography

Crystal data for **1**: $C_{74}H_{82}Fe_4Mn_4N_{14}O_{26}$, M = 2026.70, monoclinic, $P2/c$, a = 16.509(2) Å, b = 11.1843(17) Å, c = 27.176(4) Å, β = 122.487(10)°, V = 4232.6(10) $Å^3$, Z = 2, d_{calc} = 1.590 g sm^{-1}, μ = 1.326 mm^{-1}, F(000) = 2072. 33 908 reflections (7469 independent, R_{int} = 0.155) were collected on an "Xcalibur-3" diffractometer (MoK_α radiation, CCD-detector, graphite monochromator, ω-scanning, $2\theta_{max}$ = 50°). The empirical absorption correction was provided with a multi-scan method using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm of the CrysAlisPro program package ($T_{\min}$ = 0.970, $T_{\max}$ = 1.000).[26] The structure was solved by direct methods and refined against F^2 within the anisotropic approximation for all non-hydrogen atoms using the OLEX2 program package[27] with SHELXS and SHELXL modules.[28] All H atoms were placed in idealized positions and constrained to ride on their parent atoms with $U_{\text{iso}} = nU_{\text{eq}}$ (n = 1.5 for CH_3 groups and n = 1.2 for other H atoms). During the refinement, bonds in the solvent DMF molecule were constrained to have fixed values (1.25 Å for O1S–C1S, 1.35 Å for C1S–N1S, and 1.45 Å for N1S–C2S and N1S–C3S) to be within 0.01 Å. Also, anisotropic thermal parameters of all non-hydrogen atoms in this molecule were restrained to be approximately equal within 0.02 Å^2. The final refinement converged at wR_2 = 0.152 for all 7391 reflections (R_1 = 0.071 for 3849 reflections with $F > 4\sigma(F)$, S = 0.92). CCDC 1049390.

Magnetic measurements

The magnetic data were obtained with the SQUID apparatus (MPMS-XL7, Quantum Design) using the RSO mode of detection. The susceptibility measured at B = 0.1 T has been corrected for the underlying diamagnetism and converted to the effective magnetic moment. The magnetization has been measured at two temperatures: T = 2.0 and 4.6 K.

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