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## Introduction

In recent years, heterometallic polynuclear complexes have attracted much attention mainly due to their sophisticated crystal structures and possibility of possessing high-spin ground states as well as "single molecular magnet" (SMM) behaviour. Such an amazing combination of complicated architectures and fascinating magnetic properties was

## Magnetic, high-field EPR studies and catalytic activity of Schiff base tetranuclear Cu<sup>II</sup><sub>2</sub>Fe<sup>III</sup><sub>2</sub> complexes obtained by direct synthesis<sup>†</sup>

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Two novel heterometallic complexes  $[Cu_2Fe_2(HL^1)_2(H_2L^1)_2]\cdot 10DMSO (1)$  and  $[Cu_2Fe_2(HL^2)_2(H_2L^2)_2]\cdot 2DMF$ (2) have been prepared using the open-air reaction of copper powder, iron(II) chloride and DMSO (1) or DMF (2) solutions of the polydentate Schiff base  $(H_4L^1, 1; H_4L^2, 2)$  formed *in situ* from salicylaldehyde (1) or 5-bromo-salicylaldehyde (2) and tris(hydroxymethyl)aminomethane. Crystallographic analysis revealed that both compounds are based on the centrosymmetric tetranuclear core  $\{Cu^{II}_2Fe^{III}_2(\mu-O)_6\}$  where metal centres are joined by  $\mu$ -O bridges from the deprotonated ligands forming a nonlinear chain-like arrangement. Variable-temperature (1.8–300 K) magnetic susceptibility measurements of 1 and 2 showed a decrease of the effective magnetic moment value at low temperature, indicative of antiferromagnetic coupling  $(J_{Cu-Fe}/hc = -10.2 \text{ cm}^{-1}, J_{Fe-Fe}/hc = -10.5 \text{ cm}^{-1}$  in 1,  $J_{Cu-Fe}/hc = -10.5 \text{ cm}^{-1}$ ,  $J_{Fe-Fe}/hc =$ -8.93 cm<sup>-1</sup> in 2) between the magnetic centres in both compounds. They reveal an exceptionally high catalytic activity in the oxidation of cyclohexane with hydrogen peroxide under mild conditions, with the best observed yield/TON combined values of 36%/596 and 44%/1.1 × 10<sup>3</sup> for 1 and 2, respectively.

> demonstrated, for example, in the large Mn<sup>III</sup><sub>28</sub>Mn<sup>II</sup><sub>8</sub>Ni<sup>II</sup><sub>4</sub> assembly with a high ground spin state value,<sup>1</sup> a bell-shaped Mn<sub>11</sub>Gd<sub>2</sub> aggregate<sup>2</sup> or octanuclear Cr<sub>4</sub>Dy<sub>4</sub> cluster<sup>3</sup> with SMM behaviour, a calix[4]arene based Mn<sub>4</sub>Gd<sub>4</sub> complex with the behaviour of a magnetic refrigerant for low-temperature applications,<sup>4</sup> etc. Obviously, by incorporating different spins within one molecule, it is possible to affect the spin ground state, magnetic anisotropy, and magnetic exchange interactions and try to predetermine the desired magnetic properties. In spite of considerable success in the investigation of structure-magnetism correlations, another important application field for heterometallic coordination compounds with classical donor ligands, catalysis, is still poorly explored.<sup>5</sup> For instance, it was shown that heterometallic precatalysts, oxo-centred M<sub>2</sub>Ni (M = Fe, Cr) triangles and Cr<sub>7</sub>Ni wheels,<sup>6</sup> reveal a high catalytic activity in the vinyl/addition polymerization of norbornene. Further, chiral heterometallic d/s, d/d and d/f complexes were found to catalyze various asymmetric transformations.<sup>5</sup> In the field of alkane functionalization under mild conditions, the heterometallic CuCo<sub>3</sub>,<sup>7</sup> Cu<sub>2</sub>Co<sub>2</sub>Fe<sub>2</sub><sup>8</sup> and Co<sub>4</sub>Fe<sub>2</sub><sup>9</sup> polynuclear assemblies, as well as  $\{Cu_6Fe\}_n$  coordination polymers,<sup>10</sup> were recognized as highly efficient catalysts. Moreover, the catalytic activity (as measured by the yields of products, TONs and TOFs) of heterometallic Co/Fe complexes<sup>8,9</sup> was found to be among the highest ones, demonstrating the catalytic potential of the synergistic effect of a few different metals.

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<sup>†</sup>Electronic supplementary information (ESI) available: Selected bond lengths and angles for crystal structures of **1** and **2**, plots of the hydrogen-bonding schemes for **1** and **2**, IR spectra of **1** and **2**. CCDC 907644 for **1** and 908089 for **2**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt51800k

In pursuit of our research on the preparation and investigation of heterometallic polynuclear complexes, we continued to apply the direct synthesis method of coordination compounds.<sup>11</sup> This strategy, based on spontaneous self-assembly of free metal ions with commonly simple and flexible ligands without significant geometrical restrictions, already resulted in a great diversity of high-nuclearity assemblies with two<sup>12</sup> or even three<sup>13</sup> different metals. In addition to sophisticated crystal structures, the complexes synthesized in this way show interesting magnetic, spectroscopic and catalytic properties, e.g. strong exchange interaction in the Cu<sub>2</sub>Zn<sub>2</sub> complex mediated by diamagnetic metal atoms,<sup>14</sup> a single-ion contribution to the zero field splitting parameters in the Zn<sub>2</sub>Cr<sub>2</sub> tetramer determined by using high-field, high-frequency EPR spectroscopy,<sup>15</sup> and highly active and selective oxidation of cycloalkanes by Cu<sub>2</sub>Co<sub>2</sub>Fe<sub>2</sub> and Co<sub>4</sub>Fe<sub>2</sub> complexes.<sup>8,9</sup> Working with N,O-donor ligands, namely with aminoalcohols,<sup>16</sup> under the direct synthesis conditions we tried to expand this direction and started to explore the possibilities of constructing novel high-nuclearity aggregates using polydentate Schiff base ligands.<sup>17</sup> The tendency of Schiff bases to form oxo- and hydroxo-bridges between different metal centres is of great importance for magnetic materials design. Also, the synergistic effect of dissimilar metals linked only by single bridging atoms, instead of bridging groups, could have a significant influence on the catalytic behaviour of coordination compounds. Herein we report synthetic and structural features, as well as spectroscopic, magnetic and catalytic investigations of the two novel tetranuclear complexes [Cu<sup>II</sup><sub>2</sub>Fe<sup>III</sup><sub>2</sub>(HL<sup>1</sup>)<sub>2</sub>- $(H_2L^1)_2$ ]·10DMSO (1) and  $[Cu^{II}_2Fe^{III}_2(HL^2)_2(H_2L^2)_2]$ ·2DMF (2).

## **Results and discussion**

## Synthesis and spectroscopic analysis

The synthetic procedures to obtain 1 and 2 are similar and can be divided into two stages. In the first stage, the Schiff bases  $H_4L^1$  and  $H_4L^2$  (Scheme 1) were obtained by condensation of the appropriate aldehyde [salicylaldehyde (1) or 5-bromosalicylaldehyde (2)] and primary amine [tris(hydroxymethyl)aminomethane] in DMSO (1) or DMF (2) solution in a basic (triethylamine) medium.

Then the copper powder and iron(II) chloride were added to the hot yellow solutions of the ligands and the reactions were brought to completion by heating and stirring until the total dissolution of copper was observed (approximately 5 h). Dark-



red solutions were obtained at the end of both reactions. Redbrown microcrystals of **1** and **2** that showed analytical data consistent with the Cu( $\pi$ ): Fe( $\pi$ ) = 1:1 stoichiometry were formed within two days after addition of <sup>i</sup>PrOH (1) or Et<sub>2</sub>O (2). The general reaction for the syntheses of both compounds can be written as follows (Solv = DMSO, DMF; *n* = 10, 2):

$$Cu^0 + FeCl_2 \cdot 4H_2O + 2H_4L + 2Et_3N + 0.75O_2 + 0.5nSolv$$
  
→  $0.5[Cu_2Fe_2(HL)_2(H_2L)_2] \cdot nSolv + 2Et_3N \cdot HCl + 5.5H_2O$ 

Although the stoichiometry of both reactions could suggest  $Cu: FeCl_2 \cdot 4H_2O: H_4L = 1:1:2$  as the best initial ratio, the experimental results pointed to the  $Cu: FeCl_2 \cdot 4H_2O: H_4L = 2:1:4$  system as the most appropriate one, which results not only in higher yields but also in more favorable conditions for crystal growth in both cases.

The <sup>1</sup>H-NMR spectra (in DMSO–CCl<sub>4</sub>) of yellow crystals of  $H_4L^1$  and  $H_4L^2$ , obtained in separate reactions in CH<sub>3</sub>OH without addition of the metals, confirmed the *in situ* formation of the Schiff bases. The singlet peak observed at 8.55 ppm for  $H_4L^1$  (1) and at 8.51 ppm for  $H_4L^2$  (2) corresponds to the –CH=N– proton in the Schiff base.<sup>18</sup>

The IR spectra of **1** and **2** in the 4000–400 cm<sup>-1</sup> range showed all the characteristic ligand peaks (Fig. S3 and S4<sup>†</sup>). The broad medium-intensity bands in the 3330–3470 cm<sup>-1</sup> region were assigned to  $\nu$ (O–H) of the Schiff base ligands, while the very strong ones at 1618 (1) and 1621 cm<sup>-1</sup> (2) were assigned to  $\nu$ (C=N). The presence of DMSO and DMF molecules was identified by the peaks at 1026 and 950 cm<sup>-1</sup> (1) and the band at 1674 cm<sup>-1</sup> (2), respectively.

### Crystal structures

Complexes 1 and 2 (Fig. 1 and 2) reveal similar structural configurations with relatively small changes in bond lengths and angles (Tables S1 and S2<sup>†</sup>). Both compounds are centrosymmetric and based on the tetranuclear core {Cu<sub>2</sub>Fe<sub>2</sub>( $\mu$ -O)<sub>6</sub>} where the metals are joined by O bridges from the deprotonated Schiff base ligands forming a nonlinear Cu<sup>II</sup>...Fe<sup>III</sup>... Fe<sup>III</sup>...Cu<sup>II</sup> chain-like arrangement (Fig. 3). Despite the M<sub>4</sub>( $\mu$ -O)<sub>6</sub> molecular structural type belonging to the widespread family of M<sub>4</sub>( $\mu$ -X)<sub>6</sub> tetranuclear complexes where the metal centres are linked by two bridging atoms (*ca.* 250 hits according to CSD<sup>19</sup>), complexes 1 and 2 represented the first



**Fig. 1** Left: molecular structure of **1** with the atom numbering (H atoms are omitted for clarity, the non-hydrogen atoms are shown as 50% thermal ellipsoids). Right: schematic representation of the molecular structure of **1**.



**Fig. 2** Left: molecular structure of **2** with the atom numbering (H atoms are omitted for clarity, the non-hydrogen atoms are shown as 40% thermal ellipsoids). Right: schematic representation of the molecular structure of **2**.



Fig. 3 The ball-and-stick (a) and polyhedral (b) representations of the tetra-nuclear {Cu\_2Fe\_2( $\mu$ -O)\_6} core in 1 and 2. Color codes: Cu, cyan; Fe, olive; O, red; N, blue.

examples of heterometallic  $Cu^{II}Fe^{III}$  compounds with such a molecular core.

The Schiff bases in 1 and 2 have quite similar structural formulae and differ only by the presence of the Br substituent in the ligand of 2. In both compounds, two types of Schiff bases exist: a doubly deprotonated, of the tridentate (N,O,O) fashion, and a triply deprotonated, of the tetradentate (N,O,O,O) fashion. The coordination environments around all Fe<sup>III</sup> and Cu<sup>II</sup> metal atoms in 1 and 2 are formed exclusively by the Schiff base ligand. Moreover, the deprotonated ligands play a role of the charge compensators. Each Fe atom, in both complexes, adopts a distorted octahedral geometry formed by the O and N atoms of the ligands with the Fe-O(N) distances varying from 1.926(2) to 2.127(6) Å. The cis and trans O-Fe-O(N) bond angles range from 76.84(16) to 102.46(17)° and from 163.37(17) to 171.30(7)°, respectively. All Cu atoms, in 1 and 2, are four coordinated and have NO<sub>3</sub> donor sets. The Cu-O(N) bonds in 1 and 2 lie in the range from 1.873(5) to 1.934(5) Å. The cis and trans O-Cu-O(N) bond angles vary from 79.55(17) to 100.00(17)° and from 164.32(19) to 177.40(6)°, respectively.

In spite of the similarity of the crystal structures of 1 and 2 their molecular packings are quite different, which could be caused by the presence of different solvent molecules in the crystal lattice. In 1 (Fig. S1<sup>†</sup>), each tetranuclear aggregate is

H-bonded to six DMSO molecules  $[O4-H4A\cdots O5S, D-A = 2.739(4)$ Å, D-H···A = 178.44(14)°; O6-H6A···O2S, D-A = 2.685(4) Å, D-H···A = 158.78(14)°; O3-H3A···O4SA, D-A = 2.828(48) Å, D-H···A = 165.92(18)°]. In 2 (Fig. S2†), only two DMF molecules are involved in hydrogen bonding with the complex molecule by strong O-H···O interaction  $[O7-H7A\cdots O9, D-A = 2.666(7) Å,$ D-H···A = 168.69(31)°]. Although the compounds have rather different amounts of solvent molecules, uncoordinated DMSO and DMF provide steric hindrance around the tetranuclear aggregates that prevents their joining into polymeric supramolecular architectures.

### Thermal analysis

The thermal analysis curves of 1 and 2 revealed two main decomposition steps over the 40-700 °C temperature range (Fig. 4). For both compounds, the first step involved the elimination of the solvated molecules, DMSO in 1 (40-254 °C, calculated and observed mass residues are 84.8 and 85.1%, respectively) and DMF in 2 (40-155 °C, calculated and observed mass residues are 90.8 and 90.7%, respectively). In the case of compound 2, no weight loss occurred in the 155–272 °C region, revealing that the  $[Cu_2Fe_2(HL^2)_2(H_2L^2)_2]$ molecule is stable below 272 °C. A broad weight loss in the 254-390 °C (1) and 272-462 °C (2) ranges revealed a decomposition of the organic ligands, resulting in an oxide material  $2CuO + Fe_2O_3$  (calculated and observed mass residues for 1 are 23.9 and 26.4%, respectively, and calculated and observed mass residues for 2 are 20.1 and 20.6%, respectively). In general, the thermal behaviour of 1 and 2 exhibits an oxidative character being typical for other copper-containing complexes with similar ligands.<sup>8,20</sup>

#### Magnetic properties

Thermal variations of the effective magnetic moment in complexes 1 and 2 are very similar and are displayed in Fig. 5 and 6, respectively. It can be seen that the room-temperature value



**Fig. 4** Thermogravimetric plot showing the weight loss with the temperature increase for complexes **1** (blue) and **2** (red) at 10° min<sup>-1</sup> heating speed.



**Fig. 5** Magnetic functions for **1**. Left – temperature dependence of the effective magnetic moment, right – field dependence of the magnetization, inset – temperature dependence of the molar magnetic susceptibility. Open circles – experimental data. lines – fitted.

corresponds to  $\mu_{eff} = 8.1\mu_{B}$  and this is still increasing. The theoretical value for the uncoupled {Cu<sup>II</sup>-Fe<sup>III</sup>-Fe<sup>III</sup>-Fe<sup>III</sup>-Cu<sup>II</sup>} system is

$$\mu_{\rm eff} = \left[2g_{\rm Fe}^2 s_{\rm Fe}(s_{\rm Fe}+1) + \left[2g_{\rm Cu}^2 s_{\rm Cu}(s_{\rm Cu}+1)\right]\right]^{1/2} \mu_{\rm B} \qquad (1)$$

which yields an estimate  $\mu_{\rm eff} = 8.7\mu_{\rm B}$  when uniform *g*-factors (g = 2) are assumed. On cooling the effective magnetic moment decreases gradually and this is a fingerprint of the dominating antiferromagnetic interaction. This conclusion is confirmed by the magnetization data: the magnetization for *T* = 2.0 K is lower than for *T* = 4.6 K. With antiferromagnetic interaction, the susceptibility should pass through a maximum, which is seen at  $T_{\rm max} = 47$  K for 1 and  $T_{\rm max} = 44$  K for 2.

The magnetic data were fitted by considering the following spin Hamiltonian

$$\begin{aligned} \hat{H} &= -J_{\text{Cu}-\text{Fe}}[(\vec{S}_{\text{Cu}1} \cdot \vec{S}_{\text{Fe}1}) + (\vec{S}_{\text{Fe}2} \cdot \vec{S}_{\text{Cu}2})]\hbar^{-2} \\ &- J_{\text{Fe}1-\text{Fe}2}(\vec{S}_{\text{Fe}1} \cdot \vec{S}_{\text{Fe}2})\hbar^{-2} + \mu_{\text{B}}\vec{B} \cdot [g_{\text{Cu}}(\vec{S}_{\text{Cu}1} + \vec{S}_{\text{Cu}2}) \\ &+ g_{\text{Fe}1}(\vec{S}_{\text{Fe}1} + \vec{S}_{\text{Fe}2})]\hbar^{-1} \end{aligned}$$
(2)

where the isotropic exchange for adjacent centres is considered along with the spin-Zeeman term. The *g*-factor asymmetry was omitted in order to avoid overparametrization. The Hamiltonian produced a matrix of  $144 \times 144$  dimension, which after diagonalization gave the energy levels for three field values; then the partition function and its derivatives were obtained and inserted in the thermodynamic formulae for the magnetization and magnetic susceptibility, respectively.<sup>21</sup> The fitting procedure was applied simultaneously to the susceptibility and magnetization data sets by minimizing the error functional

$$F = \left[\sum_{i}^{N} \left|\chi_{i}^{c} - \chi_{i}^{0}\right| / \chi_{i}^{0}\right] \times \left[\sum_{j}^{M} \left|M_{j}^{c} - M_{j}^{0}\right| / M_{j}^{0}\right] \to \min \qquad (3)$$

The final set of magnetic parameters for 1 reads  $J_{\text{Cu-Fe}}/hc = -10.2 \text{ cm}^{-1}$ ,  $J_{\text{Fe-Fe}}/hc = -10.5 \text{ cm}^{-1}$ ,  $g_{\text{Cu}} = 2.00 \text{ (}g_{\text{Fe(III)}} = 2.0\text{-}$ fixed). The discrepancy factors for the susceptibility and



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Fig. 6 Magnetic functions for 2. Left – temperature dependence of the effective magnetic moment, right – field dependence of the magnetization, inset – temperature dependence of the molar magnetic susceptibility. Open circles – experimental data, lines – fitted.



**Fig. 7** Energy levels for **1** and **2** sorted by the total spin: one S = 6 state, 3S = 5 states, 4S = 4, 4S = 3, 4S = 2, 4S = 1, and 2S = 0 states.

magnetization are  $R(\chi) = 0.050$  and R(M) = 0.121, respectively. For 2 the magnetic parameters were  $J_{\text{Cu-Fe}}/hc = -10.5 \text{ cm}^{-1}$ ,  $J_{\text{Fe-Fe}}/hc = -8.93 \text{ cm}^{-1}$ ,  $g_{\text{Cu}} = 2.00 \text{ (}g_{\text{Fe(III})} = 2.0-\text{ fixed}\text{)}$ ;  $R(\chi) = 0.075$  and R(M) = 0.133. The energy spectrum sorted according to the spin value is displayed in Fig. 7.

When magnetic data of **1** and **2** are analyzed, the following can be concluded. The negative value of the Cu( $\pi$ )–Fe( $\pi$ ) exchange coupling constant matches the high Cu–O–Fe angle of the superexchange path. The Fe( $\pi$ )–Fe( $\pi$ ) coupling constant is also negative. Some discrepancies seen at the highest fields of the magnetization can be ascribed to the simplifications in the model: no *g*-factor anisotropy, an average of the magnetization over three Cartesian components. The improvement of the model by the single-ion anisotropy at the Fe( $\pi$ ) centres is also possible; however, with antiferromagnetic exchange the *D*-values are fixed with high uncertainty and also the sign of the *D*-parameter is problematic when |D| is small.

#### **EPR spectra**

A coupled Fe<sub>2</sub>Cu<sub>2</sub> system consists of 144 energy levels, grouped into one S = 6 state, 3 S = 5 states, 4 S = 4, 4 S = 3, 4 S = 2, 4 S =1 and 2 S = 0 states (see Fig. 7). These states are very closely spaced because of weak exchange interactions as revealed by the magnetic susceptibility data. The 144 states are eigenfunctions of the isotropic HDVV Hamiltonian, as well as of the



**Fig. 8** 216 GHz EPR spectra of **2** at 5 K and at 10 K showing increasing thermal population of the S = 2 spin state lying above the lowest triplet.

total spin-squared operator of the system,

$${\hat S_{
m T}}^2 = ({\hat S_{
m Fe1}} + {\hat S_{
m Fe2}} + {\hat S_{
m Cu1}} + {\hat S_{
m Cu2}})^2$$

They, however, are mixed under the Zeeman interaction and the zero-field splitting interactions. Accordingly, the "giant spin" approximation (that is treating each of the total spin states separately), which would be appropriate in the case of larger isotropic exchange interactions, is not strictly applicable in the present systems. Zero-field splitting on individual Fe(m) ions is expected to provide the main contribution to the zfs of the coupled system, but both the magnitude of the anisotropic Cu–Fe and Fe–Fe interactions (not included in the spin Hamiltonian (eqn (2))) and the orientation of the Cu–Fe zfs tensor *versus* the Fe–Fe zfs tensor must affect the EPR spectra. The number of variable parameters combined with the size of the spin Hamiltonian matrix indicates that attempts to simulate a powder spectrum would not be realistic and only a limited interpretation of the EPR spectra is possible.

With the exchange coupling constants of the order of  $J = -10 \text{ cm}^{-1}$ , as found from the magnetic susceptibility for 1, the lowest spin state is a singlet (S = 0), followed by a triplet (S = 1), a quintet (S = 2) and two other triplet states. The same holds true for 2. Triplet state EPR spectra were indeed recognized at very low temperatures (Fig. 8 and 9). Attempts to simulate them using the "giant spin" model with a standard spin Hamiltonian

$$\hat{H} = \mu_{\rm B} B \cdot \{g_S\} \cdot \hat{S} + D_S \{ \hat{S}_z^2 - S(S+1)/3 \} + E_S (\hat{S}_x^2 - \hat{S}_y^2) \quad (4)$$

resulted in  $D_{S=1} = 3.1 \text{ cm}^{-1}$  and  $E_{S=1} = 1.0 \text{ cm}^{-1}$  for 1; analogously,  $D_{S=1} = 2.7 \text{ cm}^{-1}$  and  $E_{S=1} = 0.4 \text{ cm}^{-1}$  for 2. Fig. 8 shows an increase in the thermal population of the S = 2 spin state lying above the lowest triplet caused by heating from 5 to 10 K.

## Mössbauer spectra

A small isomer shift (IS) and quadrupole splitting (QS) observed in the room-temperature Mössbauer spectra (Fig. 10) confirm the presence of alkoxo-bridges (rather than oxo) between the  $Fe^{3+}$  ions.<sup>22</sup>



Fig. 9 Comparison of the 10 K, 216 GHz spectra of 1 and 2. Resonances corresponding to the "Z" molecular orientation and to the "half-field" transitions in the triplet state are indicated.



Fig. 10 Mössbauer spectra at room temperature. Circles: experimental, solid lines: calculated with the isomer shift and quadrupole splitting as given. Top: 1 (IS = 0.391(1) mm s<sup>-1</sup>, QS = 0.614(1) mm s<sup>-1</sup>); bottom: 2 (IS = 0.383(1) mm s<sup>-1</sup>, QS = 0.505(1) mm s<sup>-1</sup>).

## Catalytic properties

Complexes 1 and 2 were investigated as catalytic precursors for the oxidation of cyclohexane to cyclohexanol and cyclohexanone by aqueous hydrogen peroxide under mild conditions. Cyclohexane has been used as a recognized substrate model for C-H bond activation investigations. No alkane oxidation products (or only traces) were obtained in the absence of catalyst or hydrogen peroxide (Scheme 2). The absence of a nitric acid promoter results in much lower yields for both the 1 and 2 complexes. The final concentrations of the ketone and alcohol were measured after the addition of PPh<sub>3</sub> in accord with the method developed earlier by Shul'pin.<sup>23</sup> Cyclohexanol





**Fig. 11** Effect of the catalyst concentration on the total yield of cyclohexanol and cyclohexanone (circle symbols, determined by GC after reduction with PPh<sub>3</sub>) and total TONs (square symbols) in the oxidation of cyclohexane with  $H_2O_2$  (1.0 M) catalyzed by complexes **1** (above) and **2** (below) in the presence of HNO<sub>3</sub> (0.04 M) in acetonitrile (the total volume of the reaction solution was 5 mL), room temperature, 5 h reaction time.

and cyclohexanone were essentially the only reaction products detected by GC-MS studies.

The dependence of the product yield (sum of cyclohexanol and cyclohexanone) on catalyst concentration after 5 h is depicted in Fig. 11. The yield curve for 1 rises up to 36% in the  $0 < [\mathbf{1}]_0 < 2 \times 10^{-4}$  M region, giving a maximum TON value of 596. Further increase of the concentration of 1 does not lead to a yield increase (Fig. 11). This could be associated with the overoxidation effect as well as the catalase activity of 1. Compound 2 exhibits, in general, similar behaviour (Fig. 11). In the lowest concentration range,  $[2]_0 < 2 \times 10^{-4}$  M, the maximum yield of 44% was observed for  $[2]_0 = 1.38 \times 10^{-4}$  M, supported by a TON of 1060. As for 1, after reaching a maximum, the yield undergoes a slight decay with the increase of  $[2]_0$ . The points  $[1]_0 = [2]_0 = 7.6 \times 10^{-5}$  M were chosen for all further experiments because they concern the "half yield" of ca. 20%, where both promotion (increase up to 40%) and suppression (decrease down to 0%) effects could be detected.

Recently, it was observed for the heterometallic complex  $[Co_4Fe_2O(Sae)_8]$  (H<sub>2</sub>Sae = salicylidene-2-ethanolamine) that the initial concentration increase of cyclohexane up to 0.6 M could improve the TON values significantly.<sup>9</sup> However, the dependence of the overall TON on the substrate concentration for 1 and 2 shows that the initial  $[CyH]_0 = 0.2$  M is optimal (see also below the yield dependence) for the present systems (Fig. 12). In contrast to  $[Co_4Fe_2O(Sae)_8]$ , where the yield was found to be



**Fig. 12** Effect of the cyclohexane (CyH) concentration on the total yield of cyclohexanol and cyclohexanone (circle symbols) and total TONs (square symbols) in the oxidation of cyclohexane with  $H_2O_2$  (1.0 M) catalyzed by complexes **1** and **2** (above and below, respectively;  $[\mathbf{1}]_0 = [\mathbf{2}]_0 = 7.6 \times 10^{-5}$  M) in the presence of HNO<sub>3</sub> (0.04 M) in acetonitrile at room temperature, 5 h reaction time. The total initial volume of the reaction solution was 5 mL. For the tests with  $[CyH]_0 > 0.4$  M complete dissolution of cyclohexane was observed in *ca.* 30 min.

stable in the  $[CyH]_0 = 0.2-0.4$  region,<sup>9</sup> the catalytic systems based on 1 and 2 show a gradual yield decay with  $[CyH]_0$  increase (Fig. 12), while the TON is stable in the  $[CyH]_0 = 0.2-0.5$  M region.

The study of the influence of the oxidant (hydrogen peroxide) amount on the overall yield (Fig. 13) reveals that the optimal concentration of  $[H_2O_2]_0$  *ca.* 0.6 M is surprisingly low, with an  $[H_2O_2]/[CyH]$  ratio of 2.9. In accord, the relatively high yield of 10.3% based on hydrogen peroxide is achieved. Typically, complexes of copper and iron under similar conditions exhibit the best yields based on cycloalkane in the  $[H_2O_2]/[CyH] = 5-10$  region with the yield based on hydrogen peroxide lower than 5%.<sup>7,24</sup>

The yield *versus*  $[H_2O]_0$  dependencies for 1 and 2, studied for  $[H_2O_2]_0 = 0.6$  M (highest yield based on cyclohexane) and 0.4 M (for comparative purpose), are shown in Fig. 14. Water typically has been considered an unwanted component of the catalytic systems, although for some cases it was found to have no influence until  $[H_2O]_0 = 10 \text{ M}^7$  or even to show promoting activity by catalyzing H<sup>+</sup>-transfer steps from coordinated  $H_2O_2$ towards the formation of hydroxyl radicals.<sup>25</sup> As can be seen, in both the  $[H_2O_2]_0 = 0.6$  M and 0.4 M cases, an increase of water concentration leads to a yield decay (Fig. 14). This indicates a suppressing effect of the water in the concentration



**Fig. 13** Effect of the oxidant ( $H_2O_2$ ) concentration on the total yield of cyclohexanol and cyclohexanone on the basis of cyclohexane (circle symbols) and of the total  $H_2O_2$  (square symbols) in the oxidation of cyclohexane (0.2 M) with  $H_2O_2$  catalyzed by complexes **1** and **2** (above and below, respectively; [**1**]<sub>0</sub> = [**2**]<sub>0</sub> = 7.6 × 10<sup>-5</sup> M) in the presence of HNO<sub>3</sub> (0.04 M) in acetonitrile at room temperature, 5 h reaction time. The total volume of the reaction solution was 5 mL.

ranges studied, although one cannot exclude an eventual promoting effect of water<sup>25</sup> at lower concentrations.

On the basis of previous studies, one may expect a free radical mechanism for the catalytic systems based on 1 and 2, with the hydroxyl radicals (generated from  $H_2O_2$ ) as the main reacting species with the alkane.<sup>7,9,23–25</sup> This assumption is partially confirmed by the typical maximum yield of no higher than 40%,<sup>26</sup> demonstrated by the yield *versus* [Cat] dependence (Fig. 11) and by the higher alcohol/ketone ratio (Cy–OH : Cy=O up to 10 : 1) observed after reduction of the reaction mixture by PPh<sub>3</sub>, in comparison with the ratio obtained prior to the phosphine addition.<sup>23</sup>



**Fig. 14** Effect of the water concentration on the total yield of cyclohexanol and cyclohexanone on the basis of cyclohexane in the oxidation of cyclohexane (0.2 M) with  $H_2O_2$  (0.6 M or 0.4 M for circle and triangle symbols, respectively) catalyzed by complexes **1** and **2** (above and below, respectively;  $[\mathbf{1}]_0 = [\mathbf{2}]_0 = 7.6 \times 10^{-5}$  M) in the presence of HNO<sub>3</sub> (0.04 M) in acetonitrile at room temperature, 5 h reaction time. The total volume of the reaction solution was 5 mL.

To confirm this assumption, the selectivity parameters on the oxidation of normal octane were studied (Tables 1 and 2). It was found that the catalytic systems based on 1 and 2 possess low regioselectivity, close to that found for the catalytic systems where participation of hydroxyl radicals was detected.<sup>9,23,27</sup>

The stereoselectivity of the catalytic systems based on 1 and 2 was studied under conditions that could suppress the free radical mechanism:<sup>28</sup> low concentrations of substrate, *cis*-1,2-dimethylcyclohexane (*cis*-DMCH, 0.09 M), and oxidizer (H<sub>2</sub>O<sub>2</sub>, 0.1 M in total), at 0 °C (hydrogen peroxide was added gradually for 10 min). The amounts of *trans*- and

Time (min)	Products (							
	one-2	one-3	one-4	ol-1	ol-2	ol-3	ol-4	$C(1): C(2): C(3): C(4)^{b}$
30	1.02	0.77	0.62	0.98	3.09	3.05	2.88	1:6.3:5.8:5.3
60	2.01	1.66	1.35	1.56	5.44	5.81	5.45	1:7.2:7.2:6.5
90	2.81	2.49	2.08	1.65	5.67	5.50	5.27	1:7.7:7.3:6.7
120	3.35	3.05	2.55	1.80	5.60	5.83	5.41	1:7.4:7.4:6.6
150	3.61	3.54	2.93	2.56	10.32	10.73	9.59	1:8.1:8.4:7.3
180	3.97	3.96	3.33	2.31	9.64	8.62	8.18	1:8.9:8.2:7.5
210	2.88	3.37	2.69	4.01	21.45	23.36	21.68	1:9.1:10:9.1

Table 1 Selectivity parameters in oxidation of *n*-octane catalyzed by complex 1<sup>a</sup>

<sup>*a*</sup> Reaction conditions:  $[1]_0 = 4.7 \times 10^{-4}$  M;  $[H_2O_2]_0 = 1$  M;  $[HNO_3]_0 = 0.04$  M; [n-octane $]_0 = 0.25$  M; MeCN up to 5 mL. <sup>*b*</sup> Normalized by taking into account the numbers of H atoms at each of the C atoms.

Time (min)	Products (							
	one-2	one-3	one-4	ol-1	ol-2	ol-3	ol-4	$C(1): C(2): C(3): C(4)^{b}$
30	0.42	0.34	0.27	0.63	2.69	2.57	2.26	1:7.4:6.9:5.9
60	1.61	1.39	1.11	0.65	2.54	2.55	2.28	1:9.7:9.2:7.9
90	1.22	1.01	0.88	1.62	7.52	7.60	6.81	1:8.1:7.9:7.1
120	2.88	2.99	2.54	0.66	2.70	1.99	1.86	1:12.6:11.3:10.0
150	2.22	2.10	1.77	1.83	8.41	8.64	7.99	1:8.8:8.8:8
210	2.86	2.70	2.33	2.51	11.30	11.88	10.72	1:8.5:8.7:7.8

 Table 2
 Selectivity parameters in oxidation of *n*-octane catalyzed by complex 2<sup>a</sup>

<sup>*a*</sup> Reaction conditions:  $[2]_0 = 4.8 \times 10^{-4}$  M;  $[H_2O_2]_0 = 1$  M;  $[HNO_3]_0 = 0.04$  M; [n-octane $]_0 = 0.25$  M; MeCN up to 5 mL. <sup>*b*</sup> Normalized by taking into account the numbers of H atoms at each of the C atoms.

*cis*-dimethylcyclohexanol (after addition of PPh<sub>3</sub> upon cooling) were found to be similar both for **1** and **2** after a short accumulation time (15 min), as well as after 5 h. The absence of stereo-selectivity, as well as the low regioselectivity, clearly confirms the proposed free radical mechanism for the catalytic systems with complexes **1** and **2** as catalysts.

## Conclusions

Using the "direct synthesis" approach, we have synthesized two novel heterometallic coordination compounds containing the chain-like  $\{Cu_2Fe_2(\mu-O)_6\}$  core supported by Schiff base ligands. Polynuclear heterometallic complexes are a class of compounds that deserves special attention pertaining to the development of novel magnetic and catalytic materials. The magnetic studies of complexes **1** and **2** revealed the antiferromagnetic nature of the couplings between the paramagnetic metal centres. These studies are supported by high-field EPR investigations.

Both compounds were shown to act as catalyst precursors in the mild oxidation of cyclohexane with hydrogen peroxide. The catalytic activities were found to be among the highest ones for this type of reaction, presumably due to a synergistic effect of two different metals present in 1 and 2. The results reported here demonstrate the power of the direct synthesis method to generate polynuclear heterometallic assemblies, possessing sophisticated structures. These heterometallic complexes are novel catalytic materials, potentially of bio-mimicking significance. These studies are going to be expanded to a wider range of catalytic reactions, namely towards an understanding of the synergistic catalytic effect associated with the presence of a few different metals in a molecule.

## **Experimental section**

#### General

All chemicals were of reagent grade and used as received. All experiments were carried out in air. Elemental analyses for CHNS were provided by the Microanalytical Service of the Instituto Superior Técnico. Infrared spectra  $(4000-400 \text{ cm}^{-1})$ 

were recorded using a BX-FT IR "Perkin Elmer" instrument in KBr pellets.

Synthesis of  $[Cu_2Fe_2(HL^1)_2(H_2L^1)_2]$ ·10DMSO (1). Salicylaldehyde (0.53 mL, 5 mmol), tris(hydroxymethyl)aminomethane (0.61 g, 5 mmol) and triethylamine (0.7 mL, 5 mmol) were dissolved in DMSO (25 mL) in this order, forming a yellow solution which was magnetically stirred at 50-60 °C (10 min). Then, copper powder (0.16 g, 2.5 mmol) and FeCl<sub>2</sub>·4H<sub>2</sub>O (0.25 g, 1.25 mmol) were added to the hot yellow solution of the ligand and magnetically stirred until the total dissolution of copper powder was observed (5 h). Red-brown crystals suitable for X-ray crystallographic studies were formed in two days after addition of <sup>i</sup>PrOH into the resulting dark-red solution. Yield: 0.73 g, 61% (per iron). The crystals are not stable in air and after several days they have lost a part of DMSO molecules and finally, according to the elemental analysis, the complex formula can be written as [Cu<sub>2</sub>Fe<sub>2</sub>(HL<sup>1</sup>)<sub>2</sub>(H<sub>2</sub>L<sup>1</sup>)<sub>2</sub>]·2.6DMSO. Magnetic and catalytic investigations were made using the following data of elemental analysis. Anal. calc. for C49.2H65.6Cu2- $Fe_2N_4O_{18.6}S_{2.6}$  (*M* = 1332.78): C, 44.34; N, 4.21; H, 4.97; S, 6.25%. Found: C, 44.0; N, 4.2; H, 4.9; S, 5.9%. The compound is sparingly soluble in DMSO and DMF and insoluble in water.

Synthesis of  $[Cu_2Fe_2(HL^2)_2(H_2L^2)_2]$ -2DMF (2). This complex was prepared in a way similar to that of 1, but in DMF solution and using 5-bromo-salicylaldehyde (1.01 g, 5 mmol). Redbrown crystals suitable for X-ray analysis grew within two days after addition of diethyl ether into the resulting dark-red solution. Yield: 0.54 g, 54% (per iron). Anal. calc. for C<sub>50</sub>H<sub>58</sub>Br<sub>4</sub>Cu<sub>2</sub>-Fe<sub>2</sub>N<sub>6</sub>O<sub>18</sub> (Mr = 1589.44): C, 37.78; N, 5.29; H, 3.68%. Found: C, 37.4; N, 5.2; H, 3.9%. The compound is sparingly soluble in DMSO and DMF and insoluble in water.

#### Crystallography

The X-ray diffraction study of **1** was performed on an "Xcalibur 3" diffractometer (graphite-monochromated MoK $\alpha$  radiation, CCD detector,  $\omega$ -scans). Empirical correction for absorption was provided with a multi-scan method using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm of the CrysAlis Red program package.<sup>29</sup> The structure was solved by direct methods and refined against  $F^2$  within anisotropic approximation for all non-hydrogen atoms using the SHELXTL package.<sup>30</sup> All H atoms were placed in idealized

positions and constrained to ride on their parent atoms with  $U_{\rm iso} = nU_{\rm eq}$  (n = 1.5 for CH<sub>3</sub> and OH groups and n = 1.2 for all the other H atoms). Two solvent molecules of DMSO were disordered, each one over two sites, with refined occupancy factors 0.77(1)/0.23(1) for S(4A)–O(4SA)/S(4B)–O(4SB), and 0.94 (1)/0.06(1) for S(5A)/S(5B). Anisotropic displacement parameters of non-hydrogen atoms of these molecules were restrained within "rigid bond" approximation. Additionally, S–O bonds in each disordered molecule were restrained to be of the same lengths within an effective standard deviation of 0.01 Å.

A suitable single crystal of 2 was chosen for the X-ray diffraction experiment. Image frames were collected using a Bruker SMART APEX2 diffractometer, equipped with MoKa graphite monochromated ( $\lambda = 0.71073$  Å) radiation, in the nitrogen stream at 173 K. The cell parameters were determined using 436 reflections from 3 short runs. Image frames were integrated using the SAINT v7.68a program.<sup>31</sup> The intensities were corrected for Lorentz and polarization effects as well as semiempirical (multiscan) adsorption correction using SADABS.<sup>32</sup> The structure was solved by direct methods and refined by the full matrix least-squares method on F<sup>2</sup> using SHELXTL software.<sup>30</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms, connected to correspondent carbon parent atoms, were refined in geometrically calculated positions using the "riding" model. Hydrogens connected to oxygen atoms were found from the difference Fourier map and refined with AFIX 83 instruction. During the structure refinement, one DMF lattice molecule per asymmetric unit was modeled from the difference Fourier map. Further lattice solvent molecules, supposedly diethyl ether and/or water molecules, were found to be highly disordered. This may be connected with very high flexibility of the molecule combined with the absence of strong intermolecular interactions. On this ground, it was impossible to model it with acceptable geometrical and thermal parameters. The SQUEEZE procedure was used to modify the reflection intensities, related to disordered lattice solvent molecules.33 It resulted in 377 electrons, squeezed from a 796  $\text{\AA}^3$  void with the centre in the 0.033 1/2 1/2 position.

Crystal data for 1:  $C_{64}H_{110}Cu_2Fe_2N_4O_{26}S_{10}$ , M = 1910.94, triclinic,  $P\bar{1}$ , a = 12.8911(4) Å, b = 13.6193(4) Å, c = 13.7806(4) Å,  $\alpha = 70.429(3)^\circ$ ,  $\beta = 65.864(3)^\circ$ ,  $\gamma = 85.283(2)^\circ$ , V = 2076.14(11)Å<sup>3</sup>, T = 100(2) K, Z = 1, 24 097 reflections measured, 11 889 independent reflections ( $R_{int} = 0.0565$ ),  $R_1 = 0.0408$  ( $I > 2\sigma(I)$ ), w $R(F^2) = 0.0533$  (all data), GoF = 0.763.

Crystal data for 2:  $C_{50}H_{58}Br_4Cu_2Fe_2N_6O_{18}$ , M = 1589.44, triclinic,  $P\bar{1}$ , a = 12.7243(5) Å, b = 12.8239(6) Å, c = 13.7739(6) Å,  $a = 105.861(2)^\circ$ ,  $\beta = 92.703(2)^\circ$ ,  $\gamma = 103.364(2)^\circ$ , V = 2088.78(16) Å<sup>3</sup>, T = 173(2) K, Z = 1, 25 610 reflections measured, 8393 independent reflections ( $R_{int} = 0.0979$ ),  $R_1 = 0.0549$  ( $I > 2\sigma(I)$ ),  $wR(F^2) = 0.1263$  (all data), GoF = 0.807.

#### Magnetic measurements

The magnetic data were taken with the SQUID apparatus (MPMS-XL7, Quantum Design) using the RSO mode of

detection. The susceptibility taken at B = 0.1 T was corrected for the underlying diamagnetism and converted to the effective magnetic moment. The magnetization was measured at two temperatures: T = 2.0 and T = 4.6 K.

#### High-field and high-frequency EPR spectroscopy

High-frequency EPR spectra were recorded using a home-built spectrometer at the EMR facility of NHMFL.<sup>34</sup> The instrument is a transmission-type device in which waves are propagated in cylindrical lightpipes. The microwaves were generated by a phase-locked oscillator (Virginia Diodes) operating at a frequency of  $13 \pm 1$  GHz and generating its harmonics, of which the 4th, 8th, 16th, 24th and 32nd were available. A superconducting magnet (Oxford Instruments) capable of reaching a field of 17 T was employed.

#### Thermogravimetric measurements

A Perkin-Elmer STA-6000 model thermogravimetric analyzer was used for determination of the thermal stability of complexes **1** and **2**. Samples weighing 5–30 mg were heated from 30 to 1000 °C at a heating rate of 1-50 °C min<sup>-1</sup> in open air.

### Catalytic activity studies

The reaction mixtures were prepared in two ways. (I) To 0.6-17 µmol of catalyst weighed into the reaction flask, 4.5 mL CH<sub>3</sub>CN, 0.2 mmol HNO<sub>3</sub> (65%, aqueous), 1.0 mmol of cycloalkane and 4.00-20.0 mmol (typically 5.00 mmol) H<sub>2</sub>O<sub>2</sub> (30% aqueous) were added in this order. (II) The catalyst precursor and the co-catalyst HNO3 were used in the form of stock solutions in acetonitrile. To aliquots of these solutions, 1.0 mmol of cycloalkane and 4.00-20.0 mmol (typically 5.00 mmol)  $H_2O_2$  (30% aqueous) were added, giving the total volume of the reaction solution of 5 mL. (CAUTION: the combination of air or molecular oxygen and H2O2 with organic compounds at elevated temperatures may be explosive!). The oxidation reactions were typically carried out in air in thermostated Pyrex cylindrical vessels with vigorous stirring at room temperature and atmospheric pressure. At the end of the reaction (typically 5 h), 5 mL of diethyl ether and 90 µL of cycloheptanone (as GC internal standard) were added and the system was refluxed for 5 min. Then, an aliquot of ca. 0.5 mL was taken and transferred, upon cooling, into a vial containing an excess (ca. 150 mg) of solid PPh<sub>3</sub>. A Perkin-Elmer Clarus 500 gas chromatograph with a BP-20 capillary column (SGE, 30 m  $\times$  0.32 mm  $\times$  25  $\mu$ m) and a Perkin-Elmer Clarus 600 gas chromatograph, equipped with a Perkin-Elmer Clarus 600 C mass-spectrometer (electron impact), with a BPX5 capillary column (SGE, the same dimensions) and helium carrier gas were used for quantitative analyses of the reaction mixtures.

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## Notes and references

- M. Charalambous, E. E. Moushi, C. Papatriantafyllopoulou, W. Wernsdorfer, V. Nastopoulos, G. Christou and A. J. Tasiopoulos, *Chem. Commun.*, 2012, 48, 5410.
- 2 V. Mereacre, Y. Lan, R. Clérac, A. M. Ako, W. Wernsdorfer,
  G. Buth, C. E. Anson and A. K. Powell, *Inorg. Chem.*, 2011,
  50, 12001.
- 3 J. Rinck, G. Novitchi, W. Van den Heuvel, L. Ungur, Y. Lan,
  W. Wernsdorfer, C. E. Anson, L. F. Chibotaru and
  A. K. Powell, *Angew. Chem., Int. Ed.*, 2010, 49, 7583.
- 4 G. Karotsis, M. Evangelisti, S. J. Dalgarno and E. K. Brechin, *Angew. Chem., Int. Ed.*, 2009, **48**, 9928.
- 5 J. Park and S. Hong, Chem. Soc. Rev., 2012, 41, 6931.
- 6 P.-G. Lassahn, V. Lozan, G. A. Timco, P. Christian, C. Janiak and R. E. P. Winpenny, *J. Catal.*, 2004, 222, 260.
- 7 D. S. Nesterov, V. N. Kokozay, J. Jezierska, O. V. Pavlyuk, R. Boča and A. J. L. Pombeiro, *Inorg. Chem.*, 2011, **50**, 4401.
- 8 D. S. Nesterov, V. N. Kokozay, V. V. Dyakonenko, O. V. Shishkin, J. Jezierska, A. Ozarowski, A. M. Kirillov, M. N. Kopylovich and A. J. L. Pombeiro, *Chem. Commun.*, 2006, 4605.
- 9 D. S. Nesterov, E. N. Chygorin, V. N. Kokozay, V. V. Bon, R. Boča, Y. N. Kozlov, L. S. Shul'pina, J. Jezierska, A. Ozarowski, A. J. L. Pombeiro and G. B. Shul'pin, *Inorg. Chem.*, 2012, 51, 9110.
- Y. Y. Karabach, M. F. C. Guedes da Silva, M. N. Kopylovich,
   B. Gil-Hernández, J. Sanchiz, A. M. Kirillov and
   A. J. L. Pombeiro, *Inorg. Chem.*, 2010, 49, 11096.
- A. D. Garnovskii and B. I. Kharissov, *Direct Synthesis of Coordination and Organometallic Compounds*, Elsevier Science, Amsterdam, 1999; V. N. Kokozay and D. V. Shevchenko, *Mater. Sci.-Poland*, 2005, 23, 287.
- E. A. Buvaylo, V. N. Kokozay, O. Yu. Vassilyeva,
   B. W. Skelton, I. L. Eremenko, J. Jezierska and
   A. Ozarowski, *Inorg. Chem.*, 2009, 48, 11092; E. A. Buvaylo,
   V. N. Kokozay, O. Yu. Vassilyeva, B. W. Skelton, J. Jezierska,
   L. C. Brunel and A. Ozarowski, *Inorg. Chem.*, 2005, 44, 206.
- 13 D. S. Nesterov, C. Graiff, A. Tiripicchio and A. J. L. Pombeiro, *Cryst. Eng. Commun.*, 2011, 13, 5348; D. S. Nesterov, V. N. Kokozay and B. W. Skelton, *Eur. J. Inorg. Chem.*, 2009, 5469; D. S. Nesterov, V. N. Kokozay, B. W. Skelton, J. Jezierska and A. Ozarowski, *Dalton Trans.*, 2007, 558.
- 14 E. A. Buvaylo, V. N. Kokozay, O. Yu. Vassilyeva, B. W. Skelton, J. Jezierska, L. C. Brunel and A. Ozarowski, *Chem. Commun.*, 2005, 4976.

- V. V. Semenaka, O. V. Nesterova, V. N. Kokozay,
   V. V. Dyakonenko, R. I. Zubatyuk, O. V. Shishkin, R. Boča,
   J. Jezierska and A. Ozarowski, *Inorg. Chem.*, 2010, 49, 5460.
- 16 V. V. Semenaka, O. V. Nesterova, V. N. Kokozay, R. I. Zybatyuk, O. V. Shishkin, R. Boča, C. J. Gomez-Garcia, J. M. Clemente-Juan and J. Jezierska, *Polyhedron*, 2010, 29, 1326; V. V. Semenaka, O. V. Nesterova, V. N. Kokozay, R. I. Zybatyuk, O. V. Shishkin, R. Boča, D. V. Shevchenko, P. Huang and S. Styring, *Dalton Trans.*, 2010, 2344; V. V. Semenaka, O. V. Nesterova, V. N. Kokozay, V. V. Semenaka, O. V. Nesterova, V. N. Kokozay, V. V. Dyakonenko, O. V. Shishkin, R. Boča and J. Jezierska, *Dalton Trans.*, 2010, 1734.
- 17 E. N. Chygorin, O. V. Nesterova, J. A. Rusanova, V. N. Kokozay, V. V. Bon, R. Boča and A. Ozarowski, *Inorg. Chem.*, 2012, 51, 386.
- 18 Spectral Database for Organic Compounds (SDBSWeb): http:// riodb01.ibase.aist.go.jp/sdbs/, National Institute of Advanced Industrial Science and Technology (AIST), Japan.
- 19 Cambridge Structural Database (CSD), version 5.33 (August 2012); F. H. Allen, Acta Crystallogr., Sect. B: Struct. Sci., 2002, 58, 380.
- 20 V. T. Yilmaz, Y. Topcu, F. Yilmaz and C. Thoene, *Polyhedron*, 2001, **20**, 3209; A. Karadag, V. T. Yilmaz and C. Thoene, *Polyhedron*, 2001, **20**, 635.
- 21 R. Boča, *Theoretical Foundations of Molecular Magnetism*, Elsevier, Amsterdam, 1999; R. Boča, *A Handbook of Magnetochemical Formulae*, Elsevier, Amsterdam, 2012.
- 22 P. Gütlich, E. Bill and A. X. Trautwein, Mössbauer Spectroscopy and Transition Metal Chemistry Fundamentals and Applications, Springer-Verlag, Berlin, Heidelberg, 2011; D. P. E. Dickson and F. J. Berry, Mössbauer Spectroscopy, Cambridge University Press, Cambridge, 2005; S. Menage and L. Que, Inorg. Chem., 1990, 29, 4293.
- 23 (a) G. B. Shul'pin, J. Mol. Catal. A: Chem., 2002, 189, 39;
  (b) G. B. Shul'pin, C. R. Chim., 2003, 6, 163.
- 24 (a) C. D. Nicola, F. Garau, M. Gazzano, M. F. C. Guedes da Silva, A. Lanza, M. Monari, F. Nestola, L. Pandolfo, C. Pettinari and A. J. L. Pombeiro, Cryst. Growth Des., 2012, 12, 2890; (b) R. R. Fernandes, J. Lasri, M. F. C. Guedes da Silva, J. A. L. da Silva, J. J. R. F. da Silva and A. J. L. Pombeiro, Appl. Catal., A, 2011, 402, 110; (c) C. D. Nicola, Y. Y. Karabach, A. M. Kirillov, M. Monari, L. Pandolfo, C. Pettinari and A. J. L. Pombeiro, Inorg. Chem., 2007, 46, 221; (d) A. M. Kirillov, M. V. Kirillova and A. J. L. Pombeiro, Coord. Chem. Rev., 2012, 256, 2741; (e) A. M. Kirillov, M. V. Kirillova, L. S. Shul'pina, P. J. Figiel, K. R. Gruenwald, M. F. C. Guedes da Silva, M. Haukka, A. J. L. Pombeiro and G. B. Shul'pin, J. Mol. Catal. A: Chem., 2011, 350, 26; (f) M. N. Kopylovich, A. C. Nunes, K. T. Mahmudov, M. Haukka, T. C. O. Mac Leod, L. M. D. R. S. Martins, M. L. Kuznetsov and J. L. Pombeiro, Dalton Trans., 2011, 40, 2822; A. (g) M. N. Kopylovich, M. J. Gajewska, K. T. Mahmudov, M. V. Kirillova, P. J. Figiel, M. F. C. Guedes da Silva, B. Gil-Hernández, J. Sanchiz and A. J. L. Pombeiro, New J. Chem., 2012, 36, 1646.

- 25 (a) M. V. Kirillova, Y. N. Kozlov, L. S. Shul'pina,
  O. Y. Lyakin, A. M. Kirillov, E. P. Talsi, A. J. L. Pombeiro and G. B. Shul'pin, *J. Catal.*, 2009, 268, 26;
  (b) M. L. Kuznetsov and A. J. L. Pombeiro, *Inorg. Chem.*, 2009, 48, 307.
- 26 G. B. Shul'pin, Y. N. Kozlov, L. S. Shul'pina, A. R. Kudinov and D. Mandelli, *Inorg. Chem.*, 2009, **48**, 10480.
- 27 L. S. Shul'pina, M. V. Kirillova, A. J. L. Pombeiro and G. B. Shul'pin, *Tetrahedron*, 2009, 65, 2424.
- 28 L. Gomez, I. Garcia-Bosch, A. Company, J. Benet-Buchholz, A. Polo, X. Sala, X. Ribas and M. Costas, *Angew. Chem., Int. Ed.*, 2009, 48, 5720.

- 29 CrysAlis PRO, CrysAlis CCD, CrysAlis Red, Oxford Diffraction Ltd, Abingdon, England, 2010.
- 30 G. M. Sheldrick, Acta Crystallogr., Sect. A: Fundam. Crystallogr., 2008, 64, 112.
- 31 SAINT: Area-Detector Integration Software, Siemens Industrial Automation, Inc., Madison, WI, 1995.
- 32 *SADABS: Area-Detector Absorption Correction*, Siemens Industrial Automation, Inc., Madison, WI, 1996.
- 33 A. L. Spek, Acta Crystallogr., Sect. D: Biol. Crystallogr., 2009, 65, 148.
- 34 A. K. Hassan, L. A. Pardi, J. Krzystek, A. Sienkiewicz, P. Goy, M. Rohrer and L.-C. Brunel, J. Magn. Reson., 2000, 142, 300.