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# Introduction

Polynuclear transition metal complexes are attractive objects in modern coordination chemistry since they can reveal a wide range of interesting features – from sophisticated crystal struc-

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# Details make the difference: a family of tetranuclear Cu<sup>II</sup>Mn<sup>III</sup> complexes with cube-like and double open cube-like cores<sup>†</sup>

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The "direct synthesis" approach, namely one-pot reaction of metal powders and ammonium salt with a methanol solution of a polydentate Schiff base (H<sub>2</sub>L) formed in situ from salicylaldehyde and ethanolamine, has been successfully used for the preparation of the new heterometallic compounds [Cu<sub>3</sub>Mn (L)<sub>4</sub>(CH<sub>3</sub>OH)<sub>3</sub>]I<sub>3</sub> (**1**), [Cu<sub>3</sub>Mn(L)<sub>4</sub>(CH<sub>3</sub>OH)<sub>3</sub>(H<sub>2</sub>O)]NCS·H<sub>2</sub>O (**2**), [Cu<sub>3</sub>Mn(L)<sub>4</sub>(CH<sub>3</sub>OH)(H<sub>2</sub>O)<sub>2</sub>, 55]Br·0.45H<sub>2</sub>O (**3**) and  $[Cu_3Mn(L)_4(H_2O)_{3,4}]BF_4 \cdot 0.6H_2O$  (4). Crystallographic analysis revealed that 1-4 are based on the tetranuclear core  $\{Cu_{1}^{H}Mn^{H}(\mu_{3}-O)_{4}\}$  where the metal centres are joined by the oxygen bridges of Schiff base ligands forming a cube-like arrangement. The novel heterometallic compound  $[Cu_3Mn(L)_4(CH_3OH)_3]_2[Mn$  $(NCS)_4$ -2CH<sub>3</sub>OH (5) has been obtained by the "building block" approach using the reaction of  $[Cu(HL)_2]$ with manganese acetate and NH<sub>4</sub>NCS in methanol. The crystal structure of **5** revealed the  $\{Cu_{1}^{I}Mn^{III}(\mu O_{2}(\mu_{3}-O_{2})$  metal core which can be viewed as a double open cube. In spite of a similar {Cu<sub>3</sub>MnO<sub>4</sub>} atom set in the cores of 1-5, the complexes show rather different molecular structures and significantly differ by the number and combinations of coordinated CH<sub>3</sub>OH/H<sub>2</sub>O solvent molecules. Variable-temperature (2-300 K) magnetic susceptibility along with variable-field magnetization measurements of 1-5 showed a decrease of the effective magnetic moment value at low temperature, indicative of the antiferromagnetic coupling of medium size  $(-55 \text{ to } -22 \text{ cm}^{-1})$ . For these systems resembling a compressed prism the coupling constant in walls  $J_4$  correlates with the averaged bonding angles in walls  $\alpha$ :  $J_4$  vs.  $\alpha$  develops approximately according to a straight line.

tures to outstanding physico-chemical properties. It is known that a synergetic effect caused by the presence of a few dissimilar metals within one close-packed molecule can be responsible for a fascinating magnetic behaviour, such as single-molecule magnetism, a possibility to possess large spin ground states or large anisotropy barriers.<sup>1–9</sup> Furthermore, this effect can promote a significant influence on the catalytic activity of the compounds in various processes.<sup>10–13</sup>

The Cu/Mn pair is among the most interesting combinations used for the construction of heterometallic complexes due to the possibility to show various oxidation states and particularly flexible coordination spheres of the metals, what can allow the formation of complicated and specific architectures. According to the Cambridge Structural Database (CSD, v. 5.37),<sup>14</sup> 69 structures of Cu/Mn complexes where at least one pair of metal atoms is joined by a single bridging atom (the carbonyl, organometallic and heterotrimetallic Cu/Mn/M compounds were excluded according to the search conditions) have been reported. They reveal a variety of Cu<sub>m</sub>Mn<sub>n</sub> combi-

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<sup>†</sup> Electronic supplementary information (ESI) available: Tables and figures with calculated magnetic parameters and correlations for 1–5. CCDC 1516021, 1516022, 1453203, 1453204 and 1516023. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt00957g † Deceased

nations, from a quite simple, from the structural point of view, binuclear antiferromagnet  $[CuLMn(H_2O)_3](ClO_4)_2^{15}$  and a single-molecule magnet  $[MnCuCl(5\text{-}Br\text{-}sap)_2(MeOH)]^{16}$  to the polynuclear cluster with a high spin ground state  $[Cu_{17}Mn_{28}O_{40}(tea)_{12}(HCO_2)_6(H_2O)_4]\cdot 36H_2O^{17}$  and the high nuclear aggregate  $[Mn_{18}Cu_6O_{14}(H_2L)_6Cl_2(H_2O)_6]Cl_6\cdot H_2O.^{18}$  Among them, only 8 tetranuclear Cu/Mn molecular complexes where the metal atoms are linked by one bridging atom were found.

In spite of the fact that a huge number of polynuclear complexes have already been prepared, the prediction of the composition and crystal structure of the final product is a very complicated task, especially if the spontaneous self-assembly method has been used for the synthesis. The large number of initial reagents under such conditions leads to a great variety of their possible combinations, thereby the study of synthesisstructure correlations in terms of the self-assembly approach towards polynuclear species is a considerable challenge. Following our interest in the preparation and study of polynuclear heterometallic complexes based on polydentate O,Ndonor ligands<sup>19</sup> we have continued to apply the "direct synthesis" method hereby expanding the classical spontaneous self-assembly approach where the formation of a polynuclear complex occurred upon one experimental stage. Among the many different ligands that can be used in such synthetic systems, the Schiff bases occupy a strong position since they have the tendency to form single oxido- and hydroxido-bridges between different metal centres which is of great importance for magnetic materials design. In the cases of 1-4, we applied the simplest way of the "direct synthesis" method using copper and manganese powders as metal sources. The utilization of a "building block" approach for comparative purposes allowed us to obtain complex 5, revealing a rather rare type of the molecular core, observed for the first time for heterometallic transition metal complexes. Herein, we describe the synthesis of five novel tetranuclear complexes containing the {Cu<sub>3</sub><sup>II</sup>Mn<sup>III</sup>O<sub>4</sub>} core, the detailed analysis of their crystal structures and the results of magnetic investigations.

# **Experimental section**

## General

All chemicals were of reagent grade and used as received. Complex  $[Cu(HL)_2]$  was prepared as reported previously.<sup>20</sup> All experiments were carried out in air. Infrared spectra (4000–400 cm<sup>-1</sup>) were recorded on a BX-FT IR "PerkinElmer" instrument in KBr pellets.

# Synthesis of $[Cu_3Mn(L)_4(CH_3OH)_3]I_3(1)$

Salicylaldehyde (0.31 ml, 3.0 mmol) and ethanolamine (0.18 ml, 3.0 mmol) were dissolved in methanol (20 ml), forming a yellow solution of  $H_2L$  (salicylidene-2-ethanolamine) which was magnetically stirred at 50–60 °C (10 min). Then, manganese powder (0.05 g, 1.0 mmol), copper powder (0.06 g, 1.0 mmol), calcium oxide (0.05 g, 1.0 mmol) and  $NH_4I$  (0.29 g,

2.0 mmol) were added to the hot yellow solution of the ligand and magnetically stirred until the total dissolution of metal powders was observed (4 h). Dark-green crystals of tetrakis ( $\mu_3$ -salicylidene-2-ethanolamine)-tris-methanol-tri-copper(II)manganese(III) triiodide suitable for X-ray analysis were isolated after one day from the resulting dark-brown solution. Yield: 0.25 g, 61% (per Cu). Anal. calc. for C<sub>39</sub>H<sub>48</sub>N<sub>4</sub>O<sub>11</sub>I<sub>3</sub>Cu<sub>3</sub>Mn: C, 34.06; H, 3.52; N, 4.07; Mn, 4.00; Cu, 13.86%. Found: C, 33.70; H, 3.25; N, 3.89; Mn, 3.6; Cu, 13.6%. IR (KBr, cm<sup>-1</sup>): 3290(br), 2915(w), 2868(w), 1633(s), 1538(s), 1447(s), 1392(m), 1297(s), 1192(m), 1148(s), 1041(s), 936(m), 896(m), 757(s), 650(s), 579(m), 526(w), 467(m), 435(m). The compound is soluble in DMSO, DMF and CH<sub>3</sub>CN and insoluble in water.

### Synthesis of [Cu<sub>3</sub>Mn(L)<sub>4</sub>(CH<sub>3</sub>OH)<sub>3</sub>(H<sub>2</sub>O)]NCS·H<sub>2</sub>O (2)

This complex was prepared in a way similar to that of 1, but using barium oxide (0.15 g, 1.0 mmol) and NH<sub>4</sub>NCS (0.15 g, 2.0 mmol) instead of calcium oxide and NH<sub>4</sub>I. Dark-green crystals suitable for X-ray analysis were obtained after one day from the resulting dark-brown solution. Yield: 0.13 g, 40% (per Cu). Anal. calc. for  $C_{40}H_{52}N_5O_{13}SCu_3Mn$ : C, 44.14; H, 4.82; N, 6.43; S, 2.95; Mn, 5.05; Cu, 17.51%. Found: C, 43.90; H, 4.55; N, 6.15; S, 2.88; Mn, 5.3; Cu, 17.2%. IR (KBr, cm<sup>-1</sup>): 3372(br), 2915(w), 2868(w), 2056(s), 1631(s), 1532(s), 1443(s), 1390(m), 1296(s), 1191(m), 1034(s), 971(w), 756(s), 646(s), 579(m), 525(w), 462(m), 437(m). The compound is soluble in DMSO, DMF and CH<sub>3</sub>CN and insoluble in water.

## Synthesis of [Cu<sub>3</sub>Mn(L)<sub>4</sub>(CH<sub>3</sub>OH)(H<sub>2</sub>O)<sub>2.55</sub>]Br·0.45H<sub>2</sub>O (3)

This complex was prepared in a way similar to that of 1, but using barium oxide (0.15 g, 1.0 mmol) and NH<sub>4</sub>Br (0.19 g, 2.0 mmol) instead of calcium oxide and NH<sub>4</sub>I. Dark-green crystals suitable for X-ray analysis were formed after one day from the resulting dark-brown solution. Yield: 0.19 g, 59% (per Cu). Anal. calc. for  $C_{37}H_{46}N_4O_{12}BrCu_3Mn$ : C, 41.76; H, 4.36; N, 5.26; Mn, 5.16; Cu, 17.91%. Found: C, 41.23; H, 3.95; N, 4.90; Mn, 5.1; Cu, 16.8%. IR (KBr, cm<sup>-1</sup>): 3350(br), 2896(w), 1638(s), 1541(s), 1444(s), 1388(m), 1300(s), 1198(m), 1035(s), 978(w), 759(s), 657(s), 580(m), 533(w), 467(m), 436(m). The compound is soluble in DMSO, DMF and CH<sub>3</sub>CN and insoluble in water.

## Synthesis of $[Cu_3Mn(L)_4(H_2O)_{3.4}]BF_4 \cdot 0.6H_2O(4)$

This complex was prepared in a way similar to that of **1**, but using barium oxide (0.15 g, 1.0 mmol) and NH<sub>4</sub>BF<sub>4</sub> (0.21 g, 2.0 mmol) instead of calcium oxide and NH<sub>4</sub>I. Dark-green crystals suitable for X-ray analysis were isolated after one day from the resulting dark-brown solution. Yield: 0.16 g, 51% (per Cu). Anal. calc. for  $C_{36}H_{44}N_4O_{12}BF_4Cu_3Mn$ : C, 40.90; H, 4.20; N, 5.30; Mn, 5.05; Cu, 18.03%. Found: C, 40.25; H, 3.89; N, 4.90; Mn, 5.6; Cu, 18.1%. IR (KBr, cm<sup>-1</sup>): 3338(br), 2933(w), 2870(w), 1638(s), 1541(s), 1444(s), 1395(m), 1297(s), 1190(m), 1035(s), 981(w), 759(s), 649(s), 581(m), 533(w), 464(m), 435(m). The compound is sparingly soluble in DMSO, DMF and CH<sub>3</sub>CN and insoluble in water.

#### Synthesis of [Cu<sub>3</sub>Mn(L)<sub>4</sub>(CH<sub>3</sub>OH)<sub>3</sub>]<sub>2</sub>[Mn(NCS)<sub>4</sub>]·2CH<sub>3</sub>OH (5)

Manganese acetate tetrahydrate (0.12 g, 0.5 mmol),  $[Cu(HL)_2]$ (0.18 g, 0.5 mmol), and NH<sub>4</sub>NCS (0.08 g, 1.0 mmol) were dissolved in methanol (20 ml) and magnetically stirred at 50–60 °C (60 min). Dark-green crystals suitable for X-ray analysis were isolated after one day from the resulting dark-brown solution. Yield: 0.06 g, 31% (per Cu). Anal. calc. for  $C_{84}H_{104}N_{12}O_{24}S_4Cu_6Mn_3$ : C, 43.11; H, 4.48; N, 7.18; S, 5.48; Mn, 7.04; Cu, 16.29%. Found: C, 42.80; H, 4.00; N, 6.95; S, 5.10; Mn, 6.9; Cu, 16.8%. IR (KBr, cm<sup>-1</sup>): 3500(br), 3050(w), 2900(w), 2080(m), 1620(s), 1510(s), 1480(s), 1250(s), 1050(s), 680(m), 470(m). The compound is sparingly soluble in DMSO, DMF and CH<sub>3</sub>CN and insoluble in water.

#### Crystallography

Details of the data collection and processing, structure solution and refinement are summarized in Table 1.

The diffraction data for 1, 2 and 5 were collected with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) using a Stoe Image Plate Diffraction System (for 1 and 2), numerical absorption correction using X-RED and X-SHAPE,<sup>21</sup> and a Bruker APEXII CCD area-detector diffractometer ( $\omega$  scans) (for 5). The data were corrected for Lorentz-polarization effects and for the effects of absorption (multi-scans method). The structures were solved by direct methods and refined by full-matrix least-squares on  $F^2$  using the SHELX-97 package.<sup>22</sup> All atoms of the cationic framework were refined anisotropically. The OH-hydrogen atoms were located and then fixed

with  $U_{iso} = 1.5U_{eq}(O, N)$ . The CH-hydrogen atoms were added geometrically  $[U_{iso} = 1.2U_{eq}(C)]$  and refined as riding. For 2, the hydrogen atoms of the solvate water molecule were not located and the positions of Cu and Mn ions were not distinguishable. Therefore, they were refined as mixed atoms with estimated partial contribution factors of 0.75 (Cu) and 0.25 (Mn). For 1, partial isomorphic substitution was suggested by mean square displacement amplitude (MSDA) analysis and parameters of Hirshfeld rigid-bond tests. In this case, the refinement of isotropic thermal parameters suggested the presence of one Cu position, one preferable Mn position (0.6) and two mixed positions with partial contributions of 0.8 (Cu) and 0.2 (Mn). In 2, the NCS counter anion and solvate water molecule are disordered over two unequally populated positions (0.65 and 0.35). These atoms were left isotropic and the NCS<sup>-</sup> anion was refined with a set of geometry restraints. Graphical visualization of the structures was made using the program Diamond 2.1e.23

X-Ray diffraction studies of 3 and 4 were performed on an "Xcalibur 3" diffractometer (graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$ ), 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 CrysAlisPro program package.<sup>24</sup> Structures were solved by direct methods and refined against  $F^2$  within anisotropic approximation for all non-hydrogen atoms using the OLEX2 program package<sup>25</sup> with SHELXS and SHELXL modules.<sup>26</sup> All H atoms were placed in idealized positions and constrained to ride on their parent

Complex	1	2	3	4	5
Empirical formula	C20H40C112I2MnN4O11	C40H52C112MnN5O12S	C27H46N4O12BrCU2Mn	CaeH44N4O4aBF4CuaMn	CeaH104CUcMn2N12O24S4
Formula weight	1375.07	1088.49	1064.25	1057.12	2340.09
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	PĪ
a/Å	13.3737(11)	18.5500(12)	17.9628(14)	16.8093(9)	13.5453(4)
b/Å	15.6103(8)	12.9260(8)	13.0651(9)	13.6009(7)	15.1781(4)
c/Å	23.0857(18)	19.8784(14)	19.7336(14)	19.1235(10)	26.9837(9)
$\alpha/^{\circ}$	90	90	90	90	90.892(2)
$\beta/^{\circ}$	92.535(9)	98.170(10)	96.001(7)	93.479(5)	103.293(2)
$\gamma/^{\circ}$	90	90	90	90	114.678(2)
$V/Å^3$	4814.8(6)	4718.0(5)	4605.8(6)	4364.0(4)	4866.7(3)
Z	4	4	4	4	2
Calculated density/g cm <sup>-3</sup>	1.897	1.532	1.535	1.613	1.597
Experiment temperature/K	213	213	105	298	173
$\mu$ (Mo-K <sub><math>\alpha</math></sub> )/mm <sup>-1</sup>	3.544	1.705	2.560	1.804	1.821
F(000)	2676	2236	2156	2148	2394
Reflections collected/unique	38 085/10 399	35 799/9684	23 351/10 477	51 481/14 779	55 094/18 104
R <sub>int</sub>	0.0368	0.0456	0.1225	0.0746	0.1120
Reflections with $F^2 > 2\sigma(F^2)$	7203	6144	4162	5567	9405
$\Theta_{\min}, \Theta_{\max} / ^{\circ}$	2.20, 27.00	4.14, 26.73	2.866, 28.997	2.930, 32.711	1.72, 25.50
$R_1, F^2 > 2\sigma(F^2)$	0.0309	0.0466	0.1023	0.0778	0.0573
$wR_2$ (all data)	0.0718	0.1394	0.3183	0.2870	0.1118
GoF	0.859	0.928	0.978	0.993	0.904

<sup>*a*</sup> For 3 and 4 the formula, formula weight, density, F(000) and  $\mu$  parameters are calculated without masked solvent molecules.

#### Paper

atoms with  $U_{iso} = nU_{eq}$  (n = 1.5 for OH and CH<sub>3</sub> groups and n =1.2 for all other H atoms). H atoms of water molecules were positioned to fit the hydrogen bond system. In 3, the Br1 anion, O4S water molecule, and C1S atom of the O1S-C1S methanol molecule were disordered each one over two sites. Their relative occupancy factors were refined in isotropic approximation and fixed at the final steps of refinement at the values of 0.68/0.32, 0.60/0.40, and 0.50/0.50, respectively. O1S-C1SA and O1S-C1SB bonds were restrained to be approximately equal to within 0.01 Å. Anisotropic thermal parameters of disordered C1S(A,B) and O4S(A,B) atoms were restrained to be the same within 0.04 Å and approximately equal to within 0.02 Å<sup>2</sup>. In 4, three F atoms of the BF<sub>4</sub> anion were disordered around the B(1)-F(1) rotation axis over two sites with relative occupancies of 0.55/0.45. All B-F bonds were restrained to be approximately equal to within 0.01 Å. Anisotropic thermal parameters of all atoms of the anion were restrained to be approximately equal to within 0.02 Å<sup>2</sup>. O4W molecule was disordered over two sites with relative occupancies of 0.60/0.40. All oxygen atoms of water molecules in 4 were restrained to be approximately isotropic to within 0.02 Å<sup>2</sup>. All occupancy factors were obtained by full-matrix refinement and fixed in the final refinement cycles.

For 4, the low quality and small size of the crystals cause a rather weak signal with small  $I/\sigma$  values of the reflections, up to the total absence of strong reflections in the area of higher angles  $(2\theta > 35-40^\circ)$ . This makes the assignment of the metal types a troublesome question, since the atomic scattering factors of the Cu and Mn atoms are rather close. Thus the relative Cu/Mn content was determined from the elemental analysis, and the position of the Mn(1) cation was located on the basis of the refinement indicators and coordination features of the metal centres. It should be noted that the Mn(1) position cannot be determined undoubtedly in this case and it can be disordered among all positions of the metal centres. Assuming the Mn/Cu disorder over all four metal positions, one can obtain the  $R_1$  value of 0.0673 that is lower than the actual value of 0.0778. Disordering over any two sites gives the  $R_1$ value in the range of 0.070-0.073. However, the metal coordination features and the absence of strong high-angle reflections do not allow us to ensure the Cu/Mn disorder, and thus we have decided to maintain the non-mixed metal positions in 4.

In structures of 3 and 4, several isolated electron density peaks were located during the refinement, which were believed to be of a highly disordered solvent molecule(s). Satisfactory results ( $R_1 = 0.108$  in 3 and 0.081 in 4) were obtained modelling the disordered C, N and O atoms, but very large displacement parameters for them were observed. The SQUEEZE procedure implemented in PLATON<sup>27</sup> indicated solvent cavities (2 cavities of 168 Å<sup>3</sup> each containing approximately 49 electrons, in 3, and 4 cavities of 30 Å<sup>3</sup> each containing approximately 4 electrons, in 4). In the final refinement, this contribution was removed from the intensity data that produced better refinement results.

Crystallographic data for the structures reported can be obtained by quoting the deposition numbers CCDC 1516021 (1), 1516022 (2), 1453203 (3), 1453204 (4) and 1516023 (5).

#### Magnetic measurements

A SQUID magnetometer (MPMS-XL7, Quantum Design) has been used for obtaining magnetic data using the RSO mode of detection. The susceptibility taken at B = 0.1 T between T =2–300 K 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 T = 4.6 K.

# **Results and discussion**

#### Synthesis and spectroscopic analysis

Complexes 1–4 were obtained from the reaction of manganese powder, copper powder, ammonium salt (NH<sub>4</sub>I for 1, NH<sub>4</sub>NCS for 2, NH<sub>4</sub>Br for 3 and NH<sub>4</sub>BF<sub>4</sub> for 4) and calcium (1) or barium oxide (2–4) with a methanol solution of the chelating polydentate ligand source (H<sub>2</sub>L), formed *in situ*, using a molar ratio of Mn:Cu:NH<sub>4</sub>X:H<sub>2</sub>L = 1:1:2:3. The ratio in the initial reaction mixture is fundamental, since only this stoichiometry afforded the heterometallic complexes 1–4.

The Schiff base  $H_2L$  (Scheme 1) was obtained by condensation of salicylaldehyde and ethanolamine. The reaction was initiated and brought to completion by heating and stirring in open air. Dark-brown solutions were obtained at the end of all reactions. Dark-green crystals of 1–4 that showed analytical data consistent with the Mn: Cu = 1:3 stoichiometry were formed after standing at room temperature within one day. The general reactions can be written as follows:

$$\begin{split} & 4Mn + 12Cu + 16H_2L + 12NH_4I + 12CH_3OH + 11O_2 \\ & \rightarrow 4[Cu_3Mn(L)_4(CH_3OH)_3]I_3 + 12NH_3 + 22H_2O \end{split}$$

$$\begin{split} & 4\text{Mn} + 12\text{Cu} + 16\text{H}_{2}\text{L} + 4\text{NH}_{4}\text{NCS} + 12\text{CH}_{3}\text{OH} + 9\text{O}_{2} \\ & \rightarrow 4[\text{Cu}_{3}\text{Mn}(\text{L})_{4}(\text{CH}_{3}\text{OH})_{3}(\text{H}_{2}\text{O})]\text{NCS}\cdot\text{H}_{2}\text{O} + 4\text{NH}_{3} + 10\text{H}_{2}\text{O} \end{split}$$

$$\begin{split} 4Mn + & 12Cu + 16H_2L + 4NH_4Br + 12CH_3OH + 9O_2 \\ & \rightarrow 4[Cu_3Mn(L)_4(CH_3OH)(H_2O)_{2.55}]Br\cdot 0.45H_2O + 4NH_3 + 6H_2O \end{split} \label{eq:4}$$

$$\begin{split} & 4Mn + 12Cu + 16H_2L + 4NH_4BF_4 + 9O_2 \\ & \rightarrow 4[Cu_3Mn(L)_4(H_2O)_{3,4}]BF_4 \cdot 0.6H_2O + 4NH_3 + 2H_2O \end{split} \eqno(4)$$



Scheme 1 The tridentate Schiff base H<sub>2</sub>L

We suppose that the role of calcium (or barium) oxide is to promote complete deprotonation of the amino alcohol Schiff base ligand. Although the "direct synthesis" method foresees deprotonation upon reaction of zerovalent metal,<sup>19</sup> in our case an additional deprotonating reagent (base) was required. None of complexes 1–4 were reproduced in the absence of the s-metal oxide. Compound 1 could also be obtained using barium oxide instead of calcium oxide without any difference in the crystallization process and composition. It should be noted that only the systems with methanol as the solvent resulted in the precipitation of the heterometallic compounds. Such complexes, if formed, were not isolated from DMF, DMSO and acetonitrile probably because of their high solubility in these solvents.

Complex 5 was formed through the reaction of  $[Cu(HL)_2]$  with manganese acetate and NH<sub>4</sub>NCS in methanol solution, using the molar synthetic ratio of  $[Cu(HL)_2]:Mn(OAc)_2:NH_4NCS = 1:1:2$ . Dark-green microcrystals of 5 were isolated from the dark-brown solution after one day standing at room temperature. The reaction proceeds in the following way:

$$\begin{split} & 6[\text{Cu}(\text{HL})_2] + 3\text{Mn}(\text{OAc})_2 + 4\text{NH}_4\text{NCS} + 8\text{CH}_3\text{OH} + 1/2\text{O}_2 \\ & \rightarrow [\text{Cu}_3\text{Mn}(\text{L})_4(\text{CH}_3\text{OH})_3]_2[\text{Mn}(\text{NCS})_4]\cdot 2\text{CH}_3\text{OH} + 4\text{H}_2\text{L} \\ & + 4\text{NH}_4\text{OAc} + 2\text{HOAc} + \text{H}_2\text{O} \end{split}$$

(5)

The IR spectra of 1–5 in the 4000–400 cm<sup>-1</sup> range confirmed the presence of the Schiff base ligands. The very strong bands at 1633 (1), 1631 (2), 1638 (3, 4) and 1620 cm<sup>-1</sup> (5) were assigned to the  $\nu$ (C=N) stretching vibrations of the Schiff bases. The broad bands in the region of 3600–3100 cm<sup>-1</sup> in the spectra of all compounds included the  $\nu$ (O-H) frequencies of the CH<sub>3</sub>OH or/and H<sub>2</sub>O molecules. The presence of the uncoordinated thiocyanate ligand in 2 can be identified by the strong  $\nu$ (C-N) absorption peak at 2056 cm<sup>-1</sup> and the weak  $\nu$ (C-S) vibration at 750 cm<sup>-1</sup>. In the spectrum of 5 the strong band at 2080 cm<sup>-1</sup> and the weak peak at 790 cm<sup>-1</sup> are attributed to the  $\nu$ (C-N) and  $\nu$ (C-S) vibrations, respectively, that imply coordination of the NCS-group through the nitrogen atom.<sup>28</sup>

#### Crystal structures

The single crystal X-ray analysis shows that the overall structural configurations of the heterometallic Cu<sup>II</sup>Mn<sup>III</sup> complexes 1–4 are similar. All of them are based on the tetranuclear core {Cu<sub>3</sub>Mn( $\mu_3$ -O)<sub>4</sub>} (Fig. 1), where the metal centres are joined by the  $\mu_3$ -O bridges of Schiff base ligands forming a cube-like arrangement. The Schiff base molecules, H<sub>2</sub>L, in 1–4 are doubly deprotonated and show tridentate (N,O,O) coordination. The tetranuclear core {Cu<sub>3</sub>Mn( $\mu_3$ -O)<sub>4</sub>} belongs to the {M<sub>4</sub>( $\mu_3$ -X)<sub>4</sub>} (M = metal atom, X = bridging atom) molecular structure type (MST), obtained by excluding all non-bridging non-metal atoms of the structure. This MST, according to the CSD, dominates over all other tetranuclear MSTs, taking almost 30% of all known tetranuclear complexes.

Complex 1 contains three crystallographically independent  $copper(\pi)$  atoms, two of which, Cu(1) and Cu(2), have distorted



Fig. 1 The ball-and-stick representation of the  $\{Cu_3Mn(\mu_3-O)_4\}$  molecular core in 1–4. Color scheme: Cu, cyan; Mn, magenta; O, red.

octahedral environments with O5N donor sets formed by oxygen and nitrogen atoms from the Schiff base ligands and oxygen atoms from the coordinated molecules of methanol (Fig. 2). The coordination geometry around the Cu(3) atom is square pyramidal with the O4N donor set. The equatorial Cu–O(N) bond lengths range from 1.901(2) to 1.992(2) Å, while the apical Cu-O distances vary from 2.379(3) to 2.580(2) Å (Table 2). The O-Cu-O(N)<sub>cis</sub> bond angles vary from 72.63(8)° to 109.52(9)°, while O-Cu-O(N)<sub>trans</sub> angles span from 155.88(8) to 177.40(11)°. A weak contact [3.8604(6) Å] between the Cu(3) atom of the metal core and the I(1) atom of the uncoordinated  $I_3^-$  anion exists and, in spite of the fact that it is greater than the sum of the van der Waals radii of the respective atoms, 3.38 Å,<sup>29,30</sup> it should not be ignored. The value of the angle  $O(3)-Cu(3)\cdots I(1) = 162.99(5)^{\circ}$  also supports this assumption. The Mn(III) atom adopts a distorted octahedral geometry with the {MnO<sub>5</sub>N} chromophore formed by the O and N atoms of the Schiff bases and methanol with the equatorial Mn-O(N) distances varying from 1.8675(2) to 1.958(3) Å and the apical Mn–O bond distances equal to 2.320(3) and 2.411(2) Å (Table 2). The cis and trans O-Mn-O(N) bond angles range from 75.26(8) to 101.81(9)° and from 159.06(9) to 176.71(11)°, respectively. The intermetallic M····M non-bonded distances within the metal core lie in the range of 3.115(1) - 3.520(9) Å.

Strong intramolecular O–H···O hydrogen bonding in **1** involving the oxygen atoms from Schiff bases and the coordinated  $CH_3OH$  molecules strengthens the overall tetra-



Fig. 2 The crystal structure of 1 with atom numbering. The hydrogen atoms are omitted for clarity.



Fig. 3 The crystal structure of 2 with atom numbering. The hydrogen atoms are omitted for clarity.



Fig. 4 The crystal structure of 3 with atom numbering. The hydrogen atoms are omitted for clarity.



**Fig. 5** The structure of **4** with atom numbering. The hydrogen atoms are omitted for clarity.

second part as the non-coordinated one. This results in a mixed  $O_5N$  octahedral/ $O_4N$  square pyramidal coordination environment of Cu2 in 3 and Cu3 in 4, so that 55% of complex cations in 3 and 40% in 4 reveal octahedral coordination of all metal centres, similar to 2, while 45% of cations in 3 and 60% in 4 reveal coordination type similar to 1, where one of the metal centres has a square pyramidal coordination environment. The O-M-O(N)<sub>cis</sub> bond angles in 2–4 range from 72.4(2)°

Cu1-O1	1.992(2)	Cu3-O1	1.963(2)
Cu1-O2	1.909(2)	Cu3-O3	2.474(2)
Cu1-O3	1.958(2)	Cu3-O5	1.968(2)
Cu1-07	2.580(2)	Cu3-O6	1.901(2)
Cu1-O9	2.501(3)	Cu3-N3	1.929(3)
Cu1-N1	1.942(3)	Mn1-O1	2.411(2)
Cu2-O3	1.972(2)	Mn1-O5	1.942(2)
Cu2-O4	1.904(2)	Mn1-O7	1.944(2)
Cu2-O5	2.576(2)	Mn1-O8	1.865(2)
Cu2-O7	1.968(2)	Mn1-011	2.320(3)
Cu2-O10	2.379(3)	Mn1-N4	1.958(3)
Cu2-N2	1.938(3)		
O1-Cu1-O2	169.24(10)	O1-Cu3-O3	75.07(8)
O1-Cu1-O3	87.58(9)	O1-Cu3-O5	86.11(9)
01-Cu1-07	74.83(8)	O1-Cu3-O6	95.60(10)
O1-Cu1-O9	91.88(9)	O1-Cu3-N3	168.50(11)
01-Cu1-N1	83.86(10)	O3-Cu3-O5	78.82(8)
O2-Cu1-O3	94.68(9)	O3-Cu3-O6	99.70(9)
O2-Cu1-O7	95.76(9)	O3-Cu3-N3	109.52(9)
O2-Cu1-O9	98.69(10)	O5-Cu3-O6	177.40(11)
O2-Cu1-N1	94.14(11)	O5-Cu3-N3	84.53(10)
O3-Cu1-O7	72.81(8)	O6-Cu3-N3	93.99(11)
O3-Cu1-O9	88.41(8)	O1-Mn1-O5	75.26(8)
O3-Cu1-N1	171.17(10)	O1-Mn1-O7	79.84(8)
O7-Cu1-O9	157.15(8)	O1-Mn1-O8	100.06(10)
07-Cu1-N1	106.83(9)	O1-Mn1-O11	159.06(9)
O9-Cu1-N1	89.72(10)	O1-Mn1-N4	101.81(9)
O3-Cu2-O4	170.35(10)	O5-Mn1-O7	89.50(9)
O3-Cu2-O5	76.22(8)	O5-Mn1-O8	93.66(11)
O3-Cu2-O7	88.11(9)	O5-Mn1-O11	89.31(11)
O3-Cu2-O10	91.16(8)	O5-Mn1-N4	172.86(10)
O3-Cu2-N2	83.52(9)	O7-Mn1-O8	176.71(11)
O4-Cu2-O5	95.08(9)	O7-Mn1-O11	86.06(10)
O4-Cu2-O7	93.32(9)	O7-Mn1-N4	83.55(10)
O4-Cu2-O10	98.45(10)	O8-Mn1-O11	94.89(12)
O4-Cu2-N2	94.21(10)	O8-Mn1-N4	93.27(11)
O5-Cu2-O7	72.63(8)	O11-Mn1-N4	91.81(11)
O5-Cu2-O10	155.88(8)		
O5-Cu2-N2	100.93(9)		
O7-Cu2-O10	86.69(9)		
O7-Cu2-N2	170.52(10)		
O10-Cu2-N2	97.88(10)		

nuclear structure of the complex [the O···O distances vary from 2.672(8) to 2.691(12) Å, while the O–H···O bond angles range from 166.71(22) to  $175.17(19)^{\circ}$ ].

In the crystal structures of compounds 2, 3 and 4 all metal atoms reveal an octahedral O5N coordination environment with strong axial distortion (Fig. 3, 4 and 5). The equatorial O<sub>3</sub>N donor set of each metal centre is formed by oxygen and nitrogen atoms from the Schiff base ligand with the M-O(N) bond lengths ranging from 1.862(5) to 1.986(3) Å. One of the axial oxygen atoms belongs to the Schiff base too while the second one belongs to the coordinated methanol or water molecule, with M-O bonds ranging from 2.355(9) to 2.741(11) Å (Tables 3–5). In the case of 3 and 4 a high degree of thermal and/or structural disorder of coordinated water molecules was observed. Particularly, atoms O4S in 3 and O4W in 4 are both disordered in such a way that the Cu-O bond length floats from 2.536(18) to 3.56(3) Å and from 2.45(2) to 3.055(12) Å, respectively. Therefore, the first part of each of these water molecules can be treated as coordinated to Cu centres and the

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Table 3 Selected geometrical parameters (distances/Å and angles/°) for 2

Table 4 Selected geometrical parameters (distances/Å and angles/°) for 3

M1-O1	1.986(3)	M3-O1	1.956(3)	Cu1-O1	1.894(7)	Cu3-O4	2.553(7)
M1-O2	1.916(3)	M3-O3	2.489(3)	Cu1-O2	1.985(7)	Cu3-O6	1.961(6)
M1-O3	1.957(2)	M3-O5	1.964(3)	Cu1-O6	2.508(7)	Cu3-07	1.883(7)
M1-08	2.564(2)	M3-O6	1.904(3)	Cu1-O8	1.983(7)	Cu3-O8	1.970(6)
M1-09	2.466(4)	M3-O12	2.476(4)	Cu1-O2S	2.472(7)	Cu3-O3S	2.382(10)
M1-N1	1.934(3)	M3-N3	1.929(4)	Cu1-N1	1.901(9)	Cu3-N4	1.927(8)
M2-O3	1.957(3)	M4-01	2.480(3)	Cu2-O2	1.953(7)	Mn1-O2	2.451(7)
M2-O4	1.898(3)	M4-O5	1.949(3)	Cu2-O3	1.892(6)	Mn1-O4	1.948(6)
M2-O5	2.544(3)	M4-07	1.895(3)	Cu2-O4	1.951(7)	Mn1-O5	1.883(7)
M2-O8	1.964(3)	M4-08	1.949(3)	Cu2-O8	2.438(7)	Mn1-O6	1.940(6)
M2-O10	2.373(3)	M4-011	2.383(5)	Cu2-O4SA	2.536(18)	Mn1-O1S	2.355(9)
M2-N2	1.943(3)	M4-N4	1.943(4)	Cu2-N2	1.932(8)	Mn1-N3	1.960(8)
O1-M1-O2	170.58(13)	O1-M3-O3	74.59(9)	O1-Cu1-O2	170.9(3)	O4-Cu3-O6	72.4(2)
O1-M1-O3	87.47(11)	O1-M3-O5	87.59(11)	O1-Cu1-O6	95.9(3)	O4-Cu3-O7	95.8(3)
O1-M1-O8	75.85(10)	O1-M3-O6	94.49(13)	O1-Cu1-O8	94.3(3)	O4-Cu3-O8	75.6(3)
O1-M1-O9	91.70(13)	O1-M3-O12	86.73(14)	O1-Cu1-O2S	98.2(3)	O4-Cu3-O3S	157.4(3)
O1-M1-N1	83.80(13)	O1-M3-N3	169.98(13)	01-Cu1-N1	93.9(3)	O4-Cu3-N4	103.9(3)
O2-M1-O3	94.64(11)	O3-M3-O5	79.36(10)	O2-Cu1-O6	75.9(2)	O6-Cu3-O7	94.3(3)
O2-M1-O8	95.96(10)	O3-M3-O6	95.64(11)	O2-Cu1-O8	87.2(3)	O6-Cu3-O8	88.0(3)
O2-M1-O9	97.58(13)	O3-M3-O12	157.66(13)	O2-Cu1-O2S	90.8(3)	O6-Cu3-O3S	88.1(3)
O2-M1-N1	94.33(13)	O3-M3-N3	109.25(12)	O2-Cu1-N1	84.9(3)	O6-Cu3-N4	170.7(3)
O3-M1-O8	72.93(9)	O5-M3-O6	173.89(13)	O6-Cu1-O8	73.8(2)	O7-Cu3-O8	170.0(3)
O3-M1-O9	86.73(12)	O5-M3-O12	87.86(13)	O6-Cu1-O2S	158.3(2)	O7-Cu3-O3S	96.9(3)
O3-M1-N1	171.00(13)	O5-M3-N3	84.13(13)	O6-Cu1-N1	106.9(3)	O7-Cu3-N4	94.6(3)
O8-M1-O9	156.38(11)	O6-M3-O12	97.98(14)	O8-Cu1-O2S	88.7(3)	O8-Cu3-O3S	93.0(3)
O8-M1-N1	106.89(12)	O6-M3-N3	94.32(15)	O8-Cu1-N1	171.6(3)	O8-Cu3-N4	82.8(3)
O9-M1-N1	91.30(15)	O12-M3-N3	87.31(15)	O2S-Cu1-N1	88.5(3)	O3S-Cu3-N4	93.6(3)
O3-M2-O4	173.58(13)	O1-M4-O5	74.46(10)	O2-Cu2-O3	94.9(3)	O2-Mn1-O4	73.9(3)
O3-M2-O5	78.09(9)	O1-M4-O7	97.81(11)	O2-Cu2-O4	86.4(3)	O2-Mn1-O5	98.1(3)
O3-M2-O8	88.30(11)	O1-M4-O8	78.55(11)	O2-Cu2-O8	76.2(3)	O2-Mn1-O6	78.1(3)
O3-M2-O10	88.84(12)	O1-M4-O11	156.06(13)	O2-Cu2-O4SA	83.9(5)	O2-Mn1-O1S	156.7(3)
O3-M2-N2	83.52(12)	O1-M4-N4	109.33(14)	O2-Cu2-N2	168.1(3)	O2-Mn1-N3	105.6(3)
O4-M2-O5	96.81(11)	O5-M4-O7	95.30(12)	O3-Cu2-O4	176.9(3)	O4-Mn1-O5	94.3(3)
O4-M2-O8	93.92(13)	O5-M4-O8	88.01(11)	O3-Cu2-O8	98.8(3)	O4-Mn1-O6	88.3(3)
O4-M2-O10	97.20(13)	O5-M4-O11	85.46(15)	O3-Cu2-O4SA	94.1(5)	O4-Mn1-O1S	86.7(3)
O4-M2-N2	94.02(14)	O5-M4-N4	170.42(14)	O3-Cu2-N2	94.0(3)	O4-Mn1-N3	171.8(3)
O5-M2-O8	72.54(10)	O7-M4-O8	174.27(14)	O4-Cu2-O8	78.8(3)	O5-Mn1-O6	174.6(3)
O5-M2-O10	157.89(11)	O7-M4-O11	96.89(15)	O4-Cu2-O4SA	88.9(5)	O5-Mn1-O1S	96.1(3)
O5-M2-N2	103.91(11)	O7-M4-N4	92.90(14)	O4-Cu2-N2	85.1(3)	O5-Mn1-N3	93.9(̀3)
O8-M2-O10	89.49(12)	O8-M4-O11	88.02(14)	O8-Cu2-O4SA	157.1(5)	O6-Mn1-O1S	88.8(3)
O8-M2-N2	171.64(13)	O8-M4-N4	84.24(13)	O8-Cu2-N2	110.2(3)	O6-Mn1-N3	83.6(3)
O10-M2-N2	92.09(14)	O11-M4-N4	88.65(18)	O4SA-Cu2-N2	87.6(5)	O1S-Mn1-N3	91.8(3)

to  $112.96(16)^{\circ}$ , while the O–M–O(N)<sub>trans</sub> angles span from  $155.29(15)^{\circ}$  to  $176.9(3)^{\circ}$ . Systematic differences between bonds and angles involving Cu and Mn centres are negligible.

The M···M non-bonded distances within the metal core for complexes 2–4 vary in the 3.1040(18)–3.5242(7) Å range. Similar to 1, the tetranuclear cations in 2–4 are fastened by strong intramolecular O–H···O hydrogen bonds involving the oxygen atoms from Schiff bases that act as acceptors and the coordinated solvent molecules (CH<sub>3</sub>OH or H<sub>2</sub>O) as donors (Table 6). In each of these compounds, uncoordinated anions occupy cavities between closely packed bulky cations and are linked to them *via* non-directional electrostatic forces as well as intermolecular H-bonding.

Crystallographic analysis reveals that complex 5 consists of two heterometallic  $[Cu_3Mn(L)_4(CH_3OH)_3]^{2+}$  cations having slightly different geometries, the  $[Mn(NCS)_4]^{2-}$  anion and two uncoordinated molecules of methanol. Each cation is based on the  $\{Cu_3Mn(\mu-O)_2(\mu_3-O)_2\}$  metal core which can be viewed as the double open cube  $\{M_4(\mu-X)_2(\mu_3-X)_2\}$  (Fig. 6). According to the CSD, only two complexes of this MST were found:  $[(\mu_2\text{-}SC_6H_4\text{NO}_2\text{-}4)_2(\mu_3\text{-}SC_6H_4\text{NO}_2\text{-}4)_2(\text{CuPPh}_3)_4]^{31}$  and  $[\text{Li}_3(\text{tmeda})_2\text{Cp}\text{+}\text{TaS}_3\text{Cl}]_2(\mu\text{-}\text{tmeda})$  (tmeda = tetramethyl-ethylenediamine,  $\text{Cp}\text{+}=\text{C}_5\text{Me}_5$ ).<sup>32</sup> Hence, 5 represents the first example of a heterometallic transition metal complex with the  $\{M_4(\mu\text{-}X)_2(\mu_3\text{-}X)_2\}$  molecular structure type. The O atoms from the deprotonated Schiff bases bridge the Cu and Mn centres in both double open cube-like cations, whereby two  $\mu_3$  [O2, O6] and two  $\mu_2$  bridge atoms [O4, O8] exist in one cation and two  $\mu_3$  [O10, O12] and two  $\mu_2$  bridge atoms [O14, O16] in another one (Fig. 7).

All copper atoms in 5 have five-coordinated distorted square-pyramidal coordination environments with  $O_4N$  donor sets which in the case of Cu1, Cu3, Cu4 and Cu5 are formed by donor atoms of two Schiff base ligands and one coordinated molecule of methanol, while in the case of Cu2 and Cu6 they are formed exclusively by three deprotonated Schiff bases. The equatorial Cu–O(N) distances vary from 1.889(4) to 1.996(4) Å, while the apical Cu–O bond lengths lie in the 2.376(4)–2.504(5)

Table 5 Selected geometrical parameters (distances/Å and angles/°) for 4

Table 6 Hydrogen bonding distances (Å) and angles (°) for complexes  $1{-}5$ 

Cu1-O2	2.451(4)	Cu3-O2	1.965(3)
Cu1-O6	1.967(4)	Cu3-O4	2.534(5)
Cu1-07	1.894(4)	Cu3-O5	1.880(4)
Cu1-O8	1.965(4)	Cu3-O6	1.949(4)
Cu1–OW1	2.606(6)	Cu3-OW4B	2.45(2)
Cu1-N4	1.940(4)	Cu3-N3	1.926(5)
Cu2-O1	1.862(5)	Mn1-O3	1.882(4)
Cu2-O2	1.942(4)	Mn1-O4	1.955(4)
Cu2-O4	1.977(4)	Mn1-06	2.475(4)
Cu2-O8	2.501(4)	Mn1-08	1.947(4)
Cu2–OW3	2.465(7)	Mn1-OW2A	2.741(11)
Cu2-N1	1.948(5)	Mn1-N2	1.940(5)
O2-Cu1-O6	73.80(13)	O2-Cu3-O4	72.80(14)
O2-Cu1-O7	93.81(16)	O2-Cu3-O5	95.45(16)
O2-Cu1-O8	79.99(15)	O2-Cu3-O6	171.46(19)
O2-Cu1-OW1	157.86(13)	O2-Cu3-OW4B	89.7(5)
O2-Cu1-N4	112.96(16)	O2-Cu3-N3	169.37(19)
06-Cu1-O7	94.97(17)	O4-Cu3-O5	92.87(15)
O6-Cu1-O8	87.74(16)	O4-Cu3-O6	79.71(15)
O6-Cu1-OW1	85.99(16)	O4-Cu3-OW4B	160.7(4)
O6-Cu1-N4	167.78(19)	O4-Cu3-N3	109.25(19)
O7-Cu1-O8	172.28(17)	O5-Cu3-O6	171.46(19)
O7-Cu1-OW1	96.91(17)	O5-Cu3-OW4B	97.0(4)
07-Cu1-N4	94.70(18)	O5-Cu3-N3	94.87(18)
O8-Cu1-OW1	90.47(17)	O6-Cu3-OW4B	91.4(4)
08-Cu1-N4	83.63(17)	O6-Cu3-N3	83.73(18)
OW1-Cu1-N4	85.44(18)	OW4B-Cu3-N3	86.5(5)
O1-Cu2-O2	174.55(19)	O3-Mn1-O4	173.7(2)
O1-Cu2-O4	95.0(2)	O3-Mn1-O6	94.06(16)
O1-Cu2-O8	96.93(17)	O3-Mn1-O8	95.57(17)
O1-Cu2-OW3	98.26(19)	O3-Mn1-OW2A	101.5(2)
O1-Cu2-N1	94.3(2)	O3-Mn1-N2	93.9(2)
O2-Cu2-O4	87.44(17)	O4-Mn1-O6	81.16(16)
O2-Cu2-O8	79.10(15)	O4-Mn1-O8	87.26(16)
O2-Cu2-OW3	86.66(17)	O4-Mn1-OW2A	84.43(18)
O2-Cu2-N1	83.47(18)	O4-Mn1-N2	83.7(2)
O4-Cu2-O8	72.84(14)	O6-Mn1-O8	75.02(14)
O4-Cu2-OW3	88.5(2)	O6-Mn1-OW2A	155.29(15)
O4-Cu2-N1	170.4(2)	O6-Mn1-N2	108.5(2)
O8-Cu2-OW3	156.87(15)	O8-Mn1-OW2A	84.37(18)
08-Cu2-N1	108.37(18)	O8-Mn1-N2	169.6(2)
OW3-Cu2-N1	87.8(2)	OW2A-Mn1-N2	89.6(2)

D-H···A	D-H	Н…А	D····A	D-H···A
1				
O9-H9O…O6	0.85	1.84	2.687(4)	175
O10-H10O…O2	0.85	1.85	2.691(12)	171
011-H110····04	0.85	1.84	2.672(8)	167
2				
O9-H1W…O6	0.85	1.84	2.679(6)	173
O10-H2W…O2	0.85	1.86	2.688(8)	165
011-H3W…04	0.85	1.89	2.716(16)	162
O12-H5W…O7	0.85	1.92	2.734(6)	161
3				
O1S-H1S…O7	0.86	1.80	2.635(11)	162.6
O2S-H2SA····O3	0.87	1.87	2.696(10)	157.4
O3S-H3SA…O1	0.85	1.93	2.706(11)	151.1
O4SA-H4SB…O5	1.03	1.92	2.75(2)	135.6
4				
OW1-HW1A····O3	0.86	1.95	2.790(4)	166.0
OW2A-HW2A…O1	0.85	1.96	2.761(5)	157.4
OW3-HW3A····O5	0.87	1.85	2.665(4)	155.7
OW4B-HW4D····O7	0.85	2.08	2.897(19)	159.7
5				
O17-H17O…O5	0.85	1.84	2.664(7)	163
O19-H19O…O3	0.85	1.89	2.678(7)	154
O18-H18O…O20	0.85	1.80	2.602(7)	157
O20-H20O…O1	0.85	1.83	2.668(7)	168
O21-H21O…O13	0.85	1.93	2.733(6)	152
O22-H22O…O9	0.85	1.89	2.674(7)	154
O24-H24O…O11	0.85	1.80	2.653(8)	178
O23-H23O…O24	0.85	1.88	2.644(7)	148



Fig. 6 The ball-and-stick representation of the  $\{Cu_3Mn(\mu-O)_2(\mu_3-O)_2\}$  molecular core in 5. Color scheme: Cu, cyan; Mn, magenta; O, red.

Å range. The cis angles around the Cu atoms range from 73.39(15) to  $124.94(17)^{\circ}$  and the *trans* bond angles span from 158.44(19) to 179.13(16)° (Table 7). In assessing the molecular core type for all 1-5 complexes the upper limits of the apical Cu-O bond lengths were set using the sum of van der Waals radii of the respective atoms, 2.92 Å (van der Waals radius of Cu is 1.4 Å and of O is 1.52 Å (ref. 29 and 30)). All apical Cu–O distances in 1-4 are lower than this value. In the case of 5, the distances over or close to it, namely Cu1-O4 = 2.888(4), Cu3-O8 = 2.907(4), Cu4-O16 = 2.819(5) and Cu5-O14 = 3.044(5) Å, were excluded during the core type definition. The correctness of such differentiation and assignment of the molecular core type in 1-4 and 5 to the cube and double open cube realizations, respectively, are supported by the data obtained from the magnetic studies of 1-5 and are in agreement with established magnetostructural correlations (see below).

Both Mn1 and Mn2 atoms of the double open cube-like cations adopt a distorted octahedral geometry formed by the O and N atoms of the ligands and methanol with the Mn–O(N)

distances varying from 1.857(4) to 2.331(4) Å. The *cis* and *trans* O–Mn–O(N) bond angles range from 76.60(14) to  $102.76(16)^{\circ}$  and from 165.12(16) to  $173.75(16)^{\circ}$ , respectively. The Mn3 atom from the  $[Mn(NCS)_4]^{2-}$  anion has distorted tetrahedral coordination geometry with Mn–N bond lengths in the 2.020(6)-2.061(7) Å range and N–Mn–N bond angles ranging from  $102.8(3)^{\circ}$  to  $118.4(3)^{\circ}$ . The intermetallic M…M non-bonded distances within both metal cores are in the range of 3.087(2)-3.608(2) Å. Similar to 1–4, the tetranuclear cations in 5 are reinforced by strong intramolecular O–H…O hydrogen bonds involving the oxygen atoms from Schiff bases and coordinated methanol molecules. Besides, each tetranuclear cation in 5 is H-bonded to the uncoordinated molecule of methanol that additionally stabilizes the overall double open cube-like metal cores (Table 6).

In spite of the similarity of the crystal structures of 1-4 they drastically differ by the number and combinations of



Fig. 7 The crystal structure of 5 with atom numbering. The hydrogen atoms are omitted for clarity.

coordinated CH<sub>3</sub>OH and H<sub>2</sub>O molecules. In the case of 1, only methanol molecules are coordinated to the tetranuclear metal core forming the  $\{Cu_3Mn(\mu_3-O)_4\}(CH_3OH)_3$  fragment (Fig. 8). The coordination of a fourth solvent molecule has not occurred, possibly due to the existence of a weak contact between the five-coordinated copper atom of the core and the uncoordinated  $I_3^-$  anion. Complex 2 displays coordination of four solvent molecules (one to each metal atom) to the core with mixed-solvent CH<sub>3</sub>OH<sub>3</sub>/H<sub>2</sub>O combination, while, due to the disorder, the formation of two mixed-solvent {Cu<sub>3</sub>Mn( $\mu_3$ - $O_{4}(H_{2}O_{3}(CH_{3}OH))$  and  $\{Cu_{3}Mn(\mu_{3}-O)_{4}\}(H_{2}O_{2}(CH_{3}OH))$  fragments is observed in 3. In the case of compound 4, similarly to 1, only one type of solvent molecule, namely water, is coordinated to the metal core. Taking into account the disorder of one of the coordinated water molecules, the two  $\{Cu_3Mn(\mu_3-\mu_3)\}$  $O_{4}(H_{2}O)_{4}$  and  $\{Cu_{3}Mn(\mu_{3}-O)_{4}\}(H_{2}O)_{3}$  fragments can be selected (Fig. 8) in 4. Such a diversity of the observed combinations of coordinated solvent molecules in 1-4 could be a result of a whole set of different factors. The pronounced influence of the synthetic conditions (temperature, kinetics, etc.) and the chemical composition of the synthetic mixture can be understood if one considers these mixtures as dynamic combinatorial libraries (DCL). The DCL concept,33,34 introduced by Jean-Marie Lehn, describes a library of components, which can interact in a reversible manner (such as coordination bondings). In this way, the structure and composition of a reaction product is a complex function of all possible equilibria in such systems and, moreover, may be influenced by the crystallization process, as the latter is also a reversible one. Hence, even the lattice energy may be crucial in determining which structure (coordination compound) will dominate and crystallize from the solution phase.

In the crystal structure of 5 both tetranuclear metal cores take part in the formation of similar  $\{Cu_3Mn(\mu_3-O)_4\}(CH_3OH)_3$  fragments (Fig. 9) showing the coordination of three methanol

 Table 7
 Selected geometrical parameters (distances/Å and angles/°)

 for 5

Cu1-O1	1.929(4)	Cu5-O22	2.376(4)
Cu1-O2	1.996(4)	Cu5-N6	1.937(5)
Cu1-O8	1.965(3)	Cu6-O10	1.967(4)
Cu1-O17	2.278(3)	Cu6-O12	2.466(4)
$\Omega u_1 = IN I$ $\Omega u_2 = \Omega 2$	2.379(3)	Cuo-O13 Cu6-O14	1.890(4) 1.958(3)
Cu2-O3	1.889(4)	Cu6-N7	1.918(5)
Cu2-O4	1.954(4)	Mn1-O4	1.916(3)
Cu2-O6	1.985(3)	Mn1-O6	2.330(4)
Cu2-N2	1.923(4)	Mn1-07	1.878(3)
Cu3-O2	1.945(3)	Mn1-08	1.899(3)
Juo-Oo Juo-Oo	1.906(3)	Mn1-018 Mn1-N4	2.223(4) 1.967(4)
Cu3-O19	2.504(4)	Mn2-O10	2.315(4)
Cu3-N3	1.926(4)	Mn2-O14	1.937(4)
Cu4-O9	1.904(4)	Mn2-O15	1.857(4)
Cu4-O10	1.975(4)	Mn2-O16	1.917(4)
Cu4-012	1.958(4)	Mn2-O23	2.215(4)
04-021 014-N5	2.435(4) 1.938(5)	Mn3-N9	1.977(5) 2.060(7)
Cu5-O11	1.916(4)	Mn3-N10	2.060(7)
Cu5-O12	1.964(4)	Mn3-N11	2.020(6)
Cu5-O16	1.953(4)	Mn3-N12	2.040(̈́7)́
O1-Cu1-O2	174.81(15)	O16-Cu5-N6	172.12(19)
D1-Cu1-O8	94.88(15)	O22-Cu5-N6	89.00(18)
J1-Cu1-017	91.25(15) 01.42(18)	010-Cu6-012	/3.39(15)
02-Cu1-M1	51.42(18) 89.62(14)	010-0uo-013 010-0u6-014	95.77(16) 84.97(15)
02-Cu1-O17	91.39(14)	O10 Cu6 O14 O10-Cu6-N7	158.44(19)
D2-Cu1-N1	83.76(17)	O12-Cu6-O13	92.95(17)
08-Cu1-O17	89.46(14)	O12-Cu6-O14	87.69(16)
08-Cu1-N1	169.72(17)	O12-Cu6-N7	124.94(17)
J1/-Cu1-N1	98.54(16) 96.26(12)	013-Cu6-014	1/9.13(16)
02-Cu2-03	85.27(13)	013-Cuo-N7	34.64(18)
D2-Cu2-O6	74.81(12)	O4-Mn1-O6	76.76(13)
D2-Cu2-N2	113.99(15)	O4-Mn1-O7	97.04(15)
O3-Cu2-O4	178.43(15)	O4-Mn1-O8	88.32(15)
03-Cu2-O6	95.91(15)	04-Mn1-018	91.67(15)
J3-CU2-N2 D4-Cu2-O6	94.68(17) 84.83(17)	04-Mn1-N4 06-Mn1-07	1/1.1/(16)
04-Cu2-N2	84.36(17)	06-Mn1-08	87.39(14)
D6-Cu2-N2	165.38(16)	O6-Mn1-O18	168.39(13)
O2-Cu3-O5	95.69(14)	O6-Mn1-N4	100.75(15)
D2-Cu3-O6	85.76(13)	07-Mn1-08	173.74(16)
02-Cu3-O19	92.70(14)	07-Mn1-018	89.77(15)
02-043-193 05-043-06	169.72(16)	07-MIII-N4 08-Mn1-018	91.42(16) 93.31(15)
O5-Cu3-O19	94.59(16)	08-Mn1-N4	83.09(16)
D5-Cu3-N3	94.49(16)	O18-Mn1-N4	90.84(17)
D6-Cu3-O19	95.28(14)	O10-Mn2-O14	76.57(14)
D6-Cu3-N3	83.96(16)	O10-Mn2-O15	89.84(15)
J19-Cu3-N3	8/.90(16)	010-Mn2-016	88.41(14)
0.00000000000000000000000000000000000	107.09(10) 96.81(16)	010-Mn2-N8	105.20(15) 102.76(17)
09-Cu4-O21	97.73(15)	014-Mn2-015	95.35(16)
O9-Cu4-N5	94.36(18)́	O14-Mn2-O16	90.60(15)
D10-Cu4-O12	85.84(15)	O14-Mn2-O23	88.63(16)
010-Cu4-O21	94.89(14)	O14-Mn2-N8	173.56(19)
J10-Cu4-N5 D12-Cu4-O21	83.23(17) 90.09(15)	015-Mn2-016 015-Mn2-022	1/3.24(17) 92 14(17)
D12-Cu4-N5	168.84(18)	O15-Mn2-N8	92.14(17) 91.05(19)
D21-Cu4-N5	88.58(16)	O16-Mn2-O23	91.22(16)
O11-Cu5-O12	173.89(17)	O16-Mn2-N8	82.98(18)
O11-Cu5-O16	94.31(16)	O23-Mn2-N8	91.88(18)
011-Cu5-O22	94.65(16)	N9-Mn3-N10	102.8(3)
J11-Cu5-N6	92.15(19)	N9-Mn3-N11	105.9(3)
012 - Cu5 - O10 012 - Cu5 - O22	90.68(14)	N10-Mn3-N11	118.4(3)
D12-Cu5-N6	84.94(18)	N10-Mn3-N12	106.6(3)
D16-Cu5-O22	94.95(15)	N11-Mn3-N12	112.8(3)

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Fig. 8 Ball-and-stick representations showing the coordination of the solvents to molecular cores in 1–4. Color scheme: Cu, cyan; Mn, magenta; O, red; C, light grey.



Fig. 9 Ball-and-stick representations showing the coordination of the solvents to molecular cores in 5. Color scheme: Cu, cyan; Mn, magenta; O, red; C, light grey.

molecules to two Cu(II) and one Mn(III) metal centre in each tetranuclear core. The absence of such solvent coordination to the remaining copper (Cu2 and Cu6) atoms of the cores can be explained as follows: in the case of Cu2 – by the manner of the molecular cation packing that leads to the appearance of steric hindrance and formation of insufficient space for the solvent coordination and, in the case of Cu6 – by the existence of a very weak copper–sulfur contact (Cu6…S3 = 4.701(2) Å).

Finally, when analyzing the crystal structures of 1–5, it can be concluded that all of them have similar metal atom arrangements described by the general tetranuclear  $M_4X_4$  group, in which the molecular { $Cu_3Mn(\mu_3-O)_4$ } and { $Cu_3Mn(\mu-O)_2$ ( $\mu_3-O)_2$ } cores for 1–4 and 5, respectively, can be assigned. In the cases of 1–4, the cube-like shape of the heterometallic cores is supported by the coordination of four or three solvent molecules with mixed or single-type solvent combination, while in 5, a similar coordination of three methanol molecules to both double open cube-like cores is observed. Therefore, the various synthetic mixtures, as well as the different synthetic approaches, used for complex 1–5 preparation lead to the formation of the products showing quite similar but at the same time rather different molecular structures.

Analysis of the MSTs of known crystal structures of the tetranuclear Cu/Mn molecular complexes (according to the CSD), where all metal atoms are linked by a single bridging atom, is shown in Fig. 10. Depending on the number of bridging atoms, two groups with general formulae  $M_4X_4$  and  $M_4X_6$  can be distinguished. The  $M_4X_4$  group includes three MSTs with the following realizations: diamond-like O-bridged { $M_4(\mu-X)_4$ },<sup>35</sup> consecutive N-bridged { $M_4(\mu-X)_4$ },<sup>36</sup> double open O-bridged cube { $M_4(\mu-X)_2(\mu_3-X)_2$ } [complex 5] and more numer-



Fig. 10 The MSTs and distribution of known tetranuclear Cu/Mn complexes (according to the CSD) and compounds 1–5.

ous MST  $\{M_4(\mu_3-X)_4\}$ , where in all cases the bridging atoms are oxygens [ref. 37 and 38 and complexes 1-4]. In the  $M_4X_6$ group the star-like MST  $\{M_4(\mu\text{-}X)_6\}^{39,40}$  and MST  $\{M_4(\mu\text{-}X)_4$  $(\mu_3-X)_2$ <sup>38,41</sup> which can be viewed as combination of uncompleted cubes, were found. Obviously, the synthetic procedure used for the complex preparation can be one of the main determining factors for the MST formation. While complexes from the  $M_4X_4$  group with MST { $M_4(\mu-X)_4$ } were obtained using metal salts or metal complexes as sources of the metals, the compounds from this group with MST  $\{M_4(\mu_3-X)_4\}$  were synthesized using the direct synthesis approach only. For the M<sub>4</sub>X<sub>6</sub> group, the complexes with star-like MST  $\{M_4(\mu-X)_6\}$  were obtained using the "complex as ligand" strategy only, while compounds possessing MST  $\{M_4(\mu-X)_4(\mu_3-X)_2\}$  were prepared by the "complex as ligand" strategy and by direct synthesis. Thus, in some cases, the preparation methodology is just a way for obtaining the desired compound, while in other cases it is the only possible way to prepare a complex with a certain molecular structural type.

#### **Magnetic properties**

Three Cu(II) centres and one Mn(III) centre yield a high-temperature limit for the effective magnetic moment  $\mu_{eff} = [3g_{Cu}^2S_{Cu}(S_{Cu} + 1) + g_{Mn}^2S_{Mn}(S_{Mn} + 1)^{1/2}\mu_B$  which amounts to  $5.7\mu_B$  when all g = 2.0 ( $S_{Cu} = 1/2$ ,  $S_{Mn} = 2$ ). On cooling from room temperature the effective magnetic moment for 1 gradually decreases from  $\mu_{eff} = 5.54\mu_B$  to the value of  $1.98\mu_B$  at T = 2.0 K (Fig. 11). This feature indicates that an antiferromagnetic coupling among the magnetic centres applies. Down to 2.0 K the molar magnetic susceptibility only increases showing that S > 0 is the ground state. At a very low temperature, also some (mononuclear) fragments of the tetranuclear bulk complex might be present; a modeling of such paramagnetic impurities is rather problematic though they could influence the low-temperature susceptibility data.

The molar magnetization per formula unit possesses the saturation limit  $M_1 = M_{\rm mol}/N_A\mu_B = 3g_{\rm Cu}S_{\rm Cu} + g_{\rm Mn}S_{\rm Mn}$  which



**Fig. 11** Magnetic functions for **1** and **2**. Left – Effective magnetic moment, right – magnetization per formula unit, inset – molar magnetic susceptibility (SI units). Solid lines – fitted: blue – fit-a, red – fit-b.

yields  $M_1 = 7$  for  $S_{\text{max}} = 7/2$ . The measured magnetization adopts a value of only  $M_1 = 1.2$  at T = 2.0 K and B = 7 T. This reduction is a fingerprint of a considerable antiferromagnetic exchange, eventually combined with single-ion zero-field splitting at the Mn(m) centre.

The susceptibility and magnetization data were fitted simultaneously by applying an error functional  $F = E(\chi) \times E(M)$  that accounts uniformly for the relative errors in susceptibility and magnetization. The calculated values have been reconstructed by considering the following spin Hamiltonian

$$\begin{aligned} \hat{H}_{a}^{\text{ex}} &= -\left[J_{2}(\vec{s}_{\text{Mn}}\cdot\vec{s}_{\text{Cu1}}) + J'_{2}(\vec{s}_{\text{Cu2}}\cdot\vec{s}_{\text{Cu3}})\right]\hbar^{-2} \\ &+ J_{4}[(\vec{s}_{\text{Cu1}}\cdot\vec{s}_{\text{Cu2}}) + (\vec{s}_{\text{Cu1}}\cdot\vec{s}_{\text{Cu3}}) \\ &+ (\vec{s}_{\text{Cu2}}\cdot\vec{s}_{\text{Mn}}) + (\vec{s}_{\text{Cu3}}\cdot\vec{s}_{\text{Mn}})\right]\hbar^{-2} \\ &+ D_{\text{Mn}}(\hat{s}_{\text{Mn},z}^{2} - \hat{s}_{\text{Mn}}^{2}/3)\hbar^{-2} \\ &+ \mu_{\text{B}}B_{a}(g_{\text{Mn}}\hat{s}_{\text{Mn},a} + g_{\text{Cu}}\hat{s}_{\text{Cu1},a} + g_{\text{Cu}}\hat{s}_{\text{Cu2},a} + g_{\text{Cu}}\hat{s}_{\text{Cu3},a})\hbar^{-1} \end{aligned}$$
(6)

(a = x, y, z) where the first term refers to the isotropic exchange, the second – the zero-field splitting, and the third – the Zeeman term. In the isotropic exchange part several different coupling constants occur. The constants  $J_2$  and  $J'_2$ reflect open angles between Mn–O–Cu1 (100°, 105°) and Cu2– O–Cu3 (101°, 104°) centres and they are expected to be negative (an antiferromagnetic exchange interaction).<sup>42</sup> The remaining four interactions precede along the superexchange paths which involve pairs of sharp and open angles so that a competition between ferromagnetic and antiferromagnetic interactions is expected: Mn–O–Cu2 (88°, 107°), Mn–O–Cu1 (91°, 106°), Cu1–O–Cu2 (87°, 108°), and Cu1–O–Cu3 (89°, 104°). Thus  $J_4$  could be positive or negative, but less negative than  $J_2$  and  $J'_2$ . During the fitting procedure it was found that  $J_2 = J'_2$  can be safely fixed.

The diagonalization of the above Hamiltonian produces a set of eigenvalues entering the partition function. Then the magnetic susceptibility and the magnetization are evaluated by using the formulae of the statistical thermodynamics.<sup>43</sup> The susceptibility data were corrected for the molecular-field correction (*zj*) and the temperature-independent magnetism  $\chi_{\text{TIM}}$  via  $\chi_{\text{corr}} = \chi_{\text{mol}}/[1 - (zj)\chi_{\text{mol}}] + \chi_{\text{TIM}}$ . The latter term accounts for the uncompensated underlying diamagnetism and the temperature-independent paramagnetism, along with the diamagnetic signal of the sample holder.

An advanced fitting procedure using a genetic algorithm has been applied. The final set of magnetic parameters for **1** through **4** is listed in Table 8. In accordance with expectations,  $g_{Mn} < 2$  for the d<sup>4</sup> system and  $g_{Cu} > 2$  for the d<sup>9</sup> complex hold true. (There is a second set of magnetic parameters with  $|J_2| < |J_4|$  fitting well the magnetic functions listed in the ESI<sup>†</sup> – fitb.) The magnetic properties of complex **2** are analogous to those of complex **1** (Fig. 11) and an almost identical set of magnetic parameters was obtained.

The magnetic functions for complex **3** are a bit different: (i) the susceptibility at T = 2 K is much lower; (ii) the magnetization at B = 7 T is much lower (Fig. 12). This indicates an increase of the antiferromagnetic exchange. The last complex **4** behaves analogously to **3**.

Compound 5 consists of two  $[Cu_3Mn^{III}]$  cubes of the open type and one  $[Mn^{II}(NCS)_4]^{2-}$  anion. The high-temperature limit of the effective magnetic moment is  $\mu_{eff} = [6g_{Cu}^2S_{Cu}(S_{Cu} + 1) + 2g_{Mn}^2S_{Mn}(S_{Mn} + 1) + g_{Mn'}^2S_{Mn'}(S_{Mn'} + 1)]^{1/2}\mu_B$  which amounts to 10.34 $\mu_B$  when all g = 2.0 ( $S_{Cu} = 1/2$ ,  $S_{Mn} = 2$ ,  $S_{Mn'} = 5/2$ ). At room-temperature, however,  $\mu_{eff}$  is much higher (12.7 $\mu_B$ ) owing to higher g-factors (Fig. 13). At the same time the magnetization per formula unit should saturate to  $M_1 = 6g_{Cu}S_{Cu} + 2g_{Mn}S_{Mn} + g_{Mn'}S_{Mn'} = 19$  but its value at T = 2.0 K and B = 7 T is only  $M_1 = 7.4$ . This again confirms a dominating antiferromagnetic coupling along with sizable zero-field splitting.

The data fitting for 5 has been based upon the assumption that the formula unit contains 2/3 of the  $[Cu_3Mn^{III}]$  cube and 1/3 of the  $[Mn^{II}]$  complex (S = 5/2, g = 2). Thus the magnetic data were divided by a factor of 3, then fitted as before with a paramagnetic impurity of  $Mn^{II}$  ( $x_{PI} = 1/3$ ) and the fitted data were backtransformed to the original scale by multiplying the calculated susceptibility and magnetization by a factor of 3. The final set of magnetic parameters is also listed in Table 8 and it is seen that the coupling constants for such an open-structure system are much lower relative to compounds 1–4.

#### Magnetostructural $J-\alpha$ correlations

The magnetic parameters of the complexes under study are listed in Table 9 along with structural parameters that charac-

Table 8 Calculated magnetic parameters for 1-5<sup>a</sup>

Complex	ġмn	$g_{ m Cu}$	$J_2/hc$	$J_4/hc$	$D_{\mathrm{Mn}}/hc$	(zj )/hc	$\chi_{ ext{tim}}{}^{b}$	$R(\chi)/\%$	R(M)/%
1	1.859	2.313	-54.8	-27.0	-13.6	-0.075	+0.2	4.0	3.4
2	1.869	2.349	-54.8	-27.0	-14.4	-0.013	+14.4	3.5	4.3
3	1.988	2.009	-45.0	-37.5	-2.8	-0.079	+12.2	2.2	0.7
4	2.000	2.000	-52.5	-39.1	-2.5	$\sim 0$	+15.0	1.9	1.0
5	$1.851^{c}$	2.178	-22.7	-11.6	-23.4	0.268	+40.0	2.5	3.3

<sup>*a*</sup> Coupling constants confirming the definition  $\hat{H}_{ii} = -J(\vec{s}_i \cdot \vec{s}_j)$  in cm<sup>-1</sup>.  $J_2$  – in two bases,  $J_4$  – within four walls. <sup>*b*</sup> Temperature independent magnetism  $\chi_{\text{TIM}}$  in units of 10<sup>-9</sup> m<sup>3</sup> mol<sup>-1</sup> (SI). <sup>*c*</sup>  $g(\text{Mn}^{\text{II}}) = 1.950$  and 1.956.



**Fig. 12** Magnetic functions for **3** and **4**. Left – Effective magnetic moment, right – magnetization per formula unit, inset – molar magnetic susceptibility (SI units). Solid lines – fitted: blue – fit-a, red – fit-b (in fact coincide).



Fig. 13 Magnetic functions for 5. Left – Effective magnetic moment, right – magnetization per formula unit, inset – molar magnetic susceptibility (SI units). Solid lines – fitted: blue – fit-a, red – fit-b.

terize the cube-like core. Data for two analogous complexes have been retrieved from the CSD and added for comparison.<sup>37,38</sup>

These data form a basis for magnetostructural correlations. The problem is that there are six M····M contacts, twelve M–O distances, twelve M–O–M angles, but only two *J*-constants at the disposal. This causes that some selection and/or averaging of geometrical parameters is necessary. An attempt to correlate the bonding angle  $\beta$  in the basal planes (defined by the longest Cu···Cu contacts) with the coupling constant occurring twice ( $J_2$ ) appeared recently for tetrahedro-{Cu<sub>4</sub>O<sub>4</sub>} complexes.<sup>44</sup>

An enlarged set of 41 complexes has been treated by methods of chemometry giving rise to six clusters according to their similarity by means of Cluster Analysis (CA).<sup>45</sup> Magnetic and structural data for 1–4 were added to this set and renumbered as complexes 42–45. Complex 5 possesses two structural units but the common set of magnetic parameters giving rise to members 46 and 47. Then CA was repeated as displayed in Fig. 14. Four heterometallic cubes span the cluster 1 (no. 42, 43, 44, 45) and cluster 3 (no. 46 and 47). In these cases the core of the complex refers to a compressed prism ( $R_4 < R_2$ ). (The clusters 4, 5, and 6 resemble an elongated prism with  $R_4 > R_2$ .)

For such a case the appropriate magnetostructural correlation is represented by the  $J_4$  vs.  $\alpha$  plot as displayed in Fig. 15. Here the new members (complexes 1–5, no. 42–47) are distinguished by triangle symbols. It can be concluded that the coupling constant within the walls of the compressed prism  $J_4$ approximately correlates with the averaged Cu–O–Cu angle in walls  $\alpha$  according to a straight line with a negative slope. However, a better correlation would be a curved line of the hyperbolic nature.

# Conclusions

The present study shows the successful utilization of the "direct synthesis" approach for the preparation of highly nuclear heterometallic complexes with polydentate Schiff base ligands formed *in situ*. Open-air reactions of copper and manganese powders with a solution containing the condensation product of salicylaldehyde and ethanolamine yielded four new Cu<sup>II</sup>Mn<sup>III</sup> complexes [Cu<sub>3</sub>Mn(L)<sub>4</sub>(CH<sub>3</sub>OH)<sub>3</sub>]I<sub>3</sub> (1), [Cu<sub>3</sub>Mn(L)<sub>4</sub>(CH<sub>3</sub>OH)<sub>3</sub>(H<sub>2</sub>O)]NCS·H<sub>2</sub>O (2), [Cu<sub>3</sub>Mn(L)<sub>4</sub>(CH<sub>3</sub>OH)

	J4 te Wa	lls &M	1n ŏ	Cu	$\mathcal{U}_{Mn}$	M-M Base	M-M Walls	M-O Base	M-O Walls	M-O-M Base	M-O-M Walls	$R_{M-M}$ Base	$R_{M-M}$ Walls	$P_{\rm M-O}$ Base	$R_{\rm M-O}$	$R_{M-O}$ Walls	$eta_{M-O-M}$ Base	α <sub>M−O−M</sub> Walls
Abbrev.→ J2	J4	gl	An g	,Cu	D	2007						d2	d4	POb	R2	R4	be	al
1 -5.	4.8 -25	7.0 1.5	859 2	313	-13.6	3.500	3.123	1.943, 2.580	1.945	100.42, 104.83	88.52, 103.93	3.510	3.144	1.968	2.239	1.959	102.53	97.47
						3.520	3.163	1.993, 2.411	1.959	100.76, 104.12	87.60, 107.83							
							3.115	1.964, 2.577	1.962		87.44, 107.82							
							3.176	1.972, 2.474	1.971		90.55, 106.07							
2 -5	4.8 -27	7.0 1.8	869 2	2.349	-14.4	3.477	3.135	1.966, 2.542	1.949	100.13, 102.19	88.90, 108.38	3.501	3.177	1.964	2.253	1.957	101.96	97.81
						3.525	3.137	1.960, 2.488	1.957	101.82, 103.71	88.96, 105.46							
							3.263	1.948, 2.656	1.958		87.53, 107.74							
							3.173	1.984, 2.480	1.965		89.09, 106.41							
3 -4.	5.0 -37	7.5 1.5	988 2	000.	-2.8	3.492	3.136	1.939, 2.527	1.942	102.05, 102.64	88.27, 106.57	3.496	3.136	1.960	2.226	1.950	102.81	97.82
						3.498	3.157	1.993, 2.464	1.938	101.05, 105.52	90.06, 107.38							
							3.104	1.950, 2.554	1.954		88.11, 108.41							
							3.147	1.960, 2.420	1.967		89.44, 104.31							
4 -5.	2.5 -35	9.1 2.(	000 2	0.000	-2.5	3.409	3.127	1.955, 2.527	1.946	98.24, 100.15	89.04, 108.60	3.407	3.158	1.955	2.220	1.961	99.55	98.61
						3.406	3.180	1.954, 2.470	1.965	98.69, 101.13	88.86, 106.14							
							3.151	1.965, 2.500	1.966		90.42, 108.31							
							3.176	1.946, 2.444	1.967		90.56, 106.96							
5, unit A -2.	2.7 -1	1.6 1.8	851 2	2.178	-23.4	3.514	3.087	1.898, (2.907)	1.916	(91.52), 109.02	90.53, 102.37	3.542	3.210	1.957	2.292	1.953	100.64	99.27
						3.570	3.100	1.978, 2.331	1.945	(92.96), 109.05	(86.83), 121.78							
							3.279	1.954, (2.888)	1.966		(82.14), 112.55							
							3.376	1.995, 2.379	1.985		91.48, 106.47							
unit B -2.	2.7 -1	1.6 1.8	851 2	2.178	-23.4	3.411	3.107	1.917, (2.818)	1.937	(90.09), 105.04	90.04, 105.97	3.509	3.235	1.954	2.307	1.854	98.32	99.88
						3.608	3.149	1.976, 2.314	1.953	(89.57), 108.57	(83.39), 123.90							
							3.268	1.964, (3.045)	1.958		(84.40), 112.89							
							3.415	1.959, 2.465	1.968		92.67, 105.78							
$6^{37 b}$		1.5	98 2	0.19		3.489	3.112	1.955, 2.507	1.947	102.18, 102.79	89.94, 106.26	3.478	3.136	1.956	2.224	1.957	102.21	97.64
						3.468	3.138	1.962, 2.484	1.953	100.93, 102.94	88.36, 106.95							
							3.146	1.943, 2.528	1.961		88.23, 104.85							
							3.147	1.965, 2.452	1.967		88.53, 107.96							
7 <sup>38 c</sup> n.a	. n.a	. n.;	a. n	ı.a.	n.a.	3.426	3.159	1.952, 2.512	1.952	99.44, 99.44	89.05, 107.63	3.456	3.178	1.957	2.240	1.954	100.18	99.08
						3.486	3.159	1.952, 2.512	1.952	100.92, 100.92	89.96, 109.70							
							3.197	1.962, 2.533	1.957		89.05, 107.63							
							3.197	1.962, 2.533	1.957		89.96, 109.70							

Magnetic and structural parameters of the complexes under study (fit-a)<sup>a</sup>

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Fig. 14 Cluster analysis for 41  $\{Cu_4O_4\}$  cubes and 6 additional  $\{Cu_3MnO_4\}$  cubes. Ward's method, city-block metrics.



Fig. 15 Magnetostructural correlation for cubes resembling a compressed prism with  $\{Cu_4O_4\}$  and  $\{Cu_3MnO_4\}$  cores; confidence and prediction intervals are shown at 95% probability level, correlation coefficient r = -0.47.

 $(H_2O)_{2.55}$ ]Br·0.45H<sub>2</sub>O (3) and [Cu<sub>3</sub>Mn(L)<sub>4</sub>(H<sub>2</sub>O)<sub>3.4</sub>]BF<sub>4</sub>·0.6H<sub>2</sub>O (4). The use of the "building block" approach for comparative purposes allowed us to synthesize the novel compound  $[Cu_3Mn(L)_4(CH_3OH)_3]_2[Mn(NCS)_4]\cdot 2CH_3OH$  (5). Both the used preparation methodologies afforded complexes with tetranuclear crystal structures but with different molecular core types cube-like  $\{Cu_3Mn(\mu_3\text{-}O)_4\}$  in 1–4 and the rather rare double open cube  $\{Cu_3Mn(\mu-O)_2(\mu_3-O)_2\}$  in 5, which is the first heterometallic example with such a metal arrangement built by oxygen bridges only. Moreover, the different numbers and combinations of coordinated to the metal core methanol and water molecules in 1-5 allowed us to disclose a wide range of mixed-solvent or single-type solvent heterometallic {Cu<sub>3</sub>Mn  $(O)_4$   $(H_2O)_x(CH_3OH)_v$  fragments. Magnetic susceptibility data along with variable-field magnetization measurements of 1-5 showed an antiferromagnetic coupling of medium magnitude  $(-55 \text{ to } -22 \text{ cm}^{-1})$ . For these systems resembling a compressed prism the coupling constant in walls  $J_4$  correlates with the averaged bonding angles in walls  $\alpha$ : the function  $J_4$  vs.  $\alpha$  develops approximately according to a straight line with a negative slope.

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