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ARTICLE TYPE

Trinuclear heterometallic Cu^{II}–Mn^{II} complexes of a salen type Schiff base ligand: anion dependent variation of phenoxido bridging angles and magnetic coupling

Piya Seth[a], Soumavo Ghosh[a], Albert Figuerola[b] and Asutosh Ghosh*[a]

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Five new trinuclear heterometallic Cu^{II}–Mn^{II} complexes $[(CuL)_2Mn(O_2CPh)_2]$ (**1**), $[(CuL)_2Mn(N_3)_2]$ (**2**), $[(CuL)_2Mn(NCO)_2]$ (**3**), $[(CuL)_2Mn(NO_3)_2]$ (**4**) and $[(CuL)_2Mn(Sal)_2]\cdot CH_2Cl_2$ (**5**) have been synthesized with the di-Schiff base ligand H_2L (where, H_2L= N,N'-bis(salicylidene)-1,3-propanediamine and Sal= salicylate). These complexes with different anionic co-ligands have been synthesized to attain a large variation in phenoxido bridging angles and to investigate its consequence on magnetic properties. Single crystal X-ray diffraction analyses reveal that complexes **1**, **2**, **4** and **5** are linear, whereas **3** has an angular geometry. Variable temperature magnetic susceptibility measurements suggest that all five complexes possess an overall antiferromagnetic interaction between Cu^{II} and Mn^{II} ions, which results in a final ferrimagnetic ground state with spin 3/2 in the Cu^{II}-Mn^{II}-Cu^{II} trinuclear structure. The weakest antiferromagnetic interaction (J_{Cu-Mn}= -7.0 cm^{-1}) is observed for **2** having the lowest value of the Cu-O-Mn angle (92.0°), while the strongest antiferromagnetic interaction (J_{Cu-Mn}= -26.5 cm^{-1}) is observed for **3** having the largest Cu-O-Mn angle (101.4°). Complexes **1**, **4** and **5** show an average Cu-O-Mn angles of 98.2°, 97.6° and 97.7°, respectively, that lead to intermediate antiferromagnetic interactions (J_{Cu-Mn} = -9.6, -9.7, -9.3 cm^{-1} respectively).

Introduction

The ongoing interest in heterometallic transition metal complexes derived from N, O donor ligands arises mainly due to their potential applications in the area of magnetism and catalysis.[1,2] One of the important aspects of research in the field of hetero-polynuclear metal complexes is to explore the exchange interactions between multiple non-equivalent spin carrying centers in a single molecule.[3] The magnetic interactions between nearest nonequivalent neighboring spin carriers may be ferromagnetic; it may also be antiferromagnetic but with noncompensation of the local spins that may result in ferrimagnetic behavior. The combination between two or more hetro-spin carriers can also lead to a new generation of molecule-based magnetic materials especially when the metal ions are strongly anisotropic, a requirement for obtaining single molecule magnets[4] or single chain magnets.[5] In this regard, the synthesis of Cu^{II}–Mn^{II} complexes with S_{Cu} = 1/2 and S_{Mn} = 5/2 is an active area of research because of the large difference in the local spin.[6]

Employment of appropriate types of bridging ligands which can efficiently mediate the magnetic coupling between the local spin carriers has allowed access to a variety of polynuclear complexes with interesting structures and magnetic properties. Among them, the oxido or phenoxido bridged compounds deserve special mention as numerous such compounds with various nuclearity have been studied in order to understand the factors that govern the coupling between the metal ions.[7] However, most of the compounds that have been studied are homometallic and are usually of Cu^{II}, Ni^{II} and $Mn^{II/III}$. It is now well established that for phenoxido bridged homo-metallic Cu^{II} complexes the Cu-O-Cu crossover angle from ferro to antiferromagnetic value is *ca.* 97°.[8] For Ni^{II} complexes, when Ni-O-Ni angles are close to 90°, the magnetic coupling is ferromagnetic. As the angle increases from 90°, the ferromagnetic coupling decreases and it becomes antiferromagnetic at values ca. 93.5 and 99.0° for the corresponding μ_2 and μ_3 bridging modes of phenoxido oxygen atoms.[9] For oxido bridged Mn^{III} complexes the ferro to antiferro crossover angle is reported to be much higher at 120°.[7c] However, for heterometallic complexes such correlations are rarely been made presumably due to the scarcity of the reported complexes. For example, if we focus on the double phenoxido-bridged Cu^{II}–Mn^{II} complexes of salen type Schiff base ligand about fifteen examples are known.[10] Among these complexes ten are magnetically characterized and the average Cu-O-Mn angle varies from 95.6 to 103.7º in these complexes. All of them exhibit antiferromagnetic interactions with $J_{Cu\text{-}Mn}$ in the range -22.0– -41.6 cm^{-1}. In order to draw any meaningful magneto-structural correlation and to have an idea about the crossover angle, synthesis of more complexes especially with the lower bridging angle is needed.

Our recent approach for the synthesis of hetero metallic complexes using [CuL] type metalloligands (where H_2L = N,N'-bis(salicylidene)-1,3-propanediamine) reveals that di-, tri-, tetra nuclear phenoxido bridged complexes can easily be prepared.[11] Among them the triuclear complexes are of special interest because the geometry and bridging angle can potentially be tailored by proper choice of anionic coligands. It has been found that when a carboxylate ion acts as bridge between the terminal and central metal ions in addition to the diphenoxido bridge, the trinuclear complexes are linear with phenoxido bridging angle in the range of 92.8-102.4º.[12] Whereas, when halide or pseudo halide ions are present in the molecule, they may act as single atom bridge[11b,13] between terminal and central metal atoms or remain monodentate[11b,14] and the resulting trinuclear complexes may be linear or bent with the phenoxido bridging angles in the ranges of 90.5-92.4º and 96.0-105.1º respectively. Taking into account of these structural features, we have designed and synthesized some Cu^{II}–Mn^{II} complexes by carefully selecting the anionic coligands so that a large variation of phenoxido bridging angles can be achieved.

We report here the synthesis, crystal structure and magnetic properties of five new complexes $[(CuL)_2Mn(O_2CPh)_2]$ (**1**), $[(CuL)_2Mn(N_3)_2]$ (**2**), $[(CuL)_2Mn(NCO)_2]$ (**3**), $[(CuL)_2Mn(NO_3)_2]$ (**4**) and $[(CuL)_2Mn(Sal)_2]\cdot CH_2Cl_2$ (**5**) with the N_2O_2 donor Schiff base ligand H_2L (where, H_2L= N,N'-bis(salicylidene)-1,3-propanediamine) (Scheme 1). Among these five complexes, **2** exhibits weakest antiferromagnetic interaction with the lowest Cu-O-Mn angle (92º) and **3** exhibits the strongest antiferromagnetic interaction with the highest Cu-O-Mn angle (101º). To the best of our knowledge, such a wide variation in phenoxido bridging angle in Cu^{II}–Mn^{II} complexes containing the same phenoxido bridging ligand is unprecedented and the Cu-O-Mn bridging angle in **2** is the lowest among all the di-phenoxido bridged Cu^{II}–Mn^{II} complexes reported so far. We take this opportunity to draw a magneto-structural correlation for the di-phenoxido bridged trinuclear Cu^{II}–Mn^{II}–Cu^{II} complexes.

Experimental Section

Starting materials

Salicylaldehyde, 1,3-diaminopropane, manganese(II) nitrate tetra hydrate, sodium azide, sodium cyanate, benzoic acid and salicylic acid were of AR grade and were used without further purification.

Caution! Azide and perchlorate salts are potentially explosive. Only small amounts should be used and handled with great care.

Synthesis of the Schiff-base ligand N,N'-bis(salicylidene)-1,3-propanediamine (H_2L): The di-Schiff base ligand, H_2L, was synthesized in our laboratory by standard methods.[15] Salicylaldehyde (1.05 mL, 10 mM) was mixed with 1,3-propanediamine (0.42 mL, 5 mM) in methanol (20 mL). The resulting mixture was refluxed for *ca.* 1.5 h and allowed to cool. The desired yellow crystalline solid ligand was filtered, washed with methanol, and dried in a vacuum desiccator that contained anhydrous $CaCl_2$.

Preperation of the 'metalloligand' [CuL]: To a methanolic solution (20 mL) of $Cu(ClO_4)_2\cdot 6H_2O$ (1.852 g, 5 mM) was added a methanolic solution of H_2L (5 mmol, 10 mL) to prepare the 'metalloligand' [CuL] as reported earlier.[16]

Synthesis of complexes $[(CuL)_2Mn(O_2CPh)_2]$ (1), $[(CuL)_2Mn(N_3)_2]$ (2), $[(CuL)_2Mn(NCO)_2]$ (3), $[(CuL)_2Mn(NO_3)_2]$ (4) and $[(CuL)_2Mn(Sal)_2]\cdot CH_2Cl_2$ (5): Complxes **1** and **5** were synthesized following the same procedure. To a methanolic solution (10 mL) of [CuL] (0.686 g, 2 mM), a 1:10 H_2O-MeOH (v/v, 10 mL) mixture of $Mn(ClO_4)_2\cdot 6H_2O$ (0.362 g, 1 mM) and corresponding carboxylic acid i.e. benzoic acid (0.244 g, 2 mM) for **1**, salicylic acid (0.276 g, 2 mM) for **5** was added drop wise. The resulting mixture was stirred for *ca* 1 h at room temperature. It was filtered and the filtrate was kept in a beaker inside a desiccator. X-ray quality single-crystals of **1** appeared at the wall of the beaker on evaporation of the solvent after 2-3 days. Microcrystalline compound of **5** obtained from the corresponding beaker, which was dissolved in dichloromethane. Layering it with n-hexane in a tube resulted in X-ray quality single crystals after 5-6 days.

Complexes **2** and **3** were obtained by mixing a methanolic solution (10 mL) containing [CuL] (0.686 g, 2 mM) with an aqueous solution of $Mn(ClO_4)_2\cdot 6H_2O$ (0.362 g, 1 mM) and NaN_3 (0.130 g, 2 mM) for **2**, NaOCN (0.130 g, 2 mM) for **3**. In both cases a green precipitate appeared immediately. It was filtered and the filtrate was allowed to stand overnight in open atmosphere. X-ray quality single-crystals appeared at the wall of the vessel on the following day. Complex **4** was obtained by stirring a methanolic solution of [CuL] (0.686 g, 2 mM) with $Mn(NO_3)_2\cdot 4H_2O$ (0.233 g, 1mM) in MeOH solvent for ~1 h. The resulting solution was filtered and the filtrate was kept in a beaker, covered with parafilm for slow evaporation of solvent at room temperature. X-ray quality single crystals obtained at the wall of the beaker after 2 days.

Complex **1**: Yield: 0.740 g (75%). $C_{48}H_{42}N_4O_8Cu_2Mn$ (984): calcd. C, 58.54; H, 4.39; N, 5.76; found C, 58.49; H, 4.28; N, 5.61. IR (KBr pellet, cm^{-1}) 1629 ν(C=N), 1599 ν_{as}(COO), 1553 ν_s(COO).

Complex **2**: Yield: 0.595 g (72%). $C_{34}H_{32}N_{10}O_4Cu_2Mn$ (826): calcd. C, 49.34; H, 3.85; N, 16.98; found C, 49.45; H, 3.91; N, 16.88. IR (KBr pellet, cm^{-1}) 1613 ν(C=N), 2048 ν(N_3).

Complex **3**: Yield: 0.627 g (76%). $C_{36}H_{32}N_6O_6Cu_2Mn$ (826): calcd. C, 52.39; H, 3.78; N, 10.27; found C, 52.27; H, 3.92; N, 10.11. IR (KBr pellet, cm^{-1}) 1613 ν(C=N), 2185 ν(OCN).

Complex **4**: Yield: 0.590 g (68%). $C_{34}H_{32}N_6O_{10}Cu_2Mn$ (866): calcd. C, 47.04; H, 3.65; N, 9.78; found C, 47.19; H, 3.74; N, 9.63. IR (KBr pellet, cm^{-1}) 1621 ν(C=N), 1293 ν(NO_3).

Complex **5**: Yield: 0.770 g (65%). $C_{50}H_{46}N_4O_{10}Cl_4Cu_2Mn$ (1186): calcd. C, 50.68; H, 3.97; N, 4.60; found C, 50.55; H, 3.90; N, 4.75. IR (KBr pellet, cm^{-1}) 1625 ν(C=N), 1462 ν(COO), 3433 ν(OH).

Physical measurements

Elemental analyses (C, H, and N) were performed with a Perkin–Elmer 240C elemental analyzer. IR spectra in KBr (4000–500 cm^{-1}) were recorded with a Perkin–Elmer RXI FTIR spectrophotometer. Temperature-dependent molar susceptibility measurements of powdered samples of **1-5** were carried out at the ''Servei de Magnetoquimica (Universitat de Barcelona)'' in a Quantum Design SQUID MPMSXL susceptometer with an applied field of 3000 and 198 G in the temperature ranges 2–300 and 2–30 K, respectively.

Crystal data collection and refinement

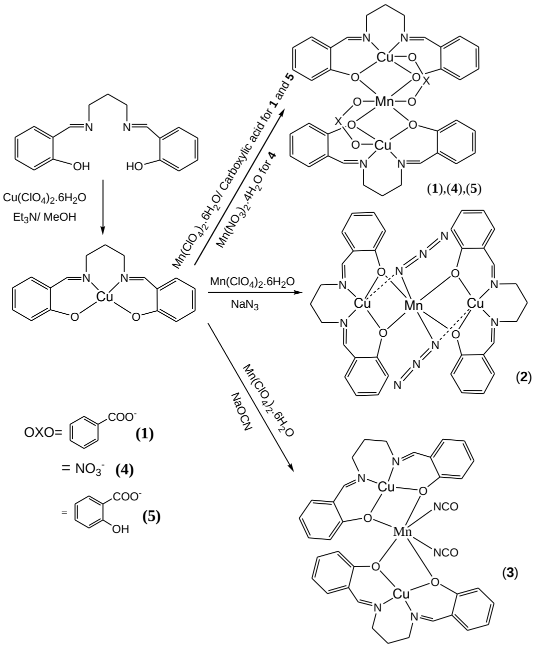
Suitable single crystals of compounds **1-5** were mounted on a Bruker-AXS SMART APEX II diffractometer equipped with a graphite monochromator and Mo-K_α (λ = 0.71073 Å) radiation. The crystals were positioned at 60 mm from the CCD. 360 frames were measured with a counting time of 10 s. The structures were solved using Patterson method by using the SHELXS97. Subsequent difference Fourier synthesis and least-square refinement revealed the positions of the remaining non-hydrogen atoms that were refined with independent anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and their displacement parameters were fixed to be 1.2 times larger than those of the attached non-hydrogen atom. Absorption corrections were carried out using the SADABS program.[17] All calculations were carried out using SHELXS 97,[18] SHELXL 97,[19] PLATON 99,[20] ORTEP-32[21] and WinGX system Ver-1.64.[22] Data collection, structure refinement parameters and crystallographic data for the five complexes are given in Table 1.

Results and Discussion

Syntheses and IR spectra of the complexes

Five new heterometallic complexes containing Cu^{II} and Mn^{II} have been prepared with the symmetrical tetradentate Schiff base ligand H_2L (where, H_2L= N,N'-bis(salicylidene)-1,3-propanediamine). For this purpose, we have first prepared the 'metalloligand' [CuL] by a reported procedure.[16] When [CuL] was made to react with $Mn(ClO_4)_2{\cdot}6H_2O$ in presence of different carboxylic acids (*viz.* benzoic acid, salicylic acid) the linear trinuclear diphenoxido and carboxylato bridged complexes $[MnCu_2L_2(O_2CPh)_2]$ (**1**), $[MnCu_2L_2(Sal)_2]{\cdot}CH_2Cl_2$ (**5**) resulted. Similar reaction with sodium salts of pseudo halides (*viz.* NaN_3, NaOCN) in H_2O-MeOH solvent produced a linear double phenoxido and $\mu_{1,1}$ azido bridged complex $[MnCu_2L_2(N_3)_2]$ (**2**) and an angular trinuclear complex $[MnCu_2L_2(NCO)_2]$ (**3**) containing terminally coordinated isocyanate. Another reaction of [CuL] with $Mn(NO_3)_2{\cdot}4H_2O$ in MeOH solvent resulted in a diphenoxido and nitrato bridged linear complex $[MnCu_2L_2(NO_3)_2]$ (**4**) which is structurally similar to **1** and **5**.

Besides elemental analysis, all the complexes were initially characterized by IR spectra. The precursor 'metalloligand' [CuL] is neutral and obviously there is no counter anion. All five synthesized hetero-nuclear complexes contain anions e.g. benzoate, azide, cyanate, nitrate and salicylate in **1-5** respectively. These anions show their characteristic absorption in IR spectra. For **1** there are two sharp peaks at 1599 and 1553 cm^{-1} due to asymmetric and symmetric stretching of benzoate. Similarly, the appearance of a strong and sharp peak at 2048 cm^{-1} is for N_3^- in **2**, at 2185 cm^{-1} is for NCO^- in **3**, at 1293 cm^{-1} is for NO_3^- in **4** and a broad band at 1462 cm^{-1} is for salicylate in **5**. All five complexes exhibit a sharp peak due to the azomethine (C=N) group of the Schiff base in the range 1613-1629 cm^{-1}. The rest of the spectral patterns and band positions of the complexes **1-5** and the precursor, [CuL], is very similar.



Scheme 1: Formation of complexes **1-5**.

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Table 1 Crystal data and structure refinement parameters for complexes **1-5**.

	1	**2**	**3**	**4**	**5**
Formula	$C_{48}H_{42}N_4O_8Cu_2Mn$	$C_{34}H_{32}N_{10}O_4Cu_2Mn$	$C_{36}H_{32}N_6O_6Cu_2Mn$	$C_{34}H_{32}N_6O_{10}Cu_2Mn$	$C_{50}H_{46}N_4O_{10}Cl_4Cu_2Mn$
Formula weight	984.90	826.74	826.72	866.70	1186.75
Space group	Pna21	P21/c	P-1	P21/c	Pbca
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Orthorhombic
a/ Å	24.025(3)	9.453(5)	10.077(5)	9.140(5)	10.532(5)
b/ Å	9.4782(1)	11.210(5)	11.887(5)	11.616(5)	17.981(5)
c/ Å	18.775(2)	15.890(5)	13.944(5)	16.367(5)	26.275(5)
α/deg			92.246(5)		
β/deg		101.832(5)	100.840(5)	100.173(5)	
γ/deg			91.095(5)		
V/Å^3	4275.3(9)	1648.1(1)	1638.6(1)	1710.4(1)	4976(3)
Z	4	2	2	2	4
Cal. Density gcm^{-3}	1.530	1.666	1.676	1.683	1.584
(μ) mm^{-1}	1.338	1.713	1.724	1.664	1.375
R(int)	0.029	0.049	0.030	0.077	0.093
No. of unique data	8116	8171	5786	2831	4340
Data with I > 2σ(I)	7326	5264	4378	2086	2751
R1 on I>2σ(I)	0.0299	0.0419	0.0406	0.0511	0.0596
wR2 on I>2σ(I)	0.0737	0.1138	0.1101	0.1402	0.1735
Goof Value	1.036	1.034	1.050	0.996	1.018

Description of structures

The molecular structure of complex **1** consists of a discrete trinuclear complex of formula $[(CuL)_2Mn(O_2CPh)_2]$ where the two terminal Cu^{II} and a central Mn^{II} are in a linear disposition (Fig. 1). The six-coordinated manganese is in a distorted octahedral environment and is bonded to four oxygens from the two metalloligands [CuL], at distances ranging between 2.173(2)–2.213(2) Å, forming the basal plane of the Mn^{II}. The trans axial positions are occupied by the oxygen atoms O(6) and O(7) of the *syn-syn* bridging benzoate (1*κO*:2*κO'*) at distances of 2.160(2) and 2.172(2) Å respectively. (see ST 1 in supporting information) The deviation of trans angles [176.71(8)−179.58(9)°] and cis angles [71.69(8)−91.42(8)°] indicate slight distortions from ideal octahedral geometry around Mn(II). The two terminal Cu^{II} atoms are penta-coordinated with a geometry closest to the square pyramid. Each of them bonded to the four donor atoms of ligand L with Cu(1)–O distances at 1.962(2)–1.970(2) Å, Cu(1)–N distances at 1.984(3)–1.997(3) Å and Cu(2)–O distances at 1.954(2)–1.965(2) Å, Cu(2)–N distances at 1.978(4)–1.992(3) Å in the equatorial plane. One of the axial positions is occupied by bridging oxygen atom of the *syn-syn* benzoate with Cu(1)–O(5) 2.173(3) and Cu(2)–O(8) 2.194(3) Å. The four donor atoms in the equatorial plane show r.m.s. deviation of 0.002 and 0.008 Å for Cu(1) and Cu(2) respectively with the copper atoms 0.192(4), 0.165(4) Å from the plane towards the carboxylato oxygen O(5) and O(8) respectively. The two planes intersect at 3.41°. The two Cu···Mn distances are 3.142(7) and 3.145(7) Å. Addison parameters for Cu atoms are 0.004 and 0.018 for Cu(1) respectively indicating very slight distortion towards trigonal bipyramid geometry. No significant hydrogen bonding is present in this structure.

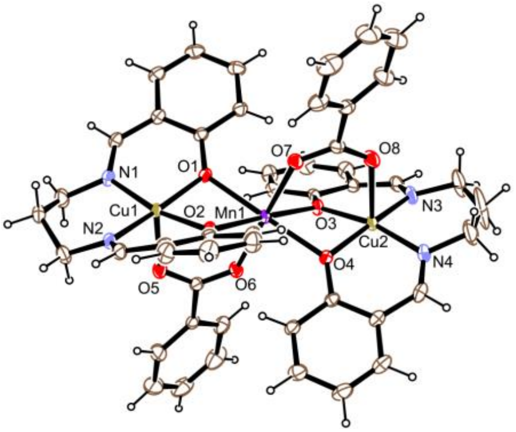


Fig. 1 ORTEP-3 view of the asymmetric unit of **1** with ellipsoids at 20% probability.

Complex **2** $[(CuL)_2Mn(N_3)_2]$ crystallizes in a centro-symmetric space group where the two terminal Cu^{II} and a central Mn^{II} are in a linear disposition. (Fig. 2) The six-coordinated manganese is in a distorted octahedral environment and is bonded to four oxygens from the two ligands L, at distances 2.172(2) and 2.200(2) Å, which form the basal plane of the Mn^{II}. (see ST 2 in supporting information) The two trans axial positions are occupied by the bridging nitrogen atom N(3) of the azide at distance of 2.194(2) Å. Due to the presence of centre of inversion, all the *trans* angles are ideal (180°), but the *cis* angles [71.19(4)−96.63(5)°] deviate considerably from the ideal value (90°). The two terminal Cu^{II} atoms are penta-coordinated with a geometry closest to the square pyramid. Each of them bonded to the four donor atoms of ligand L with Cu–O distances 1.935(2) and 1.947(2) Ǻ, Cu–N distances 1.943(2) and 1.973(2) Ǻ. The azide ion bridges the copper atom to an axial position at a distance Cu(1)–N(1)^a 2.649(2) Å to complete the square pyramidal geometry. The r.m.s. deviation of the four equatorially coordinating atoms from their respective mean plane is 0.253 Å. The metal atom is 0.051(2) Å from this plane towards the axially coordinating nitrogen atom N(1). The Mn···Cu distance is 2.973(2) Ǻ, and the Addison parameter is 0.092 which is slightly higher than that in **1**. The hydrogen atom H(8) from salicylaldehyde moiety forms a donor intermolecular hydrogen bond with azido nitrogen N(3) (1-x,-y,1-z) with dimensions C(11)···N(3) 3.43(3) Å, C(11)–H(8)···N(3) 163.1(2)° and H(8)···N(3) 2.47 Å to result in a 1D chain along the crystallographic *a* axis. (Fig. 3)

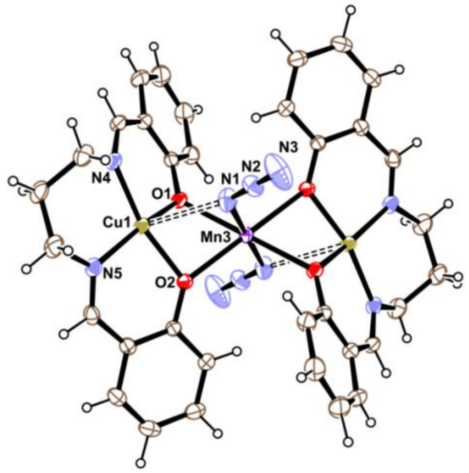


Fig. 2 ORTEP-3 view of the asymmetric unit of **2** with ellipsoids at 30% probability.

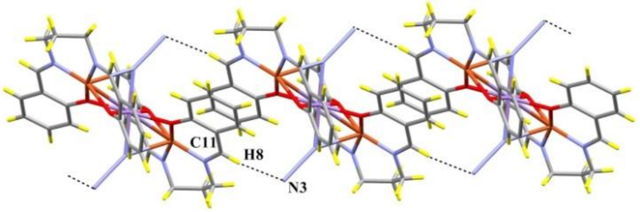


Fig. 3 Hydrogen bonded 1D chain in **2**.

The X-ray crystal structure determination reveals that complex **3** consists of a trinuclear unit $[(CuL)_2Mn\ (NCO)_2]$ as shown in Fig. 4 together with the atomic numbering scheme in the coordination spheres. Selected bond lengths and bond angles are summarized in ST 3 (supporting information). The structure contains a six-coordinate manganese in a distorted octahedral environment together with two four-coordinate square planar copper atoms with equivalent geometries. The manganese atom is bonded to four oxygens from the two metalloligands [CuL], at distances of 2.276(3), 2.268(3), 2.345(3), 2.227(3) Å which is somewhat longer than those in **1** and **2** but is very similar to those in the previously reported angular trinuclear structures.[10a] The two oxygen atoms from one ligand bridge one copper and the two oxygen atoms from the other ligand to the second copper. In addition the manganese atom is bonded to two mutually cis nitrogen atoms of terminal cyanate co-ligands at distances 2.092(4), 2.107(4) Å. Both the cis [64.54(9)−103.93(1)°] and trans [153.68(1)−160.50(8)°] angles indicate significant distortions from ideal octahedral geometry around Mn^{II}. The two copper atoms are each bonded to the four donor atoms of ligand L with Cu(1) bonded to oxygen atoms at 1.921(2), 1.938(3) Ǻ and nitrogen atoms at 1.957(3), 1.980(3) Ǻ and Cu(2) to oxygen atoms at 1.914(3), 1.925(2) Ǻ and nitrogen atoms at 1.955(3), 1.959(4) Ǻ. By using τ_4 index[23] distortion between perfect tetrahedron (τ_4=1) and perfect square planar (τ_4=0) can be calculated with the formula: $\tau_4 = [360° – (\alpha + \beta)]/141°$, with α and β (in °) being the two largest angles around the central metal in the complex. τ_4 value for Cu(1) and Cu(2) are 0.153 and 0.185 respectively, confirming slightly distorted square planar geometry around them. The donor atoms in the equatorial planes show r.m.s deviations of 0.089 and 0.175 Å for Cu(1) and Cu(2) respectively. The two planes intersect at 19.36°. The two Mn···Cu distances are 3.258(2), 3.261(2) Å respectively.

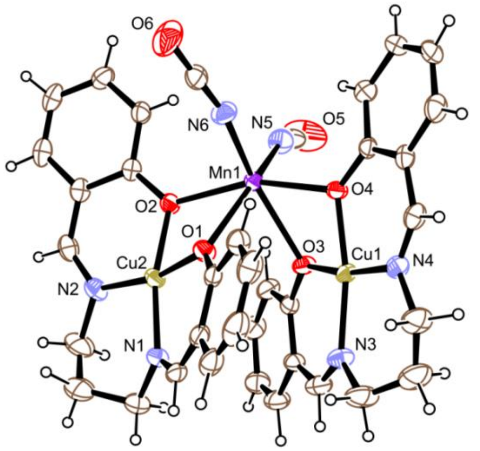


Fig. 4 ORTEP-3 view of the asymmetric unit of **3** with ellipsoids at 30% probability.

Each of the isocyanato oxygen (O5, O6) participates in intermolecular hydrogen bonding with the hydrogen atoms (H1, H4, H22B) of ligand moiety with dimensions in the range C···O 3.332(8)–3.399(6)Å, C–H···O 140.0(3)- 150.0(3)° and H···O 2.54-2.55 Å. (Fig. 5)

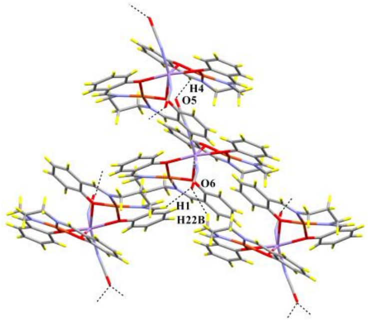


Figure 5. Hydrogen bonded polymeric structure in **3**.

Complex **4** $[(CuL)_2Mn(NO_3)_2]$ and **5** $[(CuL)_2Mn(Sal)_2]\cdot CH_2Cl_2$ crystallizes in centro-symmetric space group. (Ortep view of the structures are shown in Fig. 6 and 7 respectively) Selected bond lengths and bond angles are summarized in ST 4 (Supporting information). The connectivity of both of them is similar as in **1** but the dimensions in the metal coordination spheres differ to some extent. In **4,** the Mn–O distances to the bridging oxygen atoms of the ligands are considerably shorter [2.137(3)–2.142(3) Å] than those in **1** [2.173(2)-2.213(2) Å], whereas the distance to *syn-syn* bridging nitrato oxygen (1*κO*:2*κO'*) is slightly longer at 2.241(4) Å. In **5**, Mn–O distances in the basal plane ranges 2.161(4)- 2.193(3) Å, and the one of the trans axial positions is occupied by O(4) of the *syn-syn* bridging salicylato oxygen (1*κO*:2*κO'*) at a distance of 2.149(4) Å. Due to the presence of the centre of inversion, all the trans angles are ideal (180°) in both the structures but the cis angles [73.71(1)–94.18(1)° for **4**, 72.50(1)–91.01(1)° for **5**] deviate slightly from the ideal value (90°).

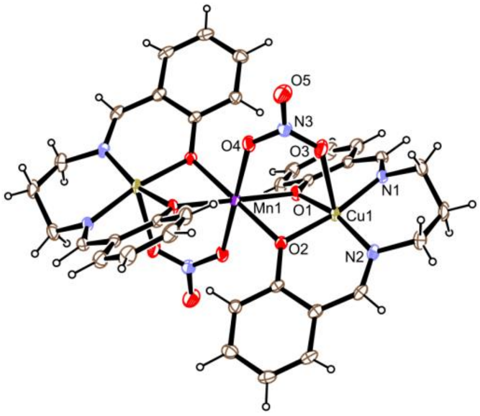


Fig. 6 ORTEP-3 view of the asymmetric unit of **4** with ellipsoids at 20% probability.

The two equivalent terminal Cu^{II} atoms labeled Cu(1) and Cu(1^a) are related through the symmetry operation (^{a}= 2-x,-y,2-z for **4** and -x,-y,-z for **5**). The bond lengths around the copper atoms are similar to those found in **1,** with Cu–O distances in the basal plane ranging 1.943(3)–1.950(3) Å in **4** and 1.958(4)–1.964(3) Å in **5**, whereas Cu–N distances in the range 1.958(5)–1.966(4) Å in **4** and 1.972(5)–1.994(5) Å in **5**. By contrast, the distance to the oxygen atom of bridging nitrate is considerably longer [Cu(1)–O(3)= 2.410(4) Å] in **4** and that of bridging salicylate is slightly longer [2.246(5) Å] in **5,** compared to **1** [2.173(3), 2.194 Å]. The mean deviation of four donor atoms in the equatorial plane from their respective mean plane is 0.182 Å in **4** and 0.065 Å in **5**. The deviation of Cu atom from this plane towards the axially coordinating oxygen O(3) is 0.085(5) Å in **4** and 0.144(1) Å in **5**. The two Cu···Mn distances are 3.076(2), 3.118(2) Å in **4** and **5** respectively. Addison parameter is 0.129 and 0.089 for **4** and **5** respectively which are comparable to **2** but are slightly higher than **1**.

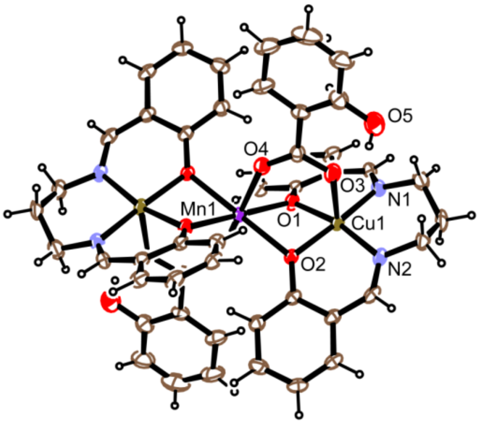


Fig. 7 ORTEP-3 view of the asymmetric unit of **5** with ellipsoids at 20% probability.

In complex **4** the nitrato oxygen (O5) forms intermolecular hydrogen bonding with hydrogen atom (H10) of the ligand moiety with dimensions C(14)···O(5) 3.465(8) Å, C(14)–H(10)···O(5) 166(4)° and H(10)···O(5) 2.59 Å. (Fig. 8) In **5** phenolic oxygen (O5) of salicylate forms intermolecular hydrogen bonding with methylene hydrogen (H3D) of dichloromethane solvent with dimensions C(35)···O(5) 3.354(2) Å, C(35)–H(3D)···O(5) 155.3° and H(3D)···O(5) 2.45 Å. (Fig. 9)

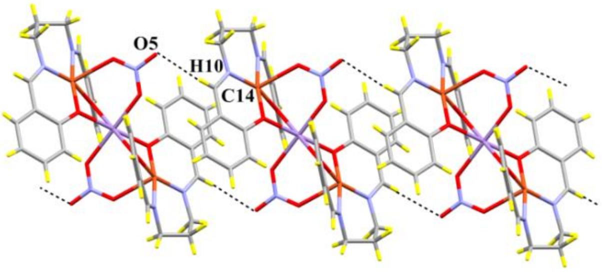


Fig. 8 Hydrogen bonded 1D chain in **4**.

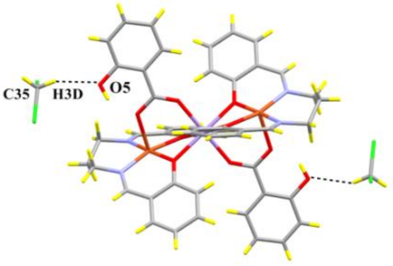
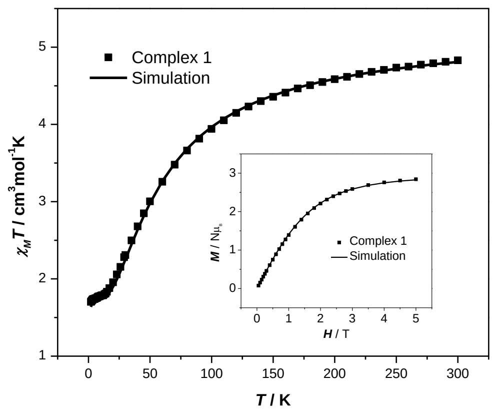


Fig. 9 Hydrogen bonding with solvent molecule (CH_2Cl_2) in **5**.

A CSD search reveals that there are 26 Cu^{II}-Mn^{II} complexes containing double oxido/phenoxido-brigde, among which 21 complexes have been magnetically characterized. These 26 complexes include 12 dimers, 6 trimers, 2 tetramers, 1 hexamer formed by connecting three dimers and 5 chains. If we limit to double phenoxido bridge Cu^{II}-Mn^{II}-Cu^{II} trinuclear complexes derived from di-Schiff base ligand the number reduces to only five; four of them are angular, three having phenoxido bridging angle ~103°, Cu···Mn distances in the range 3.158-3.205 Å and one with average Cu-O-Mn of 99°, Cu···Mn distance 3.218 Å. The remaining one is linear with Cu-O-Mn angle 101° and Cu···Mn distance 3.167 Å. The structure of complex **3** of present work is very similar to the three complexes reported by our group previously.[10a] The phenoxido bridging angle (101.40°) and Cu···Mn distance (3.258 Å) are also very close to those of the reported ones. Complexes **1**, **4** and **5** are linear with additional carboxylato or nitrato bridge ($1\kappa O$:$2\kappa O'$) which causes a slight lowering of Cu-O-Mn angles (97-98°) as well as shortening of Cu···Mn distances (3.076-3.142 Å) in these complexes. Complex **2** is also linear but here the additional bridge is $\mu_{1,1}$ azido and it exhibits very low phenoxido bridging angle (92°) and rather short Cu···Mn distance (2.973 Å). The single atom bridge ($\mu_{1,1}$ azido) in **2** brings the neighboring Cu^{II} and Mn^{II} atoms closer than the three atom bridges in complexes **1**, **4** and **5**.[7b] As a consequence, the phenoxido bridging angle decreases considerably in **2** than those in **1**, **4** and **5** compared to the diphenoxido bridging angles without the additional bridge as in **3**.

Magnetic properties

Temperature-dependent magnetic susceptibility measurements on powdered samples of **1-5** were carried out in an applied field of 0.3 T in the temperature range 1.9-300 K. The data are shown in the $\chi_M T$ versus T plot in Fig.10, where χ_M is the molar magnetic susceptibility and T is the absolute temperature. In all cases the room temperature $\chi_M T$ value roughly matches with the expected value 5.135 cm^3Kmol^{-1} obtained from the sum of one Mn(II) and two Cu(II) magnetically isolated ions, being 4.83, 4.91, 4.45, 5.09 and 4.97 cm^3Kmol^{-1} for complexes **1-5** respectively. Upon cooling, $\chi_M T$ continuously decreases until a plateau is reached between 50 and 20 K depending on the compound with a $\chi_M T$ value close to 1.87 cm^3Kmol^{-1} which corresponds to a ground state with S = 3/2. At very low temperature and depending on the strength of the intermolecular interactions, the $\chi_M T$ versus T curve further decreases in the case of complexes **1-3** and **5** or stabilizes at that value as is the case of complex **4**. The behavior displayed by all complexes suggests the presence of an overall antiferromagnetic interaction between Cu^{II} and Mn^{II} ions which, due to the Cu^{II}-Mn^{II}-Cu^{II} trinuclear structure, leads to a final ferrimagnetic ground state with spin 3/2, further confirmed in all cases by the field-dependent magnetization measurements at 2 K that indicate a saturation value close to 3 $N\mu_B$, that is 2.84, 2.88, 2.92, 3.08 and 3.08 $N\mu_B$ for complexes **1-5**, respectively. The skeleton of the five complexes can be considered magnetically symmetric even if crystallographically this is not always the case. Each Cu^{II} ion presents a Schiff base-derived tetradentate ligand that fills the four equatorial coordination sites of the metal, leaving its axial positions free for other ligands to coordinate.



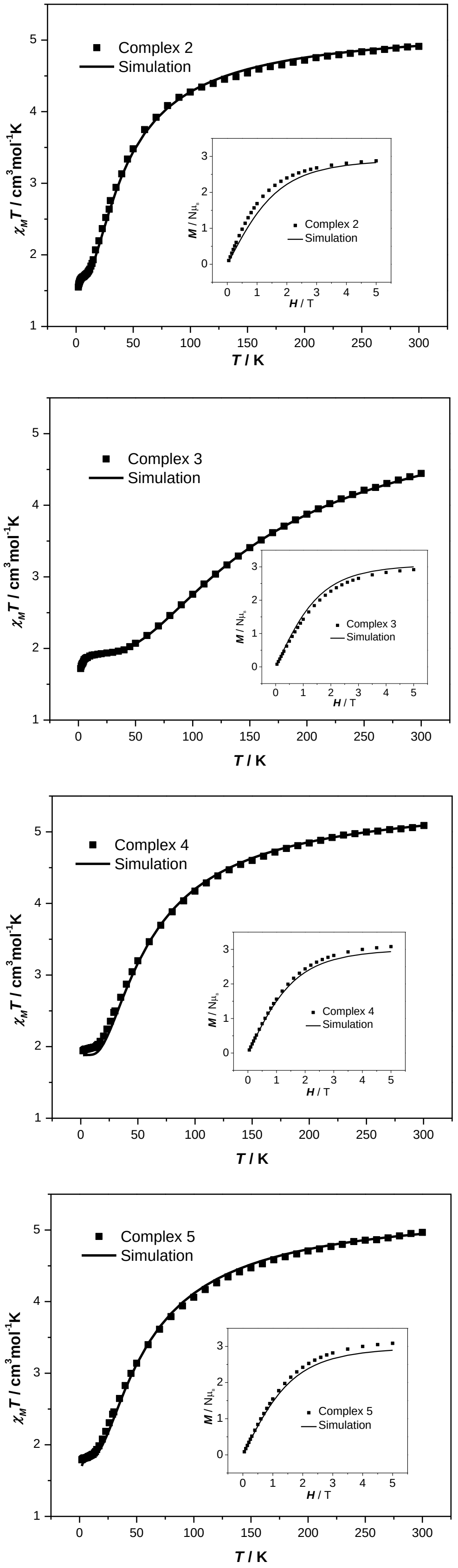


Fig. 10 Thermal dependence of the $\chi_M T$ for complexes **1-5**. Symbols represent experimental data while straight lines represent the simulations obtained from the parameters indicated in the main text. Insets: Field-dependent magnetization measurements at 2K with their corresponding simulations.

The equatorial plane of the Cu^{II} ions is composed then of two N atoms from the imine groups of the ligand plus two oxygen atoms from the two phenoxido functional groups of the same. The latter work also as bridging atoms between each Cu^{II} ion and the central Mn^{II} ion, forming a double phenoxido bridged Cu-Mn system. The differences among the five compounds are strictly related to the occupancy of the Cu^{II} axial positions which are filled by a *syn-syn* carboxylate molecule acting as additional bridging ligand in **1** and **5**, an end-on azide anion which also connects the Cu^{II} and Mn^{II} ions in **2**, a terminal cyanate ligand in complex **3** and a nitrate bridging ligand in **4**. All these axial ligands are placed along the elongated Jahn-Teller axes of the Cu^{II} ions that represent the orientation of the non-magnetic dz^2 orbitals. Consequently they are not expected to have a predominant role in the magnetic superexchange between Cu^{II} and Mn^{II} ions. This will be mainly determined by the phenoxido equatorial bridges mentioned before, which agrees quite well with the fact that the four complexes show very similar magnetic behaviors. In order to quantitatively interpret the magnetic data, simulations of the experimental curves were done by using the MAGPACK program with a Hamiltonian of the type $H= -J\,[S_1S_2+S_1S_3]$, where $S_1= S_{\mathrm{Mn}}$ and $S_2= S_3= S_{\mathrm{Cu}}$.ref needed: (a) J.J.Borràs-Almenar, J. M. Clemente-Juan, E. Coronado and B.S.Tsukerblat, J. Comput. Chem., 2001, 22, 985; (b) J.J.Borràs-Almenar, J. M. Clement-Juan, E. Coronado and B. S. Tsukerblat, Inorg. Chem., 1999, 38, 6081. In the model, the crystallographic equivalence of the two Cu^{II} ions in the trinuclear unit was considered by assigning one single g value for that ion. Simulations were carried out considering that the exchange coupling between these two terminal ions was zero ($J_{Cu\text{-}Cu}$= 0 cm^{-1}) due to the linear geometry of the complex. Moreover, a term accounting for intermolecular interactions (zJ') was also included. A good agreement between the experimental and simulated curves was found by using the following parameters: g_{Cu}= 2.16, g_{Mn}= 2.00, $J_{Cu\text{-}Mn}$= -9.6 cm^{-1} and zJ' = -0.1 cm^{-1} for complex **1**, g_{Cu}= 2.16, g_{Mn}= 2.00, $J_{Cu\text{-}Mn}$= -7.0 cm^{-1} and zJ'= -0.2 cm^{-1} for complex **2**, g_{Cu}= 2.20, g_{Mn} = 2.09, $J_{Cu\text{-}Mn}$ = -26.5 cm^{-1} and zJ' = -0.2 cm^{-1} for complex **3**, g_{Cu} = 2.20, g_{Mn} = 2.06, $J_{Cu\text{-}Mn}$= -9.7 cm^{-1} and zJ' = 0.0 cm^{-1} for complex **4** and g_{Cu} = 2.16, g_{Mn} = 2.03, $J_{Cu\text{-}Mn}$ = -9.3 cm^{-1} and zJ' = 0.0 cm^{-1} for complex **5**. The simulated curves are represented together with the experimental values in Fig.10. In the insets, the field-dependent magnetization curves at 2 K are shown with the simulated curves obtained by using the same set of magnetic parameters.

The coupling constants $J_{Cu\text{-}Mn}$ obtained are consistent with that of heterometallic Cu^{II}-Mn^{II} complexes reported previously.[10a,b,g,24] In order to evaluate the magnitude and nature of the magnetic superexchange, one should keep in mind that all the five d orbitals of Mn^{II} ion are occupied by unpaired electrons while in the case of Cu^{II} the only unpaired electron is located in the $d_{x^2-y^2}$ orbital. This implies that the Cu^{II} magnetic orbital is directly overlapped with the phenoxido ligand orbitals and hence this will be the main superexchange pathway. Although the $d_{x^2-y^2}$(Cu)- $d_{x^2-y^2}$(Mn) pathway gives rise to an antiferromagnetic interaction, the other routes through the four remaining Mn^{II} *d* orbitals could provide a ferromagnetic contribution; hence, the overall magnetic interaction between these two ions is expected to be weakly antiferromagnetic which agrees well with the present results. In the case of phenoxido-bridged dinuclear Cu^{II} complexes, the Cu-O-Cu angle has been observed as the main structural parameter dictating the nature and strength of the magnetic exchange constant. More specifically, the J_{Cu-Cu} becomes more antiferromagnetic when the Cu-O-Cu angle increases with a crossover angle from ferro to antiferromagnetic values at 97°.[8] In the case of phenoxido-bridged Cu^{II}-Mn^{II} complexes, the small number of examples present in the literature of such kind of compounds make it difficult to extract clear correlations.

However, considering all the structurally and magnetically characterized double or single oxido bridged Mn^{II}-Cu^{II} complexes reported in the literature, some of us described in a recent publication some general trends of the nature and strength of the magnetic exchange interaction with four structural parameters, namely the Cu-O and Mn-O bond distance, the Cu-O-Mn bond angle and the dihedral angle in the central CuO_2Mn unit.[10a] No obvious correlation was found with only one of those four structural parameters and the magnetic exchange interaction, even if generally speaking all of them seem to show a certain trend. If we focus more specifically on trinuclear Cu^{II}-Mn^{II}-Cu^{II} double phenoxido-bridged complexes, such as the ones reported in this work, and considering the previously mentioned structural parameters, it seems clear that the Cu-O-Mn bond angle and the Cu-O and Mn-O bond lengths show a correlation with the *J* value. Instead, the CuO_2Mn dihedral angles experimentally measured in those complexes only help to increase the dispersity of values found in the literature with no significant and clear correlation with the *J* magnetic exchange constant parameter. Thus, the data seem to confirm that the strength of the antiferromagnetic exchange increases with increasing Mn-O bond distance (Fig. 11a), with decreasing Cu-O bond distance (Fig. 11b) and with increasing Cu-O-Mn bond angle (Fig. 11c). *Focusing only on the Cu-O bond distances, it seems obvious that a shorter Cu-O bond leads undoubtedly to a stronger antiferromagnetic coupling, which is in agreement with what could be expected due to the larger overlap of magnetic orbitals. However, compound 3, which shows the most antiferromagnetic coupling (J= -26.50cm^{-1}), is at the same time the compound with the shortest Cu-O bond distance and the one with the largest Mn-O bond distance. This trend may suggest a competition between ferro and antiferromagnetic terms in this type of compounds, confirming that a decrease of the Cu-O bond distance is more effective in increasing the antiferromagnetic exchange than an increase of the Mn-O bond distance in increasing the ferromagnetic component*

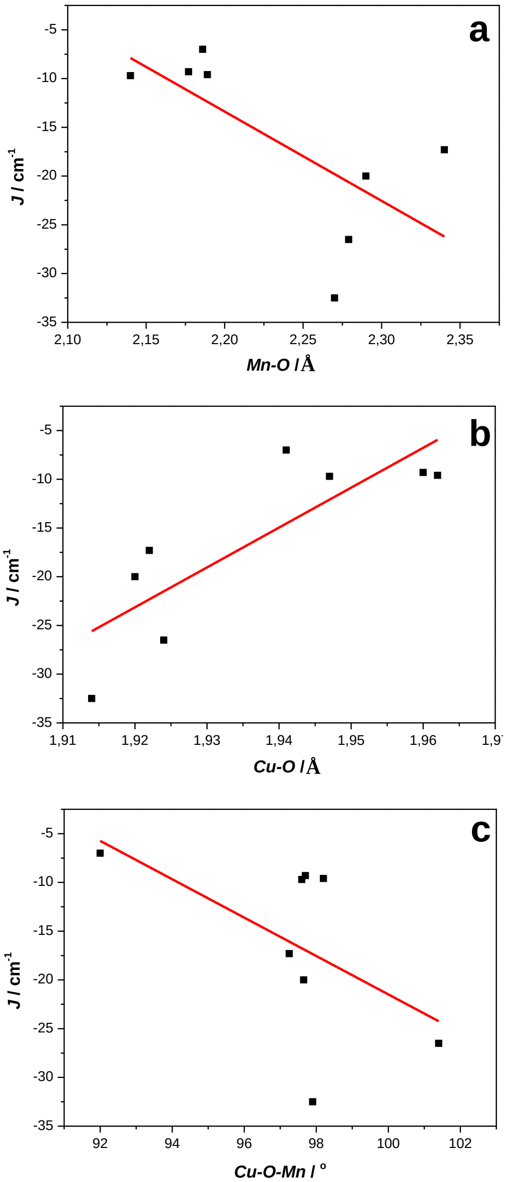


Fig. 11 Variation of the magnetic coupling (*J*) in trinuclear Cu^{II}-Mn^{II}-Cu^{II} double phenoxido-bridged complexes with: (a) the average Mn-O bond distance, (b) the average Cu-O bond distance and (c) the average Cu-O-Mn bond angle. Data are extracted from complexes **1-5** of the present work and from complexes **2-4** from reference 10a.

For what concerns the Cu-O-Mn bond angle, this behaves similar to what observed in the case of phenoxido-bridged homometallic complexes.[8-9] In the case of heterometallic Cu^{II}-Mn^{II}-Cu^{II} complexes however, the crossover angle could not be determined due to the lack of systems with Cu-O-Mn bond angle values low enough. In the present systems, the weakest antiferromagnetic interaction is observed for complex **2** that shows the lowest value of the Cu-O-Mn angle, being this equal to 92.0°, while the strongest antiferromagnetic interaction is observed for complex **3** that shows a Cu-O-Mn angle of 101.4°, being this one the largest among all our complexes. Complexes **1**, **4** and **5** show Cu-O-Mn angles of average values 98.2°, 97.6° and 97.7°, respectively, that lead to intermediate antiferromagnetic interactions as expected.

Conclusions

Five heterometallic trinuclear complexes **1-5** have been synthesized by selecting various types of coligands to acquire different geometries with diverse phenoxido bridging angles. Complexes **1**, **4** and **5** are linear with carboxylato or nitrato bridge (1*κO*:2*κO′*) along with phenoxido bridge. Complex **2** is linear containing additional $\mu_{1,1}$ azido bridge and **3** is angular with terminally coordinated isocyanato ligand. This diversity in geometry of the complexes is reflected in Cu-O-Mn angle which varies in a wide range from 92º to 101º. To the best of our knowledge, we have achieved the lowest phenoxido bridging angle in **2** among all the reported trinuclear Cu^{II}-Mn^{II}-Cu^{II} complexes. Magnetic interaction present in all five complexes is overall antiferromagnetic, leading to a final ferrimagnetic ground state with spin 3/2. The antiferromagnetic exchange coupling is weakest for **2** ($J_{Cu\text{-}Mn}$= -7.0 cm^{-1}) and strongest for **3** ($J_{Cu\text{-}Mn}$= -26.5 cm^{-1}). From magneto structural correlation it can be concluded that lowering in Cu-O-Mn angle causes antiferromagnetic interaction to decrease but the cross over angle is yet to be achieved.

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Notes and references

[a] *Department of Chemistry, University College of Science, University of Calcutta, 92, A.P.C. Road, Kolkata-700 009, India; E-mail: ghosh_59@yahoo.com*

[b] *Department of Inorganic Chemistry and Nanoscience and Nanotechnology Institute (IN2UB), University of Barcelona, Martí i Franqués 1-11, 08028 Barcelona, Spain; E-mail: albert.figuerola@antares.qi.ub.edu*

†Electronic supplementary information (ESI) available: The electronic supplementary information file contains IR spectra of the complexes, Figure S1-S6. Table ST1-ST4. CCDC 951180-951184 for ***1-5****. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/*

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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