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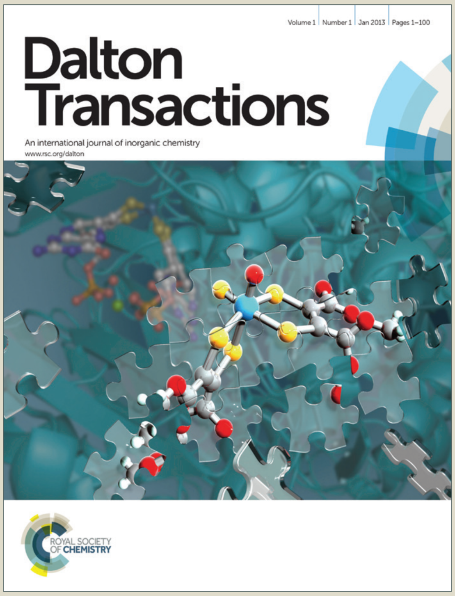

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ARTICLE TYPE

pH dependent facile synthesis of di- and tri-nuclear oxime based Cu(II) complexes: strong antiferromagnetic coupling in the dinuclear complexes and spin frustration in the trinuclear complex

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Oxime based tridentate Schiff base ligand 3-[3-(dimethylamino)propylimino]butan-2-one oxime (HL) produced two dinuclear compounds $[Cu_2L_2(H_2O)](ClO_4)_2$ (**1**) and $[Cu_2L_2(H_2O)](BF_4)_2$ (**2**), and a hexanuclear compound $[\{Cu_3(HL)_3(O_3ClO)(\mu_3\text{-}O)\}_2(\mu\text{-}H)](ClO_4)_7$ (**3**) when it was reacted with $Cu(ClO_4)_2\cdot 6H_2O$ or $Cu(BF_4)_2\cdot 6H_2O$ at different pH. All three compounds have been structurally and magnetically characterized. Compounds **1** and **2** are dinuclear species in which the two square planar copper(II) ions are joined solely by the double oximato bridges. On the other hand, the hexanuclear compound **3** consists of two triangular Cu_3O cores held together by a proton separated by an O···O distance of 2.498(10) Å. The three square pyramidal copper(II) ions at the corners of an isosceles triangle form a triangular core through a central oxido (μ_3-O) and peripheral oximato bridges. Each triangular Cu_3O core is capped by an unusual triply coordinated (μ_3-perchlorato-O,O',O'') perchlorate anion. Variable-temperature (2-300 K) magnetic susceptibility measurements show that compounds **1-3** exhibit strong antiferromagnetic interaction with J values -562.6, -633.1 and -636.0 cm^{-1} respectively. The X-band EPR data at low temperature clearly indicate the presence of spin frustration phenomenon in complex **3**.

Introduction

Exchange coupled polymetallic complexes, in which spin coupling between paramagnetic metal centers is propagated *via* bridging atoms, are a very popular research topic due to their potential applications as molecule-based magnetic materials.[1-5] Oxime based ligands have been widely used for the synthesis of polynuclear spin coupled magnetic molecules because they can connect metal ions through N as well as O atoms and generate both homo- and hetero-metallic M–N–O–M' bridging cores within a molecular unit.[6] Generally, the nuclearity and topology of the spin centers of oximato bridged complexes depend on the ligand backbone. Therefore, several dinuclear[7-9] and a few tri-[10,11] and tetranuclear[12] copper(II) oximato complexes are synthesized by the modification of the ligand backbone. A detailed investigation of the magnetic properties of these complexes reveals that the in-plane oximato bridge between magnetic centers in dicopper(II) complexes displays strong antiferromagnetic coupling due to effective overlap of magnetic orbitals ($d_{x2-y2}\|\sigma_{sp2}(NO)\| d'_{x2-y2}$) whereas out-of-plane oximato bridge orbitals ($d_{x2-y2}\|\sigma_{sp2}(NO)\perp d'_{x2-y2}$) reduces the overlap of magnetic orbitals and exhibits weak ferro- or antiferromagnetic coupling.[13] Moreover, the oxime-based triangular core containing an additional central μ_3-oxido or the μ_3-hydroxido bridge can interact magnetically *via* super exchange involving Cu^{II}–O–Cu^{II} pathways.[11,14] This type of triangular core could exist either in a spin-frustrated[11] (S_{total} = 1/2, doubly degenerate) state or in a quartet state (S_{total} = 3/2). Spin frustration occurs when only two of the three spins are achieved full spin compensation simultaneously and is especially observed in highly symmetrical triangular cores having antiferromagnetically coupled spins.[15] Recently, using oxime based Ni(II) compounds we prepared di-tri and tetranuclear species by using the Schiff-base ligands by varying the pH of the reaction mixture.[16] In the present work, our aim is to synthesize oxime based polynuclear Cu(II) compounds of different nuclearity using a fixed oxime backbone by varying the reaction conditions and counter anions and to study their magnetic behavior. In the course of our endeavor, we succeeded in preparing three Cu(II) compounds; two dinuclear $[Cu_2L_2(H_2O)](ClO_4)_2$ (**1**), and $[Cu_2L_2(H_2O)](BF_4)_2$(**2**) and one hexanuclear complex $[\{Cu_3(HL)_3(O_3ClO)(\mu_3\text{-}O)\}_2(\mu\text{-}H)](ClO_4)_7$ (**3**) by reacting amono-condensed oxime based Schiff-base ligand, 3-[3-(dimethylamino)propylimino]butan-2-one oxime (HL) with copper(II) perchlorate hexahydrate or copper(II) tetrafluroborate hexahydrate at different pH (Scheme 1). It should be noted that a similar approach was taken to synthesize Cu(II) complexes with a different oxime based ligand, 4-amino-4-methylpentan-2-one oxime by varying pH.[17] However, the results obtained by us are very different as in discussed below. The hexanuclear compound **3** in the present paper is a rare example of a structure[18-20] in which two Cu_3O triangular cores are connected solely by a single hydrogen bridge. The variable-temperature (2-300 K) magnetic susceptibility measurements of the three compounds **1-3** are performed in detailed.

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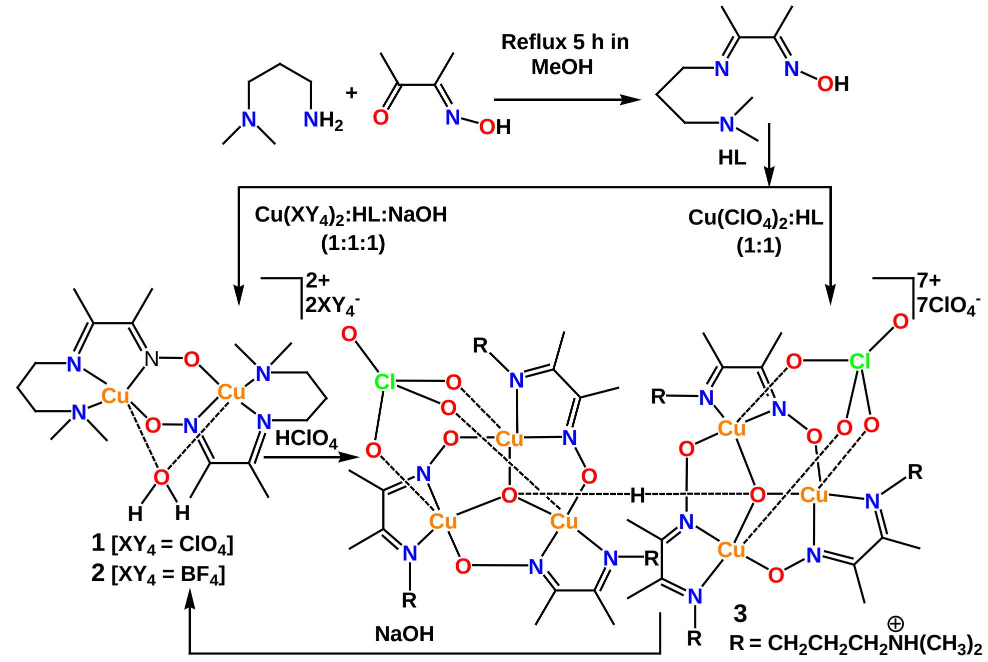

Scheme 1. Formation of complexes (**1**-**3**) and interconversion between the complexes **1** and **3**.

Experimental

Starting materials

Diacetylmonoxime, 3-dimethylamino-1-propylamine and NaOH were purchased from commercial sources and used as received. Copper(II) perchlorate hexahydrate and copper(II) tetrafluroborate hexahydrate were prepared by the standard laboratory method; solvents were of reagent grade and used without further purification.

Caution! Perchlorate salts of metal complexes coordinated with organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with care.

Preparation of Cu(ClO$_4$)$_2$·6H$_2$O and Cu(BF$_4$)$_2$·6H$_2$O

To a 20 ml of 1:1 HClO$_4$ or HBF$_4$ and H$_2$O solutions, solid CuCO$_3$ was added with continuous stirring by glass rod until evolution of CO$_2$ ceased. The mixtures were filtered and the blue filtrates were evaporated in a water bath to reduce the volume half of its initial volume. The solutions were cooled to room temperature to obtain a light blue crystalline solid which was isolated by filtration. The solid was recrystallized from water and stored in a desiccator.

Synthesis of Schiff base ligand (HL)

The mono-condensed Schiff-base ligand, 3-[3-(dimethylamino)propylimino]butan-2-one oxime (HL) was prepared by standard methods. 8 mmol of diacetylmonoxime (0.808 g) were mixed with 8 mmol of 3-dimethylamino-1-propylamin (1.008 mL) in methanol (20 mL). The resulting solution was refluxed for *ca*. 5 h and allowed to cool. The yellow coloured methanolic solution was used directly for complex formation.

Synthesis of complexes [Cu$_2$L$_2$(H$_2$O)](ClO$_4$)$_2$ (1) and [Cu$_2$L$_2$(H$_2$O)](BF$_4$)$_2$ (2)

A methanolic solution (20 mL) of Cu(ClO$_4$)$_2$·6H$_2$O (0.740 g, 2 mmol) was allowed to react with a mixture containing a methanol solution of HL (2 mmol, 5 mL) and NaOH (0.080 g, 2 mmol). The green coloured mixture was stirred for 1 h at room temperature and it was filtered. The filtrate was allowed to stand overnight at open atmosphere when needle shaped green (**1**) X-ray quality single crystals appeared at the bottom of the vessel. Similarly, green single crystals of **2** were obtained by following the same procedure for **1**, but using copper(II) tetrafluroborate hexahydrate instead of copper(II) perchlorate hexahydrate. Both **1** and **2** were then washed with diethyl ether and dried in a desiccator containing anhydrous CaCl$_2$, then characterized by elemental analysis, spectroscopic methods and X-ray diffraction.

Complex **1**: Yield: 0.650 g (91%). *Anal.* calc. for $C_{18}H_{38}Cl_2Cu_2N_6O_{11}$: C 30.34, H 5.38, N 11.79. found: C 30.61, H 5.52, N 11.99 %. IR (KBr pallet, cm^{-1}): 3467mb, 2899mb, 1631w, 1527m, 1223m, 1096sb and 621m. UV/Vis: λ_{max} (nm) [ε_{max}(M^{-1} cm^{-1})] in (MeOH) = 636 (709), 427 (2700) and 317 (28497) and λ_{max} (solid, reflectance) = 671, 427 and 351 nm.

Complex **2**: Yield: 0.595 g (87%). *Anal.* calc. for $C_{18}H_{38}F_8B_2Cu_2N_6O_3$: C 31.46, H 5.57, N 12.23. found: C 31.97, H 5.35, N 12.49 %. IR (KBr pallet, cm^{-1}): 3567mb, 3502mb, 2905m, 1635w, 1529m, 1222m, 1061sb and 509m. UV/Vis: λ_{max} (nm) [$\varepsilon_{max}(M^{-1}\ cm^{-1})$] in (MeOH)= 635 (670), 426 (2572) and 317 (26333) nm and λ_{max} (solid, reflectance) = 670, 424 and 351 nm.

Synthesis of complex $[\{Cu_3(HL)_3(O_3ClO)(\mu_3\text{-}O)\}_2(\mu\text{-}H)](ClO_4)_7$ (3)

Compound **3** was prepared by mixing the same components with same stoichiometry as for **1** but in the absence of NaOH. A methanolic solution (20 mL) of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.740 g, 2 mmol) was added to a methanol solution of HL(2 mmol, 5 mL). The deep green coloured mixture was stirred for 1h at room temperature. It was then filtered and allowed to stand overnight at open atmosphere. In this case, deep green, hexagonal shaped crystals of complex **3** suitable for single crystal X-ray diffraction were then obtained at the bottom of the vessel.

Complex **3**: Yield: 0.685 g (85%). *Anal*. calc. for $C_{54}H_{115}Cl_9Cu_6N_{18}O_{44}$: C 26.79, H 4.79, N 10.41. found: C 26.83, H 4.72, N 10.47%. IR (KBr pallet, cm^{-1}): 3504mb, 3168w, 1639w, 1555m, 1216w, 1100sb and 625m. UV/Vis: λ_{max} (nm) [$\varepsilon_{max}(M^{-1}\ cm^{-1})$] in (MeOH) = 635 (602), 423 (2370) and 317 (32558) nm and λ_{max} (solid, reflectance) = 641, 421 and 351 nm.

Physical Measurements

Elemental analyses (C, H and N) were performed using a Perkin-Elmer 2400 series II CHN analyzer. IR spectra in KBr pellets (4000–500 cm^{-1}) were recorded using a Perkin-Elmer RXI FT-IR spectrophotometer. Electronic spectra in methanol as well as in solid state were recorded in a Hitachi U-3501 spectrophotometer. Powder X-ray diffraction patterns are recorded on a Bruker D-8 Advance diffractometer operated at 40 kV voltage and 40 mA current and calibrated with a standard silicon sample, using Ni-filtered Cu-Kα (α = 0.15406 nm) radiation. The magnetic measurements were carried out in the "Servei de Magnetoquimica (Universitat de Barcelona)" on polycrystalline samples (20 mg) with a Quantum Design SQUID MPMSXL magnetometer in an applied field of 10000 G and 500 G in the temperature ranges of 2–300 K and 2–30 K, respectively. The experimental magnetic susceptibility data are corrected for the diamagnetism estimated from Pascal's tables.[21] EPR spectra were recorded on powder samples at X-band frequency with a Bruker 300E automatic spectrometer, varying the temperature between 300 and 17 K.

Crystallographic data collection and refinement

6164 and 9258 independent reflection data for **1** and **2** were collected with MoKα radiation at 293K using the Bruker-AXS SMART APEX II diffractometer. The crystals were positioned at 60 mm from the CCD. 360 frames were measured with a counting time of 5 s in both the cases. 14430 independent reflection data for **3** was collected with MoKα radiation at 150K using the Oxford Diffraction X-Calibur CCD System. The crystal was positioned at 50 mm from the CCD. 321 frames were measured with counting times of 50s. Data analyses were carried out with the CrysAlis program.[22] All three structures were solved using direct methods with the Shelxs97 program.[23] The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon, and to nitrogen in 3, were included in geometric positions and given thermal parameters equivalent to 1.2 times (or 1.5 times for methyl groups) those of the atom to which they were attached. Absorption corrections were carried out using the SADABS program[24] for **1** and **2**,and ABSPACK program[25] for **3**.The structures (**1**-**3**) were refined on F^2 to R1 0.0408, 0.0486, 0.0932; wR2 0.0531, 0.0808, 0.2580 for 5189, 6316, 4005 data with $I > 2\sigma(I)$. Data collection and structure refinement parameters and crystallographic data for the three complexes are given in Table 1.

Results and Discussion

Syntheses

When Schiff-base ligand HL is allowed to react at room temperature with copper(II) perchlorate hexahydrate or copper(II) tetrafluroborate hexahydrate separately in MeOH medium in the presence of NaOH, (the pH of the mixtures were 9-10) the dinuclear species $[Cu_2L_2(H_2O)](ClO_4)_2$ (**1**) or $[Cu_2L_2(H_2O)](BF_4)_2$ (**2**) was produced. In both compounds, the oximato oxygen atoms of the Schiff-base ligand were deprotonated and coordinated to Cu(II). In contrast, the same Schiff-base ligand HL reacted with copper(II) perchlorate hexahydrate in MeOH medium in the absence of NaOH (pH of the mixture 4.5) produced a hexanuclear compound $[\{Cu_3(HL)_3(O_3ClO)(\mu_3\text{-}O)\}_2(\mu\text{-}H)](ClO_4)_7$ **(3)**. Here, the tertiary nitrogen atoms of amine groups of the Schiff base ligand act as a base to generate the hydroxyl ion *in situ* and deprotonate the oximato oxygen atoms. As a result, the tertiary nitrogen atoms being protonated remained unbonded as pendant arms (Scheme 1). The phase purity of these three isolated compounds (**1**-**3**) was confirmed by their powder XRD pattern (Fig.S1). Interestingly, when copper(II) tetrafluroborate hexahydrate was mixed with HL in MeOH medium in the absence of NaOH (pH of the mixture 5.2), we could not isolate X-ray quality single crystals instead we got a green residue. Moreover, the green compound is not analogous to compound **3** as its elemental analyses (C, H and N) and powder pattern is completely different from compound **3**. However, crystallization of this green sample from acetonitrile resulted in crystals of **2** and a known Cu(I) compound, $[Cu(NCCH_3)_4]BF_4$.[26] This fact indicates that the green sample is a mixture of two compounds.

The interconversion of compounds **1** and **3** has been studied by electronic spectra in methanol (see Figs. S2 and S3 in supporting information). It is found that the spectrum pattern of complex **1** changes to that of complex **3** when the pH is brought about 4.5 by adding $HClO_4$ drop wisein methanol solution. Similarly, the spectrum pattern of complex **3** transforms to that of complex **1** if NaOH is added to the methanol solution of complex **3** to raise the pH to *ca.* 9.5. The interconversion is also confirmed by the determination of the cell dimensions as well as the powder XRD patterns of the crystals obtained from these solutions.

IR and UV-Vis spectra

IR spectra of the compounds (**1**-**3**) show the characteristic bands of the coordinated oxime based Schiff base ligands (Figs. S4-S6). The bands in the regions 1639-1631 and 1223-1216 cm^{-1} are due to ν(C=N) and ν(N–O) vibrational modes, respectively. In addition, the appearance of a broad band in the region 3550-3450 cm^{-1} in the spectrum of **1** and **2** indicates the presence of water molecule in both of them whereas compound **3** displays one broad band of medium intensity centered at 3504 cm^{-1} and a weak band at 3168 cm$^{–1}$, which may be attributed to the ν(O–H) and ν(N–H) stretching modes of hydroxido and –NH groups respectively. Moreover, strong intensity bands at 1096 and 1100 cm$^{–1}$ for **1** and **3** respectively confirm the presence of perchlorate anion in both compounds. Similarly, compound **2** displays a strong intensity band at 1061 cm$^{–1}$ due to the tetrafluroborate anion.

The electronic spectra of all three compounds are recorded in methanol as well as in solid state and these are shown in Figs. S2, S3 and S7. The compounds exhibit broad absorption bands in the visible region at 636, 635 and 635 nm in methanol for **1**-**3** respectively. These bands are attributed to d–d transitions of Cu(II) ions in the square based environment. In addition, sharp, single absorption bands are found near 427, 426 and 423 nm for **1-3** respectively, which can be attributed to ligand-to-metal charge transfer transitions. Moreover, absorption bands at 317 nm in methanol assignable to intra-ligand charge transfer transitions are observed for all three compounds. However, in solid state, the positions of ligand-to-metal charge transfer transitions (427, 424 and 421 nm for **1-3** respectively) are similar but the patterns are somewhat different from that observed in methanol. On the other hand, both the pattern and position of d–d transitions (671, 670 and 641 nmfor **1-3** respectively) and intra ligand charge transfer transitions (351 nm in all three complexes) in solid state differ appreciably from those in methanol solution. Therefore, it is concluded that the structural identities of the complexes in the solid state are probably changed in the solution.

Structure descriptions

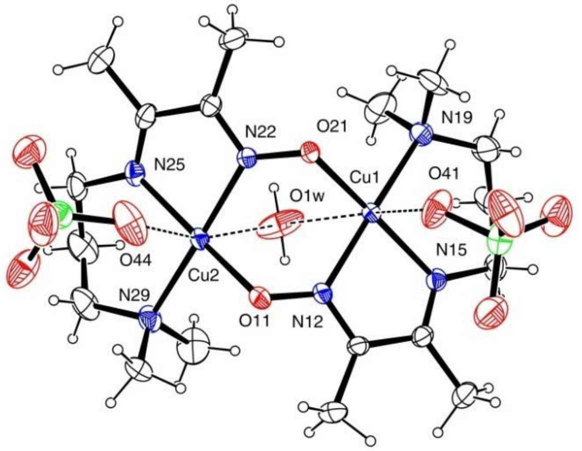

Fig. 1. The structure of **1** with ellipsoids at 20% probability. Weak interactions are shown as dotted lines.

The structures of **1** and **2** consist of [Cu$_2$L$_2$]$^{2+}$ cationic dinuclear units with two anions and a coordinated water molecule O(1W). The two structures are shown in Figs. 1 and 2, respectively, while selected bond lengths and angles are summarized in Table 2. The two copper atoms can be considered as having four coordinate square planar environments being bound to three nitrogen atoms of one ligand and oxygen of a second ligand. In **1** and **2**, the bonds to oxygen are 1.937(3), 1.935(2) Å for Cu(1)-O(21) and 1.940(3), 1.938(3) Å for Cu(2)-O(11). The distances to two of the nitrogen atoms are similar Cu(1)-N(12) 1.978(3), 1.984(3) Å, Cu(1)-N(15) 2.005(3), 1.999(3) Å and Cu(2)-N(22) 1.984(3), 1.988(3) Å, Cu(2)-N(25) 1.982(4), 1.982(4) Å but are shorter than those to the tertiary nitrogen Cu(1)-N(19) 2.05.7(4), 2.054(4) Å, Cu(2)-N(29) 2.069(4), 2.056(4) Å. The four donor atoms in the equatorial planes show r.m.s. deviations of 0.124, 0.130 Å in **1** and 0.102, 0.126 Å in **2** with the metal atoms Cu(1) and Cu(2) 0.059(2), 0.098(2) Å in **1** and 0.105(2), 0.089(2) Å in **2** from their respective planes. Both copper atoms are displaced from the planes in the direction of the water molecule O(1W) which forms weak interactions in axial positions with the two copper atoms in the cation at distances of 2.595(8), 2.775(9) Å in **1** and 2.663(10), 2.739(8) Å in **2**. As is apparent from Figs. 1 and 2, the water molecule has high thermal motion in both structures but refining a disordered model gave no significant reduction in R value.

In addition there are weak interactions in the other axial positions, with oxygen (in **1**) or fluorine (in **2**) atoms in the anions, *viz* in **1** Cu(1)···O(41) (-x, ½+y, 3/2-z) 2.785(3) Å, Cu(2)···O(44) 2.587(4) Å, and in **2** Cu(1)···F(41) (-x, ½+y, 3/2-z) 2.786(6) Å, Cu(2)···F(44) 2.602(4) Å. Therefore the cation and one anion form one dimensional polymer (Fig. 3 for **1** and Fig. S8 for **2**) along a screw axis parallel to the *b* axis.

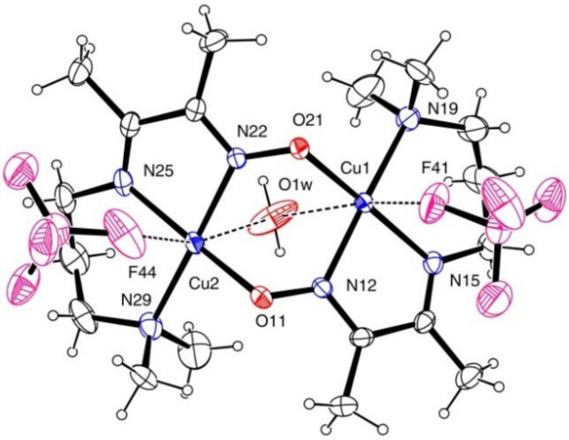

Fig. 2. The structure of **2** with ellipsoids at 20% probability. Weak interactions are shown as dotted lines.

The second anion is involved in hydrogen bonds from the water molecule namely in **1** O(1W)-H(1)···O(51) and O(1W)-H(2)···O(52) (x+½, -½-y, -z) with dimensions H···O 2.00 and 2.13 Å, O-H···O 151 and 124^{o} and O···O 2.887(9) and 2.795(8) Å and in **2** to F(51) i.e. O(1W)-H(1)···F(51) with dimensions H···F 1.92 Å, O-H···F 148^{o}, O···F 2.791(7) Å and to F(52) (x+½, -½-y, -z) O(1W)-H(2)···F(52) H···F 2.02 Å, O-H···F 126^{o}, and O···F 2.712(7) Å.

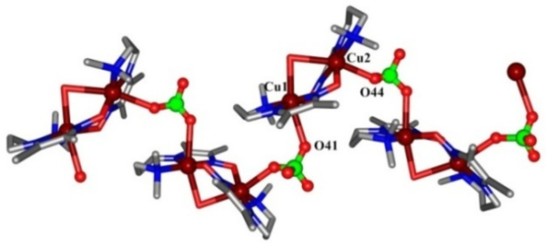

Fig. 3. The 1D zigzag coordination polymer of **1**. H-atoms have been removed for clarity.

The structure of **3** contains two trinuclear $[Cu_3(HL)_3(OClO_3)(\mu_3\text{-}O)]^{3+}$ moieties which are bridged *via* a hydrogen atom bonded to the oxygen O(1) to form a dimeric centrosymmetric cation $[\{Cu_3(HL)_3(O_3ClO)(\mu_3\text{-}O)\}_2(\mu\text{-}H)]^{7+}$. The trinuclear moiety is shown in Fig. 4 and the dimer in Fig. 5. Selected bond lengths and angles are summarized in Table 3.

In the trinuclear moiety shown in Fig. 4, the environments of the three copper atoms are equivalent showing a square planar equatorial plane, being bound to an oxygen from one ligand and two nitrogen atoms from another ligand together with the oxygen atom O(1) which bridges all three metal atoms. Thus the third protonated nitrogen in each ligand remains unbonded. These four donor atoms are approximately planar showing r.m.s. deviations of 0.007, 0.009, 0.010 Å around Cu(1), Cu(2) and Cu(3) respectively. The metal atoms are 0.117(3), 0.023(3), 0.100(3) Å from these planes. Bond lengths to the bridging oxygen atom O(1) are 1.909(5), 1.902(5), 1.879(5) Å, to the ligand oxygen 1.938(5), 1.962(5), 1.958(5) Å and to the nitrogen atoms in the range 1.936(6)–1.994(7) Å. The bridging oxygen atom O(1) lies 0.380(5) Å from the plane of the three copper atoms. In addition to the equatorial plane described above, each copper atom was also bonded to a different oxygen atom of a perchlorate anion in approximately axial positions at distances of 2.471(8), 2.594(10), 2.547(7) Å respectively. Thus, the perchlorate anion acts as a capping ligand and its bridging mode (μ_3-perchlorato-O,O',O") is rare in literature.[18]

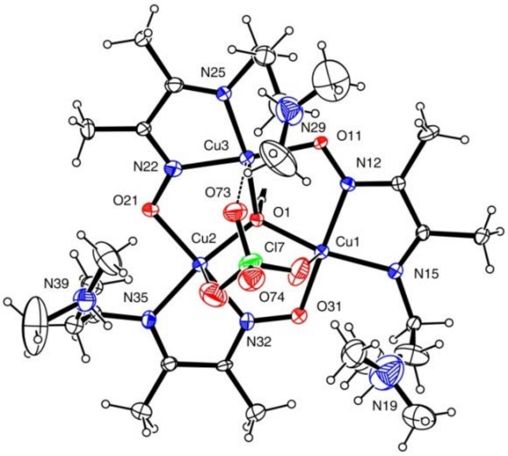

Fig. 4. The structure of the $[Cu_3(HL)_3(ClO_4)(\mu_3\text{-}O)]^{3+}$ moiety in **3** with ellipsoids at 30% probability. Weak bonds are shown as dotted lines.

This oxygen atom O(1) lies 2.498(10) Å from its symmetry related counterpart across a centre of symmetry. While a difference Fourier map did not show a strong region of electron density at or close to the centre of symmetry, it seems obvious that a hydrogen must be present between oxygen atoms this close though it is not clear whether it is positioned at the centre of symmetry equidistance from the two oxygen atoms or closer to one or the other. A symmetric hydrogen bond is often found when with such a short O···O distance and the atom were therefore refined on the centre of symmetry.

The presence of one hydrogen atom between oxygen atoms gave the formula $[\{Cu_3(HL)_3(O_3ClO)(\mu_3\text{-}O)\}_2(\mu\text{-}H)]^{7+}$ to the dimer. For charge balance, it was necessary to include 3.5 perchlorates per Cu_3 unit, and this was achieved by including one with 100%, two with 75% and two with 50% occupancy. Charge balance also requires that the nitrogens not bonded to the metal are protonated so that the ligands are neutral in the complex. These hydrogen atoms were not clearly observed in a difference Fourier map, presumably because of the high thermal motion of the nitrogen atoms but their presence can be inferred by the fact that on inclusion in calculated positions, they formed hydrogen bonds to oxygen atoms, albeit to those with 50% occupancy, thus N(19)-H(19)...O(104), N(29)-H(29)...O(102)(x-1, y-1, z) and N(39)-H(39)···O(112) with dimensions N···O 3.02(2), 3.49(2), 2.81(2) Å, N-H···O 145, 159, 170° and H···O 2.28, 2.63, 1.91 Å.

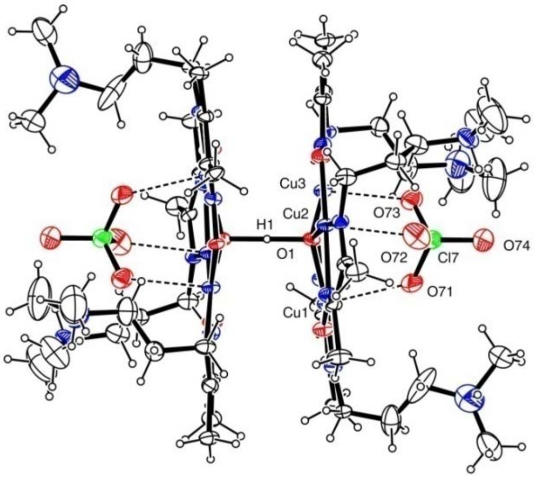

Fig. 5. The structure of the $[\{Cu_3(HL)_3(O_3ClO)(\mu_3\text{-}O)\}_2(\mu\text{-}H)]^{7+}$cation in **3** with ellipsoids at 20% probability. Weak bonds are shown as dotted lines.

Magnetic properties

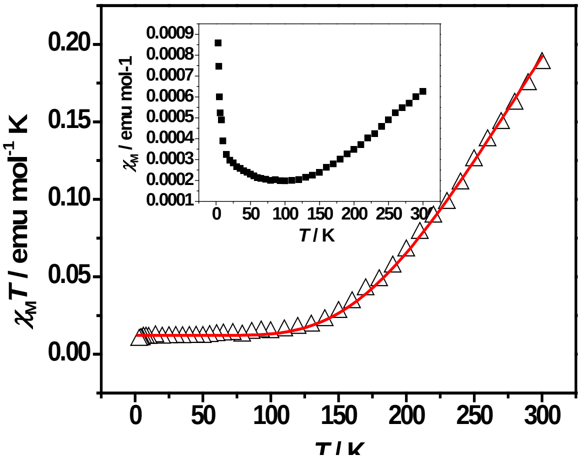

Fig 6. Plot of $\chi_M T$ vs T plot for **1**.The solid line represents the best fit to the experimental data. The χ_M vs T plot is shown inset.

The temperature dependent magnetic susceptibilities for complexes **1** and **2** were investigated in the temperature ranges of

The temperature dependent magnetic susceptibilities for complexes **1** and **2** were investigated in the temperature ranges of 2–300 K and 2–30 K in applied field of 10000 G and 500 G, respectively. The direct current (dc) magnetic properties of the complexes **1** and **2** in the form of $\chi_M T$ versus T plot (χ_M being the magnetic susceptibility per Cu_2 unit and T the absolute temperature) are shown in Fig. 6 and 7. At room temperature, $\chi_M T$ is equal to 0.19 emu mol^{-1} K for **1** and 0.143 emu mol^{-1} K for **2**. These values are much lower than the expected for the sum of two non-interacting Cu^{II} centers (0.75 emu mol^{-1} K,S$_{cu}$= 1/2, g$_{Cu}$ = 2.0), providing evidence of strong antiferromagnetic interactions. For both complexes, the $\chi_M T$ product rapidly decreases with decreasing temperature, reaching a constant value of 0.013 and 0.017 emu mol^{-1} K for **1** and **2**, respectively, near to 100 K and these values remain practically constant down to 2 K. For both dinuclear complexes the χ_M vs T curve show a rapid increase of the χ_M value below ~ 100K, due to the presence of small amount of paramagnetic impurities (Figs. 6 and 7 (inset)). Their structures reveal that both dinuclear complexes contain two symmetry-related Cu^{II} ions; the two pairs of metal ions Cu···Cu are double bridged by two N,O oximato ligands and an additional water molecule. However, the O1W atom from the water molecule are weakly bonded, in the axial position, Cu(1)-O(1W) = 2.595 Å and Cu(2)-O(1W) = 2.775 Å for **1** and Cu(1)-O(1W) = 2.663 Å and Cu(2)-O(1W) = 2.739 Å for **2,** thus the interaction between the two Cu^{II} ions through the O(1W) should be negligible.

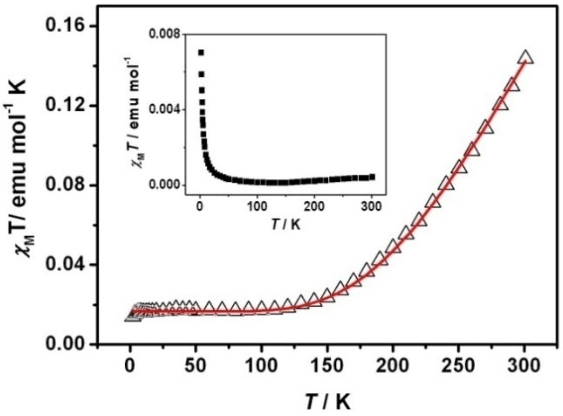

Fig. 7. Plot of $\chi_M T$ vs T plot for **2**.The solid line represents the best fit to the experimental data.The χ_M vs T plot is shown inset.

The fitting of the experimental data was performed using the Bleaney-Bowers equation for dinuclearCu^{II} complexes, derived from the Hamiltonian: $H = -J(S_1S_2)$, and introducing a ρ term to evaluate the paramagnetic impurity.[27] Best fit parameters are J = -562.6 cm^{-1}, g = 2.1, ρ= 2.9% and R = 4x10^{-5} for **1** and J = -633.1 cm^{-1}, g = 2.05, ρ= 4.2% and R = 5x10^{-6} for **2**, $(R = \Sigma_i(\chi T_{icalc} - \chi T_{iexp})^2 / \Sigma_i(\chi T_{iexp})^2)$. The best fit curves are plotted in Figs. 6 and 7 along with the experimental data.

A limited number of dinuclear Cu^{II} complexes doubley bridges by two N,O oximato ligands have been reported showing strong antiferromagnetic coupling,[7,8] usually displaying J values, in absolute value, higher than -500 cm^{-1} (even diamagnetism at room temperature in some cases), so the strong antiferromagnetic coupling for complexes **1** and **2** was not unexpected. Previous works, in this field, have shown that the mechanism of the interaction between the two Cu^{II} ions and the double oximato-bridge depends on the good orbital overlap in Cu-(R=NO)$_2$-Cu core (R = different groups), as the most relevant factor.[8] The unpaired electron of each Cu^{II} ion is located on the d_{x2-y2} magnetic orbital, so the planarity of the bringing region favors stronger antiferromagnetic coupling. The deviation from planarity of the Cu-(R=N-O)-Cu moieties for complexes **1** and **2** is significant with analogous values of 50.4°, 50.7° respectively. A comparison between compounds **1** and **2** show that the exchange coupling value among these complexes is in the same range and this result agrees with the similarity of their structural parameters. Mitra et all[8c] have plotted, for several analogous complexes, the magnetic exchange constants as a function of the average Cu-N-O-Cu dihedral angle, since this angle reflects the planarity of the Cu(R=NO)$_2$Cu ring and an approximately linear relationship was found. In Fig. 8 we have added the points corresponding to complexes **1** and **2**, and it is observed a very good agreement.

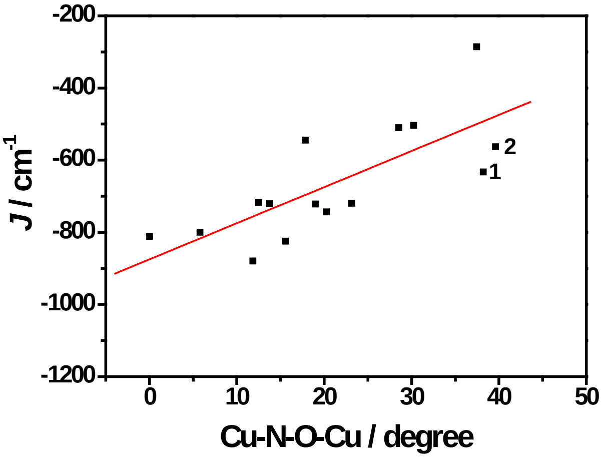

Fig. 8. J vs the average value of the Cu-N-O-Cu dihedral angle. The regression line is indicated.

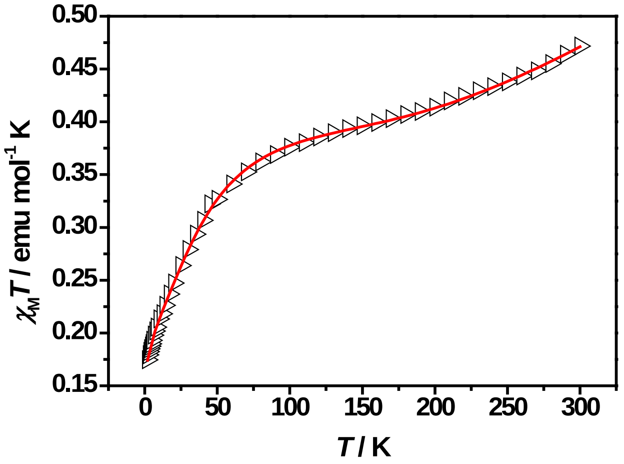

Fig. 9. Plot of $\chi_M T$ vs T plot for **3**.The solid line represents the best fit to the experimental data.

Variable temperature measurements of compound **3** were investigated in the temperature ranges of 2–300 K and 2–30 K in applied field of 10000 G and 500 G, respectively. The temperature dependence of the $\chi_M T$ product (χ_M being the magnetic susceptibility per trinuclear unit) for complex **3** is shown in Fig. 9. At room temperature, $\chi_M T$ is equal to 0.47 emu mol^{-1} K, this value are much lower than the expected for the sum of three non-interacting S = 1/2 spin(~1.2 emu mol^{-1} K), providing evidence of strong antiferromagnetic interactions even at 300 K. The $\chi_M T$ product rapidly decreases with decreasing the temperature reaching a value of 0.17 at 2 K. The magnetic behavior of **3** must be dominated by the magnetic coupling into the trinuclear core. The typical plateau, at low temperatures, corresponding to isolated trinuclear Cu^{II} complexes with antiferromagnetic coupling between the metal ions (spin doublet state, $\chi_M T \approx 0.4$ emu mol^{-1} K, and reasonable g value) does not appear. The use of the isotropic Heisemberg-Dirac-van Vleck (HDVV) Hamiltonian formalism: $H = -J_{12}S_1S_2 - J_{23}S_2S_3 - J_{13}S_1S_3$, and the expression of the magnetic susceptibility from this Hamiltonian in which the Weiss-like parameter θ was considered to analyze the experimental variation of $\chi_M T$ at low temperatures, was failed in all the attempts. The results obtained considering one, two or three coupling constants give in all cases serious discrepancies between the theory and the experimental data in the low temperature region. It is well known that triangular complexes that show intramolecular antiferromagnetic coupling exhibit spin frustration effects: it is impossible for all possible pairing of spins to be simultaneously antiferromagnetic. As is pointed out in the literature,[11,28-30] to interpret the magnetic properties of this kind of systems it is necessary to introduce an antisymmetric exchange interaction (ASE) in the above isotropic exchange model. Taking into account that the Cu···Cu distances in the trinuclear unit are 3.215, 3.215 and 3.227 Å, we can consider the copper atoms in complex **3** as forming an isosceles triangle. Thus the Hamiltonian used to investigate the magnetic interaction between the metal centers, is:

$$H = -J(S_1.S_2 + S_2.S_3) - j(S_1.S_3) + G_Z\left[(S_1 \times S_2) + (S_2 \times S_3) + (S_1 \times S_3)\right]$$

Where $J = J_{1,2} = J_{2,3}$, $j = J_{1,3}$ and $G_z$is the antisymmetric exchange vector parameter.

The expression of the magnetic susceptibility, from this Hamiltonian, derived by Lloret and coworkers,[19] in which the parallel and the perpendicular susceptibility components must be considered separately, because they are affected differently by the G_z vector is:

$$\chi_M^{||} = \frac{N\beta^2 g_{||}^2}{4kT}\left[\frac{\cosh(x) + 5\exp(3J_{av}/2kT)}{\cosh(x) + \exp(3J_{av}/2kT)}\right]$$

$$\chi_M^{\perp} = \frac{N\beta^2 g_{\perp}^2}{4kT}\left[\frac{\rho^2\cosh(x) + 5\exp(3J_{av}/2kT) + (1-\rho^2 senh(x)/x}{\cosh(x) + \exp(3J_{av}/2kT}\right]$$

$$\chi_M^{av} = \frac{\chi_M^{||} + 2\chi_M^{\perp}}{3}$$

where $x = \Delta/2kT$ and $\rho = \delta/\Delta$

The best fit obtained, introducing the Weiss parameter θ to take into account the additional antiferromagnetic interactions between the trinuclear units, are: J_{av} = -636 cm^{-1}, $g_{||}$ = 2.05, $g_{\perp}$ = 2.11 , Δ= 87.3 cm^{-1}, δ = 36.8 cm^{-1}, θ = -0.18 K and R = 2.65x10^{-6} ($R = \Sigma_i(\chi T_{icalc} - \chi T_{iexp})^2/\Sigma_i(\chi T_{iexp})^2$). Introducing these parameters to the equation $G_z = ((\Delta^2-\delta^2)/3)^{1/2}$, a G_z value of 45.5 cm^{-1} was obtained for the antisymmmetric interaction. The exchange interaction between the Cu^{II} ions in the trinuclear unit considering an isosceles arrangement can be deduced from the equations $J_{av} = (2J+j)/3$ and $\delta = J-j$ that give values of J = 623.7 cm^{-1} and j = 660.7 cm^{-1}. All these results are in good agreement with those reported in the literature for other trinuclear Cu^{II} complexes in which the antisymmetric interaction was taken into account; the observed ranges are 17.7-63 cm^{-1} for δ, 15-47 cm^{-1} for G_z and 39.7-103 cm^{-1} for Δ.[11,29-31]

According to the structural data of complex **3**, it could be consider that the hexanuclear units are isolated, thus the θ value obtained of -0.18 K (-0.125 cm^{-1}) is related with the antiferromagnetic interaction *via* the H-bridged bonds in the $[Cu_3O\cdots H\cdots Cu_3O]$ units. Its small θ value indicates its low contribution to the magnetic coupling.

The large J_{av} value of -636 cm^{-1} found un complex **3** is consistent based on a combination of the N,O oximato and μ_3-O bridges between the Cu^{II} ions. Literature works have established relationships between the magnetic coupling and structural features for trinuclear complexes with $[Cu_3O]$ core and the principal structural factors are:

(a) The Cu-O(H)-Cu bridging angles, are the major factor controlling the spin coupling between the metal centers in hydroxido, alkoxido or phenoxido bridged compounds, for angles greater than 97.5°, the antiferromagnetic interaction predominates.[32]

(b) The deviation of the μ_3-O atom from the centroid of the Cu_3 triangular motif plays an important role on the antiferromagnetic coupling between the Cu^{II}centers. This feature is evidenced by the excellent linear correlation of the coupling constant J with this deviation.[11] Less deviation provides strong antiferromagnetic coupling.

(c) The higher coplanarity of the equatorial coordination plane around each Cu^{II} atom. It has been shown that the more flattened the $Cu_3O(H)$ bridge , the stronger the magnetic interaction .[33]

Complex **3** has an average Cu-O(H)-Cu angle of 116°, and a average deviation of the μ_3-O atom from the centroid of the Cu_3 triangular of 0.38 Å , and dihedral angles between the three CuONNO planes of 16.6°, 15.4° and 16.6°. These three factors justify their antiferromagnetic behavior and especially the high degree of coplanarity justifies the high J value.

EPR spectroscopy

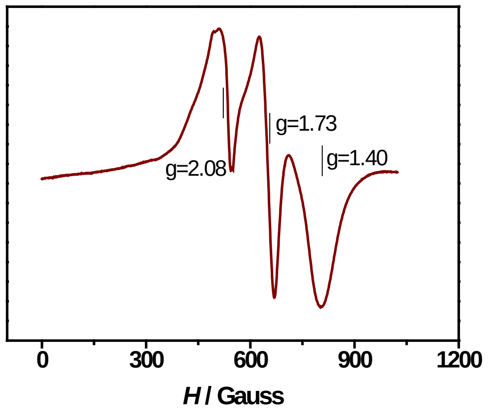

Fig. 10. X-band EPR spectra of powder sample of **3** recorded at 17 K.

The X-band EPR spectra of complex **3** was recorded on power sample,in an applied field of 0-50000 Gauss, varying the temperature between 300 and 17 K (Fig. S9, Supporting Information). At 17 K the spectra are similar to that show by others triangular complexes of S = 1/2 centers showing antisymmetric exchange.[29] Three EPR signals appears at g values of 2.08, 1.73 and 1.40 (Fig. 10). The first one correspond to $g_{\parallel}$ = 2.08, which is a typical g value for $(d_{x2-y2})^1$or $(d_{z2})^1$$Cu^{II}$centers in an axial symmetry, and the other additional two bands, at g< 2, must be related to the perpendicular component. The presence of extra peaks, in the region corresponding to the $g_{\perp}$ component, could be explained by the presence of an additional transition from the antisymmetrically coupled S =1/2 spin states, that becomes allowed in more strongly axial or rhombic spin environment.[30]

Conclusions

The oxime based Schiff base, 3-[3-(dimethylamino)propylimino]butan-2-one oxime (HL) on reaction with copper(II) perchlorate produced dinuclear (**1, 2**) and hexanuclear (**3**) compounds at different pH. Thus, here we have shown that even on keeping the oxime backbone unchanged, the nuclearity of the complexes and coordination environment of the Cu(II) can be modified by changing the pH of the reaction mixture. Formation of **3** demonstrates the importance of hydrogen bonding in the formation of unusual compounds – a knowledge that may be helpful in the rapidly developing field of crystal engineering and material chemistry. The variable temperature magnetic measurements show that the Cu(II) ions are strong antiferromagnetically coupled in all the three compounds (**1**-**3**) through the oximato group in **1** and **2**, and the oximato- and central oxido groups within the trinuclear units in **3**. Fitting of magnetic data by introducing an antisymmetric exchange interaction and the $g_{\perp}$ componentat low temperature in the EPR spectra clearly indicate the presence of spin frustration in complex **3**.

We pay attention to develop several homo- and hetero-metallic polynuclear nuclear systems with similar oxime backbones by varying the metal ions, substitution of ligand system, counter ions, pH, temperature and solvent systems, which are in progress in our laboratory.

Acknowledgements

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Notes and references

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† Electronic Supplementary Information (ESI) available powder XRD, IR spectra, electronic spestra and EPR spectra (Figs. S1–S10). CCDC. 973637-973639 contain the supplementary crystallographic data in CIF format for **1-3** respectively. See DOI: 10.1039/b000000x/

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Tables

pH dependent facile synthesis of di- and tri-nuclear oxime based Cu(II) complexes: strong antiferromagnetic coupling in the dinuclear complexes and spin frustration in the trinuclear complex

Lakshmi Kanta Das, Michael G.B. Drew, Carmen Diaz* and Ashutosh Ghosh*

Table 1. Crystal data and structure refinement of complexes **1-3**.

Complex	**1**	**2**	**3**
Formula	$C_{18}H_{38}Cl_2Cu_2N_6O_{11}$	$C_{18}H_{38}F_8B_2Cu_2N_6O_3$	$C_{54}H_{115}Cl_9Cu_6N_{18}O_{44}$
M	712.52	687.24	2420.99
Crystal System	Orthorhombic	Orthorhombic	Triclinic
Space Group	$P2_12_12_1$	$P2_12_12_1$	$P\bar{1}$
a/Å	10.456(5)	10.4206(3)	13.7881(15
b/Å	13.413(5)	13.2830(3)	13.8192(14)
c/Å	21.207(5)	21.0965	15.706(3)
α/°	90	90	92.716(13)
β/°	90	90	96.802(13)
γ/°	90	90	119.851(11)
V/Å^3	2974.2(19)	2920.11(13)	2557.6(7)
Z	4	4	1
D_c/g cm^{-3}	1.591	1.563	1.572
μ/mm^{-1}	1.672	1.538	1.551
F (000)	1472	1388	1244
R(int)	0.037	0.051	0.054
Total Reflections	36491	50961	18227
Unique reflections	6164	9258	14301
$I>2\sigma(I)$	5189	6316	4005
R1, wR2	0.0408, 0.1046	0.0486, 0.1262	0.0932, 0.2580
Temp (K)	293	293	150
GOF	1.03	1.05	0.82

Table 2. Bond distances (Å) and angles (°) around metal atoms for complexes **1** and **2**.

	1	**2**		**1**	**2**
Cu(1) – O(21)	1.937(3)	1.935(2)	Cu(2) – O(11)	1.940(3)	1.938(3)
Cu(1) – N(12)	1.978(3)	1.984(3)	Cu(2) – N(22)	1.984(3)	1.988(3)
Cu(1) – N(15)	2.005(3)	1.999(3)	Cu(2) – N(25)	1.982(4)	1.982(4)
Cu(1) – N(19)	2.057(4)	2.054(4)	Cu(2) – N(29)	2.069(4)	2.056(4)
O(21)– Cu(1)–N(12)	96.04(12)	94.76(11)	O(11)–Cu(2)–N(22)	94.03(13)	93.60(11)
O(21)–Cu(1)–N(15)	167.89(13)	167.69(12)	O(11)–Cu(2)–N(25)	165.47(14)	165.16(13)
O(21)–Cu(1)–N(19)	88.15(15)	87.73(13)	O(11)–Cu(2)–N(29)	88.38(16)	88.46(14)
N(12)–Cu(1)–N(15)	79.92(15)	80.24(13)	N(22)–Cu(2)–N(25)	80.00(15)	80.34(13)
N(12)–Cu(1)–N(19)	175.27(18)	177.24(16)	N(22)–Cu(2)–N(29)	177.30(17)	177.76(15)
N(15)–Cu(1)–N(19)	97.62(16)	97.55(14)	N(25)–Cu(2)–N(29)	97.92(17)	97.87(16)

Table 3. Bond distances (Å) and angles (°) around metal atoms for complex **3**.

Complex **3**					
Cu(1) – O(1)	1.909(5)	Cu(2) – O(1)	1.902(5)	Cu(3) – O(1)	1.879(5)
Cu(1) – O(31)	1.938(5)	Cu(2) – O(21)	1.962(5)	Cu(3) – O(11)	1.958(5)
Cu(1) – N(12)	1.982(6)	Cu(2) – N(32)	1.974(7)	Cu(3) – N(22)	1.960(7)
Cu(1) – N(15)	1.994(7)	Cu(2) – N(35)	1.975(7)	Cu(3) – N(25)	1.936(6)
Cu(1) – O(71)	2.471(8)	Cu(2) – O(72)	2.594(10)	Cu(3) – O(73)	2.547(7)
O(1)–Cu(1)–O(31)	93.7(2)	O(1)–Cu(2)–O(21)	92.7(2)	O(1)–Cu(3)–O(11)	94.0(2)
O(1)–Cu(1)–N(12)	86.6(2)	O(1)–Cu(2)–N(32)	89.8(3)	O(1)–Cu(3)–N(22)	86.9(3)
O(1)–Cu(1)–N(15)	167.8(2)	O(1)–Cu(2)–N(35)	171.1(2)	O(1)– Cu(3)–N(25)	167.7(3)
O(31)–Cu(1)–N(12)	172.7(3)	O(21)– Cu(2)–N(32)	176.9(3)	O(11)–Cu(3)–N(22)	174.6(3)
O(31)–Cu(1)–N(15)	96.3(3)	O(21)–Cu(2)–N(35)	96.2(3)	O(11)–Cu(3)–N(25)	96.0(2)
N(12)– Cu(1)–N(15)	82.6(3)	N(32)–Cu(2)–N(35)	81.3(3)	N(22)–Cu(3)– N(25)	82.5(3)

Graphical Abstract

pH dependent facile synthesis of di- and tri-nuclear oxime based Cu(II) complexes: strong antiferromagnetic coupling in the dinuclear complexes and spin frustration in the trinuclear complex

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New oxime based Cu(II) compounds containing the dinuclear and trinuclear core have been synthesized from the same oxime back bone by changing the pH of the reaction mixture. The dinuclear cores exhibit strong antiferromagnetism while the trinuclear core represents a good model for spin frustration.