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# Rare trinuclear $Ni^{II}_{2}M^{II}$ complexes ( $M^{II} = Mn$ , Fe and Co) with a reduced Schiff base ligand: Synthesis, structures and magnetic properties

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### ABSTRACT

Three new trinuclear hetero-metallic Ni<sup>II</sup><sub>2</sub>M<sup>II</sup> complexes with M<sup>II</sup> = Mn, Fe and Co have been synthesized using a [NiL<sup>R</sup>] "metalloligand", where  $H_2L^R = N,N'$ -bis(2-hydroxybenzyl)-1,3propanediamine. All complexes have been characterized by elemental analysis, spectroscopic methods, single crystal XRD and magnetic and electrochemical studies. In the three complexes, in addition to the double phenoxido bridges, the two terminal Ni<sup>II</sup> atoms are linked to the central  $M^{II}$  [M = Mn(1), Fe(2) and Co(3)] ion by means of a bridging carboxylato co-anion, giving rise to a linear Ni<sup>II</sup>-M<sup>II</sup>-Ni<sup>II</sup> structure. Variable temperature magnetic susceptibility measurements show the presence of weak ferromagnetic and antiferromagnetic exchange interactions mediated through the phenoxido bridges with J values of +8.5 and -3.0 cm<sup>-1</sup> for complexes 1 and 2, respectively. Compound 3 shows the presence of antiferromagnetic interactions. Cyclic voltammetry shows a common quasi-reversible one electron oxidation corresponding to the Ni(II)/Ni(III) process in 1-3 and an irreversible M(II)/M(III) oxidation for Mn(1) and Fe(2).

#### Keywords: Nickel(II), Manganese(II), Iron(II), Cobalt(II), Magnetic properties

### **1. Introduction**

The chemistry of hetero-metallic polynuclear clusters of transition metals have attracted considerable interest to the inorganic chemists not only for their attractive structural features but also for their applications in various fields such as magnetism, photoluminescence and multifunctional molecular materials [1-4]. There are various synthetic strategies to build hetero-

metallic coordination clusters. Among them, the use of previously synthesized metal complexes with active bridging groups/atoms has shown to be a very efficient one [5-6]. Thus, neutral transition metal chelates of tetradentate N<sub>2</sub>O<sub>2</sub> donor salen type Schiff bases have been employed as chelating bidentate "metalloligands" by different groups, including ours, since these metalcontaining ligands are well adapted for building poly-nuclear hetero-metallic clusters with interesting structures and intriguing magnetic properties [7]. Recently, we have found that complexes of reduced Schiff bases can also be used as "metalloligands" like their non-reduced analogues [8]. Moreover, they may give rise to different structures, thanks to the higher flexibility of the ligand backbone and the ability to form hydrogen bonds [8-9]. Since "metalloligands" of Cu(II) or Ni(II) are the most stable ones among the divalent first row transition metals, they have been widely used for this purpose leading to a vast library of heteronuclear species with different combination of transition metal ions [10]. Among these, trinuclear  $MCu_2$  [11] or  $MNi_2$  [12] (where M = any divalent hetero-metal atom) species are arguably the most common ones but for  $M = Co^{II}$  ion, the numbers of trinuclear structures are only 5 for Ni<sup>II</sup> and 3 for Cu<sup>II</sup> chelates [13-14]. With the salen type Schiff base ligand, the number of Mn<sup>II</sup>Cu<sub>2</sub> and Mn<sup>II</sup>Ni<sub>2</sub> species are 9 and 13, respectively [13,15-16]. Surprisingly, there is no single example of trinuclear MNi<sub>2</sub> nor MCu<sub>2</sub> complex for  $M = Fe^{II}$  with any type of Schiff base ligand.

One of the main reasons to synthesize phenoxido-bridged polynuclear complexes is to study their magnetic properties. Accordingly, most of the species studied till date are homonuclear first row transition metal ions such as  $Cu^{II}$ ,  $Ni^{II}$ ,  $Fe^{II}$ ,  $Fe^{III}$ ,  $Mn^{II/III/IV}$ , and  $Cr^{III}$  [17]. The study of hetero-nuclear systems is relatively rare. Thus, there are only three  $Ni^{II}$ - $Co^{II}$  [13] and six  $Ni^{II}$ - $Mn^{II}$  [16] magnetically characterized hetero-metallic diphenoxido-bridged trinuclear species with  $N_2O_2$  donor salen type Schiff base ligands. Furthermore, there is no single report so far of any magnetically characterized  $Ni^{II}$ - $Fe^{II}$  species (either dinuclear, trinuclear or tetranuclear) with a  $N_2O_2$  donor salen type Schiff base ligand.

Herein, we report the synthesis, crystal structure, magnetic and electrochemical properties of three new hetero-metallic complexes,  $[(NiL^R)_2Mn(CH_3COO)_2(H_2O)_2]\cdot 2CH_3OH$  (1)  $[(NiL^R)_2Fe(CH_3COO)_2(H_2O)_2]\cdot 3H_2O$  (2) and  $[(NiL^R)_2Co(CH_3COO)_2(H_2O)_2]\cdot 2CH_3OH$  (3) with the reduced N<sub>2</sub>O<sub>2</sub> donor di-Schiff base ligand, H<sub>2</sub>L<sup>R</sup> (N,N'-bis(2-hydroxybenzyl)-1,3propanediamine). Among these, complex 2 is the first example of Ni<sup>II</sup><sub>2</sub>Fe<sup>II</sup> trinuclear cluster with

a tetradentate Schiff base ligand. Complex **3** is also a rare example of a trinuclear  $Ni^{II}_{2}Co^{II}$  cluster with a Schiff base ligand. The magnetic measurements show the presence of ferromagnetic interactions in **1** and antiferromagnetic interactions in **2** and **3** between the Ni<sup>II</sup> and the respective hetero-metal ion (Mn<sup>II</sup>, Fe<sup>II</sup> and Co<sup>II</sup> for **1-3**, respectively) within the trinuclear cluster.

### 2. Experimental

#### 2.1. Starting Materials

1,3-propanediamine, salicylaldehyde and sodium borohydride were purchased from Lancaster and were of reagent grade. They were used without further purification.

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

2.2. Synthesis of the reduced Schiff base ligand, N,N'-bis(2-hydroxybenzyl)-1,3-propanediamine  $(H_2L^R)$  and its "metalloligand" [NiL<sup>R</sup>]

The di-Schiff base ligand derived from 1,3-propanediamine and salicyldehyde was synthesized by a standard reported method [11(a)]: 1,3-propanediamine (5 mmol, 0.42 mL) was mixed with salicylaldehyde (10 mmol, 1.04 mL) in methanol (30 mL). The resulting mixture was refluxed for *ca.*1 h and allowed to cool. Then 30 mL (5 mmol) of the resulting yellow ligand solution (H<sub>2</sub>L) was cooled to 0°C and solid sodium borohydride (456 mg, 12 mmol) was added to this solution with constant stirring. The resulting solution was acidified with concentrated HCl (15 mL) and then evaporated to dryness on a hot water bath [18]. The reduced Schiff base ligand H<sub>2</sub>L<sup>R</sup> was extracted from the solid residue with methanol, and the resulting colourless solution (*ca.* 30 mL) was added to a methanolic solution (20 mL) containing Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (1.820 g, 5 mmol) and 10 mL of ammonia solution (20%) to prepare the "metalloligand" [NiL<sup>R</sup>] as a solid green powder [19] that was filtered, washed with methanol and dried in a desiccator containing anhydrous CaCl<sub>2</sub> [Yield: 1.245 g, 69%].

2.3. Syntheses of the compounds  $[(NiL^R)_2Mn(CH_3COO)_2(H_2O)_2] \cdot 2CH_3OH$  (1)  $[(NiL^R)_2Fe(CH_3COO)_2(H_2O)_2] \cdot 3H_2O$  (2) and  $[(NiL^R)_2Co(CH_3COO)_2(H_2O)_2] \cdot 2CH_3OH$  (3)

The precursor complex  $[NiL^R]$  (0.708 g, 2 mmol) was dissolved in methanol (20 mL) and then an aqueous solution (1 mL) of Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.364 g, 1 mmol), followed by an aqueous solution (1 mL) of sodium acetate (0.164 g, 2 mmol), was added to this solution. The mixture was stirred for one hour and then filtered. The filtrate was allowed to stand overnight to obtain rhombic-shaped light violet coloured X-ray quality single crystals of **1**. Needle-shaped red crystals of **2** and square brown plates of **3** were prepared using a similar synthetic procedure with the same stoichiometry of reactants as used for **1** but using Fe(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and Co(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, for **2** and **3**, respectively, instead of Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O. The crystals (**1-3**) were washed with a methanol-water mixture and dried in a desiccator containing anhydrous CaCl<sub>2</sub> and then characterized by elemental analysis, spectroscopic methods, and X-ray diffraction.

Compound **1**. Yield: 0.604 g, 63%. Anal. Calc. for  $C_{40}H_{58}MnN_4Ni_2O_{12}$ : C 50.08, H 6.09, N 5.84%. Found: C 50.12, H 6.35, N 5.65%. UV/vis:  $[\lambda_{max} \text{ in nm} (\varepsilon_{max} \text{ in } M^{-1} \text{ cm}^{-1})]$  (MeCN) = 522(450), 290(18863) and 250(31168). IR (KBr) cm<sup>-1</sup>: v(N-H) 3259, v(CH<sub>3</sub>COO<sup>-</sup>) 1580. (Figs. S1, S4 and S5)

Compound **2**. Yield: 0.541 g, 57%. Anal. Calc. for  $C_{38}H_{56}FeN_4Ni_2O_{13}$ : C 48.04, H 5.94, N 5.90%; Found: C 48.27, H 5.75, N 5.85%; UV/vis:  $[\lambda_{max} \text{ in nm} (\epsilon_{max} \text{ in } M^{-1} \text{ cm}^{-1})]$  (MeCN) = 470(1110), 279(16224), and 238(26192). IR (KBr) cm<sup>-1</sup>: v(N-H) 3267, v(CH<sub>3</sub>COO<sup>-</sup>) 1574. (Figs. S2, S4 and S5)

Compound **3**. Yield: 0.664 g, 69%. Anal. Calc. for  $C_{40}H_{58}CoN_4Ni_2O_{12}$ : C 49.88, H 6.07, N 5.82%; Found: C 49.72, H 6.15, N 5.76%. UV/vis:  $[\lambda_{max} \text{ in nm } (\epsilon_{max} \text{ in } M^{-1} \text{ cm}^{-1})]$  (MeCN) = 591(297), 284(18190) and 249(30042). IR (KBr) cm<sup>-1</sup>: v(N-H) 3261, v(CH<sub>3</sub>COO<sup>-</sup>) 1587. (Figs. S3-S5)

### 2.4. Physical Measurements

Elemental analyses (C, H and N) were performed using a Perkin-Elmer 2400 series II CHN analyzer. IR spectra in KBr pellets (4000-400 cm<sup>-1</sup>) were recorded using a Perkin- Elmer RXI FT-IR spectrophotometer. Electronic spectra in acetonitrile (800-200 nm) were recorded in a Hitachi U-3501 spectrophotometer. The DC magnetic susceptibility measurements were carried out in the temperature range 2-300 K with an applied magnetic field of 0.1 T on polycrystalline samples of compounds 1-3 (with masses of 22.65, 16.37 and 16.25 mg, respectively) with a Quantum Design MPMS-XL-5 SQUID susceptometer. The isothermal magnetization was performed on the same samples at 2 K with magnetic fields up to 5 T. The susceptibility data

were corrected for the sample holders previously measured using the same conditions and for the diamagnetic contributions of the salt as deduced by using Pascal's constant tables ( $\chi_{dia} = -529.6 \times 10^{-6}$ , -531.6 x 10<sup>-6</sup> and -528.9 x 10<sup>-6</sup> emu.mol<sup>-1</sup>, respectively) [20].

#### 2.5. Electrochemical Measurements

The electrochemical measurements of the three complexes were performed using an Epsilon Basi-C3 Cell instrument at a scan rate of 100-300 mV s<sup>-1</sup> within the potential range of 0 to +2.00 V *vs* Ag/AgCl. Cyclic voltammograms were carried out using 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte and  $1.0 \times 10^{-3}$  M solutions of the complexes in acetonitrile previously deoxygenated with argon. The working electrode was a glassy-carbon disk (0.32 cm<sup>2</sup>) that was polished with alumina solution, washed with absolute acetone and acetonitrile and air-dried before each electrochemical run. The reference electrode was Ag/AgCl, with platinum as the counter electrode. All experiments were performed in standard electrochemical cells at 25 °C.

#### 2.6. Crystallographic data collection and refinement

Well formed single crystals of each complex were mounted on a Bruker-AXS SMART APEX II diffractometer equipped with a graphite monochromator and Mo K $\alpha$  ( $\lambda = 0.71073$  Å) radiation. The crystals were positioned at 60 mm from the CCD and frames (360) were measured with a counting time of 5 s. The structures were solved using the Patterson method through the SHELXS 97 program. Non hydrogen atoms were refined with independent anisotropic displacement parameters, while difference Fourier synthesis and least-squares refinement showed the positions of any remaining non-hydrogen atom. The hydrogen atoms bound to carbon atoms were included in geometric positions and given thermal parameters equivalent to 1.2 (or 1.5 for methyl groups) times those of the atom to which they were attached. Hydrogen atoms bonded to N or O was located in a difference Fourier map and refined with distance constraints. The H-atoms of the three crystallization water molecules in **2** and of all the coordinated water molecules in **1-3** could not be located. One of the crystallization water molecules in **2** was refined isotropically using distance constraints with 50% occupancy. Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle of the least-squares refinement. Absorption corrections were carried out using the SADABS

program [21], while all calculations were made *via* SHELXS 97 [22], SHELXL 97 [23], PLATON 99 [24], ORTEP-32 [25], WINGX system ver-1.64 [26] and refined using refined using SHELXL-2014 [27]. Data collection, structure refinement parameters, and crystallographic data for the three complexes are given in Table 1.

### **3. Results and discussion**

#### 3.1. Syntheses of the complexes

The reduced Schiff-base ligand  $(H_2L^R)$  and the corresponding metalloligand  $[NiL^R]$  were synthesized using the reported procedures [11a,19]. The metalloligand  $[NiL^R]$  on reaction with Mn(II) or Fe(II) or Co(II) and sodium acetate in a 2:1:2 molar ratio in MeOH:H<sub>2</sub>O 10:1(v/v) resulted in three new trinuclear complexes:  $[(NiL^R)_2Mn(CH_3COO)_2(H_2O)_2]\cdot 2CH_3OH$  (1)  $[(NiL^R)_2Fe(CH_3COO)_2(H_2O)_2]\cdot 3H_2O$  (2) and  $[(NiL^R)_2Co(CH_3COO)_2(H_2O)_2]\cdot 2CH_3OH$  (3), respectively (Scheme 1).





#### 3.2. Crystal Structures

 $[(NiL^R)_2Mn(CH_3COO)_2(H_2O)_2]$ ·2CH<sub>3</sub>OH (1). The linear trinuclear structure of compound 1, together with the atomic numbering scheme is shown in Fig. 1. The bond distances around the metals are given in Table 2 and the bond angles in Table 3. The structure contains a crystallographic inversion centre that sits on the central manganese atom, Mn(1). The asymmetric unit consists of one terminal Ni(II) centre, half central Mn(II) ion, one reduced

deprotonated di-Schiff base ligand  $[(L^R)^2]$ , one bridging acetate ligand and one coordinated water molecule. The terminal nickel centre shows a distorted octahedral NiO<sub>4</sub>N<sub>2</sub> geometry where the two axial positions are occupied by an oxygen atom of the acetate ligand at a distance of 2.057(3) Å and by a coordinated water molecule at 2.181(3) Å. The basal plane is formed by the two N atoms and two phenoxido O-atoms from the dianioinc tetradentate reduced Schiff-base ligand  $[(L^{R})^{2}]$ . The basal Ni-N bond distances [2.075(4)-2.089(4) Å] are slightly greater than the basal Ni-O ones [2.035(3)-2.046(3) Å] (Table 2). The four donor atoms in the equatorial plane show root mean squared deviation (r.m.s.) of 0.045(1) Å with the nickel atom 0.035(1) Å shifted from the mean plane towards O(2). The dihedral angle between two N-Ni-O planes [4.5(1)°] and the range of *cis*  $[81.7(1)-95.2(2)^{\circ}]$  and *trans* angles  $[172.2(1)-176.7(1)^{\circ}]$  (Table 3) of the terminal nickel centre also indicate the presence of a distortion from the ideal octahedral geometry. The central manganese atom, Mn(1), presents an octahedral  $MnO_6$  geometry where the basal plane is formed by the coordination of four  $\mu_2$ -phenoxido O-atoms from two dianionic reduced Schiffbase ligand  $[(L^R)^2]$  and the axial positions are occupied by two oxygen atoms from acetate anions. The basal Mn-O bond distances are almost similar [2.120(3)-2.132(3) Å] but they are slightly shorter than the axial one [2.245(3) Å] (Table 2).



Fig. 1. The structure of 1 with ellipsoids at 30% probability. Symmetry element  $^{a} = 2-x, 1-y, 1-z$  for 1. Methanol solvent molecules outside the coordination sphere are also removed.

The range of *cis* angles  $[77.7(1)-86.4(1)^{\circ}]$  (Table 3) around central Mn centre also indicate a distortion from ideal octahedral geometry. The Ni(1)…Mn(1) distance is 3.140(2) Å and the two Ni-O-Mn bond angles are equal within experimental error: 97.79(11)° and 97.76(12)°.

 $[(NiL^R)_2Fe(CH_3COO)_2(H_2O)_2]\cdot 2H_2O$  (2). The linear trinuclear structure of compound 2, together with the atomic numbering scheme is shown in Fig. 2. The bond distances around the metals are given in Table 2 and the bond angles in Table 3. This structure also contains a crystallographic inversion centre at the central Fe atom. The structure of this compound is very similar to that of previously described compound 1. The central Fe also has a FeO<sub>6</sub> distorted octahedral geometry where the two axial O atoms belong to two acetate ligands and the basal plane is formed by four phenoxido oxygen atoms from two dianionic tetradentate reduced Schiff base ligands  $[(L^R)^2]$ . The basal Fe(1)-O bond lengths are shorter than the axial one (Table 2) and the *cis* angles [80.1(1)-86.3(1)°] deviate from the ideal value (90°) (Table 3) indicating distortions in the octahedral coordination geometry.

The basal plane of the terminal Ni atom is constructed by the coordination of two imine nitrogen atoms and two oxygen atoms from the reduced Schiff base ligand  $[(L^R)^2]$ . One oxygen atom from a bridging acetate ion and one O-atom from a water molecule coordinate to the axial positions to complete the octahedral NiO<sub>4</sub>N<sub>2</sub> coordination environment. As in **1**, the basal Ni-O bond distances [2.034(3)-2.045(3)Å] are shorter than the Ni-N ones [2.089(3)-2.090(3)Å]. It is noticeable that the Ni-O bond distances are shorter in **2** than those in **1** but the Ni-N distances show the opposite trend (Table 2). This fact is due to a shortening of the two axial Ni-O bonds in **2** (since the basal Ni-O bonds are equal in **1** and **2**, Table 2) probably due to the smaller size of Fe(II) compared with Mn(II) that allows the acetato ligand to get closer to the Ni<sub>2</sub>M core in **2**. The distortion from the ideal octahedral geometry of the Ni atom is smaller in **2** than in **1** as evidenced by the dihedral angle between the two N-Ni-O planes  $[3.2(1) \text{ and } 4.5(1)^{\circ}$  for **2** and **1**, respectively]. The r.m.s deviation [0.014(1) Å] of the four basal atoms from their mean plane and the range of *cis*  $[80.2(1)-94.1(1)^{\circ}]$  and *trans*  $[172.7(1)-176.8(1)^{\circ}]$  angles (Table 3) also confirm this fact. The Ni(1)...Fe(1) distance is 3.075(2) Å and the two Ni-O-Fe bond angles are equal within experimental error:  $97.70(10)^{\circ}$  and  $97.79(10)^{\circ}$ .



**Fig. 2.** The structure of **2** with ellipsoids at 30% probability. Symmetry element  $^{a} = 2-x,-y,2-z$  for **2**. Water solvent molecules outside the coordination sphere are also removed.

[(NiL<sup>R</sup>)<sub>2</sub>Co(CH<sub>3</sub>COO)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·2CH<sub>3</sub>OH (3). Fig. 3 shows the trinuclear complex 3 with the atomic numbering scheme. The bond distances around the metals are given in Table 2 and the bond angles in Table 3. Compound 3 shows a structure similar to those of 1 and 2. Thus, 3 also contains a crystallographic inversion centre, located at the central atom (Co in this case). The asymmetric unit of 3 consists of a terminal Ni(II) atom, half a Co(II) atom located at the inversion centre, one deprotonated reduced di-Schiff base ligand  $[(L^R)^2]$ , one bridging acetato ligand and one coordinated water molecule. The terminal nickel centre [Ni(1)] presents a distorted octahedral geometry as in 1 and 2. The basal plane of Ni(1) is formed by the two imine N atoms and two phenoxido O atoms whereas the axial positions are occupied by one O-atom from a bridging acetato ligand and a water molecule. The basal Ni-O bond distances are shorter than the basal Ni-N and the axial Ni-O ones (Table 2), as is observed in 1 and 2. The range of *cis* angles [80.3(7)-94.7(1)°] and *trans* angles [172.2(1)-176.2(1)°] around Ni(1) indicate that the distortion of the coordination sphere from the ideal octahedral geometry in 3 is intermediate between 1 and 2. This is confirmed by the root mean square deviations of the four basal atoms from the mean plane which is 0.044(2) Å with the metal atom 0.026(1) Å shifted from this mean plane towards O(2) and also from the dihedral angle between two N-Ni-O planes [4.0 (1)°].



Fig. 3. The structure of 3 with ellipsoids at 30% probability. The crystallization methanol molecules are omitted for clarity. Symmetry element a = 1-x, 1-y,2-z.

The central Co(II) atom is bonded to four phenoxido oxygen atoms of two deprotonated tetradentate reduced Schiff base ligands and two oxygen atoms from two bridging acetato ligands as in **1** and **2**. The basal Co-O bond distances are very similar, as observed in **1** and **2**, and are shorter than those of **1** but longer than those of **2**. The central cobalt atom also shows a slightly distorted octahedral geometry, as confirmed by the range of *cis* angles [79.0(1)-86.4(1)°]. The Ni(1)···Co(1) distance is 3.093(1) Å and the two Ni-O-Co bond angles are equal within experimental error: 98.29(8)° and 98.23(8)°.

### 3.3. Electrochemistry

The cyclic voltammogram (CV) of the metallo-ligand,  $[NiL^R]$  in acetonitrile shows a quasireversible oxidation process with an anodic peak at  $E_a = +0.97$  V with the corresponding cathodic peak at +0.75 V in the reverse scan (Fig. S6) and a peak separation value ( $\Delta E_{pa} = E_{anode}$ - $E_{cathode}$ ) of +0.22 V. This quasi-reversible oxidation process is ascribed to the one electron Ni(II)/Ni(III) oxidation process. On the other hand, complex **1** shows two peaks at  $E_1 = +1.45$  V

and  $E_2 = +1.04$  V on the anodic scan and only one peak at  $E_2 = +0.52$  V on the reverse scan with a peak separation value,  $\Delta E_{pa}$  of +0.52 V (Fig. 4).



**Fig. 4.** Cyclic voltammograms (CVs) of  $10^{-3}$  M solution of complex **1** in acetonitrile at room temperature and different scan rates (100-300), using TBAP as supporting electrolyte.

Complex 2 also shows one irreversible and one quasi-reversible peaks at  $E_1 = +1.12$  V and  $E_2 = 0.78$  V on the anodic potential scan and one peak at  $E_2 = +0.55$  V on the reverse scan (Figs. S7 and S8) with a peak separation of +0.57 V, very similar to that of complex 1. Complex 3 only shows one anodic peak at  $E_a = +1.12$  V with the corresponding cathodic peak at  $E_c = +0.47$  V and with a peak separation of +0.65 V (Fig. S9). If we compare the cyclic voltammograms (CV) of complexes 1-3 with that of the metalloligand [NiL<sup>R</sup>], we can see a common quasi-reversible peak in all cases (at +1.04 in 1, +1.12 V in 2 and 3, and +0.97 V in [NiL<sup>R</sup>]). This common one-electron process is, accordingly, attributed to the Ni(II)/Ni(III) oxidation in the metalloligand [NiL<sup>R</sup>] and in complexes 1-3. The second irreversible wave observed in the anodic scan only in complexes 1 and 2 (at E = +1.45 V in 1, +0.78 V in 2) can be attributed to the M(II)/M(III) oxidation of the central ion with the corresponding irreversible complex rupture.

#### 3.4. Magnetic properties

The thermal variation of the product of the molar magnetic susceptibility per Ni<sub>2</sub>Mn trimer times the temperature ( $\chi_m T$ ) for compound 1 shows a room temperature value of ca. 7.0 cm<sup>3</sup> K mol<sup>-1</sup>, close to the expected value for two isolated Ni(II) ions with  $g \approx 2.2$  plus a Mn(II) ion with  $g \approx 2$  (Fig. 5). When the sample is cooled, the  $\chi_m T$  product increases and reaches a maximum of *ca.* 9.1 cm<sup>3</sup> K mol<sup>-1</sup> at *ca.* 6.5 K. Below this temperature  $\chi_m T$  sharply decreases to reach a value of ca. 5.7 cm<sup>3</sup> K mol<sup>-1</sup> at 2 K. The increase observed with cooling suggests the presence of predominant ferromagnetic Ni-Mn exchange interactions in the trimer whereas the sharp decrease at low temperatures can be attributed to the zero field splitting (ZFS) of the resulting S = 9/2 ground spin state in the cluster. Given the centro-symmetric nature of the complex, we have fitted the magnetic properties of compound 1 with a symmetric linear trimer model with only one coupling constant (J, Fig. 6) using the Hamiltonian:  $H = -J (S_1S_2 + S_2S_3)$  with  $S_1 = S_3 =$ 1 and  $S_2 = 5/2$  with the MAGPACK programme [28,29]. This model reproduces very satisfactorily the magnetic properties of compound 1 above the maximum with g = 2.239, J =+8.5 cm<sup>-1</sup> and a 8.7 % of paramagnetic impurity (solid line in Fig.5). The paramagnetic impurities may be due to the presence of defective clusters or monomeric species formed from the trimeric Ni<sub>2</sub>Mn cluster.



Fig. 5. Thermal variation of the  $\chi_m T$  product per Ni<sub>2</sub>Mn trimer for compound 1. Solid line is the best fit to the model (see text).



Fig. 6. View of the Ni<sub>2</sub>M linear complexes in 1-3 showing the magnetic exchange scheme.

In order to explain the ferromagnetic coupling observed in complex 1 we must take into account that previous magneto structural correlations for double oxido bridges connecting different transition metal ions (mainly Cu) show that the coupling passes from ferro- to antiferromangetic when the M-O-M' angles overpass a certain value [16,30-38]. This value depends on the metal ions and also on other structural parameters as the MO<sub>2</sub>M' dihedral angle [30-38]. As far as we know, there are only seven magnetically and structurally characterized Ni<sub>2</sub>Mn complexes with a double oxido and a syn-syn carboxylato bridges [16d-e,38]. These compounds present very weak antiferromangetic (J = -0.60, -0.30 and -0.24 cm<sup>-1</sup>) [16d-e.38] or ferromagnetic  $(J = +2.0, +1.1, +0.50 \text{ and } +1.38 \text{ cm}^{-1})$  [16d-e] Ni-Mn couplings, mainly depending on the Ni-O-Mn bond angle with a crossing angle of ca. 98°. Thus, for angles below ca. 98° the coupling is ferromagnetic and when the angle is above ca. 98° the coupling is antiferromagnetic. This value is further confirmed by compound 1 where the two Ni-O-Mn bond angles are identical within experimental error (97.78(11)° and 97.77(11)°) and slightly below 98° and, thus, a ferromagnetic coupling is expected. Accordingly, compound 1 presents a weak ferromagnetic coupling. Note that the larger value of J found in 1 may be related to the larger dihedral NiO<sub>2</sub>Mn angle found in 1 (157.7°), compared with the other four ferromagnetic compounds (where the dihedral angles are 154.1°, 153.9°, 151.8° and 151.3°). These lower values simply a reduction of the orbital overlap and, accordingly, of the magnetic coupling, in agreement with the experimental results. Of course, the presence of an additional syn-syn carboxylate bridge is expected to increase the antiferromagnetic coupling in all cases unless counter-complementarity takes place.

The  $\chi_m T$  value at room temperature per Ni<sub>2</sub>Fe trimer in **2** is *ca*. 5.0 cm<sup>3</sup> K mol<sup>-1</sup>, close to the expected value for two isolated Ni(II) ions plus a Fe(II) ion (Fig. 7). When the sample is

cooled,  $\chi_m T$  decreases to reach a value of *ca*. 1.2 cm<sup>3</sup> K mol<sup>-1</sup> at 2 K. This behaviour indicates the presence of an antiferromagnetic coupling of the two S = 1 Ni(II) ions and the central S = 2 Fe(II) ion in the trimer leading to a S = 0 ground spin state. As in **1**, given the symmetric nature of complex **2**, we have fitted the magnetic properties of compound **2** with the same symmetric linear trimer model with one coupling constant (J, Fig. 6) using the Hamiltonian: H = -J (S<sub>1</sub>S<sub>2</sub> + S<sub>2</sub>S<sub>3</sub>) but now with S<sub>1</sub> = S<sub>3</sub> = 1 and S<sub>2</sub> = 2 with the MAGPACK programme [28,29]. This model reproduces very satisfactorily the magnetic properties of compound **2** in the whole temperature range with g = 2.101, J = -3.0 cm<sup>-1</sup> and a 4.1 % of paramagnetic impurity (solid line in Fig.7). As in compound **1**, the paramagnetic impurities may be attributed to the presence of defective clusters or monomeric species formed from the trimeric Ni<sub>2</sub>Fe cluster.



Fig. 7. Thermal variation of the  $\chi_m T$  product per Ni<sub>2</sub>Fe trimer for compound 2. Solid line is the best fit to the model (see text).

Since there is no other magnetically and structurally characterized  $Ni^{II}_{2}Fe^{II}$  trimers with a double phenoxido and a *syn-syn* carboxylato bridges, we cannot establish any magneto-structural correlation to explain the weak antiferromagnetic coupling found in compound **2**. Since the Ni-O-Fe bond angles (97.87(10)° and 97.77(11)°) and the dihedral NiO<sub>2</sub>Fe angle (160.2°) in compound **2** are similar to those observed in compound **1** (where the coupling is weak but ferromagnetic), we can conclude that the main difference between **1** and **2** (besides the central metal atom) is the much shorter M-O<sub>acetato</sub> bond distances in **2** (Table 2). These shorter bond distances are expected to give rise to a larger (in module) antiferromagnetic contribution in **2**, resulting in an overall antiferromagnetic coupling, as observed experimentally.

The thermal variation of  $\chi_m T$  for compound **3** shows a room temperature value of *ca*. 5.0 cm<sup>3</sup> K mol<sup>-1</sup>, close to the expected value for two isolated Ni(II) ions (ca. 2 cm<sup>3</sup> K mol<sup>-1</sup>) plus one isolated Co(II) ion with an orbital contribution (ca. 2.8-3.4 cm<sup>3</sup> K mol<sup>-1</sup>). When the sample is cooled  $\chi_m T$  shows a progressive decrease reaching a minimum of *ca*. 4.3 cm<sup>3</sup> K mol<sup>-1</sup> at *ca*. 25 K. Below 25 K  $\chi_m T$  increases and reaches a maximum of *ca*. 4.5 cm<sup>3</sup> K mol<sup>-1</sup> at *ca*. 8 K followed by a sharp decrease to *ca*. 3.9 cm<sup>3</sup> K mol<sup>-1</sup> at 2 K (Fig. 8). This behaviour suggests the presence of antiferromagnetic Ni-Co exchange interactions in the trimer, leading to a ferri-magnetic exchange since the Ni(II) and Co(II) spins cannot cancel each other. The sharp decrease observed at very low temperatures can be attributed to the presence of a zero field splitting on the ground spin state and/or weak inter-trimer antiferromagnetic interactions.



Fig. 8. Thermal variation of the  $\chi_m T$  product per Ni<sub>2</sub>Co trimer for compound 3

The ferri-magnetic Ni-Co coupling found in compound **3** cannot be easily rationalized since there are no magneto-structural correlations in other Ni-Co clusters with similar bridges. Nevertheless, in a similar trinuclear Ni<sub>2</sub>Co complex (**A**) with a double oxido and a *syn-syn* carboxylato bridges, the coupling found was weak and ferromagnetic [38]. This result contrast with the weak antiferromagnetic coupling observed in **3**. In compound **A** the two oxido bridges are quite different (one is a phenoxido and the other is a carboxylato) and the Ni-O-Co bond angles are also very different (102.110(4)° and 94.380(4)° with an average value of 98.245°). In contrast, in **3** the two phenoxido bridges are very similar and the Ni-O-Co bond angles are equal within experimental error (98.24(7)° and 98.26(7)°) and also equal to the average value in **A**. Besides the different nature of the double oxido bridge, the main differences between **3** and **A** 

are: (i) the dihedral angle in the NiO<sub>2</sub>Co unit (157.1° in **A** and 159.9° in **3**) and (ii) the M-O<sub>acetato</sub> bond distances which are significantly longer in compound **3** (Co-O = 2.183(2) Å and Ni-O = 2.048(2) Å) than in **A** (Co-O = 2.045(4) Å and Ni-O = 2.064(4) Å) [38]. These two differences play opposite roles (in **3** the larger dihedral angle is expected to increase the antiferromagnetic coupling but the longer Co-O bond distance is expected to decrease it). Since the coupling is weak antiferromagnetic in **3** and weak ferromagnetic in **A**, we can conclude that the dihedral angle in the NiO<sub>2</sub>Co unit may be the dominant factor. Nevertheless, we cannot exclude the possibility that the double phenoxido/carboxylato bridge in **3** shows complementarity (*i.e.*, the antiferromagnetic interactions add each other) in contrast to compound **A** where the counter-complementarity of the triple oxido/phenoxido/carboxylato bridge was pointed as the origin of the weak ferromagnetic coupling found in **A** [38].

### 4. Conclusions

The metalloligand synthetic approach has proved once again to be a very useful and simple synthetic tool to synthesize polynuclear hetero-metallic clusters. Here we have shown how the use of a  $[NiL^R]$  complex  $[H_2L^R =$  tetradentate reduced di-Schiff base] as a "metalloligand" towards divalent first row transition metal ions,  $M^{II} = Mn$ , Fe and Co has yielded three new trinuclear linear  $Ni^{II}-M^{II}-Ni^{II}$  clusters where the central  $M^{II}$  ion is coordinated to the terminal  $[NiL^R]$  *via* a double phenoxido bridge along with a *syn-syn* carboxylato bridge. Complexes **1-3** are among the very few known  $Ni_2M^{II}$  complexes with double oxido bridges and  $N_2O_2$  donor Schiff bases. Even more, complex **2**  $(Ni^{II}_2Fe^{II})$  is the first example of a trinuclear  $Ni^{II}-Fe^{II}-Ni^{II}$  metal cluster with a salen type Schiff base ligand. In complexes **1-3** the double phenoxido and *syn-syn* carboxylato bridges mediate ferromagnetic (in **1**), antiferromagnetic (in **2**) and ferrimagnetic (in **3**) interactions between the terminal  $Ni^{II}$  ions and the central  $M^{II}$  one  $(M^{II} = Mn$  (**1**), Fe (**2**) and Co (**3**)). Despite the lack of magneto-structural correlations for this kind of clusters, given the very reduced number of known examples, the magnetic interactions could be rationalized with the help of previous studies on related examples.

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### Appendix A. Supplementary data

CCDC 1565583-1565585 contains the supplementary crystallographic data for (1–3). These data can be obtained free of charge via <u>http://www.ccdc.cam.ac.uk/conts/retrieving.html</u>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data (Discussion of IR and UV–Vis spectroscopy (Figs. S1-S5), CV Plots (Figs. S6-S9) associated with this article can be found, in the online version.

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### **Highlights:**

C

- > Trinuclear hetero-metallic  $Ni^{II}_2M^{II}$  complexes ( $M^{II} = Mn$ , Fe and Co) have been synthesized using a [NiL<sup>R</sup>] "metalloligand" synthetic approach.
- >  $Ni^{II}_{2}Fe^{II}$  trinuclear complex is the first example of a  $Ni^{II}$ -Fe<sup>II</sup>-Ni<sup>II</sup> metal cluster with a reduced salen type Schiff base ligand.
- > The double phenoxido and *syn-syn* carboxylato bridges mediate ferromagnetic in 1, antiferromagnetic in 2 and ferrimagnetic in 3 exchange interaction between the terminal Ni<sup>II</sup> ions and the central M<sup>II</sup> one (M<sup>II</sup> = Mn (1), Fe (2) and Co (3))

#### Table 1

Crystal data and structure refinement of complexes 1-3.

	1	2	3
Formula	$C_{40}H_{58}Mn_1N_4Ni_2O_{12}\\$	$C_{38}H_{54}Fe_1N_4Ni_2O_{13}$	$C_{40}H_{58}Co_1N_4Ni_2O_{12}\\$
Μ	959.23	950.10	963.23
Crystal System	Triclinic	Triclinic	Triclinic
Space Group	$P\overline{1}$	$P\overline{1}$	Pī
Temperature (K)	293	293	293
a/Å	10.178(5)	9.927(5)	10.117(5)
$b/{ m \AA}$	10.438(5)	10.470(5)	10.412(5)
$c/{ m \AA}$	10.946(5)	10.845(5)	10.903(5)
$lpha / ^{\circ}$	67.583(5)	68.184(5)	67.669(5)
$eta\!\!/^{\circ}$	80.703(5)	81.311(5)	81.390(5)
$\gamma^{\prime \circ}$	87.614(5)	86.255(5)	87.835(5)
$V/Å^3$	1060.6(9)	1034.4(9)	1050.2(9)
Ζ	1		1
$D_c/g \text{ cm}^{-3}$	1.498	1.512	1.521
$\mu/\mathrm{mm}^{-1}$	1.238	1.314	1.345
F (000)	499	488	501
R(int)	0.069	0.029	0.025
<b>Total Reflections</b>	12221	8904	11681
Unique reflections	3739	3608	3690
$I > 2\sigma(I)$	2622	3050	3172
$R1^a$ , $wR2^b$	0.0509, 0.1188	0.0377, 0.1286	0.0308, 0.0926
GOF <sup>c</sup> on F <sup>2</sup>	1.05	1.07	1.06
R (all)	0.0785	0.0462	0.0375

 ${}^{a}\mathrm{R1} = \sum ||F_{\rm o}| - |F_{\rm c}|| / \sum |F_{\rm o}|, {}^{b}w\mathrm{R2} (F_{\rm o}{}^{2}) = [\sum [w(F_{\rm o}{}^{2} - F_{\rm c}{}^{2})^{2} / \sum w F_{\rm o}{}^{4}]^{\frac{1}{2}};$ 

 $^{c}\text{GOF} = [\sum [w(F_{o}^{2} - F_{c}^{2})^{2}/(N_{obs} - N_{params})]^{\frac{1}{2}}$ 

C

#### Table 2

Bond distances (Å) for complexes 1-3.

atoms	1	2	3	
Ni(1)-O(10)	2.046(3)	2.045(3)	2.032(2)	
Ni(1)-O(30)	2.035(3)	2.034(3)	2.032(2)	
Ni(1)-N(18)	2.089(4)	2.090(3)	2.096(2)	
Ni(1)-N(22)	2.075(4)	2.089(3)	2.077(3)	
Ni(1)-O(1)	2.180(3)	2.149(3)	2.162(2)	
Ni(1)-O(2)	2.057(3)	2.046(3)	2.048(2)	
M(1)*-O(10)	2.120(3)	2.039(2)	2.057(2)	
M(1)*-O(30)	2.132(3)	2.045(3)	2.060(2)	
M(1)*-O(3)	2.245(3)	2.143(2)	2.183(2)	
* M = Mn, Fe	or Co in <b>1</b>	3, respectiv	vely	
es 1-3.				
atoms	1	2	3	
	-	_	U	

#### Table 3

Bond angles (°) for complexes 1-3.

atoms	1	2	3
O(10)-Ni(1)-O(30)	81.7(1)	80.2(1)	80.3(7)
O(10)-Ni(1)-N(18)	91.2(1)	93.0(1)	92.0(8)
N(18)-Ni(1)-N(22)	95.2(2)	94.1(1)	94.7(1)
O(30)-Ni(1)-N(22)	92.0(1)	92.6(1)	93.1(1)
O(1)-Ni(1)-O(10)	88.3(1)	91.0(1)	89.5(8)
O(1)-Ni(1)-O(30)	91.0(1)	90.5(1)	92.4(1)
O(1)-Ni(1)-N(18)	89.6(1)	86.8(1)	88.9(1)
O(1)-Ni(1)-N(22)	87.3(2)	88.0(1)	86.7(1)
O(2)-Ni(1)-N(18)	89.2(1)	90.4(1)	89.4(1)
O(2)-Ni(1)-N(22)	89.7(2)	90.7(1)	90.1(1)
O(2)-Ni(1)-O(10)	94.8(1)	90.8(1)	93.9(1)
O(2)-Ni(1)-O(30)	90.6(1)	92.5(1)	89.7(1)
O(10)-Ni(1)-N(22)	172.2(1)	172.8(1)	172.2(1)
O(30)-Ni(1)-N(18)	172.8(1)	172.7(1)	172.2(1)
O(1)-Ni(1)-O(2)	176.7(1)	176.8(1)	176.2(1)
O(10)-M(1)*-O(30)	77.7(1)	80.1(1)	79.0(1)
O(3)-M(1)*-O(30)	85.2(1)	86.3(1)	85.3(1)
O(3)-M(1)*-O(10)	86.4(1)	85.9(1)	86.4(1)
Ni(1)-O(10)-M(1)*	97.79(11)	97.70(10)	98.29(8)
Ni(1)-O(30)-M(1)*	97.76(12)	97.89(10)	98.23(8)

\* M = Mn, Fe or Co in 1-3, respectively

### **Highlights:**

- > Trinuclear hetero-metallic  $Ni_{2}^{II}M^{II}$  complexes ( $M^{II} = Mn$ , Fe and Co) have been synthesized using a [NiL<sup>R</sup>] "metalloligand" synthetic approach.
- ➢ Ni<sup>II</sup><sub>2</sub>Fe<sup>II</sup> trinuclear complex is the first example of a Ni<sup>II</sup>-Fe<sup>II</sup>-Ni<sup>II</sup> metal cluster with a reduced salen type Schiff base ligand.
- > The double phenoxido and syn-syn carboxylato bridges mediate ferromagnetic in  $\mathbf{1}$ , (3) antiferromagnetic in 2 and ferrimagnetic in 3 exchange interaction between the terminal

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### **Graphical Abstract**

Rare trinuclear  $Ni^{II}_{2}M^{II}$  complexes ( $M^{II} = Mn$ , Fe and Co) with a reduced Schiff base ligand: Synthesis, structures and magnetic properties

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Three new trinuclear  $Ni_{2}^{II}M^{II}$  structures (M = Mn, Fe and Co) with reduced salen-type Schiff base ligand show ferromagnetic, antiferromagnetic and ferrimagnetic exchange interactions respectively, within the trimer.

