

Phenolate- and Acetate (Both μ_2 -1,1 and μ_2 -1,3 Mode)-Bridged Face-Shared Trioctahedral Linear Ni^{II}_3 , $\text{Ni}^{\text{II}}_2\text{M}^{\text{II}}$ (M = Mn, Co) Complexes: Ferro- and Antiferromagnetic Coupling

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The complexes $[(\text{L})_2\text{Ni}^{\text{II}}_2\text{M}^{\text{II}}(\mu_2\text{-1,3-OAc})_2(\mu_2\text{-1,1-OAc})_2(\text{S})_2] \cdot x\text{MeOH}$ [HL = *N*-methyl-*N*-(2-hydroxybenzyl)-2-aminoethyl-2-pyridine; M = Ni, S = MeOH, $x = 6$ (1); M = Mn, S = H₂O, $x = 0$ (2); M = Co, S = MeOH, $x = 6$ (3)] have been synthesized. Crystal structures reveal that three octahedral M^{II} ions form a linear array with two terminal moieties $\{(\text{L})\text{Ni}^{\text{II}}(\mu_2\text{-1,3-OAc})(\mu_2\text{-1,1-OAc})(\text{MeOH}/\text{H}_2\text{O})\}^-$ in a facial donor set and a central M^{II} ion which is connected to the terminal ions via bridging phenolate and two types of bridging acetates. Magnetic measurements reveal that the Ni^{II}_3 and $\text{Ni}^{\text{II}}_2\text{Co}^{\text{II}}$ centers are ferromagnetically and $\text{Ni}^{\text{II}}_2\text{Mn}^{\text{II}}$ center is antiferromagnetically coupled. An attempt has been made to rationalize the observed magneto-structural behavior.

Rational design and synthesis of polynuclear coordination compounds with predictable magnetic properties have always attracted the attention of inorganic chemists.^{1,2} From this viewpoint, in recent years a handful of linear homo- Ni^{II}_3 and heterotrimeric $\text{Ni}^{\text{II}}_2\text{M}^{\text{II}}$ complexes have been synthesized and structurally characterized.^{3,4} Notably, most of these complexes are supported by phenol-based chelating ligands (*salen*-type tetradentate terminal and bridging ligands in particular) with or without additional acetate bridging in the $\mu_{1,3}$ mode. Moreover, it is worth noting that only in a few cases have magneto-structural studies been done.^{3a,b,d,e,g,4d,5} Face-sharing systems are of special importance in understanding overlapping magnetic orbitals, since both $d_{x^2-y^2}$ and

d_{z^2} orbitals are involved in bridging. Understandably, the ligand disposition around the paramagnetic metal ions and the nature of the bridging atoms/groups influence these magnetic exchange interactions. In view of the above, the preparation of complexes with new chelating ligands to create new homo- and heterotrimeric magnetic materials to arrive at to any trend is a challenge. From this perspective we have synthesized a new family of Ni^{II}_3 , $\text{Ni}^{\text{II}}_2\text{Mn}^{\text{II}}$, and $\text{Ni}^{\text{II}}_2\text{Co}^{\text{II}}$ complexes with invariant metal–ligand bonding characteristics, using a phenol-based potential tridentate ligand *N*-methyl-*N*-(2-hydroxybenzyl)-2-aminoethyl-2-pyridine,^{6–8} in its deprotonated form, and present the magneto-structural behavior of these complexes.

Reactions of HL with $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and $\text{M}^{\text{II}}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (M = Ni, Mn, Co) in a 2:2:1 molar ratio⁷ in MeOH readily afforded microcrystals of composition $[(\text{L})_2\text{Ni}^{\text{II}}_2\text{M}^{\text{II}}(\text{OAc})_4$

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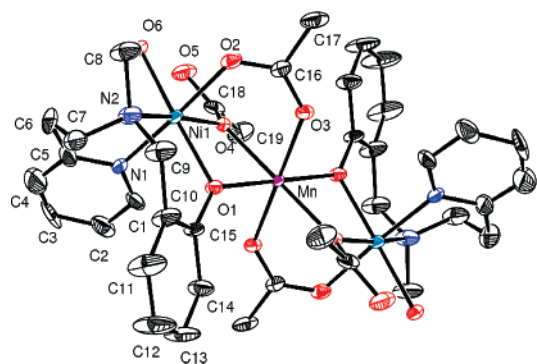


Figure 1. Perspective view of **2**. Selected distances (Å): Ni(1)–N(1) 2.080(6), Ni(1)–N(2) 2.138(6), Ni(1)–O(1) 1.988(4), Ni(1)–O(2) 2.078(4), Ni(1)–O(4) 2.136(4), Ni(1)–O(6) 2.086(4), Mn–O(1) 2.095(4), Mn–O(3) 2.144(4), Mn–O(4) 2.197(4).

(S₂)_xMeOH [M = Ni, S = MeOH, x = 6 (**1**); M = Mn, S = H₂O, x = 0 (**2**); M = Co, S = MeOH, x = 6 (**3**)]. The identities of **1–3** were elucidated from physicochemical measurements [elemental analysis, IR, UV–vis spectra (Figures S1–S3, Supporting Information), XRPD (Figures S4–S6)]⁷ and X-ray crystal structure analysis.^{7,9}

Complexes **1–3** [space groups $P\bar{1}$ (**1** and **3**) and $P2_1/c$ (**2**)] exhibit an analogous structure, containing centrosymmetric trimers. The central M^{II} ion (Ni₂ in **1**; Mn in **2**; Co in **3**) is situated on an inversion center, forming linear Ni₃, Ni₂Mn, and Ni₂Co complexes. Perspective views are presented in Figure S7, Figure 1, and Figure S8, respectively.⁷ The terminal Ni^{II} ions [Ni(1) and Ni(1')] are coordinated by a pyridyl nitrogen N(1), a tertiary amine nitrogen N(2), and a bridging phenolate oxygen O(1) from L⁻, two bridging carboxylate oxygens [O(2) of η¹:η¹:μ₂-bidentate and O(4) of μ₂-1,1-monatomic bridging mode], and an oxygen O(6) of H₂O/MeOH. The coordination environment around terminal Ni^{II} ions in **2** and that in **1** and **3** are almost identical, the only difference being the presence of coordinated MeOH in the place of H₂O. The coordination around the central M^{II} ion is also pseudo-octahedral, involving a bridging phenolate oxygen O(1), two bridging carboxylate oxygens [O(3) of η¹:η¹:μ₂-bidentate and O(4) of μ₂-1,1-monatomic bridging mode], and their symmetry-related ones. Thus, the three pseudo-octahedral M^{II} ions form a linear array with two terminal moieties in a facial N₂O donor set from L⁻. The coordination spheres of terminal Ni^{II} ions are, however, severely distorted from ideal octahedral geometry.⁷ The distances (Å) between the terminal–central M^{II} ions are 3.139(9) (**1**), 3.181(3) (**2**), and 3.161(3) (**3**); between the terminal Ni^{II} ions are 6.278(17) (**1**), 6.362(5) (**2**), and 6.322-

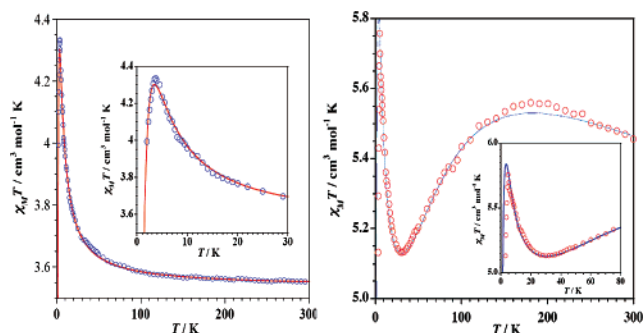


Figure 2. Plots of $\chi_M T$ vs T for **1** (left) and **3** (right). The behavior below 30 K for **1** and below 80 K for **3** are presented as insets.

(**5**) (**3**). The M^{II}₂O₂ core is not planar, as indicated by torsion angles [26.768(17)° (**1**), 28.216° (**2**), and 27.192(20)° (**3**)], defined among the Ni(1), O(1), Ni(2)/Mn/Co, and O(4) atoms. The relevant bridging angles are 101.755(16)° and 94.794(15)° (**1**); 102.328(3)° and 94.441(3)° (**2**); 102.110(4)° and 94.380(4)° (**3**).

Measurements of the susceptibility were carried out^{7,10} for solid samples, collected in the temperature range 2–300 K. The data for Ni^{II}Ni^{II}Ni^{II} system [d⁸-d⁸-d⁸ ($S = 1$)] **1** as $\chi_M T$ (cm³ mol⁻¹ K) versus T (K) are displayed in Figure 2. This behavior clearly indicates that the Ni^{II} centers in **1** are ferromagnetically coupled (magnetization plot: Figure S9). Applying the spin Hamiltonian (eq 1) for a linear Ni^{II}₃,

$$\hat{H} = -J\hat{S}_{\text{Ni1}}[\hat{S}_{\text{Ni1}} + \hat{S}_{\text{Ni3}}] + \sum_{i=1}^3 D_i[\hat{S}_{z_{\text{Ni},i}}^2 - 2/3] + \sum_{i=1}^3 \beta H g_{\text{Ni},i} \hat{S}_{\text{Ni},i} \quad (1)$$

with an approximation that the magnetic interaction between terminal Ni^{II} centers (6.278 Å apart) could be neglected,¹¹ and taking into account the zero-field splitting parameter, D (the same value for the three Ni(II) ions and the same g value), a good fit of the temperature-dependent magnetic susceptibility data was obtained. $g_{\text{iso}} = 2.18$, $J(\text{Ni}–\text{Ni}) = +1.10(1)$ cm⁻¹, and $D = +3.49(5)$ cm⁻¹.¹²

The magnetic behavior of Ni^{II}Mn^{II}Ni^{II} system [d⁸ ($S = 1$)-d⁵ ($S = 5/2$)-d⁸ ($S = 1$)] **2** is completely different from that of **1** and **3**. The profile of the $\chi_M T$ vs T curve (Figure S10) indicates that the magnetic interaction is antiferromagnetic. Fits to the experimental data (eq 2) were performed using $g(\text{Ni}) = 2.09(1)$, $g(\text{Mn}) = 2.0$ (fixed),

(9) Crystal data [100(2) K] for **1** [**2**; **3**]: C₄₆H₆₈N₄Ni₃O₁₈ [C₃₈H₄₆N₄Ni₂MnO₁₂; C₄₆H₇₀N₄Ni₂CoO₁₈], fw = 1141.17 [923.15; 1143.41], space group $P\bar{1}$ (No. 2) [$P2_1/c$ (No. 14); $P\bar{1}$ (No. 2)], $a = 9.468(5)$ Å [10.3362(9) Å; 9.4765(10) Å], $b = 10.980(5)$ Å [18.2471(16) Å; 10.9764(11) Å], $c = 13.280(5)$ Å [12.2056(11) Å; 13.3235(14) Å], $\alpha = 80.237(5)^\circ$ [90.0°; 80.140(2)°], $\beta = 82.486(5)^\circ$ [113.853(2)°; 82.215(2)°], $\gamma = 86.234(5)^\circ$ [90.0°; 86.197(2)°], $V = 1347.6(11)$ Å³ [2105.4(3) Å³; 1351.5(2) Å³], $Z = 1$ [2; 1], $\rho_{\text{calcd}} = 1.406$ g cm⁻³ [1.456 g cm⁻³; 1.405 g cm⁻³]. Bruker SMART CCD diffractometer, Mo K α radiation, graphite monochromator, 6411 [5198; 6401] unique reflections, 4674 [3007; 5140] observed [$I > 2\sigma(I)$] reflections, $R1 = 0.0573$ [0.0829; 0.0735], $wR2 = 0.1407$ [0.1687; 0.1471]; calculation programs: Bruker SAINT-PLUS, SIR-97.

(10) The measurements were carried out using a Quantum Design SQUID Magnetometer (València) at 0.1 T for $T < 50$ K in order to avoid saturation effects and 0.01 T for $T > 50$ K. Diamagnetic corrections were estimated from Pascal's constants.

(11) $H = -\{J_{12}(S_1S_2) + J_{23}(S_2S_3) + J_{13}(S_1S_3)\}$; considering $J = J_{12} = J_{23}$ and assuming the interaction between the terminal Ni^{II} ions $J_{13} = 0$. In the absence of clearly defined exchange pathway between the terminal metal ions, it is justifiable: Zhao, Q.; Li, H.; Chen, Z.; Fang, R. *Inorg. Chim. Acta* **2002**, *336*, 142–146 and references therein.

(12) The ground spin state of **1** is $S = 3$ and this state is split by the ZFS ($D_{S=3}$). Its value obeys to the expression $D_{S=3} = (D_C + 2D_T)/15$, where D_C and D_T are the local central and terminal ZFS values. In the fitting process we assumed that $D_C = D_T$ and therefore $D_{S=3} = 0.70$ cm⁻¹. The value of $D_{S=3} = 0.70$ cm⁻¹ is the only relevant parameter to account for the magnetic susceptibility at low temperature. Thus, any set of values of D_C and D_T providing $D_{S=3} = 0.70$ cm⁻¹ is possible. Consequently, the local D values cannot be determined from magnetic susceptibility measurements. Moreover, the D_C and D_T tensors are not coaxial and so the D_C tensor should contain the coefficient corresponding to the rotation matrix referred to the D_T direction.

$$\hat{H} = -J\hat{S}_{\text{Mn}}[\hat{S}_{\text{Ni1}} + \hat{S}_{\text{Ni2}}] + \sum_{i=1}^2 D_i[\hat{S}_{\text{zNi},i}^2 - 2/3] + \sum_{i=1}^2 \beta H g_{\text{Ni},i} \hat{S}_{\text{Ni},i} + \beta H g_{\text{Mn},i} \hat{S}_{\text{Mn},i} \quad (2)$$

$J(\text{Ni-Mn}) = -0.30(1) \text{ cm}^{-1}$, and axial splitting parameter for the Ni(II) ions, $D = +3.49 \text{ cm}^{-1}$ (fixed).¹³

The χ_{MT} vs T data for Ni^{II}Co^{II}Ni^{II} system [d^8 ($S = 1$)- d^7 ($S = 3/2$)- d^8 ($S = 1$)] **3** (Figure 2) suggest that the Ni^{II}Co^{II}-Ni^{II} centers are also ferromagnetically coupled. The Co(II) d^7 ion is strongly anisotropic, and the first-order orbital momentum is no longer negligible so the isotropic exchange interaction HDvV model is insufficient to discuss Co(II) complexes and must be supplemented by consideration of the spin-orbit coupling (λ).¹⁴ Considering this we analyzed the temperature-dependent magnetic data using five variables from the Hamiltonian (eq 3). The best-fit is obtained with

$$\hat{H} = -J\hat{S}_{\text{Co}}[\hat{S}_{\text{Ni1}} + \hat{S}_{\text{Ni2}}] + \alpha\lambda\hat{L}_{\text{Co}}\hat{S}_{\text{Co}} + \Delta[\hat{L}_{\text{zCo}}^2 - 2/3] + \sum_{i=1}^2 D_i[\hat{S}_{\text{zNi},i}^2 - 2/3] + \beta H[-\alpha\hat{L}_{\text{Co}} + g_e\hat{S}_{\text{Co}}] + \sum_{i=1}^2 \beta H g_{\text{Ni},i} \hat{S}_{\text{Ni},i} \quad (3)$$

values of $g(\text{Ni}) = 2.20(1)$, $J(\text{Ni-Co}) = +1.06(3) \text{ cm}^{-1}$, $\lambda = -114(2) \text{ cm}^{-1}$, $\alpha = kA = 1.30(1)$ and $D_{\text{Ni}} = +3.49 \text{ cm}^{-1}$ (fixed) [A is the ligand-field parameter that takes into account the mix of the ground triplet, 4T_1 , of the Co(II) ion (from the F term) and the excited one (from the P term)], and k , the orbital reduction parameter, and $\Delta = 100(20) \text{ cm}^{-1}$ [the splitting of the ground triplet of the Co(II) ion by an axial distortion]. For $A = 1.5$ (usual value for this kind of ligand),¹⁴ $k = 0.87$. In the free-ion the k is known to be ≈ 0.93 .¹⁴ For $A = 1.5$ (usual value for this kind of ligand),¹⁴ $k = 0.87$. In the free-ion the k is known to be ≈ 0.93 .¹⁴ The reasonably good fit of data suggests that the model used is quite acceptable.

In order to understand the magnetic exchange mechanism, it is important to note that compounds **1-3** have two monatomic bridges (from carboxylate and phenoxide) and a syn-syn carboxylate bridge. For this last bridge, it is well-known that its presence in a syn-syn conformation causes antiferromagnetic coupling.^{1a} The nature of magnetic interaction is very dependent on the bond angle M-O-M for the monatomic bridge. This dependence has been well-studied for Cu^{II} polynuclear complexes, in contrast to scarce studies for other metal ions.^{1a}

However, for di- or trinuclear¹⁵ Ni^{II} complexes, the ferromagnetic interaction is observed for Ni-O-Ni angles lower than 93.5° (magic angle).^{3d} The magnetic coupling is antiferromagnetic for greater values. For other metal ions or heteropolynuclear complexes, this dependence is quite

unknown. Moreover, it is possible that the magic angle may be lower than 93.5° for other metal ions such as Mn(II) or Co(II). In this sense, for tri- μ -phenoxide bridging trinuclear complexes of formula M_3L_2 ($LH_3 = P(S)[N(\text{Me})N=CH-C_6H_4-o-O]$ and $M = \text{Ni}^{\text{II}}, \text{Co}^{\text{II}},$ and Mn^{II}) which present M-O-M angles in the range $85-87^\circ$, ferro- [Ni(II) complexes] and antiferromagnetic [Co(II) and Mn(II) complexes] interactions have been observed.^{3g}

Given that the bond angles of **1-3** are greater than 93.5° ($\sim 102^\circ$ for phenoxide and $\sim 94.5^\circ$ for carboxylate) and taking into account the above comments, an antiferromagnetic coupling for **1-3** would be expected. However, when the bridging ligands are different, the two bridges may either add (complementarity) or counterbalance (countercomplementarity) their effects.^{16,17} It has been shown that the syn-syn μ_2 -1,3-carboxylate and monatomic μ_2 -1,1-azide bridges are countercomplementary and hence the antiferromagnetic contributions of each bridge cancel each other, and the ferromagnetic term dominates.¹⁸ This situation is observed for **1** and **3**, whereas in the case of **2**, the cancellation is not complete and a very weak antiferromagnetic contribution remains.

In summary, we have demonstrated the construction of three linear trinuclear complexes comprising a similar terminal coordination environment around Ni^{II} ion and variable central ions with invariant nature and number of bridging ligand interactions. In two complexes Ni^{II}₂M^{II} ($M = \text{Ni}$ and Co), ferromagnetic and in Ni^{II}₂Mn^{II} antiferromagnetic interactions are observed between neighboring metal ions. The tunable magnetic interactions arise from controlled variation of the spin-state of central M^{II} ion (Ni, $S = 1$; Mn, $S = 5/2$; Co, $S = 3/2$) giving rise to magnetic interactions involving $\{t_{2g}^6 e_g^2\}^2$ - $t_{2g}^6 e_g^2/t_{2g}^3 e_g^2/t_{2g}^5 e_g^2$ spins. This study showed that judicious combination of terminal and bridging ligand affording invariant terminal and central metal ion coordination environment is a useful approach for the construction of a series of linear trinuclear complexes with tunable ground spin states. Bulky substituents on the phenol moiety may bring about a change in the nuclearity. Such an endeavor is on in this laboratory.

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Supporting Information Available: CIF files for **1**, **2**, and **3**; UV-vis spectra of **1-3** (Figures S1-S3), experimental and simulated X-ray powder diffraction patterns (Figures S4-S6), perspective view of the structure of **1** and **3** (Figure S7 and S8, respectively), magnetization plot of **1** (Figure S9), χ_{MT} vs T data for **2** (Figure S10). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(13) Given that the ground spin state for **2** is $S = 1/2$, there is no ZFS for it. For such a case, the magnetic susceptibility data have no sensibility to the values of the local ZFS.

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