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Synthesis and magnetic properties of two-step-coordination Schiff base clusters

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Abstract: A new family of paramagnetic coordination compounds based on a diimine-pyridine pincer ligand has been prepared, using a two-step synthetic approach. The sequential introduction of identical or different transition metals (Co, Mn, Ni, Zn) afforded mono-, di-, triand tetranuclear clusters, whose crystal structure has been determined. Magnetic studies reveal that the metals within the trinuclear manganese cluster engage in a small ferromagnetic exchange interaction (J = 0.15 K). These studies enable the design of new clusters with specific magnetic properties.

Introduction

The introduction of coordination chemistry ^[1] has led to the emergence of a wide range of new functional materials, which have found their way into fields such as catalysis, electronics, magnetism and medicine.^[2] The design of coordination compounds with a specific function is governed by our ability to control their synthesis and understand their resulting electronic behavior. The electronic and magnetic properties of coordination compounds often strongly depend on their geometry. The inherently flexible and versatile nature of their organic (ligand) and inorganic (metal) building blocks therefore makes systematic correlation studies and the design of functionality challenging. To overcome this obstacle, rigid ligands can be used, which results in more predictable coordination products. Examples of such ligands are the so-called pincer ligands, which have at least three adjacent, coplanar binding sites, forming a strong coordination pocket. In this work, we explore the coordination compounds based on the Schiff base pincer ligand H_2L shown in Figure 1.

The ligand was synthesized by a template-free double condensation of 2,6-diformylpyridine and *o*-aminophenol.^[3] Its rigidity comes from its pyridine and phenol rings, which are linked through two rigid imine bonds. Three nitrogen lone pairs and two oxygen (covalent or donative) bonds bring about a five-fold coordination pocket, which can host various metal ions. Since its first publication, the coordination of H₂L to a range of transition and rare earth metals has been reported.^[4] In addition, H₂L based

coordination compounds have been investigated towards their catalytic,^[5] antibacterial,^[6] radio therapeutic,^[7] and their cytotoxic, anti-inflammatory and antioxidant^[8] activity. Recently, the magnetic properties of dysprosium-based complexes using the same ligand have been studied.^[9] Our interest in this ligand originates from its rigid five-fold coordination pocket. This constrained coordination geometry is particularly interesting from a magnetic point of view, since it enforces an approximate axial D_{5h} symmetry on the central ion, which has been shown to generate a high degree of either in-plane or out-of-plane axial anisotropy. $\ensuremath{^{[2c,\ 10]}}$ Therefore, this family of coordination compounds is of interest for the potential formation of single molecule magnets (SMMs).^[9, 11] In addition, the oxygen atoms can simultaneously bind a second metal ion on the outside of the coordination pocket, to extent the magnetic system and facilitate a Heisenberg super-exchange interaction between the metal ions. This second (weaker) coordination site is in competition with the (stronger) five-fold site with respect to the binding of metal ions. This competition has been shown to produce hetero metallic clusters,[12] which can possess magnetic ground states (ferrimagnetism).



Figure 1. Molecular structure of the H₂L ligand.

We synthesized paramagnetic H_2L -based coordination compounds by the subsequent addition of a transition metal chloride followed by an acetate salt, shown in Scheme 1. In addition, we synthesized a compound by the direct addition of an acetate salt only. These strategies afforded seven new coordination compounds **1-7**, of which we have investigated the

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magnetic properties of compounds **3** and **5**. Since magnetic properties are very sensitive to minute structural changes,^[13] we have determined the crystal structures of these compounds to correlate structure to magnetic behavior.



Scheme 1. Overview of the synthesis route and reaction products of the paramagnetic H_2L -based coordination compounds.



Figure 2. Crystal structure of tetranuclear cobalt cluster **1**. The thermal ellipsoids of the ORTEP representation have been set at 50% probability. Carbon = grey, cobalt = blue, nitrogen = light blue and oxygen = red. All non-coordinated solvent molecules, a front facing acetate ligand on M_2 (upper), and hydrogen atoms have been omitted for clarity.

Results and Discussion

Crystal structures

The direct addition of cobalt(II) acetate to H_2L afforded tetranuclear cluster 1 (Figure 2). The cluster contains two L ligands (deprotonated), of which both the coordination pocket M_1 and the outer position M_2 are occupied. These two ligands stack, while rotated 90°, to form a tetranuclear cluster. The four 2+ charges on the metal ions are compensated by the double

deprotonation of the H_2L ligands, and four acetate ligands. M_1 has the expected (but slightly distorted) pentagonal bipyramidal coordination, while M_2 has a near octahedral coordination.

The addition of manganese(II) chloride or cobalt(II) chloride to H₂L afforded isostructural complexes 2 and 3 respectively (Figure 3). These complexes consist of a single metal ion, located in the coordination pocket of H₂L. The ligand's geometry enforces an approximate five-fold rotational symmetry on the central ion, which in case of cobalt cluster 3 results in equatorial bond angles of 73.68° (O-M-O), 70.47° (O-M-N) and 72.67° (N-M-N). These angles closely agree with the ideal pentagonal surrounding of 360/5 = 72°. Upon coordination the ligand remains protonated, and the metal ion's 2+ charge is compensated by both an axially coordinated chloride ligand and a chloride ion in the second coordination sphere. The 2+ oxidation state is confirmed by the M-O and M-N bond distances for both metal ions (~2.3 Å for manganese(II) and ~2.2 Å for cobalt(II)).^[14] Interestingly, for the manganese complex, a longer reaction time at much higher concentration afforded a complex where both chloride ions reside on the axial position of Mn(II).[5c]



Figure 3. Crystal structure of manganese complex 2. The crystal structure is isostructural to cobalt complex 3. The thermal ellipsoids of the ORTEP representation have been set at 50% probability. Carbon = grey, chloride = yellow, manganese = green, nitrogen = light blue and oxygen = red. All non-coordinated solvent molecules and hydrogen atoms have been omitted for clarity.

The addition of nickel(II) chloride to H_2L gave complex **4** (Figure 4). Although the nickel ion occupies the ligand's coordination pocket, it only binds to the three nitrogen donors. Instead, the ion has an octahedral coordination geometry, with two chloride ions as axial ligands and a coordinated THF molecule in the equatorial plane. The phenol oxygen atoms do not coordinate to the metal and therefore they rotate out of the ligand plane to reduce steric hindrance.

Adding a half equivalent of manganese(II) acetate to **2** gave trinuclear manganese cluster **5** (Figure 5). A similar complex with bridging acetates rather than chloride ligands was studied as a catalase mimic.^[5c] The cluster consists of two deprotonated ligands, L, which still have manganese ions in their coordination pockets (M₁), but now share a third manganese ion (M₂). Therefore, the addition of manganese(II) acetate has effectively "glued" two complexes **2** together. In doing so, both H₂L ligands are doubly deprotonated and both initial complexes **2** have lost a chloride counter ion. The connecting ion, M₂, binds the four available oxygen atoms and an additional ethanol ligand, to adopt

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a slightly distorted trigonal bipyramidal coordination geometry. The total 6+ charge of the three Mn(II) ions is compensated by the chloride and deprotonated ligands, yielding an overall neutral cluster.



Figure 4. Crystal structure of nickel complex **4**. The thermal ellipsoids of the ORTEP representation have been set at 50% probability. Carbon = grey, chloride = yellow, nitrogen = light blue, nickel = cyan, and oxygen = red. All non-coordinated solvent molecules and hydrogen atoms have been omitted for clarity.



Figure 5. Crystal structure of linear Mn₃ cluster **5**. The thermal ellipsoids of the ORTEP representation have been set at 50% probability. Carbon = grey, chloride = yellow, manganese = green, nitrogen = light blue and oxygen = red. All non-coordinating solvent molecules, and hydrogen atoms have been omitted for clarity. The ethanol oxygen atom on the central ion M₂ can occupy two different crystal sites, which are both shown in this figure.

Alternatively, adding an equivalent of zinc(II) acetate to **2** gave heterometallic manganese-zinc cluster **6** (Figure 6). Similar to starting complex **2**, this cluster still contains a single ligand L with a manganese ion in its coordination pocket (M_1). However, the second coordination site (M_2) is now occupied by a Zn(II) ion. Interestingly, the two chloride ions of starting complex **2** (both axial and second coordination sphere) have migrated to the zinc ion. Therefore, the zinc ion adopts a tetrahedral coordination geometry. The axial position on the Mn(II) ion has been replaced by a water ligand. The total 4+ positive charge of both metal ions

is balanced by the fully deprotonated ligand and the chloride ligand to result in an overall neutral cluster. Although the additional Zn(II) ion is diamagnetic, and therefore has little influence on the dominating paramagnetic magnetic behavior of the clusters, it does demonstrate the controlled occupation of the second coordination site. Particularly the controlled synthesis of heterometallic clusters with unequal numbers of unpaired electrons on M₁ and M₂ is of interest, since this can produce ferrimagnetic ground states.



Figure 6. Crystal structure of heterometallic manganese-zinc cluster **6**. The thermal ellipsoids of the ORTEP representation have been set at 50% probability. Carbon = grey, chloride = yellow, manganese = green, nitrogen = light blue, oxygen = red and zinc = brown. All non-coordinated solvent molecules, and hydrogen atoms have been omitted for clarity.



Figure 7. Crystal structure of tetranuclear cobalt cluster **7**. The thermal ellipsoids of the ORTEP representation have been set at 50% probability. Carbon = grey, chloride = yellow, cobalt = blue, nitrogen = light blue and oxygen = red. All non-coordinated solvent molecules, and hydrogen atoms have been omitted for clarity.

The addition of an equivalent of cobalt(II) acetate to **3** gave tetranuclear cobalt cluster **7** (Figure 7). The cluster consists of two ligands L, each still having their Co(II) ions in their coordination

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pockets (M_1), and an additional Co(II) ion in the outer position (M_2). This additional cobalt ion has a tetrahedral coordination geometry. These two LM_1M_2 moieties are bridged by the axial chloride ligands on M_1 , to give a tetranuclear cluster. The total 8+ charge

of the four Co(II) ions is compensated by the chloride ligands and two doubly deprotonated ligands, yielding an overall neutral cluster. Details on the crystallographic data and the refinement details are presented in Table 1.

Table 1. Crys	able 1. Crystallographic Data and Structure Refinement Details.						
	1	2	3	4	5	6	7
Formula	C46C04H38N6O12	$C_{20}CIH_{19}MnN_3O_3$	C ₂₀ Cl ₂ CoH ₁₇ N ₃ O ₃	C23Cl2H23N3NiO3	C44Cl2H45Mn3N6O7	C ₂₀ Cl ₂ H ₁₉ MnN ₃ O ₄ Zn	C44Cl4C04H38N6O6
Weight	1102.56	439.77	511.26	519.05	1004.58	556.61	1124.35
Space group	C 2/c	P -1	C 2/c	C 2/c	C 2/c	P 21/n	P 21/c
a (Å)	20.0548(9)	6.9184(3)	28.7972(18)	26.235(3)	25.714(5)	12.5181(13)	17.631(4)
b (Å)	11.7054(6)	12.6804(9)	6.8035(7)	13.6726(14)	11.401(2)	13.1870(7)	13.245(3)
c (Å)	21.5865(15)	13.6337(8)	21.938(3)	15.1306(12)	21.561(4)	14.2358(14)	19.258(4)
α (deg)	90	84.880(6)	90	90	90	90	90
β (deg)	91.363(6)	83.552(4)	92.111(7)	95.654(8)	119.81(3)	95.737(5)	98.52(3)
γ (deg)	90	78.555(5)	90	90	90	90	90
V (Å ³)	5066.0(5)	1162.10(12)	4295.2(8)	5400.9(9)	5485(2)	2338.2(4)	4549.4(18)
Ζ	4	2	4	8	4	4	4
<i>Т</i> (К)	208(2)	208(2)	208(2)	208(2)	208(2)	208(2)	208(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
µ (cm⁻¹)	1.569	0.835	1.078	0.952	0.823	1.831	1.723
R (F _o) ^[a]	0.0372	0.0632	0.0425	0.0434	0.0632	0.0281	0.0412
$R_{\rm w} ({\rm F_o})^{\rm [b]}$	0.0964	0.1576	0.0983	0.1045	0.1746	0.0719	0.0975

[a] Residual factor for the reflections judged significantly intense and included in the refinement. [b] Weighted residual factors for significantly intense reflections included in the refinement.

Magnetic properties

The magnetization and susceptibility of linear Mn₃ cluster 5 has been determined using low-temperature high-field cantilever magnetometry and SQUID measurements respectively. Figure 8 shows the parallel magnetization of a powdered sample of 5 (solid black line), measured at T = 4.2 K at magnetic fields of B = 0 to 20 T through cantilever magnetometry. It shows a steep increase of the magnetization at low fields, which saturates around B = 10T. The inset shows the inverse molar susceptibility (solid triangles) at a constant magnetic field of B = 0.1 T at a temperature range of T = 1.8-300 K. It follows the Curie–Weiss law down to low temperatures, with an extracted experimental moment of μ_{eff} = 5.78 μ_B (spin-only gives μ_{eff} = 5.82 μ_B , see below) per Mn(II) ion and a Weiss constant θ_{W} = 1.02 K (fit down to 40 K). Since the Mn(II) ions are expected to be in a ⁶S ground state, we ignore spin-orbit contributions and describe the system using a spin-only Hamiltonian containing only Zeeman and Heisenbergexchange contributions. Concerning the exchange interaction, we expect an open triplet spin topology based on the structure, with identical exchange couplings between M_1 and M_2 (labelled J_{12}) and between $M_{1'}$ and M_2 (labelled $J_{21'}$) and a negligible exchange between M₁ and M₁. Based on the Weiss constant, the couplings $J_{12} = J_{21}$ would be ferromagnetic and have a magnitude of J = 0.22 K. A similarly small ferromagnetic interaction is found with the cantilever measurement, for which the T = 4.2 K trace overlaps with the simulated spin-only curve corresponding to a coupling of J = 0.15 K.

Recently, it has been shown^[15] that a single Co(II) ion in a pentagonal surrounding can result in slow relaxation of its magnetization (Single Ion Magnet behavior). Therefore, we have performed low temperature AC susceptibility measurements on Co(II) complex **3**. The measurements have been taken at temperatures between *T* = 1.8 and 50 K and at frequencies in the range *f* = 0.1-1500 Hz at a drive field of 3.78 Oe. We did not observe any out-of-phase signals, which means that $\tau \ll 1/2\pi f$, i.e. there is no indication of single ion magnet behavior.

The coordination compounds in this work show that the two-step approach employed here (subsequent addition of metal chloride and -acetate) enables the synthesis of several new homo- and heterometallic magnetic clusters. The controlled placement of metal ions in sites M_1 and M_2 gives direct control over the magnetic properties of the resulting clusters. However, this method only works when the added metal acetate in the second

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step has a lower affinity to the pentagonal coordination pocket (M₁) than the metal ion already present in the precursors complex. These affinities have been determined using mass spectrometry, where the abundant HLM+ fragment could be used to determine the occupation of the pentadentate coordination pocket. The HLM⁺ fragment of several first row transition metals are listed in Table 2.



Figure 8. Magnetic properties of linear Mn₃ cluster **5**. The solid black line represent the parallel magnetization, as measured by cantilever magnetometry at *T* = 4.2 K between *B* = 0 and 20 T. The black and red dotted lines are simulated traces which correspond to the uncoupled *J* = 0 and the ferromagnetically coupled *J* = 0.15 K situations. The inset shows the inverse molar susceptibility (solid triangles) at a constant magnetic field of *B* = 0.1 T at a temperature range of *T* = 1.8-300 K. Its linear shape up until low temperatures corresponds to Curie-Weiss behavior, through which the effective moment ($\mu_{\text{eff}} = 5.78 \, \mu_{\text{B}}$) and Weiss constant ($\theta_{\text{W}} = 1.02 \, \text{K}$) are extracted by a linear fit down to 40 K.

Table 2. Dominant LC/MS electrospray ion-trap mass fragments						
Experiment	m/z	Fragment				
MnCl ₂ vs. CoCl ₂	371.3	H[LMn(II)]*				
CoCl ₂ vs. ZnCl ₂	375.2	H[LCo(II)] ⁺				
Synthesis of 4	374.2	H[LNi(II)]⁺				
ZnCl ₂ vs. NiCl ₂	382.3	H[LZn(II)]⁺				

The relative affinities were determined by simultaneously adding equimolar quantities of two different metal chlorides to a solution of H₂L. In each case we observed dominating fragment species containing only one of the two metal ions. From these experiments we observe a bonding affinity to H₂L of order: Ni(II) < Zn(II) < Mn(II) < Co(II). The lowest affinity of the Ni(II) ion to H₂L is easily explained by the fact that according to the Jahn-Teller theorem, a regular stereochemistry of seven-coordinate pentagonal bipyramidal high-spin Ni(II) complex is unstable.^[16] Therefore, as seen in complex **4**, the ion only engages in four bonds with the ligand which reduces its affinity relative to a pentadentate coordination. Attempting to insert a second metal into M₂ for this precursor would only be possible if a metal ion is found with an even weaker affinity for M₁. The remaining three ions, Zn(II), Mn(II), and Co(II) all bind in a similar fashion to H₂L.

Their affinities are governed by their σ -acceptor (the ligand donates five lone pairs) and π^* -acceptor properties. The latter interaction has been shown to be exceptionally strong in diimine-pyridine ligands.^[17] The relative affinities of the Zn(II), Mn(II) and Co(II) ions to H₂L resemble the Irving-Williams series,^[18] with the exception of Mn(II) binding stronger than Zn(II). This might be explained by an increased back-bonding interaction of Mn(II) compared to Zn(II).

Depending on the counter ions (acetate and/or chloride), we were able to produce coordination compounds which contain 1, 2, 3 or 4 ions using H₂L. Each of these compounds contain the rigid [LM] fragment, which are organized in different ways in case of the polymetallic clusters. This is exemplified by tetranuclear cobalt clusters 1 and 7, which adopt a double-decker like structure of the two [LM] fragments while in Mn₃ cluster 5 the two fragments face each other on a single axis. Moreover, cobalt cluster 1 is the only compound in which the phenol oxygen atoms on the ligand are used to bind three different metal ions, compared to two metal ions in clusters 5-7. The extra bond results in a tetrahedral sp³ geometry of this oxygen atom. In contrast to the completely planar ligands in compounds 2-7, this bends the ligand significantly through a rotation around its C_{phenol}-N_{imine} bonds (~23 degrees).

In terms of geometry, manganese-zinc cluster **6** is the most straightforward result we obtained. The addition of zinc acetate to the manganese precursor complex **2** resulted only in the occupation of the zinc ion on site M_2 . In principle, the tetranuclear cobalt cluster **7** has a very similar structure, but in this case the structure is extended by stacking two binuclear clusters on top of each other. A similar structure has been observed for this ligand before, by using a one-pot synthesis with cadmium acetate.^[19]

The found ferromagnetic interaction between the metal ions in Mn(II) cluster **5** is rather surprising. In an earlier publication on a Mn(II) cluster highly similar to compound **1** (both in geometry and ligand),^[14] a small antiferromagnetic coupling of $J_{12} = 1.1$ K, between ions M_1 and M_2 was found. A large difference between these clusters is the local coordination geometry of M_2 , which in cluster **5** is distorted trigonal bipyramidal and for the published tetranuclear compound is octahedral. In the latter case, the Goodenough-Kanamori-Anderson rule indeed predicts an antiferromagnetic interaction. However, in case of the distorted trigonal bipyramidal case these rules do not apply.

Although exchange interaction between M_1 and M_2 mainly determines the magnetic ground state (magnetic/non-magnetic) of the system, magnetic anisotropy is needed to induce SMM behavior. A detailed analysis of the magnetic anisotropy (easy-plane/axis) on coordination sites M_1 and M_2 in case of Mn(II) ions have been determined by cantilever magnetometry on a single crystal, and will be published separately.

Conclusion

We have developed a new two-step synthesis approach, through which we were able to synthesize a family of paramagnetic coordination compounds based on diimine-pyridine ligand H₂L. By sequentially introducing different transition metal salts, we can, to a large extent controllably, insert (different) metal ions in the coordination sites, M₁ and M₂. In addition, these metal ions are shown to engage in an exchange interaction. This enables the design of new clusters with specified magnetic properties.

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Experimental Section

Commercially available reagents were used without further purification. All reactions were carried out under atmospheric conditions unless mentioned otherwise. Mass spectra were taken on a LCQ Advantage Max LC/MS electrospray ion-trap mass spectrometer (positive ion mode, MeOH). SQUID magnetization and susceptibility measurements in the ranges of 1.8 < T < 300 K and 0 < B < 70 kOe were taken on a Quantum Design SQUID magnetometer (MPMS-XL). Cantilever magnetometry measurements were performed on an in-house build cantilever magnetometer at the High Field Magnet Laboratory in Nijmegen, The Netherlands. Single-crystal diffraction was performed on a Nonius KappaCCD single crystal diffractometer θ and ω scan mode) using graphite-monochromated Mo Ka radiation. Diffraction images were integrated using Eval14.^[20] Intensity data were corrected for Lorentz and polarization effects. A semiempirical multiscan absorption correction was applied (SADABS).^[21] The structure was solved by the DIRDIF program system using the program PATTY to locate the heavy atoms. Refinement was performed with standard methods (refinement against F2 of all reflections with SHELXL97) with anisotropic displacement parameters for the non-hydrogen atoms.^[22] All hydrogen atoms were placed at calculated positions and refined riding on the parent atoms. CCDC 2086935 -2086941 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Synthesis of 2,6-bis(2-hydroxyphenyliminomethyl)pyridine (H₂L). This compound was synthesized according to a method published earlier [6]: Boiling solutions of o-aminophenol (2.50 g, 22.9 mmol) in 270 mL water and 2,6-diformylpyridine (1.55 g, 11.5 mmol) in 155 mL were mixed, and refluxed for another 30 minutes. After being stored overnight in the refrigerator, a yellow precipitate could be filtered off. The filtrate was washed with hot water and recrystallized from methanol to afford 3.10 g of product (yield 86%). Anal.: Calcd. for C₁₉H₁₅N₃O₂: C 71.94%; H 4.73%; N 13.24%. Found: C 71.87%; H 4.90%; N 13.11%.

Synthesis of Co(II)₄L₂(CH₃COO⁻)₄ (1). To a solution of 2,6-diformylpyridine (0.1 g, 0.74 mmol) and o-aminophenol (0.16 g, 1.48 mmol) in 200 mL methanol was added Co(CH₃COO⁻)₂·4H₂O (0.262 g, 1.48 mmol). The mixture was refluxed for 24 hours to obtain a dark brown solution. The solvent was removed through rotary evaporation. Residual acetic acid was stripped away through azeotropic evaporation of toluene. The strongly hygroscopic powder was dissolved in ~50 mL of methanol, and upon addition of diethyl ether (250 mL), the product precipitated and was isolated by filtration. The product was crystallized from a dichloromethane solution top-layered with *n*-pentane to yield dark brown crystal needles which were analyzed using single crystal X-ray diffraction. ESI-MS MeOH *m/z*: [HL₂Co₂]⁺, 748.9, 73%; [H(L)Co]⁺, 375.3, 100%.

Synthesis of [$Mn(II)H_2LCI(CH_3OH)$]Cl (2). To a solution of H₂L (0.10 g, 0.32 mmol) in 100 mL methanol was added MnCl₂·4H₂O (0.08 g, 0.42 mmol). The mixture was refluxed for two hours, after which the amount of solvent was lowered (to ~20 mL) under reduced pressure. Upon addition of diethyl ether (150 mL), the red product precipitated and was obtained by filtration. The brown-red product was crystallized from a methanol solution top-layered with diethyl ether to yield red-brown crystals which were analyzed using single crystal X-ray diffraction. ESI-MS MeOH m/z: [HL₂Mn₂]⁺, 741.1, 50%; [H(L)Mn(MeO-)]⁺, 402.1, 22%; [H(L)Mn]⁺, 371.3, 100%.

Synthesis of $[Co(II)H_2LCI(CH_3OH)]CI(3)$. To a solution of H_2L (0.10 g, 0.32 mmol) in 100 mL methanol was added CoCl₂·6H₂O (0.08 g, 0.32 mmol). The mixture was refluxed for two hours, after which the amount of solvent was lowered (~20 mL) under reduced pressure. Upon addition of diethyl ether (150 mL), the brown product precipitated and was obtained by filtration. The product was crystallized from an ethanol solution top-layered with diethyl ether to yield brown crystals which were analyzed using single crystal X-ray diffraction. ESI-MS MeOH m/z: $[HL_2Co_2]^+$, 749.0, 33%; $[H(L)Co]^+$, 375.2, 100%.

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Synthesis of Ni(II)H₂LCl₂(THF) (4). To a solution of H₂L (0.10 g, 0.32 mmol) in 100 mL methanol was added NiCl₂·6H₂O (0.08 g, 0.34 mmol). The mixture was refluxed for two hours, after which the amount of solvent was lowered (~20 mL) under reduced pressure. Upon addition of diethyl ether (150 mL), the red product precipitated and was isolated by filtration. The product was crystallized from a THF solution top-layered with diethyl ether to yield brown crystals which were analyzed using single crystal X-ray diffraction. ESI-MS MeOH m/z: [HL₂Ni₂]⁺, 754.9, 100%; [HLNi]⁺, 374.2, 79%.

Synthesis of $Mn(II)_{3L_2}Cl_2(EtOH)_3$ (5). To a solution of 2 (0.15 g, 0.31 mmol) in 100 mL methanol was added a small excess of $Mn(CH_3COO^-)_2 \cdot 4H_2O$ (0.08 g, 0.38 mmol). The red solution was stirred overnight, after which the solvent was removed under reduced pressure. The orange powder was dissolved in ~20 mL of methanol, and upon addition of diethyl ether (100 mL), the product precipitated and was isolated by filtration. The product was crystallized from an ethanol solution top-layered with diethyl ether to yield red-orange crystal bars which were analysed using single crystal X-ray diffraction. ESI-MS MeOH m/z: [H(L)Mn]⁺, 371.3, 41%; [not attributed] 263.7, 100%.

Synthesis of $Mn(II)Zn(II)L(MeOH)(H_2O)$ (6). To a solution of 2 (13.0 mg, 0.03 mmol) in 15 mL methanol was added an excess of $Zn(CH_3COO)_2 \cdot 2H_2O$ (7.70 mg, 0.04 mmol). The orange mixture was stirred overnight, after which the solvent was removed under reduced pressure. The product was crystallized from a methanol solution top-layered with diethyl ether to yield red crystals which were analysed using single crystal X-ray diffraction. ESI-MS MeOH m/z: $[HL_2MnZn]^+$, 749.9, 26%; $[HL_2Mn_2]^+$, 741.1, 28%; $[H(L)Mn(MeO^-)]^+$, 402.1, 24%; $[H(L)Mn]^+$, 371.2, 100%.

Synthesis of $Co(II)_{4}L_{2}Cl_{4}(acetone)_{2}$ (7). To a solution of 3 (0.15 g, 0.31 mmol) in 100 mL methanol was added $Co(CH_{3}COO)_{2}$ · $4H_{2}O$ (0.08 g, 0.31 mmol). The dark red-brown solution was stirred overnight, after which the solvent was removed under reduced pressure. The brown powder was dissolved in ~20 mL of methanol, and upon addition of diethyl ether (100 mL) the product precipitated and was isolated by filtration. The product was crystallized from an acetone solution top-layered with diethyl ether to yield dark brown crystal hexagonal bars which were analysed using single crystal X-ray diffraction. ESI-MS MeOH m/z: $[HL_2Co_2]^+$, 749.1, 79%; $[H(L)Co]^+$, 375.3, 100%.

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Keywords: Magnetic properties • Pincer ligand • Manganese • Cobalt

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In the quest for single molecule magnets (SMMs), several new homo- and heterometallic (Co, Mn, Ni, Zn) paramagnetic coordination compounds have been synthesized, based on a rigid diimine-pyridine pincer ligand. X-ray crystallography reveals their structure, while magnetic studies reveal ferromagnetic exchange interactions in some of them.