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Trinuclear first row transition metal complexes of a hexapyridyl, trialkoxy 1,3,5-triarylbenzene ligand†

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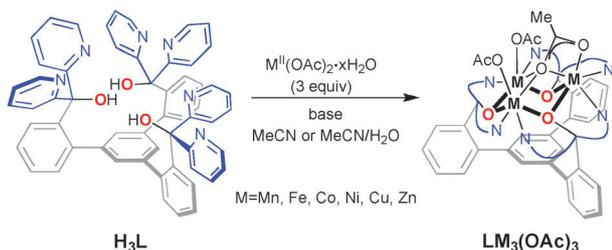
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Trinuclear complexes of Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} were synthesized using a ligand architecture based upon a 1,3,5-triarylbenzene core decorated with six pyridines and three alkoxide moieties. Characterization via X-ray diffraction, NMR, and magnetism studies is discussed.

The active sites of several enzymes involved in dioxygen chemistry (laccase, ascorbate oxidase, the oxygen evolving center of photosystem II) display three or more first row transition metal centers.¹ Synthetic catalysts for water oxidation are also proposed to be multinuclear.²

In continued efforts to rationally design multinucleating scaffolds, a 1,3,5-triarylbenzene framework was utilized to hold three multidentate binding sites near each other. 1,3,5-tris(2-(di(2-pyridyl)hydroxymethyl)phenyl)benzene (**H₃L**, Scheme 1) is accessible in two steps from commercially available starting materials.³ Trinuclear copper complexes supported by framework **L** have been synthesized containing a conserved Cu₃(μ-OR)₃ central moiety; varying the capping anions from halides, phosphate, tetrafluoroborate, and triflate causes subtle structural changes that affect the magnetism of these complexes.³

Protonated and deprotonated dipyridylhydroxymethyl moieties are known to exhibit an array of coordination modes, from tridentate N,O,N coordination of a single metal center to



Scheme 1 Synthesis of first row divalent trinuclear metal complexes with deprotonated **H₃L**. Acetate binding mode is variable (see text).

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more complicated bridging patterns of up to three metals.⁴ Although the M^{II}₃(μ-OR)₃ structural motif is commonly found in higher nuclearity clusters in complexes of 2,2'-dipyridylketone⁴ and as part of self-assembled tetranuclear clusters such as cubanes⁵ and defective dicubanes,⁶ the motif is less common in trinuclear complexes.⁷ To further investigate the metal coordination potential of **H₃L** and its control over cluster nuclearity, trinuclear complexes of **L** containing other first row transition metals were targeted.

Metallation studies were initiated with the acetate salts of the first-row metals Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} in the presence of base. Addition of three equivalents of solid M^{II}(OAc)₂·xH₂O to a suspension of **H₃L** in acetonitrile or a mixture of acetonitrile–water followed by three equivalents of a base such as sodium hydroxide or triethylamine resulted in complete dissolution of insoluble materials within 12 h. Analytically pure crystals were obtained by vapor diffusion of diethyl ether into dichloromethane or chloroform solutions of the reaction products.

Single crystal X-ray diffraction (XRD) studies demonstrate the trinucleating nature of the deprotonated **H₃L** framework to give complexes generally formulated as LM₃(OAc)₃ (Fig. 1a). The three metal centers are bridged by three alkoxides forming a six membered ring, and the pendant pyridines coordinate with the two pyridines of each dipyridyl moiety bound to adjacent metal centers. The coordination environment is completed by acetate counterions.

The LM₃ core displays pseudo-C₃ symmetry induced by a twist of each dipyridylmethoxide arm. This binding mode renders the two pyridines of each arm different, which is reflected in variations in the M–N bond lengths (Table 1). The M–O (alkoxide) bonds are also differentiated albeit less than the M–N bonds—the largest difference observed is about 0.05 Å. The elongated M–N bonds correspond to the three pyridines *trans* to alkoxide ligands. The pyridines located below the plane of the three metals and displaying shorter M–N distances are roughly *trans* to the bridging acetates. M–O (alkoxide) bonds *trans* to acetates are slightly shorter than those *trans* to pyridines. These variations may be caused by the larger *trans* influences of pyridine and alkoxide *vs.* acetate, but distortions caused by steric strain in the ligand framework cannot be ruled out. Consistent with the increase in the ionic radius, the metal–ligand distances increase from Ni to Mn and the M–M distances increase from 3.182(4) Å for Ni to 3.415(1)–3.464(1) Å for Mn. The ligand

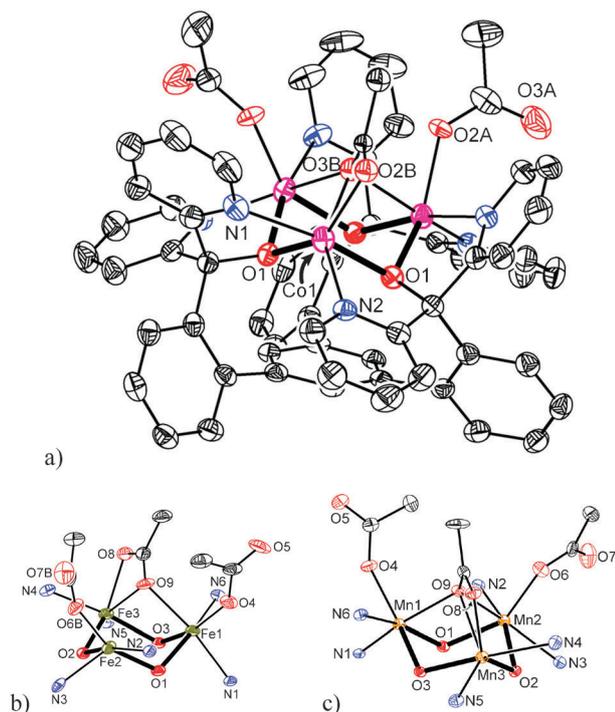


Fig. 1 (a) Solid-state structure of $\text{LCo}_3(\text{OAc})_3$. Coordination environments of (b) $\text{LFe}_3(\text{OAc})_3$ and (c) $\text{LMn}_3(\text{OAc})_3$ taken from the solid-state structures. The $\text{M}^{\text{II}}_3(\mu\text{-OR})_3$ structural motif is in bold; hydrogen atoms and solvent are not shown for clarity.

Table 1 Metal–metal and average metal–nitrogen distances

Compound	M–N <i>trans</i> to alkoxide (Å)	M–N <i>trans</i> to acetate (Å)	M–M (Å)
$\text{LMn}_3(\text{OAc})_3$	2.336(3)	2.232(6)	3.415(1)–3.464(1)
$\text{LFe}_3(\text{OAc})_3$	2.232(3)	2.150(3)	3.238(6)–3.456(6)
$\text{LCo}_3(\text{OAc})_3$	2.213(2)	2.091(2)	3.228(2)
$\text{LNi}_3(\text{OAc})_3$	2.127(3)	2.037(3)	3.182(4)
$\text{LCu}_3(\text{OAc})_3$	2.027(5)	2.081(5)	3.1822(7)–3.3282(7)
$\text{LZn}_3(\text{OAc})_3$	2.229(7)	2.056(7)	3.1975(9)–3.4199(9)

framework accommodates the different size metals by allowing for twist around the aryl–aryl bonds and of the C–O vector vs. the plane of the pendant arene.

Systematically changing the nature of the metal centers from Mn^{II} to Zn^{II} does not disrupt the trinuclear core, but changes the binding mode of the acetates. Three capping acetates are present for $\text{LM}_3(\text{OAc})_3$ ($\text{M} = \text{Mn–Ni}$); two acetates bind in monodentate and one in bidentate fashion. The bidentate acetate bridges two or three metal centers *via* a μ_2 - or μ_3 -oxygen atom. For $\text{M} = \text{Cu}$ and Zn , single crystal XRD studies show two acetates bound to the trimetallic core (see ESI†). However, a third outer sphere acetate required for charge balance could not be located due to disorder. This change in coordination mode may be due to the smaller size of Cu^{II} and Zn^{II} hindering the binding of a third acetate.

^1H NMR spectroscopy and mass spectrometry studies confirm that the trinuclear cores of the complexes are maintained in solution. The ^1H NMR spectra of $\text{LM}_3(\text{OAc})_3$ ($\text{M} = \text{Fe–Zn}$) display fourteen resonances, with chemical shifts between -20 and 160 ppm for the paramagnetic species.⁸ Thirteen signals correspond to protons on framework L, consistent with the

*pseudo-C*₃-geometry observed in the solid-state. The single peak assigned to the acetate counterions is indicative of fluxional processes that exchange the capping ligands on the NMR time scale.

The magnetism of triangular clusters has been studied in the context of spin frustration and molecular magnets.⁹ Although several alkoxo-bridged Ni^{II}_3 and Cu^{II}_3 complexes have been studied,^{7d,10} there have been fewer investigations of Mn^{II}_3 , Fe^{II}_3 , and Co^{II}_3 cores. Triangular clusters of manganese and iron more commonly contain higher oxidation state metal centers.¹¹ The present $\text{LM}_3(\text{OAc})_3$ family provides an opportunity to systematically study the magnetic interactions of several divalent transition metals in a single trinuclear system, allowing for better understanding of the magneto-structural characteristics of trinuclear complexes.

Magnetic susceptibility measurements were performed on powdered crystalline samples of $\text{LM}_3(\text{OAc})_3$ ($\text{M} = \text{Mn, Fe, Co, Ni, Cu}$) in the temperature range 4–300 K. At room temperature, the $\chi_M T$ values approach 12.0, 9.0, 6.7, 3.3, and $1.0 \text{ cm}^3 \text{ K mol}^{-1}$, respectively (Fig. 2). The difference between these and the spin-only values may be due to spin–orbit coupling and population of excited states.¹² Upon cooling, the $\chi_M T$ values decrease gradually and then drop sharply below 40 K, indicating the presence of antiferromagnetic exchange interactions. With the exception of the $\chi_M T$ values of $\text{LCu}_3(\text{OAc})_3$, which approach a plateau near the expected value for the spin-only $S = 1/2$ state (*ca.* $0.4 \text{ cm}^3 \text{ K mol}^{-1}$), the $\chi_M T$ plots do not approach obvious limiting values at 4 K.

To determine the magnitude of exchange between neighboring metal centers, the magnetic behavior of the compounds was analyzed using the isotropic spin Hamiltonian [eqn (1)] considering the two exchange pathways of an isosceles triangular arrangement. Application of the Van Vleck equation according to the Kambe vector method¹³ yields the magnetic susceptibility equation [eqn (2)].

$$H = -2J[(S_1S_2) + (S_2S_3)] - 2J_{13}(S_3S_1) \quad (1)$$

$$\chi_M = \frac{N_A \beta^2 g^2}{3kT} \left(\frac{\sum S'(S'+1)(2S'+1)\Omega(S') \exp(-W(S')/kT)}{\sum (2S'+1)\Omega(S') \exp(-W(S')/kT)} \right) \quad (2)$$

The Curie–Weiss parameter θ was included to account for possible intermolecular interactions.¹⁴

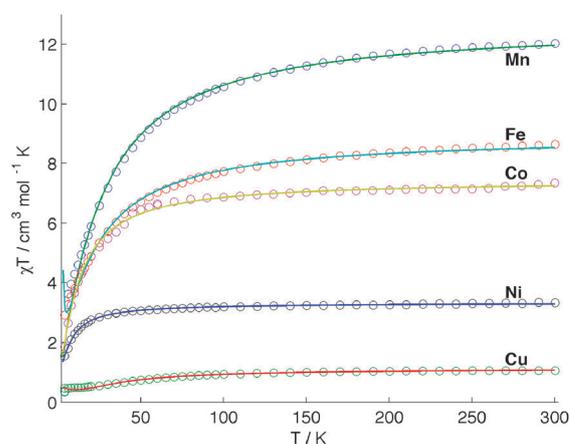


Fig. 2 Plots of $\chi_M T$ vs. T . Solid lines show the best fits obtained.

Table 2 Magnetic susceptibility parameters¹⁷

Compound	J (cm ⁻¹)	g	θ (K)	R ($\times 10^{-4}$)
LMn ₃ (OAc) ₃	-1.1	1.97	0.53	10
LF ₃ (OAc) ₃	-1.4	1.99	2.35	1.6
LCO ₃ (OAc) ₃	-1.2	2.30	0.23	1.9
LNi ₃ (OAc) ₃	-1.2	2.11	0.74	0.4
LCu ₃ (OAc) ₃	-13.7	2.01	0.75	12

The fits were not appreciably improved when modeling two J values instead of one; as a result, the magnetism data were simulated for an equilateral triangle arrangement of spins, corresponding to the approximate C_3 -symmetry of the $M_3(OR)_3$ cores (without acetates).¹⁵ It should be noted that the modeled parameters approximate the spins of each compound as isotropic and do not account for the lowered symmetry of each complex induced by the coordinated acetates. Nevertheless, the simulated magnetic susceptibility parameters (Table 2) show a good fit to the experimental data ($R \sim 10^{-4}$). In accordance with the $\chi_M T$ plots, the simulated parameters show that compounds LM₃(OAc)₃ display weak antiferromagnetic exchange coupling (Table 2). Except for LCu₃(OAc)₃ ($J = -13.7$ cm⁻¹), the best fits were obtained with $|J| < 2$ cm⁻¹. Although the ground states are predicted to be $S = 0$ or $S = 1/2$ for an equilateral triangle of antiferromagnetically coupled ions, such small J values indicate that higher spin states are thermally populated even at low temperatures.¹⁶ For these complexes, the presence of spin equilibria between these states is consistent with the observation that no limiting values of $\chi_M T$ are reached at 4 K.

Due to the presence of multiple types of bridging ligands, it is difficult to definitively assign the exchange pathways in these LM₃(OAc)₃ complexes.¹⁸ Since there are few alkoxo-bridged trinuclear complexes containing metals other than Cu^{II}—and none with Fe^{II} to our knowledge—there is yet no clear correlation between the J constants and common structural parameters such as M–M distances or M–O–M angles.¹⁹ Previously studied acetate-bridged trinuclear clusters of divalent metals have been shown to have similar intramolecular exchange interactions.²⁰ Alkoxo- and phenoxo-bridged tricobalt(II), trinickel(II), and triiron(III) clusters all show small antiferromagnetic coupling.^{7e,21} While there are no examples of Mn^{II} bridged by alkoxides, amido-bridged²² or carboxylate-bridged²³ Mn^{II} clusters also demonstrated antiferromagnetic coupling of magnitudes similar to LMn₃(OAc)₃.

In summary, the trinucleating ligand described above is a scaffold capable of supporting different first-row transition metals in a conserved trinuclear core geometry. These trimetallic complexes have been structurally and spectroscopically characterized. Current efforts are underway to explore multielectron reactivity and small molecule activation with these clusters.

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