Correlating Bridging Ligand with Properties of Ligand-Templated $[Mn^{II}_{3}X_{3}]^{3+}$ Clusters (X = Br⁻, Cl⁻, H⁻, MeO⁻)

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Supporting Information



ABSTRACT: Polynuclear manganese compounds have garnered interest as mimics and models of the water oxidizing complex (WOC) in photosystem II and as single molecule magnets. Molecular systems in which composition can be correlated to physical phenomena, such as magnetic exchange interactions, remain few primarily because of synthetic limitations. Here, we report the synthesis of a family of trimanganese(II) complexes of the type Mn_3X_3L (X = Cl⁻, H⁻, and MeO⁻) where L^{3-} is a tris(β -diketiminate) cyclophane. The tri(chloride) complex (2) is structurally similar to the reported tri(bromide) complex (1) with the Mn_3X_3 core having a ladder-like arrangement of alternating M–X rungs, whereas the tri(μ -hydride) (3) and tri(μ -methoxide) (4) complexes contain planar hexagonal cores. The hydride and methoxide complexes are synthesized in good yield (48% and 56%) starting with the bromide complex employing a metathesis-like strategy. Compounds 2–4 were characterized by combustion analysis, X-ray crystallography, X-band EPR spectroscopy, SQUID magnetometry, and infrared and UV–visible spectroscopy. Magnetic susceptibility measurements indicate that the Mn_3 clusters in 2–4 are antiferromagnetically coupled, and the spin ground state of the compounds (S = 3/2 (1, 2) or S = 1/2 (3, 4)) is correlated to the identity of the bridging ligand and structural arrangement of the Mn_3X_3 core (X = Br, Cl, H, OCH₃). Electrochemical experiments on isobutyronitrile solutions of 3 and 4 display broad irreversible oxidations centered at 0.30 V.

he synthesis and design of polynuclear manganese compounds has been motivated by two main goals: (i) to develop models that shed light on the mechanism of the Mn₄Ca water oxidizing complex (WOC) in photosystem II¹ and (ii) to synthesize clusters that display single molecule magnetism by harnessing the magnetic anisotropy of the Mn^{III} cation.²⁻⁵ The water oxidizing complex in photosystem II catalyzes the four-electron oxidation of two molecules of water to liberate dioxygen.⁶ The individual Mn cation formal oxidation states in the reduced S₀ state of the cofactor remain unclear with many models suggesting a high oxidation model, $(Mn^{III})_3Mn^{IV}$, whereas others propose a low oxidation model, $(Mn^{III})_3Mn^{II}$.⁷ As such, most targeted attempts toward modeling the WOC focus on 3+ and higher metal oxidation states. Both research directions described above are informed by a fundamental understanding of the relationships between structure, composition, and electronic structure, including how exchange interactions between the metal centers are mediated by intervening ligands.

Superexchange between metal centers is governed by the interaction of magnetic orbitals on transition metals through bridging ligands. Typically, coupling in multinuclear systems obeys the Goodenough–Kanamori–Anderson (GKA) rules.^{8–10} These rules correlate the M–L–M bond angle, where L is a single-atom bridging ligand, to the magnitude and sign of the exchange interaction; linear M–L–M units afford antiferromagnetic exchange, whereas M–L–M angles approaching 90° lead to ferromagnetic exchange. In addition, contracted metal–metal separations, which can result from short M–L distances and/or higher metal oxidation states, can

Received: August 8, 2017 Published: September 18, 2017 enhance the exchange interaction between magnetically coupled metal centers by strengthening through-space interactions or direct metal-metal exchange.^{8,11,12} In the ideal scenario, one would describe the effect of a particular parameter by selectively varying that structural or electronic feature (e.g., bridging ligand identity) across a series of compounds. Although many such studies have been conducted on families of mono- and dinuclear compounds,¹³⁻²⁰ structurally related families of higher-nuclearity compounds are rare, as most current methods rely on complex self-assembly processes in which subtle changes can lead to large perturbations (e.g., altered cluster nuclearity).^{4,21-23} If accessible, however, families of this type offer a unique opportunity to correlate specific parameters with magnetic phenomena in polynuclear materials.^{24–26} Indeed, similar ideas have been applied to study charge delocalization in multinuclear systems.²⁷⁻³² With respect to polynuclear manganese chemistry, manganese(III) and -(IV) complexes have received particular attention because of their large magnetic anisotropy and biological relevance (e.g., WOC, class 1B ribonucleotide reductases).^{6,33} Contrastingly, detailed analysis on polynuclear Mn^{II} compounds remains underexplored.

Murray and co-workers have previously demonstrated that a tris(β -diketimine) cyclophane templates the assembly of trimetallic clusters of the type M_3X_3L with two possible arrangements of the $[M_3X_3]^{3-}$ core: a hexagonal form with alternating M^{n+} and X^{z-} ions, and a ladder-like arrangement where the order of M^{n+} and X^{z-} alternates from rung to rung. In addition, ligand substitution on these complexes can be readily accomplished using a simple metathesis approach.^{34–39} Here, we report the application of this approach to the synthesis and characterization of a series of $Mn^{II}_3X_3L$ complexes ($X^- = Br^-$, Cl^- , H^- , and MeO⁻, the first of which was reported previously³⁴), with specific attention to the electrochemical properties and magnetic exchange interactions.

RESULTS AND DISCUSSION

Synthesis and Structures of Trimanganese(II) Complexes. As expected, a synthetic procedure analogous to that reported for Mn_3Br_3L (1)³⁴—viz., deprotonation of H_3L with benzyl potassium (BnK) followed by addition of $MnCl_2$ yields Mn_3Cl_3L (2) as a yellow powder (60%, Scheme 1),



Scheme 1. Synthesis of Trimanganese(II) Complexes 1-4

which can be obtained as needle-like crystals from evaporation of a benzene solution. From single crystal X-ray diffraction data, we were able to obtain a molecular structure of **2**; however, the structure solution models best as a contamination of the central μ_3 -chloride with a lighter atom, selected for simplicity as partial contribution from an O atom. We speculate that the presence of a light-atom impurity in the structure may arise from minor decomposition over the course of the several days required to obtain X-ray quality crystals. This formulation does not agree with combustion analysis or infrared spectra of the bulk powder, and we failed to obtain crystals that afforded a structure consistent with our other analyses despite numerous attempts. We, therefore, present our analysis of the structure with the highest chloride content.

In the solid-state structure of 2, each Mn^{II} center is coordinated by the N,N-chelate of a β -diketiminate arm and μ - and μ_3 -chlorides, adopting either a pseudotetrahedral (Mn2 and Mn3, $\tau_4 = 0.87-0.91$) or pseudotrigonal bipyramidal (Mn3, $\tau_5 = 0.63$) geometry (Figure 1).⁴⁰ The dihedral angle between the two arene linkers in 2 $(7.01(7)^{\circ})$ is surprisingly larger than that of 1 $(4.68(3)^\circ)$ despite the significant decrease in the radius of the μ_3 donor from 2 to 1. We suggest that the larger angle is a consequence of the shorter distance between the two μ -chlorides (Cl1 and Cl3) and the Mn cations, which in turn creates greater steric conflicts with the ethyl groups on the aryl caps. The Mn-(μ -Cl) bond lengths in 2 are asymmetric with long interactions (>2.6 Å) to the trigonal bipyramidal Mn^{II} (Mn3) and shorter ones to the four coordinate Mn^{II} centers (~2.4 Å). The longer interactions are at the upper end of the reported distances for four or five coordinate Mn^{II} centers as reported in the Cambridge Structural Database (Figure S14), but consistent with the short Mn3–(μ_3 -Cl) and Mn3–N_L bond distances (where N_L = N-donor of β -diketiminate arm). The μ_3 -Cl is nearly coplanar with the three manganese(II) ions (deviation from Mn_3 plane = 0.011(2) Å). The pseudo planar $Mn_3(\mu_3-Cl)$ unit is rare in manganese chemistry, the only other reported examples being a series of Mn_8 helicates in which the $Mn-(\mu_3-Cl)$ distances (2.368(1)-2.836(3) Å)⁴¹⁻⁴³ are significantly longer than in 2 (2.093(2)-2.193(2) Å). The N_L-Mn-N_L angles in 2 are smaller than in 1, and consistent with the shorter Mn…Mn distances and greater M-N_L bond lengths in 2 as compared to 1. The N···N distances in 2 are similar to those in compounds 1, 3, and 4, but longer than those observed in the mono- and dimetallic β -diketiminate Mn^{II} chlorides complexes reported by Roesky and co-workers (2.959(9)-3.021(3) Å).⁴⁴ Taken together, these trends are consistent with a smaller guest atom occupying the central cavity of 2 as compared to 1 (ionic radius of Cl, 1.81 Å, vs Br, 1.96 Å).45 It is interesting that the $[Mn_3Cl_3]^{3+}$ core of 2 does not adopt the planar hexagonal structure observed in the trihydride and -methoxide analogues (vide infra) or in the Co₃Cl₃L (unpublished data) and Zn₃Cl₃L³⁷ congeners. Possible explanations for the observed halide bonding modes in 2 include both steric and electronic effects. Namely, the metal ion identity influences the N_L...N_L distance,⁴⁶ which modulates the steric conflicts between μ ligands and the ethyl substituents on the benzene caps.³⁴ We cannot exclude distortions arising from spin-frustration;⁴⁷ however, large structural changes as would be required here (i.e., hexagonal vs ladder-like) are very rare and only implicated for trimetallic clusters with direct exchange pathways.⁴

Addition of KBEt₃H to a toluene solution of 1 afforded the corresponding tri(hydride) complex, Mn_3H_3L (3), in modest yield (48%, Scheme 1) after recrystallization from benzene. X-ray quality single crystals of 3 were obtained from toluene solutions stored at -35 °C. The tri(hydride) crystallizes in the $P6_3/m$ space group and has a 3-fold crystallographically imposed symmetry axis. In the solid-state structure each Mn^{II} ion is pseudotetrahedral ($\tau_4 = 0.90$) with each metal atom



Figure 1. Solid-state structures of 1-4 (from left to right) with C, N, Mn, O, Cl, Br, and H atoms illustrated as gray, blue, yellow, red, green, and maroon 50% ellipsoids, respectively. Cl2 in 2 is partially occupied with chloride and a light atom, modeled as O. Hydride ligands in 3 are shown as dark gray spheres. Hydrogen atoms and solvents of crystallization omitted for clarity. Structure 1 previously reported in ref 34.

	Mn_3X_3L	$\mathbf{X} = \mathrm{Br} \left(1 \right)^{\mathbf{b}}$	X = Cl(2)	X = H (3)	$X = OCH_3 (4)$				
	N_{L} - Mn - N_{L}^{a} (deg)	98.04(7)-101.24(7)	94.35(9)-99.28(1)	92.1(2)	96.5(3)-97.6(3)				
	Mn–X–Mn (deg)	79.70(3)-159.42(3)	80.17(3)-159.2(1)	117.1(5)	115.9(4)-121.8(4)				
	N…N (Å)	3.105(2)-3.150(2)	3.022(3)-3.148(3)	3.036(5)	3.09(1)-3.137(9)				
	Mn–X (Å)	2.4435(4)-2.6483(4)	2.093(2)-2.665(1)	1.94(1)	1.998(7)-2.023(8)				
	M…M (Å)	3.280(1)-5.093(1)	3.273(1)-4.1503(8)	3.317(1)	3.414(3)-3.518(2)				
	Mn $-N_L$ (Å)	2.035(2) - 2.070(2)	2.060(3) - 2.079(2)	2.109(3)	2.065(9)-2.10(1)				
$^{a}N_{L}$ = two N atoms on one diketiminate arm bound to an Mn ^{II} ion. ^b First reported in ref 34.									

Tab	le 1	1.	Relevant	Bond	Angles	s (deg) and	D	Distances	(A	L)	for	1-4	1
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Table 2. Relevant Bond Angles	(deg) and Distances ((Å) for	Isostructural	Trinuclear H	vdrides
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M_3H_3L	$M = Mn^{II}$	$M = Fe^{II}$	$M = Co^{II}$	$M = Zn^{II}$					
$N_L-M-N_L^a$ (deg)	92.1(2)	90.23(8)-91.11(9)	92.1(1)-92.6(1)	93.3(2)-94.3(2)					
M…M (Å)	3.317(1)	3.2570(5)-3.3562(5)	3.3226(7)-3.3473(7)	3.271(1)-3.3418(8)					
N…N (Å)	3.036(5)	2.911(3)-2.914(3)	2.905(4) - 2.924(4)	2.971(5) - 2.985(6)					
М - Н (Å)	1.94(1)	1.79(3) - 1.86(2)	1.83(2) - 1.97(2)	1.74(6) - 1.82(5)					
$M-N_L$ (Å)	2.109(3)	2.039(2) - 2.057(2)	2.013(2) - 2.034(3)	2.034(4) - 2.044(4)					
${}^{3}N_{I}$ = two N atoms on one diketiminate arm bound to an M ^{II} ion.									

coordinated by the N,N-chelate of a β -diketiminate arm and two bridging μ -hydride ligands. The $[Mn_3(\mu-H)_3]^{3+}$ core adopts a planar hexagonal arrangement and is isostructural with other tri(hydride) clusters reported by our group $[M_3(\mu -$ H)₃L, M = Fe^{II}, Co^{II}, and Zn^{II}].^{37,39} With the caveat that the hydride positions are not unambiguously determined because of the limitations of the experimental method, we briefly consider a comparison of the structure of 3 vis-à-vis other highspin Mn^{II} hydride complexes. The Mn-H bond length in 3 is longer than in the related dimer $[^{Dep}L(MnH)]_2$ ($^{Dep}L =$ $CH[C(Me)N(2,6-Et_2C_6H_3)$ reported by Driess et al. $(1.86(2)-1.87(2) \text{ Å})^{49}$ and in an amidinate-supported cluster with an isostructural $Mn_{3}^{II}(\mu-H)_{3}$ core (1.84(5)-1.87(5)).⁵⁰ We speculate that the unusually long Mn-H interactions result from the ability of the relatively rigid cyclophanate ligand to impose long M…M distances, as has been observed for the other previously reported members of the isostructural M₃H₃L series (Table 2).^{37,39} A similar conclusion is obtained if one considers the metal metal-metal distances rather than the purported metal-hydride bond lengths.

Using a metathesis strategy, a mixture of 1 and NaOCH₃ in THF was stirred at 60 °C for 12 h yielding the trimanganese-(II) tri(methoxide), $Mn_3(OCH_3)_3L$ (4), in reasonable yield (56%, Scheme 1) after crystallization by slow evaporation of a dichloromethane solution. In HRMS/ESI measurements collected on dichloromethane solutions of 4, we observed a

molecular ion with the expected isotopic pattern and mass-tocharge ratio for $[Mn_3(OCH_3)_3L + H]^+$ (Figure S4). An intense peak is observed at 499 cm⁻¹ in IR spectra of 4 (Figure S3), which is assigned to the Mn–O–Mn vibration and compares well with Fe₃(OCH₃)₃L (508 cm⁻¹).⁵¹ We were unable to generate single crystals of 4, obtaining twinned crystals in all cases. Consequently, all structure solutions of 4 have distorted thermal ellipsoids at a number of atom positions (Figure 1). In the solid-state structure of 4 each Mn^{II} center is pseudotetrahedral ($\tau_4 = 0.88 - 0.92$), ligated by the N,N-chelate of a β diketiminate arm and two μ -methoxide ligands. The Mn…Mn distances in 4 are slightly longer than in 3 as might be expected given the larger covalent radius of O vs H. The Mn-OMe bond lengths (1.998(7)-2.023(8) Å, Table 1) are comparable to the di- and trimanganese(II) alkoxides synthesized by Power and co-workers $(1.851(5)-2.095(4) \text{ Å})^{52,53}$ but shorter than those in coordination polymers and tetramanganese(II) cubane clusters (2.152(5)-2.219(1) Å) reported by Du and Lippard, respectively.54,55

Murray and co-workers have previously suggested that the observed structure type—that is, the ladder-like array with alternating orientation of M–X rungs vs the hexagonal configuration—is dictated by a balance between the electronic demands of the metal centers and a steric conflict between the size of the anionic X⁻ donor and the distance between two adjacent ethyl groups on opposite arene caps.³⁴ Consistently,

we observe that the hydride (3) and methoxide (4) adopt M_3X_3 hexagonal arrangements comparable to those seen in the triiron(II) and -cobalt(II) compounds with bridging hydride, methoxide, and formate ligands, $^{39,51}_{39,51}$ whereas the chloride (2) adopts the ladder-like arrangement. However, the μ -chlorides both lie nearly eclipsed with the methylene C atoms of the proximal ethyl groups on the upper and lower arene caps. The position of these Cl⁻ donors contrasts with that of the μ and terminal bromides in 1 and the related iron and cobalt congeners in which the bromide lies beyond the methylene units of the ethyl substituents as expected to minimize steric conflicts.^{34,39} Moreover, the tri(μ -sulfido)triiron(III) core of the related Fe₃S₃L species adopts a hexagonal arrangement, which is relevant insofar as the metal ions in both 2 and Fe_3S_3L are d^5 and the ionic radius of S^{2-} is greater than that of Cl^{-,45} Although the N···N distances within the β -diketiminate arms of Fe_3S_3L are similar to those of 2, upon closer examination of this structure as compared to that of 2, we observe that the ethyl $-CH_2-\cdots S^{2-}$ distances in Fe₃S₃L (3.190(3) Å) are shorter than the $-CH_2-...(\mu-Cl^-)$ distances in 2 (3.282(2)-3.321(3) Å), indicating that there is a steric penalty associated with the shorter, more covalent $\text{Fe}^{\text{III}} - (\mu \text{-}\text{S}^{2-})$ bonds. This steric penalty is relieved in **2** by the longer, asymmetric $\text{Mn}^{\text{II}} - (\mu \text{-}\text{Cl}^{-})$ interactions and the shift of the third chloride from μ to μ_3 to give the ladder-like structure. This comparison, in which the larger, more covalent S²⁻ anion promotes the more sterically hindered hexagonal structure type, intimates that a fine balance between steric and electronic effects determines the structure type of members of the M₂X₂L series. A subset of us has also previously reported structures in which a μ_3 -sulfide or a μ_3 bromide is present within the internal cavity,^{35,56} suggesting that the ligand has sufficient flexibility to accommodate interstitial donors of various sizes. We therefore surmise that (i) the ligand is more flexible than one might anticipate based solely on the solid-state structure of the free base ligand and chemical intuition, which consequently allows the resultant trimetallic complexes to adopt various possible cluster motifs, and (ii) the observed structure type results from the balance between the electronics of the M-X interaction and the steric clash of the X anion with the ligand's ethyl groups. As a result, we hypothesize that electronic factors typically considered as weak relative to changes in the coordination environment (e.g., exchange interactions) may play a more dominant role in the structure type, as suggested in a triiron cluster from Betley and co-workers,⁴⁸ even in the absence of strong direct exchange interactions. NMR and other spectroscopic data collected on all trinuclear compounds supported by this ligand to date do not support that a mixture of more than one conformation is present in solution and that only one configuration selectively crystallizes, although this possibility cannot be rigorously excluded.

With this in mind, we turned to magnetic susceptibility measurements and cyclic voltammetry to evaluate possible electronic contributions to the structure type variation observed in this series.

Magnetic Susceptibility Measurements. To examine the electronic interactions between Mn^{II} centers in compounds 2–4, we measured and simulated the temperature-dependent magnetic susceptibility data collected at 100 G in the temperature range of 5–300 K (Figure 2), as well as the isothermal (8 K) magnetization up to 70 kG (Figures S8–S10). Magnetic susceptibility measurements for 1 were previously reported and are included here for comparison.³⁴



Figure 2. Temperature-dependent magnetic susceptibility plots for 1 (green triangles), 2 (blue diamonds), 3 (red circles), and 4 (black squares) collected at 100 G (top). Simulations (colored lines) were generated using the parameters shown in Table 3. Superexchange pathways (bottom) are shown for complexes 1-4 from left to right, respectively.

The Mn^{II} centers in compounds 1-4 are antiferromagnetically coupled at 300 K as evidenced by $\chi_{\rm M}T$ values below that anticipated for the spin-only moment for three non-interacting Mn^{II} centers (6.59–12.1 cm³·K·mol⁻¹ observed vs 13.1 cm³·K· mol^{-1} expected for g = 2.00 and three S = 5/2 ions). One possible explanation is that all centers are intermediate-spin S =3/2 ions, as reported for phthalocyanine complexes;⁵⁷ however, only the high-spin state is possible for pseudotetrahedral geometries and the weak ligand field surrounding the Mn^{II} centers. In addition, our simulations employing three S = 3/2centers give poor agreement with the experimental susceptibility (data not shown). We, therefore, considered each Mn^{II} center as S = 5/2 in our analyses. The magnetic moments of 1– 4 steadily decrease upon cooling to 5 K to final values of 2.70, 2.17, 0.783, and 0.357 $\text{cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ for 1–4, respectively. Using the observed $\chi_{\rm M}T$ values at 5 K as a guide, the ground-state spin state for 3 and 4 could correlate to S = 1/2 whereas 1 and 2 would be more consistent with an S = 3/2 ground state. In all cases, the slightly larger than expected magnetic moment at 5 K is attributed to population of thermally accessible low lying excited states as reported for other polynuclear manganese compounds supported by weak-field donors.⁵⁸⁻⁶¹

Magnetic susceptibility data for trinuclear metal complexes with antiferromagnetic exchange interactions typically cannot be simulated or fit using a spin Hamiltonian containing a single J term (i.e., an equilateral model), but require a Hamiltonian with at least two or three J terms (i.e., isosceles or scalene triangles, respectively).⁴⁷ Indeed, idealized 3-fold symmetric

systems composed of half-integer spins with a single *J* value are susceptible to magnetic Jahn–Teller distortion, in which the molecular symmetry is lowered to relieve the degeneracy of the ground state.^{62,63} Consistently, we were unable to simulate the data collected on solid samples of 2-4 using an equilateral model, and resorted to an isosceles rather than a scalene one to avoid overparametrization of the simulations.

The magnetic data obtained on samples of 2-4 were simulated as we have previously described for 1 using Easyspin⁶⁴ and a spin Hamiltonian with two *J* terms, *J* and *J'*, and a zero-field splitting term, *D*, as given below.³⁴

$$\mathcal{H} = -2J_{12}\vec{S}_1\cdot\vec{S}_2 - 2J_{13}\vec{S}_1\cdot\vec{S}_3 - 2J_{23}\vec{S}_2\cdot\vec{S}_3 + \sum_{i=1}^3 \left(D(S_i^z)^2 + \vec{B}\langle g \rangle \vec{S}_i\right)$$

Here, *D* is considered the same for all spins and the *g* tensor is assumed to be isotropic and identical for all spins. Each d⁵ metal ion in these compounds is anticipated to be S = 5/2based on the donor environment, which would suggest a small absolute value for D, as most D values measured for high-spin Mn^{II} complexes have magnitudes of less than 1 cm^{-1.19} Simulations of magnetometry data for such complexes have been previously restricted to $|D| < 1 \text{ cm}^{-1}$ or have forced D = $0.^{58,59,65-67}$ Here, we considered $-3 \text{ cm}^{-1} < D < 1 \text{ cm}^{-1}$ as the lower and upper bounds, respectively. Exchange pathways J = J_{12} and $J' = J_{13} = J_{23}$ were drawn to reflect the larger simulated value as coupling Mn^{II} centers through the shortest bonds in the case of 2 or the shortest through-space Mn...Mn distances. Specific parameters used to model magnetic susceptibility data (i.e., g, D, J, and J') are shown in Table 3. Murray and coworkers have previously used this approach to simulate the susceptibility data for other trimetallic complexes.^{34,68}

Table 3. Magnetic Parameters for 1-4

					Xn	$\chi_{ m M} T$		
	g	$J(cm^{-1})$	$J' ({\rm cm}^{-1})$	$D (cm^{-1})$	300 K	5 K		
1	2.02	-5.1	-1.7	+0.60	12.1	2.70		
2	2.02	-10.2	-4.6	-0.35	9.14	2.17		
3	2.02	-19.1	-11.8	+0.17	6.59	0.783		
4	1.99	-10.6	-10.6	0	7.08	0.357		

Overall, the exchange coupling constants for 1-4 (-1.7 to -19.1 cm^{-1}) are consistent with antiferromagnetic exchange between the Mn^{II} centers in the four compounds. These values are comparable to those reported by Johnson and co-workers for triamidophosphine-supported trimanganese(II) compounds $(-7.0 \text{ to } -11.0 \text{ cm}^{-1})^{69}$ but larger than reported for carboxylate-bridged trimanganese(II) complexes $(-0.63 \text{ to} -2.36 \text{ cm}^{-1})$.^{58,59,67,70} Our values here border on those reported by Betley and co-workers $(-17.5 \text{ to } -49.0 \text{ cm}^{-1})$ for Mn_3 clusters supported by a tris(*o*-phenylenediamide) ligand, in which the acute $Mn-(\mu-N)-Mn$ bond angles imposed by the ligand are the proposed reason for the larger values of J.61 As expected from the GKA rules, the magnitude of the antiferromagnetic exchange scales reasonably well with the Mn-X-Mn angles where the largest angles correspond to the most negative J values and the most acute angles with the least negative J values. As might be anticipated, we also observe a trend between the magnetic susceptibility and structure type and the identity of the bridging ligand in 1-4. For example, the configuration of the Mn₃X₃ core as an alternating hexagonal array (viz., 3 and 4) correlates with larger average values for the

exchange constants as compared to the distorted ladder-like configuration (viz., 1 and 2). Thus, our discussion will focus on 1 and 2 and then consider simulations of 3 and 4 together.

Previous experimental and theoretical investigations have demonstrated larger antiferromagnetic coupling mediated by bromide versus chloride bridges between Cu^{II} and Mn^{II} centers in polynuclear compounds, 71-75 although the opposite has been reported in one case in which the Cu-X distances are extremely long.⁷⁶ Here, we observe the inverse of the reported trend in our simulation parameters for the tri(chloride) (2) and tri(bromide) (1); that is, more negative J values are observed for 2 vs 1 (c.f. -10.2 and -4.6 cm⁻¹ vs -5.1 cm⁻¹ and -1.7 cm^{-1}). However, the trend observed for |D|, which is larger for 1 than for 2, agrees with that expected from previous reports for mononuclear high-spin Mn^{II} halides, in which $|D|_{Br}$ > | $D|_{Cl}$.^{77–83} The departure from the anticipated exchange constant trend as a function of halide (i.e., Br > Cl) could arise from the additional exchange pathway(s) in 2 as compared to 1. For example, there are two μ -chlorides and one μ_3 chloride in **2** vs one μ -, one μ_3 -, and one terminal bromide in **1**. In addition, the Mn…Mn distances are shorter for 2 vs 1 as expected from the smaller radius of Cl⁻ vs Br⁻ and resulting shorter Mn-Cl bonds. Similar to 1, the ground state for 2 corresponds to one of the molecular quartets in the S = 3/2state.

From our simulations, 3 and 4 both have the S = 1/2molecular doublets as their ground states. This spin ground state is characteristic of Jahn-Teller distorted spin-frustrated triangular trimetallic systems containing metal ions with noninteger spins.^{66,67,69,84,85} Although the low-temperature magnetic susceptibility of 4 is in reasonable agreement with an S = 1/2 ground state, the 5 K χT value of 3 lies between that expected for an S = 1/2 and an S = 1 state. Given that a ground state of S = 1 is unlikely for a noninteger spin system (e.g., S =15/2), the observed magnetic data are consistent with occupation of an S = 1/2 ground state along with thermal population of excited states (e.g., S = 3/2 and 5/2). This population of low-lying excited spin states is confirmed in our EPR measurements (vide infra). One notable difference between 3 and 4 is that the susceptibility data for 4 were well-simulated with $J = J' = -10.6 \text{ cm}^{-1}$, consistent with a spinfrustrated system, whereas data for 3 could be readily modeled using two distinct values for I = -19.05 cm⁻¹ and J' = -11.8cm⁻¹. Initially, we were somewhat surprised by the relative magnitudes of the I values from the simulations of the susceptibility data for 3 and 4. Analysis of the role of bridging hydrides in mediating superexchange in dinuclear complexes is typically obscured by the presence of direct exchange through metal-metal bonding,⁸⁶ but was anticipated to afford weaker coupling than pseudohalides, which can be rationalized by the additional overlap expected for methoxide (i.e., $\sigma + \pi$) as compared to hydride. However, in the case of three high-spin Mn^{II} centers, the lack of π interactions in 3 may eliminate potential competing coupling pathways, thereby mediating stronger antiferromagnetic coupling when compared to 4. Additionally, hydride bridging ligands were previously reported to mediate strong magnetic coupling in polynuclear compounds owing to the covalent metal-hydride interaction and large diffuse radius of the hydride donor (~ 2 Å).⁸⁷ We are aware of another particular example in which bridging hydrides were reported to mediate magnetic exchange comparable to O^{2-,88} but this trend is rare for molecular species. Another possible rationale for the larger coupling constants in 3 may be spinpolarization or long-range coupling mediated by the π -system of the aryl caps. Similar phenomena have been reported in related 2- and 3-fold symmetric benzene templated copper cyclophane complexes.^{89–92} Consistently, Ermert et al. noted that the Zn–H resonances were unusually far upfield in ¹H NMR spectra of the zinc(II) congener of **3**, Zn₃H₃L. That result was attributed to ring-current effects based on the position of the hydrides relative to the π -clouds of the two arene caps. Similarly, the [Mn₃X₃]³⁺ ring is expected to weakly interact with the π -cloud of the two arene caps, thereby allowing polarization of the benzene π -systems that influences Mn^{II} exchange within clusters templated with L^{3–37}

We simultaneously modeled the isothermal magnetization and the dc susceptibility data in our EasySpin simulations. As noted above we placed a constraint on the magnitude of D, primarily because of the expected quenched orbital angular momentum in the d⁵ $S_{Mn(II)} = 5/2$ ions. We note that these parameters, however, fail to faithfully reproduce the low temperature data in the susceptibility measurements. By relaxing our D constraint in our simulations of the dc susceptibility and isothermal magnetization data of 2 and 3, we were able to improve the agreement between our calculated values and those in the low temperature region of the experimental data (Figures S8 and S9). Such large values of D (e.g., -7.0 cm^{-1} for 3 in Figure S9) are unphysical for highspin Mn^{II}, and we have therefore reported our simulations employing smaller D values.

In an effort to refine our simulated values of D, we then measured X-band EPR spectra on solutions of 2-4 at 293 and 5 K. The X-band EPR spectrum of 1 has been reported previously.³⁴ A common feature in the 293 K spectra of this series of compounds is a single broad absorption centered at g \approx 2.02, which is retained upon cooling to 5 K (Figures S11-\$13). In addition, absorptions are also observed starting near zero field in the low temperature spectra for 2-4; however, the intensity of the $g \approx 2$ feature relative to some of the absorptions at lower field varies between the different compounds. Frozen solutions of 3 at 5 K display broad absorptions from nearly zero field up to $g \approx 2.02$ with hyperfine coupling—likely to the I =5/2 Mn nuclei—apparent for the absorptions at ~2000 G and \sim 800 G (Figure S12). Spectra recorded on frozen solutions of 4 at 5 K display a broad multiline absorption centered at $g \approx$ 2.0, consistent with an S = 1/2 ground state coupled to the three Mn^{II} centers, and a broad absorption centered at ~1500 G likely arising from a low-lying S = 3/2 excited state (Figure S13). In each case, thermal population of low-lying excited states present at 5 K in EPR spectra of 2-4 agrees with the observed intermediate χT values (i.e., between S = 1/2 and 3/2for 3 and 4) measured at 5 K in the temperature-dependent magnetization studies. We attempted to model these spectra using the parameters derived from our magnetometry data, but were unable to obtain satisfactory fits without overparametrization of the simulations. From these attempts, however, we could surmise that inclusion of small zero-field splitting of rhombic symmetry (due to the presence of the local crystal field or anisotropic interactions, which would violate EPR selection rules) is necessary for each compound; however, the magnetic response of 4 is quite well modeled without zero-field splitting, so we report the simpler fit here. The ground S = 1/2 state and the excited states in 4 are well separated, yielding more distinct features with effective $g \approx 2$ and $g \approx 4.4$ with their relative intensity changing with the temperature. On the other hand, excited states for 2 and 3 are closer in energy to the ground

state (with higher thermal population) and distributed more evenly through the energy spectrum. This is manifested by the relatively minor changes to the components of the complicated EPR spectra of these compounds from 5 to 293 K (data not shown).

Cyclic Voltammetry. To further explore the effect of the bridging ligand on the electronic communication between the metal centers, we collected cyclic voltammograms on solutions of 1-4 in isobutyronitrile under ambient conditions. Guillet et al. have previously reported cyclic voltammograms on a tetrahydrofuran solution of $1;^{34}$ however, the measurement was repeated here using isobutyronitrile as the solvent for a direct comparison with 2-4 (Figure 3). We do not observe



Figure 3. Cyclic voltammograms of 1 (black), 2 (red), 3 (blue), and 4 (green) in isobutyronitrile at a scan rate of 100 mV·s⁻¹ with 0.3 M TBAPF₆ as a supporting electrolyte. All scans were recorded in the reductive direction. Working electrode: 1 mm Pt. Reference electrode: Ag/AgNO₃. Auxiliary electrode: Au flag. Referenced to Fc/Fc⁺.

reversible processes within the solvent window for 1–4, but there are notable differences between the voltammograms across the series. For 1, we observe a broad irreversible oxidative event with an onset near 0 V vs Fc/Fc⁺ that increases with no well-defined wave as the potential continues to increase. Murray and co-workers reported similar irreversible events with onsets near 0 V vs Fc⁺/Fc in triiron(II) and tricopper complexes supported by this cyclophanate.^{34,35,38,39,56} This observation is consistent with the reported oxidation of the nonbonding π -type orbitals in bis(β -diketiminate) complexes^{93–95} and in DFT calculations on Cu₃(N₂)L,³⁶ which indicate that the HOMO is composed of β -diketiminate nonbonding π -type orbitals. We, therefore, assign this process as a ligand-based oxidation. The contribution of this process is serially diminished from 2 to 4, and additional oxidative and reductive features are observed. For example, a well-defined wave at +0.10 V is observed in samples of 2, a broad poorly defined oxidation is present at \sim +0.32 V for 3, and a feature at +0.28 V is observed for 4. In the halide-bridged compounds, no reductive features are present, whereas waves at -1.48, -1.70, and -2.17 V are observed for 3 and one at -2.26 V is observed for 4. The voltammograms for the halide-bridged compounds are comparable to those reported for Fe₃Br₃L.³⁴ The absence of a reversible redox process for 3 at strongly reducing potentials contrasts with the previously reported data for the triiron and tricobalt congeners as well as the μ -formato-di(μ -hydrido)triiron(II) and -cobalt(II) complexes at similar potentials,³⁹ although we cannot exclude the possibility that a reversible reduction for 3 may occur outside the solvent window of isobutyronitrile. We speculate that this difference likely arises from poorer delocalization of charge within the trimetallic unit upon reduction or oxidation, as might be anticipated from the weaker metal-ligand interactions for Mn^{II} relative to the later divalent 3d metal ions.

CONCLUSIONS

Consistent with prior reports on triiron and -cobalt complexes,^{39,51} and expanding on the previous work with manganese,³⁴ we have demonstrated that the β -diketiminatederived macrobicyclic ligand provides facile access to trimanganese(II) tri(chloride) and tri(bromide) clusters, and that these can be derivatized readily to yield the tri(hydride) and tri(methoxide) clusters. The resultant Mn₂X₂L complexes fall into two relatively isostructural families, which allowed for a comparison of the magnetic exchange interactions and electrochemical properties as a function of the bridging ligands. The exchange interactions are best simulated using two inequivalent J terms for all compounds except the tri(μ methoxide), 4, for which the data could be simulated as a frustrated system with a single J term. Our results indicate that this ligand platform can support a variety of trimanganese clusters of predictable geometry with substantially different bridging ligands leading to different magnetic exchange properties. In addition, we envision that minor variations to the cyclophane ligand and the bridging donor, such as the alkoxide substituent for a derivative series based on 4, will allow for rational fine-tuning of the exchange interactions in these multimetallic systems. Surprisingly, our results point to unusually large coupling mediated by hydride donors, prompting ongoing studies to explore these exchange interactions in related complexes. The results are supported by X-band EPR spectra, although better estimates of D will require measurements at higher applied fields. In all cases, only irreversible redox events were observed by cyclic voltammetry, precluding an estimate of electronic coupling.

Dissecting the factors that determine the preferred structure type of the $[M_3X_3]^{3-}$ clusters supported by this cyclophanate will require a broader survey of trimetallic species across a series in which the metal ion, the metal oxidation states, and the bridging ligands are systematically varied. However, the data presented here for the series of Mn^{II} compounds as well as the prior reports of the triiron(II/III) and tricobalt(II) congeners provide strong evidence for ligand flexibility and point to electronic effects as a more influential structural determinant.

EXPERIMENTAL SECTION

General Considerations. All reactions were performed under a dinitrogen atmosphere in an Innovative Technologies glovebox. Solvents were purchased from Sigma-Aldrich, then dried using an Innovative Technologies solvent purification system, and stored over activated 3 Å molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Laboratories, purified according to reported procedures, and then stored over activated 3 Å molecular sieves.⁹ NaOMe, MnBr₂, and MnCl₂ were purchased from Sigma-Aldrich or Fisher Scientific and dried under vacuum at 150 °C overnight. TBAPF₆ was purchased from Sigma-Aldrich, recrystallized from ethanol, and dried with P2O5 under vacuum. Isobutyronitrile was purchased from Acros Organics, dried by refluxing over CaH₂, distilled, and stored over 3 Å sieves in a dinitrogen glovebox after three freeze-pump-thaw cycles. IR spectra were collected in a nitrogenfilled glovebox using a Bruker Alpha with an ATR diamond crystal stage using the Opus 7.0 software package. UV-visible spectra were recorded on a Varian Cary 50 UV/vis spectrophotometer using screwtop quartz cuvettes with a l cm path length. Cyclic voltammetry was performed under a nitrogen atmosphere using a standard three electrode setup. Electrodes were purchased from either BASi, Inc., or CH Instruments, Inc. Potential sweeps were controlled by a Princeton Applied Research Versastat II potentiostat. Magnetic data were collected on a commercial Quantum Design MPMS XL-7; samples were held in a drinking straw and oriented perpendicular to the applied magnetic field. EPR measurements were recorded on a Bruker Elexsys E580 with a Bruker 4116DM resonator. Data was collected in the field from 50 to 7000 G with the following parameters for 4: temperature = 5 K, power = 6.30×10^{-2} mW, frequency = 9.629 GHz, modulation frequency = 100.00 kHz, modulation amplitude = 10.00 G, and gain = 60 dB. Electrospray mass spectra were collected by direct injection into an Agilent 6120 TOF spectrometer at a gas temperature of 100 °C and fragmentation voltage of 120 V on solution samples prepared in a nitrogen atmosphere glovebox and transported in Hamilton gastight sample-lock syringes. Complete Analysis Laboratories, Inc. (Parsippany, NJ) conducted elemental analyses on samples shipped under vacuum. H₃L,³⁴ Mn₃Br₃L (1),³⁴ benzylpotassium,⁹⁷ and KBEt₃H⁹⁸ were synthesized as described previously. Searches of the Cambridge Structural Database (CSD) were performed with Cambridge Crystallographic Data Center ConQuest software package using CSD version 5.38 Update 3 (May 2017).

 Mn_3Cl_3L (2). BnK (59.4 mg, 0.456 mmol) and H_3L (100 mg, 0.145 mmol) were placed in a 20 mL vial and dissolved in THF (10 mL) to form a dark purple solution. $MnCl_2$ (56.5 mg, 0.449 mmol) was added and the mixture stirred at room temperature overnight. The solvent was removed under reduced pressure, the product extracted with hot benzene (2 × 15 mL), filtered through Celite, and the solvent removed *in vacuo* to yield crude Mn_3Cl_3L (2) as a yellow powder (83.3 mg, 0.0868 mmol, 60%), which was used for all spectroscopic measurements and combustion analysis. X-ray quality crystals were grown from evaporation of a saturated benzene–toluene (5:1) solution. Anal. found (calcd) for $C_{45}H_{63}Cl_3Mn_3N_6$: C, 56.11 (56.35); H, 6.61 (6.62); N, 8.59 (8.76). IR (cm⁻¹): 1521, 1402, 1320, 1013, 719, 459.

 Mn_3H_3L (3). A solution of KBEt₃H (39.8 mg, 0.289 mmol) in toluene (2 mL) was cooled to -35 °C and added dropwise to a solution of Mn_3Br_3L (100 mg, 0.0915 mmol) in toluene (10 mL) at -35 °C, after which the reaction mixture was warmed to room temperature and stirred for 2 h. The volatiles were removed under reduced pressure and the product washed with hexanes (5 mL), redried *in vacuo*, extracted with toluene (10 mL), filtered through Celite, and the solvent removed *in vacuo* to yield crude 3, which was crystallized as amber needles from cooling a hot benzene solution (37.6 mg, 0.0439 mmol, 48%). X-ray quality crystals were grown from cooling a saturated benzene solution. Anal. found (calcd) for C₄₅H₆₆Mn₃N₆: C, 62.97 (63.15); H, 7.89 (7.77); N, 9.73 (9.82). IR (cm⁻¹): 1530, 1397, 1325, 1022, 724, 600, 454.

 $Mn_3(OCH_3)_3L$ (4). Mn_3Br_3L (100 mg, 0.0915 mmol) and NaOMe (15.6 mg, 0.288 mmol) were placed in a 20 mL vial, followed by THF

(15 mL), and stirred overnight at 60 °C. The solvent was then removed under reduced pressure, the resulting solid extracted with hot toluene (20 mL) and filtered through Celite, and the solvent removed under reduced pressure to yield crude 4 as a pale yellow powder. X-ray quality crystals were grown from a diffusion of a DCM solution into toluene (48.1 mg, 0.0509 mmol, 56%). Anal. found (calcd) for C₄₈H₇₂Mn₃N₆O₃: C, 60.74 (60.95); H, 7.73 (7.67); N, 8.81 (8.88). IR (cm⁻¹): 1521, 1054, 1013, 728, 712, 499. HRMS (ESI-TOF) *m/z*: [M + H]⁺ C₄₈H₇₃Mn₃N₆O₃ found (calculated): 946.3866 (946.3891).

X-ray Crystallography. X-ray intensity data were collected at 100 K on a Bruker DUO diffractometer using Mo K α radiation (λ = 0.71073 Å) and an APEXII CCD area detector. Raw data frames were read by the program SAINT⁹⁹ and integrated using 3D profiling algorithms. The resulting data were reduced to produce *hkl* reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects, and numerical absorption corrections were applied based on indexed and measured faces. The structure was solved and refined in SHELXTL2014 or 2013,¹⁰⁰ using full-matrix least-squares refinement. The non-H atoms were refined with anisotropic thermal parameters, and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. Refinement was carried out by minimizing the wR2 function using F^2 rather than F values. R1 is calculated to provide a reference to the conventional R value, but its function is not minimized.

 Mn_3Cl_3L (2). The asymmetric unit consist of the Mn3 complex, one benzene molecule in general position, and two half benzene molecules with each being located on an independent inversion center. Two of the three Mn atoms are disordered with Mn1 refined in three positions and Mn2 in two positions. The core center is occupied by a combination of 40% Cl and 30% oxygen adding up to an anion with a -1 charge. In each disorder case, site occupation factors of partial atoms were refined until the last refinement cycles when they were fixed. In the final cycle of refinement, 12189 reflections (of which 10389 are observed with $I > 2\sigma(I)$) were used to refine 646 parameters, and the resulting R1, wR2, and S (goodness of fit) were 4.01%, 11.25%, and 1.050, respectively.

 Mn_3H_3L (3). The asymmetric unit consists of a 1/6 Mn3 complex located on a -6 center, one benzene solvent molecule on a -3 center, and another on a mirror plane of symmetry. Thus, the stoichiometry of the structure is one complex to four benzene solvent molecules. The benzene molecule located on -3 symmetry element could not be modeled properly, thus program SQUEEZE, a part of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. As other experimental results confirm the absence of any Br in the sample, the small electron density forming a hexagon with the three Mn atoms, which is more than that of a hydrogen atom, is attributed to a 60° rotation of 6% of the complexes. Although the electron density peak of 6% of Mn can be observed, this percentage of light atoms cannot be observed in electron density maps. Thus, the bridging hydride ligand position is disordered between H and Mn with a ratio of 0.94 to 0.06, respectively. In the final cycle of refinement, 2511 reflections (of which 1804 are observed with $I > 2\sigma(I)$) were used to refine 126 parameters, and the resulting R1, wR2, and S (goodness of fit) were 6.96%, 17.11%, and 1.051, respectively.

 $Mn_3(OCH_3)_3L$ (4). The asymmetric unit consists of one and a third Mn3 complexes (one molecule is located on a 3-fold rotational axis of symmetry) and four dichloromethane solvent molecules. The solvents are disordered where two were refined in two parts each, although another has both Cl atoms disordered and the last has only one Cl disordered. None of the solvent molecules' H atoms were included in the final cycle of refinement. The data was checked for higher symmetry and was also refined in space group P6(3)/m but could not be refined properly. The data is clearly twinned and was refined as such, with the twin law being a mirror plane in the *c*-direction. In the final cycle of refinement, 12436 reflections (of which 9011 are observed with $I > 2\sigma(I)$) were used to refine 822 parameters, and the resulting R1, wR2, and S (goodness of fit) were 8.68%, 16.50%, and 1.063, respectively.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b02004.

Experimental methods (PDF)

Accession Codes

CCDC 1566891–1566893 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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