Synthetic investigation of competing magnetic interactions in 2D metal–chloranilate radical frameworks

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The discovery of emergent materials lies at the intersection of chemistry and condensed matter physics. Synthetic chemistry offers a pathway to create materials with the desired physical and electronic structures that support fundamentally new properties. Metal–organic frameworks are a promising platform for bottom-up chemical design of new materials, owing to their inherent chemical predictability and tunability relative to traditional solid-state materials. Herein, we describe the synthesis and magnetic characterization of a new 2,5-dihydroxy-1,4-benzoquinone based material, (NMe$_2$)$_3.5$Ga$_2$(C$_6$O$_4$Cl$_2$)$_3$ (1), which features radical-based electronic spins on the sites of a kagomé lattice, a geometric lattice known to engender exotic electronic properties. Vibrational and electronic spectroscopies, in combination with magnetic susceptibility measurements, revealed 1 exhibits mixed valency between the radical-bearing trianionic and diamagnetic tetraanionic oxidation states of the ligand. This unpaired electron density on the ligand forms a partially occupied kagomé lattice where approximately 85% of the lattice sites are occupied with an $S = \frac{1}{2}$ spin. We found that gallium mediates ferromagnetic coupling between ligand spins, creating a ferromagnetic kagomé lattice. By modulation of the interlayer spacing with the In$^3+$ analogue, (NMe$_4$)$_3.5$In$_2$(C$_6$O$_4$Cl$_2$)$_3$ (2) and (NEt$_2$)$_2$(NMe$_4$)$_1.5$Ga$_2$(C$_6$O$_4$Cl$_2$)$_3$ (3), we determined the nature of the magnetic coupling between neighboring planes is antiferromagnetic. Additionally, we determined the role of the metal in mediating this magnetic coupling by comparison of 2 with the In$^3+$ analogue, (NMe$_2$)$_3.5$In$_2$(C$_6$O$_4$Cl$_2$)$_3$ (4), and we found that Ga$^{3+}$ supports stronger superexchange coupling between ligand-based spins than In$^{3+}$. The combination of intraplanar ferromagnetic coupling and interplanar antiferromagnetic coupling exchange interactions suggests these are promising materials to host topological phenomena.

Introduction

The discovery of new materials which host emergent phenomena lies at the intersection of condensed matter physics and synthetic chemistry. Certain lattice topologies, for example the kagomé lattice, which consists of corner sharing equilateral triangles, promote the creation of excitations which are different from those that occur in the building units of the lattice. This phenomenon is referred to as an emergent property – a property in the collective which does not occur in the core unit. Beyond emergent electronic properties, many new magnetic phases arise in spin-based materials through exchange interactions governed by the lattice geometry and the active spin and orbital degrees-of-freedom dictated by the underlying chemistry. Creating these materials from the ground up is a significant synthetic challenge which necessitates simultaneous control over both the local and extended structure and the electron filling of the frontier orbitals.

The kagomé lattice is an especially promising structure to target as either antiferromagnet or ferromagnetic interactions within the lattice lead to emergent phenomena. Antiferromagnetic coupling of electronic spins on the kagomé lattice leads to magnetic frustration, which arises from the competing magnetic interactions that cannot be simultaneously satisfied. This magnetic frustration prevents the onset of magnetic ordering and results in a state known as a quantum spin liquid. This state features an infinite number of degenerate magnetic ground states, and is predicted to host exotic fractionalized quasiparticles with applications in quantum computation and high temperature superconductivity. Alternatively, ferromagnetic coupling of electronic spins on a kagomé lattice leads to a different family of
interesting electronic properties, and includes materials that are topological magnon band insulators, exhibit skyrmionic excitations, or host Dirac fermions.

Two-dimensional (2D) metal–organic frameworks (MOFs) are an attractive platform for the targeted design of such new emergent materials. In contrast to traditional solid-state materials such as metal oxides and minerals, which have inherently little chemical tunability, MOFs possess a high degree of modularity as they can be built up from molecular building blocks. This modularity encompasses the identity of the metal centre, the organic bridging ligand, and the interlayer spacing. In these systems, the unpaired spin density that gives rise to exotic electronic behaviour can reside on either the metal site or on the organic ligand, expanding the number of viable synthetic targets. In these materials, the two primary components that dictate the electronic and magnetic properties are the intralayer interactions and the interlayer interactions. The former leads to the desired exotic properties of interest, while the latter often extinguishes the phenomena of interest. A prominent example is observed in antiferromagnetic kagomé materials, wherein the interlayer interactions often alleviate magnetic frustration. Judicious chemical design of both metal ion and organic ligand enables fine-tuning the electronic and magnetic properties of the intralayer kagomé lattice via a bottom-up chemical approach. Additionally, in 2D MOFs, the interlayer spacing in these materials can be modulated by intercalation of organic cations. We hypothesize that this will enable deconvolution of the magnetic behaviour as either the result of 2D interactions arising from the kagomé lattice or more complicated 3D interactions. This is an especially attractive feature of 2D MOFs over metal oxides and minerals.

Towards this end, we synthesized a series of 2D honeycomb MOFs composed of 2,5-dichloro-3,6-dihydroxy-p-benzoquinone (chloranilic acid) and group 13 metals (gallium and indium). In this system, chloranilate (Fig. 1a) hosts a stable organic radical in its trianionic oxidation state, localizing unpaired spin density onto the vertices of the kagomé lattice (Fig. 1b). This leads to the formation of an electronic spin based kagomé lattice on top of the structural honeycomb framework. In order to ensure the only unpaired spin density resides on the desired kagomé lattice sites, group 13 metals were chosen as the metal nodes for their diamagnetism and relative redox inertness. By preparing both the gallium and indium analogues, we are able to assess how the radial extent of the metal orbitals affect the strength of the spin–spin coupling mediated by metal–ligand superexchange. Finally, we modulate the interlayer spacing of the gallium chloranilate framework, enabling deconvolution of the inter- vs. intralayer magnetic interactions.

Results and discussion

We synthesized the first 2D MOF of the series by reaction of Ga(NO)₃·xH₂O with chloranilic acid in dimethylformamide (DMF) and trace amounts of water at 130 °C for 16 hours to produce green hexagonal crystals with the composition (NMe₃H₂)₃₆Ga₆CA₆ (1). The structure of 1 was determined from Rietveld refinement of laboratory powder X-ray diffraction (PXRD) data. The PXRD pattern revealed the framework is isostructural with the known aluminum analogue (Fig. 1b) confirming it maintains the desired kagomé lattice structure. The Ga³⁺ ions are octahedrally coordinated by three deprotonated chloranilate ligands to form the nodes of the honeycomb net. The pores of the honeycomb are 15.56 Å in diameter and are filled with DMF solvent molecules and dimethylammonium cations formed from the decomposition of DMF during the reaction. Based upon structurally analogous frameworks and elemental analysis, these cations charge balance the anionic framework. The layers are eclipsed and are separated by an interlayer distance of 8.835(1) Å. The layers stack in an ABAB pattern where neighboring layers are related by a mirror plane perpendicular to the c axis (Fig. S5†).

To assess the ligand oxidation state in 1, we performed vibrational spectroscopy as the C–C and C–O stretching modes are highly sensitive to the chloranilate ligand oxidation state. The frequency of the C–O stretching vibration should be largest in the CA²⁻ oxidation state and weaken as the ligand is reduced, whereas the C–C stretching vibration follows an opposite trend. After probing 1 using Raman spectroscopy, close inspection of the main band at 1453 cm⁻¹ reveals an additional band at 1440 cm⁻¹ (Fig. 2a). The closeness in energy of the two bands complicates assigning either as definitively to the C–C or C–O stretch. However, either band, if assigned to the C–C stretch in 1, occurs at a much higher frequency than observed in the structural analogues (NMe₃H₂)₅Zn₂(CA²⁻)₃ and

![Fig. 1](image-url)
(NMe₂H₂)₃(CoCp₂)₃Fe₂(CA₃)₃ frameworks, which are iso-
valent in the dianionic and trianionic oxidation states of the
ligand, respectively; the remaining band assigned as the C–O
stretch is also concomitantly much weaker in 1. Based on the
observed vibrational frequencies and their near coalescence, it
is evident the ligand is spontaneously reduced beyond a fully
CA³⁻⁻ system. Comparison with fully reduced chloranilic acid
(H₂CA), which displays two C–O stretches at 1448 and
1500 cm⁻¹, eliminates the possibility that the bridging ligands
in 1 are solely in the CA⁴⁻ state. Based on the aggregate of these
data, we propose 1 hosts mixed valency between CA³⁻⁻ and
CA⁴⁻. To test our hypothesis of mixed valency, we investigated 1
by Fourier transform infrared (FTIR) spectroscopy. FTIR spec-
troscopy can often reveal low-lying intervalence charge transfer
(IVCT) transitions in the near IR characteristic of delocalized
mixed-valent species. While the FTIR spectrum of 1 did not
reveal any features characteristic of mixed valency, comparison
of the spectrum of 1 to molecular compounds with chloranilic
acid in well-defined oxidation states, namely [PPh₃]₂[Ga(CA³⁻⁻)₃] and
[Ga(tren)]₂(CA⁴⁻)(BPh₄)₂ (tren = tris[2-aminoethyl]amine),
which feature chloranilic exclusively in exclusively the CA³⁺
and CA⁴⁺ states, respectively, allows for further characterization
of the ligand oxidation state. The FTIR spectrum of 1 has two
intense peaks closely spaced in energy at 1403 and 1383 cm⁻¹
(Fig. S6f). Both of these peaks are far weaker than would nor-
mally be assigned to the C–O double bond stretching vibration,
and are much lower in energy than the C–O stretch at 1644 cm⁻¹
in [PPh₃]₂[Ga(CA³⁻⁻)₃] supporting the absence of CA³⁺. Addi-
tionally, the peak at 1383 cm⁻¹ is considerably lower in energy
than the C–C stretching mode in [Ga(tren)]₂(CA⁴⁺)(BPh₄)₂
(1467 cm⁻¹). However, in the case of mixed valency of CA³⁻⁻ and
CA⁴⁺, there should only be one or two formal C–O double bonds
per every three ligands. This change in bonding should signif-
cantly weaken (and strengthen) the C–O (and C–C) stretching
vibrational mode. The aggregate of this data further supports
our assignment of mixed-valent ligand oxidation states in 1
(Table 1).

The absence of an IVCT band by FTIR spectroscopy moti-
vated us to examine electronic absorption spectroscopy to
further probe the ligand mixed valency in these frameworks.
The diffuse reflectance data (Fig. 2b) collected for 1 featured
many transitions across the energy range of inspection (7500–
45 000 cm⁻¹). The peak at ~21 000 cm⁻¹ was assigned as the
π* → π* transition of CA³⁻⁻ and features a fine structure
associated with the C–O vibrational modes which has been
previously observed in molecular species containing CA³⁻⁻.²⁶,²⁷
The broad, intense electronic transition at 35 000 cm⁻¹ is
analogous to the π → π* transition of 1,2-dihydroxy-
benzoquinone and was likewise assigned to the same transi-
tion in chloranilinate.²²,²⁶

Of more immediate interest is the presence of a broad, low-
intensity peak at 14 400 cm⁻¹ which is tentatively assigned as an
IVCT band. Due to the broadness, weak intensity, and relatively
high energy of the peak, we assigned 1 as a weakly exchanging
Class II Robin–Day mixed-valent material.²⁸ Similar low inten-
sity features in the near IR were also observed in a structurally
similar chromium(III) chloranilate framework and were
assigned to an IVCT consistent with a localized electronic
structure.²⁹ Conversely, strongly exchanging Class II and Class
III Robin–Day mixed-valent chloranilate frameworks have lower
energy and more intense IVCT bands.²⁹,³⁰ The presence of an
IVCT band in 1 is in contrast to mononuclear homoleptic gal-
lium(III) complexes that are mixed-valent in the ligand oxidation
state but lack an IVCT band in their electronic spectra.²⁹,３²

Table 1 Summary of C–O and C–C bond frequencies of 1 and molecular comparison species as determined with Raman spectroscopy

| Compound | ν (C–O) [cm⁻¹] | ν (C–C) [cm⁻¹] |
|----------|---------------|---------------|
| 1 (NMe₂H₂)₃(CoCp₂)₃Fe₂(CA₃⁻⁻)₃ (ref. 22) | 1437 | 1450 |
| (NMe₂H₂)₃Zn₃(CA⁻⁻)₃ (ref. 22) | 1487 | 1390 |
| H₄CA | 1617 | 1360 |

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Fig. 2 (a) Raman spectrum collected for a solid sample of 1 from 400 to 1900 cm⁻¹ following excitation at 473 nm. The plot to the right highlights the main peak at 1453 cm⁻¹ which has a shoulder at 1440 cm⁻¹. (b) Diffuse reflectance spectrum collected for a solid sample of 1 under a N₂ atmosphere, with arrows highlighting relevant transitions. (c) DC magnetic susceptibility for 1 at 0.1 T. Inset shows magnetization curves from 0 to 7 T at temperatures of 1.8, 5, and 10 K. Lines are guides to the eye.
these complexes, gallium(III) is a poor bridging metal ion and does not facilitate strong electronic communication between the two oxidation states of the ligands. This suggests that interligand electronic communication is stronger in the framework than in corresponding molecular complexes. To test these assignments of the electronic transitions, we exposed 1 to air, leading to oxidation of the CA$^{3-}$ ligands to their CA$^{2-}$ forms. Indeed, the ligands in 1 are oxidized to CA$^{2-}$, and as a result, the peaks assigned to CA$^{3-}$ and the IVCT disappear, concurrent with the appearance of a peak at 18 700 cm$^{-1}$, which is assigned to the $\pi \rightarrow \pi^*$ transition of CA$^{2-}$ (see Fig. S13 and S14 and ESI for extended discussion).

To quantify the degree of mixed valency in 1, we investigated its magnetic properties using SQUID magnetometry. Specifically, variable-temperature dc magnetic susceptibility measurements allow us to directly assess the number of unpaired spins in the framework by quantitation of the high-temperature $\chi_MT$ value, thus elucidating the ratio of CA$^{3-}$ to CA$^{4-}$ in 1. The 300 K $\chi_MT$ value of 1 is 0.96 cm$^3$ K mol$^{-1}$, which persists down to 100 K (Fig. 2c). This value is below the $\chi_MT$ value of 1.125 cm$^3$ K mol$^{-1}$ expected for 3 uncoupled radical spins but above the $\chi_MT$ value of 0.750 cm$^3$ K mol$^{-1}$ expected for 2 uncoupled radical spins. This $\chi_MT$ value corresponds to approximately 83% of the ligands being in the CA$^{3-}$ state, and 17% in the CA$^{4-}$, and further supports the ligand mixed valency suggested by our analysis of the vibrational and diffuse-reflectance data.

Below 100 K, $\chi_MT$ rises and reaches a maximum value of 12.82 cm$^3$ K mol$^{-1}$ at 2 K. This rise in $\chi_MT$ is attributed to ferromagnetic coupling between the ligand-based spins that does not however lead to magnetic ordering. To support the presence of significant ferromagnetic coupling in 1, we measured the magnetization of 1. At 1.8 K, the magnetization rapidly saturates (Fig. 2c, inset). By 0.15 T, the magnetization curve is no longer linear with field, and by 0.50 T the material is fully saturated. We hypothesize the ferromagnetic coupling arises from intralayer coupling of spins within the same 2-D layer of the framework, as intralayer interactions are expected to be much stronger than interlayer interactions. This type of ferromagnetic interligand coupling was also observed in molecular complexes of Ga(III) tris–semiquinone complexes.31,33,34 It was proposed that the empty 4p orbitals of Ga(III) mediated a ferromagnetic superexchange interaction between the radical bearing $\pi^*$ orbitals of the semiquinone ligands.31 This pathway could also be responsible for the ferromagnetic coupling in 1.

As noted above, competing magnetic interactions arising from interlayer and intralayer magnetic coupling often have dramatic effects on any potential exotic electronic behavior hosted by these materials. The synthetic modularity of this 2D framework yields an opportunity to investigate the nature of the interlayer magnetic coupling, and deconvolute it from intralayer magnetic interactions. We can probe the relative magnitude and nature of the interlayer coupling by modulation of the interlayer spacing by post-synthetic cation exchange. Based on literature reports of anilate MOFs synthesized with different alkyl ammonium cations without a distortion of the 2D lattice, we pursued the intercalation of bulky quaternary alkyl ammonium cations to expand the interlayer spacing without distorting the kagome lattice.35,36

Soaking 1 in a 0.15 M solution of NMe$_4$OH in DMF at 75 °C for 12 hours led to the isolation of [NMe$_4$]$_3$Ga$_2$CA$_3$ (2). Subsequently, soaking 2 in a 0.1 M solution of tetraethylammonium bromide in DMF at 75 °C for 12 hours resulted in the formation and isolation of [NEt$_4$]$_2$(NMe$_4$)$_2$Ga$_2$CA$_3$ (3). Comparison of the PXRD data across the series revealed a clear dependence of the (002) peak on cation metathesis, with a shift in the (002) peak from 10.21$^\circ$ to 8.61$^\circ$ in moving from 1 to 3 (Fig. 3a). These shifts in 2$\theta$ point to changes in the interlayer spacing across the series, ranging from 8.835(1) Å to 10.06(2) Å to 10.155(4) Å, from 1 to 3, respectively. These data suggest that as in isostructural frameworks with transition metal nodes, the NR$_4^+$ cations reside between the Ga$^{3+}$ centres of neighbouring layers and act to modulate the interlayer spacing.35,36 When this interlayer site is fully occupied, these sites account for two of the cations per formula unit; by

![Fig. 3](image-url) (a) PXRD of 1, 2, and 3 collected with Cu Kα$_2$ radiation showing the expansion of the interlayer spacing with intercalation of tetraethylammonium cations. The arrows point to the (002) peak of each pattern that corresponds to the interlayer spacing and is modulated by the size of the cation. (b) DC magnetic susceptibility of 1, 2, and 3, displaying the dependence of the low temperature magnetic behaviour on the interlayer spacing. The inset highlights the dependence of $\chi_MT_{max}$ on 1/R$^2$, where R is the interlayer spacing. The data are fit to a linear relationship with an R$^2$ of 0.981, demonstrating the strong correlation between the maximum magnetic moment and the interlayer spacing.
elemental analysis, the remaining one and a half negative
charges from the framework are charge balanced by tetrame-
thylammonium ions we believe reside in the pore of the
framework. Importantly, the incorporation of NR4+ cations does
not distort the 2D framework as the only affected peaks
observed by PXRD are those associated with the c-axis, corre-
sponding to the interlayer direction. Additionally, this cation
metathesis process does not affect the ligand oxidation state, as
the relevant vibrational modes observed by Raman and FTIR
spectroscopy remain unchanged (see ESI Fig. S8–S10†).

To further probe the ligand oxidation states of 2 and 3, and to
evaluate their magnetic properties, we collected variable-
temperature dc magnetic susceptibility data. The 300 K
evaluation of these compounds was performed using the Vienna Ab initio Software Package (VASP) with the
projected augmented wave method.36 The aforementioned
compounds were modelled using the experimental structures
as initial atomic configurations without solvent molecules, i.e.,
as Ga4CA3 (P63/mmc symmetry) and In4CA3 (P3).44 We achieved a CA− (spin ½) configuration by electron doping the chlor-
inate anions and then imposing ferromagnetic spin align-
ment among these ligands within the 2D kagomé layers, which
couple antiferromagnetically. The internal atomic positions of
each structure was relaxed using the experimental volume.

First, we found that the diamagnetic metal–oxygen bond
lengths from the bidentate CA− ligands were shorter for
Ga4CA3 (1.98 Å) compared to In4CA3 (2.16 Å), consistent with
the smaller ionic radius of Ga3+ (187 pm) compared to In3+ (220
pm). This leads to larger orbital overlap and enhanced charge
density in the bonding region (indicated in Fig. S19†), which
initiates the superexchange path between sites, Ga–O–C–C–C–
O–Ga; although the S = ½ spin state is distributed about the
chlorinate anion, it is predominately localized on the oxygen
anions. In addition, the GaO6 octahedral units are closer to
ideal compared to the InO6 owing to deviations of the intra-
ocahedral oxygen–metal–oxygen angles from 90°, which
narrow the electronic bandwidth. As a result, the direct distance
between coupled chlorinate anions and cations is significantly
shorter in Ga4CA3 (3.84 Å) compared to In4CA3 (4.049 Å).

Second, analysis of the electronic density-of-states reveals that
in both compounds, the valence band is mainly comprised of
the chlorinate anion states with chloride 3p orbitals located
below (from −5 to −3.5 eV) the oxygen 2p states (spanning −3 to
−1.5 eV), whereas the conduction band consists of the main
group s and p states. Although the empty gallium states are
located at higher energy than those of indium (Fig. S19†), they
show a small overlap with the occupied oxygen 2p bands. This
mixing is stronger for gallium compared to indium over the −4
to −2 eV energy range (Fig. S19†). Furthermore, the Ga
compound exhibits greater p-orbital occupancy (0.35e) than In
(0.31e), demonstrating that there is stronger hybridization
about the p states than s states (0.31e, 0.32e; Fig. S20†).

We therefore concluded that chelated diamagnetic metals favor ferromagnetic spin–spin coupling, owing to orthogonal
symmetry of the p orbitals from the metal and oxide ligands
consistent with trends reported for iminobenzosemiquinonato
group 13 molecular complexes.34,42 Moreover, because stronger
spin–spin interactions arise when there are stronger hybrid-
ization (covalent bonding) among the active orbitals
participating in superexchange, this coupling is greater for
gallium owing to the greater exchange propagated by the orbital
hybridization. Indeed, upon approximating the exchange
interaction by finding the energy difference between the FM and
AFM configurations (where a C ring has an opposite spin with
respect to the other two rings), we found that energy difference
was larger for Ga (40 K) compared to In (17 K).
The observation of topological behaviour necessitates that each kagomé lattice site hosts a full $S = \frac{1}{2}$ spin, leading us to pursue post-synthetic chemical oxidation of the ligand to achieve a purely CA$^{3−}$ framework. Previous work has demonstrated that honeycomb-type MOFs of chloranilate can successfully undergo single-crystal to single-crystal post-synthetic chemical reduction from a mixed-valent CA$^{2+/3−}$ system to a fully CA$^{3−}$ system.23 Thus motivated, we sought to treat the framework with an oxidant with the ability to oxidize CA$^{4−}$ to CA$^{3−}$, without effecting the oxidation of CA$^{3−}$ to CA$^{2−}$. Soaking 1 in a solution of ferrocenium hexafluorophosphate in acetonitrile results in oxidation of the CA$^{3−}$ ligand to CA$^{3−}$, as evidenced by vibrational and electronic spectroscopies. Peaks in the Raman spectrum grow in at 1390 and 1505 cm$^{-1}$ (Fig. S29†), which are consistent with the C–C and C–O stretches previously observed for CA$^{3−}$.23 However, a remnant Raman peak at 1445 cm$^{-1}$ suggests incomplete oxidation of the CA$^{4−}$ ligand to the CA$^{3−}$-based framework. The IR peaks in 1 at 1405 and 1381 cm$^{-1}$ undergo significant shifts to 1481 and 1361 cm$^{-1}$ (Fig. S30†), which is attributed to a strengthening of the C–O bond and weakening of the C–C bond, respectively, as the percentage of CA$^{3−}$ in the framework increases. Further, the oxidation of CA$^{4−}$ to CA$^{3−}$ goes to completion as evidenced by the disappearance of the IVCT band at 14 500 cm$^{-1}$ after post-synthetic oxidation (Fig. S31†). Accurate quantitation of the magnetic properties of the oxidized material is precluded by the presence of excess ferrocenium ions in the pores of the framework. Ongoing work is focused on post-synthetic oxidation of 1–3 to the fully CA$^{3−}$-based framework with the exclusion of paramagnetic cations convoluting our interpretation of the magnetic properties.

Conclusions

The bottom-up design of 2D materials with the potential to display exotic, emergent properties is an emerging challenge for synthetic chemists. Creating a pathway to realize these materials is a crucial step forward in an area dominated by traditional solid-state chemistry. The foregoing results demonstrate the synthesis of a series of 2D honeycomb MOFs using molecular building blocks geared towards accessing a kagomé lattice of unpaired electronic spins. The synthetic modularity of these 2D frameworks enables clear deconvolution of the inter- vs. intralayer magnetic interactions allowing the confirmation of ferromagnetic coupling within the kagomé plane and antiferromagnetic coupling between kagomé layers. Our data enabled us to establish the form of magnetic coupling within the layer and between the layers, thereby enabling us to assign intraplane ferromagnetic coupling interactions. The observation and confirmation of ferromagnetic coupling interactions within a kagomé plane suggests this may be a candidate for future study, in particular with the fully radical-bearing end member of the series.

Conflicts of interest

There are no conflicts to declare.

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