Hydroxido-Supported and Carboxylato Bridge-Driven Aggregation for Discrete [Ni₄] and Interconnected [Ni₂]ₙ Complexes

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ABSTRACT: Four different carboxylato bridges have been efficiently utilized for growth of three tetranuclear nickel(II) complexes [Ni₄(μ₂-H₂L)(μ₂-OH)](μ₃-CH₂CO₂)(ClO₄)₂ (1), [Ni₄(μ₂-H₂L)(μ₂-OH)](μ₃-C₆H₄CO₂)(ClO₄)₂·1/2H₂O (2), and [Ni₄(μ₂-H₂L)(μ₂-OH)](μ₃-O₂C-CH₃-H₂-pNO₂)₂[(ClO₄)(p-NO₂-C₆H₄-CO₂)]DMF·5H₂O (3) and one dinuclear nickel(II)-based chain complex {[Ni₂(μ-H₂L)(μ₁-3-OH)](μ₁-3-OH)}₂(μ₃-CH₂CO₂)₂·1/2(CH₃OH)·6H₂O with H₃L [2,6-bis((2-(2-hydroxyethylamino)ethylimino)methyl)-4-methylphenol] and RCO₂Na (R = CH₃,C₂H₅, bis((2-(2-hydroxyethylamino)ethyilmino)methyl)-4-methylphenol) and RCO₂Na (R = CH₃,C₆H₅, p-NO₂-C₆H₄ and PhCH₂). This family of complexes is developed from [Ni₄(μ₂-H₂L)]₅⁻ fragments following self-aggregation. The complexes were characterized by X-ray crystallography and magnetic measurements. The changes from acetate, propionate, and p-nitrobenzoate to phenylacetate groups resulted in two different types of coordination aggregation. These compounds are new examples of [Ni₄] and [Ni₂]ₙ complexes where organization of the building motifs are guided by the type of the carboxylate groups responsible for in-situ generation and utilization of HO⁻ bridges with alteration in the aggregation process within the same ligand environment. Studies on the magnetic behavior of the compounds reveal that the exchange coupling within 1–4 is predominantly antiferromagnetic in nature.

INTRODUCTION

Recent intense interest in the synthesis and characterization of high-nuclearity coordination cluster complexes of 3d metal ions is driven by a variety of reasons, such as their relevance to biologically significant structural motifs and to aid new members to the ever growing family of magnetic materials.¹ Incorporation of nickel(II) ions within these from the coordination support of phenol-based ligands has been receiving increasing attention in recent years in the field of molecular magnetism and electronics.² The presence of nickel(II) ions is thus promising in the synthesis of both molecule-based magnets³ and spin-phonon traps⁴,⁵. Synthetic protocols for self-assembly reactions of building blocks within complex clusters often allow the isolation of a single thermodynamic product having high-order molecular architecture in high yield. Schiff bases are ideal candidates for supporting such cage structures due to the easy preparation procedure and easier handling of reaction conditions. Ancillary bridges work in collaboration with the primary ligand to stabilize the coordination assembly. A new family of phenol-bearing “dinucleating ligands”, while simultaneously binding two nickel(II) ions, can be useful for the generation of Ni₄L₅ type building blocks. In the following step, depending upon the reaction condition and available ancillary bridges, these blocks can assemble into various molecular topologies, and the assembly process is sensitive to the nature of the side arms of the ligand backbone. Ancillary bridges such as HO⁻, RO⁻, and N₃⁻ are known to be crucial to support the cubane, defective cubane, and other higher order topologies.⁶ Until now numerous topologies have been reported, for example, cubane⁷,a,b open dicubane⁷,c stepped cubane⁷,d tetrahedron⁷,e and pentanuclear vertex-shared double cubane of hourglass type (Scheme S1 in the Supporting Information, SI)⁸.

The utility of carboxylate ancillary bridges for coordination aggregates has been observed mainly for their linking potential in basal–apical positions around any square-pyramidal and distorted octahedral geometry. They connect via μ₁,1 in syn-anti mode, μ₁,3 in syn-syn, syn-anti, and anti-anti modes, μ₁,1,3 in anti-syn-syn and anti-syn-anti modes, and μ₁,1,3,3 in anti-anti-syn-anti mode.⁹ From the viewpoint of their function as magnetic...
couplers, the syn-syn and anti-anti modes of binding result in antiferromagnetic interactions.

In the present course of work, we investigated the coordination behavior of a new Schiff base ligand H₄L (Chart 1; 2,6-bis[(2-(2-hydroxyethylamino) ethylimino)methyl]-4-methylphenol) toward nickel(II) ions in solution, followed by isolation of the products in the solid state. The ligand H₄L is new in coordination chemistry; only a group of [Cu₆] complexes has been reported by our group with dumbbell-shaped topologies. The bridging properties of carboxylate- and solvent-derived hydroxide groups (Scheme S2) have been exploited to stabilize cluster-like coordination aggregates.

The presence of carboxylic anions the Schiff base remains in the H₂L⁻ form and binds three nickel(II) ions in μ₁, forms.

Herein, we report two unique carboxylate coordination-driven self-organization reactions for the synthesis of three tetranuclear nickel(II) complexes [Ni₄(μ₁-H₂L)(μ₁,H₂L)(μ₁,3-O₂CR)]⁴⁺. A general method was used for preparation of all complexes. To a yellow MeOH (10 mL) solution of H₄L (0.36 g, 1.0 mmol) was added Ni(ClO₄)₂·6H₂O (0.73 g, 2 mmol) with stirring at room temperature. After 15 min, aqueous solutions of the respective sodium carboxylates (2.0 mmol) were added to the previous reaction mixture. The whole reaction mixture was then stirred for 30 min and further refluxed for 1 h. The resulting clear reaction mixture was then cooled and filtered. The filtrate was then kept undisturbed for slow evaporation of solvent and growth of single crystals.

**EXPERIMENTAL SECTION**

**Materials.** The solvents and chemicals used in this work were obtained from commercial sources like SRL, India, Sigma-Aldrich, and Loba Chemie Laboratory Reagents & Fine Chemicals, India. Sources: Sodium acetate, propionic acid, and phenylactic acid from SD Finechem Limited and p-nitrobenzoic acid from Alfa Aesar. The chemicals used in this work were reagent-grade materials and used as received without further purification. Nickel(II) perchlorate hexahydrate was synthesized following a literature procedure with modification providing better yield. Synthesis of Ligand H₄L [2,6-Bis{(2-(2-hydroxyethylamino)ethylimino)methyl}-4-methylphenol]. To a MeOH solution (10 mL) of 2,6-Diformyl-4-methylphenol (1.0 g, 6.1 mmol) was added a MeOH solution (10 mL) of N-(hydroxyethyl)ethylenediamine (1.3 g, 12.2 mmol) dropwise with constant stirring. After completion of the reaction, the solvent was removed from the reaction mixture by rotary evaporator, and H₄L was obtained as an orange oily mass. The ligand was characterized by FTIR, NMR, and ESI-MS spectroscopy and used directly for reaction without further purification.

**Complexes.** A general method was used for preparation of all complexes. To a yellow MeOH (10 mL) solution of H₄L (0.36 g, 1.0 mmol) was added Ni(ClO₄)₂·6H₂O (0.73 g, 2 mmol) with stirring at room temperature. After 15 min, aqueous solutions of the respective sodium carboxylates (2.0 mmol) were added to the previous reaction mixture. The whole reaction mixture was then stirred for 30 min and further refluxed for 1 h. The resulting clear reaction mixture was then cooled and filtered. The filtrate was then kept undisturbed for slow evaporation of solvent and growth of single crystals.

**FTIR (cm⁻¹, KBr disk):** 3437(vs), 2981(w), 1637(s), 1054(w). **¹H NMR (600 MHz, CDCl₃, ppm):** 8 2.83 (2H, imine-H), 6.80–6.60 (3H, Ar–H), 3.54 (2H, methylene CH₂), 3.83 (3H, methylene CH₂ attached with O atom), 1.30 (3H, methyl-H). **¹³C NMR (101.4 MHz, CDCl₃, ppm):** 162.23 (imine C), 157.01, 114.04, 70.71, 56.16, 50.94, 23.77. ESI-MS (MeOH solution, m/z): 251.14 (C₁₂H₁₉N₂O₄), 265.15 (C₁₂H₁₅N₂O₄), 160.05 (C₆H₄O₂), 399.19 (C₁₇H₂₉N₄O₄).
Molar conductance, $A_m$ (MeCN solution, $\Omega^{-1}$ cm$^2$ mol$^{-1}$): 155. UV–vis spectra $[\lambda_{max} \text{nm} (\epsilon, \text{L mol}^{-1} \cdot \text{cm}^{-1})]$ (MeCN solution): 579 (102), 892 (72), 947 (44), 387 (5700).

Caution! Though we have not faced any problem while dealing with the title compounds, complexes of metal ions containing organic ligands along with perchlorate counterions are explosive in nature. Therefore, it is safe to prepare a small amount of sample and handle it with care.

Physical Measurements. Elemental analyses (C, H, and N) of the compounds were performed with a PerkinElmer model 240C elemental analyzer. A Shimadzu UV 3100 UV–vis–NIR spectrophotometer and a PerkinElmer RXI spectrometer were used to record the solution electronic absorption spectra and FTIR spectra, respectively. The purity of the powder compounds was determined by powder X-ray diffraction (see SI) patterns using a Bruker AXS X-ray diffractometer ($40 \text{ kV, } 20 \text{ mA}$) using Cu K$_\alpha$ radiation ($\lambda = 1.5418$ Å) within a $5°$–$50°$ (20') angular range and a fixed-time counting of 4 s at 25 °C.

Magnetic Measurements. Direct current (dc) magnetic measurements were performed on polycrystalline samples of complexes 1–4 constrained in eicosane using a Quantum Design SQUID magnetometer equipped with a 5 T magnet in the School of Chemistry at the University of Glasgow. The dc measurements were carried out in the temperature range 290–2.0 K under an applied field of 1000 Oe. Data were corrected for the diamagnetism of the compound through the approximation that $\chi_{D\alpha} \approx 0.5 \times MW \times 10^{-6}$ cm$^3$ mol$^{-1}$ (MW = molecular weight) and for the magnetic contributions of the sample holder and eicosane through measurements.

Crystal Data Collection and Refinement. Suitable single crystals of 1–4 were chosen for X-ray diffraction. The data were collected on a Nonius Kappa CCD for 1 and a Bruker SMART APEX-II CCD diffractometer for 2–4 using a graphite-monochromated Mo K$_\alpha$ ($\lambda = 0.71073$ Å) radiation. The data were collected by $\omega$ scan (width of 0.3° frame$^{-1}$) method with a scan rate of 4 s per frame at 293 K for 1–3 and at 100 K for 4. Data processing and space group determination were performed with SAINT and XPREP software. The structures were solved by direct method using SHELXS-97$^{12b}$ and refined with the SHELXL (2014/7)$^{12c}$ program package included into WINGX system Version 1.80.05. Data were corrected for Lorentz and polarization effects, and multiscan empirical absorption correction was applied using the SADABS program.$^{13}$ The locations of the heaviest atoms (Ni) were determined easily, and the difference Fourier maps were used to determine the position of O, N, and C. These atoms were refined anisotropically. The H atoms were incorporated at calculated positions and refined with fixed geometry and riding thermal parameters with respect to their carrier atoms. Crystallographic diagrams were prepared using DIAMOND software.$^{14}$ A summary of the crystal data and relevant refinement parameters is provided in Table S1. CCDC 1491624, 1491625, 1491626, and 1491627 contain the supplementary crystallographic data for complexes 1–4.

## RESULTS AND DISCUSSION

**Synthetic Protocol.** The Schiff base ligand $2,6$-bis((2-hydroxyethylamino)ethylimino)methyl)-4-methylphenol (H$_3$L) was prepared (Scheme S3) following a modified literature procedure,$^{15}$ and its reaction with nickel(II) perchlorate has been examined. The suitability of this ligand has been explored for the synthesis of multimetallic complexes. The reaction of Ni(ClO$_4$)$_2$·6H$_2$O with H$_3$L and different carboxylate salts [(RCOO)$_2$Na, R = Me$^–$, Et$^–$, $p$-NO$_2$-Ph$^–$, PhCH$_2$−] in MeOH in a 2:1 molar ratio led to formation of compounds 1–4 (Scheme 1).

Use of sodium acetate in a MeOH solution provided a brown reaction mixture from which green block-shaped crystals were isolated in 75% yield. The C, H, N analysis and single-crystal X-ray diffraction data (vide supra) confirm the formula for 1. Conductivity measurement results are characteristic of 1:1 electrolyte which is in accordance with the presence of dinuclear fragments in solution state, confirmed from ESI-MS experiment (vide supra). The formation of 1 can be demonstrated by eq 1, which clearly justifies the suitability of CH$_3$COO$^−$ ions to produce HO$^−$ ions. (vide infra, mass spectral analysis) to connect two nickel(II) ions initially in {Ni$_2$(μ-H$_2$L)(μ-OH)} fragments.

$$2\text{H}_2\text{L} + 4\text{Ni(ClO}_4)_2\cdot\text{6H}_2\text{O} + 6\text{NaO}_2\text{CCH}_3 \rightarrow \ \text{MeOH} \rightarrow [\text{Ni}_4(\mu_4\text{-OH})_2(\mu_4\text{-H}_2\text{L})_2(\mu_3\text{-O}_2\text{CCH}_3)_2](\text{ClO}_4)_2 + 6\text{NaClO}_4 + 4\text{HO}_2\text{CCH}_3 + 22\text{H}_2\text{O} \quad (1)$$

We examined the reactivity pattern of other carboxylate salts keeping the molar ratio of the reagents unchanged with the hope to obtain a new family of Ni$_4$-based coordination aggregates. We were able to incorporate C$_2$H$_4$CO$_3^−$ and...
formation of green powder from the reaction mixture in 66% and 42% yields.

The formation of 2 and 3 can be summarized in eqs 2 and 3. In the latter case, slow crystallization from DMF medium for a longer time period trapped both NO2-C6H4CO2- and ClO4- in the crystal lattice.

\[
\text{H}_2\text{L} + 2\text{Ni}([\text{ClO}_4])_2 \cdot 6\text{H}_2\text{O} + 2\text{NaO}_2\text{C}_2\text{H}_5 \xrightarrow{\text{MeOH}} \left[\text{Ni}_4(\mu_3\text{-OH})_2(\mu_3\text{-H}_2\text{L})_2(\mu_3\text{-O}_2\text{C}_2\text{H}_5\text{H}_2\text{O})_2\right] \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \ quad
The tetranuclear complex units consist of two monodeprotonated (only the phenol unit) ligands (H$_2$L$^-$), each of them delivering a set of N$_2$O donor atoms to the tetrametallic coordination cluster unit that organizes around two solvent water-derived μ$_3$-OH groups (O4 and O4*) located at the two corners of the distorted cube. The Ni···Ni separations vary from 2.958 to 3.216 Å (Table S2 in SI). The molecular structure of 1 can be assumed to grow from spontaneous aggregation of two {Ni$_4$(μ-L)(μ$_3$-OH)} units, within which the phenoxido-hydroxido-bridged Ni1···Ni2 separation is shortest (2.958 Å). Three faces are distinctly different due to the presence of capping carboxylates.

All four Ni$^{II}$ ions remain in a distorted octahedral N$_2$O$_4$ coordination environment (Figure 2 and Figure S5 in the SI).

The Ni–O distances vary within the 2.008–2.210 Å range versus the Ni–N distances at 2.001–2.116 Å. The phenoxido bridges tune the Ni–O–Ni angles within the cube in the 89.05–101.44° range, while the HO$^-$ bridges record Ni–O–Ni angles in the 92.38–103.05° range. The double phenoxido-bridged face records the longest Ni···Ni distance of 3.317, 3.329, and 3.304 Å for 1, 2, and 3, respectively, while the double hydroxido-bridged face has an intermediate separation of 3.216, 3.211, and 3.209 Å for 1, 2, and 3, respectively. The μ$_3$-phenoxido bridge supports, observed in 1–3, for the growth of the cubes is exceptional in comparison to the μ$_3$-OH bridges. μ$_3$-OH and μ$_3$-OMe bridges most readily can use three available lone pairs to bind three different metal ions. As a result both hydroxido and methoxido groups can support cubane and dicubane structures quite readily. On the other hand, μ$_3$ bridging is not seen commonly with phenoxido ion. Only in a few cases it has been known for [Ni$_4$] and [Ni$_6$] complexes.

Within the Ni$_4$O$_4$ cube clusters the Ni$^{II}$ centers in distorted octahedral geometry only help the formation of the cubic arrangement. On the other hand, tetrahedral O centers were responsible for the distortion in the cubic structure.

All three cationic complexes crystallize with perchlorate anions and water molecules. In the case of 1 and 2 the dangling hydroxyl groups of the ligand arms are engaged in intra- as well as intermolecular hydrogen-bonding interactions with each other. The perchlorate anions on the other hand establish hydrogen-bonding interactions with two μ$_3$-OH groups per Ni$_4$ cubane. Such connectivity results in hydrogen-bonded double-chain structures within the crystal lattice of 1 and 2. The D···A distances range from 2.474 to 3.227 Å (Table S3), which confirms reasonably strong hydrogen-bonding interactions within the crystal lattice. Figure 3 and Figure S6 clearly describe the formation of H-bonded double-chain structures in 1 and 2, respectively.

In the case of 3 strong hydrogen-bonding interactions between pendant alcohol arms of the ligand and available carboxylate anions are responsible for the partial substitution of perchlorate anions within crystal lattice. Lattice water molecules also take part in hydrogen-bond formation, reinforcing the supramolecular hydrogen-bonding interaction to stabilize the aggregate further (Figure 4). The D···A distances for all donors and acceptors involved in hydrogen-bonding range from 2.686 to 3.046 Å (Table S3), which confirms strong H-bonding interaction within the complexes. The D–H···A angles also fall in a wide range of 105–170°.

$\{[Ni_4(\mu_3-H_2L)(\mu_3-C_1H_3Ph)_3(\mu_3-O_2CPh)_2(\mu_3-OMe)_3)\}^+ \cdot [\text{ClO}_4^-] \cdot [\text{H}_2\text{O}]_4 \cdot 2\text{MeOH}$ (4).

Complex 4 crystallizes in the monoclinic P2$_1$/c space group, and the asymmetric unit contains a ligand-bound dinuclear fragment [Ni$_4$(μ$_3$-H$_2$L)(μ$_3$-O$_2$CPh)$_3$(μ$_3$-OMe)$_3$]**. The molecular structure of 4 is shown in Figure 5, and selected bond lengths and angles are listed in Table S2. Compound 4 has a 1D coordination polymeric structure based on [Ni$_4$(μ$_3$-H$_2$L)$(\mu_3$-C$_1H_3Ph)(\mu_3$-OMe)$_3$]** repeating units. The use of PhCH$_2$CO$_2$$^-$ anions in the reaction medium did not generate HO$^-$ ions in good number to bridge two nickel(II) ions in comparison to PhCH$_2$CO$_3$$^-$ ions. This is also matching with the least basic nature of the phenylacetate moiety among all four carboxylates used in this study. Coordination of carboxylate modulates the structure of the {Ni$_4$(H$_2$L)}$^+$ fragment and fixes the position of the H$_2$L$^-$ bridging hydroxido ion, which in turn helps in the organization of {Ni$_3$} fragments for the product.

The asymmetric units are linked through the coordination of a dangling alcohol O–OH group of one end of a nickel(II)-bound H$_2$L$^-$ unit to one of the nickel(II) ions of the next unit. The distorted octahedral coordination geometry around two nickel(II) ions is shown in Figure 6.

The repeating {Ni$_3$} fragment consists of one singly deprotonated H$_2$L$^-$ ligand providing a set of N$_2$O$_4$ donor atoms, two carboxylate bridges, and one coordinated water molecule. These {Ni$_3$} units are very loosely bridged by the oxygen atom (O2*) of a dangling alcohol arm of the adjacent unit. The Ni–O distances in the 2.016–2.174 Å range are close to the Ni–N separations at 1.985–2.210 Å. The Ni–O(H) bond distance is 2.160 Å, while the Ni–Ow is the longest and has a bond length of 2.174 Å. The distorted octahedral environments around each Ni$^{II}$ ion are reflected in the variation...
of the cis and trans angles in the 79.4°–99.7° and 169.5°–174.3° ranges. The phenoxido (O1) and double carboxylato-bridged Ni···Ni distance is 3.435 Å, whereas the Ni···Ni separation within interdimeric units is in the 5.704–8.840 Å range (Figure 7).

Intramolecular hydrogen-bonding interactions further stabilize the weak interdinuclear link formed from alcoholic HO−coordination (Figure S7). Both the nickel(II)-bound −OH group (O2) and the dangling −OH arm (O3) within the \{Ni2(H2L)\} fragment are hydrogen bonded to the O donors (O4 and O7) of bound carboxylates and one −NH (N2) group of another \{Ni2(H2L)\} unit. Characteristic hydrogen-bonding parameters are listed in Table S3 in SI.

Mass Spectroscopic Identification of the Fragments.
The existence of different \{Ni3(H2L)\}-based key fragments in solution were established from mass spectral (ESI-MS positive) analysis of compounds 1–4 in MeOH solutions (Figure S8–S11). Aggregation of these fragments resulted in the products during synthesis and crystallization in the solid state.

Complex 1: In the spectra of 1 in MeOH solution two intense peaks were obtained at \(m/z = 449.06\) (calcd 449.06) and 499.06 (calcd 499.10) which can be attributed to the \([\text{Ni}_3L]^+\) (C17H25N4Ni2O3) and \([\text{Ni}_3(\text{HL})(\text{OH})(\text{CH}_3\text{OH})]^+\) (C18H31N4Ni2O5) fragments, respectively. The medium-intensity peak observed at \(m/z = 549.02\) (calcd 549.01) can be assigned to the fragment \([\text{Ni}_3(\text{HL})(\text{ClO}_4)]^+\) (C17H35Cl1Ni3O7). ESI-MS showed no evidence in support of a \([\text{Ni}_4]\) aggregate in the solution phase. The acetate-bound \{Ni2\} fragment produced in solution is manifested by a small peak at \(m/z = 650.97\) (calcd 649.03) of molecular formula \([\text{Ni}_2(\text{H}_2\text{L})(\text{OH})(\text{O}_2\text{CCH}_3)-\text{Na}]^+\) (C19H31ClN4NaNi2O10). During crystallization two such fragments collapse to yield 1 as crystals from solution.
Complex 2: In this case the peaks at 449.06 and 549.02 for molecular fragments [Ni2L]+ and [Ni2(HL)(ClO4)]+ are also present in the ESI-MS spectrum of 2 in MeOH. The base peak at m/z = 307.05 (calc 307.06) can be assigned to the hydrolyzed ligand part in the molecular fragment [Ni(HL’)]+ (C13H17N2NiO3). The presence of a mononcationic [Ni3] fragment [Ni3(H2L)(ClO4)(O2CC2H5)]+ (C26H32ClINi3O9) in solution phase, characteristic for bound C2H5CO2, originating from 2 is confirmed by a medium-intensity peak at m/z = 623.10 (calc 623.05).

Complex 3: All previously mentioned peaks at m/z = 449.06, 499.06, and 549.02 for [Ni2L]+, [Ni2(HL)(OH)(CH3OH)]+, and [Ni2(HL)(ClO4)]+ fragments are present in the ESI-MS spectrum of 3 in MeOH. Additionally, the most characteristic p-nitrobenzoate-bound {Ni3} distinguishing fragment [Ni3(HL)(p-NO-C6H4-CO2)]+ (C24H30N5Ni2O7) in 3 has been identified by a medium-intensity peak in the ESI-MS spectrum at m/z = 616.08 (calc 616.09).

Complex 4: Along with the common peaks at m/z = 449.06 and 549.02 in the ESI-MS of 4, the obtained distinctive and medium-intensity peak at m/z = 307.06 can be assigned to the mononuclear nickel(II)-bound hydrolyzed ligand fragment [Ni(HL’)]+ (C21H27N2NiO4). Dissolution of 4 in MeOH resulted in the solution-stable monophenylacetate-bound dinuclear fragment [Ni2(H2L)(O2CCH2Ph)]+ (C33H41N4Ni2O5) and bis-phenylacetate-bound fragment [Ni2(HL)(O2CCH2Ph)2]+ (C32H33N4Ni2O7) corresponding to the characteristic peaks at m/z = 585.12 (calc 585.11) and 721.17 (calc 721.16) in the ESI-MS spectrum.

The mass spectral (ESI-MS positive) evidence thus established the self-aggregation of dimeric fragments in one way for production of 1–3 and the polymeric nickel complex 4 via a different route.

Magnetic Studies. The temperature dependence of the molar magnetic susceptibility, χm, of compounds 1–4 was measured under a magnetic field of 0.1 T over the temperature range 290–2 K. Figure 8 shows the plots of χmT versus temperature, T, for compounds 1 and 2 (compound 3 is omitted for clarity and shown in Figure S12 in the SI). At 290 K, the values of χmT are 4.86, 4.96, and 5.13 cm³ mol⁻¹ K for 1, 2, and 3, respectively, which are all in line with expected values for four uncoupled NiII ions with g ≈ 2.2 within these multimetallic assemblies. On decreasing the temperature, 1–3 show a continual decrease in the value of χmT, which may be caused by predominant antiferromagnetic exchange interactions between the NiII ions but also by zero-field splitting (zfs) and antiferromagnetic intermolecular interactions at low temperature.

These data were fitted with the program Phi 2.0. The asymmetric nature of the cubanes means that they require four different exchange interactions to be considered; Figure 9 illustrates the different faces found in compound 1. For 1–3, the top and bottom faces of the distorted cubane were taken as those capped by the syn,syn-carboxylate groups and correspond to J1 between Ni1 and Ni2 and Ni1’ and Ni2’; the two lateral, opposing faces bridged by one hydroxyl group and a phenoxy oxygen atom are represented by J2 between Ni1 and Ni2’ and Ni2 and Ni1’. The coupling constant J2 corresponds to the face bridged by two phenoxy O atoms, mediating the interaction between Ni2 and Ni2’, and J2 corresponds to the pathway between Ni1 and Ni1’, which are bridged by two hydroxido groups. The same bridges and cubane faces are found in each complex and represented by the same coupling constant, but the exact label for the NiII ions depends on the crystallographic symmetry. To avoid overparameterization of the fit, the g values were fixed, while the possible contribution from zfs associated

Figure 8. Plot of χmT vs T for 1 and 2. Solid lines represent fits of the data as described in the text.

Figure 9. View of the cubane core in 1, highlighting the different types of bridge on each face as described in the text.
with the Ni\textsuperscript{II} ions was neglected. The Hamiltonian employed was

\[
\hat{H} = -2J_{1}(\hat{S}_{Ni1}\hat{S}_{Ni2} + \hat{S}_{Ni1}\hat{S}_{Ni3}) - 2J_{2}(\hat{S}_{Ni1}\hat{S}_{Ni2} + \hat{S}_{Ni1}\hat{S}_{Ni3})
- 2J_{3}(\hat{S}_{Ni3}\hat{S}_{Ni2}) - 2J_{4}(\hat{S}_{Ni4}\hat{S}_{Ni1}) + g\mu_{B}H \sum_{i=1}^{4} \hat{S}_{i}
\]

The $\chi_M T$ curves resulting from these fits are shown in Figure 8, and the derived parameters are given in Table 1.

### Table 1. Summary of the Exchange Interactions Derived from the Fits of the Magnetic Data for 1–3

<table>
<thead>
<tr>
<th>complex</th>
<th>$g$</th>
<th>$I_{1}$ (cm\textsuperscript{-1})</th>
<th>$I_{2}$ (cm\textsuperscript{-1})</th>
<th>$I_{3}$ (cm\textsuperscript{-1})</th>
<th>$I_{4}$ (cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.24</td>
<td>-2.03</td>
<td>+0.98</td>
<td>+0.32</td>
<td>-7.31</td>
</tr>
<tr>
<td>2</td>
<td>2.26</td>
<td>-2.58</td>
<td>+1.21</td>
<td>+0.70</td>
<td>-7.26</td>
</tr>
<tr>
<td>3</td>
<td>2.27</td>
<td>-2.03</td>
<td>+1.30</td>
<td>+0.04</td>
<td>-6.78</td>
</tr>
</tbody>
</table>

Previous magneto-structural correlations have shown that the average Ni–O–Ni angle is one of the most important parameters in deciding the nature and strength of the exchange coupling interactions mediated across the faces of a cubane.\textsuperscript{25} At angles of approximately 99°, the exchange interaction between Ni\textsuperscript{II} ions changes sign, with angles closer to 90° leading to stronger ferromagnetic coupling, while angles above 100° lead to antiferromagnetic coupling. Broadly, this trend is observed in compounds 1–3 (Table 1), where the interaction across the largest average Ni–O–Ni angle, $I_{4}$ [101.8(3)° in 1, 101.9(2)° in 2, and 102.5(3)° in 3], leads to the strongest antiferromagnetic coupling interaction between the Ni\textsuperscript{II} ions. The exchange across the faces with average Ni–O–Ni angles that lie close to 99° is weaker [98.2(1)° in 1, 97.9(1)° in 2, and 98.5(1)° in 3] and found to be ferromagnetic in all three cases.

An exception to this correlation is provided by the interactions across the carboxylate-capped faces, which are found to be antiferromagnetic despite the average Ni–O–Ni angles for all three compounds lying close to 90° [91.1(1)°, 90.9(1)°, and 91.6(1)° for 1, 2, and 3, respectively]. However, the correlation established is considered\textsuperscript{26} in only those cubanes that were bridged by μ-OR groups (RO = hydroxido, methoxido, alkoxido, and phenoxido) and ignored those containing a secondary bridge such as carboxylate groups. Other previous papers have found the presence of syn,syn-carboxylate bridges to result in strong deviations from the coupling anticipated based on magneto-structural correlations, often favoring antiferromagnetic exchange.\textsuperscript{20,27}

Figure 10 displays the plot of $\chi_M T$ versus temperature, $T$, for compound 4. The room-temperature value of $\chi_M T = 2.53$ cm\textsuperscript{3} mol\textsuperscript{-1} K is in line with that expected for two uncoupled Ni\textsuperscript{II} ions with $g \approx 2.25$. To fit the magnetic data with Phi 2.0, compound 4 was considered as discrete dinuclear units that are linked together into a chain. One coupling constant was considered between the Ni1 and the Ni2 ions ($J_{1}$), and the interaction between the neighboring dimers and chains was introduced as an intermolecular interaction ($zJ'$). As with compounds 1–3, the $g$ factors were assumed to be the same for each Ni\textsuperscript{II} ion, and any zfs associated with the Ni\textsuperscript{II} ions was neglected. The results of the fit yielded $g = 2.29$, $J_{1} = -1.56$ cm\textsuperscript{-1}, and $zJ' = -0.93$ cm\textsuperscript{-1}. The $g$ value and strength of the antiferromagnetic coupling are in line with those previously observed for other comparable, triply bridged, dinuclear Ni\textsuperscript{II} units.\textsuperscript{28} Due to the model employed, the intermolecular interaction is larger than expected, because it takes into account intrachain interactions between dinuclear units, as well as any possible interchain interactions and any decrease in $\chi_M T$ caused by zfs.

### CONCLUSIONS

Utilization of the coordination potential of 2,6-bis[2-(2-hydroxyethylamino)ethylamino[methyl]-4-methylphenol with nickel(II) perchlorate and aggregation propensity of the fragments thus formed have been studied in this work. In the presence of four different carboxylates these fragments led to the generation and isolation of two types of self-organized aggregates depending on the nature and number of bound carboxylate anions. The use of acetate, propionate, and p-nitrobenzoate to phenylacetate groups in the reaction medium resulted in two distinct courses of aggregation reactions. In one case, three [Ni\textsubscript{4}] coordination clusters have been grown from in-situ trapping of HO\textsuperscript{+} ions from H\textsubscript{2}O of the reaction medium. In the other case, use of phenylacetate bridges provided a [Ni\textsubscript{3}]\textsubscript{6} chain complex through linking of [Ni\textsubscript{4}(μ-H\textsubscript{2}L)]\textsuperscript{3+} units by dangling alcohol arms of the ligands. In the reaction medium H\textsubscript{2}L\textsuperscript{-} was used initially to trap two Ni\textsuperscript{II} ions, leaving behind available coordinating sites for hydroxide and carboxylate binding followed by assembly of two or more ligand-bound [Ni\textsubscript{4}(μ-H\textsubscript{2}L)]\textsuperscript{3+} units for tetrameric [Ni\textsubscript{4}] and interconnected [Ni\textsubscript{3}]\textsubscript{6} complex formation. Two solvent-derived HO\textsuperscript{+} groups present in one face of the [Ni\textsubscript{4}] distorted cube do bring Ni–Ni separations within 2.958–3.216 Å, whereas in the case of the polynuclear 1D chain the phenoxido and double carboxylato bridges result in shorter Ni–Ni separations of 3.435 Å, which is considerably shorter than the Ni–Ni separation within interdimeric units at 5.704–8.840 Å. In three of the discrete [Ni\textsubscript{4}] complexes the face-wise dependence of Ni–O–Ni angles for ferromagnetic and antiferromagnetic interactions was observed. In the case of complex 4, the single important coupling constant ($J_{1}$) was found to be antiferromagnetic in nature with a small value of $-1.56$ cm\textsuperscript{-1}. As a continuation of the work, we are exploring the bridging potential of in-situ-derived carbonate and externally available nitrate, cyanate, oxalate, sulfide, thiocyanate, peroxide, and azide ions systematically in this reaction protocol to obtain other types of self-assembled and interlinked [Ni\textsubscript{4}] aggregates.
Topologies of nickel complexes known in the literature, metal binding modes of ancillary ligands, formation of H\textsubscript{2}L\textsubscript{2}, FTIR spectra of 1–4, comparative powder XRD patterns of 1–4, charge transfer and d–d transition bands for 1–4, POV ray representation for [Ni\textsubscript{4}(H\textsubscript{2}L)\textsubscript{2}][\mu\textsubscript{3}-OH]\textsubscript{3}(\mu\textsubscript{1},\textsubscript{3}-O\textsubscript{2}C\textsubscript{2}H\textsubscript{5})\textsubscript{3}]\textsuperscript{2+} unit in 2 and [Ni\textsubscript{4}(H\textsubscript{2}L)\textsubscript{2}][\mu\textsubscript{3}-OH]\textsubscript{3}(\mu\textsubscript{1},\textsubscript{3}-O\textsubscript{2}C\textsubscript{2}H\textsubscript{5}NO\textsubscript{2})\textsubscript{3}]\textsuperscript{2+} unit in 3 with partial atom-numbering scheme, core structures of 2 and 3, H-bonded double-chain formation within 2, intramolecular H bonding within 1D coordination polymer 4, ESI MS spectra of 1 in MeOH, ESI MS spectra of 2 in MeOH, ESI MS spectra of 3 in MeOH, ESI MS spectra of 4 in MeOH, \(X_{\text{ref}}^\text{T}\) versus T plot for 3, crystal data and structure refinement details for compounds 1–4, selected bond distances and bond angles for 1–4, hydrogen-bonding parameters for 1–4, and carboxylate stretching frequencies of complexes 1–4 (PDF).

X-ray crystallographic data (ZIP)

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**Notes**

The authors declare no competing financial interest.

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