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The Structural Manipulation of a Series of Ni₄ Defective Dicubanes: Synthesis, X-ray Structures, Magnetic and Computational Analyses.†

Sidney S. Woodhouse, Tyson N. Dais, Emily H. Payne, Mukesh K. Singh, Euan K. Brechin, and Paul G. Plieger

We report the synthesis and characterization of four new tetranuclear Ni(II) complexes, C1-C4, all of which exhibit defective dicubane cores. C1-C4 are derived from the same salicylaldoxime derived ligand, H₂L₁. Complexes C1 and C4 have isostructural cores, differing in structure only by solvate molecules. Magnetic and computational analyses have revealed that complexes C1, C2, and C4 exhibit competing ferro- and antiferromagnetic interactions, however the different solvated species in C1 and C4 leads to notably different magnitudes in their magnetic coupling constants. Theoretical magneto-structural studies show that the pairwise magnetic exchange interaction is highly dependent on the Ni–X–Ni angle, as revealed by orbital overlap calculations.

Introduction

The last few years have seen an increased interest in transition metal (3d) based polynuclear coordination complexes, due to continued interest in fields such as catalysis, luminescence, and single molecule magnetism. A popular topology found in both of these fields is defective dicubanes, more commonly known as butterfly complexes. Defective dicubane refers to tetranuclear complexes where two face-sharing cubanes, each missing an opposite vertex, form the metallic core (Fig. 1). Defective dicubanes have gained popularity due to the coordination chemist's ability to manipulate exchange interactions through synthetic chemistry. For example, tuning of exchange interactions has been shown to be an effective method for quenching quantum tunnelling of magnetization (QTM). Common manipulation methods include changing the bridging groups between the metal ions, or introducing groups either coordinated or free that can form inter/intramolecular interactions, which change the bridging angles, and therefore change the sign and/or magnitude of magnetic interactions. This is well reported in the literature, with examples by Oyarzabal et al. and Jiang et al. who show that by switching the central bridging group from a methoxy group to an azido group, a stronger ferromagnetic exchange between the two metal centres can be achieved.

The salicylaldoxime moiety is commonly found in 3d based coordination clusters. The popularity surrounding salicylaldoxime derivatives as chelating ligands arises from the number of coordination sites (phenoxo oxygen and oximato nitrogen and oxygen) present, but more importantly, from its ability to impart structural torsion through M–N–O–M (M = metal ion) bridging (Fig. 2), often resulting in interesting magnetic properties. This structural torsion is commonly seen in complexes with a triangular metallic core such as the MnIII complex produced by Brechin and coworkers which exhibited single molecule magnetism, and at the time, was a record breaking single molecule magnet (SMM). Although this structural torsion is more commonly seen in triangular topolo-
reaction between $\text{H}_2\text{L}1$. The solid-state complexes, as previously mentioned, are reported examples of this occurring in both cubes and defective dicubanes. The $[\text{Co}^\text{II},\text{Co}^\text{III}]_2(\text{L})_2(\text{N}_2)_4(\text{EtOH})_2$ butterfly reported by Yao et al. utilises the ligand 3-methoxysalicylaldoxime with the phenoxo oxygen and oximato group coordinating to the metal centres. The deprotonation of the oximato oxygen causes distortion within the metallic core, as the exchange coupling resembles the well known M–N–O–M oximato bridging rather than the more typical M–X–M (X = bridging group) bridging.

Our aim for this investigation was to synthesise and characterize, both magnetically and computationally, a series of Ni(II) defective dicubanes to explore how minor structural changes can affect the overall magnetic properties of a complex. The structural changes investigated involved changing the coordinated anions, and lattice solvent molecules. Four Ni(II) defective dicubanes have been synthesized, utilizing the salicylaldoxime derived ligand $\text{H}_2\text{L}1$ (5-tert-butyl-3-(N-methyl-N-(2,2-dimethoxyethyl)amino)methyl salicylaldoxime, Fig. 2). $[\text{Ni}_4(\text{HL1})_2(\text{OMe})_2(\text{OAc})_2\text{Cl}_2\cdot(\text{Et}_2\text{O})_3$ (C1), $[\text{Ni}_4(\text{HL1})_2(\text{OMe})_2(\text{MeOH})_2\text{Cl}_4\cdot(\text{Et}_2\text{O})_3$ (C2), $[\text{Ni}_4(\text{HL1})_2(\text{OMe})_2(\text{MeOH})_2\text{Cl}_2\text{F}_2\cdot(\text{Et}_2\text{O})_3$ (C3), and $[\text{Ni}_4(\text{HL1})_2(\text{OMe})_2(\text{OAc})_2\text{Cl}_2\cdot(\text{MeOH})_2$ (C4). We report the synthesis, X-ray structures, magnetic, and computational analysis of complexes C1-C4.

Results and discussion

Structural Analysis
The solid-state complexes, C1-C4, have been synthesized from the reaction between $\text{H}_2\text{L}1$ and Ni(II) metal salts ($\text{Ni(OAc)}_2\cdot3\text{H}_2\text{O}$, $\text{NiCl}_2\cdot6\text{H}_2\text{O}$, and $\text{NiBF}_4\cdot2\cdot6\text{H}_2\text{O}$) in MeOH at room temperature (RT). Successful coordination between $\text{H}_2\text{L}1$ and the Ni(II) ions was confirmed visually by the yellow ligand solution turning green. Isolation of complexes C1-C4 was achieved by slow vapour diffusion of Et$_2$O into the concentrated green methanolic solution.

All complexes are monoclinic, crystallizing in the $P_2_1/c$ space group (Table S1). The general structure of C1-C4 consists of a defective dicubane with four Ni(II) ions, each with distorted octahedral geometries (Tables 1 and S2) and donor sets consisting of oxygen, nitrogen, chloride, and fluoride atoms. For complexes C1 and C4, the asymmetric unit contains half of the structure, with the remainder symmetry generated and for complexes C2 and C3, the symmetric unit contains the whole structure (the full structures of C1-C4 can be seen in Figs. 2-5).

The metallic cores of the four Ni(II) defective dicubanes have similar coordination environments, with complexes C1 and C4 being isostructural. For all complexes, the central Ni(II) ions, nicknamed the “body” ions, have a coordination environment consisting of a terminal $\text{N}_{\text{oximato}}$ and bridging $\text{H}_2\text{O}_{\text{phenoxo}}$ from the ligand and three additional bridging groups: two $\text{M}_3\text{O}_{\text{methoxo}}$ and a $\mu_2\text{X}_{\text{halide}}$ ($\mu_2\text{Cl}$ for C1, C2, and C4 and $\mu_2\text{Cl}/\mu_2\text{F}$ in a 40:60 ratio for C3). The coordination environment of the Ni(II) ions is completed by either a $\mu_2\text{OAc}$ (C1 and C4) or a MeOH molecule (C2 and C3). The outer Ni(II) ions, nicknamed the “wingtip” ions, have coordination environments consisting of terminal $\text{O}_{\text{OMe}}$ and $\text{N}_{\text{amino}}$ groups and a bridging $\mu_2\text{O}_{\text{phenoxo}}$ all from the ligand. The remainder of the coordination environment is made up of a $\mu_3\text{O}_{\text{methoxo}}$, a $\mu_2\text{X}_{\text{halide}}$ ($\mu_2\text{Cl}$ for C1, C2, and C4 and $\mu_2\text{Cl}/\mu_2\text{F}$ in a 40:60 ratio for C3) and either a $\mu_2\text{OAc}$ (C1 and C4) or a terminal chloride (C2 and C3). For all complexes, hydrogen bonds can be found between the oximato OH group and the bridging $\mu_2\text{X}_{\text{halide}}$. Additional hydrogen bonds can be found for complexes C2 and C3 between the terminal chlorides and MeOH groups. For all complexes, solvent molecules are found within the crystal lattices. For complexes, C1-C3, Et$_2$O...
molecules (one molecule for both C2 and C3, and two molecules, with one positionally disordered over two sites for C1) are found in the crystal lattice. For complex C4, two MeOH solvates each form a hydrogen bond with an oxygen atom of the bridging acetate groups.

The main structural difference between complexes C1 and C4 are the solvate molecules in the lattice (Et₂O and MeOH respectively). The additional hydrogen bonding between the methanol solvate and the metallic core of C4 results in different crystal packing, with the intramolecular Ni1–Ni’1 distances of C1 and C4 being 13.86 Å and 10.91 Å within the same crystal plane respectively, and 9.94 Å and 10.15 Å between different crystal planes respectively (Figs. S2 and S3), but more importantly, results in small changes to the Ni–X–Ni angles of the exchange pathways in C1 and C4 (Tables 1 and S3) resulting in significant difference in the magnetic properties.

For complex C3, the presence of bridging fluoride anions has resulted in a large amount of disorder, with the μ₂-halide bridges being both fluoride and chloride (60:40 respectively). The initial goal for this structure was to retain the bridging chloride groups while incorporating fluoride caps, as a mixed-halide analogue to complex C2. This small difference between complexes C2 and C3, has resulted in large changes in the magnetic properties.

Magnetic Analysis

The direct-current molar magnetic susceptibilities, χₘ, of polycrystalline samples of complexes C1-C4 were measured in an applied magnetic field, B = 0.1 T, over the 290 - 2 K temperature range. The experimental results are shown in Fig. 7 as the χₘT product versus T. At 300 K, the χₘT products (5.12 (C1), 5.25 (C2), 4.91 (C3), 5.48 (C4) cm³Kmol⁻¹) are consistent with the expected value for four uncorrelated Ni(II) ions (Sₙi = 1; 5.06 cm³Kmol⁻¹) with gₙi = 2.25. Upon cooling, the χₘT products of C1, C2 and C4 rise slowly reaching maximum values of 5.82 (T = 22 K), 5.62 (T = 18 K) and 10.72 (T = 3.7 K) cm³Kmol⁻¹, respectively. Upon further cooling, the χₘT products fall to 4.43 (C1), 4.42 (C2) and 9.87 (C3) cm³Kmol⁻¹ at 2 K. Given that the expected χₘT value for a ferromagnetically coupled [Ni²⁺₄] unit (S = 4) is 12.66 cm³Kmol⁻¹ the experimental susceptibility data is likely due to competing ferro- and antiferromagnetic exchange interactions, in tandem with zero-field splitting effects and/or antiferromagnetic intermolecular interactions at the lowest temperatures. For C3, the χₘT product remains constant with decreasing temperature until ~77 K, at which point it falls sharply to a minimum value of 1.58 cm³Kmol⁻¹ at 2 K. This is indicative of the presence of dominant antiferromagnetic exchange.

To better define the low-temperature magnetic properties, variable-temperature-variable-field (VTVB) magnetization measurements were performed in the temperature and field ranges of 3 - 6 K and 0.5 - 7 T (Fig. 8). The magnetization reaches a maxima (3 K, 7 T) of 7.59 (C1), 7.02 (C2), 7.02 (C3), and 8.77 (C4) μₜ. The susceptibility and magnetization data of C1, C2, and C4 were fitted simultaneously using the program PHI [29] with the following spin-Hamiltonian (1):

where the summation indices ij label consecutive metal cen-

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**Fig. 5** Molecular structure of C2. Lattice solvent molecules and non-interacting hydrogen atoms removed for clarity. Colour code: Ni = light green, N = blue, O = red, Cl = dark green, C = grey, and H = white. Hydrogen bonds represented as black dotted lines.

**Fig. 6** Molecular structure of C3. Lattice solvent molecules and non-interacting hydrogen atoms removed for clarity. Colour code: Ni = light green, N = blue, O = red, Cl = dark green, F = yellow, C = grey, and H = white. Hydrogen bonds represented as black dotted lines.
Table 1 Averaged bond lengths (Å) and bond angles (°) of complexes C1-C4

<table>
<thead>
<tr>
<th></th>
<th>C1</th>
<th>C2*</th>
<th>C3*</th>
<th>C4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni1-Cl1</td>
<td>2.50(8)</td>
<td>2.40</td>
<td>2.29</td>
<td>2.42(1)</td>
</tr>
<tr>
<td>Ni1-O1</td>
<td>2.04(19)</td>
<td>2.00</td>
<td>2.01</td>
<td>2.00(3)</td>
</tr>
<tr>
<td>Ni1-O2</td>
<td>2.01(19)</td>
<td>2.07</td>
<td>2.06</td>
<td>2.05(3)</td>
</tr>
<tr>
<td>Ni1-O6</td>
<td>2.11(2)</td>
<td>—</td>
<td>—</td>
<td>2.07(3)</td>
</tr>
<tr>
<td>Ni1-O11</td>
<td>—</td>
<td>2.08</td>
<td>2.10</td>
<td>—</td>
</tr>
<tr>
<td>Ni1-N1</td>
<td>1.98(2)</td>
<td>2.05</td>
<td>2.01</td>
<td>2.05(3)</td>
</tr>
<tr>
<td>Ni1-O2</td>
<td>2.12(19)</td>
<td>2.08</td>
<td>2.05</td>
<td>2.07(3)</td>
</tr>
<tr>
<td>Ni1-F1</td>
<td>—</td>
<td>—</td>
<td>2.10</td>
<td>—</td>
</tr>
<tr>
<td>Ni2-O1</td>
<td>1.95(19)</td>
<td>2.02</td>
<td>2.03</td>
<td>2.00(3)</td>
</tr>
<tr>
<td>Ni2-O2</td>
<td>2.08(19)</td>
<td>2.08</td>
<td>2.09</td>
<td>2.06(3)</td>
</tr>
<tr>
<td>Ni2-O7</td>
<td>2.07(2)</td>
<td>—</td>
<td>—</td>
<td>2.02(3)</td>
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<tr>
<td>Ni2-O3/5</td>
<td>2.09(2)</td>
<td>2.17</td>
<td>2.17</td>
<td>2.16(3)</td>
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<td>Ni2-N2</td>
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<td>2.09</td>
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<td>2.56(8)</td>
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<td>Ni2-Cl3</td>
<td>—</td>
<td>2.37</td>
<td>2.36</td>
<td>—</td>
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<td>Ni2-F1</td>
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<td>—</td>
<td>2.04</td>
<td>—</td>
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<tr>
<td>Ni1-O2-Ni1/3</td>
<td>98.8(8)</td>
<td>95.64</td>
<td>94.96</td>
<td>98.24(11)</td>
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<td>Ni1-O1-Ni2/4</td>
<td>95.4(8)</td>
<td>100.35</td>
<td>99.64</td>
<td>94.76(12)</td>
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<tr>
<td>Ni1-Cl1-Ni2</td>
<td>86.3(2)</td>
<td>86.79</td>
<td>84.82</td>
<td>85.60(3)</td>
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<tr>
<td>Ni1-F1-Ni2</td>
<td>—</td>
<td>—</td>
<td>102.09</td>
<td>—</td>
</tr>
<tr>
<td>Ni1-O2-Ni2</td>
<td>92.1(8)</td>
<td>106.91</td>
<td>102.25</td>
<td>108.08(18)</td>
</tr>
<tr>
<td>Ni2-O2-Ni1/3</td>
<td>111.3(8)</td>
<td>96.81</td>
<td>96.03</td>
<td>91.22(14)</td>
</tr>
</tbody>
</table>

* Averaged values, non-averaged values found in Table S2

a 1-X, -Y, 1-Z
b 1-X, 1-Y, 1-Z
In order to estimate the exchange coupling values (J1, J2, and J3) we have performed DFT calculations on the full X-ray structures of complexes C1-C4. Pairwise exchange interaction calculations were performed by keeping only two paramagnetic Ni(II) centres, replacing the remaining two with Zn(II). See Computational Details section for more information. For μ3-Cl/F moieties, we consider only the F-bridged structure, since the Cl-bridged structure is analogous to compound C2. The DFT calculated J values (Table 3) are in excellent agreement with the experimental values (Table 2). The J1 exchange interaction, which is mediated via μ3-O_methoxo, μ2-O_phenoxo, and μ2-OAc groups for C1 and C4, with average Ni-μ2/3-O-Ni angles of 93.7/93.0°, respectively (Table S4), is estimated to be moderately ferromagnetic (+9.7 cm⁻¹ (C1), +9.2 cm⁻¹ (C4)).

Overlap calculations suggest one moderate overlap for both C1 and C4: \((\langle \text{Ni}(1)d_{x^2}\rangle_p\langle \text{Ni}(2)d_{x^2}\rangle_p = 0.041\) for both C1 and C4, Table S5; Fig. S4) and three small/orthogonal magnetic orbital overlaps resulting in ferromagnetic exchange. Previous studies on polymeric Ni(II) complexes highlight the importance of the Ni-μ2/3-O-Ni angle on the magnetic exchange coupling value: the larger the angle the larger the antiferromagnetic contribution, the crossover between ferro- and antiferromagnetic being ~97.98°\(^{34,37}\). In addition to this, it has been shown previously that the presence of a bridging phenoxo group in tandem with a bridging carboxylate group exhibits a counter-complementary effect, often resulting in a ferromagnetic interaction.\(^{38}\)

The J1 magnetic exchange interaction for complexes C2 and C3, mediated by μ3-O_methoxo and μ2-O_phenoxo bridging groups with average Ni-μ2/3-O-Ni angles of 98.6° and 97.8°, respectively (Table S4), shows weak antiferromagnetic exchange (-2.3 cm⁻¹ (C2) and -0.3 cm⁻¹ (C3)). One strong \((\langle \text{Ni}(1)d_{x^2}\rangle_p\langle \text{Ni}(2)d_{x^2}\rangle_p = 0.061\) (C2) and \((\langle \text{Ni}(1)d_{x^2}\rangle_p\langle \text{Ni}(2)d_{x^2}\rangle_p = 0.050\) (C3), Table S5) and three small/orthogonal magnetic orbital overlaps result in weak antiferromagnetic exchange.

The J2 exchange interaction is mediated by μ3-O_methoxo and μ2-Cl/F groups with average Ni-μ2/3-O(OCl/F)-Ni angles of 98.8°(C1), 96.8°(C2), 102.4°(C3), and 96.7°(C4) (Table S4), resulting in weak antiferromagnetic interactions in C1 and C4 (-1.5 cm⁻¹ and -0.8 cm⁻¹, respectively), a moderate antiferromagnetic interaction in complex C3 (-7.7 cm⁻¹) and a weak ferromagnetic interaction for complex C2 (+2.1 cm⁻¹). Overlap calculations suggest two moderate overlap interactions for C1 \((\langle \text{Ni}(2)d_{x^2}\rangle_p\langle \text{Ni}(3)d_{x^2}\rangle_p = 0.034\) and \((\langle \text{Ni}(2)d_{x^2}\rangle_p\langle \text{Ni}(3)d_{x^2}\rangle_p = 0.036\), Table S5) and one strong interaction for C4 \((\langle \text{Ni}(2)d_{x^2}\rangle_p\langle \text{Ni}(3)d_{x^2}\rangle_p = 0.055\), Table S5), leading to a small antiferromagnetic interaction. For C3, one strong and one moderate magnetic orbital overlap \((\langle \text{Ni}(2)d_{x^2}\rangle_p\langle \text{Ni}(3)d_{x^2}\rangle_p = 0.061\) and \((\langle \text{Ni}(2)d_{x^2}\rangle_p\langle \text{Ni}(3)d_{x^2}\rangle_p = 0.036\), Table S5) results in a moderate antiferromagnetic interaction. For C2, only one moderate interaction \((\langle \text{Ni}(2)d_{x^2}\rangle_p\langle \text{Ni}(3)d_{x^2}\rangle_p = 0.035\), Table S5) is observed resulting in a small ferromagnetic interaction between the Ni(II) centres. Note that C3 contains the more electron-repulsed F-bridging group with a smaller average Ni-F distance resulting in a much stronger antiferromagnetic interaction compared to the Cl analogue. Although the average structural parameters for C2 and C4 are similar, there is a significant difference in sign and magnitude of the magnetic coupling (+2.1 cm⁻¹ and -0.8 cm⁻¹, respectively). The Ni-μ2Cl-Ni angle is 86.7°(C2) and 85.6°(C4) whereas the Ni-μ2O-Ni angle is 107.0°(C2) and 107.8°(C4). In agreement with previously published magnetostructural studies\(^{39}\) the change in Ni-O-Ni angle gives a more dominant shift to antiferromagnetic coupling, compared to the small increased ferromagnetic contribution due to narrowing of the Ni-Cl-Ni angle, as supported by overlap calculations.

The J3 exchange interaction for complexes C1-C4 is mediated by two μ3-O_methoxo groups with average Ni-μ2-O-Ni angles of 98.9°, 95.7°, 95.0°, and 98.2°, respectively. This results in weak ferromagnetic exchange in complexes C1 (+1.7 cm⁻¹) and C4...
Fig. 8 Field dependence of the magnetization ($M$) measured in the $T = 3 - 6$ K and $B = 0.1 - 7.0$ T temperature and field ranges for C1, C2, C3, and C4. The solid lines are a fit of the experimental data. See main text for details.

### Table 2

<table>
<thead>
<tr>
<th></th>
<th>$J_1$(cm$^{-1}$)</th>
<th>$J_2$(cm$^{-1}$)</th>
<th>$J_3$(cm$^{-1}$)</th>
<th>$g$</th>
<th>$D_{Ni}$(cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>+1.92(±0.08)</td>
<td>-1.77(±0.07)</td>
<td>+8.19(±0.26)</td>
<td>2.22(±0.002)</td>
<td>-9.3(±0.07)</td>
</tr>
<tr>
<td>C2</td>
<td>-0.27(±0.02)</td>
<td>-0.17(±0.02)</td>
<td>+4.73(±0.07)</td>
<td>2.25(±0.001)</td>
<td>-15.1(±0.09)</td>
</tr>
<tr>
<td>C4</td>
<td>+7.94(±0.13)</td>
<td>-1.31(±0.12)</td>
<td>+6.67(±0.48)</td>
<td>2.28(±0.002)</td>
<td>-3.99(±0.07)</td>
</tr>
</tbody>
</table>
(± 1.3 cm$^{-1}$) and moderate ferromagnetic exchange for complexes C2 (+9.7 cm$^{-1}$) and C3 (+10.7 cm$^{-1}$). Overlap calculations suggest the presence of one moderate overlap interaction for C1 and C4 ($\langle Ni(1) d_{xy} \cdot Ni(3) d_{xy} \rangle = 0.043$ and 0.044 respectively, Table S5), which leads to a small ferromagnetic interaction. For C2 and C3, none of the magnetic orbitals are interacting (Table S5), affording a relatively large exchange interaction exchange.

The spin density plots for C1-C4 (Fig. 10, Fig. S5) suggest a spin delocalization mechanism with the spin density on the Ni(II) atoms (0.068-0.074), since the 3p orbitals of Cl are energetically higher than the 3p orbitals of O (0.097-0.112) is greater than that on the µ$_2$-Cl bridging atoms (0.068-0.074), since the 3p orbitals of Cl are energetically closer to the 3d orbitals of the Ni(II) ions.

**Conclusions**

The reaction between ligand, H$_2$L1, and Ni(II) metal salts, Ni(OAc)$_2$, 4H$_2$O, NiCl$_2$, 6H$_2$O, and Ni(BF$_4$)$_2$, 6H$_2$O, has resulted in the formation of four new tetracnular Ni(II) defective dicubanes ((Ni$_4$(HL1)$_2$(OMe)$_2$(OAc)$_2$Cl$_2$) · (Et$_2$O)$_3$ (C1), [Ni$_4$(HL1)$_2$(OMe)$_2$(MeOH)$_2$Cl$_2$] · Et$_2$O (C2), [Ni$_4$(HL1)$_2$(OMe)$_2$(MeOH)$_2$Cl$_2$] · 2.8F$_1$Cl$_2$ · Et$_2$O (C3), and [Ni$_4$(HL1)$_2$(OMe)$_2$(OAc)$_2$Cl$_2$] · (MeOH)$_2$ (C4)). The Ni(II) ions are bridged by a series of phenoxy, methoxy, chloride, and fluoride atoms originating from the Ni(II) metal salt used. Despite the similarities in the formulae and general structural topology of C1-C4 there are significant geometric differences that result in rather different magnetic properties. Perhaps the most striking example comes from a comparison of isomorphous C1 and C4. Here different solvation leads to different packing in the extended structure which in turn leads to different intramolecular Ni-X-Ni angles and thus different magnetic exchange interactions. This study highlights the subtle intricacies involved in controlling intramolecular geometries and hence the sign and magnitude of magnetic coupling constants, particularly those relating to non-coordinating species such as anions/cations and solvent of crystallization.

**Experimental Section**

**General Details**

All reactions were performed under aerobic conditions using chemicals and solvents as received, unless otherwise stated. The ligand starting materials, 5-tert-butylsalicylaldehyde and 3-(bromomethyl)-5-tert-butylsalicylaldehyde, were prepared as described in the literature. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer and reported relative to residual solvent. Mass spectra were obtained using a Dionex UltiMate 3000 spectrometer. IR spectra were recorded on a Nicolet 5700 FT-IR spectrometer using an ATR sampling accessory. UV/Vis spectra were collected using a Shimadzu UV-3101PC spectrophotometer. Elemental analyses were determined by the Campbell Microanalytical Laboratory at the University of Otago. Variable temperature, solid-state DC magnetic susceptibility data down to 2 K was performed on polycrystalline samples embedded in eicosane and was collected on a Quantum Design MPMS XL-5 SQUID magnetometer equipped with a 7 T DC magnet at The University of Edinburgh. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal's constants. All crystalline samples originated from single bulk complexation reactions, which were analysed by unit cell checks, IR spectroscopy, and elemental analysis.

**X-ray Crystallography**

The X-ray data for complexes C1-C4 (Table S1) was collected at 1.661 - 1.717. This is as expected since the unpaired electrons reside in the e$_g$ orbitals. Of all the bridging atoms, the largest spin density is detected on the µ$_3$-O$_{methoxy}$ atoms (0.162-0.168). The spin density on the µ$_2$-Cl bridging atoms (0.097-0.112) is greater than that on the µ$_2$-F bridging atoms (0.068-0.074), since the 3p orbitals of Cl are energetically closer to the 3d orbitals of the Ni(II) ions.
iso-density surface shown corresponds to a value of 0.005 e-/bohr³.

\[
\hat{H} = -2J_1(\hat{S}_{N1} \cdot \hat{S}_{N2} + \hat{S}_{N3} \cdot \hat{S}_{N4}) \\
-2J_2(\hat{S}_{N1} \cdot \hat{S}_{N4} + \hat{S}_{N2} \cdot \hat{S}_{N3}) \\
-2J_3(\hat{S}_{N1} \cdot \hat{S}_{N3})
\] (2)

Computational Details

The Gaussian 16 program suite\(^{55}\) was used to estimate the magnetic exchange coupling constants present in complexes C1-C4, employing the hybrid B3LYP functional\(^{51,54}\) along with the TZV basis set\(^{55,57}\) for Ni, Zn, Cl, F, O, N atoms and the 6-31G* basis set\(^{58}\) for the C and H atoms. Density Functional Theory together with the broken symmetry approach\(^{50,62}\) is known to be a reliable tool for estimating magnetic exchange interactions with a high level of accuracy. Eight spin configurations were used to calculate three possible exchange coupling constants. The computed spin configurations comprise a high spin configuration with all spins up (\(S = 4\)), four other spin configurations with one of the spin centres down (\(S = 2\)) and three remaining spin configurations with two spin centres down (\(S = 0\)). See Table S6 for full details. Pairwise exchange interaction calculations were performed by keeping only two paramagnetic centres, replacing the remaining two with Zn(II). We have performed overlap integral calculations\(^{63}\) between non-orthogonal singly occupied molecular orbitals of the Ni(II) ions to analyse the sign and magnitude of magnetic exchange parameters for C1-C4 using the Heisenberg-Dirac-Van Vleck Hamiltonian\(^{64}\)(2).

Ligand and Complex Syntheses

5-tert-Butyl-3-(N-methyl-N-(2,2-dimethoxyethyl)amino)methyl salicylaldehyde (HL1a)

Solutions of 2,2-dimethoxy-N-methylethanamine (0.47 mL, 3.71 mmol) and 3-(bromomethyl)-5-tert-butyrsalicylaldehyde (1.03 g, 3.71 mmol), each in CHCl₃ (20 mL) were simultaneously added dropwise to a stirred solution of Et₃N (0.51 mL, 3.71 mmol) in CHCl₃ (20 mL). The resulting bright yellow solution was stirred at RT for 24 hours. The solution was washed with deionised H₂O (3 x 60 mL), and the combined organic layers were dried over anhydrous MgSO₄, filtered and concentrated \textit{in vacuo} to afford a yellow oil (1.10 g, 97%).

1H NMR (500 MHz, CDCl₃): δ 10.33 (s, 1H, CH=O), 7.62 (d, \(J = 2.2\) Hz, 1H, Ar-H(σ-amine)), 7.35 (d, \(J = 2.2\) Hz, 1H, Ar-H(σ-oxide)), 4.59 (t, \(J = 5.4\) Hz, 1H, CH₂-CF), 3.77 (s, 2H, Ar-CH₃-N), 3.38 (s, 6H, O-CH₃), 2.66 (d, \(J = 5.4\) Hz, 2H, N-CH₂-CH), 2.37 (s, 3H, N-CH₃), 1.30 (s, 9H, "Bu); 13C NMR (125.7 MHz, CDCl₃): δ 192.4, 159.2, 141.9, 133.3, 125.0, 123.7, 122.0, 102.2, 59.6, 58.2, 53.7, 42.6, 34.1, 31.3; IR: \(\tilde{\nu} = 2957\) (C-H), 1678 (C=O), 1652 (C-H), 1604 (C=C), 1395 (C-H), 1364 (O-H), 1124 (C=N), 1073 (C-O) cm⁻¹; MS: \(m/z\) (ESI) 310 [M+H]+; UV/Vis (\(\epsilon\), L/mol cm) in MeOH: 337.0 (3286), 259.5 (7360), 218.0 (14258); elemental analysis calcd (%) for C₁₇H₂₇NO₄: C 65.99, H 8.80, N 4.53; found: C 66.55, H 8.64, N 4.76.

5-tert-Butyl-3-(N-methyl-N-(2,2-dimethoxyethyl)amino)methyl salicylaldoxime (H₂L1)

A solution of NH₄OH-HCl (0.24 g, 3.53 mmol) in EtOH (30 mL) was neutralised with a solution of KOH (0.20 g, 3.53 mmol) in EtOH (30 mL). The filtered solution was added dropwise to a solution of HL1a (0.98 g, 3.53 mmol) in EtOH (50 mL). The resulting solution was stirred for 24 hours at RT. The light yellow
solution was concentrated in vacuo affording an oil, which was redissolved in CHCl₃ (30 mL). This solution was washed with deionised H₂O (3 x 30 mL) and the combined organic layers were dried over anhydrous MgSO₄, filtered and concentrated in vacuo affording H₂L₁ as a yellow oil (0.94 g, 91%). ¹H NMR (500 MHz, CDCl₃): δ 8.37 (s, 1H, CH=N), 7.36 (d, J = 2.5 Hz, 1H, Ar-H(σ-amine)), 7.13 (d, J = 2.5 Hz, 1H, Ar-H(σ-oxime)), 4.62 (t, J = 5.2 Hz, 1H, CH₂CH₂), 3.74 (s, 2H, Ar-N=C-N), 3.36 (s, 6H, O=C), 3.02 (2H, 2H, O=CH₂), 2.67 (d, J = 5.2 Hz, 2H, CH₂-N=CH₂), 2.36 (s, 3H, N-CH₃), 1.27 (s, 9H, Bu₃). ¹³C NMR (125.7 MHz, CDCl₃): δ 154.2, 148.6, 141.6, 128.2, 123.6, 122.4, 117.7, 102.2, 60.2, 58.2, 53.6, 42.5, 34.0, 31.4; IR: ν = 3279 (O-H), 2959 (C-H), 1616 (C=C), 1394 (C-H), 1363 (O-H), 1126 (C-O), 1070 (C-O) cm⁻¹; MS: m/z (%) for [Ni(HL₁)₂(OEt₂)(OMe)]·2H₂O: C 315.0 (3693), 261.0 (8515), 217.5 (18479).

[Ni₄(HL₁)₂(OMe)₂(OAc)₂Cl₂] (C₁). To a solution of H₂L₁ (0.421 g, 1.66 mmol) in MeOH (10 mL) was added solutions of Ni(OAc)₂·2H₂O (0.526 g, 2.11 mmol) and NH₄Cl (0.0565 g, 1.06 mmol), both in MeOH (10 mL). The bright green solution was stirred at RT for 30 minutes. Isolation of the complex was achieved by the diffusion of Et₂O into the reaction solution. Green prism shaped X-ray quality crystals were produced after a period of eight weeks. The crystals were crushed and air dried prior to further analysis. Yield (0.169 g, 12%); IR: 3159 (O-H), 2617 (C-H), 1575 (C=N), 1486 (C=C), 1463 (C-H), 1414 (N-O), 1219 (C-O), 1030 (C-N) cm⁻¹; elemental analysis calcd. (%) for C₄₀H₆₆N₄O₁₄Cl₂Ni₄·Et₂O·3H₂O: C 41.92, H 6.56, N 4.44; found: C 41.80, H 6.64, N 4.44.  

[Ni₄(HL₁)₂(OMe)₂(OAc)₂Cl₂] (C₂). To a solution of H₂L₁ (0.0530 g, 0.163 mmol) in MeOH (10 mL) was added a solution of NiCl₂·6H₂O (0.0775 g, 0.326 mmol) in MeOH (20 mL). The green solution was stirred at RT for 10 minutes, followed by the addition of Et₂N (0.140 mL, 0.979 mmol). The solution was stirred for a further 10 minutes at RT. Isolation of the complex was achieved by the diffusion of Et₂O into the reaction solution. Green platelet shaped X-ray quality crystals were produced after a period of three weeks. The crystals were crushed and air dried prior to further analysis. Yield (0.030 g, 15%); IR: ν = 3291 (O-H), 2966 (C-H), 1560 (C-N), 1479 (C=C), 1462 (C-H), 1221 (C-O), 1128 (C-O), 1024 (C-N), 986 (C=C) cm⁻¹; elemental analysis calcd. (%) for C₃₈H₆₈N₄O₁₂Cl₂Ni₄·0.25Et₂O·3H₂O: C 40.62, H 5.36, N 4.19; found: C 40.25, H 5.71, N 5.07.

[Ni₄(HL₁)₂(OMe)₂(MeOH)₂Cl₂·(C₂H₂)₂] (C₃). To a solution of H₂L₁ (0.100 g, 0.308 mmol) in MeOH (5 mL) was added solutions of Ni(BF₄)₂·6H₂O (0.105 g, 0.308 mmol, 1 eq.) and NiCl₂·6H₂O (0.0732 g, 0.308 mmol, 1 eq.), both in MeOH (7.5 mL). The green solution was stirred at RT for 10 minutes, followed by the addition of Et₂N (0.260 mL, 1.85 mmol, 6 eq.). The solution was stirred for a further 10 minutes at RT. Isolation of the complex was achieved by the diffusion of Et₂O into the reaction solution. Green platelet shaped X-ray quality crystals were produced after three weeks. The crystals were crushed and air dried prior to further analysis. Yield (0.070 g, 19%); IR: ν = 3159 (O-H), 2947 (C-H), 1559 (C-N), 1463 (C=C), 1279 (O-H), 1218 (C-O), 1127 (C-O), 1020 (C-N) cm⁻¹; elemental analysis calcd. (%) for C₃₈H₆₈N₄O₁₂Cl₂·C₂H₂·Ni₄·Et₂O: C 41.90, H 6.53, N 4.65; found: C 41.80, H 6.64, N 4.44.

[Ni₄(HL₁)₂(OMe)₂(OAc)₂Cl₂] (C₄) To a solution of H₂L₁ (0.200 g, 0.616 mmol, 1 eq.) in MeOH (20 mL) was added solutions of Ni(OAc)₂·4H₂O (0.153 g, 0.616 mmol, 1 eq.) and NiCl₂·6H₂O (0.146 g, 0.616 mmol, 1 eq.), both in MeOH (15 mL). The green solution was stirred at RT for 10 minutes, followed by the addition of Et₂N (0.520 mL, 3.70 mmol, 6 eq.). The solution was stirred for a further 10 minutes at RT. Isolation of the complex was achieved by the diffusion of Et₂O into the reaction solution. Green prism shaped X-ray quality crystals were produced after three weeks. The crystals were crushed and air dried prior to further analysis. Yield (0.140 g, 19%); IR: ν = 3255 (O-H), 2944 (C=C), 1575 (C=C), 1487 (C=C), 1472 (C=H), 1417 (C-N), 1331 (O-H), 1219 (C-O), 1131 (C-O), 1027 (C-N) 990 (C=C) cm⁻¹; elemental analysis calcd. (%) for C₄₀H₆₆N₄O₁₄Cl₂Ni₄·2H₂O: C 42.28, H 6.06, N 4.81; found: C 42.82, H 6.07, N 4.83.

Conflicts of interest

There are no conflicts to declare.
131–143.
