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ARTICLE

## Effects of electron donating/withdrawing groups in the 5-substituted-2-hydroxybenzaldehyde on the synthesis of neutral cubanes with a Ni<sup>II</sup><sub>4</sub>O<sub>4</sub> core: Synthesis, crystal structures and magnetic properties†

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Hadi Amiri Rudbari,<sup>\*a</sup>, Francisco Lloret,<sup>\*b</sup>, Mahsa Khorshidifard,<sup>a</sup> Giuseppe Bruno<sup>c</sup> and Miguel Julve<sup>b</sup>

Two tetranuclear cubane-like nickel(II) complexes of formula [Ni<sub>4</sub>(CH<sub>3</sub>O)<sub>4</sub>(L<sup>1</sup>)<sub>4</sub>(CH<sub>3</sub>OH)<sub>4</sub>] (**1**) and [Ni<sub>4</sub>(CH<sub>3</sub>O)<sub>4</sub>(L<sup>2</sup>)<sub>4</sub>(CH<sub>3</sub>OH)<sub>4</sub>] (**2**) (HL<sup>1</sup> = 2-hydroxybenzaldehyde and HL<sup>2</sup> = 2-hydroxy-5-methylbenzaldehyde) have been prepared by the reaction of NiCl<sub>2</sub> · 6H<sub>2</sub>O with methanolic solutions of HL<sup>1</sup> and HL<sup>2</sup> in the presence of triethylamine at room temperature. Complexes **1** and **2** have been characterized by elemental analyses, IR spectra and single-crystal X-ray diffraction. The X-ray crystal structure analysis revealed that **1** and **2** have a cubane-type structural topology with four Ni(II) ions and four methoxy-oxygen atoms regularly alternating at the corners. Each metal ion in **1** and **2** is six-coordinate in a distorted octahedral geometry defined by three bridging methoxy-oxygens, one oxygen atom from a methanol molecule and two oxygen atoms from the bidentate L<sup>1</sup> (**1**)/L<sup>2</sup> (**2**) ligands. The magnetic properties of **1** and **2** were investigated in the temperature range 1.9–300 K. They are indicative of an overall ferromagnetic behaviour, the decrease in the very low temperature region being due to zero-field splitting and intermolecular interactions. A detailed analysis of the magnetic data of **1** and **2** assuming an idealized D<sub>2d</sub> symmetry for the Ni<sub>4</sub>O<sub>4</sub> unit shows the occurrence of a low-lying spin nonet and two opposite magnetic interactions, one being ferromagnetic [*J*<sub>a</sub> = +12.6 (**1**) and +10.5 cm<sup>-1</sup> (**2**)] and the other antiferromagnetic [*J*<sub>b</sub> = -4.10 (**1**) and -2.10 cm<sup>-1</sup> (**2**)]. These values fit well the linear correlation between the exchange coupling parameter (*J*) and the Ni–O–Ni angle (α) which was established for Ni<sub>4</sub>O<sub>4</sub> cubane motifs in previous works.

### 1. Introduction

Polynuclear complexes of paramagnetic metal centres are viable candidates for applications in various fields, as biomimetic systems used for the study of enzyme active sites and multielectron transfer processes [1–3], and as catalytic [4–6] or magnetic materials [7–14]. The magnetic exchange between paramagnetic metal ions is important not only from a theoretical point of view [15], which aims to understand the fundamental correlation between the structure and magnetic properties, but also targets the development of single-molecule magnets (SMMs) [16–26].

One promising motif for SMMs is based on nickel(II)-hydroxo

cubane-type tetranuclear compounds, which recently received increasing attention [16, 27–32]. The crystal structures and magnetic properties of these symmetric Ni<sub>4</sub>O<sub>4</sub> cores are well-understood and it has been found that the exchange interaction in these compounds is correlated to the Ni–O–Ni angle (α). The magnetic coupling is ferromagnetic when α is smaller than 99.0° and it is antiferromagnetic for values of α greater than 99.0° [16, 33–34].

Although, some tetranuclear Ni(II), Co(II) and Mn(II) complexes with different substituted 2-hydroxybenzaldehyde have been synthesized and characterized [32, 35–39], the synthesis of tetranuclear compounds with these divalent first-row transition metal ions with 5-substituted-2-hydroxybenzaldehyde has received less attention. In order to evaluate the effect of the electron donating and withdrawing groups in the 5-position of 2-hydroxybenzaldehyde on the synthesis of tetranuclear Ni(II) compounds, we have used the deprotonated forms of 2-hydroxybenzaldehyde (HL<sup>1</sup>), 2-hydroxy-5-methylbenzaldehyde (HL<sup>2</sup>) and 2-hydroxy-5-nitrobenzaldehyde (HL<sup>3</sup>) as ligands towards the nickel(II) ion. In this work we present the synthesis and magneto-structural study of the cubane-type complexes of formula [Ni<sub>4</sub>(CH<sub>3</sub>O)<sub>4</sub>(L<sup>1</sup>)<sub>4</sub>(CH<sub>3</sub>OH)<sub>4</sub>] (**1**) and [Ni<sub>4</sub>(CH<sub>3</sub>O)<sub>4</sub>(L<sup>2</sup>)<sub>4</sub>(CH<sub>3</sub>OH)<sub>4</sub>] (**2**).

<sup>a</sup> Department of Chemistry, University of Isfahan, Isfahan 81746-73441, Iran. E-mail: h.a.rudbari@sci.ui.ac.ir; hamiri1358@gmail.com; Fax: +98-31-36689732; Tel: +98-31-37934918

<sup>b</sup> Departament de Química Inorgànica/Institut de Ciència Molecular (ICMol), Universitat de València, C/ Catedrático José Beltrán 2, 46980 Paterna, València, Spain. E-mail: francisco.lloret@uv.es; Tel: +34 96 3544441.

<sup>c</sup> Department of Chemical Sciences, University of Messina, Via F. Stagno d'Alcontres 31, 98166 Messina, Italy.

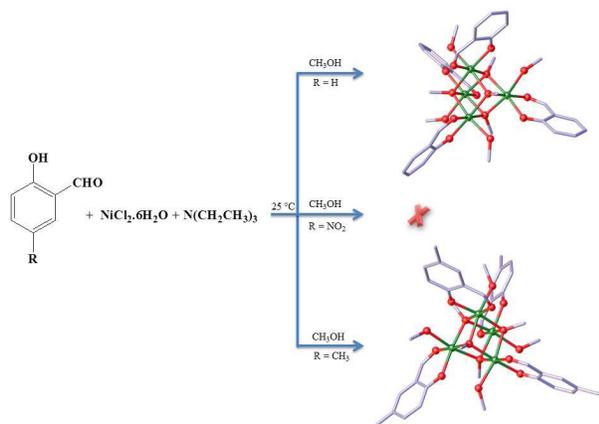
†Electronic Supplementary Information (ESI) available: Crystal data and structure refinement (Table S1 and S2 for **1** and **2**) and X-ray crystallographic files (CIF for **1** and **2**). CCDC 1440698 (**1**) and 1440699 (**2**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

## 1. Results and discussion

### 2.1. Synthesis and general characterization

Tetranuclear cubane-like nickel(II) complexes with the deprotonated forms of HL<sup>1</sup> HL<sup>2</sup> as chelating ligands have been prepared with a simple method with high yield at ambient temperature. Unfortunately, our efforts to obtain the corresponding tetranuclear Ni(II) compound with 2-hydroxy-5-nitrobenzaldehyde (HL<sup>3</sup>) as chelating ligand was not successful. As shown in Fig. 1, electron donating (–CH<sub>3</sub>) and withdrawing (–NO<sub>2</sub>) groups are very far from the Ni(II) centre. For this reason, the methyl and nitro groups cannot cause any steric effect on the formation of the tetranuclear Ni(II) compounds with these ligands. Then, the only effective parameter is the electronic factor. This means that the preparation of the tetranuclear M(II) complexes has a direct relationship with the electron donating and withdrawing effect in 5-position of the 2-hydroxybenzaldehyde.

The IR spectra show broad peaks at 3346 and 3431 cm<sup>-1</sup> for **1** and **2** respectively, because of the OH group of the methanol molecule. The  $\nu(\text{C}-\text{O}_{\text{phen}})$  stretching mode occurs as a very strong band at 1148 (**1**) and 1206 cm<sup>-1</sup> (**2**). The peaks at 1041 and 1152 cm<sup>-1</sup> are assigned to alcoholic C–O stretches for **1** and **2**, respectively. Several weak peaks observed in the range 3000 – 2760 cm<sup>-1</sup> are attributed to the aromatic and aliphatic C–H stretches of these two complexes.



Scheme 1 Preparative route for **1** and **2**

### 2.2 Crystal structures

Single crystal X-ray analysis reveals **1** and **2** crystallize in the monoclinic system with  $P2_1/n$  and  $P2_1/c$  space groups, respectively. Selected bond distances and angles for both complexes **1** and **2** are listed in Table S1. As shown in Figs. 1 and 2, four nickel(II) ions and four methoxo-oxygen atoms, occupy alternate corners of the cubane unit where each Ni atom is surrounded by six oxygen atoms two of them from the chelating L1 (**1**) and L2 (**2**) ligands, one from a methanol molecule and the other three from three bridging methoxo-oxygens to form a distorted octahedral geometry (Fig 3a). Looking down the crystallographic *b*-axis, the cubane cores are

slightly distorted in the complex **1** and **2** and the top face is slightly rotated in comparison with the bottom one.

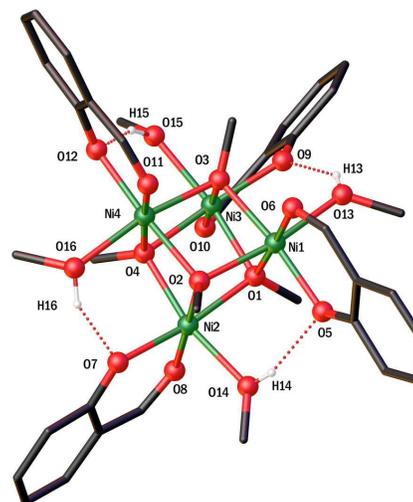


Fig. 1 Molecular structure of complex **1**. Hydrogen atoms (except those involved in hydrogen bonding interactions) have been omitted for clarity. Hydrogen bonds are represented by dashed lines.

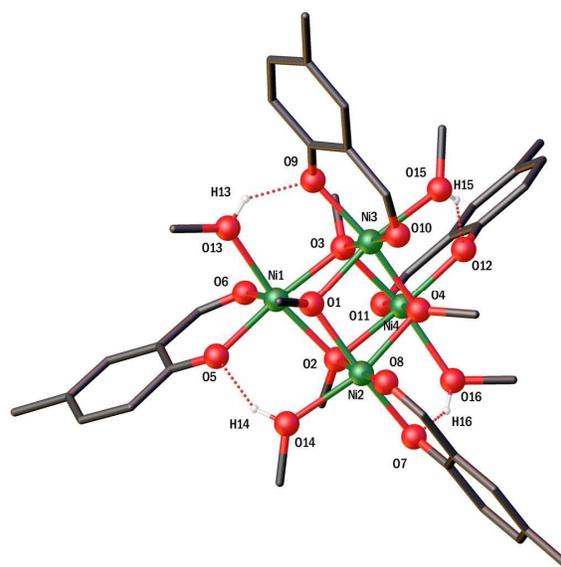
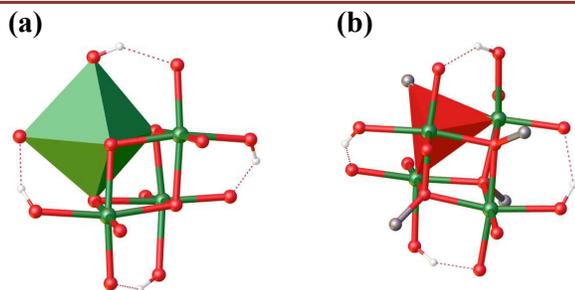


Fig. 2 Molecular structure of complex **2**. Hydrogen atoms (except those involved in hydrogen bonding interactions) have been omitted for clarity. Hydrogen bonds are represented by dashed lines.

The tetranuclear core is bridged solely by  $\mu_3$ -methoxide groups resulting in one unique exchange pathway between the metal centres. Each of the bridging oxygen atoms has a remarkably distorted tetrahedral geometry (Fig. 3b). The Ni–O<sub>MeOH</sub> bond lengths are longer than those for Ni–O<sub>MeO</sub>.



**Fig. 3** (a) Coordination polyhedron at each nickel(II) ion in complex **1** and **2**. (b) Environment of each bridged oxygen atom in complex **1** and **2**.

The values of the Ni–O bond lengths are in the range 2.0474(19)–2.084(2) Å (average value 2.0602 Å) (**1**) and 2.0417(19)–2.0637(18) Å (mean value, 2.0547 Å) (**2**). The *cis* O–Ni1–O angles vary in the narrow ranges 95.32(8)–100.18(9) (**1**) and 95.61(7)–99.60(8)° (**2**) (Table S1) whereas the *trans* O–Ni1–O angles cover the ranges 166.60(8)–177.83(9) (**1**) and 166.15(8)–179.29(8)° (**2**). Most of the Ni–O bonds in **1** are longer than the corresponding bonds in **2**. An interesting feature of these two complexes is the stabilization of the cubane core by hydrogen bonds between the exogenous methanol molecule and the phenolate-oxygen atom which act as hydrogen bond acceptor and donor, respectively (Figs. 1 and 2 and Table 1). Thereby four of the six faces of the {Ni<sub>4</sub>O<sub>4</sub>} cube are spanned by hydrogen bonds, resulting in somewhat different bond lengths and angles for the involved atoms compared to those at the two remaining faces at opposite sides of the cube (Table S1). Thus, the complexes **1** and **2** display approximate S<sub>4</sub> site symmetry, while the exact crystallographic point symmetry is C<sub>1</sub>. These differences, primarily in the bridging Ni–O–Ni angles (Table S1), are crucial factors that determine the sign of the magnetic exchange interactions through the methoxo-oxygen bridges; their modulation has drastic effects on the ground state of the complexes (see below).

**Table 1** Intramolecular hydrogen bond geometries (Å, deg) for **1** and **2**

D–H...A	D–H (1/2)	H...A(1/2)	D...A (1/2)	D–H...A (1/2)
O(13)–H(13)...O(9)	0.86/0.86	1.94/1.93	2.6879/2.659(3)	145/141
O(14)–H(14)...O(5)	0.72/0.87	2.00/1.93	2.6907/2.687(3)	161/145
O(15)–H(15)...O(12)	0.87/0.87	1.88/1.90	2.6907/2.697(3)	154/152
O(16)–H(16)...O(7)	0.87/0.86	1.95/2.01	2.6916/2.747(3)	143/142

The cubane units in **1** and **2** are well isolated from each other, the centroid-centroid distance between adjacent {Ni<sub>4</sub>O<sub>4</sub>} entities along the crystallographic *a*, *b*, *c* axes are 14.645, 9.386, 13.887 Å for **1** and 9.323, 17.467, 9.926 Å for **2**.

### 3.2. Magnetic Properties

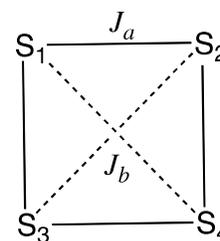
The magnetic properties of **1** and **2** under the form of the  $\chi_M T$  against *T* plot [ $\chi_M$  is the magnetic susceptibility per four nickel(II) ions] are shown in Figure 4. They are indicative of the presence of a global ferromagnetic exchange coupling between the four nickel(II) ions. At room temperature,  $\chi_M T$  for **1** and **2** is ca 4.72 cm<sup>3</sup> mol<sup>-1</sup> K, a value which is slightly higher than those expected for four magnetically isolated spin triplets, *S* = 1, ( $\chi_M T$  = 4.41 cm<sup>3</sup> mol<sup>-1</sup> K for *g* = 2.1). Upon cooling down, the values of the  $\chi_M T$  product for **1** and **2** increase to reach maximum values of 7.90 (**1**) and 8.15 cm<sup>3</sup>

mol<sup>-1</sup> K (**2**) at 11.0 and 10.8 K respectively, and they further decrease to 4.03 (**1**) and 4.55 cm<sup>3</sup> mol<sup>-1</sup> K (**2**) at 1.9 K. The values of the maximum of  $\chi_M T$  for **1** and **2** may be compared with the calculated spin-only value of 11.0 cm<sup>3</sup> mol<sup>-1</sup> K for a spin-nonet ground state (*S* = 4) with *g* = 2.1. In principle, intermolecular antiferromagnetic interactions ( $\theta$ ) and/or zero-field splitting (*D*) effects within the ground spin state (*S* = 4) would account for the smaller value of the maxima of the  $\chi_M T$  product in **1** and **2**.

The magnetic exchange pathway for each pair of Ni(II) ions in **1** and **2** takes place through a double( $\mu$ -methoxo) bridge and the Ni–O–Ni angles play a crucial role in determining both the nature (ferro- or antiferromagnetic) and magnitude of the magnetic interaction [40]. Magneto-structural studies with distorted {Ni<sub>4</sub>O<sub>4</sub>} cubane structures, whose exchange interactions are mediated by  $\mu_3$ -OR (alkoxo) bridges, have allowed to establish a linear correlation between the exchange coupling parameter (*J*) and Ni–O–Ni ( $\alpha$ ) bond angles as indicated by eqn (1) [16].

$$J = -4.69\alpha + 464.4 \quad (1)$$

According to this expression, the magnetic interaction is expected to be ferromagnetic (*J* > 0) for  $\alpha < 99.0^\circ$  and antiferromagnetic (*J* < 0) for  $\alpha > 99.0^\circ$ . In principle, due to the low symmetry of **1** and **2**, each face of the cubane in them represents a magnetic coupling parameter (*J<sub>i</sub>*) and then, six different *J<sub>i</sub>* values could be considered. However, due to the existence of two types of [Ni<sub>2</sub>( $\mu$ -MeO)<sub>2</sub>] faces present in the cubane (see the crystallographic part), an idealized *D<sub>2d</sub>* symmetry could be considered. The network of exchange pathways is displayed in Scheme 2 and the corresponding spin Hamiltonian is shown in eqn (2). *J<sub>b</sub>* corresponds to the interaction across the two faces of the cubane not spanned by hydrogen bonds and having very close average Ni(i)–O–Ni(j) angles ( $\alpha_{ij}$ ) [ $\alpha_{23} \approx \alpha_{14} \approx 99.4^\circ$  (**1**) and  $99.3^\circ$  (**2**)] and *J<sub>a</sub>* accounts for the interaction across the four faces that are spanned by hydrogen bonds and implying similar average values of  $\alpha_{ij}$  [ $\alpha_{12} \approx \alpha_{13} \approx \alpha_{24} \approx \alpha_{34} \approx 95.7^\circ$  (**1**) and  $96.1^\circ$  (**2**)] (see Table S1).



**Scheme 2** Intramolecular exchange pathways in **1** and **2**

In order to avoid overparametrization, we considered only two magnetic coupling parameters ( $J_{12} = J_{13} = J_{24} = J_{34} = J_a$  and  $J_{23} = J_{14} = J_b$  according to an idealized *D<sub>2d</sub>* symmetry) and assumed that all Ni(II) ions were equivalent ( $g_1 = g_2 = g_3 = g_4 = g$  and  $D_1 = D_2 = D_3 = D_4 = D$ ).

$$H = H_{isotropic} + H_{anisotropic} + H_{Zeeman} \quad (2)$$

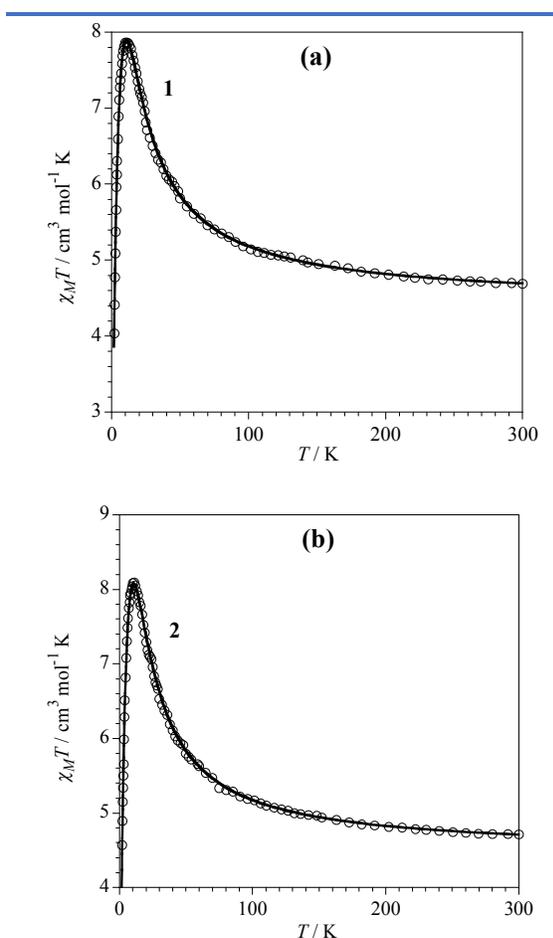
where

$$H_{isotropic} = -J_a(\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_3 + \hat{S}_2\hat{S}_4 + \hat{S}_3\hat{S}_4) - J_b(\hat{S}_1\hat{S}_4 + \hat{S}_2\hat{S}_3) \quad (2a)$$

$$H_{\text{anisotropic}} = \sum_{i=1}^4 D(S_{zi}^2 - 2/3) \quad (2b)$$

and

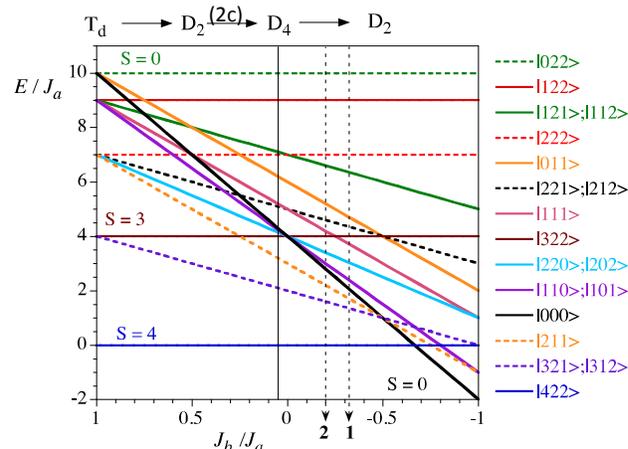
$$H_{\text{Zeeman}} = \beta H g \sum_{i=1}^4 \hat{S}_i \quad (2c)$$



**Fig. 4** Plot of  $\chi_M T$  vs.  $T$  for powdered samples of **1** (a) and **2** (b). The solid lines represent the best-fit curves described in the text.

Given that no analytical expression for the magnetic susceptibility can be derived through this Hamiltonian because of the zero-field splitting term ( $D$ ), numerical matrix diagonalisation techniques by means of a Fortran program [41] were used in the fitting procedure. A very good fit can be obtained by using the Hamiltonian of eqn (2). A Weiss constant ( $\theta$ ), in the form  $T - \theta$ , was introduced to account for the intermolecular interactions. The least-squares best-fit parameters were:  $J_a = 12.6 \text{ cm}^{-1}$ ,  $J_b = -4.10 \text{ cm}^{-1}$ ,  $g = 2.11$ ,  $D = 6.10 \text{ cm}^{-1}$  and  $\theta = -0.36 \text{ K}$  with  $R = 3.1 \times 10^{-5}$  for **1** and  $J_a = 10.50 \text{ cm}^{-1}$ ,  $J_b = -2.10 \text{ cm}^{-1}$ ,  $g = 2.12$ ,  $D = 6.50 \text{ cm}^{-1}$  and  $\theta = -0.34 \text{ K}$  with  $R = 5.2 \times 10^{-5}$  for **2** [ $R$  is the agreement factor defined as  $R = \sum_i [(\chi_M T)_i^{\text{obsd}} - (\chi_M T)_i^{\text{calc}}]^2 / [(\chi_M T)_i^{\text{obsd}}]^2$ ]. The observed values for the magnetic coupling parameters are very close to those expected from the magneto-structural study [eqn (1)] [40]. So, from the average values of the Ni-O-Ni angle and using eqn (1), the following values of the magnetic coupling are obtained:  $J_a = +15.6$

$\text{cm}^{-1}$  and  $J_b = -1.8 \text{ cm}^{-1}$  for **1** and  $J_a = +13.7 \text{ cm}^{-1}$  and  $J_b = -1.3 \text{ cm}^{-1}$  for **2**.



**Fig. 5** Energy diagram for **1** and **2** showing the low-lying states ( $E/J_a$  vs.  $J_b/J_a$  ratio), deduced from Hamiltonian **2a**, with labelling according to the spin functions  $|S_T, S_A, S_B\rangle$  being  $S_A = S_1 + S_3$ ,  $S_B = S_2 + S_4$  and  $S_T = S_A + S_B$ .

The energies of the low-lying states ( $E/J$  versus the  $J_b/J_a$  ratio) deduced from the isotropic Hamiltonian [eqn. (2a)] and labelled according to the spin wave functions  $|S_T, S_A, S_B\rangle$  where  $S_A = S_1 + S_3$ ,  $S_B = S_2 + S_4$  and  $S_T = S_A + S_B$ , are displayed in Figure 5. The relative energies, which depend on  $S_T$ ,  $S_A$  and  $S_B$ , are expressed by eqn (3). There are nineteen spin states involving values for  $S_A$  and  $S_B$  of 2, 1, 0 and  $S_T$  varying from  $|S_A + S_B|$  to  $|S_A - S_B|$  in integer increments.

$$E(S_T, S_A, S_B) = -J_a[S_T(S_T + 1) - S_A(S_A + 1) - S_B(S_B + 1)] - J_b[S_A(S_A + 1) + S_B(S_B + 1)] \quad (3)$$

Figure 5 shows the distortion of an ideal tetrahedron ( $T_d$ ,  $J_a = J_b$ ) as a function of the  $J_b/J_a$  ratio to yield a flattened tetrahedron ( $D_2$ ,  $J_a \neq J_b$ ) and a square topology ( $D_4$ ,  $J_b = 0$ ). One can see that  $S = 4$  is the low-lying level when  $J_a > 0$  and  $J_b/J_a > -2/3$ . Both compounds, with a  $J_b/J_a$  ratio of  $-0.32$  (**1**) and  $-0.20$  (**2**) present a spin nonet ( $S = 4$ ) as ground spin state.

The X-band EPR spectra of powdered samples of **1** and **2** are silent in the temperature range investigated (4.0 – 300 K), a feature that supports the occurrence of a zero-field splitting with  $D_{S=4} > h\nu \approx 0.3 \text{ cm}^{-1}$  (9.5 GHz) [42]. Considering that the local  $D_{Ni}$  tensors are collinear and using the Wigner-Eckart theorem [43], one can estimate the value of the  $D$  parameter for the nonet ( $S = 4$ ) ground spin state  $D_{S=4} = (1/7)D_{Ni} = 0.87$  (**1**) and  $0.93 \text{ cm}^{-1}$  (**2**). Both values are greater than the energy of the X-band frequency.

### 3. Conclusions

The synthesis and characterization of polynuclear nickel(II) complexes have been the focus of research since the discoveries that those molecules display the single-molecule magnetic property, biomimetic activity and structural diversity in cluster constructing. In this work, our efforts to synthesize tetranuclear cubane-like nickel(II) complexes with 5-substituted-2-

hydroxybenzaldehyde ligands yielded the compounds  $[\text{Ni}_4(\text{CH}_3\text{O})_4\text{L}^1_4(\text{CH}_3\text{OH})_4]$  (**1**) and  $[\text{Ni}_4(\text{CH}_3\text{O})_4\text{L}^2_4(\text{CH}_3\text{OH})_4]$  (**2**) ( $\text{HL}^1 = 2\text{-hydroxybenzaldehyde}$  and  $\text{HL}^2 = 2\text{-hydroxy-5-methylbenzaldehyde}$ ) whereas those with 2-hydroxy-5-nitrobenzaldehyde ( $\text{HL}^3$ ) were unsuccessful. The result showed that the preparation of tetranuclear M(II) compounds has a direct relationship with electron donating and withdrawing group in the 5-position of the 2-hydroxybenzaldehyde. The X-ray crystal structure analyses revealed that **1** and **2** have cubane-type structural topology with four Ni(II) ions and four methoxo-oxygen atoms regularly alternating at the corners. Each metal ion in **1** and **2** is six-coordinate in a distorted octahedral geometry defined by three bridging methoxo-oxygens, one oxygen atom from a methanol molecule and two oxygen atoms from the bidentate  $\text{L}^1$  (**1**)/ $\text{L}^2$  (**2**) ligands. The magnetic properties of **1** and **2** are indicative of an overall ferromagnetic behaviour, the detailed analysis of their magnetic data assuming an idealized  $D_{2d}$  symmetry for the  $\text{Ni}_4\text{O}_4$  unit shows the occurrence two opposite magnetic interactions, one being ferromagnetic [ $J_a = +12.6$  (**1**) and  $+10.5 \text{ cm}^{-1}$  (**2**)] and the other antiferromagnetic [ $J_b = -4.10$  (**1**) and  $-2.10 \text{ cm}^{-1}$  (**2**)]. These values fit well the linear correlation between the exchange coupling parameter ( $J$ ) and the Ni-O-Ni angle ( $\alpha$ ) which was established for  $\text{Ni}_4\text{O}_4$  cubane motifs in previous works. The energy diagram under the form of  $E/J_a$  against  $J_b/J_a$  shows that the  $S = 4$  is the low-lying level when  $J_a > 0$  and  $J_b/J_a > -2/3$ , conditions which are fulfilled by **1** and **2**.

## 4. Experimental

### 1.1. Materials and general methods

All reagents and solvents for the synthesis and analysis were commercially available and they were used as received without further purifications. The FT-IR spectra were recorded on a JASCO, FT/IR-6300 spectrometer ( $4000\text{--}400 \text{ cm}^{-1}$ ) as KBr pellets. The elemental analysis (C, H, N, Ni) was performed on Leco, CHNS-932 and Perkin-Elmer 7300 DV elemental analyzers.

### 1.2. Synthesis of $[\text{Ni}_4(\text{CH}_3\text{O})_4(\text{L}^1)_4(\text{CH}_3\text{OH})_4]$ (**1**) and $[\text{Ni}_4(\text{CH}_3\text{O})_4(\text{L}^2)_4(\text{CH}_3\text{OH})_4]$ (**2**)

The two complexes were synthesized using identical reaction conditions, therefore only the synthesis of **1** will be described in detail. The addition of 10 mmol of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  to a MeOH solution (30 mL) of 2-hydroxybenzaldehyde (10 mmol) and triethylamine (15 mmol) at room temperature yielded a green precipitate almost immediately. The reaction mixture was stirred for two hours, then the green precipitate was collected by filtration, washed with methanol, and dried in air. The filtrate was allowed to stand at room temperature and dark green rectangular crystals suitable for single crystal X-ray diffraction analysis were obtained after 1-2 days. Yield: 82 (**1**), 76% (**2**). Anal. Calc. for  $\text{C}_{36}\text{H}_{48}\text{O}_{16}\text{Ni}_4$  (**1**): C, 44.51; H, 4.98%; Found: C, 44.48; H, 4.97%. Anal. Calc. for  $\text{C}_{40}\text{H}_{56}\text{O}_{16}\text{Ni}_4$  (**2**): C, 46.75; H, 5.49%; Found: C, 46.73; H, 5.46%.

### 1.3. Magnetic measurements

Magnetic susceptibility measurements on crushed crystals of **1** and **2** were carried out with a Superconducting Quantum Interference Design (SQUID) magnetometer in the temperature range 1.9 – 300

K and under an applied magnetic field of 0.01 Tesla for  $T < 50$  K in order to avoid saturation effects and 1 Tesla for  $T > 50$  K. Diamagnetic corrections were estimated from Pascal's constants. X-band EPR spectra on polycrystalline samples of **1** and **2** were performed with a Brüker ER 200 spectrometer equipped with a helium continuous-flow cryostat.

### 1.4. Single crystal diffraction studies

X-ray data for single crystals of  $[\text{Ni}_4(\text{CH}_3\text{O})_4\text{L}^1_4(\text{CH}_3\text{OH})_4]$  (**1**) and  $[\text{Ni}_4(\text{CH}_3\text{O})_4\text{L}^2_4(\text{CH}_3\text{OH})_4]$  (**2**) were collected on a STOE IPDS-II diffractometer with graphite monochromated Mo-K $\alpha$  radiation. Data were collected at 298(2) K in a series of  $\omega$  scans in  $1^\circ$  oscillations and integrated using the Stöe X-AREA [44] software package. A numerical absorption correction was applied using the X-RED [45] and X-SHAPE [46] softwares. The data were corrected for Lorentz and Polarizing effects. The structures were solved by direct methods using SIR2004 [47]. The non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method on  $F^2$  using the SHELXL program [48]. Hydrogen atoms attached to carbon were located in their idealized positions by using appropriate HFIX instructions in SHELXL and included in subsequent refinement cycles in riding-motion approximation with isotropic thermal displacements parameters ( $U_{\text{iso}}$ ) fixed at 1.2 times  $U_{\text{eq}}$  of the carbon atom to which they are attached. The hydrogen atoms of the –OH group of the methanol molecules were found in difference Fourier maps and refined isotropically.

Crystallographic data for the structures of **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre with the CCDC reference numbers 1440698 (**1**) and 1440699 (**2**). See the ESI<sup>†</sup> for crystallographic data in CIF format.

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This work reports synthesis, crystal structures and magnetic properties of two tetranuclear cubane-like nickel(II) complexes of formula  $[\text{Ni}_4(\text{CH}_3\text{O})_4(\text{L}^1)_4(\text{CH}_3\text{OH})_4]$  (**1**) and  $[\text{Ni}_4(\text{CH}_3\text{O})_4(\text{L}^2)_4(\text{CH}_3\text{OH})_4]$  (**2**) ( $\text{HL}^1 = 2\text{-hydroxybenzaldehyde}$  and  $\text{HL}^2 = 2\text{-hydroxy-5-methylbenzaldehyde}$ ).

