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Magnetic ordering of Ni<sup>II</sup><sub>4</sub> Cubane complexes through hydrogen bondsJean-Pierre Costes<sup>a,\*,b</sup>, Ghenadie Novitchi<sup>c</sup>, Laure Vendier<sup>a,b</sup>, Guillaume Pilet<sup>c</sup>,  
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## ABSTRACT

The serendipity synthesis of the 2-hydroxy-3-methoxy-benzaldehyde or *o*-vanillin nickel(II) cubane complex, obtained by ourselves and other workers, can be rationalized to give the cubane in a high yield by direct use of 2-hydroxy-3-methoxy-benzaldehyde (H-ovan). The structural determinations of crystals obtained according to the two experimental processes show that the complex formulated [(MeOH)Ni(μ<sub>3</sub>-OMe)(ovan)]<sub>4</sub> (ovan = deprotonated form of *o*-vanillin) is characterized in the two cases. Ni-Ni ferromagnetic interactions ( $J_{NiNi} = 5.8 \text{ cm}^{-1}$ ) giving an  $S = 4$  ground state are active in the Ni<sub>4</sub> cubane. Replacement of methanol molecules coordinated to the Ni ions by a diol, an amino-alcohol or an amino-ether allows self-association of these Ni<sub>4</sub> units according to two different ways: by direct coordination bonds through the diol ligand or by hydrogen bonds involving the OMe groups of *o*-vanillin located at the periphery of the cubane and the hydrogen atoms of the primary amine functions. This association is suggested in the two cases by the presence of out-of-phase signals ( $\chi''$ ) when ac susceptibility measurements are performed at different frequencies. These molecules do not behave as SMM for these  $\chi''$  signals, that are not frequency-dependent, correspond to the establishment of a three-dimensional ordering.

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## R É S U M É

Un complexe tétranucléaire du nickel, obtenu par hasard dans un premier temps, a été ensuite préparé en grande quantité grâce à un procédé décrit dans cet article. Les déterminations structurales des cristaux obtenus selon les deux processus expérimentaux montrent que l'on isole un même complexe de formule [(MeOH)Ni(μ<sub>3</sub>-OMe)(ovan)]<sub>4</sub>. Ce cubane Ni<sub>4</sub> est le siège d'interactions Ni-Ni ferromagnétiques ( $J_{NiNi} = 5,8 \text{ cm}^{-1}$ ) conduisant à un état fondamental  $S = 4$  mais il ne se comporte pas comme une molécule-aimant. Le remplacement des molécules de méthanol coordonnées au nickel par un diol, le 1,3-propanediol, permet d'associer ces cubanes. Une autre façon d'assembler ces entités tétranucléaires consiste à remplacer les molécules de méthanol par autant de molécules amino-alcool ou amino-éther. Ces dernières se complexent au nickel par leurs fonctions oxygénées tandis que leurs fonctions amine primaire établissent un réseau de liaisons hydrogène avec les groupements OMe portés par l'*o*-vanilline et situés à la périphérie du cubane. Cette auto-association est confirmée par l'apparition d'un signal de susceptibilité magnétique imaginaire ( $\chi''$ ) obtenu lors de mesures de susceptibilité en mode alternatif à différentes fréquences. La non-dépendance en fréquence de ces signaux ne correspond pas à un comportement de molécule-aimant mais est liée à l'établissement d'un ordre magnétique tridimensionnel.

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## 1. Introduction

Tetranuclear complexes involving nickel ions and diketones or diketone-equivalent ligands such as salicylaldehyde have been known for a long time [1–5]. The vertexes of the cubane structure are alternately occupied by four Ni atoms and four methoxo groups, so that each Ni ion is surrounded by three  $\mu_3$ -methoxo groups. There are also examples in which the  $\mu_3$ -methoxo groups have been replaced by  $\mu_3$ -N<sub>3</sub> azido bridges [6,7]. In a large majority of cases ferromagnetic Ni–Ni interactions are active in these nickel cubane complexes, thus giving a  $S = 4$  ground state. Furthermore, magnetic anisotropy can also be present. The growing interest in single-molecule magnets (SMM), molecules that require high-spin ground state and appreciable negative magnetic anisotropy, has thus given a new interest to these cubane complexes [8–12]. Being interested in the syntheses of 3d–4f complexes, we have shown that the *o*-vanillin ligand is able to link 3d ions through its phenoxo and aldehyde oxygen atoms when 4f ions prefer coordination through the phenoxo and methoxy oxygen atoms [13]. We [14] and other workers [15] have also shown that free methoxy groups can be involved in hydrogen bonds in presence of hydrogen-donor molecules. Recently, the structural determinations of nickel cubane complexes derived from 2-hydroxy-3-methoxy-benzaldehyde (*o*-vanillin) [16–18] or 2-hydroxy-3-ethoxy-benzaldehyde [19] appeared in the literature. Surprisingly, they were prepared according to a reaction process resulting from hydrolysis of a Schiff base ligand in presence of potassium hydroxide [16] or by reaction of the *o*-vanillin or equivalent ligands in presence of nickel salts, chloride or perchlorate, and different bases used as deprotonating agents [17–19]. In the present work, we want to describe a more direct synthesis of the nickel cubane complex, starting with *o*-vanillin and nickel acetate, along with the structural determination and a complete study of the isolated Ni<sub>4</sub> complex. Then two chemical ways that allow a self-assembling of these Ni<sub>4</sub> units by direct coordination bonds or by introduction of a hydrogen-bond network will be described.

## 2. Experimental

### 2.1. Materials

The metal salts, Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Dy(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, and *o*-vanillin (2-hydroxy-3-methoxy-benzaldehyde), L-valine, 1,3-propanediol, 2-methoxyethylamine, 3-methoxypropylamine, triethylamine (Aldrich) were used as purchased. High-grade solvents were used for preparing the complexes.

### 2.2. Complexes

**[(MeOH)Ni(OMe)(ovan)]<sub>4</sub> (1).** (A) *o*-vanillin (0.15 g, 1 mmol), L-valine (0.12 g, 1 mmol) and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.29 g, 1 mmol) were dissolved with stirring in methanol (30 mL) at room temperature. A methanol solution (10 mL) of Dy(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.45 g, 1 mmol), followed by 0.5 mL of triethylamine were added. The intense green solution was

filtered 1 hour later. Slow evaporation yielded green crystals 2 days later. Yield: 0.09 g (33%). Anal. Calcd for C<sub>40</sub>H<sub>56</sub>Ni<sub>4</sub>O<sub>20</sub> (1091.6): C, 44.0; H, 5.2. Found: C, 43.8; H, 5.0. IR (ATR): 3251l, 2928w, 2822w, 1625s, 1606m, 1538m, 1468m, 1434m, 1417m, 1336m, 1239m, 1201s, 1169w, 1073w, 1054m, 1037 m, 961m, 857w, 746m, 725m, 643w cm<sup>-1</sup>.

(B) *o*-vanillin (1.5 g, 10 mmol) and Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (2.5 g, 10 mmol) were dissolved with stirring in methanol (60 mL) at room temperature. Then 2 mL of triethylamine were added and the mixture was heated to 50 °C for 40 min. The cooled mixture was filtered, yielding a green precipitate that was washed with diethyl ether. Yield: 2.3 g (83%). Slow diffusion of diethyl ether to a methanol solution of the green precipitate gave green crystals suitable for XRD analysis. Anal. Calcd for C<sub>40</sub>H<sub>56</sub>Ni<sub>4</sub>O<sub>20</sub> (1091.6): C, 44.0; H, 5.2. Found: C, 43.9; H, 5.1. IR (ATR): 3251l, 2928w, 2822w, 1625s, 1606m, 1538m, 1468m, 1434m, 1417m, 1336m, 1239m, 1201s, 1169w, 1073w, 1054m, 1037m, 961m, 857w, 746m, 725m, 643w cm<sup>-1</sup>.

**(HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>Ni<sub>4</sub>(OMe)<sub>4</sub>(ovan)<sub>4</sub> (2).** Complex **1** (0.2 g, 0.18 mmol) was partially dissolved in acetone (10 mL) and 1,3-propanediol (0.2 g, 2.6 mmol) was added. The resulting mixture was stirred and heated to 40 °C for 30 min, then filtered and left to evaporate. A green powder was filtered off 3 h later, washed with diethyl ether and dried. Yield: 0.13 g (65%). Anal. Calcd for C<sub>42</sub>H<sub>56</sub>Ni<sub>4</sub>O<sub>20</sub> (1115.6): C, 45.2; H, 5.1. Found: C, 45.3; H, 5.1. IR (ATR): 3493l, 3146l, 2937w, 2857w, 1619s, 1541m, 1467m, 1439m, 1413m, 1338m, 1240m, 1203s, 1168w, 1072w, 1051m, 963m, 859w, 723m, 644w cm<sup>-1</sup>.

**(CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>4</sub>Ni<sub>4</sub>(OMe)<sub>4</sub>(ovan)<sub>4</sub> (3).** Complex **1** (0.2 g, 0.18 mmol) was partially dissolved in acetone (10 mL) and 2-methoxyethylamine (0.2 g, 2.7 mmol) was added. The resulting mixture was stirred for 2 hours, yielding a green precipitate that was filtered off, washed with diethyl ether and dried. Yield: 0.13 g (54%). Anal. Calcd for C<sub>48</sub>H<sub>76</sub>N<sub>4</sub>Ni<sub>4</sub>O<sub>20</sub> (1263.9): C, 45.6; H, 6.1; N, 4.4. Found: C, 45.3; H, 6.2; N, 4.2. IR (ATR): 3332w, 3241w, 3163m, 2942w, 2876m, 2800m, 1622s, 1604m, 1536m, 1470m, 1435m, 1416m, 1342m, 1234m, 1200s, 1145w, 1122w, 1073w, 1055m, 959m, 855w, 746m, 722 m, 641w cm<sup>-1</sup>.

**(CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>4</sub>Ni<sub>4</sub>(OMe)<sub>4</sub>(ovan)<sub>4</sub> (4).** The same experimental procedure and use of an excess of 3-methoxypropylamine (0.2 g, 2.2 mmol) instead of 2-methoxyethylamine yielded a green precipitate that was filtered off, washed with diethyl ether and dried. Yield: 0.13 g (55%). Anal. Calcd for C<sub>52</sub>H<sub>84</sub>N<sub>4</sub>Ni<sub>4</sub>O<sub>20</sub> (1320.0): C, 47.3; H, 6.4; N, 4.2. Found: C, 47.0; H, 6.2; N, 4.1. IR (ATR): 3330w, 3243w, 3162m, 2928w, 2880m, 2803m, 1625s, 1604m, 1536m, 1472m, 1438m, 1410m, 1343m, 1235m, 1200s, 1165w, 1112m, 1072w, 1054m, 1016m, 958m, 856w, 744w, 734w, 722m, 640w cm<sup>-1</sup>.

**(HOCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>4</sub>Ni<sub>4</sub>(OMe)<sub>4</sub>(ovan)<sub>4</sub> (5).** The same experimental procedure and use of an excess of ethanolamine (0.2 g, 3.3 mmol) yielded a green precipitate that was filtered off, washed with diethyl ether and dried. Yield: 0.18 g (82%). Anal. Calcd for C<sub>44</sub>H<sub>68</sub>N<sub>4</sub>Ni<sub>4</sub>O<sub>20</sub> (1207.8): C, 43.8; H, 5.7; N, 4.6. Found: C, 43.5; H, 5.5; N, 4.4. IR (ATR): 3465l, 3336w, 3254w, 3174w, 2939w, 2881w, 2808w,

1626s, 1606m, 1538m, 1469m, 1436m, 1419w, 1345m, 1237m, 1203s, 1167w, 1061m, 1030w, 959m, 856w, 747m, 744m, 642w cm<sup>-1</sup>.

### 2.3. Materials and methods

All starting materials were purchased from Aldrich and were used without further purification. Elemental analyses were carried out by the Service de microanalyse du laboratoire de chimie de coordination, Toulouse (C, H, N). Magnetic data were obtained with a Quantum Design MPMS SQUID susceptometer. Magnetic susceptibility measurements were performed in the 2–300 K temperature range in a 0.1 T or 1 T applied magnetic field, and diamagnetic corrections were applied by using Pascal's constants [20]. Isothermal magnetization measurements were performed up to 5 T at 2 K. The magnetic susceptibilities have been computed by exact calculations of the energy levels associated to the spin Hamiltonian through diagonalization of the full matrix with a general program for axial symmetry [21], and with the MAGPACK program package [22] in the case of magnetization. Least-squares fittings were accomplished with an adapted version of the function-minimization program MINUIT [23].

#### 2.3.1. Crystallographic data collection and structure determination for (1)

Crystals of **1** were kept in the mother liquor until they were dipped into oil. The chosen crystals were mounted on a Mitegen micromount and quickly cooled to 180 K. The selected crystal of **1** (green, 0.25 × 0.15 × 0.05 mm<sup>3</sup>) was mounted on an Oxford-Diffraction XCALIBUR (**4**) using a graphite monochromator ( $\lambda = 0.71073 \text{ \AA}$ ) and equipped with an Oxford Cryosystems cooler device. The data were collected at 180 K. The unit cell determination and data integration were carried out using the CrysAlis RED package for the data recorded on the Xcalibur [24]. Seventeen thousand three hundred and ninety-five reflections were collected for **1**, of which 2420 were independent ( $R_{\text{int}} = 0.0302$ ). The structure has been solved by Direct Methods using SIR92 [25], and refined by means of least-squares procedures on a F2 with the aid of the program SHELXL97 [26] included in the software package WinGX version 1.63 [27]. The Atomic Scattering Factors were taken from International tables for X-Ray Crystallography [28]. All hydrogen atoms were geometrically placed and refined by using a riding model. All non-hydrogen atoms were anisotropically refined, and in the last cycles of refinement a weighting scheme was used, where weights are calculated from the following formula:  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$  where  $P = (F_o^2 + 2F_c^2)/3$ . Drawings of molecules are performed with the program ORTEP32 [29] with 30% probability displacement ellipsoids for non-hydrogen atoms. CCDC 863778 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) or from Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [fax: Internat +44 1223/336 033; [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

### 3. Results and discussion

The reaction of *o*-vanillin with nickel acetate in ethanol and a 2/1 ratio yields the well-known Ni(ovan)<sub>2</sub>·2H<sub>2</sub>O complex. In order to find a synthetic route to the cubane complex **1**, which was first prepared by pure serendipity, we made several trials. Indeed, heating with stirring a methanol solution of *o*-vanillin with nickel acetate in a 1/1 ratio and in presence of triethylamine, gives a green precipitate that corresponds to the expected cubane complex in correct yield. Analytical data and structural determination do confirm its [(MeOH)Ni(OMe)(ovan)]<sub>4</sub> formulation. This cubane possesses a methanol molecule in the nickel coordination sphere, as cubanes resulting from bidentate ligands. Working in acetone solution, we tried to replace this coordinated methanol molecule by a diol such as 1,3-propanediol. Although we could not obtain crystals, analytical data for the isolated powder complexes are in agreement with a [(HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>Ni<sub>4</sub>(OMe)<sub>4</sub>(ovan)<sub>4</sub>]<sub>n</sub> formulation. Presence of only two diol molecules in the complex corresponds to an assembling of the cubane units through diol bridges. On the contrary, the [(MeOH)-Ni(OMe)(ovan)]<sub>4</sub> complex does not react with pyridine or a primary amine ligand. And reaction with an amino-alcohol or an amino-ether ligand yields new compounds in which each methanol molecule is replaced by the reacting amino-alcohol (ethanolamine) or an amino-ether (2-methoxyethylamine or 3-methoxypropylamine) ligand. From these experimental results, it becomes clear that the oxygen atom of the amino-alcohol or an amino-ether ligand is linked to the nickel ion. A confirmation is given by visible spectra of the complexes **3** and **4** that give absorption bands at 590 nm, similar to the one of the starting [(MeOH)Ni(OMe)(ovan)]<sub>4</sub> entity (600 nm), in agreement with a O<sub>6</sub> environment of the nickel ions.

#### 3.1. Structural study of [(MeOH)Ni(OMe)(ovan)]<sub>4</sub> (**1**)

The crystallographic data of complex **1** are summarized in Table 1 while a view of the structure is reported in Fig. 1. Relevant bond distances and angles are collated in the figure caption. The structure crystallizes in the tetragonal I4<sub>1</sub>/a space group. The vertexes of the cubane structure are alternately occupied by four Ni atoms and four methoxy groups, so that each Ni ion is surrounded by three  $\mu_3$ -methoxy groups. The octahedral Nickel coordination sphere is completed by two oxygen atoms coming from an *o*-vanillin ligand (phenoxo and aldehyde oxygen atoms) and by the oxygen atom of a methanol molecule. The Ni-O bond lengths of the chelating ovan ligand are slightly shorter (2.000(1) and 2.027(1) Å) than the three Ni-O(OMe) bonds (2.035(1), 2.039(1) and 2.058(1) Å) of the  $\mu_3$ -bridging methoxy groups, the Ni-O(methanol) bond being slightly longer, 2.097(1) Å. The Ni-O-Ni angles involving the bridging OMe ligands are very similar, 96.41(5), 97.17(5) and 97.87(5)° so that the intramolecular Ni...Ni distances are homogeneous, 3.0332(3), 3.0332(3) and 3.0861(3) Å. The OH groups of the methanol molecules coordinated to the nickel ions act as donors for the phenoxo and methoxy oxygen atoms of the nearest *o*-vanillin ligand, thus

**Table 1**  
Crystallographic data for [(MeOH)Ni(OMe)(ovan)]<sub>4</sub> **1**.

<b>1</b>	
Chemical formula	C <sub>40</sub> H <sub>56</sub> Ni <sub>4</sub> O <sub>20</sub>
Formula weight	1091.61
Space group	I 4 <sub>1</sub> /a (No. 88)
a, Å	22.2370 (4)
b, Å	22.2370 (4)
c, Å	9.5830 (3)
α, deg	90
β, deg	90
δ, deg	90
V, Å <sup>3</sup>	4738.64 (19)
Z	4
ρ <sub>calcd</sub> , g cm <sup>-3</sup>	1.530
λ, Å	0.71073
T, K	180
Gof	1.046
μ <sub>MolKor</sub> , mm <sup>-1</sup>	1.640
R <sup>a</sup> obs, all	0.0231, 0.0317
wR <sup>b</sup> obs, all	0.0577, 0.0596
Δρ <sub>max</sub> , Δρ <sub>min</sub> , eÅ <sup>-3</sup>	0.294–0.411

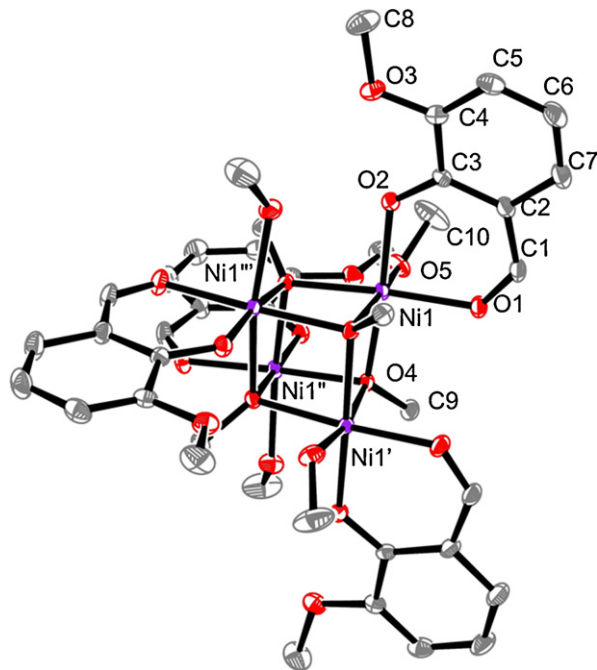
$$^a R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR = \left[ \frac{\sum w(|F_o|^2 - |F_c|^2)^2}{\sum w|F_o|^2} \right]^{1/2}$$

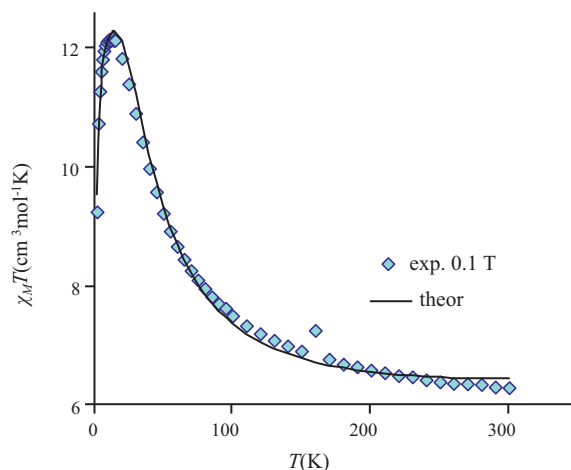
establishing intramolecular bifurcated hydrogen-bond interactions [17]. The Ni ions belonging to two different cubanes are separated by 9.540(4) Å.

### 3.2. Magnetic properties

We report in Fig. 2 the magnetic behavior of complex **1** in the form of the thermal variation of the  $\chi_M T$  product



**Fig. 1.** Plot of complex **1** with ellipsoids drawn at the 30% probability level and with partial atom numbering. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ni(1)–O(1) 2.026(1), Ni(1)–O(2) 2.000(1), Ni(1)–O(4) 2.035(1), Ni(1)–O(4') 2.039(1), Ni(1)–O(4'') 2.058(1), Ni(1)–O(1) 2.097(1), Ni(1)–O(4)–Ni(1'), 97.17(5), Ni(1)–O(4)–Ni(1''), 97.87(5), Ni(1')–O(4)–Ni(1'') 96.41(5). Symmetry operations: ' :  $y-1/4, -x+1/4, -z+1/4$ ; '' :  $-x, -y+1/2, z$ ; #3 :  $-y+1/4, x+1/4, -z+1/4$ .



**Fig. 2.** Temperature dependence of the  $\chi_M T$  product for complex **1**. Solid line corresponds to the best data fit (see the text).

( $\chi_M$  is the molar magnetic susceptibility corrected for the diamagnetism of the ligands) [20]. In the present case, the  $\chi_M T$  product, which is equal to 6.2 cm<sup>3</sup> mol<sup>-1</sup> K at 300 K, increases slowly to 100 K (7.5 cm<sup>3</sup> mol<sup>-1</sup> K), then more abruptly to 11 K where it passes by a maximum (12.2 cm<sup>3</sup> mol<sup>-1</sup> K) before decreasing to 9.1 cm<sup>3</sup> mol<sup>-1</sup> K at 2 K. The  $\chi_M T$  at room temperature is larger than expected for four isolated Ni<sup>II</sup> ions with  $g = 2$  but we must remember that  $g$  is larger than two for nickel ions. The experimental data indicate the occurrence of an overall ferromagnetic interaction in complex **1**. Finally fitting the experimental data to a simple model derived from the spin only Hamiltonian for a tetranuclear (Ni<sub>4</sub>) complex,  $H = -2J_{NiNi} (S_{Ni1} \cdot S_{Ni2} + S_{Ni1} \cdot S_{Ni3} + S_{Ni1} \cdot S_{Ni4} + S_{Ni2} \cdot S_{Ni3} + S_{Ni2} \cdot S_{Ni4} + S_{Ni3} \cdot S_{Ni4})$  yields the following data,  $J_{NiNi} = 5.8$  cm<sup>-1</sup>,  $g = 2.26$  with a  $R$  factor equal to  $4.0 \times 10^{-4}$ ,  $R = \frac{\sum [(\chi_M T)^{obs} - (\chi_M T)^{calc}]^2}{\sum [(\chi_M T)^{obs}]^2}$ . In order to fit the  $\chi_M T$  decrease below 12 K, we first introduced a common molecular-field parameter  $zJ$  that was found equal to  $-0.027$  cm<sup>-1</sup>. As we are dealing with a tetranuclear nickel complex, the single-ion anisotropy of nickel ions induces presence of zero-field splitting terms (ZFS) that can be responsible for the  $\chi_M T$  decrease at low temperature. The measured value of magnetization at 5 T and 2 K temperature (Fig. 3) indicates that we have a  $S = 4$  ground state,  $M = 8.5$  N $\beta$  against the expected value of 8 for  $g = 2$ . With use of the MAGPACK program, the best simulation reported in Fig. 3 gives  $J_{NiNi} = 5.9$  cm<sup>-1</sup>,  $g = 2.26$ ,  $D_{Ni} = 2.0$  cm<sup>-1</sup>, along with a low rhombic term  $E$ ,  $E_{Ni} = 0.4$  cm<sup>-1</sup>.

The temperature dependence of the magnetic susceptibility for complex **3** in the 2–300 K temperature range and at different fields is shown in Fig. 4 in the  $\chi_M T$  vs.  $T$  form.  $\chi_M T$  is equal to 4.9 cm<sup>3</sup> mol<sup>-1</sup> K at 300 K and remains practically constant to 100 K (5.5 cm<sup>3</sup> mol<sup>-1</sup> K) under an applied 0.1 T field. The  $\chi_M T$  product increases first gradually to 30 K (8.5 cm<sup>3</sup> mol<sup>-1</sup> K) and then sharply below 30 K to a maximum value of 24.2 cm<sup>3</sup> mol<sup>-1</sup> K at 14 K before decreasing to 7.2 cm<sup>3</sup> mol<sup>-1</sup> K at 2 K. This sharp  $\chi_M T$  increase suggests the onset of a ferromagnetic order.

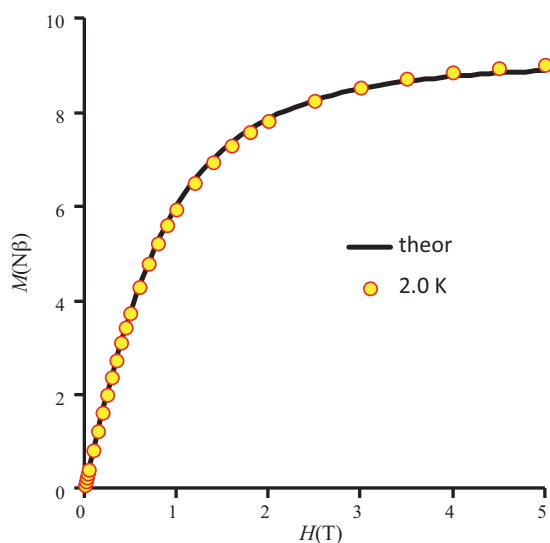


Fig. 3. Field dependence of magnetization for complex 1. Solid line corresponds to the best data fit (see the text).

Measurements at different and higher magnetic fields confirm that the magnetic ordering is suppressed with an applied field equal or higher than 1.0 T (Fig. 4 and Fig. S1). The magnetic susceptibility data registered under a 1.0 T field have been computed by the exact calculation of the energy levels through diagonalization of the full energy matrix with a Hamiltonian similar to the one described above but in which an axial ZFS term for Ni<sup>II</sup> ions is introduced. The best fit (solid line, Fig. 5) yields the following data:  $J_{NiNi} = 3.9 \text{ cm}^{-1}$ ,  $g = 2.11$ ,  $D_{Ni} = 7.6 \text{ cm}^{-1}$  with  $R = 7 \times 10^{-4}$ . In order to check the validity of these results, MAGPACK simulation of magnetization data at 2 K with the above parameters confirms that a lower  $D_{Ni}$  value ( $4.0 \text{ cm}^{-1}$ ), associated to a low  $E_{Ni}$  term ( $0.3 \text{ cm}^{-1}$ ), appears more appropriate (Fig. 6).

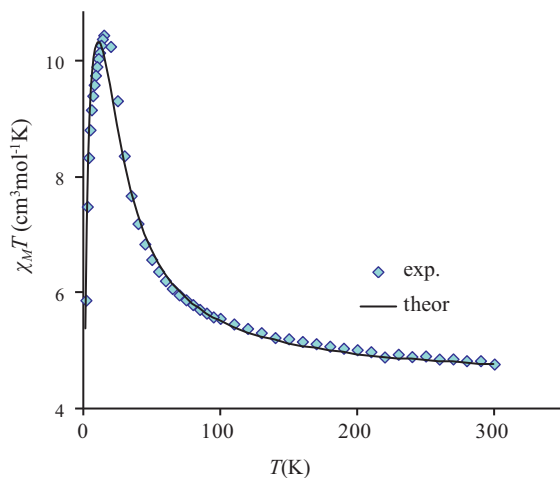


Fig. 5. Temperature dependence of the  $\chi_M T$  product for complex 3 under a 1 T applied field. Solid line corresponds to  $J_{NiNi} = 3.9 \text{ cm}^{-1}$ ,  $D_{Ni} = 7.6 \text{ cm}^{-1}$ ,  $g = 2.11$ .

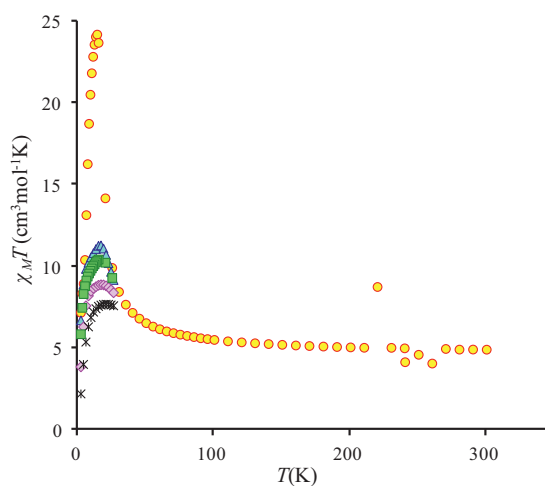


Fig. 4. Temperature dependence of the  $\chi_M T$  product for complex 3 at different applied magnetic fields: 0.1 T (circles), 0.7 T (triangles), 1.0 T (squares), 2.0 T (diamonds) and 5.0 T (stars).

To confirm the magnetic phase transition, alternating current susceptibility measurements have been investigated on complex 3. These ac susceptibility measurements show in-phase and out-of-phase signals, the latter being not frequency-dependent. Indeed the  $\chi''$  maxima at 10, 200, 400 and 800 Hz (Fig. 7 and Fig. S2) centered around 13.5 K are characteristic of a three-dimensional weak ferromagnetic ordering. Unfortunately in-phase and out-of-phase signals are not observed when ac susceptibility measurements are made on the tetranuclear complex 1, which means that it cannot be considered as a single-molecule magnet.

Similar observations have been made for complexes 4 and 5. Under a 0.1 T applied field, the  $\chi_M T$  maxima observed at 14 K are respectively equal to 27.2 and 19.3  $\text{cm}^3 \text{ mol}^{-1} \text{ K}$  (Figs. S3 and S4) while these maxima

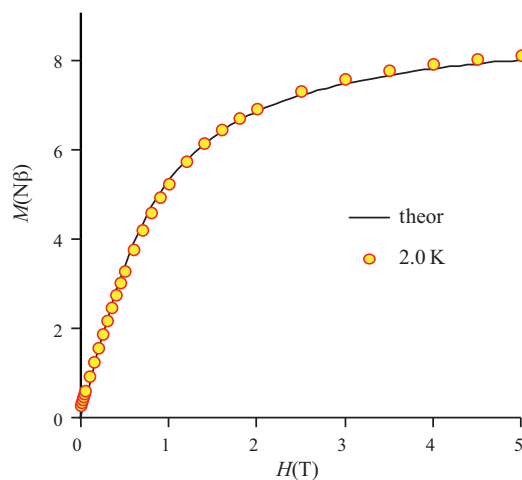


Fig. 6. Field dependence of magnetization for complex 3. Solid line corresponds to  $J_{NiNi} = 3.9 \text{ cm}^{-1}$ ,  $g = 2.11$ ,  $D_{Ni} = 4.0 \text{ cm}^{-1}$ ,  $E_{Ni} = 0.3 \text{ cm}^{-1}$ .



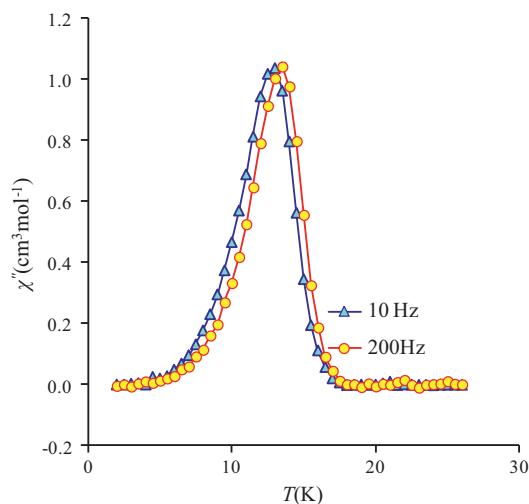


Fig. 7. Out-of-phase susceptibilities ( $\chi''$ ) against temperature measured in a 2.7 G ac magnetic field oscillating at 10 (triangles) or 200 Hz (circles) frequencies for **3**.

decrease to  $9.5 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  for measurements made with a 1.0 T applied field. Out-of-phase signals centered at 12 and 13.5 K are again observed (Figs. S5 and S6). On the contrary, complex **2** presents a slightly different behavior. Indeed the  $\chi_{MT}$  difference at 1 and 0.1 T is much less important, 11.8 against  $9.9 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  and the out-of-phase signal is weaker than in complexes **3**, **4**, **5**, and centered at 8 K (Figs. S7 and S8).

### 3.3. Discussion

If the tetranuclear nickel cubane complex has been first prepared by serendipity, an experimental process allowing its preparation in a correct yield is reported. It belongs to the family of diketone or salicylaldehyde cubane complexes in which the four nickel ions are linked together by  $\mu_3$ -OMe bridges and with very similar Ni-O(OMe) bond lengths. As a consequence, the six Ni-Ni magnetic interactions can be considered as equivalent. Indeed, use of an Hamiltonian with two different  $J$  parameters does not give a better result. The structural determination also indicates that the Ni-O-Ni angles are quite homogeneous and vary from  $96.41(5)$  to  $97.87(5)^\circ$ . The dependence of the interaction parameter  $J_{NiNi}$  has been previously noted and bridging angle values lower than  $100^\circ$  are known to give ferromagnetic interactions, which explains the  $J_{NiNi}$  value of  $5.8 \text{ cm}^{-1}$  found for complex **1** and the  $S = 4$  ground state. In a recent work, a  $J_{NiNi}$  value of  $6.2 \text{ cm}^{-1}$  has been deduced from an Hamiltonian that does not take into account the zero-field splitting parameter [18], what explains why our value ( $J_{NiNi} = 5.8 \text{ cm}^{-1}$ ) is slightly lower. On the contrary, the determination of the ZFS parameters is not so easy. While in mononuclear complexes the anisotropy can be usually enlarged by maximizing the geometrical distortions of the first coordination sphere and corroborated by *ab initio* calculations [30], in polynuclear complexes the anisotropic intersite interactions are difficult to predict and hence the property of the whole system is far from being

predictable. A recent reinvestigation of the axial zero-field splitting [31] allows to determine a tetragonality parameter  $D_{str}$  by knowing the metal-ligand bond lengths and eventually an estimation of a  $D_{mag}$  term defining the Ni single-ion magnetic anisotropy. Applied to complex **1**, the  $D_{str}$  term of the Ni metal ion is equal to 10.6, that gives a  $D_{mag}$  value of  $7.1 \text{ cm}^{-1}$ . This analysis confirms the presence of single-ion anisotropy in this complex, that cannot be determined in a straightforward way from experiment. On another side, the SHAPE program [32] indicates that the Ni coordination sphere is better described as a slightly deformed octahedron ( $S_{Oh} = 0.43$ ), the  $S$  coefficient varying from zero for an ideal octahedron to 100. A slight octahedral deformation should be associated to low ZFS terms. Nevertheless, these two approaches of the ZFS problem do not disagree with the data calculated in the above section. Furthermore, the increase of the axial zero-field splitting term  $D$  on going from the tetranuclear cluster to the complex **3** strongly suggests that the three-dimensional arrangement must induce a larger deformation of the Ni coordination spheres.

The most original point developed in the present paper concerns the different ways used to assemble the tetranuclear Ni cubane units. Surprisingly, these  $\text{Ni}_4$  complexes are well separated from each other and there are no intermolecular hydrogen bonds in between these units. Furthermore these high-spin units with their ferromagnetic interactions and their  $S = 4$  ground state do not behave as single-molecule magnets, what is confirmed by the absence of out-of-phase signals when alternating current (ac) susceptibility measurements are performed in the 2–25 K temperature range. A first way to associate such units consists in replacing the methanol molecules coordinated to the Ni ions by a diol molecule. Although we could not obtain crystals suitable for XRD study, analytical data of the resulting complex **2** do suggest that 1,3-propanediol links these  $\text{Ni}_4$  units for only two diol molecules are introduced in place of the four methanol molecules. This association is confirmed by ac susceptibility measurements performed in the 2–20 K temperature range. Observation of out-of-phase signals that are not frequency-dependent implies that magnetic ordering occurs. Unfortunately, these weak signals centered at 8 K appear on a large domain, from 6 to 10 K.

The situation becomes more interesting when amino-alcohol or amino-ethers are used, as in complexes **3**, **4** and **5**. The analytical data indicate that each methanol molecule is replaced by an amino-alcohol or amino-ether. The oxygen atom of the introduced ligands is coordinated to the nickel centre. This is demonstrated by the fact that primary amine  $\text{RNH}_2$  ligands are not able to replace methanol molecules of the  $\text{Ni}_4$  units and also by observation of visible absorption bands similar to those obtained with the starting complex **1**. If the present cubane structure belongs to an old family of cubane units involving diketone or salicylaldehyde ligands, it presents the advantage of having at the periphery free methoxy groups that are prone to make hydrogen bonds with the introduced primary amine functions. Such a behavior has been observed in several metal complexes containing *o*-vanillin ligands [14,15]. Although we could not isolate

crystals for XRD studies, the magnetic properties of complexes **3**, **4** and **5**, with the observed sharp  $\chi_{MT}$  increase and the appearance of well-defined out-of-phase  $\chi''$  susceptibility signals in the 12–14 K temperature range, evidence that self-assembling occurs. These signals cannot be associated to a SMM behavior for they are not frequency-dependent but they do confirm the presence of a three-dimensional magnetic ordering.

#### 4. Conclusion

We have described in this work an experimental process that allows direct preparation of a tetranuclear nickel cubane derived from *o*-vanillin (2-hydroxy-3-methoxy-benzaldehyde) without hydrolysis of a Schiff base ligand. Contrary to what was previously published [16], this complex presents ferromagnetic Ni–Ni interactions with a  $S=4$  ground state. Magnetic susceptibility studies reveal that positive anisotropy terms  $D_{Ni}$  are active but ac susceptibility measurements confirm that the  $D_{mol}$  is not negative for the nickel cubane does not behave as a SMM. Replacement of methanol molecules coordinated to the Ni ions by a diol ligand such as 1,3-propanediol creates coordination bonds bridging these  $Ni_4$  entities through the diol ligand, as demonstrated by analytical results and ac susceptibility measurements.

Finally, it can be assumed that the interactions between tetranuclear units through a hydrogen-bonding network involving the pendant primary amine functions and the peripheral *o*-vanillin methoxy groups promote a three-dimensional ferromagnetic ordering when methanol molecules of the tetranuclear  $Ni_4$  complex **1** are replaced by amino-alcohol or amino-ether molecules.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.crci.2012.03.008.

X-ray crystallographic file in CIF format for **1**. CCDC 863778 for **1** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Temperature dependence of the  $\chi_{MT}$

product for complexes **2**, **3**, **4**, **5** at different applied magnetic fields; in-phase ( $\chi'$ ) and out-of-phase susceptibilities ( $\chi''$ ) against temperature measured in a 2.7 G ac magnetic field oscillating at different frequencies for complexes **2**, **3**, **4**, **5** available with the electronic version.

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