

Solvent-Dependent Access to Two Different Ni₄^{II} Core Topologies from the First Use of Pyridine-2,6-dimethanol in Nickel(II) Cluster Chemistry

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The use of pyridine-2,6-dimethanol, pdmH₂, in reactions with nickel(II) acetate has led to two Ni₄ clusters, depending on the solvent. [Ni₄(O₂CMe)₄(pdmH)₄]·MeCN (**1**·MeCN) can be obtained from MeCN and [Ni₄(O₂CMe)₆(pdmH)₂(EtOH)₂]·1.2EtOH (**2**·1.2EtOH) from EtOH. Each cluster can be converted into the other in the appropriate solvent. The tetranuclear cluster molecule **1** possesses a distorted cubane {Ni₄(μ₃-OR)₄}⁴⁺ core (RO⁻ = pdmH⁻) with the Ni^{II} atoms and the alkoxide-type oxygen atoms from the η³:η¹:μ₃ pdmH⁻ ligands occupying alternate vertices of the cube; four η¹:η¹:μ MeCO₂⁻ groups cap four faces of the cube. The four Ni^{II} atoms in molecule **2** are located at four vertices of a defective dicubane and are bridged by six oxygen atoms, two μ₃ from the η³:η¹:η¹:μ₃ pdmH⁻ ligands and four from four monoatomically bridging MeCO₂⁻ groups; peripheral ligation is provided by two η¹:η¹:μ MeCO₂⁻ groups and two terminal EtOH ligands. IR data are discussed in terms of the coordination modes of the ligands. Variable-temperature direct-current magnetic susceptibility data of **1** and **2** were modelled with two and three *J* values respectively, indicating diamagnetic ground states (*S* = 0). The sign and the magnitude of the *J* values are discussed in terms of structural features of the complexes.

Manuscript received: 14 September 2012.

Manuscript accepted: 14 October 2012.

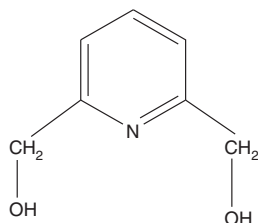
Published online: 16 November 2012.

Introduction

There are various reasons for the current interest by groups around the world in the synthesis and study of polynuclear 3d-metal complexes^[1] (coordination clusters^[2] or simply clusters^[3]). This interest is a result of their relevance to bio-inorganic chemistry,^[4] to magnetic refrigeration^[5] and to the special class of molecule-based materials known as single-molecule magnets (SMMs).^[6] Restricting further discussion to the latter area, SMMs are molecules that behave as nanoscale magnetic particles, thus providing a bottom-up, molecular approach to nanomagnetism. They are typically polynuclear assemblies of exchanged-coupled paramagnetic metal ions, usually bridged by ligands with O-ligation. As molecular crystals provide 3D organization of monodisperse particles of a well-defined size and a single orientation, the molecular nature of SMMs brings several advantages to the field of

nanomagnetism. The significant barrier to magnetization relaxation in SMMs is the result of a combination of a high ground-state spin (*S*) value and large easy axis magnetic anisotropy, as gauged by a negative, second-order axial zero-field splitting parameter (*D*), which lead to the appearance of magnetization hysteresis, the signature property of a classic magnet. SMMs also straddle the classical–quantum interface by displaying quantum tunnelling of magnetization^[7] and quantum phase interference,^[8] which have attracted the intense interest of physicists. As a consequence of this combination of classical and quantum properties, SMMs have a variety of potential advanced applications, including ultra-high-density information storage, spintronics and quantum computation.^[9]

An important factor in the construction of coordination clusters and SMMs is the choice of the primary organic ligand, because this often dictates not only cluster symmetry, topology



Scheme 1.

and the number of paramagnetic metal ions present, but also the nature of the intramolecular magnetic-exchange interactions. Thus, the use of new or less investigated ligands or a combination of ligands remains important in the field.

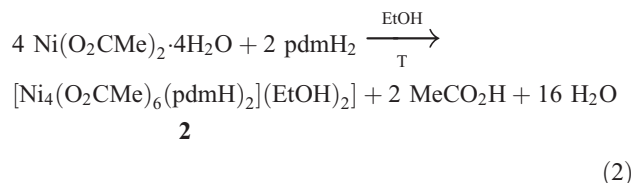
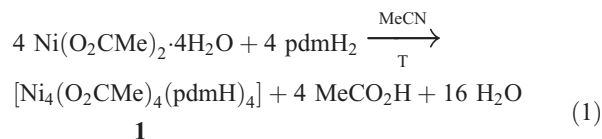
In the last 10 years or so, we have been exploiting the coordination ability of, among others, pyridyl (mono)alcohols and pyridyl *gem*-diols for 3d-metal cluster synthesis.^[10] Recently, we turned our attention to the use of pyridine-2,6-dimethanol (pdmH₂, see Scheme 1). On deprotonation, this ligand provides alkoxido groups, which are excellent bridging units that can foster the formation of high-nuclearity complexes and often propagate ferromagnetic exchange interactions. Despite its rather extensive use in trivalent and mixed-valence 3d-metal cluster chemistry,^[11] there has been only very limited use of pdmH₂ in divalent 3d-metal cluster chemistry, because it readily forms mononuclear [M^{II}(pdmH₂)₂]²⁺- or [M^{II}(pdmH)₂]-type species.^[12] Our first efforts in M^{II}-pdmH₂ chemistry produced [Cu₃^{II} + Cu₄^{II}],^[13a] [Cu₄^{II}],^[13a,b] [Cu₅^{II}]^[13a] and [Zn₆^{II}]^[13c] molecules. Herein, we extend these efforts to nickel(II) and report two Ni₄^{II} clusters with cubane and defective-dicubane cores, obtained from the reactions of Ni(O₂CMe)₂·4H₂O and pdmH₂; importantly, the product identity depends on the nature of the solvent used. It is noteworthy that only salts of the mononuclear cations [Ni(pdmH₂)₂]²⁺ have been reported so far.^[12b,14]

Ni^{II} has shown some promise in the synthesis of both SMMs^[15] (some of them contain the monoalcohol version of pdmH₂, i.e. 2-(hydroxymethyl)pyridine^[15c,15g,15i]) and spin phonon traps,^[16] the former taking advantage of its significant single-ion anisotropy^[17] and the latter its paramagnetic nature when confined within a highly symmetric cage.

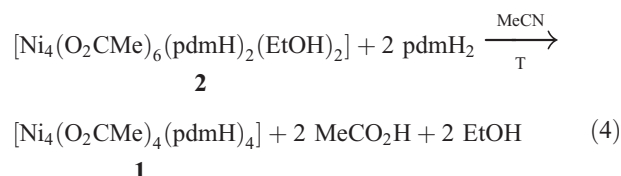
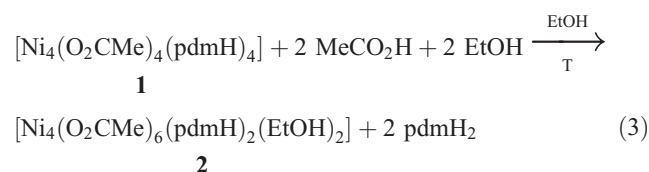
Results and Discussion

Synthetic Comments and IR Spectra

A variety of Ni(O₂CMe)₂/pdmH₂ reaction systems involving different reagent ratios, solvent media and crystallization conditions was explored to develop the procedures described here. Reaction of Ni(O₂CMe)₂·4H₂O and pdmH₂ in a 1 : 1 molar ratio in MeCN under reflux afforded a green solution that on slow evaporation at room temperature gave pale green crystals of [Ni₄(O₂CMe)₄(pdmH)₄]·MeCN (**1**·MeCN) in ~70 % yield. Assuming that **1** is the only product from this reaction system, its formation can be summarized by Eqn 1. When the same reaction and crystallization process was repeated in EtOH under reflux, the MeCO₂⁻-richer and pdmH⁻-poorer complex [Ni₄(O₂CMe)₆(pdmH)₂(EtOH)₂]·1.2EtOH (**2**·1.2EtOH) was isolated in 45 % yield (Eqn 2). The MeCO₂⁻ ions play a double role; some act as a base deprotonating the pdmH₂ ligand, whereas the remaining acetates function as ligands. The Ni(O₂CMe)₂·4H₂O : pdmH₂ reaction ratio (2 : 1, 1 : 1, 1 : 2) does not affect the product identity in either solvent.



Complex **1** can be converted into **2** in EtOH under reflux in ~20 % yield, but the yield increases to 60 % on addition of 2 equiv. of MeCO₂H per **1**. This transformation is summarized in Eqn 3. Similarly, **2** is converted into **1** in MeCN under reflux in low yield (~25 %), but the yield increases to 75 % on reaction of **2** with two equiv. of pdmH₂ in MeCN (Eqn 4). It is clear that the solvent plays a crucial role on product identity through complicated mechanisms that likely involve factors such as relative solubilities, lattice energies and crystallization kinetics among others.^[18]



We are not sure if the chemical Eqns 3 and 4 represent ‘true’ reaction chemistry of clusters **1** and **2** respectively. Another possibility is that these complexes do not retain their structures in solution (a prerequisite for ‘true’ reactivity), but instead they undergo decomposition, and then the stable compound in the specific solvent forms. We tried to clarify this issue by UV-vis (ligand-field) spectroscopy comparing the solid-state (diffuse reflectance) spectra of **1** and **2** with their solution absorption spectra in EtOH and MeCN respectively. Unfortunately, neither **1** nor **2** have satisfactory solubilities; it seems that the complexes become soluble during their interconversion by reaction with the appropriate reagent in the suitable solvent.

The pdmH₂ ligand is singly deprotonated in **1** and **2**. Thus, it was logical to target its double deprotonation to obtain different products. Addition of external bases (Et₃N, NaOMe, Me₄NOH) in the reaction mixtures that lead to **1** and **2**, or reactions of pre-isolated **1** and **2** with 2–4 equiv. of base gave insoluble amorphous powders; such products, analysed as Ni(pdm)-*n*solvent, were not further characterized.

A characteristic feature in the IR spectrum of dried **1** is a broad band of medium intensity assignable to the ν(OH) vibration of the hydroxyl group of pdmH⁻.^[13c] The broadness and relatively low wavenumber of this band are both indicative of hydrogen bonding (see below).^[19] The IR spectrum of a vacuum-dried sample of **2** exhibits strong to medium bands at

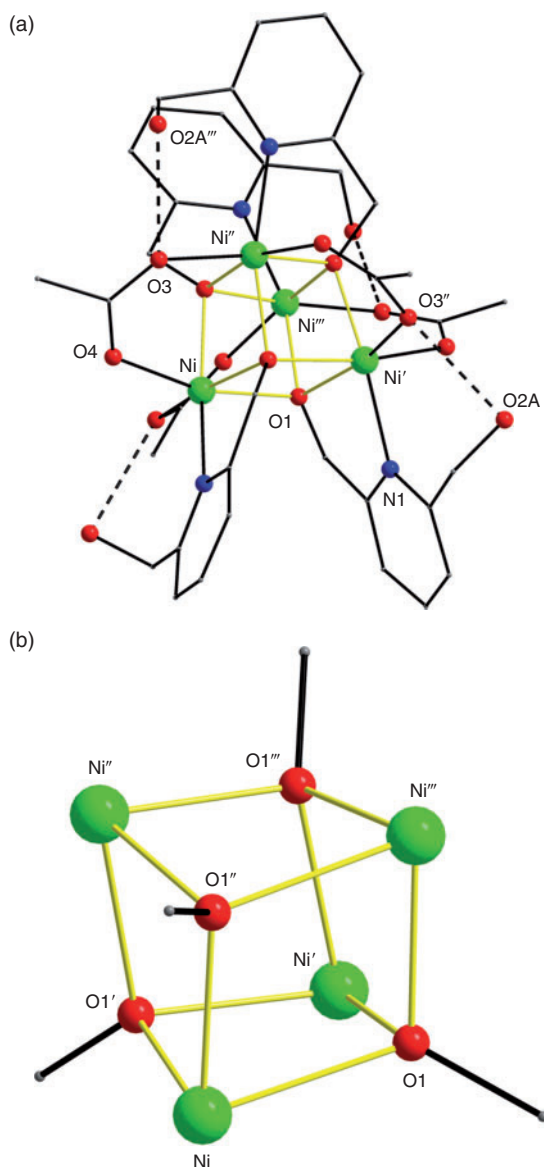


Fig. 1. (a) Molecular structure of complex **1**. The cubane core of the Ni_4 cluster is outlined in yellow bold. The dashed lines represent the intramolecular H bonds. (b) *PovRay* representation of the complete $\{\text{Ni}_4(\mu_3\text{-OR})_4\}^{4+}$ core. Single, double and triple primes are used for symmetry-related atoms; see Table 1.

3444 and 3255 cm^{-1} , tentatively assigned to $\nu(\text{OH})_{\text{coord.EtOH}}$ and $\nu(\text{OH})_{\text{pdmH}^-}$ respectively; their relatively low wavenumbers are due to the coordination of these hydroxyl groups. The in-plane and out-of-plane deformation bands of the 2,6-pyridyl ring appear at 660 and 426 cm^{-1} respectively for **1** and at 666 and 428 cm^{-1} respectively for **2**; the higher wavenumbers of these modes compared with the free ligand confirm the involvement of the ring N atom in coordination.^[12c,14] Several bands appear in the $1610\text{--}1360\text{ cm}^{-1}$ range in the spectra of both complexes. These are due to contributions from the stretching vibrations of the pyridyl ring and the MeCO_2^- carboxylate group. As overlap cannot be ruled out, the bands most probably do not represent pure vibrations, and this renders exact assignments and studies of the coordination shifts tentative. The bands at 1578 and 1420 cm^{-1} in the spectrum of **1** are assigned^[20] to the $\nu_{\text{as}}(\text{CO}_2)$ and $\nu_{\text{s}}(\text{CO}_2)$ vibrations respectively of the acetato ligands,

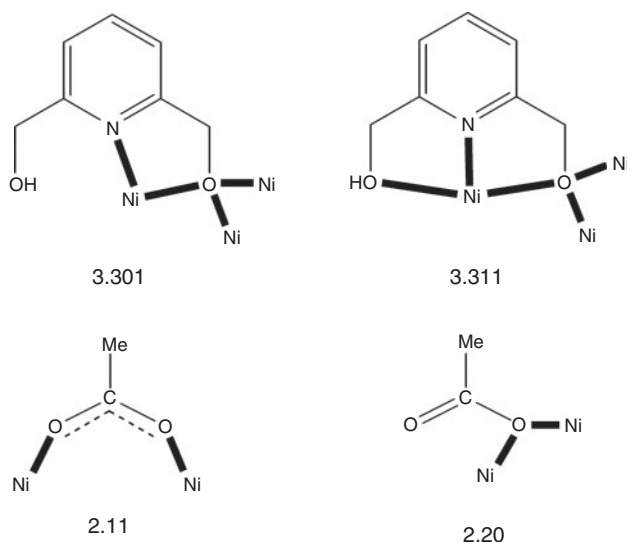


Fig. 2. The crystallographically established coordination modes of the ligands in complexes **1** and **2**, and the Harris notation that describes these modes.

coupled with ring stretching vibrations. The difference Δ , where $\Delta = \nu_{\text{as}}(\text{CO}_2) - \nu_{\text{s}}(\text{CO}_2)$, is 158 cm^{-1} , less than that for NaO_2CMe (164 cm^{-1}), as expected for the bidentate bridging mode of carboxylate ligation.^[20] Owing to the presence of two different types of carboxylate ligation in **2** (monoatomic bridging, bidentate bridging; see below), two $\nu_{\text{as}}(\text{CO}_2)$ and two $\nu_{\text{s}}(\text{CO}_2)$ bands appear in its spectrum, at least two having also a ring stretching character. The $1606, 1366\text{ cm}^{-1}$ pair ($\Delta = 240\text{ cm}^{-1}$) were assigned to the monoatomically bridging acetates, and the $1567, 1423\text{ cm}^{-1}$ pair ($\Delta = 144\text{ cm}^{-1}$) to the bidentate bridging carboxylate groups.^[20]

Description of Structures

Various structural plots of complexes **1**·MeCN and **2**·1.2EtOH are shown in Figs 1 and 3–5; the coordination modes of pdmH^- in the two complexes are illustrated in Fig. 2. Selected interatomic distances and angles are listed in Tables 1 and 2.

Complex **1**·MeCN crystallizes in the tetragonal space group $I4_1/acd$ and has crystallographic S_4 symmetry. Its structure consists of tetranuclear $[\text{Ni}_4(\text{O}_2\text{CMe})_4(\text{pdmH})_4]$ and solvate MeCN molecules. The tetranuclear cluster molecule has a distorted cubane $\{\text{Ni}_4(\mu_3\text{-OR})_4\}^{4+}$ core (Fig. 1, bottom) with the four, distorted octahedral Ni^{II} atoms and the deprotonated $\mu_3\text{-O}$ atoms from the four $\eta^3 : \eta^1 : \mu_3$ (or 3.301 using Harris notation^[21]) pdmH^- ligands (Fig. 2) occupying alternate vertices of the cube ($\text{RO}^- = \text{pdmH}^-$). Thus, the molecule consists of two interpenetrating cocentric tetrahedra, one of four metal ions and the other of four triply bridging oxygen atoms. There is a four-fold rotoinversion axis passing through the centre of the cubane, and as a result, all the Ni^{II} and $\mu_3\text{-O}$ atoms are crystallographically equivalent. In addition to the three $\mu_3\text{-O}$ atoms, each Ni^{II} centre is coordinated to two O atoms belonging to two different *syn,syn*- $\eta^1 : \eta^1 : \mu$ (or 2.11^[21]) acetate groups and to one pyridyl N atom of pdmH^- to complete an NiO_5N chromophore. One octahedral face of Ni^{II} is occupied by three alkoxide-type oxygen atoms and the other contains the remaining donor atoms.

The six faces of the cubane are not all equivalent. The side faces of the cube (using the view in Fig. 1) are capped by four 2.11 bridging acetates that lie across the face diagonals. The four

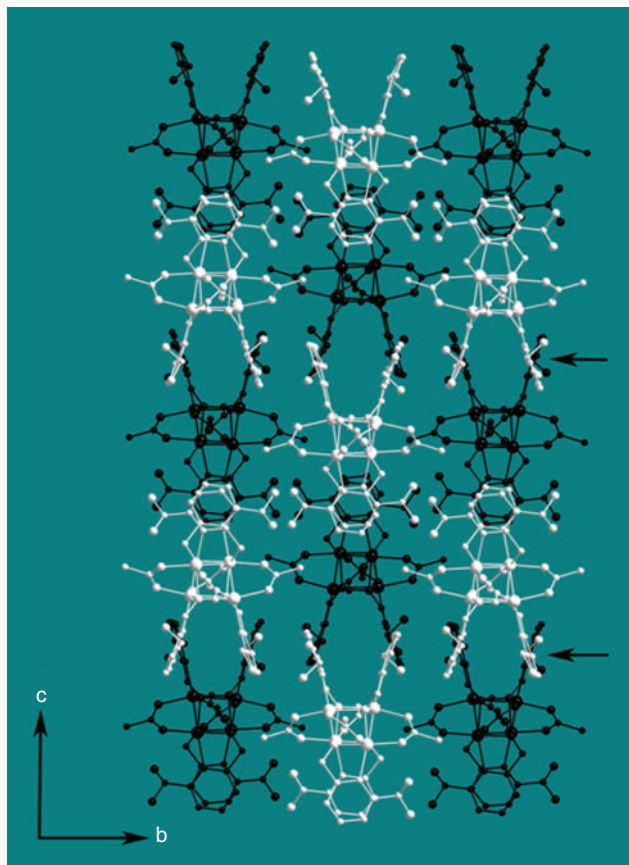


Fig. 3. 3D packing of compound **1**. White molecules form the top and black ones the bottom layer. The pyridyl rings indicate the directions of π - π stacking along the *a* crystallographic direction (normal to the plane of the figure) and the small arrows at the right of the picture indicate the directions of π - π stacking along the *b* crystallographic direction (in the plane of the picture).

faces of the cubane spanned by the MeCO_2^- ligands have shorter Ni...Ni distances (2.997 Å) and more acute Ni-O-Ni angles (92.6, 95.4°) than the two faces not bridged in this fashion (Ni...Ni = 3.199 Å, Ni-O-Ni = 102.7°). Thus, the Ni_4 tetrahedron is distorted by compression along an S_4 axis, giving four Ni...Ni separations shorter than average and two longer. The internal cube angles at the metal vertices (RO-Ni-OR) average 82.1°. Based on the Ni-O(1, 1', 1'') bond distances, and the Ni-O(1)-Ni and O(1)-Ni-O(1) bond angles, it is obvious that the cube deviates from the ideal geometry. The Ni-O (average 2.062 Å) and Ni-N (2.146 Å) distances are typical for six-coordinate Ni^{II} complexes.^[22]

The unbound O atoms of each pdmH^- ligand are in disorder and lie at two different sites with half occupancy. The atom at the O(2A) site is intramolecularly hydrogen-bonded to an O atom of an MeCO_2^- ligand ($\text{O}(2\text{A})\cdots\text{O}(3'') = 2.710$ Å, $\text{O}(2\text{A})-\text{HO}(2\text{A})\cdots\text{O}(3'') = 166.4^\circ$). The lattice MeCN also occupies two disorder sites with half occupancy each. The molecule possesses a four-fold rotoinversion axis and this symmetry arranges the pyridyl rings of the four pdmH^- bonded ligands in groups of two along the *a* and *c* crystallographic axes (Fig. 3). This is the key characteristic that governs the 3D architecture of compound **1**, through π - π stacking interactions (Fig. 3).

Complex **1** joins a large family of Ni_4^{II} cubanes with an $\{\text{Ni}_4(\mu_3\text{-OR})_3\}^{4+}$ core.^[10b,15c,15d,15g,15i,15m,23,24] Using the

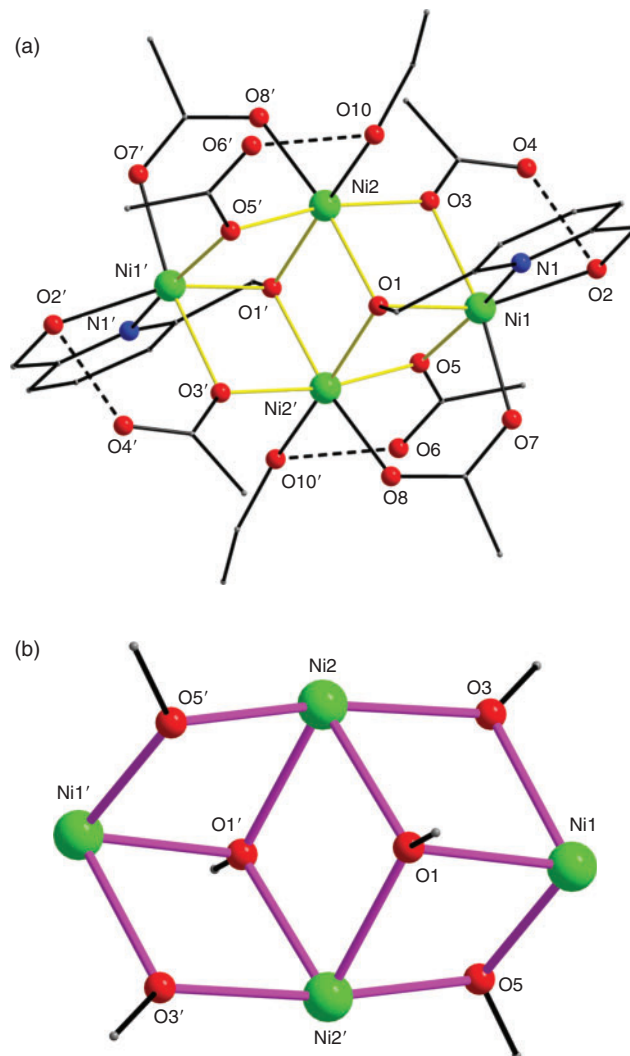


Fig. 4. (a) Partially labelled ORTEP plot of the tetranuclear molecule present in **2**·1.2EtOH. The defective dicubane core is highlighted in yellow bold. The dashed lines represent the intramolecular H bonds. (b) PovRay representation of the complete $\{\text{Ni}_4(\mu_3\text{-OR})_2(\mu\text{-OR}')_4\}^{2+}$ core. Primed and non-primed atoms are related by the crystallographic inversion centre; see Table 2.

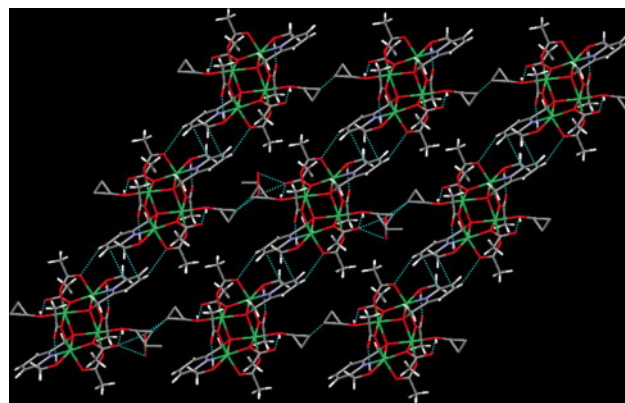


Fig. 5. A section of the 2D hydrogen-bonded network present in the crystal structure of complex **2**·1.2EtOH. Ni^{II} , green; O, red; N, blue; C, grey; H, white.

Table 1. Selected interatomic distances and angles for complex **1**·MeCNSymmetry codes: (') = $-x, -y + 3/2, z$; (") = $-y + 3/4, x + 3/4, -z + 1/4$; (""') = $y - 3/4, -x + 3/4, -z + 1/4$

Interatomic distance [Å]	
Ni...Ni'	3.199(1)
Ni...Ni''	2.997(1)
Ni–O(1)	2.093(2)
Ni–O(1')	2.002(2)
Ni–O(1'')	2.050(2)
Ni–O(3''')	2.047(3)
Ni–O(4)	2.116(3)
Ni–N(1')	2.146(3)
Bond angle [°]	
O(1)–Ni–O(4)	164.46(9)
O(1')–Ni–O(3''')	165.15(10)
O(1'')–Ni–N(1')	164.38(10)
Ni–O(1)–Ni'	102.71(10)
Ni–O(1)–Ni''	92.66(9)
Ni'–O(1)–Ni''	95.39(9)

notation introduced by Williams, Decurtins and coworkers for cubanes,^[25] we code **1** as whole by Ni₄/1s₄/d₄. The symbol s indicates that the bridging atoms of pdmH[−] are supported, the number 1 designating that one arm of pdmH[−] links the bridging O atom to a terminal donor atom (the pyridyl nitrogen); the symbol d indicates that ligands bridge two metal ions across a face diagonal of the cube, the subscript 4 designating that there are four such ligands.

The arrangement of four metal ions and four bridging ligands at alternating corners of a cube is a well-known unit in inorganic chemistry.^[26] Among the most thoroughly studied members of the cubane family are {Fe₄S₄}ⁿ⁺ clusters, many of which were prepared and characterized as models for the active sites of iron–sulfur proteins.^[27] Later, following the proposal of a cubic arrangement of Mn ions and bridging monoatomic ligands for the oxygen-evolving centre (OEC) of photosystem II (PSII),^[28] several {Mn₄X₄}ⁿ⁺ complexes with X = O^{2−}, Cl[−], RO[−], ... were synthesized as models for this postulated unit.^[29] Several crystal structures of cyanobacterial PSII, which initially suggested^[30] and recently proved^[31] that the OEC contains a cubane-like {Mn₃CaO₄} cluster linked to a fourth, external Mn by a cubane oxide and a fifth oxide that is outside the cube, have inspired synthetic chemists to prepare and study Ca and Mn-containing cubane cluster units.^[4b,32] It has also been suggested^[23h,33] that cubanes offer a way to model, and so better understand, the properties of extended networks that are based on a cubane repeating unit. Finally, 3d-metal cubanes continue to attract the intense interest of scientists working in the interdisciplinary field of molecular magnetism because some of them exhibit SMM behaviour.^[6c,15c,15d,15g,15i,34]

Complex **2**·1.2EtOH crystallizes in the triclinic space group *P*-1. Its structure consists of centrosymmetric [Ni₄(O₂CMe)₆(pdmH)₂(EtOH)₂] and solvate EtOH molecules; the latter will not be further discussed. The four Ni^{II} atoms are located at four vertices of a defective dicubane, i.e. two cubanes sharing a face (Ni(2)O(1)Ni(2')O(1')) and each missing one metal vertex. The Ni^{II} centres are bridged by means of O atoms from the η³:η¹:η¹:μ₃ (3.311) pdmH[−] ligands and four η²:μ

Table 2. Selected interatomic distances and angles for complex **2**·1.2EtOHSymmetry code: (') = $-x, -y + 1, -z + 1$

Interatomic distance [Å]	
Ni(1)···Ni(1')	5.282(3)
Ni(1)···Ni(2)	3.177(1)
Ni(1)···Ni(2')	2.959(1)
Ni(2)···Ni(2')	3.130(2)
Ni(1)–O(1)	2.034(2)
Ni(1)–O(2)	2.166(2)
Ni(1)–O(3)	2.139(2)
Ni(1)–O(5)	2.033(2)
Ni(1)–O(7)	2.056(3)
Ni(1)–N(1)	1.975(3)
Ni(2)–O(1)	2.047(2)
Ni(2)–O(1')	2.041(2)
Ni(2)–O(3)	2.110(2)
Ni(2)–O(5')	2.157(2)
Ni(2)–O(8')	2.009(2)
Ni(2)–O(10)	2.040(3)
Bond angle [°]	
O(1)–Ni(1)–O(2)	155.7(1)
O(3)–Ni(1)–O(7)	170.4(1)
O(5)–Ni(1)–N(1)	168.1(1)
O(1)–Ni(2)–O(8')	171.7(1)
O(1')–Ni(2)–O(10)	171.2(1)
O(3)–Ni(2)–O(5')	167.5(1)
Ni(1)–O(1)–Ni(2)	102.2(1)
Ni(1)–O(1)–Ni(2')	93.1(1)
Ni(1)–O(3)–Ni(2)	96.8(1)
Ni(1)–O(5)–Ni(2')	89.8(1)
Ni(2)–O(1)–Ni(2')	99.9(1)

(2.20) MeCO₂[−] groups (Fig. 2). Thus, the core is {Ni₄(μ₃-OR)₂(μ-OR')₄}²⁺ (Fig. 4, bottom), where RO[−] = pdmH[−] and R'O[−] = MeCO₂[−]. Peripheral ligation is provided by four O atoms of two *syn,syn*-η¹:η¹:μ (2.11, Fig. 2) acetato ligands that bridge the Ni(1)Ni(2') and Ni(1')Ni(2) pairs, two terminal –OH oxygen atoms (O(2), O(2')) that belong to the pdmH[−] ligands and form bonds to Ni(1) and its symmetry equivalent, two pyridyl nitrogen atoms (N(1), N(1')) that are coordinated to Ni(1) and Ni(1'), and two terminal (η¹ or 1.1) EtOH molecules that are bound to Ni(2) and its symmetry equivalent. In the centrosymmetric tetranuclear molecule, two types of distorted octahedral Ni^{II} atoms can be distinguished, Ni(1) and Ni(2). The two chromophores are Ni(1)O₅N and Ni(2)O₆. The bridging Ni–O_{acetate} distances (2.109 and 2.141 Å for O(3), 2.034 and 2.155 Å for O(5)) are slightly to moderately asymmetric. The three Ni–O bonds involving the triply bridging alkoxido oxygen atom of pdmH[−] (O(1)/O(1')) are strong (2.034, 2.041, 2.047 Å).

Complex **2** can alternatively be described^[35] as containing a butterfly of Ni^{II} sites with the 'body' of the butterfly (Ni(2) and Ni(2')) bridged by two deprotonated μ₃-O atoms from the 3.311 pdmH[−] ligands; these O atoms also bridge to Ni^{II} 'wing-tip' sites (Ni(1) and Ni(1')). Each of the four edges of the closed-type butterfly is bridged by one 2.20 MeCO₂[−] group, while two opposite edges are also bridged by one 2.11 MeCO₂[−] ligand. The octahedral coordination sphere at the body sites is completed by a terminal EtOH molecule, whereas at the wing-tip sites, the coordination is completed by a pyridyl nitrogen and the –OH

Table 3. Structurally characterized clusters with nuclearities equal to or higher than 3 of the various forms of pdmH₂ and coordination modes of the ligandsAbbreviations: pdmH₂, pyridine-2,6-dimethanol; hmpH, 2-(hydroxymethyl)pyridine; LH₂, (6-hydroxymethylpyridin-2-yl)-(6-hydroxymethylpyridin-2-yl)methoxy)methanol; nmpdH₂, 2-nitro-2-methyl-1,3-propanediol; teaH₃, triethanolamine; thmeH₃, 1,1,1-tris(hydroxymethyl)ethane

Cluster ^A	Coordination modes ^{B,C}	Ref.
[Mn ^{II} ₂ Mn ^{II} (O ₂ CMe) ₂ (pdmH) ₆](ClO ₄) ₂	$\eta^2: \eta^1: \mu; \eta^3: \eta^1: \mu_3; \eta^2: \eta^1: \eta^1: \mu$	[11c], [38a]
[Mn ^{II} ₂ Mn ^{III} (N ₃) ₄ (teaH) ₂ (pdmH) ₂	$\eta^2: \eta^1: \eta^1: \mu$	[38b]
[Mn ^{II} ₇ Mn ^{III} (O ₂ CET) ₁₂ (pdm)(pdmH) ₂ (L) ₂]	$\eta^3: \eta^1: \mu_3; \eta^2: \eta^1: \mu_3$	[38c]
[Mn ^{II} ₄ Mn ^{III} O ₂ (N ₃) ₆ (thme) ₄ (pdmH) ₄]	$\eta^2: \eta^1: \eta^1: \mu$	[38b]
[Mn ^{II} ₄ Mn ^{III} O ₂ (OH) ₂ (nmpd)(pdm) ₅ (pdmH) ₅ Cl ₆]	$\eta^2: \eta^1: \eta^1: \mu; \eta^2: \eta^1: \mu; \eta^2: \eta^2: \eta^1: \mu_3$	[38d]
[Mn ^{II} ₆ Mn ^{III} Mn ^{IV} O ₁₈ (OH) ₂ (N ₃) ₁₂ (pdm) ₆ (pdmH) ₆ Cl ₂]	$\eta^3: \eta^3: \eta^1: \mu_5; \eta^3: \eta^1: \eta^1: \mu_3$	[38e], [38f]
[Mn ^{II} ₆ Mn ^{III} Mn ^{IV} O ₁₈ (OH)(OMe)(hmp) ₆ (pdm) ₆ (pdmH) ₆](N ₃) ₂ (ClO ₄) ₆	$\eta^3: \eta^3: \eta^1: \mu_5; \eta^3: \eta^1: \eta^1: \mu_3$	[38g], [38h]
[Fe ^{III} ₈ O ₃ (OMe)(pdm) ₄ (pdmH) ₄ (MeOH) ₂](ClO ₄) ₅	$\eta^3: \eta^1: \eta^1: \mu_3; \eta^3: \eta^1: \mu_3$	[11a]
[Fe ^{III} ₉ O ₄ (OH) ₂ (O ₂ CMe) ₁₀ (pdm)(pdmH) ₄](NO ₃)	$\eta^2: \eta^2: \eta^1: \mu_3; \eta^2: \eta^1: \mu$	[38i]
[Fe ^{III} ₁₈ O ₆ (OH) ₈ (pdm) ₁₀ (pdmH) ₄ (H ₂ O) ₄](ClO ₄) ₁₀	$\eta^2: \eta^2: \eta^1: \mu_3; \eta^2: \eta^1: \eta^1: \mu$	[38i]
[Fe ^{III} ₂ Y ₂ (pdmH) ₆ Cl ₄ Cl ₂]	$\eta^2: \eta^1: \eta^1: \mu; \eta^2: \eta^1: \mu$	[38j]
[Fe ^{III} ₂ Ho ₂ (pdmH) ₆ Cl ₄ Cl ₂]	$\eta^2: \eta^1: \eta^1: \mu; \eta^2: \eta^1: \mu$	[38j]
[Co ^{II} ₂ Ln ^{III} (O ₂ CBu ^t) ₆ (pdmH) ₄] ^D	$\eta^3: \eta^1: \eta^1: \mu_3; \eta^3: \eta^1: \mu_3$	[38k]
[Co ^{II} ₂ Y ^{III} (O ₂ CBu ^t) ₆ (pdmH) ₄]	$\eta^3: \eta^1: \eta^1: \mu_3; \eta^3: \eta^1: \mu_3$	[38k]
[Ni ₄ (O ₂ CMe) ₄ (pdmH) ₄] (1)	$\eta^3: \eta^1: \mu_3$	Present work
[Ni ₄ (O ₂ CMe) ₆ (pdmH) ₂ (EtOH) ₂] (2)	$\eta^3: \eta^1: \eta^1: \mu_3$	Present work
[Cu ₄ (NO ₃) ₂ (pdmH) ₄ (H ₂ O)(MeOH)](NO ₃) ₂	$\eta^2: \eta^1: \eta^1: \mu$	[13b]
[Cu ₄ ^{II} (O ₂ CMe) ₂ (pdm) ₂ (MeOH) ₂][Cu ₄ ^{II} (O ₂ CMe) ₂ (pdmH) ₄](ClO ₄) ₂	$\eta^3: \eta^1: \eta^1: \mu_3; \eta^2: \eta^1: \eta^1: \mu$	[13a]
[Cu ₄ ^{II} (O ₂ CMe) ₂ (pdmH) ₄](O ₂ CMe) ₂	$\eta^3: \eta^1: \eta^1: \mu_3$	[13a]
[Zn ₃ (salphen) ₂ (pdmH) ₂]	$\eta^2: \eta^1: \eta^1: \mu$	[38l]
[Zn ₄ (O ₂ CMe) ₄ (pdmH) ₄]	$\eta^3: \eta^1: \eta^1: \mu_3; \eta^2: \eta^1: \mu$	[38m]
[Zn ₆ (OH) ₂ (O ₂ CPh) ₈ (pdmH) ₂]	$\eta^3: \eta^1: \eta^1: \mu_3$	[13c]
[Zn ₆ (OH) ₂ (O ₂ CBu ^t) ₈ (pdmH) ₂]	$\eta^3: \eta^1: \eta^1: \mu_3$	[13c]
[Hg ₃ ^I Cl ₅ (pdmH)(pdmH ₂) ₂]	Tridentate chelating ($\eta^1: \eta^1: \eta^1$)	[38n]
[Dy ₄ (O ₂ CPh) ₂ (pdm) ₄ (pdmH) ₂ (PhCO ₂ H) ₄]	$\eta^2: \eta^1: \eta^1: \mu$	[38o]
[Yb ₄ (O ₂ CPh) ₂ (pdm) ₄ (pdmH) ₂ (PhCO ₂ H) ₂ (H ₂ O) ₂]	$\eta^2: \eta^1: \eta^1: \mu$	[38p]
[Ln ₄ (NO ₃) ₂ (pdmH) ₆ (pdmH ₂) ₂](NO ₃) ₄ ^E	$\eta^2: \eta^1: \eta^1: \mu; \eta^1: \eta^1: \eta^1$	D. I. Alexandropoulos and Th. C. Stamatatos, unpubl. data

^ASolvate molecules have been omitted.^BThe superscript of η indicates the hapticity of each donor atom, that is, the number of metal ions to which a donor atom is attached.^CThe last η refers to the pyridyl nitrogen atom.^DLn = Gd, Tb, Dy, Ho.^ELn = Tb, Dy.

oxygen of the pdmH⁻ ligand. The body and wing-tip Ni...Ni distances are 3.130 and 5.282 Å respectively.

Within the cluster, there are four strong hydrogen bonds. The donors are the coordinated -OH groups of the pdmH⁻ and EtOH ligands, and the acceptors are the uncoordinated O atoms of the 2.20 MeCO₂⁻ groups (O(2)...O(4) = 2.580 Å, O(2)-HO(2)...O(4) = 178.2°; O(10)...O(6') = 2.622 Å, O(10)-HO(10)...O(6') = 162.6°). The Ni₄ molecules in the crystal link through O-H...O hydrogen-bonding interactions to create a 2D network (Fig. 5) and π - π stacking interactions.

Tetranuclear Ni^{II} clusters with the defective dicubane unit have been reported,^[24c,35,36] but these are significantly fewer than Ni^{II} cubanes. A critical structural analysis of Ni₄ clusters with a defective dicubane core was recently provided by Coronado, Cortes and coworkers,^[36b] and by Papaefstathiou and coworkers.^[36a] It is noteworthy that this structural motif is also known for other divalent, trivalent and mixed-valence 3d metals.^[37] Complexes **1** and **2** join a family of clusters containing pdmH₂, pdmH⁻ and pdm²⁻ as ligands.^[11a,11c,13,38] As most of them were reported only recently, we felt it timely to collect the complexes with nuclearities equal to or higher than 3 in Table 3, together with the coordination modes of the ligands. It is obvious that the pdmH⁻ and pdm²⁻ groups exhibit a variety of bridging coordination modes favouring cluster formation.

It should also be mentioned that the anionic forms of pdmH₂ participate in several coordination polymers.^[11b,13a,39]

Magnetochemistry

Variable-temperature direct-current (DC) magnetic susceptibility studies were performed on powdered samples of compounds **1** and **2** in an applied field of 0.1 T. The data are plotted as $\chi_M T$ versus T in Fig. 6, where χ_M is the molar magnetic susceptibility and T is the absolute temperature.

The values of the $\chi_M T$ product at 300 K are 4.87 (**1**) and 3.60 (**2**) emu mol⁻¹ K, very close to and lower than, respectively, the 4.84 emu mol⁻¹ K value (calculated with $g = 2.2$; g is the Landé g -factor) expected for a cluster of four non-interacting Ni^{II} ($S = 1$) atoms. For **1**, the value of $\chi_M T$ remains constant in the 300–100 K range and then decreases rapidly with decreasing T to reach an almost zero value at 2 K. For **2**, $\chi_M T$ gradually decreases with decreasing T to 2.60 emu mol⁻¹ K at 100 K, and then decreases rapidly to reach an almost zero value at 2 K. The data indicate an overall antiferromagnetic behaviour, which appears stronger in **2** and an $S = 0$ ground state for both clusters.

In order to quantify the nature of the magnetic exchange within the cubane cluster **1**, theoretical expressions of χ_M as a function of T were derived and fitted to the experimental data.

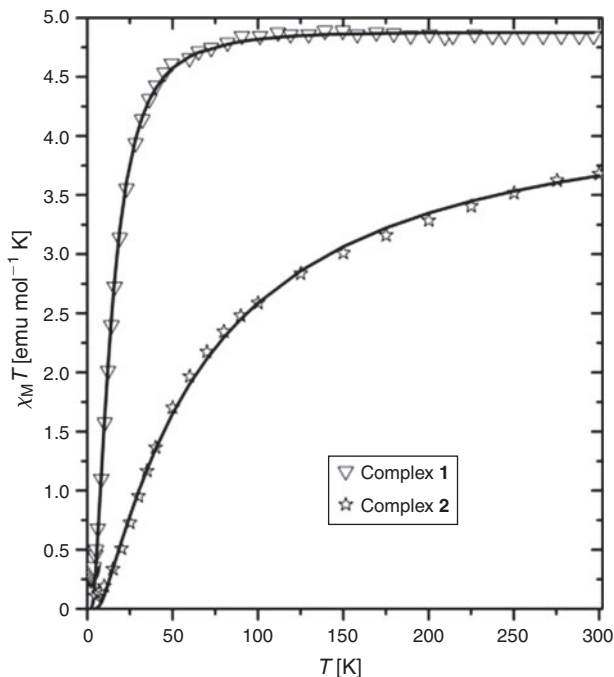


Fig. 6. $\chi_M T$ versus T plots for **1** and **2**. The solid lines are the fit of the data; see text for the fit parameters. χ_M , molar magnetic susceptibility; T , absolute temperature.

For this, a Heisenberg spin Hamiltonian (using the atomic numbering in Fig. 1), Eqn 5, was considered, where the crystallographic S_4 symmetry of the molecule was taken into account. Therefore, two types of magnetic Ni...Ni interactions were included. As an approximation, zero field splitting (ZFS) parameters, usually small in this type of systems,^[23h] were not included in the model.

$$H = -2J(S_{\text{Ni}'} \cdot S_{\text{Ni}''} + S_{\text{Ni}'} \cdot S_{\text{Ni}'''} + S_{\text{Ni}''} \cdot S_{\text{Ni}'''} + S_{\text{Ni}'''} \cdot S_{\text{Ni}''}) - 2J_1(S_{\text{Ni}'} \cdot S_{\text{Ni}''} + S_{\text{Ni}''} \cdot S_{\text{Ni}'''}) \quad (5)$$

In the above Hamiltonian, J_1 describes the interactions between the Ni^{II} atoms bridged exclusively by the μ_3 -O atoms from the pdmH⁻ ligands, while J corresponds to the exchange between Ni^{II} atoms bridged additionally by carboxylate groups. The best set of parameters are $J = +3.2(1) \text{ cm}^{-1}$, $J_1 = -6.0(1) \text{ cm}^{-1}$ and $g = 2.2$.

The most important parameter in the magnetostructural correlation of tetranuclear clusters possessing the $\{\text{Ni}_4(\mu_3\text{-OR})_4\}^{4+}$ cubane core has been reported^[23-25] to be the average Ni–O–Ni angle of a cubane face. A ferromagnetic exchange is observed for Ni–O–Ni angles lower than 99° and the positive coupling constant value increases as the angle decreases. However, Ni–O–Ni angles in the vicinity of, and larger than, 99° lead to antiferromagnetic interactions and the absolute value increases as the angle increases. The mean Ni–O–Ni angle for the four Ni₂ pairs described by J in **1** is 94.0°; thus, the coupling is predicted to be ferromagnetic, and indeed, it is ($J = +3.2(1) \text{ cm}^{-1}$). What was unexpected was the *small* value of J . The value of $+3.2(1) \text{ cm}^{-1}$ does not at all match the linear coupling constant versus Ni–O–Ni bridging angle curve established by Christou and coworkers for complexes containing the $\{\text{Ni}_4(\mu_3\text{-OR})_4\}^{4+}$ core,^[23k] the 94.0° angle would normally lead to a much larger J value. The smaller than expected value of

J (which is responsible for the $S = 0$ state) is attributed^[10b,23h,23k,25] to the presence of an additional *syn,syn* carboxylate bridge that caps each of the cube faces, magnetically characterized by J in Eqn 5, and which offers a supplementary antiferromagnetic contribution to the coupling. This situation is not without precedent. An analogous effect has previously been reported for complexes $[\text{Ni}_4(\text{OH})_2(\text{O}_2\text{CMe})_2(\text{NCS})_2(\text{pympentO})(\text{hmp})(\text{H}_2\text{O})]$,^[23a] where *pympentO*⁻ and *hmp*⁻ are the deprotonated forms of 1,5-bis[(2-pyridylmethyl)amino]pentane-3-ol and 2-(hydroxymethyl)pyridine respectively, and $[\text{Ni}_4(\text{OMe})_4(\text{O}_2\text{CMe})_2(\text{TMB})_4](\text{BPh}_4)_2$,^[40] where TMB is 2,5-dimethyl-2,5-diisocyanohexane. These complexes have two *syn,syn*- $\eta^1 : \eta^1 : \mu$ (2.11) acetates on opposite faces of the cube; in the two complexes, the exchange interaction characterizing these two faces is ferromagnetic, but in both cases the J value is much lower than that predicted on the basis of the correlation established by Christou's group.^[23k] It should be mentioned at this point that a similar explanation was used by Winpenny and coworkers^[23h] and by us^[10b] to explain the magnetic properties of the $[\text{Ni}_4(\text{O}_2\text{CBu})_4(\text{Mq})_4]$ and $[\text{Ni}_4(\text{O}_2\text{CMe})_4(\text{hmp})_4(\text{H}_2\text{O})_2]$ cubanes respectively (Mq⁻ is the monoanion of 8-hydroxyquinaldine). In both cases, according to the established magnetostructural criteria,^[23k] the coupling characterizing the faces capped by the carboxylates was predicted to be ferromagnetic, but the analysis of the data revealed antiferromagnetic coupling; it seems that the additional pathway for antiferromagnetic exchange provided by the carboxylate groups is strong enough to overcome the ferromagnetic exchange arising from the small Ni–O–Ni angles. In complete agreement with the above explanation, the cubane complexes $[\text{Ni}_4\text{X}_4(\text{hmp})_4(\text{ROH})_4]$,^[15c,15g,15j] which do not contain additional bridging ligands, are all characterized by ferromagnetic exchange interactions and an $S = 4$ ground state. The Ni–O–Ni value of 102.7° (Table 1) for the remaining two faces of the cube in **1**, i.e. the faces NiO(1)Ni'O(1') and Ni''O(1'')Ni'''O(1''') (Fig. 1) not capped by acetates, justifies the antiferromagnetic value of J_1 (-6.0 cm^{-1}).^[23h,23k]

The best set of parameters obtained taking into account the molecular structure and symmetry of **2**, and using the analytical equation derived from the spin-Hamiltonian of Eqn 6, are $J = -14.0(1) \text{ cm}^{-1}$, $J_1 = J_2 = -10.0(1) \text{ cm}^{-1}$ and $g = 2.2$.

$$H = -2J(S_{\text{Ni}1} \cdot S_{\text{Ni}2'} + S_{\text{Ni}1'} \cdot S_{\text{Ni}2}) - 2J_1(S_{\text{Ni}2} \cdot S_{\text{Ni}2'}) - 2J_2(S_{\text{Ni}1} \cdot S_{\text{Ni}2} + S_{\text{Ni}1'} \cdot S_{\text{Ni}2'}) \quad (6)$$

The double oxygen bridge that mediates the J_1 and J_2 interactions (-10 cm^{-1}) has a mean angle of 99.9° and 99.5°, angles that are known to lead to weak antiferromagnetic interactions.^[41] Although the two Ni–O–Ni angles associated with J are small (89.8, 93.1°), the third *syn,syn*- $\eta^1 : \eta^1 : \mu$ MeCO₂⁻ bridge seems to be responsible^[23k] for the overall antiferromagnetic coupling that characterizes the Ni(1)...Ni(2') and Ni(1')...Ni(2) exchange interactions. Most of the previously characterized defective dicubane Ni₄ clusters possessing *exclusively* monoatomic oxygen bridges, i.e. the $\{\text{Ni}_4(\mu_3\text{-OR})_2(\mu\text{-OR}')_4\}^{2+}$ core, are characterized by ferromagnetic exchange interactions and an $S = 4$ ground state.^[36e,36f,36j] Clusters **2** and $[\text{Ni}_4(\text{O}_2\text{CMe})_4(\text{dpk}\cdot\text{OH})_4]$,^[24c] where dpk·OH⁻ is the monoanionic *gem*-diol form of di-2-pyridyl ketone, have a diamagnetic ground state; in the latter, competing ferromagnetic and antiferromagnetic interactions are observed as a result of two types of Ni–O–Ni angle values (94.8–96.8°, 100.6–103.7°).

Conclusions and Perspectives

We believe that the chemical messages of this work are important: (1) the reported complexes are the first Ni^{II} coordination clusters containing any form of pyridine-2,6-dimethanol as ligand. The bi- or tridentate monoanions of the ligand can support cluster chemistry when coupled with appropriate ancillary groups, such as carboxylate ligands. (2) Compounds **1** and **2** have the same nuclearity and the same bridging ligands, but their core topology depends exclusively on the reaction solvent. Our preliminary conclusion was that the compound formula determines the topology. For example, the presence of four pdmH⁻ ligands (per four Ni^{II} sites) can provide the four μ_3 -O atoms that are required for the formation of a cubane, whereas two pdmH⁻ ligands (per four Ni^{II} sites) favour the defective dicubane topology as this requires only two μ_3 -O atoms. However, this initial conclusion was ruled out later because we discovered that the Ni(O₂CMe)₂·4H₂O : pdmH₂ reaction ratio does not affect product identity in either solvent. The dependence of product identity on the solvent raises the possibility that change of other synthetic parameters (e.g. pH, presence of bulky counterions, use of other solvents, solvothermal conditions) can divert this chemistry into new reaction pathways. (3) The two clusters can be interconverted, leaving open the possibility of their use as starting materials for further reactivity chemistry. Equally important is the magnetochemical lesson of the research presented herein: the well-established Ni–O–Ni magnetostructural correlation in Ni^{II} cluster chemistry should be used with caution; the expected magnetic-exchange interaction in Ni^{II}–(μ -OR)₂–Ni^{II} units may be strongly modified in the presence of an additional bridge, e.g. a *syn,syn* carboxylate group. Our belief is that we have only scratched the surface of Ni^{II} cluster chemistry based on the pyridine-2,6-dimethanol ligand; indeed, ongoing studies show that the reactions of this metal ion (and other divalent 3d metals, such as Co^{II}) with pdmH₂ in the presence of various ancillary ligands (e.g. carboxylates other than acetate, NO₃⁻, N₃⁻, NCO⁻, N(CN)₂⁻, SO₄²⁻) deliver clusters with unusual structural types and interesting properties. We are also pursuing reactions to obtain Ni^{II} (and Co^{II}) clusters with the doubly deprotonated form of the ligand.

Experimental

Materials and Methods

All manipulations were performed under aerobic conditions using reagents and solvents as received. Elemental analyses (C, H, N) were performed by the in-house facilities of the University of Patras (Greece). IR spectra (4000–400 cm⁻¹) were recorded using a Perkin–Elmer 16PC Fourier-transform (FT)-IR spectrometer with samples prepared as KBr pellets. Variable-temperature DC magnetic studies for **1** and **2** were performed using a cryogenic S600 SQUID magnetometer operating at 0.1 T; the polycrystalline powders were pressed in a pellet to prevent preferential crystallite orientation with the magnetic field. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal's constants. The data were fitted using the *MAGPACK* program,^[42] employed with the non-linear least-squares curve-fitting program *DSTEPIT*.^[43]

Syntheses of **1** and **2**

[Ni₄(O₂CMe)₄(pdmH)₄]·MeCN (**1**·MeCN)

To a stirred pale-green slurry of Ni(O₂CMe)₂·4H₂O (0.124 g, 0.50 mmol) in MeCN (25 mL) was added solid pdmH₂ (0.070 g,

0.50 mmol). The reaction mixture was refluxed for 30 min. The resulting bright-green solution was filtered and solvent allowed to slowly evaporate at room temperature. After 4 days, green crystals of the product formed in 70% yield. The crystals were collected by filtration, washed with Et₂O (2 × 3 mL) and dried in air (yield ~70%). The air-dried sample was analysed as MeCN-free. Anal. calc. for C₃₆H₄₄Ni₄N₄O₁₆: C 42.24, H 4.34, N 5.47. Found: C 42.34, H 4.42, N 5.56%. ν_{\max} (KBr)/cm⁻¹ 3248mb, 2928m, 2850w, 1578vs, 1450s, 1420m, 1342m, 1238w, 1158w, 1034m, 786m, 660m, 426m.

[Ni₄(O₂CMe)₆(pdmH)₂(EtOH)₂]·1.2EtOH (**2**·1.2EtOH)

To a stirred pale-green solution of Ni(O₂CMe)₂·4H₂O (0.124 g, 0.50 mmol) in EtOH (25 mL) was added pdmH₂ (0.070 g, 0.50 mmol). The solid soon dissolved, and the resulting green solution was refluxed for 30 min and the solvent allowed to slowly evaporate at room temperature. After 3 days, green crystals of the product formed; these were washed with cold EtOH (1 mL) and Et₂O (2 × 5 mL), and dried in a vacuum desiccator over silica gel (yield ~45% based on the Ni^{II} available). The vacuum-dried sample was analysed as EtOH-free. Anal. calc. for C₃₀H₄₆Ni₄N₂O₁₈: C 37.63, H 4.85, N 2.93. Found: C 37.57, H 4.72, N 3.07%. ν_{\max} (KBr)/cm⁻¹ 3444s, 3255mb, 2927m, 2858w, 1606vs, 1567s, 1462m, 1447m, 1423vs, 1366m, 1343m, 1044m, 787m, 666m, 428m.

Compound Transformations

Transformation of **1** to **2**

Method A. A stirred pale-green slurry of [Ni₄(O₂CMe)₄(pdmH)₄] (**1**) (0.256 g, 0.25 mmol) in EtOH (25 mL) was refluxed overnight to give a green solution that was filtered to remove a tiny amount of green precipitate. The filtrate was allowed to slowly evaporate at room temperature. After 2 days, green crystals of the product formed, which were collected by filtration, washed with cold EtOH (1 mL) and Et₂O (2 × 3 mL), and dried in a vacuum desiccator over silica gel (yield 20% based on half the amount of Ni^{II} available). The vacuum-dried solid was analysed as [Ni₄(O₂CMe)₆(pdmH)₂(EtOH)₂] (**2**). Anal. calc for C₃₀H₄₆Ni₄N₂O₁₈: C 37.63, H 4.85, N 2.93. Found: C 37.41, H 4.93, N 2.85%. The IR spectrum of the product was identical to that of the authentic material prepared by the direct reaction of Ni(O₂CMe)₂·4H₂O and pdmH₂ in EtOH.

Method B. To a stirred pale-green slurry of [Ni₄(O₂CMe)₄(pdmH)₄] (**1**) (0.256 g, 0.25 mmol) in EtOH (20 mL) was added glacial MeCO₂H (0.030 mL, 0.50 mmol). The reaction mixture was refluxed for 30 min and the resulting green solution was allowed to slowly evaporate at room temperature. After 3 days, green crystals of the product formed, which were collected by filtration, washed with cold EtOH (1 mL) and Et₂O (2 × 3 mL), and dried in a vacuum desiccator over silica gel (yield ~60% based on the Ni^{II} available). The vacuum-dried solid was analysed as [Ni₄(O₂CMe)₆(pdmH)₂(EtOH)₂] (**2**). Anal. calc. for C₃₀H₄₆Ni₄N₂O₁₈: C 37.63, H 4.85, N 2.93. Found: C 37.85, H 4.88, N 3.01%. The IR spectrum of the product was identical to that of the authentic material prepared by the direct reaction of Ni(O₂CMe)₂·4H₂O and pdmH₂ in EtOH.

Transformation of **2** to **1**

Method A. A stirred pale-green slurry of [Ni₄(O₂CMe)₆(pdmH)₂(EtOH)₂] (**2**) (0.239 g, 0.25 mmol) in MeCN (30 mL) was refluxed overnight to give a green solution that was filtered

Table 4. Crystallographic data and structure refinement summary for complexes **1**·MeCN and **2**·1.2EtOH

Parameter	1·MeCN	2·1.2EtOH
Formula ^A	C ₃₈ H ₄₇ Ni ₄ N ₅ O ₁₆	C _{32.4} H _{53.2} Ni ₄ N ₂ O _{19.2}
Formula weight	1064.65	1012.81
Crystal system	Tetragonal	Triclinic
Space group	<i>I</i> 4 ₁ / <i>acd</i>	<i>P</i> -1
<i>a</i> [Å]	16.411(6)	11.707(4)
<i>b</i> [Å]	16.411(6)	11.950(4)
<i>c</i> [Å]	33.876(12)	9.185(3)
α [°]	90	75.966(1)
β [°]	90	84.205(10)
γ [°]	90	65.568(9)
<i>V</i> [Å ³]	9124(6)	1134.9(6)
<i>Z</i>	8	1
<i>T</i> [K]	298	298
Radiation, λ [Å]	Mo Ka, 0.71073	Mo Ka, 0.71073
<i>D</i> _(calcd) [g cm ⁻³]	1.550	1.482
μ [mm ⁻¹]	1.698	1.705
Refl. collected	3876	4025
Refl. unique (<i>R</i> _{int})	1993 (0.0194)	3771 (0.0194)
Refl. with <i>I</i> > 2 σ (<i>I</i>)	1731	3337
<i>R</i> ₁ ^{B,C}	0.0367	0.0460
<i>wR</i> ₂ ^{C,D}	0.1045	0.1240
GoF on <i>F</i> ²	1.157	1.067

^AIncluding solvate molecules.

^B $R_1 = \Sigma(|F_o| - |F_c|) / \Sigma(|F_o|)$.

^CFor observed [*I* > 2 σ (*I*)] reflections.

^D $wR_2 = [\Sigma[w(F_o)^2 - |F_c|^2] / \Sigma[w(F_o)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_o^2]/3$.

to remove a tiny amount of green powder. The filtrate was allowed to slowly evaporate at room temperature. After 3 days, green crystals of the product formed, which were collected by filtration, washed with cold Et₂O (2 × 2 mL), and dried in air (yield ~25 % based on double the amount of pdmH₂ available). The air-dried solid was analysed as [Ni₄(O₂CMe)₄(pdmH)₄] (**1**). Anal. calc. for C₃₆H₄₄Ni₄N₄O₁₆: C 42.24, H 4.34, N 5.47. Found: C 41.99, H 4.28, N 5.42 %. The IR spectrum of the product was identical to that of the authentic material prepared by the direct reaction of Ni(O₂CMe)₂·4H₂O and pdmH₂ in MeCN.

Method B. To a stirred pale-green slurry of [Ni₄(O₂CMe)₆(pdmH)₂(EtOH)₂] (**2**) (0.239 g, 0.25 mmol) in MeCN (25 mL) was added solid pdmH₂ (0.070 g, 0.50 mmol). The ligand soon dissolved and the reaction mixture was refluxed for 30 min. The resulting green solution was allowed to slowly evaporate at room temperature. After 3 days, green crystals of the product formed, which were collected by filtration, washed with Et₂O (2 × 3 mL), and dried in air (yield ~75 % based on the Ni^{II} available). The air-dried solid was analysed as [Ni₄(O₂CMe)₄(pdmH)₄] (**1**). Anal. calc. for C₃₆H₄₄Ni₄N₄O₁₆: C 42.24, H 4.34, N 5.47. Found: C 42.43, H 4.19, N 5.60 %. The IR spectrum of the product was identical to that of the authentic material prepared by the direct reaction of Ni(O₂CMe)₂·4H₂O and pdmH₂ in MeCN.

X-Ray Crystallography

Green prismatic crystals of **1**·MeCN (0.13 × 0.35 × 0.45 mm) and **2**·1.2EtOH (0.26 × 0.30 × 0.40 mm) were mounted in air. Diffraction data were collected on a Crystal Logic dual

goniometer diffractometer using graphite monochromated Mo K α radiation. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centred reflections in the range 11 < 2 θ < 23°. Intensity data were recorded using a θ -2 θ scan. Three standard reflections monitored every 97 reflections showed less than 3 % variation and no decay. Lorenz-polarization and Ψ -scan absorption corrections were applied using Crystal Logic software. The structures were solved by direct methods using *SHELXS-97*^[44] and refined by full-matrix least-squares techniques on *F*² with *SHELXL-97*.^[45] Important crystallographic data together with refinement details for the complexes reported in this work are summarized in Table 4. Further crystallographic details for **1**·MeCN: 2 θ _{max} = 50°, 170 parameters refined, (Δ/σ)_{max} = 0.000, ($\Delta\rho$)_{max}/_{min} = 0.573/−0.280 e Å⁻³, *R*₁/*wR*₂ (for all data) = 0.0434/0.1087. Further crystallographic details for **2**·1.2EtOH: 2 θ _{max} = 49°, 299 parameters refined, (Δ/σ)_{max} = 0.003, ($\Delta\rho$)_{max}/_{min} = 1.112/−0.679 e Å⁻³, *R*₁/*wR*₂ (for all data) = 0.0506/0.1294. Hydrogen atoms were introduced at calculated positions as riding on their respective bonded atoms. Hydrogen atoms for the solvate molecules in **1** were not included in the refinement. All non-H atoms were refined anisotropically. The O atom of the solvate EtOH in **2**·1.2EtOH was found disordered over two orientations. The methyl carbon of the coordinated EtOH was also found disordered over two positions. CCDC-825651 and CCDC-825652 contain the supplementary crystallographic data for complexes **1**·MeCN and **2**·1.2EtOH. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, at www.ccdc.cam.ac.uk/data_request/cif. Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk.

Supplementary Material

Cifs and Checkcifs for the two structures presented in the article are available on the Journal's website.

Acknowledgements

This research was co-financed by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program ‘Education and Lifelong Learning’ of the National Strategic Reference Framework (NSRF) – Research Funding Program ‘Heracleitus II. Investing in knowledge society through the European Social Fund’.

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