

A tetranuclear complex from the employment of pyridine-2,6-dimethanol in copper(II) nitrate chemistry: Synthetic, structural and magnetic studies

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Dedicated to Dr. Aris Terzis on the occasion of his retirement and for his enormous contribution to the advancement of inorganic chemistry in Greece through X-ray crystallography.

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ABSTRACT

The use of pyridine-2,6-dimethanol (pdmH₂) in copper(II) nitrate chemistry is reported. The reaction of Cu(NO₃)₂·3H₂O with one equivalent of pdmH₂ in MeCN affords the known mononuclear complex [Cu(pdmH₂)₂](NO₃)₂ (**1**) in high-yield. The reaction of **1** and NaOMe in an 1:1 ratio, as well as the reaction between Cu(NO₃)₂·3H₂O, pdmH₂ and NaOMe in an 1:1:1 ratio, in MeOH gives the tetranuclear complex [Cu₄(NO₃)₂(pdmH)₄(H₂O)(MeOH)](NO₃)₂ (**2**) in moderate yields. The cation of **2** possesses a slightly distorted tetrahedral Cu₄ topology with a [Cu₄(μ₂-OR)₄]⁴⁺ core. The pdmH⁻ ions behave as η¹:η¹:η²:μ₂ ligands. Strong intramolecular hydrogen bonds and π–π stacking interactions provide thermodynamic stability on compound **2**. Variable-temperature, solid-state dc magnetic studies were carried out on complex **2** in the 2.0–300 K range. The data indicate predominant antiferromagnetic exchange interactions and a resulting *S* = 0 ground state, which is expected for a solely, μ₂-alkoxide-bridged system with obtuse Cu–O–Cu bond angles that magnetically behaves as a Cu₄ ring. A simplified 1 – *J* model was found to be adequate to describe the variable-temperature dc susceptibility data. The data were fitted to the appropriate equation derived from the Hamiltonian $H = -J_1(S_1 \cdot S_2 + S_2 \cdot S_4 + S_3 \cdot S_4 + S_1 \cdot S_3)$, giving the parameters $J_1 = -99.5 \text{ cm}^{-1}$ and $g = 2.11(4)$. The combined work demonstrates the ligating flexibility of the pdmH₂ chelate and its usefulness in the synthesis of oligo- and polynuclear Cu^{II}_{*x*} clusters with interesting structural and magnetic properties, without requiring the co-presence of carboxylate ligands.

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1. Introduction

The last two decades have witnessed an explosive growth in the interest of polynuclear complexes (clusters) of 3d-metals at moderate oxidation states with primarily oxygen- and/or nitrogen-based ligation [1]. Among the diverse reasons for this are (i) the aesthetically pleasing structures that many such molecular clusters possess [2], (ii) the search for various nuclearity oxide-bridged metal clusters to model M_{*x*} sites in biomolecules [3], and (iii) the discovery of compounds with interesting magnetic properties, such as single-molecule magnetism (SMM) behaviours [4]. The latter are molecules with both a large ground state spin (*S*) and a significant easy-axis magnetic anisotropy, as reflected in a negative zero-field splitting parameter (*D*).

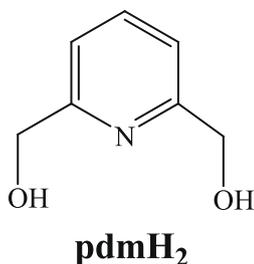
The future health of the field of 3d-metal clusters, and the chances of discovering high-spin molecules and/or new SMMs will

both benefit from the continuing development of new synthetic procedures to high-nuclearity species. There are now several empirically established approaches to a variety of clusters [5]. In Mn and Fe chemistry, for example, alcoholysis has proven to be a very useful method for obtaining both oxo- and hydroxo-containing complexes [2a,6]. Another fertile approach is the investigation of new reaction systems using appropriate chelating organic ligands, such as those containing alkoxide [5b] or oximate [7] functionalities since these are good bridging groups that can foster formation of polynuclear products. Indeed, alkoxide-based ligands such as pyridyl alcohols [8], diols [9] and triols [10], and oximates such as 2-pyridyl oximes [7b,11], R-substituted salicylaldoximes [12] and dioximes [13], have yielded a number of 3d-metal clusters with various structural motifs and interesting magnetic properties.

A modern synthetic trend is the employment of two or even three ligands in the reaction systems (combination of ligands or "ligand blends"). The loss of a degree of the synthetic control [5] is more than compensated for by the vast diversity of structural types using the combination of ligands. Carboxylates (RCO₂⁻) and/or pseudohalides (i.e., N₃⁻, OCN⁻) are excellent ancillary bridging groups in 3d-metal chemistry when they are combined

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Scheme 1. Structural formula and abbreviation of pyridine-2,6-dimethanol.

with suitable chelates (generally denoted as “L”) [14]. Thus, we and others have been exploring various such binary (L/RCO_2^- or L/N_3^-) and ternary ($L/RCO_2^-/N_3^-$) reaction schemes as potentially new routes to high-nuclearity molecular species with unprecedented structural motifs.

In particular, some of our current efforts are focused on copper(II) chemistry and, for example, we have recently reported Cu_4^{II} and 1D (Cu_4^{II})_n and 2D (Cu_2^{II})_n cluster and coordination polymers, respectively, by using the di-2-pyridyl ketone [(py)₂CO]/PhCO₂⁻/N₃⁻ ‘ligand blend’ [15]. Across this line, the initial employment of the pyridyl alkoxide ligand pyridine-2,6-dimethanol (pdmH₂, Scheme 1) in $Cu^{II}/MeCO_2^-$ chemistry has provided access to a compound consisting of cocrystallized Cu_3^{II} and Cu_4^{II} clusters, the individual Cu_4^{II} component of the latter “mixed”-species through a designed synthesis, and a unique 1D (Cu_5^{II})_n coordination polymer [16]. Despite its rather extensive use in trivalent 3d-metal cluster chemistry [8a,b,17], there has been only very limited use of pdmH₂ in Cu^{II} chemistry (and generally in the divalent 3d-metal chemistry), and only one dinuclear [18] and few mononuclear [18] complexes were further reported.

As an extension of the work with pdmH₂, we have now asked what kind of products might result from the use of this ligand in Cu^{II} non-carboxylate chemistry. Since the RCO_2^- ions are structure-determining components in the [Cu_3].[Cu_4], Cu_4 and (Cu_5)_n complexes [16], we anticipated that the absence of RCO_2^- from the reactions would give distinctly different products, and we have therefore explored this possibility. In the present work, we have explored the reactions between pdmH₂ and a Cu^{II} non-carboxylate starting material, namely copper(II) nitrate, under basic conditions. This has successfully led to the known [18] mononuclear Cu^{II} compound with a Jahn–Teller distorted octahedral geometry and a new Cu_4^{II} cluster possessing a distorted tetrahedral metal arrangement; the latter was prepared by using both the “metal complexes as ligands” strategy [19] and “one-pot” procedures. The synthesis, structure and magnetochemical characterization of the tetranuclear compound are described in this paper.

2. Experimental

2.1. General and physical measurements

All manipulations were performed under aerobic conditions using materials (reagent grade) and solvents as received.

Microanalyses (C, H, N) were performed by the University of Ioannina (Greece) Microanalytical Laboratory using an EA 1108 Carlo Erba analyser. IR spectra (4000–450 cm^{-1}) were recorded on Perkin–Elmer 16 PC and Nicolet 520 FTIR spectrometers with samples prepared as KBr pellets, and as Nujol and hexachlorobutadiene mulls between CsI discs. Variable-temperature magnetic studies for complex **2** were performed using a Quantum Design SQUID magnetometer at the Magnetochemistry Service of the University of Barcelona. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal’s constants.

2.2. Compound preparation

2.2.1. [$Cu(pdmH_2)_2$](NO₃)₂ (**1**)

Solid pdmH₂ (0.28 g, 2.00 mmol) was added to a pale blue solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.48 g, 2.00 mmol) in MeCN (30 mL). The solid soon dissolved to give a blue solution. The solution was stirred for 30 min, filtered and the filtrate was layered with Et₂O (60 mL). After 6 days, X-ray quality, blue prismatic crystals of **1** were collected by filtration, washed with MeCN (2 × 5 mL) and Et₂O (2 × 5 mL), and dried in air. Yield: 80% (based on the ligand). Anal. Calc. for $C_{14}H_{18}CuN_4O_{10}$: C, 36.10; H, 3.89; N, 12.03. Found: C, 36.21; H, 3.94; N, 11.95%. Selected IR data (KBr pellet, cm^{-1}): 3220mb, 2820m, 1612s, 1580m, 1476m, 1380vs, 1292s, 1232m, 1164m, 1102w, 1024vs, 828m, 798s, 660m, 622m.

2.2.2. [$Cu_4(NO_3)_2(pdmH)_4(H_2O)(MeOH)$](NO₃)₂ · H₂O · MeOH (**2** · H₂O · MeOH)

Method A. To a pale blue solution of **1** (0.47 g, 1.00 mmol) in MeOH (30 mL) was added solid NaOMe (0.05 g, 1.00 mmol). The solid soon dissolved to give a pale green solution. The solution was stirred for 40 min, during which time no further colour change occurred. The resulting solution was filtered and the filtrate was layered with Et₂O/*n*-hexane (1:1 v/v, 60 mL). After 10 days, pale green prismatic crystals of **2**·H₂O·MeOH were collected by filtration, washed with cold MeOH (2 × 2 mL) and Et₂O (2 × 5 mL), and dried in air. Yield: 40%. The air-dried sample analyzed as **2**·H₂O. Anal. Calc. for $C_{29}H_{40}Cu_4N_8O_{23}$: C, 31.02; H, 3.59; N, 9.98. Found: C, 31.13; H, 3.62; N, 9.85%. Selected IR data (KBr pellet, cm^{-1}): 3428mb, 3074sb, 2836m, 2360m, 1610s, 1586m, 1452vs, 1383vsb, 1317s, 1224m, 1162m, 1040vs, 826m, 790m, 696m, 634w, 574m, 432w.

Method B. To a stirred, colourless solution of pdmH₂ (0.28 g, 2.00 mmol) and NaOMe (0.11 g, 2.00 mmol) in MeOH (30 mL) was added solid $Cu(NO_3)_2 \cdot 3H_2O$ (0.48 g, 2.00 mmol). The resulting pale green solution was stirred for 40 min, filtered and the filtrate was layered with Et₂O/*n*-hexane (1:1 v/v, 60 mL). After 7 days, pale green prismatic crystals of **2**·H₂O·MeOH were collected by filtration, washed with cold MeOH (2 × 2 mL) and Et₂O (2 × 5 mL), and dried in air. Yield: 70%. The IR spectrum of the product was identical with that of the authentic material prepared by Method A. The purity of the sample prepared from this method was also confirmed by microanalytical data.

2.3. Single-crystal X-ray crystallography

The crystallographic data and structure refinement details for the two complexes are summarized in Table 1. It should be mentioned at this point that the crystal structure of **1** was reported five years ago [18]. Since the X-ray analysis by our group has led to a better quality structure due to the better quality of crystals [e.g., the reported R_1 ($I > 2\sigma(I)$) is 0.0564 [18], while our solution leads to 0.0286], we have included data for this mononuclear compound in Tables 1 and 2, and we briefly discuss its structure in the text of the present paper (vide infra). A selected crystal of **1** (0.50 × 0.40 × 0.35 mm) was mounted in air, whereas a selected crystal of **2**·H₂O·MeOH (0.30 × 0.20 × 0.15 mm) was mounted in capillary filled with drops of mother liquor. Diffraction measurements for **1** and **2**·H₂O·MeOH were made on a Crystal Logic Dual Goniometer diffractometer using graphite-monochromated Mo radiation. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range $11^\circ < 2\theta < 23^\circ$. Intensity data were recorded using a θ – 2θ scan to a maximum 2θ value of 50° . Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization corrections were applied using Crystal Logic software. Both structures were solved by direct

Table 1
Crystallographic data for complexes **1** and **2** · H₂O · MeOH.

Parameter	1	2 · H ₂ O · MeOH
Formula	C ₁₄ H ₁₈ CuN ₄ O ₁₀	C ₃₀ H ₄₄ Cu ₄ N ₈ O ₂₄
Formula weight	465.86	1154.89
Crystal system	monoclinic	monoclinic
Space group	C2/c	P2 ₁ /n
a (Å)	13.931(5)	10.132(3)
b (Å)	9.044(3)	16.605(5)
c (Å)	15.031(5)	25.813(7)
α (°)	90	90
β (°)	100.72(1)	97.33(1)
γ (°)	90	90
V (Å ³)	1860.7(11)	4307(2)
Z	4	4
ρ _{calc} (g cm ⁻³)	1.663	1.781
Radiation, λ (Å), Mo Kα	0.71073	0.71073
T (K)	298	298
μ (mm ⁻¹)	1.237	2.046
Data collected/unique (R _{int})	1702/1635 (0.0240)	8030/7570 (0.0552)
Data with I > 2σ(I)	1542	6785
R ₁ (I > 2σ(I)) ^a	0.0286	0.0431
wR ₂ (I > 2σ(I)) ^b	0.0749	0.1145

$$^a R_1 = \sum(|F_o| - |F_c|) / \sum(|F_o|)$$

$$^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

Table 2
Selected bond lengths (Å) and angles (°) for complex **1**.^a

Parameter	Parameter		
Cu(1)–O(1)	2.163(2)	Cu(1)–N(1)	1.936(2)
Cu(1)–O(2)	2.192(2)		
O(1)–Cu(1)–O(2)	156.8(6)	O(1)–Cu(1)–N(1')	97.5(7)
N(1)–Cu(1)–N(1')	174.3(1)	O(2)–Cu(1)–O(2')	91.9(1)
O(1)–Cu(1)–O(1')	104.6(1)	O(2)–Cu(1)–N(1)	79.2(7)
O(1)–Cu(1)–O(2')	86.1(8)	O(2)–Cu(1)–N(1')	104.9(7)
O(1)–Cu(1)–N(1)	79.0(7)		

^aPrimed atoms are related to the unprimed ones by the symmetry operation $-x, y, -z + 1/2$.

methods using SHELXS-97 [20a] and refined on F² by full-matrix least-squares techniques with SHELXL-97 [20b]. All H atoms were located by Fourier difference maps and refined isotropically. All non-H atoms were refined anisotropically.

3. Results and discussion

3.1. Brief synthetic comments and IR spectra

Many synthetic procedures [5,10,14a] to polynuclear 3d-metal clusters rely on the reactions of carboxylate starting materials such as M(O₂CR)₂ (R = various) with a potentially chelating/bridging ligand. This route was also known from our previous work to yield magnetically and structurally interesting Cu^{II} complexes upon reaction with pdmH₂ [16]. In the present study we have investigated the reactions with a simple Cu^{II} source, i.e. Cu(NO₃)₂·3H₂O, in the absence of carboxylate groups.

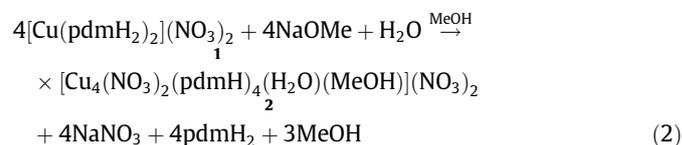
Various reactions have been systematically explored with differing reagent ratios, reaction solvents, and other conditions. The reaction of Cu(NO₃)₂·3H₂O with pdmH₂ in a 1:1 molar ratio in MeCN gave a blue solution and the subsequent isolation of well-formed blue crystals of the known complex [18] [Cu(pdmH₂)₂](NO₃)₂ (**1**) in excellent yield (~80%). The formation of **1** is summarized in Eq. (1). The “wrong” reaction ratio employed for the preparation of the complex, compared to the stoichiometric ratio (1:2) required by Eq. (1), obviously did not prove detrimental to the formation of the product. The “correct” stoichiometric ratio,

i.e. Cu^{II}:pdmH₂ = 1:2, was also employed and led to the pure compound in an excellent yield (>80%). Complex **1** was isolated from Weber's group [18] in EtOH/H₂O. Since (i) we have prepared this complex in MeCN and (ii) we have used it as starting material, we give its detailed preparation in Section 2 (Experimental) of this paper.

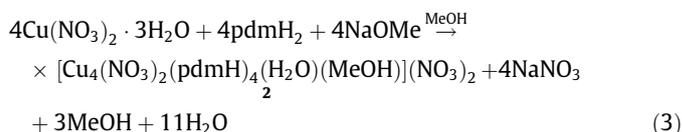


In an attempt to obtain higher nuclearity Cu^{II} products, several reactions were performed with higher Cu^{II}:pdmH₂ ratios, up to 4:1. However, complex **1** was still the only isolable product, in comparable (1.5:1 ratio) or lower (3–4:1 ratio) yields. Complex **1** was also obtained when the reaction was performed in MeOH, EtOH [18] or MeNO₂, but in much lower yields (~20–35%), whereas no significant reaction was observed when the solvent was CH₂Cl₂ or CHCl₃.

Since we could not easily divert the Cu^{II}/pdmH₂ reaction system to higher nuclearity products, we instead decided to investigate reactions of pre-isolated **1**, i.e., we suspected that this mononuclear Cu^{II} compound could act as “ligand” (the so-named “metal complexes as ligands strategy” [19,21]). Its insolubility in many common solvents limited our choices, and we thus employed MeOH in which **1** is very soluble. Given the neutral form of pdmH₂ in **1**, we targeted its deprotonation by reaction of **1** with 1–3 equiv. of base, either NEt₃ or NaOMe. Such reactions with NEt₃ gave insoluble amorphous powders that perhaps were polymeric; these products were not further characterized. However, when NaOMe was reacted with one equivalent of **1** in MeOH (Method A of Section 2) a pale green solution was obtained which led to subsequent isolation of well-formed pale green crystals of [Cu₄(NO₃)₂(pdmH)₄(H₂O)(MeOH)](NO₃)₂ · H₂O · MeOH (**2** · H₂O · MeOH) in good yield (~40%) upon layering of the reaction solution with Et₂O. Its formation is summarized in Eq. (2).



Once the identity of **2** had been established, we also sought and devised a convenient preparation of **2** in MeOH involving the *in situ* deprotonation of pdmH₂ (Method B of Section 2). This was the reaction between Cu(NO₃)₂ · 3H₂O, pdmH₂ and NaOMe in a 1:1:1 ratio in MeOH, which gave **2** in high-yield (~70%) upon layering of the reaction solution with precipitation solvents; the reaction is summarized in Eq. (3).



Note that prolonged solvent evaporation should be avoided because the crystals of the product are contaminated with NaNO₃, requiring copious washing with MeOH to obtain an analytically pure sample. An increase in the NaOMe:pdmH₂ ratio up to 3:1 gave comparable (or slightly decreased) yields of complex **2** rather than a higher nuclearity product resulting from complete deprotonation of pdmH₂ groups. Further increases in the amount of NaOMe led to insoluble amorphous precipitates that may be polymers formed from this further deprotonation.

The IR spectrum of a vacuum-dried sample of complex **1**, arising from a KBr pellet, exhibits a medium intensity band at 3220 cm⁻¹, assignable to ν(OH)_{pdmH₂} [22]. The broadness and relatively low frequency of this band are both indicative of strong hydrogen-bonding. Several bands appear in the 1610–1383 cm⁻¹ range in

the spectra of both **1** and **2**. These are assigned to contributions from the stretching vibrations of the aromatic ring, which overlap with stretches of the nitrate bands; they, thus, do not represent pure vibrations and render exact assignments difficult. The presence of ionic NO_3^- in **1** (established by crystallography) follows from the spectrum of this compound through the appearance of the $\nu_3(E')$ [$\nu_d(\text{NO})$] mode of the D_{3h} ionic nitrate at $\sim 1380\text{ cm}^{-1}$ [23]. The nitrate vibrations in the mull and KBr spectra of **2** are indicative of the simultaneous presence of coordinated and ionic nitrates (also established by crystallography). The bands at ~ 1452 and $\sim 1317\text{ cm}^{-1}$ may be assigned to the $\nu_5(B_2)$ and $\nu_1(A_1)$ stretching modes (under C_{2v} symmetry), respectively, of the nitrate ligands [23]; their separation is small ($\sim 135\text{ cm}^{-1}$) in accordance with the monodentate character of two nitrate groups [23]. It should be mentioned at this point that the highest-frequency NO stretching mode belongs to the A_1 species in complexes containing bidentate and to the B_2 species in complexes containing monodentate nitrate ligands [23]. As expected, the strong and broad band at $\sim 1383\text{ cm}^{-1}$ is present in both the KBr and mull spectra of **2**; this band is assigned (as in **1**) to the $\nu_3(E')$ mode of the ionic nitrate [23].

3.2. Description of structures

The molecular structures of the cations of complexes **1** and **2** are depicted in Figs. 1 and 2, respectively. Selected interatomic distances and angles are listed in Tables 2 and 3.

Complex **1** crystallizes in the monoclinic space group $C2/c$. Its asymmetric unit contains half of the mononuclear $[\text{Cu}(\text{pdmH}_2)_2]^{2+}$ cation in a general position (Fig. 1) and one NO_3^- anion. The Cu^{II} center is coordinated by two N,O,O' -tridentate chelating (η^3) pdmH_2 ligands. The pdmH_2 donor atoms are the nitrogen atom of the pyridyl group and the two oxygen atoms of the neutral alcohol arms. Thus, the Cu^{II} atom is six-coordinate with a compressed, *trans*-octahedral N_2O_4 environment [24]. The pyridyl nitrogen atoms can be viewed as strongly coordinating to the metal [$\text{Cu}(1)-\text{N}(1) = 1.936(2)\text{ \AA}$] in the axial direction ($\text{N}(1)-\text{Cu}(1)-\text{N}(1') = 174.3(1)^\circ$), while the four alcohol-type oxygen atoms of the equatorial plane form weaker bonds to Cu^{II} [$\text{Cu}(1)-\text{O}(1) = 2.163(2)/\text{Cu}(1)-\text{O}(2) = 2.192(2)\text{ \AA}$].

The pyridyl rings of the two pdmH_2 ligands are planar and almost perpendicular to each other, forming an angle of 71.4° [$\text{N}(1)\text{C}(2)\text{C}(3)\text{C}(4)\text{C}(5)\text{C}(6)/\text{N}(1')\text{C}(2')\text{C}(3')\text{C}(4')\text{C}(5')\text{C}(6')$]. The two five-membered chelating rings, $\text{Cu}(1)-\text{N}(1)-\text{C}(6)-\text{C}(7)-\text{O}(2)$ and $\text{Cu}(1)-\text{N}(1)-\text{C}(2)-\text{C}(1)-\text{O}(1)$, share the common $\text{Cu}(1)-\text{N}(1)$ edge. The dihedral angle formed between the mean planes $\text{Cu}(1)-\text{C}(6)-$

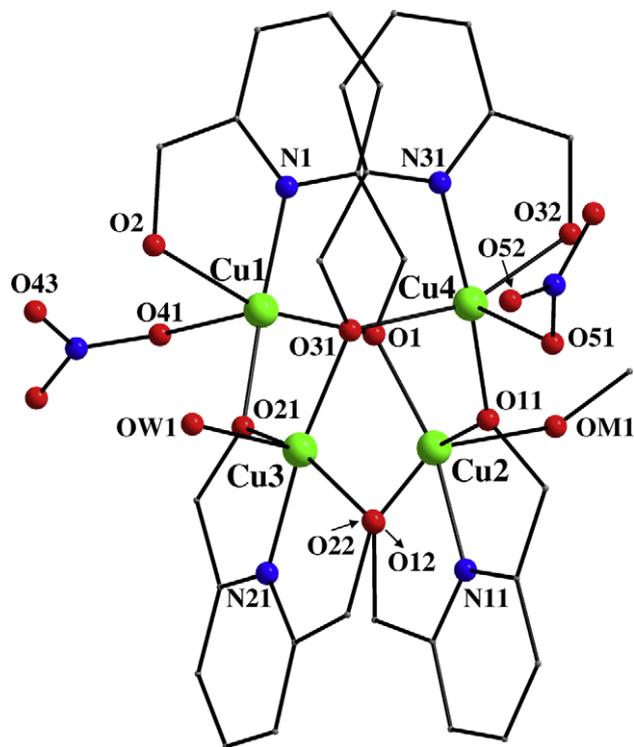


Fig. 2. Partially labelled plot of the cation of complex **2**. H atoms have been omitted for clarity. Colour scheme: Cu^{II} , green; O, red; N, blue; C, gray. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$\text{C}(7)-\text{O}(2)$ and $\text{Cu}(1)-\text{C}(2)-\text{C}(1)-\text{O}(1)$ is 7.9° . There are four symmetry-equivalent, interionic $\text{OH}\cdots\text{O}$ hydrogen bonds involving the protonated pdmH_2 O atoms as donors and NO_3^- counterion O atoms as the acceptors. Their dimensions are: $\text{O}(1)\cdots\text{O}(4)$ $2.639(4)\text{ \AA}$, $\text{HO}(1)\cdots\text{O}(4)$ $1.948(4)\text{ \AA}$, $\text{O}(1)-\text{HO}(1)\cdots\text{O}(4)$ $156.3(1)^\circ$ and $\text{O}(2)\cdots\text{O}(3)$ $2.739(4)\text{ \AA}$, $\text{HO}(2)\cdots\text{O}(3)$ $2.063(4)\text{ \AA}$, $\text{O}(2)-\text{HO}(2)\cdots\text{O}(3)$ $158.5(1)^\circ$. These H bonds serve to link neighbouring Cu^{II} monomers into one-dimensional, linear chains along the b -axis (Fig. S1) and their existence rationalizes the high thermodynamic stability of **1**.

Complex **2** $\cdot \text{H}_2\text{O} \cdot \text{MeOH}$ crystallizes in the monoclinic space group $P2_1/n$. Its structure consists of $[\text{Cu}_4(\text{NO}_3)_2(\text{pdmH})_4(\text{H}_2\text{O})(\text{MeOH})]^{2+}$ cations (Fig. 2), NO_3^- anions, and solvate H_2O and MeOH molecules; the latter two will not be further discussed.

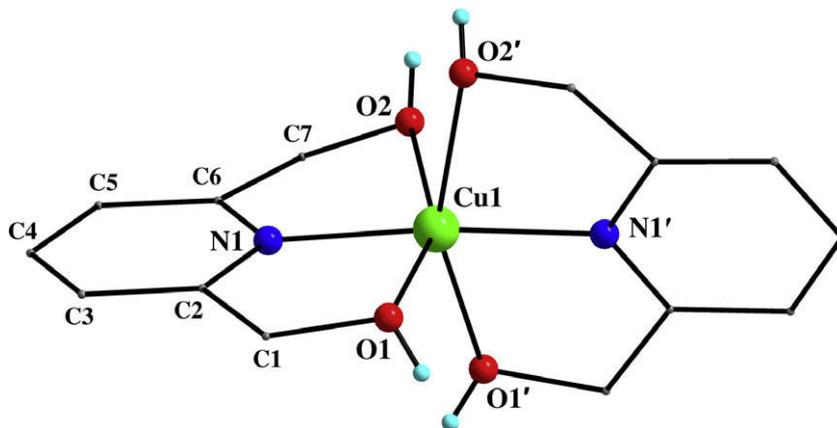


Fig. 1. Partially labelled PovRay representation of the cation of **1**, with some H atoms omitted for clarity. Colour scheme: Cu^{II} , green; O, red; N, blue; C, gray; H, sky blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3
Selected interatomic distances (Å) and angles (°) for complex **2** · H₂O · MeOH.

Parameter	Parameter	Parameter	Parameter
Cu(1)···Cu(2)	3.339(8)	Cu(2)···Cu(3)	3.762(1)
Cu(1)···Cu(3)	3.223(1)	Cu(2)···Cu(4)	3.304(8)
Cu(1)···Cu(4)	3.505(3)	Cu(3)···Cu(4)	3.373(3)
Cu(1)–O(1)	1.950(3)	Cu(3)···O(11)	3.158(6)
Cu(1)–O(2)	2.090(3)	Cu(3)–O(21)	1.937(3)
Cu(1)–O(21)	1.874(3)	Cu(3)–O(22)	2.036(3)
Cu(1)···O(31)	2.812(1)	Cu(3)–O(31)	1.904(3)
Cu(1)–O(41)	2.353(3)	Cu(3)–OW(1)	2.313(4)
Cu(1)–N(1)	1.902(3)	Cu(3)–N(21)	1.923(3)
Cu(2)–O(1)	1.899(3)	Cu(4)···O(1)	3.047(7)
Cu(2)–O(11)	1.942(3)	Cu(4)–O(11)	1.879(3)
Cu(2)–O(12)	2.034(3)	Cu(4)–O(31)	1.965(3)
Cu(2)···O(21)	3.191(4)	Cu(4)–O(32)	2.021(3)
Cu(2)–OM(1)	2.247(4)	Cu(4)–O(51)	2.396(4)
Cu(2)–N(11)	1.923(3)	Cu(4)–N(31)	1.903(3)
Cu(1)–O(1)–Cu(2)	120.3(1)	Cu(2)–O(1)···Cu(4)	80.2(1)
Cu(1)–O(1)···Cu(4)	86.1(1)	Cu(2)–O(11)···Cu(3)	91.9(1)
Cu(1)–O(21)···Cu(2)	77.7(1)	Cu(2)–O(11)–Cu(4)	119.7(1)
Cu(1)–O(21)–Cu(3)	115.5(1)	Cu(2)···O(21)–Cu(3)	91.0(1)
Cu(1)···O(31)–Cu(3)	83.9(1)	Cu(3)···O(11)–Cu(4)	79.7(1)
Cu(1)···O(31)–Cu(4)	92.6(1)	Cu(3)–O(31)–Cu(4)	121.3(1)
O(1)–Cu(1)–O(2)	163.0(1)	O(21)–Cu(3)–O(22)	156.5(1)
O(21)–Cu(1)–N(1)	171.7(1)	O(31)–Cu(3)–N(21)	166.1(1)
O(1)–Cu(2)–N(11)	163.0(1)	O(11)–Cu(4)–N(31)	171.0(1)
O(11)–Cu(2)–O(12)	159.0(1)	O(31)–Cu(4)–O(32)	159.5(1)

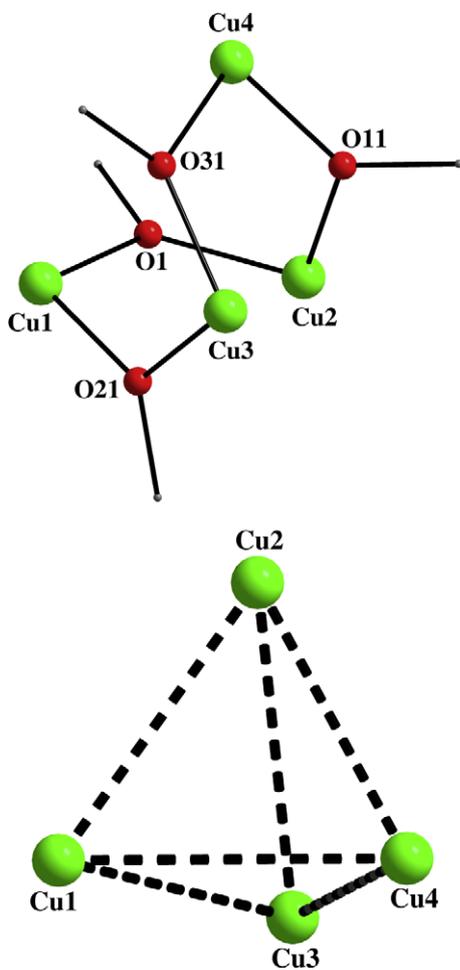


Fig. 3. (top) PovRay representation of the $[\text{Cu}_4(\mu_2\text{-OR})_4]^{4+}$ core of complex **2**. (bottom) The Cu_4 skeleton of **2**, emphasizing its slightly distorted tetrahedral metal topology. Colour scheme: Cu^{II}, green; O, red; C, gray. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The core of the cation of **2** (Fig. 3, top) consists of four Cu^{II} ions arranged at the vertices of a *slightly* distorted tetrahedron. The Cu_4 topology of **2** is shown in the bottom of Fig. 3. It can be alternatively described as a *very* distorted, non-planar “ring”, at the “corners” of which are lying the four Cu^{II} centers (Fig. S2); the deviation of the metal ions from their best least-squares plane ranges from 0.92 to 1.15 Å.

The Cu^{II} ions are held together by four monoatomic RO[−] bridges [O(1), O(11), O(21), O(31)] of four pdmH[−] groups to give a $[\text{Cu}_4(\mu_2\text{-OR})_4]^{4+}$ core (Fig. 3, top). Each O atom of the $\mu_2\text{-OR}$ bridges spans an edge of the tetrahedron. The Cu_4^{II} tetrahedron is only slightly distorted; the bridged Cu···Cu distances are within the 3.223(1)–3.373(3) Å range, while the unbridged Cu···Cu separations are 3.505(3) and 3.762(1) Å for Cu(1)···Cu(4) and Cu(2)···Cu(3), respectively. The Cu···Cu···Cu and Cu–OR–Cu angles are all acute and obtuse, respectively, varying from 53.6(1) to 68.6(1)° and 115.5(1) to 121.3(1)°. The alkoxide bridges involving O(1), O(11), O(21) and O(31) are slightly asymmetrical, with Cu–O distances ranging from 1.874(3) to 1.965(3) Å.

All Cu^{II} ions are five-coordinate with almost ideal [Cu(2) and Cu(3); $\tau = 0.07$ and 0.02, respectively] or slightly distorted [Cu(1)

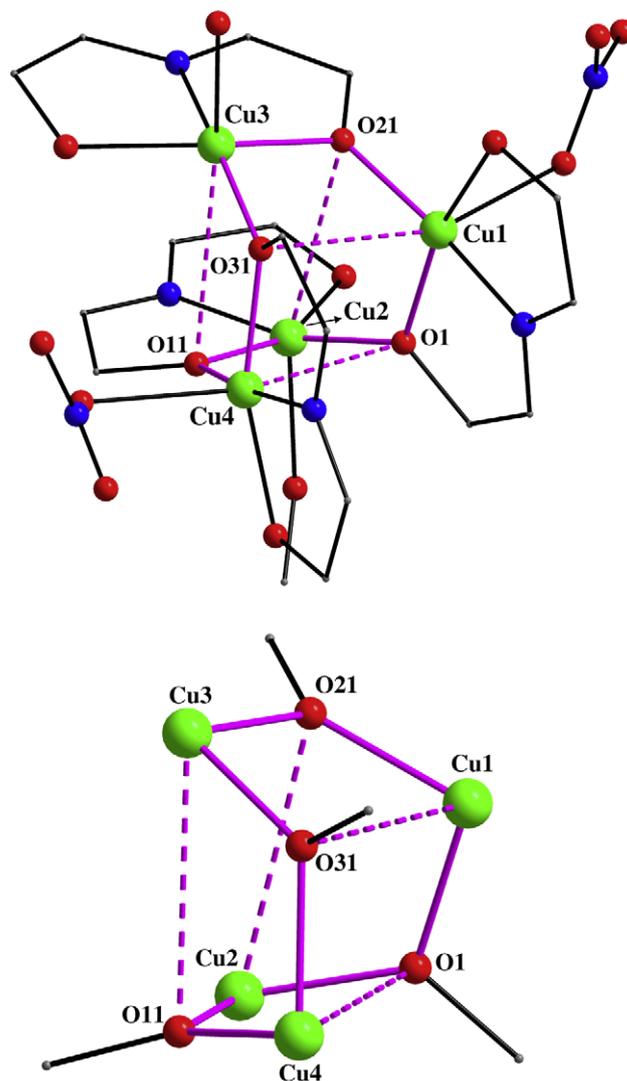


Fig. 4. (top) Molecular structure of the cation of **2**, and (bottom) its $[\text{Cu}_4(\mu_3\text{-OR})_4]^{4+}$ core, emphasizing the very distorted cubane description (purple thick lines). The purple dashed lines represent the four long distances (edges) of the cubane unit. Colour scheme: Cu^{II}, green; O, red; N, blue; C, gray. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and Cu(4); $\tau = 0.15$ and 0.19 , respectively] square pyramidal geometry, where τ is 0 and 1 for perfect square pyramidal and trigonal bipyramidal geometries [25], respectively. The basal planes of the square pyramidal Cu^{II} ions are of the same type, and consist of one N and two O atoms belonging to the 'chelate' part of one pdmH⁻ ligand and one bridging O atom from an adjacent pdmH⁻ ligand; these groups are thus $\eta^1:\eta^1:\eta^2:\mu_2$. The two coordinated monodentate NO₃⁻ ions, as well as the H₂O and MeOH molecules, are each terminally bound to Cu(1)/Cu(4), Cu(3) and Cu(2), respectively, occupying the apical positions of the square pyramids; the Cu^{II} ions lie 0.111 [Cu(1)], 0.230 [Cu(2)], 0.236 [Cu(3)] and 0.177 Å [Cu(4)] Å above the O₃N least-squares basal planes, towards the apical donor atom.

In addition to the tetrahedral or non-planar, ring-like description of **2**, an alternative way of describing it can be presented if we consider as bonding the four, abnormally long Cu(1)–O(31) [2.812(1) Å], Cu(2)–O(21) [3.191(4) Å], Cu(3)–O(11) [3.158(6) Å] and Cu(4)–O(1) [3.047(7) Å] distances that involve the RO⁻ bridges, which thus become μ_3 (Fig. 4, top). Thus, the resulting [Cu₄(μ_3 -OR)₄]⁴⁺ core (Fig. 4, bottom) can be described as a very distorted cubane with the four, distorted octahedral Cu^{II} atoms (now six- instead of five-coordinate) and the deprotonated μ_3 -O atoms from the four $\eta^1:\eta^1:\eta^3:\mu_3$ (instead of $\eta^1:\eta^1:\eta^2:\mu_2$) pdmH⁻ ligands occupying alternate vertices.

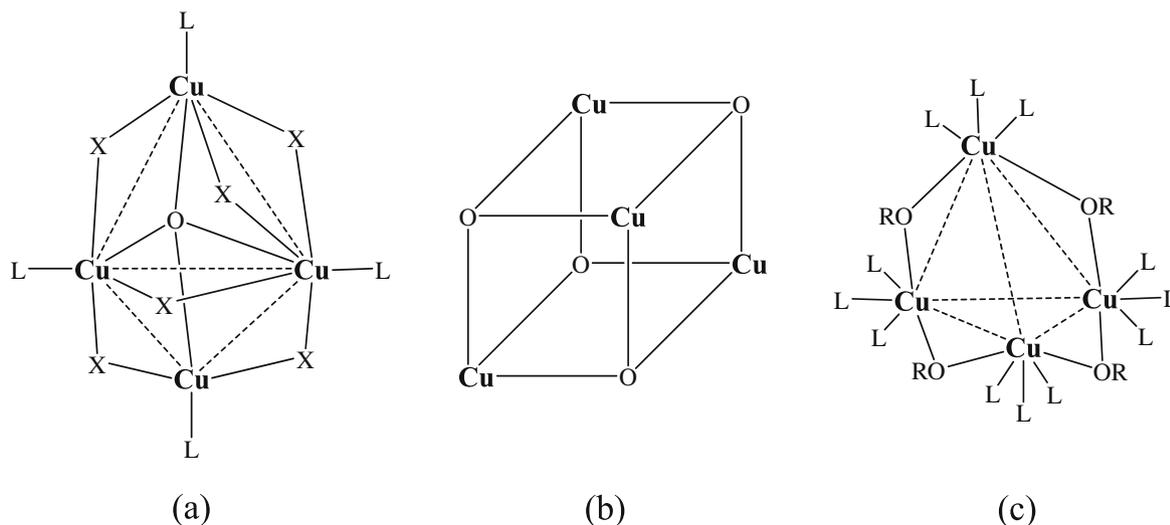
The structure of complex **2** is stabilized by two strong hydrogen bonds between the protonated, bound OH groups of two pdmH⁻ ligands and the O atoms of a monodentate or ionic NO₃⁻ group. The dimensions are: O(2)···O(43) 2.606(4) Å, HO(2)···O(43) 1.768(4) Å, O(2)–HO(2)···O(43) 170.6(1)° and O(32)···O(72) 2.705(3) Å, HO(32)···O(72) 1.918(3) Å, O(32)–HO(32)···O(72) 160.7(1)°. There are also many weak hydrogen bonds involving the remaining protonated OH groups of pdmH⁻ ligands and the terminal H₂O and MeOH molecules as donors and the monodentate/ionic NO₃⁻ groups as acceptors, with O···O distances in the 2.9–3.1 Å range, or slightly greater. These serve to link neighbouring Cu₄ cations and NO₃⁻ anions in the crystal into a 3D H-bonded network. The tetrahedral arrangement of the four Cu^{II} in the 'folded' crystal structure of complex **2** is further stabilized by two intramolecular π - π stacking interactions [26] on the two sides of the molecule that involve the pyridyl groups of two sets of pdmH⁻ ligands, i.e., those containing N(1)/N(31) and N(11)/N(21). In both sets, the aromatic rings of the pdmH⁻ ligands are nearly parallel, the angle between their mean planes being 10.3 and 3.9°, respectively.

Moreover, the distances between the centroids of rings containing N(1)/N(31) and N(11)/N(21) are 3.805 and 3.755 Å, respectively.

Tetranuclear copper(II) coordination complexes with N- and/or O-based ligands show a variety of structural types [24,27]. Well known examples are the clusters having the metal ions in a tetrahedral arrangement bridged over the edges by μ_2 -halide ions and by a μ_4 -O²⁻ in the center of the tetrahedron (Scheme 2a) [28]. More recently tetranuclear compounds of the cubane type have been studied extensively, structurally as well as with respect to their magnetic properties, by Haase, Ruiz and Alvarez, among others (Scheme 2b) [16,29]. The common feature characterizing the tetranuclear compounds studied so far is the fact that monoatomic bridges interconnect the metal ions. Tetranuclear Cu^{II} complexes containing diatomic bridges are also known [30]. Complex **2** joins a handful of structurally characterized Cu₄^{II} complexes with a tetrahedral metal topology that contain solely monoatomic bridges (Scheme 2c) [31].

3.3. Magnetochemistry

Variable-temperature dc magnetic susceptibility data in a 0.1 T field and in the 2.0–300 K range were collected on a powdered microcrystalline sample of **2**·H₂O restrained in eicosane to prevent torquing. The obtained data are plotted as $\chi_M T$ and χ_M vs. T in Fig. 5. The $\chi_M T$ value at 300 K is 1.23 cm³ mol⁻¹ K. This value is slightly less than that expected for a cluster comprising four Cu^{II} non-interacting ions (1.50 cm³ mol⁻¹ K with $g = 2$). The $\chi_M T$ product continuously decreases with decreasing temperature and gradually tends to 0 cm³ mol⁻¹ K at the very low temperature range (<20 K). This behaviour is indicative of predominant antiferromagnetic interactions between the metal centers with the low temperature value suggesting a ground state spin of $S = 0$. The shape of the $\chi_M T$ vs. T plot indicates an overall, moderate antiferromagnetic coupling between the four metal centers. On the other hand, the molar magnetic susceptibility χ_M shows a continuous increase upon cooling, but below ~110 K it exhibits a sudden drop, thus revealing a well-defined maximum. This further supports antiferromagnetic interactions, which are expected to be of moderate strength considering the position of the maximum, and an $S = 0$ ground state. The Curie tail in the low temperature susceptibility data reveals the existence of a paramagnetic, possibly monomeric, impurity.



Scheme 2. Common structural types in Cu₄^{II} clusters: (a) halide- and oxo-bridged, tetrahedral clusters; (b) cubanes; (c) alkoxide-bridged, tetrahedral clusters (X = halide ion, L = monodentate ligand).

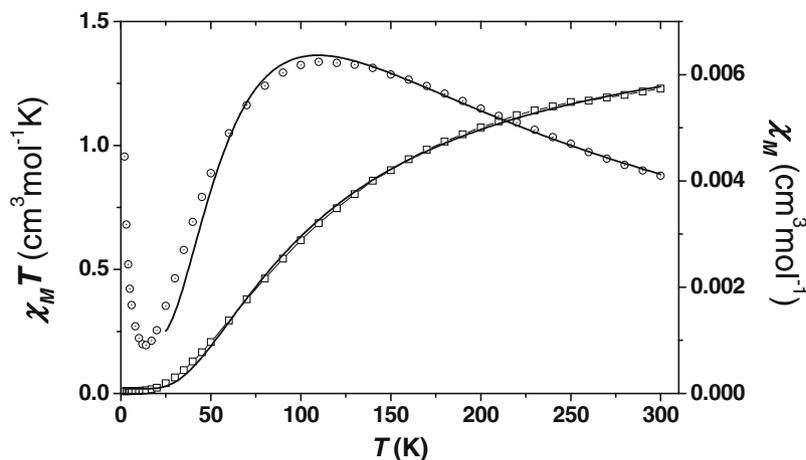


Fig. 5. χ_M vs. T (open circles) and $\chi_M T$ vs. T (open squares) plots for $2 \cdot \text{H}_2\text{O}$ in a 1 kG field. The solid lines are the fit of the data; see the text for the fit parameters.

As we mentioned before, from a structural viewpoint, complex **2** adopts a slightly distorted tetrahedral metal topology; however, magnetically, the system behaves as a ring (vide infra). Considering as bonding the four long Cu(1)–O(31), Cu(2)–O(21), Cu(3)–O(11), and Cu(4)–O(1) distances the system could potentially behave magnetically as a cube; however, given the real rigid shape of the structure, this is clearly not the case and thus there are no superexchange pathways that involve these axial Cu–O–Cu interactions. Nevertheless, from the magnetic point of view, the exact geometric arrangement of the spin carriers in a molecule is of less importance compared with the actual number of interactions through the exchange pathways. In the case of **2**, the system is magnetically defined by four exchange interactions, J_{ij} (Scheme 3).

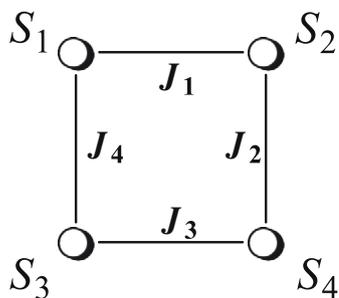
From examination of the structural data of **2**, there are strictly four different Cu–O–Cu bond angles, thus four different superexchange pathways from which derives the spin Hamiltonian (using the atomic numbering in Scheme 3) shown in Eq. (4).

$$H = -J_1(S_1 \cdot S_2) - J_2(S_2 \cdot S_4) - J_3(S_3 \cdot S_4) - J_4(S_1 \cdot S_3) \quad (4)$$

However, the Cu–O–Cu bond angles have similar values (120.3, 119.7, 121.3 and 115.5°); thus, assuming that the four J coupling constants are not identical, an attempt to differentiate J_1 , J_2 , J_3 and J_4 is not reliable because three of them should be extremely similar to each other, and only the coupling constant related to the smaller angle can be slightly different. Then, the only possibility to simplify the system is to assume a mean value defined by the spin Hamiltonian:

$$H = -J_1(S_1 \cdot S_2 + S_2 \cdot S_4 + S_3 \cdot S_4 + S_1 \cdot S_3) \quad (5)$$

A fit of the experimental data of $2 \cdot \text{H}_2\text{O}$ to the expression derived from the simplified spin Hamiltonian shown in Eq. (5), i.e. assuming that all the coupling constants are equal, gives the



Scheme 3. The magnetic coupling scheme of **2** involving four J parameters.

parameters $J_1 = -99.5 \text{ cm}^{-1}$ and $g = 2.11(4)$, which lead to an overall $S = 0$ ground state. The large, obtuse Cu–O–Cu angles are considered responsible for the moderately strong antiferromagnetic J_1 coupling [15,16,22,29c,32].

4. Conclusions

The present work extends the body of results that emphasize the ability of pdmH₂ to form interesting structural types in copper(II) cluster chemistry. In addition to the $\{[\text{Cu}_3(\text{O}_2\text{CMe})_2(\text{pdm})_2(\text{MeOH})_2][\text{Cu}_4(\text{O}_2\text{CMe})_2(\text{pdmH})_4](\text{ClO}_4)_2, [\text{Cu}_4(\text{O}_2\text{CMe})_2(\text{pdmH})_4](\text{O}_2\text{CMe})_2$ and $[\text{Cu}_5(\text{O}_2\text{CMe})_6(\text{pdm})_2]_n$ carboxylate-based complexes reported previously [16], the Cu/NO₃[−]/pdmH₂ reaction system has provided access to the tetranuclear cluster **2** and the known [18] mononuclear compound **1**. Complex **2** is a new addition to the small Cu₄ family of clusters with a tetrahedral metal arrangement bridged solely by monoatomic alkoxide bridges. This compound has been found to possess a $S = 0$ spin ground state and its magnetic behaviour can be interpreted considering a simplified $1 - J$ model as a result of its folded ring-like $[\text{Cu}_4(\mu_2\text{-OR})_4]^{4+}$ core. The monomeric complex **1** has been also used as a “ligand” for the construction of the larger, tetranuclear cluster **2** under basic conditions. Thus, from the synthetic inorganic chemistry viewpoint, this work further demonstrates the utility of the “metal complexes as ligands” approach in transition metal cluster chemistry. Preliminary experiments show that the reactions of **1** with sources of other divalent 3d or 4f metals under strong basic conditions lead to a variety of mixed-metal Cu^{II}/M complexes (M = Fe, Mn, Ni, Co, Ln). Finally, an important chemical message from this and our previous [16] work is that the pdmH₂/X[−] (X[−] = RCO₂[−], NO₃[−]) ligand combination looks like a promising candidate system for the generation of interesting new 3d-metal (other than Cu^{II}) clusters and coordination polymers, whose structure may be dependent on the nature of X[−].

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Appendix A. Supplementary data

CCDC 727367 and 727366 contain the supplementary crystallographic data for **1** and **2** · H₂O · MeOH. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12

Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2009.05.047.

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