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Benzoate as terminal ligand in the defective double-cubane, tetranuclear cobalt(II) complex $[\text{Co}_4(\text{N}_3)_2(\text{O}_2\text{CPh})_2\{(\text{py})_2\text{C}(\text{OH})\text{O}\}_4] \cdot 2\text{DMF}$ with simultaneous $\mu_{1,1}$ -azido and μ -O bridges $[(\text{py})_2\text{C}(\text{OH})\text{O} = \text{the monoanion of the hydrated, } gem\text{-diol form of di-2-pyridyl ketone}]$

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Abstract

The reaction of $\text{Co}(\text{O}_2\text{CPh})_2$ with di-2-pyridyl ketone, $(\text{py})_2\text{CO}$, and NaN_3 in DMF allows isolation of the tetranuclear compound $[\text{Co}_4(\text{N}_3)_2(\text{O}_2\text{CPh})_2\{(\text{py})_2\text{C}(\text{OH})\text{O}\}_4] \cdot 2\text{DMF}$ (**2**) instead of the expected nonanuclear cage $[\text{Co}_9(\text{N}_3)_2(\text{O}_2\text{CPh})_8\{(\text{py})_2\text{CO}_2\}_4]$. The X-ray diffraction analysis reveals a defective double-cubane, tetrameric entity in which the Co^{II} atoms are linked by $\eta^1, \mu_2\text{-N}_3$ azide ligand and two kinds of O-bridges. The molar magnetic susceptibility measurements of **2** in the 2–300 K range indicate bulk ferromagnetic coupling. Some synthetic aspects of the $\text{Co}^{\text{II}}/(\text{py})_2\text{CO}/\text{N}_3^-$ reaction system are also discussed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Benzoate ligands; Cobalt(II) complexes; Di-2-pyridyl ketone complexes; End-on azide ligands; Magnetic properties

1. Introduction

The development of routes and strategies for the synthesis of polynuclear complexes (clusters) of 3d metals in moderate oxidation states is of great importance because these species provide substantial impetus for developments in several fields, including bioinorganic chemistry, magnetochemistry, materials chemistry and solid-state physics [1–4].

The ligand di-2-pyridyl ketone, $(\text{py})_2\text{CO}$ (Fig. 1), has been recently proved to be a central player in 3d-metal cluster chemistry. The neutral molecule has three potential donor groups, two 2-pyridyl nitrogens and the carbonyl oxygen. It has been found in metal

complexes as terminal, either monodentate [5] or bidentate chelating [6], purely bridging [5] and mixed bridging/chelating [5,7] ligand. The resulting products are mononuclear, dinuclear, trinuclear or polymeric, depending on the metal ion, the coordination mode of $(\text{py})_2\text{CO}$ and the nature of the inorganic anion present.

There is a chemical characteristic of $(\text{py})_2\text{CO}$ that makes this molecule special as ligand; this is its carbonyl group. Water and alcohols have been shown to add the carbonyl group upon coordination of $(\text{py})_2\text{CO}$ to the metal producing the ligands $(\text{py})_2\text{C}(\text{OH})_2$ (*gem*-diol form) and $(\text{py})_2\text{C}(\text{OR})(\text{OH})$, respectively (Fig. 1). The neutral ligands $(\text{py})_2\text{C}(\text{OH})_2$ and $(\text{py})_2\text{C}(\text{OR})(\text{OH})$ coordinate to metal centers as tridentate chelates via the two nitrogen atoms and one oxygen atom, with the M–O bond often being weak. Thus, both neutral ligands do not present interest from the cluster formation point of view leading to mononuclear [8], dinuclear [9,10] or polymeric [10] complexes; in the last two cases, the metal

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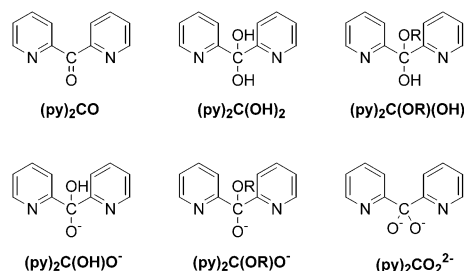


Fig. 1. Some of the ligands discussed in the text; note that (py)₂C(OH)₂, (py)₂C(OR)(OH) and all three anions do not exist as free species but exist only in their complexes.

ions are bridged by anionic ligands present in the complexes, e.g. Cl⁻ or SCN⁻.

Completely different and much more interesting (for cluster chemistry) coordination modes are seen when ligands (py)₂C(OR)(OH) and (py)₂C(OH)₂ become deprotonated. Upon deprotonation, the former becomes monoanionic, while the latter can function either as monoanion or dianion. The presence of deprotonated hydroxy groups within (py)₂C(OR)O⁻, (py)₂C(OH)O⁻ and (py)₂CO₂²⁻ (Fig. 1) leads to a great coordinative flexibility, due to the well known ability of the negatively charged oxygen to bridge two or three metal ions. The monoanionic forms usually bridge two (μ_2) or three (μ_3) metal ions, while the dianionic form can bridge as many as five metal sites. The ability of these forms to adopt a variety of coordination modes has resulted in the isolation of clusters with nuclearities ranging from 4 to 14 [11–13]. It is not known [14] whether the coordination of the oxygen to the metal center occurs *after* the hydration/alcoholysis reaction or *prior* to this reaction; in the former case there is a polarization effect of the metal upon the hydroxy group leading to its deprotonation, while in the latter case there is a direct activation of the carbonyl group towards nucleophilic attack.

Our groups are engaged in developing the polynuclear 3d-metal chemistry of di-2-pyridyl ketone [12,13]. Our main contribution to this area is twofold: firstly, the realisation that (py)₂C(OH)₂ can be doubly deprotonated leading to structurally impressive clusters [12] and, secondly, the incorporation of end-on azido ligands into the chemistry of (py)₂CO₂²⁻ and (py)₂C(OH)O⁻ / (py)₂C(OR)O⁻ as a means to introduce specifically ferromagnetic components in the superexchange schemes, thus increasing the ground-state S values of clusters [12,13].

We recently reported [12] that the reaction of Co(O₂CMe)₂·4H₂O with (py)₂CO and NaN₃ (9:4:2, 2:1:1 ratios) in DMF under heating led to the non-nuclear cage [Co₉(N₃)₂(O₂CMe)₈{(py)₂CO₂}₄] (1), in which the nine Co^{II} atoms adopt a topology of two square pyramids sharing a common apex. Salient features of the structure are the unique η^1, μ_4 coordination mode of the azido ligands, the μ_5 coordination

mode of (py)₂CO₂²⁻ and the extremely rare coordination number 8 for the Co^{II} atom lying at the common apex of the pyramids. The magnetic study revealed ferromagnetic coupling mediated by the azido bridges giving a total S value of seven times the local spin and leading to a high-spin ferrimagnetic system.

We were interested to study whether and how the nature of the carboxylate ligands affects the structural and magnetic identity of the products resulting from the Co^{II}/RCO₂⁻/N₃⁻ reaction mixtures in DMF. For example, we wondered if replacement of acetates with benzoates in this reaction mixture would give a cluster structurally and magnetically similar to 1. In this report, we describe the identity, single-crystal X-ray structure and magnetic properties of the product from the Co^{II}/PhCO₂⁻/N₃⁻ reaction mixture in DMF.

2. Experimental

2.1. Preparation of

[Co₄(N₃)₂(O₂CPh)₂{(py)₂C(OH)O}₄]·2DMF (2)

DMF (20 ml) was added to a solid mixture containing Co(O₂CPh)₂ (0.18 g, 0.60 mmol), (py)₂CO (0.06 g, 0.31 mmol) and NaN₃ (0.02 g, 0.31 mmol). The solid dissolved upon stirring under heating to give a dark blue solution. The solution was allowed to stand undisturbed at room temperature for 3 days. Well-formed, X-ray quality pink crystals of the product appeared within this period. The crystals were collected by filtration, washed with DMF and Et₂O, and dried in vacuo over silica gel. Yield: 40% [based on (py)₂CO]. *Anal.* Found: C, 50.8; H, 3.9; N, 14.8. Calc. for C₆₄H₆₀Co₄N₁₆O₁₄: C, 50.8; H, 4.0; N, 14.8%. Complex 2 can also be isolated by employing an 1:1:0.5 Co(O₂CPh)₂–(py)₂CO–NaN₃ molar ratio.

Caution: azide salts are potentially explosive and should be handled in small quantities.

2.2. Physical measurements

Magnetic susceptibility measurements were carried out for a polycrystalline sample of 2 with a SQUID susceptometer working in the range 2–300 K under magnetic fields of approximately 0.1 T. Diamagnetic corrections were estimated from Pascal Tables. IR spectra (4000–400 cm⁻¹) were recorded from KBr pellets on a Nicolet 520 FTIR spectrometer.

2.3. X-ray crystallography

Analyses on pink prismatic single crystal of 2 were carried out with an MAR345 diffractometer with image plate detector. Intensities were collected with graphite

Table 1
Crystallographic data for complex $[\text{Co}_4(\text{N}_3)_2(\text{O}_2\text{CPh})_2\{(\text{py})_2\text{C}(\text{O}-\text{H})\text{O}\}_4]\cdot 2\text{DMF}$ (**2**)

Parameter	1
Empirical formula	$\text{C}_{64}\text{H}_{60}\text{Co}_4\text{N}_{16}\text{O}_{14}$
Formula weight	1513.02
Colour and habit	pink, prism
T (°C)	20
λ (Mo $K\alpha$) (Å)	0.71069
Crystal system	monoclinic
Space group	$C2/c$
a (Å)	14.242(8)
b (Å)	16.075(8)
c (Å)	28.844(3)
α (°)	90.00
β (°)	92.36(4)
γ (°)	90.00
V (Å ³)	6598(5)
Z	4
D_{calc} (Mg m ⁻³)	1.523
μ (mm ⁻¹)	1.066
$F(000)$	3104
Crystal size (mm)	0.10 × 0.10 × 0.20
$2\theta_{\text{max}}$ (°)	28.87
Index ranges (°)	$-15 \leq h \leq 15, 0 \leq k \leq 18, 0 \leq l \leq 38$
Reflections collected	8219
Independent reflections/ R_{int}	5024/0.031
Data with $I > 2\sigma(I)$	3903
Parameters refined	507
R_1 ^a	0.0324
wR_2 ^b	0.0903
Goodness-of-fit (on F^2)	1.073
Residuals (e Å ⁻³)	0.508/−0.467

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

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

monochromatized Mo $K\alpha$ radiation. A summary of the crystallographic data is reported in Table 1. Unit cell parameters for **2** were determined from automatic centering of 8219 reflections ($3^\circ < \theta < 30^\circ$) and refined by the least-squares method. Five thousand and twenty-four reflections were measured in the range $2.81^\circ < \theta < 28.87^\circ$. Three thousand nine hundred and three reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Lp but no absorption corrections were made.

The structure was solved by direct methods using the SHELXS computer program [15] and refined by full-matrix least-squares method, with the SHELX-97 computer program [16] using 5024 reflections. The function minimized was $\Sigma w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0655P)^2]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$. f , f' and f'' were taken from *International Tables of X-ray Crystallography* [17]. Sixteen hydrogen atoms were located from a difference synthesis and 12 H atoms were computed. All were refined with an isotropic temperature factor equal to 1.2 times the equivalent isotropic temperature factor of the bonded atom. A riding model was used for computed hydrogen atoms. The number of

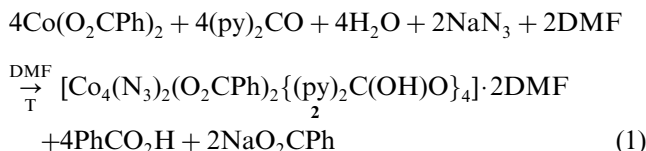
parameters refined was 507. Max. shift/esd = 0.002. Mean shift/esd = 0.000.

3. Results and discussion

3.1. Synthesis

As stated in Section 1, the initial goal of this work was the preparation of a cobalt(II) benzoate cluster with a structure and magnetic properties similar to those of **1**. Our general synthetic approach for the isolation of heteroleptic $\text{RCO}_2^-/(\text{py})_2\text{CO}_2^{2-}/\text{N}_3^-$ metal clusters is to react an excess of the metal carboxylate with $(\text{py})_2\text{CO}$ and N_3^- in DMF under heating [12]. Obviously $(\text{py})_2\text{C}(\text{OH})_2$ is fully deprotonated by the basic carboxylate groups and polynuclear $\text{M}^{\text{II}}/\text{RCO}_2^-/(\text{py})_2\text{CO}_2^{2-}/\text{N}_3^-$ complexes result from the reactions [as long as the $\text{RCO}_2^-/(\text{py})_2\text{CO}$ ratio is high enough to leave an amount of nonprotonated RCO_2^- in the reaction mixture], given the fact that the RCO_2^- , $(\text{py})_2\text{CO}_2^{2-}$ and azido ligands can potentially adopt a variety of terminal and bridging modes.

Reaction of $\text{Co}(\text{O}_2\text{CPh})_2$ with $(\text{py})_2\text{CO}$ and NaN_3 (2:1:1 molar ratio) in DMF under heating resulted in a blue solution from which the pink tetranuclear complex $[\text{Co}_4(\text{N}_3)_2(\text{O}_2\text{CPh})_2\{(\text{py})_2\text{C}(\text{OH})\text{O}\}_4]\cdot 2\text{DMF}$ (**2**) was isolated in moderate yield. We did not try to optimize the yield. The low to moderate yield in our experiments is presumably a consequence of the crystallization method (see Section 2.1). The extremely slow evaporation of the solvent (DMF) at room temperature and the relatively short time (~ 3 days) of the storage of the open reaction flask before filtration may both be responsible for the obtained yields. The stoichiometric reaction is represented by Eq. (1):



Surprisingly, a seemingly subtle change in the reaction conditions that gave complex **1** (i.e. changing the acetates with benzoates) led to a dramatic change in the type of complex produced. Complex **1** is a non-nuclear cage containing doubly deprotonated $(\text{py})_2\text{CO}_2^{2-}$ ligands, whereas **2** is a tetranuclear cluster containing singly deprotonated $(\text{py})_2\text{C}(\text{OH})\text{O}^-$ ligands. Further increase in the 'base' (PhCO_2^-) to 'acid' [$(\text{py})_2\text{C}(\text{OH})_2$] ratio, either by increase of the $\text{Co}(\text{O}_2\text{CPh})_2/(\text{py})_2\text{CO}$ molar ratio from 2:1 to 3:1 or by employment of external PhCO_2^- s, and longer reaction times did not give any evidence for the formation of a complex containing dianions $(\text{py})_2\text{CO}_2^{2-}$ as ligands. We strongly believe that the

lower basicity of PhCO_2^- (the $\text{p}K_a$ value of its conjugate acid, PhCO_2H , is 4.19) compared to MeCO_2^- ($\text{p}K_a$ of $\text{MeCO}_2\text{H} = 4.75$) is responsible for the inability of PhCO_2^- s to doubly deprotonate $(\text{py})_2\text{C}(\text{OH})_2$ and the failure to isolate the benzoate analogue of **1**.

Use of external hydroxides (LiOH , Me_4NOH) to help double deprotonation of the *gem*-diol form of $(\text{py})_2\text{CO}$ complicates the reaction mixture leading to non-crystalline hydroxo products with poor analytical results.

Looking for an alternative method of preparing the benzoate analogue of **1**, we anticipated that complex **1** would be capable of acetate substitution on treatment with PhCO_2H . Such a reactivity pattern is consistent with the known acidities of the RCOOH molecules as reflected in the $\text{p}K_a$ values (see above) and the probable mechanism [18] involves protonation of bound acetates by more acidic PhCO_2H molecules, followed by their displacement by generated PhCO_2^- s. Such ligand substitution reactions have been widely used in metal carboxylate cluster chemistry [18,19]. Unfortunately, we could not confirm this type of reactivity for **1**. Addition of excess of PhCO_2H to **1** in MeOH or DMF gives a mixture of products (including **2**) depending on the reaction conditions; the separation of these products was impossible.

With the identity of **2** established by single-crystal X-ray crystallography (vide infra), a modified preparative procedure (not reported in detail in Section 2) was devised by adjusting the $\text{Co}(\text{O}_2\text{CPh})_2-(\text{py})_2\text{CO}-\text{NaN}_3$ reaction ratio in DMF from 2:1:1 to 1:1:0.5 (Eq. (1)). We have also found that heating is not necessary for the preparation of **2**.

3.2. Description of structure

A plot of the structure of the tetranuclear compound $[\text{Co}_4(\text{N}_3)_2(\text{O}_2\text{CPh})_2\{(\text{py})_2\text{C}(\text{OH})\text{O}\}_4]\cdot 2\text{DMF}$ (**2**) is shown in Fig. 2(a). Fig. 2(b) emphasizes the core of the tetranuclear molecule and shows the numbering scheme. Selected distances and angles are listed in Table 2.

The structure consists of centrosymmetric tetranuclear molecules. The four Co^{II} atoms are located at four corners of a defective double cubane (two cubanes sharing one face and each missing one vertex, see Fig. 2(b)) and bridged by means of two end-on (η^1, μ_2) azido ligands and O atoms from the $(\text{py})_2\text{C}(\text{OH})\text{O}^-$ anions. Peripheral ligation is provided by two O atoms of the terminal benzoate ligands and the N atoms of the eight 2-pyridyl rings. Atoms O(1) of two $(\text{py})_2\text{C}(\text{OH})\text{O}^-$ ligands are triply bridging with distances to Co^{II} atoms of 2.225(2), 2.155(2) and 2.015(2) Å for $\text{Co}(1)-\text{O}(1)$, $\text{Co}(2)-\text{O}(1)$ and $\text{Co}(2)\#1-\text{O}(1)$, respectively. The $\text{Co}(1)-\text{O}(1)-\text{Co}(2)$ and $\text{Co}(1)-\text{O}(1)-\text{Co}(2)\#1$ angles are $97.4(1)^\circ$ and $96.2(1)^\circ$, respectively. Atoms O(3) of the two other $(\text{py})_2\text{C}(\text{OH})\text{O}^-$ ligands are doubly brid-

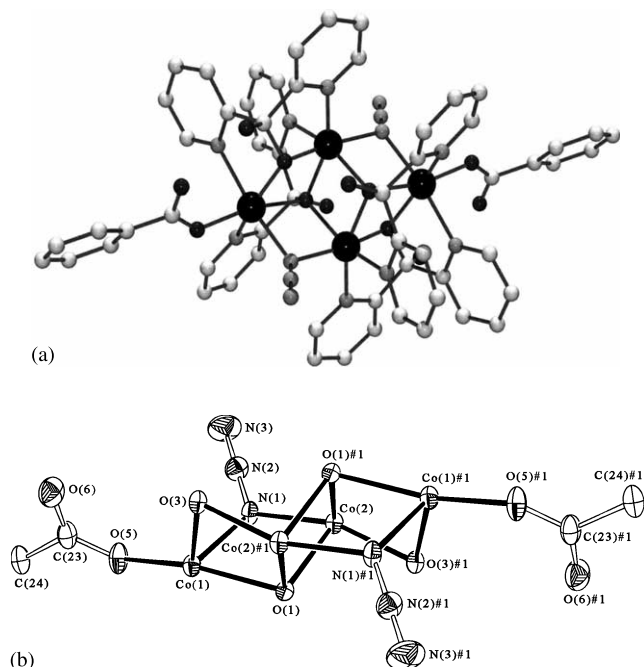


Fig. 2. (a) Plot of $[\text{Co}_4(\text{N}_3)_2(\text{O}_2\text{CPh})_2\{(\text{py})_2\text{C}(\text{OH})\text{O}\}_4]\cdot 2\text{DMF}$ (**2**); the solvate DMF molecules have been omitted. (b) Labeled plot of the defective, double-cubane core present in complex **2**.

ging with distances of 2.012(2) and 2.154(2) Å to $\text{Co}(1)$ and $\text{Co}(2)\#1$, respectively. The $\text{Co}(1)-\text{O}(3)-\text{Co}(2)\#1$ angle is $98.5(1)^\circ$. One O atom of each $(\text{py})_2\text{C}(\text{OH})\text{O}^-$ ligand remains protonated and unbound to the metals. Therefore, two $(\text{py})_2\text{C}(\text{OH})\text{O}^-$ ions adopt the $\eta^1:\eta^3:\eta^1:\mu_3$ coordination mode and the other two bind with the $\eta^1:\eta^2:\eta^1:\mu_2$ mode (Fig. 3). $\text{Co}(1)$ and $\text{Co}(2)$ are also bridged by the N(1) atom of the η^1, μ_2 azido ligand (end-on). The $\text{Co}(1)-\text{N}(1)$ and $\text{Co}(2)-\text{N}(1)$ distances are 2.158(2) and 2.103(2) Å, respectively. The $\text{Co}(1)-\text{N}(1)-\text{Co}(2)$ angle is $101.1(1)^\circ$. The azido ligand is practically linear with a $\text{N}(1)-\text{N}(2)-\text{N}(3)$ angle of $179.5(3)^\circ$.

The metal ions have distorted octahedral geometries. The $\text{Co}(1)$ octahedral coordination is completed by the N(4) and N(6) atoms of two $(\text{py})_2\text{C}(\text{OH})\text{O}^-$ ligands, and the O(5) atom of the terminal benzoate ligand. The $\text{Co}(2)$ octahedral coordination is completed by the N(5)#1 and the N(7)#1 atoms of two $(\text{py})_2\text{C}(\text{OH})\text{O}^-$ ligands with $\text{Co}(2)-\text{N}(5)\#1$ and $\text{Co}(2)-\text{N}(7)\#1$ distances of 2.168(2) and 2.079(2) Å, respectively.

3.3. IR spectroscopy

The presence of DMF in **2** is manifested by a medium-intensity band at 1669 cm^{-1} and a weak band at 645 cm^{-1} , assigned to $\nu(\text{C}=\text{O})$ and $\delta(\text{OCN})$, respectively [20]. The absence of shifts of these bands in the complex, when compared with the corresponding bands in the spectrum of free DMF [21], implies that there is no interaction between DMF and the Co^{II} atoms. The complex exhibits an intense band at 2076 cm^{-1} ,

Table 2
Selected interatomic distances (Å) and angles (°) for
[Co₄(N₃)₂(O₂CPh)₂{(py)₂C(OH)O}₂]₄ 2DMF (**2**)

Bond distances			
Co(1)···Co(2)	3.2897(19)	Co(2)–N(1)	2.103(2)
Co(1)···Co(2)#1	3.1581(18)	Co(2)–O(3)#1	2.154(2)
Co(1)···Co(1)#1	5.631(1)	Co(2)–O(1)	2.155(2)
Co(2)···Co(2)#1	3.1442(1)	Co(2)–N(5)#1	2.168(2)
Co(1)–O(3)	2.012(2)	N(1)–N(2)	1.207(3)
Co(1)–O(5)	2.034(2)	N(2)–N(3)	1.140(4)
Co(1)–N(4)	2.150(2)	O(2)–C(6)	1.420(2)
Co(1)–N(1)	2.158(2)	O(4)–C(17)	1.399(3)
Co(1)–N(6)	2.176(2)	O(6)–C(23)	1.247(3)
Co(1)–O(1)	2.225(2)	O(1)–C(6)	1.372(3)
Co(2)–O(1)#1	2.015(2)	O(3)–C(17)	1.383(2)
Co(2)–N(7)#1	2.079(2)	O(5)–C(23)	1.255(3)
Bond angles			
O(3)–Co(1)–O(5)	115.8(1)	N(7)#1–Co(2)–O(3)#1	76.4(1)
O(3)–Co(1)–N(4)	150.5(1)	N(1)–Co(2)–O(3)#1	162.8(1)
O(5)–Co(1)–N(4)	91.9(1)	O(1)#1–Co(2)–O(1)	82.2(1)
O(3)–Co(1)–N(1)	92.1(1)	N(7)#1–Co(2)–O(1)	105.5(1)
O(5)–Co(1)–N(1)	96.2(1)	N(1)–Co(2)–O(1)	81.4(1)
N(4)–Co(1)–N(1)	94.9(1)	O(3)#1–Co(2)–O(1)	84.3(1)
O(3)–Co(1)–N(6)	75.7(1)	O(1)#1–Co(2)–N(5)#1	76.7(1)
O(5)–Co(1)–N(6)	85.5(1)	N(7)#1–Co(2)–N(5)#1	98.4(1)
N(4)–Co(1)–N(6)	97.8(1)	N(1)–Co(2)–N(5)#1	93.1(1)
N(1)–Co(1)–N(6)	167.1(1)	O(3)#1–Co(2)–N(5)#1	103.8(1)
O(3)–Co(1)–O(1)	80.2(1)	O(1)–Co(2)–N(5)#1	155.9(1)
O(5)–Co(1)–O(1)	163.6(1)	Co(1)–O(3)–Co(2)#1	98.5(1)
N(4)–Co(1)–O(1)	73.2(1)	Co(2)–O(1)–Co(1)	97.4(1)
N(1)–Co(1)–O(1)	78.6(1)	Co(2)#1–O(1)–Co(1)	96.2(1)
N(6)–Co(1)–O(1)	103.1(1)	Co(2)#1–O(1)–Co(2)	97.8(1)
O(1)#1–Co(2)–N(7)#1	155.9(1)	Co(2)–N(1)–Co(1)	101.1(1)
O(1)#1–Co(2)–N(1)	105.4(1)	N(2)–N(1)–Co(1)	126.3(2)
N(7)#1–Co(2)–N(1)	98.4(1)	N(2)–N(1)–Co(2)	122.0(2)
O(1)#1–Co(2)–O(3)#1	81.9(1)	N(1)–N(2)–N(3)	179.6(3)

Symmetry transformations used to generate equivalent atoms:
#1 – $x+2, -y, -z+1$.

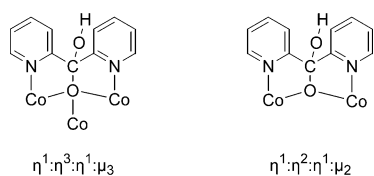


Fig. 3. The crystallographically established coordination modes of the (py)₂C(OH)O[−] ligands in complex **2**.

assigned to the asymmetric stretching mode of the azido ligands [13]. The strong bands at 1601 and 1388 cm^{−1} are assigned to the $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ modes, respectively [22]; the former should also involve a pyridine stretching character. The difference Δ [$\Delta = \nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$] for **2** (213 cm^{−1}) is more than that for NaO₂CPh, as expected for the monodentate mode of carboxylate ligation [22]. The spectrum of **2** also exhibits a strong band at 3445 cm^{−1}, assignable to $\nu(\text{OH})_{(\text{py})_2\text{C}(\text{OH})\text{O}^-}$. The broadness and relatively low frequency of this band are both indicative of hydrogen bonding.

3.4. Magnetochemistry

The $\chi_{\text{M}}T$ product versus T of **2** in the 300–2 K range is shown in Fig. 4 (χ_{M} is the corrected molar magnetic susceptibility per tetramer). $\chi_{\text{M}}T$ increases quickly on cooling from 10.8 cm³ K mol^{−1} at 300 K to a maximum of 16.9 cm³ K mol^{−1} at 11 K, and then decreases to 14.6 cm³ K mol^{−1} at 2 K. χ_{M} increases upon cooling and does not have any maximum in the temperature range studied. The overall behaviour of **2** corresponds to a ferromagnetically coupled system. The strong ferromagnetic interaction in **2** is confirmed by the molar magnetization measurement at 2 K, which shows a quick increase of $M/N\beta$ by increasing the external field, arriving to a final value of 10.37 at 5.0 T (Fig. 5). This strong coupling between Co(2) and Co(1) permits us to assume that the interactions through the $\eta^1, \mu_2\text{-N}_3^-$ and the $\mu\text{-O}^-$ bridge with the Co(1)–O(1)–Co(2) angle of 97.4(1)° are both ferromagnetic, indicating a magnetic behaviour similar to that found for the structurally related Co(II) derivatives [Co₄($\eta^1, \mu_2\text{-N}_3^-$)₂(N₃)₂{(py)₂C(OH)O}₂{(py)₂C(OMe)O}₂]₂·2H₂O (**3**) [13] and [Co₄($\eta^1, \mu_2\text{-N}_3^-$)₂(H₂O)₂{(py)₂C(OH)O}₂{(py)₂C(OMe)O}₂](BF₄)₂·4H₂O (**4**) [11]. All three complexes have the same defective double-cubane core. Analysis of the coupling constants for a high-spin rhombic cobalt(II) tetramer is not possible by means of an effective Hamiltonian based on four $S = 3/2$ spins, due to the large anisotropy of this ion [11,13]. At low temperature the local spin of Co^{II} is closer to $\frac{1}{2}$, and then the low temperature data are better defined as an $S_{\text{T}} = 2$ system with a large g_{eff} value.

3.5. Synthetic aspects of the Co^{II}(py)₂CO/N₃[−] reaction system

Complex **2** is structurally related to complexes [Co₄($\eta^1, \mu_2\text{-N}_3^-$)₂(N₃)₂{(py)₂C(OH)O}₂{(py)₂C(OMe)O}₂]₂·2H₂O (**3**) [13] and [Co₄($\eta^1, \mu_2\text{-N}_3^-$)₂(H₂O)₂{(py)₂C(OH)O}₂{(py)₂C(OMe)O}₂](BF₄)₂·4H₂O (**4**) [11], prepared from the Co(O₂CMe)₂·4H₂O/(py)₂CO/NaN₃ (1:1:1, 1:2:2, 1:3:3, 1:2:4, 1:4:4) and CoCl₂·6H₂O/(py)₂CO/NaN₃/NaBF₄ (1:1:0.5:0.5) reaction mixtures, respectively, in MeOH/H₂O. All three complexes have a defective, double-cubane motif. There are two chemical

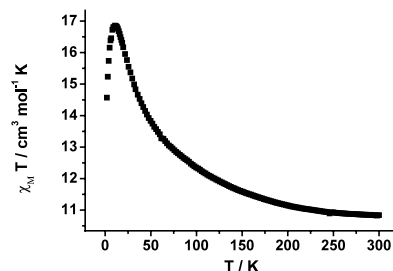


Fig. 4. $\chi_{\text{M}}T$ plot vs. T for compound **2**.

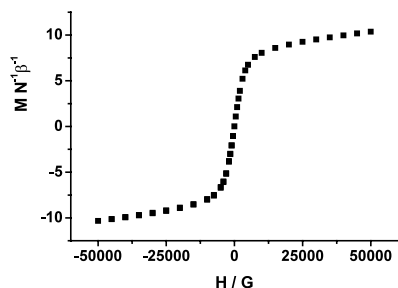


Fig. 5. Plot of the magnetization ($M/N\mu_B$) vs. H for **2** at 2 K.

differences along the series which have no structural effect. First, complexes **3** and **4** have two $(py)_2C(OH)O^-$ and two $(py)_2C(OMe)O^-$ ligands; this is a consequence of MeOH present in the reaction systems that lead to **3** and **4**. Second, the two terminal monodentate ligands differ in the three complexes; these are $PhCO_2^-$ ions in **2**, N_3^- ions in **3** and H_2O molecules in **4** (giving rise to a cationic species). The presence of benzoate ligands in **2** is a result of the high $PhCO_2^- - N_3^-$ ratio used (4:1), whereas the presence of the two terminal azide ligands in **3** can be explained by the lower $MeCO_2^- - N_3^-$ ratios used (2:1, 1:1, 1:1.5, 1:2) in the reaction mixtures. The existence of aqua ligands in the structure of **4** is certainly due to the presence of BF_4^- ions in the reaction system; the latter favour formation of cationic species.

4. Supplementary material

Further details (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 180597 for compound **2**. Copies of the data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccd.cam.ac.uk>).

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