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Synthesis and structural study of two decanuclear cobalt(II) cages incorporating pyridonates and benzoate-based carboxylates[☆]

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Abstract

In this paper, we report the synthesis and the structures of two new decanuclear cobalt(II) cages including carboxylate and pyridonate ligands. The carboxylates are related to benzoic acid. Complex **1** has the formula $[\text{Co}_{10}(\text{OH})_6(\text{chp})_6(o\text{-MeBz})_7(n\text{-C}_3\text{H}_7\text{OH})_5][o\text{-MeBz}]$ where chp = 2-chloro-6-pyridonate and $o\text{-MeBz}$ = 2-methylbenzoate. The second cage, **2**, has the formula $[\text{Co}_{10}(\text{OH})_6(\text{mhp})_6(p\text{-tBuBz})_8(\text{Hmhp})_2(\text{CH}_3\text{CN})_2]$, where mhp = 2-methyl-6-pyridonate, Hmhp = 2-methyl-6-hydroxypyridine and $p\text{-tBuBz}$ = 4-tertbutylbenzoate. The cobalt ions of **1** form a centred-tricapped-trigonal prism, whereas the metal core of **2** is based on a centred tetraicosahedron where five metal ions are missing. **To cite this article:** C. Cadiou et al., C. R. Chimie 6 (2003).

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Résumé

Cet article reporte la synthèse et la structure de deux nouvelles cages décanucléaires du cobalt(II) comprenant des ligands carboxylates et pyridonates. Les carboxylates utilisés sont dérivés de l'acide benzoïque. Le complexe **1** a pour formule $[\text{Co}_{10}(\text{OH})_6(\text{chp})_6(o\text{-MeBz})_7(n\text{-C}_3\text{H}_7\text{OH})_5][o\text{-MeBz}]$, où chp = 2-chloro-6-pyridonate et $o\text{-MeBz}$ = 2-méthylbenzoate. La seconde cage, **2**, a pour formule $[\text{Co}_{10}(\text{OH})_6(\text{mhp})_6(p\text{-tBuBz})_8(\text{Hmhp})_2(\text{CH}_3\text{CN})_2]$, où mhp = 2-méthyl-6-pyridonate, Hmhp = 2-méthyl-6-hydroxypyridine et $p\text{-tBuBz}$ = 4-tertbutylbenzoate. Les ions cobalt de **1** forment un prisme triangulaire centré ou trois Co(II) chapeautent les faces rectangulaires, tandis que le cœur métallique de **2** est basé sur un tétra-icosaèdre centré où cinq ions métalliques sont absents. **Pour citer cet article :** C. Cadiou et al., C. R. Chimie 6 (2003).

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1. Introduction

In 1993, Sessoli et al. showed the existence of slow relaxation of the magnetisation at low temperature for the cage complex $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4]$ [1]. This observation that a discrete cluster could show hysteresis of molecular origin has given birth to a new type of molecules called ‘single molecule magnets’ (SMMs). Since then, other manganese complexes [2] but also iron [3], vanadium [4] and more recently a dodecanuclear cyclic nickel complex [5] have shown this remarkable property. The interest in this type of compounds comes from their ability to store magnetic information and also in the fact that they can exhibit quantum tunnelling of the magnetisation [6]. Therefore, there is currently a great deal of interest in the synthesis of high-nuclearity clusters and one of the major challenges is to understand the correlations between the structures of the complexes and their magnetic properties.

In order to deal with this problem, our group is studying cobalt and nickel cages formed after ‘blend’ reactions of the metal salts with 2-pyridonate and carboxylates ligands [7, 8]. Recently, a family of these complexes has been reported with nuclearities from ten to twelve, the metal core of all these molecules being related to a trigonal prismatic geometry [7]. Benzoate was included in two of the clusters reported, an undecanuclear nickel cage with 2-chloro-6-pyridonate (chp) and a decanuclear cobalt compound with 2-methyl-6-pyridonate (mhp). We wanted to see if a modification of the solubility and/or the steric hindrance of the aromatic ring of the benzoate could influence the formation of new structures. Therefore we have used two substituted carboxylates, 2-methylbenzoate (*o*-MeBz) and 4-*tert*-butylbenzoate (*p*-*t*BuBz). Here we report the synthesis and the crystal structure of two decanuclear cobalt cages incorporating these ligands.

2. Experimental

All reagents, metal salts and ligands were used as obtained from Aldrich. Sodium salts of pyridone ligands were obtained by deprotonation of the corresponding hydroxypyridine in methanol using sodium methoxide followed by evaporation to dryness. Ana-

lytical data were obtained using an EA1108 elemental analyzer from Carlo Erba Instruments.

2.1. Synthesis of $[\text{Co}_{10}(\text{OH})_6(\text{chp})_6(\text{o-MeBz})_7(\text{n-C}_3\text{H}_7\text{OH})_5][\text{o-MeBz}]$ **1**

Hydrated cobalt nitrate (1.00 g, 3.4 mmol), Na(*o*-MeBz) (0.54 g, 3.4 mmol) and Na(chp) (0.52 g, 3.4 mmol) were added to MeOH (80 ml), and the solution stirred for 24 h before being filtered and evaporated to dryness under reduced pressure. The purple powder obtained was dried under vacuum for several hours and then extracted with *n*-propanol (20 ml) to give a pink solution which was filtered, and from which pink crystals of **1** grew from slow evaporation of the solvent in a 35% yield after four days. Elemental analysis calculated for $\text{C}_{109}\text{H}_{120}\text{O}_{33}\text{N}_6\text{Cl}_6\text{Co}_{10}$: C, 46.03; H, 4.25; N, 2.95; found: C, 45.74; H, 4.05; N, 3.10.

2.2. Synthesis of $[\text{Co}_{10}(\text{OH})_6(\text{mhp})_6(\text{p-tBuBz})_8(\text{Hmhp})_2(\text{CH}_3\text{CN})_2]$ **2**

Hydrated cobalt nitrate (1.00 g, 3.4 mmol), Na(*p*-*t*BuBz) (1.37 g, 6.8 mmol) and Na(mhp) (0.89 g, 6.8 mmol) were added to MeOH (80 ml), and the solution stirred for 24 h before being filtered and evaporated to dryness under reduced pressure. The powder obtained was dried in vacuum for several hours and then extracted with acetonitrile (15 ml) to give a pink solution which was filtered, and from which pink crystals of **2** grew from diethyl ether diffusion in a 25% yield after 7 days. Elemental analysis calculated for $\text{C}_{140}\text{H}_{166}\text{O}_{30}\text{N}_{10}\text{Co}_{10}$: C, 54.98; H, 5.47; N, 4.58; found: C, 54.77; H, 5.35; N, 4.32.

2.3. Structural studies

Crystal data, data collection and refinement parameters for compounds **1** and **2** are given in Table 1. Selected bond lengths and angles for these two complexes are given in Tables 2–5.

3. Results

3.1. Crystal structure of **1**

The structure of the cationic part of $[\text{Co}_{10}(\text{OH})_6(\text{chp})_6(\text{o-MeBz})_7(\text{n-C}_3\text{H}_7\text{OH})_5][\text{o-MeBz}]$ **1** is shown

Table 1
Experimental data for the X-ray diffraction studies of compounds **1** and **2**.

Compound	1	2
Formula	C ₁₀₉ H ₁₂₀ Cl ₆ Co ₁₀ N ₆ O ₃₃	C ₁₄₀ H ₁₆₆ Co ₁₀ N ₁₀ O ₃₀ ·C ₂ H ₃ N·3 H ₂ O
<i>M</i>	2844.11	3153.23
Crystal system	monoclinic	orthorhombic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>Ccca</i>
<i>a</i> (Å)	16.202(10)	32.75(2)
<i>b</i> (Å)	28.91(3)	34.68(2)
<i>c</i> (Å)	27.973(10)	29.352(19)
β (°)	90.46(4)	
<i>U</i> (Å ³)	13103(16)	33342(38)
<i>T</i> (K)	293(2)	150(2)
<i>Z</i>	4	8
ρ_{calcd} (g cm ⁻³)	1.442	1.256
Crystal shape and colour	pink plate	pink plate
Crystal size (mm)	0.30 × 0.15 × 0.08	0.20 × 0.15 × 0.05
<i>M</i> (mm ⁻¹)	1.425	1.035
<i>F</i> (000)	5808	13104
Theta range (°)	1.89 to 25.04	1.71 to 25.02
Limiting indices	0 ≤ <i>h</i> ≤ 19, 0 ≤ <i>k</i> ≤ 34, -33 ≤ <i>l</i> ≤ 33	-38 ≤ <i>h</i> ≤ 30, -41 ≤ <i>k</i> ≤ 40, -34 ≤ <i>l</i> ≤ 25
Reflections collected / unique	21197/21197	83608/14711
Data / restraints / parameters	21197/3197/1423	14711/467/783
<i>R</i> 1, <i>wR</i> 2	0.0643, 0.1887	0.0841, 0.2358
Goodness of fit	0.942	0.871

in Fig. 1. The compound crystallises in the monoclinic space group *P*2₁/*n*. The ten cobalt atoms of **1** form a centred-tricapped-trigonal prism bridged by hydroxide, carboxylate and pyridonate ligands. The central cobalt atom Co1 is bound to six μ_3 -hydroxide ligands, which are bridging to the nine remaining metals to form the tricapped-trigonal prism. The six metal atoms

at the vertices of the trigonal prism (Co3, Co4, Co6, Co7, Co9 and Co10) are sharing one μ_3 -OH with the central cobalt and the metal atoms capping the rectangular faces of the prism (Co2, Co5 and Co8) are sharing two μ_3 -OH ligands with this same cobalt atom.

Table 2
Cobalt bond length ranges (Å) with e.s.d.s between parentheses for **1**.

Bonds involving central Co atom (Co1)	
Co–OH	2.090(4)–2.125(4)
Bonds involving metal atoms capping square faces of trigonal prism (Co2, Co5 and Co8)	
Co–OH	2.048(4)–2.096(4)
Co–O (bridging O ₂ CR)	2.012(5)–2.040(5)
Co–O (chp)	2.183(4)–2.263(4)
Bonds involving metal atoms at vertices of trigonal prism (Co3, Co4, Co6, Co7, Co9 and Co10)	
Co–OH	1.999(4)–2.034(4)
Co–O (bridging O ₂ CR)	2.000(5)–2.017(5)
Co–O (terminal O ₂ CR)	2.072(6)
Co–O (chp)	2.172(5)–2.316(4)
Co–O (n-PrOH)	2.111(5)–2.182(5)
Co–N (chp)	2.111(6)–2.166(5)

Six chp ligands and six 2-methylbenzoate ligands bridge the exterior of the prism. Each chp ligand binds through its N-donor atom to one of the cobalt atoms at the vertices of the prism, and μ_3 -bridges through the O-atom. Following the Harris notation, the chp are adopting the 3.31 bridging mode. The Harris notation [9] describes the binding mode as [X·Y₁Y₂Y₃...Y_{*n*}], where X is the overall number of metals bound by the whole ligand, and each value of Y refers to the number of metal atoms attached to the different donor atoms. Therefore for both acetate and chp, there will be two values for Y. The ordering of Y is listed by the Cahn-Ingold-Prelog priority rules, hence O before N. The O-atom of chp is attached to: the metal vertex to which the N-atom is bound, the other vertex forming a side of the trigonal prism and a cobalt site capping a square face of the prism. The six O-atoms from the pyridonate ligand are then occupying the six triangular faces

Table 3

Cobalt bond angle ranges (°) with e.s.d.s. between parentheses for **1**.

Angles involving central Co atom (Co1)	
OH–Co–OH cis	81.44(16)–106.86(16)
OH–Co–OH trans	161.54(16)–161.95(16)
Angles involving metal atoms capping square faces of trigonal prism (Co2, Co5 and Co8)	
OH–Co–OH	83.06(16)–83.27(17)
OH–Co–O (bridging O ₂ CR) cis	91.76(17)–94.48(18)
OH–Co–O (bridging O ₂ CR) trans	168.72(18)–171.86(17)
OH–Co–O (chp)	75.78(16)–94.02(16)
O (bridging O ₂ CR)–Co–O (chp)	92.73(17)–98.24(19)
O (bridging O ₂ CR)–Co–O (bridging O ₂ CR)	90.9(2)–92.02(19)
O (chp)–Co–O (chp)	162.78(15)–163.84(14)
Angles involving metal atoms at vertices of trigonal prism (Co3, Co4, Co6, Co7, Co9 and Co10)	
OH–Co–O (bridging O ₂ CR)	94.45(18)–96.91(18)
OH–Co–O (chp) chelating metal site	98.80(15)–102.66(16)
OH–Co–O (chp) bridging metal site	76.11(16)–78.90(16)
OH–Co–O (<i>n</i> -PrOH)	87.86(19)–92.5(2)
OH–Co–O (terminal O ₂ CR)	96.6(2)
OH–Co–N (chp)	158.2(2)–163.40(19)
O (bridging O ₂ CR)–Co–O (chp) chelating	161.39(18)–163.71(17)
O (bridging O ₂ CR)–Co–O (chp) bridging	95.5(2)–98.5(2)
O (bridging O ₂ CR)–Co–O (<i>n</i> -PrOH)	94.1(2)–95.3(2)
O (bridging O ₂ CR)–Co–O (terminal O ₂ CR)	93.4(2)
O (bridging O ₂ CR)–Co–N (chp)	101.2(2)–104.8(2)
O (chp) chelating–Co–O (chp) bridging	78.37(16)–81.68(17)
O (chp) chelating–Co–O (<i>n</i> -PrOH)	91.2(2)–92.60(19)
O (chp) chelating–Co–O (terminal O ₂ CR)	94.9(2)
O (chp) chelating–Co–N (chp)	59.29(19)–60.99(17)
O (chp) bridging–Co–O (<i>n</i> -PrOH)	162.27(19)–167.4(2)
O (chp) bridging–Co–O (terminal O ₂ CR)	169.0(2)
O (chp) bridging–Co–N (chp)	94.87(19)–99.63(18)
O (<i>n</i> -PrOH)–Co–N (chp)	90.2(2)–91.8(2)
O (terminal O ₂ CR)–Co–N (chp)	88.8(2)

formed by the nine cobalt atoms: they are at the centre of the faces formed by a side of the prism and one of the caps.

Six of the seven 2-methylbenzoate ligands (*o*-MeBz) are bridging in a 2.11 fashion (Harris notation [9]) between cap and vertex sites, each cap being attached to two carboxylate ligands. To complete the structure, the last *o*-MeBz is in apical position to one of the metal vertex (Co7), at hydrogen bond distance of two *n*-propanol, whereas five *n*-propanol molecules from the crystallisation are attached to the five remaining cobalt atoms of the trigonal prism. The positive charge of the cluster is countered by the presence of an *o*-MeBz anion in the lattice.

Table 4

Cobalt bond length ranges (Å) with e.s.d.s. between parentheses for **2**.

Bonds involving central Co atom (Co1)	
Co–OH	2.089(7)–2.167(6)
Bonds involving metal atoms at vertices (Co2 to Co6)	
Co–OH	1.987(6)–2.077(7)
Co–O (bridging O ₂ CR)	2.008(8)–2.125(7)
Co–O (chelating O ₂ CR)	2.128(7)–2.245(7)
Co–O (μ_3 -mhp)	2.131(7)–2.272(7)
Co–O (μ_2 -mhp)	2.031(7)–2.167(7)
Co–O (Hmhp)	2.110(7)
Co–N (μ_3 -mhp)	2.090(9)–2.135(9)
Co–N (μ_2 -mhp)	2.166(9)
Co–N (MeCN)	2.108(10)

The structure of **1** is based once again on the centred-tricapped-trigonal prismatic metal core [M₁₀(μ_3 -OH)₆(η_2 , μ_3 -xhp)₆(η_2 , μ_2 -O₂CR)₆]²⁺ (several complexes have been previously obtained with M = Co or Ni, xhp = 2-chloro or 2-methylpyridonate and O₂CR = chloroacetate, dimethylacetate, diphenylacetate, trimethylacetate or benzoate) [7]. Obviously, the substituted benzoate used does not induce the formation of a new cage structure, probably because it is not bulky enough. This is the first time that such a compound is obtained with cobalt when 2-chloropyridonate is used as the N-donor ligand. This novelty may be due to the improved solubility of the cage, provoked by the substituted benzoate. Using *n*-propanol as crystallisation solvent is not very common, which may also explain the isolation of **1**.

3.2. Crystal structure of **2**

The structure of [Co₁₀(OH)₆(mhp)₆(*p*-tBuBz)₈(Hmhp)₂(CH₃CN)₂] **2** is shown in Fig. 2. The cluster crystallises in the orthorhombic space group *Ccca*. A two-fold symmetry axis passes through Co1 and Co5. The central cobalt atom Co1 is surrounded by six μ_3 -hydroxide ligands, which are bridging to the nine remaining metals. The 4-tertbutylbenzoate ligands are adopting two coordination modes: six of them are bridging between two cobalt atoms (2.11 mode) and each of the remaining two is chelating one metal (1.11 mode). The eight pyridonate ligands are adopting three coordination modes: four of them are bridging between three cobalt centres (in a 3.31 fashion according to Harris notation [9]), two other mhp are only bridging

Table 5
Cobalt bond angle ranges (°) with e.s.d.s between parentheses for **2**.

Angles involving central Co atom (Co1)	
OH–Co–OH cis	80.1(4)–105.0(3)
OH–Co–OH trans	160.1(2)–168.7(4)
Angles involving metal atoms at vertices (Co2 to Co6)	
OH–Co–OH	81.7(4)–83.8(3)
OH–Co–O (bridging O ₂ CR) cis	93.8(3)–102.2(3)
OH–Co–O (bridging O ₂ CR) trans	168.9(3)–174.8(3)
OH–Co–O (chelating O ₂ CR)	89.3(3)–94.6(3)
OH–Co–O (μ ₃ -mhp)	76.7(3)–106.5(3)
OH–Co–O (μ ₂ -mhp)	84.4(3)–98.7(3)
OH–Co–O (Hmhp)	83.5(3)–91.4(3)
OH–Co–N (μ ₃ -mhp)	160.1(3)–167.4(3)
OH–Co–N (μ ₂ -mhp)	158.7(3)
OH–Co–N (MeCN)	88.3(3)
O (bridging O ₂ CR)–Co–O (bridging O ₂ CR)	80.8(3)–92.4(4)
O (bridging O ₂ CR)–Co–O (chelating O ₂ CR)	97.4(3)–155.5(3)
O (bridging O ₂ CR)–Co–O (μ ₃ -mhp)	90.3(3)–165.5(3)
O (bridging O ₂ CR)–Co–O (μ ₂ -mhp)	94.4(3)–96.6(3)
O (bridging O ₂ CR)–Co–O (Hmhp)	91.3(3)–94.1(3)
O (bridging O ₂ CR)–Co–N (μ ₃ -mhp)	93.6(4)–105.5(4)
O (bridging O ₂ CR)–Co–N (μ ₂ -mhp)	88.6(3)
O (bridging O ₂ CR)–Co–N (MeCN)	95.3(4)
O (chelating O ₂ CR)–Co–O (chelating O ₂ CR)	59.9(3)
O (chelating O ₂ CR)–Co–O (μ ₂ -mhp)	105.3(3)–160.8(3)
O (chelating O ₂ CR)–Co–N (μ ₂ -mhp)	88.1(3)–103.4(3)
O (μ ₃ -mhp)–Co–O (μ ₃ -mhp)	78.0(3)–169.1(4)
O (μ ₃ -mhp)–Co–O (μ ₂ -mhp)	90.1(3)–158.4(3)
O (μ ₃ -mhp)–Co–O (Hmhp)	169.3(3)
O (μ ₃ -mhp)–Co–N (μ ₃ -mhp)	97.7(3)–104.9(3)
O (μ ₃ -mhp)–Co–N (MeCN)	98.2(4)–162.5(4)
O (μ ₂ -mhp)–Co–N (μ ₃ -mhp)	93.3(3)
O (μ ₂ -mhp)–Co–N (μ ₂ -mhp)	61.8(3)
N (μ ₃ -mhp)–Co–N (MeCN)	87.9(4)

two metal sites (2.21 bridging mode) and each of the remaining two are linked through the oxygen to only one cobalt, which shows that they are in their protonated form: Hmhp. To complete this structure, two acetonitrile from the crystallisation solvent are also present, linked to two cobalt atoms through their nitrogen.

The structure of **2** is not directly related to a trigonal prismatic metal core: the 4-*tert*-butylbenzoate ligand has induced the formation of a different cage structure. This type of core has been previously seen in three compounds when pivalate (piv) was used as the carboxylate in blend reactions [7]. The geometry of these

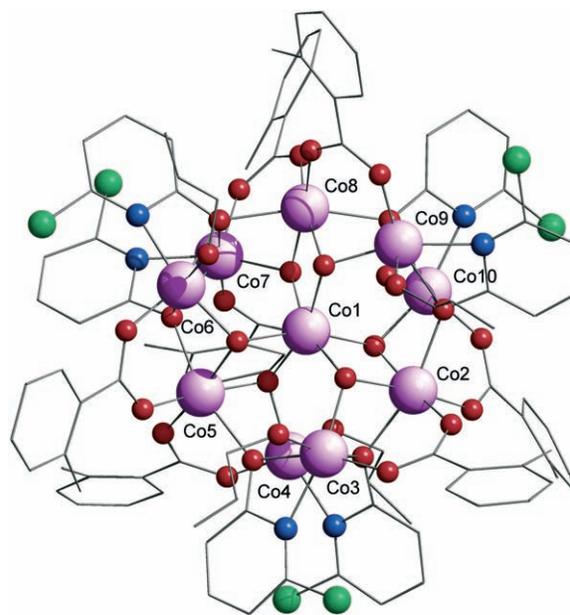


Fig. 1. Structure of the cationic part of **1** in the crystal. Colour scheme: Co, pink; O, red; N, blue, Cl, green; C, grey.

three compounds of formula $[M_{10}(\text{OH})_4(\text{xhp})_{10}(\text{piv})_6(\text{S})_2]$ (where $M = \text{Ni}$ or Co , $\text{xhp} = \text{chp}$ or mhp and $\text{S} = \text{MeOH}$ or EtOH) was related to a centred tetracosahedron where five vertices are missing [10]. This structure has also been described as a centred pentacapped trigonal prism missing one edge of the prism [7]. This second description seems a little artificial, but it does recognize the similarity between structures such as **1** and **2**.

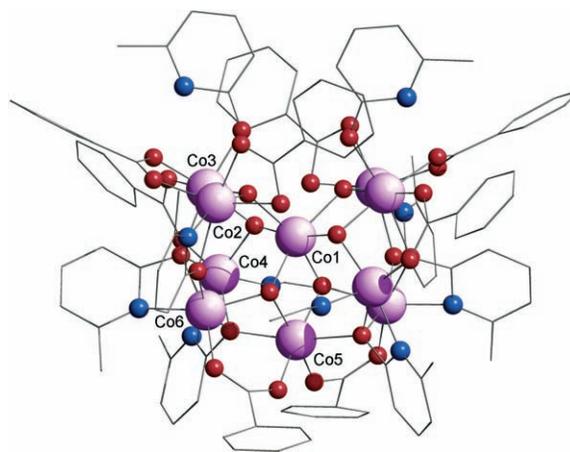


Fig. 2. Structure of **2** in the crystal. Colour scheme as in Fig. 1.

While the core of **2** is similar to these previous examples its general formula differs from the three previous examples: two more hydroxides and two more carboxylates are present but there are only six pyridonate ligands instead of ten, and two protonated pyridonates are coordinated to **2**. The three crystallographically distinct μ_3 -OH are respectively bridging between Co1, Co2 and Co3; Co1, Co3 and Co4; and Co1, Co5 and Co6. As for **1**, the central cobalt is sharing two hydroxo bridges with Co5, Co3 and the symmetry equivalent of Co3. Three of the four crystallographically independent carboxylates act as 2.11-bridges between Co2 and Co3, Co3 and Co4, and Co5 and Co6, whereas the remaining *p*-*t*BuBz chelates Co2. Concerning the three independent mhp ligands: the first one is linked to Co4 through its nitrogen and bridges between Co4, Co5 and Co6 through its oxygen; the second one is nitrogen bounded to Co6 and the oxygen is linked to Co3, Co4 and Co6 and finally the nitrogen of the last one is linked to Co2 and its oxygen is coordinated to Co2 and Co6. The 2-methyl-6-hydroxypyridine (Hmhp) is oxygen bounded to Co3 and the acetonitrile from the crystallisation solvent is linked to Co4.

4. Conclusion

The use of the benzoate-based carboxylates *o*-MeBz and *p*-*t*BuBz in blend reactions with cobalt salts and pyridonates ligands has allowed us to isolate two new cobalt cages **1** and **2**. In each case, the structure obtained has already been seen, but some differences have been observed due to the change in the size of the ligand and/or its solubility. We had previously assumed that it was the steric demands imposed by pivalate that led to the formation of the distorted core, as found in **2**, in preference to the more regular trigonal prismatic core, as found in **1**. However here the steric requirements imposed by the benzoate ligand substituted at the ortho position must be greater than the requirements of the para-substituted ligand but the structures found are reversed, i.e. the ‘more distorted’ core is found with the less sterically demanding ligand. This argues the structural control is subtler.

It is very easy to neglect reaction conditions when considering structure, and consider only the components found in the final crystal. However, here it may

be we are seeing the influence of the relative solubilities imposed by differing carboxylates. The distorted tetraicosahedral core is *only* found when a *t*-butyl-group is found in the carboxylate – either directly attached (as in pivalate) or attached to a benzoate ligand. It seems possible that these highly solubilising groups are keeping the cages in solution longer, and hence leading to new topologies. We intend to hypothesise this theory by looking at other ligands featuring a tertiary butyl group. This hypothesis also suggests a new direction for study: use of ligands substituted to induce new solubilities, e.g. polyfluorinated carboxylates.

The use of more sterically demanding ligands, e.g., triphenylacetate lead to greater changes in the structures observed [11, 12]. At present, we can only take note of the differences and similarities between structures in order to understand the conditions that favour certain topologies. Then, hopefully, by varying parameters in the synthesis and comparing the results obtained, we will be able to control the properties of the cages formed.

5. Supplementary material

Full details of the crystal structure investigations have been deposited. CCDC-190087 and CCDC-190088 contain the supplementary crystallographic data for the structures reported in this paper, including atom coordinates, thermal parameters and remaining bond lengths and angles. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, or on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ (UK) on quoting the full journal citation.

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