

The structure of $\{[\text{Co}(\text{pht})(\text{bpy})(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}\}_n$ (pht is phthalate and bpy is 4,4'-bipyridine) and the role of solvent water clusters in structure stability

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The Co^{II} cation in poly[[aqua(μ -benzene-1,2-dicarboxylato- $\kappa^3\text{O}^1, \text{O}^2: \text{O}^1$)(μ -4,4'-bipyridine- $\kappa^2\text{N}: \text{N}'$)cobalt(II)] trihydrate], $\{[\text{Co}(\text{C}_8\text{H}_4\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}\}_n$, is octahedrally coordinated by two N atoms of two 4,4'-bipyridine ligands, three O atoms from phthalate anions and a fourth O atom from a coordinated water molecule. The packing consists of planes of coordination polymers linked by hydrogen bonds mediated by three solvent water molecules; the linkage is achieved by the water molecules forming intricate oligomeric clusters which also involve the O atoms of the phthalate ligands.

Keywords: crystal structure; hydrated cobalt complex; two-dimensional covalent arrays; two-dimensional coordination polymer; stabilizing water clusters; TBG porous coordination polymer.

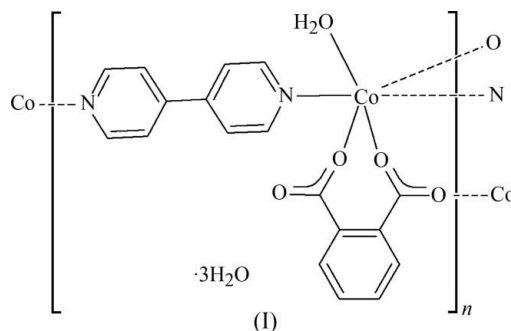
1. Introduction

The design and synthesis of structures with one-, two- or three-dimensional architectures is nowadays a feasible and well established field (Desiraju, 1989; Simon & Bassoul, 2000). The general strategy relies on the use of multidentate O- or N-donor ligands with the ability to bridge metal centres into a varied range of polymeric structures, from very simple to extremely intricate ones. In this respect, the 4,4'-bipyridine (bpy) ligand is perhaps the most commonly used linear spacer, able to form (on its own) polymers of different dimensionality, *viz.* one- (Liu *et al.*, 2009), two- (Habermehl & Loeb, 2007) or, in conjunction with polycarboxylic acids, three-dimensional (Li *et al.*, 2005).

From the many systems with bpy ligands studied so far, that involving transition metal centres (Tr) and benzene-1,2-dicarboxylate (pht) attracted our interest due to the many different species obtainable through slight variations in the synthetic conditions, differences which involve not only the cation-to-ligands ratio, but also the number of aqua ligands and solvent water molecules. For simplicity, in what follows we shall represent a general formula of the form $\text{Tr}(\text{pht})_{n1}\text{-(bpy)}_{n2}(\text{H}_2\text{O})_{n3}\cdot(\text{H}_2\text{O})_{n4}$ by the shorthand notation $n1:n2:n3:(n4)$.

A search of the Cambridge Structural Database (CSD, Version 5.34; Allen, 2002) revealed five different formulations within this general family (see Table 1). Analysis of the original reports allows us to infer some general trends regarding the sensitivity of the formulation towards synthetic conditions (temperature), namely that compounds in the most populated group A [1:1:2:(2)] derive from lower-temperature conditions (thermodynamic control), while the rest appear at higher temperatures (kinetic control).

Trying to fine-tune this temperature dependence in the case of $\text{Tr} = \text{Co}$, we obtained (see *Experimental*) the so far unreported 1:1:1:(3) polymeric complex poly[[aqua(μ -benzene-1,2-dicarboxylato- $\kappa^3\text{O}^1, \text{O}^2: \text{O}^1$)(μ -4,4'-bipyridine- $\kappa^2\text{N}: \text{N}'$)cobalt(II)] trihydrate], $\{[\text{Co}(\text{pht})(\text{bpy})(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}\}_n$ (pht is phthalate and bpy is 4,4'-bipyridine), (I). The complex is the Co isologue of its previously reported Ni counterpart (Yang *et al.*, 2003).



2. Experimental

2.1. Synthesis and crystallization

The title compound was synthesized hydrothermally from cobalt(II) chloride hexahydrate (0.119 g, 0.5 mmol), 4,4'-bipyridine (0.156 g, 1.0 mmol) and potassium hydrogen phthalate (0.102 g, 0.5 mmol) mixed with water (10 ml). The mixture was heated in a 23 ml Teflon-lined stainless steel vessel to 473 K for 4 d. The vessel was then cooled to room temperature at a rate of 5 K h⁻¹. Beautiful red prismatic crystals of (I) were separated from the solution. Analysis for $\text{C}_{18}\text{H}_{20}\text{CoN}_2\text{O}_8$ found (calculated): C 48.3 (47.91), H 4.3 (4.47), N 6.4% (6.21%).

Differential scanning calorimetry (DSC) experiments on selected single crystals were conducted on a Shimadzu DSC-50 apparatus at a heating rate of 5 K min⁻¹ under an N₂ atmos-

Table 1

Summary of transition metal complexes of the general formula $\text{Tr}(\text{pht})_{n1}(\text{bpy})_{n2}(\text{H}_2\text{O})_{n3} \cdot (\text{H}_2\text{O})_{n4}$, represented by the shorthand notation $n1:n2:n3:(n4)$.

CSD refcode	Tr	Space group	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)	<i>V</i> (Å ³)	ρ (g cm ⁻³)
Group A, formula 1:1:2:(2)										
BASMIS01 ^a	Mn	<i>P2</i> / <i>n</i>	7.69	11.59	10.75	90	92.67	90	957.16	1.552
JEKTUP ^b	Zn	<i>P2</i> / <i>n</i>	7.63	11.32	10.81	90	92.44	90	933.35	1.629
NEDXEZ ^c	Cd	<i>P2</i> / <i>n</i>	7.79	11.65	10.70	90	92.59	90	969.73	1.729
NEDXOJ01 ^d	Co	<i>P2</i> / <i>n</i>	7.61	11.36	10.81	90	92.28	90	933.65	1.605
QEHUC ^e	Fe	<i>P2</i> / <i>n</i>	7.65	11.39	10.79	90	92.67	90	939.15	1.585
TEJKUP ^f	Cu	<i>P2</i> / <i>c</i>	7.70	11.10	12.97	90	123.7	90	922.25	1.642
WIPFOR ^{†g}	Ni	<i>P2</i> / <i>c</i>	7.62	11.37	12.95	90	123.6	90	934.16	1.604
Group B, formula 2:1:0:(0)										
FEQSO ^h	Cd	<i>I4</i> 22	8.29	8.29	33.75	90	90	90	2321.90	1.713
LESBEQ ⁱ	Co	<i>I4</i> 122	8.16	8.16	32.93	90	90	90	2190.30	1.654
Group C, formula 2:2:0:(0)										
IZASIL ^j	Zn	<i>P</i> $\bar{1}$	7.51	10	22.08	84.31	88.08	71.02	1560.50	1.507
Group D, formula 1:1:2:(0.5)										
WEDNEA ^k	Ni	<i>P4</i> ₁ 2 ₁ 2	11.30	11.27	29.90	90	90	90	3796.60	1.484
Group E, formula 1:1:1:(3)										
KAQEP ^l	Ni	<i>P2</i> ₁	11.10	8.38	11.27	90	115.4	90	949.42	1.578
(I)	Co		11.10	8.40	11.37	90	115.6	90	956.85	1.566

† In spite of being refined in the space group *P2*/*c*, these structures are isomorphous with those described in *P2*/*n*. References: (a) Koeflerstein & Robl (2007a); (b) Li *et al.* (2006); (c) Suresh *et al.* (2001); (d) Koeflerstein & Robl (2007b); (e) Fan *et al.* (2006); (f) Xu *et al.* (2006); (g) Zhang *et al.* (2008); (h) Wang *et al.* (2005); (i) Lightfoot & Snedden (1999); (j) Tang *et al.* (2004); (k) Gong *et al.* (2012).

Table 2

Experimental details.

Crystal data	
Chemical formula	[Co(C ₈ H ₄ O ₄)(C ₁₀ H ₈ N ₂)(H ₂ O)]·3H ₂ O
<i>M_r</i>	451.30
Crystal system, space group	Monoclinic, <i>P2</i> ₁
Temperature (K)	294
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.0975 (6), 8.4039 (3), 11.3732 (6)
β (°)	115.564 (7)
<i>V</i> (Å ³)	956.85 (10)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.95
Crystal size (mm)	0.35 × 0.30 × 0.25
Data collection	
Diffraction	Oxford Gemini S Ultra CCD area-detector diffractometer
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Oxford Diffraction, 2009)
<i>T_{min}</i> , <i>T_{max}</i>	0.72, 0.74
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	14398, 4451, 4096
<i>R_{int}</i>	0.037
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.679
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.033, 0.084, 0.95
No. of reflections	4451
No. of parameters	286
No. of restraints	17
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.56, -0.31
Absolute structure	Flack (1983), with 2206 Friedel pairs
Absolute structure parameter	-0.016 (12)

Computer programs: *CrysAlis PRO* (Oxford Diffraction, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXTL* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

phere, using aluminium pans. Thermogravimetric analysis (TGA) was performed under similar conditions using a Shimadzu TGA-51H thermobalance. Elemental analyses were carried out at the Servicio a Terceros of INQUIMAE on a Carlo Erba CHNS-O EA1108 analyser.

Diffuse reflectance spectra were acquired on a pressed sample (Na₂SO₄ diluted) on an Ocean Optics instrument (OOIBase32) with a 50 mm integrating sphere. Typical corrections were applied; the corrected reflectance value for a given sample was thus calculated as $R = (S_a - D)/(R_{\text{ref}} - D)$, where *S_a*, *R_{ref}* and *D* stand for the measured values for that sample, for the reference and in the dark, respectively. The *K/S* coefficient, where $K = (1 - R)^2$ and $S = 2R$, has been plotted against λ . For compound (I): $\lambda_{\text{max}} = 490$ nm; for the dehydration product: $\lambda_{\text{max}} = 550$ nm

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. In the specimen analysed, water atoms O3W and O4W appeared slightly underpopulated, but refinement of their site-occupancy factors showed an oscillating behaviour due to severe correlation with the corresponding displacement parameters. In order to circumvent this problem, after a few cycles of refinement they were kept fixed at the average value (0.8 and 0.7, respectively) of those they had attained in the preceding cycles. H atoms attached to atoms O1W and O2W were clearly seen in the difference map; those for atoms O3W and O4W could not be reliably assigned, and the most probable peaks were included in the model and refined with stringent internal restraints [$\text{O}-\text{H} = 0.850$ (1) Å and $\text{H}\cdots\text{H} = 1.35$ (1) Å] subject to

Table 3
 Selected bond lengths (Å).

Co1—O21	2.0710 (18)	Co1—O1W	2.1141 (17)
Co1—O41 ⁱ	2.0819 (16)	Co1—N12	2.1486 (17)
Co1—O31	2.0947 (18)	Co1—N22 ⁱⁱ	2.1678 (17)

 Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + 1$; (ii) $x, y, z - 1$.

Table 4
 π - π contacts (Å, °).

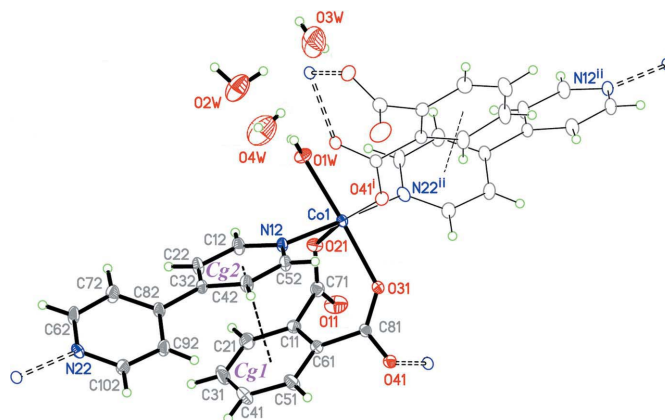
*Cg*1 is the centroid of the C11/C21/C31/C41/C51/C61 ring and *Cg*2 that of the N12/C12/C22/C32/C42/C52 ring. IPD is the mean interplanar distance (average distance from one of the planes to the neighbouring centroid), CCD the centre-to-centre distance and DA the dihedral angle between planes; for details, see Janiak (2000).

<i>Cg</i> ... <i>Cg</i> '	CCD (Å)	IPD (Å)	DA (°)
<i>Cg</i> 1... <i>Cg</i> 2	3.5851 (17)	3.48 (5)	16.39 (14)

nearest-neighbour anti-bumping constraints [$H \cdots H' > 2.25$ (1) Å]. After convergence, all water H atoms appeared in positions compatible with the difference map and were involved in hydrogen bonding. In all cases, $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(\text{parent})$

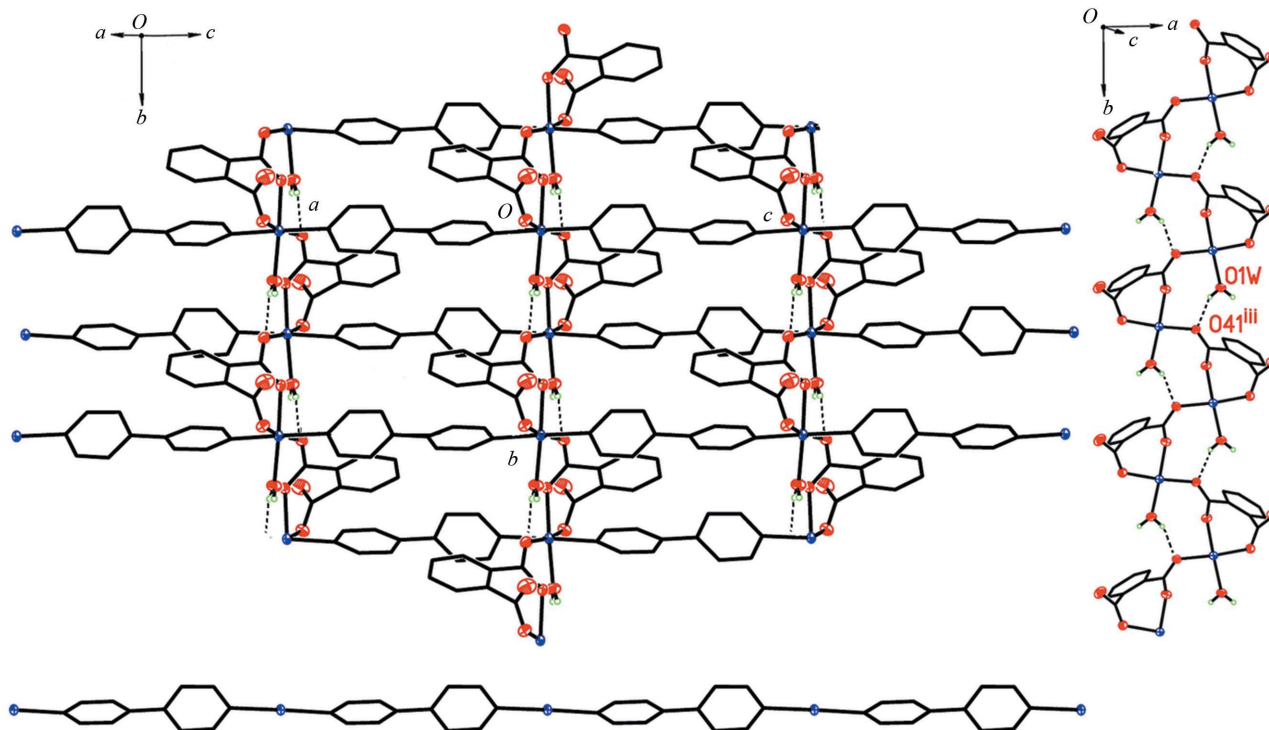
3. Results and discussion

Fig. 1 shows an ellipsoid plot of the asymmetric unit of (I) and Table 3 provides the coordination distances. The cobalt(II) cation has a CoN_2O_4 octahedral coordination, the N atoms


Figure 1

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. Single dashed lines indicate π - π contacts and double-dashed lines indicate the coordination to vicinal Co^{II} cations. [Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + 1$; (ii) $x, y, z - 1$.]

being provided by two 4,4'-bipyridine (bpy) ligands, three O atoms by phthalate anions (pht) and the fourth O atom coming from a coordinated water molecule. In spite of the coordination distances being rather even in each group [Co—O = 2.0710 (18)–2.1141 (17) Å and Co—N = 2.1486 (17)–2.1678 (17) Å], the octahedron appears somewhat distorted due to the coordination angles departing significantly from their ideal values, mainly due to chelation of pht [*cis/trans* angles = 90 ± 7.52 (7) and 180 ± 10.29 (7)°]. The stability of the


Figure 2

A packing view of one of the (100) planes. On both sides (right and bottom) are given detailed views of the columnar arrays defining the (vertical and horizontal) linking units. Dashed lines represent hydrogen bonds. [Symmetry code: (iii) $x, y + 1, z$.]

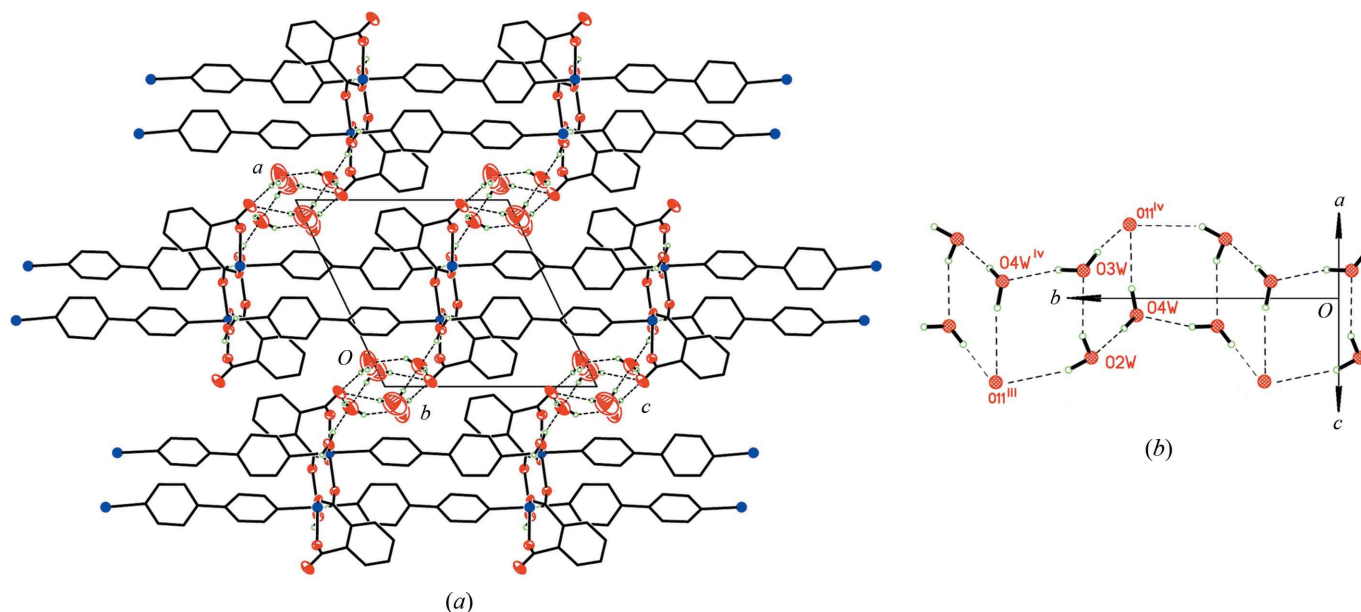


Figure 3 Packing views of (I), along [010], showing (a) a projection in the (100) plane and (b) the [010] hydrogen-bonded water ribbons. Dashed lines represent hydrogen bonds. [Symmetry codes: (iii) $x, y + 1, z$; (iv) $-x, y + \frac{1}{2}, -z$.]

coordinated assembly is enhanced by an intramolecular π - π interaction between the pht group and one of the substituted aromatic rings in bpy (Fig. 1 and Table 4). The overall structure can be described as formed by columnar Co-pht arrays (Fig. 2, right inset), with the tricoordinated anions binding one Co^{II} cation in chelating mode *via* atoms O21 and O31 from two different carboxylate groups, while bridging a second cation through atom O41. The result is a zigzag chain built up around a 2_1 axis, running along [010], as shown in the inset. The chain cohesion is enhanced by an intra-chain hydrogen bond (first entry in Table 5). These one-dimensional structures are in turn linked along [001] by the bpy ligand, acting in its usual bridging mode (Fig. 2, lower inset), to form a firmly bound two-dimensional structure parallel to (100).

Finally, these sheets are stacked along [100] to form the final crystal structure (Fig. 3a). This stacking of planes is held together by the solvent water molecules (O2W, O3W and O4W, the latter two being slightly underpopulated in the specific sample measured; see *Refinement* for details), hydrogen bonded to each other (third, sixth and eighth entries in Table 5) to form very labile zigzag ribbons (Fig. 3b) parallel

to the Co-pht chains and filling the interplanar spacing. This hydrophilic structure is parallel to the shortest crystallographic direction, as predicted by the empirical rule of Infantes & Motherwell (2002), and provides the interplanar linkage. This connection is achieved through outgoing hydrogen bonds (having the only uncoordinated carboxylate O atom, O11, as the acceptor; fourth, fifth and seventh entries in Table 5) and incoming ones (second entry in Table 5), thus generating the resulting three-dimensional framework. Compound (I) can thus be considered as a TBG (templated by guests) porous coordination polymer, following Kitagawa's classification (Tanaka & Kitagawa, 2008).

Water cyclic oligomers are often found in metal-organic frameworks (MOFs) and are nowadays actively investigated as models for understanding the properties of bulk water (Mascal *et al.*, 2006). Dimers, tetramers, pentamers, hexamers, octamers and decamers have been identified (Bernini *et al.*, 2012; Colak *et al.*, 2010; Ghosh & Bharadwaj, 2003; Ma *et al.*, 2005; Song *et al.*, 2006; Sun *et al.*, 2007; Yang *et al.*, 2003, 2006; Zhang *et al.*, 2005) in different compounds. In most cases, these oligomers contain only water molecules and are attached to the MOF structure *via* hydrogen bonds. In (I), two kinds of tetramers are found, *viz.* O2W-O3W-O11ⁱⁱⁱ-O4W (type **A**, an *AD-AD-AA-DD* cluster, where *A* indicates a hydrogen-bond acceptor and *D* a hydrogen-bond donor) and O2W-O3W-O4W^{iv}-O11ⁱⁱⁱ (type **B**, a *DD-AD-AD-AA* cluster) which also involves an O atom belonging to the MOF framework; this type is quite rare (Colak *et al.*, 2010; Yang *et al.*, 2003) [symmetry code: (iii) $x, y + 1, z$; (iv) $-x, y + \frac{1}{2}, -z$]. Individual O...O distances lie in the usual range of 2.70–3.05 Å, with the only exception being O3W...O4W^{iv}, which exhibits a significantly shorter value of 2.576 (6) Å. Average O...O distances are 2.86 (13) and 2.80 (19) Å for type **A** and type **B** tetramers, respectively, in agreement with the previous

Table 5 Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O1W–H1WA...O41 ⁱⁱⁱ	0.85 (2)	2.02 (1)	2.810 (2)	154 (1)
O1W–H1WB...O2W	0.85 (1)	1.91 (1)	2.743 (3)	167 (1)
O2W–H2WA...O3W	0.85 (1)	2.01 (1)	2.751 (5)	145 (1)
O2W–H2WB...O11 ⁱⁱⁱ	0.85 (1)	2.05 (1)	2.867 (4)	161 (2)
O3W–H3WA...O11 ^{iv}	0.85 (1)	2.02 (1)	2.843 (4)	162 (2)
O3W–H3WB...O4W ^{iv}	0.85 (2)	1.80 (1)	2.576 (6)	152 (2)
O4W–H4WB...O11 ^{iv}	0.85 (2)	2.28 (2)	3.038 (4)	150 (2)
O4W–H4WA...O2W	0.85 (1)	1.98 (1)	2.799 (5)	162 (2)
O4W–H4WB...O3W	0.85 (2)	2.51 (3)	3.096 (7)	127.5 (14)

Symmetry codes: (iii) $x, y + 1, z$; (iv) $-x, y + \frac{1}{2}, -z$.

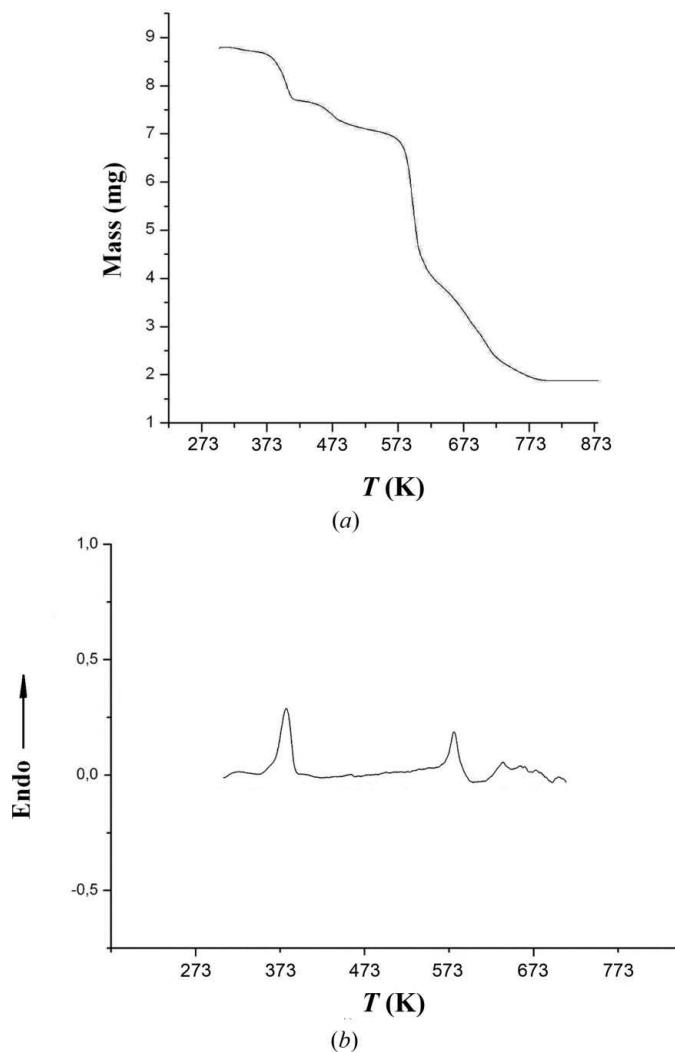


Figure 4
(a) TGA and (b) DSC diagrams for (I).

comment. Three different factors seem to influence the O···O distances in water clusters in confined environments: the nuclearity of each cluster, the degree of condensation of adjacent clusters, and the influence of the framework. The lack of a clear means of establishing their relative influences precludes further interpretations.

The crystallographic characteristics of the water ‘substructure’ suggested that gentle heating of (I) could result in the loss of all three solvent water molecules in a low temperature range. TGA and DSC analyses (Fig. 4) gave quantitative results consistent with an overall loss of three H₂O molecules per formula unit in the temperature range 380–400 K. In particular, DSC runs on individual single crystals of (I) showed an endothermic peak from 370 to 400 K with an enthalpy change of 116 kJ mol⁻¹, consistent with the vaporization heat of 3 moles of water at 370 K (Dortmund Data Bank; <http://www.ddbst.com>). On the other hand, TGA studies on higher masses showed a 12.5% mass loss at 375–405 K (calculated for three H₂O molecules: 12.0%). A ca 5.5%

mass loss, consistent with the leaving of the fourth water molecule (calculated 4.0%), was detected at ca 450 K. Consistent with the important stabilizing role fulfilled by the solvent water molecules, the resulting dehydration product was a powder of poor crystallinity.

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Supporting information for this paper is available from the IUCr electronic archives (Reference: YF3058).

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supplementary materials

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The structure of $\{[\text{Co}(\text{pht})(\text{bpy})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}\}_n$ (pht is phthalate and bpy is 4,4'-bipyridine) and the role of solvent water clusters in structure stability

Miguel Angel Harvey, Sebastián Suarez, Fabio Doctorovich, Fabio D. Cukiernik and Ricardo Baggio

Computing details

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2009); data reduction: *CrysAlis PRO* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

Poly[[aqua(μ -benzene-1,2-dicarboxylato- $\kappa^3\text{O}^1, \text{O}^2: \text{O}^1$)(μ -4,4'-bipyridine- $\kappa^2\text{N}: \text{N}'$)cobalt(II)] trihydrate]

Crystal data

$[\text{Co}(\text{C}_8\text{H}_4\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$

$M_r = 451.30$

Monoclinic, $P2_1$

Hall symbol: P 2yb

$a = 11.0975$ (6) Å

$b = 8.4039$ (3) Å

$c = 11.3732$ (6) Å

$\beta = 115.564$ (7)°

$V = 956.85$ (10) Å³

$Z = 2$

$F(000) = 466$

$D_x = 1.566$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3445 reflections

$\theta = 3.8\text{--}27.9^\circ$

$\mu = 0.95$ mm⁻¹

$T = 294$ K

Prism, red

$0.35 \times 0.30 \times 0.25$ mm

Data collection

Oxford Gemini S Ultra CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans, thick slices

Absorption correction: multi-scan

(*CrysAlis PRO*; Oxford Diffraction, 2009)

$T_{\min} = 0.72$, $T_{\max} = 0.74$

14398 measured reflections

4451 independent reflections

4096 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.037$

$\theta_{\max} = 28.9^\circ$, $\theta_{\min} = 3.6^\circ$

$h = -15 \rightarrow 15$

$k = -11 \rightarrow 11$

$l = -14 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.084$

$S = 0.95$

4451 reflections

286 parameters

17 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0448P)^2 + 0.4467P]$$

where $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\max} = 0.006$$

$$\Delta\rho_{\max} = 0.56 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack (1983), with 2206

Friedel pairs

Absolute structure parameter: -0.016 (12)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Co1	0.35427 (3)	0.50053 (6)	0.41073 (2)	0.02221 (7)	
O11	0.0305 (2)	0.2427 (3)	0.2280 (2)	0.0559 (6)	
O21	0.15083 (17)	0.4560 (2)	0.32261 (18)	0.0326 (4)	
O31	0.39059 (19)	0.2551 (2)	0.42902 (16)	0.0292 (4)	
O41	0.44053 (15)	0.0217 (2)	0.52815 (15)	0.0281 (4)	
C11	0.1390 (2)	0.2443 (3)	0.4571 (2)	0.0288 (5)	
C21	0.0448 (3)	0.2621 (3)	0.5065 (3)	0.0397 (6)	
H21	-0.0332	0.3187	0.4587	0.048*	
C31	0.0648 (3)	0.1978 (4)	0.6243 (3)	0.0484 (8)	
H31	0.0012	0.2125	0.6561	0.058*	
C41	0.1780 (3)	0.1122 (4)	0.6954 (3)	0.0481 (8)	
H41	0.1920	0.0696	0.7757	0.058*	
C51	0.2719 (3)	0.0893 (4)	0.6464 (3)	0.0399 (6)	
H51	0.3469	0.0271	0.6927	0.048*	
C61	0.2552 (2)	0.1586 (3)	0.5287 (2)	0.0277 (5)	
C71	0.1063 (2)	0.3192 (3)	0.3255 (3)	0.0319 (5)	
C81	0.3688 (2)	0.1452 (3)	0.4906 (2)	0.0232 (5)	
N12	0.37286 (17)	0.5158 (3)	0.60643 (16)	0.0253 (4)	
N22	0.34412 (18)	0.4913 (4)	1.21618 (16)	0.0295 (4)	
C12	0.2668 (3)	0.5679 (4)	0.6219 (2)	0.0340 (6)	
H12	0.1949	0.6083	0.5493	0.041*	
C22	0.2578 (3)	0.5651 (3)	0.7385 (2)	0.0347 (6)	
H22	0.1814	0.6027	0.7437	0.042*	
C32	0.3635 (2)	0.5059 (4)	0.84854 (19)	0.0268 (4)	
C42	0.4757 (3)	0.4573 (3)	0.8339 (2)	0.0346 (6)	
H42	0.5505	0.4203	0.9054	0.041*	
C52	0.4761 (2)	0.4637 (3)	0.7132 (2)	0.0318 (6)	
H52	0.5523	0.4300	0.7057	0.038*	
C62	0.2767 (3)	0.5978 (4)	1.1257 (2)	0.0403 (7)	
H62	0.2239	0.6707	1.1438	0.048*	
C72	0.2803 (3)	0.6066 (4)	1.0062 (3)	0.0414 (7)	
H72	0.2326	0.6852	0.9468	0.050*	
C82	0.3556 (2)	0.4975 (4)	0.97543 (19)	0.0280 (4)	
C92	0.4228 (3)	0.3828 (3)	1.0675 (2)	0.0369 (6)	
H92	0.4732	0.3057	1.0503	0.044*	
C102	0.4148 (3)	0.3834 (3)	1.1853 (2)	0.0367 (6)	

H102	0.4607	0.3053	1.2462	0.044*	
O1W	0.30884 (19)	0.74617 (19)	0.39430 (17)	0.0359 (4)	
H1WA	0.3694 (9)	0.8086 (14)	0.4445 (19)	0.043*	
H1WB	0.2452 (8)	0.8072 (13)	0.3472 (15)	0.043*	
O2W	0.1079 (2)	0.9216 (3)	0.2094 (3)	0.0914 (10)	
H2WA	0.1460 (8)	0.947 (2)	0.1613 (9)	0.110*	
H2WB	0.0868 (16)	1.0100 (13)	0.232 (2)	0.110*	
O3W	0.1274 (5)	0.9518 (4)	-0.0226 (3)	0.132 (2)	0.80
H3WA	0.0890 (15)	0.8997 (18)	-0.0931 (9)	0.159*	0.80
H3WB	0.093 (2)	1.0440 (12)	-0.041 (3)	0.159*	0.80
O4W	-0.0925 (4)	0.7527 (6)	0.0073 (3)	0.124 (2)	0.70
H4WB	-0.0722 (18)	0.788 (4)	-0.0518 (11)	0.149*	0.70
H4WA	-0.0434 (19)	0.8035 (15)	0.0761 (8)	0.149*	0.70

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.02774 (13)	0.02391 (12)	0.01810 (12)	0.00001 (15)	0.01284 (10)	0.00015 (14)
O11	0.0597 (14)	0.0495 (12)	0.0385 (11)	-0.0157 (11)	0.0023 (11)	-0.0059 (10)
O21	0.0305 (8)	0.0311 (10)	0.0351 (9)	-0.0013 (7)	0.0130 (8)	0.0044 (6)
O31	0.0391 (9)	0.0255 (8)	0.0319 (9)	0.0032 (8)	0.0236 (8)	0.0034 (7)
O41	0.0297 (7)	0.0250 (9)	0.0317 (8)	0.0021 (7)	0.0153 (6)	0.0043 (7)
C11	0.0273 (11)	0.0261 (11)	0.0356 (12)	-0.0056 (9)	0.0159 (10)	-0.0039 (10)
C21	0.0295 (12)	0.0413 (14)	0.0528 (16)	-0.0012 (12)	0.0221 (13)	-0.0015 (13)
C31	0.0427 (15)	0.0610 (19)	0.0571 (18)	-0.0113 (14)	0.0364 (15)	-0.0095 (15)
C41	0.0511 (17)	0.0612 (19)	0.0448 (16)	-0.0056 (15)	0.0329 (14)	0.0074 (14)
C51	0.0411 (15)	0.0473 (15)	0.0379 (14)	0.0019 (13)	0.0233 (13)	0.0106 (12)
C61	0.0290 (11)	0.0268 (11)	0.0322 (12)	-0.0012 (9)	0.0178 (10)	-0.0006 (9)
C71	0.0257 (11)	0.0353 (13)	0.0351 (13)	0.0016 (10)	0.0135 (11)	-0.0008 (10)
C81	0.0243 (11)	0.0265 (11)	0.0198 (10)	-0.0033 (9)	0.0104 (9)	-0.0034 (8)
N12	0.0290 (8)	0.0289 (10)	0.0210 (8)	0.0021 (10)	0.0136 (7)	-0.0019 (9)
N22	0.0337 (9)	0.0376 (10)	0.0211 (8)	0.0003 (12)	0.0156 (7)	0.0027 (11)
C12	0.0347 (13)	0.0477 (14)	0.0209 (11)	0.0086 (11)	0.0132 (10)	0.0017 (10)
C22	0.0337 (13)	0.0502 (14)	0.0256 (12)	0.0070 (11)	0.0178 (11)	-0.0002 (10)
C32	0.0355 (10)	0.0289 (10)	0.0208 (9)	0.0012 (14)	0.0166 (8)	-0.0024 (14)
C42	0.0340 (12)	0.0468 (17)	0.0225 (11)	0.0113 (10)	0.0118 (10)	0.0051 (9)
C52	0.0322 (11)	0.0406 (16)	0.0275 (11)	0.0086 (10)	0.0176 (10)	0.0014 (9)
C62	0.0553 (17)	0.0465 (15)	0.0269 (13)	0.0215 (13)	0.0250 (13)	0.0056 (11)
C72	0.0567 (17)	0.0472 (15)	0.0243 (12)	0.0206 (13)	0.0212 (12)	0.0089 (11)
C82	0.0331 (10)	0.0340 (10)	0.0195 (9)	0.0039 (15)	0.0136 (8)	0.0007 (14)
C92	0.0516 (16)	0.0389 (13)	0.0276 (12)	0.0141 (12)	0.0241 (12)	0.0033 (10)
C102	0.0526 (16)	0.0367 (13)	0.0251 (12)	0.0102 (13)	0.0209 (12)	0.0054 (10)
O1W	0.0405 (10)	0.0263 (9)	0.0335 (10)	-0.0014 (9)	0.0089 (8)	-0.0038 (7)
O2W	0.100 (2)	0.0791 (19)	0.0711 (19)	0.0338 (18)	0.0147 (17)	-0.0068 (15)
O3W	0.177 (5)	0.141 (6)	0.071 (3)	0.019 (4)	0.047 (3)	-0.025 (3)
O4W	0.138 (5)	0.124 (5)	0.084 (3)	0.012 (4)	0.024 (3)	-0.012 (3)

Geometric parameters (Å, °)

Co1—O21	2.0710 (18)	N22—Co1 ^{iv}	2.1678 (17)
Co1—O41 ⁱ	2.0819 (16)	C12—C22	1.373 (3)
Co1—O31	2.0947 (18)	C12—H12	0.9300
Co1—O1W	2.1141 (17)	C22—C32	1.387 (3)
Co1—N12	2.1486 (17)	C22—H22	0.9300
Co1—N22 ⁱⁱ	2.1678 (17)	C32—C42	1.387 (3)
O11—C71	1.244 (3)	C32—C82	1.485 (3)
O21—C71	1.257 (3)	C42—C52	1.375 (3)
O31—C81	1.244 (3)	C42—H42	0.9300
O41—C81	1.265 (3)	C52—H52	0.9300
O41—Co1 ⁱⁱⁱ	2.0819 (16)	C62—C72	1.380 (4)
C11—C21	1.392 (4)	C62—H62	0.9300
C11—C61	1.392 (3)	C72—C82	1.383 (4)
C11—C71	1.516 (4)	C72—H72	0.9300
C21—C31	1.371 (4)	C82—C92	1.381 (4)
C21—H21	0.9300	C92—C102	1.380 (3)
C31—C41	1.368 (5)	C92—H92	0.9300
C31—H31	0.9300	C102—H102	0.9300
C41—C51	1.391 (4)	O1W—H1WA	0.8501 (10)
C41—H41	0.9300	O1W—H1WB	0.8501 (10)
C51—C61	1.396 (3)	O2W—H2WA	0.8501 (10)
C51—H51	0.9300	O2W—H2WB	0.8500 (10)
C61—C81	1.504 (3)	O3W—H3WA	0.8500 (10)
N12—C52	1.333 (3)	O3W—H3WB	0.8503 (10)
N12—C12	1.336 (3)	O4W—H4WB	0.8500 (10)
N22—C62	1.325 (4)	O4W—H4WA	0.8501 (10)
N22—C102	1.341 (4)		
O21—Co1—O41 ⁱ	169.71 (7)	C52—N12—C12	116.54 (19)
O21—Co1—O31	89.59 (7)	C52—N12—Co1	125.78 (15)
O41 ⁱ —Co1—O31	85.12 (7)	C12—N12—Co1	117.34 (15)
O21—Co1—O1W	88.01 (7)	C62—N22—C102	116.84 (19)
O41 ⁱ —Co1—O1W	97.52 (7)	C62—N22—Co1 ^{iv}	122.12 (19)
O31—Co1—O1W	177.00 (8)	C102—N22—Co1 ^{iv}	120.85 (17)
O21—Co1—N12	96.29 (7)	N12—C12—C22	123.9 (2)
O41 ⁱ —Co1—N12	92.68 (6)	N12—C12—H12	118.1
O31—Co1—N12	91.59 (8)	C22—C12—H12	118.1
O1W—Co1—N12	86.89 (8)	C12—C22—C32	119.4 (2)
O21—Co1—N22 ⁱⁱ	86.21 (7)	C12—C22—H22	120.3
O41 ⁱ —Co1—N22 ⁱⁱ	84.92 (7)	C32—C22—H22	120.3
O31—Co1—N22 ⁱⁱ	89.38 (9)	C22—C32—C42	116.8 (2)
O1W—Co1—N22 ⁱⁱ	92.25 (9)	C22—C32—C82	120.8 (2)
N12—Co1—N22 ⁱⁱ	177.33 (9)	C42—C32—C82	122.4 (2)
C71—O21—Co1	120.77 (16)	C52—C42—C32	119.9 (2)
C81—O31—Co1	135.33 (16)	C52—C42—H42	120.1
C81—O41—Co1 ⁱⁱⁱ	128.39 (15)	C32—C42—H42	120.1
C21—C11—C61	119.1 (2)	N12—C52—C42	123.4 (2)
C21—C11—C71	116.8 (2)	N12—C52—H52	118.3

C61—C11—C71	124.0 (2)	C42—C52—H52	118.3
C31—C21—C11	121.2 (3)	N22—C62—C72	123.7 (2)
C31—C21—H21	119.4	N22—C62—H62	118.2
C11—C21—H21	119.4	C72—C62—H62	118.2
C41—C31—C21	120.3 (3)	C62—C72—C82	119.4 (2)
C41—C31—H31	119.8	C62—C72—H72	120.3
C21—C31—H31	119.8	C82—C72—H72	120.3
C31—C41—C51	119.5 (3)	C92—C82—C72	117.3 (2)
C31—C41—H41	120.3	C92—C82—C32	122.1 (2)
C51—C41—H41	120.3	C72—C82—C32	120.6 (2)
C41—C51—C61	120.9 (3)	C102—C92—C82	119.6 (2)
C41—C51—H51	119.6	C102—C92—H92	120.2
C61—C51—H51	119.6	C82—C92—H92	120.2
C11—C61—C51	118.9 (2)	N22—C102—C92	123.1 (2)
C11—C61—C81	123.4 (2)	N22—C102—H102	118.4
C51—C61—C81	117.6 (2)	C92—C102—H102	118.4
O11—C71—O21	124.8 (3)	Co1—O1W—H1WA	117.0 (9)
O11—C71—C11	116.6 (2)	Co1—O1W—H1WB	138.3 (10)
O21—C71—C11	118.4 (2)	H1WA—O1W—H1WB	104.6 (9)
O31—C81—O41	123.5 (2)	H2WA—O2W—H2WB	104.6 (11)
O31—C81—C61	119.8 (2)	H3WA—O3W—H3WB	104.3 (11)
O41—C81—C61	116.6 (2)	H4WB—O4W—H4WA	105.5 (11)

Symmetry codes: (i) $-x+1, y+1/2, -z+1$; (ii) $x, y, z-1$; (iii) $-x+1, y-1/2, -z+1$; (iv) $x, y, z+1$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1WA \cdots O41 ^v	0.85 (2)	2.02 (1)	2.810 (2)	154 (1)
O1W—H1WB \cdots O2W	0.85 (1)	1.91 (1)	2.743 (3)	167 (1)
O2W—H2WA \cdots O3W	0.85 (1)	2.01 (1)	2.751 (5)	145 (1)
O2W—H2WB \cdots O11 ^v	0.85 (1)	2.05 (1)	2.867 (4)	161 (2)
O3W—H3WA \cdots O11 ^{vi}	0.85 (1)	2.02 (1)	2.843 (4)	162 (2)
O3W—H3WB \cdots O4W ^{vi}	0.85 (2)	1.80 (1)	2.576 (6)	152 (2)
O4W—H4WB \cdots O11 ^{vi}	0.85 (2)	2.28 (2)	3.038 (4)	150 (2)
O4W—H4WA \cdots O2W	0.85 (1)	1.98 (1)	2.799 (5)	162 (2)

Symmetry codes: (v) $x, y+1, z$; (vi) $-x, y+1/2, -z$.

Summary of transition metal complexes of general formula $Tr(pht)_{n1}(bpy)_{n2}(H_2O)_{n3}\cdot(H_2O)_{n4}$, represented by the shorthand notation $n1:n2:n3:(n4)$

CSD refcode	Tr	Space group	a (\AA)	b (\AA)	c (\AA)	α ($^\circ$)	β ($^\circ$)	γ ($^\circ$)	V (\AA^3)	ρ (g cm^{-3})
Group A , formula 1:1:2:(2)										
BASMIS01 Mn		$P2/n$	7.69	11.59	10.75	90	92.67	90	957.16	1.552
JEKTUP Zn		$P2/n$	7.63	11.32	10.81	90	92.44	90	933.35	1.629
NEDXEZ Cd		$P2/n$	7.79	11.65	10.70	90	92.59	90	969.73	1.729
NEDXOJ01 Co		$P2/n$	7.61	11.36	10.81	90	92.28	90	933.65	1.605

QEHCUC	Fe	$P2/n$	7.65	11.39	10.79	90	92.67	90	939.15	1.585
TEJKUP*	Cu	$P2/c$	7.70	11.10	12.97	90	123.7	90	922.25	1.642
WIPFOR*	Ni	$P2/c$	7.62	11.37	12.95	90	123.6	90	934.16	1.604
Group B, formula 2:1:0:(0)										
FEQSOK	Cd	$I4_122$	8.29	8.29	33.75	90	90	90	2321.90	1.713
LESBEQ	Co	$I4122$	8.16	8.16	32.93	90	90	90	2190.30	1.654
Group C, formula 2:2:0:(0)										
IZASIL	Zn	$P\bar{1}$	7.51	10	22.08	84.31	88.08	71.02	1560.50	1.507
Group D, formula 1:1:2:(0.5)										
WEDNEA	Ni	$P4_12_12$	11.30	11.27	29.90	90	90	90	3796.60	1.484
Group E, formula 1:1:1:(3)										
KAGQEP	Ni	$P2_1$	11.10	8.38	11.27	90	115.4	90	949.42	1.578
(I)	Co		11.10	8.40	11.37	90	115.6	90	956.85	1.566

(*): In spite of being refined in space group $P2/c$, these structures are isomorphous with those described in $P2/n$.

π - π contacts (\AA , $^\circ$)

$Cg \cdots Cg'$	CCD (\AA)	IPD (\AA)	DA ($^\circ$)
$Cg1 \cdots Cg2$	3.5839 (19)	3.48 (5)	16.42 (16)

$Cg1$ is the centroid of the C11/C21/C31/C41/C51/C61 ring and $Cg2$ that of the N12/C12/C22/C32/C42/C52 ring. IPD is the interplanar distance, CCD the centre-to-centre distance and DA the dihedral angle between planes; for details, see Janiak (2000).