

Influence of solvent on the structures of two one-dimensional cobalt(II) coordination polymers with tetrachloroterephthalate

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The title cobalt coordination polymers, *catena*-poly[[[aqua-tri-pyridinecobalt(II)]- μ -tetrachloroterephthalato] pyridine solvate], $\{[\text{Co}(\text{C}_8\text{Cl}_4\text{O}_4)(\text{C}_5\text{H}_5\text{N})_3(\text{H}_2\text{O})]\cdot\text{C}_5\text{H}_5\text{N}\}_n$, (I), and *catena*-poly[[[diaquadipyridinecobalt(II)]- μ -tetrachloroterephthalato] 1,4-dioxane trihydrate], $\{[\text{Co}(\text{C}_8\text{Cl}_4\text{O}_4)(\text{C}_5\text{H}_5\text{N})_2(\text{H}_2\text{O})_2]\cdot\text{C}_4\text{H}_8\text{O}_2\cdot 3\text{H}_2\text{O}\}_n$, (II), have been prepared with tetrachloroterephthalic acid ($\text{H}_2\text{BDC-Cl}_4$) under different solvent media. Both complexes form infinite cobalt(II)-tetrachloroterephthalate polymeric chains. In (I), two independent Co^{II} ions are six-coordinated through N_3O_3 donor sets in slightly distorted octahedral geometries provided by two carboxylate and three pyridine ligands, and one water molecule. The structure of (II) contains two independent Co^{II} atoms, each lying on a twofold axis, which adopt a tetragonally distorted N_2O_4 octahedral geometry *via* two carboxylate

groups, two pyridine ligands and two water molecules. The different stoichiometry of coordinated and solvent guest molecules leads to different two-dimensional supramolecular networks, with (I) utilizing $\text{C}-\text{H}\cdots\pi$ and weak $\pi-\pi$ interactions and (II) utilizing mainly conventional hydrogen bonding.

Comment

The rapid development in crystal engineering of coordination polymers has afforded access to crystalline solid-state materials with potential applications in the areas of catalysis, magnetism, gas absorption, nonlinear optics and drug delivery (Férey, 2008; Wang *et al.*, 2008). To date, the aromatic bridging ligand benzene-1,4-dicarboxylate (BDC) has been widely utilized to fabricate coordination polymers based on paddle-wheel units with robust networks and attractive properties as conventional porous materials (Li *et al.*, 1999; Serre *et al.*, 2002; Xiao *et al.*, 2005; Du *et al.*, 2007). Derivatives of BDC with electron-donating or -accepting substituents, such as 2,3,5,6-tetramethylbenzene-1,4-dicarboxylate (TBDC) and 2,3,5,6-tetrafluorobenzene-1,4-dicarboxylate (BDC- F_4), have also received considerable attention in the design of porous materials with an efficient hydrogen-storage capacity (Kitaura *et al.*, 2004; Chun *et al.*, 2005). Few investigations of solvent effects have been carried out on crystalline compounds using substituted BDC building blocks (Chen *et al.*, 2008). In the latter report, solvent-regulated assemblies of manganese(II) coordination polymers with 2,3,5,6-tetrachlorobenzene-1,4-dicarboxylic acid ($\text{H}_2\text{BDC-Cl}_4$) exhibit different binding modes and dimensionality in the final coordination networks with variable auxiliary solvent co-ligands. As part of our investigation of the coordination behavior of $\text{H}_2\text{BDC-Cl}_4$ and divalent transition metal ions, we report the solvent-directed assembly of two Co^{II} coordination polymers, $\{[\text{Co}(\text{BDC-Cl}_4)(\text{C}_5\text{H}_5\text{N})_3(\text{H}_2\text{O})]\cdot\text{C}_5\text{H}_5\text{N}\}_n$, (I), and $\{[\text{Co}(\text{BDC-Cl}_4)(\text{C}_5\text{H}_5\text{N})_2(\text{H}_2\text{O})_2]\cdot\text{C}_4\text{H}_8\text{O}_2\cdot 3\text{H}_2\text{O}\}_n$, (II).

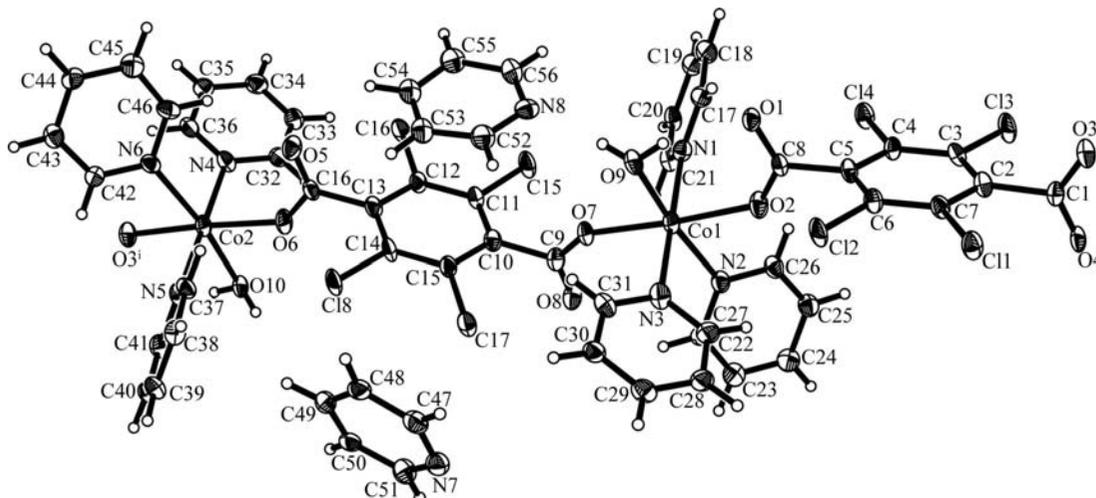
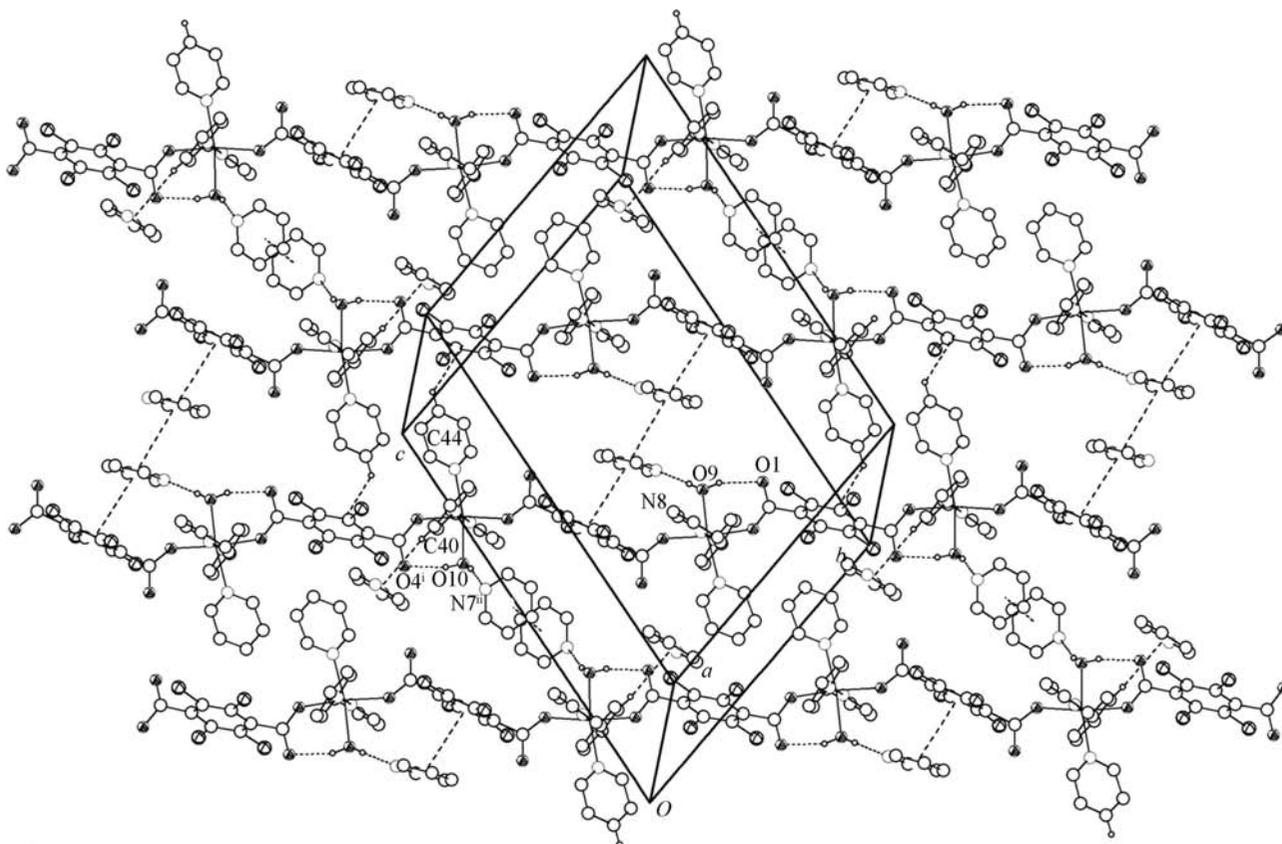
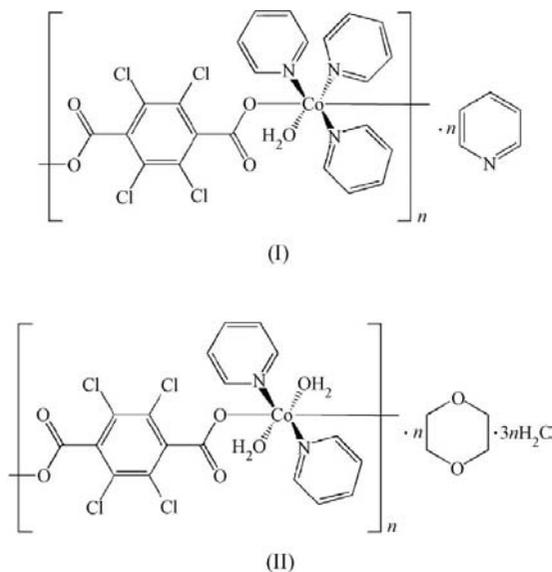


Figure 1

The structure of (I), with displacement ellipsoids drawn at the 30% probability level. [Symmetry code: (i) $x - 1, y - 1, z + 1$]

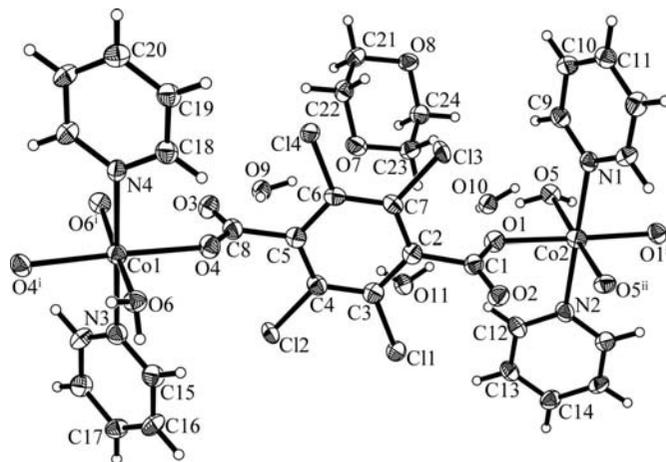

Figure 2

A view of part of the two-dimensional supramolecular network of (I), approximately normal to the *bc* plane. Hydrogen bonds and aromatic interactions are shown as dashed lines. [Symmetry codes: (i) $x - 1, y - 1, z + 1$; (ii) $-x + 1, -y, -z + 1$.]

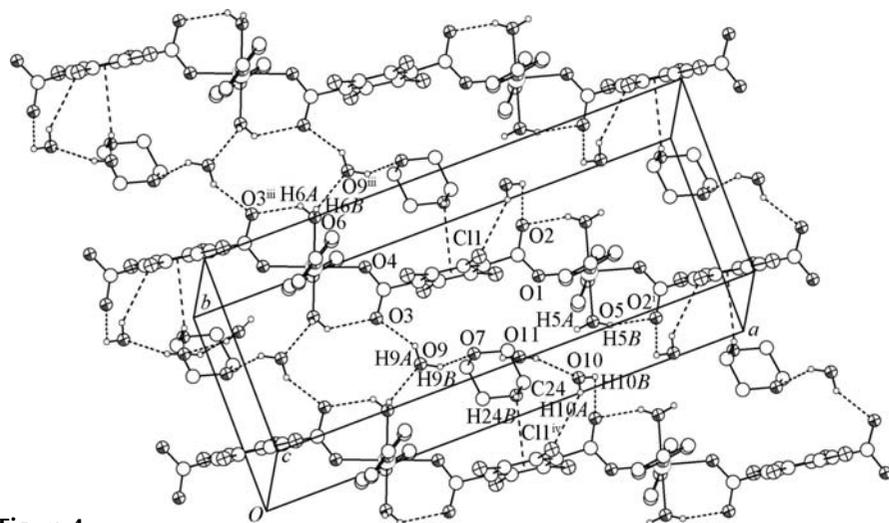


The asymmetric unit of (I) contains two Co^{II} atoms, two BDC-Cl_4 ligands, six coordinated pyridine molecules and two water molecules, along with two pyridine molecules of crystallization (Fig. 1 and Table 1). The two Co^{II} atoms exhibit similar slightly distorted octahedral coordination geometries, with the N_3O_3 coordination environment comprising two BDC-Cl_4 anions, one aqua ligand and three pyridine mol-

ecules. In the $\text{Mn}^{\text{II}}\text{-BDC-Cl}_4$ polymer crystallized from a similar pyridine–water medium, the Mn^{II} ion is six-coordinated through two BDC-Cl_4 anions, two aqua ligands and two pyridine molecules (Chen *et al.*, 2008). Within the anionic unit, the rotation angles (φ_{rot}) of the tetrachlorinated benzene rings relative to the carboxylate groups are in the range 81.0 (2)–86.2 (1)°, similar to the corresponding values for other polychlorinated carboxylate compounds (Maspoeh *et al.*, 2004).


Figure 3

The structure of (II), with displacement ellipsoids drawn at the 30% probability level. [Symmetry codes: (i) $-x + \frac{1}{2}, -y + 2, z$; (ii) $-x + \frac{3}{2}, -y + 1, z$.]


Figure 4

A view of part of the two-dimensional hydrogen-bonding network in (II), approximately normal to the *ab* plane. O—H...O and C—H... π interactions are shown as dashed lines. [Symmetry codes: (i) $-x + \frac{3}{2}, -y + 1, z$; (ii) $-x + \frac{1}{2}, -y + 2, z$; (iii) $x, y + 1, z$; (iv) $x, y - 1, z$.]

Each BDC-Cl₄ ligand adopts a bis-monodentate coordination mode, bridging adjacent Co^{II} centers into an infinite linear chain with decorated pyridine molecules, which runs along the [111] direction, as illustrated in Fig. 2.

There exist strong intramolecular O—H...O interactions (entries 2 and 3 in Table 2) between the carboxylate O atoms and the aqua ligands, which further stabilize the one-dimensional polymeric chain motif. Intermolecular O—H...N bonds (entries 1 and 4 in Table 2) join the uncoordinated pyridine molecules and the coordination chain together. Because there are a large number of coordinated and uncoordinated pyridine molecules in the structure, multiple weak π - π interactions are noted between the benzene and pyridine rings and between the pyridine rings (e.g. C10—C15, N7/C47—C51 and N8/C52—C56), with centroid-to-centroid distances in the range 3.508 (2)–3.641 (2) Å; these link the one-dimensional hydrogen-bonded chains into a two-dimensional supramolecular network (Fig. 2). The supramolecular architecture is further consolidated by multiple C—H... π interactions between CH groups and the centroids of the N3/C27—C31 pyridine and C2—C7 benzene rings (Fig. 2 and Table 2).

The crystal structure of complex (II) also exhibits a one-dimensional coordination motif. In the asymmetric unit, two crystallographically independent centers, Co1 and Co2, lie on twofold rotation axes at $(\frac{1}{4}, 1, y)$ and $(\frac{3}{4}, \frac{1}{2}, y)$, respectively. Each Co^{II} center is coordinated by two carboxylate groups in a monodentate mode from two symmetry-related BDC-Cl₄ ligands, and by two pyridine and two aqua ligands (Table 3). The asymmetric unit also contains one dioxane and three water molecules as guests. The N₂O₄ coordination geometry, provided by two carboxylate O atoms, two pyridyl N atoms and two water molecules, can be described as an elongated octahedron with two pyridyl N atoms occupying the axial sites. Neighboring Co1 and Co2 atoms are bridged by the BDC-Cl₄ dianion in a *trans* fashion (Fig. 3). Propagation of this arrangement generates a one-dimensional linear array, which

is similar to that of complex (I) but with fewer coordinated pyridine molecules and more water molecules. Similar to (I), the two carboxylate groups within each BDC-Cl₄ group make φ_{rot} dihedral angles of 81.6 (1) and 87.7 (1)° with the central benzene plane. Analogous intramolecular O—H...O bonds (entries 1 and 2 in Table 4) between uncoordinated carboxylate O atoms and aqua ligands consolidate the one-dimensional polymeric chain. Analysis of the crystal packing shows the existence of two main types of conventional hydrogen-bonding interactions (O—H...O and O—H...Cl; Table 4), which connect the polymeric chains, solvent water molecules and dioxane molecules to form a two-dimensional network parallel to the *ab* plane (Fig. 4). Notably, one hydrogen-bonded pattern (entries

2–4 in Table 4), denoted as $R_6^6(12)$ (Etter, 1990), is observed in this layer array. Additionally, the dioxane solvent molecule has a C—H... π interaction with the benzene ring of the BDC-Cl₄ anion (Table 4). However, in contrast to (I), adjacent layers have no significant aromatic ring-based stacking interactions.

Experimental

To a solution of CoCl₂·6H₂O (23.8 mg, 0.1 mmol) in a mixture of pyridine and water (1:1 *v/v*, 10 ml) was added a solution of H₂BDC-Cl₄ (30.4 mg, 0.1 mmol) in water (5 ml). After stirring for 30 min, the reaction mixture was filtered and left to stand at room temperature. After 3 d, pink block-shaped crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of the filtrate in a yield of 78% (54.2 mg, based on H₂BDC-Cl₄). Analysis found: C 48.42, H 3.18, N 8.13%; calculated for C₅₆H₄₄Cl₈Co₂N₈O₁₀: C 48.37, H 3.19, N 8.06%. For the preparation of (II), an aqueous solution (5 ml) of CoCl₂·6H₂O (23.8 mg, 0.1 mmol) was added to a dioxane and water solution (1:1 *v/v*, 10 ml) of H₂BDC-Cl₄ (30.4 mg, 0.1 mmol) with stirring for 30 min. Pyridine (0.5 ml) was then added and allowed to diffuse into the mixture at room temperature. After 7 d, pink block-shaped crystals of (II) suitable for X-ray diffraction were collected by slow evaporation of the filtrate in a yield of 67% (46.4 mg, based on H₂BDC-Cl₄). Analysis found: C 37.73, H 3.94, N 4.09%; calculated for C₂₂H₂₈Cl₄CoN₂O₁₁: C 37.90, H 4.05, N 4.02%.

Compound (I)

Crystal data

[Co(C₈Cl₄O₄)(C₅H₅N)₃·(H₂O)]·C₅H₅N
M_r = 695.23
 Triclinic, $P\bar{1}$
a = 8.7128 (10) Å
b = 17.8408 (17) Å
c = 21.227 (2) Å
 α = 67.879 (1)°

β = 79.839 (2)°
 γ = 84.962 (1)°
V = 3007.9 (5) Å³
Z = 4
 Mo *K* α radiation
 μ = 0.97 mm⁻¹
T = 291 (2) K
 0.30 × 0.26 × 0.24 mm

Data collection

Bruker SMART APEXII CCD diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.76$, $T_{\max} = 0.79$

23660 measured reflections
11691 independent reflections
8460 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.109$
 $S = 1.01$
11691 reflections

757 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.27 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.62 \text{ e } \text{\AA}^{-3}$

Table 1

Selected bond lengths (Å) for (I).

Co1—O7	2.0619 (19)	Co2—O6	2.066 (2)
Co1—O9	2.122 (2)	Co2—O3 ⁱ	2.127 (2)
Co1—O2	2.126 (2)	Co2—O10	2.144 (2)
Co1—N3	2.155 (3)	Co2—N5	2.167 (3)
Co1—N1	2.158 (2)	Co2—N4	2.170 (2)
Co1—N2	2.171 (3)	Co2—N6	2.190 (3)

Symmetry code: (i) $x - 1, y - 1, z + 1$.

Table 2

Hydrogen-bond geometry (Å, °) for (I).

Cg1 and Cg2 denote the centroids of the N3/C27—C31 and C2—C7 rings, respectively.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O9—H9A \cdots N8	0.85	1.91	2.718 (3)	159
O9—H9B \cdots O1	0.85	1.97	2.768 (3)	157
O10—H10B \cdots O4 ⁱ	0.85	1.85	2.686 (3)	166
O10—H10A \cdots N7 ⁱⁱ	0.85	1.98	2.814 (3)	167
C40—H40 \cdots Cg1 ⁱⁱⁱ	0.93	2.99	3.813 (4)	149
C44—H44 \cdots Cg2 ⁱⁱⁱ	0.93	2.94	3.638 (4)	133

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

Compound (II)

Crystal data

$[\text{Co}(\text{C}_8\text{Cl}_4\text{O}_4)(\text{C}_5\text{H}_5\text{N})_2 \cdot (\text{H}_2\text{O})_2] \cdot \text{C}_4\text{H}_8\text{O}_2 \cdot 3\text{H}_2\text{O}$
 $M_r = 697.19$
Orthorhombic, $Pcca$
 $a = 21.4257 (19) \text{ \AA}$
 $b = 8.6567 (8) \text{ \AA}$
 $c = 33.537 (3) \text{ \AA}$

$V = 6220.3 (10) \text{ \AA}^3$
 $Z = 8$
Mo $K\alpha$ radiation
 $\mu = 0.95 \text{ mm}^{-1}$
 $T = 291 (2) \text{ K}$
 $0.28 \times 0.24 \times 0.22 \text{ mm}$

Data collection

Bruker SMART APEXII CCD diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.77$, $T_{\max} = 0.81$

46466 measured reflections
6133 independent reflections
4296 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.066$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.077$
 $S = 1.02$
6133 reflections

366 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.48 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.42 \text{ e } \text{\AA}^{-3}$

Table 3

Selected bond lengths (Å) for (II).

Co1—O6 ⁱ	2.0971 (15)	Co2—O5 ⁱⁱ	2.1043 (15)
Co1—O6	2.0971 (15)	Co2—O5	2.1043 (15)
Co1—N4	2.146 (3)	Co2—O1 ⁱⁱⁱ	2.1302 (17)
Co1—O4 ⁱ	2.1469 (17)	Co2—O1	2.1302 (17)
Co1—O4	2.1469 (17)	Co2—N1	2.172 (3)
Co1—N3	2.171 (3)	Co2—N2	2.177 (3)

Symmetry codes: (i) $-x + \frac{1}{2}, -y + 2, z$; (ii) $-x + \frac{3}{2}, -y + 1, z$.

Table 4

Hydrogen-bond geometry (Å, °) for (II).

Cg1 denotes the centroid of the C2—C7 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5B \cdots O2 ⁱⁱ	0.85	1.97	2.657 (3)	137
O6—H6A \cdots O3 ⁱ	0.85	2.24	2.684 (2)	113
O6—H6B \cdots O9 ⁱⁱⁱ	0.85	2.10	2.629 (2)	120
O9—H9A \cdots O3	0.85	2.09	2.829 (2)	145
O9—H9B \cdots O7	0.85	2.03	2.726 (3)	138
O10—H10A \cdots Cl1 ^{iv}	0.85	2.71	3.3714 (19)	136
O11—H11A \cdots O10	0.85	2.37	3.199 (3)	164
C24—H24B \cdots Cg1 ^{iv}	0.97	2.97	3.715 (3)	135

Symmetry codes: (i) $-x + \frac{1}{2}, -y + 2, z$; (ii) $-x + \frac{3}{2}, -y + 1, z$; (iii) $x, y + 1, z$; (iv) $x, y - 1, z$.

H atoms bonded to C atoms were positioned geometrically (C—H = 0.93 and 0.97 Å for pyridine and dioxane H atoms, respectively) and included in the refinement in the riding-model approximation. All water H atoms were located in difference maps and then subsequently geometrically optimized. $U_{\text{iso}}(\text{H})$ values for all H atoms were set at $1.2U_{\text{eq}}(\text{C}, \text{O})$. The electron-density trough in (I) ($-0.62 \text{ e } \text{\AA}^{-3}$) is 0.66 Å from atom Co1.

For both compounds, data collection: *APEX2* (Bruker, 2003); cell refinement: *APEX2* and *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3116). Services for accessing these data are described at the back of the journal.

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