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Two isomorphous cobalt(II) complexes: poly[[diaqua-μ-2,5-dicarboxybenzene-1,4-dicarboxylato-μ-1,2-di-4-pyridylethene-cobalt(II)] 1,2-di-4-pyridylethene solvate] and the 1,2-di-4-pyridylethane analogue

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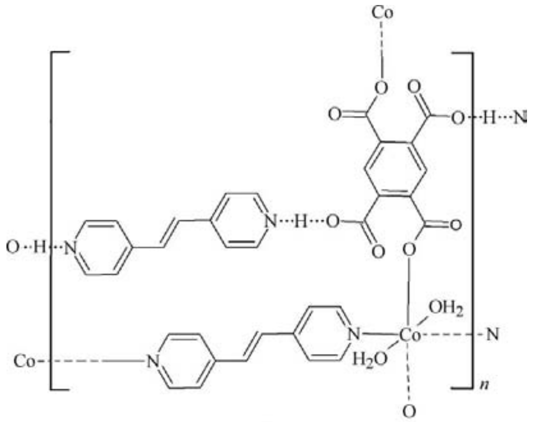
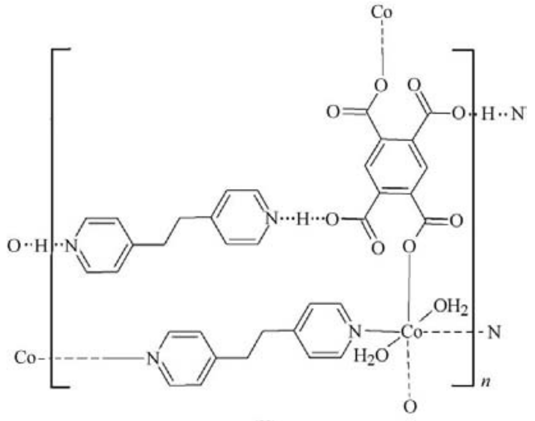
The two isomorphous title structures, formulated as $\{[Co(C_{10}H_4O_8)(C_{12}H_{10}N_2)(H_2O)_2]\cdot C_{12}H_{10}N_2\}_n$, (I), and $\{[Co(C_{10}H_4O_8)(C_{12}H_{12}N_2)(H_2O)_2]\cdot C_{12}H_{12}N_2\}_n$, (II), respectively, are reported. They crystallize in the space group $P\overline{1}$ with only one formula unit in the asymmetric unit, so that the organic ligands lie about inversion centres and the Co atom lies on an inversion centre. The Co atoms are octahedrally coordinated by a carboxylate O atom from 2,5-dicarboxybenzene-1,4-dicarboxylate (H_2btc), one N atom from 1,2-di-4-pyridylethene (*L*) in (I) or from 1,2-di-4-pyridylethane (*L*) in (II), and one coordinated water molecule, plus their inversion-related species. This particular coordination results in a two-dimensional array, with an elemental unit in the shape of a parallelogram having the Co^{II} cations at the corners, linked in one direction by *L* bridges and in the opposite direction by H_2btc groups. The *L* solvent molecules act as pillars between parallel planes, linking them by strong hydrogen bonds where the H atoms lie midway between the formal donor/acceptor atoms in a 'shared' mode. Comparison is made with structures presenting the same structural motif, strongly suggesting that the two-dimensional arrangement reported here might be a very stable robust building block for molecular engineering purposes.

Comment

The *ab initio* design of supramolecular materials starting from molecular building blocks is an active research field in molecular engineering. In particular, great effort is currently dedicated to the assembly of metal ions and organic ligands in polymeric complexes (Moulton & Zaworotko, 2001; Janiak, 2003), in a process which can in principle be understood as one where the 'interactive' information carried by the ligands is to be 'decoded' by the metal ions through the 'algorithm' determined by their coordination capabilities (Lehn, 1995). This process can lead to the formation of reproducible primary structures, which can in turn be used as secondary building units in the construction of even more complex structures, and the usefulness of these relies heavily on their stability. If one such structure is shown to be robust enough to survive almost unchanged in a number of compounds where it is subject to a diversity of interaction environments, it can then be considered an interesting target for crystal engineering. We report here a structural investigation of the isomorphous cobalt complexes poly[[diaqua-μ-2,5-dicarboxybenzene-1,4-dicarboxylato-μ-1,2-di-4-pyridylethene-cobalt(II)] 1,2-di-4-pyridylethene solvate], (I), and the 1,2-di-4-pyridylethane analogue, (II), characterized by one such seemingly robust structural motif.



(I)



(II)

The title compounds are formulated as $[Co(H_2btc)(L)(H_2O)_2]\cdot L$, where H_4btc is benzene-1,2,4,5-tetracarboxylic acid in both structures and *L*, the ligand differentiating them, is 1,2-di-4-pyridylethene (bpe1) in (I) and 1,2-di-4-pyridylethane (bpe2) in (II). For the sake of simplicity, we shall only discuss isologue (I) as representative of both, commenting on the corresponding differences when significant.

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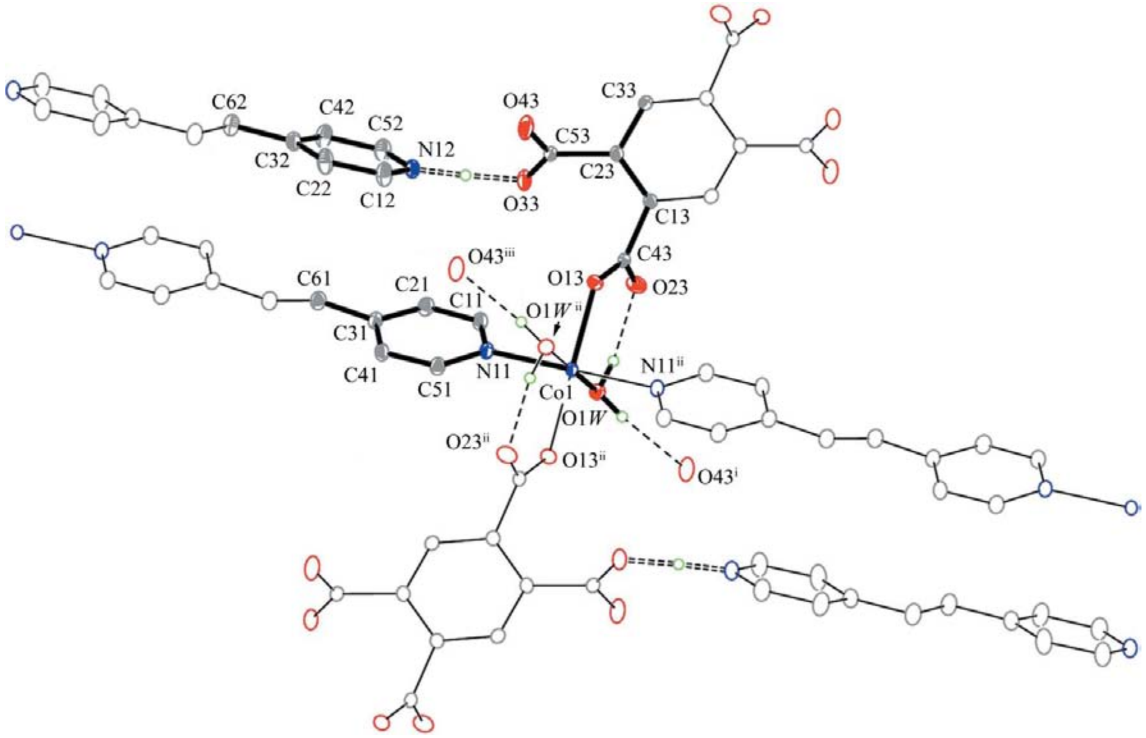

Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms have been omitted for clarity. Independent atoms are shown with heavy bonds and filled ellipsoids, and symmetry-related atoms are shown with light bonds and empty ellipsoids. [Symmetry codes: (i) $1 + x, y, z$; (ii) $2 - x, 1 - y, 1 - z$; (iii) $1 - x, 1 - y, 1 - z$.] The structure of (II) is analogous and is available with the deposited material.

Fig. 1 shows a molecular view of (I), while Tables 1 and 3 present some selected coordination parameters and Tables 2 and 4 the main hydrogen-bonding interactions for (I) and (II), respectively.

Compound (I) crystallizes in the triclinic space group $P\overline{1}$ with only one formula unit per unit cell. Thus, the organic ligands lie about inversion centres and the Co atom lies on an inversion centre. The Co^{II} cation has an octahedral coordination provided by a carboxylate O atom from H$_2$btc, an N atom from bpe1 and one coordinated water molecule, plus their inversion-related species. The O atoms define the square equatorial plane, with a tight Co—O span [2.0824 (10)–2.1171 (11) Å for (I) and 2.0819 (10)–2.0919 (9) Å for (II)], while the N atoms occupy the apical positions, with Co—N = 2.1251 (12) Å in (I) and 2.1316 (11) Å in (II). The angles are also quite regular, with departures from ideal values of less than 1.8° in (I) and less than 2.4° in (II).

The organic ligands are regular and show no unusual features. The only obvious difference between the two structures is due to the double/single-bond character of the central C—C bonds in bpe1 and bpe2 and, correspondingly, the number of H atoms attached. The coordinated bpe1 and H$_2$btc ligands act in a similar bridging mode, the former through its two N atoms and the latter *via* two opposite carboxylate O atoms, binding in its most outstretched fashion. The result is a two-dimensional array (Fig. 2) with an elemental unit presenting a parallelogram shape with the Co^{II} cations at the corners, linked in one direction (horizontally in Fig. 2) by the bpe1 bridges and in the opposite direction (vertically in Fig. 2) by H$_2$btc groups. For clarity, Fig. 2 has been drawn in a 'channelling' view, along the crystallographic *b* axis. However, the two-dimensional structures are not parallel to the projection plane but run in a slanted manner, parallel to the $(1\overline{1}1)$ planes instead. This particular view was chosen to make the mesh-like structure more clearly visible, as well as to make obvious the linking role of the bpe1 solvent molecule, which runs from top to bottom in Fig. 2 and acts as an acceptor of two extremely strong hydrogen bonds (see below for details) to carboxylate O—H groups in two adjacent planes (above and below the solvent molecule), thus configuring a very tight hydrogen-bonded three-dimensional structure. Fig. 3 shows a lateral view of that presented in Fig. 2, showing the planes sideways (bold horizontal lines), connected by the interleaved bpe1 ligands, shown as weak quasi-vertical lines.

A completely analogous two-dimensional motif has recently been reported in poly[[diaquacobalt(II)]-μ-2,5-dicarboxybenzene-1,4-dicarboxylato-μ-di-4-pyridylethene] (Xing & Li, 2006), [Co(H$_2$btc)(*L*)(H$_2$O)$_2$], (III), which uses the same ligands disposed in a topologically similar way but does not have the additional *L* solvent molecule as in (I). This results in a comparable two-dimensional structure characterized by a unit mesh motif of 13.681 (1) × 11.420 (1) Å/106.7 (1)° compared with 13.578 (1) × 11.296 (1) Å/101.5 (1)° for (I) and 13.567 (1) × 11.201 (1) Å/109.9 (1)° for (II). This metric conservation suggests that the two-dimensional structure might be considered a robust building layer, in particular when other

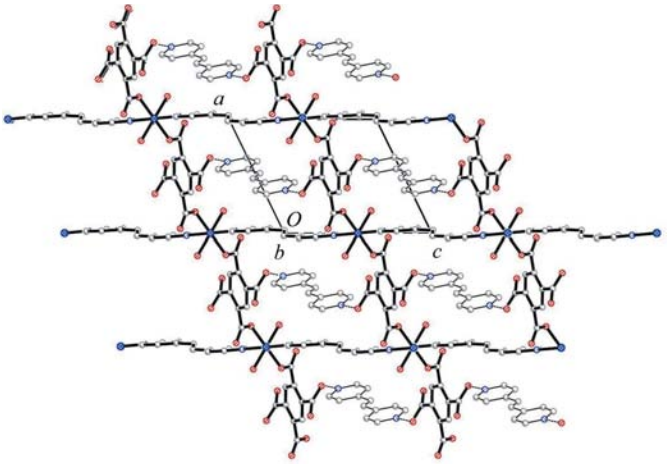

Figure 2
A packing view of (I) along the *b* axis. Heavy lines show the slanting and perfectly overlapping two-dimensional structures parallel to $(1\bar{1}1)$. Thin lines show the interleaved bpe1 ligands bridging adjacent planes through O33—H33*A*···N12 hydrogen bonds.

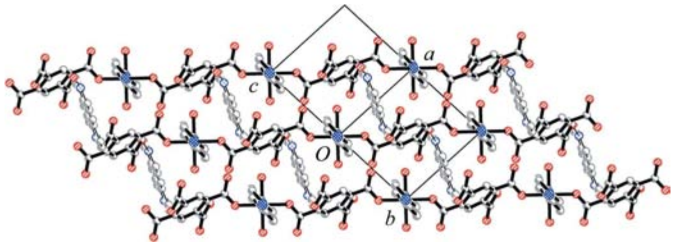

Figure 3
A side view of that presented in Fig. 2, showing the two-dimensional structures sideways (heavy lines) and the bridging bpe1 ligands (thin lines) in between.

parameters in the corresponding structures are significantly different. There is nothing occupying the interplanar space in (III) and neighbouring planes are simply linked by strong hydrogen bonds mediated by the coordinated water molecules. This leads to an extremely short interplanar spacing of 3.18 (1) Å. In compounds (I) and (II), the planes are supported by slanting *L* molecules [the N···N axes subtend to the plane normals angles of 66.1 (1)° in (I) and 65.88 (1) in (II)], leading to interplanar spacings of 5.118 (1) and 5.052 (1) Å, respectively. This suggests that the planes might 'sandwich' a variety of different molecules in a pre-designed fashion and so be a potentially useful tool for use in molecular engineering.

The hydrogen bond linking atoms O33 and N12 deserves some attention. In both (I) and (II) it presents the same delocalized character, with the H atom 'shared' by both eventual donor/acceptor atoms. Difference map plots show these H atoms with prolate spheroid shapes in both cases, and free refinement of the low-temperature data takes atom H33*A* quite close to the mid-point between atoms O33 (the expected donor) and N12 (the expected acceptor). In the case of (I), the H atom lies even slightly nearer to N12 (Table 3). These hydrogen bonds might be considered a measure of the strength of the interaction and, accordingly, of the stability of the three-dimensional structure derived from it.

In order to assess how common this kind of *D*—H—*A* interaction could be, we looked for comparable cases in the Cambridge Structural Database (CSD, Version of 2008; Allen, 2002) where the *D*—H···*A* hydrogen bond could be described as a hard *D*—H—*A* synthon with the H atom simultaneously bound to both neighbours. Very often (about 50% of the situations found) the whole group appears to be riding on a special position (inversion centre or twofold axis), thus forcing *D* and *A* to be of the same species, with the bridging H atom appearing midway between them on the special position. The most frequent case is that in which *D* = *A* = O (337 cases), followed by *D* = *A* = N (28 cases). However, the case with *D* = O and *A* = N (reported here) appears just twice, and in one of the occurrences, bis(1,2-di-4-pyridylethene) (2*R*,3*R*)-tartaric acid (2*R*,3*R*)-tartrate (Farrell *et al.*, 2002), the N atom corresponds to the bpe1 ligand, as in (I) reported here. The other case is 4-methylpyridine pentachlorophenol (Steiner *et al.*, 2001).

In addition to the short O···H···N hydrogen bonds found in both (I) and (II), there are strong hydrogen bonds (H···O = 1.86–1.92 Å) involving the water H atoms and the uncoordinated H_2btc carboxylate O atoms which, being internal to the two-dimensional structures, contribute even further to their overall stability (Fig. 1 and Tables 2 and 4).

Experimental

An aqueous solution (50 ml) containing cobalt(II) acetate tetrahydrate (0.33 mmol) was added to an aqueous solution (50 ml) containing benzene-1,2,4,5-tetracarboxylic acid (0.33 mmol) and NaOH (1.33 mmol). The mixture was heated under reflux for 20 min. An ethanolic solution (20 ml) containing the ligand [0.33 mmol; bpe1 for (I) and bpe2 for (II)] was added slowly and the final solution was maintained under reflux for 4 h. Single crystals suitable for X-ray diffraction studies were obtained by slow concentration of the solutions.

Compound (I)

Crystal data

$[Co(C_{10}H_4O_8)(C_{12}H_{10}N_2)(H_2O)_2]\cdot C_{12}H_{10}N_2$
$M_r = 711.53$
Triclinic, $P\bar{1}$
$a = 9.0283$ (2) Å
$b = 9.6152$ (2) Å
$c = 10.1064$ (3) Å
$\alpha = 93.1051$ (14)°
$\beta = 113.8441$ (13)°
$\gamma = 106.2234$ (14)°
$V = 756.41$ (3) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 0.64$ mm^{-1}
$T = 150$ (2) K
0.55 × 0.42 × 0.23 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS* in *SAINT*; Bruker, 2002)
$T_{min} = 0.70$, $T_{max} = 0.86$
12370 measured reflections
3331 independent reflections
3132 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$

Table 1
Selected geometric parameters (Å, °) for (I).

Co1—O13	2.0824 (10)	Co1—N11	2.1251 (12)
Co1—O1*W*	2.1171 (11)		
O13—Co1—O1*W*	90.01 (4)	O1*W*—Co1—N11	88.35 (4)
O13—Co1—N11	88.87 (4)		

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O33—H33*A*···N12	1.35 (3)	1.22 (3)	2.5759 (16)	177 (3)
O1*W*—H1*WB*···O43^{i}	0.81 (3)	1.92 (3)	2.7210 (16)	174 (2)
O1*W*—H1*WA*···O23	0.83 (2)	1.83 (2)	2.6414 (16)	165 (2)

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

Table 3
Selected geometric parameters (Å, °) for (II).

Co1—O13	2.0990 (9)	Co1—N11	2.1341 (11)
Co1—O1*W*	2.1049 (9)		
O13—Co1—O1*W*	90.15 (4)	O1*W*—Co1—N11	88.65 (4)
O13—Co1—N11	89.34 (4)		

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O33—H33*A*···N12	1.23 (3)	1.34 (3)	2.5695 (15)	174 (3)
O1*W*—H1*WB*···O43^{i}	0.85 (2)	1.87 (2)	2.7252 (14)	174 (2)
O1*W*—H1*WA*···O23	0.79 (2)	1.86 (2)	2.6265 (14)	164 (2)

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.078$
$S = 1.04$
3331 reflections
235 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

Compound (II)

Crystal data

$[Co(C_{10}H_4O_8)(C_{12}H_{12}N_2)(H_2O)_2]\cdot C_{12}H_{12}N_2$
$M_r = 715.57$
Triclinic, $P\overline{1}$
$a = 9.0933$ (4) Å
$b = 9.5887$ (5) Å
$c = 10.0058$ (5) Å
$\alpha = 92.2999$ (7)°
$\beta = 111.9705$ (6)°
$\gamma = 105.6443$ (7)°
$V = 769.33$ (7) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 0.63$ mm^{-1}
$T = 150$ (2) K
0.29 × 0.21 × 0.18 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS* in *SAINT*; Bruker, 2002)
$T_{min} = 0.84$, $T_{max} = 0.89$
16531 measured reflections
3442 independent reflections
3363 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.076$
$S = 1.05$
3442 reflections
235 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

All H atoms were originally found in a difference Fourier map, but they were treated differently. H atoms bonded to C atoms were repositioned at their expected locations and allowed to ride, with C—H = 0.93–0.97 Å and U_{iso}(H) = 1.2 or 1.5U_{eq}(C). Water H atoms were refined with O—H distances restrained to 0.85 (1) Å but free U_{iso}(H) values. Finally, atom H33*A*, which forms a very strong O—H···N hydrogen bond that forces it to lie essentially midway between the two atoms in a 'shared' mode, was refined freely.

For both compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; 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: *SHELXTL* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3070). Services for accessing these data are described at the back of the journal.

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