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Poly[bis(μ_3-benzene-1,3,5-tricarboxylato-κ^3O^1:O^3:O^5)tris[μ_2-1,3-bis(imidazol-1-ylmethyl)benzene-κ^2N:N']tricobalt(II)] and poly[[diaquabis(μ_3-benzene-1,3,5-tricarboxylato-κ^3O^1:O^3:O^5)tris[μ_2-1,4-bis(imidazol-1-ylmethyl)benzene-κ^2N:N']tricobalt(II)] monohydrate]

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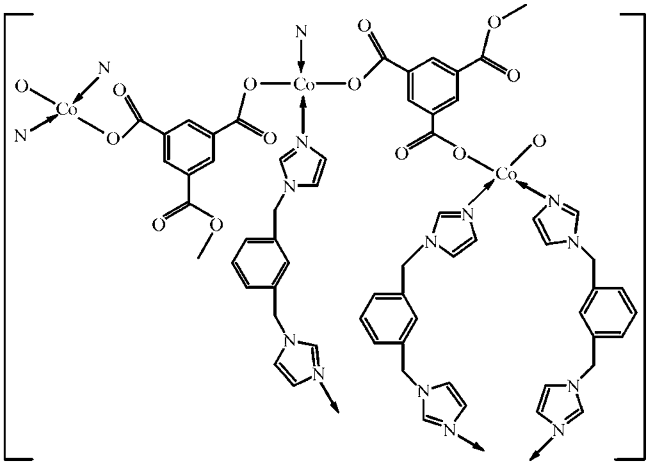
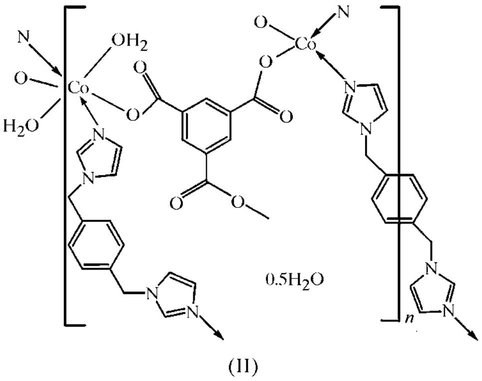
The title cobalt(II) coordination polymers, $[Co_3(C_9H_3O_6)_2(C_{14}H_{14}N_4)_3]_n$, (I), and $\{[Co_3(C_9H_3O_6)_2(C_{14}H_{14}N_4)_3(H_2O)_2]\cdot H_2O\}_n$, (II), present very different coordination and packing properties in spite of the ligand similarity. In (I), three crystallographically distinct Co^{II} cations are all four-coordinated by O_2N_2 donor sets in distorted tetrahedral geometries. The Co^{II} centres are connected by benzene-1,3,5-tricarboxylate (BTC) anions and 1,3-bis(imidazol-1-ylmethyl)benzene (L^1) ligands into a $(6^4.8^2)_2(8^6)(6.8^2)_2$ topology framework. The structure of (II) contains two kinds of crystallographically unique Co^{II} cations. One Co atom lies on a symmetry centre and is six-coordinated by an O_4N_2 donor set, and the other Co atom is four-coordinated by an O_2N_2 donor set. The Co^{II} centres are connected by BTC anions and 1,4-bis(imidazol-1-ylmethyl)benzene (L^2) ligands into a $(6^2.8^4)_2(6^4.8^2)(6^3)_2$ framework.

Comment

Extended framework solids are of current importance because they may offer new materials with a range of potentially useful properties, as well as intriguing molecular topological nets and entanglements (Huang *et al.*, 2004; Kitagawa *et al.*, 2004). The main strategy popularly used in this area is a building-block approach (Eddaoudi *et al.*, 2001), and much effort has been made towards the connection of suitable predetermined building blocks into networks in order to obtain the desired materials. In this regard, the characterization of metal–organic hybrid materials based on carboxylates and flexible ligands is a domain of special interest (Li *et al.*, 2006; Lu *et al.*, 2007). As an extension of our previous work (Yang *et al.*, 2006), we present here the two title compounds, (I) and (II), both of which were obtained by combining benzenetricarboxylic and bis(imidazole) ligands and both of which yield (3,4)-connected non-uniform entangled frameworks.



(I)



(II)

As shown in Fig. 1, the structure of (I) contains three crystallographically distinct Co^{II} cations, two kinds of unique benzene-1,3,5-tricarboxylate (BTC) anions and three kinds of unique 1,3-bis(imidazol-1-ylmethyl)benzene (L^1) ligands. Each Co^{II} cation has a distorted tetrahedral coordination environment and is coordinated by two O atoms from two BTC anions and two N atoms from two L^1 ligands (Table 1). Each BTC anion coordinates to three Co^{II} ions, and a rhomb-like chain propagated by BTC anions *via* fusing Co^{II} cations is formed along the *c* axis (Fig. 2*a*).

The three crystallographically distinct L^1 ligands adopt two kinds of conformations. One is in a *trans* conformation (Sun *et al.*, 2000), with a Co$\cdots$Co distance of 13.870 (3) Å. Each *trans* L^1 molecule coordinates to two Co3 cations, acting as a bridging ligand to form an infinite zigzag chain structure. The $[Co_3(BTC)_2]$ chains are extended by these zigzag chains to form a two-dimensional network (Fig. 2*b*). The other two L^1 ligands display *cis* conformations (Hammes *et al.*, 2005), linking cations at Co$\cdots$Co distances of 7.275 (2) and 7.416 (2) Å. Atoms Co1 and Co2 are connected by *cis* L^1 ligands to form a helix (Fig. 2*c*). These helices further link the two-dimensional networks, as shown in Fig. 2(*b*), to form a complicated three-dimensional structure. If the BTC anions

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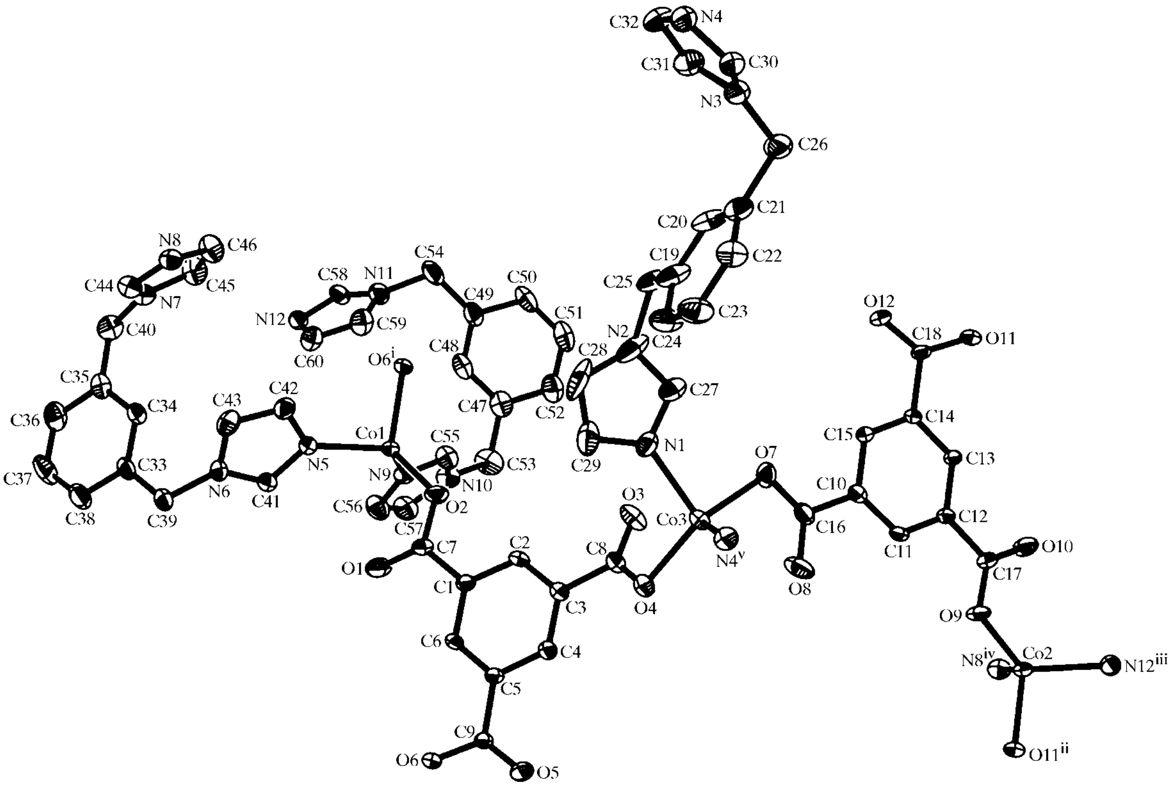

Figure 1
A view of the local coordination of the Co^{II} cations in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity. [Symmetry codes: (i) $x, -y+1, z+\frac{1}{2}$; (ii) $x, -y+1, z-\frac{1}{2}$; (iii) $x-\frac{1}{2}, y-\frac{1}{2}, z-1$; (iv) $x-\frac{1}{2}, y+\frac{1}{2}, z-1$; (v) $x, -y-1, z-\frac{1}{2}$.]

are considered as three-connected nodes, the structure of (I) can be simplified to a unique (3,4)-connected net with $(6^4.8^2)_2(8^6)(6.8^2)_2$ topology (Fig. 2*d*) (Wells, 1977, 1979; Dolomanov *et al.*, 2003).

A related compound, (III) (Liu *et al.*, 2007), displays a quite different structure, though it features the same general formula as (I), $\{[Co_3(BTC)_2(L^1)_3]\}_n$. The structure of (III) can be symbolized as a net with $(6^4.8^2)_2(6^2.8^2.10^2)(6^3)_2$ topology. Although it is hard to propose definitive reasons as to why compounds (I) and (III) adopt different configurations, it can be speculated that pH values may exert an important influence on the resulting architectures.

As illustrated in Fig. 3, the structure of (II) contains two unique Co^{II} cations (one of them, Co1, lies on an inversion centre), one BTC anion and two unique 1,4-bis(imidazol-1-ylmethyl)benzene (L^2) ligands, one of which is also bisected by a symmetry centre. Atom Co1 is six-coordinated by two O atoms from two BTC anions, two aqua ligands and two N atoms from two L^2 ligands. Atom Co2 is four-coordinated by two O atoms from two BTC anions and two N atoms from two L^2 ligands (Table 2). Each BTC anion coordinates to three Co^{II} cations, and the Co atoms are bridged by BTC anions to form a ladder (Fig. 4*a*). The two unique L^2 ligands display different conformations. One L^2 ligand shows a *cis* conformation (Carlucci *et al.*, 2005), spanning a Co$\cdots$Co distance of 11.782 (3) Å, while the other adopts a *trans* conformation

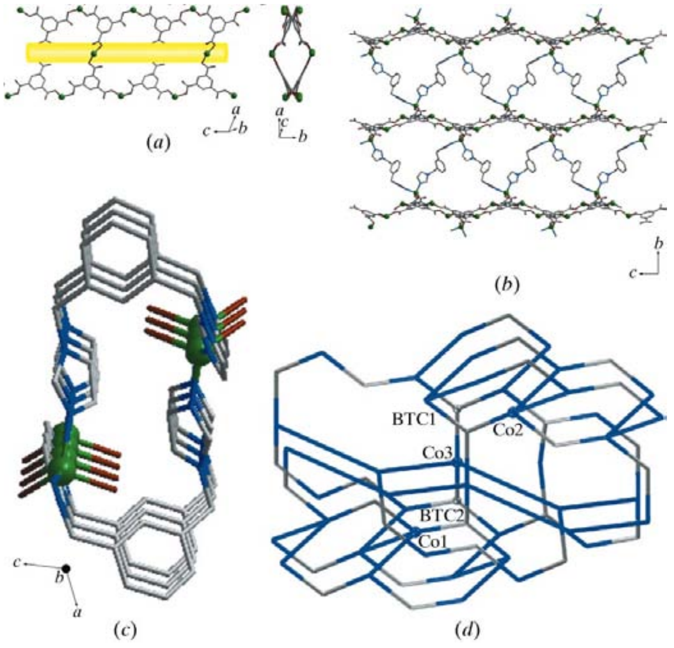

Figure 2
(*a*) Side and front views of the one-dimensional rhomb-like chain constructed from Co^{II} atoms and BTC anions in (I). (*b*) The two-dimensional structure of (I) extended by *trans* L^1 ligands between adjacent $[Co_3(BTC)_2]$ chains. (*c*) The helix formed by Co^{II} and the *cis* L^1 ligands in (I). (*d*) Schematic diagram (*OLEX*; Dolomanov *et al.*, 2003) showing the $(6^4.8^2)_2(8^6)(6.8^2)_2$ topology network of (I).

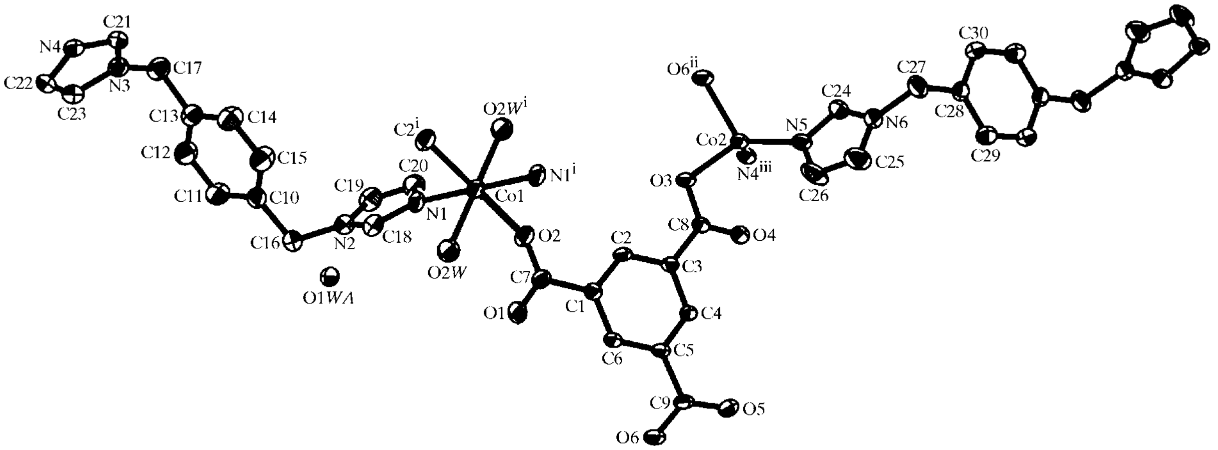

Figure 3

A view of the local coordination of the Co^{II} cations in (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity. [Symmetry codes: (i) $-x, -y, -z$; (ii) $x, y-1, z$; (iii) $x-1, -y-\frac{1}{2}, z+\frac{1}{2}$.]

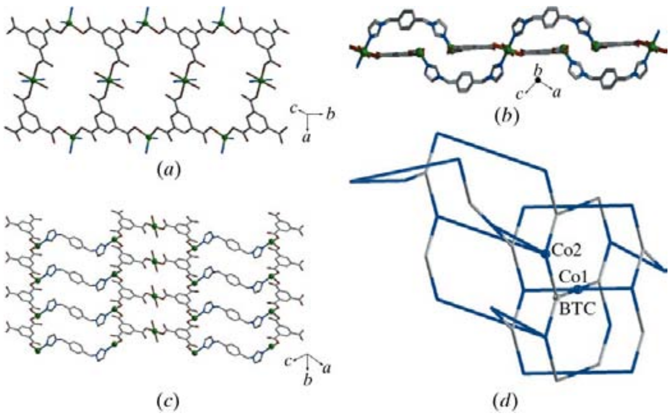

Figure 4

(*a*) View of the one-dimensional ladder made of Co^{II} atoms and BTC anions in (II). (*b*) The extended two-dimensional structure of (II) when *trans* L^2 ligands are neglected. (*c*) The extended two-dimensional structure of (II) when *cis* L^2 ligands are neglected. (*d*) Schematic diagram (*OLEX*; Dolomanov *et al.*, 2003) showing the $(6^2.8^4)_2(6^4.8^2)(6^3)_2$ topology network of (II).

instead (Fan *et al.*, 2006), with a Co$\cdots$Co distance of 14.388 (3) Å. The [$Co_3(BTC)_2$] ladders are connected by these two L^2 ligands to form two kinds of two-dimensional networks (Figs. 4*b* and 4*c*) The whole structure displays a unique (3,4)-connected three-dimensional framework (Fig. 4*d*). The structure can be symbolized as a net with $(6^2.8^4)_2(6^4.8^2)(6^3)_2$ topology, with the BTC anions being considered as three-connected nodes.

Experimental

Ligands L^1 and L^2 were synthesized according to the literature (Liu *et al.*, 2007). A mixture of $Co(NO_3)_2{\cdot}6H_2O$ (0.12 g, 0.45 mmol), H_3BTC (0.06 g, 0.30 mmol), L^1 (0.11 g, 0.45 mmol) and water (7 ml) was stirred for 10 min in air. The mixture was sealed in a Teflon reactor (15 ml) and heated at 433 K for 3 d. After the mixture had been cooled to room temperature at a rate of 10 K h^{-1}, purple crystals of (I) were obtained.

A mixture of $Co(NO_3)_2{\cdot}6H_2O$ (0.12 g, 0.45 mmol), H_3BTC (0.10 g, 0.15 mmol), L^2 (0.11 g, 0.45 mmol) and water (7 ml) was stirred for 10 min in air. The mixture was sealed in a Teflon reactor and heated at 433 K for 3 d. After the mixture had been cooled to room temperature at a rate of 10 K h^{-1}, purple crystals of (II) were obtained.

Compound (I)

Crystal data

$[Co_3(C_9H_3O_6)_2(C_{14}H_{14}N_4)_3]$
$M_r = 1305.89$
Monoclinic, *Cc*
$a = 40.152$ (9) Å
$b = 8.353$ (3) Å
$c = 18.842$ (5) Å
$\beta = 113.138$ (9)°

$V = 5811$ (3) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.92$ mm^{-1}
$T = 293$ (2) K
0.33 × 0.26 × 0.22 mm

Data collection

Bruker APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.74$, $T_{max} = 0.82$

27961 measured reflections
11621 independent reflections
10356 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.091$
$S = 1.04$
11621 reflections
800 parameters
2 restraints

H-atom parameters constrained
$\Delta\rho_{max} = 1.08$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-3}
Absolute structure: Flack (1983), with 4958 Friedel pairs
Flack parameter: 0.246 (10)

Table 1

Selected bond lengths (Å) for (I).

Co1—O2	1.929 (2)	Co2—N12^{iii}	2.014 (3)
Co1—O6^{i}	1.976 (2)	Co2—N8^{iv}	2.019 (3)
Co1—N5	2.007 (3)	Co3—O4	1.968 (2)
Co1—N9	2.012 (3)	Co3—O7	1.986 (2)
Co2—O9	1.945 (2)	Co3—N4^{v}	2.036 (3)
Co2—O11^{ii}	1.975 (2)	Co3—N1	2.067 (3)

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

Compound (II)

Crystal data

$[Co_3(C_9H_3O_6)_2(C_{14}H_{14}N_4)_3(H_2O)_2]\cdot H_2O$
$M_r = 1359.94$
Monoclinic, $P2_1/c$
$a = 14.160\ (4)$ Å
$b = 10.105\ (3)$ Å
$c = 20.927\ (4)$ Å
$\beta = 99.730\ (6)^\circ$
$V = 2951.3\ (14)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.91$ mm^{-1}
$T = 293\ (2)$ K
$0.31 \times 0.28 \times 0.21$ mm

Data collection

Bruker APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.77$, $T_{max} = 0.83$
24924 measured reflections
6651 independent reflections
3309 reflections with $I > 2\sigma(I)$
$R_{int} = 0.114$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.074$
$wR(F^2) = 0.165$
$S = 1.13$
6651 reflections
413 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.71$ e Å^{-3}
$\Delta\rho_{min} = -0.69$ e Å^{-3}

Table 2
Selected bond lengths (Å) for (II).

Co1—O2	2.033 (4)	Co2—O3	2.008 (3)
Co1—N1	2.146 (4)	Co2—N4^{ii}	2.010 (4)
Co1—O2*W*	2.178 (4)	Co2—N5	2.015 (4)
Co2—O6^{i}	2.003 (3)		

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

A *PLATON* (Spek, 2003) alert on a possible *C*2/*c* symmetry in structure (I) proved to be false, since the position of the eventual symmetry centre was incompatible with the remaining symmetry elements. In addition, the structure presented a refined Flack (1983) parameter of 0.246 (10), suggesting a considerable degree of inversion twinning.

H atoms bound to carbon were located in idealized positions and refined using a riding model, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic and C—H = 0.97 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for CH_2 hydrogens. The water H atoms in (II) could not be positioned reliably and were omitted from the final model.

For both compounds, data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3062). Services for accessing these data are described at the back of the journal.

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