Poly[[cobalt(II)-di-μ_3-3,5-diamino-benzoato-$\kappa^3 N$:N':O] monohydrate]

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In the title compound, $\{[Co(C_7H_7N_2O_2)_2]\cdot H_2O\}_n$, the Co^{II} atom lies on an inversion centre and has octahedral geometry, defined by two O atoms in axial positions and four N atoms in equatorial sites from six different 3,5-diaminobenzoate ligands. Each 3,5-diaminobenzoate anion acts as a μ_3-bridging ligand, linking three adjacent Co^{II} ions through one O atom and two N atoms to form a three-dimensional coordination polymer.

Comment

In recent years, a large number of metal–organic compounds have been prepared because of the fascinating structural and topological features of these compounds and their potential applications as functional materials, such as catalysts, optical materials and molecule-based magnets (Hagrman *et al.*, 1999; Moulton & Zaworotko, 2001; Janiak, 2003). In this field, many organic bridging ligands, such as bipyridine, polyaromatic

(I)
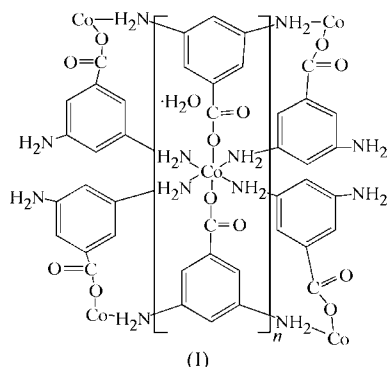
carboxylates and their related species, are often selected to coordinate to metal centres to obtain various types of polymeric structures, including one-, two- and three-dimensional network structures (Blake *et al.*, 1999; Eddaoudi *et al.*, 2001;

James, 2003). 3,5-Diaminobenzoic acid, a polydenate organic ligand containing two amino groups and a carboxyl group, can be used as a bridging and/or terminal ligand when it coordinates to various metallic ions. Complexes of this ligand with lanthanide metals, yttrium, molybdenum and tin have been reported (Rzaczynska & Belsky, 1994; Rzaczynska & Sobolev, 1994; Rzaczynska *et al.*, 1994; Udovic *et al.*, 1999; Pruchnik *et al.*, 2002, 2003). However, complexes of the first row transition metals with 3,5-diaminobenzoic acid have not yet been published. In this paper, we report the hydrothermal synthesis and structural characterization of the title complex, (I), which exhibits a three-dimensional network structure through bridging by the 3,5-diaminobenzoate anion.

In complex (I), the repeat unit is composed of one Co^{II} atom, two 3,5-diaminobenzoate anions and a solvent water molecule. The Co^{II} atom, lying on an inversion centre, is six-coordinated by four N atoms and two O atoms from six different 3,5-diaminobenzoic acid ligands, forming a slightly distorted octahedral coordination geometry (Fig. 1). The equatorial positions are occupied by the four N atoms. The N2^{iv}—Co1—N2^{v} and N1^{ii}—Co1—N1^{iii} bond angles are both 180°, and the N1^{ii}—Co1—N2^{iv} and N1^{iii}—Co1—N2^{iv} bond angles are 91.05 (5) and 88.95 (5)°, respectively [symmetry codes: (ii) $x - 1$, $-y + \frac{1}{2}$, $z - \frac{1}{2}$; (iii) $-x + 1$, $y - \frac{1}{2}$, $-z + \frac{1}{2}$; (iv) $-x + 1$, $-y$, $-z$; (v) $x - 1$, y, z]. The Co—N bond distances are 2.2094 (13) and 2.2567 (13) Å (Table 1). The axial positions are occupied by two O atoms, with the O1—Co1—O1^{i} bond angle being 180° [symmetry code: (i) $-x$, $-y$, $-z$] and the Co—O bond distances being 2.0441 (11) Å. The longer Co1···O2 distance (3.339 Å) and the larger Co1—O1—C1 angle [129.57 (11)°] suggest there is no bonding interaction between atoms Co1 and O2. Thus, the carboxyl group of the
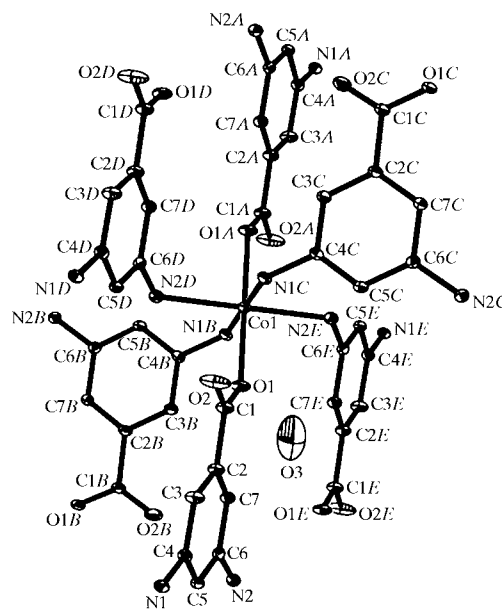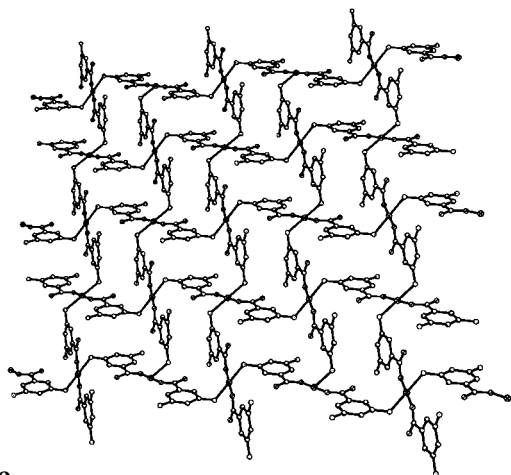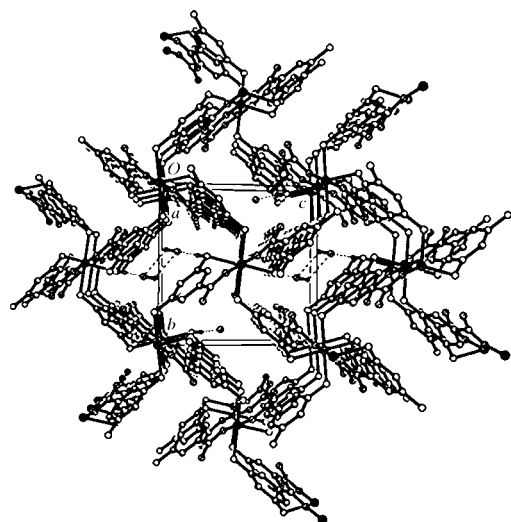

Figure 1
A view of part of the polymeric structure of (I). Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. Atoms labelled with the suffixes *A*–*E* are at the symmetry positions $(-x, -y, -z)$, $(x - 1, -y + \frac{1}{2}, z - \frac{1}{2})$, $(-x + 1, y - \frac{1}{2}, -z + \frac{1}{2})$, $(-x + 1, -y, -z)$ and $(x - 1, y, z)$, respectively.

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3,5-diaminobenzoate anion coordinates to the Co^{II} atom in a monodentate mode (Li *et al.*, 2005).

In complex (I), each 3,5-diaminobenzoate ligand provides two amine N atoms and one carboxylate O atom to coordinate to three Co^{II} atoms, thus acting as a μ_3-bridging ligand. The bridging of the 3,5-diaminobenzoate anion *via* its O atom and an N atom links the Co^{II} atoms into a two-dimensional network in the *bc* plane (Fig. 2). The distance between two adjacent Co^{II} atoms in the plane is 9.267 Å, which is comparable with the largest of several Co$\cdots$Co distances found in [Co(3,4-pyda)(H$_2$O)$_2$]$_n$·H$_2$O (9.269 Å; 3,4-pyda is the pyridine-3,4-dicarboxylate dianion; Tong *et al.*, 2004). The large Co$\cdots$Co distance in (I) indicates the absence of any interaction between the Co^{II} atoms. The coordination of another N atom of the 3,5-diaminobenzoate anion (which is not coordinated to a Co^{II} atom within the two-dimensional network) to a Co^{II} ion of an adjacent two-dimensional network leads to the generation of a three-dimensional network (Fig. 3).

Figure 2
A view of the two-dimensional sheet in the *bc* plane. All H atoms have been omitted for clarity.

Figure 3
A packing diagram for complex (I), viewed along the *a* direction of the unit cell.

In the extended structure, the uncoordinated carboxylate O atoms, the solvent water molecules and the amino groups of the 3,5-diaminobenzoate ligand are involved in hydrogen bonding. The uncoordinated carboxyl O atoms form hydrogen bonds with the amino groups of the 3,5-diaminobenzoate anion [N2—H2A$\cdots$O2^{iii} = 3.012 (2) Å and N1—H1A$\cdots$O2^{iv} = 2.8357 (19) Å], and the solvent water molecules also form hydrogen bonds with the amino groups of the ligand, as well as with other solvent water molecules [N2—H2B$\cdots$O3^{ii} = 3.165 (8) Å and O3—H3A$\cdots$O3^{i} = 2.977 (16) Å]; the geometry of the hydrogen bonding is given in Table 2. The formation of these hydrogen bonds further stabilizes the three-dimensional structure of the complex.

Experimental

Crystal data

[Co(C$_7$H$_7$N$_2$O$_2$)$_2$]·H$_2$O	D_x = 1.690 Mg m^{-3}
M_r = 379.24	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 3477
a = 7.4666 (6) Å	reflections
b = 10.0219 (8) Å	θ = 2.8–27.9°
c = 10.3856 (8) Å	μ = 1.19 mm^{-1}
β = 106.4440 (10)°	T = 294 (2) K
V = 745.36 (10) Å^3	Block, brown
Z = 2	0.22 × 0.20 × 0.16 mm

Data collection

Bruker SMART CCD area-detector diffractometer	1646 reflections with $I > 2\sigma(I)$
φ and ω scans	R_{int} = 0.012
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)	θ_{max} = 27.9°
	$h = -9 \rightarrow 9$
	$k = -13 \rightarrow 9$
4846 measured reflections	$l = -13 \rightarrow 13$
1771 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0423P)^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.028	$+ 0.6967P]$
$wR(F^2)$ = 0.079	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.05	$(\Delta/\sigma)_{max}$ = 0.003
1771 reflections	$\Delta\rho_{max}$ = 0.59 e Å^{-3}
115 parameters	$\Delta\rho_{min}$ = −0.35 e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Co1—O1	2.0441 (12)	Co1—N2^{iv}	2.2567 (14)
Co1—N1^{ii}	2.2094 (14)		
O1—Co1—N1^{ii}	87.65 (5)	O1—Co1—N2^{v}	89.37 (5)
O1—Co1—N1^{iii}	92.35 (5)	N1^{ii}—Co1—N2^{v}	88.95 (5)
O1—Co1—N2^{iv}	90.63 (5)	C1—O1—Co1	129.57 (11)
N1^{ii}—Co1—N2^{iv}	91.05 (5)		

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

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

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
O3—H3A···O3^{vi}	0.87	2.39	2.977 (16)	126
N2—H2B···O3^{vii}	0.90	2.27	3.165 (8)	173
N2—H2A···O2^{ii}	0.90	2.21	3.012 (2)	148
N1—H1A···O2^{viii}	0.90	2.07	2.8357 (19)	142

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

All H atoms were positioned geometrically and treated as riding, with C—H distances of 0.93 Å, N—H distances of 0.90 Å and O—H distances of 0.87 Å, and with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C,N})$ for aromatic and amine H atoms or $1.5U_{\text{eq}}(\text{O})$ for water H atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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