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Tetraaquabis(3,5-dicarboxybenzoato-*O*)cobalt(**II**)

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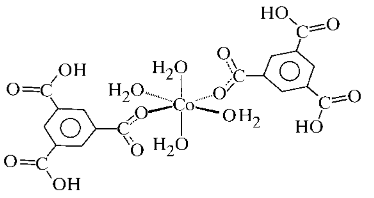
The hydrothermal reaction of cobalt(II) chloride with trimesate (3,5-dicarboxybenzoate) ions in aqueous solution gives the novel title complex, $[Co(C_9H_5O_6)_2(H_2O)_4]$. The Co^{II} ion lies on an inversion centre and is octahedrally coordinated to two trimesate anions and four water molecules. Hydrogen bonds ensure the three-dimensional architecture of the structure.

Comment

Over the last decade, significant research effort has been focused on the use of organic molecular building blocks to generate three-dimensional porous solids *via* hydrogen bonding or copolymerization of metal ions (Palmans *et al.*, 1997; Livage *et al.*, 1998, 1999). Trimesic acid (benzene-1,3,5-tricarboxylic acid, TMA) has been successfully used by several authors to design organic supramolecular networks (Kolotuchin *et al.*, 1999; Sharma & Zaworotko, 1996; Melendez *et al.*, 1996). Its geometry and hydrogen-bonding capability (three carboxylic acid groups) make it an interesting tool for crystal engineering. Condensation of TMA with metal



(I)

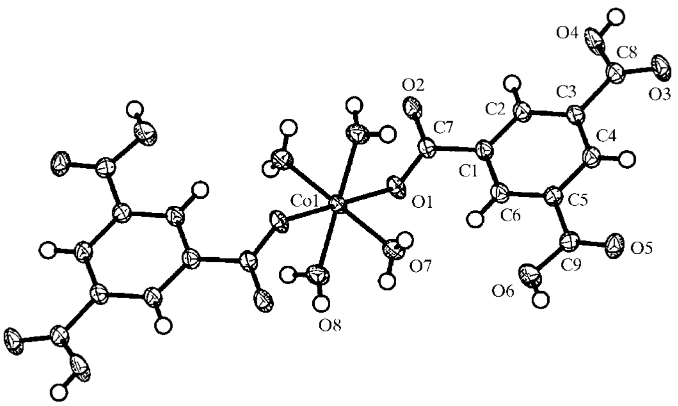


Figure 1
A view of complex (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as spheres of arbitrary radii.

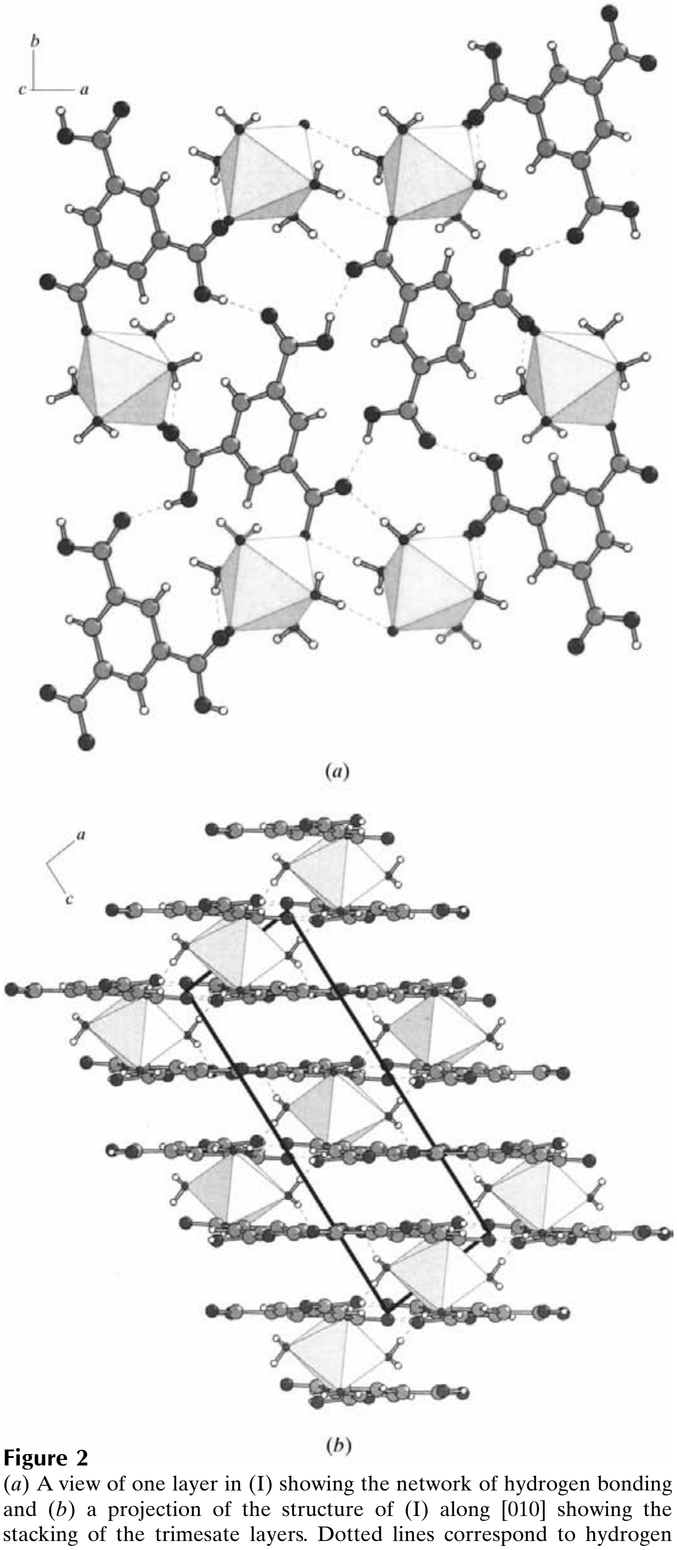


Figure 2
(*a*) A view of one layer in (I) showing the network of hydrogen bonding and (*b*) a projection of the structure of (I) along [010] showing the stacking of the trimesate layers. Dotted lines correspond to hydrogen bonds.

ions was first developed by Yaghi *et al.* (1996, 1997, 1998) to generate coordination polymers (Chui *et al.*, 1999; Chui, Los *et al.*, 1999; Daiguebonne *et al.*, 1999; Li *et al.*, 1999). Herein, we describe the synthesis and crystal structure of a new cobalt(II)–TMA complex, (I), and demonstrate that this species can be used as a synthon to generate supramolecular networks.

The centrosymmetric structure of (I) is shown in Fig. 1 with the atom-labelling scheme. Two monodentate carboxylate groups and four water molecules octahedrally coordinate the Co atom. Each trimesate ligand presents one bonding and two pendant protonated carboxylate groups, leading to a single negative charge on the ligand. The TMA^- anion and two of the coordinated water molecules lie in planes, the Co atom being located between these planes. A network of strong hydrogen bonds (Table 2), between TMA^- ions, and between TMA^- ions and water molecules, provides the basis of this two-dimensional network (Fig. 2*a*). The Co atom ensures the three-dimensionality of the architecture by linking adjacent layers (Fig. 2*b*).

These results illustrate the clear tendency of trimesate complexes to pack into planes in order to maximize hydrogen bonding. The solid-state arrangement is therefore dominated by the formation of trimesate layers, as previously described for lanthanide complexes by Daiguebonne *et al.* (1999).

Experimental

Complex (I) was hydrothermally synthesized from a mixture of cobalt(II) chloride hexahydrate, trimesic acid, potassium hydroxide and water in the molar ratio 1:1:1:60. The starting mixture was heated for 12 h at 453 K under autogenous pressure (final pH = 2). The resulting solid phase, consisting of pink needles of (I), was filtered off and dried at room temperature.

Crystal data

$[Co(C_9H_5O_6)_2(H_2O)_4]$
$M_r = 549.26$
Monoclinic, $P2_1/c$
$a = 5.1160\ (1)$ Å
$b = 13.0080\ (2)$ Å
$c = 15.1890\ (1)$ Å
$\beta = 96.853\ (1)°$
$V = 1003.59\ (3)$ Å^3
$Z = 2$
$D_x = 1.818$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5763 reflections
$\theta = 2.07$–$29.77°$
$\mu = 0.946$ mm^{-1}
$T = 296\ (2)$ K
Needle, pink
$0.76 \times 0.14 \times 0.08$ mm

Data collection

Siemens SMART 1K diffractometer
ω scans
Absorption correction: semi-empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.533$, $T_{max} = 0.928$
6860 measured reflections
2590 independent reflections
2281 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 29.77°$
$h = -6 \rightarrow 7$
$k = -17 \rightarrow 14$
$l = -20 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.073$
$S = 1.090$
2590 reflections
179 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.042P)^2 + 0.0785P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.031 (2)

Table 1
Selected geometric parameters (Å, °).

Co1—O1	2.1117 (9)	Co1—O8	2.1107 (10)
Co1—O7	2.0720 (9)		
O1—Co1—O7	90.52 (4)	O7—Co1—O8	88.86 (4)
O1—Co1—O8	88.24 (4)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4*A*···O2^{i}	0.82	1.80	2.589 (2)	161
O6—H6*A*···O3^{ii}	0.82	1.81	2.631 (2)	175
O7—H7*A*···O5^{ii}	0.80 (2)	1.95 (3)	2.740 (2)	168 (2)
O7—H7*B*···O1^{iii}	0.86 (2)	1.89 (2)	2.748 (2)	175 (2)
O8—H8*A*···O2^{iv}	0.87 (2)	1.86 (3)	2.726 (2)	177 (2)

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

H atoms from the water molecules were found *via* difference Fourier maps and isotropically refined. H atoms from the trimesate molecules were treated as riding (O—H = 0.82 and C—H = 0.93 Å). All H-atom positions (trimesate and water) could be deduced from difference Fourier maps. However, H atoms from the trimesate were placed in calculated positions in order to have perfect sp^2 geometry.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1105). Services for accessing these data are described at the back of the journal.

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