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Key indicators

Single-crystal X-ray study
T = 298 K
Mean $\sigma(\text{C}-\text{C}) = 0.018 \text{ \AA}$
R factor = 0.092
wR factor = 0.259
Data-to-parameter ratio = 15.3

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Bis[[tris(1*H*-benzimidazol-2-ylmethyl)amine]-chlorocobalt(II)] tetrachlorocobaltate(II) methanol tetrasolvate

In the title compound, $[\text{CoCl}(\text{C}_{24}\text{H}_{21}\text{N}_7)]_2[\text{CoCl}_4] \cdot 4\text{CH}_3\text{OH}$, the crystal packing is stabilized by $\text{O}-\text{H} \cdots \text{Cl}$, $\text{N}-\text{H} \cdots \text{Cl}$ and $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds, weak $\text{C}-\text{H} \cdots \text{Cl}$ interactions, and $\pi-\pi$ stacking. The anion lies on a twofold rotation axis.

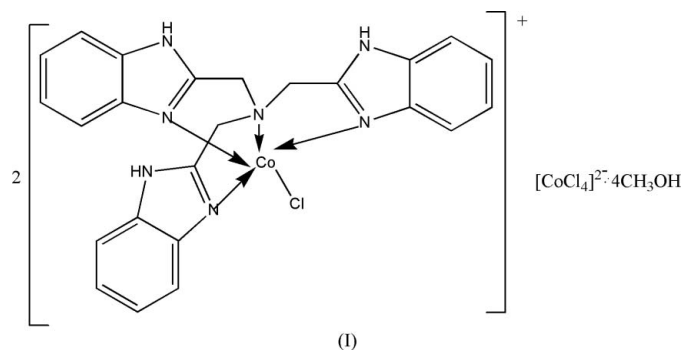
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Comment

Imidazole (Im) and benzimidazole (Bzim) are common species in biological and biochemical structure and function (Sundberg *et al.*, 1977; Santoro *et al.*, 2000). Their derivatives have also found application in drug design in the form of antitumour (Arrowsmith *et al.*, 2002) and anticancer (Hay *et al.*, 2003) agents. In an effort to explore these types of species in more detail, we have synthesized tris(benzimidazol-2-ylmethyl)amine (NTB), which contains three benzimidazole rings, and report one of its complexes here.



The molecular structure of the title compound, (I), is shown in Fig. 1 and selected geometric data are listed in Table 1. The asymmetric unit consists of a $[\text{Co}(\text{NTB})\text{Cl}]^+$ cation, half of a $[\text{CoCl}_4]^{2-}$ anion and two solvent methanol molecules. The complete tetrachlorocobaltate anion is generated by twofold symmetry (atom Co2 lies on the twofold axis). The cation has a trigonal-bipyramidal coordination geometry around the Co1 centre, and the three benzimidazolyl N atoms make up the trigonal plane. The apical N atom of NTB and the Cl^- anion occupy the axial positions (Table 1). The dihedral angles between the Bzim rings are $111.9 (2)^\circ$ between plane 1 (C2–C8/N2/N3) and plane 2 (C10–C16/N4/N5), $125.5 (3)^\circ$ between plane 2 and plane 3 (C19–C24/N6/N7), and $118.6 (2)^\circ$ between planes 1 and 3. The $\text{Co}-\text{N}(\text{Bzim})$ bond lengths range from 2.016 (8) to 2.053 (7) \AA , which is slightly longer than in related structures [2.008 (2)–2.031 (2) \AA ; Hammes *et al.*, 2002]. This difference may be a consequence of the steric constraint imposed by the chelate coordination.

As shown in Table 2 and Fig. 2, the crystal packing of (I) is stabilized by $\text{O}-\text{H} \cdots \text{Cl}$, $\text{N}-\text{H} \cdots \text{Cl}$ and $\text{N}-\text{H} \cdots \text{O}$ hydrogen

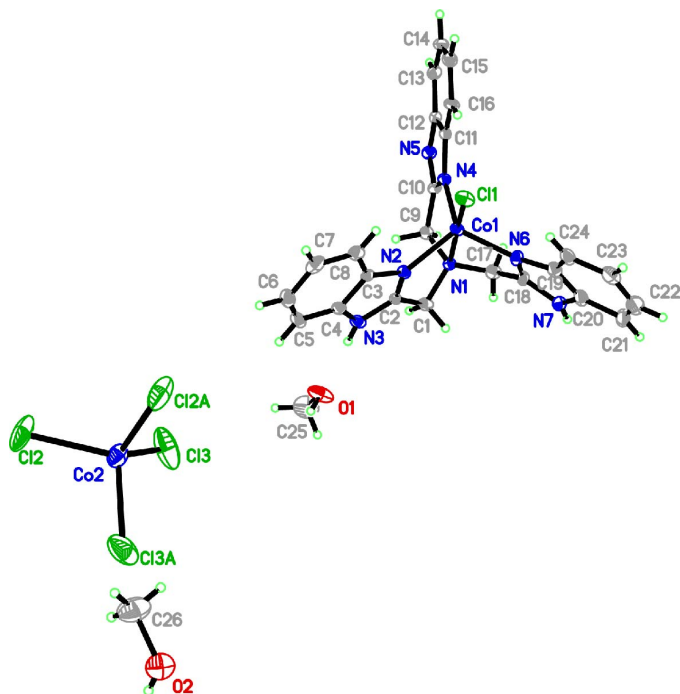


Figure 1
View of (I), showing 50% displacement ellipsoids (arbitrary spheres for H atoms). Atoms with the suffix *A* are generated by the symmetry operation $(2 - x, y, \frac{1}{2} - z)$.

bonds, and weak C—H...Cl interactions. In addition, neighbouring aromatic rings interact by way of π – π stacking interactions, with distances of 3.54 (2) [plane 1/plane 1($\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$)] and 3.58 (2) Å [plane 2/plane 2($-x, 1 - y, 1 - z$)].

Experimental

All chemicals were of reagent grade and commercially available, and were used without further purification. Nitrilotriacetic acid (0.4790 g, 2.5 mmol) and 1,2-diaminobenzene (0.8123 g, 7.5 mmol) and 10 ml of glycol were mixed in 250 ml beaker. The mixture was irradiated for 15 min intermittently with a WP700 LG microwave oven (output power 350 W), and then cooled to room temperature. Distilled water (about 80 ml) was added and a yellow precipitate formed immediately; this was filtered off and washed with distilled water, yielding a light-yellow product of tris(benzimidazol-2-ylmethyl)amine. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.0602 g, $\frac{1}{4}$ mmol) was added to a solution of NTB (0.0510 g, $\frac{1}{3}$ mmol) in a mixture of methanol (5 ml) and absolute ethanol (5 ml), and stirred at room temperature for 2 h. The deep-red solution was left at room temperature and black crystals of (I) were obtained by slow evaporation of the solvent over several days.

Crystal data

$[\text{CoCl}(\text{C}_{24}\text{H}_{21}\text{N}_7)]_2[\text{CoCl}_4] \cdot 4\text{CH}_4\text{O}$	$D_x = 1.402 \text{ Mg m}^{-3}$
$M_r = 1332.61$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 1380 reflections
$a = 23.432 (7) \text{ \AA}$	$\theta = 2.7\text{--}16.1^\circ$
$b = 16.752 (5) \text{ \AA}$	$\mu = 1.09 \text{ mm}^{-1}$
$c = 16.134 (5) \text{ \AA}$	$T = 298 (2) \text{ K}$
$\beta = 94.372 (5)^\circ$	Block, black
$V = 6315 (3) \text{ \AA}^3$	$0.30 \times 0.20 \times 0.10 \text{ mm}$
$Z = 4$	

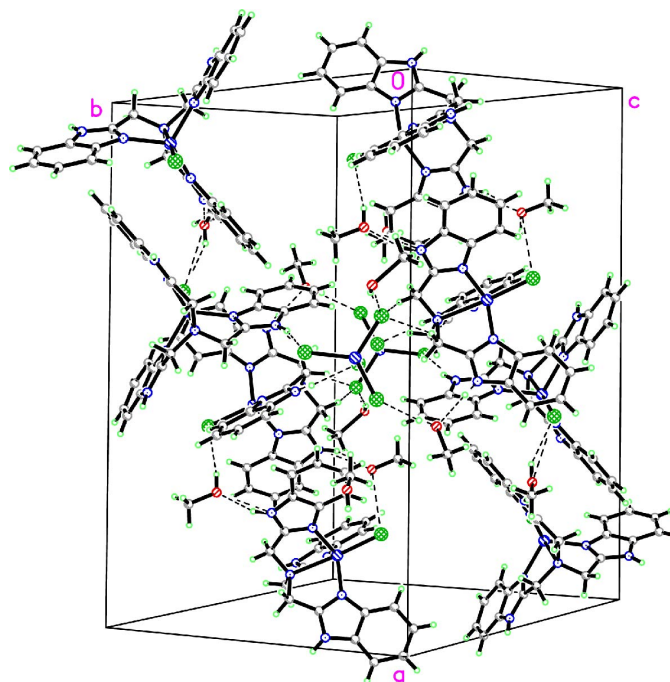


Figure 2
The packing in (I), showing intermolecular interactions as dashed lines.

Data collection

Bruker SMART 1K CCD area-detector diffractometer	5539 independent reflections
ω scans	2235 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2000)	$R_{\text{int}} = 0.085$
$T_{\text{min}} = 0.737, T_{\text{max}} = 0.899$	$\theta_{\text{max}} = 25.0^\circ$
15 114 measured reflections	$h = -27 \rightarrow 24$
	$k = -14 \rightarrow 19$
	$l = -19 \rightarrow 18$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.092$	$w = 1/[\sigma^2(F_o^2) + (0.1169P)^2]$
$wR(F^2) = 0.259$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.94$	$(\Delta/\sigma)_{\text{max}} = 0.002$
5539 reflections	$\Delta\rho_{\text{max}} = 0.70 \text{ e \AA}^{-3}$
361 parameters	$\Delta\rho_{\text{min}} = -0.64 \text{ e \AA}^{-3}$

Table 1
Selected geometric parameters (Å, °).

Co1—N6	2.016 (8)	Co1—N1	2.375 (7)
Co1—N4	2.019 (7)	Co2—Cl3	2.214 (5)
Co1—N2	2.053 (7)	Co2—Cl2	2.248 (3)
Co1—Cl1	2.269 (3)		
N6—Co1—N4	113.7 (3)	N2—Co1—Cl1	103.6 (2)
N6—Co1—N2	115.8 (3)	N6—Co1—N1	76.0 (3)
N4—Co1—N2	112.2 (3)	N4—Co1—N1	76.2 (3)
N6—Co1—Cl1	102.9 (3)	N2—Co1—N1	74.1 (3)
N4—Co1—Cl1	107.3 (3)	Cl1—Co1—N1	176.44 (19)
N6—Co1—N2—C3	133.0 (7)	N4—Co1—N6—C19	129.1 (9)
N2—Co1—N4—Cl1	124.0 (8)		

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...C11 ⁱ	0.82	2.41	3.152 (8)	152
N7—H7...C12 ⁱⁱ	0.86	2.31	3.145 (11)	163
N5—H5...O2 ⁱⁱⁱ	0.86	1.93	2.786 (12)	178
N3—H3...O1	0.86	1.89	2.706 (12)	158
C8—H8...C11	0.93	2.81	3.545 (12)	137
C16—H16...C11	0.93	2.85	3.616 (10)	140
C24—H24...C11	0.93	2.73	3.477 (13)	138
C16—H16...C16 ^{iv}	0.93	2.90	3.357 (18)	112

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

H atoms were placed in geometrically idealized positions with C—H = 0.93–0.97 Å, N—H = 0.86 Å and O—H = 0.82 Å, and refined as riding with the constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{NTB carrier})$ or $1.5U_{\text{eq}}(\text{methanol carrier})$ applied.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

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