

**(1*H*-Benzotriazole- κ N³)trichlorocobalt(III)–
1*H*-benzotriazole–water (1/1/1)****Ze-Feng Zhang, Li-Xin Li,
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Shen**Department of Chemistry, Tsinghua University,
Beijing 100084, People's Republic of ChinaCorrespondence e-mail:
xqwang@tsinghua.edu.cn**Key indicators**Single-crystal X-ray study
T = 293 K
Mean σ (C–C) = 0.007 Å
R factor = 0.029
wR factor = 0.064
Data-to-parameter ratio = 11.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, the new phase [CoCl₃(BTA)]·BTA·H₂O (BTA is benzotriazole, C₆H₅N₃), has been synthesized and characterized by X-ray single-crystal diffraction methods. In the monomeric complex, the Co³⁺ ion is four-coordinated by three Cl[−] anions and one N atom of the BTA, forming a distorted tetrahedral coordination. There are also uncoordinated BTA molecules in the crystal structure, lying between the parallel ring planes of the coordinated BTA ligands and involved in π – π interactions. The asymmetric unit, which is the entire unit cell in space group *P*1, contains two molecules each of the complex, uncoordinated BTA and water.

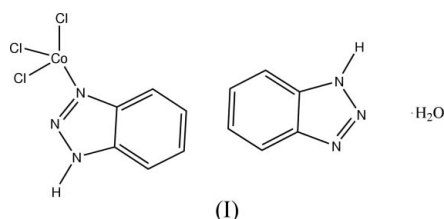
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Comment

The protection of metals with reactive materials capable of forming surface–phase coordination compounds (Wang *et al.*, 1997) is an area of chemistry which is of considerable scientific and technological importance (Sha *et al.*, 1996). Besides their uses as antiwear and antifouling agents, the ability of benzotriazole (BTA) and its derivatives to inhibit corrosion has attracted attention to transition metal complexes of BTA, especially Cu, Zn and Co compounds. Numerous complexes have been synthesized and a few compounds have shown some special structures in which the BTA ligand adopts a variety of coordination modes (Hursthouse *et al.*, 1986; Himes *et al.*, 1981). However, despite the extensive use of BTA as a corrosion inhibitor for Zn, Cu and their alloys, only a few compounds have been structurally characterized by X-ray diffraction (Hashemi & Hogarth, 1998; Yang *et al.*, 1994; Mishra *et al.*, 1982; Brusic *et al.*, 1993). Here, we report the synthesis and crystal structure of the title novel neutral tetrahedral complex of Co^{III} with BTA, (I) (Fig. 1).



Compound (I) is a mononuclear complex, in which the central Co³⁺ ion is coordinated by three Cl[−] anions and one N atom from the BTA ligand, forming a distorted tetrahedron. There are two molecules of the complex, two of uncoordinated BTA and two of water in the asymmetric unit, which is the entire unit cell in space group *P*1. The Co–N bond distances of 2.028 (3) and 2.021 (3) Å are shorter than the values in a

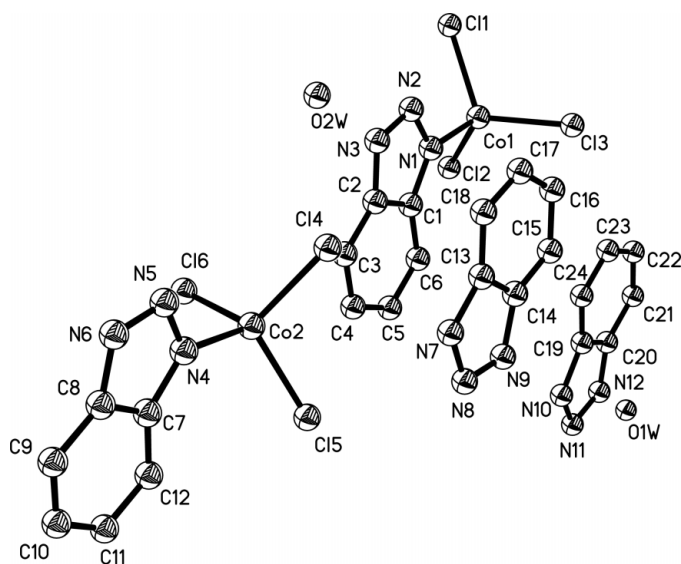


Figure 1
The asymmetric unit of (I), with 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

previous report (Zhang *et al.*, 2000). The average Co—Cl bond length is 2.248 (1) Å.

Fig. 2 shows the packing arrangement for (I). An intermolecular hydrogen-bonding network is present (Table 1), which connects the complex molecules, water molecules and free BTA ligands into a multi-layer structure. The uncoordinated BTA ligands are parallel to the ring planes of the coordinated BTA ligands, giving strong face-to-face π – π interactions between the aromatic rings. The distance between the two parallel ring planes is about 3.48 Å.

Experimental

Ethanol (1 ml) was added to a stirred aqueous (20 ml) solution of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ (0.2378 g, 0.001 mol). A few minutes later, BTA (0.2385 g, 0.002 mol) was added to the solution. A blue precipitate was produced immediately. Using HCl to adjust the pH to 4, the blue precipitate dissolved to give a clear solution. By slow evaporation of the filtrate at room temperature for several weeks, single crystals of (I) suitable for X-ray analysis were obtained. The IR spectrum shows the distinct bands, at 1612.76 and 1222.00 cm^{-1} , respectively, of the stretching vibrations of N=N and C—N.

Crystal data

$[\text{CoCl}_3(\text{C}_6\text{H}_5\text{N}_3)] \cdot \text{C}_6\text{H}_5\text{N}_3 \cdot \text{H}_2\text{O}$
 $M_r = 421.56$
 Triclinic, P1
 $a = 6.8760$ (8) Å
 $b = 7.8033$ (12) Å
 $c = 16.657$ (3) Å
 $\alpha = 95.450$ (13)°
 $\beta = 95.962$ (8)°
 $\gamma = 103.989$ (9)°
 $V = 855.8$ (2) Å³

$Z = 2$
 $D_x = 1.636$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 28 reflections
 $\theta = 5.3$ – 12.6 °
 $\mu = 1.48$ mm⁻¹
 $T = 293$ (2) K
 Prism, blue
 $0.4 \times 0.4 \times 0.2$ mm

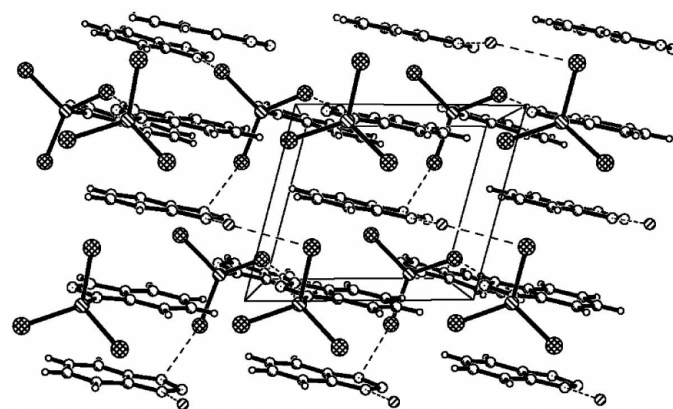


Figure 2
A unit-cell packing diagram for (I). Hydrogen bonds are indicated by dashed lines.

Data collection

Bruker P4 diffractometer
 ω scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\min} = 0.611$, $T_{\max} = 0.744$
 4906 measured reflections
 4846 independent reflections
 4528 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.078$
 $\theta_{\max} = 27.5$ °
 $h = -8 \rightarrow 1$
 $k = -9 \rightarrow 10$
 $l = -21 \rightarrow 21$
 3 standard reflections
 every 100 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.065$
 $S = 1.02$
 4846 reflections
 416 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + 0.65P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.31$ e Å⁻³
 $\Delta\rho_{\min} = -0.27$ e Å⁻³
 Extinction correction: SHELXL97
 (Sheldrick, 1997)
 Extinction coefficient: 0.0215 (4)
 Absolute structure: Flack (1983),
 920 Friedel pairs
 Flack parameter = -0.016 (14)

Table 1

Hydrogen-bonding geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
N3—H3A...O2W ⁱ	0.86	1.86	2.716 (5)	173
N6—H6A...Cl2 ⁱⁱ	0.86	2.28	3.128 (3)	170
N9—H9B...Cl1 ⁱⁱⁱ	0.86	2.30	3.123 (4)	160
N10—H10B...Cl3 ^{iv}	0.86	2.61	3.218 (4)	129
O1W—H1A...Cl4	0.85	2.89	3.692 (7)	158
O1W—H1B...Cl6	0.85	2.64	3.272 (5)	132
O2W—H2A...O1W ^v	0.93	2.22	3.148 (7)	172
O2W—H2B...Cl6	0.85	2.46	3.306 (5)	172

Symmetry codes: (i) $x, y - 1, z$; (ii) $x, y, z - 1$; (iii) $1 + x, 1 + y, z$; (iv) $x - 1, 1 + y, z - 1$; (v) $x, 1 + y, z$.

H atoms were positioned geometrically and refined riding on their parent atoms, with C—H = 0.93, N—H = 0.86 and O—H = 0.85–0.93 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent})$.

Data collection: XSCANS (Bruker, 1997); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXL97.

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