

# Structure of the five-coordinate $\text{Co}^{\text{II}}$ complex (1*H*-imidazole){tris[(1-benzyltriazol-4-yl)- $\kappa\text{N}^3$ ]-methyl]amine- $\kappa\text{N}$ }cobalt(II) bis(tetrafluoroborate)

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Received 22 February 2024

Accepted 15 April 2024

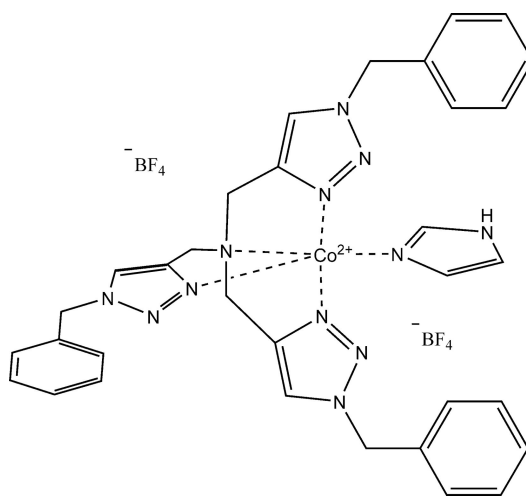
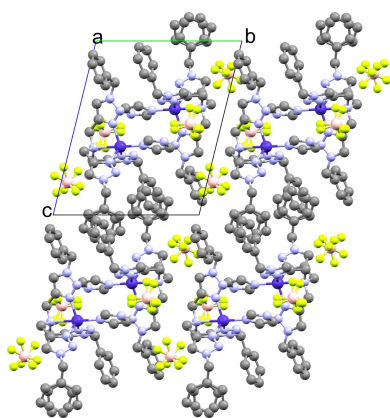
Edited by J. Reibenspies, Texas A &amp; M University, USA

**Keywords:** cobalt(II); five-coordinate; tbta; imidazole; crystal structure.**CCDC reference:** 2348506**Supporting information:** this article has supporting information at journals.iucr.org/e

The title compound,  $[\text{Co}(\text{C}_3\text{H}_4\text{N}_2)(\text{C}_{30}\text{H}_{30}\text{N}_{10})](\text{BF}_4)_2$ , is a five-coordinate  $\text{Co}^{\text{II}}$  complex based on the neutral ligands tris[(1-benzyltriazol-4-yl)methyl]amine (tbta) and imidazole. It exhibits a distorted trigonal bipyramidal geometry in which the equatorial positions are occupied by the three N-atom donors from the triazole rings of the tripodal tbta ligand. The apical amine N-atom donor of tbta and the N-atom donor of the imidazole ligand occupy the axial positions of the coordination sphere. Two tetrafluoroborate anions provide charge balance in the crystal.

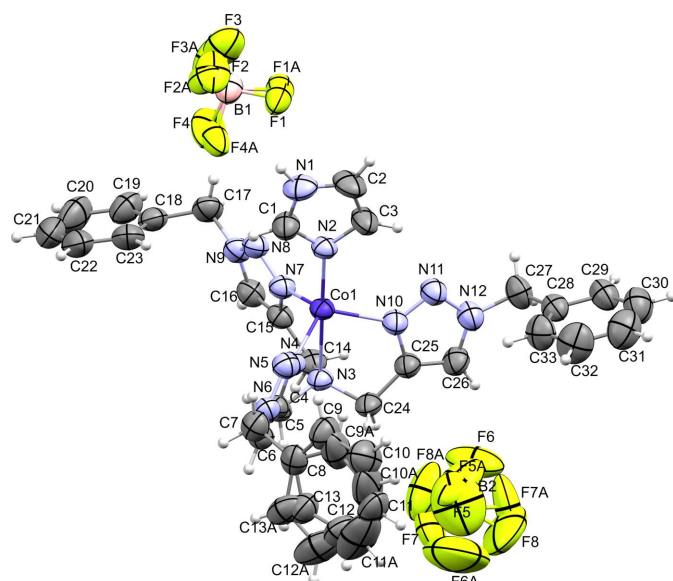
## 1. Chemical context

Five-coordinate complexes of  $\text{Co}^{\text{II}}$  are under intense investigation as potential single ion magnets, owing to unusually large magnetic anisotropy. The novel five-coordinate  $\text{Co}^{\text{II}}$  title complex is expected to exhibit similar axial magnetic anisotropy, as it shares a similar geometry with related complexes of tris[(1-benzyltriazol-4-yl)methyl]amine (tbta) (Mondal *et al.*, 2017; Schweinfurth *et al.*, 2015, 2017), which have shown promising slow magnetic relaxation. This complex pairs two neutral N-atom donor ligands with  $\text{Co}^{\text{II}}$ . Notably, the title complex,  $[\text{Co}(\text{imidazole})(\text{tbta})](\text{BF}_4)_2$ , represents the first of its kind with a neutral fifth donor, expanding the scope of potential applications within this structural motif.



## 2. Structural commentary

The central metal ion coordinates five N-atom donors, four from the tbta ligand and one from imidazole (Fig. 1). The Co atom sits 0.51 Å above the equatorial plane (N4/N7/N10)



**Figure 1**  
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

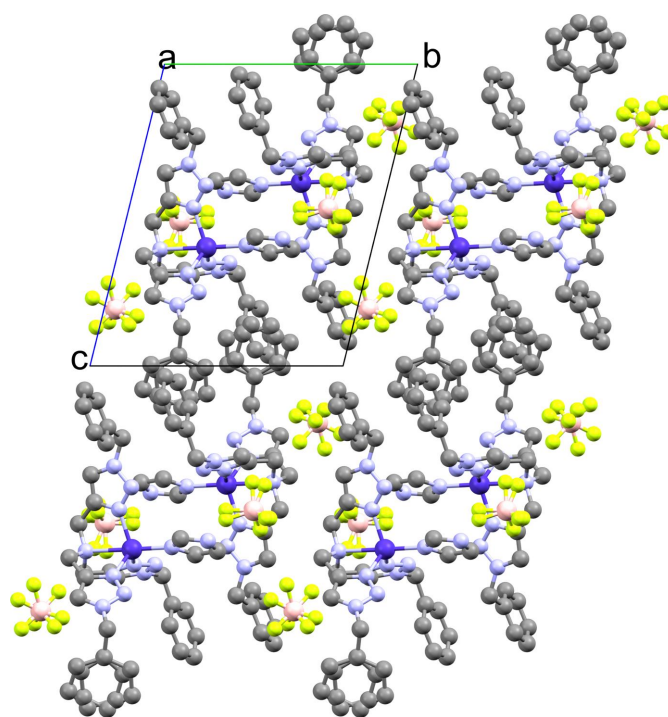
**Table 1**  
Selected bond angles ( $^{\circ}$ ).

N2—Co1—N7	103.73 (6)	N4—Co1—N10	112.62 (7)
N2—Co1—N4	105.56 (6)	N2—Co1—N3	178.95 (6)
N7—Co1—N4	117.04 (6)	N7—Co1—N3	75.67 (6)
N2—Co1—N10	104.25 (6)	N4—Co1—N3	75.50 (6)
N7—Co1—N10	112.12 (7)	N10—Co1—N3	75.26 (6)

generated by the triazole units of tbta, while the apical N-atom donors form an angle of  $178.95(6)^{\circ}$  with respect to the cobalt ion. The geometry about the cobalt center is distorted trigonal bipyramidal ( $\tau_5 = 1.03$ ; Addison *et al.*, 1984). A complete list of angles in the coordination sphere is given in Table 1. Equatorial N-atom donors are present at an average distance of  $2.04 \text{ \AA}$  from the metal ion, and the imidazole N-atom donor is at  $2.02 \text{ \AA}$ . The apical amine N atom of tbta is found at  $2.34 \text{ \AA}$  from the central metal (Table 2). Two tetrafluoroborate counter-ions balance the charge on the metal ion. Both counter-ions, and one of the terminal arene rings, are disordered. The terminal benzyl groups of the tbta ligand, rather than packing upright to form a pocket around the imidazole, are rotated away (Fig. 2). Two are nearly coplanar at angles of  $19.18$  (C18–C23) and  $15.92^{\circ}$  (C28–C33) with respect to the trigonal plane, while the third (C8–C13) is almost normal at an

**Table 2**  
Structural parameters for five-coordinate  $\text{Co}^{\text{II}}$  complexes based on the tbta ligand (distances in  $\text{\AA}$ ).

Compound	Co—N <sub>eq</sub> (tbta)	Co—N <sub>ax</sub> (tbta)	Co—X <sub>ax</sub>	Reference	CSD refcode
[Co(tbta)(Im)](BF <sub>4</sub> ) <sub>2</sub>	2.04	2.34	2.02 (N)	This work	This work
[Co(tbta)(N <sub>3</sub> )]ClO <sub>4</sub> ·3CH <sub>3</sub> CN	2.04	2.37	1.96 (N)	Schweinfurth <i>et al.</i> (2015)	RUDDUR
[Co(tbta)(NCS)]BF <sub>4</sub>	2.03	2.37	1.98 (N)	Schweinfurth <i>et al.</i> (2017)	HAWYOW
[Co(tbta)Cl]BF <sub>4</sub>	2.04	2.39	2.26 (Cl)	Schweinfurth <i>et al.</i> (2017)	HAWXEL
[Co(tbta)(NCS)]BF <sub>4</sub> ·3CH <sub>3</sub> CN	2.03	2.35	1.95 (N)	Schweinfurth <i>et al.</i> (2017)	HAWXAH
[Co(tbta)(Br)]ClO <sub>4</sub>	2.05	2.33	2.40 (Br)	Mondal <i>et al.</i> (2017)	KENWUY
[Co(tbta)(Cl)]ClO <sub>4</sub> ·2CH <sub>3</sub> CN·H <sub>2</sub> O	2.04	2.34	2.26 (Cl)	Mondal <i>et al.</i> (2017)	KENWOS



**Figure 2**  
The crystal packing of the title compound. H atoms have been omitted for clarity.

angle of  $72.57^{\circ}$ . The counter-ions pack nearly along the axial direction of the trigonal bipyramid, where one appears hydrogen bonded to the imidazole N—H group ( $\sim 2.2 \text{ \AA}$  N—H...F). The second is translated to a position directly opposite the imidazole, appearing to be shared between two complex molecules.

### 3. Supramolecular features

The packing of the tbta terminal benzyl groups, as noted above, facilitates the stacking of complexes seen in the extended structure. The complexes pack antiparallel, with the imidazoles of adjacent complexes approximately coplanar and  $4.1 \text{ \AA}$  apart. The counter-ion hydrogen bonded to the imidazole N—H group appears to be tightly associated with one complex. In contrast, the other counter-ion occupies a position that suggests it is shared between two unit cells. This counter-ion exhibits significantly more disorder than the other, owing to its placement in the lattice. No intermolecular hydrogen bonding is observed in the extended structure.

#### 4. Database survey

The title compound marks the seventh Co<sup>II</sup> complex with tbta and an ancillary ligand that presents a distorted five-coordinated structure. It is the first with a neutral ancillary ligand, requiring two counter-anions. The neutral imidazole ligand occupies a position closer to the Co<sup>II</sup> ion, more like the thiocyanate and azide complexes. The equatorial triazole N-atom donors are remarkably similar across the entire set of compounds. Meanwhile, the apical Co–N distance shows some small variation, trending longer when *trans* to an anionic N-atom donor. This distance in the parent molecule is uniquely short among ancillary N-atom donors in Table 2.

#### 5. Synthesis and crystallization

The click-derived tbta ligand was synthesized according to the literature (Mondal *et al.*, 2017). The title complex was formed under an inert atmosphere by first preparing a solution of 0.1 mmol tbta and 0.14 mmol imidazole in 10 ml of degassed acetonitrile, then adding 0.1 mmol of solid CoBF<sub>4</sub>·6H<sub>2</sub>O. The mixture was stirred for 2 h at room temperature. The solvent was removed under vacuum to reveal a dark-blue crude product. The methanol-soluble fraction produced brown block-shaped crystals by slow evaporation over a period of 2 d.

#### 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The H atoms were positioned geometrically (*sp*<sup>2</sup>-C–H = 0.93 Å, *sp*<sup>3</sup>-C–H = 0.97 Å and N–H = 0.86 Å) and were refined using a riding model, with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C) for CH<sub>2</sub> and C–H hydrogens, and 1.5*U*<sub>eq</sub>(N) for N–H hydrogens.

#### Acknowledgements

The authors wish to thank Dr John Rakovan and Dr Monu Joy for helpful discussions.

#### Funding information

Funding for this research was provided by: National Science Foundation (grant No. CHE-1152755 to D. L. Tierney; grant No. CHE-1532042 to Miami University).

**Table 3**  
Experimental details.

Crystal data	
Chemical formula	[Co(C <sub>3</sub> H <sub>4</sub> N <sub>2</sub> )(C <sub>30</sub> H <sub>30</sub> N <sub>10</sub> )](BF <sub>4</sub> ) <sub>2</sub>
<i>M</i> <sub>r</sub>	831.27
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	297
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.6861 (4), 13.0639 (5), 15.7006 (6)
$\alpha$ , $\beta$ , $\gamma$ (°)	96.304 (2), 107.142 (2), 110.766 (2)
<i>V</i> (Å <sup>3</sup> )	1901.24 (13)
<i>Z</i>	2
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.53
Crystal size (mm)	0.23 × 0.16 × 0.13
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2016; Krause <i>et al.</i> , 2015)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.681, 0.746
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	212950, 11085, 8422
<i>R</i> <sub>int</sub>	0.053
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.705
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.049, 0.118, 1.04
No. of reflections	11085
No. of parameters	622
No. of restraints	19
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.30, -0.31

Computer programs: *APEX3* (Bruker, 2016), *SAINT* (Bruker, 2016), *SHELXT2018* (Sheldrick, 2015a), *SHELXL2019* (Sheldrick, 2015b), *publCIF* (Westrip, 2010) and *Mercury* (Macrae *et al.*, 2020).

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