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Crystal structure of azido- k^1N -{6,6'-(((methyazanediyl)bis(propane-3,1-diyl))bis(azanylylidene))bis(methanylylidene))bis(2,4-dibromophenolato)} k^5N,N',N'',O,O' cobalt(III)-methanol (1/1), $C_{21}H_{23}Br_4CoN_6O_3$

Table 1: Data collection and handling.

Crystal:	Black block
Size:	0.22 × 0.20 × 0.18 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	6.73 mm ⁻¹
Diffractometer, scan mode:	Xcalibur Eos, φ and ω
$\theta_{\max}$, completeness:	26.4°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	37,075, 5358, 0.045
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4612
$N(\text{param})_{\text{refined}}$:	318
Programs:	CrysAlis ^{PRO} [1], Olex2 [2], SHELX [3, 4]

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Abstract

$C_{21}H_{23}Br_4CoN_6O_3$, monoclinic, $P2_1/c$ (no. 14), $a = 16.2300(4)$ Å, $b = 20.9661(6)$ Å, $c = 7.8269(2)$ Å, $\beta = 97.2250(11)^\circ$, $V = 2642.19(12)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0336$, $wR_{\text{ref}}(F^2) = 0.0981$, $T = 150.0$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

N' , N -bis(3-aminopropyl) methylamine (0.81 mL, 5 mmol) was added into an anhydrous ethanol solution (40 mL) of 3,5-bromosalicylaldehyde (1.90 g, 10 mmol). The solution was refluxed at 60 °C for ca. 3 h, the yellow suspension was then stirred at 60 °C for 30 min. Then, $Co(NO_3)_2 \cdot 6H_2O$ (0.145 g, 0.5 mmol) was added and the resulting brown mixture was further stirred for another 30 min and filtered. The black crystals of the title compound were obtained after one week by slow evaporation.

Experimental details

The crystal sample was selected by microscope and mounted on a glass fiber. Structure solution and refinements were carried out using the Olex2 software package [2]. All the hydrogen atoms were theoretically placed onto the ligand and refined using the riding model approximation. For the $-CH_2$ -groups, C–H bonds length were fixed at 0.97 Å and for the aromatic C–H distances 0.93 Å was used.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Br1	0.35748 (3)	0.70775 (2)	−0.06633 (6)	0.04175 (12)
Br2	0.04508 (3)	0.71859 (2)	−0.47685 (6)	0.05029 (13)
Br3	0.15392 (3)	0.31527 (2)	0.34082 (6)	0.04569 (13)
Br4	0.44511 (3)	0.20401 (3)	0.15173 (8)	0.06241 (16)
CoOA	0.25949 (3)	0.51921 (2)	0.19441 (6)	0.02955 (12)
O1	0.27174 (16)	0.60307 (13)	0.1100 (3)	0.0352 (6)
O2	0.24622 (16)	0.43650 (12)	0.2831 (3)	0.0338 (6)
N1	0.14114 (19)	0.53000 (15)	0.1745 (4)	0.0316 (7)
N2	0.2715 (2)	0.55001 (17)	0.4342 (4)	0.0385 (7)
H2	0.295521	0.512652	0.502650	0.046*
N3	0.37812 (19)	0.50775 (17)	0.2161 (4)	0.0348 (7)
N4	0.24707 (19)	0.48515 (16)	−0.0407 (4)	0.0341 (7)
N5	0.3028 (2)	0.48924 (19)	−0.1266 (4)	0.0426 (8)
N6	0.3556 (3)	0.4933 (3)	−0.2144 (5)	0.0677 (13)
C1	0.1363 (2)	0.60913 (18)	−0.0521 (5)	0.0328 (8)
C2	0.2207 (2)	0.62761 (18)	−0.0143 (5)	0.0322 (8)
C3	0.2471 (2)	0.67741 (19)	−0.1175 (5)	0.0349 (8)
C4	0.1962 (2)	0.70480 (19)	−0.2525 (5)	0.0365 (8)
H4	0.216392	0.737577	−0.319905	0.044*
C5	0.1146 (3)	0.68336 (19)	−0.2876 (5)	0.0361 (8)
C6	0.0844 (2)	0.63690 (19)	−0.1874 (5)	0.0350 (8)
H6	0.028116	0.623734	−0.210636	0.042*
C7	0.0994 (2)	0.56606 (18)	0.0611 (5)	0.0325 (8)
H7	0.040537	0.564193	0.051346	0.039*
C8	0.0943 (2)	0.49533 (19)	0.2959 (5)	0.0355 (8)
H8A	0.096260	0.448933	0.273255	0.043*
H8B	0.035481	0.508991	0.279128	0.043*
C9	0.1325 (3)	0.5092 (2)	0.4826 (6)	0.0488 (11)
H9A	0.086820	0.518868	0.551364	0.059*
H9B	0.160327	0.469974	0.530908	0.059*
C10	0.1937 (3)	0.5628 (2)	0.5046 (6)	0.0487 (11)
H10A	0.167669	0.601304	0.447785	0.058*
H10B	0.206682	0.572366	0.628934	0.058*
C11	0.3343 (3)	0.6009 (3)	0.4743 (6)	0.0525 (11)
H11A	0.335212	0.613296	0.596492	0.063*
H11B	0.317119	0.638722	0.402972	0.063*
C12	0.4200 (3)	0.5826 (3)	0.4442 (6)	0.0541 (12)
H12A	0.438148	0.546369	0.520901	0.065*
H12B	0.457501	0.618895	0.478634	0.065*
C13	0.4309 (3)	0.5640 (2)	0.2608 (5)	0.0416 (9)
H13A	0.414041	0.599564	0.180935	0.050*
H13B	0.489826	0.553584	0.252583	0.050*
C14	0.4129 (2)	0.4536 (2)	0.2032 (5)	0.0378 (9)
H14	0.471080	0.453426	0.197924	0.045*
C15	0.3711 (2)	0.3925 (2)	0.1959 (5)	0.0382 (9)
C16	0.4164 (3)	0.3376 (2)	0.1652 (5)	0.0426 (9)
H16	0.470606	0.341411	0.132326	0.051*
C17	0.3825 (3)	0.2787 (2)	0.1826 (6)	0.0442 (10)
C18	0.3039 (3)	0.2717 (2)	0.2326 (6)	0.0440 (10)
H18	0.281083	0.230470	0.244834	0.053*
C19	0.2600 (2)	0.3253 (2)	0.2639 (5)	0.0384 (9)
C20	0.2900 (2)	0.38790 (19)	0.2461 (5)	0.0344 (8)

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
O3	0.09136 (19)	0.42434 (16)	−0.1247 (5)	0.0555 (8)
H3	0.135219	0.445995	−0.110078	0.083*
C21	0.1106 (3)	0.3611 (2)	−0.1612 (7)	0.0587 (13)
H21A	0.132326	0.359242	−0.272361	0.088*
H21B	0.060295	0.334921	−0.166228	0.088*
H21C	0.152491	0.344889	−0.070615	0.088*

Comment

Since the N atoms in −C=N− in Schiff bases have the advantages of a high affinity and coordination ability for different transition metal ions, Schiff base ligands can construct versatile functional complexes, and the design and synthesis of Schiff base complexes arouse great interest [5, 6]. Structures with corresponding halogenated ligands are still rare [7–9]. As a part of our current research the title complex was studied.

The Co(III) ion adopts a distorted octahedral geometry with a CoN₄O₂ core in the title compound. The environment around Co(III) comprises an azide ion and a nitrogen atom at the apical position and two nitrogen atoms and two oxygen atoms in the basal plane of which all the nitrogen and oxygen atoms (N1, N3, O1, O2) are from the pentadentate Schiff base ligand. Not surprisingly, the Co–N bond distances are longer than the Co–O bonds in the basal plane. The bond angles range from 87.34(13)° to 179.43(14)° in the title compound and are all in the expected ranges [10, 11].

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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