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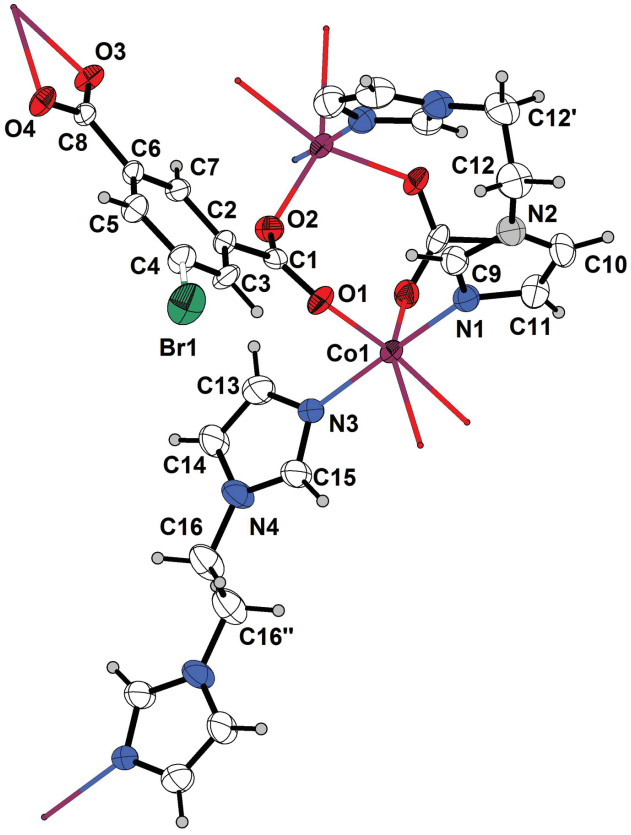
Crystal structure of catena-(μ$_3$-5-bromoisophthatato-κ*O*,*O*′: *O*″,*O*‴)-(1,2-bis(imidazol-1-yl) ethane-κ*N*:*N*′)cobalt(II), $C_{16}H_{13}CoN_4O_4Br$



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Abstract

$C_{16}H_{13}CoN_4O_4Br$, orthorhombic, *Pnna* (no. 52), $a = 16.921(2)$ Å, $b = 19.211(2)$ Å, $c = 10.2928(12)$ Å, $V = 3345.9(7)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0335$, $wR_{ref}(F^2) = 0.0713$, $T = 296$ K.

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A part of the polmeric title crystal structure is shown in the figure. (The asymmetric unit is labelled only. ′ = x, 0.5 − y, 0.5 − z; ″ = 1 − x, 1 − y, −z.) Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Block, clear light pink
Size:	0.24 × 0.13 × 0.08 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	3.45 mm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ and ω-scans
$2\theta_{max}$, completeness:	25.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	24093, 3124, 0.076
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2268
$N(param)_{refined}$:	235
Programs:	Bruker programs [1], SHELX [2], OLEX2 [3]

Source of material

A mixture of 5-bromoisophthalic acid ($BripH_2$, 24.5 mg, 0.1 mmol), $Co(OAc)_2{\cdot}2H_2O$ (24 mg, 0.1 mmol), and 1,2-bis(imidazol-1-yl)ethane (bia, 16.2 mg, 0.1 mmol), were added to water (9 mL) and [BMI]Br (BMI = 1-butyl-3-methylimidazolium, 1 mL) in a 25 mL Teflon-lined autoclave. The mixture was heated at 413 K for 3 days and then slowly cooled down to room temperature. Pink block crystals of the title compound were obtained.

Experimental details

The hydrogen atoms were placed in calculated positions and refined using a riding on attached atoms with isotropic thermal parameters 1.2 times those of their carrier atoms. The U_{iso} values of the hydrogen atoms of methyl groups and oxygen were set to $1.5U_{eq}$(C, O).

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.22044(3)	0.32154(2)	0.08236(4)	0.02094(12)
Br1	0.08106(3)	0.56854(2)	0.54190(4)	0.05075(15)
O1	0.19571(14)	0.35370(12)	0.2673(2)	0.0292(6)
O2	0.25928(14)	0.28021(11)	0.4000(2)	0.0270(6)
O3	0.22894(14)	0.31685(12)	0.8765(2)	0.0279(6)
O4	0.18512(15)	0.41658(12)	0.9505(2)	0.0304(6)
N1	0.09937(17)	0.29198(15)	0.0682(3)	0.0273(7)
N2	−0.02621(18)	0.27984(16)	0.1216(3)	0.0324(8)
N3	0.33233(17)	0.36901(14)	0.1036(3)	0.0267(7)
N4	0.42776(18)	0.44668(16)	0.0950(3)	0.0380(8)
C1	0.2203(2)	0.33445(17)	0.3768(3)	0.0232(8)
C2	0.1985(2)	0.38137(16)	0.4893(3)	0.0207(8)
C3	0.1602(2)	0.44395(17)	0.4673(3)	0.0275(8)
H3	0.1501	0.4587	0.3828	0.033*
C4	0.1372(2)	0.48439(18)	0.5715(3)	0.0291(8)
C5	0.1526(2)	0.46462(17)	0.6974(3)	0.0263(8)
H5	0.1380	0.4932	0.7663	0.032*
C6	0.19028(19)	0.40135(16)	0.7204(3)	0.0198(7)
C7	0.2134(2)	0.36010(17)	0.6164(3)	0.0217(8)
H7	0.2389	0.3180	0.6317	0.026*
C8	0.20239(19)	0.37745(18)	0.8580(3)	0.0214(8)
C9	0.0441(2)	0.30757(18)	0.1531(4)	0.0307(9)
H9	0.0527	0.3347	0.2266	0.037*
C10	−0.0147(2)	0.2433(2)	0.0095(4)	0.0397(10)
H10	−0.0525	0.2177	−0.0358	0.048*
C11	0.0618(2)	0.2513(2)	−0.0229(4)	0.0371(10)
H11	0.0858	0.2322	−0.0961	0.045*
C12	−0.0966(2)	0.2803(2)	0.2016(4)	0.0419(11)
H12A	−0.1429	0.2770	0.1464	0.050*
H12B	−0.0994	0.3240	0.2488	0.050*
C13	0.3912(2)	0.3511(2)	0.1870(4)	0.0415(11)
H13	0.3901	0.3124	0.2411	0.050*
C14	0.4512(2)	0.3970(2)	0.1808(4)	0.0433(11)
H14	0.4988	0.3951	0.2258	0.052*
C15	0.3564(2)	0.4275(2)	0.0511(4)	0.0400(10)
H15	0.3274	0.4527	−0.0096	0.048*
C16	0.4730(2)	0.5090(2)	0.0549(4)	0.0440(11)
H16A	0.5036	0.5262	0.1278	0.053*
H16B	0.4368	0.5454	0.0279	0.053*

Discussion

Design and construction of Co(II)-based metal-organic frameworks (MOFs) is of interest in the field of molecular magnetism and materials chemistry due to their fascinating structural diversities and potential application as functional materials [4–8]. Flexible diimine-type *N*-donor co-ligands, 1,3-bis(imidazol-1-yl)ethane (bia) serve as bridging bidentate ligands to coordinate two metals [9–12]. On the other hand, ionic liquids have received increasing attention as the solvent of choice for the syntheses of crystalline materials. Ionothermal methods are of interest in coordination chemistry for the preparation of unusual MOFs [13–15].

There are one Co(II) ion, one anionic Brip ligand, and one bbip ligand, in the asymmetric unit of the title structure. Co1 is six-coordinated with a distorted octahedral geometry by four O atoms from three Brip ligands, located at the basal equatorial plane, and a pair of N atoms of one cis-bia and one bia ligand (*trans* conformation) from the axial positions with a N1—Co1—N3 angle of 169.61(11)°. The Co—N bond lengths are 2.113(3) and 2.131(3) Å and the Co—O ones are in the range of 2.044(2) and 2.352(2) Å. Each Brip ligand serves as a triply bridging ligand, in which one carboxylate group adopts a bi-monodentate mode while another adopts a chelating fashion and link the Co(II) centers to a 1-D polymeric motif, with the Co$\cdots$Co distance in the $[Co_2(COO)_2]$ unit of 3.39 Å. These 1D motifs are joined by a bia ligand (*cis* conformation) to form a 2-D layer. Topologically, each dimeric unit can be defined as a 4-connected node, and the overall structure of the title complex can be described as a 4-connected sql (shubnikov tetragonal plane) layer.

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