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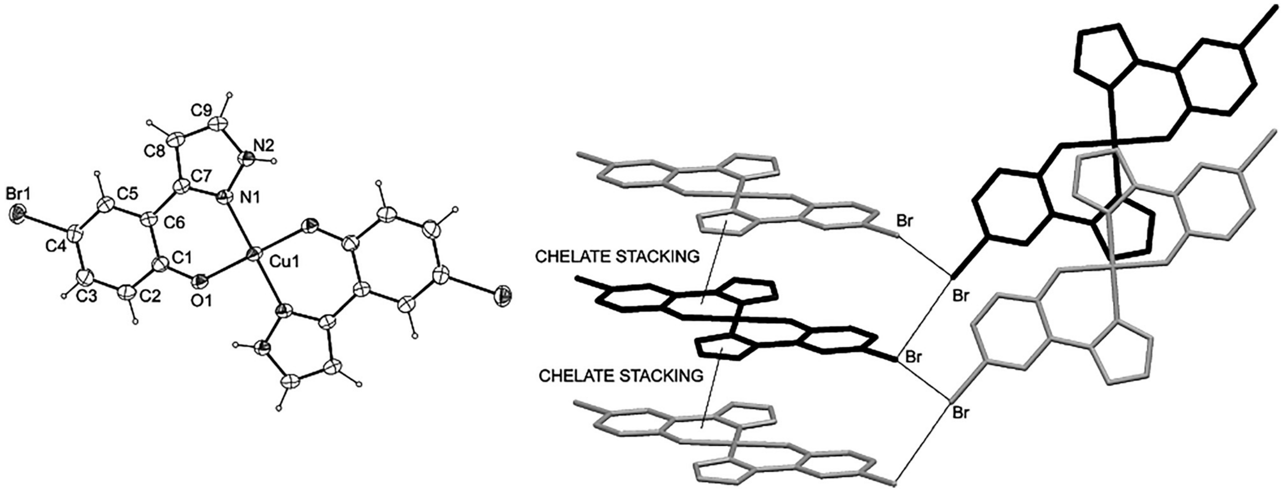
The crystal structure of bis[4-bromo-2-(1*H*-pyrazol-3-yl) phenolato-κ^2*N*,*O*] copper(II), $C_{18}H_{12}Br_2CuN_4O_2$



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Abstract

$C_{18}H_{12}Br_2CuN_4O_2$, monoclinic, $P2_1/c$ (no. 14), $a = 11.5165(11)$ Å, $b = 5.4369(5)$ Å, $c = 14.4872(14)$ Å, $V = 873.52(14)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0232$, $wR_{ref}(F^2) = 0.0559$, $T = 200$ K.

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Table 1: Data collection and handling.

Crystal:	Green prism
Size:	0.25 × 0.10 × 0.08 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	5.85 mm^{-1}
Diffractometer, scan mode:	Bruker Apex-II, *φ* and *ω*
θ_{max}, completeness:	30.6°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	24890, 2680, 0.031
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2239
$N(param)_{refined}$:	128
Programs:	Bruker [1], SHELX [2], Mercury [3], PLATON [4], WinGX/ORTEP [5, 6]

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

A warm DMF (3 cm^3) $Cu(NO_3)_2{\cdot}3H_2O$ solution (0.5 mmol) was slowly heated with a warm DMF (3 cm^3) 4–bromo-2-(1*H*-pyrazol-3-yl) phenol (0.25 mmol) ligand solution. The resulting green-brown solution was allowed to crystallize by slow evaporation at room temperature. After two days, the dark green single crystals of the complex were filtered

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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}
Br1	0.92682 (2)	0.29323 (4)	0.29381 (2)	0.03565 (7)
C1	0.71540 (16)	0.8184 (3)	0.45057 (13)	0.0247 (3)
C2	0.83933 (18)	0.8481 (4)	0.45822 (16)	0.0351 (4)
C3	0.90086 (18)	0.6939 (4)	0.41266 (17)	0.0364 (5)
C4	0.84106 (17)	0.5011 (3)	0.35819 (13)	0.0271 (4)
C5	0.72055 (16)	0.4605 (3)	0.34963 (12)	0.0247 (3)
C6	0.65605 (15)	0.6163 (3)	0.39524 (11)	0.0213 (3)
C7	0.52762 (15)	0.5696 (3)	0.38121 (11)	0.0211 (3)
C8	0.45589 (16)	0.3758 (3)	0.33160 (12)	0.0260 (4)
C9	0.34164 (16)	0.4199 (4)	0.33940 (13)	0.0270 (4)
Cu1	0.5000	1.0000	0.5000	0.02228 (7)
H1	0.295 (2)	0.704 (5)	0.4089 (17)	0.037 (7)*
H2	0.2671	0.3376	0.3185	0.032*
H3	0.4793	0.2475	0.2959	0.031*
H4	0.6821	0.3254	0.3085	0.030*
H5	0.9829	0.7163	0.4192	0.044*
H6	0.8764	0.9900	0.4923	0.042*
N1	0.45866 (13)	0.7188 (3)	0.41696 (10)	0.0227 (3)
N2	0.34578 (14)	0.6249 (3)	0.39083 (11)	0.0258 (3)
O1	0.66406 (11)	0.9777 (2)	0.49569 (10)	0.0290 (3)

and washed with a small amount of DMF. Yield: 0.01 g. **FTIR–ATR** (Bruker Tensor 27 FTIR–ATR spectrometer) ν (cm^{-1}): 3330, 3145, 1487, 1431, 1402, 1369, 972.

Experimental details

All hydrogen atoms were located from a difference Fourier map. The nitrogen-bound H atom was refined freely, along with its isotropic displacement parameter. The remaining H atoms were constrained to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$.

Comment

Pyrazolyl molecules exhibit various biologically relevant properties including anti-inflammatory, analgesic and anti-cancer effects [7, 8]. Due to their various coordination capabilities, pyrazole derivatives are used for the extraction of metal ions [9] and also for the formation of metal organic frameworks [10]. Usage of pyrazole derivatives in processes involving metal atoms is related to their versatile coordinating properties. Rigidity of the pyrazole ring diminishes potential variation of the steric properties of the pyrazole derivatives, which makes these molecules a convenient choice in attempts to control the influence of the various substituents on the complexation properties as well as intra and inter molecular interactions. As part of our ongoing research on the synthesis, physico-chemical and structural properties of pyrazole based coordination compounds [11, 12] herein we report the crystal structure of the title compound. We reported previously the crystal structure of uncoordinated 4-bromo-2-(1H-pyrazol-3-yl) phenol [13]. Addition of halogenated phenols to the pyrazolyl ring adds new possibilities for both coordination, and intermolecular interactions. Geometrical constraints make the deprotonated phenolic oxygen the likely site for bonding to metal, while the halogen substituent can potentially form hydrogen bond or halogen-halogen interaction [14]. The structure is built up of isolated units with a copper(II) ion located on an inversion center. Two molecules of the [4-bromo-2-(1*H*-pyrazol-3-yl) phenolato ligand are coordinated through the phenolate-*O* and pyridine-like nitrogen of the pyrazole moiety arranged in a square-planar geometry resulting in a trans disposition of these ligands (left part of the Figure). To gain better insight into the coordinating properties of this ligand we performed a CSD search [15] (CSD version 5.41) using the chemical structure of the title ligand, with exclusion of hydrogen atoms, and Br substituted by any halogen atom, as a template. This search returned only seven hits, having the CSD refcodes AHIZIB, AHIZIB01, CIVVEJ, CIVVIN, CIVVOT, TEQHEE and TEQHII (the last two structures contain Cl instead of Br). As opposed to the mononuclear complex found in the title structure, all seven structures consist of trinuclear complexes. This is associated with different coordinating capabilities of the pyrazolyl ligand achieved through additional deprotonation at pyrrolic–N thus making it a tridentate ligand. The title complex possesses capabilities for hydrogen bonding involving Br [14], however, association of molecules is achieved through chelate-chelate stacking [16] and Br···Br interactions [17]. Figure, on the right, depicts associations of molecules into the chains through the stacking interactions between the six-membered chelate ring and pyrazole ring at a distance of 3.2848(10) Å. Neighboring chains are connected by Br···Br interactions (Br1···Br1 = 3.6050(5) Å, C4–Br1···Br1 = 95°, Br1···Br1–C4 = 167°. The geometry of the C–Br···Br–C contacts indicates that it is a type II halogen···halogen contact [17] which represents an attractive interaction [18].

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