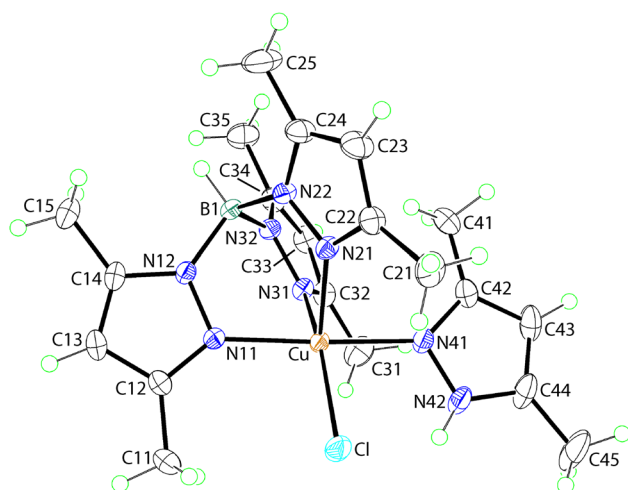


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Crystal structure and spectroscopic properties of chlorido{hydridotris[3-,5-dimethylpyrazol-1-yl- κN^3]borato}(3-,5-dimethylpyrazol-1-yl- κN) copper(II), $C_{20}H_{30}BClCuN_8$

**Table 1:** Data collection and handling.

Crystal:	Green needle
Size:	0.25 × 0.05 × 0.05 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	1.04 mm ⁻¹
Diffractometer, scan mode:	Rigaku Mercury70, ω
θ_{\max} , completeness:	27.5°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	18647, 5501, 0.022
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5223
$N(\text{param})_{\text{refined}}$:	291
Programs:	REQAB [1], CrystalClear [2], SIR2014 [3], SHELX [4], WinGX/ORTEP [5]

<https://doi.org/10.1515/ncrs-2020-0412>

Received July 28, 2020; accepted September 8, 2020;

published online October 5, 2020

Abstract

$C_{20}H_{30}BClCuN_8$, monoclinic, $P2_1/c$ (no. 14), $a = 17.1345(7)$ Å, $b = 7.8207(2)$ Å, $c = 19.0213(8)$ Å, $\beta = 108.268(1)^\circ$, $V = 2420.46(16)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0322$, $wR_{\text{ref}}(F^2) = 0.0876$, $T = 184$ K.

CCDC no.: 2027354

The molecular structure is shown in the Figure. Table 1 contains crystallographic data and Table 2 contains the list

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of the atoms including atomic coordinates and displacement parameters.

Source of material

A solution of $\text{Na}\{\text{HB}(3,5\text{-Me}_2\text{pz})_3\}$ (100.5 mg, 0.313 mmol) [6] in dichloromethane (13 mL) was added slowly to a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (61.0 mg, 0.358 mmol) in acetone (13 mL). In addition, one equivalent of 3,5-Me₂pzH (30.1 mg, 0.313 mmol) in dichloromethane (13 mL) was dropped carefully into this solution. After the mixture was stirred overnight, the solvent was evaporated under vacuum. The resulting solid was extracted with dichloromethane (20 mL). The filtrate was evaporated under vacuum, and a green powder was obtained. Green crystals were obtained by slow evaporation of a saturated dichloromethane/*n*-octane solution at room temperature. Yield: 62% (95.8 mg, 0.195 mmol). **Anal. Calcd.** for $C_{20}H_{30}BClCuN_8$. C, 48.79; H, 6.14; N, 22.76%. Found: C; 48.48, H; 6.02, N; 22.54%. **IR** (JASCO FT/IR-550 spectrophotometer, KBr; cm⁻¹): 3211 (m) $\nu(\text{N-H})$, 2927 (m) $\nu(\text{C-H})$, 2511 (m) $\nu(\text{B-H})$, 1567 (m) $\nu(\text{C=N})$, 1542 (s) $\nu(\text{C=N})$. **UV-Vis** (JASCO V-570 at 298 K in dichloromethane); λ_{max} , nm

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

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Cu	0.26204 (2)	0.12884 (2)	0.19167 (2)	0.01650 (7)
Cl	0.23805 (3)	-0.01354 (6)	0.28935 (3)	0.03204 (12)
N11	0.37327 (8)	0.02157 (17)	0.20311 (8)	0.0185 (3)
N12	0.39609 (8)	0.02229 (17)	0.13957 (8)	0.0185 (3)
N21	0.21502 (8)	-0.00725 (18)	0.08711 (8)	0.0194 (3)
N22	0.25958 (9)	0.01586 (17)	0.03908 (8)	0.0193 (3)
N31	0.30330 (9)	0.33060 (18)	0.14730 (8)	0.0191 (3)
N32	0.32879 (8)	0.29815 (18)	0.08695 (8)	0.0188 (3)
N41	0.15275 (9)	0.25600 (18)	0.17602 (8)	0.0221 (3)
N42	0.12066 (10)	0.2654 (2)	0.23280 (9)	0.0273 (3)
H42N	0.1445 (13)	0.203 (3)	0.2717 (9)	0.033*
C11	0.43654 (12)	-0.0759 (3)	0.33436 (11)	0.0339 (4)
H11A	0.423730	0.033881	0.353069	0.051*
H11B	0.491504	-0.113169	0.364326	0.051*
H11C	0.395926	-0.161461	0.337332	0.051*
C12	0.43421 (10)	-0.0558 (2)	0.25567 (10)	0.0222 (3)
C13	0.49568 (11)	-0.1068 (2)	0.22598 (11)	0.0267 (4)
H13	0.545249	-0.165018	0.251111	0.032*
C14	0.46997 (10)	-0.0560 (2)	0.15341 (10)	0.0240 (3)
C15	0.51228 (13)	-0.0791 (3)	0.09596 (12)	0.0361 (5)
H15A	0.477457	-0.147612	0.054939	0.054*
H15B	0.564828	-0.137743	0.118032	0.054*
H15C	0.522216	0.033035	0.077374	0.054*
C21	0.08398 (13)	-0.1345 (3)	0.08674 (13)	0.0352 (5)
H21A	0.107531	-0.116502	0.140223	0.053*
H21B	0.067897	-0.254652	0.077043	0.053*
H21C	0.035546	-0.061417	0.067228	0.053*
C22	0.14649 (11)	-0.0904 (2)	0.04968 (10)	0.0246 (3)
C23	0.14640 (13)	-0.1214 (3)	-0.02276 (11)	0.0325 (4)
H23	0.104976	-0.178056	-0.060836	0.039*
C24	0.21882 (12)	-0.0527 (2)	-0.02769 (10)	0.0278 (4)
C25	0.25174 (16)	-0.0501 (4)	-0.09226 (12)	0.0451 (6)
H25A	0.255806	0.068475	-0.107451	0.068*
H25B	0.214560	-0.113889	-0.133648	0.068*
H25C	0.306310	-0.103057	-0.077757	0.068*
C31	0.27966 (14)	0.5805 (3)	0.21757 (13)	0.0364 (5)
H31A	0.220371	0.602436	0.201885	0.055*
H31B	0.309425	0.688642	0.231413	0.055*
H31C	0.294377	0.503118	0.260244	0.055*
C32	0.30219 (11)	0.5004 (2)	0.15545 (10)	0.0232 (3)
C33	0.32633 (12)	0.5789 (2)	0.09957 (11)	0.0282 (4)
H33	0.330712	0.698151	0.092141	0.034*
C34	0.34252 (11)	0.4483 (2)	0.05736 (10)	0.0241 (3)
C35	0.37099 (14)	0.4584 (3)	-0.00928 (12)	0.0358 (4)
H35A	0.423883	0.399517	0.000987	0.054*
H35B	0.377389	0.578533	-0.021043	0.054*
H35C	0.330362	0.403687	-0.051417	0.054*
C41	0.11463 (13)	0.3682 (3)	0.04744 (11)	0.0332 (4)
H41A	0.147908	0.470950	0.049066	0.050*
H41B	0.061519	0.381148	0.008724	0.050*
H41C	0.143411	0.268385	0.036519	0.050*
C42	0.10100 (11)	0.3442 (2)	0.12042 (11)	0.0259 (4)
C43	0.03564 (12)	0.4065 (3)	0.14299 (14)	0.0356 (5)
H43	-0.009678	0.472329	0.114116	0.043*

Table 2: (continued)

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
C44	0.04986 (13)	0.3539 (3)	0.21465 (14)	0.0357 (5)
C45	0.00349 (18)	0.3768 (3)	0.26903 (19)	0.0577 (8)
H45A	0.011081	0.275640	0.300867	0.087*
H45B	-0.055094	0.391742	0.242239	0.087*
H45C	0.024191	0.478073	0.299539	0.087*
B1	0.34288 (12)	0.1108 (2)	0.06774 (10)	0.0187 (3)
H1	0.371706	0.107742	0.029464	0.022*

(ϵ , mol⁻¹ cm⁻¹) 341 (1100), 430 (shoulder, 230), 730 (100).
ESR Bruker EMX-T, 5 mm ϕ quartz tube, dichloromethane:
 1,2-dichloroethane = 1:1, 124 K: g_{\parallel} , 2.32 (A_{\parallel} , 159 G); g_{\perp} , 2.07.

Experimental details

The C- and B-bound H atoms were geometrically placed (C–H = 0.95–0.98 Å & B–H = 1.00 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5 U_{\text{eq}}(\text{C})$ and $1.2 U_{\text{eq}}(\text{B})$. The N-bound H atom was refined with N–H = 0.88 ± 0.01 Å, and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{N})$.

Comment

Boron-substituted poly(1-pyrazolyl)borates occupy a prominent position in current coordination chemistry [6]. Among this class of ligand, the methyl substituted hydridotris(3,5-dimethyl-pyrazolyl-1-yl)borato- κN^3 anion is very common. It has been designated as “Tp*” [7–10] and also named “homoscorpionates-first generation” [7, 10]. The Tp* ligand is relatively sterically unhindered so it can readily form coordinatively saturated six-coordinate, bis-chelate complexes, formulated as $[\text{M}(\text{Tp}^*)_2]$. For copper(II), the structure of $[\text{Cu}(\text{Tp}^*)_2]$ has been reported [11]. To avoid the formation of this bis-chelate complex, the synthetic methodology needs to be carefully modified: the solution containing the Tp* ligand needs to be added slowly to a solution containing a small amount of excess metal salt [12]. This work reports the crystal structure and some properties of a five-coordinate copper(II) complex with the first generation Tp* ligand, also containing a coordinated 3,5-dimethylpyrazol-1-yl molecule, i.e. $[\text{Cu}(\text{Cl})(3,5\text{-Me}_2\text{pzH})\{\text{HB}(3,5\text{-Me}_2\text{pz})_3\}]$, (I).

It is well-known that four-coordinate copper(II) geometries are not so common in coordination chemistry [13]. In particular, the tetrahedral geometry is very unstable for

less sterically hindered ligands such as Tp^* . Indeed, the slow reaction of a copper(II) salt, such as $CuCl_2$, with Tp^* yielded a mixture of four- (red) and five-coordinate (green) complexes. To ensure the formation of a five-coordinate complex, one equivalent of pyrazole was also added to the reaction mixture. In the IR spectrum of (I), the ν (C=N) signals were split, with absorptions at 1567 and 1542 cm^{-1} , reflecting the presence of two kinds of pyrazole ligands. The IR also provides evidence for hydrogen bonding by the $pzH-N-H$ residue with a very sharp absorption noted at 3211 cm^{-1} . The ground state of (I) is $d_{x^2-y^2}$, as confirmed by ESR [14]. This ground state is also supported by UV-Vis spectroscopy. For (I), the d-d transition occurs at 730 nm ($100 M^{-1} cm^{-1}$) which is shifted by approximately 200 nm to higher energy compared with that of 996 nm ($150 M^{-1} cm^{-1}$) for $[Cu(Cl)\{HB(3,5-iPr_2pz)_3\}]$ [15] and 906 nm ($180 M^{-1} cm^{-1}$) for $[Cu(Cl)\{HB(3-Ph-5-Mepz)_3\}]$ [13].

The molecular structure determined by X-ray diffraction of (I) is shown in figure (50% probably displacement ellipsoids). The Cu atom is coordinated by a Cl, three pyrazolyl-N11, N21 and N31 atoms of the tripodal ligand and a pyrazolyl-N41 atom derived from a neutral 3,5-dimethylpyrazol-1-yl molecule. The Cu-Cl bond length in (I) of 2.3107(5) Å is slightly longer than the equivalent Cu-Cl bonds in other five-coordinated chlorido copper(II) complexes, viz. 2.260(2) Å in $[Cu(Cl)(dmf)\{HB(3,5-iPr_2pz)_3\}]$ [15] and 2.2833(8) Å in $[Cu(Cl)(3-Ph-5-MepzH)\{HB(3-Ph-5-Mepz)_3\}]$ [16]. These bond lengths are approximately 0.1 Å longer compared with the Cu-Cl bond lengths in four-coordinate, chlorido copper(II) complexes [13].

Each of the four Cu-N bond lengths in (I) is experimentally distinct from the others. The Cu-N11 [2.0305(14) Å] and Cu-N31 [2.0189(14) Å] bond lengths are different and significantly shorter than the Cu-N21 [2.1756(14) Å] separation. The Cu-N41 bond length [2.0579(14) Å] is intermediate between the extreme Cu-N values formed by the tripodal ligand. The ClN_4 donor set defines, to a first approximation a distorted square-pyramidal geometry, with the less tightly bound pyrazolyl-N21 atom occupying the axial position with the N11 and N31 atoms approximately trans to the N41 [N11-Cu-N41 = 174.93(6)°] and Cl [N31-Cu-Cl = 152.45(4)°] atoms. The distortion in the coordination geometry is quantified by the value of $\tau = 0.37$ which compares with values of 0.0 and 1.0 for ideal square-pyramidal and trigonal-bipyramidal geometries, respectively [17]. The orientation of the 3-phenyl-5-methylpyrazol-1-yl ligand is to place the amine-N42-H group in close proximity with the Cl atom which enables the formation of an intramolecular N-H...Cl [N42-H42n...Cl: H42n...Cl = 2.28(2) Å,

N42...Cl = 2.9335(17) Å with angle at H42n = 131.3(17)°] hydrogen bond.

In the molecular packing, the only directional contact is a long pyrazolyl-C-H... π (pyrazolyl) [C33-H33...Cg(N21, N22, C22-C24)ⁱ: H33...Cg(N21, N22, C22-C24)ⁱ = 2.98 Å with angle at H33 = 129° for symmetry operation (i): $x, 1 + y, z$] contact. The result is the formation of a linear, supramolecular chain parallel to the *b*-axis. To investigate the molecular packing further, with the aid of Crystal Explorer 17 [18] and following literature methods [19], the Hirshfeld surface along with the full and delineated two-dimensional fingerprint plots were calculated. Consistent with the lack of evident directional interactions in the crystal of (I), the major contribution to the surface comes from H...H contacts, at 73.9%. After this are H...C/C...H [10.9%], H...N/N...H [8.0%] and H...C/C...H [6.8%] contacts.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: KF is grateful for support from the joint usage/research programme “Artificial Photosynthesis” based at Osaka City University. Sunway University Sdn Bhd is thanked for financial support of this work through Grant No. STR-RCTR-RCCM-001-2019.

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

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