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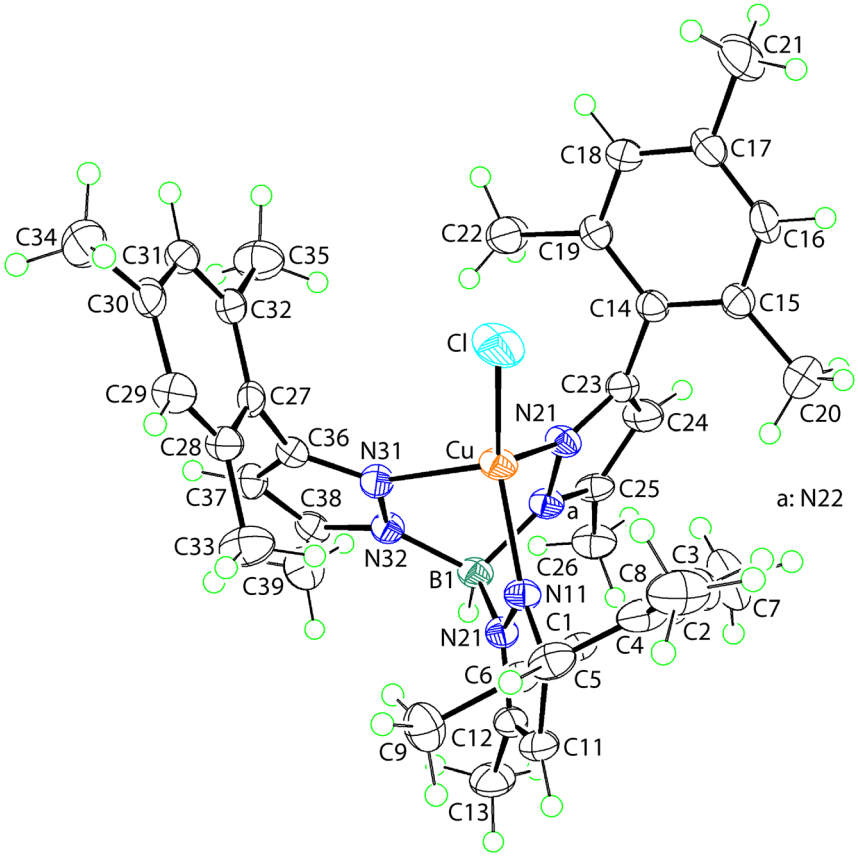
Crystal structure of chlorido{hydridotris[3-mesityl-5-methyl-1*H*-pyrazol-1-yl-κN^3]borato}-copper(II) dichloromethane monosolvate



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Abstract

$C_{39}H_{46}BClCuN_6 \cdot CH_2Cl_2$, monoclinic, *C*2/*c* (no. 15), a = 18.1441(7) Å, b = 15.6735(8) Å, c = 28.1341(13) Å, β = 90.247(4)°, V = 8000.7(6) Å^3, Z = 8, $R_{gt}(F)$ = 0.0563, $wR_{ref}(F^2)$ = 0.1306, T = 168 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.

1 Source of material

A solution of {hydridotris[3-mesityl-5-methyl-1*H*-pyrazol-1-yl-κN^3]borato}thallium(I)[5] ([Tl{HB(3–Mes-5–Mepz)$_3$}], 144.36 mg, 0.178 mmol) in dichloromethane (15 mL) was added slowly to a solution of $CuCl_2 \cdot 2H_2O$ (34.7 mg, 0.204 mmol) in methanol (5 mL). After the mixture was stirred for 60 min, the solvent was evaporated under vacuum and the resulting solid was extracted with dichloromethane (25 mL) to separate the

Table 1: Data collection and handling.

Crystal:	Red prism
Size:	0.25 × 0.13 × 0.05 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.78 mm^{-1}
Diffractometer, scan mode:	Rigaku XtaLAB P200, ω scan
θ_{max}, completeness:	27.5°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	31658, 9164, 0.050
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5,911
$N(param)_{refined}$:	472
Programs:	CrysAlis^{PRO},[1] IL MILIONE,[2] SHELX,[3] WinGx[4]

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu	0.26421 (2)	0.01644 (3)	0.10440 (2)	0.02686 (11)
Cl1	0.21368 (5)	0.01407 (7)	0.17240 (3)	0.0519 (3)
N11	0.33615 (12)	0.07677 (16)	0.06479 (9)	0.0251 (6)
N12	0.34979 (12)	0.04100 (16)	0.02147 (9)	0.0243 (6)
N21	0.18930 (13)	0.01001 (17)	0.05018 (9)	0.0264 (6)
N22	0.22011 (12)	−0.00805 (17)	0.00684 (9)	0.0250 (6)
N31	0.31034 (13)	−0.10051 (17)	0.08635 (9)	0.0265 (6)
N32	0.31682 (13)	−0.11085 (16)	0.03788 (9)	0.0247 (6)
C1	0.38309 (15)	0.1962 (2)	0.11361 (11)	0.0255 (7)
C2	0.32592 (16)	0.2548 (2)	0.12103 (12)	0.0334 (8)
C3	0.32716 (17)	0.3056 (2)	0.16155 (13)	0.0366 (8)
H3	0.288139	0.344936	0.166534	0.044*
C4	0.38347 (17)	0.3006 (2)	0.19495 (12)	0.0336 (8)
C5	0.44039 (17)	0.2445 (2)	0.18596 (12)	0.0322 (8)
H5	0.480152	0.241483	0.207975	0.039*
C6	0.44190 (15)	0.1925 (2)	0.14617 (11)	0.0271 (7)
C7	0.2642 (2)	0.2635 (3)	0.08477 (15)	0.0543 (11)
H7A	0.233766	0.313138	0.092666	0.081*
H7B	0.233653	0.211913	0.085213	0.081*
H7C	0.285253	0.271000	0.053035	0.081*
C8	0.3820 (2)	0.3539 (3)	0.23946 (14)	0.0487 (10)
H8A	0.347434	0.401405	0.235217	0.073*
H8B	0.431441	0.376510	0.245849	0.073*
H8C	0.366198	0.318628	0.266294	0.073*
C9	0.50672 (17)	0.1334 (2)	0.13858 (13)	0.0401 (9)
H9A	0.488956	0.078247	0.126763	0.060*
H9B	0.532875	0.125025	0.168768	0.060*
H9C	0.540311	0.158595	0.115284	0.060*
C10	0.38347 (15)	0.1416 (2)	0.07084 (11)	0.0245 (7)
C11	0.42890 (16)	0.1467 (2)	0.03106 (11)	0.0302 (7)
H11	0.467577	0.186425	0.025914	0.036*
C12	0.40658 (15)	0.0826 (2)	0.00072 (11)	0.0278 (7)
C13	0.43632 (19)	0.0585 (2)	−0.04693 (13)	0.0416 (9)
H13A	0.481968	0.090127	−0.052852	0.062*
H13B	0.399958	0.072516	−0.071576	0.062*
H13C	0.446520	−0.002869	−0.047569	0.062*
C14	0.06661 (15)	0.0413 (2)	0.08312 (11)	0.0250 (7)
C15	0.03953 (16)	0.1231 (2)	0.09150 (12)	0.0296 (7)
C16	−0.00651 (16)	0.1361 (2)	0.12996 (12)	0.0327 (8)
H16	−0.024367	0.192021	0.135901	0.039*
C17	−0.02744 (16)	0.0711 (2)	0.15995 (12)	0.0323 (8)
C18	−0.00135 (17)	−0.0098 (2)	0.15020 (12)	0.0354 (8)
H18	−0.015699	−0.055775	0.170163	0.043*
C19	0.04493 (16)	−0.0262 (2)	0.11237 (12)	0.0310 (7)
C20	0.0588 (2)	0.1974 (3)	0.05985 (16)	0.0550 (11)
H20A	0.106613	0.187025	0.044891	0.083*
H20B	0.061344	0.249672	0.078900	0.083*
H20C	0.020852	0.203788	0.035196	0.083*
C21	−0.0785 (2)	0.0877 (3)	0.20142 (15)	0.0558 (11)
H21A	−0.061264	0.055835	0.229273	0.084*
H21B	−0.128534	0.069300	0.193070	0.084*
H21C	−0.078786	0.148886	0.208715	0.084*
C22	0.0706 (2)	−0.1160 (2)	0.10319 (16)	0.0578 (12)
H22A	0.058360	−0.132137	0.070426	0.087*
H22B	0.046011	−0.155075	0.125245	0.087*
H22C	0.124041	−0.119398	0.107905	0.087*
C23	0.11748 (15)	0.0245 (2)	0.04264 (11)	0.0266 (7)
C24	0.10205 (16)	0.0173 (2)	−0.00548 (12)	0.0344 (8)
H24	0.055528	0.025339	−0.020441	0.041*
C25	0.16784 (16)	−0.0038 (2)	−0.02754 (11)	0.0280 (7)
C26	0.18343 (18)	−0.0172 (3)	−0.07905 (12)	0.0383 (8)
H26A	0.137231	−0.014500	−0.097160	0.057*
H26B	0.206244	−0.073332	−0.083533	0.057*
H26C	0.217048	0.027273	−0.090273	0.057*
C27	0.33158 (15)	−0.18728 (19)	0.15870 (11)	0.0254 (7)
C28	0.39049 (16)	−0.1535 (2)	0.18510 (12)	0.0297 (7)
C29	0.39646 (17)	−0.1730 (2)	0.23303 (12)	0.0340 (8)
H29	0.436063	−0.149279	0.250846	0.041*
C30	0.34633 (17)	−0.2262 (2)	0.25598 (12)	0.0309 (7)
C31	0.28692 (16)	−0.2560 (2)	0.22951 (12)	0.0292 (7)
H31	0.250578	−0.289676	0.244835	0.035*
C32	0.27878 (15)	−0.2382 (2)	0.18164 (11)	0.0270 (7)
C33	0.44760 (19)	−0.0978 (3)	0.16150 (13)	0.0465 (10)
H33A	0.423220	−0.049098	0.146229	0.070*
H33B	0.474004	−0.131044	0.137492	0.070*
H33C	0.482624	−0.077013	0.185460	0.070*
C34	0.35854 (19)	−0.2526 (3)	0.30682 (12)	0.0435 (9)
H34A	0.373630	−0.202849	0.325587	0.065*
H34B	0.397232	−0.296145	0.308260	0.065*
H34C	0.312695	−0.275959	0.319726	0.065*
C35	0.21411 (18)	−0.2749 (3)	0.15440 (13)	0.0449 (9)
H35A	0.196330	−0.232814	0.131277	0.067*
H35B	0.174424	−0.288952	0.176580	0.067*
H35C	0.229669	−0.326662	0.137684	0.067*
C36	0.32879 (15)	−0.1749 (2)	0.10646 (11)	0.0254 (7)
C37	0.34756 (16)	−0.2330 (2)	0.07111 (12)	0.0292 (7)
H37	0.363071	−0.290358	0.075600	0.035*
C38	0.33931 (15)	−0.1914 (2)	0.02856 (11)	0.0265 (7)
C39	0.35084 (19)	−0.2245 (2)	−0.02078 (12)	0.0390 (9)
H39A	0.366304	−0.284312	−0.019326	0.058*
H39B	0.389093	−0.190651	−0.036495	0.058*
H39C	0.304683	−0.220029	−0.038832	0.058*
B1	0.30227 (18)	−0.0346 (2)	0.00414 (13)	0.0269 (8)
H1	0.317126	−0.051942	−0.033230	0.032*
C40	0.31133 (19)	0.0121 (3)	0.27321 (13)	0.0437 (9)
H40A	0.303123	−0.040660	0.254541	0.052*

Table 2: (continued)

	x	y	z	U_{iso}*/U_{eq}
H40B	0.264487	0.044430	0.273681	0.052*
Cl2	0.37910 (6)	0.07350 (8)	0.24567 (4)	0.0652 (3)
Cl3	0.33624 (6)	−0.01559 (7)	0.33200 (4)	0.0537 (3)

resulting salts. A red powder was obtained after evaporation of the solvent. Red crystals for X-ray crystallography were obtained by the slow evaporation of a saturated dichloromethane/n-heptane (1:1 v/v) solution held at room temperature which were characterised as [Cu(Cl){HB(3–Mes-5–Mepz)$_3$}]·CH_2Cl_2 (72.2 mg, 0.102 mmol, 58 %). Anal. calcd. for $C_{39}H_{46}BClCuN_6$: C, 66.10; H, 6.54; N, 11.86. Found: C; 65.94, H; 6.58, N; 11.90 %. **IR** (KBr, cm^{-1}): 3002 m ν(C–H), 2954 s ν(C–H), 2920 s ν(C–H), 2858 m ν(C–H), 2527 s ν(B–H), 1615 s ν(C=N). **Far–IR** (CsI, cm^{-1}): 383 ν(Cu–Cl). **UV–Vis** (CH_2Cl_2, λ_{max}, nm (ε, M^{-1} cm^{-1})) 298 (1100), 376 (2400), 505 (480), 1020 (180).

2 Experimental details

The B- and C-bound H atoms were geometrically placed (B–H = 1.12 Å and C–H = 0.95–1.00 Å) and refined as riding with U_{iso}(H) = 1.2–1.5 U_{eq}(B, C).

3 Discussion

Hyridotris(pyrazolyl)borate ligands are still recognised as one of the most well-studied classes of ligands in contemporary coordination chemistry. The reason for their popularity relates their easy derivatisation to introduce substituents of varying steric and electronic profiles into the pyrazolyl rings. This key feature of this ligands flexibility for the fine-tuning of the coordination environments for a wide range of metal centres. In 2016, the structure and properties of a thallium(I) salt ligated by a relatively sterically hindered mesityl-substituted pyrazolyl ring, i.e. [Tl{HB(3–Mes-5–Mepz)$_3$}], were described.[5] Herein, in continuation of these studies, a related chlorido copper(II) complex, [Cu(Cl){HB(3–Mes-5–Mepz)$_3$}], isolated as its dichloromethane mono-solvate, (I), is described.

The complex, [Cu(Cl){HB(3–Mes-5–Mepz)$_3$}], was obtained by the reaction of [Tl{HB(3–Mes-5–Mepz)$_3$}] with $CuCl_2 \cdot 2H_2O$ in 58 % yield. The IR spectrum of [Cu(Cl){HB(3–Mes-5–Mepz)$_3$}] shows the B–H stretching band at 2527 cm^{-1} is slightly shifted from the absorption band at 2522 cm^{-1} for [Tl{HB(3–Mes-5–Mepz)$_3$}].[5] In the far–IR spectrum, [Cu(Cl){HB(3–Mes-5–Mepz)$_3$}] shows a characteristic band at 383 cm^{-1}, which is assignable to Cu–Cl stretching. Similar bands were also observed at 375 cm^{-1} for the phenyl analogue [Cu(Cl){HB(3–Ph-5–Mepz)$_3$}][6] and at 359 cm^{-1} for the *t*-butyl/*i*-propyl analogue, [Cu(Cl){HB(3-tBu-5-iPrpz)$_3$}].[7] The d-d transition band was observed at 1020 nm (180 M^{-1} cm^{-1}), which compares to 960 nm (180 M^{-1} cm^{-1}) reported for [Cu(Cl){HB(3–Ph-5–Mepz)$_3$}].[6] This low-energy shift of the d-d transition arises from the ground state change from d(x^2 – y^2) to d(z^2).[6,7]

The molecular structure of (I) is shown in figure (50 % probability ellipsoids; the solvent dichloromethane molecule is not shown). The copper(II) centre exists within a ClN_3 donor set defined by a chlorido ligand and three pyrazolyl-nitrogen atoms derived from a tridentate {HB(3–Mes-5–Mepz)$_3$}$^-$ anion. The angles subtended at the copper(II) atom range from 90.96(10)°, for N11–Cu–N31, to 144.09(8)°, for N11–Cu–Cl1. Using the τ_4 parameter as a guide,[8] which is calculated from the equation, τ_4 = [360 − (α + β)/141], the α and β angles being the two widest angles subtended at the copper(II) centre, an indication of the nature of the coordination geometry is given. In (I), τ_4 computes to 0.73, a value intermediate between 0.64, for a see-saw geometry, and 0.85, for a trigonal-pyramidal geometry.[8] The angles substended at the copper(II) atom by the tridentate ligand span a narrow range, i.e. 90.96(10)° [N11–Cu–N31] to 92.40(10)° [N11–Cu–N21] and are systematically narrower than the N–Cu–Cl angles. The latter fall in two distinct values, i.e. 112.54(7) and 112.34(8)° for N21, N31–Cu–Cl1, respectively, and a wide 144.09(8) for N11–Cu–Cl1. The pattern of bond lengths indicates a significant deviation from the putative three-fold axis incorporating the Cu, Cl and B atom. The reason for the wide N11–Cu–Cl1 angle could relate the presence of a weak Cl···H contact between the complex and solvent dichloromethane molecule [C40–H40b···Cl1: H40b···Cl1 = 3.03 Å with angle at H40b = 100°] as well as a relatively close intramolecular contact [C22–H22c···Cl1: H22c···Cl1 = 3.21 Å with angle at H22c = 123°]. It is also noted the Cu–N11 bond length of 1.963(2) Å is significantly shorter than the Cu–N21, N31 bond lengths of 2.041(2) and 2.079(3) Å, respectively.

The Cu–Cl bond length in (I) is 2.1253(9) Å, which can be compared with other Cu–Cl bonds in related tetrahedral chlorido copper(II) complexes having tridentate hydridotris(pyrazolyl)borate ligands. Thus, the Cu–Cl bond in (I) is experimentally equivalent to the Cu–Cl bond length of 2.125(6) Å in [Cu(Cl){HB(3,5-iPr$_2$pz)$_3$}],[9] but shorter than 2.167(1) Å, in [Cu(Cl){HB(3-tBu-5-iPrpz)$_3$}],[7] 2.1706(9) Å, in [Cu(Cl){HB(3–Ad-5-iPrpz)$_3$}],[7] and 2.1738(14) and 2.1760(13) Å for the two independent molecules in [Cu(Cl){HB(3-tBu-5–Mepz)$_3$}].[10]

In the crystal of (I), several interactions are noted. First and foremost are the interactions between the complex molecule and the dichloromethane molecule of crystallisation. Here, the solvent molecule bridges two mesityl substituents via C–Cl···π [C40–Cl2···Cg(C1–C6): Cl2···Cg(C1–C6) = 3.7745(18) Å with angle at Cl2 = 136.31(14)°] and C–H···π [C40–H40a···Cg(C27–C32): H40a···Cg(C27–C32) = 2.98 Å, C40···Cg(C27–C32) = 3.916(5) Å with angle at H40a = 158°] interactions to form a two-molecule aggregate. These form a linear chain along [1 –1 0] featuring C–H···π [C21–H21c···Cg(C27–C32)^{i}: H21c···Cg(C27–C32)^{i} = 2.73 Å, C21···Cg(C27–C32)^{i} = 3.576(5) Å with angle at H21c = 145° for symmetry operation (i) –1/2 + x, 1/2 + y, z] interactions. Centrosymmetrically related chains assemble into double-chains which feature additional C–H···π [C26–H26a···Cg(C14–C19)^{ii}: H26a···Cg(C14–C19)^{ii} = 2.99 Å, C26–H26a···Cg(C14–C19)^{ii} = 3.907(4) Å with angle at H26a = 157° for (ii) –x, –y, –z] interactions. The chains assemble in the crystal without directional interactions between them.

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