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Crystal structure of carbonyl{hydridotris[3-phenyl-5-methylpyrazol-1-yl]borato- $\kappa^3 N, N' N''$ } copper(I), $C_{31}H_{28}BCuN_6O$

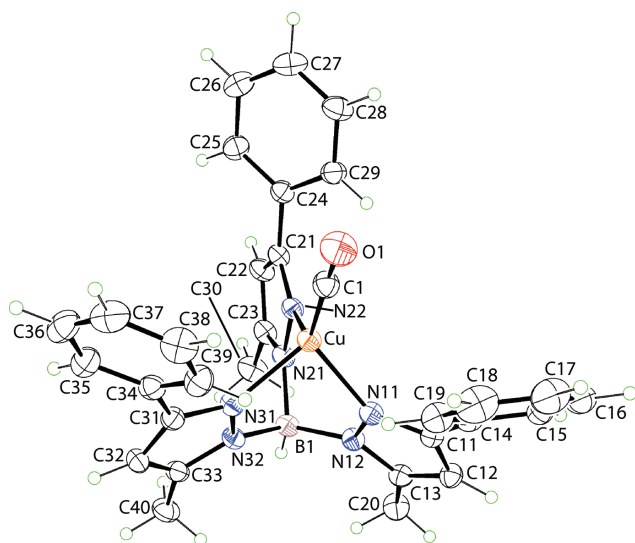


Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.20 × 0.20 × 0.15 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.79 mm ⁻¹
Diffractometer, scan mode:	Rigaku Mercury70, ω
θ_{\max} , completeness:	27.5°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	23366, 6621, 0.036
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5228
$N(\text{param})_{\text{refined}}$:	364
Programs:	NUMABS [1], CrystalClear [2], SIR2014 [3], SHELXL [4], WinGX/ORTEP [5]

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

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu	0.74718(2)	0.98921(2)	0.24222(2)	0.03256(11)
O1	0.99344(17)	0.94528(16)	0.29757(14)	0.0665(7)
N11	0.69655(17)	1.10374(13)	0.19476(11)	0.0328(5)
N12	0.57718(16)	1.11603(13)	0.18393(11)	0.0315(5)
N21	0.61847(17)	0.98178(13)	0.31923(11)	0.0314(5)
N22	0.50906(17)	1.00824(13)	0.28039(12)	0.0320(5)
N31	0.63509(17)	0.93639(13)	0.14306(11)	0.0332(5)
N32	0.52426(17)	0.97067(13)	0.12963(11)	0.0330(5)
C1	0.8973(2)	0.96113(18)	0.27700(16)	0.0416(6)
C11	0.7453(2)	1.17768(15)	0.18444(13)	0.0312(5)
C12	0.6577(2)	1.23809(16)	0.16838(15)	0.0360(6)
H12	0.668424	1.295612	0.159172	0.043*
C13	0.5527(2)	1.19759(16)	0.16858(14)	0.0343(6)
C14	0.8724(2)	1.18797(16)	0.18742(13)	0.0345(6)
C15	0.9275(2)	1.26026(18)	0.22223(15)	0.0427(7)
H15	0.882919	1.301090	0.246113	0.051*
C16	1.0461(3)	1.2729(2)	0.2223(2)	0.0585(9)
H16	1.083276	1.321953	0.246707	0.070*
C17	1.1096(3)	1.2146(3)	0.1870(2)	0.0737(11)
H17	1.190996	1.223845	0.186230	0.088*
C18	1.0577(3)	1.1425(3)	0.1524(2)	0.0696(10)
H18	1.103328	1.101968	0.129008	0.083*
C19	0.9381(2)	1.1294(2)	0.15193(17)	0.0486(7)
H19	0.901502	1.080243	0.127282	0.058*
C20	0.4306(2)	1.23183(18)	0.15595(17)	0.0460(7)
H20A	0.378740	1.196866	0.115305	0.069*
H20B	0.430852	1.288382	0.133245	0.069*
H20C	0.401891	1.232724	0.211010	0.069*

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Abstract

$C_{31}H_{28}BCuN_6O$, monoclinic, $P2_1/n$ (no. 14), $a = 11.506(3)$ Å, $b = 16.122(3)$ Å, $c = 15.805(3)$ Å, $\beta = 99.433(3)^\circ$, $V = 2892.2(11)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0501$, $wR_{\text{ref}}(F^2) = 0.1260$, $T = 193(2)$ 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.

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
C21	0.6022(2)	0.94688(16)	0.39344(13)	0.0326(5)
C22	0.4848(2)	0.95077(18)	0.40248(14)	0.0386(6)
H22	0.450589	0.930475	0.449217	0.046*
C23	0.4275(2)	0.98984(16)	0.33037(15)	0.0352(6)
C24	0.7006(2)	0.91015(16)	0.45356(13)	0.0340(6)
C25	0.6834(2)	0.83614(18)	0.49447(15)	0.0418(6)
H25	0.609718	0.808507	0.481444	0.050*
C26	0.7725(3)	0.8018(2)	0.55430(17)	0.0508(8)
H26	0.759528	0.751194	0.582024	0.061*
C27	0.8800(3)	0.8416(2)	0.57331(16)	0.0514(8)
H27	0.940585	0.818709	0.614800	0.062*
C28	0.8991(2)	0.9142(2)	0.53221(15)	0.0490(7)
H28	0.973565	0.940851	0.544651	0.059*
C29	0.8102(2)	0.94876(18)	0.47255(14)	0.0397(6)
H29	0.824236	0.999039	0.444517	0.048*
C30	0.3001(2)	1.0107(2)	0.30622(18)	0.0514(8)
H30A	0.291189	1.070767	0.297982	0.077*
H30B	0.257583	0.992944	0.352009	0.077*
H30C	0.267663	0.982140	0.252819	0.077*
C31	0.6317(2)	0.86951(16)	0.09190(13)	0.0352(6)
C32	0.5173(2)	0.86038(16)	0.04630(14)	0.0388(6)
H32	0.490372	0.817944	0.006145	0.047*
C33	0.4521(2)	0.92407(16)	0.07059(13)	0.0356(6)
C34	0.7365(2)	0.81759(17)	0.09184(14)	0.0386(6)
C35	0.7278(3)	0.73230(18)	0.09048(17)	0.0495(7)
H35	0.652370	0.707167	0.085825	0.059*
C36	0.8264(3)	0.6827(2)	0.09572(18)	0.0579(8)
H36	0.818380	0.624096	0.095934	0.070*
C37	0.9352(3)	0.7176(2)	0.10061(17)	0.0597(9)
H37	1.003315	0.683518	0.105191	0.072*
C38	0.9454(3)	0.8027(2)	0.09884(18)	0.0597(9)
H38	1.020753	0.827380	0.100644	0.072*
C39	0.8468(3)	0.85251(19)	0.09445(16)	0.0481(7)
H39	0.854825	0.911126	0.093216	0.058*
C40	0.3256(2)	0.9450(2)	0.04172(16)	0.0472(7)
H40A	0.282056	0.937562	0.089511	0.071*
H40B	0.292689	0.908444	−0.005719	0.071*
H40C	0.318967	1.002844	0.022393	0.071*
B1	0.4940(2)	1.04216(19)	0.18780(16)	0.0322(6)
H1	0.410622	1.060150	0.168994	0.039*

Source of material

A solution of K{HB(3-Ph-5-Mepz)₃} (400 mg, 0.766 mmol) in dichloromethane (30 mL) was added to a solution of CuCl (74.3 mg, 0.751 mmol) in acetonitrile (10 mL). After the mixture was stirred for 5 h, the solution was cooled to 273 K in an argon atmosphere, after which the argon was replaced by CO. After the mixture was stirred overnight, the solvent was evaporated under vacuum. The resulting solid was extracted with dichloromethane (15 mL). The filtrate was evaporated under reduced pressure and a white powder was obtained. Recrystallisation from dichloromethane/*n*-heptane at 243 K gave colourless crystals. Yield: 60% (259.7 mg, 0.452 mmol).

Anal. calcd. for C₃₁H₂₈BCuN₆O · 0.5(H₂O) (bulk material): C, 63.76, H, 5.01, N, 14.39%. Found: C, 63.91, H, 4.96, N, 14.61%. IR (JASCO FT/IR-6300 spectrophotometer, KBr; cm^{−1}): 3060 (m) ν(C—H), 2961 (m) ν(C—H), 2926 (m) ν(C—H), 2526 (m) ν(B—H), 2072 (s) ν(C=O), 2024 (w), 1545 (s) ν(C=N). ¹H NMR (Bruker AVANCE III-500 NMR spectrometer, chemical shifts relative to CDCl₃ at 298 K; ppm): δ 2.50 (s, Me, 9H), 6.15 (s, pyrazole-4, 3H), 7.31 (t, *J* = 7.25 Hz, phenyl-para, 3H), 7.37 (t, *J* = 7.25 Hz, phenyl-meta, 6H), 7.64 (d, *J* = 6.5 Hz, phenyl-ortho, 6H); the B—H signal was not observed. ¹³C{¹H} NMR (as for ¹H NMR): δ 12.9 (methyl), 104.3 (pyrazole-4), 127.8 (phenyl-ortho), 128.3 (phenyl-meta), 134.3 (phenyl-ipso), 137.9 (phenyl-para), 144.5 (pyrazole-5), 152.0 (pyrazol-3); the signal due to CO was not observed.

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95–1.00 Å & B—H = 1.00 Å) and refined as riding with *U*_{iso}(H) = 1.2–1.5*U*_{eq}(C) and 1.2*U*_{eq}(B).

Comment

Copper(I) carbonyl complexes are well-known and the ligand electron-donating properties are readily obtained by IR through the measurement of the ν(CO) frequency. Previously, N3-type hydrotris(pyrazolyl)borate ligands have been employed in bioinorganic chemistry to synthesise copper and iron complexes in order to contribute to the understanding of the reaction mechanisms associated with enzymatic processes [6–8]. As a continuation of these studies, a new aryl and alkyl substituted hydrotris(pyrazolyl)copper(I) carbonyl complex, [Cu{HB(3-Ph-5-Mepz)₃}(CO)], (I), was prepared to study the electron-donating property of the HB(3-Ph-5-Mepz)₃ anion towards copper(I) via IR. Herein, the synthesis, characterisation and crystal structure determination of (I) are described.

Complex (I) has been synthesised in good yield as detailed in Source of Material. The key spectroscopic observation relates to the ν(CO) frequency, i.e. 2072 cm^{−1}, which lies between 2080 cm^{−1} observed in [Cu{HB(3,5-Ph₂pz)₃}(CO)] [9, 10] and 2066 cm^{−1} observed in [Cu{HB(3,5-Me₂pz)₃}(CO)] [9], i.e. the symmetric di-phenyl and di-methyl complexes, respectively.

The molecular structure of (I) is illustrated in the figure (35% displacement ellipsoids). The copper(I) centre is coordinated by a carbonyl-C [Cu—C1 = 1.784(3) Å] atom and three N atoms of the HB(3-Ph-5-Mepz)₃ anion. The Cu—N11, N21 and N31 bond lengths of 2.042(2), 2.069(2) and 2.0450(18) Å are experimentally equivalent at the 5σ level. The range of N—Cu—N angles spans nearly 5°, i.e. 89.36(8)°, for N11—Cu—N31, to 94.58(8)° for N11—Cu—N21. The C—Cu—N angles are approximately 30° wider, and range from 123.12(11)°, for

C1—Cu—N11, to $126.01(10)^\circ$ for C1—Cu—N31. When viewed down the Cu—C1—O1 axis, the molecule approximates 3-fold symmetry.

The crystal structures of both the $[Cu\{HB(3,5-Ph_2pz)_3\}(CO)]$ [10] and $[Cu\{HB(3,5-Me_2pz)_3\}(CO)]$, as the acetonitrile mono-solvate [11], complexes are available for comparison. $[Cu\{HB(3,5-Ph_2pz)_3\}(CO)]$ has crystallographic 3-fold symmetry with Cu—C1 = $1.776(13)$ Å and Cu—N11 = $2.058(6)$ Å. In $[Cu\{HB(3,5-Me_2pz)_3\}(CO)]$, Cu—C1 = $1.785(4)$ Å and the range of Cu—N bond lengths is $2.033(2)$ to $2.054(2)$ Å.

In the crystal, methyl-C—H... (pyrazolyl) $[C40-H40 \cdots Cg(N31, N32, C31-C33)]^i$: $H40 \cdots Cg(N31, N32, C31-C33)^i = 2.92$ Å, with angle at H40 = 129° for symmetry operation (i) $1 - x, 2 - y, -z$ and $\pi(\text{pyrazolyl}) \cdots \pi(\text{phenyl})$ $[Cg(N11, N12, C11-C13) \cdots Cg(C34-C39)]^{ii} = 3.8808(18)$ Å with angle of inclination = $10.48(13)^\circ$ for (ii) $3/2 - x, 1/2 + y, 1/2 - z$ interactions link molecules into a supramolecular layer parallel to (1 0 -1). The layers stack without directional interactions between them.

In order to probe the supramolecular aggregation further, the Hirshfeld surface and the full and delineated two-dimensional fingerprint plots were calculated following literature methods [12] using Crystal Explorer 17 [13]. Reflecting the general lack of directional interactions between molecules, H...H contacts contribute 51.4% of all contacts to the Hirshfeld surface, with the next most significant being H...C/C...H contacts, at 30.3%. The only other contributions to the calculated surface are from H...O/O...H [7.4%], H...N/N...H [7.1%] and C...C [2.7%] contacts.

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