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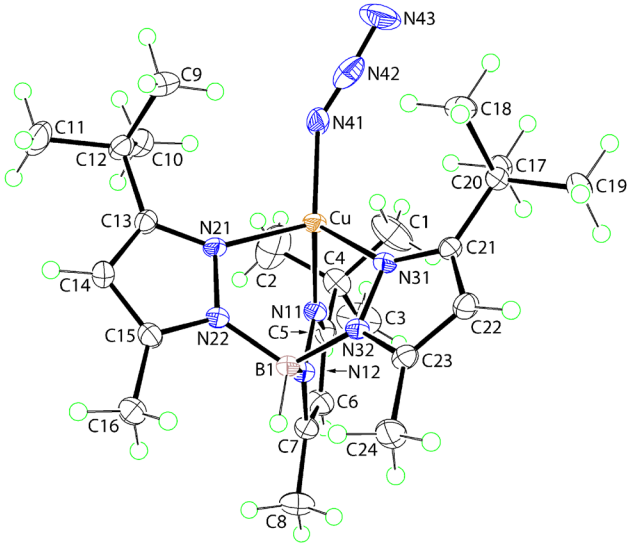
Crystal structure of azido-κ^1N\{hydridotris(3-*tert*-butyl-5-methylpyrazol-1-yl)borato-κ^3N,N',N''\} copper(II), $C_{24}H_{40}BCuN_9$



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Abstract

$C_{24}H_{40}BCuN_9$, monoclinic, $P2_1/c$ (no. 14), a = 15.3310(6) Å, b = 9.8056(3) Å, c = 19.1252(6) Å, β = 107.751(4)°, V = 2738.20(17) Å^3, Z = 4, $R_{gt}(F)$ = 0.0332, $wR_{ref}(F^2)$ = 0.0857, T = 178 K.

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The molecular structure is shown in the figure. Table 1 contains the crystallographic data and the list of the atoms including atomic coordinates and displacement parameters can be found in the cif- file attached to this article.

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1 Source of material

The starting copper(II) chlorido complex was obtained by the reaction of the ligand, potassium hydridotris(3-*tert*-butyl-5-methylpyrazol-1-yl)borate (denoted as KL) with $CuCl_2{\cdot}2H_2O$.[1] A solution of the resulting complex [CuCl(L)] (501 mg, 0.959 mmol) in CH_2Cl_2 (10 mL) was added slowly to a solution of NaN_3 (140 mg, 2.15 mmol) in $(CH_3)_2CO$ (20 mL). After the stirring for 2 h at room temperature, the solvent was evaporated under reduced pressure to afford a purple powder. The resulting solid was extracted with dichloromethane (20 mL) to separate any residual salts. Purple crystals were obtained from concentrated $C_6H_5CH_3/CH_2Cl_2$ (1:2 v/v) solution at 253 K as [Cu(N_3)(L)] (310 mg, 0.586 mmol, 61 % yield). Crystals suitable for X-ray crystallography were obtained by the slow evaporation of a saturated $C_6H_5CH_3/CH_2Cl_2$ (1:2 v/v) solution held at room temperature. In the same way, isotopic [Cu($^{15}N_3$)(L)] was synthesised. **Anal. Calcd.** for $C_{24}H_{40}BCuN_9{\cdot}0.25(H_2O)$; bulk material: C, 54.03; H, 7.65; N, 23.63 %. Found: C, 54.38; H, 7.78; N, 23.23 %. **IR** (KBr, cm^{-1}): 2,962 s ν(C–H), 2,929 m ν(C–H), 2,866 w ν(C–H), 2,549 m ν(B–H), 2,070 vs $\nu_{asym}(N_3)$, 1,541 m, 1,424 s, 1,362 s $\nu_{sym}(N_3)$, 1,189 s, 1,065 s, 648 m, 521 w ν(Cu–Npz). For [Cu($^{15}N_3$)(L)]: 2,960 s ν(C–H), 2,928 s ν(C–H), 2,866 m ν(C–H), 2,549 m ν(B–H), 2,002 vs $\nu_{asym}(^{15}N_3)$, 1,541 m, 1,424 s, 1,362 s, 1,314 w $\nu_{sym}(^{15}N_3)$, 1,189 s, 1,065 s, 648 m, 521 w ν(Cu–Npz). **Far–IR** (CsI, cm^{-1}): 646 s, 521 m ν(Cu–Npz), 450 m, 395 s ν(Cu–N_3), 288 m. For [Cu($^{15}N_3$)(L)]: 646 s, 521 m ν(Cu–Npz), 450 m, 391 s ν(Cu–N_3), 292 m. **UV–vis** (CH_2Cl_2, λ_{max}, nm (ε, M^{-1} cm^{-1})): 268 (2,710), 564 (4,600), 973 (620). **ESR** ($C_6H_5CH_3$, 130 K): g_1 2.32, g_2 2.17, g_3 2.00 (A_3 13.5 mT).

Table 1: Data collection and handling.

Crystal:	Purple block
Size:	0.16 × 0.12 × 0.09 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.83 mm^{-1}
Diffractometer, scan mode:	Rigaku XTALAB P200, ω scan
θ_{max}, completeness:	26.4°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	26891, 5594, 0.034
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 4796
$N(param)_{refined}$:	328
Programs:	Rigaku,[2] IL MILION,[3] SHELX,[4] WinGX[5]

2 Experimental details

The B- and C-bound H atoms were geometrically placed (B–H = 1.12 Å and C–H = 0.95–0.98 Å) and refined as riding with U_{iso}(H) = 1.2–1.5 U_{eq}(B, C).

3 Discussion

The azide anion, one of the "pseudohalide" ligands, has a unique absorption band in IR spectroscopy. Moreover, the azide anion can be a bridging ligand, complementing classical terminal binding. For these reasons, and others, the coordination chemistry of the azide anion has been studied extensively.[6,7] We have already succeeded in selectively synthesising and structurally characterising mononuclear complexes using ligands with bulky substituents, e.g. the *tert*-butyl group. For example, previously we reported a mononuclear, four-coordinate copper(II) chlorido complex, [CuCl(L)], with a hindered ligand, hydridotris(3-*tert*-butyl-5-methylpyrazol-1-yl)borate anion viz. [L$^-$].[1] In this study, we report the synthesis, structure determination and spectroscopic properties of a four-coordinate copper(II) azido complex, [Cu(N_3)(L)]. The reaction of [CuCl(L)] with an excess amount of NaN_3 led to the isolation of the title complex [Cu(N_3)(L)], as a purple solid. The IR spectrum of [Cu(N_3)(L)] exhibited a strong absorption band at 2070 cm^{-1}, which was shifted clearly, to 2002 cm^{-1}, in the complex with ^{15}N, i.e. of [Cu($^{15}N_3$)(L)].[8,9] This strong band was assignable to antisymmetric stretching, i.e. $\nu_{asym}(N_3)$. Moreover, the band at 1362 cm^{-1} was also shifted, to 1314 cm^{-1}, which was assignable to symmetric stretching, i.e. $\nu_{sym}(N_3)$. In the far–IR region, the isotopically active band at 395 cm^{-1} is assigned to ν_{sym}(Cu–N_3), which was shifted to 391 cm^{-1} in [Cu($^{15}N_3$)(L)].[8,9] The strong band at 521 cm^{-1} was not shifted by isotopic substitution; the band was attributed to ν(Cu–Npz). The equivalent absorption at 523 cm^{-1} was also observed in [Cu(Cl)(L)].[1] There is a strong absorption band in the UV–vis spectrum at 564 nm, so this complex is deep-purple, and is assignable to a [N_3]$^-$ to copper(II) charge transfer band. The d-d transition energy of four-coordinate species (distorted tetrahedral geometry) occurs at low energy, at 973 nm. The energy of this d-d transition is very close to other tetrahedral copper(II) complexes, viz. 1025 nm for [Cu(Cl)(L)],[1] indicating a d_{z2} ground state. This observation was confirmed by ESR spectroscopy, with g_1 = 2.32, g_2 = 2.17 and g_3 = 2.00 (A_3 = 13.5 mT). These ESR parameters were also similar those in [Cu(Cl)(L)] (g_1 = 2.39, g_2 = 2.20 and g_3 = 2.01 (A_3 = 10.2 mT)).[1]

The crystal and molecular structure of [Cu(N_3)(L)], hereafter (I), is also described, with the latter illustrated in the figure (50 % displacement ellipsoids). The molecule comprises a copper(II) atom coordinated by a tridentate pyrazolate anion with the four-coordinate geometry completed by a terminally bound azide anion. The range of angles subtended at the copper centre is broad, i.e. from a narrow 91.90(6)°, for N11–Cu–N31, to a wide 140.87(8)° for N11–Cu–N41. This implies the azide anion deviates significantly from the putative 3-fold axis through the remaining part of the molecule. The geometric parameter, τ_4 [= (360 – (α + β))/141], is a descriptor for four-coordinate geometries;[10] where α and β are the greatest angles subtended at the central atom. For the title structure, τ_4 computes to 0.73 which is close to the ideal value for a trigonal-pyramidal geometry (0.85) and represents a significant distortion from ideal tetrahedral (τ_4 = 1.0).

The distortions from the ideal tetrahedral angles are also reflected in significant differences in bond lengths subtended at the copper(II) centre. The shortest Cu–N bond of 1.9302(18) Å is formed by the azido ligand. Of the Cu–N(pyrazolyl) bond lengths, that involving the N11 atom [1.9434(15) Å] is significantly shorter than each of the Cu–N21, N31 bond lengths [2.0851(15) and 2.0543(15) Å, respectively]. Globally, in the molecule, the *tert*-butyl groups are orientated towards the azido ligand. The N41–N42–N43 angle [176.9(2)°] within the azido ligand is close to linear.

In the crystal, molecules assemble into a zigzag chain (glide symmetry) along the c-axis and feature pyrazolyl–C–H···N(azido) interactions [C14–H14···N43^i: H14···N43^i = 2.62 Å, C14···N43^i = 3.421(3) Å with the angle subtended at the H14 atom = 143° for symmetry operation (i) x, –1/2 - y, –1/2 + z]. The chains lie in a layer in the bc-plane and feature methyl–C–H···π(pyrazolyl) [C19–H19c···Cg(N21,N21,C13–C15)^{ii}: H19c···Cg(N21,N21,C13–C15)^{ii} = 2.80 Å with angle at H19c = 140° for (ii) 1 - x, 1/2 + y, 3/2 - z] interactions between the chains. This interaction may provide an explanation for the slight elongation of the Cu–N21 bond length cf. the Cu–N31 bond (see above). The layers stack along the a-axis without directional interactions between them.

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

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