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Redetermination of the crystal structure of bis {hydridotris(3,5-dimethylpyrazol-1-yl-κN³)borato} copper(II), C₃₀H₄₄B₂CuN₁₂

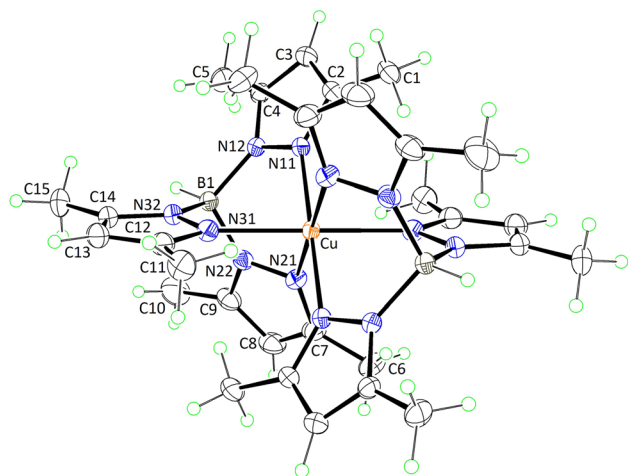


Table 1: Data collection and handling.

| | |
|--|--|
| Crystal: | Blue prism |
| Size: | 0.17 × 0.15 × 0.03 mm |
| Wavelength: | Mo K α radiation (0.71073 Å) |
| μ : | 0.70 mm ⁻¹ |
| Diffractometer, scan mode: | Rigaku XtaLAB P200, ω |
| θ_{\max} , completeness: | 29.8°, >99% |
| $N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} : | 27,784, 4444, 0.029 |
| Criterion for I_{obs} , $N(hkl)_{\text{gt}}$: | $I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4288 |
| $N(\text{param})_{\text{refined}}$: | 211 |
| Programs: | CrysAlis ^{PRO} [1], SIR2014 [2], SHELX [3], WinGX/ORTEP [4] |

Source of material

A mixed solvent system comprising acetone (20 mL) and dichloromethane (20 mL) was added to a mixture of K {HB(3,5-Me₂pz)₃} (369 mg, 1.097 mmol) [5] and Cu(NO₃)₂·3H₂O (150 mg, 0.621 mmol). After the mixture was stirred for 30 min, the solvent was evaporated under vacuum. The resulting solid was washed with distilled water (10 mL) to remove side-products, e.g. KNO₃. Pale-blue crystals were obtained by the crystallisation of the remaining solid from a dichloromethane/hexane (10 mL/5 mL) solution at –30 °C. Yield: 34% (121 mg, 0.184 mmol). **Anal. Calcd.** for C₃₀H₄₄B₂CuN₁₂(H₂O). C; 53.31, H; 6.86, N; 24.87%. Found: C; 53.08, H; 6.62, N; 24.87%. **IR** (JASCO FT/IR-550 spectrophotometer, KBr; cm⁻¹): 2925 (s) ν (C–H), 2506 (s) ν (B–H), 1541 (s) ν (C=N). **Far-IR** (JASCO FT/IR-6700 spectrophotometer, CsI; cm⁻¹): 649 (s), 471 (s), 277 (s) ν (Cu–N). **UV–Vis** (JASCO V-570 at 298 K) in dichloromethane: $\lambda_{\text{max}}/\text{nm}$ (ϵ , mol⁻¹ L cm⁻¹) 313 (800), 645 (24). **ESR** (JEOL JES-RE2X, 5 mm ϕ quartz tube, dichloromethane, 143 K): g_{\parallel} , 2.22 (A_{||}, 154 G); g_{\perp} , 2.07.

Experimental details

The C- and B-bound H atoms were geometrically placed (C–H = 0.95–1.00 Å & B–H = 1.12 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C})$ and $1.2U_{\text{eq}}(\text{B})$. Owing to poor agreement, two reflections, i.e. (0 0 1) and (3 1 1), were omitted from the final cycles of refinement.

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Abstract

C₃₀H₄₄B₂CuN₁₂, triclinic, $P\bar{1}$ (no. 2), $a = 8.6801(1)$ Å, $b = 10.1688(2)$ Å, $c = 10.7290(2)$ Å, $\alpha = 62.672(2)^\circ$, $\beta = 84.3550(10)^\circ$, $\gamma = 78.9700(10)^\circ$, $V = 825.71(3)$ Å³, $Z = 1$, $R_{\text{gt}}(F) = 0.0318$, $wR_{\text{ref}}(F^2) = 0.0961$, $T = 178$ 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: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> _{iso} [*] / <i>U</i> _{eq} |
|------|--------------|---------------|---------------|---|
| Cu | 0.5 | 0.0 | 0.0 | 0.02311 (8) |
| N11 | 0.33323 (12) | 0.13068 (11) | 0.05647 (10) | 0.0253 (2) |
| N12 | 0.26240 (12) | 0.06437 (11) | 0.18590 (10) | 0.02460 (19) |
| N21 | 0.33535 (15) | -0.18292 (13) | 0.10693 (12) | 0.0341 (2) |
| N22 | 0.29741 (13) | -0.21090 (12) | 0.24250 (11) | 0.0294 (2) |
| N31 | 0.59981 (12) | -0.07955 (12) | 0.19672 (11) | 0.0283 (2) |
| N32 | 0.50163 (12) | -0.11339 (11) | 0.31202 (11) | 0.0270 (2) |
| C1 | 0.3007 (2) | 0.38129 (16) | -0.15342 (15) | 0.0423 (3) |
| H1A | 0.372813 | 0.327324 | -0.197144 | 0.063* |
| H1B | 0.350881 | 0.458072 | -0.150016 | 0.063* |
| H1C | 0.204608 | 0.429309 | -0.208628 | 0.063* |
| C2 | 0.26060 (16) | 0.27329 (14) | -0.00778 (13) | 0.0311 (3) |
| C3 | 0.14323 (18) | 0.29895 (15) | 0.08067 (15) | 0.0365 (3) |
| H3 | 0.074381 | 0.390549 | 0.061542 | 0.044* |
| C4 | 0.14663 (15) | 0.16573 (15) | 0.20102 (13) | 0.0300 (2) |
| C5 | 0.04264 (19) | 0.13038 (19) | 0.32779 (16) | 0.0411 (3) |
| H5A | -0.024877 | 0.060968 | 0.333001 | 0.062* |
| H5B | -0.022640 | 0.223152 | 0.321545 | 0.062* |
| H5C | 0.107154 | 0.083814 | 0.412066 | 0.062* |
| C6 | 0.3280 (3) | -0.3044 (2) | -0.0445 (2) | 0.0563 (5) |
| H6A | 0.227680 | -0.274389 | -0.092734 | 0.085* |
| H6B | 0.373402 | -0.406957 | -0.027818 | 0.085* |
| H6C | 0.400202 | -0.235867 | -0.102880 | 0.085* |
| C7 | 0.30140 (19) | -0.29826 (17) | 0.09246 (18) | 0.0415 (3) |
| C8 | 0.2450 (2) | -0.40158 (17) | 0.2190 (2) | 0.0471 (4) |
| H8 | 0.213570 | -0.493283 | 0.237044 | 0.057* |
| C9 | 0.24417 (18) | -0.34353 (15) | 0.31214 (17) | 0.0390 (3) |
| C10 | 0.1980 (3) | -0.4069 (2) | 0.4638 (2) | 0.0590 (5) |
| H10A | 0.287533 | -0.419705 | 0.519670 | 0.088* |
| H10B | 0.165917 | -0.504398 | 0.493623 | 0.088* |
| H10C | 0.110358 | -0.338098 | 0.477757 | 0.088* |
| C11 | 0.88668 (17) | -0.0853 (2) | 0.14792 (18) | 0.0433 (3) |
| H11A | 0.937875 | -0.181575 | 0.151466 | 0.065* |
| H11B | 0.960456 | -0.044066 | 0.178246 | 0.065* |
| H11C | 0.853973 | -0.015059 | 0.051646 | 0.065* |
| C12 | 0.74626 (16) | -0.10832 (15) | 0.24292 (15) | 0.0338 (3) |
| C13 | 0.74209 (17) | -0.16084 (17) | 0.38809 (16) | 0.0388 (3) |
| H13 | 0.829419 | -0.189445 | 0.447220 | 0.047* |
| C14 | 0.58605 (17) | -0.16321 (15) | 0.42930 (14) | 0.0330 (3) |
| C15 | 0.5142 (2) | -0.2093 (2) | 0.57286 (15) | 0.0456 (4) |
| H15A | 0.428982 | -0.129921 | 0.571193 | 0.068* |
| H15B | 0.594323 | -0.225928 | 0.639203 | 0.068* |
| H15C | 0.472382 | -0.302272 | 0.602181 | 0.068* |
| B1 | 0.32444 (16) | -0.09898 (15) | 0.29440 (14) | 0.0258 (2) |
| H1 | 0.264735 | -0.123218 | 0.393853 | 0.031* |

Comment

Since their earliest reports, poly(1-pyrazolyl)borates have been established as an important class of ligands in contemporary coordination chemistry [5]. Among these ligands, the methyl substituted mono-anion, hydridotris{(3,5-dimethylpyrazolyl-1-yl)borato-κN³} anion, denoted as HB{(3,5-Me₂pz)₃}, is prototypical of the substituted

derivatives [5–7]. This ligand is relatively sterically unhindered so it can readily form coordinatively saturated six-coordinate complexes, formulated as [M{HB(3,5-Me₂pz)₃}]₂. The crystal structure of the copper(II) derivative [Cu{HB(3,5-Me₂pz)₃}]₂, has been described previously [8] but was experimentally flawed and subsequently was subjected to a space group change [9]. However, the derived Cu–N bond lengths, being close to equivalent, do not match

expectation; another room temperature determination exhibits relatively high standard uncertainty values on derived parameters [10]. Hence, it was thought worthwhile to redetermine this benchmark structure at reduced temperature in order to reliably determine the crucial intramolecular parameters; new spectroscopic data are also presented.

The molecular structure of $[Cu\{HB(3,5-Me_2pz)_3\}_2]$ is shown in the figure (35% displacement ellipsoids). The copper(II) centre lies on a centre of inversion being coordinated by the six nitrogen atoms derived from two symmetry related tripodal $\{HB(3,5-Me_2pz)_3\}^-$ anions. The Cu–N bond lengths span a range of 0.34 Å with the shortest Cu–N11 bond being 2.0147(10) Å compared to the longest bond of 2.3567(12) for Cu–N21; at 2.0936(11) Å, the Cu–N31 bond length is intermediate between these extremes. These observations suggest a significant deviation from putative three-fold symmetry along the HB···Cu axis, being consistent with an elongated rhombic octahedral geometry. Further, the sequence of dihedral angles between the N11-/N21, N11-/N31- and N21-/N31-pyrazolyl rings is 54.95(9), 58.55(9) and 69.60(10)°, respectively. The d^9 electronic configuration of the copper(II) ion gives three electrons in the doubly degenerate e_g orbitals, therefore the relative elongation of the Cu1–N21 bond is traced to the Jahn–Teller distortion, an effect which lowers the electrostatic repulsion between the electron-pairs on the Lewis basic pyrazole ligands, with the result the overall energy of the complex decreases [11].

The elongated rhombic octahedral structure just described was not observed in other metal(II) complexes of comparable formulation: $[M\{HB(3,5-Me_2pz)_3\}_2]$ for M = Fe [12], M = Co [13] and M = Zn [14], forming instead close to regular octahedral coordination geometries.

In the far-IR spectrum, the strong peak at 277 cm^{-1} can be assigned as $\nu(\text{Cu–N})$. This observation is consistent with $\nu(\text{Fe–N})$, which was assigned by far-IR spectroscopy at 192 cm^{-1} and NRSV (nuclear resonance vibrational spectroscopy) at 197 cm^{-1} [15]. The ground state of the title complex is dx^2-y^2 , which was observed in its ESR spectrum with its ESR parameter g_{\parallel} being 2.22 (A \parallel , 154 G) [11]. This ground state also support by UV–Vis spectroscopy as the d–d transition occurs at 645 nm ($24\text{ mol}^{-1}\text{ cm}^{-1}\text{ L}$), which is shifted by 85 nm to higher energy compared with that of 730 nm ($100^{-1}\text{ cm}^{-1}\text{ L}$) observed for the recently reported complex $[Cu(\text{Cl})(3,5-Me_2pzH)\{HB(3,5-Me_2pz)_3\}_2]$ [16]. This difference arises from the different coordination geometries: elongated rhombic octahedral and distorted square pyramidal geometries, respectively.

An analysis of the molecular packing employing PLATON [17] suggests the absence of directional interactions between molecules. This analysis was

complemented by the calculation, using Crystal Explorer 17 [18], of the Hirshfeld surfaces and of the full and delineated two-dimensional fingerprint plots conducted employing literature protocols [19]. These calculations show that H···H contacts contribute 85.7% to the calculated surface with the only other contacts of note being C···H/H···C [11.5%] and N···H/H···N [2.9%].

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

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