

Bis[tris(3-cyclohexylpyrazol-1-yl)-hydridoborato]copper(II) dichloromethane disolvate

Malcolm A. Halcrow,* Colin A. Kilner and Mark Thornton-Pett

School of Chemistry, University of Leeds, Woodhouse Lane, Leeds LS2 9JT, England
Correspondence e-mail: m.a.halcrow@chem.leeds.ac.uk

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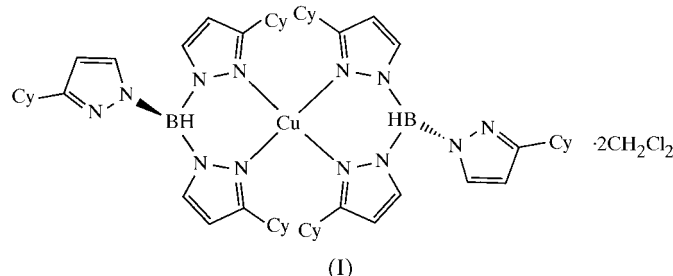
The title compound, $[\text{Cu}(\text{C}_{27}\text{H}_{40}\text{BN}_6)_2] \cdot 2\text{CH}_2\text{Cl}_2$, contains a four-coordinate Cu^{II} ion lying on a crystallographic inversion centre, giving rise to a near-regular square-planar stereochemistry. There is an axial contact of 2.71 Å between the Cu ion and ligand B—H group, although this is unlikely to correspond to a significant 'agostic' interaction.

Comment

The complexes $[\text{CuTp}_2]$ [Tp^- = hydridotris(pyrazol-1-yl)borate] and $[\text{CuTp}^*_2]$ [Tp^{*-} = hydridotris(3,5-dimethylpyrazol-1-yl)borate] adopt distorted octahedral molecular structures in their crystals, with the expected Jahn–Teller elongation along one N—Cu—N axis (Murphy *et al.*, 1979; Kitajima *et al.*, 1988; Marsh, 1989). However, some analogous Cu^{II} complexes containing more sterically hindered pyrazolylborate derivatives, which have not been crystallographically characterized, have been proposed to adopt tetrahedral stereochemistries. This suggestion appears to have been made largely on the basis of their brown colouration, which is often a characteristic of tetrahedral Cu^{II} centres (Trofimenko *et al.*, 1989; Hannay *et al.*, 1994; Trofimenko, 1999), and also because Co^{II} or Zn^{II} complexes of the same ligands have been shown to contain tetrahedral metal ions by crystallography (Trofimenko *et al.*, 1989; Hartmann *et al.*, 1993). We have prepared several compounds of this type during our own studies of copper/hydridotris(pyrazol-1-yl)borate chemistry (Halcrow *et al.*, 1997, 1998; Chia *et al.*, 2000; Liu *et al.*, 2000), and report here the single-crystal structure of one such species, (I).

Brown prisms of formula (I) were grown from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$. The asymmetric unit of the crystals contains half a molecule of the complex, with Cu1 lying on the inversion centre at $(0, 0, \frac{1}{2})$, and one disordered molecule of CH_2Cl_2 lying on a general position. The four-coordinate Cu ion is strictly planar due to the crystallographic inversion symmetry, with N—Cu—N angles that deviate only slightly from a regular square plane owing to the bite angle of the chelating ligand.

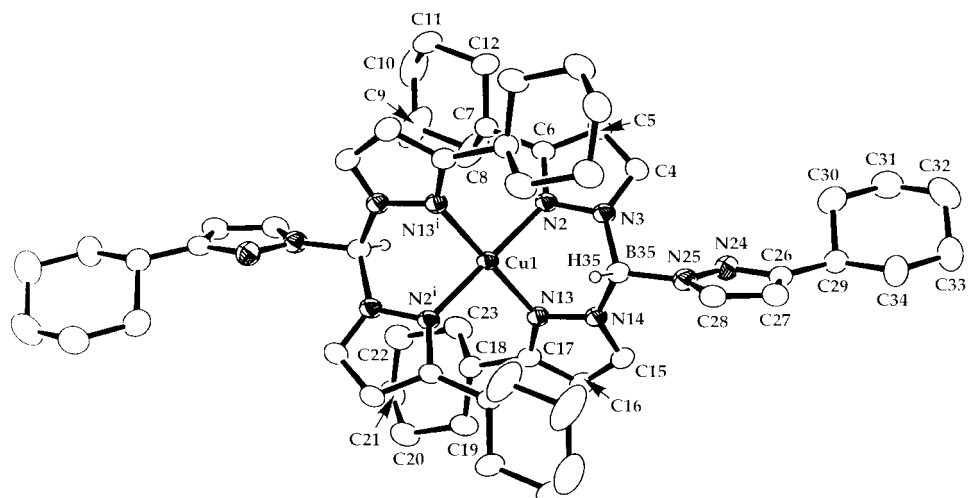
The Cu—N bond lengths in (I) compare well with those derived by EXAFS for the closely related brown-coloured (and presumed tetrahedral) complex $[\text{Cu}(\text{pz}^0\text{Tp}^{\text{Pr}})_2]$, (II) $\{[\text{pz}^0\text{Tp}^{\text{Pr}}]^-$ = tetrakis(3-isopropylpyrazol-1-yl)borate}, of 1.93 (2) and 1.94 (2) Å (Hannay *et al.*, 1994). Hence, given the steric similarity between the 3-cyclohexylpyrazole ligating



groups in (I) and the 3-isopropyl donors in (II), it seems likely that the latter compound in fact also has a square-planar, rather than tetrahedral, Cu^{II} centre. The caveat must be added, however, that different tetrahedral hydridotris(pyrazol-1-yl)borate-containing Cu^{II} complexes have been shown to exhibit Cu—N bonds in the range 1.928 (3)–2.127 (3) Å (Han *et al.*, 1993; Yoon & Parkin, 1995), so that Cu—N distances are not an infallible guide to coordination geometry in these compounds. Adjacent molecules in the extended lattice of this structure interact through van der Waals contacts only.

The upper and lower faces of the ligand square plane in (I) are efficiently shielded by the ligand cyclohexyl substituents, which would prevent the approach of exogenous ligands to this Cu^{II} centre. However, H35 is oriented towards Cu1 in a geometry that is suggestive of an 'agostic' interaction, with $\text{Cu1} \cdots \text{H35} = 2.71$ Å and $\text{B35} - \text{H35} \cdots \text{Cu1} = 94.1^\circ$. This $\text{Cu} \cdots \text{H}$ distance is longer than for other B—H $\cdots M$ (M = first row transition ion) interactions that have been crystallographically characterized, for which $M \cdots \text{H}$ distances of ≤ 2.4 Å are typical (see *e.g.* Dias *et al.*, 1996; Kremer-Aach *et al.*, 1997; Kiani *et al.*, 1997; Ghosh, Bonanno & Parkin, 1998; Ghosh, Hascall *et al.*, 1998). The only previous Cu^{II} /pyrazolylborate complex we are aware of, where an agostic B—H $\cdots \text{Cu}$ interaction was proposed, is $[\text{Cu}\{\text{Bp}^{(\text{CF}_3)_2}\}_2]$ $\{[\text{Bp}^{(\text{CF}_3)_2}]^-$ = dihydridobis[3,5-bis(trifluoromethyl)pyrazol-1-yl]borate}, for which a $\text{Cu} \cdots \text{H}$ distance of 2.58 Å was measured crystallographically (Dias & Gorden, 1996). Therefore, given the long $\text{Cu1} \cdots \text{H35}$ distance it seems likely that there is no significant bonding interaction between Cu1 and H35 in (I), beyond possibly a weak electrostatic attraction between the hydridic H atom and the positively charged void perpendicular to the square plane of ligand donor atoms.

Complex (I) represents only the second structurally authenticated example of a square-planar homoleptic complex of a hydridotris(pyrazol-1-yl)borate derivative, after $[\text{PdTp}_2]$ (Canty *et al.*, 1986). Interestingly, in the Pd complex, the ligand conformation is substantially different from that in (I), in that the axial sites above and below the coordination plane are occupied by the non-coordinated pyrazole rings, rather than the hydridic B—H groups. This is the conformation usually


Figure 1

The molecular structure of (I) with 35% probability displacement ellipsoids, showing the atom-numbering scheme employed. For clarity, solvent molecules and all C-bound H atoms have been omitted. [Symmetry code: (i) $-x, -y, 1 - z$.]

(but not exclusively) adopted in the crystal by κ^2 -hydrido-tris(pyrazol-1-yl)borate derivatives, which are quite common in heteroleptic Rh^I, Ir^I, Pd^{II}, Pt^{II} and Au^{III} complexes of these ligands (Trofimenko, 1999). However, this conformation is impossible for (I), since it would lead to substantial steric repulsions between the axial pendant pyrazole ring of one ligand, and the cyclohexyl substituents on the coordinated pyrazole rings of the other. Hence the ligand conformation in (I), which brings Cu1 and H35 into close proximity, is probably imposed by steric factors.

Experimental

Potassium hydridotris[3-(cyclohexyl)pyrazol-1-yl]borate (1.00 g, 2.0 mmol) and CuCl₂ (0.14 g, 1.0 mmol) were refluxed in CH₃OH (50 ml) for 1 h. The resultant red precipitate was filtered off, washed with CH₃OH and dried *in vacuo*. Brown crystals of the complex were grown by diffusion of CH₃OH into a solution of the compound in CH₂Cl₂ at room temperature. The powdered crystals retain some of the lattice solvent upon drying, with different samples analysing approximately as the dichloromethane hemisolvate. Found: C 63.1, H 8.0, N 16.4%; calculated for C₅₄H₈₀B₂CuN₁₂·0.5CH₂Cl₂: C 63.8, H 8.0, N 16.4%.

Crystal data

[Cu(C₂₇H₄₀BN₆)₂]₂·2CH₂Cl₂
 $M_r = 1152.31$
 Monoclinic, $P2_1/c$
 $a = 13.0758$ (2) Å
 $b = 18.3961$ (3) Å
 $c = 13.0405$ (2) Å
 $\beta = 104.6939$ (12)°
 $V = 3034.22$ (8) Å³
 $Z = 2$

$D_x = 1.261$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 33672 reflections
 $\theta = 2.7$ – 27.5°
 $\mu = 0.58$ mm⁻¹
 $T = 150$ (2) K
 Rectangular prism, brown
 $0.86 \times 0.40 \times 0.37$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
 Area-detector scans
 Absorption correction: multi-scan (Blessing, 1995)
 $T_{\min} = 0.634$, $T_{\max} = 0.813$
 33672 measured reflections

6916 independent reflections
 5524 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.057$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -16 \rightarrow 16$
 $k = -20 \rightarrow 23$
 $l = -16 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.058$
 $wR(F^2) = 0.173$
 $S = 1.04$
 6916 reflections
 363 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0947P)^2 + 1.9928P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.93$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.62$ e Å⁻³
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.011 (3)

Table 1

Selected geometric parameters (Å, °).

Cu1—N2	1.9788 (18)	Cu1—N13	1.995 (2)
N2—Cu1—N13 ⁱ	92.13 (8)	N2—Cu1—N13	87.87 (8)

Symmetry code: (i) $-x, -y, 1 - z$.

The dichloromethane molecule is disordered over four orientations: C36—C138, occupancy 0.3; C39—C141, occupancy 0.2; C42—C144, occupancy 0.2; and C45—C147, occupancy 0.3. All C—Cl distances were restrained to 1.78 (2) Å, and non-bonded Cl···Cl contacts within each disorder orientation to 2.91 (2) Å. Slightly high displacement parameters on individual C atoms in all three cyclohexyl rings may be evidence for libration of these groups in the crystal. However, since the metric parameters in all three of these substituents are typical for a saturated six-membered ring, these groups are not conformationally disordered. All ordered non-H atoms were refined anisotropically, while H atoms were placed in calculated positions and refined using a riding model. The C—H distances employed for the final refinement were 0.95 Å for the pyrazole H atoms, 0.99 Å for the cyclohexyl CH₂ groups and 1.00 Å for the cyclohexyl tertiary C—H bonds, while the B—H distances were 1.00 Å.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1996); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: local program.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1451). Services for accessing these data are described at the back of the journal.

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