

Two complexes of CuBr₂ with 5-*tert*-butylpyrazole

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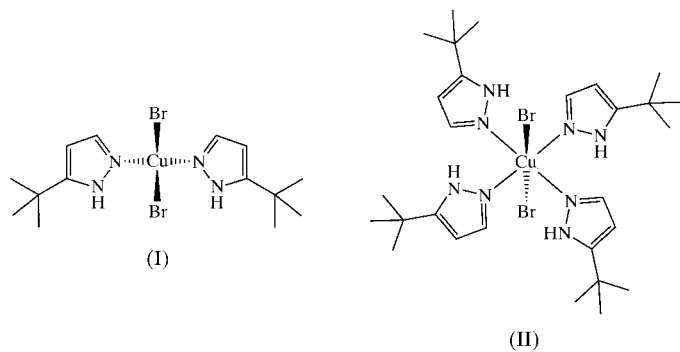
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trans-Dibromobis(5-*tert*-butylpyrazole-*N*²)copper(II), *trans*-[CuBr₂(H₅pz^{*t*Bu})₂] (H₅pz^{*t*Bu} is 5-*tert*-butylpyrazole, C₇H₁₂N₂), exhibits a distorted square-planar geometry with a significant tetrahedral twist, while *trans*-dibromotetrakis(5-*tert*-butylpyrazole-*N*²)copper(II), *trans*-[CuBr₂(H₅pz^{*t*Bu})₄], adopts a distorted octahedral geometry across a crystallographic inversion centre. Both compounds exhibit intramolecular N—H···Br hydrogen-bonding interactions.

Comment

We have recently discovered that complexation of CuCl₂ or CuBr₂ by H₅pz^{*t*Bu} [H₅pz^{*t*Bu} is 3-*tert*-butylpyrazole] in basic MeOH leads to a novel heptacopper aggregate structure, which appears to be templated by N—H···X (X[−] = Cl[−], Br[−]) hydrogen-bonding interactions to non-coordinated anions (Liu *et al.*, 2001). As a result of a more in-depth study of this system, we have isolated two more adducts of CuBr₂ and H₅pz^{*t*Bu}, namely *trans*-dibromobis(5-*tert*-butylpyrazole-*N*²)copper(II), [CuBr₂(H₅pz^{*t*Bu})₂], (I), and *trans*-dibromotetrakis(5-*tert*-butylpyrazole-*N*²)copper(II), [CuBr₂(H₅pz^{*t*Bu})₄], (II). The Trofimenko nomenclature for substituted pyrazoles is employed throughout this discussion (Trofimenko, 1999).



The asymmetric unit of (I) contains one molecule of the complex lying on a general position. The Cu^{II} centre in (I) is four-coordinate, with *trans*-disposed Br[−] and H₅pz^{*t*Bu} ligands;

the latter are coordinated as the less sterically hindered 5-*tert*-butylpyrazole tautomer. The two Cu—N bond lengths in the molecule are crystallographically identical. However, the Cu1—Br20 bond is 0.0713 (6) Å longer than Cu1—Br21, which presumably reflects the presence of two hydrogen bonds to Br20 (see below). Although clearly derived from a square plane, the coordination sphere at Cu1 has a significant tetrahedral twist, which can be expressed by the dihedral angle of 45.71 (6)° between the Cu1/N2/Br20 and Cu1/N11/Br21 planes. This angle would be 0° for ideal square-planar geometry and 90° for tetrahedral geometry. The N—H groups on each pyrazole ligand form an intramolecular hydrogen bond to Br20, leading to a distorted pyramidal geometry for this atom, defined by the angles H3···Br20—Cu1 = 70.0°, H12···Br20—Cu1 = 73.4° and H3···Br20···H12 = 108.2°.

Several 2:1 adducts of pyrazole derivatives with copper dihalides have been crystallographically characterized by other workers. Bis-pyrazole complexes of CuF₂ and CuCl₂ most commonly adopt dimeric structures in the solid state of general formula [CuX(μ-X)L₂]₂ (X[−] = F[−], Cl[−]; L is a pyrazole derivative; ten Hoedt *et al.*, 1981; Reitmeijer *et al.*, 1984; Keij *et al.*, 1991; Malecka *et al.*, 1998; Chandrasekhar *et al.*, 2000). Two coordination polymers with this stoichiometry (Keij *et al.*, 1988; Malecka *et al.*, 1998) and a number of monomeric [CuCl₂L₂] structures (Francisco *et al.*, 1980; Watson *et al.*, 1989; Hergold-Brundic *et al.*, 1991; Valle *et al.*, 1995; Malecka *et al.*, 1998) have also been reported. The only CuBr₂ bis-pyrazole adduct whose crystal structure has been determined previously is the mononuclear complex [CuBr₂(H₅pz^{Ph2})₂] (H₅pz^{Ph2} is 3,5-diphenylpyrazole; Murray *et al.*, 1988). Interestingly, this compound exhibits *cis*-disposed Br[−] and H₅pz^{Ph2} ligands in the solid, but otherwise adopts an almost identical coordination geometry to (I).

Compound (II) contains discrete six-coordinate Cu^{II} centres, with Cu1 lying on a crystallographic inversion centre. As for (I), the H₅pz^{*t*Bu} ligands in (II) are coordinated as the 5-*tert*-butylpyrazole tautomer. The four pyrazole *N*-donor atoms are strictly coplanar and form an almost perfect square

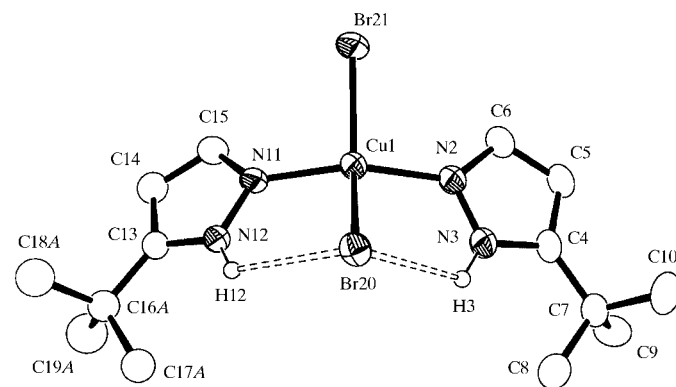


Figure 1

The molecular structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme employed. H atoms have arbitrary radii. For clarity, only one orientation of the disordered *tert*-butyl group (C16A—C19A) is shown, while all C-bound H atoms have been omitted.

plane, although the two unique Cu–N bond lengths differ by 0.006 (2) Å, which is of borderline crystallographic significance. The axial Cu1–Br20 distance of 3.02801 (16) Å is substantially longer than the sum of the covalent radii of Cu (1.38 Å) and Br (1.14 Å) (Gordon & Ford, 1972), so that this 'bond' is probably better considered as a weak electrostatic interaction between the Br[−] anion and the positively charged void perpendicular to the molecular tetragonal plane. This suggestion is supported by the fact that the Cu1–Br20 'bond' fails the Hirschfeld rigid-bond test (Hirschfeld, 1976) by almost

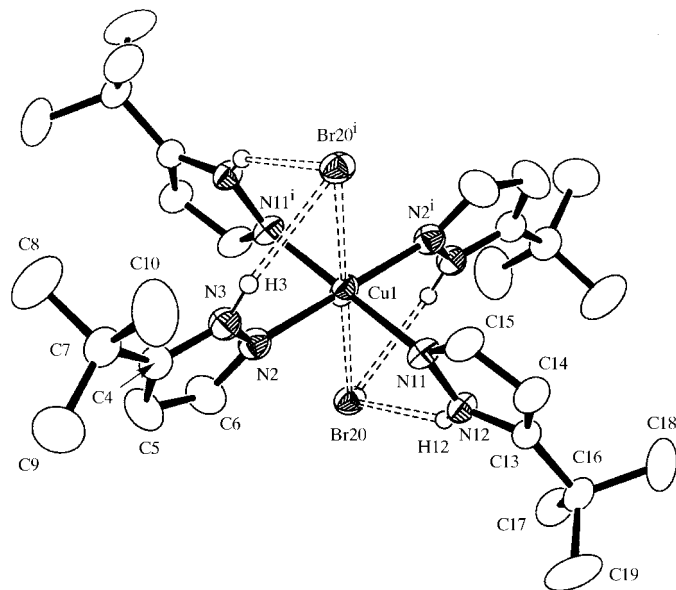


Figure 2
The molecular structure of (II) showing 50% probability displacement ellipsoids and the atom-numbering scheme employed. H atoms have arbitrary radii. For clarity, all C-bound H atoms have been omitted. [Symmetry code: (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$.]

80 s.u.'s, which implies that there is negligible covalent interaction between these two atoms. Each Br[−] ligand accepts two hydrogen bonds from *cis*-disposed pyrazole ligands, forming an approximately pyramidal geometry with angles H3...Br20–Cu1 = 64.1 (5)°, H12...Br20–Cu1 = 63.0 (5)° and H3...Br20...H12 = 76.1 (7)°. The crystal structures of two other 4:1 pyrazole–Cu^{II} dihalide adducts have been reported previously, namely [CuCl₂(Hpz)₄] (Mighell *et al.*, 1975; Casellato *et al.*, 2000) and *catena*-[CuCl₂(μ-dpm)₂]_n [dpm is bis(pyrazol-4-yl)methane; Broomhead *et al.*, 1998]. Both of these exhibit an essentially identical coordination geometry to (II) and show the same pattern of N–H...Cl intramolecular hydrogen bonding.

Experimental

For the preparation of compound (I), anhydrous CuBr₂ (0.22 g, 1.0 mmol) and Hpz^{tBu} (0.18 g, 1.5 mmol) were stirred in a 4:1 CH₂Cl₂–acetone mixture (50 ml) at room temperature for 2 h. The solvent was then removed *in vacuo* and the residue redissolved in a minimum

volume of CH₂Cl₂, yielding a dark-green solution and some insoluble material which was removed by filtration. Slow diffusion of pentane into the filtrate gave a brown microcrystalline product which was removed by filtration. Slow evaporation of the remaining solution yielded green crystals of (I). Analysis, found: C 35.7, H 5.1, N 12.0%; calculated for C₁₄H₂₄Br₂CuN₄: C 35.6, H 5.1, N 11.9%. For the preparation of compound (II), anhydrous CuBr₂ (0.22 g, 1.0 mmol) and Hpz^{tBu} (0.37 g, 3.0 mmol) were reacted in CH₃OH (50 ml) at room temperature for 30 min. The solvent was then removed *in vacuo* and the residue redissolved in a minimum volume of CH₂Cl₂, yielding a dark-green solution and some insoluble material which was removed by filtration. Slow diffusion of pentane into the solution gave a mixture of deep-blue well formed crystals of (II), together with a turquoise by-product which was removed manually. Analysis, found: C 46.8, H 6.7, N 15.7%; calculated for C₂₈H₄₈Br₂CuN₈: C 46.7, H 6.7, N 15.6%.

Compound (I)

Crystal data

[CuBr₂(C₇H₁₂N₂)₂]
M_r = 471.73
Orthorhombic, Pca2₁
a = 17.4947 (2) Å
b = 9.8730 (1) Å
c = 11.1165 (1) Å
V = 1920.10 (3) Å³
Z = 4
D_x = 1.632 Mg m^{−3}

Mo Kα radiation
Cell parameters from 37 366 reflections
θ = 4.1–27.5°
μ = 5.30 mm^{−1}
T = 150 (2) K
Column, green
0.48 × 0.18 × 0.14 mm

Data collection

Nonius KappaCCD diffractometer
Area-detector scans
Absorption correction: multi-scan (SORTAV; Blessing, 1995)
T_{min} = 0.185, T_{max} = 0.524
37 366 measured reflections
4373 independent reflections

4268 reflections with I > 2σ(I)
R_{int} = 0.056
θ_{max} = 27.5°
h = −22 → 22
k = −12 → 12
l = −14 → 14

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.024
wR(F²) = 0.060
S = 1.06
4373 reflections
203 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 0.6531P]$
where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} = 0.001
Δρ_{max} = 0.25 e Å^{−3}
Δρ_{min} = −0.47 e Å^{−3}
Absolute structure: Flack (1983)
Flack parameter = −0.006 (8)

Table 1

Selected geometric parameters (Å, °) for (I).

Cu1–N2	1.951 (2)	Cu1–Br20	2.4479 (4)
Cu1–N11	1.948 (2)	Cu1–Br21	2.3766 (4)
N2–Cu1–N11	152.26 (9)	N11–Cu1–Br20	93.97 (6)
N2–Cu1–Br20	94.09 (6)	N11–Cu1–Br21	94.75 (6)
N2–Cu1–Br21	94.96 (7)	Br20–Cu1–Br21	142.27 (2)

Table 2

Hydrogen-bonding geometry (Å, °) for (I).

D–H...A	D–H	H...A	D...A	D–H...A
N3–H3...Br20	0.88	2.69	3.200 (2)	118
N12–H12...Br20	0.88	2.64	3.194 (2)	122

Compound (II)

Crystal data

[CuBr₂(C₇H₁₂N₂)₄]
M_r = 720.10
 Monoclinic, *C*2/*c*
a = 19.5985 (3) Å
b = 11.9918 (2) Å
c = 15.9131 (2) Å
 β = 109.8260 (6)°
V = 3518.24 (9) Å³
Z = 4

D_x = 1.359 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 29 739 reflections
 θ = 3.7–27.5°
 μ = 2.92 mm⁻¹
T = 150 (2) K
 Rectangular prism, deep blue
 0.49 × 0.34 × 0.17 mm

Data collection

Nonius KappaCCD diffractometer
 Area-detector scans
 Absorption correction: multi-scan
 (SORTAV; Blessing, 1995)
T_{min} = 0.329, *T_{max}* = 0.637
 29 739 measured reflections
 4019 independent reflections

3655 reflections with *I* > 2σ(*I*)
R_{int} = 0.077
 θ_{max} = 27.5°
h = -25 → 25
k = -15 → 15
l = -20 → 20

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.026
wR (*F*²) = 0.070
S = 1.07
 4019 reflections
 187 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0327P)^2 + 2.2831P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.44 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0027 (2)

Table 3

Selected geometric parameters (Å, °) for (II).

Cu1–N2	2.0094 (14)	Cu1–Br20	3.02801 (16)
Cu1–N11	2.0032 (14)		
N2–Cu1–N11	92.96 (6)	N11–Cu1–Br20	88.63 (4)
N2–Cu1–Br20	92.62 (4)		

Table 4

Hydrogen-bonding geometry (Å, °) for (II).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N3–H3...Br20 ⁱ	0.86 (2)	2.45 (2)	3.2195 (15)	148 (2)
N12–H12...Br20	0.80 (2)	2.51 (2)	3.2275 (15)	149 (2)

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, -z$.

The Flack parameter (Flack, 1983) for (I) was determined using 2070 Friedel pairs. One *tert*-butyl group in (I) was found to be disordered during refinement. Three equally occupied disorder orientations were modelled: C16*A*–C19*A*, C16*B*–C19*B* and C16*C*–C19*C*. All C–C bonds within the disordered group were restrained to 1.53 (2) Å, and non-bonded 1,3-C...C contacts within a given disorder orientation were restrained to 2.50 (2) Å. All wholly occupied non-H atoms were refined anisotropically. All H atoms were placed in calculated positions and refined using a riding model, with fixed C–H distances of 0.95 Å for *Csp*²–H bonds and 0.98 Å for methyl C–H bonds, and an N–H distance of 0.88 Å. No disorder was detected in (II). All C-bound H atoms were placed in calculated

positions and refined using a riding model, with fixed C–H distances of 0.95 Å for *Csp*²–H bonds and 0.98 Å for methyl C–H bonds. The N-bound H atoms H3 and H12 were located in a difference Fourier map and were allowed to refine freely.

For both compounds, data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); 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: BM1461). Services for accessing these data are described at the back of the journal.

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