

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: MU1108). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetrakis(imidazole)copper(II) Dibromide, [Cu(Him)₄]Br₂

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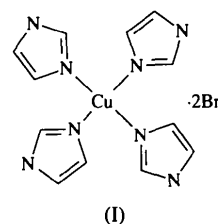
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Abstract

The structure of blue [Cu(C₃H₄N₂)₄]Br₂ consists of discrete [Cu(Him)₄]²⁺ ions (Him = imidazole), with the Cu atom on an inversion center [Cu—N 1.997 (4) and 2.008 (3) Å, N—Cu—N 89.9 (1) and 90.1 (1)°], and bromide ions [unique Cu···Br[−] 3.3767 (4) Å] in the fifth and sixth octahedral sites above and below the CuN₄ plane. The Br[−] ions also take part in a network of N—H···Br[−] hydrogen bonds [N···Br[−] 3.343 (4) and 3.383 (4) Å].

Comment

The [Cu(Him)₄]Br₂ complex has been prepared previously (Goodgame, Goodgame, Hayward & Rayner-Canham, 1968), and its vibrational bands, diffuse reflectance spectra and magnetic moment reported. The analogous iodide complex, [Cu(Him)₄]I₂, has also been prepared, and its molecular and crystal structure determined (Akhtar, Goodgame, Goodgame, Rayner-Canham & Skapski, 1968; Ballester, Parker & Breneman, 1993). The molecular determination of the iodide complex showed that the copper-to-iodide distances were long and unequal [3.406 (2) and 3.865 (2) Å (Ballester, Parker & Breneman, 1993)] in the pseudo tetragonal stereochemistry. The present work was undertaken in order to determine whether or not the analogous bromide complex, (I), had the same type of distorted tetragonal core.



An *ORTEP* (Johnson, 1965) plot of the complex is shown in Fig. 1 with the atomic numbering system. The structure consists of a discrete [Cu(Him)₄]²⁺ square-planar cation with two bromide anions, at best, weakly interacting with the copper(II) in the fifth and sixth octahedral positions. The Cu atom lies on an inversion center which requires the CuN₄ moiety of the cation to be precisely planar and also requires the Cu···Br distances to be equivalent. The Cu···Br distances of 3.3767 (4) Å are long for tetragonal copper(II) complexes. The compound CuBr₂ has short Cu—Br distances of 2.40 Å and long Cu—Br distances of 3.18 Å (Huheey, 1983). The complex [CuBr(NCS)(phen)₂] (phen = 1,10-phenanthroline) has a long Cu—Br distance of 2.820 (2) Å (Parker & Breneman, 1995) and the five-coordinate complex [CuBr(phen)₂]ClO₄ has a short copper-to-bromide distance of 2.496 (1) Å (Parker, Greiner, Breneman & Willett, 1994).

The Cu—N(Him) distances of 2.008 (3) and 1.997 (4) Å fall in the normal range for the equatorial bond lengths in tetragonal copper(II) complexes. These distances are comparable with those found in [Cu(Him)₄]I₂, [Cu(Him)₄SO₄], [Cu(Him)₄(ClO₄)₂], [Cu(Him)₄(H₂O)₂]F₂ and [Cu(Him)₄(NO₃)₂], with values of 1.996 (4)–2.026 (5), 2.000–2.021, 1.998–2.010, 1.984–2.033 and 2.008–2.018 Å, respectively (Ballester, Parker & Breneman, 1993; Fransson & Lundberg, 1972; Ivarsson, 1973; Vreugdenhil, Birker, ten Hoedt, Verschoor & Reedijk, 1984; McFadden, McPhail, Garner & Mabbs, 1976).

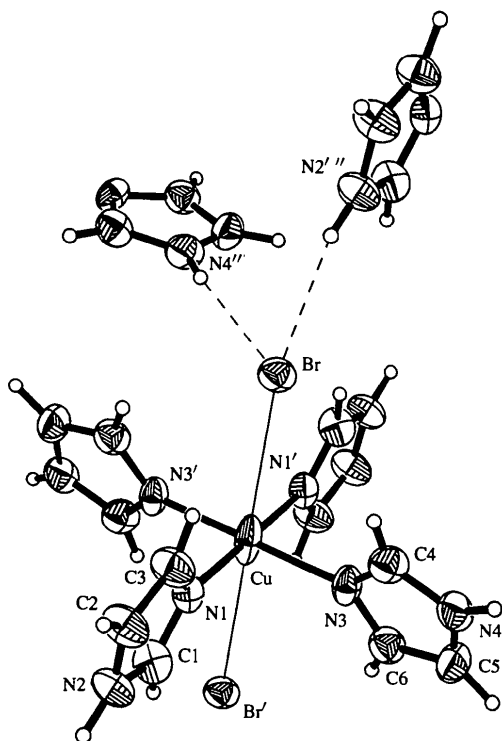


Fig. 1. Displacement ellipsoid plot (50% probability) of the title complex showing the atom-numbering scheme. Hydrogen bonding between molecules is shown by dashed lines.

The Cu···Br interactions are weak but are definitely in the fifth and sixth coordination sites, as indicated by the angles around the Cu atom: Br···Cu—N 190.4 (1) and Br···Cu—N3 88.2 (1)°. The Br···Cu···Br' axis is closer to being collinear with one of the pairs of imidazole ligands than it is with the remaining pair. The Br[−] ions also take part in a network of N—H···Br[−] hydrogen bonds to imidazole rings from neighboring cations, as shown in Fig. 1. These hydrogen-bond distances are N···Br[−] 3.343 (4) and 3.383 (4) Å, and H···Br[−] 2.55 and 2.52 Å, and the N—H···Br[−] angles are 148 and 160°. The N···Br[−] distance is about 82% of the expected van der Waals distance. Hydrogen-bonding networks are also present in the structure of [Cu(Him)₄]I₂ (Ballester, Parker & Breneman, 1993), with each iodide hydrogen bonded to two distinct imidazole rings. These hydrogen-bond distances are N···I[−] 3.54–3.65 and H···I[−] 2.68–2.80 Å, and the N—H···I[−] angles are 140–169°. The N···I[−] distance is about 85% of the expected van der Waals distance. The [Pt(Ph₂PCH₂)₂]I₂·2CDCl₃ complex (Ferguson, Lough, McAlees & McCrindle, 1993) has reported hydrogen-bonding geometry of I···C 3.891 (8), I···D 2.96 Å and I···D—C 166°; the distance is 92% of the expected van der Waals distance.

Bond distances and angles within the imidazole rings are within the normal range of values. The present

complex has the non-coordinated N atoms on opposite imidazole rings in inverted positions with respect to each other, as required by the inversion center. The [Cu(Him)₄(H₂O)₂]F₂ complex also has the Cu atom on a center of inversion (Vreugdenhil, Birker, ten Hoedt, Verschoor & Reedijk, 1984). The complex [Cu(Him)₄]I₂ has the non-coordinated N atoms of the rings in a similar inverted position but the Cu atom is not on a center of inversion and the two Cu···I distances are unequal (Ballester, Parker & Breneman, 1993). The orientation of the Him ligands with respect to the CuN₄ coordination plane is defined by the dihedral angles which the ligand planes make with the CuN₄ plane, *i.e.* 83.6 (2) for the plane formed by N1, C1, N2, C2 and C3, and 72.2 (2)° for the plane through N3, C4, N4, C5 and C6.

Experimental

The title compound was prepared by dissolving CuBr₂ (1.12 g, 5 mmol) in 50 ml of absolute ethanol, followed by slow addition of imidazole (2.04 g, 30 mmol) with gentle heating. Crystals were obtained from the solution by slow evaporation of the solvent.

Crystal data

[Cu(C₃H₄N₂)₄]Br₂

M_r = 495.667

Monoclinic

*C*2/*c*

a = 14.739 (4) Å

b = 9.029 (1) Å

c = 14.269 (4) Å

β = 115.95 (1)°

V = 1707.4 (8) Å³

Z = 4

D_x = 1.928 Mg m^{−3}

Data collection

Enraf–Nonius CAD-4 diffractometer

θ/2θ scans

Absorption correction:

ψ scan

T_{min} = 0.349, *T_{max}* = 0.989

1723 measured reflections

1673 independent reflections

Refinement

Refinement on *F*

R = 0.038

wR = 0.050

S = 2.09

1359 reflections

106 parameters

H atoms riding with C—H

0.95 and N—H 0.90 Å

w = 1/[σ²(*F*) + 0.0004*F*²]

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 19.98–23.81°

μ = 5.97 mm^{−1}

T = 293 K

Plate

0.40 × 0.35 × 0.07 mm

Purple

1359 observed reflections

[*I* > 3σ(*I*)]

R_{int} = 0.021

θ_{max} = 25.0°

h = −17 → 15

k = 0 → 10

l = 0 → 16

1 standard reflection

frequency: 167 min

intensity decay: 0.91%

(Δ/σ)_{max} = 0.01

Δρ_{max} = 0.54 e Å^{−3}

Δρ_{min} = −1.13 e Å^{−3}

Atomic scattering factors

from Cromer & Mann

(1968) and *International*

Tables for X-ray

Crystallography (1974,

Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Br	0.40448 (3)	1.04636 (5)	0.08556 (3)	0.0396 (1)
Cu	1/4	3/4	0	0.0481 (3)
N1	0.3694 (2)	0.6134 (4)	0.0599 (2)	0.0351 (9)
N2	0.4560 (2)	0.4088 (4)	0.1050 (3)	0.042 (1)
N3	0.2643 (2)	0.7610 (4)	-0.1327 (2)	0.0360 (9)
N4	0.3189 (2)	0.8098 (4)	-0.2492 (3)	0.045 (1)
C1	0.3640 (3)	0.4703 (5)	0.0605 (3)	0.043 (1)
C2	0.5242 (3)	0.5217 (5)	0.1346 (4)	0.047 (1)
C3	0.4700 (3)	0.6474 (5)	0.1063 (4)	0.046 (1)
C4	0.3336 (3)	0.8294 (5)	-0.1507 (3)	0.043 (1)
C5	0.2340 (3)	0.7241 (6)	-0.2978 (3)	0.048 (1)
C6	0.2009 (3)	0.6948 (5)	-0.2248 (3)	0.042 (1)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Cu...Br	3.3767 (4)	N3—C6	1.373 (6)
Cu—N1	2.008 (3)	N4—C4	1.336 (6)
Cu—N3	1.997 (4)	N4—C5	1.373 (6)
N1—C1	1.295 (7)	C2—C3	1.345 (6)
N1—C3	1.368 (6)	C5—C6	1.354 (7)
N2—C1	1.341 (6)	Br...N2 ⁱ	3.343 (4)
N2—C2	1.363 (6)	Br...N4 ⁱⁱ	3.383 (4)
N3—C4	1.312 (6)		
Br...Cu—N1	90.4 (1)	C4—N3—C6	106.2 (4)
Br—Cu—N3	88.2 (1)	C4—N4—C5	107.4 (4)
N1—Cu—N3	89.9 (1)	N1—C1—N2	111.4 (4)
Cu—N1—C1	124.8 (3)	N2—C2—C3	106.1 (4)
Cu—N1—C3	129.1 (3)	N1—C3—C2	109.4 (4)
C1—N1—C3	106.1 (4)	N3—C4—N4	111.2 (4)
C1—N2—C2	107.0 (4)	N4—C5—C6	106.1 (4)
Cu—N3—C4	128.6 (3)	N3—C6—C5	109.1 (4)
Cu—N3—C6	125.2 (3)		

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

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *MolEN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1007). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans-Dichlorobis(7-thiabicyclo[2.2.1]-heptane)palladium(II) and *trans*-Dichlorobis(7-thiabicyclo[2.2.1]heptane)platinum(II)

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Abstract

The asymmetric unit of the title Pd complex, $[\text{PdCl}_2(\text{C}_6\text{H}_{10}\text{S})_2]$, consists of two independent half molecules lying on inversion centres. The Pd atoms have square-planar coordination with Pd—S distances of 2.300 (2) and 2.313 (2) \AA , Pd—Cl distances of 2.300 (2) and 2.307 (2) \AA , and S—Pd—Cl angles of 88.21 (8) and 90.12 (8)°. The Pt complex, $[\text{PtCl}_2(\text{C}_6\text{H}_{10}\text{S})_2]$, has the Pt atom lying on an inversion centre, also has square-planar coordination, and has a Pt—S distance of 2.286 (2), a Pt—Cl distance of 2.300 (2) \AA and a S—Pt—Cl angle of 89.25 (8)°.

Comment

Platinum group metals occur in low amounts in association with other metal ores (e.g. Ni and Cu) (Hartley, 1973). One possible method for concentrating these metals is to take advantage of the ability of chloride derivatives to complex with thioether compounds to form hydrocarbon-soluble complexes. The base metals and