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LETTER

The crystal and molecular structure of bromo bis(1-phenyl-3,5-dimethylpyrazole)-copper(I), $CuBr(pdmp)_2$

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Much of the recent activity in the area of copper(I) chemistry is inspired not only by the versatility of copper catalysts in oxidation processes, but also for their important role in the redox-active copper containing proteins. This has led to extensive efforts in biomimetics chemistry to simulate the protein active sites in order to learn about its structure and mechanism of action. As part of a series of crystallographic studies of Cu(I) complexes [1, 2] we report here the crystal and molecular structure of the title compound.

Experimental

The title complex was obtained by heating solid CuBr and an ethanolic pdmp solution. After 3 h the excess of solid CuBr was separated and on cooling the solution colorless crystals were obtained.

X-ray data for $CuBr(pdmp)_2$

A crystal of maximum linear dimensions 0.7 mm was mounted on an Enraf-Nonius CAD-4 diffractometer. Unit cell dimensions were obtained by least-squares on setting angles of 25 reflections collected in the range $16 < 2\theta < 38°$.

Crystal data for $BrCuC_{22}H_{24}N_4$. $FW = 487.91$, monoclinic, $P2_1/n$, $a = 9.502(4)$, $b = 14.605(3)$, $c = 15.851(6)$ Å, $\beta = 102.17(7)°$, $V = 2150(3)$ Å^3, $Z = 4$, $D_c = 1.507$ g cm^{-3}, λ(Mo Kα) = 0.71073 Å, μ(Mo Kα) = 3.04 cm^{-1}. The crystal was stable under radiation. A total of 2618 unique reflections was collected in the range $0 < \theta < 22°$, the intensities of which were corrected for Lp and for absorption [3]; of these, 1450 with $I > 3\sigma(I)$ were retained for structure refinement.

The structure was solved by Patterson and difference Fourier techniques. In the final cycles of least-squares refinement all non-H atoms were treated anisotropically. H atoms were included as fixed contributors all with a common isotropic temperature factor that refined to $U = 0.10$ Å^2. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w^{-1} = [\sigma^2(F_o) + 0.005F_o^2]$ and 254 parameters were refined; excluding unobserved reflections the refinement converged to $R = 0.046$ and $R_w = 0.050$. Programs used were SHELX76 [4] and ORTEP [5]. Bonded H-atom scattering factors [6] and complex scattering factors [7, 8] for the remaining atoms were employed.

Final atomic parameters are listed in Table 1; interatomic distances and angles around the Cu(I) are given in Table 2.

X-ray structure for $CuBr(pdmp)_2$

A projection of the complex showing the atom numbering is given in Fig. 1. The main result of this communication is that the coordination around the Cu(I) is essentially trigonal-planar, the distance of Cu(I) to the N(1), N'(1), Br plane being 0.037(1) Å. The Cu–Br distance of 2.372(2) Å is in good agreement with the value found in $[(PPh_3)CuBr]_4$ [9]. The Cu–N distances of 1.976(7) and 1.977(7) Å are comparable to those found in the trigonal complex $(C_6H_7N)_3CuClO_4$ [10].

The phenyl and pyrazole rings are planar to within experimental accuracy: σ_{av} defined as $\Sigma(d_i^2/N-3)^{1/2}$ are 0.013 and 0.010 for the Ph rings and 0.016 and 0.006 for the pyrazole rings of the unprimed

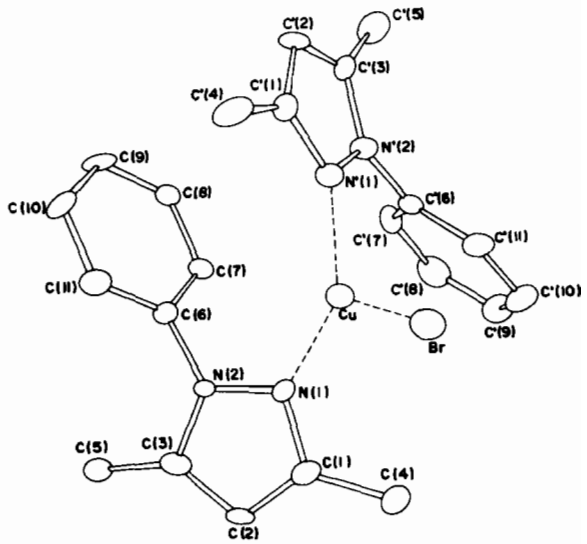

Fig. 1. Projection of the complex showing the atom numbering.

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TABLE 1. Fractional atomic coordinates and equivalent isotropic temperature factor (Å²)

Atom	x/a	y/b	z/c	B_{iso}[a]
Cu	−0.2319(1)	0.2472(1)	0.3038(1)	3.35(4)
Br	0.0128(1)	0.2817(1)	0.3065(1)	4.36(4)
N(1)	−0.3599(8)	0.2105(5)	0.1941(4)	3.0(2)
N(2)	−0.4519(8)	0.1376(5)	0.1867(4)	2.7(2)
C(1)	−0.351(1)	0.2307(6)	0.1130(6)	3.4(3)
C(2)	−0.443(1)	0.1723(6)	0.0547(5)	3.3(3)
C(3)	−0.503(1)	0.1133(6)	0.1039(5)	3.0(3)
C(4)	−0.266(1)	0.3115(7)	0.0955(6)	4.9(4)
C(5)	−0.612(1)	0.0403(6)	0.0805(5)	4.1(3)
C(6)	−0.5027(9)	0.1075(6)	0.2590(6)	2.4(3)
C(7)	−0.463(1)	0.0210(7)	0.2959(6)	3.7(3)
C(8)	−0.517(1)	−0.0042(7)	0.3688(6)	4.1(3)
C(9)	−0.604(1)	0.0542(8)	0.4019(6)	4.1(4)
C(10)	−0.644(1)	0.1367(6)	0.3644(5)	3.5(3)
C(11)	−0.595(1)	0.1641(6)	0.2922(5)	3.2(3)
N′(1)	−0.2880(8)	0.2514(5)	0.4170(5)	3.2(2)
N′(1)	−0.3854(8)	0.3138(5)	0.4342(4)	3.3(3)
C′(1)	−0.256(1)	0.1985(7)	0.4857(6)	3.8(3)
C′(2)	−0.332(1)	0.2271(8)	0.5471(6)	5.0(4)
C′(3)	−0.413(1)	0.3009(7)	0.5139(7)	4.7(4)
C′(4)	−0.156(1)	0.1206(8)	0.4882(6)	5.9(4)
C′(5)	−0.511(2)	0.3610(8)	0.5521(7)	6.7(5)
C′(6)	−0.439(1)	0.3829(6)	0.3721(5)	3.1(3)
C′(7)	−0.585(1)	0.3950(7)	0.3408(7)	4.2(4)
C′(8)	−0.631(1)	0.4606(8)	0.2797(8)	5.2(4)
C′(9)	−0.537(1)	0.5150(7)	0.2465(7)	4.9(4)
C′(10)	−0.390(1)	0.5001(8)	0.2776(6)	4.8(4)
C′(11)	−0.341(1)	0.4345(7)	0.3399(6)	3.8(3)

[a] $B_{iso} = \frac{4}{3}\Sigma_i\Sigma_j B_{ij}(a_i \cdot a_j)$.

TABLE 2. Distances (Å) and angles (°) around Cu(I)

Cu–Br	2.372(2)
Cu–N(1)	1.976(7)
Cu–N′(1)	1.977(7)
Br–Cu–N(1)	119.6(2)
Br–Cu–N′(1)	115.3(2)
N(1)–Cu–N′(1)	125.0(3)

and primed molecules. Dihedral angles between the rings in each molecule are 73.1(3) and 54.0(4)°, respectively.

Supplementary material

Tables of anisotropic thermal parameters, H-atom coordinates and structure factors are available from the authors on request.

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