

Di- μ -bromo-bis[(pyridine)(triphenylphosphine)copper(I)]

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Abstract. $[\text{Cu}_2\text{Br}_2(\text{C}_5\text{H}_5\text{N})_2\{\text{P}(\text{C}_6\text{H}_5)_3\}]$, $M_r = 970.0$, monoclinic, $C2/c$, $a = 26.188(7)$, $b = 14.222(3)$, $c = 11.259(4)$ Å, $\beta = 94.51(2)^\circ$, $V = 4180(2)$ Å³, $Z = 4$, $D_x = 1.54$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 2.90$ mm⁻¹, $F(000) = 1944$, $T = 296$ K, $R = 0.047$ for 1271 observed reflections. The compound is in a dimeric form; the metal atom is tetrahedrally coordinated to pyridine [Cu–N 2.053(9) Å], two Br atoms [Cu–Br 2.538(2), 2.507(2) Å; Br–Cu–Br 108.50(8)°] and triphenylphosphine [Cu–P 2.209(3) Å] and is slightly distorted, with a dihedral angle between the [BrCuBr] and [PCuN] planes of 90.9(2)°. The Cu...Cu' distance is 2.948(2) Å.

Introduction. Monodentate tertiary phosphines form many complexes with Cu^I that show a variety of stoichiometries and structures (Gill, Mayerle, Welcker, Lewis, Ucko, Barton, Stowens & Lippard, 1976). Considerable interest exists in structural studies of copper(I) derivatives, not only because of their stereochemistry but also for their importance in oxidation–reduction reactions in enzymes containing copper (Peisach, Aisen & Blumberg, 1966) and in organic synthesis (Tsuda, Fujii, Kawasaki & Saegusa, 1980). Some years ago, Jardine, Rule & Vohra (1970) reported the preparation of halogenocopper(I) complexes using tertiary phosphines as ligands. We synthesized one of them, the title compound, and proceeded with its crystal structure determination because the only characterizations in the Jardine *et al.* (1970) paper were analytical data and molecular weight and to elucidate their hypothesis that the compound, though monomeric in solution, may be dimeric in the solid state.

Experimental. Irregular colourless crystals from butanol at 277 K, max. and min. linear dimensions 0.30, 0.15 mm; Nonius CAD-4 diffractometer,

graphite-monochromated Mo $K\alpha$; cell parameters by least squares on setting angles for 22 reflections, $9 < \theta < 30^\circ$; ω – 2θ scans, scan width $(0.80 + 0.35 \tan\theta)^\circ$, scan speed $6.7^\circ \text{ min}^{-1}$; max. range of hkl : $-27 < h < 27$, $k < 15$, $l < 11$, $\theta_{\text{max}} = 22^\circ$; standards 060, $10\bar{4}$, 2 varied $\pm 2.4\%$ of mean intensities over data collection; 2086 reflections measured, 2553 unique, $R_{\text{int}} = 0.014$, 1271 observed above $3\sigma(I)$, Lp corrections; structure solved by direct methods. In final cycles of full-matrix least-squares refinement all non-hydrogen atoms anisotropic. Py H atoms included at constrained positions [C–H = 1.00(1) Å] based on those found in difference synthesis, all with fixed isotropic $U = 0.06$ Å²; phenyl rings of triphenylphosphine as rigid bodies (C–C = 1.395, C–H = 1.08 Å, all angles 120° , H atoms with common $U = 0.06$ Å²). Function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = [\sigma^2(F_o) + 0.00075F_o^2]^{-1}$; max. $\Delta/\sigma = 0.005$; 135 parameters refined; excluding unobserved reflections $R = 0.047$, $wR = 0.050$; inspection of F_c and F_o values indicated correction for secondary extinction required;* max. $\Delta/\sigma = 0.002$, $\Delta\rho$ excursions within -0.44 and 0.56 e Å⁻³; scattering factors for non-H atoms from Cromer & Mann (1968) with corrections for anomalous dispersion from Cromer & Liberman (1970), for H from Stewart, Davidson & Simpson (1965); programs used: MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); SHELX76 (Sheldrick, 1976) and ORTEP (Johnson, 1965). Most of the calculations were performed on a VAX 11/780 computer of the Instituto de Física e Química de São Carlos.

Discussion. A projection of the crystallographically independent moiety is shown in Fig. 1. Positional

* $F_{\text{corr}} = F_c/[1.0 - \chi F_c^2/\sin(\theta)]$, where χ refined to 6×10^{-8} in the final run.

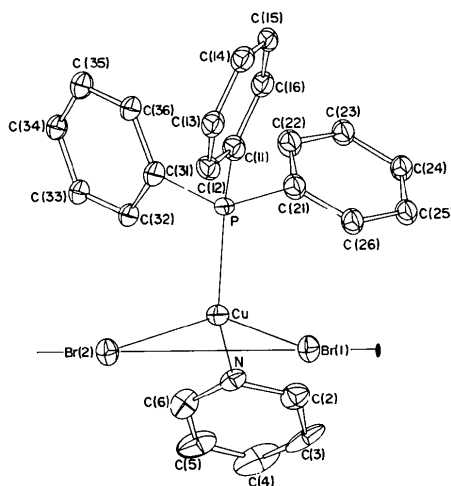


Fig. 1. Projection of the crystallographically independent moiety, with the thermal ellipsoids drawn at 45% probability.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters with *e.s.d.*'s in parentheses

For each rigid phenyl ring only the coordinates of three C atoms are given.

	<i>x</i>	<i>y</i>	<i>z</i>	* <i>B</i> _{eq} (Å ²)
Br(1)	0	0.3812 (1)	0.25	4.50 (8)
Br(2)	0	0.0933 (1)	0.25	4.24 (7)
Cu	0.0310 (1)	0.2359 (1)	0.3651 (1)	4.01 (5)
P	0.1148 (1)	0.2420 (2)	0.4063 (3)	3.3 (1)
C(11)	0.1545 (3)	0.2738 (5)	0.2861 (5)	4.3 (2)
C(13)	0.1637 (3)	0.2761 (5)	0.0743 (5)	4.3 (2)
C(15)	0.2315 (3)	0.3365 (5)	0.2113 (5)	4.3 (2)
C(21)	0.1339 (3)	0.3266 (5)	0.5218 (6)	4.9 (2)
C(23)	0.1825 (3)	0.3732 (5)	0.7036 (6)	4.9 (2)
C(25)	0.1173 (3)	0.4763 (5)	0.6127 (6)	4.9 (2)
C(31)	0.1434 (3)	0.1328 (4)	0.4653 (7)	4.6 (2)
C(33)	0.1366 (3)	0.0022 (4)	0.6004 (7)	4.6 (2)
C(35)	0.2139 (3)	0.0240 (4)	0.4995 (7)	4.6 (2)
N	-0.0143 (3)	0.2361 (9)	0.5059 (8)	4.4 (4)
C(2)	-0.0258 (6)	0.317 (1)	0.559 (2)	6.0 (7)
C(3)	-0.0556 (7)	0.318 (2)	0.655 (2)	8 (1)
C(4)	-0.0700 (7)	0.239 (2)	0.704 (1)	9 (1)
C(5)	-0.0586 (7)	0.157 (2)	0.652 (2)	7.9 (9)
C(6)	-0.0302 (6)	0.158 (1)	0.553 (1)	5.5 (6)

$$*B_{eq} = \frac{1}{3} \sum_{i,j} b_{ij} (a_i, a_j) \text{ (Hamilton, 1959).}$$

Table 2. Bond lengths (Å) and angles (°)

Cu—N	2.053 (9)	P—Cu—N	117.6 (3)
Cu—P	2.209 (3)	Br(1)—Cu—N	102.2 (3)
Cu—Br(1)	2.538 (2)	Br(2)—Cu—N	102.5 (3)
Cu—Br(2)	2.507 (2)	Br(1)—Cu—P	110.36 (9)
Cu—Cu'	2.948 (2)	Br(2)—Cu—P	114.60 (9)
		Br(1)—Cu—Br(2)	108.49 (6)
P—C(11)	1.827 (7)	C(11)—P—Cu	117.9 (2)
P—C(21)	1.813 (7)	C(21)—P—Cu	113.0 (3)
P—C(31)	1.826 (7)	C(31)—P—Cu	114.5 (3)
		C(11)—P—C(21)	103.1 (3)
		C(11)—P—C(31)	103.8 (3)
		C(21)—P—C(31)	102.8 (3)

atomic parameters and the equivalent values of the anisotropic temperature factors are given in Table 1.* Relevant bond lengths and angles are given in Table 2. The compound is in a dimeric form with the two bromine atoms sited on a twofold axis; this requires the Cu₂Br₂ moiety to be strictly planar. The coordination polyhedron around the copper ion is a slightly distorted tetrahedron with the dihedral angle between the [BrCuBr] and [PCuN] planes of 90.9 (2)°. The N—Cu—P angle of 117.6 (3)°, compared to 108.49 (6)° for the Br(1)—Cu—Br(2) angle, reflects the greater steric bulk of the pyridine and triphenylphosphine compared to the bromine ligands. The Cu...Cu distance of 2.948 (2) Å is sufficiently long to preclude any significant interaction.

As is general for metal-phosphine complexes (Churchill & O'Brien, 1968; Churchill & Kalra, 1974) angles about the phosphorus atom show systematic deviations from the ideal tetrahedral value, as shown in Table 2. The pyridine ring is planar to within experimental accuracy ($\chi^2 = 5.1$).

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* Lists of structure factors, anisotropic thermal parameters and a complete list of atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42622 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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