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(2,2′-Bipyridine)bromo(triphenylphosphine)copper(I), $[CuBr(C_{10}H_8N_2)\{P(C_6H_5)_3\}]$

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Abstract. $M_r = 561·93$, monoclinic, $C2/c$, $a = 34·089\ (5)$, $b = 9·370\ (3)$, $c = 18·863\ (3)$ Å, $\beta = 124·50\ (1)°$, $V = 4965\ (4)$ Å^3, $Z = 8$, $D_x = 1·50$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 2·49$ mm^{-1}, $F(000) = 2264$, $T = 296$ K, $R = 0·054$ for 1067 observed reflections. The metal atom is tetrahedrally coordinated to 2,2′-bipyridine [Cu—N 2·11 (1), 2·10 (1) Å; N—Cu—N 78·6 (5)°], Br [Cu—Br 2·428 (3) Å] and triphenylphosphine [Cu—P 2·206 (4) Å], and is distorted [N—Cu—Br 115·2 (3), 108·8 (4)°; N—Cu—P 116·2 (4), 114·8 (4)°; and Br—Cu—P 117·0 (2)°].

Introduction. Monodentate tertiary phosphines form many complexes with Cu$^{\mathrm{I}}$ 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 to its crystal-structure determination because the only characterizations in the Jardine *et al.* (1970) paper were analytical data and melting point.

Experimental. Prismatic yellow crystals from butanol at 277 K, 0·23 × 0·18 × 0·05 mm, Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$, cell parameters by least squares on setting angles for 25 reflections, $16 < 2\theta < 30°$, ω–2θ scans, scan width (0·80 + 0·14 tanθ)°, scan speed 6·7° min^{-1} max., range of hkl: $h < 37$, $k < 10$, $-20 < l < 20$; standards $60\bar{6}$, $11,\bar{1},\bar{3}$, $0\bar{8}0$, varied ±2% of mean intensities over data collection; 3520 reflections measured, 3454 unique, $R_{\mathrm{int}} = 0·039$, 1068 observed above $3\sigma(I)$. Lp and absorption corrections (transmission factors 0·51–0·89); structure solved by direct methods, H atoms located in a difference map; least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$; 196 parameters refined: coordinates and anisotropic thermal parameters for non-H atoms, phenyl rings of triphenylphosphine as rigid bodies (C—C = 1·395, C—H = 1·08 Å, all angles 120°, H atoms with common $B = 6·3$ Å^2), H atoms of bipyridine with fixed isotropic temperature factor $B = 4·7$ Å^2; excluding unobserved and one reflection ($\bar{2}04$) $R = 0·054$, $R_w = 0·048$; max. $\Delta/\sigma = 0·056$, $\Delta\rho$ excursions within $-0·40$ and 0·42 e Å^{-3}, scattering factors for non-H atoms from Cromer & Mann (1968) with corrections

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for anomalous dispersion from Cromer & Liberman (1970) and for H from Stewart, Davidson & Simpson (1965), programs used: *SHELX*76 (Sheldrick, 1976) and *ORTEP* (Johnson, 1965).

Discussion. A projection of the structure is shown in Fig. 1. Positional 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 coordination polyhedron around the copper ion is a distorted tetrahedron in which the bond angle N—Cu—N′ of 78·6 (5)°, spanned by the 2·67 (3) Å N–N′ bite of the chelate, differs significantly from the ideal value.

As is general for metal–phosphine complexes (Churchill & O'Brien, 1968; Churchill & Kalra, 1974), angles about the P atom show systematic deviations from the ideal tetrahedral value, as shown in Table 2.

Bond distances and bond angles within the pyridyl units of the bipyridyl moiety are in good agreement, to within experimental accuracy, with the values found in the literature (Cordes, Durham, Swepston, Pennington, Condren, Jensen & Walsh, 1982).

Using the Cordes *et al.* (1982) criterion, the distortion from planarity in the bipyridyl ligand is measured by a τ value of 8·5° which is approximately equal to the dihedral angle between the two pyridyl groups of 9·8°. This distortion seems to be a consequence of the fact that the tendency of Cu^I to form tetrahedral angles around it forces the N–N′ chelate bite to increase.

It can be speculated that because of a short intramolecular Br···H non-bonded contact [Br···H(C26) = 2·86 (1) Å] the Br—Cu—N angles are different.

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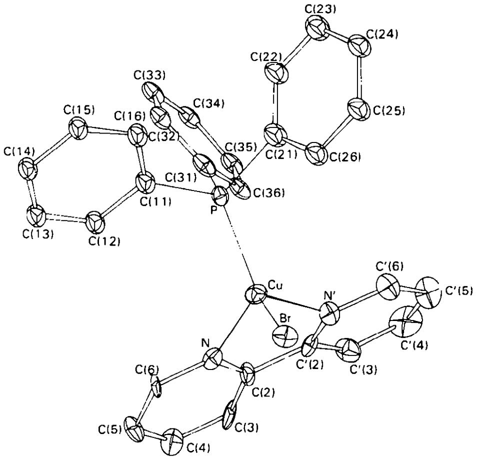

Fig. 1. Projection of the molecular structure, with the thermal ellipsoids drawn at 45% probability.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

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

	x	y	z	B_{eq}*
Br	0·3526 (1)	0·1188 (2)	0·0285 (1)	4·1 (1)
Cu	0·3539 (1)	0·3462 (2)	0·0915 (1)	3·6 (1)
P	0·3711 (2)	0·3418 (5)	0·2232 (3)	2·9 (1)
C(11)	0·3285 (3)	0·246 (1)	0·2349 (6)	3·6 (2)
C(13)	0·2461 (3)	0·214 (1)	0·1834 (6)	3·6 (2)
C(15)	0·3066 (3)	0·062 (1)	0·2962 (6)	3·6 (2)
C(21)	0·4291 (3)	0·2606 (9)	0·3037 (6)	4·8 (2)
C(23)	0·4990 (3)	0·2331 (9)	0·4487 (6)	4·8 (2)
C(25)	0·4894 (3)	0·0878 (9)	0·3340 (6)	4·8 (2)
C(31)	0·3751 (3)	0·5149 (9)	0·2717 (5)	3·6 (2)
C(33)	0·3741 (3)	0·6636 (9)	0·3753 (5)	3·6 (2)
C(35)	0·3967 (3)	0·7639 (9)	0·2852 (5)	3·6 (2)
N	0·3009 (5)	0·493 (1)	0·0057 (8)	3·4 (3)
C(2)	0·3176 (6)	0·606 (2)	−0·010 (1)	3·3 (3)
C(3)	0·2902 (7)	0·718 (2)	−0·063 (1)	4·4 (4)
C(4)	0·2420 (8)	0·706 (2)	−0·103 (1)	5·6 (4)
C(5)	0·2227 (6)	0·588 (2)	−0·090 (1)	5·8 (3)
C(6)	0·2537 (7)	0·484 (2)	−0·033 (1)	4·1 (3)
N′	0·3939 (5)	0·492 (1)	0·0726 (8)	3·6 (3)
C′(2)	0·3693 (6)	0·610 (2)	0·032 (1)	3·3 (3)
C′(3)	0·3931 (7)	0·729 (2)	0·030 (1)	5·1 (3)
C′(4)	0·4419 (9)	0·728 (2)	0·072 (1)	7·2 (4)
C′(5)	0·4669 (7)	0·609 (3)	0·109 (1)	7·0 (4)
C′(6)	0·4418 (8)	0·490 (2)	0·111 (1)	5·5 (4)

* $B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$ (Hamilton, 1959).

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

Cu—N	2·11 (1)	P—C(11)	1·824 (8)
Cu—N′	2·10 (1)	P—C(21)	1·842 (8)
Cu—P	2·206 (4)	P—C(31)	1·829 (8)
Cu—Br	2·428 (3)		
N—Cu—P	116·2 (4)	Cu—P—C(11)	115·1 (4)
N′—Cu—P	114·8 (4)	Cu—P—C(21)	114·4 (4)
N—Cu—N′	78·6 (5)	Cu—P—C(31)	116·3 (4)
Br—Cu—N	115·2 (3)	C(11)—P—C(21)	104·7 (5)
Br—Cu—N′	108·8 (4)	C(21)—P—C(31)	102·3 (4)
Br—Cu—P	117·0 (2)	C(11)—P—C(31)	102·4 (5)

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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 39822 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of Potassium Hydrogen (+)-Tartrate at 100 K, $K^+.C_4H_5O_6^-$

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Abstract. $M_r = 188{\cdot}18$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}749$ (3), $b = 10{\cdot}582$ (3), $c = 7{\cdot}604$ (4) Å, $V = 623{\cdot}5$ (8) Å^3, $Z = 4$, $D_m = 1{\cdot}96$ g cm^{-3} at room temperature according to van Bommel & Bijvoet [*Acta Cryst.* (1958). **11**, 61–70], $D_x = 2{\cdot}004$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 8{\cdot}2$ cm^{-1}, $F(000) = 384$, $T = 100\,(\pm 1)$ K, $R = 0{\cdot}0196$ for 1499 observed reflections. van Bommel & Bijvoet determined the structure of ammonium hydrogen tartrate and stated that potassium hydrogen tartrate has an isomorphous structure. The present study confirms that this is so and also confirms the absolute configuration postulated by them.

Introduction. In the history of crystallography the salts of tartaric acid have played a famous role in that they were the subject of the first studies of absolute configuration performed by Bijvoet and his group. The rubidium salt was the first compound for which an assignment of the enantiomer, based on experiment, was made. In contrast to a number of alkali salts of tartaric acid no structural data have so far been published for the optically active potassium salt. van Bommel & Bijvoet (1958) state that it is isomorphous with the ammonium salt. A description of the structure determination of the potassium salt is given in a crystallographic textbook by Luger (1980). The results of a low-temperature X-ray investigation of the title compound are now reported which are related to the ammonium hydrogen tartrate structure data.

Experimental. Platelet-like crystal, 0·4 × 0·1 × 0·7 mm, large faces (010) and $(0\bar{1}0)$. Automatic Siemens four-circle diffractometer, θ–2θ scan mode. No transition detected on cooling. Crystal kept at constant low temperature of 100 K by two coaxial gaseous nitrogen streams generated by an apparatus which was designed and built in cooperation with Dietrich & Dierks (1970). Lattice constants determined from 14 high-order reflections. One octant ($hkl \geq 0$) of independent reflections measured, $\theta_{\max} = 35°$, $(\sin\theta/\lambda)_{\max} = 0{\cdot}807$ Å^{-1}, 1571 reflections of which 72 were classified as unobserved with $I < 2\sigma(I)$. Standard reflections 400 and 060 measured every 40 reflections, statistical intensity variation of 0·5%. Corrections for Lorentz–polarization and for absorption [program *ABSCOR* in *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); minimum absorption correction factor 1·088, maximum 1·348]. Room-temperature atomic parameters given by Luger (1980) were used as input parameters for refinement. Usual parameters, including an isotropic-extinction parameter, refined by full-matrix least squares using spherical scattering factors with complex anomalous-dispersion correction from *International Tables for X-ray Crystallography* (1974). Quantity minimized $\sum w(|F_o| - |F_c|)^2$, with $w = xy$, $x = 1$ for $\sin\theta > 0{\cdot}5$, $x = (\sin\theta)/0{\cdot}5$ for $\sin\theta \leq 0{\cdot}5$, $y = 1$ if $|F_o| < 13{\cdot}0$ and $y = 13{\cdot}0/|F_o|$ otherwise. Parameters for w were chosen so as to make $w\Delta F$ almost independent of $|F_o|$ and $\sin\theta$. Unobserved reflections were included only if $|F_c| > |F_o|$. Extinction correction factor for the calculated structure factors $F_c(hkl)$ varied between 1·000 and 0·87. For observed reflections final $wR = 0{\cdot}024$ and $R = 0{\cdot}0196$. $(\Delta/\sigma)_{\max} = 0{\cdot}0002$ for non-hydrogen atoms, 0·001 for H atoms.

The absolute configuration was determined by parallel refinements of the two enantiomorphic forms with all reflections, reaching reliability indices of 0·022 and 0·027, defined by $R = [\sum_{\mathbf{h}}||F_o(\mathbf{h})| - k|F_c(\mathbf{h})||]/\sum_{\mathbf{h}}|F_o(\mathbf{h})|$. Applying the Hamilton (1965) R factor test, on the significance level of 0·005, clear preference was obtained for the configuration defined by the structure shown in the stereodiagram Fig. 1, which is the same as

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