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(2,2′-Bipyridine)chloro(triphenylphosphine)copper(I) Monohydrate,* $C_{28}H_{23}ClCuN_2P.H_2O$

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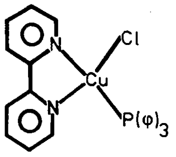
Abstract. $M_r = 535.5$, triclinic, $P\bar{1}$, $a = 16.967\ (10)$, $b = 9.426\ (5)$, $c = 8.712\ (5)$ Å, $\alpha = 65.50\ (4)$, $\beta = 88.23\ (5)$, $\gamma = 89.53\ (5)°$, $V = 1267\ (1)$ Å^3, $Z = 2$, $D_m = 1.39$, $D_x = 1.40\ (3)$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.09$mm^{-1}, $F(000) = 552$, $T = 298$ K, $R = 0.049$ for 2371 unique reflections. The metal atom is tetrahedrally coordinated to 2,2′-bipyridine [Cu—N 2.076 (5), 2.087 (6) Å; N—Cu—N 79.2 (2)°] Cl [Cu—Cl 2.330 (2) Å] and triphenylphosphine [Cu—P 2.180 (2) Å], and is distorted [N—Cu—Cl 102.9 (2), 104.5 (2)°; N—Cu—P 122.8 (2), 123.2 (1)°; and Cl—Cu—P 117.1 (1)°]. The water molecule is hydrogen bonded to Cl [Cl···O 3.25 (1), 3.30 (1) Å].

Introduction. Complexes of the type Cu$^{\rm I}$(XYZ), with X = ligands containing an N—C—C—N group, Y = Cl$^-$ or BH$_4^-$, and Z = triphenylphosphine, are currently being investigated. The title compound, [Cu(bpy)Cl(tpp)].H$_2$O, (I), where bpy = 2,2′-bipyridine and tpp = triphenylphosphine, is the first member of this series. bpy and tpp are used to stabilize Cu$^{\rm I}$ (Jardine, Rule & Vohra, 1970).



(I)

Experimental. (I) prepared by reacting [(tpp)CuCl]$_4$ with bpy in absolute alcohol (Jardine *et al.*, 1970), and recrystallized from a chloroform–xylene mixture as yellow crystals. Crystal 0.25 × 0.20 × 0.13 mm. D_m by flotation. Syntex $P2_1$ four-circle diffractometer. 15 reflections used for lattice-parameter determination. No absorption or extinction correction. $2\theta_{\max} = 50°$. Standard reflections: $I_{400} = 302\ (7) \times 10^3$; $I_{020} = 129\ (2) \times 10^3$; $I_{003} = 108\ (3) \times 10^3$. 3058 reflections measured, 2371 unique [$I > 2.5\sigma(I)$], 687 unobserved. Cu atom obtained using the *TANG* direct method of *SHELX* (Sheldrick, 1976). Remaining atoms located from a weighted difference-Fourier synthesis. H atoms located at the end of the refinement, and set at fixed positions with $U = 0.05$ Å^2. Full-matrix least-squares refinement based on F reduced R to 0.049 and wR to 0.049; $w = 2.26/[\sigma^2(F_o) + 0.0003F_o^2]$ (determined by least squares). Maximum and average Δ/σ ratios 2.4 and 0.6. Final difference electron density maximum 0.12, minimum −0.12 e Å^{-3}. Scattering factors: non-hydrogens (Cromer & Mann, 1968), H (Stewart, Davidson & Simpson, 1965).

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* Stereochemistry of Rigid Chelate–Metal Complexes. VII. Part VI: Green, Kennard, Smith, James & White (1981).

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Discussion. Atomic coordinates are given in Table 1.*

Cu^I has a distorted tetrahedral coordination in the title complex (Fig. 1 and Table 2). (I) is similar to $[Cu(phen)BH_4(tpp)]$, (II) (Green, Kennard, Smith, James & White, 1981) (phen = 1,10-phenanthroline), with differences in coordination due to bpy having greater steric freedom compared to phen and to Cl^- replacing a bidentate BH_4^-. Comparative bond distances for (I) and (II) are: Cu—N 2·076 (5), 2·087 (6), and 2·08 (1), 2·12 (1) Å; Cu—Cl 2·330 (2) Å; Cu—B 2·29 (2) Å; and Cu—P 2·180 (2), 2·212 (5) Å respectively. The distorted angles for (I) and (II) are: N—Cu—N 79·2 (2) and 77·1 (4)°; N—Cu—Cl 102·9 (2), 104·5 (2)°; N—Cu—B 107·8 (1), 116·2 (1)°; N—Cu—P 122·8 (2), 123·2 (1) and 109·9 (3), 117·4 (3)°; Cl—Cu—P 117·1 (1)°; and B—Cu—P 120·6 (1)°.

Although the Cu—N distances in (I) are longer than those found in bis(6,6′-dimethyl-2,2′-bipyridine)-copper(I) tetrafluoroborate (Burke, McMillan & Robinson, 1980) [2·018 (1), 2·052 (1) and 2·024 (1), 2·040 (1) Å], they are in the general range of Cu^I—N distances [1·990 (2) – 2·104 (5) Å] for the series (Healy, Skelton, Pakawatchai & White, 1983). The Cu—P and Cu—Cl distances are short compared to those listed by Gill, Mayerle, Welcker, Lewis, Ucko, Barton, Stowens & Lippard (1976). A characteristic feature is a common dissimilarity existing among the three phenyl-ring angles for P—C(*x*1)—C(*x*2) and P—C(*x*1)—C(*x*6), when *x* = 2, 117·0 (6), 123·7 (5)°; *x* = 3, 124·1 (4), 116·8 (5)°; *x* = 4, 123·1 (6), 117·1 (5)°. This has been found for other Cu^I complexes *e.g.* (II).

In (I), the bond angle Cl—Cu—P and torsion angle Cl—Cu—P—C(21) are 117·1 (1) and −9·9 (1)° respectively with the Cu—Cl distance 2·330 (2) Å. In (α-II) and (β-II) the Cl is replaced by the bulkier BH_4 and

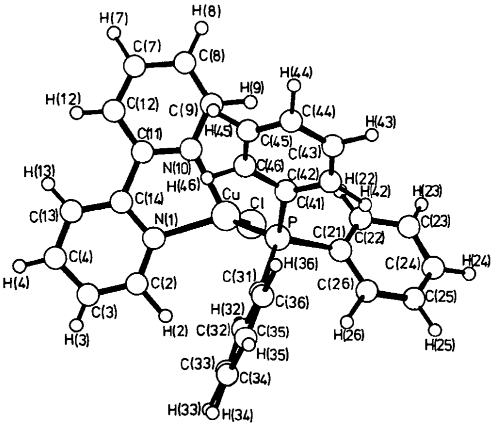

Fig. 1. The atom labelling for the title compound.

Table 1. *Atomic coordinates* (×10^4) *and isotropic thermal parameters* (Å^2 × 10^3)

$U_{eq} = (U_{11} + U_{22} + U_{33})/3$. For atoms marked with an asterisk, U_{iso} is given.

	x	*y*	*z*	U_{eq} or U_{iso}
Cu	1751·6 (5)	1392 (1)	1595 (1)	38 (1)
P	2923 (1)	1774 (2)	2316 (2)	37 (1)
N(1)	1250 (3)	−805 (6)	2346 (6)	36 (3)
C(2)	1174 (4)	−1928 (8)	3921 (8)	43 (4)
C(3)	866 (5)	−3377 (8)	4288 (9)	48 (5)
C(4)	603 (5)	−3693 (8)	2988 (10)	55 (5)
C(7)	960 (4)	1251 (10)	−3635 (9)	54 (5)
C(8)	1403 (5)	2517 (9)	−3749 (9)	50 (5)
C(9)	1675 (4)	2552 (9)	−2288 (9)	49 (5)
N(10)	1532 (3)	1378 (6)	−742 (6)	37 (1)
C(11)	1108 (4)	146 (8)	−649 (8)	37 (4)
C(12)	807 (4)	54 (8)	−2071 (8)	49 (5)
C(13)	649 (4)	−2562 (8)	1367 (8)	53 (5)
C(14)	997 (4)	−1120 (7)	1061 (8)	39 (4)
Cl	733 (1)	2921 (2)	1932 (2)	52 (1)
O(*w*)	−1108 (3)	4126 (6)	1632 (6)	78 (1)*
C(21)	3048 (4)	3475 (7)	2793 (8)	37 (2)*
C(22)	2703 (4)	4857 (8)	1715 (8)	45 (2)*
C(23)	2750 (4)	6209 (8)	2031 (9)	56 (2)*
C(24)	3127 (4)	6119 (9)	3449 (9)	60 (2)*
C(25)	3472 (4)	4778 (9)	4501 (9)	56 (2)*
C(26)	3443 (4)	3436 (8)	4192 (8)	49 (2)*
C(31)	3278 (4)	154 (7)	4201 (7)	34 (2)*
C(32)	4023 (4)	−478 (8)	4320 (8)	46 (2)*
C(33)	4225 (4)	−1789 (8)	5806 (9)	58 (2)*
C(34)	3684 (5)	−2424 (9)	7080 (10)	63 (2)*
C(35)	2945 (5)	−1794 (9)	7005 (10)	67 (2)*
C(36)	2747 (4)	−504 (8)	5536 (9)	52 (2)*
C(41)	3696 (4)	2007 (7)	704 (7)	37 (2)*
C(42)	4328 (4)	3030 (8)	370 (9)	51 (2)*
C(43)	4891 (5)	3129 (9)	−877 (10)	67 (2)*
C(44)	4825 (4)	2216 (9)	−1776 (9)	59 (2)*
C(45)	4203 (4)	1217 (9)	−1427 (9)	56 (2)*
C(46)	3633 (4)	1096 (8)	−196 (8)	47 (2)*

Table 2. *Interatomic distances* (Å) *and angles* (°)

Cu—Cl	2·330 (2)	P—C(41)	1·837 (7)
Cu—N(1)	2·076 (5)	C(21)—C(22)	1·389 (8)
Cu—N(10)	2·087 (6)	C(21)—C(26)	1·396 (10)
Cu—P	2·180 (2)	C(22)—C(23)	1·414 (12)
N(1)—C(2)	1·344 (7)	C(23)—C(24)	1·380 (12)
N(1)—C(14)	1·354 (10)	C(24)—C(25)	1·357 (9)
C(2)—C(3)	1·372 (11)	C(25)—C(26)	1·400 (12)
C(3)—C(4)	1·372 (13)	C(31)—C(32)	1·380 (9)
C(4)—C(13)	1·373 (9)	C(31)—C(36)	1·377 (9)
C(7)—C(8)	1·382 (13)	C(32)—C(33)	1·420 (8)
C(7)—C(12)	1·381 (9)	C(33)—C(34)	1·352 (10)
C(8)—C(9)	1·380 (12)	C(34)—C(35)	1·375 (11)
C(9)—N(10)	1·358 (8)	C(35)—C(36)	1·400 (9)
C(11)—N(10)	1·343 (9)	C(41)—C(42)	1·389 (10)
C(11)—C(12)	1·391 (11)	C(41)—C(46)	1·388 (12)
C(11)—C(14)	1·480 (8)	C(42)—C(43)	1·399 (11)
C(13)—C(14)	1·403 (10)	C(43)—C(44)	1·390 (14)
P—C(21)	1·831 (8)	C(44)—C(45)	1·361 (11)
P—C(31)	1·833 (5)	C(45)—C(46)	1·391 (11)
Cl—Cu—N(1)	104·5 (2)	C(21)—P—C(41)	104·2 (3)
Cl—Cu—N(10)	102·9 (2)	C(31)—P—Cu	113·9 (2)
Cl—Cu—P	117·1 (1)	C(31)—P—C(41)	103·5 (3)
N(1)—Cu—N(10)	79·2 (2)	C(41)—P—Cu	113·5 (2)
N(1)—Cu—P	123·2 (1)	P—C(21)—C(22)	117·0 (6)
N(10)—Cu—P	122·8 (2)	P—C(21)—C(26)	123·7 (5)
Cu—N(1)—C(2)	127·7 (5)	P—C(31)—C(32)	124·1 (4)
Cu—N(1)—C(14)	114·3 (4)	P—C(31)—C(36)	116·8 (5)
C(9)—N(10)—Cu	127·0 (6)	P—C(41)—C(42)	123·1 (6)
C(11)—N(10)—Cu	114·1 (4)	P—C(41)—C(46)	117·1 (5)
C(21)—P—Cu	116·7 (2)		
C(21)—P—C(31)	103·5 (3)		

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* Lists of H-atom atomic coordinates, structure factors, anisotropic thermal parameters and additional bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38954 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

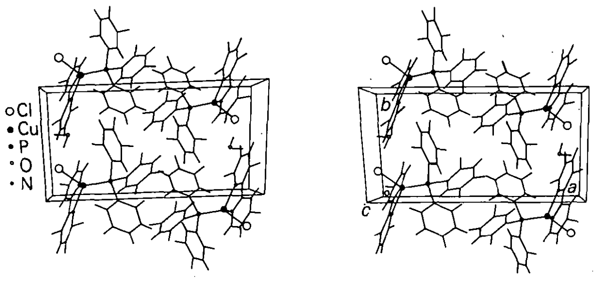

Fig. 2. A stereoview perpendicular to the *ab* plane.

BD_4 respectively in [Cu(phen)BH_4(tpp)] (Green, Kennard, Smith, Elcombe, Moore, James & White, 1984) to give the following corresponding angles and distances: B—Cu—P 120·3 (3), 116·7 (9)°; B—Cu—P—C(21) 31·6 (3), −36·6 (9)°; and Cu—B 2·28 (1), 2·29 (2) Å. These results suggest that the change in torsion angle in the two (II) examples is probably due to the steric hindrance of the bulkier BH_4 or BD_4 group.

The Cl atoms hydrogen bonded to O from one water molecule are also similarly bonded to water at a symmetry-related position down the *c* axis at $x = 0$ and $y = 0·5$ [Cl···O 3·25 (1), 3·30 (1) Å] (Fig. 2). This is comparable to the intramolecular Cl···O link of 3·109 (7) Å in aquatrichlorohydroxo[3,6-di(2-pyridyl)-pyridazine]dicopper(II), (III) (Ghedini, deMunno, Denti, Lanfredi & Tiripicchio, 1982). The pyridine rings are planar but twisted with respect to each other about the C(11)—C(14) bond [dihedral angle 5·7 (1)°, torsion angle N(1)—C(11)—C(14)—N(10) 7·8 (1)°] and this too is comparable to (III).

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Structural Studies of the System *trans*-Azobenzene/*trans*-Stilbene. II. A Reinvestigation of the Disorder in the Crystal Structure of *trans*-Stilbene, $C_{14}H_{12}$

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Abstract. $M_r = 180·25$, monoclinic, $P2_1/c$, $a = 15·709$ (3), $b = 5·723$ (1), $c = 12·374$ (2) Å, $\beta = 111·90$ (2)°, $V = 1029·9$ (2) Å^3, $Z = 4$, $D_x = 1·160$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0·33$ mm^{-1}, $F(000) = 384$, $T = 295$ K. A model in which the disorder at one of the two independent molecule sites was taken into account refined, using constraints and restraints, with 2276 observed diffractometer data to an R of 0·060. The nature of disorder and the degree of misorientation (13%) are very similar to those of *trans*-azobenzene [Bouwstra, Schouten & Kroon (1983). *Acta Cryst.* C**39**, 1121–1123].

Introduction. The crystal structure of *trans*-stilbene was determined by Robertson & Woodward (1937); the analysis was based on projection data. The molecular structure was frequently used for theoretical investigations and hence the availability of more accurate geometrical data became of interest. For that reason the structure has been redetermined: two structure refinements from different groups at room temperature (Finder, Newton & Allinger, 1974; Bernstein, 1975) and one at low temperature (113 K; Hoekstra, Meertens & Vos, 1975). From these investigations it appeared that one of the two independent

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