Crystal structure of bis(triphenylphospine-κP)(bromo-κBr)-(isoquinoline-κN)copper(I), $CuBr(PC_{18}H_{15})_2(i\text{-}C_9H_7N)$

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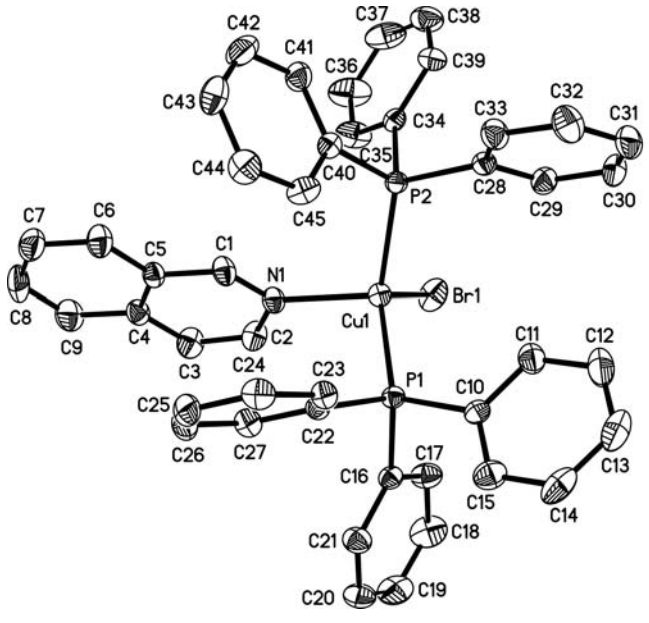

Abstract

$C_{45}H_{37}BrCuNP_2$, monoclinic, $P2_1/n$ (no. 14), a = 10.019(1) Å, b = 36.487(3) Å, c = 11.294(2) Å, β = 114.653(1)°, V = 3752.3 Å^3, Z = 4, $R_{gt}(F)$ = 0.058, $wR_{ref}(F^2)$ = 0.125, T = 298 K.

Source of material

Synthesis of the title compound was carried out by stirring the solution of the CuBr (0.0215 g, 0.15 mmol), triphenylphosphine (PPh_3, 0.0787 g, 0.3 mmol), and isoquinoline (1 ml) in the CH_3OH (5 ml) and CH_2Cl_2 (5 ml) for 4 hours at room temperature. The filtrate was allowed to stand at the room temperature. Slow evaporation of the solvent yielded yellow crystals.

Discussion

The d^{10} metal copper(I) and Ag(I) complexes containing mixed ligands such as PPh_3 (triphenylphosphine) and nitrogen ligands have been noticed for a long time because of their various interesting structures [1-3]. Quinoline and isoquinoline are good nitrogen dorners because they contain pyridine ring, the strong Lewis base group. It is difficult to synthesize copper(I) complexes because of their low solubility in the organic solvents and their instability. We succeeded in synthesizing a series of copper(I) complexes with nitrogen heterocycle complexes, halogen and triphenylphosphine as ligands. $[CuBr(PPh_3)(C_9H_7N]_2$ (**1**), $[CuI(PPh_3)(C_9H_7N)]_2$ (**2**) and $[CuCl(PPh_3)(i\text{-}C_9H_7N)]_2$ (**3**) [4-6]. The crystal structure of the title complex shows that the copper(I) atom is coordinated by two phosphorus atoms from PPh_3 groups, one nitrogen atom from isoquinoline and one bromide anion. The structure shows differences among the title complex and (**1**), (**2**) and (**3**) whose structures are inversion-symmetric dimers with a diamond-shaped Cu_2X_2 ring (X = Cl, I). The d(Cu1—Br1) = 2.4485(9) Å is shorter than d(Cu—Br) (2.520(1) - 2.573(1) Å) in **1**, but d(Cu—P) = 2.279(1) - 2.290(1) Å and d(Cu1—N1) = 2.135(4) Å are longer than d(Cu—P) and d(Cu—N) (2.216(1) Å and 2.065(3) Å) in **1** and d(Cu—P) (2.247(1) Å) in **2**, respectively. While d(Cu—P) and d(Cu1—N1) are all longer than d(Cu1—P1) and d(Cu1—N1) in (**3**) [d(Cu1—P1) = 2.1945(8) Å; d(Cu1—N1) = 2.066(2) Å]. The bond angles ∠N–Cu–P in the title complex range from 101.5(1)° to 105.3(1)° which are smaller than the ∠N–Cu–P (117.20(8)°) in **2**. While ∠N1–Cu1–Br1 (102.2(1)°) and ∠P–Cu–Br (104.76(4)° - 115.88(4)°) are smaller than ∠N–Cu–I = 106.25(8)°, ∠P–Cu–I = 114.70(3)° in **2**, ∠N–Cu–P, ∠N1–Cu1–Br1 and ∠P–Cu–Br are smaller than the ∠N–Cu–P = 120.23(7)°, ∠N–Cu–Cl = 104.11(6)° and the ∠P–Cu–Cl = 111.67(3)° in **3**.

The composition and crystal structure of the d^{10} metal complex is influenced by the molar ratio of metal : P-ligand. When this molar ratio is 1 : 2, the title complex is obtained, while this molar ratio is 1 : 1, complex **3** is obtained. So we believe, there exist at least two series of Cu(I) complexes with PPh_3 and isoquinoline, i.e., $[CuX(PPh_3)(i\text{-quinoline})]_2$ and $[CuX(PPh_3)_2(i\text{-quinoline})]$ (X = Cl, Br, I).

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.38 × 0.40 × 0.50 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	11.97 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ/ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	18561, 6602
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4459
$N(param)_{refined}$:	451
Programs:	SHELXS-97, SHELXL-97 [8]

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Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.4910	0.0951	0.7741	0.050
H(2)	4*e*	0.6093	0.1595	0.5623	0.057
H(3)	4*e*	0.8502	0.1525	0.6972	0.064
H(6)	4*e*	0.6719	0.0651	0.9686	0.066
H(7)	4*e*	0.9120	0.0532	1.1031	0.075
H(8)	4*e*	1.0981	0.0823	1.0695	0.080
H(9)	4*e*	1.0461	0.1202	0.8952	0.074
H(11)	4*e*	–0.0225	0.1648	0.4544	0.059
H(12)	4*e*	–0.2641	0.1827	0.3941	0.077
H(13)	4*e*	–0.3178	0.2314	0.4957	0.078
H(14)	4*e*	–0.1301	0.2628	0.6579	0.073
H(15)	4*e*	0.1099	0.2462	0.7145	0.061
H(17)	4*e*	0.2856	0.2218	0.4173	0.064
H(18)	4*e*	0.3775	0.2759	0.3725	0.081
H(19)	4*e*	0.4924	0.3177	0.5367	0.080
H(20)	4*e*	0.5112	0.3065	0.7415	0.073
H(21)	4*e*	0.4124	0.2540	0.7858	0.057
H(23)	4*e*	0.1512	0.1763	0.8284	0.043
H(24)	4*e*	0.2573	0.1604	1.0470	0.054
H(25)	4*e*	0.5102	0.1611	1.1608	0.059
H(26)	4*e*	0.6556	0.1757	1.0538	0.060
H(27)	4*e*	0.5501	0.1889	0.8347	0.050
H(29)	4*e*	–0.0345	0.1082	0.2850	0.054
H(30)	4*e*	–0.2871	0.1137	0.1909	0.070
H(31)	4*e*	–0.4226	0.0950	0.3027	0.073
H(32)	4*e*	–0.3052	0.0704	0.5082	0.073
H(33)	4*e*	–0.0547	0.0626	0.5998	0.057
H(35)	4*e*	0.4210	0.0676	0.4611	0.074
H(36)	4*e*	0.4788	0.0253	0.3411	0.098
H(37)	4*e*	0.3113	–0.0182	0.2211	0.091
H(38)	4*e*	0.0842	–0.0188	0.2247	0.075
H(39)	4*e*	0.0269	0.0213	0.3518	0.053
H(41)	4*e*	0.2493	0.0068	0.6198	0.056
H(42)	4*e*	0.3184	–0.0208	0.8195	0.077
H(43)	4*e*	0.3455	0.0134	0.9987	0.070
H(44)	4*e*	0.3014	0.0752	0.9791	0.064
H(45)	4*e*	0.2266	0.1030	0.7780	0.054

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	4*e*	0.29924(6)	0.13779(2)	0.53620(6)	0.0325(3)	0.0346(3)	0.0312(4)	–0.0007(3)	0.0151(3)	0.0009(3)
Br(1)	4*e*	0.29832(7)	0.14601(2)	0.32069(6)	0.0756(5)	0.0669(4)	0.0350(4)	0.0189(3)	0.0318(3)	0.0117(3)
N(1)	4*e*	0.5258(4)	0.1274(1)	0.6554(4)	0.027(2)	0.044(3)	0.040(3)	–0.001(2)	0.014(2)	0.001(2)
P(1)	4*e*	0.2591(1)	0.18930(3)	0.6308(1)	0.0345(7)	0.0282(7)	0.0287(8)	–0.0002(6)	0.0146(6)	0.0022(6)
P(2)	4*e*	0.1832(1)	0.08291(3)	0.5237(1)	0.0279(7)	0.0291(7)	0.0349(8)	0.0004(5)	0.0139(6)	–0.0009(6)
C(1)	4*e*	0.5650(5)	0.1063(2)	0.7580(5)	0.029(3)	0.059(4)	0.037(3)	–0.007(3)	0.014(3)	0.005(3)
C(2)	4*e*	0.6348(6)	0.1442(2)	0.6345(6)	0.042(3)	0.058(4)	0.047(4)	0.006(3)	0.023(3)	0.013(3)
C(3)	4*e*	0.7793(6)	0.1399(2)	0.7141(6)	0.034(3)	0.066(4)	0.067(4)	–0.001(3)	0.027(3)	0.012(4)
C(4)	4*e*	0.8213(5)	0.1165(1)	0.8211(6)	0.031(3)	0.046(3)	0.044(4)	0.003(2)	0.013(3)	–0.005(3)
C(5)	4*e*	0.7102(5)	0.0995(1)	0.8451(5)	0.034(3)	0.042(3)	0.029(3)	0.003(2)	0.011(3)	–0.002(2)
C(6)	4*e*	0.7464(7)	0.0761(2)	0.9524(6)	0.052(4)	0.068(4)	0.039(4)	0.002(3)	0.014(3)	0.007(3)
C(7)	4*e*	0.8893(8)	0.0693(2)	1.0336(6)	0.072(5)	0.063(4)	0.043(4)	0.011(4)	0.013(4)	0.009(3)
C(8)	4*e*	1.0008(7)	0.0865(2)	1.0122(7)	0.039(4)	0.091(5)	0.051(4)	0.015(4)	0.000(3)	0.003(4)
C(9)	4*e*	0.9699(6)	0.1093(2)	0.9089(7)	0.035(3)	0.072(4)	0.075(5)	–0.001(3)	0.021(3)	–0.002(4)
C(10)	4*e*	0.0693(5)	0.2041(1)	0.5898(5)	0.042(3)	0.028(3)	0.035(3)	–0.003(2)	0.016(3)	0.012(2)
C(11)	4*e*	–0.0436(6)	0.1848(2)	0.4946(6)	0.044(4)	0.053(4)	0.045(4)	–0.001(3)	0.014(3)	0.003(3)
C(12)	4*e*	–0.1885(7)	0.1955(2)	0.4593(7)	0.040(4)	0.081(5)	0.059(5)	0.000(3)	0.008(3)	0.014(4)
C(13)	4*e*	–0.2207(7)	0.2244(2)	0.5196(8)	0.046(4)	0.071(5)	0.084(6)	0.018(4)	0.033(4)	0.039(4)
C(14)	4*e*	–0.1086(7)	0.2433(2)	0.6159(7)	0.064(5)	0.052(4)	0.085(5)	0.024(3)	0.048(4)	0.023(4)
C(15)	4*e*	0.0349(6)	0.2332(2)	0.6499(6)	0.057(4)	0.044(3)	0.060(4)	0.001(3)	0.033(3)	0.003(3)
C(16)	4*e*	0.3424(5)	0.2318(1)	0.6061(5)	0.037(3)	0.031(3)	0.037(3)	–0.001(2)	0.018(3)	0.005(2)
C(17)	4*e*	0.3308(7)	0.2388(2)	0.4834(6)	0.070(4)	0.041(3)	0.054(4)	–0.004(3)	0.030(4)	0.002(3)
C(18)	4*e*	0.3863(8)	0.2713(2)	0.4564(7)	0.092(5)	0.063(5)	0.072(5)	–0.003(4)	0.058(5)	0.014(4)
C(19)	4*e*	0.4539(7)	0.2962(2)	0.5540(8)	0.071(5)	0.046(4)	0.098(6)	–0.012(3)	0.050(5)	0.014(4)
C(20)	4*e*	0.4647(7)	0.2896(2)	0.6756(7)	0.062(4)	0.036(3)	0.080(5)	–0.016(3)	0.024(4)	–0.001(3)
C(21)	4*e*	0.4075(6)	0.2579(1)	0.7026(6)	0.055(4)	0.042(3)	0.044(4)	–0.009(3)	0.020(3)	0.001(3)
C(22)	4*e*	0.3382(5)	0.1835(1)	0.8071(5)	0.034(3)	0.030(3)	0.030(3)	–0.002(2)	0.012(2)	–0.001(2)
C(23)	4*e*	0.2530(6)	0.1756(1)	0.8728(5)	0.036(3)	0.042(3)	0.033(3)	0.000(2)	0.016(3)	–0.001(3)
C(24)	4*e*	0.3164(6)	0.1666(2)	1.0047(5)	0.059(4)	0.050(3)	0.037(4)	–0.004(3)	0.031(3)	–0.001(3)
C(25)	4*e*	0.4673(7)	0.1668(2)	1.0724(6)	0.061(4)	0.054(4)	0.025(3)	0.007(3)	0.010(3)	–0.001(3)
C(26)	4*e*	0.5540(6)	0.1754(2)	1.0084(6)	0.046(4)	0.057(4)	0.038(4)	0.000(3)	0.009(3)	–0.002(3)
C(27)	4*e*	0.4906(6)	0.1834(1)	0.8771(5)	0.042(3)	0.049(3)	0.038(4)	0.000(3)	0.021(3)	–0.004(3)
C(28)	4*e*	–0.0176(5)	0.0849(1)	0.4533(5)	0.033(3)	0.032(3)	0.040(3)	0.001(2)	0.015(3)	–0.003(2)
C(29)	4*e*	–0.0887(6)	0.1003(1)	0.3299(6)	0.043(3)	0.043(3)	0.048(4)	0.006(3)	0.017(3)	–0.001(3)
C(30)	4*e*	–0.2399(6)	0.1037(2)	0.2739(7)	0.043(4)	0.057(4)	0.058(5)	0.013(3)	0.004(3)	0.004(3)
C(31)	4*e*	–0.3210(6)	0.0925(2)	0.3404(7)	0.030(3)	0.062(4)	0.083(6)	0.003(3)	0.017(4)	–0.007(4)
C(32)	4*e*	–0.2509(7)	0.0776(2)	0.4626(7)	0.040(4)	0.079(5)	0.070(5)	–0.005(3)	0.030(4)	–0.002(4)
C(33)	4*e*	–0.1007(6)	0.0733(2)	0.5180(6)	0.037(3)	0.054(4)	0.051(4)	–0.002(3)	0.018(3)	0.002(3)
C(34)	4*e*	0.2178(5)	0.0493(1)	0.4211(5)	0.035(3)	0.032(3)	0.036(3)	0.007(2)	0.016(2)	0.002(2)
C(35)	4*e*	0.3524(7)	0.0499(2)	0.4150(7)	0.062(4)	0.053(4)	0.090(5)	–0.005(3)	0.052(4)	–0.022(4)
C(36)	4*e*	0.3865(8)	0.0247(2)	0.3421(8)	0.097(6)	0.061(5)	0.127(7)	–0.002(4)	0.085(6)	–0.027(5)
C(37)	4*e*	0.2877(9)	–0.0012(2)	0.2708(8)	0.123(7)	0.044(4)	0.084(6)	0.005(4)	0.068(5)	–0.017(4)
C(38)	4*e*	0.1536(8)	–0.0016(2)	0.2743(6)	0.087(5)	0.048(4)	0.048(4)	–0.012(3)	0.024(4)	–0.010(3)
C(39)	4*e*	0.1183(6)	0.0226(1)	0.3492(5)	0.051(4)	0.037(3)	0.046(4)	–0.008(3)	0.022(3)	–0.006(3)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(40)	4*e*	0.2301(5)	0.0581(1)	0.6765(5)	0.025(3)	0.038(3)	0.041(3)	0.001(2)	0.021(2)	0.005(2)
C(41)	4*e*	0.2587(6)	0.0208(2)	0.6916(6)	0.051(4)	0.048(4)	0.036(4)	0.004(3)	0.012(3)	0.000(3)
C(42)	4*e*	0.3007(7)	0.0043(2)	0.8112(7)	0.079(5)	0.044(4)	0.062(5)	0.012(3)	0.023(4)	0.016(4)
C(43)	4*e*	0.3165(7)	0.0246(2)	0.9179(6)	0.059(4)	0.072(5)	0.044(4)	0.015(3)	0.020(3)	0.018(4)
C(44)	4*e*	0.2900(7)	0.0613(2)	0.9064(6)	0.068(4)	0.062(4)	0.035(4)	0.004(3)	0.027(3)	–0.004(3)
C(45)	4*e*	0.2459(6)	0.0779(2)	0.7856(6)	0.062(4)	0.039(3)	0.049(4)	0.004(3)	0.036(3)	0.002(3)

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