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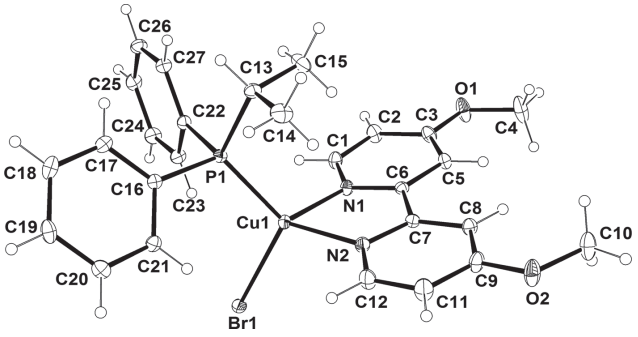
Crystal structure of bromido(4,4′-dimethoxy-2,2′-bipyridine-κ²*N*,*N*′)(isopropyl(diphenyl) phosphane-κP)copper(I), $C_{27}H_{29}BrCuN_2O_2P$



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Abstract

$C_{27}H_{29}BrCuN_2O_2P$, monoclinic, *Cc* (no. 9), $a = 15.5806(10)$ Å, $b = 10.5071(10)$ Å, $c = 16.9748(15)$ Å, $\beta = 110.729(2)°$, $V = 2599.0(4)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0186$, $wR_{ref}(F^2) = 0.0445$, $T = 120$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

Synthesis of the complex (4,4′-dimethoxy-2,2′-bipy)[(i-Pr)Ph_2P]CuBr: CuBr (1.00 mmol, 0.143 g), isopropyl (diphenyl)phosphine (1.00 mmol, 0.228 g) and 4,4′-dimethoxy-2,2′-bipyridine (1.00 mmol, 0.216 g) were reacted in dimethylformamide (30 mL) at 65 °C for 2 h. Red crystals were obtained by slow evaporation of the filtrate.

Experimental details

All hydrogen atoms were positioned at calculated positions using a riding model with C—H distances of 0.93 Å for sp^2 carbons, 0.96 Å for methyl carbons and 0.98 Å for C-$H_{i\text{-}propyl}$. The isotropic displacement parameters were $U_{iso}(H) = 1.2U_{eq}(C)$, $U_{iso}(H) = 1.5U_{eq}(C)$ and $U_{iso}(H) = 1.2U_{eq}(C)$, respectively.

Table 1: Data collection and handling.

Crystal:	Red block
Size:	0.30 × 0.28 × 0.25 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	2.47 mm^{-1}
Diffractometer, scan mode:	Bruker SMART, ω-scans
$2\theta_{max}$, completeness:	28.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	17076, 6386, 0.020
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 6057
$N(param)_{refined}$:	311
Programs:	Bruker programs [1], SADABAS [2], SHELX [3], ORTEP [4]

Discussion

2,2′-Bipyridinehalophosphinecopper(I) complexes have been reported to have interesting catalytic [5] and luminescence properties [6]. While the X-ray structures of 2,2′-bipyridine copper(I) complexes are abundant in literature, only a few copper complexes of 4,4′-dimethoxy-2,2′-bipyridine have been reported to date [7].

The compound crystallizes in the non-centrosymmetric space group *Cc* with one molecule in the asymmetric unit. The modified Flack parameter [8] was refined based on 2835 quotients to 0.010(2). The copper(I) ion is bonded to the two nitrogen atoms of 4,4′-dimethoxy-2,2′-bipyridine, the phosphorus atom of the phosphine, and to the bromido ligand. The geometry is distorted tetrahedral with the N-Cu-N bite angle of 77.82(8)° and the other coordination sphere bond angles in the range 111.32(6)–124.21(6)°. The bond distances are similar to those reported for the analogous 2,2′-bipyridine complex [5] with the Cu—N bond distances slightly shorter in the title compound. This is consistent with the stronger basic strength of 4,4′-dimethoxy-2,2′-bipyridine ligand due to the electron donating effect of the methoxy groups. Accordingly they adopt a planar conformation due to conjugation. The phosphine isopropyl group and the bromide ion adopt an anti conformation around the Cu—P bond with the torsion angle

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.42142(2)	0.18022(3)	0.68087(2)	0.01703(7)
N1	0.41062(13)	−0.00154(18)	0.62998(13)	0.0188(4)
N2	0.49433(14)	0.19712(19)	0.60151(14)	0.0204(4)
Br1	0.52202(2)	0.18245(2)	0.82829(2)	0.02199(7)
P1	0.28893(4)	0.27163(6)	0.65958(4)	0.01578(11)
C1	0.36456(17)	−0.0986(2)	0.64780(16)	0.0239(5)
H1	0.342649	−0.088689	0.691780	0.029*
C2	0.3480(2)	−0.2121(3)	0.60443(18)	0.0261(6)
H2	0.314872	−0.276622	0.618092	0.031*
C3	0.3821(2)	−0.2274(3)	0.53988(17)	0.0236(6)
C4	0.4006(3)	−0.3683(3)	0.4368(2)	0.0443(8)
H38A	0.372897	−0.310989	0.390747	0.067*
H38B	0.386266	−0.454429	0.417768	0.067*
H38C	0.465995	−0.356805	0.457568	0.067*
C5	0.42922(18)	−0.1280(2)	0.51900(16)	0.0197(5)
H4	0.451477	−0.136015	0.475118	0.024*
C6	0.44200(15)	−0.0161(2)	0.56602(14)	0.0169(4)
C7	0.49054(15)	0.0985(2)	0.54945(14)	0.0173(4)
C8	0.52792(18)	0.1031(3)	0.48641(17)	0.0210(5)
H7	0.523270	0.033940	0.450918	0.025*
C9	0.5729(2)	0.2150(3)	0.47787(19)	0.0258(6)
C10	0.6086(2)	0.1369(3)	0.3610(2)	0.0359(7)
H39A	0.637229	0.061774	0.391093	0.054*
H39B	0.640656	0.163859	0.324919	0.054*
H39C	0.545866	0.118526	0.327594	0.054*
C11	0.5789(2)	0.3154(3)	0.5324(2)	0.0330(7)
H11	0.609182	0.390036	0.528518	0.040*
C12	0.5391(2)	0.3024(2)	0.59232(19)	0.0288(6)
H10	0.543304	0.370247	0.628680	0.035*
C13	0.21655(17)	0.2895(2)	0.54765(16)	0.0210(5)
H27	0.157076	0.325803	0.543236	0.025*
C14	0.2650(2)	0.3788(3)	0.50565(18)	0.0317(7)
H28A	0.323865	0.344074	0.511174	0.048*
H28B	0.273129	0.460699	0.532384	0.048*
H28C	0.228507	0.387687	0.447040	0.048*
C15	0.2021(2)	0.1589(3)	0.50518(18)	0.0312(7)
H37A	0.163992	0.167603	0.446986	0.047*
H37B	0.172852	0.103137	0.532804	0.047*
H37C	0.260383	0.123854	0.509102	0.047*
C16	0.28936(15)	0.4294(2)	0.70581(14)	0.0171(4)
C17	0.21031(18)	0.4913(3)	0.70611(17)	0.0241(5)
H36	0.153309	0.453804	0.679393	0.029*
C18	0.2154(2)	0.6082(3)	0.74568(19)	0.0289(6)
H35	0.162213	0.648478	0.745484	0.035*
C19	0.3005(2)	0.6647(2)	0.78563(18)	0.0272(6)
H34	0.304341	0.742528	0.812783	0.033*
C20	0.37931(19)	0.6055(3)	0.78500(17)	0.0246(6)
H33	0.436105	0.643986	0.811012	0.030*
C21	0.37383(16)	0.4884(2)	0.74550(15)	0.0195(5)
H32	0.427241	0.448810	0.745558	0.023*
C22	0.21830(16)	0.1789(2)	0.70522(15)	0.0177(5)
C23	0.26381(17)	0.1078(2)	0.77705(16)	0.0219(5)
H18	0.327611	0.107907	0.799125	0.026*
C24	0.21562(17)	0.0370(2)	0.81601(16)	0.0255(6)
H19	0.247142	−0.008697	0.864583	0.031*
C25	0.12039(18)	0.0336(3)	0.78317(17)	0.0258(5)
H29	0.087975	−0.014592	0.809207	0.031*
C26	0.07425(18)	0.1029(3)	0.71116(18)	0.0242(6)
H17	0.010485	0.100753	0.688493	0.029*
C27	0.12282(17)	0.1756(2)	0.67251(17)	0.0210(5)
H16	0.091214	0.222391	0.624463	0.025*
O1	0.36623(18)	−0.34281(19)	0.50241(15)	0.0379(6)
O2	0.61159(16)	0.2354(2)	0.41937(14)	0.0357(5)

Br–Cu–P–$C_{isopropyl}$ of 172.86(9)°. The dihedral angle between the two phenyl mean planes is 79.86(7)°.

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