The Crystal Structure of Di-μ-Bromo-tris(triphenylphosphine)dicopper(II)

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Synopsis. The crystal structure of the $Cu_2Br_2(PPh_3)_3 \cdot 1.5C_6H_6$ complex has been determined by three dimensional X-ray analysis. The crystals are monoclinic, and the space group is $P2_1/c$, with unit-cell parameters of $a=14.122$ (3), $b=19.573$ (4), $c=25.985$ (7) Å, $\beta=128.99$ (1)°, and $Z=4$. In the $Cu_2Br_2(PPh_3)_3$ molecule, one copper atom is three-coordinate, and the other, four-coordinate.

It has been known that copper(I) halides form a number of complexes with tertiary phosphine. A particularly interesting series is the 2 : 3 complexes, $Cu_2X_2(PPh_3)_3$, in which three- and four-coordinated copper atoms are both present and in which the stabilities of the two atoms are similar.[1-3] In this work, the bromide complex is investigated by means of the X-ray crystal analysis and the structure and bonding are discussed in connection with the NQR study.[4]

Experimental

Preparation. $Cu_2Br_2(PPh_3)_3 \cdot 1.5C_6H_6$, prepared as has been described in the literature,[5] was recrystallized from a mixed solvent of benzene and heptane (benzene : heptane= 3 : 1). Found: C, 62.94; H, 4.55%. Calcd for $C_{63}H_{54}Cu_2Br_2P_3$: C, 63.54; H, 4.57%.

X-Ray Data Collection. All the cell constants were determined by a least-squares treatment of the setting of 24 reflections measured on a Rigaku four-circle diffractometer, AFC-5, with Mo $K\alpha_1$ radiation ($\lambda_1=0.70926$ Å); $a=14.122$ (3), $b=19.573$ (3), $c=25.985$ (7) Å, $\beta=128.99$ (1)°. $Z=4$, and calculated density $\rho(\text{calcd})=1.42$ g cm^{-3}. The intensity data were collected by the ω-2θ scan technique to a maximum 2θ value of 42° at a scan rate of 16°/min (50 KV, 170 mA). The intensities of 4890 independent reflections were collected. Reflections for which the intensities were less than three times their standard deviations were regarded as "unobserved" and were not included in subsequent calculations. Thus, 4538 independent reflections were used for the structure determination. Their intensities were corrected for Lorentz and polarization factors, but no absorption corrections were made since the μ-values were low ($\mu=25.9$ cm^{-1}).

Structure Determination. The crystal structure was (solved by the heavy-atom technique, and the refinement was performed by a block-diagonal least-squares calculation. The quantity minimized was $w(|F_o|-k|F_c|)^2$. Cruickshank's weighting scheme was used, where $w=1/(a+|F_o|+b|F_o|^2)$, with $a=6.5$ and $b=0.019$. The atomic scattering factors from the International Tables for X-Ray Crystallography[6] were used. The effects of the anomalous dispersion of the P, Cu, and Br atoms for Mo $K\alpha$ radiation were included in the calculation. The final R value was 0.070. A list of observed and calculated structure factors is preserved by the Chemical Society of Japan (Document No. 8114). The final atomic coordinates are summarized in Table 1.

TABLE 1. FINAL ATOMIC PARAMETERS FOR $Cu_2Br_2(PPh_3)_3 \cdot 1.5C_6H_6$, WITH ESTIMATED STANDARD DEVIATIONS

Atom	x	y	z	Atom	x	y	z
Cu(1)	0.58856(12)	0.18115(8)	0.18994(7)	C(55)	0.7956(14)	0.3619(8)	0.0158(7)
Cu(2)	0.74821(12)	0.21919(7)	0.15925(7)	C(56)	0.7971(13)	0.3070(7)	0.0527(7)
Br(1)	0.55725(11)	0.28104(6)	0.12707(7)	C(61)	0.8504(9)	0.1334(5)	0.0873(5)
Br(2)	0.74503(11)	0.10785(6)	0.21339(7)	C(62)	0.9130(10)	0.1507(6)	0.0630(6)
P(1)	0.4461(3)	0.1564(2)	0.1972(1)	C(63)	1.0093(11)	0.1081(7)	0.0806(6)
P(2)	0.7220(3)	0.1845(2)	0.0682(1)	C(64)	1.0476(12)	0.0547(7)	0.1219(6)
P(3)	0.9001(3)	0.2800(2)	0.2479(1)	C(65)	0.9867(12)	0.0368(7)	0.1473(6)
C(11)	0.3619(10)	0.2259(6)	0.2184(5)	C(66)	0.8864(11)	0.0780(6)	0.1293(6)
C(12)	0.4759(12)	0.2787(7)	0.2571(7)	C(71)	0.9297(10)	0.3633(6)	0.2289(5)
C(13)	0.4418(15)	0.3322(9)	0.2789(8)	C(72)	0.8279(11)	0.4032(6)	0.1806(6)
C(14)	0.3260(15)	0.3348(9)	0.2615(8)	C(73)	0.8433(13)	0.4684(7)	0.1643(7)
C(15)	0.2423(14)	0.2851(8)	0.2210(8)	C(74)	0.9647(13)	0.4921(8)	0.1956(7)
C(16)	0.2733(13)	0.2287(7)	0.1986(7)	C(75)	1.0616(12)	0.4528(7)	0.2402(7)
C(21)	0.3141(9)	0.1300(6)	0.1142(5)	C(76)	1.0486(11)	0.3880(6)	0.2594(6)
C(22)	0.2847(11)	0.0615(6)	0.0972(6)	C(81)	1.0505(10)	0.2386(6)	0.3001(5)
C(23)	0.1872(13)	0.0440(8)	0.0302(7)	C(82)	1.0699(12)	0.1874(7)	0.2712(6)
C(24)	0.1245(14)	0.0954(8)	−0.0164(8)	C(83)	1.1853(13)	0.1540(8)	0.3084(7)
C(25)	0.1504(13)	0.1625(8)	−0.0008(7)	C(84)	1.2736(13)	0.1740(8)	0.3705(7)
C(26)	0.2484(12)	0.1821(7)	0.0664(7)	C(85)	1.2596(16)	0.2234(9)	0.4013(9)
C(31)	0.4685(10)	0.0855(6)	0.2484(6)	C(86)	1.1422(14)	0.2585(8)	0.3658(7)
C(32)	0.5664(13)	0.0423(7)	0.2717(7)	C(91)	0.8674(10)	0.2996(6)	0.3043(6)
C(33)	0.5817(16)	−0.0186(9)	0.3093(9)	C(92)	0.8751(13)	0.2451(8)	0.3411(7)
C(34)	0.5005(15)	−0.0319(8)	0.3194(8)	C(93)	0.8386(14)	0.2556(8)	0.3823(8)
C(35)	0.4085(14)	0.0110(8)	0.2988(8)	C(94)	0.7942(14)	0.3204(8)	0.3803(7)
C(36)	0.3872(12)	0.0697(7)	0.2608(7)	C(95)	0.7859(14)	0.3734(8)	0.3442(7)
C(41)	0.5921(10)	0.1304(6)	0.0094(5)	C(96)	0.8227(11)	0.3627(7)	0.3041(6)
C(42)	0.4929(12)	0.1347(7)	0.0092(6)	C(101)	0.5697(15)	0.4116(9)	−0.0197(8)
C(43)	0.3858(13)	0.0909(8)	−0.0400(7)	C(102)	0.5486(14)	0.4350(8)	0.0045(8)
C(44)	0.3905(13)	0.0497(7)	−0.0810(7)	C(103)	0.4785(15)	0.4438(8)	0.0244(8)
C(45)	0.4871(12)	0.0451(7)	−0.0794(7)	C(111)	0.0157(24)	0.0735(14)	0.4320(13)
C(46)	0.5901(11)	0.0861(7)	−0.0335(6)	C(112)	0.1246(24)	0.0987(13)	0.4495(13)
C(51)	0.7084(10)	0.2526(6)	0.0183(6)	C(113)	0.2160(22)	0.1275(13)	0.5157(12)
C(52)	0.6190(12)	0.2580(7)	−0.0503(7)	C(114)	0.1923(22)	0.1372(13)	0.5591(12)
C(53)	0.6174(15)	0.3155(9)	−0.0853(8)	C(115)	0.0808(28)	0.1144(16)	0.5384(15)
C(54)	0.7076(14)	0.3638(8)	−0.0517(8)	C(116)	−0.0062(28)	0.0855(16)	0.4775(15)

TABLE 2. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (DEG.) FOR $Cu_2Br_2(PPh_3)_3 1.5CH$, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Distanes				Angles			
Cu(1)–Cu(2)	2.992(2)	Cu(2)–Br(2)	2.610(2)	Cu(1)–Br(1)–Cu(2)	71.88(5)	Br(2)–Cu(1)–P(1)	127.03(9)
Br(1)···Br(2)	4.009(2)	Cu(1)–P(1)	2.190(3)	Cu(1)–Br(2)–Cu(2)	71.66(5)	Br(2)–Cu(2)–Br(2)	101.44(5)
Cu(1)–Br(1)	2.404(2)	Cu(2)–P(2)	2.252(3)	Br(1)–Cu(1)–Br(1)	114.26(6)	Br(2)–Cu(2)–P(2)	105.41(8)
Cu(1)–Br(2)	2.370(2)	Cu(2)–P(3)	2.260(3)	Br(1)–Cu(1)–P(1)	116.91(9)	Br(2)–Cu(2)–P(3)	102.60(8)
Cu(2)–Br(1)	2.569(2)			Br(1)–Cu(2)–P(2)	110.76(8)	P(2)–Cu(2)–P(3)	130.66(11)
				Br(1)–Cu(2)–P(3)	102.27(8)		

Results and Discussion

Crystals of $Cu_2Br_2(PPh_3)_3 \cdot 1.5C_6H_6$ are composed of discrete molecular units of $Cu_2Br_2(PPh_3)_3$ and benzene. The interatomic distances and bond angles, along with their estimated standard deviations, are listed in Table 2. The molecular structure obtained and the labelling of atoms are illustrated in Fig. 1. Two kinds of benzene molecules are present in this crystal. One benzene occupies interstitial sites in the structure centered at 1/2, 1/2, 0. In the other benzene, some degree of disorder is suggested by the large thermal parameters.

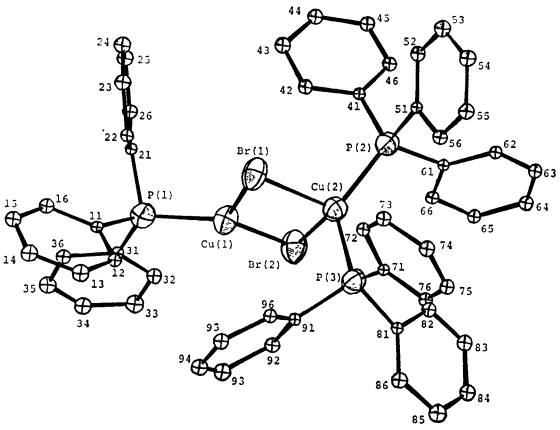

Fig. 1. View of the molecule $Cu_2Br_2(PPh_3)_3$ (drawn by use of ORTEP). The symbol, C, for each carbon atom has been omitted for clarity.

The structure of $Cu_2Br_2(PPh_3)_3$ consists of both three- and four-coordinated copper atoms. The geometry about Cu(I) is approximately trigonal planar, and the copper atom lies 0.183 Å above the plane including P(1), Br(1), and Br(2). The Cu(1)–P(1) distance, 2.190 Å, is nearly equal to the values observed cases where only one phosphine ligand is linked to the copper atom.[7,8] The environment of Cu(2) is distorted in a tetrahedral direction, and a marked departure from an idealized tetrahedral geometry is seen in the P(2)–Cu(2)–P(3) angle, which is 130.66°. The Cu(2)–P distances, 2.252 and 2.260 Å, are longer than the Cu(1)–P(1) distance in the three-coordinated copper atom.

The Cu–P distances involving the same kind of phosphines are dramatically influenced by the number of phosphine ligands bonded to the copper atom, whereas they are only slightly influenced by the coordination number of the copper atom.[7,8] In the ^{63}Cu NQR studies of $Cu_2X_2(PPh_3)_3$ (X=Cl, Br, and I),[4] the observed quadrupole coupling constant (e^2Qq/h) and the orientations of the efg principal axes of the three-coordinated copper atoms are mainly interpreted in terms of an sp^2-hybridization scheme. However, the observed frequencies are slightly higher than the maximum value expected for the sp^2 bonding. This discrepancy can be explained in terms of a bonding scheme involving 3d orbital mixing. This bonding scheme is applicable to the present compound, because the bromide complex is similar to the chloride and iodide complexes in the molecular structure as well as in ^{63}Cu NQR frequencies. In the case of the four-coordinated copper atom, the observed low frequency can be explained by sp^3 mixing only. However, from the distorted tetrahedral structure obtained in this compound, it seems likely that the Cu→P back-bonding exists and that it contributes to the Cu–P distance to some extent.

The Cu–Br distances in the four-coordinated copper atom are 0.203 Å (on the average) longer than those in the three-coordinated copper atom. In comparison with the case of the Cu–P distances, the copper-halogen distances increase with the copper coordination number. In the NQR studies of the $Cu_2X_2(PPh_3)_3$ series, it is observed that the e^2Qq/h values of the three-coordinated copper atoms decrease from X=Cl to I. This order is the reverse of the expectation for the sp^2 mixing scheme. This conflict can be explained by the existence of copper p_π-halogen p_π bonding; this π-bonding will reduce the e^2Qq/h value in this order; I>Br>Cl.[4] Therefore, the shortening of the copper-halogen distances in the three-coordinate copper atom is considered to be caused by the mixture of π-bonding.

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