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The Crystal and Molecular Structure of Dibromobis(triphenylphosphine oxide)copper(II)

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The structure of dibromobis(triphenylphosphine oxide) copper(II) has been determined by a single-crystal X-ray diffraction study. The compound crystallizes as orthorhombic crystals ($a = 17.193(6)$ Å, $b = 10.226(4)$ Å, and $c = 19.052(4)$ Å) of space group $Pca2_1$, with four molecules per unit cell ($\varrho_{obs} = 1.55(2) g\ cm^{-3}$, $\varrho_{calc} = 1.55 g\ cm^{-3}$). The structure was solved from Patterson and electron density maps and refined by least-squares methods to a conventional R value of 0.062 for 1283 independent, non-zero reflections. The coordination about copper is a slightly elongated tetrahedron with Cu–Br distances of 2.320(3) Å and 2.302(3) Å and Cu–O distances of 1.91(1) Å and 1.96(1) Å; the Cu–O–P angles are 144.0(9)° and 154.8(7)°.

Introduction

The complexes $Cu(TPPO)_2X_2$ (where TPPO represents triphenylphosphine oxide and X represents chloride or bromide) have been reported and, on the basis of spectral and magnetic properties, assigned tetrahedral structures.[1] Although it was suggested that the tetrahedron might be flattened, an elongated tetrahedron was observed[2] for $Cu(TPPO)_2Cl_2$. The structure of $Cu(TPPO)_2Cl_2$ consists of molecular units with two-fold symmetry, a Cl–Cu–Cl angle of 102.2(1)°, an O–Cu–O angle of 93.0(1)°, and a dihedral angle of 71.6° between the Cl–Cu–Cl and O–Cu–O planes. Although a linear Cu–O–P arrangement was observed[3] for $Cu_4OCl_6(TPPO)_4$, the Cu–O–P arrangement in $Cu(TPPO)_2Cl_2$ is distinctly bent (150.9°); this difference is reflected in the P–O stretching frequencies, 1195 cm^{-1} for $Cu_4OCl_6(TPPO)_4$ and 1142 cm^{-1} for $Cu(TPPO)_2Cl_2$.

The infrared spectrum of $Cu(TPPO)_2Br_2$ was also reported and two bands, 1145 and 1169 cm^{-1}, were observed in the region of P–O stretching frequencies. The position of these bands suggests a bent Cu–O–P arrangement as in $Cu(TPPO)_2Cl_2$ but the presence of two bands instead of one indicates a different structure. In order to determine the nature of this difference, an X-ray diffraction study of $Cu(TPPO)_2Br_2$ has been carried out and the results are reported in this paper.

Experimental

X-Ray Data Collection

The compound was prepared by the method reported in the literature[1] and was recrystallized from ethyl acetate. The compound crystallized as red-brown needle crystals and a crystal with approximate dimensions 0.10 × 0.20 × 0.35 mm was mounted on a glass fiber such that the longest crystal dimension (*b* axis) was approximately parallel to the fiber axis.

Unit cell parameters and the orientation matrix were determined on a Syntex $P2_1$ four-circle diffractometer equipped with a graphite monochromator (Bragg 2Θ angle = 12.2°) using MoK_α radiation at a takeoff angle of 6.5°. Fifteen reflections whose 2Θ values ranged from 5° to 17° were machine-centered and used in least-squares refinement of the lattice parameters and orientation matrix. Oscillation photographs about the axes showed mirror symmetry thus indicating that the crystal belonged to the orthorhombic system. Unit cell parameters obtained were[4] $a = 17.193(6)$ Å, $b = 10.226(4)$ Å, $c = 19.052(4)$ Å, and $V = 3350(2)$ Å^3. The calculated density of 1.55 gcm^{-3} for four molecules per unit cell agrees with the experimental density of 1.55(2) gcm^{-3} measured by the flotation method using a mixture of hexane and carbon tetrachloride. Omega scans of several low angle reflections gave peak widths at half-height of less than 0.25°, indicating a satisfactory mosaic spread for the crystal.

Intensity data for zero and upper levels were collected at a rapid scan rate and the intensities carefully examined for systematic absences. The absence of *0kl* reflections for $l = 2n+1$ and *h0l* reflections for $h = 2n+1$ is consistent with space groups $Pca2_1$ and Pcam. The strong vectors in a three-dimensional Patterson synthesis could be interpreted in terms of $Pca2_1$ but not Pcam; the successful refinement of the structure has confirmed the assignment of $Pca2_1$ (No. 29[5]).

Intensity data were collected using Θ–2Θ scans with X-ray source and monochromator settings identical to those used for determination of the unit cell parameters. A variable scan rate of from 29.3° to 7.5° min was used and a scan width of 2° was sufficient to collect all of the peak intensity. Stationary background counts were

TABLE I. Positional, Thermal, and Group Parameters for $Cu(TPPO)_2Br_2$.

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.0840(1)	0.1814(3)	0	0.0031(1)	0.0113(4)	0.0016(1)	−0.0002(2)	0.0003(1)	0.0002(2)
Brl	−0.0196(1)	0.3253(3)	0.0115(2)	0.0042(1)	0.0154(4)	0.0061(1)	0.0028(2)	−0.0010(1)	−0.0005(2)
Br2	0.1253(1)	0.1488(3)	0.1137(2)	0.0038(1)	0.0214(4)	0.0016(1)	−0.0005(2)	0.0000(1)	0.0004(2)
Pl	0.1759(3)	0.2445(6)	−0.1471(3)	0.0032(2)	0.0093(7)	0.0016(2)	−0.0012(4)	0.0004(2)	0.0005(4)
P2	0.0689(3)	−0.1415(6)	−0.0336(3)	0.0024(2)	0.0068(8)	0.0020(2)	0.003(4)	−0.0002(2)	0.0000(3)
O1	0.1422(8)	0.264(2)	−0.0733(7)	0.0046(7)	0.013(2)	0.0021(4)	−0.003(1)	0.0005(5)	0.0006(8)
O2	0.0893(7)	0.001(1)	−0.0339(5)	0.0032(6)	0.009(2)	0.0020(4)	−0.001(1)	0.0005(4)	−0.0002(8)

Group	x_c[b]	y_c	z_c	δ	ε	η
R1	0.2882(6)	−0.0027(9)	−0.1585(6)	0.053(9)	−0.143(9)	−0.827(7)
R2	0.0444(6)	0.2446(12)	−0.2632(5)	−0.744(8)	−0.173(8)	−0.171(8)
R3	0.3047(6)	0.4625(9)	−0.1716(6)	0.125(9)	−0.395(8)	0.754(9)
R4	−0.0949(5)	−0.1947(10)	0.0392(5)	0.520(9)	0.391(8)	−0.008(9)
R5	0.0695(6)	−0.2405(8)	−0.1918(5)	−0.076(7)	−0.239(8)	−0.243(9)
R6	0.1894(5)	−0.3085(10)	0.0564(5)	−0.592(8)	0.180(8)	−0.561(8)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-\beta_{12}hk-\beta_{13}hl-\beta_{23}kl]$. [b] x_c, y_c, and z_c are fractional coordinates of the rigid-group centers. The angles δ, ε, and η are used as defined previously.[10]

measured at the beginning (bgd1) and at the end (bgd2) of each scan with a total scan to background time ratio, TR, of 1.0. No significant fluctuations were observed in the intensities of three standard reflections (0,0,4; 0,3,0; 4,0,1) monitored every 100 reflections. Intensities were calculated from the total scan count (CT) and background counts by the relationship:

$$I = CT-(TR)(bgd1 + bgd2)(Scan\ Rate)$$

The intensities were assigned standard deviations according to the formula

$$\sigma(I) = [CT + (TR)^2(bgd1 + bgd2)]^{1/2}(Scan\ Rate)$$

From a total of 3483 reflections collected in a complete octant of data out to $2\Theta = 50°$, 1283 were accepted as statistically above background on the basis that I was greater than $3\sigma(I)$. Lorentz and polarization corrections were made in the usual way.

Solution and Refinement of the Structure

Computations were performed using standard programs;[6] all computations were carried out on the CDC Cyber 74 System. For structure factor calculations the scattering factors were taken from Cromer and Waber's tabulation[7] for all atoms except hydrogen; Stewart's

TABLE II. Derived Positional and Thermal Parameters for Group Atoms.

Atom[a]	Carbon				Hydrogen[c]		
	x	y	z	B[b]	x	y	z
R1C1	0.235(1)	0.097(1)	–0.155(1)	3.4(5)			
R1C2	0.252(1)	0.040(1)	–0.218(1)	4.5(6)	0.350(1)	–0.075(2)	–0.057(1)
R1C3	0.305(1)	–0.058(1)	–0.222(1)	5.4(6)	0.259(1)	0.093(2)	–0.051(1)
R1C4	0.342(1)	–0.102(1)	–0.162(1)	5.8(6)	0.198(1)	0.165(1)	–0.152(1)
R1C5	0.325(1)	–0.045(1)	–0.099(1)	5.1(6)	0.226(1)	0.070(2)	–0.260(1)
R1C6	0.271(1)	0.054(1)	–0.095(1)	4.8(6)	0.317(1)	–0.098(2)	–0.266(1)
R2C1	0.104(1)	0.243(2)	–0.215(1)	3.2(4)			
R2C2	0.086(1)	0.357(1)	–0.250(1)	4.4(5)	0.114(1)	0.434(2)	–0.241(1)
R2C3	0.026(1)	0.358(1)	–0.298(1)	5.6(6)	0.014(1)	0.437(2)	–0.322(1)
R2C4	–0.015(1)	0.246(2)	–0.311(1)	4.6(5)	–0.056(1)	0.247(2)	–0.344(1)
R2C5	0.003(1)	0.132(1)	–0.276(1)	5.2(6)	–0.026(1)	0.055(2)	–0.286(1)
R2C6	0.062(1)	0.131(1)	–0.228(1)	4.6(5)	0.075(1)	0.053(2)	–0.204(1)
R3C1	0.244(1)	0.376(1)	–0.163(1)	3.0(4)			
R3C2	0.286(1)	0.377(1)	–0.225(1)	4.9(6)	0.274(1)	0.318(2)	–0.262(1)
R3C3	0.347(1)	0.463(2)	–0.233(1)	5.3(6)	0.376(1)	0.464(2)	–0.276(1)
R3C4	0.365(1)	0.549(1)	–0.180(1)	5.4(6)	0.407(1)	0.609(2)	–0.186(1)
R3C5	0.323(1)	0.548(1)	–0.119(1)	6.3(7)	0.336(1)	0.607(2)	–0.082(1)
R3C6	0.263(1)	0.462(2)	–0.110(1)	4.1(5)	0.234(1)	0.461(2)	–0.068(1)
R4C1	–0.026(1)	–0.170(2)	0.006(1)	3.1(4)			
R4C2	–0.060(1)	–0.075(1)	0.046(1)	4.4(5)	–0.035(1)	0.008(1)	0.051(1)
R4C3	–0.129(1)	–0.099(1)	0.080(1)	4.9(6)	–0.153(1)	–0.034(2)	0.107(1)
R4C4	–0.164(1)	–0.219(2)	0.072(1)	5.3(6)	–0.212(1)	–0.236(2)	0.095(1)
R4C5	–0.130(1)	–0.314(1)	0.032(1)	6.0(6)	–0.155(1)	–0.397(1)	0.027(1)
R4C6	–0.061(1)	–0.290(1)	–0.001(1)	5.6(6)	–0.037(1)	–0.356(2)	–0.029(1)
R5C1	0.068(1)	–0.207(1)	–0.122(1)	3.2(5)			
R5C2	0.002(1)	–0.198(1)	–0.162(1)	4.5(5)	–0.045(1)	–0.169(2)	–0.141(1)
R5C3	0.003(1)	–0.231(2)	–0.231(1)	5.0(6)	–0.043(1)	–0.225(2)	–0.259(1)
R5C4	0.071(1)	–0.274(1)	–0.262(1)	5.2(6)	0.072(1)	–0.297(2)	–0.310(1)
R5C5	0.137(1)	–0.283(1)	–0.222(1)	6.3(6)	0.184(1)	–0.312(2)	–0.243(1)
R5C6	0.136(1)	–0.250(1)	–0.152(1)	4.1(5)	0.182(1)	–0.256(2)	–0.125(1)
R6C1	0.138(1)	–0.238(1)	0.017(1)	2.6(4)			
R6C2	0.127(1)	–0.370(1)	0.025(1)	4.2(5)	0.084(1)	–0.413(2)	0.004(1)
R6C3	0.179(1)	–0.440(1)	0.065(1)	5.1(6)	0.172(1)	–0.532(1)	0.071(1)
R6C4	0.241(1)	–0.379(1)	0.096(1)	5.5(6)	0.277(1)	–0.428(2)	0.123(1)
R6C5	0.252(1)	–0.247(1)	0.087(1)	4.7(5)	0.295(1)	–0.204(2)	0.109(1)
R6C6	0.200(1)	–0.176(1)	0.048(1)	4.7(5)	0.207(1)	–0.085(1)	0.042(1)

[a] RxCy designates carbon atom *y* of group *x*; in each group, C1 is bonded to phosphorus and the atoms are sequentially numbered around the ring. [b] Isotropic thermal parameters of the carbon atoms; all hydrogen atoms isotropic thermal parameters were set at 5.0. [c] Coordinates of the hydrogen atom are presented on the same row as the carbon to which it is bonded.

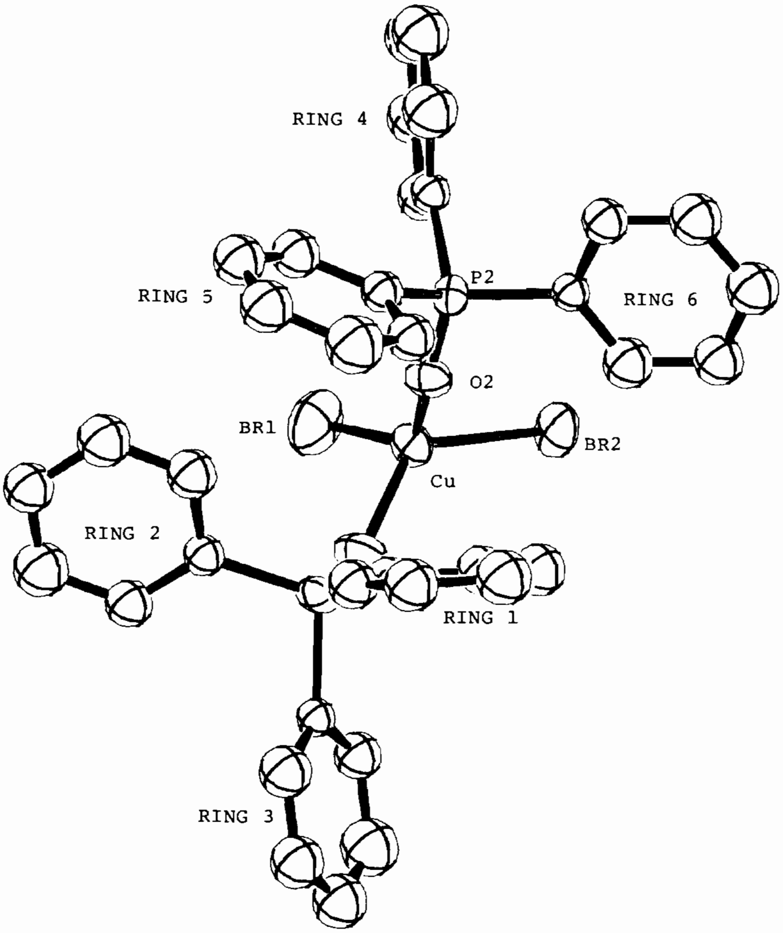

Figure 1. An ORTEP drawing of the molecular structure of Cu(TPPO)$_2$Br$_2$.

hydrogen atom scattering factors[8] were used. The scattering factor(s) for copper, bromine, and phosphorus were corrected for the real and imaginary anomalous dispersion components, using the dispersion factors given by Cromer.[9] The agreement factors are defined in the usual way as $R = (\Sigma||F_o|-|F_c||)/(\Sigma|F_o|)$ and $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$. In all least squares refinements, the quantity minimized was $w(|F_o|-|F_c|)^2$. A weighting scheme based on counting statistics, $w = 4I/\sigma^2(I)$, was employed for calculating R_w and in least-squares refinement.

Coordinates for one set of copper atoms and two sets of bromine atoms in general positions were obtained from a three-dimensional Patterson synthesis; successive cycles of least-squares refinement and electron density calculations revealed the positions of the phosphorus, oxygen, and carbon atoms. The six phenyl groups were refined as groups with fixed geometry (D_{6h} symmetry, C–C = 1.373 Å, C–H = 0.95 Å). The variable parameters for the groups included the coordinates of the group center and three orientation angles.[10] All non-group atoms were refined anisotropically, carbon atoms of the phenyl groups were refined isotropically, and phenyl hydrogen atoms were assigned isotropic temperature factors of 5.0. Least-squares refinement converged to give the residuals R = 0.062 and R_w = 0.050 (1283 observations, 136 variables). In the final refinement no parameter changed by more than one standard deviation from the previous value. The positional, thermal, and group parameters from the last cycle of least-squares refinement are given in Table I, along with the standard deviations estimated from the inverse matrix. The positional parameters of the ring carbon atoms, which may be derived from the group parameters in Table I, are presented in Table II together with thermal parameters obtained from the last cycle of refinement. A table of calculated and observed structure factors is avialable from the Editor.

Description of the Structure and Discussion

The crystal structure consists of discrete molecules of $Cu(TPPO)_2Br_2$ that are very similar to those of the corresponding chloride compounds. A view of the asymmetric unit is shown in Figure 1 and selected intramolecular distances and angles are presented in Table III along with corresponding values for $Cu(TPPO)_2Cl_2$.

The distorted tetrahedral coordination of the copper is similar to that observed for $Cu(TPPO)_2Cl_2$. The molecular symmetry is different in the two structures since the copper atoms of the chloride structure (space group Fdd2) occupy sites of two-fold symmetry and the copper atoms of the bromide structure occupy general positions. This difference in site symmetry has little effect on the structure, however, as the independent Cu–Br distances differ by only 0.018 Å (6 standard deviations) and the Cu–O distances differ by 0.042 Å (3 standard deviations). Although the tetrahedron is elongated as it was in the chloride structure, comparison of the O–Cu–O′ angles (98.7° for the bromide, 93.0° for the chloride) and the X–Cu–X′ angles (104.0° for the bromide, 102.2° for the chloride) indicates that the bromide structure is less elongated. On the other hand, comparison of the dihedral angle between the O–Cu–O′ and X–Cu–X′ planes (67.9° for the bromide, and 71.6° for the chloride) indicates a greater twist distortion for the bromide structure.

The difference in infrared spectra of the chloride and bromide in the P–O stretching region is apparently related to the difference in site symmetries. The bromide, with two independent phosphine oxide groups, shows two P–O stretching frequencies (1145 and 1169 cm^{-1}) while the more symmetric chloride shows only one P–O stretching frequency (1142 cm^{-1}). The Cu–O–P angles for the bromide structure (154.8° and 144.0°) are bent to about the same extent as in the chloride structure (150.9°). As indicated previously, bending of the Cu–O–P arrangement should change the hybridization at O, decrease the π-bonding between phosphorus and oxygen, and lower the P–O stretching frequency.

TABLE III. Comparison of Selected Intramolecular Distances (Å) and Angles (deg.) in $Cu(TPPO)_2Br_2$ and $Cu(TPPO)_2Cl_2$.

Atoms	$Cu(TPPO)_2Br_2$	$Cu(TPPO)_2Cl_2$
	Bond Distances	
Cu–X1	2.320(3)	2.170(2)
Cu–X2	2.302(3)	
Cu–O1	1.91(2)	1.958(4)
Cu–O2	1.96(1)	
O1–P1	1.54(1)	1.492(4)
O2–P2	1.50(1)	
P1–C1	1.79(1)	1.822(6)
P2–C1	1.81(1)	
P1–C2	1.82(1)	1.781(6)
P2–C2	1.82(1)	
P1–C3	1.84(1)	1.798(6)
P2–C3	1.83(1)	
	Bond Angles	
X1–Cu–X2	103.9(1)	102.2(1)
O1–Cu–O2	98.7(5)	93.0(1)
X1–Cu–O1	100.9(5)	104.7(2)
X1–Cu–O2	131.7(4)	127.5(2)
X2–Cu–O1	126.1(4)	
X2–Cu–O2	99.1(3)	
Cu–O1–P1	144.0(9)	150.9(3)
Cu–O2–P2	154.8(7)	
O1–P1–C1	113.8(9)	111.8(3)
O2–P2–C1	111.0(7)	
O1–P1–C2	112.6(9)	108.4(3)
O2–P2–C2	111.5(7)	
O1–P1–C3	107.4(9)	113.5(3)
O2–P2–C3	112.3(7)	
	Dihedral Angles	
[O1–Cu–O2]–[Br1–Cu–Br2]	67.9(4)	71.6(2)

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