ings of 0.28 and 0.27 Å are found for the chloride and bromide, respectively. To a first approximation bonding in these hexahalide species can be viewed as involving only the 5p orbitals on the antimony with the lone pair residing in the 5s orbital. This description is essentially that proposed by Rundle[21] for I_3^- and other polyhalides; it should also be noted that the lengthening of the I-I distance in I_3^- relative to I_2 is 0.27 Å.

Registry No. $Co(NH_3)_6SbCl_6$, 17805-63-9.

[21] R. E. Rundle, *J. Amer. Chem. Soc.*, 73, 4321 (1951).

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The Crystal and Molecular Structure of Bromobis(triphenylphosphine)copper(I) Hemibenzenate

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The crystal and molecular structure of bromobis(triphenylphosphine)copper(I) hemibenzenate, $[(C_6H_5)_3P]_2CuBr\cdot{}^1/_2C_6H_6$, has been determined by three-dimensional X-ray crystallographic analysis using data collected on a diffractometer. The colorless acicular crystals are triclinic, space group $P\bar{1}$, with unit cell parameters, $a = 12.870$ (6) Å, $b = 10.235$ (5) Å, $c = 13.658$ (9) Å, $\alpha = 104.97$ (3)°, $\beta = 101.81$ (4)°, $\gamma = 74.37$ (3)°, and $Z = 2$. The structure has been refined to a final R factor of 0.069 on 3484 independent observable reflections. All of the hydrogen atoms were included in the structure factor calculations, but their parameters were not refined. The structure consists of discrete molecules of $[(C_6H_5)_3P]_2CuBr$ in which the coordination geometry about the copper atom is essentially trigonal planar. This is believed to be the first X-ray structural characterization of a monomeric copper(I) complex exhibiting three-coordination. The important interatomic distances Cu-Br = 2.346 (2) Å, Cu-P(1) = 2.282 (3) Å, and Cu-P(2) = 2.263 (2) Å are consistent with those found in other complexes of copper(I). The P-Cu-P angle of 126.0 (1)° is comparable to that observed in the previously characterized $[(C_6H_5)_3P]_2CuX$ compounds in which X is a uninegative, bidentate anion and the copper is formally four-coordinate. Structural comparisons suggest that all of the bis(triphenylphosphine)copper(I) complexes thus far studied can be viewed in terms of a basic trigonal coordination for both unidentate and bidentate anions.

Introduction

During the course of a study of the molecular and electronic structure of several nickel(I) halide–triphenylphosphine complexes being carried out in this laboratory, we have prepared samples of bromobis(triphenylphosphine)copper(I) in which a portion of the copper(I) has been isomorphously replaced by nickel(I). As an aid to the interpretation of the electron spin resonance spectra of these samples we have had occasion to determine the crystal and molecular structure of the host. Structures of several bis(triphenylphosphine)copper(I) complexes involving bidentate anions and formally four-coordinate copper have been reported previously.[1-3] In the present case the copper atom is unambiguously three-coordinate; however the similarities in structure are at least as pronounced as the differences.

Experimental Section

Bromobis(triphenylphosphine)copper(I) Hemibenzenate. The compound was prepared by adding a solution of $CuBr_2$ (2.18 g, 0.01 mol) in ethanol to a warm solution of triphenylphosphine (6.55 g, 0.025 mol) in ethanol and stirring vigorously. The brown coloration due to the $CuBr_2$ in solution was discharged slowly and an off-white precipitate formed. After 20 min the precipitate was collected by suction filtration and washed with ethanol and ether. The crude product was recrystallized from a mixture of benzene and cyclohexane (benzene > cyclohexane) in which had been dissolved a small amount of triphenylphosphine. The colorless acicular crystals used in this study were grown by slow evaporation of the solvent at room temperature over a period of 12 hr. Elemental analysis indicated that the crystals contained 0.5 mol of benzene of crystallization per mol of complex, a fact confirmed in the subsequent structure determination. *Anal.* Calcd for $[(C_6H_5)_3P]_2CuBr\cdot{}^1/_2C_6H_6$: Cu, 8.99; Br, 11.30; P, 8.76; C, 66.25; H, 4.56. Found: Cu, 9.05; Br, 11.60; P, 8.89; C, 66.47; H, 4.76.

Crystal Data. For $[(C_6H_5)_3P]_2CuBr\cdot{}^1/_2C_6H_6$, $M = 707.1$, the crystals are triclinic, with $a = 12.870$ (6) Å, $b = 10.235$ (5) Å, $c = 13.658$ (9) Å, $\alpha = 104.97$ (3)°, $\beta = 101.81$ (4)°, $\gamma = 74.37$ (3)°, $V = 1656.2$ Å^3, ρ_{measd}(flotation in 1,2-dichloroethane and chloroform at 25°) = 1.41 g cm^{-3}, $Z = 2$, $\rho_{\text{calcd}} = 1.43$ g cm^{-3}, $F(000) = 722$ and μ(Mo Kα) = 20.6 cm^{-1}.[4] The presence of 0.5 mol of benzene per mole of complex, coupled with the observation of two molecules per unit cell, seemed to indicate that the centrosymmetric space group $P\bar{1}$ was the more likely of the two possible space groups. The aptness of this choice was borne out by the successful refinement of the structure in this space group. Two crystals were used for the collection of data. The first, measuring 0.10 × 0.12 × 0.35 mm, was used for reflections in the range $2\theta \leqslant 35°$, while the second, measuring 0.25 × 0.30 × 0.50 mm, was used for reflections in the range $35° \leqslant 2\theta \leqslant 55°$. The crystals were mounted on glass fibers with the length of the macroscopic crystal (approximately parallel to b) aligned along the axis of the fiber.

Data Collection and Reduction. Preliminary crystal alignment, determination of space group, and initial measurement of unit cell parameters were accomplished by means of precession photographs. Data were then collected on a Picker FACS-1 automated diffractometer (Mo Kα, λ 0.7107 Å). Refined unit cell parameters were obtained from a least-squares fit to the angular settings of 10 reflections carefully hand-centered on the diffractometer. Intensity measurements were made using the moving crystal–moving counter technique. A basic scan width of 2°(2θ) was used to which was added a dispersion factor to take into account the Kα_1-Kα_2 splitting. Reflections were scanned at a rate of 1°/min with 10-sec stationary background counts being taken at the low- and high-angle extremes of each scan.

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[1] (a) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, 6, 2223 (1967); (b) *ibid.*, 8, 2755 (1969).

[2] G. G. Messmer and G. J. Palenik, *Inorg. Chem.*, 8, 2750 (1969).

[3] S. J. Lippard and G. J. Palenik, *Inorg. Chem.*, 10, 1322 (1971), and references therein.

[4] While in the triclinic system the choice of unit cell is not dictated by symmetry, a conventional choice of axes such that $c < a < b$ has been suggested. Application of the transformation $a \rightarrow a'$, $b \rightarrow c'$, and $-c \rightarrow b'$ to the cell chosen for this study gives a cell conforming to this convention. The resultant cell also has the normal axial character representation + + +.

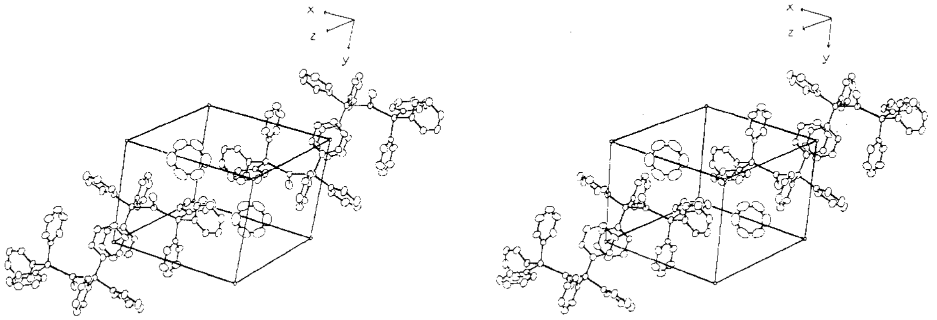

Figure 1. A stereoscopic view of the packing in $[(C_6H_5)_3P]_2CuBr \cdot {}^1/_2C_6H_6$. Atoms are represented by the envelopes of 35% probability thermal ellipsoids.

Detection was by means of a scintillation counter employing pulse height discrimination and with copper foil attenuators automatically inserted into the diffracted beam whenever the counting rate exceeded 10,000 counts/sec. Three standard reflections were measured after each block of 50 reflections to monitor the crystal alignment and stability and beam stability. The intensities of these reflections showed a roughly uniform drop to approximately 94% of their initial value during the course of the data collection. The intensities of the standard reflections were later used to correct the data for this decrease in intensity.

The raw data were corrected for background, for Lorentz and polarization effects, and for the use of attenuators. An estimated standard deviation for the intensity of each reflection was calculated from the formula

$$\sigma(I) = [P + (T_c/2T_b)^2(B_1 + B_2) + (0.05N)^2]^{1/2}$$

In the above expression P is the total counts in the peak plus background observed in a time T_c, B_1 and B_2 are the background counts observed at each extreme of the scan, each in a time T_b, and the term in N, the net count, is included to take into account deviations from sources other than counting statistics.[5] Of the 5804 reflections with $2\theta \leqslant 55°$, 2320, for which $I < 2\sigma(I)$, were considered to be unobserved and were excluded from the refinement. No absorption corrections were applied. Transmission coefficients were estimated to range from 0.60 to 0.67 and from 0.35 to 0.45 for the two crystals, respectively. Some of the effects of the relatively larger absorption of the second crystal were probably absorbed in the scale factor used to place the two data sets on a common basis.

Determination and Refinement of Structure.[6] Analysis of a three-dimensional Patterson synthesis yielded the coordinates of all four heavy atoms, and two successive Fourier syntheses, each phased by the atoms already located, revealed the positions of all phenyl ring carbon atoms. Several small, diffuse peaks in the last electron density map suggested that the molecule of benzene of crystallization was located about the inversion center at $^1/_2$, 0, 0, but it was not included in the model at this time. After two cycles of full-matrix least-squares refinement of all positional and individual atom isotropic thermal parameters, a three-dimensional difference Fourier synthesis served to locate unambiguously the three independent atoms of the molecule of benzene of crystallization in the previously suspected positions. The difference synthesis also revealed considerable anisotropy of thermal motion and all nonhydrogen atoms were assigned anisotropic thermal parameters in the subsequent refinement.

Because of limitations on the number of variables which could be refined simultaneously by full-matrix techniques, the following scheme was adopted: first, positional and thermal parameters for the heavy atoms and all carbon atoms in the phenyl rings attached to a single phosphorus atom were refined; next, positional and thermal parameters for the heavy atoms and all carbon atoms in the phenyl rings attached to the other phosphorus atom were refined; and, finally, after two cycles of the above procedure, the positional and thermal parameters of the atoms of the molecule of benzene of crystallization were refined. This procedure was repeated twice, at which point the refinement had converged with R_1 $[\Sigma||F_o| - |F_c||/\Sigma|F_o|] = 0.076$ and R_2 $[(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}] = 0.083$.

Although a difference Fourier map which was now prepared revealed 15 peaks with an electron density > 0.5 e/Å^3 and an additional 10 peaks with electron density > 0.3 e/Å^3 in positions chemically reasonable for various of the hydrogen atoms, we did not feel that definition of electron density in this map warranted its use for the determination of the coordinates of the hydrogen atoms. Instead, positions of all independent hydrogen atoms were calculated from the positions of the carbon atoms and the standard assumptions concerning the geometry of benzene rings. The hydrogen atoms were assigned isotropic thermal parameters equal to the mean thermal parameter of a phenyl ring carbon atom at the end of isotropic refinement (4.75 Å^2). Because of the observation of a positive electron density of ~1.0 e/Å^3 at the center of the bromine atom position and a negative electron density of ~0.75 e/Å^3 at the center of the copper atom position, scattering factors for Br^- and Cu^+ instead of the neutral atoms were used in the final refinement. After one further complete cycle of refinement as described above in which the hydrogen atom parameters were included in the structure factor calculation, but were not allowed to vary, the refinement converged with the residuals having the final values $R_1 = 0.069$ and $R_2 = 0.078$. Application of Hamilton's test[7] indicates that the inclusion of the hydrogen atoms produces a significant improvement in the model at greater than a 99% confidence level.

In the least-squares refinement carried out on F, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with all reflections being assigned unit weight. Scattering curves for neutral Br, Cu, P, C, and later Br^- and Cu^+ (see above) were calculated from the analytical function and coefficients tabulated by Cromer and Mann.[8] The hydrogen scattering curve was that of Stewart, Davidson, and Simpson.[9] The effects of anomalous dispersion were taken into account in the structure factor calculations using values of $\Delta f'$ and $\Delta f''$ for Br, Cu, and P given in ref 10. During the last cycle of refinement no parameter shifted by more than 0.3 times its estimated standard deviation. A final difference map was essentially featureless, the only peaks with magnitude > 0.3 e/Å^3 (on this scale the density of a typical carbon atom peak was 5.5 e/Å^3) being confined to the region near the heavy atoms. No peak had a magnitude > 0.75 e/Å^3. Final positional and anisotropic thermal parameters derived from the last cycle of least-squares refinement for all nonhydrogen atoms are contained in Table I, and the calculated, probable hydrogen atom positions in Table II. A listing of observed and calculated structure factor amplitudes is available.[11]

Results and Discussion

Description of Structure. The crystal structure, as shown in Figure 1, consists of discrete, monomeric bromobis(tri-

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[5] W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).

[6] Programs for the IBM 360/75 used in this analysis were local modifications of Rodgers and Jacobson's ALF Fourier program, Busing, Martin, and Levy's ORFLS least-squares refinement program, and Johnson's ORTEP thermal ellipsoid plotter program.

[7] W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

[8] D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

[9] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

[10] "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, pp 215, 216.

[11] A table of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N. W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-213.

Table I. Final Positional and Anisotropic Thermal Parameters for the Nonhydrogen Atoms[a]

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	16,032 (10)	44,000 (13)	17,498 (9)	992 (11)	1,298 (17)	616 (8)	−623 (11)	20 (7)	453 (10)
Cu	12,635 (9)	28,607 (12)	25,901 (9)	400 (8)	778 (15)	497 (8)	−169 (9)	82 (6)	243 (9)
P1	2,787 (2)	1,848 (3)	3,554 (2)	37 (2)	85 (3)	61 (2)	−20 (2)	2 (1)	32 (2)
P2	−408 (2)	2,405 (3)	2,345 (2)	36 (2)	79 (3)	48 (2)	−18 (2)	4 (1)	24 (2)
C11	2,728 (8)	2,039 (10)	4,905 (8)	46 (7)	78 (13)	56 (7)	−18 (8)	2 (6)	16 (8)
C12	1,782 (8)	1,974 (11)	5,191 (8)	45 (7)	122 (15)	62 (8)	−23 (8)	−4 (6)	36 (9)
C13	1,691 (9)	2,100 (14)	6,200 (9)	61 (9)	174 (20)	63 (8)	−11 (10)	12 (7)	46 (11)
C14	2,552 (11)	2,311 (13)	6,950 (9)	107 (12)	141 (18)	42 (7)	−13 (12)	15 (8)	13 (9)
C15	3,521 (11)	2,403 (16)	6,685 (10)	82 (11)	205 (24)	66 (10)	−53 (13)	−14 (8)	15 (12)
C16	3,597 (8)	2,247 (13)	5,673 (9)	47 (8)	150 (8)	55 (8)	−14 (9)	0 (6)	20 (9)
C21	4,065 (7)	2,328 (12)	3,584 (8)	32 (6)	132 (16)	62 (8)	−24 (8)	2 (5)	42 (9)
C22	5,071 (8)	1,364 (12)	3,629 (9)	49 (8)	113 (16)	83 (9)	−18 (9)	5 (7)	35 (10)
C23	6,040 (8)	1,770 (13)	3,717 (9)	25 (6)	169 (20)	78 (9)	−11 (9)	9 (6)	37 (10)
C24	6,014 (9)	3,124 (14)	3,790 (9)	48 (8)	182 (20)	72 (9)	−51 (11)	−4 (6)	46 (11)
C25	5,014 (10)	4,106 (13)	3,723 (11)	72 (10)	132 (18)	120 (12)	−49 (11)	2 (9)	50 (12)
C26	4,050 (9)	3,709 (12)	3,611 (11)	46 (8)	119 (17)	119 (12)	−32 (9)	7 (7)	44 (11)
C31	3,109 (8)	−16 (10)	3,046 (8)	51 (7)	57 (11)	56 (7)	−25 (7)	−4 (6)	13 (7)
C32	3,197 (11)	−482 (14)	2,007 (9)	99 (11)	154 (20)	50 (8)	−41 (12)	−8 (7)	43 (10)
C33	3,383 (12)	−1,910 (16)	1,564 (10)	126 (14)	154 (22)	68 (10)	−31 (14)	21 (9)	−13 (12)
C34	3,455 (11)	−2,833 (14)	2,159 (13)	81 (11)	106 (18)	125 (15)	−20 (11)	24 (10)	12 (13)
C35	3,379 (10)	−2,425 (13)	3,173 (12)	81 (10)	99 (17)	120 (13)	−28 (10)	26 (9)	44 (12)
C36	3,207 (8)	−1,008 (12)	3,598 (9)	60 (8)	109 (15)	70 (8)	−13 (9)	23 (7)	39 (9)
C41	−427 (7)	632 (12)	1,689 (8)	35 (6)	135 (16)	55 (7)	−28 (8)	10 (5)	18 (9)
C42	357 (8)	−462 (11)	2,052 (9)	55 (8)	93 (15)	67 (8)	−16 (8)	−13 (6)	24 (9)
C43	377 (10)	−1,826 (13)	1,582 (10)	61 (9)	114 (17)	94 (11)	−10 (9)	6 (8)	16 (11)
C44	−366 (10)	−2,143 (13)	754 (10)	80 (10)	103 (17)	78 (10)	−12 (11)	16 (8)	4 (10)
C45	−1,099 (11)	−1,094 (15)	354 (10)	94 (12)	139 (20)	71 (10)	−38 (12)	0 (8)	−30 (11)
C46	−1,162 (9)	294 (12)	810 (9)	69 (9)	97 (16)	64 (8)	−10 (9)	−11 (7)	10 (9)
C51	−1,593 (7)	3,479 (10)	1,709 (7)	45 (7)	86 (13)	41 (6)	−8 (7)	2 (5)	23 (7)
C52	−2,650 (8)	3,442 (14)	1,760 (9)	44 (8)	186 (20)	76 (9)	−34 (10)	1 (7)	49 (11)
C53	−3,534 (9)	4,265 (16)	1,295 (10)	50 (8)	245 (25)	71 (9)	−36 (12)	3 (7)	60 (13)
C54	−3,393 (9)	5,074 (14)	702 (9)	61 (9)	186 (22)	58 (8)	0 (11)	0 (7)	37 (11)
C55	−2,360 (11)	5,111 (14)	597 (9)	109 (12)	153 (19)	54 (8)	−6 (12)	10 (8)	49 (10)
C56	−1,452 (8)	4,306 (11)	1,115 (8)	53 (8)	109 (15)	59 (7)	−5 (8)	12 (6)	33 (8)
C61	−852 (7)	2,615 (10)	3,579 (7)	33 (6)	89 (13)	51 (7)	−20 (7)	−2 (5)	27 (8)
C62	−996 (9)	3,939 (11)	4,203 (8)	69 (8)	94 (14)	57 (7)	−26 (9)	13 (6)	18 (8)
C63	−1,231 (9)	4,121 (13)	5,175 (9)	59 (8)	127 (17)	64 (8)	−17 (10)	14 (7)	8 (9)
C64	−1,307 (8)	3,060 (14)	5,565 (8)	55 (8)	190 (21)	47 (7)	−28 (10)	11 (6)	37 (10)
C65	−1,181 (8)	1,735 (12)	4,938 (9)	54 (8)	105 (15)	71 (8)	−18 (9)	13 (6)	34 (9)
C66	−972 (8)	1,540 (11)	3,952 (8)	52 (7)	109 (14)	52 (7)	−22 (8)	11 (6)	28 (8)
C71	4,165 (25)	1,077 (33)	25 (43)	148 (29)	219 (41)	234 (36)	−7 (25)	66 (29)	86 (33)
C72	4,990 (43)	1,061 (36)	779 (22)	252 (35)	278 (50)	106 (19)	−144 (38)	67 (22)	−35 (22)
C73	4,151 (23)	30 (54)	−756 (26)	149 (26)	390 (58)	141 (24)	−80 (36)	−22 (19)	94 (32)

[a] All values in the tables are multiplied by 10^4 except for the Br and Cu atom parameters which are multiplied by 10^5. The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Estimated standard deviations in the last significant digit(s) are given in parentheses. See Figure 2 for the atom-labeling scheme (atoms C71, C72, and C73 are the independent atoms of the molecule of benzene of crystallization).

Table II. Calculated Positions of Hydrogen Atoms[a]

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
H12	1188	1821	4672	H42	866	−252	2629
H13	1027	2062	6389	H43	910	−2567	1860
H14	2485	2411	7657	H44	−341	−3100	428
H15	4188	2554	7211	H45	−1615	−1310	−227
H16	4259	2291	5490	H46	−1689	1030	528
H22	5093	403	3592	H52	−2754	2858	2161
H23	6725	1091	3751	H53	−4256	4248	1350
H24	6678	3396	3864	H54	−4008	5622	351
H25	4988	5061	3760	H55	−2256	5691	190
H26	3360	4395	3580	H56	−728	4318	1061
H32	3137	186	1604	H62	−933	4697	3947
H33	3454	−2232	844	H63	−1325	5031	5601
H34	3578	−3803	1856	H64	−1463	3228	6253
H35	3451	−3100	3570	H65	−1244	986	5202
H36	3147	−683	4314	H66	−877	634	3524
				H71	3527	1852	31
				H72	4937	1842	1357
				H73	3522	54	−1300

[a] All values in the table are multiplied by 10^4. Hydrogen atoms are given the number of the carbon atom to which they are attached.

phenylphosphine)copper(I) units separated by van der Waals distances. The molecule of benzene of crystallization does not participate in the basic structural unit but occupies interstitial sites in the structure centered at $^1/_2$, 0, 0.

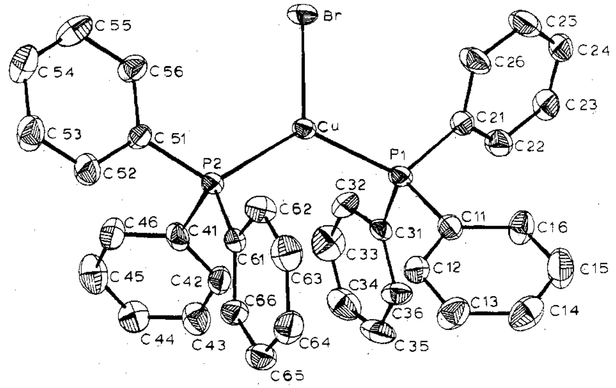

Figure 2. A perspective view of the structure of the $[(C_6H_5)_3P]_2$-CuBr molecule illustrating the trigonal-planar coordination geometry and showing the atom-labeling scheme used. Atoms are represented by 35% probability thermal ellipsoids.

A view of the molecular structure is presented in Figure 2 with the relevant interatomic distances and angles summarized in Table III. The coordination geometry about the copper atom is essentially trigonal planar, although the angles about the copper atom deviate somewhat from the idealized value of 120°. The copper atom is displaced 0.04 Å from

Table III. Summary of Important Interatomic Distances (Å) and Angles (deg)[a]

A. Coordination Geometry

Bond	Value	Angle	Value
Cu-Br	2.346 (2)	P1-Cu-P2	126.0 (1)
Cu-P1	2.282 (3)	P1-Cu-Br	112.8 (1)
Cu-P2	2.263 (3)	P2-Cu-Br	121.0 (1)

B. Geometry of the Triphenylphosphine Groups

Bond	Value	Angle	Value	Angle	Value
P1-C11	1.82 (1)	Cu-P1-C11	117.5 (3)	C11-P1-C21	102.9 (5)
P1-C21	1.83 (1)	Cu-P1-C21	117.9 (3)	C11-P1-C31	104.6 (5)
P1-C31	1.82 (1)	Cu-P1-C31	109.5 (3)	C21-P1-C31	102.8 (5)
P2-C41	1.81 (1)	Cu-P2-C41	112.9 (3)	C41-P2-C51	105.4 (5)
P2-C51	1.83 (1)	Cu-P2-C51	120.8 (3)	C41-P2-C61	105.1 (5)
P2-C61	1.83 (1)	Cu-P2-C61	110.3 (3)	C51-P2-C61	100.7 (4)

	C-C bond lengths			C-C-C bond angles		
Ring	Min	Max	Mean	Min	Max	Mean
1	1.37 (2)	1.40 (2)	1.38	117.9 (9)	121.7 (11)	120.0
2	1.36 (2)	1.41 (2)	1.39	118.7 (8)	120.8 (9)	120.0
3	1.35 (2)	1.40 (2)	1.38	117.1 (13)	123.6 (11)	120.0
4	1.36 (2)	1.41 (2)	1.38	117.8 (9)	122.5 (14)	120.0
5	1.36 (2)	1.41 (2)	1.38	118.1 (8)	121.5 (11)	120.0
6	1.36 (2)	1.39 (2)	1.38	118.6 (7)	123.0 (12)	120.0
All phenyl rings	1.35	1.41	1.38 (2)[b]	117.1	123.6	120.0 (16)[b]

C. Geometry of Benzene of Crystallization

Bond	Value	Angle	Value
C71-C72	1.32 (4)	C73-C71-C72	121 (2)
C71-C73	1.30 (4)	C71-C72-C73′	120 (2)
C72-C73′	1.35 (4)	C71-C73-C72′	118 (2)

[a] See Figure 2 for atom-labeling scheme. Carbon atoms C71′, C72′, and C73′ are related to atoms C71, C72, and C73, respectively, by inversion through (1/2, 0, 0). Estimated standard deviation in the last significant digit given in parentheses. [b] Calculated standard deviation from the mean given in parentheses.

Table IV. Distances (Å) of Atoms from Best Least-Squares Planes through Various Rings

	Ring						
Atom	1	2	3	4	5	6	7
C1	0.005	−0.016	0.003	−0.019	−0.013	−0.014	0.006
C2	−0.008	0.000	0.003	0.014	0.026	−0.001	−0.006
C3	0.003	0.017	−0.008	0.007	−0.020	0.014	−0.006
C4	0.005	−0.018	0.007	−0.022	0.001	−0.012	−0.006[a]
C5	−0.009	0.001	−0.001	0.016	0.012	−0.003	0.006[a]
C6	0.004	0.015	−0.004	0.005	−0.006	0.016	0.006[a]

[a] Carbon atoms 4, 5, and 6 of ring 7 correspond to C71′, C72′, and C73′, respectively.

the plane of the bromine and phosphorus atoms. In spite of the formal difference in coordination geometry (*vide infra*) the P-Cu-P angle of 126.0 (1)° falls in the middle of the range of values reported for other bis(triphenylphosphine)copper(I) compounds.[1-3] The Cu-P distances of 2.282 (3) and 2.263 (3) Å are comparable to those observed in these compounds. The Cu-Br distance of 2.346 (2) Å is somewhat shorter than that which has been observed previously in copper(I) compounds.[12,13]

The interatomic distances and angles within the triphenylphosphine groups (Table IIIB) are consistent with those commonly found in coordinated triphenylphosphine ligand.[14] We attach no chemical significance to the moderate deviations of several individual carbon atoms from the best least-squares planes through the phenyl rings (Table IV). The individual carbon-carbon bond lengths range from 1.354 to 1.413 Å with a mean of 1.382 Å and a computed standard deviation from the mean of 0.016 Å. Not included in the table are the 33 individual C-H distances which ranged from 0.94 to 0.98 Å with a mean of 0.96 Å and a computed standard deviation from the mean of 0.01 Å. While the independent atoms of the benzene of crystallization appeared clearly in the difference Fourier and in a final Fourier synthesis, the abnormally short bond lengths (Table IIIC) and large thermal parameters (Table I) observed for this ring suggest some degree of rotational disorder in the plane of the ring.

Comparison with Related Structures. A feature common to the structures of all $[(C_6H_5)_3P]_2CuX$ compounds thus far characterized is a value for the P-Cu-P angle in the range 120-130°. In the present case which involves obvious three-coordination, such a value is not surprising, but in compounds where X is a bidentate anion and the copper formally four-coordinate, the large deviation of this angle from the ideal tetrahedral value of 109.47° has been the subject of much discussion.[1-3] It has been pointed out by analogy with triphenylphosphine complexes with other metals that smaller angles are possible without significantly increasing the metal-phosphorus distance, so that steric interactions between the triphenylphosphine groups alone cannot account for the opening up of this angle. Likewise, while the small "bite" of the bidentate anions used and/or an increase in the electronegativity of the donor atoms of the anion would serve to open up further the P-Cu-P angle, these factors alone or in combination with the steric interactions between the phosphine groups have not seemed adequate to explain distortions of the uniformly large magnitude observed.

Figure 3 compares structures of compounds of the above formula where X^- is (a) Br^-, (b) NO_3^-, (c) BH_4^-, and (d) $B_3H_8^-$. The similarity in structure, particularly among the

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(12) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 260.

(13) B. Morosin and E. C. Lingafelter, *Acta Crystallogr.*, 13, 807 (1960).

(14) M. R. Churchill and J. A. O'Brien, *J. Chem. Soc. A*, 2970 (1968), and references cited therein.

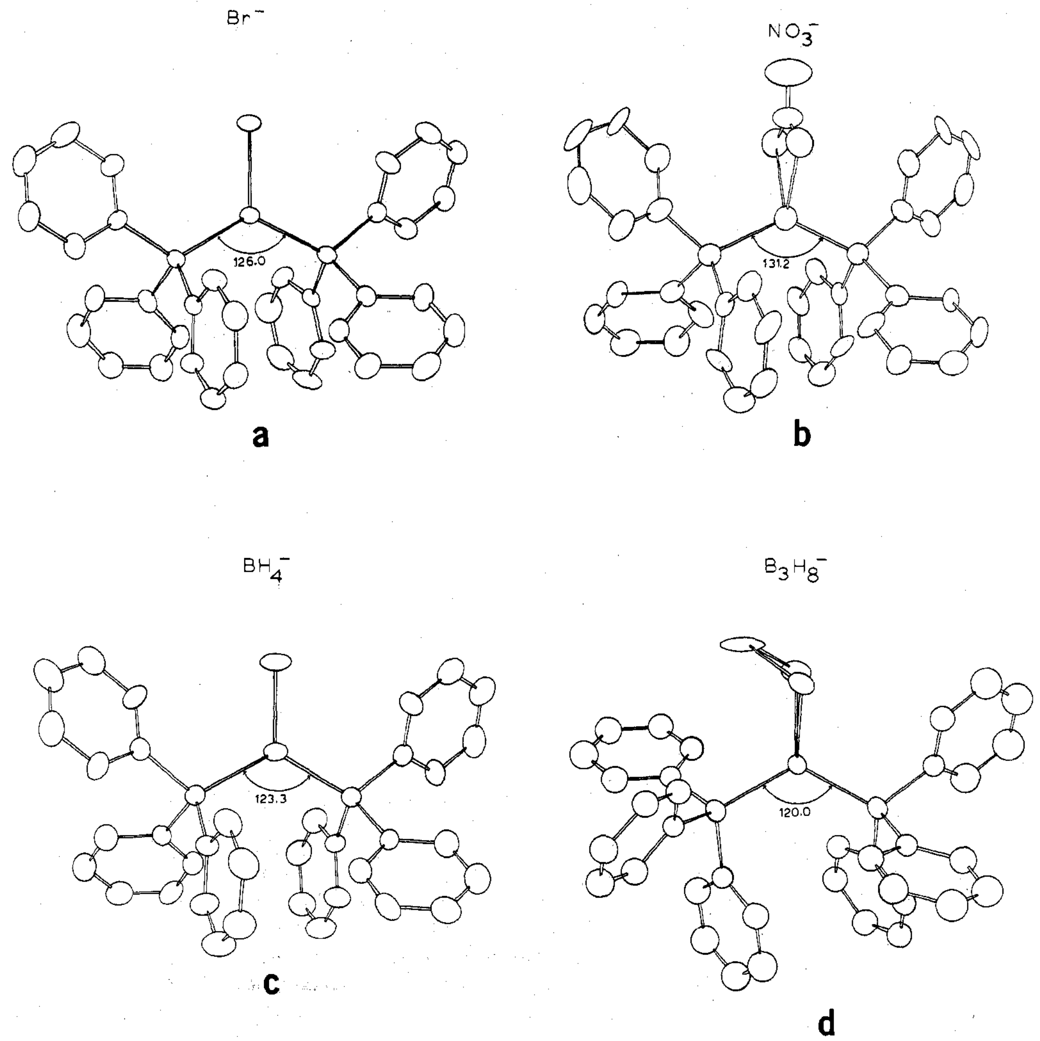

Figure 3. A comparison of the molecular structures of the complexes $[(C_6H_5)_3P]_2CuX$ where X⁻ is (a) Br⁻, (b) NO_3^-, (c) BH_4^-, and (d) $B_3H_8^-$. Hydrogen atoms have been omitted from all structures. Figures 3b, c, and d were drawn from parameters in ref 2, 1a, and 1b, respectively.

first three compounds, is striking. The differences in the structure of the complex involving the $B_3H_8^-$ ion are not as great as they might seem at first glance. The orientation with respect to one another of the phenyl rings within a single triphenylphosphine group is essentially the same in all cases and is undoubtedly arranged so as to minimize steric interactions among the rings. The plane of each ring is approximately that defined by the P-C bond to that ring and the P-C bond to the next ring in clockwise sequence when the phosphine group is viewed along the P-Cu bond from the P atom. The relative orientation of the triphenylphosphine group observed on the left-hand side of the molecule in Figure 3d can be obtained from that observed in the other structures by rotation of the phosphine group through approximately 60° in a clockwise direction about the P-Cu bond (again viewed from the P atom). Such a rotation maintains the preferred relationship among the phenyl rings while minimizing interactions with the boron atom and associated hydrogen atoms furthest from the copper. The other triphenylphosphine group in this compound has undergone a similar rotation, but only through a few degrees.

If one does not consider the individual atoms within the anion but rather considers the anion simply as a negatively charged entity, the coordination geometry in all four compounds may be appropriately described as trigonal planar. The complexes involving NO_3^- and BH_4^- both crystallize in the monoclinic space group *C*2/*c*. In the former case the copper, nitrogen, and one oxygen and in the latter case the copper and boron are located on a crystallographic twofold rotation axis. This immediately constrains the indicated atoms to be coplanar with the coordinated phosphorus atoms in each case. As noted previously the Br⁻ complex is essentially planar, although not constrained to be so by crystallographic symmetry. In fact, this compound possesses an approximate twofold rotational symmetry. Considering the "center" of the $B_3H_8^-$ ion (*e.g.*, the midpoint of the B2-B3[15] interatomic vector or the center of the triangle defined by the three boron atoms), the coordination geometry of this fourth complex is likewise essentially planar (this planarity is perhaps more obvious in Figure 1 of ref 1a).

Conclusions. It would appear that the structures of all $[(C_6H_5)_3P]_2CuX$ compounds studied thus far can be discussed in the context of a trigonal-planar coordination geometry, each consisting of a $[(C_6H_5)_3P]_2Cu^+$ unit associated with an anionic ligand *via* an interaction which is primarily electrostatic in nature and lacks strongly directional character. Purely spatial considerations would lead to an expected P-Cu-P angle of approximately 120°. One still is faced with deviations from the idealized geometry which are undoubtedly the result of steric factors, notably the tendency to maxi-

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(15) The numbering system is that used in ref 1a.

mize the separation between the triphenylphosphine groups subject to the limitations set by the spatial extent of the anion, and of localized, directional electronic interactions. It should be noted that the adoption of this viewpoint in no way diminishes the validity of the arguments previously advanced for the opening up of the P-Cu-P angle but merely requires the explanation of smaller deviations from the "expected" value.[16]

Registry No. Bromobis(triphenylphosphine)copper(I) hemibenzenate, 36273-10-6.

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(16) Subsequent to the submission of this article there appeared a preliminary communication of the structure of another monomeric, three-coordinate copper(I) complex, tris(2-picoline)copper(I) perchlorate: A. H. Lewin, R. J. Michl, P. Ganis, and U. Lepore, *J. Chem. Soc., Chem. Commun.*, 661 (1972). As in the present case the geometry of this cationic, three-coordinate copper(I) species deviates from the idealized trigonal planar. The extent of the deviation is obscured by an apparent error in reporting the bond angles about the Cu atom. As given, the sum of these angles is 370°. Geometric considerations require the sum to be $\leqslant 360°$.

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The Crystal and Molecular Structure of Tris(tetraisopropylmethylenediphosphonate)copper(II) Perchlorate with Comments on the Jahn-Teller Effect[1a]

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Tris(tetraisopropylmethylenediphosphonate)copper(II) perchlorate, $\mathrm{Cu[[(CH_3)_2CHO]_2P(O)CH_2P(O)[OCH(CH_3)_2]_2]_3(ClO_4)_2}$, crystallizes in the monoclinic space group $C2/c$ with eight molecules per unit cell. The unit cell dimensions are $a = 29.126$ (6) Å, $b = 23.399$ (4) Å, $c = 21.696$ (4) Å, and $\beta = 118.86$ (1)°. Intensity data were collected with a four-circle computer-controlled diffractometer using the θ–2θ scan technique. All 74 nonhydrogen atoms were refined anisotropically and the 90 hydrogen atoms were included as fixed atoms. Refinement by full-matrix least squares using 11,541 reflections gave a final R factor of 0.063. The $\mathrm{CuO_6}$ group is a slightly distorted octahedron. Average bond distances and bond angles with rms deviations for the chelate rings are as follows: Cu-O, 2.089 Å (range 2.067–2.111 Å); P-O, 1.478 (5) Å; P-C-(P), 1.787 (8) Å; O-Cu-O, 90.1 (8)°; Cu-O-P, 131.0 (15)°; O-P-C, 112.3 (11)°; and P-C-P, 114.1 (14)°. Structural data for six-coordinate Cu(II) complexes with equivalent donor sites are compared with data for complexes where Jahn-Teller distortions are not expected. The results are interpreted in terms of a negligible static Jahn-Teller distortion in six-coordinate Cu(II) complexes with equivalent donor sites.

Introduction

The present paper describes the crystal and molecular structure of tris(tetraisopropylmethylenediphosphonate)copper(II) perchlorate, $\mathrm{Cu[[(CH_3)_2CHO]_2P(O)CH_2P(O)[OCH(CH_3)_2]_2]_3(ClO_4)_2}$ (referred to as CuIPCP). Structural data are now available for seven complexes of six-coordinate Cu(II) which contain identical monodentate or bidentate ligands.[2] These data will be analyzed in terms of the Jahn-Teller effect.

Collection and Reduction of Data

Caution! Although the toxicity of IPCP is not known, it should be handled with care because of its similarity to OMPA, a toxic anticholinesterase agent.

The ligand IPCP was synthesized according to the procedure of Walmsley and Tyree[3]. Lannert[4] first synthesized the Cu complex by mixing hydrated copper(II) perchlorate and ligand in a 1:4 mole ratio in acetone. The compound was isolated by evaporating the acetone solution at room temperature in a desiccator. Well-formed hexagonal needles suitable for X-ray studies were obtained by using absolute ethanol rather than acetone in the above procedure. The data crystal was easily cleaved parallel to (101) to give a 0.64 × 0.94 × 0.64 mm hexagonal prism which was mounted with b^* parallel to the ϕ axis of the diffractometer. Like CuPCP, CuIPCP crystals are slightly sensitive to atmospheric moisture and X-radiation. However, special procedures were not required to protect the data crystal.

Precession photographs showed the crystals to be monoclinic with hkl reflections absent for $h + k$ odd and $h0l$ reflections absent for l odd. The space group is therefore either $C2/c$ or Cc.[5] The crystal density of 1.328 g/cm³, measured by flotation in a mixture of n-heptane and carbon tetrachloride, compares with the calculated value of 1.320 g/cm³ based on eight molecules per unit cell (volume 13037.8 Å³) and a molecular weight of 1295.42. Karle-Hauptman statistics indicated a center of symmetry,[6,7] so the space group $C2/c$ was assumed. This choice was confirmed by the structure analysis.

Accurate cell parameters were determined at 21° from 26 high-angle reflections ($2\theta > 50°$) manually centered on an accurately aligned four-circle diffractometer using the Cu $K\alpha_1$ line of the resolved doublet (λ 1.54051 Å) and a 1.0° X-ray tube takeoff angle. Least-squares refinement with diffractometer angles of 2θ, ω, and χ as observations gave $a = 29.126$ (6) Å, $b = 23.399$ (4) Å, $c = 21.696$ (4) Å, and $\beta = 118.86$ (1)°.

Intensity data were collected with a four-circle computer-controlled Picker diffractometer (FACS-I system) using a Digital Equipment Corp. PDP-8/I with a DF-32 disk memory. The data set was measured with Mo $K\alpha$ radiation complete to $2\theta = 50°$ in the hkl and $\bar{h}kl$ octants and included 11,541 reflections. A complete description of the experimental conditions and procedures for reduction of data are given in the previous paper of this series.[2]

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