distortion at the cobalt(II) ions is consistent with the smaller crystal field stabilization of the divalent d^7 ions relative to the trivalent d^6 ions.

The bond distances and bond angles for the 2,4-pentanedionate groups are listed in Table III and the least-squares planes of the rings and deviations of the individual atoms from these planes are given in Table IV; these groups do not show any unusual features when compared to 2,4-pentanedionate groups from other structures.

Within each acetate, there is a significant difference in the two carbon–oxygen distances; the long carbon–oxygen distances within the two acetates differ by less than the sum of their standard deviations and the short carbon–oxygen distances differ by the sum of their standard deviations. However, the shortest carbon–oxygen distance has an abnormally high standard deviation; the carbon–carbon distance of that acetate is extremely long and also has a high standard deviation. Attempts to find better positions for the atoms in this region resulted in refinement to the same final positions.

The difference in magnetic properties between the present compound and the nickel(II) cubanes needs further investigation; however, the difference is not surprising when one considers (1) the change in electronic structure in going from d^8 nickel(II) to d^7 cobalt(II) and (2) the additional bridging by the acetate in the present structure. The change from d^8 to d^7 provides a vacancy in the t_{2g} orbitals and the acetate provides a π pathway for superexchange; since the half-filled t_{2g} orbital can be oriented in such a way as to overlap with the acetate π system, an antiferromagnetic coupling is possible.

Registry No. $Co_4(CH_3O)_4(CH_3CO_2)_2(C_5H_7O_2)_4$, 36731-69-8.

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Crystal Structure of Hexaamminecobalt Hexachloroantimonate(III)

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Hexaamminecobalt hexachloroantimonate(III), $Co(NH_3)_6SbCl_6$, crystallizes in the orthorhombic space group *Pbca* (D_{2h}^{15}) with unit cell parameters $a = 11.50 \pm 0.03$ Å, $b = 11.53 \pm 0.03$ Å, and $c = 11.51 \pm 0.02$ Å. The observed and calculated densities were both found to be 2.19 g/cm³ with $Z = 4$. Data were collected on an automated four-circle diffractometer equipped with scintillation counter using the θ-2θ step-scan technique and Mo Kα radiation (λ 0.71069 Å). The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques to a final discrepancy index $R = 0.061$ for the 416 independent reflections significantly above background. The structure consists of $SbCl_6^{3-}$ anions and $Co(NH_3)_6^{3+}$ cations both of which have exact $\bar{1}$ crystallographic symmetry. Both also have approximately octahedral symmetry with all Sb–Cl bond lengths in $Sb^{III}Cl_6$ of 2.643 (6) Å (2.652 (6) Å when corrected for thermal motion); the mean Co–N bond distance is 1.982 (10) Å.

Introduction

The crystal structure investigation of hexaamminecobalt hexachloroantimonate(III) was undertaken as part of a series of investigations of halo-coordinated antimony compounds being performed in this laboratory.[1-7] Through these studies an attempt is being made to evaluate the effects of cation size and type on the stereochemistry of different antimony halides and to determine what effect, if any, the lone pair plays in the coordination geometry. The structures of a number of bromide complexes have previously been reported including $[(CH_3)_4N]_3Sb_2Br_9 \cdot Br_2$[2] and $(C_5H_5NH)_5Sb_2Br_9 \cdot Br_2$,[3] both of which contain $Sb_2Br_9^{3-}$ species, and $(NH_4)_4Sb^{III}Sb^{V}Br_{12}$,[4] $Rb_4Sb^{III}Sb^{V}Br_{12}$,[5] $(C_5H_5NH)_6Sb^{III}Sb^{V}_3Br_{24}$,[6] and $(C_7H_{13}NH)_4Sb^{III}Sb^{V}Br_{12} \cdot 2Br_2$,[7] all of which contain octahedral $SbBr_6^{3-}$ units. Of the chloride complexes, accurate crystal structure determinations of only $(NH_4)_2SbCl_5$[8] and $(C_5H_5NH)SbCl_4$[9] have been reported. In addition the stoichiometric formula found for the present complex indicated the presence of an $SbCl_6^{3-}$ anion; a structural study of such an anion has not been reported previously.

Experimental Section

Preparation. The salt was prepared by the reaction of hexaamminecobalt(III) chloride and antimony trioxide in a solution of 2 *M* hydrochloric acid. Hexaamminecobalt(III) chloride was first prepared by adding 24.0 g (0.1 mol) of cobalt(II) chloride hexahydrate and 16.0 g (0.3 mol) of ammonium chloride to 20.0 ml of H_2O. To this was added 0.4 g of activated decolorizing charcoal and 50.0 ml of concentrated NH_3. Air was then bubbled vigorously through the mixture for approximately 4 hr to enhance oxidation of Co(II). The crystals were filtered and then added to a solution of 3.0 ml of con-

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centrated hydrochloric acid in 150 ml of H_2O. Hexaamminecobalt(III) chloride was then precipitated by adding 40.0 ml of concentrated hydrochloric acid and cooling to 0°. The precipitate was next filtered and washed first with 60% and then with 95% alcohol before drying at 90°. Then, a hot solution of 0.15 g of antimony trioxide in 50.0 ml of 2 *M* hydrochloric acid was added to 50.0 ml of 0.02 *M* hexaamminecobalt(III) chloride in H_2O. The crystalline product which resulted was of superior quality, consisting of tetragonal prisms which exhibited a bright orange color. They were also found to be stable in the atmosphere; therefore, the crystal used for data collection was mounted on a glass fiber.

Crystal Data. Crystals of $Co(NH_3)_6SbCl_6$, examined by precession and Weissenberg film techniques, were found to exhibit *mmm* Laue symmetry indicating an orthorhombic space group. The following systematic absences were observed: $0kl$ when $k = 2n + 1$, $h0l$ when $l = 2n + 1$, and $hk0$ when $h = 2n + 1$. These absences are consistent only with the space group *Pbca*.

The unit cell parameters at 25 ± 2° are $a = 11.50 \pm 0.03$, $b = 11.53 \pm 0.03$, and $c = 11.51 \pm 0.02$ Å. The unit cell parameters and their standard deviations were obtained by a least-squares fit to 12 independent reflection angles whose centers were determined by left–right, top–bottom beam splitting on a previously aligned Hilger–Watts four-circle diffractometer (Cu Kα radiation, λ 1.5418). Any error in the instrument zero was eliminated by centering the reflection at both $+2\theta$ and -2θ.

Data were collected at room temperature utilizing an automated four-circle diffractometer designed and built in the Ames Laboratory. The upper full circle was purchased from STOE and equipped with encoders (Baldwin optical) and drive motors. The base was so designed that encoders could be directly connected to the main ω and 2θ shafts, using solid- and hollow-shaft encoders, respectively. The diffractometer is interfaced to a PDP-15 computer and is equipped with a scintillation counter. Zirconium-filtered Mo Kα radiation was used for data collection on an approximately spherical crystal of dimensions 0.104 × 0.106 × 0.100 mm and mounted such that the b^* axis was coincident with the ϕ axis of the diffractometer. The θ–2θ scan technique was employed to measure 710 reflections in one octant within a 2θ sphere of 40°, of which 416 were found to be $\geqslant 3\sigma(F)$. A takeoff angle of 3° and scan rate of 0.01°/0.1 sec were employed for the symmetric scan ranges of 1.12° in 2θ at low 2θ values to 1.72° at large 2θ. Stationary-crystal, stationary-counter background counts of half the time required to scan the peak were taken at each end of the scan. Before the scan was made, a peak height measurement was used to determine if the reflection was observed. The reflection had to exceed the background by seven counts or more to be scanned, which corresponds to approximately three standard deviations in the background for larger $(\sin\theta)/\lambda$ values.

As a general check on electronic and crystal stability, the intensities of three standards were measured every 25 reflections. These reflections showed no decrease over the entire period of data collection.

The intensity data were also corrected for Lorentz–polarization effects. The estimated error in each intensity was calculated by

$$[\sigma(I)]^2 = [C_t + C_b + (0.03C_t)^2 + (0.05C_b)^2 + (0.04C_r)^2]$$

where C_t, C_b, and C_r are the total count, background count, and net count, respectively. The estimated standard deviation in each structure factor was calculated by $\sigma(F_o) = [(I_o + \sigma(I_o))/Lp]^{1/2} - |F_o|$, a function based on the finite-difference method,[10] where Lp is the Lorentz–polarization factor. These standard deviations were used during the least-squares refinement to weight the observed structure factors, where w, the individual weighting factor, was defined by $1/\sigma(F_o)^2$. Transmission factors ranged from 0.71 to 0.68 based on a linear absorption coefficient of 39.24 cm^{-1}; no absorption corrections were therefore applied.

Solution and Refinement of Structure

Since there are eight general positions and only four formula units per unit cell, both the antimony and cobalt atoms must lie on special positions of $\bar{1}$ site symmetry. Atoms at such positions contribute only to those reflections with $h + k$, $k + l$, and $h + l = 2n$, and indeed all the strong reflections are in this subgroup. A Patterson map was computed from sharpened data[11] and revealed peaks consistent with such special positions for these atoms. The remaining atoms were found by successive structure factor and electron density map calculations after care was exercised to separate the structure from its mirror image, since both heavy atoms are positioned on planes with $y = 0, {}^1/_2$.

Table I. Final Atomic Parameters[a]

Atom	Position	*x*	*y*	*z*
Sb	4a	0.0[b]	0.0[b]	0.0[b]
Co	4b	0.0[b]	−0.5[b]	0.0[b]
Cl(1)	8c	0.1621 (5)	−0.0781 (6)	0.1436 (5)
Cl(2)	8c	0.3559 (5)	−0.1612 (5)	0.4208 (6)
Cl(3)	8c	0.0790 (6)	−0.3564 (5)	0.3383 (5)
N(1)	8c	0.4438 (17)	−0.0955 (17)	0.1312 (16)
N(2)	8c	0.3668 (15)	−0.4440 (16)	0.4050 (16)
N(3)	8c	0.0963 (17)	−0.3667 (16)	0.0556 (16)

[a] Numbers in parentheses in this and succeeding tables represent standard deviations occurring in the least significant digits of the parameter. [b] Atomic coordinate fixed by symmetry.

Table II. Final Anisotropic Thermal Parameters[a] (×10^4) for $Co(NH_3)_6SbCl_6$

Atom	Position	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb	4a	34 (1)	36 (1)	30 (1)	0 (2)	0 (1)	0 (2)
Co	4b	30 (3)	35 (3)	30 (3)	−6 (3)	2 (3)	1 (3)
Cl(1)	8c	41 (5)	81 (7)	48 (5)	16 (5)	−9 (5)	−1 (5)
Cl(2)	8c	53 (5)	51 (6)	74 (6)	−11 (5)	0 (5)	−8 (5)
Cl(3)	8c	78 (6)	49 (5)	51 (5)	0 (5)	11 (5)	5 (5)
N(1)	8c	2.4 (4)					
N(2)	8c	1.8 (4)					
N(3)	8c	2.3 (4)					

[a] The isotropic temperature factor and its corresponding standard deviation for nitrogens are listed under the heading β_{11}. The form of the anisotropic temperature factor expression is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hl + 2\beta_{13}hl + 2\beta_{23}kl)]$.

These positions were then refined by full-matrix, least-squares techniques[12] with isotropic thermal parameters to a conventional discrepancy factor of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.070$ and a weighted R factor $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.071$. The scattering factors were those of Hanson, *et al.*,[13] with antimony, cobalt, and chlorine modified for the real and imaginary parts of anomalous dispersion.[14] A difference electron density map at this stage verified that all nonhydrogen atoms had been accounted for but that some anisotropic motion, particularly of the heavier atoms, was quite evident. Accordingly, anisotropic refinement of all atoms heavier than nitrogen was begun, and after four cycles of least squares, the discrepancy factor dropped to 0.061 ($R_w = 0.060$).

A final electron density map showed no peaks higher than 0.6 e/Å^3. A final statistical analysis of the F_o and F_c values as a function of the indices, the scattering angle, and the magnitude of F_o showed no unusual trends and suggests that the relative weighting scheme used is a reasonable one. The final positional parameters are given in Table I and the final thermal parameters in Table II, along with their standard deviations as derived from the inverse matrix of the final least-squares cycle.[15] A table of observed and calculated structure factors is available.[16]

Description of the Structure

The $SbCl_6^{3-}$ and $Co(NH_3)_6^{3+}$ moieties are illustrated in Figure 1 and the interatomic distances and angles and their standard deviations are given in Table III. The average Sb–Cl bond

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(16) A table of structure factors 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-73-210.

Table III. Selected Distances (Å) and Angles (deg) in $Co(NH_3)_6SbCl_6$

Atoms	Length	Atoms	Length
Sb-Cl(1)	2.643 (6)	N(1)-N(2)	2.814 (26)
Sb-Cl(2)	2.643 (6)	N(1)-N(3)	2.801 (27)
Sb-Cl(3)	2.643 (6)	N(2)-N(3)	2.808 (26)
Co-N(1)	1.972 (19)	Cl(1)-N(3)	3.545 (22)
Co-N(2)	1.984 (18)	Cl(3)-N(3)	3.254 (21)
Co-N(3)	1.992 (19)	Cl(3)-N(1)	3.341 (21)
Cl(1)-Cl(2)	3.999 (10)	Cl(2)-Cl(3')	3.774 (11)
Cl(1)-Cl(3)	4.013 (10)	Cl(1')-Cl(3)	3.767 (11)
Cl(2)-Cl(3)	4.002 (11)		
Atoms	**Angle**	**Atoms**	**Angle**
Cl(1)-Sb-Cl(2)	90.7 (2)	N(1)-Co-N(2)	90.7 (7)
Cl(1)-Sb-Cl(3)	90.9 (2)	N(1)-Co-N(3)	89.9 (8)
Cl(2)-Sb-Cl(3)	91.1 (2)	N(2)-Co-N(3)	89.8 (7)

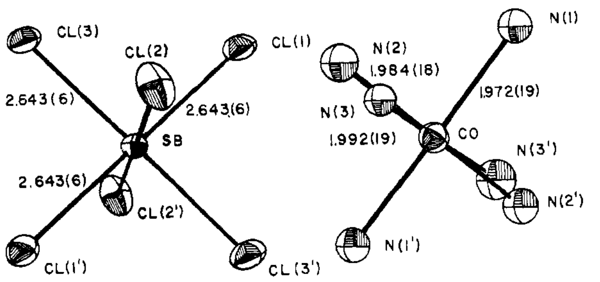

Figure 1. The $SbCl_6^{3-}$ anion and $Co(NH_3)_6^{3+}$ cation in $Co(NH_3)_6SbCl_6$.

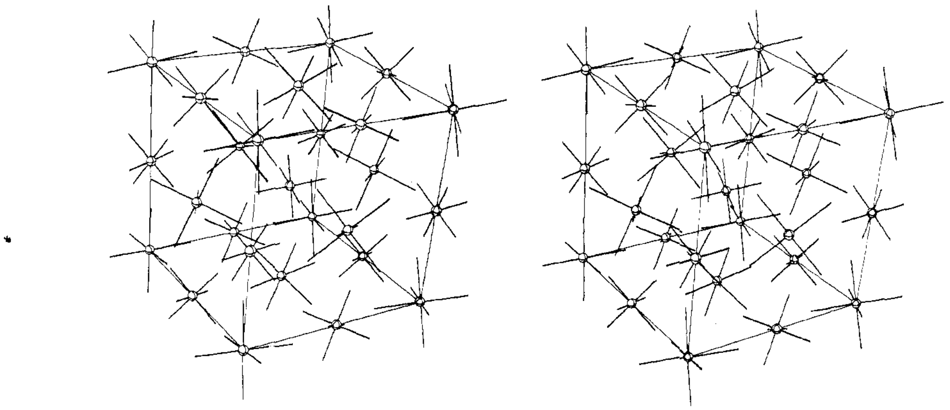

Figure 2. Stereogram of $Co(NH_3)_6SbCl_6$ with Sb at (0, 0, 0) and Co at (1/2, 0, 0).

length is 2.652 (6) Å when corrected assuming a riding model. A stereoview of the unit cell of $Co(NH_3)_6SbCl_6$ is illustrated in Figure 2 produced by Johnson's thermal-ellipsoid plot program.[17] The unit cell contains four $SbCl_6^{3-}$ anions and four $Co(NH_3)_6^{3+}$ cations, and these anions and cations pack in a NaCl-type structure. Indeed, the unit cell dimensions are all equal to within one standard deviation, although the symmetry is clearly only orthorhombic. A portion of the unit cell has been illustrated in Figure 3 along with important nonbonding distances. The dihedral angle between the planes formed by Sb, Cl(1), Cl(3) and Co, N(1), N(3) is 64.26 (5)° giving rise to an efficient packing of cations. Although no hydrogen atom positions were clearly evident on the difference map, hydrogen bonding is clearly indicated by the shorter nitrogen-chlorine distances ranging from 3.245 to 3.399 Å, well within that expected for such hydrogen bonds.[18] Also,

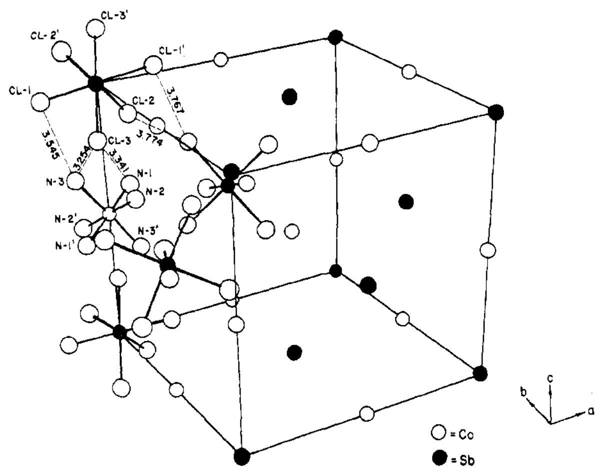

Figure 3. A portion of the unit cell of $Co(NH_3)_6SbCl_6$ illustrating intermolecular contacts.

the Co-N-Cl angles are indicative of such bonding, ranging from 108.02 to 114.78°.

Discussion

Gillespie and Nyholm[19] have suggested that the stereochemistry of most non-transition-element compounds seems to be dictated by the electrostatic repulsion between pairs of valence electrons located on the central atom, regardless of the nature of the pair of electrons, bonding or lone. Using this type of argument one would expect an $:XL_6$ compound such as $SbCl_6^{3-}$ to be either seven-coordinate, with the lone pair occupying a bonding site, or an irregular octahedron. However, the three crystallographically independent bonds in $SbCl_6^{3-}$ average 2.643 (6) Å with no significant difference between them. The Cl-Sb-Cl angles all range from 88.90 to 91.10°. The equality of all the Sb-Cl distances and the very slight variation of the Cl-Sb-Cl angles from 90° indicate that the lone pair in $SbCl_6^{3-}$ does not occupy a coordination site, but rather is in a spherically symmetric s orbital; this is also consistent with the Mossbauer work of Birchall.[20] Essentially octahedral symmetry was also found for the $SbBr_6^{3-}$ anions.[4-7] Moreover, if in each case the bond length in the anion is compared to that in the simple trihalide, lengthen-

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[17] C. K. Johnson, "ORTEP, a Fortran Thermal-Ellipsoid Plot Program for the Crystal Structure Illustrations," Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

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[19] R. J. Gillespie and R. S. Nyholm, *Quart. Rev., Chem. Soc.*, 11 339 (1957).

[20] B. Della Valle, E. Martineau, J. B. Milne, and T. Birchall, *J. Chem. Soc. A*, 1855 (1971).

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.

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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, α = 104.97 (3)°, β = 101.81 (4)°, γ = 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, α = 104.97 (3)°, β = 101.81 (4)°, γ = 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, ρ_{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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(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 + + +.