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Molecules with an M₄X₄ Core. V.[1-4] Crystallographic Characterization of the Tetrameric "Cubane-Like" Species Triethylphosphinecopper(I) Chloride and Triethylphosphinecopper(I) Bromide. Systematics in the [PEt₃CuX]₄ Series

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The tetrameric species triethylphosphinecopper(I) chloride, [PEt₃CuCl]₄, and triethylphosphinecopper(I) bromide, [PEt₃CuBr]₄, have been synthesized and their molecular parameters determined *via* single-crystal X-ray diffraction studies. Each crystallizes in the noncentrosymmetric polar space group $I\bar{4}3m$ (T_d^3; No. 217) with $Z = 2$. X-Ray diffraction data complete to $2\theta = 50°$ (Mo Kα radiation) were collected with a Picker FACS-1 automated diffractometer. Unit cell constants are $a = 12.5924$ (18) Å for [PEt₃CuCl]₄ and $a = 12.7495$ (18) Å for [PEt₃CuBr]₄. All atoms were located, final discrepancy indices being $R_F = 2.10\%$ and $R_{wF} = 2.41\%$ for [PEt₃CuCl]₄ and $R_F = 1.81\%$ and $R_{wF} = 1.73\%$ for [PEt₃CuBr]₄. Each of the tetrameric molecules lies on a site of T_d ($\bar{4}3m$) symmetry with methylene groups and methyl hydrogens disordered about crystallographic mirror planes. The four copper and four halogen atoms, taken alternately, define a "cubane-like" arrangement in which Cu–(μ_3-Cl) = 2.4383 (10) Å and Cu–(μ_3-Br) = 2.5436 (8) Å. Intramolecular Cu⋯Cu distances are 3.2111 (16) Å for [PEt₃CuCl]₄ and 3.1836 (18) Å for [PEt₃CuBr]₄; intramolecular halogen⋯halogen contacts are close to the sum of their van der Waals radii, with Cl⋯Cl = 3.6567 (22) Å and Br⋯Br = 3.9324 (13) Å. The completion of these two structural studies allows a detailed comparison of molecular parameters in the isomorphous and isostructural series [PEt₃CuX]₄ (X = Cl, Br, I).

Introduction

We have recently completed a series of X-ray diffraction studies on the tetrameric triphenylphosphinecopper(I) halides [PPh₃CuX]₄ (X = Cl,[1] Br,[2] I[4]). The most important result from this work was the discovery that the Cu₄Cl₄ core of [PPh₃CuCl]₄ has the well-known "cubane-like" stereochemistry (see structure I) whereas the Cu₄X₄ cores of both [PPh₃CuBr]₄ and [PPh₃CuI]₄ have "step" structures (see structure II). A secondary result was an indication that, regardless of the gross molecular configuration, the geometry of the individual four-membered Cu₂X₂ rings which constitute each of the structures is dictated primarily by interatomic repulsions.

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I   II
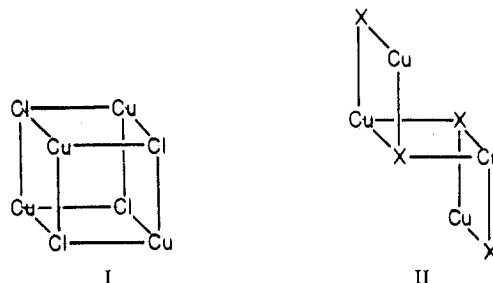
The "step" structure has been found only in those [PR₃CuX]₄ species which contain both bulky phosphine ligands and large halogen atoms. Thus [PEt₃CuI]₄ has been shown to have a "cubane-like" Cu₄I₄ core (see structure III).

III
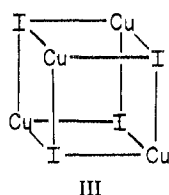
We decided to synthesize and to determine the crystal structures of [PEt₃CuCl]₄ and [PEt₃CuBr]₄ (each of which we expected to have a "cubane-like" structure analogous to the iodo derivative) so that information on the geometry of the Cu₄X₄ cores within a set of *isostructural* [PR₃CuX]₄ (X = Cl, Br, I) complexes could be collected and a detailed metric comparison made.

As outlined below, the three triethylphosphinecopper(I) halide molecules are, indeed, isostructural and comparisons of their molecular parameters are rendered even more meaningful by the discovery that the species are also isomorphous.

Experimental Section

Synthesis of [PEt₃CuCl]₄. This complex had previously been synthesized by Jardine et al.[6] via the reduction of CuCl₂·2H₂O with PEt₃ in ethanol. The sample used for our crystallographic investigation was prepared by a modification of the method used by Mann et al.[7] for preparing [PEt₃CuI]₄.

Approximately 3 ml of PEt₃ (2.4 g, 20 mmol) was added to excess CuCl (3 g, 30 mmol) in toluene (50 ml) under a positive pressure of prepurified nitrogen. The mixture was stirred for 16 hr at 80–85° and the resulting slurry was filtered hot and washed with hot toluene under nitrogen. After reheating of the filtrate with additional toluene, slow cooling yielded large (up to (~5 mm)³) colorless crystals of [PEt₃CuCl]₄. Anal. Calcd for C₂₄H₆₀Cl₄Cu₄P₄: C, 33.19; H, 6.96; Cl, 16.33; Cu, 29.26; P, 14.26. Found (Galbraith Laboratories): C, 33.37; H, 6.81; Cl, 16.49; Cu, 29.46; P, 13.90.

Note that, unlike [PEt₃CuI]₄, this complex is air sensitive and is converted slowly into [Cu₄OCl₆(OPEt₃)₄] from either solutions or the solid state.[8]

Synthesis of [PEt₃CuBr]₄. This is a new compound. It was synthesized via a modification of the procedure used by Jardine et al.[6] to prepare [PEt₃CuCl]₄.

To a solution of CuBr₂ (2.01 g, 9 mmol) in absolute ethanol (100 ml) under prepurified nitrogen was added 2 ml (1.6 g, 13.5 mmol) of PEt₃. The solution immediately decolorized and a white solid quickly appeared. The solution was stirred for 15 min at room temperature and the white solid was isolated by filtration. Colorless dodecahedral crystals suitable for X-ray diffraction studies were obtained by dissolving this material in warm (steam bath) toluene under nitrogen and allowing the solution to cool slowly.

Collection of X-Ray Diffraction Data for [PEt₃CuCl₄]. The crystal employed for data collection was an irregular block, of maximum dimensions 0.60 mm × 0.56 mm × 0.42 mm, which had been broken from a larger crystal. The crystal approximated to a polyhedron of seven faces, three of which were true crystallographic faces of the form {110} intersecting at the (defined) origin. The remaining faces were rather rough surfaces at distances ranging from 0.27 mm to 0.39 mm from the origin. The crystal was carefully wedged into a thin-walled glass capillary, which was then flushed with nitrogen, flame-sealed, and mounted in a brass pin on a eucentric goniometer.

A preliminary photographic study using precession and cone-axis photographs showed that the crystal was cubic, provided an approximate value for the cell edge, and showed the systematic absences *hkl* for *h* + *k* + *l* = 2*n* + 1 (only). The diffraction pattern seemed to have *m3m* (*O*ₕ) symmetry, but the possibility that the true Laue symmetry was only *m3* (*T*ₕ) was considered and tested (vide infra). Possible space groups based on the systematic absences are as follows: *I*23 [*T*³; No. 197], *I*2₁3 [*T*⁵; No. 199], *Im*3 [*T*ₕ⁵; No. 204]—all of *m3* Laue symmetry; *I*432 [*O*⁵; No. 211], *I*43̄*m* [*T*d³; No. 217], *Im3m* [*O*ₕ⁹; No. 229]—all of *m3m* Laue symmetry.[9] Of these, all but *I*23 and *I*43̄*m* would require disorder of *all* atoms in any tetramer. The successful solution of the structure shows the true space group to be the noncentrosymmetric polar space group *I*43̄*m*.

The crystal was transferred to a Picker FACS-1 diffractometer,[10] was accurately centered, and was aligned so that [111] was coincident

Table I. Statistical Study of the Merging of Intensity Data (Both before and after Correction for Absorption)

	Before absorption cor		After absorption cor	
	6 forms averaged (*m3m*)	3 forms averaged (*m3*)	6 forms averaged (*m3m*)	3 forms averaged (*m3*)
(A) [PEt₃CuCl]₄ (1012 Obsd Data)				
$R(F^2)^a$	5.385%	5.357%	2.229%	2.131%
$R(wF^2)^b$	6.843%	6.698%	4.082%	3.835%
$\Delta/\sigma > 1^c$	574	555	312	273
$\Delta/\sigma > 2$	300	294	44	35
$\Delta/\sigma > 3$	137	137	5	5
(B) [PEt₃CuBr]₄ (1063 Obsd Data)				
$R(F^2)$	13.662%		1.980%	
$R(wF^2)$	14.106%		3.724%	
$\Delta/\sigma > 1$	649		206	
$\Delta/\sigma > 2$	426		13	
$\Delta/\sigma > 3$	305		0	

^{a} $R(F^2) = \Sigma |F^2 - F^2_{av}|/\Sigma |F^2|$ where the sums are over every datum averaged [i.e., there are 6 (or 3) terms for each average value produced]. F^2_{av} is defined in ref 12. ^{b} $R(wF^2) = \{\Sigma[|F^2 - F^2_{av}|/\sigma(F^2)]^2/\Sigma[F^2/\sigma(F^2)]^2\}^{1/2}$ where the sums are as in footnote a. ^{c} $\Delta/\sigma = |F^2 - F^2_{av}|/\sigma(F^2)$.

with the instrumental φ axis. Using "high-resolution" conditions, the 2θ, ω, and χ settings of the resolved Mo Kα₁ components (λ 0.709300 Å)[11] of 12 high-angle reflections (9 forms of {0,10,10} and 3 forms of {0,0,14}; 2θ = 46–47°) were determined. These values were used in a least-squares refinement of cell and orientation parameters, yielding *a* = 12.5924 (18) Å at a temperature of 24.8 ± 0.5°. The unit cell volume is 1996.8 (9) Å³; the calculated density is 1.445 g cm⁻³ for mol wt 868.61 and *Z* = 2.

Prior to the collection of intensity data, the strong axial 222 reflection was measured by θ–2θ scans at χ = 90° and at 10° intervals from φ = 0° to φ = 350°. The variation in intensity as a function of φ [((maximum – minimum)/(average)) = 16.93%] indicated that an absorption correction would be required. When these "φ-scan" data were later corrected for absorption, the variation of intensity with φ was substantially reduced (to 7.42%). [This acts as a check on the validity of the absorption correction.]

The crystal was now deliberately offset (by 2.4° in a random direction) from its precise mounting along [111] so as to minimize the probability of multiple diffraction effects interfering with the intensity measurements. Following redetermination of the orientation matrix, intensity data [Mo Kα; Nb filter] for reflections of the type *h* + *k* + *l* = 2*n* in the range 1° < 2θ < 50°, with nonnegative *h*, *k*, and *l* indices, were collected using a coupled θ(crystal)–2θ(counter) scan from 0.70° in 2θ below the Mo Kα₁ peak to 0.70° above the Mo Kα₂ peak. The scan speed was 2.0°/min; backgrounds were counted for 20 sec each at the low and high 2θ limits of the scan. The takeoff angle was 3.0°, and the detector aperture was 3 mm wide (in 2θ) × 4 mm high (in χ) and was 330 mm from the crystal. Attenuators were used if the counting rate exceeded 10⁴ counts/sec. The crystal showed no evidence of decomposition over the course of data collection. During data collection, the intensities of three "check reflections" were measured after every 47 reflections. These standards remained constant, rms deviations from the mean being 0.54% for 611, 1.03% for 161, and 0.64% for 116.

The 1012 observed reflections were assigned estimated standard deviations (using counting statistics plus an "ignorance factor" of 0.02) and were reduced to values of |*F*₀| and σ(|*F*₀|) as described previously,[10] using the program RDUS2 (by B. G. DeBoer). Any reflection with a net negative count was assigned an |*F*₀| value of zero. No data were rejected on the basis of being "not significantly above background".

All data were corrected for absorption using the program DRAB by B. G. DeBoer. With μ = 26.168 cm⁻¹ for Mo Kα radiation, transmission factors ranged from 0.355 to 0.464.

Equivalent reflections were averaged,[12] using the program WAVE by B. G. DeBoer. The statistical results of this, based on data before and after correction for absorption and testing *m3m* Laue symmetry (the octant of data collected treated as six equivalent forms) vs. *m3* symmetry [one octant containing only three equivalent forms; (*hkl* = *lhk* = *klh*) ≠ (*khl* = *hlk* = *lkh*)], are collected in Table I. This tabulation provides striking evidence for the validity of the absorption

correction and suggests that the diffraction pattern has *m3m* symmetry.

Finally, those data with $(\sin \theta)/\lambda < 0.14$ were corrected for the systematic error caused by the high absorption by the Nb "β filter" of that part of the "white radiations streak" with $\lambda < 0.65291$ Å (the absorption edge for Nb). The method has been described previously.[10]

Collection of Data for [PEt₃CuBr]₄. The crystal of [PEt₃CuBr]₄ selected for the structural analysis was a quadrilateral prism bounded by $\pm(1\bar{1}0)$ and $\pm(01\bar{1})$ at separations of 0.14 and 0.16 mm, respectively. This prism was terminated by (110) and (011) at one end and by $(\bar{1}0\bar{1})$ at the other. Maximum dimensions were 0.37 mm × 0.28 mm × 0.17 mm. [Note that all three triethylphosphinecopper(I) halides crystallize in the dodecahedral {110} habit.] This crystal was caused to adhere to the interior of a thin-walled glass capillary with the aid of a small quantity of silicone grease; the capillary was flushed with nitrogen, sealed, and mounted as for the [PEt₃CuCl]₄ study (vide supra).

The course of data collection paralleled that for the isomorphous chloro analog, with the following differences.

(i) The cell edge, determined from 12 forms of {2,7,11} ($2\theta = 43.05°$) at $19.8 \pm 0.3°$, is 12.7495 (18) Å. The unit cell volume is 2072.4 (9) Å³; the calculated density is 1.677 g cm⁻³ for mol wt 1046.44 and $Z = 2$.

(ii) The variation [(maximum − minimum)/(average)] in intensity of the axial 222 reflection as a function of ϕ was 40.3%. Following correction for absorption this was reduced to 3.6%.

(iii) A total of 1063 reflections in the all-positive *hkl* octant and in the angular range $1° < 2\theta < 50°$ were measured as for the chloride, except that the offset from [111] was 2.9° and a smaller scan range [from 0.45° in 2θ below the Mo Kα₁ peak to 0.45° in 2θ above the Mo Kα₂ peak, at 1.0°/min] and detector aperture [3 mm × 3 mm] were found to be sufficient to encompass the narrower diffraction peaks.

(iv) Root-mean-square deviations in the intensities of the check reflections were 1.84% for 510, 2.50% for 105, and 1.85% for 051. However, application of a correction (to all data) for the systematic part of these fluctuations (which were apparently instrument related since they paralleled one another for all three reflections) reduced these values to 0.43%, 0.48%, and 0.55%, respectively.

(v) Corrections for absorption were calculated with a linear absorption coefficient of $\mu = 63.50$ cm⁻¹. Maximum and minimum transmission factors were 0.520 and 0.335.

(vi) Six-form averaging of the data yielded 215 independent reflections [see Table I].

(vii) Data with $(\sin \theta)/\lambda < 0.08$ were given a "β-filter" correction.

Again, the crystal gave no indication of decomposition over the course of data collection.

Solution and Refinement of the Structures. Programs used in the structure determination were as follows: LSHF (structure factor calculations and full-matrix least-squares refinement, by B. G. DeBoer), FORDAP (Fourier synthesis, by A. Zalkin), STAN1 (calculation of distances and angles, with estimated standard deviations, by B. G. DeBoer), PLOD (least-squares planes and lines, by B. G. DeBoer), and ORTEP (thermal ellipsoid drawings, by C. K. Johnson). All calculations were performed on the IBM 370/158 computer at the Computer Center of the University of Illinois at Chicago Circle.

Scattering factors used were in the analytical form of Cromer and Mann.[13] Values for neutral copper, phosphorus, bromine, chlorine, and carbon are from that compilation. For hydrogen, the "best floated spherical H atom" values of Stewart et al.[14] were converted into analytical form.[15] The values of Cromer and Liberman[16] were used for the real and imaginary components of anomalous dispersion for all nonhydrogen atoms.

The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = \sigma^{-2}$. Discrepancy indices used below are defined as

$$R_F = \left[\frac{\sum ||F_o| - |F_c||}{\sum |F_o|}\right] \times 100 \ (\%)$$

$$R_{wF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2}\right]^{1/2} \times 100 \ (\%)$$

The structure of [PEt₃CuCl]₄ was solved by assuming that the crystals were both isomorphous (space group $I\bar{4}3m$) and isostructural with the known species [PEt₃CuI]₄,[3] but with atomic coordinates
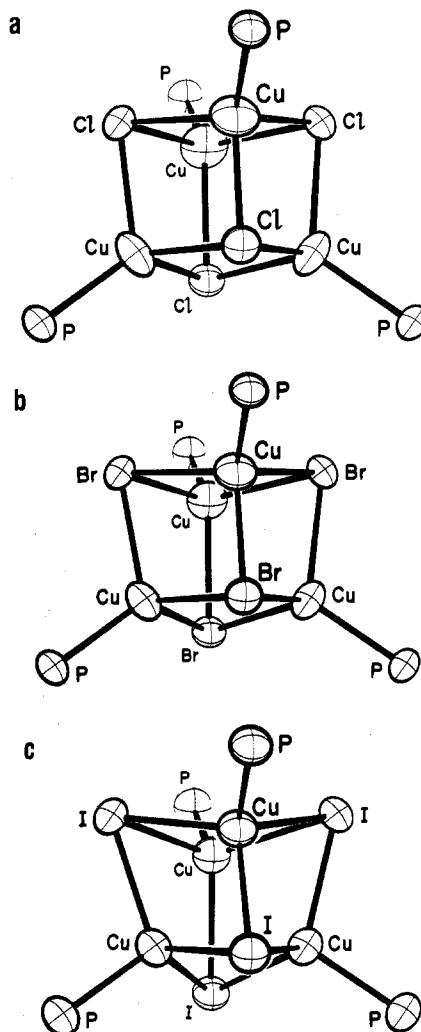

Figure 1. The $P_4Cu_4X_4$ cores of (a) [PEt₃CuCl]₄, (b) [PEt₃CuBr]₄, and (c) [PEt₃CuI]₄ showing the progressively increasing distortion from a regular "cubane-like" geometry.

slightly modified to give reasonable Cl···Cl and Cu–Cl distances. Initially, only the real parts of the anomalous dispersion corrections were included. Several cycles of least-squares refinement of the scale factor along with positional and anisotropic thermal parameters of all nonhydrogen atoms (25 variables in all) led to convergence with $R_F = 4.66\%$ and $R_{wF} = 9.78\%$ for the 205 independent (assuming *m3m* symmetry) reflections. A careful inspection of the observed and calculated structure factor amplitudes suggested that a correction for secondary extinction was necessary. A surprising observation was, however, that the worst agreement between $|F_o|$ and $|F_c|$ was for weak- or medium-intensity reflections at very low angle (002, $\Delta F = 71\sigma(|F_o|)$; 013, $\Delta F = 18\sigma$; 222, $\Delta F = 12\sigma$).

A secondary extinction parameter (*c*) was now included in the model. This parameter enters the equations for the corrected structure factor in the form[17-19]

$$F_{c,cor} = F_{c,uncor}(1 + c\beta F_{c,uncor}^2)^{-1/4}$$

where

$$\beta = \left(\frac{1 + \cos^4 2\theta}{(\sin 2\theta)(1 + \cos^2 2\theta)}\right)\left(\frac{-d \ln T}{d\mu}\right)$$

Continued refinement, now including the secondary extinction parameter (26 variables in all) led to convergence with $R_F = 3.30\%$ and $R_{wF} = 5.50\%$. An examination of observed and calculated structure factor amplitudes showed considerable improvement, but agreement for weak low-angle data was still very poor (viz.: 002, $\Delta F = 24\sigma$; 013, $\Delta F = 19\sigma$; 222, $\Delta F = 19\sigma$). We decided, therefore, to include the contributions from all hydrogen atoms. Hydrogen atoms were introduced in calculated positions[20] with $d(C-H) = 0.95$ Å.[21]

Table II. Final Positional Parameters with Esd's[a]

Atom	Site symmetry	x	y	z	B,[c] Å^2
		A. [PEt$_3$CuCl]$_4$[b]			
Cu	$3m$	0.590156 (42)	$=x$	$=x$	7.516
Cl	$3m$	0.397332 (60)	$=x$	$=x$	4.708
P	$3m$	0.689911 (62)	$=x$	$=x$	4.606
C(1)[d]	1	0.64174 (47)	0.71004 (65)	0.82406 (39)	7.073
C(2)	m	0.61105 (34)	$=x$	0.87951 (51)	12.199
H(1A)[d]	1	0.5813	0.7551	0.8210	
H(1B)[d]	1	0.6962	0.7437	0.8640	} 7.4 (13)
H(2A)[d]	1	0.5867	0.6277	0.9490	
H(2B)[d]	1	0.5560	0.5767	0.8411	} 16.0 (22)
H(2C)[d]	1	0.6708	0.5653	0.8841	
		B. [PEt$_3$CuBr]$_4$			
Cu	$3m$	0.411717 (47)	$=x$	$=x$	6.440
Br	$3m$	0.609048 (32)	$=x$	$=x$	4.751
P	$3m$	0.312119 (89)	$=x$	$=x$	4.764
C(1)[d]	1	0.35993 (57)	0.28978 (79)	0.18061 (55)	7.159
C(2)	m	0.38874 (40)	$=x$	0.12392 (59)	11.863
H(1A)[d]	1	0.4204	0.2465	0.1846	
H(1B)[d]	1	0.3068	0.2548	0.1418	} 8.6 (18)
H(2A)[d]	1	0.4133	0.3719	0.0556	
H(2B)[d]	1	0.4424	0.4243	0.1615	} 18.2 (29)
H(2C)[d]	1	0.3288	0.4326	0.1187	

[a] Esd's, shown in parentheses, are right adjusted to the last digit of the preceding number. They are derived from the inverse of the final least-squares matrix. [b] The coordinates given for [PEt$_3$CuCl]$_4$ are those for the actual crystal studied. Had a crystal of the opposite chirality fortuitously been selected, the resulting coordinates would be related to the present set by the transformation $(1 - x, 1 - y, 1 - z)$. This transformation may be used to compare coordinates for [PEt$_3$CuCl]$_4$ with those for the isomorphous species [PEt$_3$CuBr]$_4$ (see section B of this table), [PEt$_3$CuI]$_4$,[3] and [AsEt$_3$CuI]$_4$.[3] [c] For nonhydrogen atoms, the "equivalent isotropic" thermal parameters are given. For the full anisotropic thermal parameters, see Table III. [d] These atoms are disordered about the mirror plane at (x, x, z).

Table III. Anisotropic Thermal Parameters with Esd's[a,b]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U \rangle$[c]
			(A) [PEt$_3$CuCl]$_4$				
Cu	7.516 (35)	$=B_{11}$	$=B_{11}$	−2.109 (22)	$=B_{12}$	$=B_{12}$	0.204, 0.349, 0.349
Cl	4.708 (30)	$=B_{11}$	$=B_{11}$	−0.720 (29)	$=B_{12}$	$=B_{12}$	0.203, 0.262, 0.262
P	4.606 (34)	$=B_{11}$	$=B_{11}$	−0.731 (29)	$=B_{12}$	$=B_{12}$	0.200, 0.260, 0.260
C(1)	6.54 (24)	8.34 (33)	6.34 (28)	−1.31 (28)	0.42 (23)	−1.46 (29)	0.263, 0.277, 0.350
C(2)	14.64 (39)	$=B_{11}$	7.31 (30)	−6.88 (50)	1.29 (19)	$=B_{13}$	0.269, 0.344, 0.522
			(B) [PEt$_3$CuBr]$_4$				
Cu	6.440 (32)	$=B_{11}$	$=B_{11}$	−1.387 (26)	$=B_{12}$	$=B_{12}$	0.215, 0.315, 0.315
Br	4.751 (21)	$=B_{11}$	$=B_{11}$	−0.721 (16)	$=B_{12}$	$=B_{12}$	0.205, 0.263, 0.263
P	4.764 (41)	$=B_{11}$	$=B_{11}$	−0.744 (44)	$=B_{12}$	$=B_{12}$	0.204, 0.264, 0.264
C(1)	6.65 (40)	8.57 (50)	6.25 (37)	−2.10 (35)	0.24 (30)	−1.62 (37)	0.247, 0.280, 0.364
C(2)	14.19 (43)	$=B_{11}$	7.21 (36)	−6.76 (55)	0.48 (24)	$=B_{13}$	0.290, 0.319, 0.515

[a] See footnote a to Table I. [b] These anisotropic thermal parameters are analogous to the usual form of the isotropic thermal parameter and have units of Å^2. They enter the expression for the calculated structure factor amplitude in the form $\exp[-\frac{1}{4}a^{*2}(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{12} + 2klB_{23})]$. [c] These values are the root-mean-square amplitudes of vibration (in Å) of the atom along the three principal axes (minor, median, major, respectively) of its vibrational ellipsoid. For relative orientations, see the figures.

Continued refinement introducing two further parameters (overall group isotropic thermal parameters for (i) methylene hydrogens and (ii) methyl hydrogens) led to convergence with R_F = 2.83% and R_{wF} = 4.05%, and all major discrepancies between observed and calculated structure factor amplitudes were eliminated.

At this stage the imaginary components of anomalous dispersion for all nonhydrogen atoms were introduced. Since $I\bar{4}3m$ is a noncentrosymmetric space group, there are two enantiomeric crystal forms. The absolute configuration of the particular crystal selected for study was checked by refining the original set of positional parameters (x, y, z) [which now, upon inclusion of $\Delta f''$ values, converged with the increased residuals R_F = 3.60% and R_{wF} = 4.54%] and the inverted coordinates $(1 - x, 1 - y, 1 - z)$ [which converged to final values of R_F = 2.10% and R_{wF} = 2.41%]. Clearly, the inverted coordinates defined the true handedness of the crystal. The largest shift during the last cycle of refinement was 0.001σ. The final "goodness of fit", defined by $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, is 1.581 where m (the number of observations) was 205, n (the number of variables) was 28, and the ratio of observations to variables $(m{:}n)$ was 7.32:1. The final value for the secondary extinction parameter was c = 1.84 (53) × 10^{-6} mm^{-1} e^{-2}. The highest peaks on a final difference-Fourier synthesis were of height 0.19 e Å^{-3} (at 0.64, 0.56, 0.56—near Cu) and 0.18 e Å^{-3} (at 0.66, 0.66, 0.66—between Cu and P). All other peaks were less than 0.15 e Å^{-3} in height.

As a final check, we decided to test analytically whether the crystal belonged to the assumed space group $I\bar{4}3m$ [O_h diffraction symmetry] or whether it only approximated to $I\bar{4}3m$, the true space group being $I23$ [i.e., only T_h diffraction symmetry]. The lower symmetry space group corresponds to removing the mirror planes at $\{x, x, z\}$ and concomitantly changing the structure from a disordered to an ordered array. [Note that the disorder in space group $I\bar{4}3m$ involves only the methylene groups and the methyl hydrogens.]

A data set was prepared from the three-form averaged absorption-corrected data by deleting those reflections for which any pair of h, k, or l were equal (since their structure factors do not distinguish between the two sides of the "mirror plane"). Using the final parameters (methyl hydrogens omitted) from the refinement in space group $I\bar{4}3m$, we refined, in space group $I23$, the coupled occupancies of the methylene atoms on either side of the "mirror plane" using α and $1 - \alpha$ as the occupancies of the two sets. At convergence, the value of α was 0.4976 (60)—i.e., only 0.4σ from the value expected for a true crystallographic mirror plane. As α changed from its initial value of $\frac{1}{2}$, the residuals for the 268 data changed very little—from R_F = 2.543% to R_F = 2.539% and from R_{wF} = 3.111% to R_{wF} = 3.107%. An "R-factor ratio test"[22] indicates that the one-dimensional hypothesis that the final value of α is a better fit to the data may be either accepted or rejected at the 50% confidence level.

Table IV. Intramolecular Distances (Å) and Angles (deg) with Esd's for [PEt₃CuX]₄ Species[a,b]

Atoms	[PEt₃CuCl]₄	[PEt₃CuBr]₄	[PEt₃CuI]₄[c]
		Distances	
Cu···Cu	3.2111 (16)	3.1836 (18)	2.9272 (20)
X···X	3.6567 (22)	3.9324 (13)	4.3800 (11)
Cu–X	2.4383 (10)	2.5436 (8)	2.6837 (13)
Cu···X	4.2056 (16)	4.3576 (14)	4.4748 (14)
Cu–P	2.1757 (17)	2.1994 (22)	2.2538 (27)
P–C(1)	1.813 (5)	1.807 (7)	1.766 (15)
C(1)–C(2)	1.480 (10)	1.500 (11)	1.510 (21)
C(1)···C(1')	1.216 (15)	1.265 (18)	1.360 (45)
		Angles	
X–Cu–X	97.15 (4)	101.25 (3)	109.38 (4)
X–Cu–P	120.02 (3)	116.80 (2)	109.56 (8)
Cu–X–Cu	82.36 (5)	77.48 (4)	66.10 (4)
Cu–P–C(1)	115.2 (2)	115.6 (3)	117.0 (10)
C(1)–P–C(1)	103.2 (3)	102.7 (3)	101.0 (6)
P–C(1)–C(2)	114.2 (5)	113.4 (6)	113.6 (13)

[a] Esd's were calculated from the full correlation matrix, using the Fortran IV program STAN1, by B. G. DeBoer. Errors in the unit cell parameter are included. [b] Bond lengths have not been corrected for any possible systematic errors due to thermal motion. [c] These data are from ref 3.

We conclude, therefore, that the true space group is, indeed, $I\bar{4}3m$.

The structure of the bromo derivative was solved by taking all parameters from the solution of the structure of [PEt₃CuCl]₄. Refinement (omitting all $\Delta f''$ values) converged with $R_F = 2.64\%$ and $R_{wF} = 2.82\%$. Upon inclusion of $\Delta f''$ values for all nonhydrogen atoms, refinement to convergence resulted in the increased residuals $R_F = 3.82\%$ and $R_{wF} = 4.60\%$. Clearly, the crystal had the opposite hand to that which we had been assuming (i.e., we had selected a crystal with the opposite chirality to that of the chloro analog). All positional coordinates (x, y, z) were therefore inverted to the values $1 - x, 1 - y, 1 - z$; several cycles of full-matrix least-squares refinement (28 parameters) led to final convergence with $R_F = 1.81\%$ and $R_{wF} = 1.73\%$. The largest shift in the final cycle of refinement was 0.002σ. The "goodness of fit" was 1.085 where $m = 215$, $n = 28$, and $m:n = 7.68:1$. The final value for the secondary extinction parameter was $c = 4.36$ (62) $\times$ 10⁻⁶ mm⁻¹ e⁻². The largest peaks on a difference-Fourier synthesis were of height 0.23 e Å⁻³ (at 0.44, 0.44, 0.36) and 0.18 e Å⁻³ (at 0.36, 0.44, 0.34) and were each close to the position of the copper atom.

Tables of the observed and calculated structure factor amplitudes for both [PEt₃CuCl]₄ and [PEt₃CuBr]₄ appear as supplementary material. [See paragraph at the end of this article.]

Positional parameters for the two species are shown in Table II; anisotropic thermal parameters are collected in Table III.

Discussion

Views of the [PEt₃CuCl]₄, [PEt₃CuBr]₄, and [PEt₃CuI]₄[3] molecules are shown in Figure 1 and 2.

Each of the species [PEt₃CuX]₄ (X = Cl, Br, I) has a cubane-like Cu₄X₄ core of precise (i.e., crystallographically imposed) T_d symmetry. The three complexes are both isomorphous and isostructural, the molecules in each case sitting on sites of T_d symmetry with ethyl groups being disordered about the crystallographic mirror planes at {x, x, z}. The tetrameric units are mutually separated by normal van der Waals distances; there are no abnormally short intermolecular contacts.

Intramolecular distances and angles within the [PEt₃CuCl]₄ and [PEt₃CuBr]₄ molecules are compared in Table IV with those previously found for [PEt₃CuI]₄. Least-squares planes within the [PEt₃CuCl]₄ and [PEt₃CuBr]₄ molecules are collected in Table V.

As outlined in the Introduction, the basic purpose of this work was to ascertain how the geometry of [Et₃PCuX]₄ species changes as the halogen atoms are varied successively from iodine to bromine to chlorine. The most obvious effect is that the cubane framework becomes more regular (i.e., all internal angles closer to 90°) as the size of the halogen atom decreases.
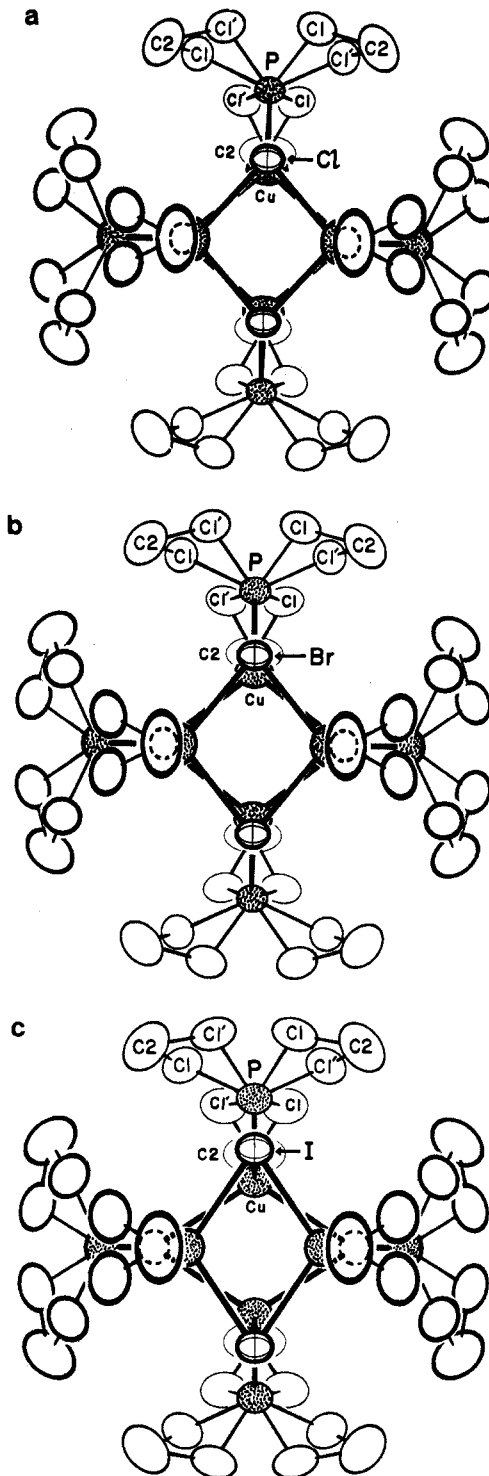

Figure 2. The "cubane-like" molecules (a) [PEt₃CuCl]₄, (b) [PEt₃CuBr]₄, and (c) [PEt₃CuI]₄ viewed down their crystallographic S_4 axes. Note the increasing acuteness of the Cu–X–Cu angles. (Copper and phosphorus atoms have been stippled for the sake of clarity.)

Other systematic changes from I to Br to Cl are as follows.

(1) The thermal parameters of the copper atoms increase systematically from 5.98 Å² for [PEt₃CuI]₄ to 6.44 Å² for [PEt₃CuBr]₄ and 7.52 Å² for [PEt₃CuCl]₄. [Values given are "equivalent isotropic" thermal parameters.] These values are all rather high for polynuclear transition metal complexes. The copper atoms are held less rigidly as the size of the halogen atoms decreases. This suggests that there are no appreciable copper···copper interactions. [Note that thermal parameters for metal atoms in metal–metal bonded clusters are frequently

Table V. Planes[a] and Dihedral Angles

Atom	Dev, Å	Atom	Dev, Å
	(A) [PEt₃CuCl]₄		

Plane I: $0.0691X + 0.0691Y + 0.9952Z = 8.422$

Atom	Dev, Å	Atom	Dev, Å
Cu(x, x, x)*	0.000	Cu(1 − x, 1 − x, x)	−0.314
Cl(x, 1 − x, 1 − x)*	0.000		
Cl(1 − x, x, 1 − x)*	0.000		

Plane II: $-0.0691X - 0.0691Y + 0.9952Z = 6.683$

Atom	Dev, Å	Atom	Dev, Å
Cu(1 − x, 1 − x, x)*	0.000	Cu(x, x, x)	−0.314
Cl(x, 1 − x, 1 − x)*	0.000		
Cl(1 − x, x, 1 − x)*	0.000		

Plane III: $-0.0607X + 0.0607Y + 0.9963Z = 7.404$

Atom	Dev, Å	Atom	Dev, Å
Cu(x, x, x)*	0.000	Cl(x, 1 − x, 1 − x)	+0.314
Cu(1 − x, 1 − x, x)*	0.000		
Cl(1 − x, x, 1 − x)*	0.000		

Plane IV: $0.0607X - 0.0607Y + 0.9963Z = 7.404$

Atom	Dev, Å	Atom	Dev, Å
Cu(x, x, x)*	0.000	Cl(1 − x, x, 1 − x)	+0.314
Cu(1 − x, 1 − x, x)*	0.000		
Cl(x, 1 − x, 1 − x)*	0.000		

Dihedral Angles: I–II = 168.79°; III–IV = 170.15°

(B) [PEt₃CuBr]₄

Plane I: $0.1160X + 0.1160Y + 0.9865Z = 6.396$

Atom	Dev, Å	Atom	Dev, Å
Cu(x, x, x)*	0.000	Cu(1 − x, 1 − x, x)	+0.522
Br(x, 1 − x, 1 − x)*	0.000		
Br(1 − x, x, 1 − x)*	0.000		

Plane II: $-0.1160X - 0.1160Y + 0.9865Z = 3.438$

Atom	Dev, Å	Atom	Dev, Å
Cu(1 − x, 1 − x, x)*	0.000	Cu(x, x, x)	+0.522
Br(x, 1 − x, 1 − x)*	0.000		
Br(1 − x, x, 1 − x)*	0.000		

Plane III: $-0.0944X + 0.0944Y + 0.9911Z = 5.202$

Atom	Dev, Å	Atom	Dev, Å
Cu(x, x, x)*	0.000	Br(x, 1 − x, 1 − x)	−0.525
Cu(1 − x, 1 − x, x)*	0.000		
Br(1 − x, x, 1 − x)*	0.000		

Plane IV: $0.0944X - 0.0944Y + 0.9911Z = 5.202$

Atom	Dev, Å	Atom	Dev, Å
Cu(x,,x, x)*	0.000	Br(1 − x, x, 1 − x)	−0.525
Cu(1 − x, 1 − x, x)*	0.000		
Br(x, 1 − x, 1 − x)*	0.000		

Dihedral Angles: I–II = 161.11°; III–IV = 164.66°

[a] Cartesian coordinates (i.e., X = ax, Y = ay, Z = az). Only atoms atoms marked with an asterisk were used in the calculation of the plane. Calculations were performed using the program PLOD, by B. B. G. DeBoer.

very low—i.e., $B < 2$ Å².] The halogen atoms have lower thermal parameters than the copper atoms and these thermal parameters decrease systematically as the size of the halogen atom decreases—5.68 Å² for I in [PEt₃CuI]₄, 4.75 Å² for Br in [PEt₃CuBr]₄, and 4.71 Å² for Cl in [PEt₃CuCl]₄.

(2) Copper–halogen distances change in the same order as the covalent radii of the halogen atoms, but (as might be expected with triply bridging halogen atoms) the magnitude of the change is less. Thus, Cu–I = 2.6837 (13) Å, Cu–Br = 2.5436 (8) Å, and Cu–Cl = 2.4383 (10) Å; the decrements are 0.1401 and 0.1053 Å, respectively. For comparison, the appropriate covalent radii are[23] 1.33 Å for I, 1.14 Å for Br, and 0.99 Å for Cl—decrements being 0.19 and 0.15 Å.

(3) Intramolecular halogen···halogen interactions appear to make an important contribution to the gross molecular stereochemistry. Thus, I···I in [PEt₃CuI]₄ is 4.3800 (11) Å, Br···Br in [PEt₃CuBr]₄ is 3.9324 (13) Å, and Cl···Cl in [PEt₃CuCl]₄ is 3.6567 (22) Å. These distances closely parallel the sums of the van der Waals radii for the appropriate interactions, i.e., 4.30 Å for I···I, 3.90 Å for Br···Br, and 3.60 Å for Cl···Cl.[24] [Note that Pauling stated that his listed van der Waals *radii* "...are to be considered as reliable only to 0.05 or 0.10 Å".]

(4) Copper···copper distances increase systematically from

2.9272 (20) Å in [PEt₃CuI]₄ to 3.1836 (18) Å in [PEt₃CuBr]₄ and 3.2111 (16) Å in [PEt₃CuCl]₄. These distances are strongly dependent on the chemically and structurally more important Cu–X and X···X distances—in fact, in the approximation that the Cu₂X₂ faces of the cubane moieties are planar, the three distances are related by the Pythagoras theorem, i.e., $(Cu-X)^2 = [^1/_2(Cu···Cu)]^2 + [^1/_2(I···I)]^2$.

(5) The angles Cu–X–Cu increase regularly from 66.10 (4)° in [PEt₃CuI]₄ to 77.48 (4)° in [PEt₃CuBr]₄ and 82.36 (5)° in [PEt₃CuCl]₄; the angles X–Cu–X concomitantly decrease, with values of 109.38 (4)° (i.e., close to a regular tetrahedral angle) for [PEt₃CuI]₄, 101.25 (3)° for [PEt₃CuBr]₄, and 97.15 (4)° for [PEt₃CuCl]₄.

(6) The X–Cu–P angles, which are directly dependent on the X–Cu–X angles, increase systematically from 109.56 (8)° in [PEt₃CuI]₄ to 116.80 (2)° in [PEt₃CuBr]₄ and 120.02 (2)° in [PEt₃CuCl]₄.

(7) Copper–phosphorus distances decrease systematically from 2.2538 (27) Å in [PEt₃CuI]₄ to 2.1994 (22) Å in [PEt₃CuBr]₄ and 2.1757 (17) Å in [PEt₃CuCl]₄. These variations *may* simply reflect changes in hybridization at the four-coordinate copper(I) atoms. However, the direction of the change is such as to lead us to suggest that the decreases in Cu–P distance make up for the increasing polarization of the Cu–X bond as the electronegativity of X increases. [The pertinent Allred–Rochow electronegativities[25] are 2.21 for I, 2.74 for Br, and 2.83 for Cl. The values for phosphorus and copper are 2.06 and 1.75, respectively.]

(8) The Cu₂X₂ faces of the cubane structures become closer to planarity as the size of the halogen atom diminishes. Thus, the dihedral angles about the X···X axes are 141.32° in [PEt₃CuI]₄, 161.11° in [PEt₃CuBr]₄, and 168.79° in [PEt₃CuCl]₄. Dihedral angles about the Cu···Cu vectors are 153.60, 164.66, and 170.15° (respectively).

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC50073L-9-75.

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to be "averaged away" by the factor $N^{1/2}$. The value of $\sigma(F^2_{av})$ was further *increased* by a factor of $\{[\sum(F^2 - F^2_{av})/\sigma^2(F^2)]/(N - 1)\}^{1/2}$ if that quantity was >1.0. (N = number of F^2 values averaged.)

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Crystal Structure and Molecular Geometry of Ir(B5H8)Br2(CO)(PMe3)2, a Product from the Oxidative Addition of Bromopentaborane to IrCl(CO)(PMe3)2, and Some Comments on the Structural Trans Influence of σ-Bonded Boron

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The complex Ir(B5H8)Br2(CO)(PMe3)2, a product from the oxidative addition of (1- or 2-) BrB5H8 to IrCl(CO)(PMe3)2, has been examined by a single-crystal X-ray diffraction study. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ [C^5_{2h}; No. 14] with $a = 13.824$ (4) Å, $b = 10.661$ (3) Å, $c = 13.611$ (3) Å, and $\beta = 104.90$ (2)°. Observed and calculated densities are ρ(obsd) = 2.012 and ρ(calcd) = 2.036 g cm^{-3} for mol wt 594.3 and $Z = 4$. X-Ray diffraction data complete to $2\theta = 45°$ (Mo Kα radiation) were collected with a Picker FACS-1 automated diffractometer and the structure was solved via the use of Patterson, Fourier, and least-squares refinement techniques. All atoms other than the hydrogen atoms associated with the methyl groups have been located, the final discrepancy indices being $R_F = 4.84\%$ and $R_{wF} = 4.88\%$ for the 2558 independent reflections. The molecular geometry thus determined shows the complex to be *cis*-dibromo-*trans*-bis(trimethylphosphine)(2-pentaboranyl)carbonyliridium(III). The geometry about the central iridium(III) atom approximates to octahedral, with cis angles ranging from 86.19 (8) to 93.54 (36)° and trans angles from 172.17 (10) to 177.81 (38)°. The two iridium–phosphorus distances are 2.362 (3) and 2.361 (3) Å, while iridium–bromine distances are Ir–Br(1) = 2.638 (1) Å [trans to σ-bonded boron] and Ir–Br(2) = 2.516 (1) Å [trans to a carbonyl ligand]. σ-Bonded boron thus seems to exert a strong trans-lengthening effect, as does σ-bonded carbon in metal alkyls. The pentaboranyl ligand is bonded to iridium via its basal (2) position, with Ir–B(2) = 2.071 (14) Å. Distances within the square-pyramidal B5H8 moiety are as follows: B(apical)–B(basal) = 1.641 (21)–1.691 (18) Å, B(basal)–B(basal) = 1.805 (20)–1.912 (18) Å, B–H(terminal) = 1.08 (8)–1.55 (11) Å, and B–H(bridging) = 1.03 (14)–1.45 (10) Å.

Introduction

The oxidative addition of boron halides and diphenylboron halides to [(C5H5)2Ti]2, (diphos)2Co, and (Ph3P)4Pt was reported some years ago.[1] Oxidative addition of boron–hydrogen bonds has been shown to lead to such species as Ir-(H)(Cl)[C2B10H10PMe2][C2B10H11PMe2]2[2] and 3-[(PPh3)2Ir(H)Cl]-1,2-C2B10H11;[3] in addition to this, hydridometallocarboranes have been used as homogeneous catalysts[4] and deuterated boron hydrides have been prepared by transition metal catalyzed exchange of deuterium gas with terminal boron–hydrogen bonds.[5]

Recently, Davison and his coworkers[6] have studied the reaction of 1-BrB5H8 and 2-BrB5H8 with IrCl(CO)(PMe3)2 and found the identical product, Ir(B5H8)Br2(CO)(PMe3)2, in each case. We have examined this product of oxidative addition and metathesis by means of a single-crystal X-ray structural analysis. A preliminary report of this work has appeared previously;[6] a full account appears below.

Collection of the X-Ray Diffraction Data

Yellow crystals of the complex were provided by Professor A. Davison of Massachusetts Institute of Technology. The crystal used for the diffraction study was needle shaped, being 0.63 mm in length (along [101]) and having a cross section of 0.175 mm × 0.191 mm. It was mounted along its extended [101] direction. Preliminary photographic studies, using Weissenberg, rotation, precession, and

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cone-axis techniques, revealed the approximate unit cell dimensions, showed C_{2h} (2/m) Laue symmetry, and indicated the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$. These extinctions suggest that the crystal belongs to the centrosymmetric monoclinic space group $P2_1/c$ [C^5_{2h}; No. 14].

The crystal was transferred to a Picker FACS-1 diffractometer, was accurately centered, and was aligned with [101] precisely coincident with the instrumental ϕ axis.

As a check on absorption, the intensity of the strong axial 202 reflection was measured at $\chi = 90°$ and at 10° intervals from $\phi = 0°$ to $\phi = 350°$. The resulting variation in intensity as a function of ϕ [(maximum – minimum)/(average) = 29%] indicated that an absorption correction would be necessary. The "ϕ-scan" data were processed along with the primary data set; following correction for absorption the ϕ dependence of the 202 reflection was reduced to 3.5%, thus confirming the validity of the absorption correction.

Details of the data collection are provided in Table I; the apparatus and experimental technique have been described previously.[7]

We note here that the crystal was severely affected by X irradiation. The three check reflections decreased steadily during data collection—202 by 41%, 502 by 23%, and 131 by 15%; all data were brought to a common scale by the use of an anisotropic linear-decay correction.[8]

Solution and Refinement of the Structure

Programs used in determining the structure include FORDAP (Fourier synthesis, by A. Zalkin), LSHF (structure factor calculations with full-matrix least-squares refinement, by B. G. DeBoer), STAN1 (distances and angles with their esd's, by B. G. DeBoer), PLOD (least-squares planes and lines, by B. G. DeBoer), and ORTEP (thermal