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Preparation, Characterization, and Solution Behavior of Tri-*tert*-butylphosphine Complexes of Copper(I) Halides and Crystal Structure of Bromo(tri-*tert*-butylphosphine)copper(I) Tetramer

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Received March 23, 1982

The 1:1 complexes $CuXP(t\text{-}Bu)_3$, X = Cl, Br, and I, have been isolated from the reaction of copper(I) halides with tri-*tert*-butylphosphine. Solutions of all the three complexes, in 1,2-dichloroethane, are nonconducting; molecular weight measurements in the same solvent indicate the presence of monomeric species in the case of the chloro complex and dimeric species in the case of the bromo as well as the iodo complex. The infrared and Raman spectra for all of the three complexes, in the solid state, are indicative of a cubane-type tetrameric structure, which has been confirmed for the bromo complex by a single-crystal structure analysis. Crystals of $[CuBrP\text{-}t\text{-}Bu_3]_4$ belong to space group $P\bar{3}$, with a = 14.008 (3) Å and c = 19.416(3) Å. The unit cell contains two tetrameric molecules with a cubane-type Cu_4Br_4 core. The molecule occupies a crystallographic threefold axis, and the overall geometry is close to T_d. The pertinent bond lengths and angles are as follows (averages): Cu–Br = 2.593 Å, Cu–P = 2.228 Å, Br–Cu–Br = 95.3°, and Cu–Br–Cu = 84.5°. The steric hindrance due to the bulky $t\text{-}Bu_3P$ ligand induces a significant lengthening of the Cu–P bonds and reduces the Br···Br contacts to 3.83 Å. The conformation of the *tert*-butyl groups in this and similar compounds is discussed. Addition of excess $P(t\text{-}Bu)_3$ to the 1:1 complexes, in dichloromethane, results in the formation of the 1:2 complexes, which are indicated to be ionic species containing the two-coordinate cation $Cu[P(t\text{-}Bu)_3]_2^+$, as shown by the $^{31}P\{^1H\}$ NMR and conductance data. Phosphorus-31 NMR measurements show that the 1:2 complexes undergo fast ligand exchange with excess phosphine at ambient probe temperature; the spectra at 183 K show characteristic resonances due to the 1:2 complexes and free phosphine.

Introduction

Monodentate tertiary phosphines and arsines form with Cu(I) a number of mono- and polynuclear complexes showing a variety of stoichiometries and structures.[2a] A series of 1:1 compounds with CuX and AgX (X = Cl, Br, and I) was investigated by Churchill and co-workers[2b-11] and by Teo and Calabrese.[12-14] The tetrameric "cubane" structure was found to be the most common, although an open "chair" (or "step") structure was also observed in several cases. For $[AgIPPh_3]_4$, both isomers were isolated in the solid state by Teo and Calabrese[13] and the structures of the two forms were compared to determine structural parameters likely to be involved in the cubane ⇌ chair isomerization. According to these authors,[13] the most important parameter is the steric repulsion of the phosphine alkyl or aryl groups with those of the adjacent phosphines and with the nearby halogens. They concluded that, when the size of the phosphine increases, the cubane core undergoes increasingly large distortions and eventually opens into the chair form. With very bulky phosphines, the latter form apparently tends to break further into smaller units, as observed by Churchill and Rotella[10] for the 1:1 complex of tricyclohexylphosphine with copper(I) chloride, which exists as a halide-bridged dimer.

Table I. ^{31}P NMR, Conductance, and Molecular Weight Data

stoichiometry	$\delta^{a,b}$	$\Lambda_M{}^c$	mol wt found^d	mol wt calcd
$CuClP(t\text{-}Bu)_3$	50.5	3.0	304	301
$CuBrP(t\text{-}Bu)_3$	44.8	0.6	625	346
$CuIP(t\text{-}Bu)_3$	...	0.2	697	393
$Cu[P(t\text{-}Bu)_3]_2Cl$	58.5	10.2		
$Cu[P(t\text{-}Bu)_3]_2Br$	58.6	11.8		
$Cu[P(t\text{-}Bu)_3]_2I$	58.6	23.9		

[a] For concentrated solutions in CH_2Cl_2 containing 20% CD_2Cl_2 at 183 K. [b] δ(free phosphine) = 55.8. [c] In Ω^{-1} cm² mol⁻¹ for 10^{-3} M solutions in 1,2-dichloroethane at 20 °C. [d] For solutions in 1,2-dichloroethane.

In a continuing investigation on tri-*tert*-butylphosphine complexes of group 1B[15,16] and 2B[17-22] metals, complexes of copper(I) halides were investigated in this work. Treatment of copper(I) halides with phosphine readily afforded the 1:1 complexes $CuXP(t\text{-}Bu)_3$. Since tri-*tert*-butylphosphine is one of the bulkiest phosphines known,[23] bulkier than tricyclohexylphosphine, the $CuXP(t\text{-}Bu)_3$ species were expected to be low-molecular-weight molecules. The molecular weight measurements for these complexes, in 1,2-dichloroethane, indeed indicated the presence of monomeric or dimeric species. However, neither the infrared nor the Raman spectra of the solid complexes showed any bands attributable to the terminal Cu–X stretching frequencies, indicating that the complexes are not monomeric in the solid state. The structure of the bromo complex, which afforded suitable crystals, was therefore

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Table II. Infrared and Raman Data[a] in the 300-50-cm^{-1} Region

$CuClP(t-Bu)_3$		$CuBrP(t-Bu)_3$[b]		$CuIP(t-Bu)_3$		
IR	R	IR	R	IR	R	assignt
	300 m		294 s		295 s	
	270 sh		268 sh		264 sh	
	208 m		202 m		202 m	
		165 w				
				154 w		
150 s, vb	151 w	120 s, vb	118 m, b	104 m, b	100 m, b	ν_b(Cu-X)
	104 mw				92 mw	ν_t(Cu-P)
94 w		87 mw		84 mw		
	80 sh		80 sh		80 sh	
72 w		73 sh		73 sh	70 sh	

[a] For the solid state. Description of abbreviations: IR, infrared; R, Raman; b, broad; m, medium; s, strong; sh, shoulder; v, very; w, weak; ν_b(Cu-X), stretching mode involving Cu-X bridge bonds; ν_t(Cu-P), stretching mode involving the Cu-P terminal bond. [b] Tetramer.

determined by a single-crystal X-ray diffraction study. Surprisingly, the crystallographic study showed that bromo(tri-*tert*-butylphosphine)copper(I) is a cubane-type tetramer.

Results and Discussion

Tri-*tert*-butylphosphine reacts with copper(I) halides to give the 1:1 complexes, $CuXP(t\text{-}Bu)_3$, which are air-stable white solids. The complexes are soluble in solvents such as benzene and dichloromethane. Analytical and ^1H NMR data for the complexes are given in the Experimental Section; conductance and molecular weight data and $^{31}P\{^1H\}$ NMR parameters are given in Table I.

The ^1H NMR spectra of all the three complexes consisted of a doublet that is ca. 0.20 ppm downfield from that for the free phosphine. The ^1H NMR parameters show that the *tert*-butyl resonance in the complexes is not very sensitive to the nature of the halide attached to the copper; the magnitude of ^3J(P–H) for the complexes is 20–25% higher than the value for the uncoordinated phosphine. The $^{31}P\{^1H\}$ NMR spectra for the chloro and the bromo complexes in dichloromethane at ambient temperature as well as at 183 K exhibited a single resonance. Attempts to obtain a ^{31}P NMR spectrum of the iodo complex failed due to its poor solubility.

The ^{31}P chemical shifts, unlike the ^1H chemical shifts, for the chloro and the bromo complexes differ significantly. However, the ^{31}P chemical shifts for both complexes are upfield from that for the free phosphine. The observed upfield ^{31}P chemical shift upon complexation is in marked contrast to the popular belief[24,25] that the ^{31}P chemical shift of the phosphine moves downfield upon complexation. Recent work has shown that a number of phosphine complexes of zinc(II)[18,26] and cadmium(II)[18,26,27] also exhibit upfield coordination shifts (δ(complex) − δ(free phosphine)).

The conductance data given in Table I show that all of the three 1:1 complexes behave as nonelectrolytes in 1,2-dichloroethane. The molecular weight data in Table I show that the chloro complex exists as a monomeric molecular species in 1,2-dichloroethane, but the bromo and the iodo complexes are indicated to be dimeric species.

The infrared and Raman spectra of the three $CuXP(t\text{-}Bu)_3$ complexes were examined in the solid state in the 4000–50-cm^{-1} region; the observed bands in the 300–50-cm^{-1} region are listed in Table II. The infrared spectrum for each complex is characterized by the presence of a broad complex band of strong to medium intensity. The frequency as well as the intensity of this band decreases with increasing mass of the halogen. Therefore, it can be attributed to vibrations involving stretching of Cu–X bonds. The frequency ratios ν(M–Br)/ν(M–Cl) and ν(M–I)/ν(M–Cl) of 0.65–0.85 and ~0.64, respectively, have often been used[28] to support the assignments of metal–halogen stretching frequencies. The ratios calculated from the halogen-sensitive infrared bands observed in the present work are ν(Cu–Br)/ν(Cu–Cl) = 0.80 and ν(Cu–I)/ν(Cu–Cl) = 0.69.

The Raman spectrum of each complex (Table II) showed a band of weak to medium intensity at a frequency similar to the halogen-sensitive infrared frequency. The remaining Raman bands, except a medium-weak band, at 104 cm^{-1} for the chloro and a similar band at 92 cm^{-1} for the iodo complex, are invariant with the nature of the phosphine.[18] The 104- and 92-cm^{-1} bands are tentatively assigned to the Cu–P stretching frequency.[29]

The Cu–X stretching frequencies[29,30] for the complexes $CuX(PPh_3)_3$, which are monomeric and contain terminal Cu–X bands, are reported to be 239–220, 160, and 145 cm^{-1} for X = Cl, Br, and I, respectively. Thus, the possibility of a monomeric solid-state structure for any of the $CuXP(t\text{-}Bu)_3$ complexes included in this work can be ruled out. Although it is difficult to deduce the solid-state structures of the $CuXP(t\text{-}Bu)_3$ complexes from their vibrational spectra, the halogen-sensitive infrared bands observed for these complexes are similar to those reported[30] for the tetramers $Cu_4Cl_4(PPh_3)_4$, $Cu_4I_4(PEt_3)_4$, and $Ag_4X_4(PPh_3)_4$ (X = Cl, Br, I) having a cubane-type structure in the solid state. In fact, the halogen-sensitive infrared bands for the $CuXP(t\text{-}Bu)_3$ complexes occur at frequencies that are even lower than those assigned for the stretching modes involving the triply bridging Cu–X bonds of the cubane-type tetramers. The lower frequencies for the tri-*tert*-butylphosphine complexes can be rationalized in terms of elongation of copper–halogen bonds to relieve the steric crowding caused by the very bulky tri-*tert*-butylphosphine ligands.

In view of the very large steric requirements[23] of tri-*tert*-butylphosphine, a cubane-type tetrameric structure for the $CuXP(t\text{-}Bu)_3$ complexes is not consistent with the conclusions arrived at by Teo and Calabrese[13] and by Churchill and Rotella[10] from their X-ray diffraction studies of steric interactions in $M_4X_4L_4$ (M = Ag or Cu, L = tertiary phosphine or arsine) tetramers. Therefore, determination of the structures of the $CuXP(t\text{-}Bu)_3$ complexes by single-crystal X-ray diffraction studies became desirable. The bromo complex afforded crystals suitable for a single-crystal structure analysis; results of the X-ray diffraction study show (vide infra) that the complex indeed has a cubane-type tetrameric structure.

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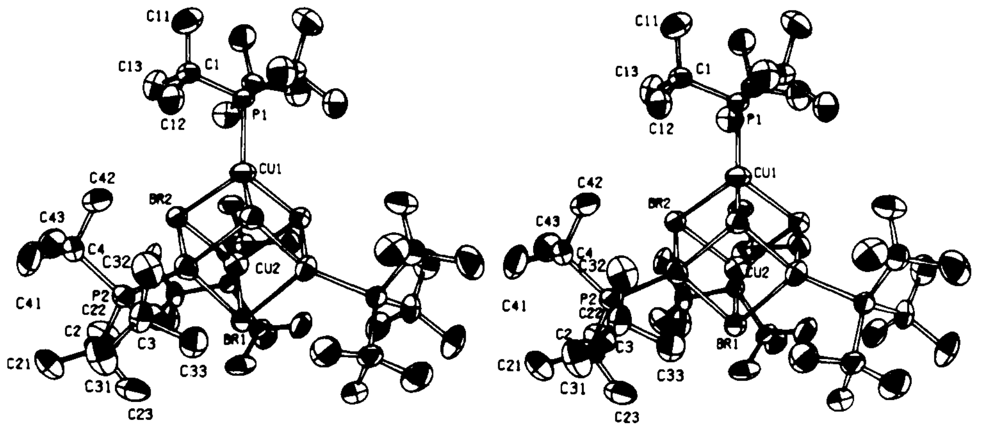

Figure 1. Stereoview of the tetramer $[CuBrP(t\text{-}Bu)_3]_4$. P1, Cu1, and Br1 lie along the crystallographic threefold axis. The ellipsoids correspond to 50% probability. The hydrogens are not shown for simplicity.

Table III. Interatomic Distances (Å) and Bond Angles (deg) in $[CuBrP(t\text{-}Bu)_3]_4$

Distances in $Cu_4Br_4P_4$

Cu1-Br2	2.598 (1)^a	Cu2-Br2^b	2.604 (1)
Cu2-Br1	2.599 (2)^a	Cu1-P1	2.228 (4)
Cu2-Br2	2.571 (1)	Cu2-P2	2.228 (3)

Angles in $Cu_4Br_4P_4$

Br2-Cu1-Br2	95.22 (4)^a	Br2-Cu2-P2	122.43 (8)
Br2-Cu1-P1	121.48 (7)^a	Br2^b-Cu2-P2	120.84 (8)
Br1-Cu2-Br2	95.50 (5)	Cu2-Br1-Cu2	84.38 (4)^a
Br1-Cu2-Br2^b	94.70 (5)	Cu1-Br2-Cu2	84.61 (4)
Br2-Cu2-Br2^b	95.74 (5)	Cu1-Br2-Cu2^c	83.95 (4)
Br1-Cu2-P2	120.92 (8)	Cu2-Br2-Cu2^c	84.85 (5)

Geometry of the Phosphine (Average, Range)^d

P-C	1.906 (9) (1.903 (9)-1.908 (8))
C-C	1.53 (1) (1.50 (1)-1.56 (1))
Cu-P-C	110.5 (3) (110.0 (4)-110.9 (4))
C-P-C	108.5 (4) (107.9 (4)-108.9 (4))
P-C-C_{top}	116.0 (6) (115.1 (6)-116.9 (6))
C-C-C_{out}	108.4 (6) (106.7 (6)-110.3 (6))
C_{out}-C-C_{top}	109.1 (8) (110.6 (8)-107.9 (8))
C_{out}-C-C_{out}	105.3 (8) (104.2 (7)-106.1 (8))

[a] Three symmetry-equivalent values. [b] $1 - x + y, 1 - x, z$. [c] $1 - y, x - y, z$. [d] Details are given in Table IX (supplementary material).

The crystal consists of individual $[CuBrP(t\text{-}Bu_3)]_4$ molecules with a cubane Cu_4Br_4 core (Figure 1). Interatomic distances and bond angles are listed in Table III.

The tetramer has a crystallographic three-fold axis through Br1 and the Cu1-P1 bond. With the exception of the compounds in which T_d symmetry is imposed by the space group, this structure is the closest to ideal T_d symmetry reported so far. Departure from this symmetry can be estimated from the scattering of the values for corresponding bond lengths or angles, which should be rigorously equal in T_d symmetry. The spreads in each case (Table IV) are actually very small.

Tri-*tert*-butylphosphine is a very bulky ligand, and its steric effects on the cubane core can be discussed in terms of various structural parameters pointed out by Teo and Calabrese.[12,13] For instance, the average distance from P to the centroid of the Cu_4Br_4 core is 0.18 Å greater than in the PEt_3 complex[6] (Table IV). This is correlated to three other structural changes: (i) the Cu-P bonds (2.228 Å) are 0.03 Å longer than the presumably normal distance of 2.20 Å found in the PEt_3 cubane complex[6] and in the PPh_3 "chair" molecule;[3] (ii) the Cu-Br distances (2.593 Å) are lengthened by 0.049 Å compared with those of the PEt_3 complex;[6] (iii) finally, the Cu_4Br_4 core is much closer to a cube than usually found, as evidenced from the difference of only 10.8° between the Br-Cu-Br and the Cu-Br-Cu angles, this difference being 23.8° in the PEt_3 compound.[6] All these peculiarities can be considered as so many ways for the system to adjust itself to the steric requirements of the phosphine. Indeed, the *tert*-butyl groups squeeze the nearby Br atoms together to 3.83 Å, a distance appreciably shorter than the normal van der Waals contact (radius of Br 1.95 Å).[31] The concomitant reduction of the Br-Cu-Br angle to 95.3° (instead of 101.3° in the PEt_3 compound[6]) makes it easier for the Cu atom to reach the lone pair of the P atom hidden inside the "mushroom cap" created by the *tert*-butyl groups.

The tetramer contains three symmetry-equivalent $P(t\text{-}Bu)_3$ ligands without imposed symmetry and a fourth molecule lying on the threefold axis of the cell. Both types, however, have very similar interatomic distances and bond angles (Table III). The distributions in space of their *tert*-butyl groups are mirror images, but in all other respects, they are almost identical, as indicated by the torsion angles of Table V (supplementary material).

Typical values of various geometrical parameters have been computed from 14 coordinated $P(t\text{-}Bu)_3$ ligands in 11 crystal structures[21,32] (Tables VI and X, supplementary material). Our own results are in good agreement with these data. Interestingly, for most of the compounds, the relative orientations of the *tert*-butyl groups, defined by the M-P-C-CH_3 torsion angle near 166°, vary within only a few degrees. This suggests that $P(t\text{-}Bu)_3$, at least when coordinated, possesses a very restricted motion about the P-C bonds. In fact, in any given ligand, the three *tert*-butyl groups assume an approximately staggered orientation with respect to the P-metal bond, the M-P-C-CH_3 angles being ~43, 166, and 288°. Thus, one C-CH_3 bond of each *tert*-butyl group ($\tau \approx 166°$) is pointed up, roughly parallel to the metal-P bond, which makes the region at the top of the "mushroom cap" very crowded. The strain shows on the C-P-C angles, which are appreciably larger (~108°) than in less bulky phosphines such as PMe_3 (~101°) or PPh_3 (~103°).[33] The strain is also absorbed to a large extent by the P-C-CH_3 angles in the crowded region, which are on the average 6° greater than the same angles for the methyl groups pointing outward. This limited mobility of the interlocked *tert*-butyl groups imparts rigidity to the organic portion.

The steric hindrance around the P-metal bonds was examined by means of the cone-angle profiles widely used by Ferguson and co-workers.[21] As usual, the depressions in the

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(32) Tables of individual distances and angles are provided in the supplementary material.

(33) These values were computed from ~130 PMe_3 and ~950 PPh_3 ligands in ~800 structures stored in the Cambridge Crystallographic Database of Organics and Organometallics in use at the National Research Council, Ottawa, Canada.

Table IV. Comparisons between Known $[CuBrPR_3]_4$ Structures[a]

	R = *t*-Bu, "cubane" (this work)				R = ethyl, "cubane"[b] (ref 6)	R = phenyl, "chair" (ref 3)			
	min	max	range	av	av	min	max	range	av
Cu–Br	2.571 (1)	2.599 (2)	0.028	2.593	2.544 (1)	2.376 (2)	2.664 (2)	0.288	2.495
Cu–P	2.228 (3)	2.228 (4)	0.000	2.228	2.199 (2)	2.207 (3)	2.194 (4)	0.013	2.200
Br···Br	3.827 (1)	3.838 (1)	0.011	3.832	3.932 (1)	3.880 (2)	3.956 (2)	0.076	3.917
Cu···Cu	3.479 (2)	3.491 (2)	0.012	3.485	3.184 (2)	2.990 (2)	3.987 (2)	0.997	3.481
P-centroid				4.333	4.149				
Br–Cu–Br	94.70 (5)	95.74 (5)	1.04	95.29	101.25 (3)	96.76 (6)	110.81 (8)	14.05	102.61
Cu–Br–Cu	83.95 (5)	84.85 (5)	0.90	84.45	77.48 (4)	71.74 (6)	107.15 (7)	35.41	84.54
P–Cu–Br	120.84 (8)	122.43 (8)	1.59	121.42	116.80 (2)	114.86 (10)	128.75 (11)	13.89	120.22

[a] Distances are in angstroms, and angles are in degrees. [b] Crystallography-imposed T_d symmetry.

profiles are occupied by the Cu–Br bonds. However, it is remarkable that these depressions are actually rather shallow, making $P(t\text{-}Bu)_3$ a bulky ligand with steric hindrance uniformly distributed around the P–metal bonds.

Proton-decoupled ^{31}P NMR spectra of solutions containing equimolar amounts of $CuXP(t\text{-}Bu)_3$ and $P(t\text{-}Bu)_3$ showed a single resonance at ambient temperatures as well as at 183 K. The observed ^{31}P chemical shifts (Table I) were invariable with the nature of the halogen X. The invariability of the ^{31}P NMR chemical shift with change in the halogen very strongly suggests that addition of 1 mol equiv of $P(t\text{-}Bu)_3$ to the 1:1 complexes results in the formation of the 1:2 complexes $[Cu(P(t\text{-}Bu)_3)_2]X$, in which X is not coordinated to the metal. Evidence for the formation of ionic species is also provided by molar conductivities of the solutions (Table I), which are markedly higher than those for the 1:1 complexes. In fact, the molar conductivity for the iodide complex, $[Cu(P(t\text{-}Bu)_3)_2]I$, is comparable to that for a tetraalkylammonium salt. Although the conductivities for the analogous chloride and bromide complexes are ~50% lower than that for the iodide complex, the values are comparable to that reported[34] for $[Ag(P(p\text{-tolyl})_3)_3]CF_3CO_2$, for which the $^1J(Ag\text{–}P)$ values[34] indicate an ionic structure. As for the silver(I) trifluoroacetate complex, the intermediate conductivity for $[Cu(P(t\text{-}Bu)_3)_2]X$, X = Cl or Br, can be attributed to an equilibrium such as represented by eq 1.

$$CuXP(t\text{-}Bu)_3 + P(t\text{-}Bu)_3 \rightleftharpoons [Cu(P(t\text{-}Bu)_3)_2]^+ + X^- \qquad (1)$$

The $^{31}P\{^1H\}$ NMR spectra of solutions of the complexes containing excess (>1 mol equiv) $P(t\text{–}Bu)_3$, at 183 K, showed a resonance due to the 1:2 complex and another resonance attributable to free phosphine. For all the three cases, relative intensities of the resonances for bound and free phosphine confirmed that only two phosphines are bound to the copper. Unfortunately, attempts to isolate the 1:2 complexes did not succeed. The $^{31}P\{^1H\}$NMR spectra of solutions containing 1:1 complex and excess phosphine, at ambient probe temperatures, showed a single resonance showing fast phosphine exchange.

In summary, tri-*tert*-butylphosphine reacts readily with copper(I) halides to form isolable 1:1 complexes, which are indicated to have a cubane-type tetrameric structure in the solid state as shown by a single-crystal X-ray diffraction study of the bromo complex. The discovery of the cubane-type tetrameric structure in the present work is in marked contrast to the conclusions arrived at by previous workers[10,13] that the tetrameric cubane-type and/or chair-type structures become unstable with increasing steric bulk of the phosphine. The tetrameric structure, however, breaks down in solution. All the three 1:1 complexes react with excess phosphine to form the 1:2 complexes, which seem to contain the cationic species $Cu[P(t\text{-}Bu)_3]_2^+$ in solution. Isolation of the 1:2 complexes seems to be difficult due to an equilibrium such as represented by eq 1.

Experimental Section

Materials and Solvents. Tri-*tert*-butylphosphine was prepared as described previously.[35] Copper(I) bromide was Fisher ACS Certified grade. Copper(I) chloride and iodide were supplied by Research Organic/Inorganic Chemical Corp. Diethyl ether, benzene, and petroleum ether were refluxed over sodium wire and subsequently distilled. Dichloromethane and 1,2-dichloroethane were dried by refluxing over calcium hydride and subsequent distillation.

General Procedures. Tri-*tert*-butylphosphine was handled under an atmosphere of oxygen-free dry nitrogen. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. Molecular weights were determined by Galbraith Laboratories, Knoxville, TN. Infrared spectra were measured in the solid state (Nujol mull) with use of a Perkin-Elmer 180 double-beam spectrophotometer. Raman spectra were measured on powdered samples with a Jarrell-Ash Raman spectrophotometer using the 5145-Å exciting line of an argon ion laser. Proton NMR spectra were recorded at ambient temperatures with a Varian A60 NMR spectrometer on solutions in CH_2Cl_2 with use of the solvent peak as internal reference; the reported chemical shifts are relative to Me_4Si. Proton-decoupled ^{31}P NMR spectra were recorded at ambient temperature as well as at 183 K on solutions in CH_2Cl_2 containing 20% CD_2Cl_2; the spectra were recorded in the Fourier transform mode with a Bruker WP60 FT spectrometer. The ^{31}P chemical shifts were measured relative to 85% H_3PO_4 external reference; the positive shifts are downfield from H_3PO_4.

Preparation of the Complexes. (a) To a suspension of CuCl in CH_2Cl_2 was added ~1.5 mol equiv of $P(t\text{-}Bu)_3$, and the mixture was stirred for several hours until all the solid dissolved to give a green solution, which was evaporated in vacuo. The green sticky residue was dissolved in petroleum ether, the solution was filtered, and the filtrate was evaporated in vacuo. The resulting light green residue was washed several times with cyclohexane to give a white crystalline solid, which was characterized to be $CuClP(t\text{-}Bu)_3$: yield 60%; mp 207–210 °C. Anal. Calcd for $C_{12}H_{27}ClPCu$: C, 47.84; H, 9.03; Cl, 11.76. Found: C, 48.07; H, 9.15; Cl, 12.01. ^1H NMR (CH_2Cl_2): δ 1.47 (d, $^3J(P\text{–}H)$ = 12.0 Hz). (b) Excess (~2 mol equiv) $P(t\text{-}Bu)_3$ was added to a suspension of CuBr in benzene, and the mixture was stirred to give a clear solution. The solvent was removed in vacuo, the residue was redissolved in benzene, and petroleum ether was added slowly to the solution to give white crystals of $CuBrP(t\text{-}Bu)_3$: yield 80%; mp 234 °C. Anal. Calcd for $C_{12}H_{27}BrPCu$: C, 41.68; H, 7.80. Found: C, 41.65; H, 8.00. ^1H NMR (CH_2Cl_2): δ 1.47 (d, $^3J(P\text{–}H)$ = 12.5 Hz). (c) A suspension of CuI in benzene containing $P(t\text{-}Bu)_3$ (~1.5 mol equiv) was stirred until a clear solution was obtained, which was evaporated in vacuo. The residue was dissolved in CH_2Cl_2, and petroleum ether was added to the solution to give white crystalline $CuIP(t\text{-}Bu)_3$: yield 80%; mp 255–256 °C. Anal. Calcd for $C_{12}H_{27}PICu$: C, 36.70; H, 6.93; I, 32.31. Found: C, 38.80; H, 6.77; I, 32.08. ^1H NMR (CH_2Cl_2): δ 1.48 (d, $^3J(P\text{–}H)$ = 12.5 Hz). (d) To an aqueous solution of 3.0 g of KI in 3 mL of H_2O was added 0.3 g of CuI with stirring. The resulting solution was filtered, and 0.3 g of $P(t\text{–}Bu)_3$ was added dropwise to the filtrate with stirring.

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The precipitated CuIP(t-Bu)$_3$ was filtered, dried in vacuo, and recrystallized from a mixture of 1,2-dichloroethane and ether; yield 80%. The analytical and spectral data and melting point for the product were identical with those for the product obtained by following procedure c.

Crystal Data: $C_{48}H_{108}Br_4Cu_4P_4$, fw = 1383.1, trigonal, space group $P\bar{3}$, a = 14.008 (3) Å, c = 19.416 (3) Å, V = 3299.4 Å^3, D_o = 1.40 (1) g cm^{-3}, D_c = 1.392 g cm^{-3}, Z = two tetramers per cell, λ(Mo K$\bar{\alpha}$) = 0.71068 Å (graphite monochromator), t = 25 °C, μ(Mo Kα) = 38.0 cm^{-1}.

Crystallographic Measurements and Structure Resolution. The crystal selected for data collection was a regular triangular plate with sides of 0.033 mm and a thickness of 0.002 mm. The trigonal Laue symmetry was observed on a set of precession photographs, and the lack of systematic absences led to two possible space groups: $P3$ and $P\bar{3}$.

The crystal was mounted on an Enraf-Nonius CAD4 diffractometer, and the data were collected with use of the $\omega/2\theta$ scan technique. A fixed slit of 2.00 mm was used, and the scan range was ω = (0.85 + 0.36 tan θ)° extended 25% on both sides for background counts. Fast prescans at 6.7° min^{-1} were made, and all reflections with a ratio $I/\sigma(I) \leq 1$ were labeled "weak" and not remeasured at slow speed. For the slow scans, speeds between 10.0 and 0.55° min^{-1} were selected in order to make the $I/\sigma(I)$ ratio equal to 100, but the scan time was limited to 135 s. The option FLAT of the CAD4 software was used to measure the intensity at the ψ angle that minimizes absorption. Three standard reflections were used as a check on instrument and crystal stability. They showed random fluctuations (σ = ±1.7%) during the experiment. Crystal orientation was checked every 100 reflections by centering three reflections. No crystal recentering was necessary during data collection.

A set of 3073 independent hkl and $hk\bar{l}$ reflections in a sphere limited by 2θ = 46° was collected. Net intensity I and the standard deviation $\sigma(I)$ were calculated as described elsewhere.[36] An absorption correction was applied (grid 10 × 10 × 10, Gaussian integration, transmission coefficient 0.30–0.53). The data were finally corrected for the Lorentz and polarization effects.

The structure was solved by the heavy-atom method and refined by full-matrix least squares. The centrosymmetric $P\bar{3}$ space group was assumed first. The choice was subsequently confirmed by successful structure refinement. The Cu_4Br_4 unit was positioned from a Patterson synthesis. All non-hydrogen atoms were located from a difference Fourier (ΔF) map. Isotropic refinement of all non-hydrogen atoms converged to $R = \sum||F_o| - |F_c||/\sum|F_o|$ = 0.117. These atoms were then anisotropically refined, which reduced R to 0.052. The next ΔF map clearly revealed the positions of 19 hydrogen atoms, and the coordinates of those missing were calculated. These 36 hydrogen positions were introduced in the structure and isotropically refined. At this stage, refinement was carried out by large blocks including the $Cu_4Br_4P_4$ unit and the carbon and hydrogen atoms of only two *tert*-butyl groups at a time. Nine hydrogens failed to converge to reasonable positions. They were repositioned and held fixed for the rest of the refinement (C–H = 0.95 Å, C–C–H = 111°, B_{iso} = 6.0 Å^2). The coordinates of the fixed hydrogens were recalculated after each cycle. In the last stage of the refinement, individual weights based on counting statistics were applied and block-diagonal least squares were used. Anisotropic refinement of the non-hydrogen atoms and isotropic refinement of 27 hydrogen atoms converged to R = 0.035 and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ = 0.049. The goodness-of-fit ratio was 1.46. The final ΔF map showed maximum peaks of 0.55 e/Å^3, whereas the deepest valley was −0.31 e/Å^3. Because the highest residual electron density was found in the ab plane at 1.65 Å from the origin, where local symmetry is $\bar{3}$, the possibility that a benzene molecule was trapped in the structure was considered. However, no vibrations due to aromatic systems were detected in the infrared spectrum taken on a KCl pellet. The density measurement was not accurate enough (1.41 (1) g cm^{-3}) to settle the question, since the value calculated above (1.392 g cm^{-3}) would increase to only 1.431 g cm^{-3}, with the assumption of full occupancy by a benzene molecule. We tried to introduce the ring carbon atoms in the refinement. The coordinates changed only slightly, but the isotropic temperature factor had increased to $B \approx 41$ Å^2 when refinement was abandoned. It is noteworthy, however, that the structure does possess around the origin a cavity large enough to contain a benzene molecule. No short van der Waals contacts were noted when an idealized benzene molecule was placed in the ab plane with its C–H bonds oriented along the a, b, and v axes. Thus, although the crystal actually used for X-ray work did not contain a detectable amount of benzene, there is still a possibility that the fresh crystals did contain trapped solvent, which slowly escaped without disrupting the overall framework.

Table VII. Coordinates (×10^4; Cu, Br, ×10^5; H, ×10^3) of [CuBrP(t-Bu)$_3$]$_4$

atom	x	y	z
Br1	66667	33333	36022 (7)
Br2	51109 (7)	17267 (7)	19951 (4)
Cu1	66667	33333	12964 (9)
Cu2	51965 (8)	32687 (9)	27570 (5)
P1	6667	3333	149 (2)
P2	3688 (2)	3242 (2)	3148 (1)
C1	5234 (6)	2914 (6)	−194 (4)
C2	3156 (7)	2356 (7)	3955 (4)
C3	4012 (6)	4702 (6)	3364 (4)
C4	2552 (6)	2666 (7)	2471 (4)
C11	5153 (8)	3176 (8)	−953 (5)
C12	4769 (7)	3488 (8)	271 (5)
C13	4498 (7)	1701 (8)	−77 (5)
C21	1982 (8)	1996 (7)	4175 (5)
C22	3273 (8)	1334 (7)	3844 (5)
C23	3914 (8)	2966 (9)	4557 (4)
C31	3166 (8)	4777 (7)	3853 (5)
C32	4121 (7)	5322 (7)	2701 (5)
C33	5155 (7)	5303 (7)	3709 (5)
C41	1612 (7)	2910 (9)	2593 (5)
C42	3099 (8)	3115 (8)	1767 (4)
C43	2054 (8)	1416 (8)	2408 (5)
H111	542 (5)	397 (5)	−98 (3)
H112	562 (5)	289 (6)	−136 (3)
H113	424 (8)	274 (8)	−114 (5)
H121	508 (8)	420 (8)	35 (5)
H122[a]	407	335	11
H123[a]	467	322	73
H131	433 (5)	135 (5)	44 (3)
H132	391 (5)	149 (5)	−17 (3)
H133	452 (5)	117 (5)	−32 (3)
H211	164 (6)	137 (6)	456 (4)
H212	145 (5)	150 (5)	393 (3)
H213	190	262	426
H221	293 (5)	93 (5)	353 (3)
H222	322 (5)	90 (6)	423 (3)
H223	406 (6)	156 (6)	367 (4)
H231	455 (5)	303 (5)	447 (3)
H232	377 (6)	251 (6)	504 (4)
H233	372 (5)	332 (5)	476 (3)
H311	296 (7)	454 (7)	436 (4)
H312[a]	334	552	391
H313[a]	244	437	367
H321	349 (6)	524 (6)	240 (4)
H322	440 (5)	600 (5)	277 (3)
H323[a]	449	514	236
H331	522 (5)	499 (5)	414 (3)
H332	545 (5)	607 (6)	394 (3)
H333[a]	571	537	340
H411	119 (4)	265 (4)	231 (3)
H412[a]	126	262	302
H413[a]	188	368	260
H421	259 (7)	300 (7)	140 (4)
H422[a]	333	383	175
H423[a]	371	300	169
H431	253 (6)	119 (6)	233 (3)
H432	165 (5)	102 (5)	277 (3)
H433[a]	156	113	203

[a] Not refined.

The refined coordinates are collected in Table VII. The scattering curves were taken from Cromer and Waber,[37] except for hydrogen.[38] The anomalous dispersion terms f' and f'' for Cu, Br, and P were

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taken from Cromer.[39] The computer programs used are listed elsewhere.[36]

Acknowledgment. This work was supported by operating grants from the Natural Sciences and Engineering Research Council of Canada and travel grants from the provincial governments of Ontario and Quebec in the framework of the Ontario–Quebec educational exchange. We wish to thank Mr. T. G. M. H. Dikhoff for technical assistance and Dr. G. S. Wood for access to the Cambridge Crystallographic Database in use at the National Research Council of Canada.

Registry No. $[CuClP(t\text{-}Bu)_3]_4$, 83731-72-0; $[CuBrP(t\text{-}Bu)_3]_4$, 83731-73-1; $[CuIP(t\text{-}Bu)_3]_4$, 83731-74-2; $[Cu(P(t\text{-}Bu)_3)_2]Cl$, 83731-75-3; $[Cu(P(t\text{-}Bu)_3)_2]Br$, 83731-76-4; $[Cu(P(t\text{-}Bu)_3)_2]I$, 83731-77-5.

Supplementary Material Available: Listings of torsion angles in the coordinated $P(t\text{-}Bu)_3$ ligand (Table V), typical values for the distances and angles in coordinated $P(t\text{-}Bu)_3$ (Table VI), anisotropic temperature factors (Table VIII), interatomic distances and bond angles in the phosphine (Table IX), the average geometry of coordinated $P(t\text{-}Bu)_3$ (Table X), and observed and calculated structure factors (Table XI) (27 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Dihydroxo(5,10,15,20-tetraphenylporphinato)phosphorus(V) Hydroxide Dihydrate[1]

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Received December 21, 1981

The structure of dihydroxo(5,10,15,20-tetraphenylporphinato)phosphorus(V) hydroxide dihydrate, $(C_{44}H_{30}O_2P^+)(OH^-)\cdot 2H_2O$, has been determined from three-dimensional diffractometer data. It crystallizes in the monoclinic space group $P2_1/c$ with $a = 14.636$ (4) Å, $b = 13.953$ (3) Å, $c = 17.592$ (4) Å, $\beta = 90.21$ (2)°, and $Z = 4$. The structure was solved by heavy-atom methods and refined by full-matrix least-squares methods to yield a final R factor of 0.090. This is the first reported structural analysis of a "metalloporphyrin" where the central ion is a nonmetal. The coordination geometry is distorted octahedral with the phosphorus atom displaced 0.09 Å from the mean plane of the pyrrole nitrogen atoms. The P–N bond lengths range from 1.87 (1) to 1.92 (1) Å. The two P–O distances are 1.644 (8) and 1.545 (8) Å. The porphyrin ring shows marked S_4 deviations from planarity. There is extensive hydrogen bonding between the axial hydroxyl groups, the hydroxide counterion and the waters of hydration forming quasi-linear hydrogen-bonded polymers.

Introduction

Porphyrin complexes of almost all the metallic elements are known.[3] Complexes with the metalloids arsenic and silicon have also been reported.[4] Complexes with a nonmetal, phosphorus, have also been characterized by using the synthetic macrocycles octaethylporphyrin (OEP)[5] and *meso*-tetraphenylporphyrin (TPP).[6] For the OEP complexes, evidence has been presented for phosphorus in both the III and V oxidation states. Surprisingly, several differences have been noted between analogous complexes with the two porphyrins. The phosphorus(V) ion was postulated to lie in the plane of the macrocycle in the OEP complex, but in some of the TPP complexes, NMR data suggested the central atom was out of the plane. The complexes of the two porphyrins also show a surprising difference in stability. While the TPP complex falls into the highest stability class (i.e., the metal is not removed by strong acid), the OEP complex is decidedly less stable, the phosphorus ion being removed by traces of HCl in CH_2Cl_2. However, the OEP complex is stable in alcoholic solvents.

Table I. Crystal Data for $(C_{44}H_{30}O_2P^+)(OH^-)\cdot 2H_2O^a$

space group: $P2_1/c$	$Z = 4$
$a = 14.636$ (4) Å	d(calcd) = 1.35 g cm^{-3}
$b = 13.963$ (3) Å	d(measd) = 1.32 g cm^{-3}
$c = 17.592$ (4) Å	$\mu = 11.2$ cm^{-1} (Cu Kα radiation)
$\beta = 90.21$ (2)°	$F(000) = 1528$
$V = 3595$ (3) Å^3	
mol wt = 730.8	

systemic absences	$h0l$, l odd; $0k0$, k odd
space group	$P2_1/c$
ω-scan rate	2–20° min^{-1}
scan range	$(0.6 + 0.14 \tan \omega)°$
max $(\sin \theta)/\lambda$	0.50° (100° in 2θ)
total unique reflcns	3623
NO (reflcns with $I > 2.5\sigma_I$)	1190
NV (no. of variables)	217
max shift/error on last cycle	0.09
$R = \Sigma \|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.090
$R_w = (\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w F_o^2)^{1/2}$	0.092
SEF = $(\Sigma w(\|F_o\| - \|F_c\|)^2/(NO - NV))^{1/2}$	1.77

[a] In this and subsequent tables, the estimated standard deviation of the least significant figure is shown in parentheses.

The structure of phosphorus(V) porphyrins would also be of interest to show the effects of small ions like phosphorus(V) on the planarity of the macrocycle. Hoard has calculated that, if the radius of the central "hole" is less than 1.96 Å, the macrocycle must undergo buckling so that there are S_4 deviations from planarity.[7] This was borne out by the two crystalline forms of nickel(II) octaethylporphyrin.[8,9] Phos-

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(1) Presented at the American Crystallographic Association Meeting, Lake Point Convention Center, AL, March 1980; Abstract I5.

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