

**Table VI.** Individual Bond Strengths and Bond Strength Sums about Oxygen Atoms (in vu)

O(1):	P(1)	1.27	O(6):	P(2)	1.27
	Co(2)	0.37		Co(2)	0.43
	Co(1)	0.33		Co(1)	0.31
	$\Sigma$	= 1.97		$\Sigma$	= 2.01
O(2):	P(1)	1.25	O(7):	P(2)	1.26
	Co(3)	0.44		Co(3)	0.45
	$\Sigma$	= 1.69		Co(3)	0.37
				$\Sigma$	= 2.08
O(3):	P(1)	1.24	O(8):	P(2)	1.23
	Co(1)	0.43		Co(3)	0.39
	Co(2)	0.29		Co(1)	0.27
	$\Sigma$	= 1.96		$\Sigma$	= 1.89
O(4):	P(1)	1.23	O(9):	Co(2)	0.30
	Co(2)	0.39		Co(2)	0.30
	Co(1)	0.35		$\Sigma$	= 0.60
	$\Sigma$	= 1.97			
O(5):	P(2)	1.29			
	Co(3)	0.47			
	Co(1)	0.37			
	$\Sigma$	= 2.13			

valence,  $R$  = bond length, and  $S_0$ ,  $R_0$ , and  $N$  are empirically fit constants for a given atom. The values<sup>13</sup> of  $S_0$ ,  $R_0$ , and  $N$  for  $\text{Co}^{2+}$  and  $\text{P}^{5+}$  are 0.333, 2.118, 5.0 and 1.25, 1.534, 3.2, respectively. Summing the individual bond strengths about the nine oxygen atoms (see Table VI) shows that, except for O(2) and O(9), the bond strength sums cluster about the expected value of 2.00 vu ( $-0.11$ ,  $+0.13$  vu; average of seven oxygens 2.00 vu). O(2) has a bond strength sum of 1.68 and O(9) of 0.60 vu. This, of course, indicates that two hydrogens are bonded to O(9) and implies hydrogen bonding to O(2). In fact, inspection of the *interpolyhedral* oxygen–oxygen distances (oxygen atoms not sharing the same cation) shows that each O(9) has two O(2) atoms at distances of 2.755 and 2.763 Å; the next longest oxygen–oxygen distance of this type is 2.954 Å. The value 2.7 Å is just the oxygen–oxygen distance

expected for a slightly strained hydrogen bond.<sup>14</sup> The bond strength of the *hydrogen bond* can be estimated as 0.20 vu<sup>14</sup> leaving a bond strength of 0.80 vu for the O–H bond. Thus O(9) (the water oxygen) will have a total bond strength sum of 2.20 vu and O(2) (the hydrogen bond acceptor) a sum of 2.08 vu.

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**Registry No.**  $\text{Co}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ , 60305-65-9.

**Supplementary Material Available:** A table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

## References and Notes

- (1) J. B. Anderson, G. L. Shoemaker, E. Kostiner, and F. A. Ruzsala, *Am. Mineral.*, in press.
- (2) F. A. Ruzsala, M. Mengeot, and E. Kostiner, Abstracts, Third Conference on Crystal Growth, Stanford University, 1975, pp 129 and 130.
- (3) J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. XIV, Longmans, Green and Co., London, 1935, p 852.
- (4) T. Ando, S. Minami, and T. Tsubota, *Bull. Osaka Ind. Res. Inst.*, **1**, 63 (1950); *Chem. Abstr.*, **46**, 6401b (1952).
- (5) "International Tables for X-Ray Crystallography", Vol. II, Kynoch Press, Birmingham, England, 1968, p 295.
- (6) J. B. Anderson, E. Kostiner, M. C. Miller, and J. R. Rea, *J. Solid State Chem.*, **14**, 372 (1974).
- (7) G. Germain, P. Main, and M. N. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368 (1971).
- (8) W. R. Busing, K. O. Martin, and H. A. Levy, Oak Ridge National Laboratory, ORNL-TM-305, Oak Ridge, Tenn., 1962.
- (9) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).
- (10) W. H. Zachariasen, *Acta Crystallogr.*, **23**, 558 (1967); *Acta Crystallogr., Sect. B*, **24**, 324 (1968).
- (11) W. R. Busing, K. O. Martin, and H. A. Levy, Oak Ridge National Laboratory, ORNL-TM-306, Oak Ridge, Tenn., 1962.
- (12) W. H. Baur, *Acta Crystallogr., Sect. B*, **28**, 1456 (1972).
- (13) I. D. Brown and R. D. Shannon, *Acta Crystallogr., Sect. A*, **29**, 266 (1973).
- (14) I. D. Brown, *Acta Crystallogr., Sect. A*, **32**, 24 (1976).

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## Sterically Hindered Solvent Extractants. 2. A Neutron-Diffraction Study of the Di-*tert*-butylphosphinic Acid Dimer Showing Strong Asymmetric Hydrogen Bonding<sup>1</sup>

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Di-*tert*-butylphosphinic acid,  $[(\text{CH}_3)_3\text{C}]_2\text{PO}(\text{OH})$ , is shown to be dimeric in the solid state with two acid molecules linked together by strong linear, 2.486 (9) Å, asymmetric hydrogen bonds forming an eight-membered centrosymmetric ring (1). The two O–H distances in the asymmetric H bond are 1.114 (15) and 1.372 (14) Å, the primary O–H being considerably lengthened. The molecule crystallizes in the monoclinic space group,  $P2_1/c$ , with unit cell parameters  $a = 8.979$  (6),  $b = 13.119$  (9),  $c = 10.576$  (7) Å,  $\beta = 118.03$  (3)°, and  $Z = 4$ . The structure was solved using the heavy-atom coordinates of the previously determined x-ray model and refined using 1001 three-dimensional neutron data by Fourier and full-matrix least-squares techniques to  $R_F = 0.048$  for 525 reflections where  $F_o > 3\sigma(F_o)$ . The P–O bond lengths are P–O(1) = 1.531 (7) Å and P–O(2) = 1.518 (9) Å.

### Introduction

Di-*tert*-butylphosphinic acid,  $[(\text{CH}_3)_3\text{C}]_2\text{PO}(\text{OH})$ , H-[Dt-BP] hereafter, is part of a wide class of sterically hindered organophosphorus solvent extractors of lanthanide and actinide metal ions which show a great selectivity of metal ion extraction.<sup>3</sup> For example, the  $[\text{UO}_2^{2+}]$  ion is extracted by H-[Dt-BP] with an efficiency which is  $10^7$  greater than for Th(IV) ions under the same pH, diluent, and temperature conditions.<sup>4</sup> Recently, we have undertaken the study of the structural characteristics of several of these extractants in order

to observe possible correlations between structure and selectivity.

Previously,<sup>5</sup> we have shown that H-[Dt-BP] exists in the crystalline state as a discrete dimer, the only discrete dimeric  $\text{R}_2\text{POOH}$  acid to be described to date. The x-ray model was ambiguous as to the position of the hydrogen atoms linking the two halves of the dimer. Fourier maps derived from the x-ray data showed an extended cylindrical trough of electron density joining the two nonequivalent oxygen atoms of the eight-membered ring but did not reliably establish whether

**Table I.** Positional Parameters of H[Dt-BP] with Estimated Standard Deviations Given in Parentheses

Atom	x	y	z
P	0.0424 (6)	0.4043 (4)	0.6687 (5)
O(1)	0.0625 (8)	0.5202 (3)	0.6845 (7)
O(2)	0.0234 (6)	0.3661 (3)	0.5264 (5)
C(1)	-0.1503 (5)	0.3723 (3)	0.6782 (5)
C(2)	0.2375 (5)	0.3516 (3)	0.8095 (5)
C(3)	-0.2886 (10)	0.4293 (8)	0.5550 (11)
C(4)	-0.1911 (11)	0.2589 (5)	0.6578 (12)
C(5)	-0.1393 (16)	0.4058 (13)	0.8203 (13)
C(6)	0.3767 (11)	0.3823 (10)	0.7743 (12)
C(7)	0.2370 (11)	0.2347 (5)	0.8154 (11)
C(8)	0.2855 (12)	0.3929 (8)	0.9580 (9)
H(1)	0.0225 (11)	0.5707 (9)	0.5894 (13)
H(2)	0.1530 (19)	0.2081 (10)	0.8571 (17)
H(3)	0.3542 (18)	0.2064 (10)	0.8822 (19)
H(4)	0.1987 (25)	0.2022 (10)	0.7074 (21)
H(5)	0.1971 (26)	0.3633 (21)	0.9991 (15)
H(6)	0.4008 (19)	0.3719 (17)	1.0314 (15)
H(7)	0.2843 (28)	0.4743 (19)	0.9564 (20)
H(8)	0.3571 (20)	0.3480 (16)	0.6722 (19)
H(9)	0.3851 (23)	0.4608 (18)	0.7658 (24)
H(10)	0.4934 (17)	0.3540 (13)	0.8498 (16)
H(11)	-0.4104 (16)	0.4160 (13)	0.5533 (17)
H(12)	-0.2982 (22)	0.4110 (22)	0.4544 (20)
H(13)	-0.2689 (20)	0.5110 (12)	0.5724 (26)
H(14)	-0.1922 (26)	0.2302 (13)	0.5604 (27)
H(15)	-0.1073 (21)	0.2152 (13)	0.7488 (23)
H(16)	-0.3136 (16)	0.2489 (11)	0.6509 (16)
H(17)	-0.2683 (20)	0.3986 (14)	0.8093 (16)
H(18)	-0.0624 (25)	0.3577 (24)	0.9009 (19)
H(19)	-0.1070 (32)	0.4856 (16)	0.8384 (30)

the hydrogen location was in accord with a symmetric, asymmetric, or a disordered hydrogen bond. In order to resolve this ambiguity and to obtain a more accurate description of all hydrogen atom positions, a complete three-dimensional neutron structure determination was undertaken.

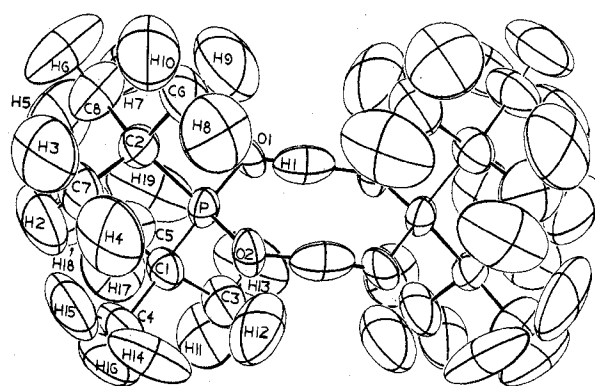
### Experimental Section

**Crystal Preparation.** Single crystals of H[Dt-BP] suitable for neutron studies were grown from benzene solution by evaporation. The crystals are transparent and air stable. The observed density is 1.015 g/cm<sup>3</sup> ( $\rho_{\text{calcd}} = 1.077$  g/cm<sup>3</sup>).

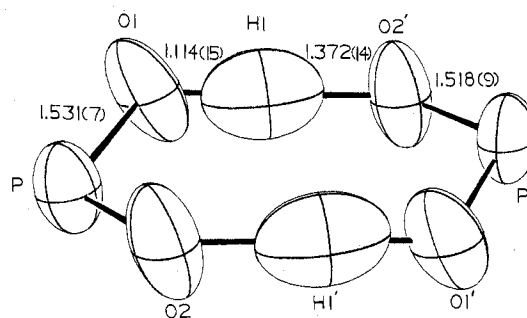
**Space Group.** A neutron survey of systematically absent reflections was carried out resulting in complete concurrence with the space group  $P2_1/c$  previously established by x-ray methods.

**Neutron Data.** The crystal selected for data collection, a rectangular prism 0.266 × 0.235 × 0.490 cm, was sealed to a glass rod and mounted on the Chemistry Division four-circle neutron diffractometer at the CP-5 reactor which has been described in detail previously.<sup>6</sup> The crystal remained clear and transparent throughout the study. The orientation was a general one with *b* approximately parallel to the  $\phi$  axis of the diffractometer. The cell parameters and orientation matrix were determined from precise angular measurement of 19 automatically centered reflections, chosen in the  $2\theta$  range of 30 to 60°. The cell parameters are  $a = 8.979$  (6),  $b = 13.119$  (9),  $c = 10.576$  (7),  $\beta = 118.03$  (3),  $Z = 4$  at 22 °C. The wavelength, 1.142 (1) Å, was obtained with a Be crystal monochromator set at  $\theta_M = 30^\circ$ . Data were collected in the  $\theta-2\theta$  step scan mode with 0.1° steps and a scan width varying from 3.2 to 5.2°. Backgrounds were measured on both sides of the peak for times ca. 0.3 to 0.5 the peak scan time. Data collection was limited to  $2\theta \leq 65^\circ$ , beyond which few reflections were observable. A total of 1001 reflections were collected in the *hkl* and  $\bar{h}\bar{k}l$  octants. Two standard reflections were checked repeatedly during the run and found to remain unchanged in intensity within the expected statistical variation. Standard errors were assigned to the data on the basis of counting statistics plus a contribution  $(0.03I)^2$  to the variance of each reflection. The data were corrected for absorption ( $\mu = 2.655$  cm<sup>-1</sup>), the transmission coefficients ranging from 0.56 to 0.52, and were reduced to scaled  $F^2$  values for structure solution and refinement.

**Structure Solution and Refinement.** The coordinates of the nonhydrogen atoms as determined by the previous x-ray determination were used to provide an initial phasing model.<sup>5</sup> A difference Fourier



**Figure 1.** H[Dt-BP] dimer showing atom labeling and 50% probability ellipsoids of thermal motion.



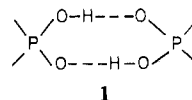
**Figure 2.** Eight-membered ring formed by strong asymmetric hydrogen bonding linking the two halves of the dimer of H[Dt-BP].

map revealed the positions of all hydrogen atoms. Anisotropic full-matrix least-squares refinement of all atom parameters, a scale factor, and a secondary extinction factor ( $G = 0.0957$ ) using all neutron data converged after six cycles. The final discrepancy indices are  $R_F = 0.048$  ( $R_F^2 = 0.066$ ) for the 525 reflections, where  $F_o > 3\sigma(F_o)$  and  $\Sigma_2 = 1.117$ , indicating the excellence of the refinement. The agreement indices are defined as  $R_F = \sum |F_o| - |F_c| / \sum |F_o|$ ,  $R_{F^2} = \sum |F_o^2 - F_c^2| / \sum F_o^2$ , and  $\Sigma_2 = [\sum w(F_o^2 - F_c^2)^2 / (N_o - N_r)]^{1/2}$ , where  $N_o$  is the number of independent observations and  $N_r$  the number of parameters varied. The data were quite weak as is shown by the large difference between the number of reflections which were collected (1001) and the number which had an observable intensity ( $>3\sigma F_o$ ). The quantity minimized in the refinement was  $\sum w(F_o^2 - F_c^2)$  where  $F_o$  and  $F_c$  are the observed and calculated structure factor amplitudes and weights  $w$  are given by  $1/\sigma^2(F_o)^2$ . The observed and calculated structure factor amplitudes are given as supplementary material. The atomic coordinates are listed in Table I, and the anisotropic temperature factors are listed in Table II. The neutron scattering amplitudes used were as follows:  $b_P = 0.510$ ,  $b_C = 0.6658$ ,  $b_O = 0.575$ , and  $b_H = -0.374$  all in units of  $10^{-12}$  cm.

The raw neutron data were reduced using the program DATALIB<sup>7</sup> for input into Fourier and least-squares refinement programs S5FOUR<sup>8</sup> and S5XFLS,<sup>8</sup> respectively. All distances, angles, and planes were calculated using the program S5FFE.<sup>8</sup> Molecular drawings were made using the program OR-TEP II.<sup>9</sup>

### Description and Discussion of the Structure

In the crystalline state, H[Dt-BP] exists as a dimer as shown in Figure 1. Table III lists interatomic distances, and Table IV lists the interatomic angles for H[Dt-BP]. The two phosphinic acid molecules are linked through a center of symmetry by strong asymmetric hydrogen bonds of 2.486 (9) Å length, forming a nonplanar eight-membered ring (1) which



has a chair configuration (see Figure 2). The hydrogen bond is clearly asymmetric, but the O-H bond distances of O(1)-H(1) = 1.114 (15) Å and O(2)'-H(1) = 1.372 (14) Å

**Table II.** Anisotropic Thermal Parameters<sup>a</sup> ( $\times 10^4$ ) of H[Dt-BP] with Estimated Standard Deviations in Parentheses

Atom	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
P	194 (11)	57 (4)	85 (8)	3 (5)	70 (7)	4 (4)
O(1)	329 (16)	26 (4)	160 (11)	-29 (5)	139 (12)	-18 (4)
O(2)	312 (13)	44 (3)	128 (9)	8 (5)	119 (9)	9 (5)
C(1)	174 (9)	62 (4)	183 (8)	11 (5)	79 (7)	24 (4)
C(2)	171 (9)	83 (4)	128 (7)	-2 (5)	64 (7)	11 (4)
C(3)	199 (16)	117 (7)	299 (18)	24 (9)	95 (17)	68 (9)
C(4)	257 (17)	61 (5)	334 (19)	-24 (8)	108 (16)	33 (8)
C(5)	368 (30)	269 (17)	275 (23)	-57 (18)	250 (21)	-64 (16)
C(6)	221 (17)	168 (9)	309 (20)	-23 (11)	144 (16)	81 (12)
C(7)	260 (17)	72 (6)	285 (16)	42 (8)	109 (14)	61 (8)
C(8)	315 (21)	168 (9)	156 (17)	34 (12)	56 (14)	9 (10)
H(1)	221 (20)	105 (11)	223 (24)	-24 (12)	114 (21)	-97 (13)
H(2)	392 (35)	104 (11)	450 (38)	16 (15)	176 (30)	111 (16)
H(3)	343 (32)	129 (12)	492 (42)	86 (16)	98 (29)	98 (18)
H(4)	707 (59)	70 (9)	411 (37)	62 (17)	253 (43)	1 (16)
H(5)	683 (68)	409 (40)	185 (22)	44 (37)	265 (35)	19 (23)
H(6)	361 (35)	317 (27)	175 (23)	62 (26)	-30 (23)	-19 (20)
H(7)	624 (60)	227 (23)	234 (29)	40 (33)	-32 (34)	-115 (24)
H(8)	435 (40)	242 (23)	330 (30)	-2 (22)	295 (33)	-12 (22)
H(9)	385 (38)	245 (24)	529 (52)	-61 (27)	196 (33)	130 (32)
H(10)	238 (28)	250 (20)	370 (30)	15 (20)	128 (25)	122 (21)
H(11)	190 (25)	234 (18)	495 (38)	92 (18)	56 (25)	137 (22)
H(12)	302 (34)	350 (38)	300 (33)	41 (25)	74 (32)	124 (32)
H(13)	433 (40)	79 (11)	735 (65)	74 (17)	198 (38)	22 (19)
H(14)	582 (54)	119 (14)	617 (56)	-138 (22)	336 (52)	-116 (26)
H(15)	432 (44)	132 (14)	569 (55)	-35 (18)	133 (39)	153 (25)
H(16)	289 (26)	155 (13)	489 (36)	-87 (17)	176 (28)	31 (18)
H(17)	444 (37)	317 (23)	467 (36)	-24 (26)	379 (33)	41 (26)
H(18)	325 (43)	432 (46)	184 (27)	-72 (33)	131 (27)	20 (30)
H(19)	808 (74)	241 (23)	586 (65)	-192 (37)	577 (62)	-249 (36)

<sup>a</sup> The form of the anisotropic temperature factor is:  $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})]$ .

**Table III.** Interatomic Distances in H[Dt-BP] with Estimated Standard Deviations in Parentheses

Bond	Distances, Å	Bond	Distances, Å
(a) Heavy-Atom Distances			
P-O(1)	1.531 (7)	C(1)-C(4)	1.523 (8)
P-O(2)	1.518 (9)	C(1)-C(5)	1.523 (17)
P-C(1)	1.829 (8)	C(2)-C(6)	1.517 (15)
P-C(2)	1.820 (6)	C(2)-C(7)	1.535 (9)
C(1)-C(3)	1.509 (10)	C(2)-C(8)	1.519 (11)
(b) Methyl Hydrogen-Carbon Distances			
C(3)-H(11)	1.098 (20)	C(6)-H(8)	1.105 (25)
C(3)-H(12)	1.054 (26)	C(6)-H(9)	1.040 (28)
C(3)-H(13)	1.088 (20)	C(6)-H(10)	1.042 (16)
C(4)-H(14)	1.093 (33)	C(7)-H(2)	1.094 (24)
C(4)-H(15)	1.068 (20)	C(7)-H(3)	1.022 (16)
C(4)-H(16)	1.074 (20)	C(7)-H(4)	1.111 (24)
C(5)-H(17)	1.113 (25)	C(8)-H(5)	1.139 (29)
C(5)-H(18)	1.024 (27)	C(8)-H(6)	0.998 (17)
C(5)-H(19)	1.078 (28)	C(8)-H(7)	1.068 (28)
(c) Hydrogen-Bonded Distances			
H(1)-O(1)	1.114 (15)	H(1)-O(2)'	1.372 (14)
(d) Dimeric Interaction			
O(1)---O(2)'	2.486 (9)		
(e) Bite Distance			
O(1)---O(2)	2.541 (8)		

show a considerable shift toward a symmetric hydrogen bond. The shift is somewhat greater ( $\sim 0.03$  Å) than the well known correlation between O-H and O-H---O distances<sup>10</sup> would predict. This tendency toward the formation of a symmetric bond is related to the strength of the hydrogen bond formed and also, undoubtedly, to the symmetry of the environment of the bonding proton. In the present case, the near equivalence of the two distinct P-O distances (see below) gives a rather strong indication that the environment of the proton is nearly symmetrical. The hydrogen bond is essentially linear, the O(1)-H(1)-O(2)' angle being  $178.8$  (10)<sup>o</sup>, in keeping with expectations for a strong hydrogen bond.

**Table IV.** Bond Angles in H[Dt-BP] with Estimated Standard Deviations Given in Parentheses

Atoms	Angle, deg	Atoms	Angle, deg
(a) Angles Involving Nonhydrogen Atoms			
O(1)-P-O(2)	112.9 (5)	P-C(2)-C(6)	106.6 (5)
C(1)-P-C(2)	116.0 (4)	P-C(2)-C(7)	113.1 (4)
C(1)-P-O(1)	106.7 (5)	P-C(2)-C(8)	114.0 (5)
C(1)-P-O(2)	108.1 (4)	C(3)-C(1)-C(4)	108.4 (6)
C(2)-P-O(1)	105.6 (4)	C(3)-C(1)-C(5)	110.7 (8)
C(2)-P-O(2)	107.6 (4)	C(4)-C(1)-C(5)	108.8 (9)
P-C(1)-C(5)	111.3 (6)	C(6)-C(2)-C(7)	107.1 (8)
P-C(1)-C(3)	104.8 (6)	C(6)-C(2)-C(8)	106.9 (7)
P-C(1)-C(4)	112.8 (6)	C(7)-C(2)-C(8)	108.6 (7)
(b) Angles Involving Methyl Hydrogen Atoms			
H(11)-C(3)-H(12)	109.8 (15)	H(14)-C(4)-H(15)	110.7 (18)
H(11)-C(3)-H(13)	103.9 (18)	H(14)-C(4)-H(16)	109.8 (16)
H(12)-C(3)-H(13)	108.9 (24)	H(15)-C(4)-H(16)	105.1 (19)
C(1)-C(3)-H(11)	110.2 (12)	C(1)-C(4)-H(14)	111.4 (14)
C(1)-C(3)-H(12)	113.7 (15)	C(1)-C(4)-H(15)	112.1 (11)
C(1)-C(3)-H(13)	109.8 (11)	C(1)-C(4)-H(16)	107.4 (11)
H(17)-C(5)-H(18)	107.2 (23)	H(8)-C(6)-H(9)	107.7 (22)
H(17)-C(5)-H(19)	106.3 (25)	H(8)-C(6)-H(10)	104.2 (18)
H(18)-C(5)-H(19)	115.4 (22)	H(9)-C(6)-H(10)	109.4 (16)
C(1)-C(5)-H(17)	106.9 (12)	C(2)-C(6)-H(8)	111.1 (13)
C(1)-C(5)-H(18)	110.4 (20)	C(2)-C(6)-H(9)	112.6 (18)
C(1)-C(5)-H(19)	110.1 (23)	C(2)-C(6)-H(10)	111.4 (15)
H(2)-C(7)-H(3)	106.6 (16)	H(5)-C(8)-H(6)	105.2 (17)
H(2)-C(7)-H(4)	110.7 (16)	H(5)-C(8)-H(7)	110.0 (23)
H(3)-C(7)-H(4)	106.9 (18)	H(6)-C(8)-H(7)	106.7 (18)
C(2)-C(7)-H(2)	110.5 (11)	C(2)-C(8)-H(5)	111.3 (12)
C(2)-C(7)-H(3)	111.7 (10)	C(2)-C(8)-H(6)	113.1 (15)
C(2)-C(7)-H(4)	110.3 (11)	C(2)-C(8)-H(7)	110.2 (13)
(c) Angles Involving the Hydrogen Bond			
O(1)-H(1)-O(2)'	178.8 (10)	P'-O(2)-H(1)	122.1 (7)
P-O(1)-H(1)	121.3 (8)		

The two P-O distances are 1.531 (7) and 1.518 (9) Å. The difference is not significant statistically; however, the longer distance involves O(1) which participates in the shorter (1.114 Å) O-H separation. The similarity of the two P-O distances implies both chemical and crystallographic near equivalence,

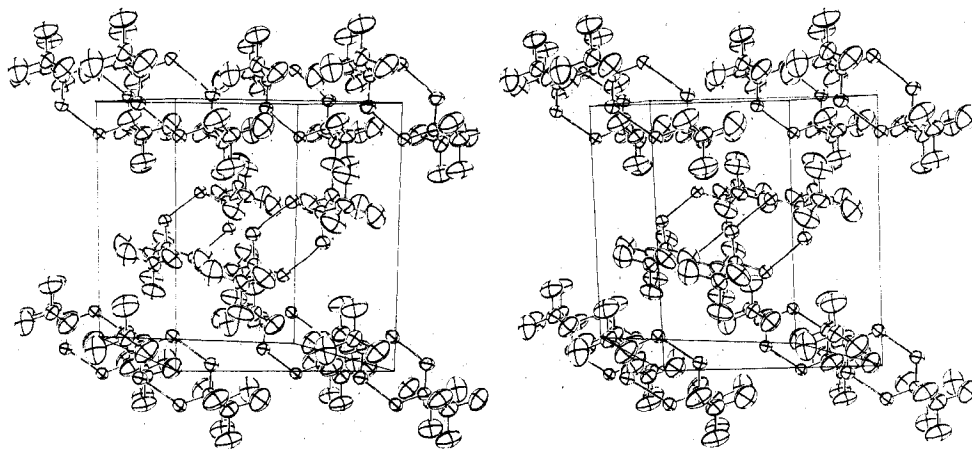
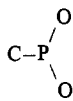


Figure 3. Stereoview showing packing of H[Dt-BP] dimers within the unit cell.

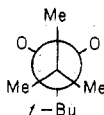
influenced undoubtedly by the symmetry of the dimer; their lengths imply partial double-bond character in both instances. The O(1)-P-O(2) angle is 112.9° giving an O(1)-O(2) distance of 2.541 (8) Å.

The methyl hydrogen positions determined by neutron diffraction generally confirm the x-ray hydrogen positions but yield an average C-H distance of 1.072 Å compared to 0.934 Å for the x-ray case. There is no evidence for disorder, rotational or otherwise. All atoms occupy fixed positions with reasonable thermal parameters (see Table II). This appears to be due to strong steric effects, which prevent rotation not only of the bulky *tert*-butyl groups about the P-C bonds but also the methyl groups about the various C-C bonds in the molecule.

The conformation of the H[Dt-BP] dimer may be described in terms of the nearly planar eight-membered ring and pairs of *tert*-butyl groups related by a pseudomirror coincident with the ring plane. The ring is slightly distorted from the plane of the four oxygen atoms by symmetric 0.24-Å P-atom displacements, above and below the plane, resulting in a chair conformation. The nearly tetrahedral geometry of P (see Table IV) plus the expected substantial barrier for rotation<sup>11</sup> of the bulky *tert*-butyl groups about the C-P bond fixes the staggered configuration (looking down the C-P bond) of the *tert*-butyl groups with respect to the



moiety as shown in the Newman projection. A nearly eclipsed



conformation of the two *tert*-butyl groups (including hydrogen atoms) when viewed down the C(1)-C(2) vector is required by the pseudomirror. The C(1)-P-C(2) bond angle of 116.0 (4)°, which is substantially larger than tetrahedral, may be attributed to the repulsions of the neighboring eclipsed *tert*-butyl methyl groups. The CH<sub>3</sub> groups are each staggered with respect to the



moieties to which they are attached. This leads to orientations of the C(3) and C(6) methyl groups which place two hydrogen atoms of each group above and below the two oxygen atoms. The H-O approaches which result are 2.64 (2) and 2.68 (2)

Table V. Short C-H...O Interactions

C-H...O	C...O distance, Å	H...O distance, Å
C(3)-H(13)...O(1)	3.031 (11)	2.639 (19)
C(3)-H(12)...O(2)	3.071 (13)	2.684 (21)
C(6)-H(8)...O(2)	3.027 (10)	2.659 (17)
C(6)-H(9)...O(1)	3.101 (13)	2.719 (22)
C(4)-H(14)...O(2)	3.185 (15)	2.777 (26)
C(5)-H(19)...O(1)	3.169 (20)	2.740 (38)
C(7)-H(4)...O(2)	3.238 (10)	2.817 (16)
C(8)-H(7)...O(1)	3.117 (11)	2.686 (19)

Table VI. Close Interdimeric Hydrogen Bonding Contacts

Atoms	Distances, Å	Atoms	Distances, Å
O(1)...H(15)	2.633 (18)	O(2)...H(15)	2.809 (22)
O(1)...H(2)	3.036 (16)	O(2)...H(18)	3.166 (31)
O(2)...H(2)	2.732 (22)		

Å for two C(3) hydrogen atoms and 2.66 (2) and 2.72 (2) Å for two C(6) hydrogen atoms with O(1) and O(2). Since these distances are slightly longer than the expected O-H van der Waals separation (2.6 Å), the forces orienting the CH<sub>3</sub> groups would appear to be largely repulsive. However, the bond angles P-C(1)-C(3) and P-C(2)-C(6), which involve methyl groups with two short H...O distances each, are 104.8 (6)° and 106.6 (5)°, while the neighboring C(4) and C(5) and C(7) and C(8) methyl groups which have rather close hydrogen approaches display the considerably larger angles P-C(1)-C(4) = 112.8 (6)°, P-C(1)-C(5) = 111.3 (6)°, P-C(2)-C(7) = 113.1 (4)°, and P-C(2)-C(8) = 114.0 (5)°. The orientations of the latter four methyl groups are such that one hydrogen atom from each is directed toward O(1) or O(2). The O-H separations range from 2.69 to 2.82 Å so it appears that repulsive interactions are indeed dominant in establishing their orientations.

The geometry of the *tert*-butyl ligands is shown by the following average bond lengths and angles: C-C = 1.521 (7) Å, C-H = 1.072 (20) Å, ∠C-C-C = 108.4 (12)°, ∠H-C-H = 108.0 (22)°, and ∠C-C-H = 110.7 (15)°. The C-C bond length is shorter than a normal C-C single-bond distance which may be rationalized in terms of hyperconjugation of the CH<sub>3</sub> groups with the C-P=O moiety.

The H[Dt-BP] dimer is distinct in the crystalline state as is evident from the packing diagram shown in Figure 3. Each dimer is related by a 2<sub>1</sub> axis to another dimer in the unit cell. The packing is relatively open in agreement with the rather low density. Table VI lists the closest interdimeric hydrogen bonding contacts; these indicate the relatively weak crystal forces present.

### Conclusions

Dimer formation in H[Dt-BP] involves very strong hydrogen

bonding which, although asymmetric, shows a strong tendency toward development of a symmetric bond. The existence of a discrete hydrogen bond dimer rather than the more usual infinite spiral hydrogen bonded polymer observed for (X)-(Y)PO(OH) compounds<sup>12</sup> is due to a steric effect as discussed previously.<sup>5</sup> The bulky *tert*-butyl groups in H[Dt-BP] are strategically located to block the directions in which a molecular approach is required to form a hydrogen-bonded spiral, while not interfering with dimer formation. Therefore dimeric hydrogen bonding is the only alternative.

The practical significance of the dimeric structure adopted by H[Dt-BP] is related to the obvious blockage of the oxygen chelation sites by the bulky *tert*-butyl groups, thus potentially interfering with extraction of metal ions of large ionic radii and high coordination number.<sup>13</sup> As reported in the Introduction, R<sub>2</sub>PO(OH) and (RO)<sub>2</sub>PO(OH) molecules, where R is a large organic ligand, extract [UO<sub>2</sub>]<sup>2+</sup> ions much more easily than ions of higher ionic radius and coordination number, e.g., Th(IV). Since the oxygen chelation sites are sterically blocked, ions of smaller radii can be expected to chelate more readily, e.g., the ionic radii of [UO<sub>2</sub>]<sup>2+</sup> and Th(IV) are 0.76 Å (coordination no. 6) and 0.98 Å (coordination no. 8), respectively.

Clearly chelation of Th(IV) solely with H[Dt-BP] is not possible in view of the large radius and high charge and coordination number of Th(IV) plus the steric blockage of the oxygen sites of the extractant. Since Th(IV) is extracted to a minor extent by H[Dt-BP], water and inorganic anions probably participate somewhat to maintain the Th(IV) coordination sphere and charge balance.

Work is continuing on the synthesis and structural determinations of several metal-phosphorus chelated materials in order to pinpoint further the selective nature of many of these sterically hindered phosphinic acid extractants.

Registry No. H[Dt-BP], 677-76-9.

**Supplementary Material Available:** A listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

### References and Notes

- (1) Work performed under the auspices of the U.S. Energy Research and Development Administration.
- (2) To whom correspondence should be addressed.
- (3) (a) D. F. Peppard, "Annual Review of Nuclear Science", Vol. 21, E. Segre, Ed., Annual Reviews Inc., Palo Alto, Calif., 1971, pp 365-396; (b) E. K. Hulet and D. D. Bode, *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One*, 1 (1972); (c) G. W. Mason, N. L. Schofer, and D. F. Peppard, *J. Inorg. Nucl. Chem.*, **32**, 3899 (1970); (d) G. W. Mason, N. L. Schofer, and D. F. Peppard, *ibid.*, **32**, 3911 (1970); (e) D. F. Peppard, G. W. Mason, A. F. Bollmeier, and S. Lewey, *ibid.*, **33**, 845 (1971); (f) G. W. Mason and S. Lewey, *ibid.*, **36**, 911 (1974).
- (4) G. W. Mason and D. F. Peppard, unpublished results.
- (5) M. E. Druyan, A. H. Reis, Jr., E. Gebert, S. W. Peterson, G. W. Mason, and D. F. Peppard, *J. Am. Chem. Soc.*, **98**, 4801 (1976).
- (6) S. W. Peterson, R. P. Willett, and J. L. Huston, *J. Chem. Phys.*, **59**, 453 (1973).
- (7) An IBM 370/195 program written by H. A. Levy.
- (8) SSFOUR, SSXFLS, and SSFFE are Sigma 5 versions of the programs FOURIER by R. J. Dellaco and W. T. Robinson, ORXFLS written by W. R. Busing and H. A. Levy, and ORFFE3 written by W. R. Busing and H. A. Levy.
- (9) "OR-TEP II" written by C. Johnson.
- (10) W. Hamilton and J. Ibers, "Hydrogen Bonding in Solids", W. A. Benjamin, New York, N.Y., 1968, pp 53 and 54.
- (11) C. H. Bushweller and J. A. Brunelle, *J. Am. Chem. Soc.*, **95**, 5949 (1973).
- (12) (a) M. Calleri and J. C. Speakman, *Acta Crystallogr.*, **17**, 1097 (1964); (b) Mazhar-ul-Haque, C. N. Caughlan, and W. L. Moats, *J. Org. Chem.*, **35**, 1446 (1970); (c) F. P. Boer, *Acta Crystallogr., Sect. B*, **28**, 1201 (1972); (d) P. J. Wheatley, *J. Chem. Soc.*, **3722** (1962); (e) T.-T. Liang and K.-C. Chi, *Chem. Abstr.*, **63**, 12441e (1965); (f) F. Giordano and A. Ripamonti, *Acta Crystallogr.*, **22**, 678 (1967); (g) D. D. Swank and C. N. Coughlan, *Chem. Commun.*, 1051 (1968); (h) E. Alver and H. M. Kjøge, *Acta Chem. Scand.*, **23**, 1101 (1969); (i) D. Fenske, R. Mattes, J. Lons, and K. F. Tebbe, *Chem. Ber.*, **106**, 1139 (1973).
- (13) The exact value for the size of an ion which will chelate has not been determined, but calculations based on extraction data seem to indicate that an ion with an ionic radius of ~0.80 Å or above will not fit satisfactorily.

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## Molecules with an M<sub>4</sub>X<sub>4</sub> Core. 8.<sup>1-7</sup> Crystal Structures of Tetrameric Triethylphosphinesilver(I) Chloride and Triethylphosphinesilver(I) Bromide

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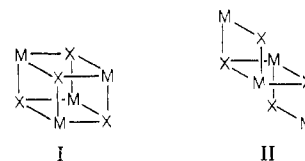
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The tetrameric species triethylphosphinesilver(I) chloride, [PEt<sub>3</sub>AgCl]<sub>4</sub>, and triethylphosphinesilver(I) bromide, [PEt<sub>3</sub>AgBr]<sub>4</sub>, have been synthesized and subjected to full three-dimensional x-ray structural analysis. The complexes each crystallize in the polar cubic space group *I*43*m* (*T*<sub>d</sub><sup>3</sup>; No. 217) with *Z* = 2. X-ray diffraction data were collected with a Picker FACS-1 automated diffractometer. Unit cell constants are *a* = 12.919 (2) Å for [PEt<sub>3</sub>AgCl]<sub>4</sub> and *a* = 13.165 (2) Å for [PEt<sub>3</sub>AgBr]<sub>4</sub>. These species are isomorphous with [PEt<sub>3</sub>CuX]<sub>4</sub> (X = Cl, Br, I) and [AsEt<sub>3</sub>CuI]<sub>4</sub>. However, satisfactory refinement of [PEt<sub>3</sub>AgCl]<sub>4</sub> and [PEt<sub>3</sub>AgBr]<sub>4</sub> occurred only after the additional assumption of threefold disorder of the silver atoms about the crystallographic C<sub>3</sub> axes. Resulting discrepancy indices are *R*<sub>F</sub> = 2.41% and *R*<sub>wF</sub> = 2.49% for [PEt<sub>3</sub>AgCl]<sub>4</sub> and *R*<sub>F</sub> = 2.70% and *R*<sub>wF</sub> = 2.52% for [PEt<sub>3</sub>AgBr]<sub>4</sub>. Each molecule has a "cubanelike" skeleton of alternating silver and halogen atoms.

### Introduction

We have recently completed crystal structure determinations on two complete series of tetrameric phosphinecopper(I) halides, [PPh<sub>3</sub>CuX]<sub>4</sub> (X = Cl,<sup>1</sup> Br,<sup>2</sup> I<sup>4</sup>) and [PEt<sub>3</sub>CuX]<sub>4</sub> (X = Cl,<sup>5</sup> Br,<sup>5</sup> I<sup>3</sup>), along with the related arsine derivative, [AsEt<sub>3</sub>CuI]<sub>4</sub>.<sup>3</sup> These results show the following pattern for copper complexes.

A. The ubiquitous "cubane" structure I is unstable with respect to the "step" structure II when large halogen atoms



and bulky phosphine ligands appear simultaneously (i.e., in [PPh<sub>3</sub>CuI]<sub>4</sub> and [PPh<sub>3</sub>CuBr]<sub>4</sub>); i.e., the transformation from "cubane" to "step" structure comes about as the result of repulsive intramolecular interactions. [Note that the step structure is not itself intrinsically unstable when intramolecular

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