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Crystal and Molecular Structure of Triphenylphosphonium Praseodymium(III) Hexachloride

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The structure of triphenylphosphonium praseodymium(III) hexachloride, $[(C_6H_5)_3PH]_3PrCl_6$, has been determined from three-dimensional x-ray data collected by counter methods. The compound crystallizes in the monoclinic space group $P2_1/c$ with four molecules in a unit cell of dimensions $a = 12.010$ (3) Å, $b = 41.574$ (3) Å, $c = 11.750$ (2) Å, and $\beta = 112.71$ (1)°. Least-squares refinement of the structure has led to a final value of a weighted $R = 0.088$ where $1/\sigma^2$ weights were used for 4061 independent reflections. The final structure shows that the $PrCl_6^{3-}$ ion very closely approximates D_{2d} symmetry instead of the previously assumed octahedral (O_h) symmetry. The average Pr–Cl bond distance is 2.745 ± 0.012 Å.

Introduction

The number of papers discussing lanthanide halides has increased so rapidly that a series of reviews regarding these have been published.[1] The structures of these compounds were originally investigated through interpretation of absorption spectra, but answers regarding chemical bonding and molecular geometries in many of those cases were not clear since the spectra were complicated and alternative models often fit the same spectra. A large body of structural information based on x-ray diffraction techniques was subsequently developed. Apparently, the structures studied were a function of the relative stability of the compound. Thus, trihalides and oxyhalides primarily, with tetrahalides and pentahalides subsequently, were studied in great depth. A limited number of pentavalent hexafluorides, of high symmetry, were studied and found to fall in various isomorphous families.[2] The structure of UCl_6 has long been known[3] having been found to be of hexagonal symmetry with the chlorines forming an almost perfect octahedron about the uranium. However, there exists a paucity of structural information for those cases in which spectroscopic studies indicate some deviation from the highly idealized O_h symmetry.[4] To help understand these spectra and to give an accurate model for quantum mechanical calculations, the x-ray crystal structures of several significant lanthanide complexes has been undertaken. The first to be completed by us, triphenylphosphonium praseodymium(III) hexachloride, $[(C_6H_5)_3PH]_3PrCl_6$, mol wt 1143, is reported herein. It represents the first hexachloride of praseodymium reported although both $PrCl_3$ and $PrBr_3$ have been shown to be isostructural to UCl_3.[5]

Experimental Section

A sample of the compound was prepared and recrystallized by Roger Mazique of Southern University using the method of Ryan and Jorgensen.[6] Since the compound is hygroscopic, the x-ray study was carried out on crystals sealed in glass capillaries containing a dry nitrogen atmosphere. One such crystal having dimensions 0.27 × 0.32 × 0.43 mm was mounted on a General Electric XRD-5 diffractometer with the $(\bar{3}06)$ axis coincident with the Φ axis of the instrument. Extinction of the ($h0l$) reflections with l odd and the ($0k0$) reflections with k odd uniquely characterizes the monoclinic space group as $P2_1/c$. Lattice constants were determined by a least-squares fit of 30 carefully measured 2θ values of the Cu $K\alpha_1$–$K\alpha_2$ doublet for $2\theta > 66°$ under fine conditions (1° takeoff angle and 0.05° slit). The resultant lattice constants and their estimated standard deviations (esd's) are $a = 12.010$ (3) Å, $b = 41.574$ (3) Å, $c = 11.750$ (2) Å, $\beta = 112.71$ (1)°, and V(cell) = 5412.2 Å^3.

The calculated density of 1.41 g/cm^3 assuming four molecules per unit cell was accepted as reasonable and subsequently confirmed by the complete structure determination. Because of the instability of the compound in solution, no experimental density was measured.

Intensity data were collected on a General Electric XRD-490 fully automated diffractometer by the stationary-crystal, stationary-counter method using balanced Ni and Co Ross filters and Cu $K\alpha$ radiation. A total of 5564 reflections were measured to a 2θ maximum of 100° ($d^* = 0.995$). Reflections were considered as statistically significant if $(I_{Ni} - 2\sigma(I_{Ni})) - (I_{Co} + 2\sigma(I_{Co})) > N$, where σ is based on counting statistics (10-s counting time) and N is based on the background cutoff level. In this study, a value of 250 was chosen for N, based on background measurements at the locations of symmetry-extinct reflections. This procedure gave a total of 4061 (73%) observed reflections. The intensities were corrected for α_1–α_2 splitting as a function of 2θ and Lorentz polarization effects in the usual manner. Normalized transmission factors ranging from 1.00 to 2.00 were corrected using an absorption correction calculated as a function of the polar angle Φ (linear absorption coefficient $\mu = 102.4$ cm^{-1} for Cu radiation).

Structure Determination

A three-dimensional Patterson function calculated using the 1100 most intense reflections led directly to trial coordinates for the Pr atoms. Least-squares refinement of these coordinates with this limited data set gave $R = 0.34$. A three-dimensional Fourier map based on Pr only showed 12 possible Cl atom positions around each Pr atom. The chlorines formed two independent but chemically reasonable sets of six each, with the two sets related to each other by the pseudosymmetry element ($y' = {}^1/_4 - y$). Close contact distances between the two sets showed that both could not be present on the same Pr atom. This condition can arise either from disordering or from pseudosymmetry due to a special position of the heavy atom. In this case the problem was presumed to be one of pseudosymmetry, since a least-squares refinement using the Pr and one set of Cl atoms led to $R = 0.26$; and a difference map based on this seven-atom model removed all 13 peaks and showed clearly the rest of the nonhydrogen atoms.

The nonhydrogen atoms were refined isotropically using all of the data and unit weights to a value of $R = 0.14$. A difference electron density map was then calculated to locate the hydrogen coordinates. Positive regions of electron density were found at most of the anticipated hydrogen positions but not at all of them. Therefore, the hydrogen atom coordinates were calculated, based upon expected geometry, and included in subsequent structure factor calculations but not refined. Refinement was continued for the nonhydrogen atoms using anisotropic temperature factors, $1/\sigma^2$ weights, and anomalous dispersion corrections for Pr, Cl, and P atoms.[7] Refinement was considered as completed with values of $R_w = 0.088$ and $R = 0.093$ and with all shifts less than one-tenth the magnitude of the estimated standard deviations of their respective parameters. A final cycle of least-squares refinement including unobserved reflections was run and led to $R = 0.114$ with no unusually large $|\Delta F|$ confirming the completion of the structure determination.

Results and Discussion

Table I lists the final coordinates and anisotropic temperature factors for all nonhydrogen atoms together with the estimated standard deviations (esd's) for all parameters. Table II lists the calculated hydrogen coordinates. Table III lists the distances and angles within the $PrCl_6^{3-}$ group. In all cases the Pr–Cl bond distances have esd's less than 0.008 Å and the Cl–Pr–Cl angles have esd's less than 0.2°.

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Table I. Fractional Coordinates and Anisotropic Thermal Parameters[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pr	0.1310 (1)	0.1324 (0)	0.3307 (1)	14 (1)	2 (0)	41 (1)	0 (0)	23 (1)	0 (0)
Cl1	0.2630 (6)	0.1591 (2)	0.2077 (6)	46 (8)	7 (1)	80 (9)	−4 (2)	51 (7)	3 (2)
Cl2	−0.0023 (6)	0.1032 (2)	0.4456 (6)	54 (8)	5 (1)	87 (9)	−3 (2)	60 (7)	0 (2)
Cl3	0.1767 (7)	0.1812 (1)	0.4979 (6)	80 (9)	4 (0)	75 (8)	−1 (2)	43 (7)	−4 (2)
Cl4	0.0674 (7)	0.0804 (2)	0.1717 (6)	110 (10)	4 (1)	84 (9)	−7 (2)	75 (8)	−6 (2)
Cl5	0.3468 (6)	0.1049 (2)	0.4739 (6)	36 (8)	7 (1)	92 (9)	7 (2)	43 (7)	6 (2)
Cl6	−0.0623 (6)	0.1641 (2)	0.1628 (6)	33 (7)	7 (1)	54 (8)	3 (2)	26 (6)	0 (2)
P1	0.0295 (7)	0.3606 (2)	0.3934 (7)	53 (9)	4 (1)	64 (9)	0 (2)	37 (7)	0 (2)
P2	0.4824 (6)	0.1951 (2)	0.5038 (7)	22 (8)	4 (1)	68 (9)	1 (2)	30 (7)	1 (2)
P3	0.8087 (7)	0.0438 (2)	0.2367 (7)	41 (8)	4 (1)	73 (9)	0 (2)	42 (7)	−1 (2)
CA1	−0.1090 (23)	0.3821 (6)	0.3137 (25)	17 (29)	5 (2)	114 (38)	0 (6)	41 (28)	−4 (7)
CA2	−0.1978 (31)	0.3833 (7)	0.3605 (29)	158 (53)	8 (3)	140 (47)	−2 (9)	112 (43)	8 (9)
CA3	−0.3048 (26)	0.3995 (8)	0.2992 (32)	12 (33)	14 (4)	232 (58)	16 (9)	62 (38)	−4 (11)
CA4	−0.3359 (29)	0.4130 (7)	0.1867 (30)	84 (43)	8 (3)	179 (52)	4 (9)	57 (40)	11 (9)
CA5	−0.2526 (27)	0.4109 (7)	0.1418 (26)	64 (38)	10 (3)	85 (39)	6 (9)	12 (32)	13 (8)
CA6	−0.1421 (27)	0.3978 (7)	0.1993 (26)	80 (40)	9 (3)	111 (42)	2 (9)	71 (35)	8 (8)
CB1	0.1516 (23)	0.3798 (6)	0.3667 (22)	28 (30)	6 (2)	63 (33)	2 (6)	39 (27)	−1 (6)
CB2	0.2254 (29)	0.4020 (7)	0.4504 (24)	135 (47)	10 (3)	47 (33)	−10 (9)	70 (34)	−8 (8)
CB3	0.3234 (30)	0.4176 (7)	0.4354 (27)	134 (50)	10 (3)	89 (41)	−11 (10)	66 (38)	−8 (9)
CB4	0.3427 (25)	0.4105 (7)	0.3345 (27)	23 (32)	9 (3)	119 (42)	2 (8)	19 (31)	7 (8)
CB5	0.2805 (30)	0.3881 (7)	0.2545 (28)	151 (50)	7 (3)	151 (46)	4 (9)	136 (42)	5 (8)
CB6	0.1741 (26)	0.3727 (6)	0.2624 (24)	99 (39)	3 (2)	91 (37)	4 (7)	35 (31)	−3 (7)
CC1	0.0149 (23)	0.3193 (6)	0.3516 (23)	25 (30)	5 (2)	91 (35)	0 (6)	48 (28)	3 (7)
CC2	−0.0330 (26)	0.3106 (7)	0.2289 (27)	42 (35)	8 (3)	130 (44)	3 (8)	34 (33)	0 (8)
CC3	−0.0373 (28)	0.2782 (7)	0.1989 (29)	76 (41)	9 (3)	169 (50)	0 (8)	75 (39)	−17 (9)
CC4	−0.0049 (28)	0.2551 (6)	0.2879 (30)	99 (42)	4 (2)	213 (54)	2 (8)	117 (41)	−10 (8)
CC5	0.0409 (26)	0.2636 (6)	0.4100 (29)	79 (38)	3 (2)	208 (50)	4 (7)	120 (38)	6 (8)
CC6	0.0494 (23)	0.2956 (6)	0.4404 (23)	35 (31)	5 (2)	87 (35)	−1 (6)	56 (28)	−2 (7)
CD1	0.5496 (21)	0.1905 (6)	0.6662 (23)	1 (26)	5 (2)	85 (34)	0 (6)	27 (26)	0 (7)
CD2	0.6624 (24)	0.2026 (7)	0.7327 (25)	16 (30)	9 (3)	82 (36)	6 (7)	6 (28)	5 (8)
CD3	0.7110 (25)	0.1996 (7)	0.8601 (27)	28 (33)	8 (3)	132 (44)	−1 (8)	20 (32)	−1 (8)
CD4	0.6451 (26)	0.1836 (8)	0.9178 (25)	37 (35)	15 (3)	55 (35)	14 (9)	9 (29)	12 (8)
CD5	0.5405 (25)	0.1709 (8)	0.8550 (28)	10 (32)	16 (4)	114 (43)	−3 (9)	−3 (31)	23 (10)
CD6	0.4894 (25)	0.1752 (7)	0.7285 (26)	26 (32)	8 (3)	109 (40)	−1 (7)	6 (30)	4 (8)
CE1	0.4181 (25)	0.2335 (6)	0.4643 (24)	80 (36)	3 (2)	96 (36)	−4 (7)	73 (31)	0 (6)
CE2	0.3443 (25)	0.2409 (6)	0.3393 (25)	54 (35)	5 (2)	108 (39)	−6 (7)	39 (31)	1 (7)
CE3	0.2990 (27)	0.2710 (8)	0.3123 (32)	46 (38)	12 (3)	230 (58)	6 (9)	61 (40)	39 (11)
CE4	0.3135 (28)	0.2928 (7)	0.3995 (33)	79 (42)	7 (3)	293 (65)	20 (9)	124 (45)	15 (11)
CE5	0.3739 (32)	0.2857 (7)	0.5115 (29)	172 (54)	6 (3)	147 (47)	10 (9)	104 (43)	7 (8)
CE6	0.4280 (28)	0.2565 (6)	0.5491 (25)	111 (43)	6 (2)	87 (38)	4 (8)	68 (34)	5 (7)
CF1	0.6036 (23)	0.1902 (6)	0.4490 (24)	24 (30)	4 (2)	89 (35)	−1 (6)	12 (27)	−3 (7)
CF2	0.6378 (27)	0.2156 (7)	0.3935 (28)	59 (37)	10 (3)	156 (47)	8 (8)	81 (36)	6 (9)
CF3	0.7351 (30)	0.2108 (8)	0.3599 (31)	104 (45)	12 (3)	206 (55)	12 (10)	135 (44)	10 (11)
CF4	0.7843 (30)	0.1825 (8)	0.3752 (30)	109 (46)	14 (4)	173 (51)	9 (10)	141 (43)	−10 (11)
CF5	0.7516 (30)	0.1580 (7)	0.4281 (34)	117 (48)	6 (3)	202 (55)	7 (9)	67 (43)	−9 (9)
CF6	0.6542 (26)	0.1612 (6)	0.4612 (26)	57 (36)	7 (2)	127 (42)	11 (8)	58 (33)	−2 (8)
CG1	0.8205 (23)	0.0164 (5)	0.3556 (21)	66 (34)	1 (2)	53 (31)	−1 (6)	23 (27)	−4 (6)
CG2	0.7861 (29)	−0.0140 (6)	0.3367 (24)	151 (48)	4 (2)	74 (36)	6 (8)	60 (35)	2 (7)
CG3	0.7906 (29)	−0.0341 (6)	0.4289 (29)	108 (44)	3 (2)	167 (48)	0 (8)	58 (39)	3 (8)
CG4	0.8365 (27)	−0.0227 (6)	0.5514 (26)	94 (41)	5 (2)	124 (42)	2 (8)	48 (35)	11 (8)
CG5	0.8682 (27)	0.0087 (6)	0.5716 (25)	100 (41)	5 (2)	93 (38)	5 (8)	66 (34)	1 (7)
CG6	0.8650 (26)	0.0278 (6)	0.4750 (26)	93 (39)	2 (2)	146 (43)	4 (7)	81 (35)	14 (7)
CH1	0.7655 (24)	0.0230 (6)	0.0964 (24)	43 (32)	3 (2)	102 (37)	1 (6)	24 (29)	−2 (7)
CH2	0.6517 (29)	0.0220 (7)	0.0118 (27)	100 (44)	8 (3)	117 (44)	−6 (9)	29 (37)	−16 (9)
CH3	0.6237 (34)	0.0062 (8)	−0.0954 (32)	177 (59)	9 (3)	174 (54)	7 (11)	62 (47)	−12 (10)
CH4	0.7028 (34)	−0.0104 (8)	−0.1241 (28)	187 (60)	10 (3)	85 (42)	−18 (11)	18 (41)	−9 (9)
CH5	0.8165 (36)	−0.0121 (7)	−0.0447 (34)	283 (70)	8 (3)	281 (65)	−15 (11)	278 (61)	−28 (11)
CH6	0.8552 (29)	0.0055 (7)	0.0756 (29)	83 (43)	10 (3)	159 (49)	−13 (9)	69 (39)	−12 (9)
CI1	0.6951 (22)	0.0731 (6)	0.2227 (20)	23 (29)	6 (2)	14 (26)	0 (6)	−8 (23)	−4 (6)
CI2	0.6069 (26)	0.0680 (7)	0.2652 (25)	77 (38)	9 (3)	91 (37)	0 (8)	79 (33)	0 (8)
CI3	0.5176 (27)	0.0902 (7)	0.2458 (29)	47 (36)	9 (3)	151 (46)	6 (8)	48 (34)	−3 (9)
CI4	0.5234 (28)	0.1193 (7)	0.1910 (29)	68 (40)	10 (3)	140 (47)	15 (9)	15 (35)	−13 (9)
CI5	0.6078 (31)	0.1242 (6)	0.1471 (26)	170 (52)	4 (2)	99 (40)	20 (8)	39 (37)	6 (7)
CI6	0.6983 (25)	0.1029 (6)	0.1652 (23)	67 (36)	5 (2)	66 (33)	−3 (7)	38 (29)	0 (7)

[a] Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Standard deviations ($\times 10^4$) are given in parentheses.

The $PrCl_6^{3-}$ group has been assumed to possess octahedral symmetry (O_h) in the solid state.[6,8] This would conform to the cubic crystal systems Cs_2NaMCl_6 (M = trivalent rare earth) which contain this MCl_6^{3-} moiety and which show O_h site symmetry about M.[9,10] Recent work has confirmed this for $Cs_2NaEuCl_6$[11] and $Cs_2NaPrCl_6$[12] although the latter praseodymium hexahalide shows O_h forbidden transitions at lower temperatures. Earlier spectral assignments in this latter compound[13] were questioned, then reassigned,[14] again questioned,[15] and presumably now assigned correctly.[12] Recent spectroscopic studies on the triphenylphosphonium complex discussed in this paper[4] show it to be of the MS_6^{3-} type with noticeable distortion from O_h symmetry and conclude that those distortions can be either trigonal or tetragonal. Infrared studies alone cannot characterize these distortions although, combined with Raman data, they could conceivably

Table II. Calculated Hydrogen Positions[a]

Atom	x	y	z
HP1	0.0566 (0)	0.3614 (0)	0.5231 (0)
HP2	0.3886 (0)	0.1719 (0)	0.4499 (0)
HP3	0.9229 (0)	0.0592 (0)	0.2647 (0)
HA2	−0.1763 (0)	0.3734 (0)	0.4461 (0)
HA3	−0.3638 (0)	0.3992 (0)	0.3403 (0)
HA4	−0.4104 (0)	0.4244 (0)	0.1475 (0)
HA5	−0.2745 (0)	0.4187 (0)	0.0565 (0)
HA6	−0.0818 (0)	0.3984 (0)	0.1608 (0)
HB2	0.2039 (0)	0.4075 (0)	0.5238 (0)
HB3	0.3756 (0)	0.4336 (0)	0.4984 (0)
HB4	0.4075 (0)	0.4226 (0)	0.3202 (0)
HB5	0.3050 (0)	0.3820 (0)	0.1849 (0)
HB6	0.1211 (0)	0.3575 (0)	0.1994 (0)
HC2	−0.0642 (0)	0.3272 (0)	0.1631 (0)
HC3	−0.0714 (0)	0.2723 (0)	0.1069 (0)
HC4	−0.0112 (0)	0.2322 (0)	0.2640 (0)
HC5	0.0657 (0)	0.2466 (0)	0.4753 (0)
HC6	0.0797 (0)	0.3023 (0)	0.5276 (0)
HD2	0.7092 (0)	0.2137 (0)	0.6885 (0)
HD3	0.7937 (0)	0.2093 (0)	0.9087 (0)
HD4	0.6711 (0)	0.1821 (0)	1.0066 (0)
HD5	0.4964 (0)	0.1571 (0)	0.8937 (0)
HD6	0.4081 (0)	0.1680 (0)	0.6819 (0)
HE2	0.3283 (0)	0.2240 (0)	0.2753 (0)
HE3	0.2539 (0)	0.2769 (0)	0.2251 (0)
HE4	0.2785 (0)	0.3151 (0)	0.3766 (0)
HE5	0.3819 (0)	0.3023 (0)	0.5757 (0)
HE6	0.4786 (0)	0.2523 (0)	0.6404 (0)
HF2	0.5953 (0)	0.2364 (0)	0.3799 (0)
HF3	0.7655 (0)	0.2285 (0)	0.3250 (0)
HF4	0.8555 (0)	0.1785 (0)	0.3502 (0)
HF5	0.8002 (0)	0.1379 (0)	0.4458 (0)
HF6	0.6216 (0)	0.1429 (0)	0.4901 (0)
HG2	0.7550 (0)	−0.0229 (0)	0.2517 (0)
HG3	0.7660 (0)	−0.0566 (0)	0.4136 (0)
HG4	0.8449 (0)	−0.0378 (0)	0.6213 (0)
HG5	0.8875 (0)	0.0175 (0)	0.6542 (0)
HG6	0.8945 (0)	0.0507 (0)	0.4916 (0)
HH2	0.5846 (0)	0.0327 (0)	0.0290 (0)
HH3	0.5397 (0)	0.0091 (0)	−0.1612 (0)
HH4	0.6783 (0)	−0.0223 (0)	−0.2046 (0)
HH5	0.8833 (0)	−0.0255 (0)	−0.0581 (0)
HH6	0.9394 (0)	0.0068 (0)	0.1353 (0)
HI2	0.6049 (0)	0.0475 (0)	0.3102 (0)
HI3	0.4519 (0)	0.0862 (0)	0.2757 (0)
HI4	0.4629 (0)	0.1362 (0)	0.1871 (0)
HI5	0.6032 (0)	0.1442 (0)	0.0969 (0)
HI6	0.7664 (0)	0.1075 (0)	0.1406 (0)

[a] The fixed isotropic temperature factor was $B = 4.0$ Å^2.

Table III. Interatomic Distances (Å) and Angles (deg) within $PrCl_6^{3-}$ Groups

Distances			
Pr–Cl1	2.757 (7)	Pr–Cl4	2.767 (7)
Pr–Cl2	2.745 (7)	Pr–Cl5	2.737 (8)
Pr–Cl3	2.726 (7)	Pr–Cl6	2.735 (7)
Angles			
Cl1-Pr-Cl2	177.1 (2)	Cl2-Pr-Cl6	94.2 (2)
Cl1-Pr-Cl3	94.7 (2)	Cl3-Pr-Cl4	173.8 (2)
Cl1-Pr-Cl4	91.5 (2)	Cl3-Pr-Cl5	89.3 (2)
Cl1-Pr-Cl5	83.7 (2)	Cl3-Pr-Cl6	92.3 (2)
Cl1-Pr-Cl6	85.9 (2)	Cl4-Pr-Cl5	92.1 (2)
Cl2-Pr-Cl3	88.1 (2)	Cl4-Pr-Cl6	87.3 (2)
Cl2-Pr-Cl4	95.7 (2)	Cl5-Pr-Cl6	169.6 (2)
Cl2-Pr-Cl5	96.1 (2)		

be more definitive in categorizing the specific distortions.

The present structural study shows that the $PrCl_6^{3-}$ ion very closely approximates D_{2d} symmetry. A previous observation by Ryan[8] that the $^3H_4 \rightarrow {}^3P_0$ transition exists in the solid-state absorption spectrum of praseodymium(III) hexahalides is consistent with this. The transition is not allowed in octahedral symmetry and was explained as being due to the pure electronic transition with vibronic transitions equally spaced at higher and lower energies (a transition allowed in D_{2d} symmetry).

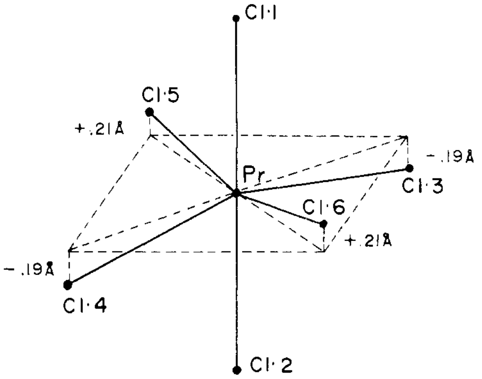

Figure 1. Distortion from octahedral to D_{2d} symmetry for $PrCl_6^{3-}$.

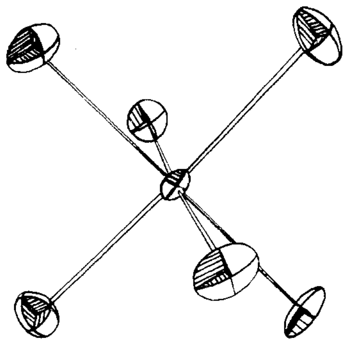

Figure 2. ORTEP view of $PrCl_6^{3-}$.

These distortions from O_h to D_{2d} symmetry can be most readily visualized in terms of the various planes formed by the Pr and the Cl atoms. Figure 1 shows these distortions in a schematic drawing of the ion, while Figure 2 gives the more exact ORTEP view of the same ion. The least-squares plane using atoms Cl1, Cl2, Cl3, Cl4, and Pr is essentially planar with standard deviations from the best plane of less than 0.01 Å for any of the aforementioned atoms. Similarly, a relatively good fit to planarity can be obtained for atoms Cl1, Cl2, Cl5, Cl6, and Pr with all standard deviations from the best least-squares fitted plane being less than 0.03 Å. However, if one attempts a similar best fit plane for Cl3, Cl4, Cl5, Cl6, and Pr, the standard deviation is 0.18 Å. The pattern for this nonplanarity is shown in Figure 1, with the D_{2d} symmetry readily evident.

The six Pr–Cl distances average 2.745 ± 0.012 Å which is in agreement with the value of 2.72 Å[17] previously found for Pr(III) to Cl bonds. The bonds show no systematic bond length distortions. The $PrCl_6^{3-}$ groups are surrounded by the bulky triphenylphosphonium ions with no significant close contact distances. The benzene ring parameters for the triphenylphosphonium ions are in agreement with the standard values[18] having an average C–C distance of 1.37 ± 0.03 Å and an average C–C–C angle of 119.9 ± 1.9°. The P–C distances average 1.78 ± 0.02 Å, which is significantly shorter than the 1.83-Å distance found in triphenylphosphorus.[19] The C–P–C angles are predictably larger in the triphenylphosphonium ion than in triphenylphosphorus averaging 109.7 ± 1.6° as compared to 103° owing to the larger repulsion of the lone-pair electrons as compared to the repulsion of electrons in bonding orbitals associated with two nuclei.

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Registry No. $[(C_6H_5)_3PH]_3PrCl_6$, 16949-62-5.

Supplementary Material Available: Listing of structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

References and Notes

(1) As an illustration of the burgeoning of this field, a series of books (three already published) have come out since 1968 entitled "Halides of the Transition Elements", Wiley-Interscience, New York, N.Y.

(2) A series of papers discuss these: L. B. Asprey et al., *Inorg. Chem.*, **3**, 126, 727 (1964); **5**, 659 (1966).

(3) W. H. Zachariasen, *Acta Crystallogr.*, **1**, 285 (1948).

(4) S. Z. Ali, Ph.D. Dissertation, University of New Orleans, 1972.

(5) J. D. Corbett, D. L. Pollard, and J. E. Mee, *Inorg. Chem.*, **5**, 761 (1966).

(6) J. L. Ryan and C. K. Jorgenson, *J. Phys. Chem.*, **70**, 2845 (1966).

(7) The conventional reliability index $R = \sum||kF_o| - |F_c||/\sum|kF_o|$ and a weighted reliability index $R_w = \sum w||kF_o| - |F_c||^2/\sum|kF_o|^2$ with $1/w = 1/\sigma^2$ are cted in the paper. Scattering factors for Pr^{3+}, Cl^-, P, and C are taken from the paper by D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965), while the scattering factor curve for hydrogen and the anomalous dispersion corrections for Pr^{3+}, Cl^-, and P are from "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1968. The programs used are part of the crystallographic package for the PDP-10 developed at the University of New Orleans by J. N. Brown, L. R. Towns, R. J. Majeste, and L. M. Trefonas (1966–1976). The package includes a modification of the LSLAT routine (K. N. Trueblood), a series of data reduction programs, a series of direct-methods programs (including FAZC and MULTAN II), Patterson and Patterson superposition programs, block diagonal least-squares and Fourier programs, and a package of figure-drawing programs (including ORTEP developed by C. K. Johnson).

(8) M. Choca, J. R. Ferraro, and K. Nakamoto, *J. Inorg. Nucl. Chem.*, **37**, 1425 (1975).

(9) L. R. Morss and J. Fuger, *Inorg. Chem.*, **8**, 1433 (1969).

(10) L. R. Morss, M. Siegal, L. Stenger, and M. Edelstein, *Inorg. Chem.*, **9**, 1771 (1970).

(11) R. W. Schwartz, *Mol. Phys.*, **30**, 1909 (1975).

(12) R. W. Schwartz, *Mol. Phys.*, **31**, 1909 (1976).

(13) D. A. Wensky and W. G. Moulton, *J. Chem. Phys.*, **53**, 3957 (1970).

(14) W. A. Hargreaves, *Phys. Rev. B*, **6** 3417 (1972).

(15) A. Kiel and K. R. German, *Phys. Rev. B*, **8** 2353 (1973).

(16) J. L. Ryan, *Inorg. Chem.*, **8**, 2053 (1969).

(17) M. D. Glick and L. J. Radonovich, Abstracts of Papers, American Crystallographic Association Summer Meeting, 1970, p 90.

(18) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, **No. 11** (1958).

(19) J. J. Daly, *J. Chem. Soc.*, 3799 (1964).

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Synthesis, Vibrational and Tin-119 Mössbauer Spectra, and Crystal and Molecular Structure of Tris(dimethyltin(IV)) Bis(orthophosphate) Octahydrate

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A single-crystal x-ray diffraction study has shown that Me_2SnCl_2 and Na_2HPO_4 react in aqueous solution to give $(Me_2Sn)_3(PO_4)_2{\cdot}8H_2O$. The colorless needle-shaped crystals are orthorhombic and belong to space group $Pn2_1a$ with a = 22.578 (4), b = 9.395 (2), c = 11.100 (2) Å, and Z = 4. The structure was solved by standard Patterson and Fourier methods and refined to a final R value of 0.080. The structure of $(Me_2Sn)_3(PO_4)_2{\cdot}8H_2O$ consists of infinite "ribbons" extending through the crystal in the b direction. One tin atom (inner) is in an almost regular octahedral environment with trans methyl groups [C–Sn–C = 178.1 (14)°], and the other two tin atoms (outer) are in highly distorted octahedral configurations [C–Sn–C = 145.4 (16), 151.1 (15)°] due to weak coordination to two water molecules. The other water molecules form a three-dimensional network of hydrogen bonds involving the phosphate oxygen atoms. The tin atoms are linked by PO_4 tetrahedra to give eight-membered rings in chair configurations. The different tin environments cannot be distinguished by ^{119}Sn Mössbauer spectroscopy (δ = 1.17; Δ = 3.68 mm s^{-1} at 77 K) although the line widths (Γ_1 = 1.37; Γ_2 = 1.32 mm s^{-1}) are somewhat broadened. It is suggested that the formation of $(Me_2Sn)_3(PO_4)_2{\cdot}8H_2O$ in aqueous solution results from the condensation reaction between 2 mol of $H_2PO_4^-$ and the polynuclear species $[(Me_2Sn)_3(OH)_4]^{2+}$.

Introduction

The reaction of dimethyltin dichloride with Na_2HPO_4 in aqueous solution produces white crystals previously assumed to be Me_2SnHPO_4.[1] We were unable to unambiguously assign a structure to this compound on the basis of infrared and ^{119}Sn Mössbauer spectral data,[2] and we therefore undertook a single-crystal x-ray structure determination which revealed the compound to be $(Me_2Sn)_3(PO_4)_2{\cdot}8H_2O$. In this paper we discuss the synthesis and vibrational and ^{119}Sn Mossbauer spectra of $(Me_2Sn)_3(PO_4)_2{\cdot}8H_2O$ in the light of the determined crystal and molecular structure. A preliminary report of the x-ray structure determination has appeared.[3]

Previous reports of x-ray structural determinations of dimethyltin compounds have been limited to derivatives of monobasic acids e.g., Me_2SnF_2,[4] $Me_2Sn(SO_3F)_2$,[5] $Me_2Sn(CNS)_2$[6], $Me_2Sn(CN)_2$,[7] $Me_2Sn(NO_3)_2$,[8] and Me_2SnCl_2.[9] In Me_2SnX_2 compounds there is a tendency for the tin atoms to become hexacoordinate either via intermolecular association (X = F, SO_3F, CNS, CN, Cl) or via intramolecular coordination (X = NO_3). The extent of intermolecular association, as determined by the geometry of the C–Sn–C arrangement, varies considerably. For X = F or SO_3F the association is strong leading to octahedral geometry about tin and trans methyl groups. For more weakly associated structures the observed geometry about tin can be viewed as either distorted tetrahedral or distorted octahedral (C–Sn–C = ca. 149°, X = CNS,[6] CN;[7] C–Sn–C = ca. 123°, X = Cl[9]).

Experimental Section

Instrumentation. The following instruments were used to obtain spectroscopic data: infrared spectra, Perkin-Elmer 337; far-infrared spectra, Digilab FTS 16; Mössbauer spectra, spectrometer described previously in ref 10. Raman spectra were obtained using a He/Ne laser operating at 6328 Å, using collinear excitation, and viewing with a Cary 81 spectrophotometer.

Synthesis. Equimolar quantities of dimethyltin dichloride and $Na_2HPO_4{\cdot}2H_2O$ in aqueous solutions (ca. 0.5 M) were mixed and allowed to stand at room temperature. Elongated, needle-shaped, colorless crystals were slowly deposited. These crystals were filtered off, washed with water, and dried in an Aberhalden pistol at 80 °C (0.1 mm); yield 52%; dec pt >350 °C. Anal. Calcd for $(Me_2Sn)_3(PO_4)_2{\cdot}8H_2O$: C, 9.23; H, 4.31. Found: C, 9.82, 9.59; H,