# Synthesis, Properties, and Structural Characterization of Lead(II) Bis(diphenylphosphinate), Pb[OP(C6H5)2O]2

P. COLAMARINO,[1a] P. L. ORIOLI,*[1a] W. D. BENZINGER,*[1b] and H. D. GILLMAN[1b]

Pure polymeric Pb[OP(C6H5)2O]2 has been prepared, and its structure has been determined by three-dimensional single-crystal x-ray techniques. The compound crystallizes in the triclinic space group $P\bar{1}$ with two formula units in a cell of dimensions $a = 12.167$ (5), $b = 10.937$ (4), $c = 8.695$ (6) Å; $\alpha = 96.40$ (3), $\beta = 105.96$ (4), $\gamma = 91.05$ (5)°; $V = 1104$ Å³; $d_{calcd} = 1.93$ g cm⁻³. Least-squares refinement of 3737 independent reflections gave a final $R$ factor of 3.5%. The structure consists of polymeric chains of lead atoms linked by double-phosphinate bridges. The coordination around each lead atom can be described as a distorted trigonal bipyramid with a lone pair of electrons occupying an equatorial site. Mean equatorial and axial Pb–O distances are 2.233 (6) and 2.435 (6) Å, respectively. The corresponding O–Pb–O angles are 88.2 (2) and 167.6 (2)°. This polymer was found to dissociate in solution, and its infrared spectrum suggests that changes in the mode of coordination of the phosphinate groups take place upon dissolution. Other forms including crystalline and amorphous modifications were found in the solid state.

## Introduction

The polymeric nature of the metal phosphinates has prompted considerable interest in these materials, and many of them have been extensively studied.[2,3] Because these polymeric systems are generally not amenable to single-crystal x-ray studies, only a few closely related materials have been definitively characterized by this technique. Thus a number of beryllium(II), zinc(II), and cobalt(II) bis(phosphinates) have been found to contain linear chains of tetrahedrally coordinated metal atoms linked by alternating single and triple O,O' symmetrically bridging phosphinate groups.[4,5] The possibility of forming linear double-phosphinate-bridged chains by incorporating bulky substituents on the phosphorus atoms has also been discussed; however, the present evidence is not definitive.[6]

In order to extend our understanding of these systems, we undertook an investigation of Pb[OP(C6H5)2O]2 including a complete crystal study of one of its solid-state forms. The only other report concerning Pb[OP(C6H5)2O]2 in the literature discusses unsuccessful attempts to prepare this material.[7]

## Experimental Section

**Materials.** All of the chemical reagents and solvents employed were obtained from commercial sources.

**Pb[OP(C6H5)2O]2.** A solution of 16.56 g of Pb(NO3)2 (0.050 mol) in 100 ml of H2O was added to another solution containing 22.91 g of (C6H5)2P(O)OH (0.105 mol) and 5.62 g of Na2CO3 (0.053 mol) in 350 ml of H2O. The white precipitate, which immediately formed, was filtered and washed with water. Additional product in the form of well-formed crystals suitable for a single-crystal x-ray study was obtained from the mother liquor after partial evaporation; total yield 28 g (88%). Anal. Calcd for C24H20O4P2Pb: C, 44.9; H, 3.14; P, 9.66. Found: C, 44.8; H, 3.15; P, 9.65. Lead analyses were run by several different methods, but the results were quite scattered, suggesting interference by the diphenylphosphinate ligand. The infrared spectra of both fractions were identical and contained no O–H bands.

**Analysis and Physical Measurements.** Elemental analyses were run by standard methods in the Pennwalt Analytical Department. Infrared spectra were recorded with a Perkin-Elmer 337 grating spectrophotometer on both Nujol and hexachlorobutadiene mulls between KBr disks and as solutions in CH2Cl2. The molecular weight was obtained with a Mechrolab Model 301A vapor pressure osmometer. The chloroform for this measurement was first washed with water, then dried with anhydrous sodium sulfate, and redistilled. The dta data were obtained with a Du Pont dta cell module and the Du Pont 900 thermal analyzer. Thermogravimetric analyses were recorded on a Du Pont 950 thermogravimetric analyzer.

**Crystal Structure Data Collection.** The crystal used for data collection had dimensions 0.27 × 0.22 × 0.32 mm parallel to the crystallographic axes [100], [010], and [001], respectively. Intensity data were collected at room temperature on a Philips automatic diffractometer without any prior knowledge of the lattice constants and orientation matrix. Automatic search routines, followed by least-squares refinement on 23 intense reflections, gave the following results: $a = 12.167$ (5), $b = 10.937$ (4), $c = 8.695$ (6) Å; $\alpha = 96.40$ (3), $\beta = 105.96$ (4), $\gamma = 91.05$ (5)°; $V = 1104.1$ Å³; $Z = 2$; $d_{calcd} = 1.93$ g cm⁻³; space group $P1$ or $P\bar{1}$; the latter was confirmed by the structure determination.

For this study Mo Kα radiation ($\lambda$ 0.7107 Å) monochromatized by means of a flat graphite crystal was used to collect the intensities of 3737 independent reflections in the range $6° < 2\theta < 50°$. The $\omega-2\theta$ scan technique was used to measure the intensities with a scan speed of 0.08°/s and a scan width of 1.4° in $\omega$. Stationary-counter, stationary-crystal background counts of 17.5 s (half the total scan time) were taken at each end of the scan range. The 3349 reflections with intensity greater than twice the standard deviation were considered observed and used for the structure solution and refinement. Standard deviations on intensities ($I$) were calculated according to the expression

$$\sigma(I) = (P + B_1 + B_2 + (kI)^2)^{1/2}$$

where $P$ is the total peak count, $B_1$ and $B_2$ are the left and right background counts, and $k = 0.004$, a constant determined by a least-squares analysis of the intensities of three reflections monitored periodically. Intensities were corrected for Lorentz–polarization and absorption effects, the linear absorption coefficient being 78.7 cm⁻¹ for Mo Kα radiation. Transmission factors were calculated by the Gaussian numerical integration method with a grid of 6 × 6 × 6, using AGNOST, in the version written by David Cahen at Northwestern University.

**Structure Solution and Refinement.** The lead atoms were easily located by means of a three-dimensional Patterson synthesis. The successive electron density syntheses, phased with the contribution of the lead atoms, showed clearly all the nonhydrogen atoms. Two cycles of isotropic refinement on all of the atoms and two cycles with anisotropic temperature factors for Pb, P, and O atoms, followed by the inclusion of the hydrogen atoms in calculated positions (C–H distance 1.01 Å) and by a final refinement cycle, gave $R$ and $R'$ values of 0.035 and 0.037, respectively, where $R'$ is defined as $[w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. The average shift per error in the last cycle was 0.73. Inclusion of the hydrogen atoms, which were assigned the temperature factors of the carbon atoms to which they are attached, improved slightly both distance and angle values in the benzene rings. The function minimized in the refinement was $\sum w(|F_o| - |F_c|)^2$ with weights $w$ taken as $4F_o^2/\sigma^2(F_o^2)$.

Scattering factors for nonhydrogen atoms were taken from Cromer and Waber,[8] and the hydrogen scattering factors were those calculated by the method of Stewart, et al.[9] The Pb and P scattering factors have been corrected for the real and imaginary part of the anomalous dispersion.[10] Atomic parameters with their standard deviations are reported in Table I. The X-Ray 72 system of programs, adapted for the CII-10070 computer of the University of Florence by C. Mealli, was used for all the calculations.

## Results and Discussion

**Description of the Structure.** The structure of lead(II)

**Table I.** Positional Parameters ($\times 10^4$), Thermal Parameters[a] ($A^2 \times 10^3$), and Estimated Standard Deviations for the Atoms of $Pb[OP(C_6H_5)_2O]_2$

| Atom | $x/a$ | $y/b$ | $z/c$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| $Pb^b$ | 2771 (3) | 25 023 (4) | 10 705 (5) | 293 (2) | 228 (2) | 250 (2) | 16 (1) | 100 (1) | 19 (1) |
| P(1) | 1570 (2) | 399 (2) | −1 022 (3) | 28 (1) | 23 (1) | 30 (2) | 1 (1) | 12 (1) | 2 (1) |
| P(2) | −1732 (2) | 4 416 (2) | −558 (3) | 26 (1) | 25 (1) | 38 (2) | 0 (1) | 9 (1) | 5 (1) |
| O(1) | 937 (5) | 1 580 (5) | −895 (7) | 35 (4) | 32 (4) | 33 (4) | 16 (3) | 17 (3) | 1 (3) |
| O(2) | 1083 (5) | −754 (5) | −615 (8) | 44 (4) | 27 (4) | 42 (4) | −9 (3) | 19 (3) | 3 (3) |
| O(3) | −1074 (5) | 3 278 (6) | −817 (8) | 32 (4) | 40 (4) | 33 (4) | 18 (3) | 4 (3) | 3 (3) |
| O(4) | −1350 (5) | 5 604 (6) | −1 019 (8) | 50 (4) | 31 (4) | 36 (4) | −11 (3) | 5 (3) | 10 (3) |

| Atom | $x/a$ | $y/b$ | $z/c$ | $U$ | Atom | $x/a$ | $y/b$ | $z/c$ | $U$ |
|---|---|---|---|---|---|---|---|---|---|
| C(1) | 1666 (7) | 151 (8) | −3078 (11) | 28 (2) | C(13) | −3187 (8) | 4024 (9) | −1734 (13) | 40 (3) |
| C(2) | 2236 (8) | 1029 (10) | −3657 (13) | 47 (3) | C(14) | −3461 (10) | 3013 (12) | −2843 (16) | 71 (4) |
| C(3) | 2260 (9) | 790 (10) | −5265 (14) | 55 (3) | C(15) | −4612 (12) | 2778 (13) | −3855 (19) | 91 (4) |
| C(4) | 1734 (9) | −237 (10) | −6235 (14) | 53 (3) | C(16) | −5399 (12) | 3543 (14) | −3607 (20) | 101 (5) |
| C(5) | 1190 (8) | −1072 (10) | −5650 (13) | 46 (3) | C(17) | −5172 (16) | 4425 (18) | −2383 (26) | 158 (8) |
| C(6) | 1153 (8) | −892 (9) | −4048 (12) | 40 (3) | C(18) | −4053 (14) | 4695 (16) | −1411 (22) | 136 (6) |
| C(7) | 3027 (8) | 694 (9) | 286 (12) | 33 (2) | C(19) | −1714 (7) | 4637 (8) | 1529 (11) | 31 (2) |
| C(8) | 3518 (10) | 1882 (11) | 620 (15) | 65 (4) | C(20) | −2144 (9) | 3692 (10) | 2197 (14) | 48 (3) |
| C(9) | 4648 (11) | 2098 (12) | 1622 (17) | 85 (4) | C(21) | −2135 (9) | 3898 (11) | 3824 (14) | 56 (3) |
| C(10) | 5221 (10) | 1098 (12) | 2244 (16) | 73 (4) | C(22) | −1675 (9) | 4975 (10) | 4774 (14) | 55 (3) |
| C(11) | 4728 (10) | −58 (11) | 1913 (15) | 65 (4) | C(23) | −1248 (9) | 5880 (11) | 4117 (15) | 60 (3) |
| C(12) | 3622 (9) | −269 (9) | 935 (13) | 49 (3) | C(24) | −1270 (9) | 5738 (10) | 2457 (14) | 49 (3) |
| H(2)$^c$ | 2613 | 1793 | −2955 | 47 | H(14) | −2837 | 2432 | −2943 | 71 |
| H(3) | 2675 | 1397 | −5712 | 55 | H(15) | −4833 | 2050 | −4709 | 91 |
| H(4) | 1753 | −382 | −7394 | 53 | H(16) | −6174 | 3459 | −4414 | 101 |
| H(5) | 805 | −1821 | −6358 | 46 | H(17) | −5866 | 4880 | −2149 | 158 |
| H(6) | 755 | −1518 | −3617 | 40 | H(18) | −3858 | 5402 | −426 | 136 |
| H(8) | 3052 | 2581 | 173 | 65 | H(20) | −2459 | 2895 | 1529 | 48 |
| H(9) | 5034 | 2943 | 1880 | 85 | H(21) | −2461 | 3247 | 4303 | 56 |
| H(10) | 6024 | 1236 | 2939 | 73 | H(22) | −1651 | 5097 | 5931 | 55 |
| H(11) | 5158 | −749 | 2379 | 65 | H(23) | −914 | 6664 | 4806 | 60 |
| H(12) | 3250 | −1114 | 691 | 49 | H(24) | −981 | 6423 | 1971 | 49 |

$^a$ Anisotropic thermal factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. $^b$ Positional parameters $\times 10^5$; thermal parameters $\times 10^4$. $^c$ Hydrogen atoms are numbered according to the carbon atom to which they are attached.

bis(diphenylphosphinate) consists of polymeric chains in which the phosphinate groups form double bridges between lead atoms (Figure 1). Each chain is formed by a right- and a left-handed helix of Pb, P, and O atoms, winding around the *b* axis and intersecting at the Pb atoms. This double-bridge system differs from that found for the tetrahedrally coordinated beryllium(II), zinc(II), and cobalt(II) phosphinates in which the phosphinate group forms alternate single and triple bridges between the metal atoms.[4,5] On the other hand, the chromium(III) dimer (CH₃COCHCOCH₃)₂Cr[OP(C₆-H₅)₂O]₂Cr(CH₃COCHCOCH₃)₂ has been found to contain double-phosphinate bridges between the metal atoms.[11] However, in this case the metal atoms are octahedrally coordinated. The coordination around the lead atom can be described as a distorted trigonal bipyramid with $O^I_2$ and $O^{II}_4$ in the axial positions and $O_1$, $O_3$, and a lone pair of electrons in the equatorial plane (Figure 2). Evidence for stereochemical activity of the electron lone pair in lead compounds has been already reported.[12] In $Pb[OP(C_6H_5)_2O]_2$ the repulsion energy of the nonbonding electron pair[13] causes elongation of the axial Pb–O distances (2.430 (6) and 2.439 (6) Å) compared with the equatorial distances (2.232 (7) and 2.234 (6) Å) and distortion of the O–Pb–O angles (Table II). The larger distortion of the equatorial O–Pb–O angle relative to the axial O–Pb–O angle is consistent with the shorter lengths of the equatorial Pb–O bonds. Steric effects due to the bridging phosphinate groups are probably also at least partially responsible for the distortion of the coordination polyhedron around the Pb atom.

The Pb–O–P angles at the axial oxygen atoms (average 159.3°) are larger than the corresponding angles at the equatorial oxygen atoms (average 128.9°) (Table II).

Bond lengths and angles in the phosphinate group and in the phenyl groups are in agreement with analogous values from the literature[5,11] (Table II). Least-squares planes through the

phenyl rings and deviations of the atoms from the planes are reported in Table III.

**Physical Properties and Structural Isomerism.** Crystals of $Pb[OP(C_6H_5)_2O]$ melt sharply at 234 °C (by dta) and are soluble in a variety of organic solvents including benzene, chloroform, and methylene chloride. The number-average molecular weight in purified chloroform was found to be 2500 (±100) which corresponds almost exactly to a tetramer. However, it is not known from this observation whether the species in solution is predominantly a tetramer or a mixture of oligomers with an average molecular weight corresponding to 4 times the molecular weight of $Pb[OP(C_6H_5)_2O]_2$. This low molecular weight in solution suggests that there is a rearrangement occurring on dissolution, a phenomenon which has been found in other phosphinate systems such as $Cu[OP(C_8H_{17})_2O]_2$ and may be associated with a change in the mode of coordination of the phosphinate groups.[3] The $PO_2$ stretching bands of the metal phosphinates, which occur in the 900–1200-cm⁻¹ region[14] of their infrared spectra, have been found to be sensitive to the mode of coordination of the phosphinate groups.[3] The infrared spectrum of crystalline $Pb[OP(C_6H_5)_2O]_2$ (designated $\alpha$) is given in Figure 3 along with its spectra in $CH_2Cl_2$ solution and as a residue (designated $\beta$) after evaporation of the $CH_2Cl_2$. The $PO_2$ stretching bands are different for all three cases, but the most obvious difference is the presence of a $PO_2$ antisymmetric stretching at 1165 cm⁻¹ in the solution spectrum which is absent in the spectra of both solid forms. This is further evidence that the structure of the compound in solution is different from the structure in the original crystal. It is not possible to assign a definite structure to the species present in solution because of the several coordination geometries possible for lead atoms as well as different modes of coordination which are possible for the phosphinate groups. It is interesting to note that solid $Pb[OP(C_6H_5)_2O]_2$ with an infrared spectrum identical with
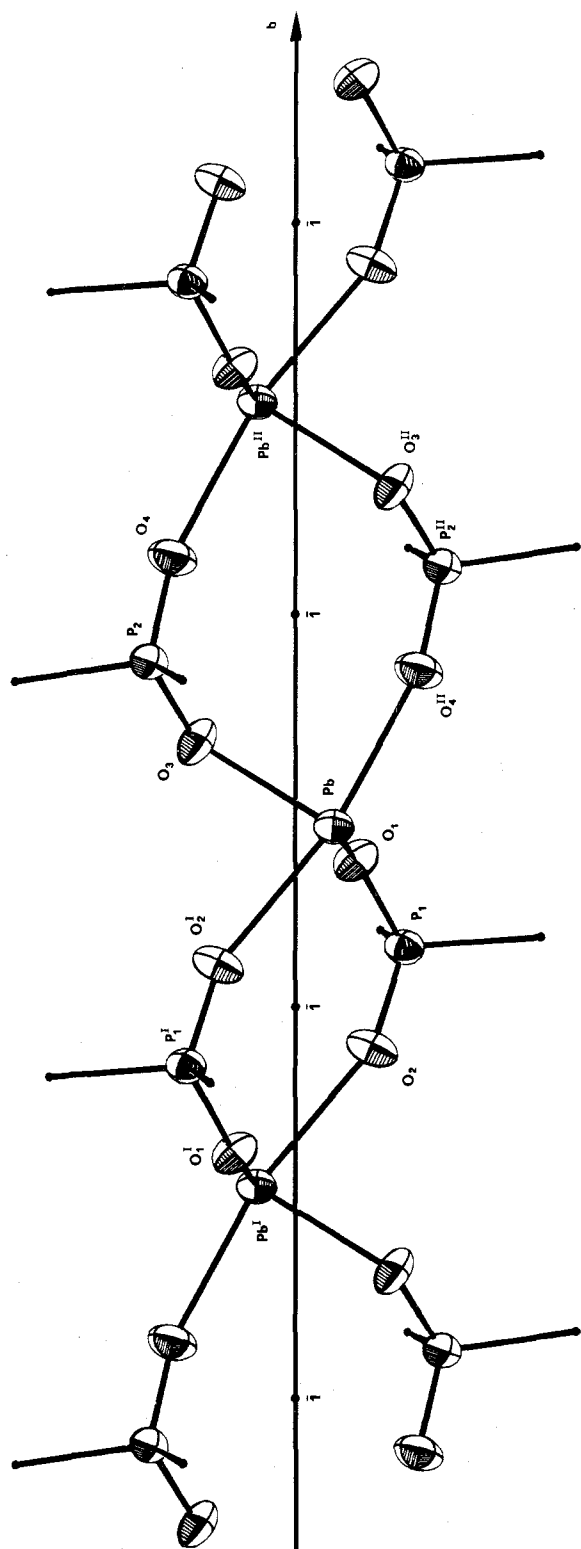
**Table II.** Bond Lengths (A) and Angles (deg) with Estimated Standard Deviations

Lengths

| | | | |
|---|---|---|---|
| Pb–O(1) | 2.232 (7) | C(7)–C(8) | 1.39 (1) |
| Pb–O(2)[I] | 2.430 (6) | C(8)–C(9) | 1.41 (2) |
| Pb–O(3) | 2.234 (6) | C(9)–C(10) | 1.39 (2) |
| Pb–O(4)[II] | 2.439 (6) | C(10)–C(11) | 1.36 (2) |
| | | C(11)–C(12) | 1.38 (1) |
| P(1)–O(1) | 1.524 (6) | C(12)–C(7) | 1.37 (1) |
| P(1)–O(2) | 1.502 (7) | | |
| P(1)–C(1) | 1.814 (10) | C(13)–C(14) | 1.35 (2) |
| P(1)–C(7) | 1.824 (8) | C(14)–C(15) | 1.43 (2) |
| | | C(15)–C(16) | 1.33 (2) |
| P(2)–O(3) | 1.521 (7) | C(16)–C(17) | 1.32 (2) |
| P(2)–O(4) | 1.504 (7) | C(17)–C(18) | 1.40 (2) |
| P(2)–C(13) | 1.800 (9) | C(18)–C(13) | 1.37 (2) |
| P(2)–C(19) | 1.797 (11) | | |
| | | C(19)–C(20) | 1.40 (2) |
| C(1)–C(2) | 1.39 (2) | C(20)–C(21) | 1.40 (2) |
| C(2)–C(3) | 1.40 (2) | C(21)–C(22) | 1.37 (1) |
| C(3)–C(4) | 1.36 (1) | C(22)–C(23) | 1.36 (2) |
| C(4)–C(5) | 1.34 (2) | C(23)–C(24) | 1.43 (2) |
| C(5)–C(6) | 1.40 (2) | C(24)–C(19) | 1.38 (1) |
| C(6)–C(1) | 1.37 (1) | | |

Angles

| | | | |
|---|---|---|---|
| O(1)–Pb–O(2)[I] | 88.1 (2) | C(1)–C(2)–C(3) | 117 (1) |
| O(1)–Pb–O(3) | 88.2 (2) | C(2)–C(3)–C(4) | 122 (1) |
| O(1)–Pb–O(4)[II] | 89.6 (2) | C(3)–C(4)–C(5) | 120 (1) |
| O(2)[I]–Pb–O(3) | 84.9 (2) | C(4)–C(5)–C(6) | 120 (1) |
| O(2)[I]–Pb–O(4)[II] | 167.6 (2) | C(5)–C(6)–C(1) | 120 (1) |
| O(3)–Pb–O(4)[II] | 82.8 (2) | | |
| | | P(1)–C(7)–C(8) | 120 (1) |
| Pb–O(1)–P(1) | 131.9 (4) | P(1)–C(7)–C(12) | 119 (1) |
| Pb–O(2)[I]–P(1)[I] | 155.1 (4) | C(12)–C(7)–C(8) | 121 (1) |
| Pb–O(3)–P(2) | 126.0 (4) | C(7)–C(8)–C(9) | 119 (1) |
| Pb–O(4)[II]–P(2)[II] | 163.5 (4) | C(8)–C(9)–C(10) | 118 (1) |
| | | C(9)–C(10)–C(11) | 122 (1) |
| O(1)–P(1)–O(2) | 118.1 (4) | C(10)–C(11)–C(12) | 120 (1) |
| O(1)–P(1)–C(1) | 106.1 (4) | C(11)–C(12)–C(7) | 120 (1) |
| O(1)–P(1)–C(7) | 107.6 (4) | | |
| O(2)–P(1)–C(1) | 109.3 (4) | P(2)–C(13)–C(14) | 122 (1) |
| O(2)–P(1)–C(7) | 108.1 (4) | P(2)–C(13)–C(18) | 120 (1) |
| C(1)–P(1)–C(7) | 107.1 (4) | C(18)–C(13)–C(14) | 119 (1) |
| | | C(13)–C(14)–C(15) | 120 (1) |
| O(3)–P(2)–O(4) | 117.8 (4) | C(14)–C(15)–C(16) | 118 (1) |
| O(3)–P(2)–C(13) | 105.4 (4) | C(15)–C(16)–C(17) | 122 (1) |
| O(3)–P(2)–C(19) | 107.8 (4) | C(16)–C(17)–C(18) | 121 (2) |
| O(4)–P(2)–C(13) | 108.5 (4) | C(17)–C(18)–C(13) | 119 (2) |
| O(4)–P(2)–C(19) | 109.2 (4) | | |
| C(13)–P(2)–C(19) | 107.8 (5) | P(2)–C(19)–C(20) | 120 (1) |
| | | P(2)–C(19)–C(24) | 120 (1) |
| P(1)–C(1)–C(2) | 120 (1) | C(24)–C(19)–C(20) | 121 (1) |
| P(1)–C(1)–C(6) | 119 (1) | C(19)–C(20)–C(21) | 118 (1) |
| C(6)–C(1)–C(2) | 121 (1) | C(20)–C(21)–C(22) | 122 (1) |
| | | C(21)–C(22)–C(23) | 119 (1) |
| | | C(22)–C(23)–C(24) | 121 (1) |
| | | C(23)–C(24)–C(19) | 118 (1) |

that of the species in solution can be obtained by precipitating the compound from benzene or chloroform solution with hexane.

The residues ($\beta$ form) obtained upon evaporation of the organic solvents from $Pb[OP(C_6H_5)_2O]_2$ solutions are either amorphous or partially crystalline and melt only a few degrees lower (228–233 °C) than the $\alpha$ form. The x-ray powder patterns of the crystalline samples of the $\beta$ form show it to be different from the $\alpha$ form. The infrared spectrum of the $\beta$ form (Figure 3) differs from that of the $\alpha$ form mainly in that the $PO_2$ antisymmetric stretching band is split in the case of the $\alpha$ form, whereas in the $\beta$ form it is not. Another form of $Pb[OP(C_6H_5)_2O]_2$ (designated $\gamma$) is obtained on cooling the melt of either of the other forms. The $\gamma$ form has an infrared spectrum identical with that of the $\beta$ form, but it is very crystalline and gives an x-ray powder pattern distinctly different from that of the $\alpha$ or the $\beta$ forms. This type of polymorphism has been observed in other metal(II) phosphinates and was attributed to changes in the orientation of the side groups.[4,5] However, in the case of $Pb[OP(C_6H_5)_2O]_2$ it is possible to retain the same coordination geometry of the



**Figure 1.** ORTEP drawing showing the polymeric chain of lead(II) bis(diphenylphosphinate). Superscripts I and II refer respectively to atoms related through the centers of symmetry at 0, 0, 0 and 0, $^1/_2$, 0.
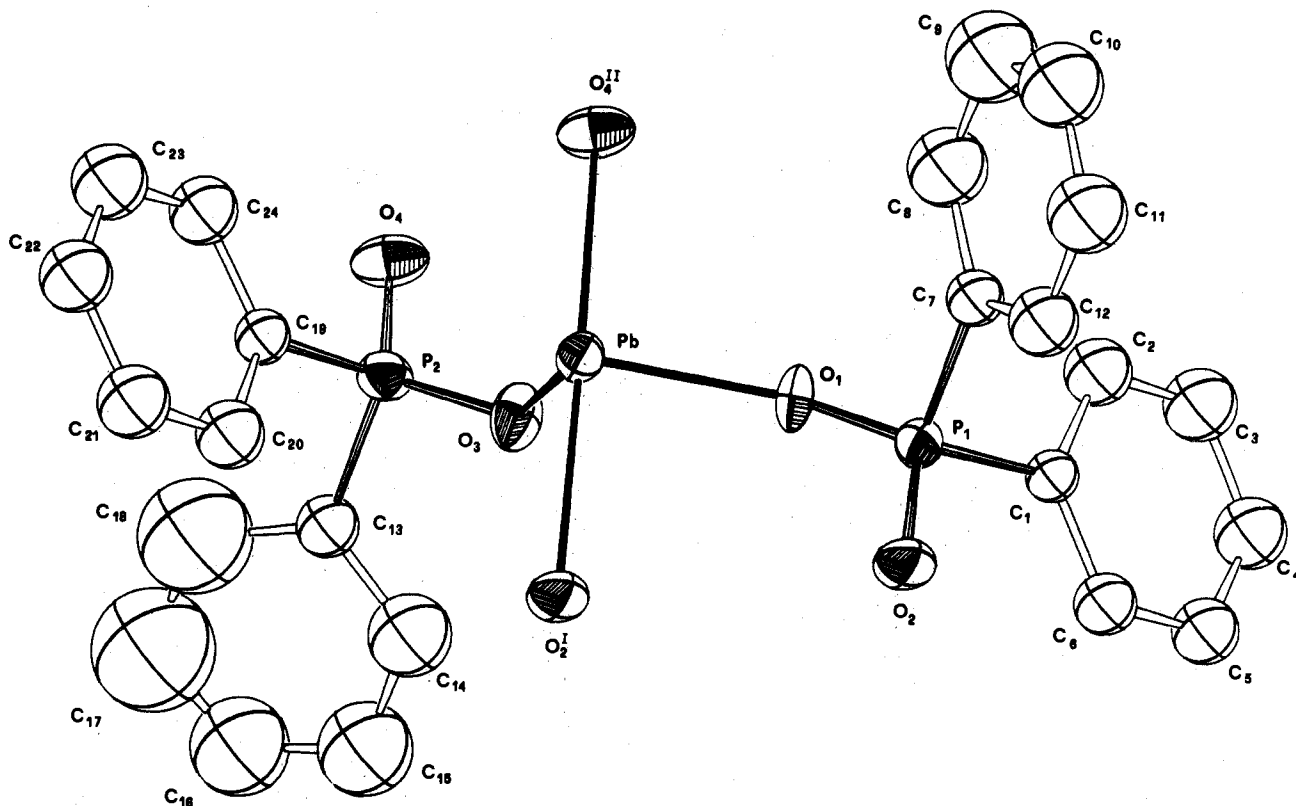
**Figure 2.** ORTEP drawing of the lead(II) bis(diphenylphosphinate) moiety, showing the coordination around the Pb atoms. The numbering scheme is the same as that used in the tables.

**Table III.** Least-Squares Plane Equations Referred to the Crystallographic Axes, with Deviations (Å) of the Atoms from the Planes

| | Eq: $AX + BY + CZ = D$ | | | | | Dev from |
|---|---|---|---|---|---|---|
| Plane | A | B | C | D | Atom | plane |
| 1 | 9.846 | −5.795 | 0.930 | 2.200 | C(1) | −0.003 |
| | | | | | C(2) | −0.004 |
| | | | | | C(3) | 0.008 |
| | | | | | C(4) | −0.005 |
| | | | | | C(5) | −0.002 |
| | | | | | C(6) | 0.006 |
| | | | | | P(1) | −0.050 |
| 2 | −7.269 | 0.815 | 7.997 | −1.911 | C(7) | −0.005 |
| | | | | | C(8) | 0.003 |
| | | | | | C(9) | 0.000 |
| | | | | | C(10) | −0.001 |
| | | | | | C(11) | −0.001 |
| | | | | | C(12) | 0.004 |
| | | | | | P(1) | −0.015 |
| 3 | 4.220 | 7.424 | −6.838 | 4.658 | C(13) | −0.063 |
| | | | | | C(14) | 0.045 |
| | | | | | C(15) | 0.013 |
| | | | | | C(16) | −0.054 |
| | | | | | C(17) | 0.034 |
| | | | | | C(18) | 0.025 |
| | | | | | P(2) | −0.163 |
| 4 | 10.656 | −4.711 | 0.375 | −0.382 | C(19) | −0.000 |
| | | | | | C(20) | −0.012 |
| | | | | | C(21) | 0.014 |
| | | | | | C(22) | −0.004 |
| | | | | | C(23) | −0.009 |
| | | | | | C(24) | 0.010 |
| | | | | | P(2) | −0.007 |

lead atoms and the same overall double-bridged structure but instead of each phosphinate group bridging between an axial and equatorial site as in the α form, the phosphinate groups can also bridge between two axial or two equatorial sites. Other possibilities for isomerism include changes of coordination geometry of the lead atoms and ligands and alternating
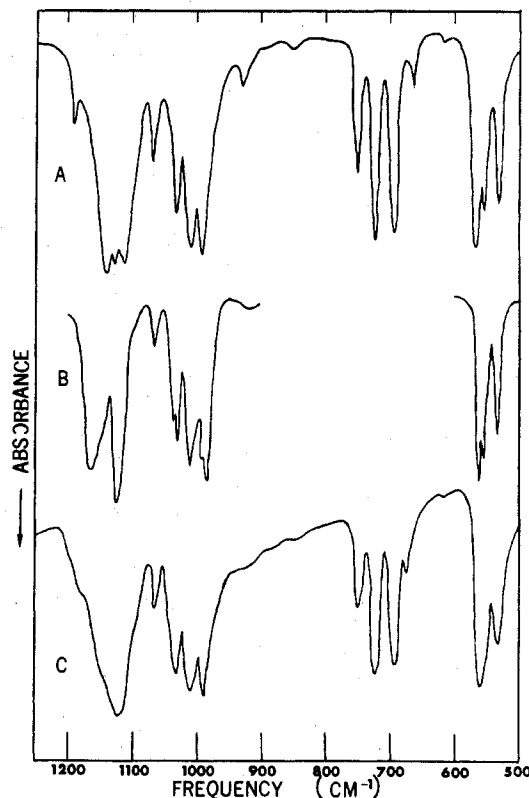


**Figure 3.** Infrared spectra of $Pb[OP(C_6H_5)_2O]_2$: (A) crystalline α form in Nujol mull; (B) compound in $CH_2Cl_2$ solution; (C) amorphous β form (residue) in Nujol mull.

single and triple bridges. The possibility of the lone pair of electrons occupying an axial site is less likely because the electron pair repulsion would be greater in an axial than in an equatorial site.

The dta diagram of the amorphous form of Pb[OP(C₆H₅)₂O]₂ obtained as a residue from solution contains an irreversible exotherm at approximately 145 °C in addition to the melting endotherm above 225 °C. Examination of this material with a light-polarizing microscope equipped with a hot stage shows crystallization occurring at the temperature of the exotherm. The dta diagrams of the crystalline polymers contain only one transition, which is the endotherm due to melting.

The thermal decomposition of Pb[OP(C₆H₅)₂O]₂ was followed by tga in both air and nitrogen with a heating rate of 5 °C/min. Under these conditions the decompositions in both atmospheres were identical, with initial weight loss occurring at 300 °C. This is well below the initial weight loss observed for other diphenylphosphinates such as Zn[O-P(C₆H₅)₂O]₂[15] and Cr[OP(C₆H₅)₂O]₂OH.[16]

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# Crystal Structure of an Adduct of Telluric Acid with Potassium Fluoride, Te(OH)₆·2KF. A Compound with Short O-H···F Hydrogen Bonds

R. ALLMANN* and W. HAASE

Te(OH)₆·2KF crystallizes in space group *Pcab* with $Z = 4$ formula units per cell: $a = 9.610$ (4) Å, $b = 8.999$ (6) Å, $c = 8.547$ (5) Å³, $V = 739.1$ Å³, $d_m = 3.08$ (3) g cm⁻³, $d_x = 3.11$ g cm⁻³. With 576 independent reflections (74 of them $<F_{min} = \sigma(F)$), which were measured on a Philips four-circle PW 1100 diffractometer, the structure could be refined to $R = 3.1\%$, using anisotropic temperature factors for all atoms except H. The structure is very similar to the cubic one of K₂PtCl₆, but to make room for the F⁻ ions, the Te(OH)₆ octahedra are slightly turned out of their regular positions (Te–O = 1.905 Å). K is ten-coordinated (K–O = 2.766–3.225 Å, eight times; K–F = 2.591, 3.125 Å). All OH groups are involved in short O-H···F hydrogen bonds of about 2.58 Å. The fluorine ions are therefore four-coordinated (plus one long K–F bond). The ir and Raman spectra are discussed.

## Introduction

Telluric acid, Te(OH)₆, forms with alkali fluorides adducts like Te(OH)₆·2KF or Te(OH)₆·NaF.[1] In the case of the sodium compound rather regular Te(OH)₆ octahedra were found[2] (Te–O = 1.92 Å). A bonding of the F⁻ ions directly to Te, as assumed by Kolditz and Fitz,[1] could not be confirmed by this, but three of the six OH groups form strong O-H···F hydrogen bonds of 2.50 Å in Te(OH)₆·NaF[2] (the other three O-H···O bonds are 2.76 Å). How the double amount of alkali and fluorine ions is assembled in the structure of Te(OH)₆·2KF shall be examined in this paper, as well as the kind of hydrogen bonds in this compound. A preliminary structure determination by Willinger[3] yielded wrong results with respect to the fluorine positions.

## Experimental Section

A colorless octahedral crystal (form {111}) of Te(OH)₆·2KF with about 0.2-mm edges was measured on a Philips four-circle PW 1100 diffractometer (Mo Kα radiation, λ 0.71069 Å, graphite monochromator, ω/2θ scan, $\theta_{max} = 24°$, scan width 1.2° in θ, time for integrated reflection 40 s, time for background 2 × 10 s, scintillation counter with discriminator). For the stronger *eee* and *ooo* reflections mostly four symmetry-equivalent reflections were measured; for the

* To whom correspondence should be addressed at the University of Marburg.

others, mostly two (altogether 1821 reflections). After applying the normal *Lp* corrections and averaging, 576 independent structure factors remained, 74 of them below the observation limit $F_{min} = \sigma(F_o)$. No absorption correction was applied ($\mu = 53.0$ cm⁻¹).

The centrosymmetric space group *Pcab* is uniquely determined by the following extinctions: 0*kl* with $l = 2n$, *h0l* with $h = 2n$, and *hk0* with $k = 2n$ only. The lattice constants $a = 9.610$ (4) Å, $b = 8.999$ (6) Å, $c = 8.547$ (5) Å, and $V = 739.1$ Å³ were derived at room temperature (~21 °C) from the 2θ values of 14 selected reflections (200, 020, 002, 111, and symmetry-related ones), which were measured six times during 3 days at the four-circle goniometer. The given values and standard deviations result when these six data sets are taken with equal weight. The equivalent positions in *Pcab* are $\pm(x, y, z; 1/2 + x, -y, 1/2 - z; 1/2 - x, 1/2 + y, -z; -x, 1/2 - y, 1/2 + z)$. With $Z = 4$ formula units of Te(OH)₆·2KF per unit cell the calculated density becomes $d_x = 3.11$ g cm⁻³, which compares well with the measured density $d_m = 3.08$ (3) g cm⁻³ (pycnometric with 189 mg of substance in 2 ml of *n*-hexane).

## Structure Determination and Refinement

Since the tellurium atoms have to be situated at centers of symmetry, they contribute only to the *eee* and *ooo* reflections. Because of the high number of 52 electrons for Te, all $F$ values of these 179 reflections are expected to become positive if Te is placed at position 4(a): 0, 0, 0; 1/2, 1/2, 0; 1/2, 0, 1/2; 0, 1/2, 1/2. A Fourier synthesis with only these structure factors (i.e., in space group *Fmmm*, all signs