

Structures of Complexes between Metal Halides and Phosphinothioethers or Related Ligands.

VI. Polymeric Diiodo[1,5-bis(diphenylphosphine)pentane]mercury(II)

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The structure of polymeric diiodo[1,5-bis(diphenylphosphine)pentane]mercury(II), $(\text{HgI}_2\text{P}_2\text{C}_{29}\text{H}_{30})_n$, has been determined by Patterson and Fourier methods and refined to $R=0.047$ and $R_w=0.062$ for 1792 independent X-ray counter intensities. The crystals are orthorhombic, space group *Pccn* with $a=8.288$ (3), $b=21.012$ (5), $c=17.044$ (5) Å, $Z=4$. The Hg atoms are four-coordinated, bonded to two I atoms and to two P atoms belonging to two different ligand molecules, $(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_5\text{P}(\text{C}_6\text{H}_5)_2$, thereby forming infinite chains which run approximately parallel to [100].

Introduction

The structures of some complexes between bis(diphenylphosphineethyl) sulphide, $(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2$, and halides of Hg, Ag and Ni have been the subject of investigations at this Institute. In the complexes of Hg (Aurivillius & Fälvh, 1973) and Ni (Fälvh, 1976) the structures are built up of monomeric molecules, $\text{MeI}_2\text{P}_2\text{SC}_{28}\text{H}_{28}$. Besides being bonded to two I atoms, Hg is coordinated to the two P atoms and Ni to the two P atoms and the S atom of one ligand molecule. The Ag complex (Aurivillius, Cassel & Fälvh, 1974; Cassel, 1975) is built up of dimeric molecules $(\text{AgXP}_2\text{SC}_{28}\text{H}_{28})_2$, $\text{X}=\text{Cl}$, I. The Ag atom is coordinated to two X atoms and to two P atoms, belonging to two different ligand molecules. The coordination involves the formation of a double halide bridge between two Ag atoms.

To study the influence of the S atom of the ligand on the structures given above, especially that of $\text{HgI}_2\text{P}_2\text{SC}_{28}\text{H}_{28}$, the present investigation was undertaken on a compound of Hg where the S atom of the ligand was replaced by a methylene group.

Experimental

Single crystals of $\text{HgI}_2\text{P}_2\text{C}_{29}\text{H}_{30}$ in the form of colourless plates were supplied by Professor G. Schwarzenbach, ETH, Zürich, Switzerland. Weissenberg photographs showed systematic absences $hk0$ for $h+k=2n+1$, $0kl$ and $h0l$ for $l=2n+1$ which are characteristic of the space group *Pccn* (No. 56). The dimensions of the cell were determined from powder photographs taken in a Guinier-Hägg focusing camera with $\text{Cu K}\alpha_1$ radiation ($\lambda=1.54051$ Å) and KCl ($a=6.2929$ Å) as an internal standard. Refinement of the cell parameters was performed by least squares. The density observed by flotation was in fair agreement with the calculated value assuming four formula units $\text{HgI}_2\text{P}_2\text{C}_{29}\text{H}_{30}$ per cell. Some crystal data are presented

in Table 1. A crystal, 0.145, 0.034 and 0.085 mm along a , b and c respectively, was chosen. Intensities were collected on a computer-controlled four-circle diffractometer (Enraf-Nonius, CAD-4) with $\text{Cu K}\alpha$ radiation and a graphite monochromator. The $\omega-2\theta$ scan technique was used with a scan interval of $(0.80+0.50 \tan \theta)^\circ$. The background was measured by extending the scan by 25% at each end of the interval. In the range $5^\circ < \theta < 70^\circ$, 2793 independent reflexions were recorded. Of these, 1792 were considered significantly above background having $I > 2\sigma(I)$, where $\sigma(I)$ is the standard deviation based on counting statistics. The intensities and their standard deviations were corrected for Lorentz, polarization and absorption effects as well as for fluctuations in the intensities of three standard reflexions (general hkl) measured at regular intervals. The crystal was described by six planes and the transmission factors, evaluated by numerical integration, varied between 0.032 and 0.393.

Table 1. *Crystal data*

| | | | |
|---|-----------------------|--------------------------|-------------------------|
| $\text{HgI}_2\text{P}_2\text{C}_{29}\text{H}_{30}$, M.W. 894.9 | | | |
| Orthorhombic, <i>Pccn</i> (No. 56) | | | |
| a | 8.288 (3) Å | D_m | 1.95 g cm ⁻³ |
| b | 21.012 (5) | D_x | 2.00 |
| c | 17.044 (5) | Z | 4 |
| V | 2968.2 Å ³ | $\mu(\text{Cu K}\alpha)$ | 304 cm ⁻¹ |

Structure determination

From a vector map the Hg and the I atoms were found to occupy the point positions 4(c) and 8(e) in *Pccn* respectively. Least-squares refinements based on deduced preliminary parameters, and followed by difference syntheses, revealed the positions of all other non-hydrogen atoms, *viz* the atoms P, C(1)–C(14) in 8(e) and C(15) in 4(d). Refinement with the deduced positions of the atoms and anisotropic temperature factors converged at $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.054$ and $R_w = [\sum w_i (|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2} = 0.065$ for 1764 reflexions. At

this stage a difference synthesis showed residuals near the positions of the Hg and the I atoms ranging from -1.1 to $2.4 \text{ e } \text{\AA}^{-3}$. The positions of the H atoms were deduced from geometrical considerations with $\text{C-H} = 0.9\text{--}1.0 \text{ \AA}$. A final least-squares refinement including the non-hydrogen atoms with anisotropic temperature factors, the H atoms of the phenyl rings and the methylene groups with fixed positional and isotropic thermal parameters ($B = 4.0 \text{ \AA}^2$) converged at $R = 0.047$ and $R_w = 0.062$ for 1792 reflexions. The function minimized was $\sum w_i(|F_o| - |F_c|)^2$, where the weights were calculated from $w_i^{-1} = \sigma^2(F_o^2)/4|F_o|^2 + a|F_o|^2$. The constant was chosen so as to give the most constant averages of

$w_i(|F_o| - |F_c|)^2$ over ranges of F and $\sin \theta$ ($a = 0.002$). The value of $S = [\sum w_i(|F_o| - |F_c|)^2 / (m - n)]^{1/2}$, where m and n are the number of observations and parameters varied, was 1.06. Scattering factors for neutral Hg and I were those of Cromer & Waber (1965), for neutral P and C those of Hanson, Herman, Lea & Skillman (1964). An anomalous dispersion correction for Hg and I (Cromer & Liberman, 1970) was included. Scattering factors for the H atoms were taken from Stewart, Davidson & Simpson (1965). Owing to the heavy absorption of the crystal, no extinction correction was made. The highest residuals near the positions of the Hg and the I atoms were $1.9 \text{ e } \text{\AA}^{-3}$ in the final difference syn-

Table 2. Positional and thermal parameters

(a) Positional fractional coordinates and root-mean-square components R_i . The values of R_i are given only for the non-hydrogen atoms. Standard deviations are given in parentheses.

| | x | y | z | R_1 (Å) | R_2 (Å) | R_3 (Å) | |
|-------|---------------|---------------|--------------|-----------|-----------|-----------|-------|
| Hg | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.69669 (4) | 0.2322 | 0.2390 | 0.2542 | |
| I | 0.00366 (13) | 0.29552 (4) | 0.79129 (5) | 0.2051 | 0.2735 | 0.2951 | |
| P | 0.34013 (38) | 0.33761 (11) | 0.60022 (16) | 0.1784 | 0.2051 | 0.2379 | |
| C(1) | 0.4490 (14) | 0.4060 (5) | 0.6408 (6) | 0.185 | 0.203 | 0.258 | |
| C(2) | 0.5510 (22) | 0.3970 (6) | 0.7051 (7) | 0.223 | 0.238 | 0.354 | |
| C(3) | 0.6394 (23) | 0.4474 (7) | 0.7342 (9) | 0.219 | 0.271 | 0.355 | |
| C(4) | 0.6289 (24) | 0.5052 (8) | 0.7005 (10) | 0.234 | 0.264 | 0.377 | |
| C(5) | 0.5300 (18) | 0.5153 (5) | 0.6364 (11) | 0.226 | 0.254 | 0.327 | |
| C(6) | 0.4384 (17) | 0.4658 (5) | 0.6067 (8) | 0.215 | 0.259 | 0.310 | |
| C(7) | 0.1746 (17) | 0.3700 (5) | 0.5447 (6) | 0.193 | 0.211 | 0.265 | |
| C(8) | 0.0463 (18) | 0.3997 (5) | 0.5845 (8) | 0.222 | 0.277 | 0.287 | |
| C(9) | -0.0836 (21) | 0.4232 (6) | 0.5447 (11) | 0.231 | 0.311 | 0.327 | |
| C(10) | -0.0929 (23) | 0.4175 (8) | 0.4653 (12) | 0.239 | 0.323 | 0.345 | |
| C(11) | 0.0257 (23) | 0.3897 (8) | 0.4261 (9) | 0.202 | 0.335 | 0.379 | |
| C(12) | 0.1633 (20) | 0.3640 (6) | 0.4638 (7) | 0.209 | 0.270 | 0.294 | |
| C(13) | 0.4821 (16) | 0.3066 (5) | 0.5275 (7) | 0.210 | 0.247 | 0.270 | |
| C(14) | 0.6176 (22) | 0.2764 (6) | 0.5684 (8) | 0.243 | 0.277 | 0.309 | |
| C(15) | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.5150 (11) | 0.190 | 0.251 | 0.342 | |
| | x | y | z | x | y | z | |
| H(2) | 0.558 | 0.356 | 0.728 | H(11) | 0.017 | 0.385 | 0.371 |
| H(3) | 0.710 | 0.440 | 0.778 | H(12) | 0.248 | 0.344 | 0.439 |
| H(4) | 0.688 | 0.537 | 0.719 | H(131) | 0.430 | 0.276 | 0.494 |
| H(5) | 0.520 | 0.555 | 0.612 | H(132) | 0.521 | 0.341 | 0.494 |
| H(6) | 0.367 | 0.471 | 0.562 | H(141) | 0.669 | 0.308 | 0.602 |
| H(8) | 0.060 | 0.403 | 0.640 | H(142) | 0.580 | 0.243 | 0.601 |
| H(9) | -0.165 | 0.443 | 0.572 | H(15) | 0.707 | 0.217 | 0.482 |
| H(10) | -0.187 | 0.434 | 0.439 | | | | |

(b) Anisotropic thermal parameters for the non-hydrogen atoms. The parameters β_{ij} are based on the expression $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

| | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|-------|--------------|--------------|--------------|---------------|--------------|--------------|
| Hg | 0.01728 (13) | 0.00262 (2) | 0.00359 (3) | -0.00039 (4) | 0 | 0 |
| I | 0.02205 (19) | 0.00363 (2) | 0.00399 (3) | 0.00010 (5) | 0.00163 (7) | -0.00092 (2) |
| P | 0.01435 (51) | 0.00213 (5) | 0.00303 (10) | -0.00039 (13) | 0.00091 (19) | -0.00007 (6) |
| C(1) | 0.0147 (21) | 0.0026 (2) | 0.0035 (4) | -0.0010 (5) | 0.0003 (7) | -0.0003 (2) |
| C(2) | 0.0369 (41) | 0.0036 (3) | 0.0035 (5) | -0.0048 (9) | 0.0000 (11) | 0.0002 (3) |
| C(3) | 0.0287 (42) | 0.0049 (5) | 0.0042 (6) | -0.0036 (11) | -0.0034 (13) | 0.0002 (4) |
| C(4) | 0.0311 (41) | 0.0039 (4) | 0.0064 (8) | -0.0046 (10) | 0.0027 (15) | -0.0019 (5) |
| C(5) | 0.0191 (28) | 0.0028 (3) | 0.0077 (8) | -0.0016 (7) | 0.0018 (13) | -0.0001 (4) |
| C(6) | 0.0180 (24) | 0.0031 (3) | 0.0054 (6) | -0.0005 (6) | 0.0007 (10) | 0.0004 (3) |
| C(7) | 0.0185 (21) | 0.0026 (3) | 0.0032 (4) | -0.0013 (6) | 0.0000 (8) | 0.0002 (2) |
| C(8) | 0.0237 (33) | 0.0031 (3) | 0.0043 (5) | 0.0016 (7) | 0.0005 (11) | -0.0004 (3) |
| C(9) | 0.0261 (34) | 0.0031 (3) | 0.0074 (8) | 0.0026 (9) | 0.0003 (15) | 0.0010 (4) |
| C(10) | 0.0210 (35) | 0.0050 (5) | 0.0071 (9) | 0.0031 (11) | -0.0024 (16) | 0.0000 (5) |
| C(11) | 0.0293 (38) | 0.0058 (5) | 0.0043 (6) | 0.0011 (12) | -0.0051 (13) | 0.0007 (4) |
| C(12) | 0.0212 (29) | 0.0041 (4) | 0.0033 (5) | 0.0013 (8) | 0.0006 (9) | -0.0005 (3) |
| C(13) | 0.0187 (23) | 0.0028 (3) | 0.0038 (4) | -0.0001 (6) | -0.0008 (9) | -0.0003 (3) |
| C(14) | 0.0296 (37) | 0.0039 (4) | 0.0040 (6) | 0.0004 (9) | 0.0001 (12) | 0.0006 (3) |
| C(15) | 0.0134 (27) | 0.0045 (5) | 0.0048 (7) | 0.0004 (12) | 0 | 0 |

thesis. Final positional and thermal parameters are given in Table 2.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31862 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

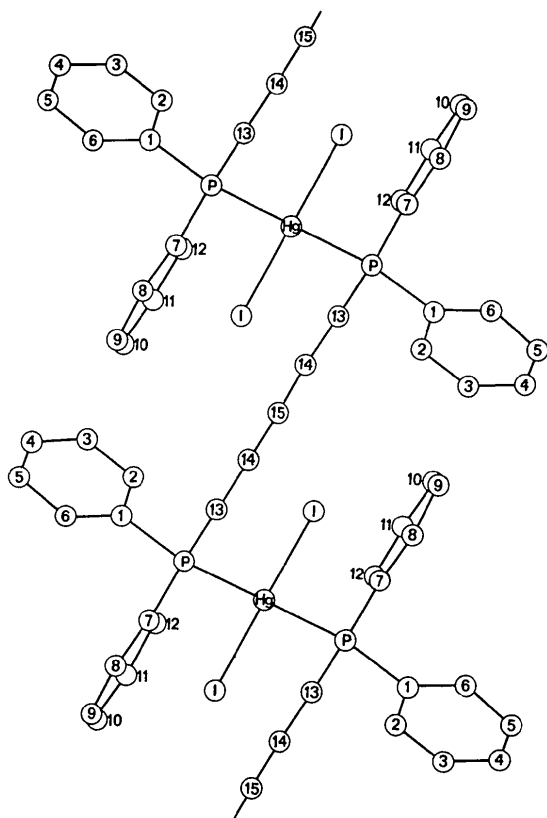


Fig. 1. Schematic drawing showing part of the infinite chains ($\text{HgI}_2\text{P}_2\text{C}_{29}\text{H}_{30}$)_n. The labelling of the atoms refers to Tables 2 and 3. Numbered circles denote carbon atoms.

Table 3. Selected interatomic distances (Å) and angles (°)

Standard deviations are given in parentheses. For labelling of the atoms, cf. Fig. 1 and Table 2(a).

| Mercury coordination | | Phosphorus coordination | |
|----------------------|-----------|-------------------------|------------|
| Hg-2P | 2.579 (3) | P-C(7) | 1.800 (13) |
| Hg-2I | 2.772 (1) | P-C(13) | 1.829 (13) |
| | | P-C(1) | 1.832 (11) |
| | | P-Hg | 2.579 (3) |

| Carbon-carbon distances outside the phenyl rings | |
|--|------------|
| C(13)-C(14) | 1.466 (21) |
| C(14)-C(15) | 1.530 (20) |

| Mean carbon-carbon distances of the phenyl rings | |
|--|-----------|
| | 1.382 (7) |
| | 1.383 (2) |

Angles in the distorted tetrahedra around the mercury and phosphorus atoms

| | | | |
|--------------|----------------|------------|----------------|
| P-Hg-P | 100.77 (12) | P-Hg-I | 113.82 (7) × 2 |
| P-Hg-I | 109.75 (7) × 2 | I-Hg-I | 108.86 (5) |
| C(1)-P-C(13) | 102.6 (5) | Hg-P-C(13) | 111.3 (4) |
| C(7)-P-C(1) | 106.1 (5) | Hg-P-C(7) | 112.6 (4) |
| C(7)-P-C(13) | 105.6 (6) | Hg-P-C(1) | 117.5 (4) |

Angles in the ligand chain

| | |
|-------------------|-------------|
| P—C(13)-C(14) | 109.0 (9) |
| C(13)-C(14)-C(15) | 115.0 (1.2) |
| C(14)-C(15)-C(14) | 106.9 (1.6) |

Discussion

Interatomic distances and angles are given in Table 3. A schematic drawing of the structure with the labelling of the atoms is presented in Fig. 1 and a stereo view in Fig. 2.

Besides being coordinated to two I atoms, the Hg atom (point symmetry 2) is bonded to two P atoms belonging to two different ligand molecules, thereby forming endless chains of formula $(\text{HgI}_2\text{P}_2\text{C}_{29}\text{H}_{30})_n$, which run approximately parallel to [100]. No intermolecular distances shorter than the sum of the van der Waals radii occur between them. The structure is thus built up by the packing of these infinite chains.

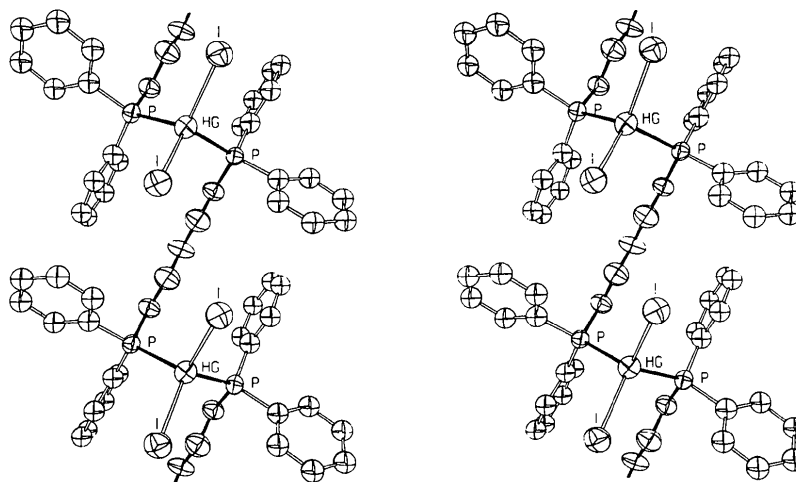


Fig. 2. Stereo view showing part of the infinite chains, which run approximately parallel to [100].

The coordination polyhedron of Hg is a tetrahedron with Hg-2I 2.772 (1) and Hg-2P 2.579 (3) Å. These distances are in good agreement with values reported earlier, e.g. Hg-4I 2.78 for tetrahedral HgI₂ (Huggins & Magill, 1927), Hg-I 2.759 (4), 2.858 (4), Hg-P 2.50 (1), 2.53 (1) Å for HgI₂P₂SC₂₈H₂₈ (Aurivillius & Fälth, 1973). The angles in the tetrahedron vary between 100.8 and 113.8° (Table 3). The coordination of P is also tetrahedral with P-Hg 2.579 (3), P-C(1) 1.83 (1), P-C(7) 1.80 (1) and P-C(13) 1.83 (1) Å. The P-C distances also agree well with analogous distances in HgI₂P₂SC₂₈H₂₈. The angles in the coordination polyhedron vary between 102.6 and 117.5°. The C-C distances in the ligand chain, 1.47 (2), 1.53 (2) Å, are normal compared with the value 1.531 (3) Å given in *International Tables for X-ray Crystallography* (1968).

The C-C distances in the phenyl rings average 1.382 (7) and 1.383 (12) Å respectively, in good agreement with values reported for similar compounds, e.g. (AgIP₂SC₂₈H₂₈)₂ (Cassel, 1975). The largest deviations of a C atom from the least-squares planes through C(1)-C(6) and C(7)-C(12) of the two phenyl rings are 0.006 and 0.008 Å.

The different arrangements in HgI₂P₂SC₂₈H₂₈, built up of monomeric molecules, and HgI₂P₂C₂₉H₃₀, built up of endless chains, may have their origin in a faint

interaction between Hg and S, the distance Hg...S being 3.71 (1) Å. In the present compound the corresponding distance Hg...C is 5.173 (2) Å.

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The Crystal Structure of Pr(OH)₂NO₃

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The structure of Pr(OH)₂NO₃ has been determined from single-crystal X-ray data and refined by least-squares methods. The crystals are monoclinic, space group *P2*₁ and the unit-cell dimensions are *a* = 6.449, *b* = 3.881, *c* = 7.747 Å and β = 98.73°. The cell contains two formula units. Each Pr atom is surrounded by a tricapped trigonal prism formed by nine O atoms. The polyhedra are linked together in the *ab* plane. Two of the three O atoms in the NO₃⁻ group are contained in the O polyhedron. The structure is closely related to the monoclinic form of Y(OH)₂Cl.

Introduction

In recent years an increasing awareness of manifold lanthanide hydroxy anion compounds has resulted primarily from low-temperature studies of crystals grown hydrothermally. Hydroxy compounds formed also contain the anions fluoride, chloride, nitrate and carbonate. Single-crystal X-ray structure examinations have been made of several trivalent metal hydroxide chloride phases including orthorhombic and mono-

clinic forms of Y(OH)₂Cl (Klevtsova & Klevtsov, 1965, 1966; Dornberger-Schiff & Klevtsova, 1967) as well as monoclinic forms of Ln(OH)₂Cl, where Ln = La (Carter & Levinson, 1969), Pr, Sm and Gd (Klevtsova & Glinskaya, 1969). All these compounds have been treated crystallographically as though they had a centrosymmetric array of atoms in the unit cell, although Carter & Levinson (1969) noticed that La(OH)₂Cl may have a noncentrosymmetric arrangement.

Haschke (1975) has recently reviewed the known structural information on the larger group of anion-substituted lanthanide and actinide MX₃ compounds and has proposed a systematization based largely upon

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