# PHENYLMERCURY CHELATES AND CHELATED TITANOXANES

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#### Summary

The reaction of phenylmercury hydroxide with chelating ligands such as salicylaldehyde, 8-hydroxyquinoline, benzoylphenyl hydroxylamine, 2-hydroxybenzophenones and some Schiff bases has been found to give chelated phenylmercury compounds. Stable phenylmercury titanoxanes containing the Hg-O-Ti group have been prepared by the reaction of chelated titanium diisopropoxides with phenylmercury hydroxide. Isopropyl titanate under similar conditions gave tetra-phenylmercury titanate.

#### 1. Introduction

Chelated organomercury compounds have not attracted much attention. Phenylmercury oxinate has been reported in the literature to have herbicidal properties [1]. The synthesis and structure of phenylmercury chelates of substituted 8-hydroxyquinolines were studied recently [2, 3]. Non-coordinated methylmercury derivatives of oximes and phenols have been reported by Glockling and Mahale [4]; these compounds were prepared by reacting the ligands with methyl-(hexamethyldisilyl-amino)-mercury. However, mercury is known to form stable complexes with coordination numbers 3 - 6 [5 - 9]. We have found that phenylmercury hydroxide gives stable coordinated derivatives with bidentate chelating ligands such as salicylaldehyde, 8-hydroxyquinoline, benzoylphenyl hydroxylamine, 2-hydroxybenzophenone, 2-hydroxy-4-methoxy-benzophenone and several Schiff bases. These coordinated derivatives are examples of 3-coordinated mercury. Hetero-metalloxanes containing titanium and elements such as silicon, germanium, tin, lead, boron, phosphorus, arsenic and antimony have been reported in the literature [10, 11]. However, titanoxanes containing mercury are rare. It should be possible to synthesize stable derivatives containing the Hg–O–Ti group.

## 2. Experimental

Dried solvents were freshly distilled before use. Isopropyl titanate was redistilled carefully every time. Experiments were carried out under dry nitrogen in apparatus with standard ground glass joints.

## 2.1. Preparation of phenylmercury hydroxide

Phenylmercury hydroxide was prepared from phenylmercury acetate (33.66 g; 0.1 mol) and sodium hydroxide (4.4 g; 0.11 mol) as described by Bloodworth [12]. The yield was 26.5 g, which represents 90% of the theoretical yield. The fine white crystals melted at 234 °C; the previously reported melting point is 234 - 236 °C.

### 2.2. Preparation of salicylaldehydo-phenylmercury

Phenylmercury hydroxide (2.95 g; 0.01 mol) and salicylaldehyde (1.34 g; 0.011 mol) were refluxed in benzene (50 ml) with a partial take-off condenser for 2 h. When the reaction was over the solvent was removed under reduced pressure. The mass was then extracted with fresh benzene (50 ml) and centrifuged to remove insoluble material; the compound was crystallized by concentration. The crystals were washed with hexane and dried in a vacuum at room temperature. The yellow solid weighed 3.46 g, which represents 85% of the theoretical yield. Analysis showed Hg 50.52%;  $C_7H_5O_2HgC_6H_5$  requires Hg 50.31%. The molecular weight determined by vapour pressure osmometry in benzene was 405; the calculated value is 399.

Other phenylmercury chelates were prepared similarly (Table 1).

### 2.3. Preparation of bis-salicylaldehydo-diisopropoxy titanium

Isopropyl titanate (2.84 g; 0.01 mol) was mixed with salicylaldehyde (2.44 g; 0.02 mol) in benzene (50 ml) and refluxed for 2 h. The solvent and the liberated isopropanol were then removed using a partial take-off condenser and finally under reduced pressure. The product was washed with hexane and the red powdery material was dried in vacuum at room temperature. The yield was 4 g, which represents 98% of the theoretical yield. Analysis showed: C 58.74, H 5.95, Ti 11.85%;  $(C_7H_5O_2)_2Ti(OC_3H_7)_2$  requires: C 58.82, H 5.88, Ti 11.76%. The molecular weight determined by vapor pressure osmometry in benzene was 410; the calculated value is 408.

Other bis-chelated diisopropoxy titaniums were prepared similarly.

### 2.4. Preparation of bis-phenylmercury-bis-salicylaldehydo-titanoxane

Bis-salicylaldehydo-diisopropoxy titanium (4.08 g; 0.01 mol) and phenylmercury hydroxide (5.9 g; 0.02 mol) were mixed in benzene (100 ml)and refluxed for 2 h. Then the liberated alcohol was removed, with the benzene, using a partial take-off condenser. The solution was concentrated in vacuum until crystals of the compound began to appear. The crystals were separated, washed with hexane and dried in vacuum at room temperature. The yellow crystals weighed 7.45 g, which represents 85% of the theoretical yield. Analysis showed: C 35.39, H 2.35, Ti 5.55, Hg 46.10%;  $(C_7H_5O_2)_2Ti(OHgC_6H_5)_2$  requires: C 35.58, H 2.28, Ti 5.47, Hg 45.78%. The compound was soluble in boiling benzene and the molecular weight determined by ebullioscopy in that solvent was found to be 849; the calculated value is 877.

Other phenylmercury titanoxanes were prepared similarly (Table 1).

### 3. Results and discussion

Phenylmercury hydroxide has been found to react with organic chelating ligands containing hydroxyl groups to give chelated phenylmercury compounds. For this reaction to proceed smoothly, it is essential that the water formed during the condensation be removed continuously. This has been achieved by carrying out the reaction in boiling benzene and removing the water formed azeotropically. Chelating ligands containing one hydroxyl group in the molecule reacted with one molecule of phenylmercury hydroxide, whereas those containing two hydroxyl groups needed two molecules of phenylmercury hydroxide. Several of the compounds formed were sufficiently soluble in benzene to allow their molecular weights to be determined; these compounds were found to be monomeric.

Bis-chelated diisopropoxy titanium compounds condensed with phenylmercury hydroxide with the elimination of two molecules of isopropanol. Isopropyl titanate under similar conditions, however, gave four molecules of isopropanol as expected. These reactions were carried out in benzene and the isopropanol liberated was removed azeotropically and was quantitatively estimated by gas chromatographic techniques. The products obtained were stable solids, slightly soluble in benzene and more soluble in alcohol; many of them decomposed on heating. Elemental analysis of these products was good; titanium was estimated by gravimetry as  $TiO_2$  and mercury either by volumetry or gravimetry [13]. The compounds prepared are listed in Table 1.

#### 3.1. IR spectra

In the IR spectrum of phenylmercury hydroxide the  $\nu(OH)$  stretching vibration is found as a strong band at 3250 cm<sup>-1</sup> and the  $\delta(OH)$  as weak bands at 925 and 910 cm<sup>-1</sup>. The spectra of the complexes showed a complete absence of the  $\nu(OH)$  band and  $\delta(OH)$  bands. The  $\delta(CH)$  of the phenyl group is located as strong bands at 730 and 695 cm<sup>-1</sup> in the ligand as well as in the complexes.

In salicylaldehydo-phenylmercury, the CO absorption band at  $1660 \text{ cm}^{-1}$  in the ligand is shifted down to  $1640 \text{ cm}^{-1}$  indicating the coordination of the CO of the ligand with mercury. In the complex of phenylmercury hydroxide with 2-hydroxybenzophenone, the CO absorption frequency at  $1640 \text{ cm}^{-1}$  in the free ligand is displaced to  $1590 \text{ cm}^{-1}$ . In the complex with 2-hydroxy-4-methoxy-benzophenone, the CO absorption value is shifted from 1620 to  $1560 \text{ cm}^{-1}$ . In the case of the 8-hydroxyquinoline

Reactants		Molar ratio	Product <sup>a</sup>	Colour	M.p. (°C)
A	B	A:B			
Salicylaldehyde 8-Hvdroxvouinoline	C <sub>6</sub> H <sub>5</sub> HgOH	1:1	C <sub>7</sub> H <sub>5</sub> O <sub>2</sub> HgC <sub>6</sub> H <sub>5</sub> C <sub>2</sub> H <sub>2</sub> NOHgC <sub>2</sub> H <sub>2</sub>	Yellow Yellow	120 182
2-Hydroxy-benzophenone		1:1	C <sub>13</sub> H9O <sub>2</sub> HgC <sub>6</sub> H5	Orange	183
2-Hydroxy-4-methoxy- benzophenone		1:1	C <sub>14</sub> H <sub>11</sub> O <sub>3</sub> HgC <sub>6</sub> H <sub>5</sub>	Yellow	165
Benzoylphenyl hydroxyl- amine		1:1	C <sub>13</sub> H <sub>10</sub> NO <sub>2</sub> HgC <sub>6</sub> H <sub>5</sub>	Pale yellow	112
Salicylaldazine		1:2	$C_{14}H_{10}N_2O_2[HgC_6H_5]_2$	Yellow	180
N, N'ethylene-bis- (salicylideneimine)		1:2	C <sub>16</sub> H <sub>14</sub> N2O2[HgC <sub>6</sub> H5]2	Yellow	135
Isopropyl titanate		1:4	Ti[OHgC <sub>6</sub> H <sub>5</sub> ] <sub>4</sub>	White	230d
Bis-salicylaldehydo- -diisopropoxy Ti		1:2	[C <sub>7</sub> H <sub>5</sub> O <sub>2</sub> ] <sub>2</sub> Ti[OHgC <sub>6</sub> H <sub>5</sub> ] <sub>2</sub>	Yellow	182d
Bis-8-hydroxyquinoline- -diisopropoxy Ti		1:2	[C9H6NO]2Ti[OHgC6H5]2	Yellow	155
Bis-2-hydroxy-benzophenoxy- -diisopropoxy Ti		1:2	[C <sub>13</sub> H <sub>9</sub> O <sub>2</sub> ] <sub>2</sub> Ti[OHgC <sub>6</sub> H <sub>5</sub> ] <sub>2</sub>	Yellow	>200d
Bis-2-hydroxy-4-methoxy- -benzophenoxy-diisopropoxy Ti		1:2	[C <sub>14</sub> H <sub>11</sub> O <sub>3</sub> ] <sub>2</sub> Ti[OHgC <sub>6</sub> H <sub>5</sub> ] <sub>2</sub>	Yellow	120
Bis-benzoylphenyl-hydroxyl- amino-diisopropoxy Ti		1:2	[C <sub>13</sub> H <sub>10</sub> NO <sub>2</sub> ] <sub>2</sub> Ti[OHgC <sub>6</sub> H <sub>5</sub> ] <sub>2</sub>	Yellow	101
Bis-acetylacetono- diisopropoxy Ti		1:2	[C <sub>6</sub> H <sub>7</sub> O <sub>2</sub> ] <sub>2</sub> Ti[OHgC <sub>6</sub> H <sub>5</sub> ] <sub>2</sub>	Yellow	>180d

TABLE 1 Phenyl mercury chelates and chelated titanoxanes

Reactants		Molar ratio	<b>Product<sup>a</sup></b>	Colour	M.p. (°C)
A	B	A:B			
Bis-benzoylacetono- diisopropoxy Ti	C <sub>6</sub> H <sub>5</sub> HgOH	1:2	[C10H9O2]2Ti[OHgC6H5]2	Yellow	145d
Bis-dibenzoylmethano- diisopropoxy Ti		1:2	[C <sub>15</sub> H <sub>11</sub> O <sub>2</sub> ] <sub>2</sub> Ti[OHgC <sub>6</sub> H <sub>5</sub> ] <sub>2</sub>	Yellow	102
N, N'-ethylene bis(sali- cylideneimino)diiso- propoxy Ti		1:2	C <sub>14</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> Ti[OHgC <sub>6</sub> H <sub>5</sub> ] <sub>2</sub>	Yellow	141
šalicylidene 2.amino-phenoxy- diisopropoxy Ti		1:2	C <sub>13</sub> H9NO2Ti[OHgC6H5]2	Brown	>180d

TABLE 1 (continued)

<sup>a</sup>Confirmed by elemental analysis. d, decomposed.

complex, the evidence for the coordination of nitrogen to mercury is seen from the splitting of the C=N band from the C=C in the original ligand at 1587 cm<sup>-1</sup> into two strong bands due to the augmentation of C=C (1600 cm<sup>-1</sup>) and C=N (1575 cm<sup>-1</sup>) vibrations. The hydrogen-bonded hydroxyl absorption bands of the ligands are totally absent from the new compounds.

In the spectrum of salazine (taken in hexachlorobutadiene), the strongly hydrogen-bonded  $\nu(OH)$  is seen at 3050 and 2650 cm<sup>-1</sup>. These and the hydroxyl deformation bands at 1330 and 1310 cm<sup>-1</sup> are absent from the spectrum of the reaction product with phenylmercury hydroxide. The CN stretching mode of the ligand at 1630 cm<sup>-1</sup> retains almost the same position in the compound with mercury, suggesting relatively weak coordination to the metal. The  $\nu(N-N)$  of the ligand observed at 905 cm<sup>-1</sup> is shifted slightly to a higher frequency region and is seen as a doublet at 910 and 920 cm<sup>-1</sup>. This may be due to the change in the planarity of the ligand with the formation of a metal compound.

The IR spectra of the condensation products of phenylmercury hydroxide with bis-chelated isopropoxy titanium compounds show the absence of alkoxy as well as hydroxy absorption bands. Furthermore, the coordination of the ligand in bis-salicylaldehydo-diisopropoxy titanium is not affected by the replacement of the alkoxy groups with  $C_6H_5HgO$  groups, as shown by the CO absorption at 1620 cm<sup>-1</sup> in both the parent and the reaction product. Similarly, in bis-phenylmercury-bis-benzoylacetonotitanoxane the CO absorption band is seen in the same place as in the parent titanium compound (1530 cm<sup>-1</sup>). In the 8-hydroxyquinoline complex also, the bands at 1600 and 1575 cm<sup>-1</sup> are not affected by the introduction of phenylmercury groups.

The IR spectra of metalloxanes are expected to show broad bands associated with symmetrical stretching of the M-O-M' group. For example, the Si-O-Hg absorption in Ph<sub>3</sub>Si-O-HgPh is seen at 882 cm<sup>-1</sup> whereas the Si-O-Pb absorption in Ph<sub>3</sub>Si-O-PbPh<sub>3</sub> appears at 948 cm<sup>-1</sup>. In functionally halo-substituted metalloxanes [11] the M-O-M' frequency is always about 50 cm<sup>-1</sup> higher than the unsubstituted compounds. All the new phenylmercury titanoxanes showed strong absorption bands in the 750 - 690 cm<sup>-1</sup> region. The Hg-O-Ti group is expected to absorb in the same region, but a correct assignment could not be made because of ligand vibrations in this region.

### 3.2. Mass spectra

Phenylmercury chelates showed only very feeble peaks for molecular ions in their mass spectra. This may be due to lack of thermal stability or volatility. However, all the complexes showed clusters attributable to  $Ph_2Hg^+$ which could arise from a transformation of the phenylmercury chelate to a symmetrical compound, either thermally or due to electron impact inside the mass spectrometer.

## 3.3. NMR spectra

The NMR spectra of the complexes in DMSO showed a total absence of hydroxyl protons of the ligands. In salicylaldehydo-phenylmercury, the methine proton of the ligand which resonates at  $\delta = 9.87$  ppm in the free ligand is seen at  $\delta = 10.37$  ppm. This shift may be due to deshielding of the methine proton by the coordination of CO to mercury. In the oxine complex, the 2 and 4 protons in the hetero (nitrogen-containing) ring are shifted down field compared with the free ligand protons. This may be ascribed to the deshielding effect of the hetero ring compared with the phenol ring; this deshielding is due to the coordination of nitrogen to mercury. Similar evidence for coordination was seen in the spectra of other complexes. The titanoxanes containing mercury were too insoluble in common solvents for NMR studies.

The IR and NMR studies show that mercury will have a planar 3-coordination in phenylmercury chelates. In phenylmercury titanoxanes containing chelated titanium, however, mercury has a 2-coordinated linear structure whereas titanium is hexa-coordinated.

The IR spectra were taken on a Perkin–Elmer 221 IR spectrometer or on an Infracord machine equipped with sodium chloride/caesium bromide optics. The mass spectra of the mercury compounds were recorded on a CEC 21-110 B mass spectrometer by a direct inlet system under the following experimental conditions: electron energy 70 eV, pressure  $1 \cdot 2 \times 10^{-7}$ mmHg, ionization current 20  $\mu$ A, source temperature 90 - 180 °C. The NMR spectra were measured on a Varian T-60 spectrometer operating at 60 MHz. Tetramethylsilane was used as an internal standard.

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