Interaction of mercury(II) halides with tertiary phosphine betaines: synthesis and structural characterization of
\[\text{[HgX}_2\text{\{Ph}_3\text{P(CH}_2\text{)}_2\text{CO}_2\}]} (X = \text{Cl, I}) \text{ and } \text{[HgCl}_\text{\mu-Cl}\text{-\{Ph}_3\text{P(CH}_2\text{)}_3\text{CO}_2\}]}_2

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Three new mercury(II) complexes containing tertiary phosphine betaine ligands \(\text{Ph}_3\text{P}^+\text{\{CH}_2\text{)}_2\text{CO}_2^-\) and \(\text{Ph}_3\text{P}^+\text{\{CH}_2\text{)}_3\text{CO}_2^-\) have been synthesized and fully characterized by single-crystal X-ray analysis: \(\text{[HgCl}_2\text{\{Ph}_3\text{P}\text{(CH}_2\text{)}_2\text{CO}_2\}]}_2\), 1, space group \(P2_1/n\), \(a = 9.819(2)\), \(b = 14.966(4)\), \(c = 14.973(5)\) \(\AA\), \(\beta = 105.67(2)^\circ\) and \(Z = 4\); \(\text{[HgCl}_2\text{\{Ph}_3\text{P}\text{(CH}_2\text{)}_3\text{CO}_2\}]}_2\), 2, \(P2_1/n\), \(a = 10.206(2)\), \(b = 14.807(3)\), \(c = 15.557(3)\) \(\AA\), \(\beta = 107.11(2)^\circ\) and \(Z = 4\); \(\text{[HgCl}_\text{\mu-Cl}\text{-\{Ph}_3\text{P}\text{(CH}_2\text{)}_3\text{CO}_2\}]}_2\), 3, \(P1\), \(a = 10.813(2)\), \(b = 11.975(3)\), \(c = 11.180(2)\) \(\AA\), \(\alpha = 87.04(2)^\circ\), \(\beta = 75.14(1)^\gamma\), \(\gamma = 81.95(1)^\circ\) and \(Z = 1\). The isomorphous complexes 1 and 2 contain discrete mononuclear molecules in which the mercury(II) atom is unsymmetrically chelated by a \(\text{Ph}_3\text{P}^+\text{\{CH}_2\text{)}_2\text{CO}_2^-\) ligand and coordinated by a pair of terminal halo ligands in a distorted tetrahedral environment, while 3 consists of discrete centrosymmetric dinuclear molecules in which the betaine ligand \(\text{Ph}_3\text{P}^+\text{\{CH}_2\text{)}_3\text{CO}_2^-\) acts in the chelate mode and the mercury(II) atoms are unsymmetrically bridged by a pair of chloro ligands.

KEY WORDS: Mercury(II) halides; tertiary phosphine betaine; triphenylphosphonicpropionate; triphenylphosphonibutyrate; crystal structure.

Introduction

Mercury(II) carboxylates, especially the acetate and trifluoroacetate, will attack unsaturated hydrocarbons to form Hg-C bonds which can be used to synthesize a wide variety of organic compounds. For example, they can be used as catalysts in the synthesis of aldehydes and ketones and of stereospecific enol derivatives from alkynes. However, the structures of simple mercury(II) carboxylates are quite rare in the literature, and many are organometallic compounds. Among the known structures of mercury(II) carboxylates, the carboxylato group exhibits a variety of coordination modes. In the organometallic complexes \(\text{[PhHg(MeCO}_2\]_\text{3}}\), \(\text{[C\{Hg(F}_3\text{CCO}_2\}_4]}\), \(\text{[C\{Hg(MeC-\text{O}_2\}_4]}\), \(\text{2H}_2\text{O}\), and \(\text{[\text{Me}_3\text{C}\{\text{CO}_2\}_2\text{CHHg(MeCO}_2\}_\text{3}}\) the carboxylato group commonly acts in a unidentate fashion. The bidentate chelate mode of the carboxylate group exists in \(\text{[Hg(PBu}_3\)\{MeCO}_2\]_\text{3}}\), \(\text{[Hg(MeS)}\text{\{MeCO}_2\text{)\{4-methylpyridine}\), and \(\text{[Hg(\text{EtS)}\{MeCO}_2\text{)\{4-methylpyridine}\). A syn-syn bidentate carboxylato-O,O' bridging mode was found in the dimeric charge-transfer complex \(\text{[Hg}_2\text{(F}_3\text{CCO}_2\}_4\{\text{C}_\text{6}\text{(CH}_3\text{)}_6\}_\text{2}}\), whereas in \(\text{[\{Hg}_2\text{(BET)}\text{Cl}_4\text{HgCl}_2\}_\text{2}}\) \(\text{(BET = Me}_3\text{N}\text{\{CH}_2\text{CO}_2\})\) the carboxylato group acts in an unusual \(\mu\)-O,O bridging mode which commonly exists in metal alkoxide complexes. In all these complexes, apart from the primary coordination bonds, there are usually secondary interactions between the mercury atom and adjacent donor atoms that lead to a complicated coordination polymeric structure.

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Recently tertiary amine betaines such as Me₃N⁺CH₂CO₂⁻ and C₆H₄N⁺CH₂CO₂⁻, which are structurally analogous to amino acids acting in the zwitterionic form, have been extensively used as ligands to prepare metal complexes in our laboratory. Our interest is further extended to triphenylphosphine betaines, whose bulky PPh₃ group would be expected to have a significant influence on their coordination behavior. This has been demonstrated in a series of tetrakis-carboxylato-O,O'-dicadmium(II) complexes of triphenylphosphoniopropionate, Ph₃P⁺(CH₂)₂CO₂ (L), the occurrence of which are ascribed to the steric requirement of the L ligand. In the present study, we report the reaction of L and triphenylphosphoniobutyrate, Ph₃P⁺(CH₂)₃CO₂ (L') with HgX₂ to yield three new mercury(II) complexes, namely, [HgCl₂{Ph₃P(CH₂)₂CO₂}] (X = Cl (1), I (2)) and [HgCl₂{μ-Cl}{Ph₃P(CH₂)₂CO₂}]₂ (3). Single crystal X-ray analysis has shown that the isostructural complexes 1 and 2 contain discrete molecules and the mercury(II) atom has a secondary interaction with an oxygen atom of the L ligand in an adjacent molecule. Compound 3 is a doubly chloro-bridged centrosymmetric dimeric molecule. In all three complexes the betaine ligands L and L' function in the asymmetric chelate mode.

**Experimental**

**Synthesis**

Ph₃P⁺(CH₂)₂CO₂⁻ (L) and Ph₃P⁺(CH₂)₃CO₂⁻ (L') were synthesized by literature methods. Solvents and other chemicals were used as purchased.

*Synthesis of [HgCl₂{Ph₃P(CH₂)₂CO₂}] 1.* HgCl₂ (137 mg, 0.5 mmol) and L (334 mg, 1.0 mmol) were dissolved in CH₃CN (ca. 10 cm³). Colorless prismatic crystals of 1 (280 mg, 92%) were obtained after the solution was allowed to stand for 1 day.

*Synthesis of [HgCl₂{Ph₃P(CH₂)₂CO₂}] 2 and [HgCl₂{μ-Cl}{Ph₃P(CH₂)₂CO₂}]₂ 3.* The isomorphous complex 1, and 2 comprise a packing of discrete [HgX₂{Ph₃P(CH₂)₂CO₂}] (X = Cl or I) molecules in the crystal lattice. As depicted in Fig. 1, the mercury(II) atom is unsymmetrically chelated by a Ph₃P⁺(CH₂)₂₂⁻ ligand with one oxygen atom strongly bonded to it [Hg-O = 2.337(12) Å for 1, and 2.355(13) Å for 2] and the other more weakly bound [2.587(15) Å for 1, and 2.629(16) Å for 2]. The distorted tetrahe-

**Results and discussion**

Reaction of Ph₃P⁺(CH₂)₂CO₂⁻ (L) with HgCl₂ or HgI₂ at a molar ratio of 2:1 in CH₃CN led to the formation of [HgCl₂{Ph₃P(CH₂)₂CO₂}] 1 and [HgI₂{Ph₃P(CH₂)₂CO₂}] 2, respectively. Reaction of Ph₃P⁺(CH₂)₃CO₂⁻ (L') with HgCl₂ at the same molar ratio in CH₃CN yielded [HgCl₂{μ-Cl}{Ph₃P(CH₂)₂CO₂}] 3.

Crystal structures of [HgCl₂{Ph₃P(CH₂)₂CO₂}] and [HgCl₂{μ-Cl}{Ph₃P(CH₂)₂CO₂}] 2

The isomorphous complex 1 and 2 comprise a packing of discrete [HgX₂{Ph₃P(CH₂)₂CO₂}] (X = Cl or I) molecules in the crystal lattice. As depicted in Fig. 1, the mercury(II) atom is unsymmetrically chelated by a Ph₃P⁺(CH₂)₂₂⁻ ligand with one oxygen atom strongly bonded to it [Hg-O = 2.337(12) Å for 1, and 2.355(13) Å for 2] and the other more weakly bound [2.587(15) Å for 1, and 2.629(16) Å for 2]. The distorted tetrahe-