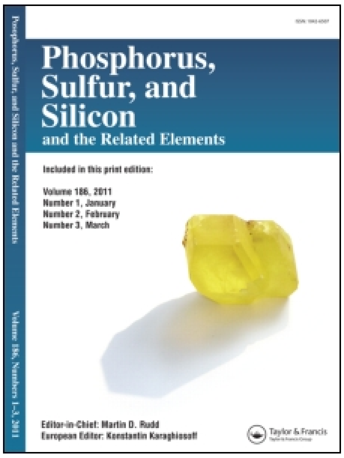

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SYNTHESIS OF FIRST ARYLTELLUROLATE—MERCURY(II) CLUSTERS HAVING Hg_4Te_6 CORE

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The reaction between $Hg(PPh_3)_2(ClO_4)_2$, $Hg(TeAr)_2$ and PPh_3 in a 1:3:2 ratio produces aryltellurolate-mercury(II) clusters—$[Hg_4(PPh_3)_4(\mu\text{-}TeAr)_6](ClO_4)_2$, where Ar = Ph, p-$MeOC_6H_4$. Studies of the electrical conductivities and molecular masses in solution are consistent with an ionic structure. The ^1H and ^{13}C NMR spectra indicate the equivalence of all tellurol and phosphine ligands. The down field chemical shift of carbon linked to tellurium is indicative of a bridging tellurol group. This is suggestive of an adamantane structure for these clusters.

Key words: Hg_4Te_6-cluster; aryltellurolate; mercury-clusters.

INTRODUCTION

Mercury(II) has been reported to displace Zn and Cd from Zn, Cd-metallothionein II (Zn, Cd-MT), producing the Hg_7-MT protein.[1] To understand the mercury-binding sites of MT, mercury clusters of the type $[Hg_4(\mu\text{-}ER)_6L_4](ClO_4)_2$ (E = S or Se; L = PPh_3)[2] having Hg_4E_6 cores and very close structural resemblance with adamantanoid anions $[(\mu\text{-}SPh)_6(MSPh)_4]^{2-}$ (M = Zn or Cd) have been prepared as possible models for the four atom sites of Zn, Cd-MT.[3] These have been recently synthesized and studied using multinuclear NMR. It was, therefore, thought to be worthwhile to attempt the synthesis of a mercury(II)-tellurolate cluster containing an Hg_4Te_6 core. In the present paper the synthesis and spectral data of $[Hg_4(PPh_3)_4(\mu\text{-}TeAr)_6](ClO_4)_2$, where Ar = Ph or p-$MeOC_6H_4$ are reported. To the best of our knowledge no other aryltellurolate-mercury(II) clusters having an Hg_4Te_6 core have been reported. This appears to be the first example of this type.[4]

RESULTS AND DISCUSSION

The reaction given in Equation (1) gives mercury(II)-aryltellurolate clusters, $[Hg_4(\mu\text{-}TeAr)_6(PPh_3)_4](ClO_4)_2$, which have been found to be soluble in chloroform, dichloromethane, acetonitrile and dimethylsulphoxide. The solubility of **1** was less than that of **2**. The mercury and tellurium analysis of both the clusters is in agreement with the proposed stoichiometries. Carbon and hydrogen analyses were not carried out because of the presence of perchlorate groups. The molar

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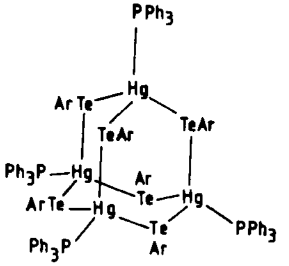
conductivities (Λ_M) at 30°C of their ~1 mM solutions in acetonitrile are 230 and 242 $ohm^{-1} cm^2 mol^{-1}$ for **1** and **2** respectively, which are the values expected for a 1:2 electrolyte. The molecular masses of **1** and **2** in chloroform were measured osmometrically and found to be 1200 and 1400, respectively. This is nearly one third of the values expected on the basis of chemical composition $[Hg_4(\mu\text{-}TeAr)_6(PPh_3)_4](ClO_4)_2$ and consistent with Λ_M values.

$$2PPh_3 + 3(ArTe)_2Hg + (PPh_3)_2Hg(ClO_4)_2 \xrightarrow[\text{Argon atm.}]{0°C} [Hg_4(PPh_3)_4(\mu\text{-}TeAr)_6](ClO_4)_2 \quad (1)$$

$$Ar = Ph\ (\mathbf{1});\quad p\text{-}MeOC_6H_4\ (\mathbf{2})$$

The ^1H NMR spectra of **1** and **2** were those expected. The ratio of methyl and phenyl protons in the spectrum of **2** concurs with its assigned chemical composition. The absence of any splitting in the methyl signal suggests that all TeAr groups are equivalent. This has been further supported by $^{13}C\{^1H\}$ NMR spectrum of **2**. The carbon linked to tellurium appears in the $^{13}C\{H\}$ NMR spectrum of **2** at δ, 131.5 ppm, further downfield than that found for diaryltellurides[5] and their complexes[6] (in which it generally appears around δ, 105–115 ppm). This observation suggests that aryltellurolate group in these Hg-clusters act as bridging ligands. Consideration of the various evidence makes it reasonable to suggest that **2** having the composition $[Hg_4(\mu\text{-}TeC_6H_4\text{-}p\text{-}OMe)_6(PPh_3)_4](ClO_4)_2$ has an adamantanoid structure (**3**) as suggested for its sulfur or selenium analogue.[2] By analogy a similar structure may be presumed for **1**. Of course a final word about the structure can not be said without determining the crystal structure, which has not been undertaken owing to our inability to obtain suitable crystals.



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EXPERIMENTAL

Published methods were used for the synthesis of $Hg(TeAr)_2$[7] and $(PPh_3)_2Hg(ClO_4)_2$[8]. Tellurium and mercury were estimated by standard methods.[9,10] The conductivity measurements were made with a WG PYE conductivity bridge. Molecular masses were determined with a Knauer vapour pressure osmometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX 100 FT-NMR spectrometer at 99.55 and 25 MHz respectively.

Synthesis of $[Hg_4(\mu\text{-}TePh)_6(PPh_3)_4](ClO_4)_2$ (**1**). All operations were performed under an atmosphere of argon. Triphenylphosphine (10 mmol) and $(PPh_3)_2Hg(ClO_4)_2$ (5 mmol) were stirred together in 50 cm^3 acetone until the solution became clear (~10 min). $Hg(TePh)_2$ solid (15 mmol) was added to this solution with continued stirring. Within 30 min a clear yellow solution was obtained. The 20 cm^3

cyclohexane was slowly added to this solution so that it formed a separate layer. The mixture was kept at 5°C for 48 h. The resulting yellow crystals were filtered, washed thoroughly with cyclohexane, recrystallized from chloroform and dried in *vacuo*. Yield 60%; m.p. was not attempted in view of explosive nature of the perchlorates. Analysis: Found: Te, 22.83; Hg, 23.28; calc.: Te, 23.36; Hg, 24.48%. NMR (^{1}H, $CDCl_3$, 25°C): δ, 6.8–7.4 (m, phenyl protons). The limited solutibility of **1** restricted from recording its $^{13}C\{H\}$ NMR spectrum satisfactorily.

Synthesis of $[Hg_4(\mu\text{-}TeC_6H_4\text{-}p\text{-}OMe)_6(PPh_3)_4](ClO_2)$ (**2**). This compound was prepared in the manner described for **1**, except that the reaction medium was chloroform. The yield of **2** after recrystallization from chloroform was 63%. The m.p. was not recorded due to the presence of perchlorate groups. Analysis: Found: Te, 21.50; Hg, 21.95; calc.: Te, 22.14; Hg, 23.20%. NMR (^{1}H, $CDCl_3$, 25°C): δ, 3.8 (s, OMe), 6.4–7.3 (m, phenyl); ($^{13}C\{H\}$, $CDCl_3$, 25°C): δ, 55.5 (OMe), 115.9 (*m* to Te), 129.1 (*m*, to P), 129.5 (*p* to P), 131.6 (C-Te), 133.6 (*o* to P), 134.1 (*o* to Te), 140.3 (C–P); 160.2 (C–OMe).

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