Synthesis of an Encapsulated Arsenic Anion via Reaction of Arsenic Acid with a Linear Catecholamide-N,N′,N″-tris(2,3-dihydroxybenzoyl)-1,5,10-triazadecane

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Abstract

The reaction of arsenic acid with N,N′,N″-Tris(2,3-dihydroxybenzoyl)-1,5,10-Triazadecane(3,4-LICAM) provides the first example of an encapsulated arsenic anion. The structural features of this compound, thought to have an octahedral configuration around the arsenic, was established by ^{13}C NMR, IR, UV and FAB mass spectroscopy as well as elemental analysis.

Introduction

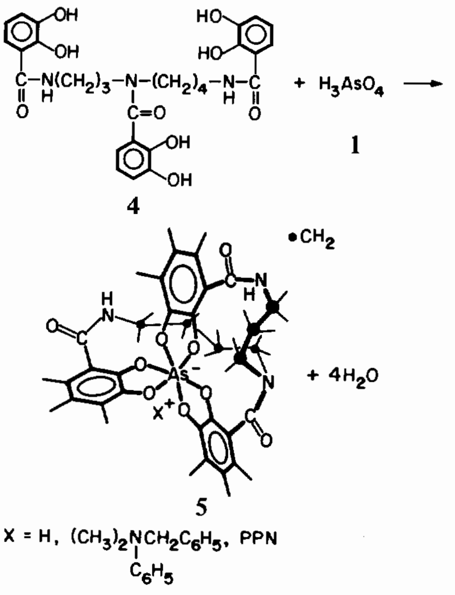
The molecular characterization of inorganic and organometallic compounds present in fossil fuel precursors and their products has become increasingly more important as our synthetic fuel industry develops. The chief reasons for this are that these compounds are thought to be responsible for the poisoning of process catalysts and their presumed effects on man and his environment [1].

We have recently characterized inorganic arsenic and organoarsenic compounds in oil shale [2], shale oil [3], and oil shale retort waters [4]. These studies have provided evidence that arsenate (AsO_4^{-3}), **1** and methyl- and phenylarsonic acids, **2** and **3**, are present in the above mentioned fossil fuel precursor and products.

While the molecular characterization of these arsenic compounds is an important first step in understanding their biogeochemical origin and their presence in fossil fuel products, the ultimate aim of removing them from these complex matrices utilizing innovative methods is also a predominant goal of our program. In this regard, we recently reported on a novel method that used substituted catechols as models for the above-stated goals with the characterized organoarsenic compounds, 2 and 3 [5].

Similar reactions with **1** have focused on a class of linear catecholamide compounds (LICAM) synthesized by Raymond *et al.* [6a–i] to be used eventually for the removal of iron and actinide metal ions in clinical applications. We were particularly interested in N,N′,N″-tris(2,3-dihydroxybenzoyl)-1,5,10-triazadecane(3,4-LICAM), **4** [6b], a ligand with three catechols on a linear amide chain, that could potentially coordinate in an octahedral configuration around an arsenic anion and that could be placed in a polymeric backbone for eventual removal of **1** from complex matrices.

In this paper, we report on the reaction of 3,4-LICAM, 4, with **1** to provide a novel encapsulated arsenic anion, 5, (eqn. 1):



(1)

Results and Discussion

The ligand, 4, reacted with **1** in an aqueous ethanol solution and after work-up gave a white powder (83%) which had a decomposition point at 275–276 °C. The material was analyzed spectrosco-

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pically by ^{13}C NMR, IR, UV, FAB–MS as well as elemental analysis to provide evidence for the structure designated as, **5** (X = H), in eqn. 1. A tetraammonium salt (X = benzyldimethylphenylammonium) and the bis(triphenylphosphoranylidene)ammonium (PPN) salt were also prepared; but unfortunately, were not found to be suitable for single crystal X-ray studies.

The ^{13}C NMR spectrum of the acid (X = H), **5**, is shown in Fig. 1 along with the ligand **4**. The arsenic anion appears to have a less complicated ^{13}C NMR spectrum than the ligand, **4**. The carbonyl region, ~160–170 ppm, should contain three carbonyl resonances, however, **4** has more carbonyl lines (~6–8) indicative of a possible role of geometrical isomers (syn and anti isomers with 8 possible carbonyl resonances). Thus, upon arsenic coordination, the carbonyl region of **5** appears somewhat simplified as compared to **4** (3–4 carbonyls) with resonances at 163.6, 164 (shoulder), 168, and 169.6 ppm. The aromatic carbons with hydroxyl groups in the ligand, **4**, (~140–152 ppm) should show six resonances; however, many more are evident, while the arsenic compound, **5**, has six phenolic carbons at 140, 143, 143.4, 144, 145, and 150 ppm. The remaining aromatic carbons are in the 110–135 ppm range (12) for **5**, while the methylene carbons (0–50 ppm, not shown in Fig. 1) were somewhat masked by the solvent, dimethylsulfoxide-d_6.

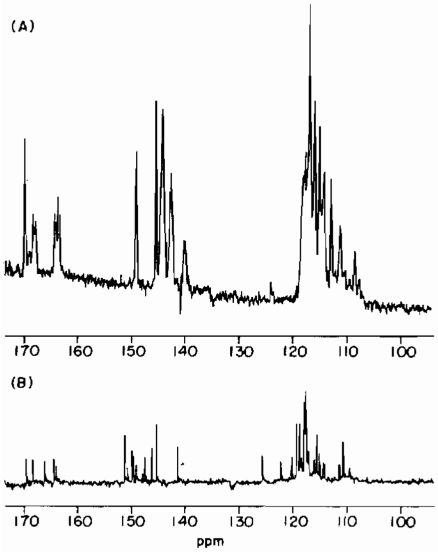

Fig. 1. ^{13}C NMR spectrum (100 Mz) of: (A) Arsenic anion (X = H) compound **5** and (B) 3,4-LICAM, **4**, in DMSO-d_6. The region from 100–170 ppm includes the carbonyl region, ~160–170 ppm, aromatic carbon-hydroxyl, ~140–152, aromatic carbon, ~110–135 ppm, while the methylene carbons, ~0–50 ppm, were masked by the solvent and are not included.

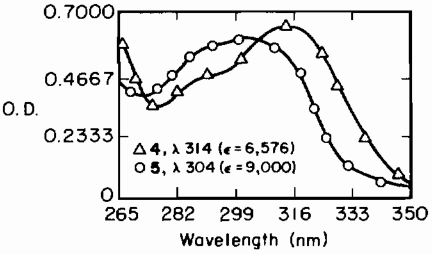

Fig. 2. Ultraviolet spectrum of compounds **4**, 1 × 10^{-4} M, (Δ) and **5**, 7 × 10^{-5} M (o) in DMSO.

The UV spectra of both **4** and **5** are shown in Fig. 2, and indicate that on formation of the arsenic anion a pronounced shift from 314 nm (ϵ = 6576) for **4** to 304 nm (ϵ = 9001) for **5** (X = H) occurs. A similar occurrence was observed by Raymond *et al.* [6b,g] in the coordination of ferric ion with a sulfonated 3,4-LICAM, where the extinction coefficient rises and the wavelength decreases upon complexation of all six phenolic oxygens. The fast atom bombardment (FAB) mass spectrum (glycerol) of **5** (X = H) provides confirmatory evidence for the molecular weight with a small parent ion at m/e 623 (2.5%) and ions at 625 (M + 2, 5%) and 626 (M + 3, 16%), while IR data (KBr) indicates As–O stretching frequencies at 650–720 cm^{-1}.

The above mentioned data is strongly supportive of structure, **5**, with a presumed octahedral configuration around the arsenic, and represents the first isolated encapsulated arsenic anion structure yet reported. The only other synthesis of a catechol–arsenic anion compound was for catechol itself [7], and a single crystal X-ray study provided unequivocal evidence for the distorted octahedral symmetry around arsenic [8]. While we were unable to prepare a suitable crystalline derivative for unequivocal, structural X-ray analysis of **5**, a Drieding model clearly indicates that the tris-catecholate coordination of 4 around arsenic can readily occur.

Finally, in recent experiments we have placed **4**, and catechol itself, on a polymer support (10% cross-linked chloromethylated polystyrene–divinylbenzene) and have been able to quantitatively remove arsenate, **1**, from an aqueous ethanol solution, which verifies the usefulness of this approach in possible synthetic fuel applications [9].

Experimental

Materials and Instrumentation

The 400 MHz NMR spectrometer for the ^{13}C (at 100 MHz) NMR spectra was located at the NBS-NML high field NMR facility located at NBS, Gaithersburg, MD. A Cary 219UV–VIS spectrophotometer–Apple II computer combination was used for the ultraviolet spectra and a Perkin–Elmer 1330 for infrared spectra. The FAB-MS of **5** (suspended in glycerol) was obtained on a Kratos MS-50 mass spectrometer located in the Department of Chemistry, U.C. Berkeley. Elemental analyses were also obtained from the Chemistry Department's microanalytical laboratory. The 3,4-dihydroxylbenzoic acid, thionyl chloride, boron tribromide and spermidine were purchased from Aldrich Chemical CO.

A Modified Procedure for the Preparation of Ligand 4 [6b]

In a 100 ml flask equipped with a drying tube was placed 4.55 g (25 mmol) of 2,3-dimethoxybenzoic acid and 24.5 g (0.206 mol) of thionyl chloride. The reaction mixture was stirred at room temperature for 2 h, after which the solution was rotary evaporated to give a white solid. The solid was then dissolved in benzene (30 ml, thrice) and rotary evaporated to give the benzene soluble acid chloride. The acid chloride was dissolved in 20 ml tetrahydrofuran along with 3.5 g (34.6 mmol) of triethylamine and 1.66 g (11.4 mmol) of spermidine. The reaction mixture was refluxed for 20 h under nitrogen (important to exclude both air and water) and then rotary evaporated to give an oil that was dissolved in chloroform. The chloroform solution was washed with 50 ml of 0.1 N hydrochloric acid, 50 ml of deionized water and 50 ml of 10% sodium hydroxide and then again with deionized water and hydrochloric acid. The chloroform layer was dried over anhydrous magnesium sulfate, filtered and rotary evaporated.

The oil was then dissolved in 75 ml of methylene chloride and placed in a round bottom flask equipped with a stirring bar, a nitrogen inlet and a dropping funnel containing 6 ml of boron tribromide in 50 ml of methylene chloride. The boron tribromide was added slowly and after addition the reaction mixture was stirred at room temperature overnight under nitrogen. To the reaction mixture was added slowly 50 ml of deionized water with stirring for 3 h. The precipitate was washed with deionized water and diethylether and attempted recrystallization from methanol/water gave an oil that was redissolved in methanol and rotary evaporated (thrice). The oil was washed well with diethylether and dried under vacuum (P_2O_5) to give a solid, amorphous material (3.5 g, 55%), m.p. 267–270 °C [lit. 267–270] [6b]. The UV spectrum (DMSO) (1×10^{-4} M) shows absorptions at 314 nm (ϵ = 6,576) and 291 nm (ϵ = 4,948).

Preparation of 5 (X= H)

In a 25 ml two-neck flask equipped with a reflux condenser with drying tube and a nitrogen gas inlet was placed 26 mg (0.11 mmol) of arsenic pentaoxide along with 0.5 ml of water. This was refluxed for a few minutes to form arsenic acid, **1**, (H_3AsO_4), and to this was added 373 mg (0.67 mmol) of 4 in 15 ml 100% ethanol and the reaction mixture refluxed for 20 h. The work-up included solvent evaporation and washing the resulting solid thoroughly with methanol and with diethylether to provide 118 mg (83% yield) of a white powder which was dried under vacuum (P_2O_5) and had a m.p. of 275–276 °C (dec).

A ^{13}C NMR spectrum (DMSO-d_6) at 100 MHz gave the following resonances: (C=O), 169.7, 168, 164.3 (shoulder) and 163.6. (Aromatic C–OH), 149.7, 145.4, 144.4, 143.4, 143, 140. (Aromatic C) 118.7, 117.5, 117, 116.3, 115, 113.8, 112.5, 111.3, 110, 109, 108, (CH_2) 0–50?. The UV spectrum of **5** (X = H) in DMSO (7×10^{-5} M) had a maximum absorption at 304 nm (ϵ = 9001) and a minimum at 291 nm (ϵ = 7480), while infrared (KBR) bands were found at 2950, 2880, 1642, 1486, 1453, 1384, 1310, 1220, 1145, 1115, 995, 900, 850, 790, 748, 720–650, 600, 415, 335, 320, and 310 cm^{-1}.

The fast atom bombardment mass spectrum (MS-50, glycerol) provided ions at m/e 623 (M, 2.5%) 625 (M + 2, 5%) and 626 (M + 3, 16%). *Anal.* Calcd. for $C_{28}H_{26}O_9N_3As \cdot H_2O$ (monohydrate): C, 52.40; H, 4.57; N, 6.55. Found: C, 52.39; H, 4.67; N, 6.50%.

Preparation of the Benzyldimethylphenylammonium Salt of 5

In a round-bottom flask was placed 200 mg (0.362 mmol) of 4, 67.3 mg (0.362 mmol) sodium arsenate and 269 mg (1.03 mmol) of benzyldimethylphenylammonium chloride dissolved in 60 ml of 50% aqueous ethanol. The reaction mixture was refluxed for 24 h and then the solvent was reduced to half its volume and refrigerated. The precipitate that formed was filtered and the filtrate was again reduced in volume and refrigerated. This method produced 100 mg (33%) of product. Attempts to obtain suitable crystals of the tetraammonium salt for X-ray studies were unsuccessful. The infrared (KBR) spectrum provided the following bands at 1650, 1505, 1490, 1480, 1245, 1215, 1115, 1060, 995, 887, 842, 790, 770, 750, 685, 595, 570 and 415 cm^{-1}. *Anal.* Calcd. for $C_{43}H_{44}N_4O_9As \cdot 2.5H_2O$, C, 52.64; H, 5.57; N, 6.36. Found: C, 52.57; H, 5.67; N, 6.64%.

Preparation of the Bis(triphenylphosphoranylidene)ammonium Salt of 5 (X= PPN)

In a round-bottom flask was placed 50 mg (0.08 mmol) of **5** (X = H) and 48 mg (0.08 mmol) of bis(triphenylphosphoranylidene)ammonium chloride dissolved in 10 ml of dimethylsulfoxide and stirred for 2 h. The DMSO was removed under vacuum and the remaining precipitate was dissolved in methylene chloride and filtered. Removal of the methylene chloride was followed by a benzene and methanol wash to give 25 mg (25%) of product. All attempts to obtain crystals for X-ray analysis were met with failure. The infrared (CH_2Cl_2) provided the following bands at 3630, 3060, 2953, 2844, 1645, 1580, 1550, 1486, 1450, 1440, 1252, 1222, 1120, 1024, 682, 550, 539 cm^{-1}. *Anal.* Calcd. for $C_{64}H_{56}N_4O_9P_2As \cdot 4H_2O$, C, 62.29; H, 5.19; N, 4.54; P, 5.03. Found: C, 62.29; H, 4.75; N, 4.61; P, 4.81%.

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