

Reaction of Trimethylaluminum with Selenium Tetrachloride. Synthesis of $[(\text{CH}_3)_3\text{Se}][\text{ClAl}(\text{CH}_3)_2(\text{Cl})\text{Al}(\text{CH}_3)_3]$. The First Selenium-Based Liquid Clathrate

SAMUEL A. SANGOKOYA and GREGORY H. ROBINSON*

Department of Chemistry, Clemson University, Clemson, South Carolina 29634-1905, U.S.A.

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Abstract. Selenium tetrachloride reacts with an excess of trimethylaluminum in the presence of aromatic solvents to afford a non-stoichiometric organoaluminum-selenonium based inclusion compound of the formula $[(\text{CH}_3)_3\text{Se}][\text{ClAl}(\text{CH}_3)_2(\text{Cl})\text{Al}(\text{CH}_3)_3] \cdot (\text{aromatic solvent})_n$. The cation of the parent compound of the inclusion complex results from the alkylation of SeCl_4 producing the $(\text{CH}_3)_3\text{Se}^+$ selenonium ion while the anion consists of a dimethylaluminum chloride unit and a trimethylaluminum unit bridged by a chlorine atom. This liquid inclusion complex, liquid clathrate, can accommodate 8.5 benzene molecules or 8.3 guest toluene molecules per anionic moiety.

Key words. Aluminum alkyl, aromatic, liquid clathrate, selenium.

1. Introduction

This laboratory has long had an interest in the organoaluminum based inclusion compounds known as liquid clathrates [1]. These interesting host-guest complexes may be traced to the reaction of neat aluminum alkyls with MX moieties (M = alkali metal or tetraalkylammonium ion; X = halide or pseudohalide ion). Ziegler reported that these reactions resulted in 1 : 1 (Equation 1) or 1 : 2 complexes (Equation 2) [2].



It was subsequently shown by Atwood that the 1 : 2 complex, upon interaction with aromatic solvents, affords the organoaluminum host-guest compounds known as liquid clathrates [3].

While, over the years, a variety of MX species have been shown to exhibit the liquid layering effect indicative of liquid clathrates, the literature reveals a paucity of data concerning selenium based organoaluminum host-guest compounds. Herein we report the unusual organoaluminum-selenonium based liquid clathrate $[(\text{CH}_3)_3\text{Se}][\text{ClAl}(\text{CH}_3)_2(\text{Cl})\text{Al}(\text{CH}_3)_3] \cdot (\text{aromatic solvent})_n$ isolated from reaction of SeCl_4 with an excess of trimethylaluminum in the presence of aromatic solvents. This $[(\text{CH}_3)_3\text{Se}][\text{ClAl}(\text{CH}_3)_2(\text{Cl})\text{Al}(\text{CH}_3)_3]$ complex represents the first report of a stable selenium based liquid clathrate.

* Author for correspondence.

2. Experimental

Standard Schlenk techniques and an inert-atmosphere drybox (Vacuum Atmospheres HE-43 Dri-Lab) were employed for the synthesis and subsequent manipulations. Trimethylaluminum (Ethyl Corporation) and selenium tetrachloride (Strem Chemical Co.) were both used without further purification. Solvents were purified and degassed in the usual manner. NMR data were recorded on a JOEL-FX 90Q NMR spectrometer.

2.1. PREPARATION OF THE $[(\text{CH}_3)_3\text{Se}][\text{ClAl}(\text{CH}_3)_2(\text{Cl})\text{Al}(\text{CH}_3)_3]$ PARENT COMPOUND

Inside the drybox a reaction vessel was charged with selenium tetrachloride (4.5 mmol) and aromatic solvent (ca. 20 mL). Trimethylaluminum (18.1 mmol) was slowly added via a syringe. Reaction was immediate and judged to be complete by the formation of two liquid layers (the liquid clathrate effect). ^1H NMR ($\text{C}_6\text{H}_5(\text{CH}_3)$): δ -0.58 (s, 15H, $\text{Al}(\text{CH}_3)_3/\text{Al}(\text{CH}_3)_2$), 1.45 (s, 9H, $\text{Se}(\text{CH}_3)_3$).

2.2. PREPARATION OF $[(\text{CH}_3)_3\text{Se}][\text{ClAl}(\text{CH}_3)_2(\text{Cl})\text{Al}(\text{CH}_3)_3] \cdot 8.5(\text{C}_6\text{H}_6)$

This host-guest compound was prepared by synthesizing the parent compound in the presence of benzene. The clathrate was shown to accommodate 8.5 guest benzene molecules.

2.3. PREPARATION OF $[(\text{CH}_3)_3\text{Se}][\text{ClAl}(\text{CH}_3)_2(\text{Cl})\text{Al}(\text{CH}_3)_3] \cdot 8.3(\text{C}_6\text{H}_5(\text{CH}_3))$

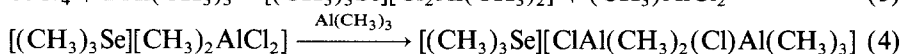
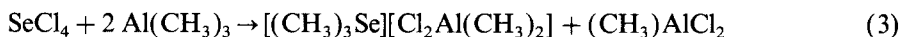
The toluene based liquid clathrate was prepared in an analogous manner to its benzene derivative. This clathrate was able to complex 8.3 toluene molecules.

3. Results and Discussion

While liquid clathrates were shown to be readily prepared by reaction of aluminum alkyls with a multitude of MX species in the presence of aromatic solvents, a considerable number of interesting MX moieties did not react according to Equation 2. As the failure of these MX species to exhibit the liquid clathrate effect was chiefly ascribed to the lattice energy of MX and/or its solubility [4], the metal-ion-coordinating ability of crown ethers was employed in these systems. It soon became apparent that in the absence of MX, crown ethers (CE) formed stable complexes with AlR_3 of the formula $[\text{CE}][\text{AlR}_3]_n$. Several such organoaluminum-oxygen [5, 6], -sulfur [7-9], and -nitrogen [10] based macrocyclic complexes have been reported. As $[\text{CE}][\text{AlR}_3]_n$ complexes were often found to serve as precursors to liquid clathrates, these complexes afforded a vast extension of those MX species exhibiting the liquid clathrate effect. Although a wide variety of MX species have been examined it is noteworthy that the organoaluminum chemistry of chalcogens relative to liquid clathrates has been largely ignored. The preparation of $[(\text{CH}_3)_3\text{Se}][\text{ClAl}(\text{CH}_3)_2(\text{Cl})\text{Al}(\text{CH}_3)_3]$ represents the first report of a stable selenium-based liquid clathrate.

The preparation of the title compound from reaction of SeCl_4 with an excess of $\text{Al}(\text{CH}_3)_3$ in the presence of aromatic solvent is interesting in that, unlike routine

$M[Al_2R_6X]$ liquid clathrates, the preparation of the parent compound proceeds in distinct stages. The initial step involves the reaction of selenium tetrachloride with two equivalents of trimethylaluminum to produce the intermediate product $[(CH_3)_3Se][(CH_3)_2AlCl_2]$ (Equation 3). The remaining trimethylaluminum subsequently reacts with the organoaluminum-selenonium product of Equation 3 to form an adduct with the dimethyldichloroaluminate ion via one of the chlorine atoms (Equation 4). Thus, the anionic species of the inclusion compound consists of a chlorine atom bridging a dimethylaluminum chloride unit and a trimethylaluminum unit. The fact that the selenium clathrate will only form when reacted in a 1 : 3 ratio ($SeCl_4$ to $Al(CH_3)_3$) is particularly noteworthy as all previously reported liquid clathrates proceed in a 1 : 2 ratio (MX to $Al(CH_3)_3$).



The parent compound given in Equation 4 was shown to accommodate 8.5 guest benzene molecules or 8.3 guest toluene molecules per anionic species.

To the best of our knowledge the literature reveals only one other report concerning the organoaluminum chemistry of $SeCl_4$. The organoaluminum complex $K[(CH_3)_3Se\{Al(CH_3)_3\}_3] \cdot (C_6H_6)_2$, isolated from the sealed tube thermal decomposition of $K[Al_2(CH_3)_3SeCN] \cdot (C_6H_6)_n$, was prepared in very low yield several years ago [11]. While the precursor material, $K[Al_2(CH_3)_3SeCN] \cdot (C_6H_6)_n$, reportedly did transiently exhibit the liquid layering effect indicative of liquid clathrate behavior, the workers were unable to isolate the compound or obtain NMR data due to instability of the complex.

As stated above, this laboratory has found that trimethylaluminum must be in excess for the title compound to form. Indeed, the 1 : 2 organoaluminum-selenonium complex indicated in Equation 3, when prepared in aliphatic solvents, undergoes disproportionation and results in a novel two-dimensional layered organoaluminum-selenonium polymer of the formula $\{[(CH_3)_3Se][(CH_3)AlCl_3]\}_n$ [12]. The reaction of tellurium tetrachloride with excess trimethylaluminum in toluene has also recently been investigated by this laboratory [13]; the crystalline product $[(CH_3)_3Te][(CH_3)_2AlCl_2]$ was isolated. This compound did not exist as discrete cation and anions but may be described as an extended one dimensional polymeric array. Importantly, regardless of the molar ratio of trimethylaluminum employed no liquid clathrate effect was observed in the tellurium system.

Perhaps the fact that the organoaluminum-tellurium system does not readily approach a layer-like orientation [13], as does the selenium system [12], contributes to its inability to exhibit the liquid clathrate effect. Future contributions from this laboratory will address other aspects of organoaluminum-selenium based host-guest compounds.

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