

Different Products from the Chemical and Electrochemical Reduction of “HgSe₂”: [K(2.2.2-cryptand)]₂[HgSe₂] and [PPh₄]₂[Hg(Se₄)₂][•]en

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Received July 3, 1996

Introduction

We have developed a technique to reduce and solubilize solid-state chalcogenides at a fixed electrical potential.¹ The electron source arises from the solvated electrons generated from the dissolution of alkali metals in NH₃(l); the reduction potential is dependent on the oxidation potential of the alkali metal. Not only has this technique proved to be useful for solubilizing several solid-state chalcogenides, but it has led to the isolation of several very simple chalcogenometalates, such as [GaTe₃]³⁻,² that have potential as precursors for more complex species. Warren et al. have reported a different method for the reduction of metal chalcogenides;^{3–5} it involves the electrochemical reduction in an electrolytic ethylenediamine (en) solution of such compounds fabricated as cathodes. In their technique both reduction potential and reduction current are variable. Here we emphasize the complementary nature of these methods. A compound of nominal composition HgSe₂ has been reduced both by K in NH₃(l) and electrochemically to afford two different products, namely [K(2.2.2-cryptand)]₂[HgSe₂] and [PPh₄]₂[Hg(Se₄)₂][•]en. ⁷⁷Se NMR studies demonstrate that the different products do not result from the use of different cations.

Experimental Section

Chemicals and Reagents. All manipulations were carried out under N₂ with the use of standard Schlenk techniques. Solvents were distilled, dried, and degassed before use. Diethyl ether was purchased from Baxter Scientific Products Inc., McGaw Park, IL and was distilled over Na/benzophenone. Ethylenediamine and CH₃CN were purchased from Aldrich Chemical Co., Milwaukee, WI, and were distilled over CaH₂. Ammonia gas (anhydrous, 99.95% purity) was purchased from Linde Gas Corp. The remaining reagents were purchased from Aldrich Chemical Co., Milwaukee, WI, and were used as received. 2.2.2-Cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) was dissolved in acetonitrile and was recrystallized by vacuum evaporation. A material of nominal composition HgSe₂, actually an intimate mixture of HgSe and Se, was prepared by the fusion under an inert atmosphere of HgSe (Johnson Matthey, 99.9%) and Se (Aldrich, 99.5%) in a fused-silica tube.

Physical Measurements. ⁷⁷Se and ¹⁹⁹Hg NMR spectra were obtained with the use of a Varian 400 MHz Unity Plus spectrometer equipped with a 10 mm tunable broad-band probe and a deuterium lock. ⁷⁷Se NMR chemical shifts are referenced to the external Ph₂Se₂ standard at 460 ppm, which in turn is referenced to (CH₃)₂Se at 0 ppm;

¹⁹⁹Hg NMR chemical shifts are referenced to the external standard (CH₃)₂Hg at 0 ppm.

[K(2.2.2-cryptand)]₂[HgSe₂] (**1**). NH₃ (60 mL) was condensed into a flask containing 2.2.2-cryptand (370 mg, 1 mmol) and K (40 mg, 1 mmol) at –195 °C. The resulting blue solution was stirred for 30 min at –77 °C until all the K had dissolved. Upon addition of finely ground HgSe₂ (179 mg, 0.5 mmol), the solution changed to orange-red and faded to pale yellow after 30 min. After the solution was stirred at –77 °C for 6 h, it was allowed to warm to 20 °C overnight. The solid residue that remained after the NH₃ had evaporated was dissolved in CH₃CN (20 mL) to give a yellow solution. The solution was filtered, and the filtrate was layered with diethyl ether (60 mL) to afford pale yellow hexagonal-shaped crystals after 5 d. Yield: 140 mg, 24% yield (based on Hg). NMR (0.1 M in 80% en / 20% acetonitrile-*d*₃, 25 °C): ⁷⁷Se, –117.4 ppm (*J*_{Se–Hg} 2263 Hz); ¹⁹⁹Hg, –954.1 ppm (*J*_{Hg–Se} 2261 Hz).

[PPh₄]₂[Hg(Se₄)₂][•]en (**2**). This compound was prepared from the electrochemical reduction of a 4 g cathode of HgSe₂ with the use of techniques developed by Warren et al.^{3–5} The cathode was fashioned by attaching copper wire to the chalcogenide with silver solder and then sealing the entire assembly in a Pyrex jacket with epoxy. Ni wire was used for the sacrificial anode. An en solution saturated with PPh₄Br (recrystallized from acetonitrile) served as the electrolyte. The reduction current was held at 300 μA, and the potential was kept at or below 5 V for 3 days. Immediately upon application of current a dark red stream was observed around the cathode. Dark red plates crystallized from this solution after 2 days. ⁷⁷Se NMR (0.1 M in 100% en; 25 °C): 79.4, 605 ppm vs 76, 594 ppm.⁶ ¹⁹⁹Hg NMR: unobserved.

Crystallographic Studies

X-ray data for **1** were collected with Cu Kα radiation on a CAD4 diffractometer while those for **2** were collected with Mo Kα radiation on a Picker diffractometer. All data were collected at 113 K. These data were processed⁷ and corrected for absorption by means of the analytical method.⁸ The structures were solved by direct methods and refined with the use of the program SHELXL-93.⁹ Hydrogen atoms were placed at calculated positions and refined according to a riding model. For structure **1** only the heavy atoms were refined anisotropically; for structure **2** anisotropic displacement parameters were refined for all but C and H atoms. In **1** the [K(2.2.2-cryptand)]⁺ cation is disordered along the three-fold axis and it was modeled in two parts, each part being a complete [K(2.2.2-cryptand)]⁺ cation. Part 1 contains atoms O(1a), O(2a), and C(1a)–C(6a); part 2 contains atoms O(3b), O(4b), and C(7b)–C(12b). Crystal and refinement data: **1**, *a* = 11.970(2) Å, *c* = 11.135(2) Å, *C*_{3i}–*P*₃, *Z* = 1, NO = 633, NV = 78, *R*_w(*F*²) = 0.122 for all data and *R*₁(*F*) = 0.052 for those 572 reflections having *F*_o² > 2σ(*F*_o²); **2**, *a* = 17.243(7) Å, *b* = 13.104(5) Å, *c* = 23.265(11) Å, β = 97.82(2)°, *C*_{2h}–*C*₂/*c*, *Z* = 4, NO = 3881, NV = 160, *R*_w(*F*²) = 0.144 for all the data and *R*₁(*F*) = 0.066 for those 2621 reflections having *F*_o² > 2σ(*F*_o²). Supporting Information provides more details.

Discussion

[K(2.2.2-cryptand)]₂[HgSe₂] (**1**) is isolated from the reduction of HgSe₂ by K in NH₃(l) in the presence of 2.2.2-cryptand. [PPh₄]₂[Hg(Se₄)₂][•]en (**2**) is synthesized by the electrochemical reduction of a cathode of HgSe₂ in an en solution saturated with PPh₄Br as the electrolyte.

HgSe₂ is an intimate mixture of HgSe and Se.¹⁰ For the reduction by K in NH₃(l), the use of this mixture gives a cleaner reaction than does the addition of HgSe and Se powders separately. Excess Se aids in the reaction, although its role is not clear since similar crystals (as characterized by EDX) can

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(10) An X-ray diffraction powder pattern of “HgSe₂” matches that calculated for the superposition of the patterns from HgSe and Se.

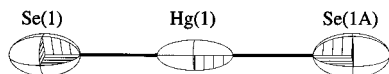


Figure 1. The $[\text{HgSe}_2]^{2-}$ anion in $[\text{K}(2.2.2\text{-cryptand})]_2[\text{HgSe}_2]$ (**1**). Here and in Figure 2 the displacement parameters are shown at the 50% probability level. The anion has crystallographically imposed $\bar{3}$ symmetry.

Table 1. ^{77}Se and ^{199}Hg NMR Chemical Shifts (ppm, 25 °C) for the $[\text{HgSe}_2]^{2-}$ Anion

solvent/concentration, M	$\delta(^{77}\text{Se})$	$\delta(^{199}\text{Hg})$
100% $\text{CH}_3\text{CN}/0.1$	-64.9	-910.4
80% en + 20% $\text{CD}_3\text{CN}/0.1$	-117.4 ($J_{\text{Se-Hg}} = 2263$ Hz)	-954.1 ($J_{\text{Hg-Se}} = 2261$ Hz)
95% en + 5% $\text{CD}_3\text{CN}/0.05$	-120.0	-954.1 ($J_{\text{Hg-Se}} = 2261$ Hz)
100% en /0.08	-131.7 ($J_{\text{Se-Hg}} = 2295$ Hz)	-966.0
100% en/0.1–0.2 ^a	-142.3	-796 ($J_{\text{Hg-Se}} = 2258$ Hz)

^a Reference 12.

be obtained from the reduction of HgSe by K in $\text{NH}_3(\text{l})$. In the electrochemical experiment, the presence of excess Se aids in the formation of an electrode with enhanced electrical conductivity to which a lead can be soldered without melting.

In $[\text{K}(2.2.2\text{-cryptand})]_2[\text{HgSe}_2]$ (**1**) the $[\text{HgSe}_2]^{2-}$ anion (Figure 1), which has a crystallographically imposed center of symmetry, is necessarily linear. The displacement parameters of the Hg and Se atoms are normal perpendicular to the Hg-Se bonds but are surprisingly large (0.147(2) and 0.143(4) Å², respectively) in the direction of the bonds, suggestive of some disorder in this direction. Nevertheless, the Hg-Se distance of 2.389(4) Å is reasonable. For example, the $[\text{Hg}_7\text{Se}_{10}]^{4-}$ anion¹¹ has four distorted tetrahedral Hg centers, two nearly linear centers (average distances and angles: $\text{Hg-Se} = 2.44$ -(1) Å, $\text{Se-Hg-Se} = 167(1)^\circ$), and one linear center ($\text{Hg-Se} = 2.399(5)$, $2.411(5)$ Å, $\text{Se-Hg-Se} = 178.9(2)^\circ$).

The compound $[\text{K}(2.2.2\text{-cryptand})]_2[\text{HgSe}_2]$ was first synthesized by extraction of KHgSe in en in the presence of 2.2.2-cryptand.¹² It was not isolated, but it was characterized by ^{199}Hg and ^{77}Se NMR spectroscopy. While the ^{77}Se chemical shift of the $[\text{HgSe}_2]^{2-}$ anion observed here is in reasonable agreement with the earlier results,¹² the ^{199}Hg chemical shift is not (Table 1). As the chemical shifts are apparently only a function of the solvent choice and not of concentration, we have no explanation for the disagreement. The ^{199}Hg chemical shift observed here is consistent with that expected for a two-coordinate Hg center.¹³

The $[\text{HgSe}_2]^{2-}$ anion is very susceptible to oxidation by air or water. $[\text{K}(2.2.2\text{-cryptand})]_2[\text{Hg}(\text{Se}_4)_2]$ ¹⁴ precipitates when a solution of $[\text{K}(2.2.2\text{-cryptand})]_2[\text{HgSe}_2]$ (**1**) is exposed to air, degassed water, or insufficiently dried counterion.

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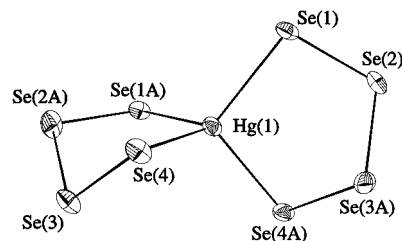


Figure 2. The $[\text{Hg}(\text{Se}_4)_2]^{2-}$ anion in $[\text{PPh}_4]_2[\text{Hg}(\text{Se}_4)_2]\cdot\text{en}$ (**2**). The anion has crystallographically imposed 2 symmetry.

In $[\text{PPh}_4]_2[\text{Hg}(\text{Se}_4)_2]\cdot\text{en}$ (**2**) the $[\text{Hg}(\text{Se}_4)_2]^{2-}$ anion comprises a Hg^{2+} cation coordinated to two bidentate Se_4^{2-} ligands (Figure 2). Metrical details (Supporting Information) are comparable with those found in previous determinations of this ubiquitous anion.^{15–17} The formation of $[\text{Hg}(\text{Se}_4)_2]^{2-}$ from $[\text{HgSe}_2]^{2-}$ in the presence of air or moisture as well the multitude of other preparative routes^{6,15–19} are strong testimony to its stability.

No evidence for the presence of the $[\text{HgSe}_2]^{2-}$ anion is observed in the ^{77}Se NMR spectrum of the preparative solution of $[\text{PPh}_4]_2[\text{Hg}(\text{Se}_4)_2]\cdot\text{en}$ (**2**), and similarly no evidence for the $[\text{Hg}(\text{Se}_4)_2]^{2-}$ anion is observed in the ^{77}Se NMR spectra of the preparative solution of $[\text{K}(2.2.2\text{-cryptand})]_2[\text{HgSe}_2]$ (**1**). We conclude that a different selenomercurate is obtained upon the reduction of HgSe_2 by K from that obtained by electrochemical methods. In neither experiment is it possible to assess the number of moles of electrons involved in the reduction. The product from the electrochemical method is less reduced than is that from the reduction by K .

Acknowledgment. This research was funded by the National Science Foundation, Grant No. CHE95-31232.

Supporting Information Available: Experimental details (Tables S1 and S6), positional parameters and equivalent isotropic displacement parameters (Tables S2 and S7), bond lengths and angles (Tables S3 and S8), anisotropic displacement parameters (Tables S4 and S9), H atom parameters (Tables S5 and S10) for **1** and **2**, metrical details for various determinations of the $[\text{Hg}(\text{Se}_4)_2]^{2-}$ anion (Table S11), and comparable details for $[\text{K}(2.2.2\text{-cryptand})]_2[\text{Hg}(\text{Se}_4)_2]$ (Tables S12–S16) (27 pages). Ordering information is given on any current masthead page.

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- (14) This was established by a crystal structure determination. Crystal data for $[\text{K}(2.2.2\text{-cryptand})]_2[\text{Hg}(\text{Se}_4)_2]$: $a = 10.834(2)$ Å, $b = 13.277(3)$ Å, $c = 20.114(4)$ Å, $\alpha = 97.83(3)^\circ$, $\beta = 96.99(3)^\circ$, $\gamma = 99.94(3)^\circ$, $C_i^1-P\bar{1}$, $Z = 2$, $\text{NO} = 4871$, $\text{NV} = 388$, $R_w(F^2) = 0.121$ for all the data and $R_1(F) = 0.061$ for those 2859 reflections having $F_o^2 > 2\sigma(F_o^2)$. Details may be found in the Supporting Information.
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