Preparation and Characterization of New Organomercury(II) Selenolates

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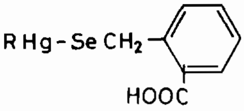
Our work is concerned with the biological interactions in aquatic life, involving mercury and selenium [1]. Although the protective effect of sodium selenite on mercury toxicity has been known for many years [2], little is still known of the biological activity of organomono- and diselenides or about the bioaccumulation and toxic effects of mercury(II) selenolates which are assumed to form in living organisms [3, 4]. Indeed, relatively few mercury–selenium complexes have been reported [5–12] and most are insoluble in water [9, 12] or relatively air-sensitive [7]. However, the recent isolation of methylmercury(II) selenocysteinate monohydrate, $CH_3HgSeCH_2CH_2(NH_3^+)COO^-\cdot H_2O$ (I) [11] has opened a new avenue in mercury toxicity studies since such an amino-acid complex may more closely reflect the behaviour of Hg–Se compounds in biological systems with respect to accumulation and transfer of these elements.

In this communication we report the synthesis of two water soluble organomercury(II) carboxybenzylselenides (**IIa** and **IIb**), and compare their properties with those of **I**.



IIa, R = Me
IIb, R = Ph

Experimental

Methylmercury(II) hydroxide, phenylmercury(II) chloride, selenium powder, and phthalide were used as received (Aldrich). Bis(2-carboxybenzyl)diselanide (**III**) was prepared by the literature method [13], melting point (m.p.) 218–20 °C (literature 217–18 °C). NMR spectra of saturated D_2O solutions were measured at 20 °C using Varian XL-200 (^1H) and XL-300 (^{77}Se and ^{199}Hg) instruments. Infrared data were obtained for samples examined as Nujol mulls using a Perkin-Elmer 297 spectrophotometer (1800–600 cm^{-1}) or a Nicolet-6000 interferometer fitted with a 6.24 μ Mylar beam splitter (600–200 cm^{-1}).

Methylmercury(II) hydroxide or phenylmercury(II) chloride in ethanol were added at −10 to 0 °C to solutions of 2-carboxylbenzyl selenol prepared by reducing **III** in ethanol with $NaBH_4$. Pouring the mixture at room temperature into dilute hydrochloric acid gave the required brown or grey crude products which were purified by solution in aqueous alkali ($pH > 10$) and reprecipitation (as white solids) by addition of conc. HCl.

Results and Discussion

By reaction of the appropriate organomercury compound with 2-carboxylbenzyl selenol generated *in situ* by reduction of the corresponding diselenide, two new mercury(II) selenolates (**IIa** and **IIb**) have been prepared. Both are thermally unstable decomposing to black solids when heated to ≃90–100 °C. Both compounds are light sensitive but **IIa** remains unchanged when stored in the dark under nitrogen at room temperature. In contrast, **IIb** decomposes slowly even when stored at −20 °C under the same conditions. Similarly, **I** was reported to be a stable compound under ambient conditions [11]. Both **IIa** and **IIb** are soluble in aqueous alkali presumably by ionisation of the ring carboxyl group. In dilute (10^{-4} M) alkaline solutions ($pH = 9–10$) prepared using both distilled water and seawater, **IIa** was stable for several days at 25 °C and was easily recovered by simple acidification of the solutions. All attempts to prepare inorganic mercury(II) selenolates were unsuccessful, yielding only black products, presumably HgSe.

Infrared Spectra

The rather small increases in the separation $\Delta\nu(CO_2) = \nu_{as}(CO_2) - \nu_s(CO_2)$, when **IIa** and **IIb** are formed from **III** (Table I) suggest only weak intramolecular interaction exists between the mercury and the carbonyl oxygen of the adjacent ring carboxyl group [14] in these compounds. For compound **IIa**, peaks at 1426 and 1188 cm^{-1} may be assigned to methyl group deformations [15] but for the phenylmercury analogue, phenyl ring modes overlap extensively with those of the benzene ring of the selenol group and cannot be readily assigned.

In the skeletal region, ν(C–Se) is assigned to an absorption at ≃300 cm^{-1} [8], the formation of the

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TABLE I. Characteristic Infrared Absorptions (cm^{-1}) for Organomercury(II) Selenolates

Compound	$\nu_{as}(CO_2)$	$\nu_s(CO_2)$	$\Delta\nu(CO_2)$	ν(C–Se)	ν(C–Hg)	ν(Hg–Se)
I[a]	1515s,br	1392s	123		536s	214m
IIa	1675vs	1401m	274	307m	532s	221m
IIb	1685vs	1400m,br	285	300m	(208w)[b]	
III	1675vs	1410m,br	265	298vs		

[a] Ref. 11. [b] See text.

TABLE II. NMR Data for Organomercury(II) Selenolates[a]

Compound	$\delta(^1H)$[b]	$\delta(^{77}Se)$[c]	$\delta(^{199}Hg)$[d]	$^2J^{199}Hg-CH_3$
I[e]	0.80s (CH_3), 3.47m (CH_2) 4.10t (CH_3)		−664	166.5
IIa	0.64s (CH_3), 4.34s (CH_2) 7.18–7.43m (ring)		−660.5	165.0
IIb	4.32s (CH_2), 7.12–7.58m (rings)			
III	4.16s (CH_2), 7.31m (ring)	386.1		

[a] In D_2O; values as ppm (δ) or Hz (J). [b] Referenced to $(CH_3)_4Si$ (int). [c] Referenced to $(CH_3)_2Se$ (ext). [d] Referenced to $Hg(CH_3)_2$ (ext). [e] Ref. 11.

organomercurial apparently causing little change in the C–Se bond. For **IIa**, ν(Hg–Me) and ν(Hg–Se) are almost the same as those reported for **I** [11], 536(s) and 214(m) cm^{-1} respectively. Unfortunately the complexity of the infrared spectrum of **IIb**, means that neither ν(Hg–Ph) or ν(Hg–Se) can be identified with certainty. Comparison with the data for PhHgBr [15] suggests ν(Hg–Ph) be assigned to a weak absorption at 208 cm^{-1} with ν(Hg–Se) perhaps overlapping benzene ring modes in the region above this.

NMR Spectra

The ^1H NMR spectra of **IIa**, **IIb**, and **III** (Table II) show resonances in the 7.1–7.6 ppm region for ring protons while benzylic CH_2 occur at 4.1 to 4.3 ppm being slightly more deshielded when mercury replaces selenium in the diselenide. For **IIa** and **I**, the $^2J^{199}Hg-^1H$ values for the methyl group are almost the same as that found for $CH_3HgSeCH_2CH_2NH_3^+Cl^-$ (162.0 Hz) [4] confirming the very similar nature of the Hg–CH_3 and thus Hg–Se bonds in these systems. In contrast, methylmercury(II)–seleno, urea adducts, $[CH_3HgSeC(CH_2)_2]^+$, have larger $^2J^{199}Hg-^1H$ values (190–192 Hz), indicative of the mercury–carbon bond having more 's' character and thus being more covalent with the coordinate Hg–Se bond being weaker in these adducts, compared with the compounds studies here.

The selenium-77 chemical shift noted for **III** (Table II) is in good agreement with those reported for organodiselenides [17] while $^2J^{77}Se-^1H = 28.3$ Hz is identical with the value found for benzyl diselenide. Unfortunately, ^{77}Se NMR data could not be obtained for compounds **IIa** and **IIb** because of their low solubility. Only for **IIa** could the mercury-199 spectrum be observed. The very small change in ^{199}Hg chemical shift from that observed for **I** is a further indication of the very similar chemical environments of the mercury atoms in these two compounds.

Supplementary Material

Full details of the preparations, microanalytical data, and complete infrared spectra are available from the authors (E.P.).

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