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Methylmercury Derivatives of Phthalocyanine and Tetraphenylporphyrin

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Inorganic mercury(II) derivatives of porphyrins are well known[1] and recently a bis(mercuryacetato)-tetraphenylporphyrin has been described.[2] This work began with attempts to demethylate methylmercury compounds using porphyrin-type ligands. Neither of the title compounds reacted thermally with dimethylmercury up to 140 °C but when the silazide $MeHgN(SiMe_3)_2$ was added to a benzene suspension of tetraphenylporphyrin the colour rapidly changed from purple to green and the bis-(methylmercury) complex, $(MeHg)_2(C_{44}H_{28}N_4)$ (I) was isolated as a blue solid. A similar reaction with phthalocyanine gave the related complex as the blue benzene solvate $(MeHg)_2(C_{32}H_{16}N_8)C_6H_6$ (II). Attempts to prepare the monomethylmercury analogues by this method were unsuccessful. It was shown, incidentally, that $Hg[N(SiMe_3)_2]$ provides a very clean and convenient way of forming mercury (II) porphyrin complexes.

Both (I) and (II) are quite stable in air; at 210 °C small proportions of methane and mercury are produced over 5 days, but extensive decomposition to mercury requires several days at 250 °C. The hydrolysis of (I) and (II) can be followed in benzene or chloroform solution by changes in the u.v.–visible spectra and, in moist benzene or chloroform, hydrolysis of (I) to tetraphenylporphyrin produces an isobestic point at 426 nm. In chloroform solution stepwise hydrolysis to $MeHg(C_{44}H_{29}N_4)$ is indicated by the short-lived presence of an absorption at 440 nm in the Soret-band region. The u.v.–visible spectrum of (II) in moist benzene suggests that the rate of hydrolysis of the first MeHg group giving $MeHg(C_{32}H_{17}N_8)$ is greater than the rate of the second stage in which insoluble phthalocyanine is formed.

Experimental

Tetraphenylporphyrinatobis(methylmercury)

Tetraphenylporphyrin[3] (2.0 g, 3.26 mmol), suspended in dry benzene (100 ml), was treated with $MeHgN(SiMe_3)_2$[4] (2.57 g, 6.84 mmol) in a pressure vessel when the colour changed from purple to green. After 19 h at 100 °C the mixture was diluted with n-hexane (100 ml) and the pale green solution decanted from the blue solid *product* (3.32 g, 98%). The pure material was obtained by Soxhlet extraction with benzene. Found: C, 53.0; H, 3.4; N, 5.3; Hg, 38.1. $C_{46}H_{34}Hg_2N_4$, calcd: C, 52.9; H, 3.3; N, 5.4; Hg, 38.4%. The ^1H nmr spectrum showed a high field methyl mercury resonance, $\delta = -4.25$, ^2JHgH = 218 Hz; *m*- and *p*-phenyl protons at $\delta \approx 7.78$; *o*-phenyl protons at $\delta \approx 9.29$, β-pyrrole protons at $\delta = 8.79$ ppm. λ_{max}(nm)/log ϵ: 418, 4.41 (due to free ligand); 440 sh, 4.80; 457, 5.47; 540, 3.53; 586, 3.78; 611, 4.00; 628, 4.09; 661, 3.96. Its mass spectrum showed a clean parent ion centred on 1044 with the inlet temperature at 295 °C. Elimination of $HgMe_2$ from the parent ion was metastable-supported and a low abundance ion corresponding to elimination of HgMe from the parent was present.

Phthalocyaninatobis(methylmercury)

Phthalocyanine (1.5 g, 2.92 mmol), $MeHgN(SiMe_3)_2$ (3.3 g, 8.78 mmol) and benzene (100 ml) were heated at 100 °C for 2 days. The pure *complex* was isolated by Soxhlet extraction with benzene as a green benzene solvate (1.7 g, 57%). Found: C, 47.0; H, 2.7; N, 10.9; Hg, 39.3. $C_{40}H_{28}N_8$, calcd: C, 47.0; H, 2.8; N, 11.0; Hg, 39.3%. It was too insoluble for ^1H nmr measurements. λ_{max}(nm)/log ϵ: 285, 4.35; 342, 4.69; 440, 4.16; 654, 4.43; 721, 5.09. Its mass spectrum showed a parent peak for $C_{34}H_{22}Hg_2N_8$ at an inlet temperature of 295 °C. Three metastable-supported transitions were present: $p \rightarrow HgMe_2 + Hg(ligand)^+$; $MeHg(ligand)^+ \rightarrow Me + Hg(ligand)^+$; $Hg(ligand)^+ \rightarrow Hg + (ligand)^+$ where ligand = $C_{32}H_{14}N_8$. For both (I) and (II) the ions $HgMe_2^{+\cdot}$, $HgMe^+$ and $Hg^{+\cdot}$ were very strong.

References

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