A Novel Mercury(II) Chloride Complex of *S*-β-(2-Pyridylethyl)-L-cysteine

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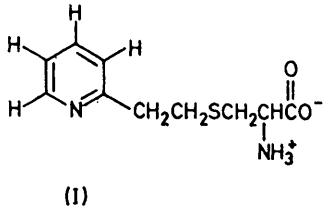
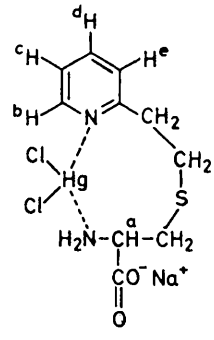
Summary Spectroscopic evidence shows that, in the complex of *S*-β-(2-pyridylethyl)-L-cysteine (I) with mercury(II) chloride, $HgCl_2$ binds to the pyridyl ring nitrogen and the amino-group but not to the sulphur or carboxylate groups.

IT has recently been observed by Natusch and Porter[1,2] that the mercury(II) ion binds to the sulphur of *S*-methylcysteine at low pD and the amino and sulphur groups at high pD. We report here our results on the interaction of *S*-β-(2-pyridylethyl)-L-cysteine (I) with $HgCl_2$ and show that they form a novel chelate (II).‡



(I)



(II)

The ^1H n.m.r. results in the Table show that at pD 7·0 (D_2O) the protons on the pyridyl ring as well as the methine proton (see II) are preferentially shifted, while those methylene protons adjacent to sulphur are not affected by $HgCl_2$.

These results confirm that the pyridyl ring nitrogen is a site of binding. The methine proton in (II) is shielded to higher field than that in (I) because of the full positive charge of the NH_3^+ group in (I) compared to the partial positive charge of $NH_2 \rightarrow Hg$ in (II). The amino-function of (I) was selectively blocked with an *N*-acetyl and the n.m.r. shifts of the pyridyl protons at pD 7·0 were compared with those of (I) providing values for protons b; c,e; d for the *N*-acetyl derivative of −1·0; −2·5; −3·0, respectively. This confirms the necessity of the amino-group in binding $HgCl_2$ along with the pyridyl group. The i.r. spectrum (KBr) (1594 and 540 cm^{-1} for antisymmetric carboxylate stretch and carboxylate rock) eliminates the carboxylate as a site of binding, while the Raman spectrum (solid) of (II) shows a strong band at 275 cm^{-1} (Hg–Cl stretch;[3] uncomplexed $HgCl_2$ 315 cm^{-1}). The intramolecular chelation of $HgCl_2$ was further substantiated by the c.d. spectra of (I) and (II), which showed a six-fold enhancement of the molecular ellipticity for (II), $[\theta]_{270}$ −2330, over that of (I), $[\theta]_{272}$ −360 at pH 4·0 (H_2O). This indicates an increase in the dissymmetric environment of the pyridyl group by restricting its rotation as in (II). The fact that $HgCl_2$ forms a nine-membered ring chelate with two nitrogen atoms as opposed to a five-membered ring chelate with sulphur and nitrogen, as in *S*-methylcysteine[1,2] can be rationalized by the known co-ordinating ability of mercury with pyridyl and amino-groups,[4] which evidently provides a more stable chelate although making a larger ring.

Chemical shift differences between the $HgCl_2$ *complex* (II) *and the corresponding free ligand* (I) *at pD* 7·0

Chemical shift differences[a]			
a[b]	b	c,e	d
+4·8	−7·2	−8·0	−2·0

[a] In plots of δΔ *vs.* pD for (I) and (II), the difference Δδ(II) − Δδ(I) is a measure of the deshielding (−ΔΔδ) or shielding (+ΔΔδ) of (II) compared to (I). [b] See structure (II) for proton designations. The measurements were performed at 100 MHz.

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‡ Prepared by mixing $HgCl_2$ and (I) (1 : 1) in water and adjusting the pH to 8·0; (II) then precipitated. Satisfactory analyses were obtained for (II).

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[3] T. B. Brill and D. W. Wertz, *Inorg. Chem.*, 1970, **9**, 2692.
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