Binding of Methylmercury by Amino-acids: X-Ray Structure of DL-Penicillaminatomethylmercury(II)

By Yau Shing Wong, Peter C. Chieh, and Arthur J. Carty*
(*Department of Chemistry, University of Waterloo, Waterloo, Ontario*)

Summary An *X*-ray structural study has established that in the 1:1 compound formed by methylmercury(II) and DL-penicillamine, the sulphur amino-acid is bound by a deprotonated sulphydryl group; this is the probable mode of binding of methylmercury(II) to sulphur-containing protein molecules.

Environmental pollution by methylmercury(II) is a matter of global concern.[1] In order to understand the harmful effects of methylmercury(II) on living cells, knowledge of the mode of binding of MeHgCl and other less toxic forms of the heavy metal ($HgCl_2$, PhHgCl *etc.*) to protein and enzyme molecules is needed. Although some solution work on Hg^{2+} complexes of amino-acids[2] and $MeHg^{II}$ complexing by glutathione[3] has recently been reported, detailed structural data on $MeHg^{II}$ complexes with sulphur amino-acids are lacking. We report here the *X*-ray crystal structure of the zwitterionic complex, $MeHg[SC(Me)_2CH(NH_3)CO_2]H_2O$.

Colourless prisms of the complex were obtained from aqueous ethanol solutions containing equimolar quantities of DL-penicillamine and MeHgOH in basic solution. *Crystal data*: $(MeHg)[SC(Me)_2CH(NH_3)CO_2]H_2O$, monoclinic crystals, space group $C2/c$, $a = 23{\cdot}331$, $b = 9{\cdot}921$, $c = 19{\cdot}496$ Å, $\beta = 106{\cdot}5$; $Z = 16$, $D_m = 2{\cdot}40$, $D_c = 2{\cdot}43$ g cm^{-3}. 1505 independent reflections measured on a G.E. XRD6 automatic diffractometer were used in the structure refinement. The structure was solved by the heavy-atom method and refined by least-squares including an anomalous dispersion correction for mercury and anisotropic thermal factors to the present R value of 0·09. The amino-acid in the zwitterionic form $SC(Me)_2CH\overset{+}{N}H_3CO_2^-$ is bonded to the methylmercury unit *via* a deprotonated sulphydryl group (Figure). The two independent Hg–S distances, Hg(1)–S(1) [2·385(14) Å] and Hg(2)–S(2) [2·376(14) Å] are similar to the Hg–S distances [av. 2·330(7) Å)] in $[PhN{=}C(OMe)S]_2Hg$[4] where mercury is two-co-ordinate, but significantly shorter than in $Hg(SCN)_2AsPh_3$[5] where mercury is three-co-ordinate.

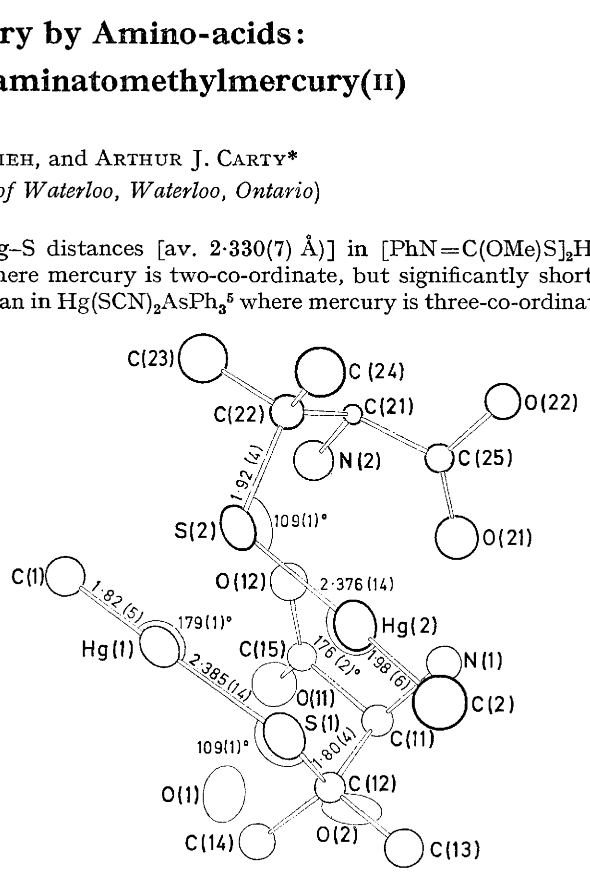

Figure. The molecular structures of the two crystallographically non-equivalent molecules of $MeHg[SC(Me)_2CH(NH_3)CO_2]$ in the asymmetric unit. O(1) and O(2) are the oxygen atoms of solvent water molecules.

In agreement with a characteristic co-ordination number of two for mercury and a mean C–Hg–S angle of 178(2)°, there is no evidence for intermolecular co-ordination of nitrogen, oxygen, or sulphur to mercury. However, the two crystallographically independent molecules are bound to each other, to solvent water molecules, and to neighbouring molecules in the unit cell by a complex system of strong hydrogen bonds.

This structure confirms the hypothesis that methylmercury is bound to sulphur amino-acid containing proteins as the linear complex Me–Hg–S–. By contrast, this seems *unlikely to be the* form of bound "inorganic" mercury in poisoned cells.[2]

We thank the Department of National Health and Welfare for financial support of this work.

(*Received, 29th June* 1973; *Com.* 936.)

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