Syntheses, *X*-Ray Crystal Structure, and Vibrational Spectra of L-Cysteinato(methyl)mercury(II) Monohydrate

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The title complex has been prepared from the reaction of L-cysteine with methylmercury hydroxide or chloride in basic solution and characterised by single-crystal *X*-ray diffractometry. Crystals are orthorhombic, space group $P2_12_12_1$, with unit cell dimensions $a = 6{\cdot}386(6)$, $b = 26{\cdot}026(13)$, $c = 5{\cdot}282(4)$ Å and $Z = 4$. The structure was solved by Patterson and Fourier techniques and refined by full-matrix least-squares methods to a final R of 0·065 for 980 independent observed reflections measured on an automatic diffractometer. The amino-acid is co-ordinated to Hg *via* a deprotonated sulphydryl group [Hg–S 2·352(12) Å]. A weak intramolecular Hg ··· O interaction [2·85(2) Å] to a carboxylate group is present. Individual molecules of the complex are linked by hydrogen bonds to solvent water molecules. The vibrational spectra of the complex are discussed [ν(Hg–S) 326 cm^{-1}].

Environmental pollution by methylmercury(II) has recently become a matter of serious global concern.[1] Fish and shellfish contaminated with methylmercury(II) in polluted waters have been the cause of several epidemics of mercury poisoning in Japan resulting in many deaths and innumerable cases of brain damage. The Japanese disaster is, however, dwarfed by events in Iraq where several thousands died as a result of eating seed grain treated with methylmercury(II) fungicides.[1] As a first step in understanding the specific deleterious effects of methylmercury(II) on living cells in general it is essential to have detailed knowledge of the mode of binding of methylmercury(II) and other less toxic forms of the heavy metal ($HgCl_2$, PhHgCl, $MeOC_2H_4HgCl$) to protein and enzyme molecules. Of the common ligand groups present in proteins, the constituent groups present in sulphur amino-acids, namely –SH, –S–S–, $-NH_2$, and $-CO_2^-$, are probably of paramount importance to mercury(II) binding. Indeed it has long been assumed that the inactivation of proteins and enzymes caused by Hg^{II} species is due to the co-ordination of mercury to deprotonated sulphydryl sites.[1] Although the co-ordination chemistry of Hg^{2+} with sulphur amino-acid has been widely studied by many different techniques,[2,3] few investigations of the complexing by amino-acids of organomercury(II) species have been reported. Recent work on glutathione–methylmercury(II) systems has shown [4,5] that the methylmercury ion is preferentially co-ordinated to the ionised sulphydryl group in aqueous solution. Complexation to other sites may, however, occur when the stoicheiometry CH_3Hg^+ : glutathione exceeds 1 : 1. As part of a programme designed to obtain detailed stereochemical information on the bonding of organomercury(II) species to amino-acids and peptides, a variety of RHg^{II} (R = Me or Ph) complexes with L-cysteine, DL-methionine, *S*-methyl-L-cysteine, and DL-penicillamine have been synthesised and structurally characterised by single-crystal *X*-ray diffractometry. Preliminary studies with the non-essential amino acid DL-penicillamine have been described.[6,7] In this paper we describe the synthesis, structural characterisation, i.r. and Raman spectra of a 1 : 1 complex between MeHg^{II} and the zwitterion $^-SCH_2{\cdot}CH(N^+H_3)CO_2^-$ derived from L-cysteine. Since cysteine residues are an integral component of many sulphur-containing proteins, a cysteine–methylmercury complex may well be involved in methylmercury poisoning.[1] In addition, cysteine neutralises, to a certain degree, the effects of toxic organomercury compounds on cells in sea-urchin eggs, presumably by complex formation with the organomercury poison.[8]

EXPERIMENTAL

Physical Methods and Materials.—Methylmercury chloride and hydroxide (Research Organic–Inorganic Chemical Corporation); L-cysteine (Sigma Chemical Company). I.r. spectra (Nujol mulls on caesium iodide plates) were run on a Perkin-Elmer 180. Raman spectra were obtained for powders by use of a rotating cell,[9] on a Jarrell–Ash 400 spectrophotometer with argon-ion (5145 Å) excitation. This sampling technique was essential to prevent extensive burn-up in the laser beam; a modified version of the cell described in ref. 9 was used.

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Synthesis.—Methylmercury hydroxide (0·50 g, 2·16 mmol) and L-cysteine (0·26 g, 2·16 mmol) were mixed in 50% aqueous ethanol (150 ml) and stirred for 3 h. The volume of the filtered solution was reduced to *ca.* 20 ml, and the almost saturated solution set aside until prismatic crystals were obtained (Found: C, 13·6; H, 3·10; N, 3·85. $C_4H_{11}HgNO_3S$ requires C, 13·58; H, 3·13; N, 3·96%). The presence of a molecule of water of crystallisation was indicated by the appearance of a ν(O–H) band in the i.r. spectrum and confirmed by the *X*-ray structure determination (*vide infra*). The same complex was prepared by reaction of MeHgCl with L-cysteine in basic aqueous ethanol (pH *ca.* 10) solution.

Crystals were grown from aqueous ethanol solutions. Weissenberg and precession photographs were used to establish cell constants which were refined by least-squares methods from the 2θ values (Mo-K_α) measured by use of a General Electric XRD 6 diffractometer for 21 reflections.

Crystal Data.—$C_4H_{11}HgNO_3S$, *M* 353·8, Orthorhombic, $a = 6{\cdot}386(6)$, $b = 26{\cdot}026(13)$, $c = 5{\cdot}282(4)$ Å; $U = 877{\cdot}9$ Å^3; $D_m = 2{\cdot}65$ g cm^{-3} (by flotation), $Z = 4$, $D_c = 2{\cdot}676$ g cm^{-3}. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 180·9 cm^{-1}; $\mu R = 1{\cdot}040$. Space group $P2_12_12_1$ (D_2^4, No. 19) from systematic absences: $h00$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$, and $00l$ for $l = 2n + 1$.

Data Collection.—A crystal of dimensions 0·13 × 0·10 × 0·22 mm was mounted on a glass fibre and aligned with c^* along the ϕ axis of a General Electric XRD 6 automatic diffractometer equipped with scintillation counter and pulse-height analyser. Zirconium-filtered Mo-K_α radiation was employed and the stationary-crystal–stationary-counter method used. A background curve was derived from measurements taken with the crystal at different orientations. The intensities of four standard reflections were monitored and diminished by 12% during the course of data collection; these were used to scale the data to a common level. Standard deviations were estimated from counting statistics. Of 2289 independent reflections measured ($2\theta \leqslant 70°$), 980 with intensities $>3\sigma$ were considered observed and used for the structure determination. Lorentz and polarisation factors were applied to the derivation of structure amplitudes. Revised versions of least-squares (Doedens and Ibers), Fourier (Zalkin), and Ranger (Corfield) programs were used. Other programs were developed in this laboratory. Calculations were carried out on an IBM 360/75 computer at the University of Waterloo computing centre. The ORTEP program of Johnson[10] was used for perspective plots of the molecule and the packing diagram.

Structure Solution and Refinement.—The co-ordinates of the mercury atom in the asymmetric unit were determined from a three-dimensional Patterson map. An initial Fourier map revealed the methyl carbon and sulphur atom positions together with those of the carboxylate group. The remaining skeleton of the amino-acid and the solvent molecule were identified from a subsequent Fourier map. A difference Fourier map revealed only ' ripples ' in the vicinity of the mercury atom. With all the non-hydrogen atoms having isotropic thermal parameters, the structure was refined by full-matrix least-squares to *R* 0·209. Scattering factors used, including anomalous scattering corrections for mercury, were taken from ref. 11. Introduction of anisotropic thermal parameters reduced *R* to 0·113. At this stage, structure factors were calculated using negative co-ordinates for all the atoms with the previous data. This gave a significantly better *R* of 0·103 with all the bond distances appearing to be chemically reasonable, so this model was taken to represent the correct configuration. A linear absorption correction was made and an empirical weighting scheme of the form $w^{-1} = 18{\cdot}077 + 0{\cdot}377|F| + 0{\cdot}00375|F|^2$ was introduced to obtain constant errors in the different ranges of $|F_o|$ values. Final refinement gave an *R* 0·065 with *R'*, the weighted residual, 0·075. In view of the presence of a heavy-metal atom, it was not possible to locate any hydrogen atoms. Final positional and thermal parameters are listed in Table 1. Bond distances and angles within the molecule are given in Table 2, together with short

TABLE 1

Atomic co-ordinates and anisotropic temperature factors

(*a*) Atomic co-ordinates (fractional, × 10^4)

	x	*y*	*z*
Hg	1536(2)	1909(0)	2893(2)
S	4218(17)	1769(3)	5867(18)
O(1)	1474(33)	353(6)	4544(30)
O(2)	2391(32)	885(5)	1319(33)
O(3)	9053(28)	505(9)	8719(41)
N	4889(38)	561(7)	7297(49)
C(1)	5707(46)	1284(9)	4246(60)
C(2)	4981(38)	750(12)	4516(56)
C(3)	2642(32)	657(8)	3556(50)
C(4)	9270(47)	2151(11)	177(76)

(*b*) Anisotropic temperature factors in the form: $\exp[-2\pi^2(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

	$10^5\beta_{11}$	$10^4\beta_{22}$	$10^5\beta_{33}$	$10^4\beta_{12}$	$10^5\beta_{13}$	$10^4\beta_{23}$
Hg	33·8(3)	10·1(1)	52·7(5)	−3·3(6)	−1·5(4)	13·6(7)
S	53(4)	13(1)	49(4)	−11(5)	−11(3)	−8(5)
O(1)	31(5)	13(3)	33(6)	−21(11)	5(7)	−9(10)
O(2)	37(6)	9(2)	24(7)	−2(9)	−6(5)	14(9)
O(3)	12(5)	28(5)	36(9)	14(11)	−2(5)	−8(16)
N	31(7)	13(3)	35(10)	−2(11)	−5(7)	19(13)
C(1)	16(8)	15(4)	46(13)	−28(13)	−4(9)	14(18)
C(2)	12(6)	19(5)	31(12)	−10(15)	−4(8)	11(21)
C(3)	7(4)	13(3)	46(12)	−6(9)	4(6)	−6(14)
C(4)	21(7)	19(5)	93(20)	13(15)	1(11)	71(26)

TABLE 2

Intramolecular and intermolecular distances and angles

(*a*) Intramolecular bond distances (Å) and angles (°)

Hg–C(4)	2·10(4)	C(4)–Hg–S	177·6(0·9)
Hg–S	2·352(12)	Hg–S–C(1)	100·4(0·9)
S–C(1)	1·81(3)	S–C(1)–C(2)	113·7(1·1)
C(1)–C(2)	1·48(4)	C(1)–C(2)–C(3)	116·1(1·3)
C(2)–C(3)	1·53(3)	C(1)–C(2)–N	115·0(1·3)
C(2)–N	1·53(4)	C(3)–C(2)–N	105·7(1·1)
C(3)–O(1)	1·24(3)	C(2)–C(3)–O(1)	123·0(1·3)
C(3)–O(2)	1·33(3)	C(2)–C(3)–O(2)	112·7(1·3)
Hg–O(2)	2·85(2)	O(1)–C(3)–O(2)	124·0(1·3)
N–O(1)	2·68(3)	S–Hg–O(2)	84·9(0·4)
		C(4)–Hg–O(2)	95·7(0·9)
		C(2)–N–O(3)	105·4(1·1)

(*b*) Some relevant intermolecular distances (Å) and angles (°)

N ··· O(3)	2·75(3)	N ··· O(3) ··· O(1)	109·9(0·6)
O(1) ··· O(3)	2·73(3)	N ··· O(3) ··· O(2)	150·3(0·6)
O(2) ··· O(3)	2·73(3)	O(1) ··· O(3) ··· O(2)	90·5(0·5)
N ··· O(1)	2·80(3)	C(3) ··· O(1) ··· O(3)	128·8(0·9)
N ··· O(2)	2·79(3)	C(3) ··· O(2) ··· O(3)	147·8(0·8)
O(1) ··· O(3)	3·48(3)		
N ··· O(3)	3·42(3)		
Hg ··· S	3·803(8)		
S ··· O(2)	3·53(2)		

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intermolecular (⩽3·5 Å) contacts. Structure-factor amplitudes are listed in Supplementary Publication No. SUP 21187 (5 pp., 1 microfiche).*

RESULTS AND DISCUSSION

I.r. and Raman Spectra.—The colourless crystalline complex formed in the reaction of MeHgOH (or MeHgCl) with equimolar quantities of L-cysteine was identified as the monohydrate of L-cysteinato(methyl)mercury(II). The i.r. and Raman spectra of MeHgCl, the material known as 'MeHg(OH),'[12] the free base L-$HSCH_2 \cdot CH(N^+H_3)CO_2^-$, and the complex were measured to provide some indication of the bonding mode of the amino-acid and to identify frequencies diagnostic of the type of bonding present. Four areas of the spectra were of particular interest namely: ν(N–H) and ν(O–H) (3100—3500 cm^{-1}), ν(S–H), δ(H–N–H), and ν(C=O), and the far-i.r. (<550 cm^{-1}), where metal–ligand modes are expected. Table 3 summarises spectral bands and, where possible, assignments in these regions. Apart from a strong ν(O–H) (solvent water) band at 3340 cm^{-1}, the i.r. spectrum of the complexed ligand in the high frequency region is typical of a strongly hydrogen-bonded zwitterionic amino-acid $-S-CH_2 \cdot CH(N^+H_3)CO_2^-$ and not of a compound with 'free' $-NH_2$ and $-CO_2H$ groups.[13,14] The band due to ν(S–H), which is weak and difficult to identify in the i.r., is the strongest band in the Raman spectrum of the free ligand. Hence the disappearance of this band in the Raman on complex formation is an excellent diagnostic test of co-ordination to a deprotonated sulphydryl ligand. In the 1700—1500 cm^{-1} i.r. region the band pattern is similar to that of the amino-acid in the zwitterionic form $HSCH_2 \cdot CH(N^+H_3)CO_2^-$ rather than that of the complex $MeHgSCMe_2 \cdot CH(NH_2\text{-}Hg^+Me)CO_2^-$ where the amino group is co-ordinated to mercury.[6] The $-N^+H_3$ group gives rise to characteristic δ_{as} and δ_s modes at 1608 and 1500 cm^{-1} respectively.[13,14] A medium intensity band in the i.r. spectrum and an intense band in the Raman spectra at 538 cm^{-1}, is probably ν(Hg–C) whilst another strong Raman band at 326 cm^{-1} is probably ν(Hg–S); a medium-weak counterpart of the latter appeared at 325 cm^{-1} in the i.r. spectrum. These assignments compare with ν(Hg–S) frequencies of 329 cm^{-1} in MeHgSMe (ref. 15) and 283 cm^{-1} in MeHgSCN.[16] The Raman spectra appear to be considerably more useful than the i.r. for diagnostic purposes. Similar spectral correlations have been found for other organo-mercury–amino-acid complexes.[17]

TABLE 3

Some characteristic infrared and Raman bands for L-cysteinato(methyl)mercury(II) monohydrate

L-$HSCH_2 \cdot CH(N^+H_3)CO_2^-$		$MeHgSCH_2 \cdot CH(N^+H_3)CO_2,H_2O$		
R	I.r.	R	I.r.	Assignments
			3340s	ν(O–H)
	3160vs, br 3060s, sh		3150s, br	$\nu(N^+H_3)$ sym, asym
2545vs	2545mw			ν(S–H)
	1640m, sh		1640m, sh	
1613w, br	1610vs, br	1608vw, br	1608s, sh	$\delta(N^+H_3)$ asym
	1588s, sh		1590s, br	$\nu(COO^-)$ asym
	1548sh			
1514w, br	1511vs	1500vw, br	1500s, br	$\delta(N^+H_3)$ sym
1398mw	1400s	1396mw	1397s	$\nu(COO^-)$ sym
		538vs	538mw	ν(Hg–C)
		326vs	325mw	ν(Hg–S)

X-*Ray Structural Results.*—An ORTEP plot of the molecular structure showing the atomic numbering is illustrated in Figure 1. Figure 2 is a packing diagram showing the four molecules in the unit cell. The structure consists of individual molecules of $MeHgSCH_2 \cdot CH(N^+H_3)CO_2^-$ packed together in pairs along the *y* axis and linked by hydrogen bonds to solvent water molecules. The amino-acid is bound to mercury *via* a deprotonated sulphydryl group with an Hg–S distance [2·352(12) Å] which compares with those [2·320(2) and 2·376(14) Å] in the penicillaminato-species $MeHgSCMe_2 \cdot CH(NH_2HgMe)\text{-}CO_2^-$ (ref. 6) and $MeHgSCMe_2 \cdot CH(N^+H_3)CO_2^-$ (ref. 7) respectively. These values are all similar to mean Hg–S distances[18] (2·330 Å) in [PhN⁚C(OMe)S]$_2$Hg where the mercury atom is two-co-ordinate. By contrast, in

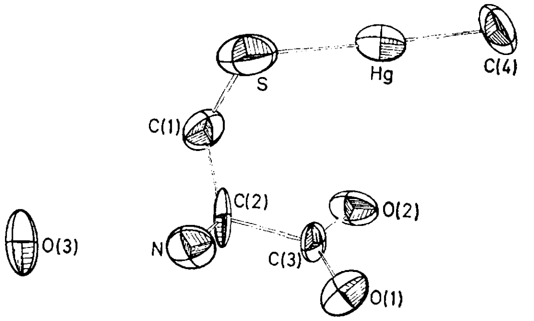

FIGURE 1 View of the molecular structure; O(3) is the oxygen atom of the molecule of water of crystallisation

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

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$Hg(SCN)_2(AsPh_3)$,[19] where three strong covalent bonds to mercury are present, mean Hg–S distances are 2·54 Å and in $[Hg(tu)_2Cl]Cl$ (tu = thiourea)[20] where the metal is co-ordinated in a trigonal planar fashion, they are 2·42(1) Å. Somewhat longer bond lengths (2·51—2·62 Å) have been found in the tetrahedrally co-ordinated mercury complexes $HgCl_2(tu)_4$[21] and $HgCl_2$(1,4-thioxan).[22] Hence a gradual progression in bond lengths with increasing co-ordination number is apparent for these Hg^{II} complexes. The Hg–C(4) distance [2·10(4) Å] does not differ significantly from values [2·06(2) Å] for gaseous MeHgCl,[23] 2·08(2) Å for $(p\text{-}CH_3\cdot C_6H_4)_2Hg$,[24] and [2·12(3) Å] $Et_2NC_2H_4HgCl$,[25] and is only marginally longer than the mean distance (1·90 Å) in related penicillamine derivatives.[6,7] Thus, in spite of the presence of ligands which, in d^8 complexes have markedly different *trans* bond-lengthening influences,[26] no regular trend in Hg–C bond lengths is apparent for these d^{10} systems.

A scan of intra- and inter-molecular bond distances <3·5 Å revealed an additional interaction with each mercury atom. If the sum of the van der Waals radii of mercury and oxygen is taken to be 3·0 Å,[27] the Hg–O(2) distance of 2·85(2) Å may represent a weak bonding interaction between the metal atom and the carboxylate group. However, there appears to be little agreement in the literature as to what constitutes a definite Hg–O bonding interaction. For PhHgOCOMe,[28] an Hg–O distance of 2·85 Å was considered non-bonding while for *cis*-β-benzoylvinylmercuric chloride[29] a corresponding distance of 2·88 Å was taken to be indicative of C=O · · · Hg bonding. These distances are much longer than normal covalent bond lengths (2·00—2·35 Å) for Hg–O in co-ordination complexes[28,30] and it seems doubtful whether the carboxylate oxygen atom can be described as being co-ordinated to mercury.

The shortest intermolecular Hg · · · S contact is 3·803(8) Å which is considerably greater than the sums of van der Waals radii (3·35 Å). Although mercury–sulphur bonds have been implied at distances up to 3·0 Å,[31] it is clear that such interactions are precluded for the present structure. Despite the presence of a weak Hg–O bond the C(4)–Hg–S angle [177·6(0·9)°] deviates only slightly from 180°. The near linearity of the C(4)–Hg–S unit may reflect a strong tendency for mercury 6*s*-orbital character to be concentrated in the Hg–C(4) and Hg–S bonds. As is commonly found for many amino-acids[32] and their complexes[33] the ligand appears to be present in the zwitterionic form: $^-S\cdot CH_2\cdot CH(N^+H_3)\cdot CO_2^-$. Although C–O bond lengths in a carboxylate group often differ for zwitterionic amino-acids, owing to different hydrogen-bonding patterns,[32] in the present case the difference in the C(3)—O(2) [1·33(3) Å] and C(3)–O(1) [1·24(3) Å] distances may be related to the weak binding of O(2) to the mercury atom. The atoms N and S are mutually *cis* with respect to the C(1)–C(2) bond, this configuration being imposed by the intramolecular co-ordination of S and O(2) to mercury. Intraligand distances appear normal and are comparable with the bond lengths in the free ligand L-cysteine.[34]

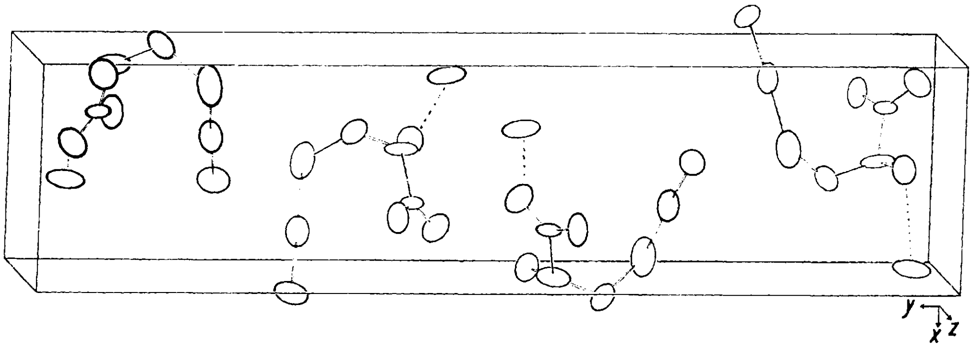

FIGURE 2 Packing diagram. Dotted lines represent hydrogen bonds

Although no attempt was made to locate hydrogen atoms it appeared likely, by analogy with structures of related amino-acid complexes,[33] that molecules of solvent water and complex would be linked by a definite pattern of hydrogen bonds. Accordingly, the presence of hydrogen bonds in the structure was inferred from oxygen–oxygen and oxygen–nitrogen distances. The oxygen atom of each water molecule is located at a distance of 2·75(3) Å from the amine nitrogen atom of a neighbouring molecule of complex. This distance is well within the range expected for an N · · · H · · · O hydrogen bond[34] and the interaction is shown in Figure 2. In

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addition, the same oxygen atom forms hydrogen bonds with O(1) of a second molecule of complex [O(3) · · · O(1) 2·73(3) Å] and O(2) of a third molecule [O(3) · · · O(2) 2·73(3) Å] outside the unit cell shown in Figure 2.

This structure determination confirms the hypothesis that reaction of methylmercury with cysteine or cystine moieties results in attachment to sulphur sites. In view of the weakness of the secondary intramolecular Hg · · · O(2) interaction it seems likely that in cells poisoned by $MeHg^{II}$, the metal is present as the linear complex Me–Hg–S. This is unlikely to be the form of bound 'inorganic' mercury in biological systems.[3] Moreover there must be subtle differences between the cysteine complex of $MeHg^{II}$ and that of $PhHg^{II}$ since the latter is considerably less toxic and is excreted more rapidly from the body.

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