Crystal Structures of Methyl(L-tyrosinato)mercury(II) Monohydrate and [L-(2-Amino-4-phenylbutanoato)]methylmercury(II)

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The crystal structures of the 1 : 1 complexes formed by methylmercury(II) with L-tyrosine (2) and L-2-amino-4-phenylbutanoic acid (3) have been determined by *X*-ray diffraction. Complex (2) crystallises as a monohydrate which is monoclinic, $P2_1$, with unit-cell dimensions a = 9.084(1), b = 6.150(1), c = 11.565(1) Å, β = 110.52(2)°, and Z = 2. Complex (3) is orthorhombic, $Pca2_1$, with dimensions a = 14.853(4), b = 9.438(3), c = 8.755(2) Å, and Z = 4. Intensities [1 078 and 674 with $I/\sigma(I) \geqslant 3.0$ for (2) and (3) respectively] have been recorded at 173 K on a four-circle diffractometer, and the structures refined by the least-squares method to yield final R values of 0.044 and 0.046 for (2) and (3) respectively. The two structures differ markedly: in (2) the amino-acid is bound to mercury *via* an amino-group [Hg–N 2.17(2) Å], and mercury has further weaker intramolecular interactions with the carboxylate group [Hg–O 2.62(2) Å] and with the phenyl ring [Hg–C 3.19(2) and 3.33(2) Å], whilst in (3) a phenyl-ring interaction is absent but the amino-group is again bound [Hg–N 2.15(3) Å] and mercury has both intramolecular and intermolecular interactions with carboxylate groups [Hg–O 2.72(2) and 2.78(3) Å respectively]. The crystal structures are compared with the structures in solution as indicated by ^1H and ^{13}C n.m.r. spectroscopy. The postulated hydrophobic interaction between the methyl group of methylmercury(II) and the phenyl ring of phenylalanine or tyrosine is shown to be an edge-on interaction between the mercury atom and two carbon atoms (1 and 2) of the phenyl group.

THE co-ordination of methylmercury(II) ion with 3-phenylalanine [$PhCH_2CH(NH_2)CO_2H$] shows a pH-dependent equilibrium between two complexes in which the ligand is bonded through either its amino- or its carboxylate group.[1] The position of this equilibrium is readily established by ^1H or ^{13}C n.m.r. spectroscopy at reduced temperatures, when separate resonances can be detected for the methyl groups of the two complexes (^1H and ^{13}C n.m.r.) [2] and for the carboxylate groups (^{13}C n.m.r., Figure 1). As expected, the equilibrium lies to the left-hand side at high pH, and the concentration of the carboxylate-bound species increases as the pH is decreased. The kinetics of equilibrium (1) are readily

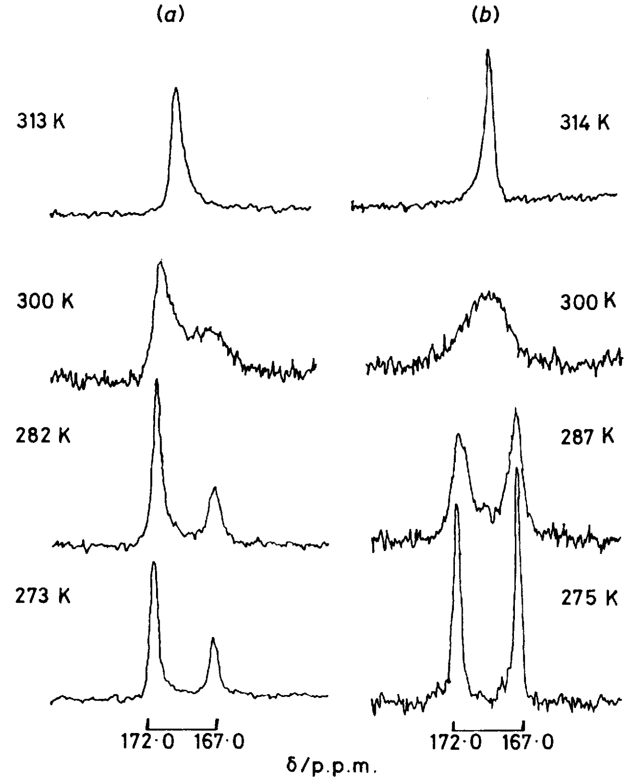

FIGURE 1 Parts of the 22.628-MHz ^{13}C n.m.r. spectra (in the carbonyl region) associated with equilibrium (1) as a function of pH and temperature. [complex] = 0.20 mol dm^{-3} (10% enriched in $^{13}CO_2^-$); each spectrum is an average of *ca.* 35 000 8K scans (sweep width 3 000 Hz) in H_2O–D_2O (9 : 1 v/v). pH 4.0 (*a*) or 2.8 (*b*)

$$H^+ + [HgMe\{H_2NCH(CO_2)CH_2Ph\}] \rightleftharpoons [HgMe\{O_2CCH(NH_3)CH_2Ph\}]^+ \quad (1)$$

studied by line shape analysis,[3] and the absence of such a dynamic process for simpler amino-acids, together with the observation of a high-field ^1H or ^{13}C chemical shift for the methyl group of the methylmercury(II), led to the suggestion that the phenyl ring of the amino-acid was interacting hydrophobically with the methyl group; [1,2] further evidence for a phenyl-ring interaction was also found in a very small shift in the ^{13}C resonance associated with C^4 of the phenyl ring, and a general broadening of the other phenyl-ring resonances.[2] Equilibria analogous to (1) have also been observed in the complexes with tyrosine [3-(*p*-hydroxyphenyl)-alanine], L-dopa [3-(3,4-dihydroxyphenyl)alanine],[2] and with 2-amino-4-phenylbutanoic acid (this work). The latter complex was investigated to discover if chelate-ring size plays an important part in effecting an interaction with the phenyl ring.

In the present study the nature of this phenyl-ring interaction has been investigated further by *X*-ray crystallography for the complexes with tyrosine (1; R = OH, n = 1) and 2-amino-4-phenylbutanoic acid

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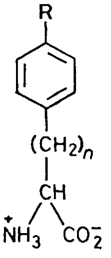
[1] D. L. Rabenstein, R. Ozubko, S. L. Libich, C. A. Evans, M. T. Fairhurst, and C. Suvanprakorn, *J. Co-ordination Chem.*, 1974, **3**, 263.

[2] A. J. Brown, O. W. Howarth, and P. Moore, *J.C.S. Dalton*, 1976, 1589; A. J. Brown, M.Sc. Thesis, University of Warwick, 1975.

[3] P. Moore, *J.C.S. Faraday I*, 1976, 826.

(1; R = H, *n* = 2). Tyrosine was used rather than 3-phenylalanine because it was difficult to grow crystals suitable for *X*-ray analysis with the latter.



(1)

There are other mercury-containing compounds in which a mercury–phenyl-ring interaction has been observed; for example, in [HgMe(SCH$_2$Ph)] (^{1}H n.m.r. studies[4]), in 3-arylpropylmercury(II) complexes (^{1}H n.m.r. and preliminary *X*-ray work),[5] and in Co[Hg$_2$(NCS)$_6$]·C$_6$H$_6$.[6] The present results are compared with other crystal structures reported recently involving methylmercury(II)–ligand interactions.[7–9]

EXPERIMENTAL

Synthesis and Study of Methyl(L-*tyrosinato*)*mercury*(II) *Hydrate*. (2).—Solutions of methylmercury(II) nitrate (0.55 g, 1.99 mmol) in water (30 cm^3) and L-tyrosine (0.36 g, 1.99 mmol) in water (30 cm^3) were mixed and the pH adjusted to *ca.* 7 with drops of HNO$_3$ or Na[OH]. The solution was reduced in volume to *ca.* 10 cm^3 on a rotary evaporator, and on standing white needles of the monohydrate precipitated. Intensity data from a crystal bounded by planes {001}, {100}, {101}, {011}, and {111} and size 0.006 × 0.009 × 0.019 mm were collected with a Syntex $P2_1$ four-circle diffractometer in the range $3 \leqslant 2\theta \leqslant 50°$ by the θ—2θ scan technique. In a preliminary data collection the crystals were found to decompose fairly rapidly, and the temperature was therefore kept at 173 K with a Syntex LT-1 attachment. Three check reflections were monitored after every 60 reflections and showed a 5% decay starting after *ca.* 20 h. These reflections were used to scale the data to a common level. A total of 1 078 observed reflections $[I/\sigma(I) \geqslant 3.0]$ was measured and corrected for absorption by the method of Alcock,[10] giving transmission factors in the range 0.321—0.609. The systematic extinction $0k0$ for $k = 2n + 1$ was observed, indicating space groups $P2_1/m$ or $P2_1$. The latter was selected because the crystal contained resolved asymmetric molecules. The crystal density was measured by flotation in chloroform–bromoform indicating two molecules per unit cell. The unit-cell dimensions and their estimated standard deviations (e.s.d.s) were obtained by a least-squares fit to 13 strong reflections. For crystal data see Table 1.

Synthesis and Study of [L-(2-*Amino*-4-*phenylbutanoato*)]-*methylmercury*(II), (3).—*Preparation*. DL-2-Amino-4-phenylbutanoic acid was prepared from diethyl acetamidomalonate by an extension of the method of Goldsmith and Tishler.[11] To t-butyl alcohol (125 cm^3) was added sodium (0.57 g, 0.025 cm^3) and the mixture was heated under reflux under nitrogen until the sodium dissolved. Diethyl acetamidomalonate (5.43 g, 0.025 mmol) was added to this warm stirred solution, followed by dropwise addition of (2-bromoethyl)benzene (BrCH$_2$CH$_2$Ph) (4.62 g, 0.025 mol). The mixture was heated under reflux for 6 h and then evaporated to dryness under reduced pressure. The residue was extracted with ethanol (250 cm^3) and the solution evaporated to dryness. Concentrated hydrochloric acid (10 cm^3) and water (40 cm^3) were added, and the mixture heated under reflux for 4 h. The resulting solution was neutralised with Li[OH], filtered, and then concentrated to 10 cm^3 on a rotary evaporator. This solution was left overnight in a refrigerator to form crystals which were filtered off and dried in air: ^{1}H n.m.r. in D$_2$O at δ 7.14 (m, 5 H, phenyl ring), 3.06 (m, 1 H, CH), 2.47 (m, 2 H, CH$_2$), and 1.68 p.p.m. (m, 2 H, CH$_2$).

TABLE 1

	Complex	
Crystal data	(2)	(3)
Molecular formula	$C_{10}H_{13}HgNO_3 \cdot H_2O$	$C_{11}H_{15}HgNO_2$
Colour	White	White
Habit	Needle	Needle
Crystal system	Monoclinic	Orthorhombic
a/Å	9.084 3(19)	14.853(4)
b/Å	6.150 6(15)	9.438(3)
c/Å	11.564 8(20)	8.755(2)
β/°	110.516(14)	
U/Å^3	605.18(22)	1 227.25(58)
T/K	173	173
Space group	$P2_1$	$Pca2_1$
μ/cm^{-1}	126.7	125.4
Relative molecular mass	413.6	393.6
D_m/g cm^{-3}	2.16	2.20
D_c/g cm^{-3}	2.27	2.13
Z	2	4
$N(3\sigma)$	1 078	674
λ(Mo-K_α)/Å	0.710 69	0.710 69

Aqueous solutions of methylmercury(II) nitrate (0.147 g, 0.5 mmol) and L-2-amino-4-phenylbutanoic acid (0.089 g, 0.5 mmol) were mixed, and the pH adjusted to *ca.* 7 with drops of HNO$_3$ or Na[OH]. The solvent was very slowly evaporated (over 2 weeks) and white needles of (3) were produced. A small crystal of dimensions 0.004 × 0.011 × 0.03 mm bounded by planes {100}, {010}, and {101} was selected and centred on the diffractometer. The observed systematic extinctions $0kl$ for $l = 2n + 1$ and $h0l$ for $h = 2n + 1$ were consistent with orthorhombic space groups $Pca2_1$ and $Pcam$. A density measurement made in chloroform–bromoform indicated four molecules per unit cell, consistent only with $Pca2_1$, in view of the lack of molecular symmetry, *i.e.* with the molecules having resolved on crystallisation. Intensity data were collected at 173 K as before. Three check reflections were monitored after every 50 reflections and showed a gradual decay of *ca.* 10%.

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[4] R. D. Bach and A. T. Weibel, *J. Amer. Chem. Soc.*, 1976, **98**, 6241.

[5] E. F. Kiefer, W. L. Waters, and D. A. Carlson, *J. Amer. Chem. Soc.*, 1968, **90**, 5127.

[6] R. Gronback and J. D. Dunitz, *Helv. Chim. Acta*, 1964, **47**, 1889.

[7] Y. S. Wong, A. J. Carty, and P. C. Chieh, *J.C.S. Dalton*, 1977, 1157, 1801.

[8] N. J. Taylor, Y. S. Wong, P. C. Chieh, and A. J. Carty, *J.C.S. Dalton*, 1975, 438.

[9] A. J. Canty and A. Marker, *Inorg. Chem.*, 1976, **15**, 425.

[10] N. W. Alcock, in 'Crystallographic Computing,' ed. F. Ahmed, Munksgaard, Copenhagen, 1970, p. 271.

[11] O. Goldsmith and M. Tishler, *J. Amer. Chem. Soc.*, 1946, **68**, 144.

These reflections were used to scale the data to a common level. A total of 674 observed reflections $[I/\sigma(I) \geqslant 3.0]$ was measured and corrected for absorption by the method of Alcock [10] giving transmission factors in the range 0.265—0.608. For crystal data see Table 1.

Structure Solution.—The structures were solved using the heavy-atom method involving a three-dimensional Patterson synthesis to locate the position of each mercury atom. The remaining atoms were located in subsequent electron-density maps and refined by minimising the function $\Sigma(F_o - F_c)^2$. The final refinement of complex (2) with anisotropic temperature factors for Hg, O(1), O(2), N, and C(1) gave an R factor of 0.044. The final refinement of complex (3) with anisotropic temperature factors for Hg and C(1) gave an R factor of 0.046. The handedness of crystal (3) was tested by carrying out a refinement with negative co-ordinates. The R value was unchanged but $\Sigma(F_o - F_c)^2$ was slightly lower with the original hand (corresponding to an L-amino-acid). This configuration for the particular crystal examined is, therefore, preferred, but from the available data cannot be regarded as conclusively demonstrated; the co-ordinates in Table 2 correspond to this hand. Unit weights were used throughout.

TABLE 2

Atomic co-ordinates ($\times 10^4$) with standard deviations in parentheses

Atom	*X*	*Y*	*Z*
(*a*) Complex (2)			
Hg	2 427.6(9)	2 500.0	431.9(7)
O(1)	1 697(18)	6 439(26)	901(14)
O(2)	910(17)	8 032(27)	2 299(15)
O(3)	8 399(14)	2 459(60)	3 626(11)
O(4)	9 462(17)	8 436(27)	3 945(13)
N(1)	788(16)	2 361(54)	1 404(14)
C(1)	3 727(36)	2 120(46)	−738(25)
C(2)	1 197(23)	6 374(36)	1 786(18)
C(3)	868(22)	4 192(35)	2 243(17)
C(4)	2 125(22)	3 573(36)	3 521(17)
C(5)	3 792(22)	3 280(32)	3 473(17)
C(6)	4 810(23)	5 054(37)	3 685(19)
C(7)	6 376(27)	4 712(38)	3 725(21)
C(8)	6 839(18)	2 785(50)	3 525(14)
C(9)	5 843(24)	903(36)	3 278(19)
C(10)	4 260(25)	1 279(38)	3 253(19)
(*b*) Complex (3)			
Hg	541.0(12)	1 212.3(7)	0.0
O(1)	2 512(27)	312(14)	1 710(24)
O(2)	1 785(29)	−805(17)	3 103(30)
N(1)	508(33)	−208(16)	−426(23)
C(1)	530(48)	2 610(21)	309(129)
C(2)	1 745(35)	−358(21)	1 954(34)
C(3)	562(42)	−783(23)	936(37)
C(4)	1 036(35)	−1 750(21)	513(34)
C(5)	−176(50)	−2 207(29)	−395(46)
C(6)	317(45)	−3 124(26)	−720(40)
C(7)	−169(40)	−3 862(26)	−22(132)
C(8)	371(52)	−4 787(26)	−304(50)
C(9)	1 335(56)	−4 904(35)	−1 227(51)
C(10)	1 931(56)	−4 173(31)	−2 111(61)
C(11)	1 484(51)	−3 262(29)	−1 812(51)

Scattering factors and anomalous-dispersion corrections from ref. 12 were used and all computation was carried out with the '*X*-RAY '76' programs [13] on a Burroughs B7600 computer. Final co-ordinates are in Table 2 and bond lengths and angles in Tables 3 and 4. Temperature factors and structure factors are listed in Supplementary Publication No. 22309 (18 pp.).*

TABLE 3

Bond lengths (Å) and angles (°) with standard deviations in parentheses for complex (2)

Hg–C(1)	2.12(5)	C(3)–C(4)	1.57(3)
Hg–N	2.17(2)	C(4)–C(5)	1.55(3)
Hg–O(1)	2.62(2)	C(5)–C(6)	1.40(3)
Hg–C(10)	3.19(2)	C(5)–C(10)	1.36(3)
Hg–C(5)	3.33(2)	C(6)–C(7)	1.42(3)
Hg–ring plane	3.11(2)	C(7)–C(8)	1.30(4)
C(2)–O(1)	1.26(3)	C(8)–C(9)	1.43(3)
C(2)–O(2)	1.25(3)	C(8)–O(3)	1.39(2)
C(2)–C(3)	1.51(3)	C(9)–C(10)	1.45(3)
C(3)–N	1.42(4)		
C(1)–Hg–N	169(1)	C(3)–C(4)–C(5)	113(2)
C(1)–Hg–O(1)	118.8(9)	C(4)–C(5)–C(6)	120(2)
N–Hg–O(1)	68(1)	C(4)–C(5)–C(10)	120(2)
Hg–N–C(3)	117(2)	C(6)–C(5)–C(10)	121(2)
Hg–O(1)–C(2)	109(1)	C(5)–C(6)–C(7)	119(2)
O(1)–C(2)–O(2)	123(2)	C(6)–C(7)–C(8)	121(2)
O(1)–C(2)–C(3)	119(2)	C(7)–C(8)–C(9)	123(2)
O(2)–C(2)–C(3)	117(2)	C(7)–C(8)–O(3)	120(3)
C(2)–C(3)–N	113(2)	C(9)–C(8)–O(3)	117(3)
C(2)–C(3)–C(4)	112(2)	C(8)–C(9)–C(10)	115(2)
N–C(3)–C(4)	108(2)	C(9)–C(10)–C(5)	121(2)

TABLE 4

Bond lengths (Å) and angles (°) with standard deviations in parentheses for complex (3)

Hg–C(1)	2.12(3)	C(4)–C(5)	1.48(5)
Hg–N	2.15(3)	C(5)–C(6)	1.46(5)
Hg–O(1)	2.72(2)	C(6)–C(7)	1.34(8)
Hg–O′(2)	2.78(3)	C(7)–C(8)	1.47(5)
C(2)–O(1)	1.22(4)	C(8)–C(9)	1.24(6)
C(2)–O(2)	1.27(4)	C(9)–C(10)	1.46(7)
C(2)–C(3)	1.56(5)	C(10)–C(11)	1.43(6)
C(3)–N	1.56(4)	C(11)–C(6)	1.48(6)
C(3)–C(4)	1.52(4)		
C(1)–Hg–N	177(2)	C(2)–C(3)–C(4)	113(3)
C(1)–Hg–O(1)	114(2)	N–C(3)–C(4)	108(3)
C(1)–Hg–O′(2)	109(2)	C(3)–C(4)–C(5)	112(3)
N–Hg–O(1)	68(1)	C(4)–C(5)–C(6)	110(3)
N–Hg–O′(2)	70(1)	C(5)–C(6)–C(7)	128(5)
O(1)–Hg–O′(2)	138(1)	C(5)–C(6)–C(11)	117(3)
Hg–N–C(3)	114(2)	C(6)–C(7)–C(8)	127(7)
Hg–O(1)–C(2)	99(2)	C(7)–C(8)–C(9)	117(5)
O(1)–C(2)–O(2)	124(3)	C(8)–C(9)–C(10)	123(4)
O(1)–C(2)–C(3)	127(3)	C(9)–C(10)–C(11)	119(4)
O(2)–C(2)–C(3)	108(3)	C(10)–C(11)–C(6)	118(4)
C(2)–C(3)–N	106(2)		

RESULTS AND DISCUSSION

A perspective view of molecule (2) is shown in Figure 2. The mercury atom is co-ordinated to tyrosine through the amino-group, and there are further interactions with a carboxylate oxygen and with the phenyl ring. The Hg–N bond length [2.17(2) Å] is approximately equal to the sum of the covalent radii of mercury (1.48 Å) and nitrogen (0.70 Å).[14] The Hg–C(1) bond length [1.12(5) Å] is also in the expected range for methylmercury(II) complexes.[7-9] The N–Hg–C(1) angle [169(1)°] is significantly distorted from linearity, apparently due to chelation of the carboxylate oxygen, O(1). The Hg–O(1)

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[12] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

[13] J. M. Stewart, University of Maryland, Report TR-446, March 1976.

[14] M. C. Bull and A. H. Nornury, 'Physical Data for Inorganic Chemists,' Longman, London, 1974, p. 140.

distance [2.62(2) Å] is greater than the sum of the covalent radii (2.14 Å) although considerably shorter than the sum of the van der Waals radii (2.90—3.13 Å).

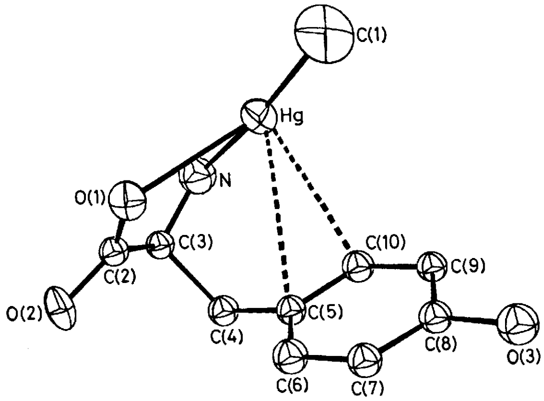

FIGURE 2 Molecular structure of complex (2)

This chelation by the carboxylate group was expected from a study of both ^{1}H and ^{13}C n.m.r. spectra.[2]

The previously postulated interaction between methylmercury(II) and the aromatic ring [1,2] appears to be due to a mercury–ring interaction rather than to a methyl group–aromatic-ring hydrophobic interaction. The mercury–ring distance is comparable with two previous observations of 3.05 [5] and 3.30 Å,[15] and rather shorter than the value (3.52 Å) observed in Co[Hg$_2$(SCN)$_6$]·C$_6$H$_6$.[6] The distance between the mercury atom and the plane of the ring is 3.11(2) Å while the C(1)–ring distance is 4.40(2) Å. The ring carbon atoms and O(3) are coplanar within experimental error, although C(4) is 0.14 Å out of the plane of the ring on the side away from the mercury atom. As shown by the non-planarity of C(4), the phenyl ring is so constrained that a closer mercury–aromatic interaction cannot occur.

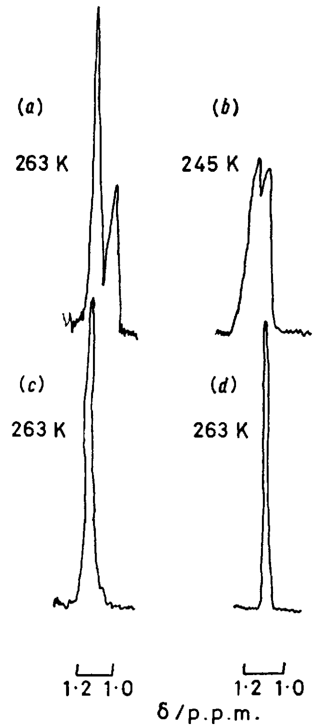

FIGURE 3 Parts of the 90-MHz ^{1}H n.m.r. spectra (in the methyl region) of complex (3) at pH 4.0 (*a*), 5.8 (*b*), 1.9 (*c*), or 7.0 (*d*)

Complex (3) was prepared in an attempt to remove the constraint which prevents any closer interaction between mercury and the aromatic ring. Its solution ^{1}H n.m.r. spectrum (Figure 3) demonstrates the presence of an equilibrium analogous to (1), the behaviour being very similar to that observed for the 1 : 1 complexes of methylmercury(II) with 3-phenylalanine, tyrosine, and L-dopa.[2] However, the methyl resonance found for (3) is at lower field than that observed in related systems, where a methylmercury(II)–phenyl ring interaction is present (Table 5). The resonances are in fact typical of simple amine-bound species,[1,2] with no evidence for the expected upfield shift arising from the close proximity of the methyl group to the aromatic ring current.[4] This observation is in complete accord with the structure in

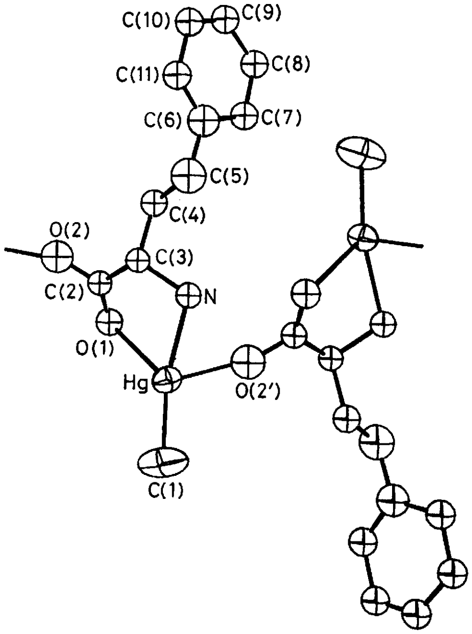

FIGURE 4 Molecular structure of complex (3)

TABLE 5

Hydrogen-1 chemical shifts (δ/p.p.m. relative to SiMe$_4$) of HgMeX in D$_2$O

HX	*N*-bound species	*O*-bound species	*T*/K
L-Phenylalanine	0.14	0.81	270
L-Tyrosine	0.22		270
L-Dopa	0.44	1.04	270
2-Phenylethylamine	0.43		303
3-Phenylpropylamine	0.99 *		303
2-Amino-4-phenylbutanoic acid	1.02 *	0.93	263

* Typical of amine-bound complexes and indicates the absence of a mercury–phenyl-ring interaction.

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[15] R. D. Bach, A. T. Weibel, W. Schmonsees, and M. D. Glick, *J.C.S. Chem. Comm.*, 1974, 961.

the crystal, where the molecule adopts an extended conformation with no mercury–aromatic interaction (Figure 4). Instead there is an intermolecular Hg–O bond as well as the previously observed intramolecular Hg–O bond between the mercury atom and the carboxylate groups. The primary binding of the amino-acid to mercury is as before through the amino-group, the Hg–N bond length [2.15(2) Å] being very close to that observed previously. The N–Hg–C(1) angle [177(2)°] is virtually linear unlike that of (2), perhaps because both O(1) and O′(2) are bonding, on opposite sides of the N–Hg–C(1) bond. The O(1)–Hg–O′(2) angle [138(1)°] is far from linear, and the mercury–oxygen bond lengths Hg–O(1) [2.72(2) Å] and Hg–O′(2) [2.78(3) Å] are notably longer than that found in (2) [2.62(2) Å] but still considerably shorter than the sum of the van der Waals radii.

Hydrogen Bonding and Packing.—In complex (2) (Figure 5), each oxygen atom O(4) of the molecule of water of crystallisation forms hydrogen bonds to three atoms arranged tetrahedrally; these are part of three separate molecules, the carboxylate oxygen O(2), the phenolic oxygen atoms O′(3) of the molecule translated one unit cell along *b*, and oxygen O″(3) of the molecule translated by the screw axis. The nitrogen atom is hydrogen-bonded to the carboxylate oxygen O′(2) of the molecule translated one unit cell along *b* and the carboxylate oxygen O″(1) of the molecule translated by the screw axis. Overall, therefore, the molecules are linked into a three-dimensional framework. The hydrogen-bond lengths and angles are in Table 6. In complex (3) (Figure 6) there are two principal packing forces, together with the Hg–O′(2) interaction. There are N · · · O′(2) and N · · · O″(2) hydrogen bonds at the edge of the unit cell which, together with the Hg–O(2) interaction, link the molecules into sheets. These are held together by hydrophobic interactions between the phenyl rings in the middle of the unit cell.

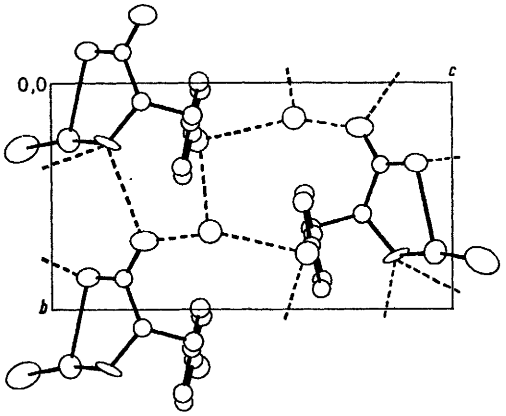

FIGURE 5 Crystal-packing diagram of complex (2) viewed along *a*

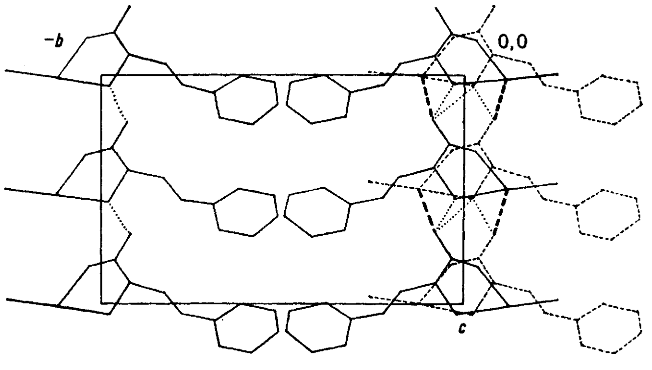

FIGURE 6 Crystal-packing diagram of complex (3) viewed along *a*. Molecules shown with full lines have Hg at $x = 0.55$, those with broken lines have Hg at $x = -0.05$ and 0.95

TABLE 6

Hydrogen bond lengths (Å) and angles (°) for complexes (2) and (3) with standard deviations in parentheses

(*a*) Bond lengths

Complex (2)		Complex (3)	
O(4) · · · O(2)	2.68(3)	O(2) · · · N′	2.90(4)
O(4) · · · O′(3)	2.64(4)	O(2) · · · N″	2.89(4)
O(4) · · · O″(3)	2.86(3)	O(2) · · · Hg′	2.78(3)
N · · · O′(2)	2.89(4)		
N · · · O″(1)	2.90(3)		

(*b*) Bond angles

Complex (2)		Complex (3)	
O(2) · · · O(4) · · · O′(3)	103.6(8)	N′ · · · O(2) · · · N″	100(1)
O(2) · · · O(4) · · · O″(3)	110.1(6)	Hg′ · · · O(2) · · · N′	44(1)
O′(3) · · · O(4) · · · O″(3)	115.1(9)	Hg · · · O(2) · · · N″	109(1)
		C(3) · · · N · · · O(2)	135(2)
		C(3) · · · N · · · O′(2)	101(2)

In (2) the phenolic oxygen O(3) is intimately involved in the hydrogen-bonding pattern, while in (3) there is only a hydrophobic interaction involving the phenyl rings, which may in part at least explain the radically different structures.

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