Methyl- and Phenyl-mercury(II) Derivatives of 2-Mercaptopyridine. Crystal and Molecular Structure of Methyl(pyridine-2-thiolato)mercury(II)†

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The compounds [HgR(L)] (R = Me or Ph, L = pyridine-2-thiolate) have been isolated by reaction of HL with methylmercury(II) hydroxide and phenylmercury(II) acetate, respectively. The crystal structure of the methyl derivative has been determined at 190 K. The compound crystallizes in the monoclinic space group $P2_1/n$ with a = 10.834(5), b = 4.206(3), c = 17.144(2) Å, β = 101.91(1)°, and Z = 4. Refinement converged to R = 0.036 for 1 676 independent observed reflections. The pyridine ligand is co-ordinated to mercury by the thiolate sulphur atom [Hg–S 2.374(2) Å]. The intramolecular mercury–nitrogen distance of 2.980(5) Å is shorter than the sum of the van der Waals radii. The vibrational spectra of the compounds are discussed. The ^{13}C n.m.r. spectra in chloroform and a dipole-moment study in benzene suggests that the secondary mercury–nitrogen interaction is maintained in these solutions.

The co-ordination chemistry of the cation $HgMe^+$ has been a subject of increasing attention,[1] largely owing to the desire to understand its toxicological behaviour and to find effective chemical antidotes. As the number of its compounds whose structures have been determined by *X*-ray diffraction studies has risen,[2] it has become clear that the co-ordination of the mercury atom can be more complex than that of simple linear two-co-ordination, if the bound ligand possesses further donor atoms in positions enabling the formation of 'secondary bonds'.[3] The same situation has been detected among the compounds of $HgPh^+$, though less research has so far been carried out on this ion.[4]

This article reports the results obtained during an investigation on the presence of secondary bonds in $HgMe^+$ and $HgPh^+$ compounds of deprotonated 2-mercaptopyridine (HL). In solution, the free ligand adopts the thione form,[5] but on binding to the organomercury ions it changes to the thiol form in which the nitrogen atom is able to function as a donor. Earlier spectroscopic studies of [HgMe(L)] have suggested that secondary bonds are present in the solid state[6] but not in $CDCl_3$ solution.[7] Our own conclusions, based on *X*-ray difraction, spectroscopic, ^{13}C n.m.r., and dipole-moment data, are that in [HgMe(L)] there is a weak interaction between the nitrogen and mercury atom in the solid state, in deuteriochloroform, and in benzene, and that the same is probably true for the phenylmercury derivative, too.

Experimental

2-Mercaptopyridine (Sigma), methylmercury(II) chloride (ROC/RIC), and phenylmercury(II) acetate (Fluka 'purum') were used as received. Di-2-pyridyl disulphide was prepared by the method of Masaki and Matsunami.[8] Analytical data (C, H) were obtained from Galbraith Lab. Inc., Knoxville, Tennessee and mercury analyses were carried out using a Varian AA-6 atomic absorption spectrometer after sample digestion with a mixture of concentrated nitric and sulphuric acids (1:1, v/v). Melting points were determined in a Electrothermal apparatus. Molecular weights were measured in benzene with a Knauer vapour-pressure osmometer and dipole moments were determined in the same solvent at 25 °C as reported previously.[9] Infrared spectra were recorded as Nujol mulls or KBr discs on a Perkin-Elmer 180 spectrometer, Raman spectra on a 500 Jarrell-ASH spectrometer (argon-ion laser, 5 145 Å), and ^{13}C n.m.r. spectra on a Bruker WM250 apparatus ($CDCl_3$ solutions).

Preparation of [HgMe(L)].—A solution of methylmercury hydroxide was prepared by stirring [HgMeCl] (0.73 g, 2.9 mmol) and freshly precipitated Ag_2O (0.36 g) for 24 h in water (*ca.* 100 cm^3). To this solution, 2-mercaptopyridine (0.34 g, 3.0 mmol) in methanol (*ca.* 30 cm^3) was added. On addition of the mercaptan a white precipitate was formed immediately. The solid was recrystallized from methanol by slow evaporation of solvent; m.p. 54—55 °C (lit.,[6] 53 °C) (Found: C, 22.0; H, 2.20. Calc. for C_6H_7HgNS: C, 22.1; H, 2.15%); *M* (ebullioscopy) 323 (calc. 326).

Preparation of [HgPh(L)].—When to a solution of phenylmercury(II) acetate (1.57 g, 4.7 mmol) in methanol (50 cm^3) was added a solution of 2-mercaptopyridine (0.52 g, 4.7 mmol) in methanol (25 cm^3) a white precipitate was formed. Recrystallization from methanol yielded a crystalline solid, m.p. 82—83 °C (Found: C, 34.1; H, 2.45; Hg, 51.1. Calc. for $C_{11}H_9HgNS$: C, 34.15; H, 2.35; Hg, 51.7%); *M* (ebullioscopy) 380 (calc. 388).

For the dipole-moment study, the following compounds were also prepared using procedures analogous to those outlined above: (4-chlorothiophenolato)methylmercury(II), m.p. 63 °C (lit.,[6] 63 °C) (Found: C, 23.6; H, 1.95. Calc. for C_7H_7ClHgS: C, 23.4; H, 1.95%); methyl(thiophenolato)mercury(II), m.p. 91—92 °C (lit.,[6] 92 °C) (Found: C, 26.0, H, 2.50. Calc. for C_7H_8HgS: C, 25.9; H, 2.50%).

Crystal Structure Determination.—The complex [HgMe(L)] was obtained as white needles. For all measurements the temperature was 190 K to avoid decomposition of the compound in the *X*-ray beam. Unit-cell dimensions were deter-

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Supplementary data available (No. SUP 56567, 3 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Non-S.I. unit employed: D ≈ 3.33 × 10^{-30} C m.

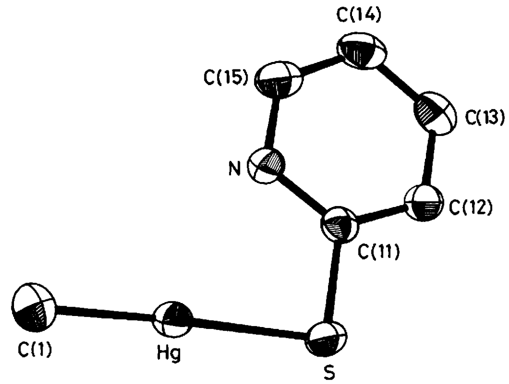

Figure 1. Structure of [HgMe(L)] with numbering scheme and thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted

Table 1. Fractional atomic co-ordinates for [HgMe(L)] with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z
Hg	0.370 76(4)	0.208 4(1)	0.060 29(2)
S	0.554 9(3)	0.517 4(8)	0.105 8(2)
N	0.406 7(8)	0.579(2)	0.211 5(5)
C(1)	0.204(1)	−0.040(4)	0.015 3(7)
C(11)	0.520 1(9)	0.660(3)	0.196 4(6)
C(12)	0.606(1)	0.843(3)	0.246 0(6)
C(13)	0.580(1)	0.949(3)	0.317 0(6)
C(14)	0.466(1)	0.867(3)	0.334 9(6)
C(15)	0.384(1)	0.687(3)	0.281 4(6)

Table 2. Selected distances (Å) and angles (°) with e.s.d.s in parentheses. Superscripts I and II represent the equivalent positions (x, $y - 1$, z) and ($1 - x$, $1 - y$, $-z$), respectively

Hg–S	2.374(2)	Hg···N	2.980(5)
Hg–C(11)	2.089(7)	$Hg \cdots S^{I}$	3.520(2)
S–C(11)	1.776(6)	$Hg \cdots S^{II}$	3.322(2)
S–Hg–C(1)	176.4(2)	Hg–S–C(11)	99.0(2)

mined on an Enraf-Nonius CAD4 automated four-circle diffractometer by least-squares refinement of 25 reflections. Systematic extinctions were characteristic of the space group $P2_1/n$.

Crystal data. C_6H_7HgNS, $M = 325.78$, monoclinic, space group $P2_1/n$ (derived from $P2_1/c$, no. 14), $a = 10.834(5)$, $b = 4.206(3)$, $c = 17.144(2)$ Å, $\beta = 101.91(1)°$, $U = 764.3$ Å^3, $Z = 4$, $D_c = 2.834$ g cm^{-3}, $F(000) = 584$, μ(Mo-K_α) = 203.32 cm^{-1}, specimen size 0.10 × 0.15 × 0.12 mm, $T = 190$ K, 99 parameters, S (the e.s.d. of an observation of unit weight) = 3.107.

Intensity data in the range $3 < \theta < 28°$ were collected by the ω—θ scan mode using graphite-monochromated Mo-K_α radiation. For the 3 885 reflections measured, Lorenz and polarization corrections and an empirical absorption correction[10] were performed. Averaging equivalent reflections gave 1 931 unique reflections ($R_{int} = 0.023$), of which 1 676 with $I > 3\sigma(I)$ were used for all calculations. The positions of the Hg and S atoms were taken from the Patterson map. Subsequent Fourier difference synthesis revealed the position of the N,C atoms and the H atoms of the pyridine ring. Methyl hydrogen atoms were not found. Full-matrix refinement, with anisotropic thermal parameters for heavy atoms, isotropic ones for hydrogen atoms, and an extinction correction in the form $F_{corr} = F_c(1 + kF_c{}^2/\sin 2\theta)^{0.25}$ with $k = 1.759 \times 10^{-7}$, converged to $R = 0.036$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.044$. Scattering factors and anomalous dispersion corrections were taken from ref. 11. Calculations were performed with SDP program system[12] on a PDP 11/60 computer.

Results and Discussion

Description of the Structure.—The atomic numbering used is shown in Figure 1, the fractional atomic co-ordinates in Table 1, and bond lengths and angles in Table 2.

With a bond angle of 176.4(2)°, the S–Hg–C(1) fragment is almost linear. The Hg–S and Hg–C(1) bond lengths are those of covalent single bonds and are within the ranges previously found in other $HgMe^+$ complexes.[2] The S–C(11) distance of 1.776(1) Å is that of a single bond as expected for the thiol form of the ligand. The ring parameters differ only slightly from those of the free ligand,[13] the most important changes being the N–C(11) and C(11)–C(12) distances, which are shortened by the recovery of aromaticity in the ring. The dihedral angle between the C(1)–Hg–S–C(11) plane and the pyridine ring is only 2.2°. Thus the molecule is almost planar, and the largest deviation from the least-squares plane is 0.05 Å.

The above geometry places the mercury atom 2.980(5) Å from the pyridine nitrogen. If the value of 1.73 Å recently proposed by Carty and Deacon[14] for the van der Waals radius of mercury is accepted, the sum of the two van der Waals radii is 3.2 Å. There is therefore a secondary bond between the mercury and nitrogen atom, as was suggested by Carty and Marker[6] based on spectroscopic data (see below). Similar structures have been found in methylmercury(II) complexes with 2-mercaptopyrimidine[15,16] and 1-methylimidazoline-2-thione.[17,*] The mechanism tentatively suggested by Domazetis *et al.*[18] for the formation of such bonds in a complex of di-n-butyltin(IV) with 2-mercapto-5-nitropyridine involves *d* orbitals, and more recently Atwood *et al.*[19] have reviewed a number of possibilities for the orbital description of N···Hg secondary bonds.

In addition to the intramolecular N···Hg interaction, there are two sulphur atoms of neighbouring molecules around the Hg atom [(x, $y - 1$, z) and ($1 - x$, $1 - y$, $-z$)]. One of these, S^{II}, is at a distance from the mercury atom shorter than the sum of the van der Waals radii (3.5 Å[14,20]). The other, S^{I}, is at a longer one [3.520(2) Å]. Therefore, the co-ordination sphere of the metal atom contains an additional weak interaction, which, together with the Hg···N bond, completes the main four-co-ordination, or a distorted trigonal bipyramid if S^{I} is included (Figure 2).

Vibrational Spectra.—The analysis of the most important i.r. and Raman bands of the free ligand, the complexes, and di-2-pyridyl disulphide in the range 1 600—1 400 cm^{-1} confirms previous suggestions[8] about the utility of this spectral zone for establishing the mesomeric form adopted by the ligand. No conclusions about the secondary bond can be drawn on the basis of the very weak shifts observed for the ligand vibrations nor from the analysis of the organometallic vibrations.

The very low position of ν(Hg–S) for the methylmercury(II) compound (233 cm^{-1}) has been considered[7] to be an effect of the Hg···N bond. In fact, the phenyl derivative shows an absorption band at 224 cm^{-1} (220vs, Raman) whose assignment as the band with the greatest contribution from ν(Hg–S) is supported by the relationship between the intensities of the ring *t* mode in the i.r. and Raman spectra.[21] It is nevertheless difficult to see why a secondary interaction that has no significant effects on the other vibrational characteristics of the complex should

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[*] The Hg–N(3) distance in this compound is 3.0 Å (A. L. Beauchamp, personal communication).

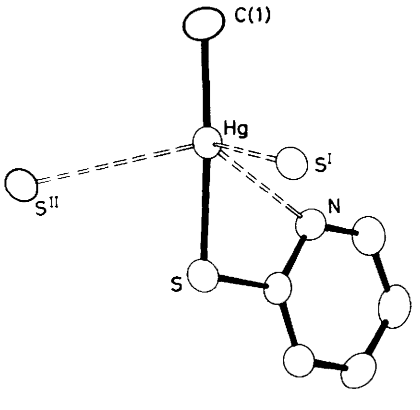

Figure 2. Structure of [HgMe(L)] showing the co-ordination around Hg

give rise to so large a shift in ν(Hg–S), and we think that this band may not be a pure vibration but the result of coupling between the sulphur–mercury stretching and a ligand mode.

The complexes studied are soluble in organic solvents such as cyclohexane, benzene, chloroform, and dimethyl sulphoxide, and molar conductivity measurements show that ionogenous solvents such as acetonitrile fail to produce significant concentrations of ionic species ($\Lambda < 1$ ohm^{-1} cm^{2} mol^{-1}).[22] When the i.r. and Raman spectra of [HgMe(L)] are recorded in cyclohexane, the bands discussed above undergo only a slight shift towards higher frequencies, so it seems that the main structural characteristics in the solid state are unaltered in this solvent.

^{13}C *N.M.R. Spectra.*—The inconclusive vibrational results can be resolved by the ^{13}C n.m.r. spectra. According to Pugmire and Grant,[23] the *ortho-*, *meta-*, and *para-*carbons of the pyridine ring are affected differently when the lone pair on the nitrogen atom is involved in bonding (*e.g.* on protonation). Whereas the *meta-* and *para-*carbon signals show a downfield shift, the α-carbons are shielded. This behaviour has been explained in terms of the bond order, which is reduced by the new interaction of the nitrogen atom.[23]

Table 3 shows the positions of the signals of the two mercury complexes and of the S-methylated ligand, which is a better reference system than the free ligand itself because like the complexes it contains the thiol form. Atoms C(11) and C(12) undergo strong deshielding induced by the bond with the metal atom. This effect diminishes as the distance from the substituted carbon increases, and is almost imperceptible in C(14). On the other hand, C(15) is shifted towards high field, and the possibility that this shift may be due to the persistence of the secondary bond involving the nitrogen lone pair is supported by the extent of the shift (*ca.* 1.5 p.p.m.) which is lower than expected for an ordinary bond,[23] and that it is also present in the spectrum of the phenylmercury complex.

Table 3. ^{13}C N.m.r. spectra (p.p.m. from $SiMe_4$ in $CDCl_3$ as solvent)

Compound	C(11)	C(12)	C(13)	C(14)	C(15)	Me or Ph
$NC_5H_4(SMe-2)$	159.9	121.4	135.7	119.0	149.3	13.2
[HgMe(L)]	165.16	125.70	136.51	118.97	147.60	11.08
[HgPh(L)]	164.70	125.13	136.55	119.18	147.74	159.6 136.7 128.9 128.7

Table 4. Dipole moments (benzene, 25 °C)

Compound	μ/D
[HgMe(L)	1.7
a	2.2
b	2.8
[HgPh(L)]	1.7

[a] Methyl(thiophenolato)mercury(II). [b] (4-Chlorothiophenolato)methylmercury(II).

Dipole Moments.—The dipole moments of the compounds can also be used as evidence of any conformational preferences in solution. Table 4 shows the dipole moments in benzene of [HgMe(L)], [HgPh(L)], and two relevant compounds. The dipole moment of [HgMe(L)] is determined by the moments of the pyridine (2.2 D)[24] and the SHgMe 'group', which, mesomeric effects apart, may be taken as approximately the same as that of methyl(thiophenolato)mercury(II) (see Table 4). The orientation of SHgMe with respect to the S–C(11) bond can be deduced from the dipole moment of (4-chlorothiophenolato)methylmercury(II) if we bear in mind that the latter is the resultant of the components SHgMe and Cl (1.6 D).[25] The value of θ obtained in this way (*ca.* 86°) is quite plausible since the moments of SHgMe must be determined by the moment of the S–Hg bond, whose angle θ (*ca.* 99° in the solid state) will be reduced by the contribution from the C–S bond.

If the SHgMe group retains the same orientation in solution as in the solid state (with the mercury atom adjacent to the nitrogen), there will be an angle of about 154° between the pyridine and SHgMe moments, giving a value of *ca.* 1.0 D for [HgMe(L)]. If, on the other hand, the mercury atom lies in the plane of the ring but adjacent to C(12), the resulting moment will be 4.2 D. If there is free rotation,[26] the moment is 3.2 D. The experimental results seem to support the hypothesis that a large proportion of [HgMe(L)] molecules in benzene solution retain a conformation involving the Hg • • • N secondary bond. The same must also be true for the phenylmercury(II) complex, whose dipole moment is similar to that of the methylmercury(II) compound.

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