Methyl(2-mercapto-4-methylpyrimidinato)mercury(II): a Methylmercury(II) Derivative with an Unusual Metal–Metal Interaction

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4-Methylpyrimidine-2-thione reacts with methylmercury hydroxide to give the thiolate derivative $HgMe(SC_4H_2N_2Me\text{-}2)$, the *X*-ray structure of which reveals pairs of molecules with a mercury–mercury distance of 3.10 Å.

For theoretical and toxicological reasons there has been a growing interest in the co-ordination chemistry of organomercuric derivatives. Structural studies using *X*-ray diffraction have shown that the co-ordination sphere of the mercury atom in these compounds always contains two strongly bonded ligands in an almost linear arrangement and can also contain other donors atoms bonded by weaker interactions; the possible metabolic interest of this has already been pointed out.[1]

As part of our study of methylmercury(II) co-ordination by mercapto-derivatives of pyridine and pyrimidine, we report here the preparation and structure of the compound formed by 4-methyl-2-mercaptopyrimidine and $MeHg^{II}$ that shows in the solid state a very short mercury–mercury distance.

The compound was prepared in water by the reaction of methylmercury(II) hydroxide [prepared from methylmercury(II) chloride and silver(I) oxide, freshly precipitated] with 4-methylpyrimidine-2-thione hydrochloride (HCl·HMePym) partially neutralized with sodium hydroxide. The yellow solid isolated was recrystallized from methanol as needles of HgMe(MePym) (**1**).†

The i.r. spectrum of (**1**) suggests co-ordination of the ligand in its thiol form.‡ This was verified by an *X*-ray crystal structure determination of a single crystal of (**1**). *Crystal data:* $C_6H_8N_2SHg$, $M = 340.8$, monoclinic, space group $C2/c$, $a = 18.281(4)$, $b = 12.170(4)$, $c = 17.350(5)$ Å, $\beta = 154.20(7)°$, $U = 1680(2)$ Å^3, $Z = 8$, $D_c = 2.690$ g cm^{-3}. 3698 Reflections were collected on an Enraf–Nonius CAD-4 instrument with Mo-K_α radiation merged to 1840 unique reflections of which 930 with $I > 3\sigma(I)$ were used in the structure solution to give $R = 0.076$ and $R_w = 0.078$. Hg co-ordinates were derived by the Patterson method. All other non-hydrogen atoms were located *via* standard Fourier techniques. The structure is shown in Figure 1.§

HgMe(MePym) HgMe(Pym)
(**1**) (**2**)

The intramolecular distances and angles closely resemble those observed in the pyrimidine-2-thione derivative HgMe(Pym)[4] (**2**) except for the C–S and N(1) · · · Hg distances. The latter is larger in the methylated compound but still shorter than the sum of the van der Waals radii.[5] Furthermore (**1**) shows two intermolecular interactions not present in (**2**): a weak one between the mercury atom of one molecule and a sulphur atom of a neighbouring one and another one that involves two mercury atoms separated by a distance of 3.10 Å, clearly less than the sum of the van der Waals radii,[5] and which to the authors' knowledge is previously unknown in methylmercury compounds. {Note that the mercury–mercury distances in mercurous compounds are close to 2.5 Å, although in $Hg[N_2(COMe)_2]_2$ a value of 2.9 Å has been observed.[6]} The mutual arrangement of molecules enables the 6p orbital not involved in the sp hybrids responsible for the Hg–C and Hg–S (intramolecular) bonds, to be involved in the mercury–mercury interaction; the molecular packing can thus be

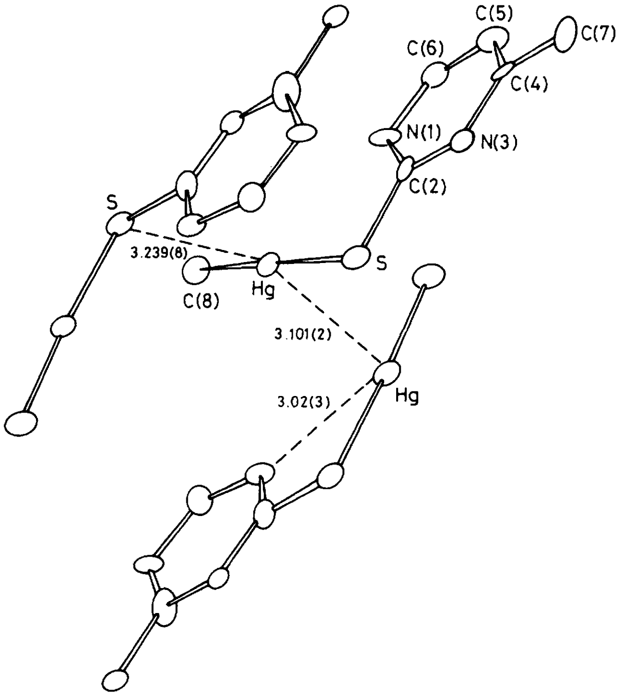

Figure 1. A view of the compound $HgMe(SC_4H_2N_2Me\text{-}2)$ showing a partial atom labelling scheme. Some important intramolecular distances (Å) and angles (°) are: C(8)–Hg, 2.15; Hg–S, 2.437(8); S–C(2), 1.81(3); C(8)–Hg–S, 176(1); Hg–S–C(2), 99.3(7).

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† Microanalytical data and conductivity measurements in MeCN [Λ (10^{-3} M) = 0.5 ohm^{-1} cm^2 mol^{-1}] are fully in accord with this formulation.

‡ The spectrum shows no bands assignable to ν(N–H) (3080 cm^{-1} in the free ligand) and it has the usual pattern observed in the spectra of the *S*-methylated or disulphide derivatives of similar ligands.[2] δ_{sym}Me (1170 cm^{-1}) and ν(Hg–C) (545 cm^{-1}) are placed in the typical range for the mercury atom co-ordinated by thiolic sulphur.[3] A band of medium intensity at 329 cm^{-1} compatible with ν(Hg–S) supports this idea.

§ Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

described as a collection of pairs of molecules associated *via* mercury atoms.

The origin of this peculiarity of (**1**) absent in (**2**) is difficult to explain with the data available, but seems to exist only in the solid state. Thus, (**1**) shows in benzene a molecular weight in agreement with isolated molecules [*M* (ebulloscopy), 348].

The ^{1}H n.m.r. spectrum of (**1**) in $CDCl_3$ has, for the organometallic part of the compound, the same spectral pattern as that for (**2**) [δ(Hg–Me) 0.95 and 0.98; $^2J(^1H-^{199}Hg)$ 170.8 and 171.5 Hz, respectively].¶ The signals for the H-5 and H-6 protons in (**1**) are shifted slightly to higher field relative to the corresponding signals in (**2**), but this can be due to an inductive effect of the 4-methyl group. Finally, the dipole moment of (**1**) (3.6 D) is similar to that observed for (**2**) (3.2 D) under the same measurement conditions (benzene, 298 K).

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¶ Compound (**2**) was prepared for comparative purposes following a similar procedure to that outlined for (**1**).