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Methylmercury Derivatives of Mercaptopyrimidines: Structures of (4-Amino-5-methyl-2-pyrimidinethiolato)methylmercury(II) and (4-Amino-2-mercapto-6-pyrimidinonato)methylmercury(II) Monohydrate

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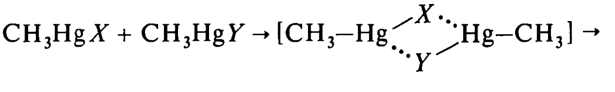
Abstract

$[Hg(CH_3)(C_5H_6N_3S)]$ (I) and $[Hg(CH_3)(C_4H_4N_3OS)].H_2O$ (II) crystallize in the space group $P2_1/c$ with $a = 11{\cdot}932\,(6)$, $b = 5{\cdot}824\,(3)$, $c = 12{\cdot}895\,(6)$ Å, $\beta = 99{\cdot}75\,(6)°$, $Z = 4$, and $a = 7{\cdot}312\,(4)$, $b = 8{\cdot}702\,(4)$, $c = 14{\cdot}911\,(7)$ Å, $\beta = 94{\cdot}43\,(5)°$, $Z = 4$, respectively. The structures were refined to a final R of 0·059 and 0·096 respectively. In both structures CH_3Hg^+ is bonded to S with a secondary intramolecular interaction to N, while in (I) there is an additional intermolecular interaction to S.

Introduction

The behaviour of the methylmercury ion, CH_3Hg^+, in biological systems is governed, for the most part, by its coordination chemistry. This ion has a strong preference for unifunctionality and, in biological ligands, sulphhydryl groups are the favoured binding sites (Rabenstein, 1978). The observation that Hg^{II} compounds denature native DNA's (Katz, 1952) and that CH_3Hg^+ causes chromosome damage and is consequently mutagenic has provided the stimulus for detailed studies of its binding to nucleosides and nucleotides in general, as well as to modified bases such as 4-thiouridine which occur in transfer RNA's (Maguire, 1976). Toxicology studies have shown methylmercury in biological complexes to be labile and there is evidence, from mechanistic studies, that exchange may take place *via* a four-centred bridged intermediate (Bach & Weibel, 1976):



$$CH_3HgX + CH_3HgY \rightarrow [CH_3{-}Hg\overset{X}{\underset{Y}{\diamond}}Hg{-}CH_3] \rightarrow CH_3HgY + CH_3HgX. \quad (1)$$

We have established the structure of two methylmercury–sulphur-substituted pyrimidine complexes in the solid state. The ligands are cytosine derivatives: 4-amino-5-methyl-2-pyrimidinethiol and 4-amino-2-mercapto-6-pyrimidinone. In the light of previous work, it was predicted that Hg would bind to the deprotonated thio group of the 2-mercaptopyrimidine moiety but it was not known how the N and O atoms would interact with the metal.

Experimental

An aqueous solution of methylmercury(II) acetate (1 mmol) was added to an aqueous solution of a mixture of the thiobase (1 mmol) and sodium hydrogen carbonate (1 mmol). The resulting precipitate was filtered and recrystallized from hot acetone. Crystals were grown from a solution of the complex in a mixture of Me_2SO, acetone and water.

Lattice constants were obtained by least squares from the settings of 25 reflections measured on a four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). Intensities were collected on the diffractometer and three reference reflections were monitored periodically to check crystal stability. The crystal data and experimental details of the data collection are listed in Table 1. The data were corrected for Lorentz–polarization effects but not for absorption.

Solution and refinement of the structures

The 5-methyl complex (I) was solved by locating the Hg atom in a Patterson map and then the remaining non-hydrogen atoms in a subsequent difference map. Least-squares refinement, in which both the Hg and S atoms were treated anisotropically, revealed the H atoms of the amino group. All the H atoms were constrained to ride at 1·00 (for N—H) or 1·08 Å (for C—H) from the atoms to which they were bonded, their positions being dictated by the geometry of the molecule. The methyl H atoms were refined as a rigid group. The isotropic temperature factors of the H

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Table 1. *Crystal data and experimental and refinement parameters for* (I) *and* (II)

	(I)	(II)
Crystal data		
Molecular formula	$C_6H_9HgN_3S$	$C_5H_7HgN_3OS.H_2O$
M_r	355	375
Space group	$P2_1/c$	$P2_1/c$
a	11·931 (6) Å	7·312 (4) Å
b	5·824 (3)	8·702 (4)
c	12·895 (6)	14·911 (7)
β	99·75 (6)°	94·43 (5)°
D_m	2·64 Mg m^{-3}	2·59 Mg m^{-3}
D_c for $Z = 4$	2·67	2·63
μ(Mo $K\alpha$)	16·96 mm^{-1}	15·84 mm^{-1}
F(000)	652	648
Data collection		
Scan mode	ω–2θ	ω–2θ
Scan width	1·2° θ	1·2° θ
Scan speed	0·04° θ s^{-1}	0·04° θ s^{-1}
Range scanned (2θ)	3–25°	3–23°
Stability of standard reflections	1·5%	3%
Number of reflections collected	1719	1415
Number of observed reflections [I(rel.) > $2\sigma I$(rel.)]	1313	1125
Final refinement		
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0·059	0·096
$R_w = \sum w^{1/2}\|\|F_o\| - \|F_c\|\|/\sum w^{1/2}\|F_o\|$	0·062	0·099
Weighting scheme, w	$(\sigma^2 F + 0{\cdot}0089F)^{-1}$	$(\sigma^2 F + 0{\cdot}021F)^{-1}$
U(amino H)	0·031 Å^2	0·052 Å^2
U(methyl H)	0·177	0·050
U(aromatic H)	0·177	0·059

Table 2. *Fractional atomic coordinates* ($\times 10^3$; *for* Hg *and* S $\times 10^4$) *and temperature factors* (Å^2 $\times 10^3$) *for the non-hydrogen atoms of* (I), *with e.s.d.'s in parentheses*

	x	y	z	U
Hg	926 (1)	1905 (1)	926 (1)	*
S	1695 (3)	4854 (7)	−39 (2)	*
C(2)	253 (1)	609 (2)	110 (1)	29 (3)
C(4)	307 (1)	595 (2)	287 (1)	26 (3)
C(5)	373 (1)	802 (2)	285 (1)	31 (3)
C(51)	440 (1)	909 (3)	381 (1)	48 (4)
C(6)	363 (1)	901 (3)	183 (1)	37 (3)
C(7)	22 (1)	−62 (3)	177 (1)	47 (3)
N(1)	305 (1)	802 (2)	95 (1)	35 (3)
N(3)	252 (1)	497 (2)	202 (1)	30 (2)
N(4)	307 (1)	485 (2)	380 (1)	38 (3)

* Anisotropic parameters in the form $T = \exp[-2\pi^2 \times (\varepsilon_i \varepsilon_j h_i h_j a_i^* a_j^* U_{ij})]$ with U_{ij} for Hg (Å^2 $\times 10^4$) and U_{ij} for S (Å^2 $\times 10^3$):

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg	410 (5)	375 (5)	265 (4)	−71 (2)	31 (3)	−60 (2)
S	45 (2)	44 (2)	20 (2)	−2 (1)	−1 (1)	−8 (2).

atoms were treated as two single parameters and refined to $U = 0{\cdot}177$ (aromatic and methyl H) and $U = 0{\cdot}031$ Å^2 (amino H). In the final refinement, a weighting scheme was introduced.

The 6-oxo complex (II) was solved in a similar manner except that the amino H atoms were not located in a difference map. These were fixed, according to the geometry of the group, with N—H = 1·00 Å. The H atoms of the water molecule could not be located and were omitted from the final model.

Table 3. *Fractional atomic coordinates* ($\times 10^3$; *for* Hg *and* S $\times 10^4$) *and temperature factors* (Å^2 $\times 10^3$) *for the non-hydrogen atoms of* (II), *with e.s.d.'s in parentheses*

	x	y	z	U
Hg	3506 (1)	1166 (1)	1061 (1)	*
S	2604 (9)	−1456 (6)	1209 (4)	*
C(2)	191 (2)	−171 (2)	6 (1)	23 (4)
C(4)	162 (3)	−99 (2)	−141 (1)	33 (5)
C(5)	86 (3)	−239 (2)	−168 (1)	34 (4)
C(6)	57 (3)	−348 (2)	−105 (1)	30 (4)
C(7)	424 (5)	347 (3)	95 (2)	73 (8)
N(1)	109 (2)	−309 (2)	−11 (1)	30 (3)
N(3)	218 (2)	−67 (2)	−52 (1)	33 (4)
N(4)	202 (2)	7 (2)	−200 (1)	36 (4)
O(6)	−2 (2)	−485 (2)	−116 (1)	37 (3)
OW	309 (3)	162 (2)	318 (1)	71 (5)

* Anisotropic thermal parameters defined as in Table 2:

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg	210 (8)	429 (9)	616 (9)	−79 (4)	60 (5)	−73 (3)
S	42 (4)	48 (3)	34 (3)	0 (2)	−1 (2)	−12 (3).

Details of the final refinement parameters are given in Table 1. Tables 2 and 3 show the final atomic coordinates and temperature factors of (I) and (II) respectively.*

Description of the structures and discussion

Figs. 1 and 2 show perspective views of the molecular structures with atomic nomenclature. Bond distances and angles are in Table 4. The C(7)—Hg—S angle is close to 180° in both structures, in common with most

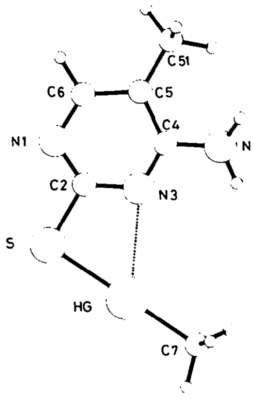

Fig. 1. A perspective view of (I).

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* Lists of hydrogen atomic coordinates and structure factors for (I) and (II) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35334 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

	(I)	(II)		(I)	(II)		(I)	(II)
Hg–S	2·393 (4)	2·390 (6)	N(3)–C(4)	1·31 (2)	1·39 (3)	C(5)–C(6)	1·42 (2)	1·36 (3)
Hg–C(7)	2·09 (1)	2·09 (2)	C(4)–N(4)	1·36 (1)	1·32 (2)	C(6)–O(6)	–	1·27 (2)
S–C(2)	1·78 (1)	1·76 (2)	C(4)–C(5)	1·44 (2)	1·39 (3)	C(6)–N(1)	1·35 (2)	1·46 (2)
C(2)–N(3)	1·36 (2)	1·28 (3)	C(5)–C(51)	1·49 (1)	–	N(1)–C(2)	1·31 (2)	1·36 (2)
C(7)–Hg–S	178·6 (4)	178·6 (9)	N(3)–C(4)–N(4)	117 (1)	116 (1)	C(51)–C(5)–C(6)	123 (1)	–
Hg–S–C(2)	94·1 (4)	95·2 (6)	N(3)–C(4)–C(5)	123 (1)	122 (1)	C(5)–C(6)–O(6)	–	129 (2)
S–C(2)–N(1)	116 (1)	112 (1)	N(4)–C(4)–C(5)	119 (1)	122 (2)	O(6)–C(6)–N(1)	–	114 (1)
S–C(2)–N(3)	116 (1)	121 (1)	C(4)–C(5)–C(51)	123 (1)	–	C(5)–C(6)–N(1)	124 (1)	117 (2)
N(1)–C(2)–N(3)	128 (1)	126 (1)	C(4)–C(5)–C(6)	113 (1)	119 (1)	C(6)–N(1)–C(2)	115 (1)	118 (1)
C(2)–N(3)–C(4)	116 (1)	117 (1)						

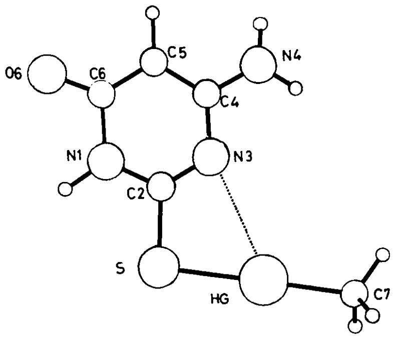

Fig. 2. A perspective view of (II).

Table 5. *Selected intra- and intermolecular distances* (Å)

Roman numeral superscripts refer to the following equivalent positions relative to the reference molecule at x,y,z:

(i) $-x,-y,-z$ (ii) $x,\frac{1}{2}-y,\frac{1}{2}+z$.

(I)		(II)	
Hg$\cdots$N(3)	2·80 (2)	Hg$\cdots$N(3)	2·95 (2)
Hg$\cdots$N(4)	4·47 (3)	Hg$\cdots$N(4)	4·70 (3)
Hg$\cdots$N(1)	3·39 (2)		
		Hg$\cdots$S$^{\rm i}$	4·59 (3)
Hg$\cdots$S$^{\rm i}$	3·67 (2)	O(6)$\cdots$N(1)$^{\rm i}$	2·76 (3)
N(4)$\cdots$N(1)$^{\rm ii}$	3·04 (3)	O(6)$\cdots$O$W^{\rm ii}$	2·98 (3)
		N(4)$\cdots$O$W^{\rm ii}$	2·99 (3)

organomercurials (Grdenić, 1965), and the Hg–S and Hg–C(7) lengths [2·393 (4) and 2·09 (1) Å for (I); 2·390 (6) and 2·09 (2) Å for (II)] are typical of digonal mercury (Wells, 1962). The methylmercury group lies off the ring plane with dihedral angles Hg–S–C(2)–N(3) of 4 (1) and 7 (1)° for (I) and (II) respectively. The Hg$\cdots$N(3) distances of 2·80 (2) (I) and 2·95 (2) Å (II) indicate a rather strong interaction, the sum of the van der Waals radii for the two atoms being 3·00 Å (Pauling, 1960). A similar situation arises in the structure of methyl(2-pyrimidinethionato)mercury(II) (Chieh, 1978), in which there is a secondary interaction with an Hg$\cdots$N distance of 2·83 Å.

The carbonyl bond in (II) appears bent in the direction of the hydrogen bond O(6)$\cdots$N(1)$^{\rm i}$ (Table 5: as the amino H atoms were not freely refined, only the O$\cdots$N contacts are given). It is possible that this strong hydrogen bond [2·76 (3) Å] may result in the unusual angles around the carbonyl C(6) atom.

Packing patterns and close contacts

Figs. 3 and 4 show [010] projections of (I) and (II) respectively. Dotted lines indicate the hydrogen-

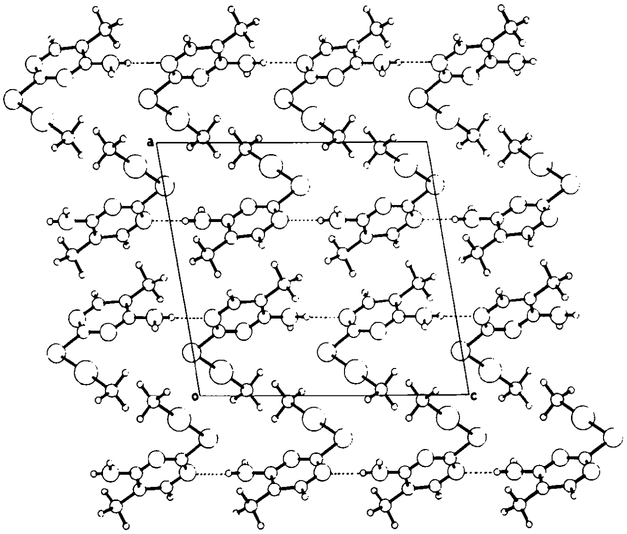

Fig. 3. [010] projection of (I). H-bonds are shown by dotted lines.

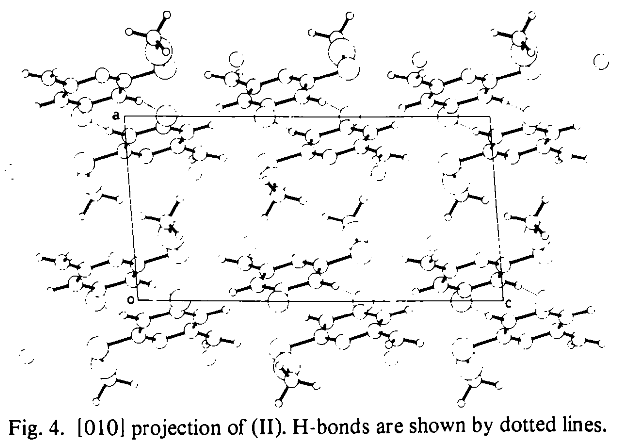

Fig. 4. [010] projection of (II). H-bonds are shown by dotted lines.

bonding scheme. There is a possibility of further hydrogen bonding in (II) [Table 5: O(6)$\cdots$O*W* and N(4)$\cdots$O*W*] but uncertainty in the positions of the H atoms of the water molecule prevents the assignment of further formal H-bonds.

In both (I) and (II), the Hg—S group is aligned about a centre of symmetry as in (*N*,*N*-diethyldithiocarbamato)methylmercury(II) (Chieh & Leung, 1976). In the latter, the intermolecular Hg$\cdots$S distance is short (3·147 Å) while in (I) and (II) it is longer 3·67 (2) and 4·59 (3) Å respectively. The sum of the van der Waals radii for Hg and S is 3·35 Å (Pauling, 1960), so in (I) and (II) the interaction cannot be considered as secondary bonding as is the Hg$\cdots$N(3) interaction. The orientation of the Hg—S groups about the centre of symmetry does, however, bear resemblance to the four-centred bridged intermediate proposed by Bach & Weibel (1976) and may provide additional support for such a mechanism of ligand exchange (equation 1).

All calculations were carried out on a Univac 1180 computer at the University of Cape Town.

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Bis(oxamide oximato)nickel(II)–Oxamide Oxime

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Abstract

$[Ni(C_2H_5N_4O_2)_2].C_2H_6N_4O_2$, $C_4H_{10}N_8NiO_4.C_2H_6N_4O_2$, $M_r = 411$, $P1$, $a = 4{\cdot}982\,(1)$, $b = 12{\cdot}133\,(3)$, $c = 12{\cdot}871\,(4)$ Å, $\alpha = 67{\cdot}67\,(2)$, $\beta = 78{\cdot}84\,(2)$, $\gamma = 78{\cdot}14\,(2)°$, $V = 698{\cdot}5$ Å^3, $Z = 2$, $d_c = 1{\cdot}95$ Mg m^{-3}; final $R = 0{\cdot}050$ for 2055 reflections. The planar complex molecules form stacks along **a**, the normals of the planes being inclined at ~50° to the stacking axis. There are axial interactions between Ni and the amino groups of adjacent complex molecules within a stack. Free oxamide oxime, present in the *s-trans* form, links the stacks to sheets by forming H bridges to the complex molecules.

Introduction

We are presently investigating the structural variability of oxamide oxime (diaminoglyoxime, oaoH$_2$) complexes of Ni, Pd, and Pt (Endres & Jannack, 1980, and references therein). As we are interested in solids with highly anisotropic structures, we focus on the complexes of oaoH$_2$ with the metals of the Ni triad, for the α,β-dione dioximato complexes of these metals are known to prefer stacked structures in the solid state (Endres, Keller, Lehmann, Poveda, Rupp & van de Sand, 1977). The structural systematics outlined by these authors are often violated in complexes of oaoH$_2$, due to the reduced acidity of the oxime H atoms and to a pronounced capability to form intermolecular H bridges.

Experimental

The preparation of the compound is similar to that of $[Ni(oaoH_2)_3]Cl_2$ (Endres & Jannack, 1980) but with more dilute solutions: 600 mg $NiCl_2.6H_2O$ and 600 mg oaoH$_2$ are dissolved in 50 ml ethanol each, and the NiCl$_2$ solution is added dropwise to the refluxing solution of the ligand. The title compound is obtained as

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