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Interaction of $MeSHgO_2CMe$ with Imidazole and Related Ligands

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The complex $MeSHgO_2CMe$ reacts with imidazole (LH) in 1:1 or 2:1 mol ratio in water at low pH to form a complex of stoichiometry $(MeSHg)_2(O_2CMe)(L)$, but in the absence of acetic acid forms a new phase of $Hg(SMe)_2$. Stirred suspensions of $MeSHgO_2CMe$ with imidazole or 2-methylimidazole in 1:1 mol ratio in ethanol form $(MeSHg)_2(O_2CMe)(L)$ and the 2-methylimidazole analogue. Solutions of $MeSHgO_2CMe$ or the new phase of $Hg(SMe)_2$ in N-methylimidazole deposit crystals of the previously known phase of $Hg(SMe)_2$.

Introduction

Complex formation between mercury(II) and thiols, *e.g.* cysteine, is believed to play a major role in the biological chemistry of mercury [1], and several studies have indicated that Hg(II) may be bonded to one thiol and one non-thiol ligand [1–7]. Most 1:1 Hg(II) thiolates that could act as models for a study of the interaction of RSHg(II) with non-thiol ligands are insoluble in water and common organic solvents, *e.g.* the cysteine complex $Hg(SCH_2CH(NH_2)CO_2)$ and RSHgX (X = halide, NO_3), but $MeSHgO_2CMe$ is water soluble [8, 9] and a study of its interaction with imidazole, 2-methylimidazole, and N-methylimidazole is presented here.

Experimental

Preparation of $MeSHgO_2CMe$ has been described [9], imidazole (ImH, Halewood Chemicals Ltd.) was recrystallized from ethanol, and both 2-methylimidazole (MeIm) and N-methylimidazole (Ega-Chemie) were used as received. Bis(methanethiolato)-mercury(II) was prepared as described earlier [10–14], and crystallized from ethanol as shiny flakes (as noted by Bradley and Kunchur), and had i.r. and Raman spectra in agreement with those reported earlier [14]. Silver(I) imidazolate was prepared as described [15]; Ag (gravimetric) 60.8. Calcd. for $C_3H_3AgN_2$ 61.7%.

Infrared spectra (4000–400 cm^{-1}) of complexes in Nujol and hexachlorobutadiene mulls, and far-infrared spectra (400–200 cm^{-1}) of complexes in Nujol mulls between polyethylene plates, were recorded with a Perkin-Elmer 577 spectrophotometer. Raman spectra were measured with a Cary 82 laser Raman spectrometer over the range 2000–100 cm^{-1}, 514.5 nm excitation being used. Maximum errors are considered to be 4 cm^{-1} for both IR and Raman spectra. X-ray powder diffraction was measured using a Philips PW 1050/25 goniometer, and PW 1965/40

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TABLE I. Analytical Data for the Complexes.

Complex	Prepn.[a]	Found %					Calcd. %				
		C	H	Hg	N	S	C	H	Hg	N	S
$(MeSHg)_2(O_2CMe)(Im)$[b]	$H_2O(2:1)$	13.7	2.0	64.7	4.2	10.2	13.5	2.0	64.6	4.5	10.3
$(MeSHg)_2(O_2CMe)(Im)$	$H_2O(1:1)$	14.1	2.3	64.3	4.4	10.1	"	"	"	"	"
$(MeSHg)_2(O_2CMe)(Im)$	EtOH(1:1)	13.8	1.9	64.2	4.1	10.4	"	"	"	"	"
$(MeSHg)_2(O_2CMe)(MeIm)$[c]	EtOH(1:1)	15.1	2.3	63.2	4.5	10.3	15.1	2.2	63.1	4.4	10.1
$Hg(Sme)_2$[d]	H_2O	8.2	2.1	67.9	–	21.4	8.1	2.1	68.0	–	21.8

[a] Solvent (mol ratio $MeSHgO_2CMe$:ligand). [b] Im = $C_3H_3N_2$. [c] MeIm = $C_4H_5N_2$. [d] New phase, from $MeSHgO_2CMe$ and imidazole in water (1:1).

detector with Cu Kα radiation. Microanalyses (C, H, Hg, N, S) were by the Australian Microanalytical Service, Melbourne, and are given in Table I.

Preparation of Complexes

Examples of preparations in water and 95% ethanol are given, together with brief details for other preparations.

$(MeSHg)_2(O_2CMe)(Im)$

(i) In water. Imidazole (0.088 g, 1.29 mmol) in water (2 ml) was added to a solution of $MeSHgO_2CMe$ (0.396 g, 1.29 mmol) in water (36 ml) and acetic acid (5*M*, 2 ml). The solution was filtered and evaporated at ambient temperature to low volume. Addition of ethanol resulted in slow precipitation of a white powder which was collected, washed with ethanol, and dried in a vacuum over phosphorus pentoxide (0.314 g, 77%), m.p. (dec.) 127–129 °C. Infrared absorptions: 3144 w, 3120 w, 2976 vw, 2923 w, 1545 vs(br), 1483 m, 1469 m, 1423 m(sh) and 1396 s(br), 1338 w, 1317 m, 1231 w, 1173 w, 1098 w, 1081 vs, 1044 w, 1009 w, 970 w and 960 w, 947 m, 844 w, 761 s, 685 w, 646 s, 616 w, 338 m, 287 w, 233 vw cm^{-1}. Raman bands: 1500 w, 1325 vw(sh) and 1316 w, 1175 vw, 1102 vw, 1079 vw, 967 s, 922 w, 696 w(br), 634 vw, 327 vs, 285 w, 243 w, 195 m cm^{-1}.

A smilar preparation using a mol ratio $MeSHgO_2CMe$: imidazole of 2:1 gave the same product (81%), m.p. (dec.) 124–127 °C.

(ii) In ethanol (95%). $MeSHgO_2CMe$ (0.206 g, 0.67 mmol) was added to a solution of imidazole (0.046 g, 0.67 mmol) in ethanol (5 ml) and the suspension stirred for 24 h. The white powder was collected, washed with water, and dried in a vacuum over phosphorus pentoxide (0.150 g, 70%), m.p. (dec.) 123–132 °C.

$(MeSHg)_2(O_2CMe)(MeIm)$

This complex was prepared using a 1:1 mol ratio of reactants in ethanol (yield 89%), m.p. (dec.) 121–123 °C. Infrared absorptions: 3123 vw, 2923 w, 1536 vs(br), 1477 vw, 1401 vs(br), 1336 w, 1309 m, 1183 w, 1154 s, 1004 w, 970 w and 954 vw(sh), 919 w, 751 m, 672 w, 653 m, 618 vw, 434 m, 347 m, 329 m, 276 m cm^{-1}. Raman bands: 1515 vw, 1474 w, 1419 vw(br), 1394 vw, 1385 vw, 1344 vw, 1317 vw, 1307 vw, 1182 vw, 1033 vw(sh) and 1020 w, 916 w, 836 vw, 692 vs, 629 vw, 347 m, 331 s, 294 w, 277 w, 205 w(sh) and 188 m, 144 m cm^{-1}.

Preparation of a New Phase of $Hg(SMe)_2$

Imidazole (0.027 g, 0.39 mmol) in water (5 ml) was added to a solution of $MeSHgO_2CMe$ (0.119 g, 0.39 mmol) in water (10 ml). A white powder which formed immediately was collected, washed with water, and dried in a vacuum over phosphorus pentoxide (0.020 g, 17%), m.p. (dec.) 127–138 °C. Infrared absorptions: 2972 w, 2911 m, 2820 vw, 1425 m(br), 1305 m, 959 m and 949 m, 694 w, 338 m and 295 vw, sh(br) cm^{-1}. Raman bands: 1396 w, *ca.* 1306 vw(br), 1136 w, *ca.* 950 vw(br), 695 m, 465 w, 401 w, 309 vs, 190 m cm^{-1}.

X-Ray Powder Diffraction for the Two Phases of $Hg(SMe)_2$

For each phase *d* spacings (Å) for only the most intense lines are given, together with relative intensities in parentheses (most intense line = 1000).

Previously known phase

9.858(1000), 6.000(29), 4.120(43), 3.275(50), 3.005(43), 2.457(100), 1.966(50), 1.903(14), 1.602-(29).

New phase

9.858(22), 8.613(1000), 4.312(107), 3.833(11), 3.294(11), 2.879(36), 2.634(11), 2.156(11), 1.726(9).

Results and Discussion

Reactions of $MeSHgO_2CMe$

Addition of aqueous solutions of imidazole (ImH) to solutions of $MeSHgO_2CMe$ (mol ratio mercury: ImH 1:1 or 2:1) resulted in precipitation of $Hg(SMe)_2$. With acetic acid present to give pH *ca.* 4, evaporation to low volume followed by addition of ethanol resulted in precipitation of a white powder of analytical composition $(MeSHg)_2(O_2CMe)(Im)$.

$$2MeSHgO_2CMe + ImH \longrightarrow (MeSHg)_2(O_2CMe)(Im) + MeCO_2H$$

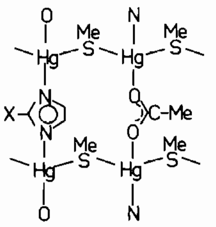
Reactions using stirred suspensions of $MeSHgO_2CMe$ in 95% ethanol solutions of ImH gave the same complex when reacted in 1:1 mol ratio, but with 2:1 mol ratio some unreacted $MeSHgO_2CMe$ was present. Low solubility of $MeSHgO_2CMe$ in 95% ethanol apparently allows the reaction to proceed (24 h) without formation of $Hg(SMe)_2$. An attempt to replace acetate completely with imidazolate by reaction in 1:10 mol ratio led to precipitation of $Hg(SMe)_2$.

An analogous complex with 2-methylimidazolate ($MeIm^-$) could not be isolated by reaction of $MeSHgO_2CME$ with MeImH in water (1:1 or 2:1 mol ratio) acidified to prevent formation of $Hg(SMe)_2$. Precipitation did not occur on addition of ethanol, and addition of acetone gave $Hg(SMe)_2$. A 'hetero geneous' reaction in ethanol in 1:1 mol ratio gave the required complex, with incomplete reaction in 2:1 mol ratio as found for imidazole.

Infrared and Raman spectra indicate the absence of Hg(SMe)$_2$ and the presence of 'MeSHg' and acetate groups in the complexes, with bands altered from their positions in MeSHgO$_2$CMe. Presence of Im$^-$, rather than ImH, was shown by comparison of IR spectra of ImH, Ag(Im), (MeSHg)$_2$(O$_2$CMe)(Im) and the complex prepared in deuterated ethanol. Silver(I) imidazolate has ν(CH) at 3115 cm^{-1} allowing assignment of bands at 3144 and 3120 cm^{-1} in (MeSHg)$_2$(O$_2$CMe)(Im) as ν(CH) rather than ν(NH). Preparation of (MeSHg)$_2$(O$_2$CMe)(Im) in EtOD gave a complex with an identical spectrum and no indication of absorption near 2200 cm^{-1} expected for presence of ν(ND). The 2-methylimidazolate complex has ν(CH) at 3123 cm^{-1}.

Mercury–sulphur vibrations have been assigned in the ranges 322–216 [9, 16] and 371 (or 405 [14])–172 cm^{-1} [12–14, 17] in RSHgO$_2$CMe (R = Me, Et, Pr^n, Bu^n) and 1:2 mercury(II) thiolates, respectively. For both complexes several bands occur below 400 cm^{-1}, and thus assignment of mercury–sulphur modes is not straightforward, *e.g.* (MeSHg)$_2$(O$_2$CMe)(Im), IR: *338 m,* 287 w, 233 vw, Raman: *327* vs, 285 w, 243 cm^{-1}, with bands *in italics* tentatively assigned as mercury–sulphur modes (*cf.* MeSHgO$_2$CMe: ν_{as}(SHgS) 322 m, br (IR), ν_s(SHgS) 274 s cm^{-1} (Raman) [9]).

All mercury(II) thiolates studied crystallographically so far have oligomeric chains (–Hg–SR–)$_n$. In the acetates RSHgO$_2$CMe (R = Me [18], ^{n}Pr, ^{n}Bu [16]) parallel chains are linked by acetate groups to form wrinkled sheets, and in the pyridine complex MeSHgO$_2$CMe·pyridine coordination of pyridine results in displacement of bridging acetate groups to give isolated chains with pyridine and acetate (bidentate) coordination at each mercury [18]. Occurrence of polymeric structures for these acetates and the ability of Im$^-$ to act as a bridging ligand [19] suggest that the imidazolate and 2-methylimidazolate complexes are polymeric, *e.g.* I with acetate bridging to give equivalent environments for all mercury atoms.



I. X = H or Me

Attempts to grow crystals of the complexes for crystallographic study were unsuccessful, *e.g.* dissolution of (MeSHg)$_2$(O$_2$CMe)(Im) in a large volume of water resulted in formation of crystalline MeSHgO$_2$CMe on slow evaporation of water.

TABLE II. Mercury–Sulphur Vibrations in Phases of Hg(SMe)$_2$ (cm^{-1})[a].

Phase	ν_{as} (SHgS)	ν_s (SHgS)
Previously known	337 vs[b]; (338 vw)[b] 338 vs[c,d]	(297 vs)[b]; 296 m[b] (298 m)[c]; (295 vs)[d]
New	338 m	(309 vs)

[a] Raman values in parentheses ( ). Abbreviations: v, very; s, strong; m, medium. [b] From reference 14. [c] From reference 13. [d] From reference 12.

Crystalline Phases of Hg(SMe)$_2$

The structure of Hg(SMe)$_2$ prepared by Wertheims' method [10] has been determined by X-ray diffraction [11]. The powders of analytical composition Hg(SMe)$_2$ obtained as a decomposition product from aqueous solutions of MeSHgO$_2$CMe and imidazole ligands have melting point *ca.* 45° lower than previous preparations which involved recrystallization from ethanol [10–14]. An X-ray powder diffractogram of Hg(SMe)$_2$ prepared in this laboratory by Wertheims' method can be indexed with the unit cell dimensions reported by Bradley and Kunchur [11], but the sample prepared from water (above) gave a different spectrum. Solutions of MeSHgO$_2$CMe or the new phase of Hg(SMe)$_2$ in N-methylimidazole deposit crystals of the previously known form.

Infrared spectra of the two phases are similar, with one absorption at 1305 m replacing two in the previously known phase [1312 w(sh) and 1307 w cm^{-1} [14] (Me sym. def. [12])] and absorptions at 959 m and 949 m replacing one at 945 s(br) cm^{-1} [14] (Me rock [12]). The IR spectrum of the new phase has lower intensity for ν(CS) at 694 cm^{-1}, and the Raman spectrum has ν_s(SHgS) at 309 cm^{-1}, 12 cm^{-1} higher than in the previously known phase. The Raman spectrum shows extra bands of low intensity at 1136, 465, and 401 cm^{-1}. Small quantities of one phase may be present in samples of the other as IR and Raman spectra are very similar with overlap of band envelopes, and in the Raman spectrum of the previously known phase ν_s(SHgS) at 297 cm^{-1} has a weak shoulder at *ca.* 310 cm^{-1}. Similarly, in X-ray powder spectra the new phase has a weak line at *d* 9.858 Å corresponding to the most intense line of the previously known phase, and the most intense line of the new phase (*d* 8.613 Å) may be present but not detected beneath the strong, broad, line of the previously known phase at *d* 9.858 Å.

Mercury–sulphur vibrations are readily assigned to medium–strong bands close to values for the previously known phase (Table II), indicating that the new phase also has a linear S–Hg–S skeleton rather than, for example, tetrahedral as in polymeric Hg(SBu^t)$_2$ [20] which has much lower frequencies associated with a higher coordination number for mercury (ν_{as}(SHgS) 172 vs(vbr) and ν_s(SHgS) 188 s cm^{-1} [47]).

Facile reaction of $MeSHgO_2CMe$ with imidazole nitrogen donor ligands under mild conditions is of interest, although the solid complexes isolated from the solution may be polymeric and thus unrelated to *in vivo* conditions.

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