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Formation of Dimeric Mercury(II) Thiolate Ions in Water

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Complexes with Hg(II):thiol ratio 1:1 studied so far by X-ray crystallography, $RSHgO_2CMe$ (R = Pr^n, Bu^n [1]; Me [2]), have polymeric structures based on zig-zag $(-Hg-SR-)_n$ chains with bridging thiolate. Mercury has coordination number greater than two and non-linear S–Hg–S (156.2–159.0°) in these complexes. In contrast ^{35}Cl NMR studies indicate that several RSHg(II) ions, *e.g.* $HOCH_2CH_2SHg(II)$, form linear, monomeric complexes with chloride ion and histidine in aqueous solution in the presence of excess chloride [3, 4]. We report here preparation and spectroscopic studies of MeSHg(II) complexes which form dimeric units "$Hg_2(SMe)_2$" in aqueous solution.

The complexes $MeSHgO_2CMe \cdot L$ [L = pyridine(py) and 4-methylpyridine (4-mpy)] form as colourless crystals from solutions of $MeSHgO_2CMe$ in the ligand, and infrared spectra show the usual shifts of ligand absorptions on coordination [5]. The complexes lose ligand at ambient temperature and pressure to give $MeSHgO_2CMe$, and have satisfactory analysis for ligand by weight loss (Table).

TABLE. Raman Spectra of Aqueous Solutions (200–350 cm^{-1})^a.

$MeSHgO_2CMe^b$	309vw,sh	277s,br		
$MeSHgO_2CMe \cdot py^c$	306vw,sh		267s,br	
$MeSHgO_2CMe$ + excess py	308vw,sh			253s,br
$MeSHgO_2CMe \cdot$ 4-mpy^d	305vw,sh			256s,br
$MeSHgO_2CMe$ + excess 4-mpy	305vw,sh	*ca.* 274m,sh		259s,br

^{a}Measured with a Cary 82 laser Raman spectrometer using 514.5 nm excitation. ^{b}Found: C, 11.9; H, 1.9; Hg, 65.9; S, 10.5. Calcd. C, 11.8; H, 2.0; Hg, 65.4; S, 10.5%. ^{c}Found: py, 21.2. Calcd. 20.5%. ^{d}Found: 4-mpy, 23.5. Calcd. 23.3%.

The complexes and $MeSHgO_2CMe$ dissolve in water to form conducting solutions, *e.g.* $MeSHgO_2CMe \cdot py$ has molar conductivity 62.8 ohm^{-1} mol^{-1} cm^2. Mercury–sulphur stretching vibrations in mercury(II) thiolates $Hg(SR)_2$ occur in the range 371 (or 405 [6]) –172 cm^{-1} [6–9], and Raman spectra of aqueous solutions of $MeSHgO_2CMe$ and the complexes have an intense, broad, strongly polarized band in the range 277–253 cm^{-1} immediately above Rayleigh scattering (Table and Figure, depolarization ratios $\rho_p < 0.1$). With the polarized band assigned as a totally symmetric mercury–sulphur stretching mode the ions containing mercury cannot be monomeric, *i.e.* based on "MeSHg", and are assumed to have structure I with tetrahedral coordination and a centre of symmetry between mercury atoms. Similar sulphur bridging occurs in polymeric $Hg(SBu^t)_2$ [10].

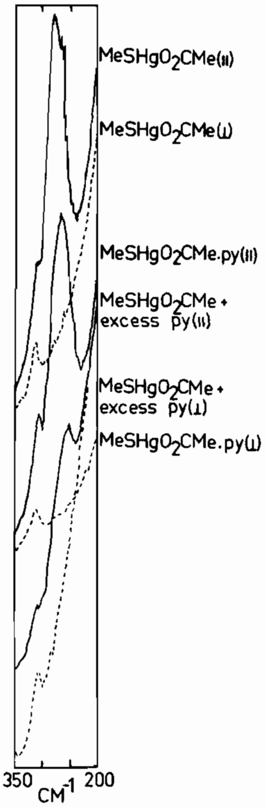
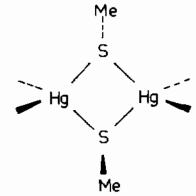


Figure. Polarized (∥) and depolarized (⊥) Raman spectra of aqueous solutions of $MeSHgO_2CMe$, $MeSHgO_2CMe \cdot py$, and a solution of $MeSHgO_2CMe$ with excess pyridine added.



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Solutions of $MeSHgO_2CMe$ are acidic, *e.g.* a 1.62 $\times 10^{-2}$ *M* solution has pH 6.0, indicating hydrolysis, and thus several species, including ones with terminal hydroxo, aquo, and acetato groups may be present. Solutions of $MeSHgO_2CMe \cdot L$ have both coordinated and free ligand, *e.g.* L = py: 1023w(coord.) and 1005s cm^{-1} (free, *cf.* py in water: 1003 cm^{-1}). The strongly polarized ν(SHgS) mode is lower than that of solutions of $MeSHgO_2CMe$ but is broad enough to include a contribution from $MeSHgO_2CMe$, and in some spectra a shoulder is present (Table). Addition of excess pyridine lowers the band even further (267 → 253), consistent with further coordination of py with replacement of more weakly coordinating ligands, *e.g.* water.

Presence of dimeric ions in water does not indicate their existence in the solid state as $MeSHgO_2CMe$ is polymeric in crystals [2]. The solid complexes have several medium–strong bands in both IR and Raman spectra that could be assigned as mercury–sulphur modes.

Further studies on the aqueous solution chemistry of mercury(II) thiolates is in progress. The results presented here suggest a structure for the 1:1 complex with L-cysteine, $Hg(SCH_2CH(NH_2)CO_2)$, [12], which has very low solubility but may be detected polarographically in dilute solution [13]. Chelation of L-cysteine cannot give linear coordination for mercury [14] and thus, in *aqueous solution,* the complex presumably adopts a dimeric structure based on an 'Hg_2S_2' ring similar to I with chelated L-cysteine.

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