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A Structural Study of 1-Butanethiolatomercury(II)perchlorate, Pyridinium Tris(1-butanethiolato)mercurate(II) and Pyridinium Tris(thiophenolato)mercurate(II) in Pyridine Solution

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Abstract

The stereochemistry around mercury(II) in the $Hg(SR)_3^-$, R = $^nC_4H_9$ and C_6H_5, and $Hg_2(SC_4H_9)_2^{2+}$, complexes in pyridine solution has been studied by means of large angle X-ray scattering (LAXS) technique. The $Hg(SR)_3^-$ complexes were found to be trigonal planar with mercury in the center of gravity and the sulfurs in the corners of an equilateral triangle. The Hg–S bond distances were refined to 2.454(11) and 2.475(7) Å in the $Hg(S^nC_4H_9)_3^-$ and $Hg(SC_6H_5)_3^-$ complexes respectively. The 1-butanethiolatomercury(II) complex is monomeric in dilute pyridine solution, but it dimerizes in concentrated solution. The Hg–S bond distance is 2.48(2) Å and the Hg–Hg distance is 3.69(5) Å in the $Hg_2(S^nC_4H_9)_2^{2+}$ complex. One or two pyridine molecules are, most probably, loosely coordinated to the mercury atoms, completing a distorted tetrahedral arrangement.

Introduction

Mercury(II) is well-known for its ability to form stable complexes with thiolates. The first mercury(II) thiolate complex was discovered by Zeise as early as 1834 [1]. The structure of the $Hg(SC_nH_{2n+1})_2$, $n = 2, 3, 5–7$, complexes were in principle solved by Wells [2]. That work contains, however, only basic information like the coordination numbers of mercury. Detailed structures including one of those compounds, have later been reported for $Hg(SCH_3)_2$ [3], $Hg(SC_2H_5)_2$ [4], $Hg(S^nC_4H_9)_2$ [5] and $Hg(S^tC_4H_9)_2$ [6].

The structures of the compound series $Hg(SR)(CH_3CO_2)$ have been reported for R = CH_3 [7], R = $^nC_3H_7$ and $^nC_4H_9$ [8], and R = C_6H_5 [9]. The alkanethiolate compounds consist of sulfur bridged (–Hg–SR–Hg–SR–) zig-zag chains linked to sheets by acetate bridges. It is noticeable that no monomeric $HgSR^+$ complexes have so far been found in the solid state.

Raman spectroscopic studies on aqueous solutions and aqueous/pyridine mixtures of $HgSCH_3(CH_3CO_2)$ have indicated predominance of dimeric $Hg_2(SCH_3)_2^{2+}$ complexes. In dilute mixtures, the $Hg_2(SCH_3)_2^{2+}$ complex dissociates to mononuclear complexes with increasing pyridine content [7].

The structures of $(C_2H_5)_4NHg(SC_6H_5)_3$ and $((C_2H_5)_4N)_2Hg(SC_6H_4Cl\text{-}p)_4$ contain mononuclear tris and tetrakis(thiophenolato)mercurate(II) complexes respectively [10, 11]. The $Hg(SC_6H_5)_3^-$ complex is in the solid state trigonal-planar, while the $Hg(SC_6H_4Cl\text{-}p)_4^{2-}$ complex is pseudotetrahedral. The structure of $(C_2H_5)_4NHg(SCH_3)_3$ is reported to consist of dimers with two bridging and four terminal thiolate groups [12].

The purpose of this work was to examine the structures of some mercury(II) thiolate complexes of varying stoichiometry, in solution. Pyridine was chosen as the solvent since mercury(II) thiolate compounds are sufficiently soluble only in strongly donating aprotic solvents. Moreover, the complex formation thermodynamics of some mercury(II) thiolate systems have recently been investigated in pyridine [13]. That study showed that three very strong mononuclear mercury(II) thiolate complexes are formed in pyridine solution; there are no indications of a fourth complex. The first and third complexes are predominating in large ranges of free ligand concentration, while the second complex, normally the most stable one never exceeds 45% of the total mercury(II) concentration.

Three mercury(II) thiolate complexes in pyridine were examined by means of large angle X-ray scattering (LAXS) technique on liquids. Two tristhiolatomercurate(II) complexes, $Hg(SC_6H_5)_3^-$ and $Hg(S^nC_4H_9)_3^-$, and the 1-butanethiolatomercury(II) complex, $Hg(S^nC_4H_9)^+$, have been studied in concentrated pyridine solutions at 25 °C.

Experimental

Preparation of Solutions

The $Hg(SR)_3^-$ complexes were prepared by adding an equivalent corresponding thiol to a mercury(II) thiolate solution according to

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TABLE I. Composition (mol dm^{-3}), Linear Absorption Coefficients, μ(Mo Kα) (cm^{-1}) for the Investigated Solutions

Solution	Hg	C_5H_6N	SR	ClO_4	C_5H_5N	μ
$HgSC_4H_9(ClO_4)$	0.600		0.600	0.600	9.2	15.5
$C_5H_6NHg(SC_4H_9)_3$	0.962	0.962	3.036		9.0	24.2
$C_5H_6NHg(SC_6H_5)_3$	0.889	0.889	2.909		9.0	22.3

$$Hg(SR)_2(py) + HSR + C_5H_5N \longrightarrow Hg(SR)_3^-(py) + C_5H_6N^+$$

The $HgSR^+$ complex was prepared by dissolving equimolar amounts of $Hg(SC_4H_9)_2$ and $Hg(C_5H_5N)_2(ClO_4)_2$ in warm pyridine, 60 °C; the mixture was slowly cooled down to room temperature. The composition of the studied solutions is given in Table I.

X-ray Scattering Measurements

The X-ray scattering from the free surface of the solutions was measured in a large angle theta–theta diffractometer [14] of Seifert GDS type. In order to avoid contact with the atmosphere and to avoid evaporation, the solutions were enclosed in a cylindrical thin-walled glass container, which was exactly half-filled. The absorption of the glass container and its angle dependence have previously been determined [15]. Mo Kα ($\lambda = 0.7107$ Å) radiation was used as the X-ray source. The scattered intensities were determined at discrete points in the interval $4° < \theta < 60°$, separated by 0.0335 in s, where $s = 4\pi\lambda^{-1} \sin\theta$, and the scattering angle is 2θ. An extrapolation of the intensity data at $\theta < 4°$ was necessary due to the upward meniscus in the glass container. A counting error of 0.35% was achieved by measuring 40 000 counts twice at each sampling point. The fraction incoherent scattering contributing to the intensities has been estimated in the usual manner [16].

Data Treatment

The same data reduction procedure and corrections as described previously were applied [16]. The experimental intensities were normalized to a stoichiometric unit of volume, containing one mercury atom. The scattering factors, corrections for anomalous dispersion and values for incoherent scattering were the same as used before [16]. The electric radial distribution functions (RDF), $D(r) - 4\pi r^2\rho_0$, were obtained by Fourier transformation from the intensity functions. The RDFs for the studied solutions are given in Fig. 1. Spurious peaks below 1.5 Å which could not be related to interatomic distances within the pyridine molecule or the perchlorate and thiolate ions have been removed by a Fourier transformation procedure [14].

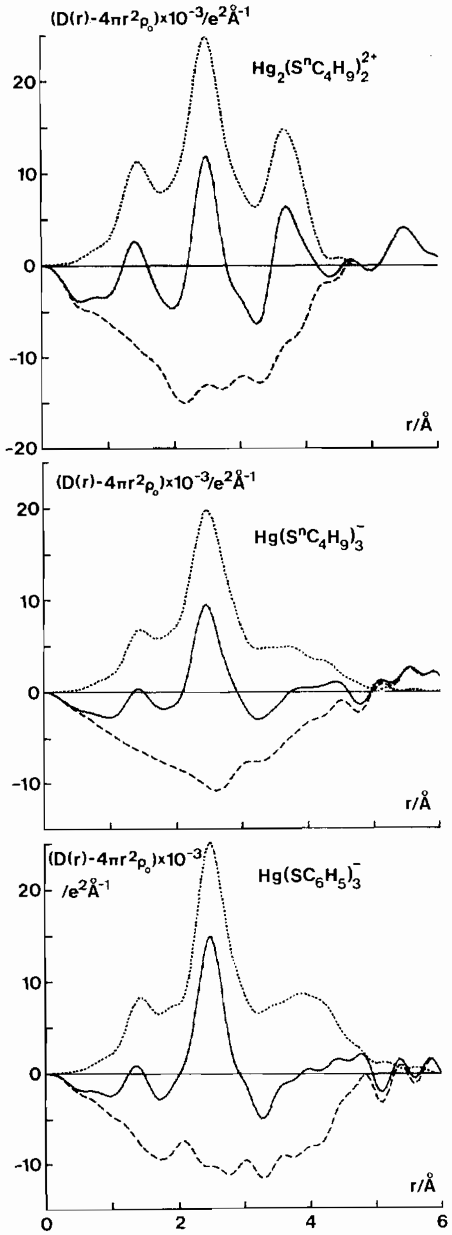

Fig. 1. Experimental radial distribution function, $D(r) - 4\pi r^2\rho_0$, for the 1-butanethiolatomercury(II)perchlorate, pyridinium tris(1-butanethiolato)mercurate(II) and pyridinium tris(thiophenolato)mercurate(II) in pyridine solution (solid lines), model functions with parameters from Table II (dotted lines) and the differences between them (dashed lines.

TABLE II. Interatomic Distances, *d* (Å), Temperature Factor Coefficients for the Distances, *b* (Å^2), and Frequencies of the Distances Relative to One Mercury Atom, *n*, for the $Hg_2(SC_4H_9)_2^{2+}$, $Hg(SC_4H_9)_3^-$ and $Hg(SC_6H_5)_3^-$ Complexes in Pyridine Solution. The Refined Parameters are those with e.s.d.s in Parentheses

Complex	Distance	*d*	*b*	*n*
$Hg_2(SC_4H_9)_2^{2+}$	Hg–S	2.48(2)	0.012(3)	2.0
	Hg–Hg	3.69(5)	0.023(5)	0.5
	S–S	3.36	0.020	0.5
	Hg–C	3.75	0.022	2.0
$Hg(S_4H_9)_3^-$	Hg–S	2.455(11)	0.0179(18)	3.1(3)
	Hg–C	3.69(7)	0.023(9)	3.0
	S–S	4.25	0.020	3.0
$Hg(SC_6H_5)_3^-$	Hg–S	2.475(7)	0.0072(9)	3.0
	Hg–C	3.76(4)	0.033(7)	6.0
	S–S	4.29	0.020	3.0

All calculations were carried out by means of the computer programs KURVLR [17] and STEPLR [18].

Results

For the tristhiolatomercurate(II) complexes a major peak in the RDFs is found at 2.5 Å. These peaks correspond to Hg–S bond distances, and the integral of the peaks indicates three Hg–S distances per mercury. Two minor peaks at about 3.8 and 4.3 Å correspond to Hg–C and S–S distances respectively, within the $Hg(SR)_3^-$ complexes. The distances, the temperature factor coefficients of the Hg–S and Hg–C distances and the number of Hg–S distances were refined in the range $3.5 \leqslant s \leqslant 13.5$ by a least-square refinement procedure. For the number of Hg–C distances and for the S–S distance, the pyridinium and thiolate ions and for free pyridine, fixed parameters were introduced. The parameters for the tristhiolatomercurate(II) complexes are given in Table II.

The radial distribution function for the $HgSC_4H_9(ClO_4)$ solution shows two distinct peaks at 2.5 and 3.7 Å, Fig. 1. These peaks correspond to Hg–S and Hg–Hg distances respectively. The peak areas indicate two Hg–S and half a Hg–Hg distance per mercury. The peak at 3.7 Å, being somewhat unsymmetrical, also incorporates the expected Hg–C distance at around 3.8 Å. The distances and the temperature factor coefficients of the Hg–S and Hg–Hg distances have been refined in the range $4.0 \leqslant s \leqslant 13.5$. The quality of the experimental intensities is not good enough to determine if any pyridine is loosely coordinated to mercury. The parameters for the bis(1-butanethiolato)dimercury(II) complex are given in Table II. The parameters for the thiolate and perchlorate ions, and free pyridine have been taken from the literature and further refinements on these parameters have not been made.

Discussion

The $Hg(SC_6H_5)_3^-$ complex is found to be trigonal-planar in pyridine solution as well as in the solid state [10]. In the structure of $(C_3H_5)_4NHg(SC_6H_5)_3$ the HgS_3 entity is strongly distorted, but the average S–Hg–S angle is 120° and the average Hg–S bond distance is 2.455 Å [10]. The Hg–S bond distance in the $Hg(SC_6H_5)_3^-$ complex is 0.020 Å longer in pyridine solution than in the solid state. This increase in the Hg–S bond distance is certainly due to the solvation of the $Hg(SC_6H_5)_3^-$ complex in pyridine. Pyridine is a strong donor to the soft acceptor mercury(II) [19], though pyridine is a much weaker donor than thiolate ions. It has not been possible from current X-ray scattering data to determine whether or not pyridine molecules are coordinated to mercury in the $Hg(SC_6H_5)_3^-$ complex. Pyridine has the possibility of solvating the mercury atom through the nitrogen atom and the phenyl rings through pi-interactions. The lengthening of 0.017 Å of the Hg–S bond in pyridine indicates that weak interactions between pyridine and mercury indeed occur, as only π-interactions should give a smaller effect. A similar lengthening of Hg–X bonds has been reported in the complexes HgX_3^-, X = Cl, Br, I, where solvent molecules are coordinated to mercury [20, 21]. Two pyridine molecules are probably coordinated in the axial positions of a trigonal bipyramid.

The Hg–S bond distance is 0.02 Å shorter in $Hg(S^nC_4H_9)_3^-$ than in $Hg(SC_6H_5)_3^-$, Table II. This is somewhat surprising since the $Hg(SC_6H_5)_3^-$ complex is the most stable of these complexes in pyridine solution [13]. The solvent interaction with a phenyl group is approximately twice as strong as with a butyl group [22, 23]. It is hard to tell if the Hg–S bond distance depends on either substantially weaker solvation of the butyl groups, or on smaller atom radius on the sulfur atom in the $SC_4H_9^-$ ion than in $SC_6H_5^-$ ion, or in fact, whether it depends on both factors.

The mononuclear $HgSC_4H_9^+$ complex exists in dilute pyridine solution [13]. This complex dimerizes when the concentration is increased. The structure of the $Hg_2(S^nC_4H_9)_2^{2+}$ complex is very similar to the units building the infinite chains in the structures of $Hg(S^tC_4H_9)_2$ [6] and $Hg(S^nC_4H_9)_2$ [5]. The Hg–S bond distance is 2.48(2) Å and the Hg–Hg distance is 3.69(5) Å. This means that the Hg–S–Hg angle is 96(3)°, and the S–Hg–S angle is 84° if the

Hg_2S_2 entity is co-planar, or somewhat smaller if the Hg_2S_2 entity is slightly out of planarity. Pyridine is definitely coordinated to mercury atoms in the $Hg_2(S^nC_4H_9)_2^{2+}$ complex. This study did not allow, however, the determination of either the number of coordinated pyridines or the Hg–N(pyridine) distance.

A change in the complex distribution can occur when the concentration is increased. The neutral copper(I) and silver(I) halide complexes in tetrahydrothiophene are monomeric in dilute solution while dimers or tetramers are formed in concentrated solution [24]. Already at 0.1 M this reaction starts. A mixture of Hg_2I^{3+} and HgI_2 complexes is formed in concentrated DMSO solutions with the Hg/I ratio one [20]. This reaction also starts at around 0.1 M. It is plausible that the $HgSR^+$ complexes in pyridine behave in a similar way.

Acknowledgements

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References

1 W. C. Zeise, *J. Prakt. Chem.*, *1*, 257; 396; 457 (1834).
2 A. F. Wells, *Z. Kristallogr.*, *96A*, 435 (1937).
3 D. C. Bradley and N. R. Kunchur, *J. Chem. Phys.*, *40*, 2258 (1964).
4 D. C. Bradley and N. R. Kunchur, *Can. J. Chem.*, *43*, 2786 (1965).
5 C. I. Stålhandske and F. Zintl, *Acta Crystallogr.*, in press.
6 N. R. Kunchur, *Nature*, *204*, 468 (1964).
7 A. J. Canty and R. K. Tyson, *Inorg. Chim. Acta*, *24*, L77 (1977).
8 H. Puff, R. Sievers and G. Elsner, *Z. Anorg. Allg. Chem.*, *413*, 37 (1975).
9 C. I. Stålhandske and F. Zintl, *Acta Crystallogr., Sect. C*, *42*, 1731 (1986).
10 G. Christou, K. Folking and J. C. Huffman, *Polyhedron*, *3*, 1247 (1984).
11 S. Choudhury, I. G. Dance, P. J. Guerney and A. D. Rose, *Inorg. Chim. Acta*, *70*, 227 (1983).
12 G. A. Bowmaker, I. G. Dance, B. C. Dobson and D. A. Rogers, *Aust. J. Chem.*, *37*, 1607 (1984).
13 F. Zintl and I. Persson, *Inorg. Chim. Acta*, *131* (1987), in press.
14 H. A. Levy, M. D. Danford and A. H. Narten, 'Data Collection and Evaluation with an X-Ray Diffractometer Designed for the Study of Liquid Structure', *Report ORNL-3960*, Oak Ridge National Laboratory, Oak Ridge, 1966.
15 I. Persson, M. Sandström, P. L. Goggin and A. Mosset, *J. Chem. Soc., Dalton Trans.*, 1597 (1985).
16 M. Sandström and G. Johansson, *Acta Chem. Scand., Ser. A*, *31*, 132 (1977).
17 G. Johansson and M. Sandström, *Chem. Scr.*, *4*, 195 (1973).
18 M. Molund and I. Persson, *Chem. Scr.*, *25*, 197 (1985).
19 I. Persson, *Pure Appl. Chem.*, *58*, 1153 (1986).
20 S. Ahrland, E. Hansson, Å. Iverfeldt and I. Persson, *Acta Chem. Scand., Ser. A*, *35*, 275 (1981).
21 M. Sandström, *Acta Chem. Scand., Ser. A*, *32*, 627 (1978).
22 K. G. Lawrence and A. Sacco, *J. Chem. Soc., Faraday Trans., 1*, *79*, 615 (1983).
23 M. Johnsson and I. Persson, *Inorg. Chim. Acta*, *127*, 15 (1987).
24 M. Johnsson and I. Persson, *Inorg. Chim. Acta*, *130* (1987), in press.