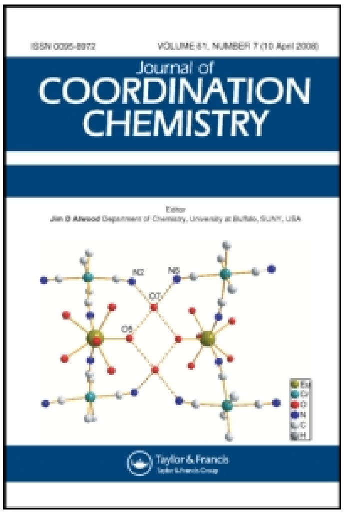

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Synthesis and characterization of bis(organothiolato)mercury(ii) complexes by disproportionation of Hg_2Cl_2 in the presence of thiols

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SYNTHESIS AND CHARACTERIZATION OF BIS(ORGANOTHIOLATO)MERCURY(II) COMPLEXES BY DISPROPORTIONATION OF Hg_2Cl_2 IN THE PRESENCE OF THIOLS

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Mercury(I) chloride disproportionates to mercury metal and bis(organothiolato)mercury(II) in the presence of some thiols in good yields. The products were analyzed by means of ^{1}H NMR and gas chromatographic–mass spectrometry (GC/MS), which indicated that the complexes are monomers in the gas phase and decomposed at elevated temperature to mercury(0) and corresponding disulfides.

Keywords: Mercury(I); Chloride; Thiols; Mercury(II) complexes

INTRODUCTION

Sustained interest in the coordination chemistry of mercury(I) and mercury(II) has resulted from the inherent toxicity of these ions. Mercury(II) and especially methylmercury(II) is extremely toxic to living organisms and, owing to its bioaccumulation in the food chain, it is dangerous to higher organisms [1,2]. Such toxic behavior derives from the affinity of mercury(II) compounds for cysteinyl sulfur residues in a variety of biosystems [3]. Heterocyclic thiones and thionates are among the ligand systems used to mimic bio-relevant mercury(II)–sulfur interactions [4].

Despite the fact that bis(organothiolato)mercury(II) compounds of composition $Hg(SR)_2$ have been known for a long time [2,5–13], questions remain concerning their chemistry, especially the reactions of thiols with mercury(I).

A literature search showed that all bis(organothiolato)mercury(II) compounds have previously been prepared from mercury(II) salts [2,10–23], or by photochemically [24] or electrochemically [25] initiated redox reactions starting from mercury and organic disulfides. To the best of our knowledge there is no report on the reaction of mercury(I) with thiols.

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The mercury(I) ion is peculiar in that it is associated into the double ion Hg_2^{2+}, not only in solution but also in its solid compounds. Some mercury(I) compounds (notably the oxide, sulfide and iodide) are unstable and undergo spontaneous decomposition to the corresponding mercury(II) compound and free mercury [26]. In continuation of our interests on thermal and photochemical reactions of mercury(I) and mercury(II) inorganic compounds with potential organic ligands [27–31], and applications of mercury(II) complexes in electrochemistry [32], in the present work we have focused on the reactions of some thiols with Hg_2^{2+} which leads to disproportionation of Hg_2^{2+} into bis(organothiolato)mercury(II) complexes and free mercury in quantitative yields. Moreover, we extended our investigation on the GC/MS and NMR data of these complexes to allow comparisons to be made both of the title compounds with each other and of the collected data with those already published.

EXPERIMENTAL

All solvents and chemicals were reagent grade and used as received. Gas chromatographic–mass spectrometry investigations (GC/MS) were performed using a Shimadzu GC/MS-QP1000EX and an AMD 604 spectrometer, EI mode at 70 eV, FT mode at 0.005 V, $\Delta m = 1$. ^{1}H NMR spectra were recorded on a Bruker Avance DPX 250 MHz in DMSO-d_6.

Caution: Because of the toxicity of mercury and related compounds, all the reactions were carried out under strong ventilation and the use of metallic apparatus was strictly avoided.

Material

2-Pyridinethiol, 4-chlorothiophenol, 4-methylthiophenol, 2-mercaptobenzothiazol, 2-mercaptobenzoxazol, 2-naphthalenethiol, 4-bromothiophenol, 2-pyrimidinethiol, 3-methoxythiophenol, 3,5-dimethyl-2-pyrimidinethiol, 4-fluorothiophenol, 2,6-dichlorothiophenol, 2-aminothiophenol and mercury(I) chloride were used as reagent grade chemicals from Merck and Aldrich.

Preparation of Bis(4-chlorothiphenolato)mercury(II) from Hg_2Cl_2 and 4-Chlorothiphenol

A methanolic solution (10 cm^3) of 4-chlorothiophenol (1 mmol, 0.144 g) was added to a suspension of Hg_2Cl_2 (0.5 mmol, 0.236 g) in methanol (10 cm^3) with stirring. The reaction mixture darkened immediately. The course of the reaction was followed by TLC (3 : 1, *n*-hexane : THF). After between 30 min and 2 h the voluminous grayish precipitate that contained free mercury and bis(4-chlorothiphenolato)mercury(II) was filtered under suction and washed twice with methanol. To separate the grayish black mercury powder (insoluble in THF) from bis(4-chlorothiophenolato)mercury(II) (soluble in THF), the precipitate was dissolved in the minimum volume of THF and filtered under suction. Evaporation of the clear solution resulted in a white precipitate of bis(4-chlorothiophenolato)mercury(II), which was identified by spectral and physical data (Tables I and II).

TABLE I ^{1}H NMR data and melting point of bis(organothiolato)mercury(II)

No	*Name*	*Chemical shift* (ppm)	*Melting point* (°C)	*Yields* (*%*)
1	Bis(2-pyridinethiolato)mercury(II)	(8.04 ppm, t, 2 H) (7.21 ppm, m, 4 H)	178	82
2	Bis(4-chlorothiophenolato)mercury(II)	(6.80 ppm, d, 2 H) (7.13 ppm, d, 4 H)	189	87
3	Bis(4-methythiophenolato)mercury(II)	(7.33 ppm, d, 4 H) (6.91 ppm, d, 4 H) (7.22 ppm, d, 4 H)	162	85
4	Bis(2-mercaptobenzothiazolato)mercury(II)	(2.33 ppm, s, 6 H) (7.62 ppm, m, 4 H)	194 (dec.)	70
5	Bis(2-mercaptobenzoxazolato)mercury(II)	(7.31 ppm, m, 4 H) (6.60 ppm, m, 4 H)	203 (dec.)	72
6	Bis(2-naphthalenethiolato)mercury(II)	(6.65 ppm, m, 4 H) (7.39 ppm, m, 4 H)	201	80
7	Bis(4-bromothiophenolato)mercury(II)	(7.54 ppm, m, 4 H) (7.69 ppm, m, 4 H)	229	83
8	Bis(2-pyrimidinethiolato)mercury(II)	(8.13 ppm, t, 2 H	215	78
9	Bis(4-fluorothiophenolato)mercury(II)	(7.29 ppm, d, 4 H)	94	88
10	Bis(3-methoxythiophenolato)mercury(II)	(7.37 ppm, d, 4 H) (8.46 ppm, m, 4 H) (7.16 ppm, t, 2 H)	119	86
11	Bis(3,5-dimethypyrimidinethiolato)mercury(II)	(7.06 ppm, t, 4 H) (7.39 ppm, t, 4 H)	219	75
12	Bis(2-aminothiophenolato)mercury(II)	(3.95 ppm, S, 6 H) (6.65 ppm, S, 2 H) (6.95 ppm, m, 4 H) (7.05 ppm, m, 2 H)	139 (dec.)	71
13	Bis(2,6-dichlorothiophenolato)mercury(II)	(2.19 ppm, S, 12 H) (6.93 ppm, m, 2 H) (5.18 ppm, d, 4 H) (6.40 ppm, m, 2 H) (6.74 ppm, 2 H) (6.90 ppm, m, 2 H) (7.50 ppm, m, 2 H) (7.44 ppm, t, 4 H) (7.15 ppm, q, 2 H)	279	85

TABLE II Mass spectral data and main fragmentation pattern of compounds **1**–**13** together with their most important decomposition products

No	*Name*	*Fragmentation* (*main peaks*)						
		M.W.	M^{+a}	*R*	*RS*	*RSSR*	*RSR*	Hg^{a}
1	Bis(2-pyridinethiolato)mercury(II)	420.7	419	78	109	220	187	202
2	Bis(4-chlorothiophenolato)mercury(II)	488.6	488	111	143	286	–	202
3	Bis(4-methylthiophenolato)mercury(II)	446.8	446	91	123	246	213	202
4	Bis(2-mercaptobenzothiazolato)mercury(II)	533.4	533	134	167	332	300	202
5	Bis(2-mercaptobenzoxazolato)mercury(II)	500.7	500	122	151	300	268	202
6	Bis(2-naphthalenethiolato)mercury(II)	518.8	520	127	159	318	285	202
7	Bis(4-bromothiophenolato)mercury(II)	576.5	576	–	187	376	–	202
8	Bis(2-pyrimidinethiolato)mercury(II)	422.7	424	79	111	222	190	202
9	Bis(4-fluorothiophenolato)mercury(II)	454.5	456	95	127	254	222	202
10	Bis(3-methoxythiophenolato)mercury(II)	478.8	480	108	139	278	245	202
11	Bis(3,5-dimethylpyrimidinethiolato)mercury(II)	478.8	480	107	139	278	245	202
12	Bis(2-aminothiophenolato)mercury(II)	448.7	450	97	124	248	216	202
13	Bis(2, 6-dichlorothiophenolato)mercury(II)	556.7	556	142	177	356	221	202

[a] Main peaks with isotopic pattern of mercury.

The procedure described here is typical for the preparation of a range of the title complexes.

RESULTS AND DISCUSSION

Synthesis

Addition of methanolic solutions of thiols to a methanolic suspension of Hg_2Cl_2 led to darkening of the reaction mixture. Stirring for between 30 min and 2 h, depending on the nature of the thiol (except for 2-mecaptobenzothiazol, and 2-mercaptobenzoxazol, which required reaction times of about 8–12 h), gave voluminous grayish precipitates containing free mercury and white bis(organothiolato)mercury(II) without the need for an auxiliary base [10]. The compounds are obtained in high yields. In this reaction mercury(I) chloride, Hg_2Cl_2, disproportionates rapidly to bis(organothiolato)mercury(II) and free mercury. The same bis(organothiolato) mercury(II) may be obtained from mercury(II) chloride, $HgCl_2$, and thiols under more severe conditions and with longer reaction times (3–4 h).

Identification of Bis(organothiolato)mercury(II) by ^{1}H NMR and GC/MS

Spectral and physical data of two known complexes, **2** and **4**, were compared with literature values (Tables I and II) [2,21]. ^{1}H NMR and gas chromatographic–mass spectrometry (GC/MS) data were successful for identification of these complexes [9]. GC/MS was also run immediately after the combination of the reagents in order to observe the Hg(I) thiolate and thereby provide support for the mechanism shown in Eq. (1). The ^{1}H NMR spectra did not show any S–H resonance in the 3.6–4.2 ppm range and other peaks in the aromatic region showed good agreement with bis(organothiolato)mercury(II) complexes (Table I).

GC/MS investigations clearly reveal the bis(organothiolato)mercury(II) molecular ions. As expected, they easily undergo decomposition at elevated temperatures and the main decomposition products are Hg, R, RS, RSSR and RSR with the mercury isotopic pattern in the molecular ion and the mercury ion fragment. Moreover, the signal intensities of the bis(organothiolato)mercury(II) complexes generally decrease with increasing molecular weight of the complexes, whereas the corresponding signals of the decomposition products increase, owing to decomposition of these complexes during progressively longer retention times on the GC column. The main fragments of all the complexes are given in Table II.

During the reaction of 2-pyridinethiol with Hg_2Cl_2 three products were recognized by TLC monitoring: free mercury, bis(organothiolato)mercury(II) and a very small amount of unidentified product. The following mechanism is proposed for the reaction of Hg_2^{2+} and thiols [10,26,33–36].

$$Hg_2Cl_2 + 2RSH \rightarrow Hg_2(SR)_2 + 2HCl \qquad (1)$$

$$\begin{tikzcd} & Hg(0) + Hg(SR)_2 & \\ Hg_2(SR)_2 \arrow[ur, "a"] \arrow[dr, "b"'] & & \\ & 2Hg(0) + RSSR \arrow[r] & Hg(0) + Hg(SR)_2 \end{tikzcd} \qquad (2)$$

Presumably the bis(organothiolato)mercury(I) complexes, RSHgHgSR formed in the first step rapidly lose mercury(0) in the second step, via two possible pathways, a and b. Electrochemically induced reactions of Hg(0) with disulfides support the step-b mechanism [37]. Somewhat longer reaction times (8–10 h) for 2-mercaptobenzothiazol, and 2-mercaptobenzoxazol (non-thiophenolic compounds) compared to other thiols (thiophenolic) support this mechanism because the softness of thiophenolic thiols increases the rate of the first step and promotes oxidation in the second step of the proposed mechanism.

CONCLUSION

In this work, we report that Hg_2Cl_2 disproportionates to bis(organothiolato) mercury(II) and free mercury powder in the presence of thiols at room temperature. ^{1}H NMR and GC/MS spectral data indicate that the mercury complexes are monomeric in the gas and solution phases. The corresponding mass spectra of bis(organothiolato)mercury(II) show molecular ions with the mercury isotopic pattern.

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