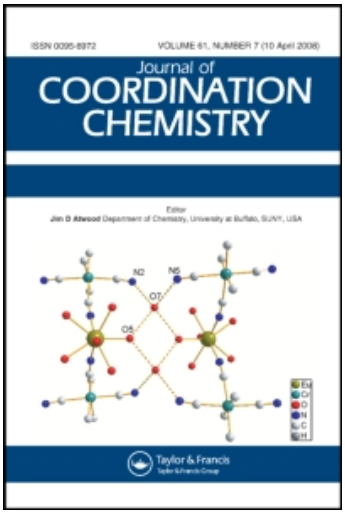

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Preparation and spectral investigation of bis[*N*-(substituted-phenyl)thiobenzamidato]mercury(II) complexes

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Preparation and spectral investigation of bis[*N*-(substituted-phenyl)thiobenzamidato]mercury(II) complexes

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Several preparative routes to bis[*N*-(substituted-phenyl)thiobenzamidato]mercury(II) complexes are presented, including the reaction of mercury(II) oxide, fluoride, chloride, bromide, cyanide, acetal and nitrate with *N*-(substituted-phenyl)thiobenzamide derivatives. ^{1}H NMR, Raman and IR measurements confirm the complexation of mercury to sulfur. The mercury(II) complexes with *N*-substituted phenylthiobenzamide ligands did not show antimicrobial activity against test organisms, unlike the starting mercury(II) compounds of high toxicity. This may allow some therapeutic uses when considered as an antidote to mercury poisoning.

Keywords: Mercury poisoning; Mercury(II); Thiobenzamide

1. Introduction

Current interest in the coordination chemistry of mercury complexes with sulfur ligands is related to mercury–cysteine thionato interactions in the toxicological behavior of this metal [1, 2], in detoxification of mercury by metallothionenes [3], in a DNA-binding protein [4] and in mercury reductase and related proteins [5]. The sustained interest in the coordination chemistry of mercury and sulfur-containing ligands is related to the environmental consequences of the high toxicity of the metal to living systems [6–11]. Consequently, a number of attempts have been made to explore the coordination chemistry of mercury(II) with sulfur-containing ligands such as phenyl thiolate and heterocyclic thiones, e.g. pyrimidine-2-thione and imidazoline-2-(OH)-thione derivatives [12–35]. Thiolate ligands have a high affinity for Hg(II), producing various complexes such as $Hg(SR)_2$, $[Hg(SR)_3]^-$ and $[Hg(SR)_2Cl_2]^2$. The common coordination form for the thiolate complexes is linear dicoordination with a short Hg–S distance

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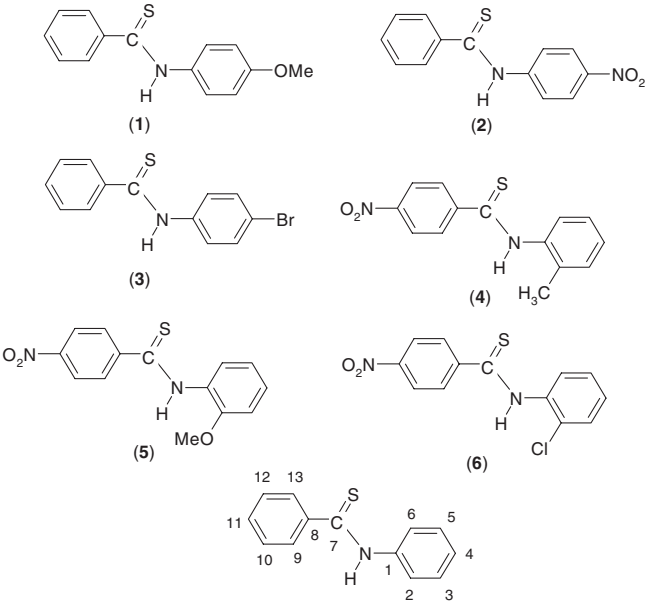


Scheme 1. The free ligands and atom numbering.

[36–40]. Mercury(II) ions interact with many biological molecules through coordination with deprotonated thiol, imidazole, disulfide, thioether, amino or carboxylate groups and its interactions in model molecules and in proteins are well known [41]. In previous papers we have reported the thermal and photochemical reactions of mercury compounds [42–45].

The only significant antidotes to the toxicity of mercury and its compounds of clinical importance are monothiols or dithiols. We are therefore interested in the study of the coordination chemistry of mercury(II) with sulfur-containing ligands such as thiobenzamides with very low toxicity, not only for clarification of the mercury poisoning mechanism but also for the development of new antidotes. To the best of our knowledge, there are no reports on the preparation and spectral characterization of mercury(II) with *N*(substituted-phenyl)thiobenzamide ligands.

Recently we reported the preparation and application of bis(2-mercaptobenzoxazolato)mercury(II) [$Hg(MBO)_2$] and bis(2-pyridinethiolato) mercury(II) [$Hg(PT)_2$] complexes as carriers for thiocyanate-selective electrodes [46, 47]. In this article, we describe the preparation and spectroscopic studies of six *N*-(substituted-phenyl)thiobenzamide complexes of mercury(II) (**7**–**12**) derived from the reaction of HgX_2 with *N*-(substituted-phenyl)thiobenzamide ligands (**1**–**6**) (scheme 1).

2. Experimental

2.1. *Materials*

N-(substituted-phenyl)thiobenzamide ligands **1**–**6** were prepared according to reported procedures [48, 49] and mercury(II) inorganic compounds were commercially available and used without further purification.

2.2. *Physical methods*

Microanalyses were carried out by Elemental Micro-Analysis Ltd. Mercury was analyzed using a Shimadzu AA-680 atomic absorption spectrometer. IR spectra of the ligands and complexes were obtained using KBr disks in the range 4000–400 cm^{-1} with a Shimadzu 430 spectrometer. Raman spectra were collected using 1800 backscattering geometry and a Bomem MB-154 Fourier Transform Raman spectrometer equipped with a ZnSe beam splitter and a TE cooled InGaAs detector. Rayleigh filtering was performed by two sets of two Holographic technology filters. The laser power at the samples was 40 mW. ^1H NMR spectra were obtained as solutions in $CDCl_3$ with a Bruker AC 250 spectrometer. Mass spectra were acquired using a Micromass platform spectrometer, EI-mode at 70 eV.

2.3. *Preparation of complexes*

2.3.1. Typical procedure: preparation of bis[*N*-(4-methoxyphenyl)thiobenzamidato] mercury(II) [Hg(Nmtptb)$_2$] (7). One mmol of mercury(II) oxide (0.216 g) (excess) was added to a solution of *N*-(4-methoxyphenyl)thiobenzamide (0.243 g, 1 mmol) at ambient temperature in acetonitrile (20 mL) for 80 min with stirring. The reaction was followed to completion by thin layer chromatography (TLC) with CCl_4/CH_3OH 15 : 1 as eluent. The complex is insoluble in acetonitrile and the white precipitate formed was filtered off, dissolved in chloroform, filtered under vacuum, recrystallized from chloroform at room temperature as fine pale yellow crystals and dried *in vacuo*. Yield: 85%. Anal. Calcd for $C_{28}H_{24}N_2O_2S_2Hg$(%): C, 49.12; H, 3.51; N, 4.09; Hg, 29.24. Found: C, 49.23; H, 3.59; N, 4.06; Hg, 29.31. m.p. 175–178°C.

2.3.2. Bis[*N*-(4-nitrophenyl)thiobenzamidato]mercury(II) [Hg(Nnptb)$_2$] (8). The same method of preparation was used as for the typical procedure but using *N*-(4-nitrophenyl)thiobenzamide (0.258 g, 1 mmol) in acetonitrile (25 mL for 180 min) and the complex was recrystallized from chloroform as yellow crystals. Yield: 94%. Anal. Calcd for $C_{26}H_{18}N_4O_4S_2Hg$(%): C, 43.69; H, 2.52; N, 7.84; Hg, 28.01. Found: C, 43.31; H, 2.47; N, 7.65; Hg, 28.13. m.p.173–175°C.

2.3.3. Bis[*N*-(4-bromophenyl)thiobenzamidato]mercury(II) [Hg(Nbptb)$_2$] (9). The same method of preparation was followed but using *N*-(4-bromophenyl)thiobenzamide (0.292 g, 1 mmol) in chloroform (10 mL for 105 min) and the complex was recrystallized from chloroform as pale yellow crystals. Yield: 95%. Anal. Calcd for $C_{26}H_{18}N_2S_2Br_2Hg$(%): C, 39.89; H, 2.3; N, 3.58; Hg, 25.57. Found: C, 39.75; H, 2.45; N, 3.41; Hg, 25.48. m.p.197–199.5°C.

2.3.4. Bis[*N*-(2-methylphenyl)-4-nitrothiobenzamidato]mercury(II) [Hg(Nmpntb)$_2$] (10). The same method of preparation but using *N*-(2-methylphenyl)-4-nitrothiobenzamide (0.273 g, 1 mmol) in chloroform (35 mL for 130 min) was followed and the complex recrystallized from chloroform as pale yellow crystals. Yield: 95%. Anal. Calcd for $C_{28}H_{22}N_4O_4S_2Hg$(%): C, 45.28; H, 2.96; N, 7.55; Hg, 26.95. Found: C, 45.12; H, 3.12; N, 7.35; Hg, 27.08. m.p. 193–195°C.

2.3.5. Bis[*N*-(2-methoxyphenyl)-4-nitrothiobenzamidato]mercury(II) [Hg(Nmtpntb)$_2$] (11). The same method of preparation was followed but using *N*-(2-methoxyphenyl)-4-nitrothiobenzamide (0.288 g, 1 mmol) in chloroform (45 mL, 330 min) and the complex recrystallized from CH_2Cl_2 as pale yellow crystals. Yield: 94%. Anal. Calcd for $C_{28}H_{22}N_4O_6S_2Hg$(%): C, 43.41; H, 2.84; N, 7.24; Hg, 25.84. Found: C, 43.56; H, 2.67; N, 7.39; Hg, 25.97. m.p. 129–131°C.

2.3.6. Bis[*N*-(2-chlorophenyl)-4-nitrothiobenzamidato]mercury(II) [Hg(Ncpntb)$_2$] (12). The same method of preparation was followed but using *N*-(2-chlorophenyl)-4-nitrothiobenzamide (0.2925 g, 1 mmol) in chloroform (50 mL, 90 min) and the complex recrystallized from chloroform as yellow crystals. Yield: 87%. Anal. Calcd for $C_{26}H_{16}N_4O_4S_2Cl_2Hg$(%): C, 39.84; H, 2.04; N, 7.15; Hg, 25.5. Found: C, 39.55; H, 1.97; N, 7.02; Hg, 25.75. m.p. 210–212.6°C.

3. Results and discussion

Complexes **7**–**12** were readily prepared in good yield by the addition of equimolar quantities of HgX_2 ($X = F^-$, Cl^-, Br^-, CN^-, NO_3^-, OAc^-) and HgO to the ligands in chloroform (table 1, scheme 2). The most common preparation used HgO, although HgF_2, $HgCl_2$, $HgBr_2$, $Hg(CN)_2$, $Hg(OAc)_2$ and $Hg(NO_3)_2$ can be used. The reaction of 1 equiv. HgO with 2 equiv. of *N*-(substituted-phenyl)thiobenzamide proceeded at lower yield and longer reaction times (1–2 days). Irradiation of the reaction mixture with a 400-W high-pressure mercury lamp enhanced the rate by 30%. No reaction was observed on photolysis of *N*-(substituted-phenyl)thiobenzamide in the absence of an acetonitrile solution of HgO. In the reaction of *N*-(substituted-phenyl)thiobenzamide with 1 equiv. of $Hg(NO_3)_2$ in chloroform, the isolated products were 30–60% benzoamide and 25–62% 1 : 2 complex. The reaction of thiobenzamide with $Hg(OAc)_2$ produced a 1 : 2 complex in a few minutes and the complex decomposed to imides in solution immediately. The same reactions proceed in the presence of catalytic amounts of triethylamine as an auxiliary base, and 1 : 2 complexes were formed at longer reaction times but decomposed to imides [50]. The reaction of *N*-phenyl-*N*-methyl-4-nitrothiobenzamide did not proceed with mercury(II) compounds in various solvents (e.g. acetonitrile, chloroform, dichloromethane, tetrahydrofuran) even at prolonged times, and under photochemical conditions. This inertness is due to the absence of the N–H bond on this ligand while ligands **1**–**6** with N–H bonds undergo complexation.

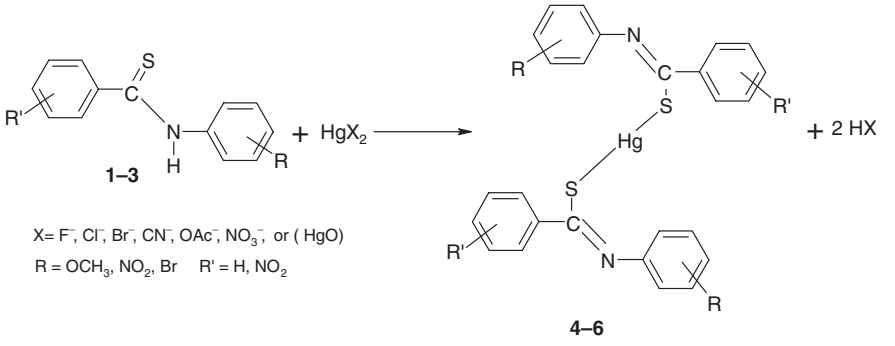
Complexes **7**–**12** melt in the range 129–212.6°C whereas the thiobenzamide analogs melt at 122–152°C. The complexes are pale yellow to yellow, whereas the parent thiobenzamides are yellow to orange. All six ligands are monodentate and coordinate to mercury through sulfur. To establish the mode of coordination in the thiobenzamide complexes, we examined their Raman spectra, as well as the ^{1}H NMR spectra of the 1 : 2 complexes.

^{1}H NMR data for all six complexes, together with those for the free ligands, recorded in $CDCl_3$ solution are listed in table 2. It would be expected that the phenyl group nearest to sulfur would be the most sensitive to coordination. In the free thiobenzamide ligands **1**–**6** the resonances at 8.88–9.35 are due to the N–H bond; these shifts are absent in ^{1}H NMR spectra of **7**–**12**. This clearly indicates the N–H bond cleavage and coordination through sulfur (table 2).

Table 1. Preparation method, reaction times and yields of **7**–**12**.

Complex	Thiobenzamide	Mercury(II) salts	Reaction time (min)	Yield (%)[a]
7	NmtptbH (**1**)	HgO	80	85
		HgF_2	120	68
		$HgCl_2$	60	81
		$HgBr_2$	100	70
		$Hg(CN)_2$	105	95
		$Hg(OAc)_2$	10	65
		$Hg(NO3)_2$	120	59
8	NnptbH (**2**)	HgO	180	94
		HgF_2	300	45
		$HgCl_2$	45	67
		$HgBr_2$	220	53
		$Hg(CN)_2$	240	95
		$Hg(OAc)_2$	20	42
		$Hg(NO3)_2$	35	40
9	NbptbH (**3**)	HgO	105	95
10	NmpntbH (**4**)	HgO	130	95
		HgF_2	90	70
		$HgCl_2$	5	89
		$HgBr_2$	15	85
		$Hg(CN)_2$	310	80
		$Hg(OAc)_2$	2	74
		$Hg(NO3)_2$	105	62
11	NmtpntbH (**5**)	HgO	330	94
12	NcpntbH (**6**)	HgO	90	87
		HgF_2	210	30
		$HgCl_2$	5	72
		$HgBr_2$	120	58
		$Hg(CN)_2$	165	83
		$Hg(OAc)_2$	3	64
		$Hg(NO3)_2$	120	25

[a]Isolated yield.



Scheme 2. Reaction scheme of *N*-(substituted-phenyl)thiobenzamide ligands with mercury(II) compounds.

Characteristic IR absorption bands in the 4000–400 cm^{-1} region and Raman bands in the 800–100 cm^{-1} region are summarized in tables 3 and 4, respectively. Shifts to lower frequency in the thioamide(IV) band as well as in the (C=S) absorption are associated with sulfur donation in which C=S gains some C–S character upon donation.

Table 2. ^{1}H NMR data (δ in ppm in $CDCl_3$) for six thiobenzamide complexes of mercury(II) and their corresponding free ligands.

	N–H	H9, H13	H2, H6	H10, H12	H3, H5	H11	H4	CH_3/OCH_3
NmtptbH **1**	8.9	7.82	7.6	7.45	6.9	7.2	–	3.8
[Hg(Nmtptb)$_2$] **7**	–	8.17	6.4	7.5	7.2	7.3	–	3.7
NnptbH **2**	9.24	8.07	8.32	7.5	7.84	7.56	–	–
[Hg(Nnptb)$_2$] **8**	–	8.39	7.97	7.56	6.72	7.56	–	–
NbptbH **3**	8.9	7.82	7.6	7.42	7.55	7.3	–	–
[Hg(Nbptb)$_2$] **9**	–	8.15	6.5	7.42	7.63	7.42	–	–
NmpntbH **4**	8.88	8.33	7.59	8.06	7.36	–	7.36	2.4
[Hg(Nmpntb)$_2$] **10**	–	8.34	6.41	8.24	7.35	–	7.21	2.02
NmtpntbH **5**	9.1	8.3	7.22	7.9	7.1	–	6.9	3.92
[Hg(Nmpntb)$_2$] **11**	–	8.4	6.24	8	7.1	–	6.8	3.79
NcpntbH **6**	9.35	8.3	7.6	8.1	7.21–7.40	–	7.6	–
[Hg(Ncpntb)$_2$] **12**	–	8.36	6.62	8.27	7.26(H5), 6.8(H3)	–	7.46(H4)	–

Table 3. Major IR bands (cm^{-1}) and their assignments for six thiobenzamide complexes of mercury(II) and their corresponding free ligands.

		Thioamide bands			
	ν(NH)	I	II	III	IV
NmtptbH **1**	3161m	1596w	1175 m	918w	620m
[Hg(Nmtptb)$_2$] **7**	–	1598vs	1163m	908s	604s
NnptbH **2**	3266m	1556m	1284m	1032w	749m
[Hg(Nnptb)$_2$] **8**	–	1568s	1261s	1021vs	691m
NbptbH **3**	3136m	1587m	1213s	889w	742s, 638m
[Hg(Nbptb)$_2$] **9**	–	1603vs	1163s	909vs	710m, 604m
NmpntbH **4**	3313m	1580w	1227m	994m	730w, 670w
[Hg(Nmpntb)$_2$] **10**	–	1585vs	1181m	920m	740w, 616m
NmtpntbH **5**	3334w	1599m	1200m	929m	736m, 641w
[Hg(Nmpntb)$_2$] **11**	–	1605vs	1187m	929s	740m, 617m
NcpntbH **6**	3328m	1595m	1207m	930w	732w, 665w
[Hg(Ncpntb)$_2$] **12**	–	1607vs	1185m	923vs	743w, 616m

s, strong; vs, very strong; m, medium; w, weak.
Thioamide-type modes are described as follows: thioamide I = ν(C–N) + δ(CH); thioamide II = ν(C–N) + δ(CH) + ν(C=S); thioamide III = ν(C–N) + ν(C=S); thioamide IV = ν_s(C=S) + ν_{as}(C=S); according to Ref. [54]. ν, stretching frequency; ν_s, symmetric stretching; ν_{as}, asymmetric (or antisymmetric) stretching; δ, bending.

Table 4. Raman data for six thiobenzamide complexes of mercury(II) and their corresponding free ligands.

	Sk	Sk*	Sk	Sk	Sk*	Sk*
NmtptbH **1**	613.2	405	364	246.8	–	
[Hg(Nmtptb)$_2$] **7**	611.3	–	378	291	217	183, 106, 75, 61.6
NnptbH **2**	673	408.8	354	235	–	
[Hg(Nnptb)$_2$] **8**	600	–	378	274	217.8	162, 111, 86
NbptbH **3**	696	407	351	239	–	
[Hg(Nbptb)$_2$] **9**	678	–	378	281	193	156, 106, 78, 64
NmpntbH **4**	644m	413m	358m	283s	–	
[Hg(Nmpntb)$_2$] **10**	694s	–	381s	281m	219m	171.6, 90.6, 57.8
NmtpntbH **5**	594w	408w	303w	–	–	
[Hg(Nmpntb)$_2$] **11**	627m	–	332m	–	219m	84.7, 69.4, 56.3
NcpntbH **6**	640m	474m	345m	276m	–	
[Hg(Ncpntb)$_2$] **12**	675m	–	372s	271m	218m	165.8, 90.6, 65.5, 46.2

Sk, skeletal bands of the ligand; Sk*, changes in the electronic structure due to complexation.

In the free thiobenzamide ligands **1**–**6** the presence of ν(NH) bands at 3161–3334 cm^{-1} is due to the N–H bond, while these ν(NH) bands are absent in IR spectra of complexes **7**–**12**. This clearly indicates that the ligands (NmtptbH, NnptbH, NbptbH, NmpntbH, NmtpntbH, NcpntbH) are coordinated through the sulfur in all six mercury complexes. The most significant change was seen for the thiobenzamide bands, especially the thioamide(IV) band, which shifted to lower frequency [51, 54]. Shifts to higher frequency in the thioamide(I) band for ν(CN) bands are associated with gaining some C=N character (table 3). Complementary information is obtained by assignment of Raman vibrational spectral features of the complexes (table 4). Structural information can be obtained for complexes in the low frequency range (below 700 cm^{-1}). The skeletal vibrations, as before, can readily be identified by comparison with the pure ligand spectrum. The remaining spectral features are due to complexation, i.e., ν(Hg–S).

Mass spectra were recorded for the NbptbH ligand and [Hg(Nbptb)$_2$] complex. The free ligand species is fully confirmed by molecular ion $(M–H)^+$ peaks of m/z 291 and the peak at $(M+2)^+$ attributed to the isotopic pattern of sulfur. The most intense peaks at m/z 170, 110, 121, 77 and 91 are attributed to $(NC_6H_4Br)^+$, $(C_6H_5SH)^+$, $(C_6H_4CS)^+$, $(C_6H_5)^+$ and $(HNC_6H_5)^+$ with abundances 27, 100, 91, 41 and 32%, respectively. The most intense peaks for the complex are attributed to $(C_6H_5CNC_6H_4Br)^+$ and $(C_6H_5)^+$ and the isotopic patterns of mercury with abundances 87, 88 and 7–20% respectively. The presence of the peak at m/z 260 with high abundance clearly indicates that the ligand is coordinated to mercury through the thiobenzamide sulfur atom.

Antimicrobial activities of the mercury(II) complexes **7**–**12** together with those of the starting mercury(II) compounds and the free thiobenzamides were measured and evaluated by the Kirby–Bauer (agar disk diffusion) method [55].

The free thiobenzamide ligands showed moderate activities against Gram-positive bacteria (*Bacillus subtilis* and *Staphylococcus aureus*) and yeast (*Saccahromyces cerevisiae*) and modest activities against molds (*Aspergillus niger* and *Pseudomonas griseofulvum*) and Gram-negative (*Escherichia coli* and *Pseudomonas aeruginosa*) bacteria. The starting mercury(II) compounds showed high activities against a Gram-positive bacterium (*B. subtilis* and *S. aureus*), molds (*A. niger* and *P. griseofulvum*), yeast (*S. cerevisiae*) and moderate activities against Gram-negative bacteria (*E. coli* and *P. aeruginosa*).

Compared with antimicrobial activities of the free ligands and starting mercury(II) compounds, the two-coordinate mercury(II) complexes showed no antimicrobial activities against selected bacteria, molds and yeast, completely different from the activity of starting mercury(II) compounds. This lack of activity may allow therapeutic uses when considered as an antidote to mercury poisoning.

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