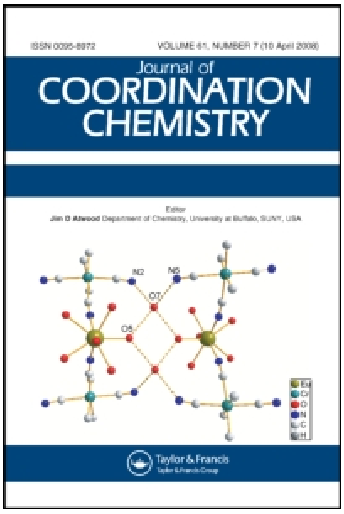

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^1H, ^{13}C AND ^{199}Hg NMR STUDIES OF THE COMPLEXATION OF $HgCl_2$ BY IMIDAZOLIDINE-2-THIONE AND ITS DERIVATIVES

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Mercury(II) complexes of imidazolidine-2-thione and its derivatives have been synthesized and their ^1H, ^{13}C and ^{199}Hg NMR spectra measured. $HgCl_2$ forms L_2HgCl_2 type complexes (where L = imidazolidine-2-thione and its derivatives). The NH group of the ligand is shifted downfield by about +1.37 ppm in the ^1H NMR after complexation. The C-2 carbon in the ^{13}C NMR is shifted by −6.50 ppm for mono *N*-substituted ligands, but by −5.30 ppm for *N,N'*-disubstituted ligands. The ^{199}Hg NMR resonance is shifted by about −60 ppm for *N*-substituted ligands, but −140 ppm shifts were observed for *N,N'*-disubstituted ligands.

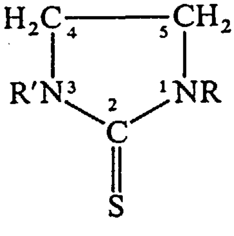
Keywords: Imidazolidine-2-thiones, Hg(II), multinuclear NMR, complexes

INTRODUCTION

As far as bioinorganic chemistry is concerned, some current interest in mercury(II) ions stems from the fact that they form complexes with sulfur-containing biological molecules.[1–6] Studies of the aqueous coordination chemistry of $CH_3Hg(II)$ and Hg(II) have shown that of the potential binding sites in amino acids, peptides and proteins, sulfhydryl groups have a high affinity for the metal ions. SH-containing ligands bind more strongly than thioether ligands. The log K_f values for $CH_3Hg(II)$–thiolate complexes were reported in the range of 14.8 to 17.3,[7] whereas log K_f for $CH_3Hg(II)$–methionine was reported to be 1.94 in acidic aqueous solution.[2]

In biological systems, a thione-containing ligand, ergothionine,[1] is also known. Very little is known about its interaction with Hg(II). However, complexation of thione-containing ligands such as imidazolidine-2-thione and its derivatives and other related ligands with Au(I), Cu(I) *etc.*, have been reported.[8–17] We report here the synthesis and ^1H, ^{13}C and ^{199}Hg NMR studies of the complexation of imidazolidine-2-thione and its derivatives with $HgCl_2$. The results show that ^{199}Hg chemical shifts are not very sensitive to mono substituents on the NH group of the imidazole ring. However, significant chemical shifts were observed with respect to mono and disubstituted imidazole rings.

Complexes of the following ligands are reported.



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(a) R = R′ = H = Imidazolidine-2-thione (Imt); (b) R = $-CH_3$ and R′ = H = *N*-methyl-imidazolidine-2-thione (MeImt); (c) R = $-C_2H_5$ and R′ = H = *N*-ethyl-imidazolidine-2-thione (EtImt); (d) R = $-C_3H_7$ and R′ = H = *N*-propyl-imidazolidine-2-thione (PrImt); (e) R = $-i\text{-}C_3H_7$ and R′ = H = *N*-*i*-propyl-imidazolidine-2-thione (*i*-PrImt); (f) R = R′ = $-CH_3$ = *N*,*N*′-dimethyl-imidazolidine-2-thione (DimeImt); (g) R = R′ = $-C_2H_5$ = *N*,*N*′-diethyl-imidazolidine-2-thione (DietImt); (h) R = R′ = $-i\text{-}C_3H_7$ = *N*,*N*′di-*i*-propyl-imidazolidine-2-thione (Di-*i*-prImt).

The work was carried out with the aim of gaining some insight into the interaction of Hg(II) with ergothionine.

EXPERIMENTAL

Chemicals

All the ligands reported here were prepared by literature methods.[17,18] Analytical grade $HgCl_2$ and DMSO-d_6 were obtained from the Fluka Chemical Company.

Preparation of the Complexes

A solution of $HgCl_2$ (0.5432 g, 2 mmol) in 20 cm^3 of ethanol was added dropwise to a solution of a ligand (4 mmol) in 100 cm^3 of ethanol. The reaction mixture was heated on a water bath for 0.5 hr., after which the solid was filtered off, washed with ethanol, and dried. The yields of the complexes were 70 to 80%. The elemental analyses of these products were carried out on a Carlo Erba (Italy) Elemental Analyzer and are given in Table I.

TABLE I

Analytical data for the L_2HgCl_2 complexes where L = imidazolidine-2-thione and its derivatives.*

Complex	M.P.(°C)	Colour	H%	C%	N%
$(Imt)_2HgCl_2$	250–251	silvery white,	2.26	14.92	11.51
		crystalline	(2.52)	(15.13)	(11.77)
$(MeImt)_2HgCl_2$	152–153	white,	2.97	18.19	10.93
		crystalline	(3.06)	(19.06)	(11.11)
$(EtImt)_2HgCl_2$	161–162	pale yellow,	3.73	21.77	10.31
		powder	(3.76)	(22.57)	(10.53)
$(PrImt)_2HgCl_2$	122–123	white, powder	4.15	24.93	10.06
			(4.28)	(25.73)	(10.07)
$(i\text{-}PrImt)_2HgCl_2$	150–151	white,	4.21	25.69	10.57
		crystalline	(4.28)	(25.73)	(10.07)
$(DimetImt)_2HgCl_2$	68–69	white,	3.73	22.86	10.84
		powder	(3.76)	(22.57)	(10.53)
$(DietImt)_2HgCl_2$	297–298	dark brown,	4.41	26.70	8.85
		powder	(4.76)	(28.59)	(9.53)
$(Di\text{-}i\text{-}PrImt)_2HgCl_2$	144–145	pale yellow,	5.32	31.88	8.37
		powder	(5.60)	(33.56)	(8.70)

* The corresponding calculated values are given in parentheses.

NMR Measurements

^1H and ^{13}C NMR spectra were measured on a Bruker AC-80 spectrometer at 80 MHz and 20 MHz, respectively. A 0.15 M solution of each sample was prepared in DMSO-d_6. All the ^1H, ^{13}C NMR and ^{199}Hg NMR spectra were measured on the same sample. The ^1H and ^{13}C NMR spectra were referenced to internal 1,4-dioxane whose ^1H and ^{13}C peaks were assigned values of +3.57 ppm and +67.4 ppm, respectively, as compared to 0.00 ppm for TMS. In certain cases, the ^{13}C NMR resonance of some ligands overlapped with DMSO-d_6 solvent resonances. The DEPT technique was used to resolve the chemical shifts of the overlapping resonances. ^{199}Hg NMR spectra were measured at 35.784 MHz on a Varian XL-200 spectrometer. The ^{199}Hg isotope has $I = 1/2$, a natural abundance of 16.9% and sensitivity of 1.4% as compared to 100% for proton. The following conditions were used: pulse width 8.0 µs (90°), pulse delay 2s, 32 K data points, spectral width 50,000 Hz, 10 mm multi-nuclear probe, ^1H noise decoupling and internal lock on the deuterium signal of the solvent. Chemical shifts for ^{199}Hg were computed with reference to $(CH_3)_2Hg$ at 0.0 ppm and checked against external $HgCl_2$ (1M) in DMSO-d_6 solvent (−1501 ppm).[19,20]

RESULTS AND DISCUSSION

Reaction of imidazolidine-2-thione and its derivatives with mercuric chloride in most cases gave a white powder or crystalline products. The analytical data and some physical properties of the complexes are listed in Table I.

^1H NMR Chemical Shifts

The ^1H NMR spectra of ligands and the complexes were measured. The chemical shifts of the NH proton of the imidazole ring were observed between 7.65 and 7.95 ppm for Imt through *iso*-propyl-Imt ligand. After complexing with Hg(II), the NH proton shifted to 9.01 for $(Imt)_2HgCl_2$ and 8.70 ppm for the $(\textit{iso}\text{-}PrImt)_2HgCl_2$ complex. For the $(Imt)_2HgCl_2$ system, the NH shift was +1.36 ppm from the free resonance of the ligand. However, for the $(\textit{i}\text{-}PrImt)_2HgCl_2$ system the shift was +0.61 ppm. There were no significant chemical shifts of other ^1H resonances between the free and the bound ligands and these are therefore not reported here. We also prepared the copper complexes $(MeImt)_2CuCl$, $(EtImt)_2CuCl$ and $(\textit{i}\text{-}PrImt)_2CuCl$ as described in the literature.[10] The NH proton resonances of these complexes in DMSO-d_6 appeared at 8.35, 8.42 and 8.29 ppm, respectively. The chemical shift difference between free and bound NH for $(\textit{i}\text{-}PrImt)_2CuCl$ was found to be +0.44 ppm less than in the $(\textit{i}\text{-}PrImt)_2HgCl_2$ system. Unfortunately, Imt reacts with $CuCl_2$ to give an insoluble ImtCuCl-type complex.[10]

^{13}C NMR Chemical Shifts

More conclusive evidence concerning the coordination sites is provided by the ^{13}C NMR spectra. The ^{13}C NMR assignments are summarized in Table II. The carbon nearest to sulfur could be expected to be the most sensitive to coordination to metal ions.[21] As expected, the C-2 carbon shifted upfield by about −6.30 to −6.71 ppm for the mono-*N*-substituted Hg^{2+} complexes and −4.99 to −5.41 ppm for disubstituted complexes. The upfield shift for the C-2 resonance is due to the decrease in the double bond character of the thione group. The C-4 and C-5 resonances shifted downfield because of the increase in the double bond character of the C=N groups.

As noted in Table II, the C-2 resonance of the mercury complexes is shifted more as compared to the copper complexes, thus showing the "soft" character of the mercury. Gold(I) complexes of the ligands under investigation such as $(Imt)_2AuCl$, $(i\text{-}PrImt)_2AuCl$, $(EtImt)_2AuCl$ have been reported.[8] In all complexes, the gold(I) is coordinated *via* the sulfur group. Since Hg(II) is isoelectronic (d^{10}) with copper(I) and gold(I), it too is expected to bind to sulfur. Therefore, the structures of the isoelectronic complexes would be similar in solution and in the solid state as revealed by ^{13}C NMR and X-ray diffraction.[8–11,22–24] All the mercury complexes would be tetrahedral in nature, as proposed for analogous complexes.[21]

TABLE II

^{13}C NMR chemical shifts for the L_2HgCl_2 complexes where L = imidazolidine-2-thione and its derivatives.*

Compound	C-2	C-4	C-5	α-CH_2	β-CH_2	-CH_3
Imt	183.72	44.13	44.13			
$(Imt)_2HgCl_2$	177.01	44.77	44.77			
	(−6.71)	(+0.64)	(+0.64)			
MeImt	183.20	40.70	50.40			33.53
$(MeImt)_2CuCl$	179.42	40.54	50.72			33.14
	(−3.78)	(+0.16)	(+0.32)			(+0.39)
$(MeImt)_2HgCl_2$	176.37	41.55	50.91			33.55
	(−6.83)	(+0.85)	(+0.51)			
EtImt	182.40	40.80	47.20	40.60		11.80
$(EtImt)_2CuCl$	178.50	41.14	47.72	41.00		11.62
	(−3.90)	(+0.80)	(+0.52)	(+0.40)		(−0.18)
$(EtImt)_2HgCl_2$	175.98	42.18	48.04	41.25		12.02
	(−6.42)	(+1.38)	(+0.84)	(+0.65)		(−0.22)
PrImt	182.79	41.77	47.84	47.50	19.92	11.03
$(PrImt)_2CuCl$	178.57	40.55	48.00	46.96	19.32	10.61
	(−4.22)	(+1.22)	(+0.16)	(+0.54)	(+0.60)	(−0.42)
$(PrImt)_2HgCl_2$	176.24	41.94	48.68	48.01	19.92	11.03
	(−6.55)	(+0.51)	(+0.84)	(+0.17)		
i-PrImt	181.70	40.93	42.15	46.70		19.00
$(i\text{-}PrImt)_2CuCl$	177.92	41.16	41.16	46.08		18.83
	(−3.78)	(+0.23)	(0.99)	(+0.62)		(+0.17)
$(i\text{-}PrImt)_2HgCl_2$	175.40	41.83	43.23	50.22		19.25
	(−6.30)	(+0.90)	(+1.08)	(+3.52)		(−0.25)
DiMeImt	182.90	47.76	47.76			34.54
$(DiMeImt)_2HgCl_2$	177.49	48.49	48.49			34.95
	(−5.41)	(+0.73)	(+0.73)			(−0.40)
DiEtImt	181.17	44.90	44.90	41.40		11.69
$(DiEtImt)_2HgCl_2$	175.74	45.60	45.60	42.14		11.99
	(−5.43)	(+0.70)	(+0.70)	(+0.74)		(−0.30)
Di-*i*-PrImt	180.31	46.17	46.17	40.12		18.75
$(Di\text{-}i\text{-}PrImt)_2HgCl_2$	175.32	47.23	47.23	40.73		19.09
	(−4.99)	(+1.06)	(+1.06)	(+0.61)		(−0.34)

* ^{13}C resonances are assigned as in reference 9. The numbers in parentheses indicate shifts with respect to the free ligands. A negative value indicates a high-field shift, whereas a positive value shows a low-field shift. The chemical shifts for the copper complexes are taken from reference 9.

^{99}*Hg NMR Chemical Shifts*

The ^{199}Hg NMR chemical shifts are listed in Table III and these indicate that ^{199}Hg NMR chemical shifts provide a sensitive probe of the complexation of Hg(II) by midazolidine-2-thione and its derivatives.

As noted in Table III, $(Imt)_2HgCl_2$ has a negative chemical shift when referenced to $CH_3)_2Hg$. The substitution of hydrogen by methyl, ethyl and propyl groups did not change the chemical shift significantly (*e.g.*, 63.1, 63.8 and 65.9 ppm, respectively). However, the substitution at both the *N* and *N′* sites of the imidazolidine ring gives ise to a greater chemical shift range for similar groups. For example, the disubstiution from methyl to ethyl groups causes a negative shift of 25 ppm, and ethyl to *so*-propyl an additional negative shift of 12 ppm. Norris *et al.*[25] reported the ^{199}Hg NMR chemical shifts of complexes of $CH_3Hg(II)$; 2-mercapto-1-methyl-imidazole in DMSO gave −717.0 ppm and when the complex was protonated the resonance hifted to −737.0 ppm. Thus it can be concluded that when sulfur is in the thiolate orm or as a thione bound to Hg(II), the chemical shifts are within the −700 to −1100 ppm range. However, *N*-bonded $CH_3Hg(II)$ imidazoles are found to have nore negative chemical shifts of about 200 ppm.[25]

TABLE III

^{99}Hg NMR chemical shifts (ppm) for the L_2HgCl_2 complexes where L = imidazolidine-2-thione and its derivatives.

Compound	^{199}Hg	$\Delta\nu_{1/2}$[a] in Hz	Δ^{199}Hg[b] in ppm	Δ^{13}C[c] in ppm
$(Imt)_2HgCl_2$	−863.7	77		−6.71
$(MeImt)_2HgCl_2$	−916.8	51	−63.1	−6.83
$(EtImt)_2HgCl_2$	−917.5	75	−63.8	−6.42
$(PrImt)_2HgCl_2$	−919.6	83	−65.9	−6.55
(*i*-PrImt)$_2$HgCl$_2$	−900.5	65	−46.8	−6.30
$(DiMeImt)_2HgCl_2$	−970.7	52	−117.0	−5.41
$(DiEtImt)_2HgCl_2$	−995.7	61	−142.0	−5.43
(Di-*i*-PrImt)$_2$HgCl$_2$	−1007.8	109	−154.1	−4.99

[a] $\Delta\nu_{1/2}$ = the peak width in hertz at half the peak height. [b] $\Delta^{199}Hg = \Delta_N - \Delta_I$ where Δ_N = ^{199}Hg chemical shifts of *N* or *N,N′*-disubstituted complexes and Δ_I = ^{199}Hg chemical shift of the $(Imt)_2HgCl_2$ complex. [c] Δ^{13}C = the ^{13}C NMR chemical shift difference of the C-2 resonance between free and bound ligand.

By comparing the differences in the ^{13}C NMR chemical shift resonances of the C-2 carbon of the free ligand and the mercury-bonded ligand, Table III, it can be seen that the difference between their chemical shifts becomes less as the size and number of groups attached to the adjacent nitrogens increases. It might be expected that as the steric hindrance around the thione increases, the strength of the sulfur to mercury bond would decrease and, as a result, the chemical shift of the carbon to decrease. This is confirmed by the results in Table III, but the change is small, about 1.7 ppm (from 6.71 ppm to 4.99 ppm).

For the ^{199}Hg NMR a similar but larger and opposite effect is observed. As the size and number of groups on the nitrogens increases the chemical shift of the mercury becomes more negative; that is it shifts in the direction of unbound $HgCl_2$ at −1501 ppm (from −63 to −154 ppm). The change here is of the order of −150 ppm. The ^{199}Hg nucleus can thus be a very sensitive probe for the study of steric interactions at thione complexation sites and should prove to be valuable in the study of these groups in biologically important molecules. It is not only much more sensitive than ^{13}C spectroscopy, but also gives more simplified spectra.

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