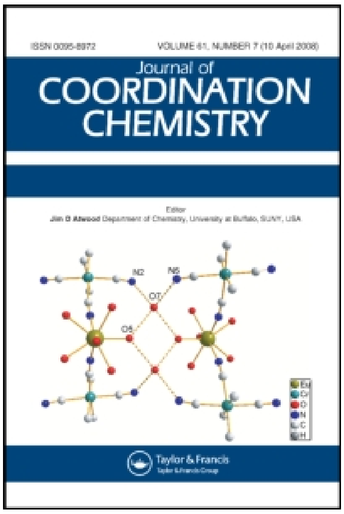

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REACTIVITY AND MECHANISMS IN THE REACTIONS BETWEEN MERCURY(II) HALIDES AND 5, 5-DIMETHYLIMIDAZOLIDINE-2-THIONE-4-ONE. CRYSTAL STRUCTURE OF A MERCURY BROMIDE COMPLEX

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REACTIVITY AND MECHANISMS IN THE REACTIONS BETWEEN MERCURY(II) HALIDES AND 5,5-DIMETHYLIMIDAZOLIDINE-2-THIONE-4-ONE. CRYSTAL STRUCTURE OF A MERCURY BROMIDE COMPLEX

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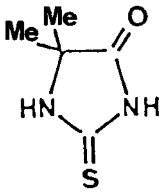
The reaction between HgX_2 (X = Cl, Br, I) and 5,5-dimethylimidazolidine-2-thione-4-one (L) yields HgLXY (Y = Cl, Br, I) and HgL′X (L′ = deprotonated L) complexes. The crystal structure, solved for $HgLBr_2$, showed it to be a polymer with a very distorted tetrahedral environment for the mercury. This is achieved by L bonded *via* S, a bromine, and two bridging bromines.

An interconversion mechanism between HgLXY and HgL′X has been suggested on the basis of the reactivity of HgLXY towards the two nucleophilic species H_2O and OH^- and of HgL′X towards KY, HY and $HClO_4$.

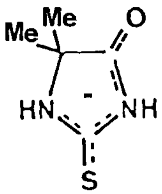
Keywords: mercury(II), 5,5-dimethylimidazolidine-2-thione-4-one, reactivity, halides, X-ray structure

INTRODUCTION

As part of our studies[1–8] on several imidazolidine derivatives having two chalcogen atoms at C-2 and C-4 (hydantoin derivatives), we have recently[6] reported complexes obtained by reacting 5,5-dimethylimidazolidine-2-thione-4-one (L) with Hg(II) halides. According to reaction conditions, L can act as a neutral or anionic (L′) ligand as shown below,



(L)



(L′)

giving HgLXY or HgL′X complexes (X, Y = Cl, Br, I).

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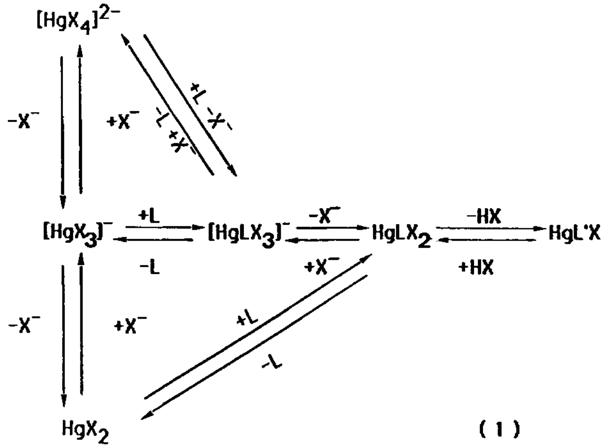
Infrared evidence showed[6] that in the HgLXY compounds, the coordinate bond is *via* the sulfur atom, whereas in HgL′X the metal is also bound by nitrogen N-3. Subsequently, an X-ray crystal structure,[8] solved for $HgLCl_2$, showed that it consists of a polymer in which the tetrahedral mercury(II) environment is achieved by two strong bonds (with a chlorine and the *S*-bonded L) and two bridging chlorines. Although HgLXY and HgL′X were first obtained by using solvents of different polarities, it was observed that the acidity of the solution and the presence of an excess of halide ions can play an important role in synthesis. In fact, HgLXY can be prepared in water by reacting either HgX_2 and L in $HClO_4$ (for HgLXY with X = Y), HgX_2 and L in KY solutions, or HgL′X and HY. A general rationalizing scheme is represented below.



(I)

In this paper we have focussed attention on the interconversion mechanism between HgLXY and HgL′X. The very low solubilities of the complexes prevented us carrying out kinetic investigations; however, some information on the mechanisms has been obtained from a study of the reactivities of HgLXY and HgL′X.

EXPERIMENTAL

Syntheses of the ligand and complexes

5,5-Dimethylimidazolidine-2-thione-4-one (L), HgLXY, HgL′X were obtained as previously described.[1]

Reaction of HgLXY with NaOH

An equivalent amount of 0.1 M NaOH was added to HgLXY dissolved in the least amount of ethanol. HgL'_2 (L′ = deprotonated L) precipitated immediately as a white powder. *Anal.*; Calcd. for $C_{10}H_{14}N_4O_2S_2Hg$: C, 24.3; H, 1.5; N, 11.3%. Found: C, 24.7; H, 1.4; N, 11.5%. Except for the chloro-compounds, this reaction was carried out also in water to yield the same product HgL'_2. For X = Y = Cl this reaction yielded HgL′Cl. The same final product, *i.e.*, HgL′Cl, was also obtained by reacting $HgLCl_2$ in absolute ethanol with an equivalent of both ethoxy anion and alcoholic potassium hydroxide.

All the complexes were characterized by elemental analysis and by their infrared spectra. Although the i.r. spectra of HgL'_2 and HgL'X are very similar, some differences are present in the regions 1450–1350, 750–650 cm^{-1}, which can be conveniently used in distinguishing between the HgL'X and HgL'_2 species.

Reaction of HgL'X with KY

HgL'X was suspended in water and treated with KY for 3–4 days, with stirring. This reaction was carried out several times for each HgL'X complex using molar ratios KY/HgL'X ranging from 1 to 100. The reactions with KCl always yielded unreacted HgL'X, and those with KI yielded HgL'_2 for a 1:1 ratio. With KBr, HgL'_2 was obtained only for ratios exceeding 20:1. The identification of the tetrahalomercury(II) anion in the mother liquor was carried out by precipitation with tetraphenylarsonium chloride.

Reaction of HgL'X with HY

A suspension of HgL'X in ethanol was treated with an equivalent amount of HY with stirring. The complex dissolved almost immediately and after some time HgLXY was isolated by slow evaporation of the solvent.

TABLE I
Crystal data and intensity collection parameters.

Compound	$HgBr_2L$
Formula	$C_5H_8Br_2HgN_2OS$
F.W.	504.60
Crystal system	monoclinic
Space Group	$P2_1/c$
a (Å)	10.389(9)
b (Å)	13.854(4)
c (Å)	7.817(7)
β (deg.)	102.91(7)
U (Å^3)	1096.7(25)
Z	4
$D_{calcd.}$ (gcm^{-3})	3.056
μ(Mo-K$_\alpha$) (cm^{-1})	213.99
Min. transmission factor	0.41
Crystal dimensions (mm)	0.2 × 0.2 × 0.1
Scan mode	ω
ω-scan width (deg.)	$1.6 + 0.35 \tan \theta$
θ-range (deg.)	3–26
Octants of reciprocal space explored	$+h, +k, \pm l$
Measured reflections	2143
Unique observed reflections with $I > 3\ \delta\ (I)$	1475
Final R and R_w indices[a]	0.036, 0.040
No. of variables	109
ESD[b]	1.383

[a] $R = [\Sigma(Fo - k|Fc|)/\Sigma Fo]$, $R_w = [\Sigma w(Fo - k|Fc|)^2/\Sigma wFo^2]^{1/2}$. [b] $ESD = [\Sigma w(Fo - k|Fc|)^2/(NO - NV)]^{1/2}$.

Reaction of HgL′X with $HClO_4$

If a suspension of HgL′X in ethanol is treated with $HClO_4$ in the molar ratios HgL′X/$HClO_4$ 1:1 and 1:2, no reaction occurs. HgLXY (X = Y) was formed by increasing the ratio to 1:10; after some time the complex precipitated by slow evaporation of the solvent.

X-ray Data Collection and Structure Determination

Crystal data and other experimental details are summarized in Table I. The diffraction experiment was carried out on an Enraf-Nonius CAD-4 diffractometer at room temperature using Mo-K_α radiation. The calculations were performed on a PDP 11/34 computer using the SDP-plus Structure Determination Package.[9] The diffracted intensities were corrected for Lorentz, polarization and absorption (empirical correction[10]). Anomalous dispersion corrections for atomic scattering factors of non-hydrogen atoms were taken from ref. 11. The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares, minimizing the function $\Sigma w(F_o - k|F_c|)^2$. Weights assigned to individual observations were $w = 1/[\sigma(F_o)]^2$, where $\sigma(F_o) = [\sigma^2(I) + (0.041)^2]^{1/2}/2F_oLp$.

Anisotropic thermal factors were refined for all non-hydrogen atoms. All the hydrogen atoms were introduced in the model at calculated positions but they were not refined. The final difference Fourier synthesis shows residuals of 1.3 e/Å^3 close to the metal atoms. The atomic coordinates are listed in Table II.

TABLE II

Atomic coordinates for non-hydrogen atoms with e.s.d.'s in parentheses.

Atom	*x/a*	*y/b*	*z/c*
Hg	−0.23897(4)	0.19896(3)	−0.25685(6)
Br(1)	−0.4060(1)	0.23835(7)	−0.5897(1)
Br(2)	−0.0796(1)	0.33143(7)	−0.2839(2)
S(6)	−0.2303(3)	0.0282(2)	−0.1794(3)
O(7)	−0.2776(7)	−0.2516(4)	−0.5790(9)
N(1)	−0.2298(8)	−0.0048(5)	−0.5239(9)
N(3)	−0.2613(8)	−0.1322(5)	−0.3737(9)
C(2)	−0.2407(9)	−0.0338(6)	−0.369(1)
C(4)	−0.2643(9)	−0.1684(6)	−0.538(1)
C(5)	−0.2454(9)	−0.0833(6)	−0.653(1)
C(8)	−0.370(1)	−0.0656(7)	−0.799(1)
C(9)	−0.123(1)	−0.0964(7)	−0.724(1)

RESULTS AND DISCUSSION

Crystal structure of catena-μ-bromobromo(5,5-dimethylimidazolidine-2-thione-4-one) mercury (II)

The $HgLBr_2$ complex is isotypic and isostructural with the homologous $HgLCl_2$ compound. For comparison the unit cell parameters for $HgLCl_2$ are *a* = 9.998(2),

b = 13.769(3), c = 7.798(1) Å, β = 100.61(4)°, V = 1055.1(4) Å^3. The mercury atom is in a very distorted tetrahedral coordination environment (Table IIIa) with two strong bonds to the sulfur atom of the organic molecule and to Br(2) [Hg–S(6) = 2.439(2) Å, Hg–Br(2) = 2.512(1) Å with an S(6)–Hg–Br(2) angle of 137.82(7) °], and two weaker bonds to Br(1) and to a symmetry-related Br(1)′, which bridge two mercury atoms asymmetrically.

TABLE III

Bond distances (Å) and angles (deg.) with e.s.d.'s in parentheses.

a) Comparison of the mercury environment for HgLX$_2$(X = Cl^a, Br^b)

	Cl	Br
Hg–X(1)	2.779(5)	2.790(1)
Hg–X(2)	2.398(6)	2.512(1)
Hg–X(1)′	2.628(6)	2.717(1)
Hg–S(6)	2.410(5)	2.439(2)
X(2)–Hg–S(6)	143.3(4)	137.82(7)
X(1)–Hg–S(6)	103.7(2)	104.92(6)
X(1)–Hg–X(2)	94.5(2)	99.89(3)
X(1)′–Hg–X(2)	100.3(2)	101.48(3)
X(1)–Hg–X(1)′	97.6(2)	95.47(3)
X(1)′–Hg–S(6)	108.4(2)	109.36(6)
Hg–S(6)–C(2)	107.3(8)	106.4(3)
Hg–X(1)–Hg′	99.9(2)	98.01(3)

b) The 5,5-dimethylimidazolidine-2-thione-4-one molecule

S(6)–C(2)	1.695(8)	C(5)–N(1)	1.468(9)
C(2)–N(3)	1.379(9)	N(1)–C(2)	1.304(10)
N(3)–C(4)	1.370(10)	C(5)–C(8)	1.540(12)
C(4)–O(7)	1.198(9)	C(5)–C(9)	1.514(12)
C(4)–C(5)	1.523(10)		

S(6)–C(2)–N(1)	130.8(6)
S(6)–C(2)–N(3)	120.2(6)
N(1)–C(2)–N(3)	109.0(6)
C(2)–N(3)–C(4)	110.9(6)
N(3)–C(4)–C(5)	106.9(6)
C(4)–C(5)–N(1)	100.1(6)
C(5)–N(1)–C(2)	113.0(6)
N(3)–C(4)–O(7)	125.7(7)
C(5)–C(4)–O(7)	127.4(7)
C(4)–C(5)–C(8)	111.4(7)
C(8)–C(5)–C(9)	112.4(7)
C(9)–C(5)–N(1)	111.7(6)

c) Hydrogen bonds and shortest contacts^c

Br(1)...H(10)	2.834(1)
Br(2)...H(10)′	2.942(1)
Br(2)...H(9)C′	2.906(1)
O(7)...H(11)″	1.894(6)
O(7)...N(3)″	2.846(9)
O(7)...H(11)″–N(3)″	175.6(5)

[a] Ref. 8. [b] This work. [c] Primed atoms at x, $\frac{1}{2}-y$, $\frac{1}{2}+z$; double primed atoms at x, $-\frac{1}{2}-y$, $z-\frac{1}{2}$.

The large deviation from the ideal tetrahedral angle of the S(6)–Hg–Br(2) linkage can be explained by the presence of a short Hg. . . .Br(2)′ contact of 3.722(1), which bisects this angle. All the other angles are in the range 95.47(3)°–104.92(6)°. Large deviations for the tetrahedral angle around a mercury atom are common. As examples we quote the complexes [$HgBr_2$(TETD)],[12] and [$HgX_2(py)_2$] (X = Br and I).[13] The Hg–Br(2) distance 2.512(1)Å can be compared with the distance of 2.504(6)Å found in $HgBr_2$(TETD), while the Hg–S(6) bond (2.439(2)Å) is considerably shorter than the value of 2.66(1)Å found in the same compound.

An alternative way of describing the coordination geometry around the metal atom is to derive it from a digonal S(6)–Hg–Br(2) system, "perturbed" by the bridging bromine atoms which increase the coordination number and cause tetrahedral distortion.

The pattern of bond distances and angles within the 5,5-dimethyl-2-thiohydantoin (Table IIIb) is very similar to that in the uncoordinated 2-thiohydantoin molecule,[7] with the exception of the C–S bond which upon coordination undergoes a reduction of double bond character. The five-membered ring of the organic ligand is strictly planar while the sulfur and the oxygen atoms are out of this plane by 0.011(3) and 0.041(7)Å, respectively. The mercury atom is 0.432(1)Å out of the "best" plane for the whole molecule.

The polymeric chains are arranged in the crystal lattice along the crystallographic *c* axis, and the packing is determined by the interactions reported in Table IIIc. A portion of these chains is shown in Figure 1.

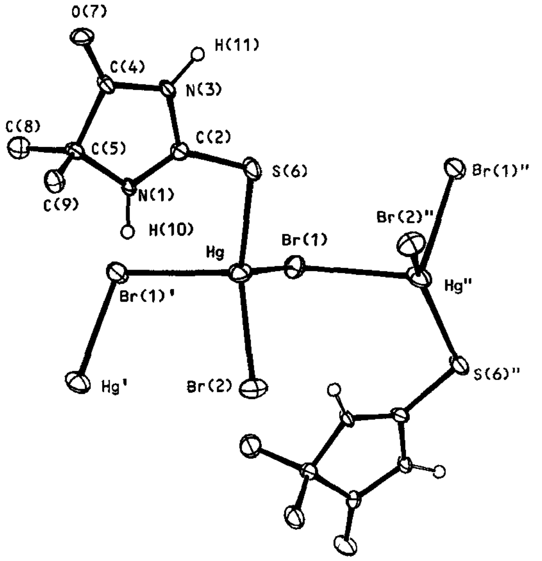
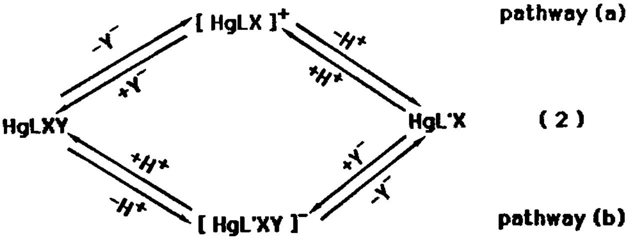


FIGURE 1 ORTEP drawing of the $Hg(C_5H_8N_2OS)Br_2$ complex with the atomic labelling scheme. The thermal ellipsoids are sealed to include 30% probability.

Dehydrohalogenation of HgLXY

Assuming a heterolytic mechanism in the dehydrohalogenation of HgLXY in water, there are only two different ways of obtaining HgL'X as shown below



(2)

where the two pathways (a) and (b) differ in priority of loss of the proton or the halogen. For $X = Y$ it was observed that $HgLCl_2$ reacts immediately in water to yield HgL'Cl, while $HgLBr_2$ needs to be slightly warmed and $HgLI_2$ does not react at all. If $X \neq Y$, the leaving halide is Cl^- for HgLClBr and HgLClI, and Br^- for HgLBrI. However, although these facts do not help to distinguish between pathways (a) and (b), they show the dehydrohalogenation reactivity sequence to be $HCl > HBr \gg HI$, indicating that the rate-determining step is the breaking of the mercury–halide bond. The problem of choosing between the two possible heterolytic pathways still remains. To clarify this, we have forced a proton loss by treating HgLXY in ethanol* with a stoichiometric amount of NaOH, in order to obtain the $[HgL'XY]^-$ ion.

Unexpectedly, all the complexes except $HgLCl_2$, which gave HgL'Cl, yielded the new compound HgL'_2 according to the reaction below.

$$2\ HgLXY \xrightarrow{+2OH^-} HgL'_2 + [HgX_2Y_2]^{2-} \qquad (3)$$

This different reactivity of $HgLCl_2$ with respect to all other complexes was at first suspected to be due to the fact that the hydrolysis of this substrate is fast. For this reason the reaction with $HgLCl_2$ was carried out in absolute ethanol using alcoholic potassium hydroxide or the ethoxy anion as base; the product was always HgL'Cl.

The behaviour of $HgLCl_2$, whose structure is known, prompted us to solve the structure of another HgLXY compound, in order to ascertain if this diversity of behaviour might be due to a different coordination environment at the mercury atom. As seen in the Experimental section, the crystal structure of the model compound $HgLBr_2$ is very similar to that of $HgLCl_2$, thus indicating that the explanation of the different reactivity must be sought elsewhere.

Formation of HgL'_2

According to the scheme, (*2*), another way of making $[HgL'XY]^-$, is to react HgL'X with KY. These reactions were carried out by treating in water a suspension of

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* A change of the solvent, required to avoid the fast hydrolyses of the chloro-derivatives, does not alter the reaction products since $HgLI_2$, $HgLBr_2$ and HgLBrI react in the same way both in water and in ethanol.

HgL'X with KY for increasing molar ratios of KY/HgL'X (from 1:1 to 100:1); the final product was unreacted HgL'X or HgL'_2, according to (*4*), with Y = Br, I.

$$2\ HgL'X \xrightarrow{+2Y^-} HgL'_2 + [HgX_2Y_2]^{2-} \qquad (4)$$

HgL'X (X = Cl, Br, I) does not react with KCl at any ratio, and with KBr for molar ratios lower than 20:1; reaction with KI gives HgL'_2 at all ratios. From this evidence, HgL'_2 could always be obtained *via* HgL'X as intermediate as shown in (*5*).

$$2\ HgLXY \xrightarrow{+2OH^-\ -2Y^-} 2\ HgL'X \xrightarrow{+2Y^-} HgL'_2 + [HgX_2Y_2]^{2-} \qquad (5)$$

When HgLXY is $HgLCl_2$, reaction (*5*) ends in HgL'Cl; in all other cases HgL'_2 is the final product. Moreover, if we consider HgLClBr or HgLClI as starting molecules and take into account the fact that HgL'Br and HgL'I do not react with Cl^-, we must conclude that in these cases the intermediate species is HgL'Cl since this compound reacts with KBr and KI to yield HgL'_2.

Consequently, when HgLXY reacts with OH^- in ethanol (or water) to give HgL'X, the leaving halide is the one that is more strongly bonded to the mercury and the reactivity sequence should be $I^- > Br^- \gg Cl^-$. This sequence is the reverse of that found in the dehydrohalogenation of HgLXY with water; these facts suggest that the two dehydrohalogenations have different mechanisms, E_1 with water and E_2 with OH^-. For this reason, HgLClI gives HgL'I in water (E_1) and HgL'Cl in NaOH solution (E_2).

The knowledge of the structures of both HgL'_2 and HgL'X might help to clarify how HgL'X reacts with Y^- (= Br^-, I^-) to give HgL'_2. Unfortunately both complexes are so insoluble that it was not possible to obtain suitable crystals for X-ray structure analysis.

Hydrohalogenation of HgL'X

By treating a suspension of HgL'X in ethanol with HY (Y = Cl, Br, I), the complex is dissolved and after some time HgLXY precipitates, according to the following reaction.

$$HgL'X + HY \rightarrow HgLXY \qquad (6)$$

Reaction (*6*) can proceed in either of the two ways reported in (*2*) and would not necessarily help in supporting either pathway. On the other hand, the reaction of HgL'X with Y^-, as reported above, does not yield HgLXY. *Vice versa*, by reacting HgL'X with an excess of $HClO_4$, HgLXY (X = Y) is obtained, thus proving that reaction (*6*) proceeds according to the pathway (a). Finally, the general results can be summarized by the following equilibria.

$$HgLXY \underset{+Y^-}{\overset{-Y^-}{\rightleftarrows}} [HgLX]^+ \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} HgL'X \qquad (7)$$

SUPPLEMENTARY MATERIAL

Full lists of anisotropic thermal parameters, hydrogen coordinates plus isotropic thermal parameters and observed calculated structure factors have been deposited with the Editor.

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