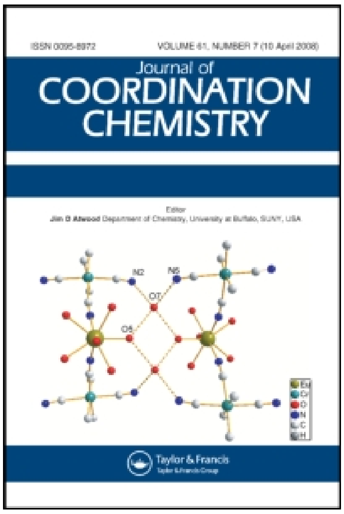

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REACTIONS BETWEEN MERCURY(II) HALIDE COMPLEXES AND 5,5-DIMETHYLIMIDAZOLIDINE-2-THIONE-4-ONE

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REACTIONS BETWEEN MERCURY(II) HALIDE COMPLEXES AND 5,5-DIMETHYLIMIDAZOLIDINE-2-THIONE-4-ONE

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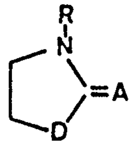
5,5-Dimethylimidazolidine-2-thione-4-one (L) has been used as a ligand towards HgX_2 (X = Cl, Br, I). Several synthetic ways have been used to prepare complexes having the general formula HgLXY (X, Y = Cl, Br, I) or HgL′X(L′ = L^- anion and X = Cl, Br, I). The coordination of L to the metal occurs through the sulfur atom, whereas L′ binds the mercury with both sulfur and nitrogen-3.

Keywords: synthesis, complexes, mercury, imidazolidines, halides

INTRODUCTION

In the course of our studies on the chemistry of coordinated sulfur and selenium, we have investigated several complexes[1-5] of a variety of heterocyclic pentaatomic rings of general formulas shown below,



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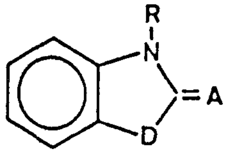
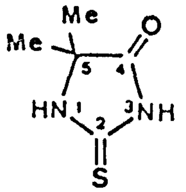
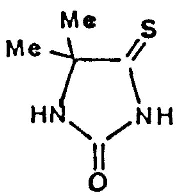
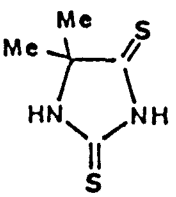


where D = O, S, NH, NMe, NEt, R = H, Me and A = S, Se. The theme of the research was the competitivity among N, A and D in forming coordinative bonds with several metal ions. On the whole these studies have shown that when the above ligands act as neutral molecules[6], they bind the metals through the *exo*-A and stabilize their low oxidation states[2,4].

Pursuant to our interest in the coordination chemistry of sulfur and selenium, we have synthesized[7] the following imidazolidines with two *exo*-atoms, as shown below,







and have used them as ligands towards mercury(II) halides.

This paper deals with the complexes obtained by reacting 5,5-dimethylimidazolidine-2-thione-4-one (L) with mercury(II) halides under several experimental conditions. 5,5-Dimethylimidazolidine-2-one-4-thione does not react and 5,5 dimethyl imidazolidine-2,4-dithione is desulfurated at the 4-position and yields L.

RESULTS AND DISCUSSION

Reactivity

The reaction between mercury(II) bromide and L yields two types of complexes: $HgLBr_2$ and HgL'Br (L' = L^- anion), whose formation can be explained according to the following equation.

$$HgBr_2 + L \longrightarrow HgLBr_2 \longrightarrow HgL'Br + HBr \qquad (1)$$

The pathway (**1**) depends on several factors, among which are the solvent (HgL'Br is obtained in water, while $HgLBr_2$ in tetrahydrofurane) and the strength of the mercury-halide bond (in ethanol, mercury(II) bromide yields $HgLBr_2$, and mercury(II) chloride a mixture of $HgLCl_2$ and HgL'Cl).

The same complexes can be prepared by reacting in ethanol the tetrahalo-complexes obtained by mixing HgX_2 and KY (X, Y = Cl, Br, I) in a 1:2 molar ratio with L. In this manner, the following complexes may be obtained according to the reactions (**2a**) to (**2c**).

$$[HgX_2Y_2]^{2-} + L \begin{array}{l} \nearrow HgLX_2 + 2Y^- \qquad (2a) \\ \longrightarrow HgLY_2 + 2X^- \qquad (2b) \\ \searrow HgLXY + X^- + Y^- \qquad (2c) \end{array}$$

In Table I the results obtained are summarized for all the possible combinations of HgX_2 and 2KY. As can be seen, the complexes agree with the rule of bond strength: Hg–I > Hg–Br > Hg–Cl. Only the reaction with potassium chloride yielded the inner complexes HgL'Cl and HgL'Br, since it was necessary to introduce some water for

TABLE I
Complexes obtained by reacting 5,5-dimethylimidazolidine-2-thione-4-one with mercury(II) halide and potassium halide in 1:1:2 and 1:1:1 molar ratios in ethanol.

Mercury(II) halide	Potassium halide	Complex	
		1:1:2	1:1:1
$HgCl_2$	KCl	$HgLCl_2$ + HgL'Cl*	HgL'Cl*
	KBr	$HgLBr_2$	HgLClBr
	KI	$HgLI_2$	HgLClI
$HgBr_2$	KCl	HgL'Br*	HgL'Br*
	KBr	$HgLBr_2$	$HgLBr_2$
	KI	$HgLI_2$	$HgLBr_2I$
HgI_2	KCl	$HgLI_2$	$HgLI_2$
	KBr	$HgLI_2$	$HgLI_2$
	KI	$HgLI_2$	$HgLI_2$

*L' = L^- anion

TABLE II

Melting points and analytical data for the complexes and selected infrared absorptions (3500-350 cm^{-1}) for ligands and complexes

Compound[a]	M.P.[b](°)	Analysis[c]			ν_{NH}		ν_{CO}	$\nu_{C_2N_1}$	$\nu_{C_4N_3}$	$\nu_{C_2N_3}$	ν_{CS}	δ_{CS}
		C	H	N								
L					3220 sh	3179 s	1742 vs	1529 s	1290 ms	1132 s	495 ms	351 ms
$HgLCl_2$	237	14.3 (14.4)	2.1 (1.9)	6.9 (6.7)	3300 m	3107 s	1767 vs	1538 vs	1277 vs	1128 s	480 ms	366 ms
$HgLBr_2$	235	11.7 (11.9)	1.6 (1.6)	5.6 (5.5)	3305 m	3130 s	1765 vs	1536 vs	1276 vs	1128 s	480 ms	355 ms
$HgLI_2$	158	10.0 (10.0)	1.2 (1.3)	4.6 (4.7)	3317 m	3153 s	1762 vs	1531 vs	1268 vs	1120 vs	480 ms	348 ms
HgLClBr	237	12.7 (13.0)	1.8 (1.8)	5.8 (6.1)	3309 m	3124 s	1765 vs	1541 vs	1277 vs	1129 vs	480 ms	366 ms
HgLClI	165	12.1 (11.8)	1.5 (1.6)	5.8 (5.5)	3300 m	3133 s	1765 vs	1536 vs	1274 vs	1125 s	480 ms	360 ms
HgLBrI	192	11.1 (10.9)	1.4 (1.5)	5.2 (5.1)	3303 m	3133 s	1764 vs	1533 vs	1272 vs	1125 s	480 ms	351 ms
NaL′					3239 vs		1640 vs	1483 vs	1305 vs	1160 vs	450 m	355 m
HgL′Cl	222 d	15.6 (15.8)	1.9 (1.9)	7.4 (7.4)	3168 s		1689 vs	1527 s	1301 vs	1147 vs	442 vw	—
HgL′Br	226 d	13.8 (14.2)	1.5 (1.6)	6.6 (6.6)	3149 s		1687 vs	1524 s	1301 vs	1148 vs	442 w	355 vw
HgL′I	260 d	12.6 (12.8)	1.4 (1.6)	6.7 (6.6)	3140 s		1685 vs	1522 s	1297 s	1148 s	442 w	356 w

[a] L = 5,5 dimethyl imidazolidine-2-thione-4-one, L′ = L^- anion; [b] d = decomposes; [c] calculated values in parentheses

solubility reasons. The same procedure was used in the case of mercury(II) iodide and potassium chloride, but no inner complex was obtained in agreement with the fact that the sequence of reactivity in water to give HgL'X is $HgLCl_2 > HgLBr_2 > HgLI_2$.[8]

In the last column of Table I, we report the complexes obtained by reacting HgX_2 and KY in a 1:1 molar ratio. This ratio has been used in order to prepare mixed complexes, according to (**3a**) and (**3b**). Also in this case, the reactions of mercury(II) chloride and mercury(II) bromide in the presence of potassium chloride yielded the inner complexes HgL'X. The analytical data for the complexes synthesized by reactions (**1**), (**2**) and (**3**) are reported in Table II.

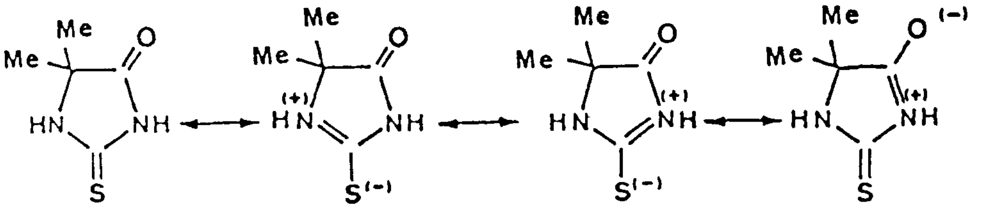
$$[\mathrm{HgX_2Y}]^- + \mathrm{L} \begin{cases} \rightarrow \mathrm{HgLX_2} + \mathrm{Y}^- & (3a) \\ \text{or} & \\ \rightarrow \mathrm{HgLXY} + \mathrm{X}^- & (3b) \end{cases}$$

Coordination

In order to identify the nature of the coordination of mercury, we have applied the infrared technique by analyzing mainly the shifts of the bands of the ligands, since we do not obtain much information from metal-ligand vibrations. In the complexes, the ligand is present as a neutral or anionic form, to which very different infrared spectra correspond. To begin with, one of the differences is due to ν_{NH}, which gives rise to two bands in the neutral and only one and in the anionic ligand. The shifts of these bands in the complexes are attributable to variations of the hydrogen bonding interaction and not to the involvement of the NH nitrogen in the coordination. As far as the ν_{CO}, ν_{CS} and ν_{CN} vibrations are concerned, they present strong variations on passing from L to L' as will be discussed later.

L Complexes

As one can see from Table II, ν_{CO} undergoes upward shifts of *ca* 22 cm^{-1} in the complexes with respect to the free ligand, indicating a reinforcement of the carbonyl bond. This excludes oxygen as the coordinating atom and consequently provides an indirect proof that the bond must occur through the sulfur atom. In this case we would expect a lowering of the π-bond order on CS, and a variation of the π-distribution on the CN groups, resulting in a higher contribution of the (B) and (C) resonating forms below.



(A) (B) (C) (D)

As expected, the bands at 1529 and 1290 cm^{-1}, assigned[7] to the prevailing contributions of $\nu_{C_2N_1}$ and $\nu_{C_4N_3}$ respectively, move towards higher and towards lower frequencies. However, the band at 1132 cm^{-1}, tentatively assigned[7] to $\nu_{C_2N_3}$, unexpectedly decreases in frequency, although the shifts are very small.

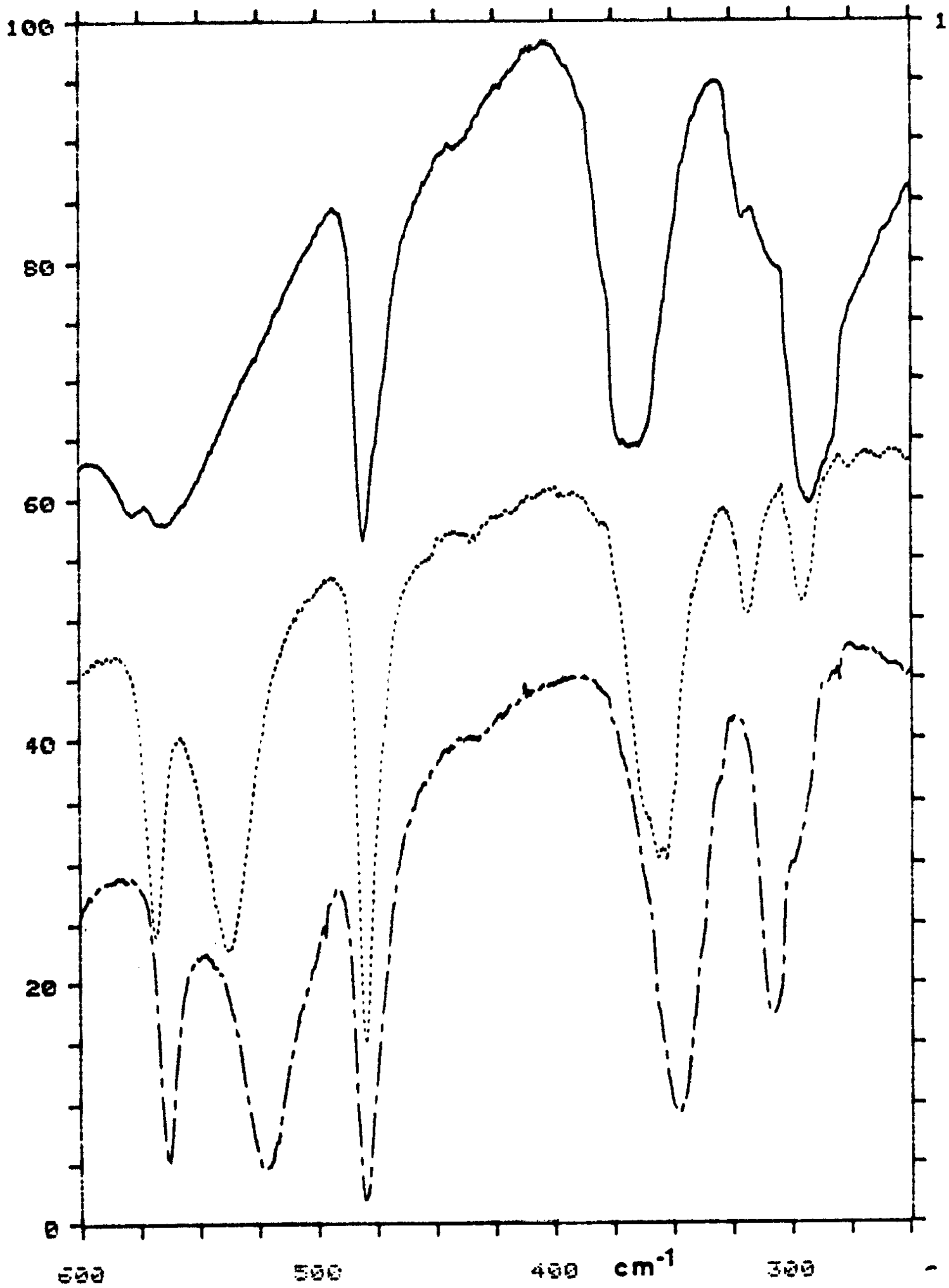


FIGURE 1 Infrared spectra (600–250 cm^{-1}) of $HgLX_2$ (X = Cl ; X = Br . . . . . ; X = I - - - -) in Nujol mulls between CsI discs.

"Selenation"[9] applied to L^7, allowed us to identify as CS modes the bands at 495 and 351 cm^{-1}, the former having a prevailing ν_{CS} and the latter a δ_{CS} contribution. In the complexes, the band at 495 cm^{-1} shifts to 480 cm^{-1} in accord with S-coordination, while the band at 351 cm^{-1} is stationary or has very small upward shifts. This behaviour is in

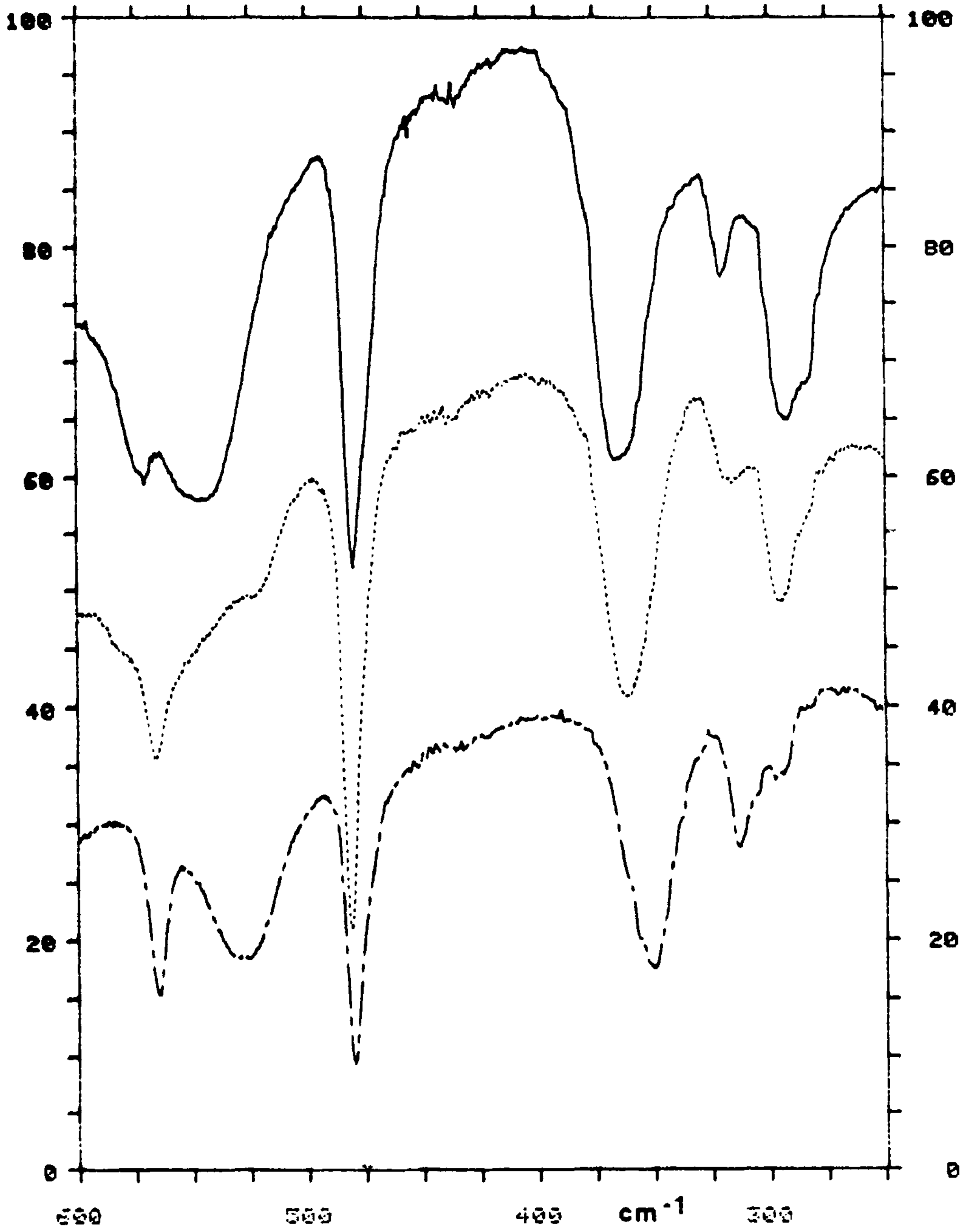


FIGURE 2 Infrared spectra (600–250 cm^{-1}) of HgLClBr (——), HgLClI (· · · · ·) and HgLBrI (- - - - -) in Nujol mulls between CsI discs.

good agreement with the attribution of the band, since the same trend was found for complexes of imidazolidine-2-thione[10] and other pentaatomic rings[11,12].

The infrared spectra of $HgLX_2$ and HgLXY, recorded in the 600–250 cm^{-1} range, are shown in Figures 1 and 2 respectively. Within the range 600–500 cm^{-1}, two bands are

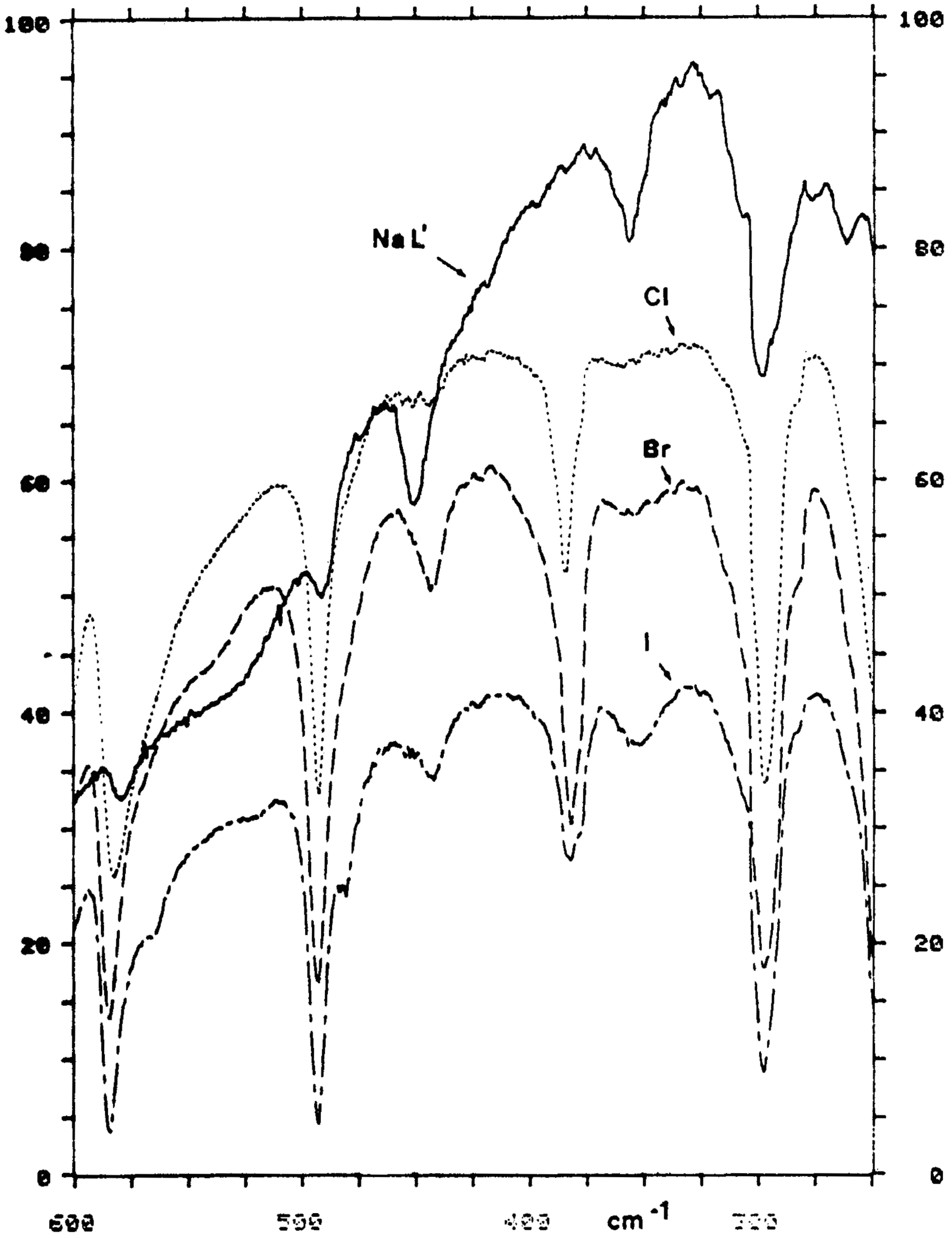


FIGURE 3 Infrared spectra (600–250 cm^{-1}) of NaL' and HgL'X (X = Cl, Br, I) in Nujol mulls between CsI discs.

present, one of which, seen at *ca* 565 cm^{-1}, is also present in the free ligand, while the other, which is halo-dependent, is seen at 577, 537 and 522 cm^{-1} (see Fig. 1) in the Cl, Br and I complexes, respectively. In the mixed complexes (see Fig. 2), the halo-dependent band can be identified at 547, 524sh and 529 cm^{-1} for Cl/Br, Cl/I and Br/I derivatives respectively. An analogous behaviour, found in some halo-complexes of imidazolidines-2-thione was attributed to the out-of-plane Δ_{NH} which interacts with the halogen by hydrogen bonding[1,13,14] All the complexes show absorptions between 250–320 cm^{-1}, in which range the ν_{HgS} vibrations should be expected.[15,16] However, in the interval also the free L shows two weak bands at 300 and 282 cm^{-1}, which make it difficult to assign the ν_{HgS} vibration. We tentatively suppose that this vibration might contribute to the band seen at *ca* 315 cm^{-1} in all complexes. As far as the $\nu_{Hg\text{-}X}$ vibrations are concerned, over 250 cm^{-1} it is possible to identify only the ν_{HgCl} vibrations[17] as the medium strong bands seen at *ca* 292 cm^{-1}, present in all the complexes containing the mercury-chloride bond.

L′ Complexes

Table II reports the bands assigned to the heterosystem of L′ and its HgL′X complexes. First some comments will be made in comparing L and L′. As can be seen from Table II, the ν_{CO} and ν_{CS} bands shift downward by 102 cm^{-1} and 45 cm^{-1} respectively. $\nu_{C_2N_1}$ moves in the same direction with a variation of 46 cm^{-1}, while $\nu_{C_4N_3}$ and $\nu_{C_2N_3}$ undergo upward shifts of 15 and 28 cm^{-1} respectively. These special variations are in good agreement with the loss of the hydrogen bonded at N-3 to yield the 5,5-dimethylimidazolidinato-2-thione-4-one anion (L^-). The comparison of the i.r. spectra of HgL′X and NaL′ shows that in these complexes, not only sulfur but also nitrogen-3 are involved in bonding to Hg. In fact, the variation of the i.r. bands in the HgL′X show, a general displacement towards the corresponding bands of L, thus indicating that the ion pair of N-3 is involved in bonding.

The infrared spectra (600–250 cm^{-1}) of NaL′ and HgL′X are shown in Figure 3. The main difference between the spectrum of NaL′ and those of the complexes is the medium strong band at 382 cm^{-1} present in all the latter, and which can be assigned to the ν_{HgN} vibration.[17] The bands at 450 and 355 cm^{-1} in NaL′, attributed to ν_{CS} and δ_{CS} respectively, undergo only very low shifts in the complexes, according to the fact that the carbon-sulfur bond is very close to a single bond.

EXPERIMENTAL

The preparation and purification of the ligands has been discussed elsewhere.[7]

$HgLCL_2$ was prepared by mixing $HgCl_2$ and L in 1:1 molar ratio in tetrahydrofuran. The reaction occurs in about 8 hours.

The complexes $HgLX_2$ (X = Br, I) were prepared by reacting HgX_2, KX and L in ethanol at room temperature for several days in a 1:2:1 molar ratio. HgLXY ($X \neq Y$ = Cl, Br, I) were prepared in the same manner using a 1:1:1 molar ratio. In the reaction with KCl it was necessary to add some water to dissolve the reactants. The presence of water promotes the formation of HgL′Cl and HgL′Br.

The complexes HgL′X(X = Cl, Br) were also obtained by reacting HgX_2 and L(1:1 molar ratio) in water at room temperature. To obtain HgL′I it was necessary to hydrolyze HgLClI. The infrared spectra were recorded, with a Perkin-Elmer 903 instrument connected with a Data Station 7500, in KBr pellets (4000–450 cm^{-1}) and in Nujol mulls between CsI discs (600–250 cm^{-1}).

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