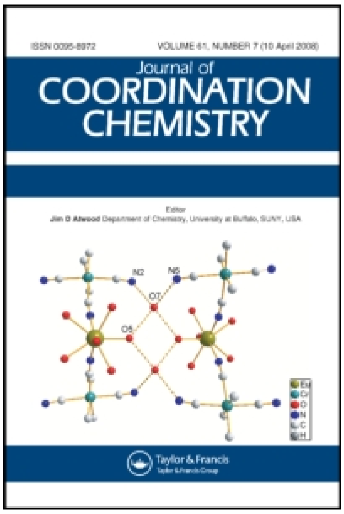

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Reactivity of Mercury(II) Perchlorate Towards 5,5 -Dimethylimidazolidine-2- Thione-4-One. Structure of Bis(5,5-Dimethylimidazolidine-2-Thione-4-One)Mercury(II) Perchlorate Triaquo

Franco Cristiani[a]; Francesco Demartin[b]; Francesco A. Devillanova[a]; Angelo Diaz[a]; Francesco Isaia[a]; Gaetano Verani[a]
[a] Dipanimenlo di Chimica e Tecnologie Inorganiche e Metallorganiche, Cagliari, Italy [b] Istituto di Chimica Slrutturistica Inorganica, Milano, Italy

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REACTIVITY OF MERCURY(II) PERCHLORATE TOWARDS 5,5 -DIMETHYLIMIDAZOLIDINE-2-THIONE-4-ONE. STRUCTURE OF BIS(5,5-DIMETHYLIMIDAZOLIDINE-2-THIONE-4-ONE)MERCURY(II) PERCHLORATE TRIAQUO

FRANCO CRISTIANI,* FRANCESCO DEMARTIN,**
FRANCESCO A. DEVILLANOVA,* ANGELO DIAZ,*
FRANCESCO ISAIA* and GAETANO VERANI*

* *Dipartimento di Chimica e Tecnologie Inorganiche e Metallorganiche, Via Ospedale 72, 09124 Cagliari, Italy*
** *Istituto di Chimica Strutturistica Inorganica, via G. Venezian 21, 20133 Milano, Italy*

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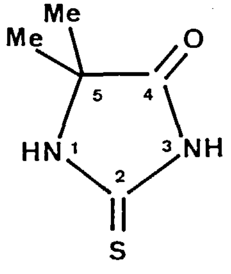
The reaction between $Hg(ClO_4)_2$ and 5,5-Dimethylimidazolidine-2-thione-4-one (L) has been investigated in water, diethylether and perchloric acid solutions. In water, three different complexes, $HgL(ClO_4)_2 \cdot nH_2O$, $HgL'ClO_4$ and HgL'_2 (L′ = deprotonated L) have been obtained; in diethylether $HgL_n(ClO_4)_2$ ($n = 1$, 3–5) was prepared, whereas in perchloric acid solutions, besides the $HgL_2(ClO_4)_2$ complex, a mercury(I) complex of formula HgL_2ClO_4 was obtained at high acid concentration. The mercury(I) complex can also be obtained at a lower acid concentration using a L:$Hg(ClO_4)_2$ molar ratio higher than 2:1. The crystal structure of bis(5,5-dimethylimidazolidine-2-thione-4-one) mercury(II) perchlorate triaquo shows the existence of the $[HgL_2]^{2+}$ cation, in which the coordination around the mercury atom is almost linear.

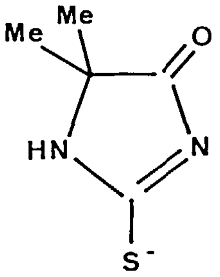
Keywords: Mercury, 5,5-dimethylimidazolidine-2-thione-4-one, hydantoin, imidazolidine, X-ray structure

INTRODUCTION

5,5-Dimethylimidazolidine-2-thione-4-one can act as neutral (L)[1–3] or anionic (L′)[1] ligand, as shown below.



L



L′

Since L′ can exist in two desmotropic forms and no structural data are available for their complexes, it has been hypothesized that L′ is the isomer which has lost the hydrogen bonded to N-3 on the basis of the higher acidity of this hydrogen.[4]

L reacts with mercury(II) halides under various conditions[1] to give the series of complexes HgLXY, HgL′X and HgL'_2 (X, Y = Cl, Br, L), where L is S-bonded to the metal and L′ coordinates the mercury(II) with both S and N-3. The interconversion between HgLXY and HgL′X

$$HgLXY \longrightarrow HgL'X + HY$$

occurs with an E_1 type mechanism in water and E_2 in ethanol/OH^- solution. However, in the latter case, HgL′X is an intermediate product while the final one is always HgL'_2 (except for HgL′Cl which does not react). The reverse reaction

$$HgL'X + HY \longrightarrow HgLXY$$

carried out in ethanol, seems to occur first with protonation of the nitrogen bonded to Hg(II) followed by an attack of Y^- on $HgLX^+$.

Pursuant to our interest in the interaction between L and Hg(II), we have undertaken a further investigation using $Hg(ClO_4)_2$ as the starting salt.

EXPERIMENTAL

Materials

5,5-Dimethylimidazolidine-2-thione-4-one (L) was prepared according to the literature.[5] $Hg(ClO_4)_2$ was obtained as a hexahydrate from HgO and $HClO_4$.

Reactions

In water, HgL'_2 is obtained by reacting $Hg(ClO_4)_2$ and L in the 1:2 molar ratio. Its identity was verified both by i.r. comparison with an authentic sample and by elemental analysis. Calcd. for $HgC_{10}H_{14}N_4O_2S_2$: C, 24.7; H, 2.9; N, 11.5%. Found: C, 24.6; H, 3.0; N, 11.4%.

For a 1:1 molar ratio, L dissolved in the least amount of water is added to a solution of $Hg(ClO_4)_2$. No precipitation is observed and the hygroscopic compound $HgL(ClO_4)_2 \cdot nH_2O$ is obtained by carefully evaporating the solvent. **WARNING: all attempts at drying this compound produced an explosion.** No analysis is reported for this compound since every analysed sample showed a variable amount of water. However, if the above solution is left at room temperature for a few days, $HgL'ClO_4 \cdot 2H_2O$ is formed. Calcd. for $HgC_5H_{11}ClN_2O_7S$: C, 12.5; H, 2.3; N, 5.8%. Found: C, 12.5; H, 2.8; N, 5.7%. Its imidazolidinato form is confirmed by i.r. comparison with HgL'_2.

The reactions in diethyl ether are carried out by dissolving $Hg(ClO_4)_2$ and L separately in the least amount of solvent; L is then added to the perchlorate dropwise in several molar ratios (see Table I). The complexes precipitate immediately or after some time by evaporation of the solvent. The complex obtained for the 1:1 molar ratio shows the same properties as that prepared from water.

TABLE I

Complexes obtained by reacting 5,5-dimethylimidazolidine-2-thione-4-one (L) and $Hg(ClO_4)_2$ at various $Hg(ClO_4)_2/L$ molar ratios in diethyl ether.

$Hg(ClO_4)_2/L$	Complex	Found (Calcd.) %		
		C	H	N
1:1	$HgL(ClO_4)_2 \cdot 5H_2O$*	9.4(9.5)	3.1(2.9)	4.3(4.4)
1:2	$HgL_3(ClO_4)_2$	22.3(21.7)	3.3(2.9)	10.5(10.1)
1:3	$HgL_3(ClO_4)_2$	21.1(21.7)	2.9(2.9)	9.8(10.1)
1:4	$HgL_4(ClO_4)_2$	25.0(24.6)	3.4(3.3)	11.8(11.5)
1:(5–10)	$HgL_5(ClO_4)_2$**	26.1(26.8)	3.2(3.6)	12.6(12.5)

* Since this compound is highly hygroscopic (see Experimental), the elemental analysis is given for one example. However, many others give CHN values for the number of water molecules ranging from 5–10.

** This complex was obtained for all molar ratios from 1/5 to 1/10.

TABLE II

(a) Complexes obtained by reacting $Hg(ClO_4)_2$ and 2L in $HClO_4$-aqueous solutions.

% $HClO_4$*	Notes	Complex	Found (Calcd.) %		
			C	H	N
5; 10	crystals + Hg after a month	$HgL_2(ClO_4)_2 \cdot 3H_2O$	15.9; 16.0 (16.2)	2.7; 3.2 (3.3)	7.4; 7.5 (7.5)
15; 20	crystals after a day	$HgL_2(ClO_4)_2 \cdot 3H_2O$	16.0; 16.2 (16.2)	2.9; 3.1 (3.3)	7.4; 7.4 (7.5)
25	crystals after a day	$HgL_2ClO_4 \cdot 3H_2O$	18.5 (18.7)	2.9 (3.4)	8.6 (8.7)

(b) Complexes obtained by reacting $Hg(ClO_4)_2$ and nL in 10% $HClO_4$.

n	Notes	Complex	Found (Calcd.) %		
			C	H	N
1	obtained after a day	$HgL(ClO_4)_2 \cdot 8H_2O$	8.6(8.7)	3.6(3.5)	4.0(4.1)
2	crystals + Hg after a month	$HgL_2(ClO_4)_2 \cdot 3H_2O$	15.9(16.2)	2.7(3.3)	7.4(7.5)
3-5	Precipitated immediately	$HgL_2ClO_4 \cdot 3H_2O$	18.5(18.7)	3.4(3.4)	8.7(8.7)

* 30 g of $HClO_4$ solution were used in each experiment. The molar ratios $HClO_4/Hg(ClO_4)_2$ were: 8.8, 17.6, 26.5, 35.3, and 44.1, for solutions of 5, 10, 15, 20, and 25% $HClO_4$ respectively.

The experiments in aqueous $HClO_4$ are performed by dissolving 1.78 g of $Hg(ClO_4)_2 \cdot 6H_2O$ (3.5 mmol) in 30 g of $HClO_4$ at various concentrations (5, 10, 15, 20 and 25%) and adding the proper amount of L. The results obtained by reacting

$Hg(ClO_4)_2$ and L at the 1:2 molar ratio in variable concentrations of $HClO_4$ are summarized in Table IIa. Table IIb reports the complexes obained by reacting $Hg(ClO_4)_2$ and nL (n = 1–5) in 10% $HClO_4$. The crystal used for the structural analysis is obtained from one of these solutions.

X-ray data collection and structure determination.

Crystal data and other experimental details are summarized in Table III. The diffraction experiment was carried out on an Enraf-Nonius CAD-4 diffractometer at room temperature, using Mo-Kα radiation (λ = 0.71073 Å). The calculations were performed on a PDP11/34 computer using the SDP-Plus Structure Determination Package.[6] The diffracted intensities were corrected for Lorentz and polarization effects and absorption (empirical correction)[7] but not for extinction. Anomalous dispersion corrections for atomic scattering factors of non-hydrogen atoms were taken from ref. 8. The structure was solved by conventional Patterson and Fourier methods and refined by full matrix least-squares methods, minimizing the function $\Sigma w(F_o - k\,|F_c|)^2$. Weights assigned to individual observations were $w = 1/[\sigma(F_o)]^2$, where $\sigma(F_o) = [\sigma^2(I) + (0.04I)^2]^{1/2}/2F_oLp$. Anisotropic thermal factors were refined for all non-hydrogen atoms. All hydrogen atoms, with the exception of those of water molecules not detected in a Fourier difference, were introduced into the model at calculated positions without refining. The final Fourier synthesis showed no residuals greater than 0.7 e/Å^3.

TABLE III
Crystal data and intensity collection parameters.

Compound	$[HgL_2][ClO_4]_2 \cdot 3H_2O$
Formula	$C_{10}H_{22}Cl_2HgN_4O_{13}S_2$
F.w.	741.93
Crystal system	monoclinic
Space Group	$P2_1/c$
a (Å)	7.505(3)
b (Å)	24.372(6)
c (Å)	13.110(6)
β (°)	99.33(3)
U (Å^3)	2366.3(28)
Z	4
D_{calc} (gcm^{-3})	2.082
μ(Mo-Kα) (cm^{-1})	69.64
Min. transmission factor	0.88
Crystal dimensions (mm)	0.20 × 0.10 × 0.10
Scan mode	ω
ω-scan width (°)	1.1 + 0.35 tanθ
θ-range (°)	3–25
Octants of reciprocal space explored	$\pm h, +k, +l$
Measured reflections	4076
Unique observed reflections with $I > 3\sigma(I)$	2989
Final R and R_w indices[a]	0.029, 0.038
No. of variables	289
ESD[b]	1.396

[a] $R = [\Sigma(Fo - k|Fc|)/\Sigma Fo]$; $R_w = [\Sigma w(Fo - k|Fc|)^2/\Sigma wFo^2]^{1/2}$.
[b] $ESD = [\Sigma w(Fo - k|Fc|)^2/(N_{observations} - N_{variables})]^{1/2}$.

Infrared Measurements

The i.r. spectra were recorded in KBr discs (3500–400 cm^{-1}) and in Nujol mulls (450–200 cm^{-1}) using a Perkin-Elmer 983 instrument connected to a Perkin-Elmer 7500 Data Station.

RESULTS AND DISCUSSION

Reactivity

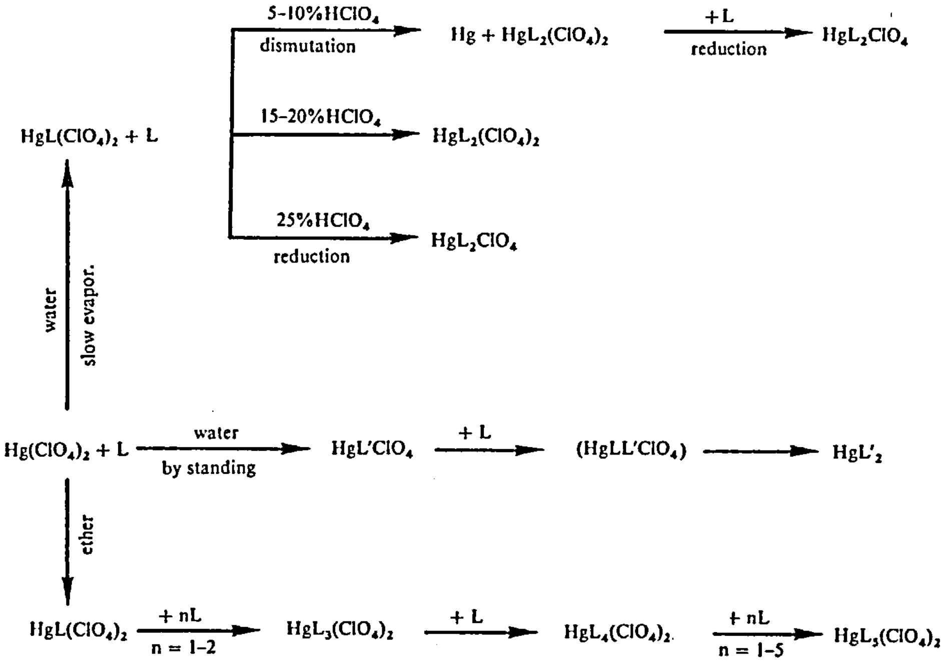
In water, three different complexes, $HgL(ClO_4)_2{\cdot}nH_2O$, $HgL'ClO_4$ and HgL'_2 are obtained. The formation of the inner complexes $HgL'ClO_4$ and HgL'_2 ($HgL'LClO_4$ is an hypothesized complex), can be explained in terms of interaction between the coordinated ligand and the solvent, which acts as a base expelling the more acid proton at N-3 from L.

The reaction between L and $Hg(ClO_4)_2$ was also carried out in diethyl ether for several $Hg(ClO_4)_2/L$ molar ratios. The results reported in Table I show that the ligand binds to mercury as L, the 1:1 molar ratio yields the hygroscopic complex $HgL(ClO_4)_2{\cdot}5H_2O$, the 1:2 molar ratio does not give $HgL_2(ClO_4)_2$, but $HgL_3(ClO_4)_2$, and molar ratios lower than 1:5 always produce $HgL_5(ClO_4)_2$.[9–10] As expected, reactivity in a solvent with a lower polarity than water favours the isolation of imidazolidine rather than imidazolidinato compounds. It is worth pointing out that $HgL_2(ClO_4)_2$ has never been obtained in this solvent despite innumerable attempts.

On the contrary, this complex is easily obtained in perchloric acid solutions as shown in Table IIa, where the results of the reaction between the Hg(II) perchlorate and L in a 1:2 molar ratio are reported. From Table IIa it appears that all the complexes contain the ligand as L, after *ca* a month in 5 and 10% $HClO_4$ the presence of metallic mercury and crystals of $HgL_2(ClO_4)_2{\cdot}3H_2O$ in the reaction mixture indicates a dismutation of a complex of Hg(I) and that the highest concentration of $HClO_4$ stabilizes the mercury(I) complex.

Both complexes of mercury(I) and $HgL_2(ClO_4)_2$ were unexpected. It seems to be interesting to ascertain the reduction mechanism of mercury(II), which occurs at a very high acid concentration. On the other hand, the Hg(I) complex must also exist at low acid concentrations, in consequence of the formation of metallic mercury. Unfortunately, all attempts at obtaining crystals of HgL_2ClO_4 suitable for X-ray analysis were unsuccessful, since the crystals were always fibrous polycrystalline aggregates. Strangely, intermediate acidity values stabilize $HgL_2(ClO_4)_2$ and no traces of dismutation were found.

To improve our knowledge of the system, we have carried out a series of reactions keeping both the acidity of the medium ($HClO_4$ = 10%) and the concentration of $Hg(ClO_4)_2$ constant, but varying the amount of L. The results are reported in Table IIb, where it can be seen that while there is no reduction for n = 1, the known hygroscopic complex $HgL(ClO_4)_2{\cdot}8H_2O$ is obtained. For n = 3–5, the mercury(I) complex precipitates immediately. Hence the reduction of mercury(II) depends on the amount of L. All of these syntheses are summarized in the following scheme.



SCHEME

Reactivity of $Hg(ClO_4)_2$ and 5,5-dimethylimidazolidine-2-thione-4-one (L) in water, in water/$HClO_4$ and diethylether. L′ is the N-3 deprotonated ligand.

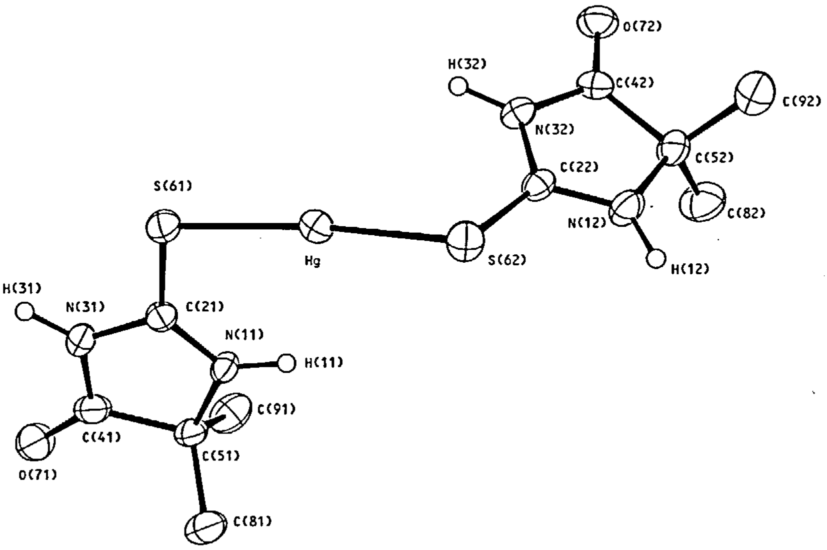


FIGURE 1 An ORTEP drawing of the $[HgL_2]^{2+}$ cation. The thermal ellipsoids enclose 30% of the electron density. The hydrogens of the methyl groups are omitted for clarity.

TABLE IV
Fractional coordinates for non-hydrogen atoms (e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c
Hg	−0.14877(3)	0.15254(1)	0.13654(2)
S(61)	−0.2087(2)	0.06173(7)	0.0790(1)
O(71)	0.1323(8)	−0.1040(2)	0.2041(4)
N(11)	0.1084(6)	0.0383(2)	0.2065(4)
N(31)	−0.0457(8)	−0.0320(2)	0.1392(4)
C(21)	−0.0370(8)	0.0239(3)	0.1469(5)
C(41)	0.104(1)	−0.0556(3)	0.1965(5)
C(51)	0.2204(9)	−0.0088(3)	0.2464(5)
C(81)	0.241(1)	−0.0117(4)	0.3627(6)
C(91)	0.400(1)	−0.0080(3)	0.2067(6)
S(62)	−0.1124(2)	0.24030(8)	0.2126(1)
O(72)	0.2364(6)	0.3050(2)	−0.0588(3)
N(12)	0.1470(8)	0.3110(2)	0.1925(4)
N(32)	0.0642(7)	0.2649(2)	0.0505(4)
C(22)	0.0398(8)	0.2724(3)	0.1488(5)
C(42)	0.1906(8)	0.3012(3)	0.0253(5)
C(52)	0.2575(9)	0.3344(3)	0.1216(5)
C(82)	0.458(1)	0.3225(4)	0.1570(7)
C(92)	0.221(1)	0.3961(4)	0.1021(7)
Cl(1)	0.3378(2)	0.13931(6)	−0.0168(1)
O(11)	0.4543(7)	0.1646(2)	0.0665(4)
O(12)	0.2467(9)	0.1787(3)	−0.0836(5)
O(13)	0.209(1)	0.1081(4)	0.0218(5)
O(14)	0.430(1)	0.1060(3)	−0.0749(6)
Cl(2)	0.2568(3)	−0.10865(9)	0.6143(1)
O(21)	0.3598(9)	−0.1374(3)	0.7013(5)
O(22)	0.231(1)	−0.1413(4)	0.5245(6)
O(23)	0.086(1)	−0.1015(5)	0.6420(6)
O(24)	0.339(2)	−0.0653(4)	0.5978(8)
OW(1)	−0.7686(6)	0.3567(2)	−0.2522(4)
OW(2)	−0.1726(6)	0.1904(2)	−0.0583(3)
OW(3)	0.5497(8)	0.2458(3)	0.3707(5)

Structure of bis(5,5-dimethylimidazolidine-2-thione-4-one) mercury(II) perchlorate triaquo

The fractional coordinates for non-hydrogen atoms with their e.s.d.'s in parentheses are reported in Table IV. Selected distances and angles are listed in Table V. An ORTEP drawing of the $[HgL_2]^{2+}$ cation is shown in Figure 1. The coordination about the mercury atom is almost linear with deviation from the ideal value of 180° due to packing interactions. Beside the two Hg–S bonds, the metal atom interacts weakly with two water molecules and with two oxygen atoms of the perchlorate anions.

As already observed in $HgLX_2$ (X = Cl, Br) complexes,[2] the C=S bond of the ligand undergoes a reduction of double bond character upon coordination to the metal. The largest variations in the geometry of the ligand regard the C(21) and C(22) atoms and their neighbours, the remaining part of the molecule being essentially

TABLE V

Selected bond distances (Å) and angles (deg).

Hg-S(61)	2.358(2)	Hg-S(62)	2.357(2)
S(61)-C(21)	1.712(5)	S(62)-C(22)	1.711(6)
C(21)-N(11)	1.283(6)	C(22)-N(12)	1.308(7)
C(21)-N(31)	1.366(7)	C(22)-N(32)	1.343(7)
N(31)-C(41)	1.373(8)	N(32)-C(42)	1.376(7)
C(41)-C(51)	1.517(8)	C(42)-C(52)	1.516(8)
C(51)-N(11)	1.469(7)	C(52)-N(12)	1.458(7)
C(41)-O(71)	1.199(7)	C(42)-O(72)	1.212(6)
C(51)-C(81)	1.508(8)	C(52)-C(82)	1.527(9)
C(51)-C(91)	1.519(9)	C(52)-C(92)	1.541(9)
Cl(1)-O(11)	1.424(4)	Cl(2)-O(21)	1.450(6)
Cl(1)-O(12)	1.400(5)	Cl(2)-O(22)	1.409(7)
Cl(1)-O(13)	1.391(6)	Cl(2)-O(23)	1.395(8)
Cl(1)-O(14)	1.374(7)	Cl(2)-O(24)	1.260(8)
Hg...OW(2)	2.695(4)	Hg...O(21)^{ii}	2.874(6)
Hg...OW(1)^{iii}	2.994(4)	Hg...O(11)^{x}	2.986(5)
OW(1)^{iii}...H(11)	1.804(4)	OW(2)...H(32)	1.850(4)
N(11)...OW(1)^{iii}	2.746(6)	N(32)...OW(2)	2.768(6)
N(11)...O(23)^{ii}	3.066(8)	N(31)...O(13)^{i}	2.925(8)
O(71)...OW(2)^{i}	2.894(6)	H(31)...O(13)^{i}	2.102(7)
O(13)...OW(1)^{iii}	3.062(8)	O(72)...OW(1)^{iv}	2.825(6)
O(72)...OW(3)^{vi}	2.936(7)	N(12)...O(12)^{v}	2.920(7)
O(12)...OW(3)^{vi}	3.060(9)	H(12)...O(12)^{v}	2.029(5)
O(21)...OW(1)^{vii}	3.036(7)	O(21)...OW(3)^{viii}	2.923(10)
OW(2)...OW(3)^{ix}	2.645(7)		
S(61)-Hg-S(62)	171.93(5)		
Hg-S(61)-C(21)	104.5(2)	Hg-S(62)-C(22)	104.4(2)
S(61)-C(21)-N(11)	131.6(4)	S(62)-C(22)-N(12)	121.8(4)
S(61)-C(21)-N(31)	118.4(4)	S(62)-C(22)-N(32)	127.8(4)
N(31)-C(21)-N(11)	110.0(5)	N(32)-C(22)-N(12)	110.3(5)
C(21)-N(31)-C(41)	110.6(5)	C(22)-N(32)-C(42)	110.4(5)
N(31)-C(41)-C(51)	106.5(5)	N(32)-C(42)-C(52)	107.0(5)
N(31)-C(41)-O(71)	125.1(6)	N(32)-C(42)-O(72)	125.2(5)
C(51)-C(41)-O(71)	128.4(6)	C(52)-C(42)-O(72)	127.8(5)
C(41)-C(51)-N(11)	100.2(4)	C(42)-C(52)-N(12)	100.1(4)
C(41)-C(51)-C(81)	110.9(5)	C(42)-C(52)-C(82)	109.1(6)
C(41)-C(51)-C(91)	110.0(5)	C(42)-C(52)-C(92)	110.9(5)
C(81)-C(51)-C(91)	113.3(5)	C(82)-C(52)-C(92)	112.2(6)
C(21)-N(11)-C(51)	112.6(4)	C(22)-N(12)-C(52)	112.1(5)
O(11)-Cl(1)-O(12)	111.1(4)	O(21)-Cl(2)-O(22)	111.6(5)
O(11)-Cl(1)-O(13)	109.5(3)	O(21)-Cl(2)-O(23)	104.5(4)
O(11)-Cl(1)-O(14)	112.2(4)	O(21)-Cl(2)-O(24)	109.0(6)
O(12)-Cl(1)-O(13)	107.7(5)	O(22)-Cl(2)-O(23)	106.3(5)
O(12)-Cl(1)-O(14)	107.3(5)	O(22)-Cl(2)-O(24)	109.6(8)
O(13)-Cl(1)-O(14)	108.8(7)	O(23)-Cl(2)-O(24)	115.8(10)
N(32)-H(32)...OW(2)	161.6(3)	N(11)-H(11)...OW(1)^{iii}	171.6(3)

Symmetry codes: i) $-x, -y, -z$; ii) $-x, -y, 1-z$; iii) $1+x, 1/2-y, 1/2+z$; iv) $1+x, y, z$; v) $x, 1/2-y, 1/2+z$; vi) $x, 1/2-y, z-1/2$; vii) $-x, y-3/2, -1/2-z$; viii) $1-x, -y, 1-z$; ix) $x-1, 1/2-y, z-1/2$; x) $-x, -y, 1-z$.

TABLE VI

Selected infrared bands (3500–300 cm^{-1}) for the ligands and their Hg complexes (KBr disc).

Complex	Reaction Solvent	ν(NH)	ν(CO)	ν(CN)	ν(CS)	Perchlorate		Other vibrations below 450 cm^{-1}
						ν_3	ν_4	
L[a]		3220sh 3179s	1742vs	1529vs 1290vs 1132vs	495ms			444w–300w
$HgL(ClO_4)_2{\cdot}5H_2O$[b]	Ether	3305ms 3130s	1768vs 1742m	1535vs 1275vs	478m	1140vs 1110vs 1085vs	635m 627s	355mbr
$HgL_3(ClO_4)_2$	Ether	3181s	1784s 1746vs	1536vs 1285s	484m	1120vsbr 1083vs	627s	347m
$HgL_4(ClO_4)_2$	Ether	3177vs	1784s 1745vs	1539vs 1286s 1132s	495m 483m	1108vsbr 1087vs	636s 628s	347ms
$HgL_5(ClO_4)_2$	Ether	3175vsbr	1784s 1745vs	1534s 1286s	495m 483m	1107vsbr 1088vs	637s 628s	347ms
$HgL_2(ClO_4)_2.3H_2O$[c]	water/ $HClO_4$	3175vsbr	1768vs 1745vs	1536vs 1276s	494m 480m	1128vsbr 1087vs	628s	347m
$HgL_2ClO_4.3H_2O$	water/ $HClO_4$	3182vsbr	1765vs 1745vs	1533vs 1279s	495m	1108vsbr	627s	347ms
NaL′[a]		3239vs	1640vs	1483vs 1305vs 1160vs	450m			355m
$HgL'ClO_4{\cdot}2H_2O$	water	3155s	1700sh 1685vs	1520vs 1300vs 1145vs*	490m 450vw	1145vs* 1113vs 1078vs	638s 628s	377w
HgL'_2	water	3134s	1674vs	1514vs 1304vs 1151s	492m 446w			371m

[a] From Ref. 1. [b] $HgL(ClO_4)_2.8H_2O$ obtained in water/$HClO_4$ and $HgL(ClO_4)_2.nH_2O$ prepared in water by slow evaporation exhibit the same i.r. bands.
[c] The crystal structure for this compound was solved.

unchanged in all the studied complexes. Here again, as verified in all the other studied hydantoin derivatives,[3,11] an asymmetry is observed for the N-C-S angles, explicable in terms of the different repulsions between the C=S bond and the two C(21)-N and C(22)-N bonds. The two five-membered rings are strictly planar and the deviations from the "best plane" of the sulphur and oxygen atoms are: S(61) 0.038(2), O(71) −0.006(6), S(62) 0.097(2) and O(72) 0.038(5) Å.

The packing of the $[HgL_2]^{2+}$ cations, the ClO_4^- anions and the water molecules is determined by a pattern of hydrogen bonds and short van der Waals interactions, as given in Table V.

Infrared Spectra

The importance of infrared spectroscopy in obtaining information on the coordination of L and L′ to mercury has been widely discussed in previous papers on complexes of mercury(II) halides.[1] It is convenient to remember that L and L′ have such different infrared spectra that it is very easy to ascertain whether the ligand is present in the neutral or the anionic form. It has also been found that N,S-coordination of L′ to a metal shows a general displacement of i.r. bands towards the corresponding bands of L, thus indicating that the lone pair of N-3 is involved in the coordination bond. Selected infrared bands of the ligands and their complexes are collected in Table VI. I.r. spectroscopy does not give any useful information on the number of the coordinated ligands. As previously found, the shifts of the bands are consistent with S-coordination for all complexes with the neutral ligand, and with N,S-coordination of the anion.

Splitting of the ν_3 and ν_4 bands of the ClO_4^- ion, verified in almost all the complexes, is indicative of a lowering of symmetry of this group, as is also demonstrated by the crystal data.

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