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On the Interaction between Mercury(II) Thiocyanate, Perchlorate or Acetate and Various Diazoles and Triazoles

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Several compounds of diazoles or triazoles with mercury(II) thiocyanate, perchlorate or acetate were obtained and characterized using analytical and spectral data. They are either adducts, e.g. $(imH)_n$-$Hg(SCN)_2$*, or mercurated species, e.g.* ImHgSCN. *The results show that the behaviour of inorganic mercury(II) with azoles is strongly dependent on the counter-ion present.*

Introduction

The complicated interactions between metal ions and natural products such as nucleosides are being studied in several laboratories, often with sophisticated techniques, and constitute a branch of bioinorganic chemistry.

From the particular point of view of a coordination chemist, a contribution to the field may be the definition of the possible ways in which a well-defined metal derivative reacts with simple, nitrogen-containing organic molecules. These results might then be utilized, *e.g.* as a pattern of reactivity, by other workers in the field dealing with biomolecules, such as nucleic acids or proteins.

Because of our previous experience in the field [1–6] we chose to investigate a series of simple organic molecules such as azoles (mainly imidazoles, but also other azoles for comparison) which are building blocks of purines. The metal of our choice was mercury, limiting our investigation to the inorganic side, since other research groups have been dealing with the reactivity of alkyl- [7–9] or aryl-mercury(II) species [10, 11].

With azoles this element is able to yield several air- and water-stable compounds containing metal–carbon or metal–nitrogen bonds, whose existence is feasible but which are not often observed with many other common elements. In addition, because of unexpected and often unexplained results the chemistry of mercury has been a source of interest since the age of alchemy [12].

In our preceding papers [2, 3] the interaction between mercury(II) chloride or cyanide and imidazoles was investigated and found to be different in the two cases, thus pointing out that what is generally called 'inorganic mercury(II)' has a behaviour strongly dependent on the counter-ion present, at least for the two derivatives mentioned.

In this paper we report our investigations on the reaction of imidazoles and of related azoles with other various mercury(II) derivatives, namely the thiocyanate, $Hg(SCN)_2$, and in a few cases the perchlorate $Hg(ClO_4)_2 \cdot 6H_2O$, or the acetate, $Hg(CH_3COO)_2$. Additional support is given here to show the dependence on the counter-ion for the chemical behaviour toward Hg(II) of such simple molecules as azoles, where the complicating features of the biomolecules derived from purines are absent.

Results and Discussion

The reaction of mercury(II) thiocyanate with several azoles was carried out in the conditions described in the experimental section. When a product was formed the reaction took place according to one or other of the following schemes:

$$\begin{tikzcd}
 & {[H\text{–}SCN] + Az\text{–}Hg\text{–}SCN} & \text{I} \\
Hg(SCN)_2 + AzR \arrow[ur, "(R = H)"] \arrow[dr, "R = H\text{ or}"', "R \neq H)"] & & \\
 & (AzR)_nHg(SCN)_2\ (n = 1, 1.5, \text{or } 2) & \text{II}
\end{tikzcd}$$

In both cases excess azole (*ca.* 1:4) was present; thiocyanic acid, an unstable species, was never isolated.

The first reaction pattern (N-mercuration) was observed with imidazole, 2-methyl–, 4-methyl–imidazole, benzoimidazole or *sym*-triazole, which gave the compounds *1*, *4*, *7*, *9*, or *12* as colourless air-stable powders, insoluble in common organic solvents except DMSO.

The second type of reaction (adduct formation) took place with N-substituted imidazoles, such as

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TABLE I.

	Compound and Formula	M.P. °C	Yield %	Elemental Analysis %[a]			Additional Data
				C	H	N	
1)	ImHgSCN	170	77	14.97	0.96	13.10	S: 9.79/9.83
	$C_4H_3HgN_3S$	(dec.)		14.74	0.92	12.90	$\Lambda = 0.11$ ohm^{-1} cm^2 mol^{-1}
							(Me_2SO, 20 °C, $1.2 \cdot 10^{-3}$ *M*)
2)	$(1\text{-}PhCH_2Im)_2Hg(SCN)_2$	48	78	41.79	3.24	13.34	
	$C_{22}H_{20}HgN_6S_2$			41.70	3.16	13.27	
3)	$(1\text{-}AllylIm)Hg(SCN)_2$	175	52	22.70	1.99	13.05	
	$C_8H_8HgN_4S_2$	(120 dec.)		22.59	1.88	13.18	
4)	2-MeImHgSCN	155	98	17.82	1.54	12.49	S: 9.42/9.42
	$C_5H_5HgN_3S$			17.66	1.47	12.36	
5)	$(2\text{-}Pr^iImH)_2Hg(SCN)_2$	105–107	86	31.15	3.77	15.82	
	$C_{14}H_{20}HgN_6S_2$			31.28	3.72	15.64	
6)	$(2\text{-}PhImH)_3 \cdot 2Hg(SCN)_2$	120	64	34.75	2.23	13.02	
	$C_{31}H_{28}Hg_2N_{10}S_4$			34.89	2.25	13.13	
7)	(BenzoIm)HgSCN	160	21	25.43	1.44	11.27	
	$C_8H_5HgN_3S$	(dec.)		25.55	1.33	11.18	
8)	$[4(5)\text{-}PhImH]_2Hg(SCN)_2$	159	77	39.72	2.65	13.80	
	$C_{20}H_{16}HgN_6S_2$			39.66	2.64	13.88	
9)	[4(5)-MeIm]HgSCN	140	18	17.78	1.55	12.43	S: 9.29/9.42
	$C_5H_5HgN_3S$	dec.		17.67	1.47	12.37	
10)	$(Im)_2Hg$	190	91	21.47	2.18	16.75	
	$C_6H_8HgN_4$			21.38	2.37	16.63	
11)	$(5\text{-}Nitroindazole)Hg(SCN)_2$	180	95	22.43	1.03	14.40	
	$C_9H_5HgN_5O_2S_2$			22.51	1.04	14.59	
12)	(1,2,4-Triazolyl)HgSCN	165	97	11.23	0.63	17.20	
	$C_3H_2HgN_4S$	(dec.)		11.02	0.61	17.14	
13)	$[(Im)_3Hg_2]^+(ClO_4)^-$	230–240	16	15.18	1.28	12.00	$\Lambda = 152$ ohm^{-1} cm^2 mol^{-1}
	$[(C_3H_3N_2)_3Hg_2]^+(ClO_4)^-$			15.39	1.28	11.97	(Me_2SO, 20 °C, $1.1 \cdot 10^{-4}$ *M*)
14)	$[(1\text{-}PhCH_2Im)_5Hg_2](ClO_4)_4 \cdot 6H_2O$	110–115	29	35.45	3.55	8.28	$\Lambda = 740$ ohm^{-1} cm^2 mol^{-1}
	$C_{50}Cl_4H_{62}Hg_2N_{10}O_{22}$			35.33	3.65	8.24	(Me_2CO, 20 °C, $1.2 \cdot 10^{-3}$ *M*)
							$\Lambda = 166$ ohm^{-1} cm^2 mol^{-1}
							(Me_2SO, 20 °C, $1.2 \cdot 10^{-3}$ *M*)

[a] Found/Calcd.

1-benzyl– or 1-isopropyl-imidazole yielding *2* or *5*, resp., white compounds soluble in organic solvents such as acetone. This reactivity, however, is not limited to N-substituted derivatives, for which N-mercuration is impossible, but was also found with 2- and 4(5)-phenylimidazole or 5-nitroindazole, giving a good yield of the corresponding adducts, *6* and *8* or *11* respectively, in spite of the modest basicity of the ligands (pK_a: 6.4 and 6.1 for 2-Ph– and 4-Ph–imH resp. [13]).

No product could be isolated when mercury thiocyanate was reacted with pyrazole, indazole, tetrazole, 4-nitroimidazole or N-methylimidazole. Owing to the existence of a large number of N-ethyl- and of N-n-propylimidazole adducts with various metal derivatives [14] the reaction with N-methylimidazole was attempted in several conditions, but no adduct was isolated.

On this evidence, the reactivity of mercury(II) thiocyanate seems to be intermediate between that of the cyanide [3] and that of the chloride [2], which are likely to be limiting cases. No other generalization can be made on the available results [2, 3, 12]; and moreover, not even the preceding generalization is valid if another azole, such as pyrazole [15], or other mercury(II) derivatives are concerned. For example, with imidazole, mercury(II) perchlorate afforded $[Hg_2(Im)_3]ClO_4$ while in different experimental conditions a species formulated as $ImHgClO_4 \cdot H_2O$ [16] was isolated; the same

TABLE II. Selected Infrared Data[a], cm^{-1}.

	Compound	ν(N–H)	ν(C–H) azole and aromatics	ν(S–C≡N)	1500–1600	low frequency region (<500)
1)	ImHgSCN		3147m, 3140m	2055vs	1525m	70m, 460m, 368m
2)	$(1\text{-}PhCH_2Im)_2Hg(SCN)_2$		3138m, 3119m	2120vs	1600m, 1515m 1502m	480w, 458w, 430w
4)	2-MeImHgSCN		3143m, 3127m	2078vs	1580m, 1530m	475m, 450m, 437s, 310m, 275m
5)	$(2\text{-}Pr^iImH)_2Hg(SCN)_2$	3160m,br; 3100–2500m,br	3120m, 3100m	2120vs	1560m	490w, 460m, 440m, 410m
6)	$(2\text{-}PhImH)_3 \cdot 2Hg(SCN)_2$	3300–2500m	3141m, 3090m	2118vs[b]	1560w	440vw, 340vw
7)	(BenzoIm)HgSCN		3119vw, 3050vw	2118vs[b]		470m, 430m
8)	$[4(5)\text{-}PhImH]_2Hg(SCN)_2$	3240s	3080m, 3020m	2130vs	1590m, 1570m	460m, 440m, 430m, 365m
9)	$[4(5)\text{-}MeIm]Hg(SCN)_2$		3130w	2110s	1568w	460m, 395m, 309m, 295m, 282m
10)	$(Im)_2Hg$		3118m			
11)	$(5\text{-}Nitroindazole)Hg(SCN)_2$[c]	3240m,br	3135w, 3110w	2150s, 2130vs	1585m, 1520m	458m, 435m, 420m, 300m
12)	(1,2,4-Triazolyl)HgSCN		3130w, 3120w	2120s	1550w, 1500s	460w, 430m, 283m
13)	$[(Im)_3Hg_2]^+(ClO_4)^-$		3140m, 3120m	d	1525w	465w, 380m, 330m
14)	$[(1\text{-}PhCH_2Im)_5Hg_2](ClO_4)_4 \cdot 6H_2O$	e	3120m, 3060w, 3030w	f	1550m, 1530m, 1500m	470w

[a] Nujol mull. [b] 50 cm^{-1} broad at half-height. [c] Nitrogroup bands at 1570–1500 and 1370–1300 cm^{-1}. [d] $\nu(ClO_4)^-$ *ca.* 1060 cm^{-1}, vs. [e] ν(OH), H_2O, 3500 cm^{-1}, m, br.
[f] $\nu(ClO_4)^-$ *ca.* 1090 cm^{-1}, vs.

TABLE III. Proton Magnetic Resonance Data.

Compound	Solvent	δ values[a] for azole substituents in position		
		1	2	4 + 5
ImH	$(CD_3)_2SO$	12.63s, NH	7.83s	7.14s
ImHgSCN	$(CD_3)_2SO$		7.90s	7.33s
1-$PhCH_2$Im	$(CD_3)_2CO$	5.10s, CH_2; 7.1–7.4m, Ph	7.65s	7.00s; 7.03s
(1-$PhCH_2$Im)$_2$Hg(SCN)$_2$	$(CD_3)_2CO$	5.35s, CH_2; 7.33s, Ph	8.20s	7.19s[b]
2-MeImH	$(CD_3)_2SO$	11.60s, v. broad, NH	2.25s, Me	6.85s
2-MeImHgSCN[c]	$(CD_3)_2SO$		2.53s, Me[d]	7.13s
2-Pr^iImH	$(CD_3)_2CO$	8.62s, NH	1.30d, Me (J = 7 Hz) 3.14sp, CH (J = 7 Hz)	6.97s
(2-Pr^iImH)$_2$Hg(SCN)$_2$	$(CD_3)_2CO$	8.68s, broad, NH	1.35d, Me (J = 7 Hz) 3.40sp, CH (J = 7 Hz)	7.15s
2-PhImH	$(CD_3)_2SO$	12.47s, broad, NH	7.1–7.6m, Ph	7.9–8.0m
(2-PhImH)$_3$·2Hg(SCN)$_2$	$(CD_3)_2SO$	10.50s, v. broad, NH	7.1–7.5m, Ph	7.5–7.8m
BenzoImH	$(CD_3)_2SO$	11.35s, broad, NH	8.40s	7.1–7.4m; 7.6–7.9m, C_6H_4
(BenzoIm)HgSCN	$(CD_3)_2SO$		8.58s	7.1–7.5m; 7.8–8.1m, C_6H_4
4(5)-PhImH	CD_3OD	not observed	[e]	7.1–7.9m[Ph + 4(5)H]
[4(5)-PhImH]$_2$Hg(SCN)$_2$	CD_3OD	not observed[f]	7.92s[g]	7.2–7.7m[Ph + 4(5)H][g]
4(5)-MeImH	$(CD_3)_2SO$	11.80s, NH	7.60s	2.18s, Me; 6.77s
[4(5)-MeIm]Hg(SCN)$_2$	$(CD_3)_2SO$		7.77s	2.28s, Me; 7.08s
5-Nitroindazole	$(CD_3)_2SO$	13.60s, v. broad, NH	8.43s[h]	7.6–8.9m, C_6H_3
(5-Nitroindazole)Hg(SCN)$_2$	$(CD_3)_2SO$	not observed[f]	8.47s[h]	7.7–8.9m, C_6H_3
$[(Im)_3Hg_2]^+(ClO_4)^-$ [c]	$(CD_3)_2SO$		7.97s	7.37s
$[(1\text{-}PhCH_2Im)_5Hg_2](ClO_4)_4 \cdot 6H_2O$	$(CD_3)_2CO$	5.47s, (N–CH_2) 7.41s, (C–H + C_6H_5)	7.41s[g]	7.60s; 8.59s[g]

[a] s = singlet; d = doublet; m = multiplet; sp = sextuplet. [b] One of these two heterocyclic protons lies below the phenyl signal. [c] Heating was required to dissolve the sample. [d] Overlaps with signal of the solvent. [e] Overlapping with phenyl signals. [f] NH evidence was found in the IR spectrum. [g] The assignment can be exchanged. [h] 3-position.

heterocycle reacted with mercury(II) acetate affording Im_2Hg, *10.* With the perchlorate an adduct was formed, $(L_5Hg_2)(ClO_4)_4 \cdot 6H_2O$, *14,* when N-benzylimidazole was employed.

The compounds reported were characterized using analytical (Table I) and spectral data (Tables II and III). The infrared spectra (Table II) of the compounds *1–9* and *10–12* show the expected ν(SCN) vibration in the 2050–2150 cm^{-1} range: those of the adducts *5, 6, 8* and *11* show also a noticeable ν(NH) which, in the case of *5* and *6* is very broad, owing to hydrogen-bonding. When instead of the adducts the N-mercurated derivatives *1, 4, 7, 9, 10, 12* or *13* are considered the region above 3000 cm^{-1} contains only absorptions of medium or weak intensity, due to ν(CH) of the azole, or of the aromatic rings where present. These same bands are observed also in the adducts of N-substituted azoles, both in those reported here or previously [2, 3], so that they are diagnostic for the presence of an azole or azolato ligand.

Although infrared criteria have often been used to establish the coordination pattern of perchlorato or thiocyanato ligands, they afford reliable information only in the former case. The perchlorate is ionic here since the very strong vibration at 1060–1090 cm^{-1} is not split. Considerable doubts have been raised [17] on the validity of the infrared criteria in establishing the coordination mode of an SCN ligand, so that these will not be applied. In our case the maority of ν(SCN) lies in the 2100–2130 cm^{-1} region (compound *2, 3, 5, 6, 7, 8, 9* and *12*), a range which is compatible with both Hg-SCN and Hg–SCN-Hg arrangements. The remaining mercurated azoles have ν(SCN) at lower values in the case of *1* and *4* (2055 and 2078 cm^{-1} resp.), while the vibration is found at higher values and is split (2150 and 2130 cm^{-1}) in the 5-nitroindazole adduct, *11.* These variations may be indicative of different arrangements of the thiocyanato group(s), but do not allow any certain conclusion to be reached.

The proton NMR spectra support the formulae proposed and rule out any rearrangement of the organic ligand or any C-mercuration. As already found in other azoles derivatives [2, 3], the signals in the derivatives are found at lower field than in the parent ligand, in agreement with electron donation from the donor atom toward the metal ion. The nmr spectra of the N-mercurated compounds, *1, 4, 7, 9* and *12*, could be registered only in dimethylsulphoxide because of solubility.

In conclusion, in our papers [2, 3] it has been shown that the interaction of the so-called 'inorganic mercury(II)' with azoles, the building block of purines, is strongly dependent on the counter-ion present. In the case of thiocyanato (and if any reaction does take place) both N-mercurated Az–HgSCN compounds or $(AzR)_n$–$Hg(SCN)_2$ adducts are obtained.

The coordination number of mercury in the adducts cannot be decided in the absence of other data, such as an X-ray crystal structure, but in the former species the usual four-coordination around mercury is likely to be achieved through bridging SCN and bridging Az^- groups, in agreement with their insolubility in most common solvents.

Experimental

The samples were pumped to constant weight (20 °C, *ca.* 0.1 torr). Carbon, hydrogen, and nitrogen analyses were carried out by Mr. A. Canu (University of Sassari), sulphur analyses by Pascher's Mikroanalytisches Laboratorium, Bonn, F.R.G. Infrared spectra (Table II) from 4000 to 250 cm^{-1} were recorded on a Perkin-Elmer 457 Instrument; proton NMR spectra were recorded on a Varian EM-390 machine operating at room temperature and 90 MHz, and are given in Table III. No attempt was made to reduce the reaction times.

(ImHgSCN), 1

To an aqueous suspension (30 ml) of mercury(II) thiocyanate (1 mmol) an aqueous solution (15 ml) of imidazole (4 mmol) was added and the mixture stirred for 5 days to yield 1 as a white precipitate. The compounds *2* (4 days), *4* (3 days), and *6* (a few hours) were obtained similarly after the time indicated in brackets.

(N-benzylimidazole)$_2$Hg(SCN)$_2$, 2

An ethanol solution (15 ml) of the ligand (4.74 mmol) was added to a stirred ethanol (50 ml) suspension of mercury thiocyanate (1.5 mmol). After keeping the mixture overnight in the refrigerator, the compound *2* was filtered. In a similar way the following compounds were obtained: *1, 3* (after 5 months at room temperature), *4, 5* (10 ml of water was added in order to precipitate the compound), *7* or *9* (20 ml of water was added to precipitate the compound), *8, 11* (after 5 days), and *12.* When the reaction was carried out in ethanol rather than in water lower yields were obtained than those reported in the Table I.

(Im)$_2$Hg, 10

The compound precipitated upon mixing aqueous mercury(II) acetate (15 ml; 1 mmol) with aqueous imidazole (15 ml; 4 mmol).

$[(Im)_3Hg_2]^+(ClO_4)^-$, 13

This was obtained as a off-white precipitate after stirring for 4 days a solution of $Hg(ClO_4)_2 \cdot 6H_2O$ (1.26 mmol in 50 ml) to which imidazole (5.6 mmol) in ethanol (5 ml) was added.

$[(1\text{-}PhCH_2Im)_5Hg_2](ClO_4)_4\cdot 6H_2O$, 14

N-benzylimidazole (4.7 mmol) was added to a stirred aqueous solution of $Hg(ClO_4)_2\cdot 6H_2O$ (1.52 mmol in 40 ml). The solution was separated by decantation from a sticky precipitate and was cooled in the refrigerator for 5 days, affording the compound *14* as a white precipitate.

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