Complexes of Pt(II), Pd(II), Rh(I) and Rh(III) with Nitrogen and Sulfur-containing Heterocyclic Ligands of Biological Interest. Synthesis, Characterization and Influence of pH

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Complexes of 2-mercapto-thiazoline (SHth) with Pt (II), Pd(II), Rh(I) and Rh(III), of 2-mercapto-benzothiazole (SHbtz) and 2-mercapto-1-methylimidazole (SHmi) with Pt(II) and Pd(II) were prepared and characterized. I.R. and far i.r. spectroscopy, ^1H n.m.r., conductivity and dipole moments measurements were used to assign the stereochemistry and to determine the mode of co-ordination. Several types of complexes have been isolated: cis- or trans-ML_2X_2 (M = Pt(II), Pd(II); L = SHth, SHbtz, SHmi; X = Cl, I); $2K^+[PtL_4]^{2-}$ and $[PtL_4]^{2+}2Cl^-$ (L = SHth); $[ML_2]_n$ (M = Pt(II), Pd(II); L = SHbtz, SHmi); $[Rh(I)(L)_3 PPh_3]^+$ and $[Rh(I)(L)_3PPh_3]^{2-}$ and their oxidative addition products with CH_3I, $[Rh(III)(L)_4Cl_2]^+$ and $[Rh(III)(L)_4Cl_2]^{3-}$, where L = SHth for the cationic complexes, L = Sth for the anionic ones.

It appears that in acid medium these ligands co-ordinate only through the N-heteroatom. When operating in basic medium, SHth is only S-coordinated to Pt(II), Rh(I) and Rh(III), whereas SHbtz and SHmi always bond through both S and N.

Introduction

The discovery of anti-tumor activity among platinum complexes[1–5] has been the most important factor in stimulating a new interest in metal complexes as a potential class of anti-tumor drugs. However, the mechanism of action of these compounds within the cell is still unknown, and one of the necessary steps for its understanding is therefore a preliminary study of "model"-complexes.

We have undertaken the synthesis and spectroscopical identification of various Pt(II), Pd(II), Rh(I) and Rh(III) complexes. Some of these indeed show strong anti-tumor action[6] and the study of their stereochemistry and chemical reactivity will help to determine what relationship exist between chemical structure and anti-cancer activity.

Until now, few complexes with ligands other than primary or alicyclic amines have been tested. We have therefore chosen three cyclic molecules (aromatic or not), containing N and S as heteroatoms and potential reaction centers:
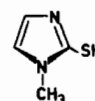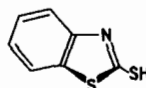

2-mercaptothiazoline (SHth)*   1-methyl,2-mercaptoimidazole (SHmi)

2-mercaptobenzothiazole (SHbtz)

Experimental

Instrumental

Analytical data for all compounds discussed are given in Table I.

I.R. spectra were carried out on a Polytec FIR 30 interferometer for the 50–400 cm^{-1} range and on a Beckman I.R. 12 spectrophotometer for the 400–4000 cm^{-1} range. The complexes were respectively sampled as polyethylene and KBr pellets.

^1H n.m.r. spectra were performed at room temperature with a Perkin–Elmer R 12B spectrometer in $CD_2 Cl_2$ or $DMSO(d_6)$ solutions, with TMS as external standard.

Dipole moments were measured with a DMO1 dipolmeter and the refractive indexes with a PULFRICH refractometer.

Preparation of the Complexes

The ligands (SHth, SHbtz, SHmi) were purchased from FLUKA AG and used without further purification. Potassium tetrachloroplatinate(II) and the tetra

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*These abbreviations have been retained for N-coordinated complexes, but changed to Sth, Smi, Sbtz for the S-coordinated compounds.

TABLE I. Analytical Data[a]

Compounds	Colour	% C		% H		% N		% M		$\Lambda^b \, \Omega^{-1}$ mol^{-1}cm^2		Yield %
		calcd	found	calcd	found	calcd	found	calcd	found	theor.	found	
1 Pt(SHth)$_2$Cl$_2$	yellow	14.35	14.3	1.99	2.0	5.58	5.5	38.70	38.5			75
2 Pt(SHth)$_2$I$_2$	brown	10.48	10.5	1.46	1.5	4.07	3.9	28.38	28.5			70
3 K$_2$[Pt(Sth)$_2$Cl$_2$]	yellow	12.30	12.2	1.38	1.5	4.83	4.7	33.61	33.8			50
4 [Pt(SHth)$_4$]Cl$_2$	pale yellow	19.38	19.6	2.70	2.8	7.54	7.7	26.28	26.3			55
5 K$_2$[Pt(Sth)$_4$]	brick	19.35	19.4	2.15	2.3	7.52	7.5	26.18	26.2			40
6 Pd(SHth)$_2$Cl$_2$[c]	brick	17.25	17.2	2.40	2.6	6.74	6.7					80
7 Pd(SHth)$_2$I$_2$	brown	12.02	12.1	1.67	1.7	4.68	4.5					80
8 Pd(Sth)$_2$	orange–yellow	21.05	21.4	2.34	2.3	8.18	8.1					75
9 [Rh(SHth)$_3$PPh$_3$]Cl	orange–yellow	42.40	41.0	3.92	4.0	5.50	5.5			75–95	78	80
10 K$_2$[Rh(Sth)$_3$PPh$_3$]	cinnamon	40.70	40.6	3.40	3.7	5.28	6.3			200	171	70
11 [Rh(SHth)$_3$PPh$_3$I$_2$]PF$_6$	violet–brown	28.65	28.8	2.65	2.7	3.71	3.8			75–95	84	75
12 K$_2$[Rh(Sth)$_3$PPh$_3$I$_2$]	violet–brown	30.60	30.8	2.54	2.7	3.96	4.1			200	150	60
13 [Rh(SHth)$_4$Cl$_2$]Cl	ochre	21.01	20.6	2.92	2.6	8.18	8.1			75–95	73	85
14 Na$_3$[Rh(Sth)$_4$Cl$_2$]	hazel–nut	20.12	20.3	2.24	2.7	7.83	7.4					82
15 Pt(SHbtz)$_2$Cl$_2$	lemon	28.01	28.1	1.67	1.7	4.67	4.8	32.50	32.3			65
16 Pt(SHbtz)$_2$I$_2$	orange	21.42	21.8	1.28	1.3	3.58	3.7	24.90	24.7			63
17 Pt(Sbtz)$_2$	straw–yellow	31.82	31.7	1.51	1.5	5.31	5.2	36.92	37.0			60
18 Pd(SHbtz)$_2$Cl$_2$[c]	orange	32.41	32.6	1.96	2.0	5.48	5.3					80
19 Pd(SHbtz)$_2$I$_2$	red–brown	24.21	24.4	1.44	1.5	4.04	4.2					82
20 Pd(Sbtz)$_2$	brick	38.26	38.9	1.82	1.9	6.38	6.5					75
21 Pt(SHmi)$_2$Cl$_2$	red	19.41	19.8	2.43	2.4	11.33	11.5	39.43	38.6			70
22 Pt(SHmi)$_2$I$_2$	red–violet	14.19	14.3	1.77	1.8	8.28	8.4	28.80	27.5			68
23 Pt(Smi)$_2$	brown	22.80	22.9	2.38	2.4	13.29	13.5	46.01	48.1			60
24 Pd(SHmi)$_2$Cl$_2$[c]	red	23.62	23.2	2.96	2.7	13.80	13.4					80
25 Pd(SHmi)$_2$I$_2$	red–violet	16.32	16.5	2.10	2.2	9.53	9.3					83
26 Pd(Smi)$_2$	brick	28.82	29.0	3.01	2.9	16.83	16.2					70

[a] Microanalyses for C, H, N were performed by the Service Central de Microanalyse of C.N.R.S. in Strasbourg. Platinum was determined by the thermogravimetric method, at 300° C. [b] Molar conductivity measurements at 25° C in $10^{-4} M$ MeNO$_2$ for 1:1 electrolytes and $10^{-4} M$ MeOH for 1:2 electrolytes. The theoretical values are indicatively given, the experimental ones agree with literature data[15,26]. [c] Dipole moment in CHCl$_3$ at 25° C : $\mu = 1.8 \pm 0.1$ D *trans*-Pd(SHth)$_2$Cl$_2$), $\mu = 1.6 \pm 0.1$ D *(trans*-Pd(SHbtz)$_2$Cl$_2$), $\mu = 1.5 \pm 0.1$ D *(trans*-Pd(SHmi)$_2$Cl$_2$).

n-butylammonium salt of tetrachloro, di-μ-chloropalladium(II) were prepared by standard methods[7].

Cis- and *trans*-ML$_2$Cl$_2$ (M = Pt(II), Pd(II); L = SHth, SHmi, SHbtz). Platinum(II) complexes were obtained by adding a hot aqueous solution of K$_2$PtCl$_4$ (10^{-3} mol) to a water–ethanol solution (1:1) of the ligand (2×10^{-3} mol). The precipitates were washed successively with water and alcohol and recrystallized from dimethylformamide (DMF)/diethylether. The palladium(II) analogues were prepared by addition of an ethanolic solution of the ligand (2×10^{-3} mol) to a hot solution of [NBu$_4$]$_2$[PdCl$_3$]$_2$ in dichloromethane (10^{-3} mol of Pd). Crystals were formed by evaporating the solution; they were washed with alcohol and recrystallized from dichloromethane/diethylether.

Tetrakis(2-mercaptothiazoline)platinum(II) chloride (4) and potassium tetrakis(2-mercaptothiazoline)platinate(II) (5) were prepared by reaction of SHth (4×10^{-3} mol) with a hot aqueous solution of K$_2$PtCl$_4$ (10^{-3} mol). For complex 4, the ligand solution was

acidified to pH = 4.5 with 0.1 N HCl; for complex 5, it was made alkaline by addition of $1N$ KOH and NH$_4$OH (2 ml) which was found to enhance the reaction. Both complexes were washed with water and alcohol and dried with diethylether.

Tris-(2-mercaptothiazoline)triphenylphosphinerhodium(I) chloride (9) and potassium tris-(2-mercaptothiazoline)triphenylphosphinerhodate(I) (10) were obtained by addition of a hot solution of Rh(PPh$_3$)$_3$Cl in dichloromethane (0.5×10^{-3} mol) to an ethanolic solution of SHth (2×10^{-3} mol), acidified to pH = 2 by $1N$ HCl for complex 9 and made alkaline to pH = 9 by $1N$ ethanolic KOH for complex 10. The salts were precipitated by addition of diethylether, and recrystallized from dichloromethane/diethylether.

The potassium derivatives of diiodo tris-(2-mercaptothiazoline)triphenylphosphinerhodium(III) hexafluorophosphate (11) and diiodo tris-(2-mercaptothiazoline)triphenylphosphinerhodate(III) (12) where synthesized by addition of an excess of methyl iodide

$(2 \times 10^{-3}$ mol) to a solution of complexes 9 and 10 $(0.5 \times 10^{-3}$ mol) respectively. Complex 12 was progressively formed, whereas complex 11 was precipitated after addition of NH_4PF_6. The products were washed with ethanol and recrystallized from dichloromethane/diethylether.

Dichlorotetrakis-(2-mercaptothiazoline)rhodium(III) chloride (13) and sodium dichlorotetrakis-(2-mercaptothiazoline)rhodate(III) (14). Hexachlororhodate(III) $(10^{-3}$ mol) dissolved in hot water was added to an ethanolic solution of 2-mercaptothiazoline $(4 \times 10^{-3}$ mol) acidified to pH $= 4$ by 1N HCl for complex 12 or under basic conditions (pH $= 9$ by addition of 1N KOH) for complex 14. The precipitates, obtained on standing overnight, were washed with water and ethanol and recrystallized from DMF/diethylether.

The $[M(L)_2]_n$ complexes (M $=$ Pt(II), Pd(II); L $=$ SHth, SHmi, SHbtz) were precipitated as powdry compounds by addition of a basic ethanolic solution of the ligand $(2 \times 10^{-3}$ mol) to an aqueous solution of K_2PtCl_4 $(10^{-3}$ mol) or to a solution of $[NBu_4]_2$ $[PdCl_3]_2$ $(10^{-3}$ mol) in dichloromethane. The complexes were washed with ethanol and dried with diethylether.

Results and Discussion

The mercapto-substituted ligands exist, when free, as two tautomeric conformations: the thiol form and the thioketo form. The latter is dominant in the case of SHbtz and SHmi, because of their entirely aromatic character, whereas the more basic SHth appears in the i.r. and n.m.r. results as a mixture of both forms.

Platinum(II), Palladium(II), Rhodium(I) and Rhodium(III) Complexes with 2-Mercaptothiazoline (SHth)

Platinum(II) afforded the widest range of complexes with the SHth ligand, and compounds having metal:ligand ratios of 1:2 and 1:4, coordinated either through the nitrogen or the sulfur, some of which already described in literature[21], have been characterized[8] (Scheme I):
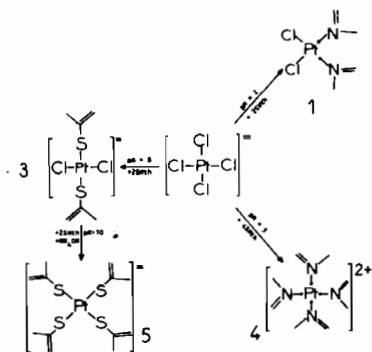
At a highly basic pH, complex 5 is obtained following addition of NH_4OH. The mechanism presumably in-

volves an intermediate substitution of two chlorines on $[PtCl_4]^{2-}$ by NH_3, followed by a nucleophilic attack of Sth$^-$. This is partially confirmed by the fact that complex 5 could also be synthesized by reaction of *cis*-$Pt(NH_3)_2Cl_2$ with SHth in a 1:4 ratio.

After reaction with the metal salt, SHth appears entirely as the thiol form, since the ν(C–N) vibration, due to the thioketo form

(initially at 1257 cm^{-1}), has disappeared after complexation. Furthermore, no absorption is visible anymore in the 3300–3000 cm^{-1} range due to a ν(N–H) vibration. Wilson[9] and Basson[10] have also observed that 2-mercaptothiazoline reacts with platinum metals by changing into the thiol form.

The medium-range i.r. vibrational frequencies (Table II) of the 2-mercaptothiazoline complexes suggest coordination through the nitrogen in acid medium, or through the sulfur in basic medium. Although a class b metal such as platinum is usually bonded via the sulfur atom[11], we observed for complexes 1 and 4 a downshift for the ν(C=N) frequency. The intensity and position of the ν(C–S) vibrations indicated that S-bonded ligands were absent. This may be explained by the fact that the ionisation of the thiol in RS$^-$ occurs only at a basic pH. In acid medium on the contrary, the thiol is not dissociated and the cyclic nitrogen is then the most probable coordination center. In the case of complexes 3 and 5, the i.r. shifts are characteristic of an S-bonded ligand, since ν(C–S), at 655 cm^{-1} in free SHth, is split into 680–640 cm^{-1} in $K_2[Pt(Sth)_2Cl_2]$ and lowered to 626 cm^{-1} in $K_2[Pt(Sth)_4]$. The ν(S–H) vibration was not considered as representative of S-coordination, because of its already weak intensity in the free ligands. The stereochemistries of the halogenated complexes, $Pt(SHth)_2Cl_2$ and $K_2[Pt(Sth)_2Cl_2]$, respectively *cis* and *trans* according to the higher *trans*-effect in the order N$<$Cl$<$S[12,13], are confirmed by the far i.r. spectra, and by the dipole moment measurements (Table I). Two ν(Pt–Cl) modes (asym. and sym.) appear at 316–310 cm^{-1} for the *cis* complex (of C_{2v} symmetry), whereas only one ν(Pt–Cl) mode appears at 338 cm^{-1} for the *trans* of D_{2h} symmetry. The iodide analogue $Pt(SHth)_2I_2$, obtained by metathesis from $Pt(SHth)_2Cl_2$, confirms the *cis* configuration of the latter since two bands are visible at 170 and 204 cm^{-1} for ν_{as} and ν_s(Pt–I).

In spite of its close analogy with platinum, we observed with palladium(II) a lower degree of substitution. The initial metal salt was

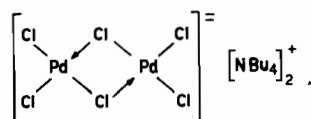TABLE II. Assignments of the Most Important I.r. and Far i.r. Bands (4000–50 cm^{-1}).[a]

Compounds	ν(C=N) + ν(N–C=S)	ν(C–N)	ν(C–S)	ν(M–X)	ν(M–N)	ν(M–S)
SHth[b]	*1586* m, *1454* m	*1257* m	*1300* m, *655* m			
1 *cis*-Pt(SHth)$_2$Cl$_2$	1656 m–1520 s, –	1250 vw	1309 s, 662 s	316 s, 310 sh	260 m, 252 m	
2 *cis*-Pt(SHth)$_2$I$_2$				204 m, 170 m	262 m, 254 m	
3 *trans*-K$_2$[Pt(Sth)$_2$Cl$_2$]	1586 m, 1452 w	–	1290 s, 680 m–640 m	338 s		365 s
4 Pt(SHth)$_4$Cl$_2$	1545 m, 1444 w	–	1300 m, 650 s		236 s[c]	
5 K$_2$[Pt(Sth)$_4$]	1590 m, 1461 w	–	1292 m, 626 m			332 s[c], 362 m
6 *trans*-Pd(SHth)$_2$Cl$_2$	1630 w–1518 s, –	1245 vw	1306 m, 658 s	332 s	264 m	
7 *trans*-Pd(SHth)$_2$I$_2$				190 m	261 m	
8 Pd(Sth)$_2$	1522 s, 1435 m	1253 vw	1285 m, –		265 s	370 m
9 [Rh(SHth)$_3$PPh$_3$]Cl	1525 s, –	1245 vw	1304 m, 680 m			
10 K$_2$[Rh(Sth)$_3$PPh$_3$]	1586 m, –	–	1295 m, –			
11 [Rh(SHth)$_3$PPh$_3$I$_2$]PF$_6$	1540 m, –	1235 vw	1300 w, 680 m			
12 K$_2$[Rh(Sth)$_3$PPh$_3$I$_2$]	1590 w, –	–	1293 m, –			
13 [Rh(SHth)$_4$Cl$_2$]Cl	1560 m, 1450 m	1246 w	1300 m, 670 m			
14 Na$_3$[Rh(Sth)$_4$Cl$_2$]	1586 m, 1461 s	–	1290 m, 650 w			
SHbtz[b]	*1600* m, *1497* s	*1248* m	*1286* m, *671* s			
15 *cis*-Pt(SHbtz)$_2$Cl$_2$	1590 m–1570 w, 1452 m	1250 m	1280 m, 679 m	318 s, 312 sh	283 s, 264 m	
16 *cis*-Pt(SHbtz)$_2$I$_2$				196 m, 160 m	290 s, 266 m	
17 Pt(Sbtz)$_2$	1576 m, –	1242 m	1265 vw, –		245 s	356 m
18 *trans*-Pd(SHbtz)$_2$Cl$_2$	1580 m, –	1245 m	1285 m, 670 m	338 s	258 s	
19 *trans*-Pd(SHbtz)$_2$I$_2$				186 m	257 s	
20 Pd(Sbtz)$_2$	1570 m, –	1235 m	1264 w, –		258 s	350 s
SHmi[b]	*1575* m, *1466* m	*1248* m	*1278* m, *675* m			
21 *cis*-Pt(SHmi)$_2$Cl$_2$	1561 s, 1460 s–1450 sh	1242 vw	1278 s, 686 m–665 m	319 sh, 312 s	260 m, 252 m	
22 *cis*-Pt(SHmi)$_2$I$_2$				192 m, 172 m	261 m, 254 m	
23 Pt(Smi)$_2$	1530 m, 1448 s	–	1270 m, 640 w		250 s	342 m
24 *trans*-Pd(SHmi)$_2$Cl$_2$	1564 s, 1460 m–1446 sh	–	1278 m, 670 m	340 s	261 s	
25 *trans*-Pd(SHmi)$_2$I$_2$				204 m	260 s	
26 Pd(Smi)$_2$	1518 m, 1448 s	–	1270 m, 620 m		252 s	348 s

[a] s, m, w = strong, medium, weak intensities. [b] ν(N–H) of free ligands: 3140 cm^{-1}, w(SHth); 3065 cm^{-1}, w(SHbtz); 3090 cm^{-1}, w(SHmi). [c] Raman active.

Reactions were performed in dichloromethane–ethanol, in which the polarity is similar to that of the water–ethanol medium used with platinum(II).

We however obtained only complexes having a metal:ligand ratio of 1:2. Those isolated in acid medium were N-bonded, whereas those obtained from a basic medium were highly insoluble polymers of general formula [Pd(Sth)$_2$]$_n$ (Scheme II):
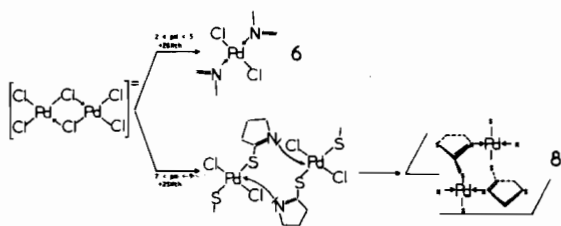

We observed for complex 6 negative shifts for the i.r. bands attributed to ν(C=N) vibrations, while the ν(C–S) modes showed a positive shift. This suggests that only the nitrogen is involved in the metal coordination bond. In the case of Pd(Sth)$_2$, coordination through both N and S is confirmed by the strong downshifts observed for ν(C=N) (64 cm^{-1}), and for ν(C–S) a decrease of 15 cm^{-1} is observed for the band at 1300 cm^{-1} in SHth, whereas the 655 cm^{-1} band is absent. A chelate form is however difficult to envisage, because of the high strain which appeared from the molecular model of a four-membered

ring, where C and N belong already to a five membered heterocycle. We therefore propose a bridged configu-

ration through the ligands, which are thus bonded to two different palladium atoms.

The *trans*-configuration in both cases is confirmed by the i.r. analysis. Only one strong band appears in the usual ν(Pd–X) vibration range[14–16], *viz.* at 332 cm^{-1} for Pd(SHth)$_2$Cl$_2$ and at 190 cm^{-1} for its iodide analogue. For [Pd(Sth)$_2$]$_n$, we observed two strong bands at 265 and 370 cm^{-1} which, compared to our results with similar complexes and in accordance with literature data, we attribute to a ν(Pd–N) and a ν(Pd–S) vibration respectively[16,17]. This confirms the *trans*-configuration around the metal atom, this symmetry being obtained first by an attack of the sulfur anion, followed by the coordination of the cyclic nitrogen (see Scheme II). With rhodium, we observed a similar reactivity of 2-mercaptothiazoline as with platinum, since N-coordinated complexes were isolated in acid medium and S-coordinated in basic medium (Scheme III):
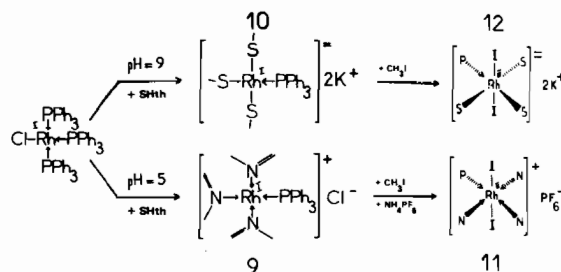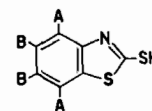
Rhodium(III) salts afforded with SHth only substitution reactions, although the presence of the thiol, a classical reducing agent, can also lead to the reduction of Rh(III). This was not observed, apparently because the octahedral environment of Na$_3$[Rh(III)Cl$_6$] stabilized the d^6 electronic configuration.

In the case of Rh(I)(PPh$_3$)$_3$Cl, we observed in both acid and basic media the substitution of the chlorine

TABLE III. ^{1}H N.m.r. Parameters (δ(TMS) = 0 ppm).

Compound	δ(S–H)	δ(N–H)	δ(CH$_2$)-4	δ(CH$_2$)-5	δ(C–H) arom	δ(CH$_3$)	Solvent	Observations
SHth	1.8	9.75	3.90	3.60			a or b	
1 Pt(SHth)$_2$Cl$_2$	2.05		4.15	3.65			a	δ(CH$_2$)-4 = doublet δ(CH$_2$)-5 = quadruplet
2 K$_2$[Pt(Sth)$_2$Cl$_2$]	–	–	4.10	3.70			a	
3 [Pt(SHth)$_4$]Cl$_2$	2.0		4.18	3.72			a	
4 [Pt(Sth)$_4$]	–	–	4.15	3.65			a	
5 Pd(SHth)$_2$Cl$_2$	2.05	–	4.00	3.65			a	
6 Rh(PPh$_3$)$_3$Cl					7.5–7.15		b	
7 [Rh(SHth)$_3$PPh$_3$]Cl	1.9	–	4.10	3.65	7.45		b	
8 K$_2$[Rh(Sth)$_3$PPh$_3$]	–	–	4.10	3.70	7.45		b	
9 [Rh(SHth)$_3$PPh$_3$I$_2$]PF$_6$	2.0	–	4.15	3.60	7.45		b	^{4}J$_{(Rh–H)}$(SH) = 18 Hz
10 K$_2$[Rh(Sth)$_3$PPh$_3$I$_2$]	–	–	4.10	3.72	7.45		b	
11 [Rh(SHth)$_4$Cl$_2$]Cl	2.05	–	4.10	3.70			a	
12 Na$_3$[Rh(Sth)$_4$Cl$_2$]	–	–	4.10	3.70			a	
SHbtz	1.95	10.20			7.70(AA')–7.40(BB')		a	
13 Pt(SHbtz)$_2$Cl$_2$	2.10	–			7.75–7.40		a	δ(CH arom) = multiplet
14 Pd(SHbtz)$_2$Cl$_2$	2.10	--			7.75–7.40		a	
SHmi	3.80	5.40			7.00–6.85	3.40	a	
15 Pt(SHmi)$_2$Cl$_2$	3.90	–			7.45–7.35	3.50	a	
16 Pt(Smi)$_2$	–	–			7.40–7.25	3.60	a	
17 Pd(SHmi)$_2$Cl$_2$	3.85	–			7.25–6.95	3.50	a	
18 Pd(Smi)$_2$	–	–			7.25–7.00	3.55	a	

^{a} = DMSO-d$_7$. ^{b} = CD$_2$Cl$_2$.

and of two of the labile triphenylphosphines by SHth. This substitution may be explained by the fact that the cyclic nitrogen or the thiol anion is more basic than the phosphine group. When Rh(I) is coordinated to three ligands, the presence of the less polarizable N or S in *trans* position with respect to the last phosphine strengthens the Rh–P bond. This may explain the observation that the complexes isolated always contained a residual PPh$_3$ group.

For the S-coordinated complex 10, the reaction time was longer than for 9, since the presence of a good π-acceptor group such as PPh$_3$ weakens the π-bonding contribution to the rhodium–sulfur bond. Oxidation to Rh(III) was observed upon addition of methyl iodide to complexes 9 and 10, and the *trans*-di-iodides were formed[18, 19].

With Na$_3$[Rh(III)Cl$_6$], substitution of four chlorines by SHth gave the tetra-N-substituted (pH = 4) and the tetra-S-substituted (pH = 8) compounds.

The i.r. results confirmed the SHth coordination to the rhodium either through the nitrogen or through the sulfur. Thus, in complexes 9, 11 and 13, prepared in acid medium, ν(C=N) is 20–60 wavenumbers lower;
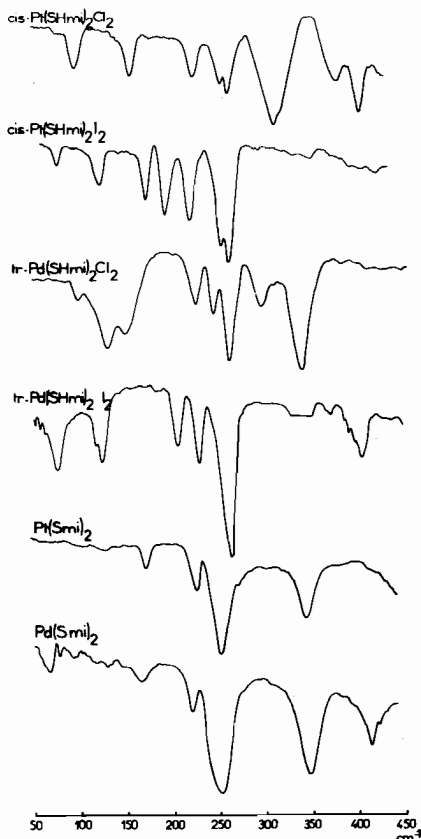

Figure 1. Far infrared spectra (450–50 cm^{-1}) of *cis*-Pt and *trans*-Pd complexes with 2-mercapto,1-methylimidazole (SHmi).

the strong shifts observed for 9 and 11 may be explained by the presence of the π-acceptor PPh$_3$. In [Rh(III)(SHth)$_3$PPh$_3$I$_2$]PF$_6$, which was obtained by oxidative addition of iodine to [Rh(I)(SHth)$_3$PPh$_3$]Cl, the ν(C=N) vibration showed a positive shift of 15 cm^{-1} from its initial value in the Rh(I) complex. This was also observed by McCleverty[19] in the oxidation of [Rh(I)(CNR)$_4$]PF$_6$ by I$_2$. With Rh(III), the σ-donation to the metal is enhanced, but the $d_\pi \rightarrow \pi^*$ transfer from the metal to the ligand orbitals is decreased; the double bond character for C(2)–N is therefore increased, and this is accompanied by an increase in its i.r. frequency.

For complexes 10, 12 and 14 on the other hand (synthesized at a basic pH), the observed i.r. frequency shifts (see Table II) show that the nitrogen is not coordinated and that the C=N double bond is entirely localized after complexation (absence of νC–N)). The thiol thus appears to have reacted under the S$^-$ form and to have formed a covalent bond with the metal. The S-coordination is confirmed by the decrease of the ν(C–S) (of about 10 cm^{-1}) and by the disappearance of the band at 655 cm^{-1}.

The far i.r. region did not give satisfactory results for the Rh–halogen stretching vibration, but a *trans*-configuration was assumed from the absence of degeneracy of the SHth bands in the medium i.r. range. The ^{1}H n.m.r. data (Table III) obtained for most of the Pt, Pd and Rh complexes with 2-mercaptothiazoline support our N- or S-bonding hypothesis in each case. The free ligands spectra show NH and SH proton resonance, with an overall integration line corresponding to only one hydrogen[20]. This is evidence that the free ligand is present under two tautomeric forms – as a thiol and as a thioketone.

The complexes prepared in acid medium are characterized by a disappearance of the NH signal and a deshielding effect both on the SH proton resonance (0.10–0.25 ppm) and on the CH$_2$(4) and CH$_2$(5) signals; the hyperfine structure of the latter is also lacking. Complexation is accompanied by an electron withdrawal by the metal from N, with the result that the SH and the CH$_2$ signals are affected[21]. In the case of [Rh(III)(SHth)$_3$PPh$_3$I$_2$]PF$_6$, the SH signal becomes a multiplet, which indicated Rh–H spin–spin coupling as well as an interaction with the adjacent phenyl groups.

When the soluble complexes studied are prepared in a basic medium, coordination through S$^-$ is confirmed by the additional disappearance of the SH proton signal.

Platinum(II) and Palladium(II) Complexes with 2-Mercaptobenzothiazole (SHbtz) and 1-Methyl, 2-mercaptoimidazole (SHmi)

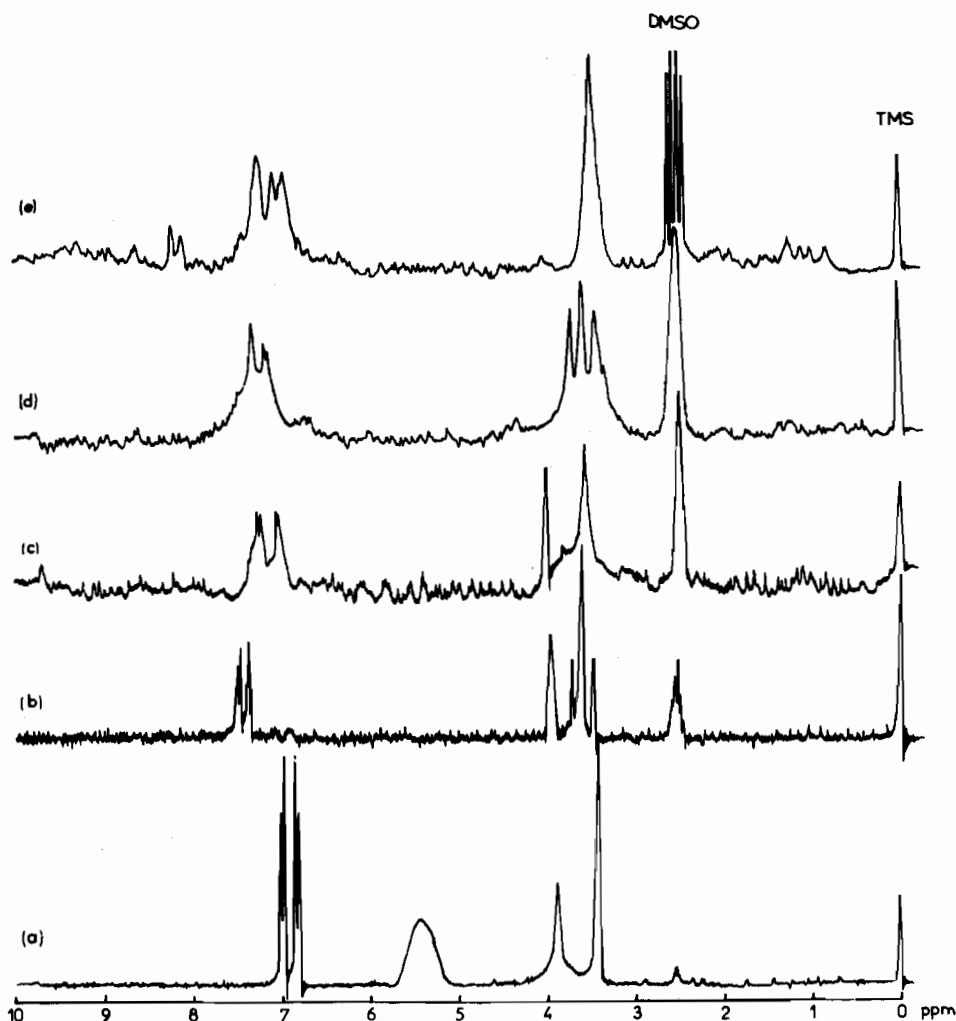Both platinum and palladium salts gave complexes of similar type with SHbtz and SHmi. At a pH less

Figure 2. ^{1}H n.m.r. spectra in DMSO-d$_7$ solution of: (a) SHmi, (b) Pt(SHmi)$_2$Cl$_2$, (c) Pd(SHmi)$_2$Cl$_2$, (d) Pt (Smi)$_2$, (e) Pd(Smi)$_2$.

than 3.5, no reaction occurred since the ring nitrogen and the thiol were both protonated. At a pH between 3.5 and 6, N is no longer protonated and N-bonded *cis*-PtL$_2$X$_2$ and *trans*-PdL$_2$X$_2$ complexes were isolated (L = SHbtz, SHmi; X = Cl, I)[22,23].

When the medium becomes alkaline (6 < pH < 10), dissociation of the thiol occurs and we obtained complexes of general formula [M(L)$_2$]$_n$ (M = Pt(II), Pd(II); L = SHbtz, SHmi). These compounds probably have a polymeric structure in which a ligand is bridged through N and S between two metal atoms. The reaction presumably occurs via the RS$^-$ ion, leading to a metal–sulfur bond of covalent type (see Scheme II).

The different reactivity observed between these two ligands and SHth at alkaline pH, where the former were always bidentate and SHth was monodentate, is possibly due to the full aromaticity of SHbtz and

SHmi. Their basicity is then decreased, N having a partial negative charge δ^- and less nucleophilic character than in SHth. The ring nitrogen and the thiol are thus equally favored co-ordination centers. I.r. data for the N-bonded complexes 15, 18, 21, 24 show a frequency decrease of ν(C=N), initially at 1600 cm^{-1} in SHbtz or 1575 cm^{-1} in SHmi, as well as of ν(N–C=S) at 1466 cm^{-1}; the latter band even disappears in the case of *trans*-Pd(SHbtz)$_2$Cl$_2$.

The S- and N-bonded complexes 17, 20, 23, 26 show an even greater frequency decrease of ν(C=N), a decrease or total disappearance of the band due to ν(N–C=S), and a frequency and intensity decrease of bands corresponding to a strong ν(C–S) contribution.

For all N-coordinated complexes, the position and the number of bands observed in the far i.r. region are characteristic of ν(M–X) and ν(M–L) (Figure 1).

The results suggest a *cis-* or *trans*-configuration around the metal atom. Thus, for *cis*-halogen disubstituted complexes (C_{2v}), two $\nu(Pt-X)$ and two $\nu(Pt-L)$ frequencies are predicted. These were in fact observed (see Table II). On the other hand, only one band was observed in each case for the homologous Pd(II) *trans*-complexes. Furthermore, the dipole moment values observed for the Pd complexes (Table II) confirm the *trans*-configuration of the latter.

The *trans*-configuration (D_{2h}) proposed for [M $(L)_2]_n$ complexes is supported by the presence of only one strong band in the 245–265 cm^{-1} range (attributed to ν_{as} (M–N)), and one medium band in the 342–370 cm^{-1} region attributed to ν_{as} (M–S). This is in accordance with our results with SHth and with literature data[16,17,24,25].

[1]H n.m.r. results confirm in most SHbtz and SHmi complexes (see Table III and Figure 2) that in acid medium the ligands are coordinated via the ring nitrogen, whereas in basic medium both N and S participate in bonding.

Acknowledgment

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