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Rh(III), Pd(II), Pt(IV) and Au(III) Complexes of 2-Thiopyrimidine Derivatives

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Some news thiopyrimidine derivatives and complexes [4-amino-5-nitroso-6-oxo-1,2,3,6-tetrahydro-2-thio-pyrimidine (*TANH*), its 2-methylthio derivative (*MTH*), the ammonium salt of *TANH* (*sTANH*) and six new complexes of formulas: $Rh(MT)_2Cl \cdot 2H_2O$, $Pd(MTH)_2Cl_2$, $Pt(MTH)_2Cl_4$, $Au(MTH)Cl_3$ $Pd(TANH)_2Cl_2$ and $Au(TAN^-)Cl$] have been synthesized and characterized by elemental analysis, IR and ^{1}H-NMR spectroscopy techniques. The thermal behaviour of all compounds has also been studied.

(Keywords: Complexes; Thermal analysis)

Rh(III), Pd(II), Pt(IV) *und* Au(III) *Komplexe von 2-Thiopyrimidin Derivaten*

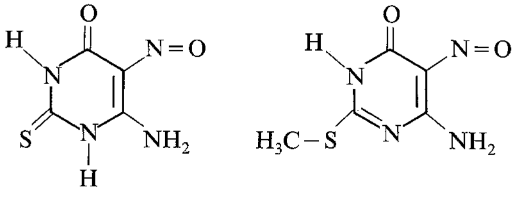
Es wurden einige neue Thiopyrimidinderivate und deren Komplexe synthetisiert und mittels Elementaranalyse, IR und ^{1}H-NMR charakterisiert: 4-Amino-5-nitroso-6-oxo-1,2,3,6-tetrahydro-2-thio-pyrimidin (*TANH*), dessen 2-Methylthio-Derivat (*MTH*), das Ammoniumsalz von *TANH* (*sTANH*) und sechs neue Komplexe der Formeln $Rh(MT)_2Cl \cdot 2H_2O$, $Pd(MTH)_2Cl_2$, $Pt(MTH)_2Cl_4$, $Au(MTH)Cl_3$, $Pd(TANH)_2Cl_2$ und $Au(TAN^-)Cl$. Das thermische Verhalten der Verbindungen wurde ebenfalls untersucht.

Introduction

The studies on metal complexes of heterocyclic thioderivatives is an area of great interest as has been indicated by *Raper* in a recent review [1]. Most IR studies carried out on these complexes indicate that the coordination of ligand to the metal ion takes place, normally, through the sulphur atom. However, in ligands of the type of pyrimidine and purine derivatives an other alternative coordination mode may exist, where nitrogen or oxygen atoms can participate.

Following our studies on metal complexes of oxopyrimidine and oxopurine derivatives [2–11] in the present paper the synthesis and characterization of six new complexes of Rh(III), Pd(II), Pt(IV) and Au(III) with 4-amino-5-nitroso-6-oxo-1,2,3,6-tetrahydro-2-thiopyrimidine (*TANH*) and its 2-methylthio derivative (*MTH*) is described (Scheme 1).

Scheme 1



(TANH) (MTH)

Experimental

The pyrimidine derivatives (*TANH* and *MTH*) were synthesized using methods previously described [12, 15]. The low solubility of *TANH* in water is increased in ammonia from which the ammonium salt of *TANH* (*s-TANH*) can be isolated.

Rh(*MT*)$_2$Cl $\cdot$ 2 H_2O, Pd(*MTH*)$_2$Cl$_2$, Pt(*MTH*)$_2$Cl$_4$ and Au(*MTH*)Cl$_3$ were synthesized as follows: 0.2 g of corresponding metallic salt ($RhCl_3H_2O$, $PdCl_2$, $PtCl_4$ and $HAuCl_4$) were added to an aqueous solution containing an equimolar amount of *MTH*. The resulting solution was stirred and heated at 60 °C for one hour. By evaporation at room temperature during one day the corresponding complexes were obtained. The precipitates were washed with water and ethanol and dried with ether.

Pd(*TANH*)$_2$Cl$_2$ and Au(*TAN*$^-$) Cl were synthesized by mixing of equimolar aqueous solutions of *s-TANH* and $K_2(PdCl_4)$ or $HAuCl_4$, respectively. In both cases brown precipitates were immediately formed, which were filtered, washed with water and ethanol and dried with ether.

Chemical analysis were realized in the Instituto de Química Biorgánica (C.S.I.C.), Barcelona. Metal ions were determined thermogravimetrically. The results obtained are summarized in Table 1.

Infrared spectra were recorded with a Beckman 4250 Spectrophotometer in the 40000–200 cm^{-1} range using KBr pellets. Likewise, the 600–200 cm^{-1} range was investigated dispersing the samples in polyethylene. TG studies were made in dynamic atmosphere of pure air and nitrogen using a gas flow of 100 ml $\cdot$ min^{-1} and a heating rate of 20 °C min^{-1} on a Mettler TG-50 thermobalance; sample weights varying in weigth from 1.677 to 11.507 mg. DSC curves were recorded on a Mettler differential scanning calorimeter mod DSC-20 at a heating rate of 5 °C min^{-1} in the 35–550 temperature range. ^{1}H-NMR spectra were recorded on a Hitachi Perkin-Elmer R-600 FT-NMR spectrometer, using dimethylsulfoxide-d_6 as solvent and *TMS* as internal reference.

Table 1. *Analytic data (%); found (theoretical)*

Compound	Colour	C	H	N	M
$Rh(MT)_2Cl \cdot 2H_2O$	ochre	22.25 (22.04)	2.36 (2.57)	20.38 (20.57)	19.0 (18.90)
$Pd(MTH)_2Cl_2$	brown	21.25 (21.83)	2.05 (2.18)	20.40 (20.37)	20.2 (19.41)
$Pt(MTH)_2Cl_4$	brown	16.71 (16.92)	1.54 (1.69)	15.38 (15.79)	28.1 (27.51)
$Au(MTH)Cl_3$	green	12.78 (12.28)	1.31 (1.02)	11.65 (11.46)	40.4 (40.31)
$Pd(TANH)_2CL_2$	brown	18.09 (18.41)	1.10 (1.15)	21.07 (21.48)	20.3 (20.40)
$Au(TAN^-)Cl$	brown	11.79 (11.92)	0.24 (0.01)	13.87 (13.91)	49.1 (48.94)

Results and Discussion

In order to establish the molecular structures of the isolated complexes, we have used elemental analysis and IR and ^{1}H-NMR techniques. In Table 2 and 3 we have collected most significant IR bands and ^{1}H-NMR signals for the complexes.

These assignments have been made on the basis of data for the free ligands (*MTH* and *TANH*), and other pyrimidine derivatives (4-amino-2,6-dioxo-5-nitroso-1,2,3,6-tetrahydropyrimidine [16]), its complexes and the spectral data observed from IR spectra of 2-thiouracil derivatives [17–20].

In the region 3 200–2 800 cm^{-1}, the IR spectra show some absorption bands assigned to stretching vibrations ν(N—H). The two bands which appear at higher wavenumbers correspond to exo-cyclic ν(N—H), the others to cyclic ν(N—H).

In the complexes $Rh(MT)_2Cl \cdot 2H_2O$ and $[Au(TAN^-)Cl]_2$ the IR spectra show only two bands at 3 280, 3 190 cm^{-1} and 3 320, 3 120 cm^{-1}, respectively, which were assigned to ν(N—H) of the amine group. For the remaining complexes the IR spectra are similar to the IR spectra of the ligands according with the action of these ligands in molecular form in the corresponding complexes, showing only a displacement to higher wavenumbers of the bands assigned to ν(N—H) which suggest an interactions by hydrogen bond decrease of amine and N—H groups.

In the range 1 700–1 550 cm^{-1} the IR spectrum of *MTH* shows bands at 1 680, 1 635 and 1 580 cm^{-1} assigned to stretching vibrations ν(C=O), ν(C=C) and ν(C=N) respectively, while the IR spectrum of *TANH*

Table 2. *Infrared*

Compound	ν(O—H)	ν(N—H)	ν(C=O)	ν(C=C)
MTH	—	3170 3010 2880	1680	1635
Rh(*MT*)$_2$Cl·2H$_2$O	3400	3280 3190	1615[a]	
Pd(*MTH*)$_2$Cl$_2$	—	3380 3270 3190	1695	1620
Pt(*MTH*)$_2$Cl$_4$	—	3390 3280 3190	1675	1620
Au(*MTH*)Cl$_3$	—	3360 3260 3200	1690	1610
TANH	—	3200 3050 2860	1685	1640
S-TANH	—	3290 3160 3070	—	1655
Pd(*TANH*)$_2$Cl$_2$	—	3190 3070 2860	1680	1635
Au(*TAN*$^-$)Cl	—	3230 3120	1670	1615

[a] Broad band

only shows two bands corresponding to ν(C=O) and ν(C=C). This suggests that in solid phase the ligand *TANH* is present in the tautomeric 2-thio form. The higher wavenumber of ν(C=C) and ν(C=N) bands are in accord with the literature data of other 2-thiopyrimidine derivatives [17, 19, 21]. In the ammonium salt (*s-TANH*)—due to deprotonation of *TANH*—the negative charge should be delocated to different atoms of the molecule. However, the tautomeric form with the negative charge on the oxygen atom should be the favoured one (Scheme 2).

The IR spectrum of *s-TANH* is in agreement with the above supposition since the ν(C=O) band is absent and on the other hand it shows

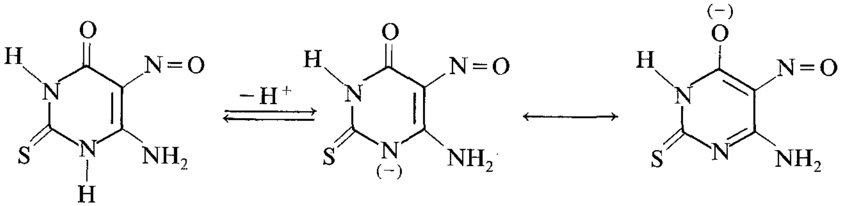
Data (cm^{-1})

$\nu(C{=}N)$	$\nu(N{=}O)$	$\nu(C{-}O)$	$\nu(NCN) +$ $+ \nu(NCS) +$ $+ \nu(C{=}S)$	$\nu(M\text{-}Cl)$	$\nu(M\text{-}N)$
1 560	1 500	—	1 265 1 185 1 130	—	—
1 520[a]		—	1 295 1 230 1 130	365	255
1 520[a]			1 300 1 235 1 140	350	240
1 530[a]			1 300 1 230 1 140	355	250
1 540	1 470	—	1 300 1 260 1 130	350	250
—	1 490	—	1 280 1 170	—	—
1 625	1 495	1 255	1 290 1 170	—	—
—	1 485	—	1 270 1 160	—	—
—	1 485	—	1 270 1 150	—	—

Table 3. *Data of* ^{1}H-NMR (*δ, ppm*)

Compound	N—H	S—CH_3	C_4—NH_2
MTH	12.75	2.60	9.10; 11.30
Rh(*MT*)$_2$Cl · 2 H_2O	—	2.50	9.30; 9.70
Pd(*MTH*)$_2$Cl$_2$	10.20	2.50	9.20; 9.60
Au(*MTH*)Cl$_3$	11.30	2.60	9.10; 10.60

Scheme 2



a new band at 1 255 cm^{-1} which can be assigned to the stretching vibrations ν(C=O) [22]. The sharp band at 1 625 cm^{-1} shows a shoulder at 1 655 cm^{-1} and we suppose that it is due to stretching vibrations ν(C=C) and ν(C=N). The bands at 1 635 and 1 565 cm^{-1} in the isolated ligand appear at lower wavenumber in the IR spectra of the complexes which suggests that the coordination of *MTH* takes place through a cyclic nitrogen.

On the other hand, the IR spectrum of Rh(*MT*)$_2$Cl · 2 H$_2$O complex shows shifts to lower wavenumbers of the band corresponding to ν (C=O) compared with the position of this band in the free *MTH* which is in accord with the participation of *MTH* as bidentate ligand through the oxygen atom of position six and a nitrogen atom.

In the region 1 300 to 1 100 cm^{-1} the IR spectrum of *MTH* shows three absorption bands while the IR spectrum of *TANH* shows only two. In this region appears the stretching vibration ν(NCN), ν(NCS) and ν(C=S) in agreement with literature [1, 17–21]. The sharper band (according to *Spinner* [21]) is due to ν(C=S) and therefore the band centered at 1 170 cm^{-1} in the IR spectra of *TANH* would correspond to ν(C=S). This band is shifted to lower wavenumbers in Pd(*TANH*)$_2$Cl$_2$ and [Au(*TAN*$^-$)Cl]$_2$ complexes which should indicate that the coordination of the ligand, in both cases, takes place through the sulphur atom.

The new bands in the spectra of complexes in the region 600 to 200 cm^{-1} have been assigned to stretching vibrations metal-ligand. Thus, the bands at 365–350 cm^{-1} have been assigned to ν (M—Cl) and the bands at 255–230 cm^{-1} to ν(M—N) [23].

The ^{1}H-NMR data of *MTH* and its complexes are summarized in Table 3. The ^{1}H-NMR spectra of *TANH* and its complexes and the ^{1}H-NMR spectrum of Pt(*MTH*)$_2$Cl$_2$ were not registered due to below to low solubility of the compounds in the solvents used (*DMSO-d*$_6$ and D$_2$O).

The ^{1}H-NMR spectrum of *MTH* indicates that this ligand is present also in the aminocetonic form in *DMSO-d*$_2$. This spectrum shows three signals of same intensity. Those at 9.10 and 11.30 ppm are due to the protons of NH$_2$, the other one at 12.75 ppm has been assigned to the proton bound to anular nitrogen. The non-equivalence of the two hy-

Table 4. *Thermoanalytical Data*

Process	T^a (°C)	ΔH (kJ mol^{-1})	% accumulate loss weight	
			exp.	calcd.
$Rh(\mathit{MT})_2Cl \cdot 2H_2O \rightarrow Rh(\mathit{MT})_2Cl$	125 (endo)	34	6.2	6.61
$Rh(\mathit{MT})_2Cl \rightarrow Rh_2O_3$	250–500 (exo)	—	76.5	76.69
$Pd(\mathit{MTH})_2Cl_2 \rightarrow PdO$	260–475 (exo)	—	76.8	77.68
$Pt(\mathit{MTH})_2Cl_4 \rightarrow Pt$	210–460 (exo)	—	71.9	72.49
$Au(\mathit{MTH})Cl_3 \rightarrow Au$	170–650 (exo)	—	59.6	59.69
$Pd(\mathit{TANH})_2Cl_2 \rightarrow PdO$	270–600 (exo)	—	76.6	76.53
$\searrow PdS$	270–800 (exo)	—	73.0	73.46
$[Au(\mathit{TAN}^-)Cl]_2 \rightarrow Au$	180–620 (exo)	—	50.9	51.06

drogens of the amine group may be due to the existence of a hydrogen intramolecular bond between a proton of the NH_2 group and the oxygen atom of the 5-nitroso group [11, 14, 24, 25].

The chemical shift of the protons of the S—CH_3 group suggests no participation of this group in the coordination to metal, since no displacement to lower field is observable. On the other hand, the value found for the chemical shift of N_1—H should be explained on the basis of a prototropy process of the N 1 to N 3 position. The 1 position is less shielded than the 3 position due to the oxo group, and therefore the proton linked to N 1 will appear at lower field than the proton bound at N 3, since this hydrogen is near an amine group and not an oxo group. From above data, N_1 would be the coordination position in all cases.

The thermal behaviour of these compounds is presented in Table 4. TG diagrams were carried out in pure air and nitrogen dynamic atmospheres. *MTH* is stable up to 220 °C. The DSC curve shows a exothermic effect centered at 244 °C ($\Delta H = 153\,\mathrm{kJ\,mol^{-1}}$), while *TANH* and its ammonium salt are stable up to 250 °C and 220 °C, with exothermic effects at 251 °C ($\Delta H = 162\,\mathrm{kJ\,mol^{-1}}$) and 233 °C ($\Delta H = 103\,\mathrm{kJ\,mol^{-1}}$), respectively. TG curves registered in nitrogen atmosphere are similar to the ones obtained in air showing the same pyrolytic processes but at higher temperature. For each complex the nature of pyrolytic residues is the same in both atmospheres, except for the $Pd(TANH)_2Cl_2$ complex (PdO in air and PdS in nitrogen) as revealed by the IR spectra. This result is in agreement with the IR data of $Pd(TANH)_2Cl_2$ suggesting that the coordination of *TANH* to Pd(II) takes place through the sulphur atom in position 2.

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