Monatshefte für Chemie 118, 553—566 (1987)

Monatshefte für Chemie
Chemical Monthly

Metal Complexes of Two 7-oxo-*vic*-Triazolo[4,5—*d*]Pyrimidine Derivatives

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(Received 10 March 1986. Accepted 28 April 1986)

Seven Hg(II), Pd(II), Cu(II), and Ag(I) complexes of two 7-oxo-*vic*-triazolo[4,5—*d*]pyrimidine derivatives have been obtained. The complexes were characterized by spectroscopic studies (IR, ^{1}H-NMR and UV-visible) and magnetic measurements. On the basis of these data both the structure of the complexes and the coordination positions of the pyrimidinic ligands have been proposed. Likewise, the thermal behaviour of the complexes has also been studied.

(Keywords: Metal complexes; Triazapurines; Spectral studies)

Metall-Komplexe von zwei 7-Oxo-vic-triazolo[4,5—d]pyrimidin-Derivaten

Sieben Hg(II)-, Pd(II)-, Cu(II)- und Ag(I)-Komplexe von zwei 7-Oxo-*vic*-triazolo[4,5—*d*]pyrimidin-Derivaten wurden hergestellt. Die Komplexe wurden durch die Daten der elementaren Analyse, spektroskopische Studien (IR, ^{1}H-NMR und UV-Vis.) und magnetische Messungen charakterisiert. Auf der Basis dieser Daten wurden die Strukturen der Komplexe und die Koordinationsstelle der Pyrimidin-Liganden bestimmt. Das thermische Verhalten der Komplexe wurde ebenfalls untersucht.

Introduction

In the last few years some triazapurine derivatives have got a special interest since they show a wide spectrum of biological activity; e.g. as antibacterial, antiviral, anticancerous or antitumoral agents [1, 2]. Thus, the study of the transition metal complexes with these compounds might be useful to elucidate the role played by the afore mentioned compounds in such biological processes [3].

In two recent papers [4, 5] we reported the characterization of two new triazapurine derivatives. 6,7-dihydro-3(*H*)-6-methyl-5-methoxy-7-oxo-*vic*-triazolo[4,5—*d*]pyrimidine (*OTH*) and 6,7-dihydro-3(*H*)-6-methyl-5-methylthio-7-oxo-*vic*-triazolo[4,5—*d*]pyrimidine (*STH*). A thermodynamic study of the complex formation equilibria in aqueous solutions of some of their metal complexes [M = Cu(II), Zn(II), Cd(II) and Hg(II)] was reported too.

Now a study and characterization of some solid metal complexes [M = Hg(II), Pd(II), Cu(II), and Ag(I)] of the afore-mentioned triazapurine derivatives is presented.

The literature data on metal complexes of triazapurine derivatives show that the N_1 and N_3 atoms of the triazolic ring are potential binding sites [6]. Nevertheless, although few N_2 bonded complexes have been described in literature, the charge density values of the triazolic N atoms in some 8-triazapurines [6] allows to suppose that the N_2 atom could be considered as potential binding site too. In addition to the three above atoms other potential binding sites in the compounds under study are the N_4 atom of the pyrimidine ring, the O atoms of the 6-oxo groups and the O (in *OTH*) and S atoms (in *STH*) of methoxy and methylthio substituents respectively. Nevertheless, some literature data on purine complexes point out that the 6-oxo groups are not good donors [7, 8]. On the other hand a coordination pattern through $N_3 \cap N_4$ bridges has been found in some purine complexes too.

Experimental

The compounds used as ligands were obtained by an adaptation of the *Gabriel* and *Colman's* method [9], and purified by recrystallization. The metallic salts used were chlorides [Hg(II), Pd(II) and Ag(I)] or sulphates [Cu(II)]. The infrared spectra were obtained from KBr (4000–200 cm^{-1}) and polyethylene (650–200 cm^{-1}) pellets on a Beckman 4250 spectrophotometer. The visible and UV spectra were recorded on a Spectronic 2000 spectrophotometer at room temperature, using H_2O (UV range) and *DMSO* (visible range) solutions of the complexes. The ^{1}H-NMR spectra were recorded on a Hitachi Perkin-Elmer R-600 spectrometer. Magnetic measurements were performed at room temperature, using a Faraday Bruker Magnet B-E 15 equipment. The ATG and DSC plots were obtained from a Mettler TA 3000 equipment with a TG-50 thermobalance and a DSC-20 differential calorimeter, respectively. Carbon, hydrogen, nitrogen and sulphur analyses were performed in the Laboratory of Microanalysis of the National Institut of Bioorganic Chemistry in Barcelona.

An aqueous solution of 4 mmole of the metallic salt in 10 ml of distilled water [in the case of Pd(II) ion a 14 m*M* NaCl aqueous solution was used as solvent], was added gradually under constant stirring to 2 mmole of the corresponding ligand (*OTH* or *STH*) dissolved in 125 ml of distilled water at 50 °C. The complexes were precipitated almost immediately from the corresponding mixtures (after twenty minutes in the case of the complex obtained from the system

OTH/Cu). However, all efforts to obtain some solid complex from the *STH*/Hg(II) system were unsuccessful.

The complexes were filtered, washed with water and ethanol and dried in a desiccator over P_2O_5.

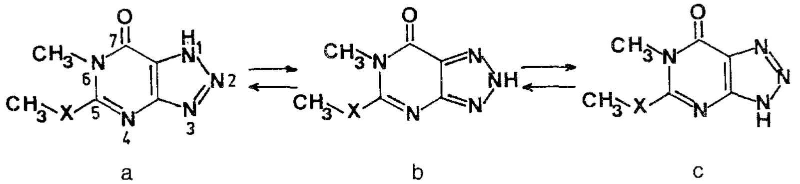
The analyses of Cu(II) in the complexes were realized volumetrically using KI and $Na_2S_2O_3$ as reactants, whereas Ag(I) was titrated following the *Volhard's* method [10]. The determination of Hg(II) was carried out spectrophotometrically in a Perkin-Elmer Mod. 290 atomic absorption spectrophotometer fitted with a graphite camera. Pd(II) in complexes was determined gravimetrically using dimethylglyoxime [11]. Finally, to analyze SO_4^{--} ions in the complex obtained from the system *OTH*/Cu, precipitation as $BaSO_4$ from an aqueous solution obtained from a sample of the complex which had previously been mineralized with HCl 12*N* [11] was used.

Results and Discussion

Ligands

The compounds used as ligands can exist under several tautomeric forms. In accordance to literature data [2] the most important of such tautomeric structures in aqueous solutions should be those three shown in Scheme 1. X-ray analysis proves that in the solid state the predominant one is **c**.

Scheme 1



The medium acidic character of *OTH* and *STH* compounds in aqueous solution [4, 5] (the thermodynamic acidic constants at 25 °C are $K_{OTH} = 2.45 \cdot 10^{-7} \mathrm{mol\,l^{-1}}$ and $K_{STH} = 2.14 \cdot 10^{-6} \mathrm{mol\,l^{-1}}$) is a fact in accordance with the existence of a tautomeric equilibrium between the three above cited forms.

Complexes

The composition of the complexes, analytical data and colour are presented in Table 1. The Pd(II) and Ag(I) complexes displayed 1 : 1 stoichiometry whereas Hg(II) and Cu(II) complexes showed a 1 : 2 ratio.

a) Hg(II) *complex*

The Hg(II) complex obtained has the formula $Hg(OT^-)_2$. The UV spectrum consists of two absorption bands centered at wavelength values

(263 nm and 203 nm) equal to those of the OT^- UV spectrum, and different from those of *OTH* (253 nm and 205 nm) thus proving that the ligand molecules are present in this complex as monoanion. This fact becomes also evident from the IR spectrum of this complex (Table 2) because of the disappearance of the ν(N—H) stretching vibration bands which appeared in the IR spectrum of *OTH* at 3 200 cm^{-1} and 3 130 cm^{-1}.

Besides that other noticeable features of the IR spectrum of this complex are the following: a) the $\nu(C=O)$ stretching vibration band suffers a slight shift (10 cm^{-1}) to a higher wavenumber value than in the free ligand, thus indicating that the $C_7 = 0$ group does not intervene in the coordination; b) the lowering in the frequency values of $\nu(C=C)$ and $\nu(N=N)$ stretching vibration bands in 30 cm^{-1} and 20 cm^{-1} respectively indicates in accordance to literature data [6, 12, 13] that the coordination of the anion OT^- occurs via the triazolic ring; c) the arising of a new weak band at 215 cm^{-1} which can be assigned at the ν(Hg—N) stretching vibrations. This value is similar to that found in the complex formed by 5,7-dimethyl-[1,2,4]-triazolo[1,5—*a*]pyrimidine with Hg(II) ions [14].

The ^{1}H-NMR data of the ligands and complexes are summarized in Table 3. Concerning the Hg $(OT^-)_2$ complex the most noticeable features are; a) the disappearance of the signal due to the hydrogen triazolic ring in accordance with the presence of the OT^- form in this complex; b) the signals corresponding to the C_5-O*Me* and N_6-CH_3 groups are singlets, at 4.05 and 3.40 ppm respectively, with satellites. In the case of the first one, two satellites at 4.25 ppm and 4.30 ppm were observed, while in the second case two at 3.25 ppm and 3.30 ppm. This fact could be explained by the spin nuclear interaction between the H atoms of the C_5-O*Me* group and the ^{199}Hg atoms present in Hg (16.9%) [15]. Thus, the satellites of the signal due to the N_6-*Me* group could be explained by the coupling of this signal with that of the C_5-O*Me*. Moreover, the resonance value of the C_5-O*Me* group signal is practically unmodified. Thus, these two data conjunctly considered suggest that the Hg(II) ions interact in this complex with a group relatively close to the C_5-O*Me* one, probably the N_4 atom of the pyrimidinic ring, but it does not interact directly with such a group.

Taking all the above information one could assume that the two OT^- anions in this complex act as bidentate bridging $N_4 \cap N_3$ ligands defining a tetrahedral arrangement around the Hg(II) ions.

b) Pd(II) *complexes*

The analytical data of the two Pd(II) complexes are in close agreement with the proposed formulae, $Pd_2(L^-)_2Cl$ OH ($L = OT^-$, ST^-). These formulae imply a square plane arrangement of the ligands in which the chlorine and hydroxy groups act as bridge ligands between two Pd(II)

Table 1. *Colour and analytical data (theoretical values in parentheses)*

Complex	Colour	C	H	N	Cl	SO_4	M
$Hg(OT^{-})_2$	white	25.10 (25.69)	2.05 (2.14)	24.20 (24.97)	—	—	33.10 (35.78)
$Pd(OT^{-})_2OH\ Cl$	brown	22.33 (22.95)	2.22 (2.07)	21.51 (22.31)	5.65 (5.66)	—	31.97 (33.92)
$Pd(ST^{-})_2OH\ Cl$	brown	22.81 (21.82)	2.15 (1.97)	21.40 (21.23)	5.22 (5.38)	—	30.83 (32.27)
$Cu(ST^{-})_2$	dark green	30.89 (31.69)	2.69 (2.63)	29.91 (30.73)	—	—	13.87 (13.95)
$Cu(OTH)_2(OT^{-})_2$ $(H_2O)_6SO_4$	pale blue	27.90 (27.35)	3.49 (3.61)	26.89 (26.84)	—	8.45 (9.11)	12.25 (12.06)
$Ag(OT^{-})$	white	24.49 (25.02)	2.07 (2.08)	23.87 (24.33)	—	—	37.85 (37.43)
$Ag(ST^{-})$	white yellow	23.63 (23.69)	1.72 (1.97)	22.61 (23.04)	—	—	36.01 (35.49)

Table 2. *IR spectral data*

Compound	(O—H)	(N—H)	(C=0)	(C=C)	(C=N)	(N=N)	(S—O)	(M—O)	(M—Cl)	(M—N)
OTH	—	3 200 s 3 130 m	1 675 s	1 610 s	1 560 s	1 520 m	—	—	—	—
STH	—	3 180 s 3 120 m	1 670 s	1 590 s	1 525 s	1 460 m	—	—	—	—
$Hg(OT^{-})_2$	—	—	1 685 s	1 580 s	1 580 s	1 500 m	—	—	—	215 w
$Pd(OT^{-})_2OH\ Cl$	3 480 s	—	1 700 s	1 570 s, wi	1 570 s, wi	1 510 m	—	500 w	350 w	255 w 250 w
$Pd(ST^{-})_2OH\ Cl$	3 480 s	—	1 700 s	1 530 s, wi	1 530 s, wi	1 410 m	—	485 w	320 w	240 w 220 w
$Cu(ST^{-})_2$	—	—	1 685 s	1 530 s	1 530 s	1 450 m	—	—	—	245 w
$Cu(OTH)_2(OT^{-})_2$ $(H_2O)_6SO_4$	3 430 s, wi	3 240 m	1 700 s, wi	1 580 s, wi	1 580 s, wi	1 505 m	1 140 m 1 120 w 1 060 w 1 020 m, sh	—	—	250 w 240 w
$Ag(OT^{-})$	—	—	1 690 s	1 580 s, wi	1 580 s, wi	1 500 m	—	—	—	245 w 240 w
$Ag(ST^{-})$	—	—	1 680 s	1 530 s, wi	1 530 s, wi	1 450 m	—	—	—	230 w 270 w

s strong, *m* medium, *w* weak, *wi* wide, *sh* shoulder ions. These facts are in accordance with the diamagnetic character of the complexes and with the high tendency of Pd(II) ions to form polymeric chains with chlorine [16] and hydroxo ions [17–19] as bridge ligands.

On the other hand, in accordance with *Martin* [20] the shift of the equilibrium that exists between the different probable complexes in aqueous Cl^- solutions of the *cis*-Cl_2 $Pd(NH_3)_2$ is conditioned by the Cl^- concentration and the *pH* of the medium. Thus, under the conditions at which the complexes under study were obtained (*pH* = 6.5 and $[Cl^-]$ = 1 m*M*) the complexes that predominated in solution were probably those of formulae: Pd *L* Cl, Pd *L* OH_2Cl and Pd *L* Cl OH from which the precipitation of the corresponding $Pd_2(L)_2Cl$ OH dimers above cited could become possible at the above *pH* value [20].

The UV-visible spectra of the complexes could not be obtained with enough resolution because of their poor solubility.

The most noticeable features in the high frequency range of the IR spectrum of both Pd(II) complexes are very much like those of the Hg $(OT^-)_2$ complex: a) the disappearance of the ν(N—H) stretching vibration bands; b) the appearing of a sharp band at 3 500 cm^{-1} [in $Pd_2(OT^-)$ Cl OH] and 3 510 cm^{-1} [in $Pd_2(ST^-)_2Cl$ OH] which have been assigned to the ν(O—H) stretching vibrations of the OH^- groups; c) the $\nu(C=O)$ stretching vibration bands are slightly shifted ($\simeq$ 15 cm^{-1}) to higher wavenumber values, thus indicating that the $C_7 = O$ group does not intervene in the coordination; d) the decrease in wavenumber values of the $\nu(C=C)$ and $\nu(N=N)$ stretching vibration bands indicating that the triazolic rings are the coordination sites in these complexes.

Likewise, there appear new bands in the low frequency range (600–200 cm^{-1}) of the IR spectra of both complexes which have been assigned to ν(Pd—O), ν(Pd—Cl) and ν(Pd—N) stretching vibration (see Table 2) in accordance to the proposed structure. It must be pointed out that the arising of two ν(Pd—N) bands in each complex might indicate the existence of two *cis*-Pd—N bonds [21].

The ^{1}H-NMR spectra of the two Pd(II) complexes were obtained from previously dehydrated samples. From the data given in Table 3 the following features become clear: a) the disappearance of the signals corresponding to he H triazolic atom, which is in agreement with the presence of the OT^- and ST^- anions in the corresponding complexes; b) the resonance values of the remaining signals (C_5-O*Me*, N_6-*Me* and C_5-S*Me*, N_6-*Me*) are practically unmodified, suggesting that the C_5-O*Me* and C_5-S*Me* groups do not participate in the coordination of the corresponding complexes; c) the arising of a new sharp and strong signal in both spectra at 3.45 ppm in Pd $(OT^-)_2Cl$ OH and 3.40 ppm in $Pd(ST^-)_2Cl$ OH assigned to the OH^- bridging groups.

Taking into consideration all these data, we propose for the two complexes under study square plane dimeric structures in which the Cl^- and OH^- ions act as bridging ligands and the remaining two positions around each Pd(II) ion are occupated by OT^- and ST^- molecules, respectively, which are linked via a $N_4 \cap N_3$ bridge like in $Hg(OT^-)_2$ described above.

Table 3. ^{1}H-*NMR data*

Compound	δ (ppm)				
	N_6-*Me*	OH	C_5-O*Me*	C_5-S*Me*	N—H triazol.
OTH	3.30 s	—	4.00 s	—	7.50 s (broad)
STH	3.35 s	—	—	2.50 s	10.00 s (broad)
$Hg(OT^-)_2$	3.40[b] d	—	4.05[b] d	—	—
$Pd(OT^-)_2Cl \cdot OH$	3.25 s	3.45 s	4.10 s	—	—
$Pd(ST^-)_2Cl \cdot OH$	3.40[a] s	3.40 s	—	2.50 s	—

[a] Overlaps with O—H signal
[b] Signals with satellites (see text)

c) Cu(II) *complexes*

The two Cu(II) complexes obtained are quite different from each other.

The proposed formula for the complex obtained from the Cu(II)/*STH* system is $Cu(ST^-)_2$ (see Table 1). The IR spectrum is very much like those of the Pd(II) and Hg(II) complexes studied before, namely; a) the disappearance of the ν(N—H) stretching vibration bands. This indicates that the 8-azapurinic ligand is present in its anionic form; b) the $\nu(C=O)$ stretching vibration band is practically unmodified, which indicates that this group is not a coordination position; c) both $\nu(C=C)$ and $\nu(N=N)$ stretching vibration bands suffer a decrease in their wavenumber values. Thus, the coordination of the ligand ST^- takes place via the triazolic ring. Finally, in the low IR range a new weak band arises at 245 cm^{-1}; this band is assigned to the ν(Cu—N) stretching vibrations.

On the basis of the analytical and IR data it could be supposed that the ST^- anions are linked as bidentate ligands via a $N_4 \cap N_3$ bridge in the complex under study as it was proposed in the cases of the Hg(II) and Pd(II) complexes studied before.

The magnetic moment of the Cu(II) ion in this complex is 1.59 MB. This value is lower than that corresponding to a d^9 system with a square-plane arrangement of the two ST^- ligands around the Cu(II) ion and could be explained on the basis of probable Cu(II)-Cu(II) interactions which are favoured by the square-plane structure of the complex.

The UV spectrum of this complex shows two defined bands centered at 267 nm and 238 nm which correspond to the ones that ST^- presents at 268 nm and 229 nm. The complex also presents a third band at λ values lower than 200 nm which could correspond to that of ST^- centered at 208 nm. In the visible range the complex presents a weak wide band (at 715 nm). In accordance with the literature [22–24] this band can be assigned to the forbidden $d_{x^2-y^2} \rightarrow d_{xy}$ transition in square planar symmetry complexes. The remaining two forbidden $d_{x^2-y^2} \rightarrow d_{z^2}$ and $d_{x^2-y^2} \rightarrow d_{yz,xz}$ transitions have not been observed probably due to the overlapping of such bands with the afore mentioned $\pi \rightarrow \pi^*$ transitions bands present in the UV range.

The analytical data for the Cu(II) complex isolated from the *OTH*/Cu(II) system are in close agreement with the formula $Cu_2(OTH)_2(OH_2)_6(OT^-)_2SO_4$.

The UV spectrum of this complex shows three clearly defined bands at 205 nm, 250 nm and 262 nm. The last band is characteristic for the OT^- form whereas the one at 250 nm is due to *OTH*; finally, the band at 205 nm corresponds to both the OT^- and the *OTH* forms.

On the other hand, the TG data of this complex (Table 4) confirm the existence of six water molecules per mol of compound. Moreover, the medium hydration enthalpy value obtained from the corresponding endothermic effect is 50.2 kJ mol^{-1}. This value suggests that the six water molecules are probably coordinated to the central Cu(II) ions in the molecule of this complex.

The most important data obtained from the IR spectrum of the complex are: a) the arising of four new weak-medium intensity bands at 1 140, 1 120, 1 060 and 1 025 (shoulder) cm^{-1}. It must be said that the ligand presents a lonely band at 1 020 cm^{-1} in this range. In accordance to literature data [25] these bands could be assigned to the four expected stretching vibration bands due to a SO_4^{--} ion with C_{2v} symmetry. This assignment implies that the said anion is probably linked as a bidentate bridge between the two Cu(II) ions of a dimeric complex molecule. Similar frequency values for the C_{2v} SO_4^{--} ions in Co(II) complexes have been described in literature [25]; b) the arising of a sharp wide band peaked at 3 420 cm^{-1} (3 700–3 000 cm^{-1}) which is assigned to ν(O—H) stretching vibrations of coordinated water. This band probably hides the expected

ν(N—H) stretching vibration bands; c) the ν(C=O) stretching vibration band is found to be wide and centered at 1 690 cm^{-1}. This band overlaps with that due to the $\delta(OH_2)$ bands from the coordinated water. So, when the complex became dehydrated by heating up to 170 °C (the dehydration temperature was obtained from the corresponding TG plot) the $\delta(OH_2)$ band was lost and the ν(C=O) stretching vibration band appeared then as a double band with peaks at 1 720 cm^{-1} and 1 680 cm^{-1}. The band at 1 720 cm^{-1} is assigned to the ν(C=O) stretching vibration of the OT^- anion; thus, this band is shifted to higher wavenumber than in the free ligand, just as was observed in the Hg(II), Pd(II) and Cu(II) complexes before studied, indicating that the ν(C=O) group of such anion does not intervene in coordination. The increase in the wavenumber value of this band could be explained on the basis of the existence of intramolecular hydrogen bridge interactions between the $C_7=O$ group and the N^1—H group; so, when the *OTH* molecule suffers deprotonation the $C_7=O$ bond becomes stronger thus increasing its wavenumber value. Consequently, the band at 1 680 cm^{-1} is assigned to the *OTH* molecule which should be protonated on N_1 of the triazolic ring; d) the ν(C=C) and ν(N=N) stretching vibration bands are 30 cm^{-1} and 15 cm^{-1} shifted to lower wavenumber values than in the IR spectrum of *OTH*. This is similar to those observed in the previously studied Hg(II), Pd(II) and Cu(II) complexes. Furthermore, these bands are single which might indicate that in the complex under study both the OT^- and *OTH* ligands are linked in a similar way through the N_3 triazolic atoms, as it is suggested by the similarity between the IR spectrum of this complex and those of Hg(II), Pd(II) and Cu(II) studied before; e) the appearance of two relatively weak bands at 240 cm^{-1} and 250 cm^{-1} which are assignable to ν(Cu—N) stretching vibrations of the Cu-*OTH* and Cu-OT^- bonds. These values are in the same range as those given in the literature for the complexes Cu(*pdz*)Cl_2 (*pdz* = pyridazine), Cu(*bipy*)$_3(NO_3)_2$ (*bipy* = bipyridile), and Cu (2,6-*Mepy*)$_2Cl_2$ (*Mepy* = methylpyridine) [21].

The magnetic moment value of the Cu(II) ions in this compound is 1.78 MB. This value is in the range corresponding to that expected for octahedral Cu(II) complexes in which no orbital contribution is expected [26].

Considering all the above data, one could suggest for this compound a dimeric structure with a octahedral arrangements of the ligands around each of the two Cu(II) ions, as follows; a) the two organic ligands (*OTH* and OT^-) would be probably in the apical positions linked through the N_3 triazolic atoms; b) three of the four equatorial plane positions would be occupyed by three water molecules. Finally, the fourth of these positions would be occupyed by the SO_4^{--} group which could act as a bridging ligand in the dimer.

d) Ag(I) *complexes*

The proposed formulae for the two Ag(I) complexes obtained are Ag(X^-) (where X^- = OT^-, ST^-). The complexes are not soluble in water or in common organic solvents. Thus, their ^{1}H-NMR spectra could not be obtained.

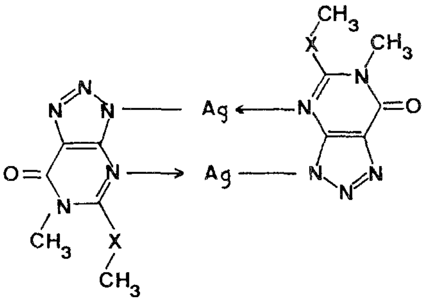
The UV spectrum of Ag(OT^-) shows two bands at 260 nm and 204 nm, which are similar to those of the OT^- UV spectrum. Likewise, the UV spectrum of Ag (ST^-) shows two bands at 267 nm, 268 nm and 208 nm (shoulder) which correspond to those previously cited (shown by the UV spectrum of ST^-).

Concerning the IR spectra of the two complexes they clearly show the same features as in the Hg(II), Pd(II) and Cu(ST^-) complexes (see Table 2). Namely: a) the loss of the ν(N—H) stretching vibration bands. This proves that both ligands are present as anions in the corresponding complexes; b) the ν(C=O) stretching vibration bands shift to slightly higher wavenumber values. Thus, the $C_7 = O$ groups do not participate in coordination; c) the decrease of the wavenumber values corresponding to the ν(C=C) and ν(C=N) stretching vibration bands. This fact might indicate that the coordination of the ligands occur via the triazolic cycle; d) the appearance of two new weak bands in the low frequency range of the IR spectrum of each complex, all of them assignable to ν(Ag—N) stretching vibration bands.

From the IR data it does not become clear by which of the three triazolic nitrogen atoms the coordination occurs. Nevertheless, the similarity in the IR spectra of these complexes and those of Hg(II) and Pd(II) complexes [in the case of Ag(OT^-)] and those of Pd(II) and Cu(II) [in the case of Ag(ST^-)] suggests that the coordination positions (and consequently the negatively charged atoms) in the two Ag(I) complexes could be the N_3 triazolic atoms. If we assume this hypothesis, two structural possibilities for the compounds under study can be considered: 1) a polymeric chain structure in which the 8-azapurinic derivatives would act as bridging ligands through either the N_1 and N_3 atoms or the N_2 and N_3 atoms. Similar N_3 and N_1 bridging structures have been proposed by *Estrella* et al. [6] for Ag(I) complexes of some 8-azapurinic derivatives; 2) a dimeric structure in which two ligand molecules would act as $N_4 \cap N_3$ bridges between two Ag(I) ions as is shown in Scheme 2. This structure would be similar to those found by other authors in complexes of Ag(I) with 4-amino-5-nitroso-6-oxo-tetrahydro-pyrimidine [27] and methylimine [28].

As mentioned already, the IR spectra of the Ag(I) complexes under study are similar to those of the corresponding OT^- and ST^- complexes in which the coordination occurred via the $N_4 \cap N_3$-bridges. So it seems

Scheme 2



probable that a structure similar to that cited in 2) could be the one corresponding to Ag(I) complexes, although further research must be done to prove it.

Thermal Study

The most significant thermal data of the compounds have been summarized in Table 4. These data have been obtained from the corresponding TG and DSC plots.

The compounds *OTH* and *STH* are both anhydrous. *STH* presents a defined melting point at 283 °C; the enthalpy value for this process has been obtained from the corresponding endothermic effect in the DSC plot. The pyrolisis of the compounds start at temperature values of 225 °C (*OTH*) and 287 °C (*STH*); the decompositions became complete at the temperatures of 650 °C (*OTH*) and 750 °C (*STH*) at which no samples remained in the crucible. On the other hand, no stable intermediate species were present in the pyrolitic processes. This prevented us from proposing the possible decomposition mechanisms. The thermal effects and the corresponding energies accompanying the pyrolitic processes are summarized in Table 4.

The temperature corresponding to the onset of the pyrolitic decomposition processes of the complexes are similar to those of the corresponding ligands in the cases of the Hg $(OT^-)_2$, Cu$(ST^-)_2$ and [Ag $(X^-)]_2$ complexes, indicating that their pyrolitic decompositions start by those of the ligands.

The three remaining $Cu_2(OTH)_2(H_2O)_6(OT^-)_2SO_4$ and Pd $(X^-)_2$Cl OH complexes start their pyrolysis at temperature values much lower than those of the ligands. The Cu(II) complex dehydrated in the 50–172 °C temperature range; at the last temperature the found weight loss (9.8%) was in good agreement with the calculated one (10.26%). The medium dehydration enthalpy (50.2 kJ mol^{-1}) indicates that the water molecules are coordinated.

Table 4. *TG and DSC data (the analytical data in parentheses are theoretical values)*

Compound	^{a}Dehydration or ^{b}Dehydroxylation			Other effects		End of the pyrolisis		
	T(°C)	Wt. loss (%)	ΔH(kJ mol)	T(°C)	ΔH(kJ mol)	Residue	Wt. loss (%)	T(°C)
$C_6H_7N_5O_2(OTH)$	—	—	—	235 (exo) 298 (exo)	—35.3 —30.6	—	—	650
$C_6H_7N_5OS(STH)$	—	—	—	290 (exo) 440 (exo)	—122.8 —58.0	—	—	770
$Hg(OT^-)_2$	—	—	—	200 (exo) 280 (exo)	—34.9 —88.9	—	—	680
$Pd_2(OT^-)_2OH\ Cl$	^{b}70 (endo)^{b}	2.6 (2.7)	^{b}48.0	296 (exo) 398 (exo) 437 (exo) 485 (exo)	—48.2 —1 014.3 —2 284.1 —	PdO	37.2 (39.1)	450
$Pd_2(ST^-)_2OH\ Cl$	^{b}80 (endo)^{b}	2.4 (2.6)	^{b}45.0	410 (exo)	—5 185.0	PdO	34.2 (37.2)	450
$Cu(ST^-)_2$	—	—	—	256 (exo) 318 (exo) 369 (exo) 542 (exo)	—94.3 —29.9 —17.7 —2 660.8	CuO	17.4 (17.5)	570
$Cu_2(OTH)(H_2O)_6$ $(OT^-)_2SO_4$	^{a}80 (endo)^{a}	9.8 (10.3)	^{a}50.2	274 (exo) 374 (exo) 518 (exo)	—164.5 —91.9 —1 882.9	CuO	15.9 (15.1)	560
$Ag(OT^-)$	—	—	—	190 (exo) 326 (exo) 348 (exo) 532 (exo)	—18.4 —45.6 —17.2 —646.0	Ag	38.1 (38.4)	570
$Ag(ST^-)$	—	—	—	208 (exo) 236 (exo) 302 (exo) 400 (exo)	—12.6 —13.9 —53.0 —15.1	Ag	36.0 (35.5)	740

The two Pd(II) complexes started their pyrolitic decompositions at 60 °C, when the ligand was OT^-, and 70 °C, when it was ST^-. In both cases, a first weight loss ending at 160 °C (in the case of the Pd(II)/OT^- complex] and 220 °C [in that of Pd(II)/ST^-] occurred. The found values for such weight losses were 2.6% [Pd(II)/OT^-] and 2.4% [Pd(II)/ST^-] and are in good agreement with those calculated for the loss of the corresponding hydroxy groups [2.72% for P(II)/PT^- and 2.60 for Pd(II)/ST^-]. The corresponding energies for the hypothetical dehydroxylation processes have been obtained from the respective endothermic effect accompanying these processes in the DSC plots. The values obtained are presented in Table 4.

On the other hand, none of the seven complexes under study form any stable intermediate during the corresponding pyrolysis. All of these processes take place through a continuous weight loss of the samples up to the end temperatures summarized in Table 4. The final sample remaining in the crucible at the end temperature of each process was characterized by IR spectroscopy, except in the case of the Hg(OT^-)$_2$ complex in which no residues were observed because of the volatility of the HgO presumably formed (b.p. = 357 °C). In Table 4 it can be seen that the found percentages of residues are in accordance with those calculated from the corresponding formula.

Finally, the thermal effects accompanying the pyrolitic decomposition processes of the complexes as well as their energies are also summarized in Table 4.

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