

Metal Complexes of 6-Chloropurine

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Summary. Five Cu(II), Pd(II), Cd(II), Pt(IV), and Au(III) complexes of 6-chloropurine have been obtained. The complexes were characterized by elemental analysis, IR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectroscopy. On the basis of these data the structure of the complexes and the coordination of the ligand have been proposed. Thus, the physical and chemical methods supported evidence that in acidic medium, with exception of the Cu(II) complex, 6-chloropurine acts in the monoprotonated form neutralizing the charge of $[\text{PdCl}_4]^{2-}$, $[\text{CdCl}_4]^{2-}$, $[\text{AuCl}_4]^-$ and $[\text{PtCl}_6]^{2-}$ anions. The thermal behaviour of the complexes has also been studied.

Keywords. 6-Chloropurine; Metal complexes; Spectroscopic studies; Thermal studies.

Metallkomplexe von 6-Chlorpurin

Zusammenfassung. Es wurden fünf Komplexe von 6-Chlorpurin mit Cu(II), Pd(II), Cd(II), Pt(IV) und Au(III) erhalten. Die Komplexe wurden mittels Elementaranalysen, IR, $^1\text{H-NMR}$ und $^{13}\text{C-NMR}$ charakterisiert. Auf der Basis dieser Daten wurde eine Komplexstruktur und eine bestimmte Koordination der Liganden vorgeschlagen. Physikalische und chemische Methoden beweisen, daß im sauren Bereich [mit der Ausnahme von Cu(II)] das 6-Chlorpurin in der monoprotonierten Form koordiniert, wobei die Ladung von $[\text{PdCl}_4]^{2-}$, $[\text{CdCl}_4]^{2-}$, $[\text{AuCl}_4]^-$ und $[\text{PtCl}_6]^{2-}$ jeweils neutralisiert wird. Das thermische Verhalten der Komplexe wurde ebenfalls untersucht.

Introduction

In the last few years some purine 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 these compounds in biological processes [3, 4].

We have previously reported [5] that the interactions of 6-chloropurine (6-ClPH) with several metal ions in aqueous medium lead to the formation of complexes which have been characterized by spectroscopic and thermal methods. IR studies of these complexes suggest that 6-ClPH acts as a bidentate ligand through the exocyclic C 6-Cl and one of the imidazolic nitrogen atoms.

In this context we report here the characterization and thermal behaviour of five new metal complexes of 6-ClPH with Cu(II), Pd(II), Cd(II), Pt(IV), and Au(III) ions obtained in acidic medium.

Experimental

6-Chloropurine was purchased from SIGMA and used as received. All the remaining chemicals were commercial analytical grade reagents and used without further purification. 6-Chloropurine monohydrochloride was prepared by evaporation of a solution of 6-ClPH in a stoichiometrical quantity of diluted hydrochloric acid.

The methods for isolating the metal complexes of this ligand have been previously described [6]. All the complexes were filtered off, washed with water, ethanol and diethylether and air-dried. Their chemical analyses and colours are given in Table 1.

Measurements

Chemical analysis of C, H and N were performed by means of microanalytical methods using a Perkin-Elmer 240C microanalyzer.

Infrared (IR) spectra were obtained from KBr (4000–250 cm^{-1} range) and polyethylene pellets (600–180 cm^{-1} range) using a Perkin Elmer 983G spectrophotometer.

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on a Bruker AM-300 spectrometer, using $\text{DMSO-}d_6$ as solvent and TMS as internal standard. In all cases, the registered intervals were 0–20 ppm and 0–200 ppm, respectively.

Thermal studies were carried out on a Mettler TA-3000 system provided with a Mettler TG 50 thermobalance and a Mettler DSC 20 differential scanning calorimeter. Thermogravimetric curves were registered under dynamic conditions using a flow rate of 100 ml min^{-1} of pure air, with samples between 7.167 and 13.317 mg and a rate of 10 $^\circ\text{C min}^{-1}$. DSC curves were obtained in static air atmosphere, using sample weights between 3.484 and 4.442 mg and at a heating rate of 10 $^\circ\text{C min}^{-1}$. The temperature ranges investigated were 35–900 $^\circ\text{C}$ (TG) and 35–600 $^\circ\text{C}$ (DSC).

Results and Discussion

The analytical data and colours together with proposed formulae for the five new complexes are given in Table 1.

The most important IR bands for the isolated complexes have been tabulated in Table 2. The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectral studies of Cd(II) and Au(III) complexes are summarized in Table 3. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of Cu(II),

Table 1. Analytical data, found % (calcd. %), and colour of the isolated complexes

Compound	Colour	C (%)	H (%)	N (%)	M (%)
$\text{Cu}(6\text{-ClPH})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (I)	blue-greenish	25.14 (25.02)	1.97 (2.08)	23.14 (23.35)	15.03 (13.25)
$\text{PdCl}_4(6\text{-ClPH}_2)_2$ (II)	ochre	21.60 (21.45)	1.34 (1.43)	20.15 (20.02)	21.82 (19.02)
$\text{CdCl}_4(6\text{-ClPH}_2)_2$ (III)	yellow	21.68 (21.23)	1.59 (1.41)	20.16 (19.81)	9.29 (19.88)
$\text{PtCl}_6(6\text{-ClPH}_2)_2$ (IV)	brown	17.30 (16.69)	1.25 (1.11)	16.38 (15.58)	28.51 (27.14)
$\text{AuCl}_4(6\text{-ClPH}_2)$ (V)	yellow	12.82 (12.14)	1.02 (0.81)	11.82 (11.33)	40.21 (39.84)

Table 2. IR spectral data (cm^{-1})

Compound ^a	$\nu(\text{O}-\text{H})$	$\nu(\text{N}-\text{H})$	$\nu(\text{C}=\text{C})$ + $\delta(\text{N}-\text{H})$	$\nu(\text{C}=\text{C})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{Cl})$	$\nu(\text{M}-\text{Cl})$
6-ClPH	—	3 101	—	1 604	1 550	671	—
(6-ClPH ₂) ⁺ Cl ⁻	—	^b	1 705	—	1 573	709	—
I	3 473	3 114	—	1 605	1 549	691	333
II	—	3 120	1 692	—	1 588	690	341
III	—	3 111	1 704	—	1 571	680	217
IV	—	3 138	1 693	—	1 594	717	348
V	—	3 116	1 694	—	1 580	710	359

^a 6-ClPH, 6-chloropurine; 6-ClPH₂⁺, 6-chloropurium ion

^b strong broad absorption, probably hiding the expected $\nu(\text{N}-\text{H})$ vibration band

Table 3. ¹H-NMR and ¹³C-NMR data (*DMSO-d*₆, δ , ppm, TMS)

	6-ClPH	(6-ClPH ₂) ⁺ Cl ⁻	III	V
¹ H-NMR				
C(2)-H	8.72	8.22	8.06	8.26
C(8)-H	8.67	9.27	8.43	9.09
¹³ C-NMR				
C(2)	151.35	148.49	151.81	149.11
C(4)	147.80	139.14	139.80	139.77
C(5)	129.05	115.85	118.09	116.17
C(6)	154.20	153.45	154.71	153.64
C(8)	146.11	148.28	145.59	147.66

Pd(II) and Pt(IV) complexes could not be obtained because of their insolubility in suitable organic solvents.

To facilitate the assignments all tables include the data for the free ligand and its monohydrochloride. The corresponding assignments have been realized on the basis of these data, the literature about spectroscopic data for 6-ClPH [7–10] and other analogous complexes previously described [11, 12].

Cu(II) Complex

The reaction between 6-ClPH and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in acidic medium gave a blue greenish precipitate (I). Its analytical data are in close agreement with the proposed formula, $\text{Cu}(\text{6-ClPH})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$.

The most significant feature in the high frequency range of the IR spectrum of this complex, as is shown in Table 2, is the wide and sharp peak at 3473 cm^{-1} which is assigned to $\nu(\text{O}-\text{H})$ stretching vibrations of hydrate water. The $\nu(\text{N}-\text{H})$ stretching vibration band remains practically unmodified, suggesting that neutral 6-ClPH ligand is present in this complex. In the low frequency range there appears one new and relatively strong band at 333 cm^{-1} , which can be assigned [13] to a $\nu(\text{Cu}-\text{Cl})$ stretching vibration.

On the basis of the analytical and IR data it could be concluded that the neutral 6-ClPH are linked as bidentate ligand (given the proclivity of copper(II) to attain coordination numbers greater than four, and the coordinative unsaturation implied by the formula, it is likely that 6-ClPH functions as a bidentate ligand) via a $N_3 \cap N_9$ bridge in the complex, as it was proposed in previous examples of copper(II)-purine derivatives complexes [13].

Pd(II) Complex

When $PdCl_2$ reacts with 6-ClPH in acidic medium an ochre complex is obtained (II). Its analytical data (Table 1) show that this complex contains four chlorine atoms and two ligands in monoprotonated form bonded to the central atom.

In the region $3\,500\text{--}2\,600\text{ cm}^{-1}$ the IR spectrum shows a strong broad absorption which has been identified (compare [14]) as being due to the NH^+ stretching vibration. A further band at $3\,120\text{ cm}^{-1}$ was assigned to the $\nu(N-H)$ stretching vibration. This absorption was similar to that of the 6-chloropurine hydrochloride spectrum, though this one shows a more strong and broad polyhumped maximum in which the $\nu(N-H)$ band could not be identified. This provides evidence that, according to literature data [15], in this complex the ligand is in its protonated form. Besides, the $\nu(C=C)$ and $\nu(C=N)$ stretching vibration bands are shifted to higher wavenumber values than in the free ligand, just as was observed in the IR spectrum of its hydrochloride. It is generally observed that skeletal stretching motions in purines increase in energy upon protonation [16, 17]. This could be explained on the basis that an increase in the electron density of a carbon atom adjacent to a nitrogen occurs if the nitrogen atom is protonated [18]. In the low IR range a new band arises at 341 cm^{-1} which is assignable to the $\nu(Pd-Cl)$ stretching vibration [19].

The data allow to conclude that this compound is a salt, where the 6-chloropurine acts in its monoprotonated form, neutralizing the negative charge of the $(PdCl_4)^{2-}$ ion, with a structure that could be similar to those found in other tetrachloropalladate(II) complexes of purines [20].

Finally, it is worth noting that the $\nu(C-Cl)$ stretching vibration band suffers a shift to a lower wavenumber value than in the 6-chloropurine hydrochloride, thus indicating that the chlorine atoms of 6-chloropurinium ions participate somehow in the coordination.

Cd(II) Complex

In acidic medium (HCl) 6-ClPH reacts with $CdCl_2 \cdot 2H_2O$ to give a pale yellow complex (III). The proposed formula for this complex is $CdCl_4(6-ClPH_2)_2$.

The most noticeable features in the high frequency range of its IR spectrum are like those of the Pd(II) complex, namely: a) In the region $3\,500\text{--}2\,600\text{ cm}^{-1}$ there is a strong band at $3\,111\text{ cm}^{-1}$ which has been assigned to the $\nu(N-H)$ stretching vibration. According to literature data [14, 15] this indicates that the ligand is present in its protonated form; b) the bands corresponding to $\nu(C=C)$ and $\nu(C=N)$ stretching vibrations are displaced to a higher wavenumber with respect to their position in the IR spectrum of the free ligand, indicating that the 6-ClPH has undergone a protonation process at one of the nitrogen atoms [16,

17]; c) the lowering in the frequency value of the $\nu(\text{C}-\text{Cl})$ stretching vibration at 29 cm^{-1} in comparison with its value in the hydrochloride indicates that in the complex the chlorine atoms of 6-chloropurinium ions are linked in a similar way like in the Pd(II) complex discussed before. Besides, in the low frequency range, it shows a new band at 217 cm^{-1} , which could be assigned [21] to the $\nu(\text{Cd}-\text{Cl})$ stretching vibration.

Moreover, it has been possible to record the $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of this complex. Chemical shifts of the individual resonances are listed and assigned in Table 3. The assignments of these signals have been made from literature data concerning the free ligand [8–10] and other purine derivatives complexes. As far as we know, no previous work has been published on the $^1\text{H-NMR}$ of 6-chloropurine hydrochloride. It shows resonances at δ 8.22 and 9.27 ppm corresponding to C_2-H and C_8-H protons, respectively. The largest shift change caused by protonation occurs for the C_8-H next to the protonation site, giving a shielding order $\text{C}_2-\text{H} > \text{C}_8-\text{H}$. This order is reversed compared to the free ligand [8] and has been found for protonation at the imidazole ring in purine derivatives [22]. With regard to the Cd(II) complex its $^1\text{H-NMR}$ spectral data shows shifts towards higher field with respect to hydrochloride, mainly the signal due to C_8-H .

From these considerations it is proposed that this compound is a salt formed by CdCl_4^{2-} and 6-chloropurinium ions. A similar coordination has been proposed by Colacio for the bis(xanthinium)tetrachloro cadmate (II) complex [20].

Pt(IV) Complex

The reaction between $\text{H}_2[\text{PtCl}_6] \cdot 2\text{H}_2\text{O}$ and 6-ClPH gave a brown solid (IV). Its analytical data are in close agreement with the proposed formula $\text{PtCl}_6(\text{6-ClPH}_2)_2$.

The IR spectrum shows the same features as the compounds (II) and (III). Thus, the $\nu(\text{N}-\text{H})$ stretching vibration band remains centered at 3138 cm^{-1} within a strong and broad absorption in the region $3500\text{--}2600\text{ cm}^{-1}$, indicating a protonation of the free ligand. Likewise, the $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$ stretching vibration bands are shifted to higher wavenumber values than in the IR spectrum of 6-ClPH. This is similar to the Pd(II) and Cd(II) complexes and indicates again protonation. In the low frequency range, between 600 and 180 cm^{-1} , a new and relatively strong band appears at 348 cm^{-1} , which is assignable to the $\nu(\text{Pt}-\text{Cl})$ stretching vibration. This value is in the same range as those given in the literature for analogous Pt(IV) complexes [23, 24]. Furthermore, this band is single which might indicate that in the complex under study the chlorine atoms are linked in a similar way to Pt(IV).

Taking into account all data, one could suggest that this compound is a salt where 6-chloropurinium ions are neutralizing the negative charge of the PtCl_6^{2-} ion, analogous to other hexachloroplatinate(IV) complexes of purines [25].

Au(III) Complex

In acidic medium (HCl) 6-ClPH reacts with tetrachloroauric acid to give a yellow solid (V). The proposed formula for this compound, in close agreement with its analytical data, is $\text{AuCl}_4(\text{6-ClPH}_2)$.

The most important data obtained from its IR spectrum in the higher frequency range are much like those of the Pd(II), Cd(II), and Pt(IV) complexes and indicate

that in this compound the 6-chloropurine is also present in its protonated form: a) there is a strong broad absorption in the region $3\,500\text{--}2\,500\text{ cm}^{-1}$, with a band at $3\,116\text{ cm}^{-1}$ which has been assigned to the $\nu(\text{N-H})$ stretching vibration, and b) both $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$ stretching vibrations bands show an increase in their wavenumber values. Furthermore, in the low IR range a new band arises at 359 cm^{-1} which is assignable [26, 27] to the $(\text{Au}-\text{Cl})$ stretching vibration.

The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of **V** (Table 3) provide additional evidence that 6-ClPH is present in its protonated form.

On the basis of the spectroscopic data obtained it seems that positively charged 6-ClPH is coordinated to the central Au(III) ion. This coordination mode has also been observed in other Au(III)-purine derivative complexes [12, 28]. In these compounds the negative charge of the square planar AuCl_4^- ion is neutralized by a protonated purine.

Thermal Studies

Thermal data of the complexes obtained from the corresponding TG and DSC curves are summarized in Table 4. These data confirm the anhydrous character of all the complexes except for $\text{Cu}(\text{6-ClPH})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (**I**). Moreover, no stable intermediate species were present in the pyrolytic processes. This prevented us from proposing a tentative pyrolytic decomposition mechanism for the complexes.

The $\text{Cu}(\text{6-ClPH})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ complex (**I**) becomes totally dehydrated in the $50\text{--}170^\circ\text{C}$ temperature range; at the last temperature the weight loss found (7.1%) is in good agreement with the calculated one (7.51%). The dehydration enthalpy is 17.0 kJ mol^{-1} , which indicates that the water is probably not coordinated. The pyrolytic decomposition of the remaining anhydrous complex begins at 250°C ; the complex undergoes a weight loss (14.5%) which ceases at 355°C . This weight loss is in good agreement with the one calculated for the dehalogenation process (14.78%).

The TG and DSC plots of the Pd(II) and Pt(IV) complexes are alike. The anhydrous complexes are stable up to 170°C (compound **II**) and 200°C (**IV**); at

Table 4. Thermoanalytical data

Compound	^a Dehydration or ^b dehalogenation		Residue	Residue (%)		T ($^\circ\text{C}$)
	T ($^\circ\text{C}$) range	Wt. loss (%)		Calc.	Found	
I	^a 50–170	7.1 (7.5) ^c	CuO	16.5	18.8	550
	^b 250–355	14.5 (14.8)				
II	^d	–	PdO	21.9	25.1	500
III	^b 250–540	25.1 (25.1)	CdO	22.7	10.6	920
IV	^d	–	Pt	27.1	28.5	500
V	^b 190–330	28.3 (28.9)	Au	40.2	39.8	640

^c The analytical data in parentheses are theoretical values

^d This dehalogenation process is overlapping with the pyrolytic process

these temperatures thermal decomposition take place in two steps (**II**) or three steps (**IV**) corresponding to the pyrolytic degradation of the samples and are reflected in the DSC curves by exothermic effects. The expected endothermic behaviour for the dehalogenation process is not observed in the DSC curves of **II** and **IV**. Instead of this there is a strong exothermic effect centered at 480°C (**II**) and 522°C (**IV**), which suggests that the above mentioned dehalogenation process occurs simultaneously with the pyrolytic decomposition. The energy values obtained for this effect are 3306.7 kJ mol⁻¹ for **II** and 4097.1 kJ mol⁻¹ for **IV**.

The TG curve of the CdCl₄(6-ClPH₂)₂ complex (**III**) reveals its anhydrous character and thermal stability. The decomposition starts at 250°C with a dehalogenation process which takes place in two steps with a weight loss (25.1%), in accordance with the calculated one for total dehalogenation (25.08%). It is responsible for the endothermic effects centered at 296°C and 396°C in the DSC curve. Dehalogenation enthalpies calculated from the areas of these effects are 19.1 kJ mol⁻¹ and 64.7 kJ mol⁻¹, respectively. This has been observed in the thermal decomposition of some purine metal complexes [26, 28] and could be explained assuming that in the dehalogenation process one chlorine atom is lost as HCl while the remaining chlorine atoms are eliminated as Cl₂.

The TG and DSC plots of the AuCl₄(6-ClPH₂) complex (**V**) show that it is stable up to 190°C. From this temperature onwards the decomposition starts with an intense effect of weight loss, in two overlapping steps ending at 330°C. The experimental value for the weight loss in this effect (28.3%) is in good agreement with that calculated for the total dehalogenation (28.89%). So it seems probable that this dehalogenation process takes place in the same way as in the Cd(II) complex (**III**).

Finally, the residues of pyrolytic decomposition of the complexes were characterized by IR spectroscopy; they are summarized in Table 4. In the case of CdCl₄(6-ClPH₂)₂ the final residue (CdO) (10.6%) is much lower than that calculated (22.71%), due to the partial sublimation of CdCl₂ in the 575–725°C temperature range [29]. In the other complexes the calculated and found residue values are in good agreement.

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Received February 14, 1991. Accepted February 27, 1991