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# Thermal and spectroscopic study of some metal complexes of 6-chloropurine

C. Valenzuela-Calahorro, F.J. García-Barros [1], M.A. Díaz-Díez,
A. Bernalte-García and E. Sabio-Rey

*Department of Inorganic Chemistry, Faculty of Sciences, University of Extremadura,*
*06071 Badajoz (Spain)*

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## Abstract

Solid complexes of 6-chloropurine (6-ClPH) with the cations Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) have been obtained and characterised on the basis of elemental analysis and IR spectroscopy. Except for the Hg(II) compound, Hg(6-ClP)Cl, the remaining complexes have the general formula $M(6\text{-ClP})_2$ with a variable amount of water. The thermal behaviour of these complexes has been studied by TG and DSC techniques. The IR spectra of the compounds are also discussed.

## INTRODUCTION

The interactions of purines with metal ions have been studied extensively in the research of bioinorganic chemistry [1–7]. Recently, it has been proposed that the role of metal ion binding to purines influences the conversions between, for example, B-DNA and Z-DNA [8].

Although the literature concerning metal complexes of purine derivatives is extensive [9–12], studies of their thermal behaviour are, however, still scarce, especially when compared with those related to other techniques [13,14]. For this reason, and because, to our knowledge, no investigation has been reported on the thermal behaviour of 6-chloropurine (6-ClPH) and its solid complexes, we report here the characterisation and thermal behaviour of the six complexes of 6-ClPH with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) ions.

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[1] Author to whom correspondence should be addressed.

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## EXPERIMENTAL

### *Reagents*

The compound 6-chloropurine was purchased from Sigma and used as received. All the remaining chemicals were commercial analytical grade reagents and were used without further purification.

### *Methods*

Chemical analyses of C, H and N were performed by microanalytical methods using a Perkin–Elmer 240C microanalyser.

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 in dynamic conditions using a flow rate of 100 ml $\mathrm{min}^{-1}$ of pure air, with sample weights between 9.397 and 15.309 mg and a heating rate of 10 °C $\mathrm{min}^{-1}$. DSC curves were obtained in static air atmosphere, using sample weights between 2.790 and 4.137 mg and a heating rate of 10 °C $\mathrm{min}^{-1}$. The temperature ranges investigated were 35–850 °C (TG) and 35–600 °C (DSC).

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

### *Samples*

The interactions of 6-ClPH in aqueous media over a wide pH range with the metal ions Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II), gave six new

TABLE 1

Analytical data: found % (calc. %), and colour of the isolated complexes

| Compound | Colour | C(%) | H(%) | N(%) | M(%) |
|---|---|---|---|---|---|
| $Co(C_5H_2ClN_4)_2\cdot 4H_2O$ (I) | Pink | 27.47<br>(27.40) | 2.59<br>(2.74) | 25.04<br>(25.57) | 12.81<br>(13.45) |
| $Ni(C_5H_2ClN_4)_2\cdot 3.5H_2O$ (II) | Green | 27.43<br>(27.98) | 2.31<br>(2.56) | 25.24<br>(26.12) | 14.13<br>(13.69) |
| $Cu(C_5H_2ClN_4)_2\cdot 4H_2O$ (III) | Blue | 27.64<br>(27.11) | 2.27<br>(2.71) | 25.28<br>(25.30) | 13.96<br>(14.35) |
| $Zn(C_5H_2ClN_4)_2\cdot 1.5H_2O$ (IV) | Yellow | 29.18<br>(30.03) | 1.29<br>(1.75) | 27.47<br>(28.03) | 16.85<br>(16.36) |
| $Cd(C_5H_2ClN_4)_2\cdot 1.5H_2O$ (V) | White | 26.76<br>(26.87) | 1.45<br>(1.57) | 25.20<br>(25.08) | 18.79<br>(28.18) |
| $Hg(C_5H_2ClN_4)Cl$ (VI) | Yellow | 15.45<br>(15.40) | 0.53<br>(0.51) | 14.53<br>(14.37) | –<br>– |

compounds of composition: $Co(C_5H_2ClN_4)_2 \cdot 4H_2O$ (I), $Ni(C_5H_2ClN_4)_2 \cdot 3.5H_2O$ (II), $Cu(C_5H_2ClN_4)_2 \cdot 4H_2O$ (III), $Zn(C_5H_2ClN_4)_2 \cdot 1.5H_2O$ (IV), $Cd(C_5H_2ClN_4)_2 \cdot 1.5H_2O$ (V) and $Hg(C_5H_2ClN_4)Cl$ (VI); their synthesis and characterisation have been described previously [15]. The complexes were prepared as follows. A hot solution (100 ml) containing 0.25 g of the ligand was mixed (slowly with stirring) in a molar ratio of 1 : 2 (M : L) with a solution of the corresponding metallic nitrate, except for Hg(II) for which the chloride was used. When the solutions were allowed to stand at room temperature, the compounds precipitated almost immediately. All the complexes were filtered off, washed consecutively with water, ethanol and diethylether, and air dried. Their chemical analyses and colour are given in Table 1.

## RESULTS AND DISCUSSION

The thermal analysis curves for 6-ClPH are shown in Fig. 1. The thermogravimetric analysis curves for some complexes of 6-ClPH are given in Fig. 2 and differential scanning calorimeter curves are given in Fig. 3.

The TG curve of 6-ClPH shows that the compound is in its anhydrous form. The decomposition starts at 165 °C and finishes at 630 °C, when all the sample has disappeared from the reaction crucible. On the other hand, the DSC curve of anhydrous 6-ClPH exhibits two endothermic effects centred at 175 and 191 °C, which correspond to the fusion process, overlapping with the dehalogenation of the sample.

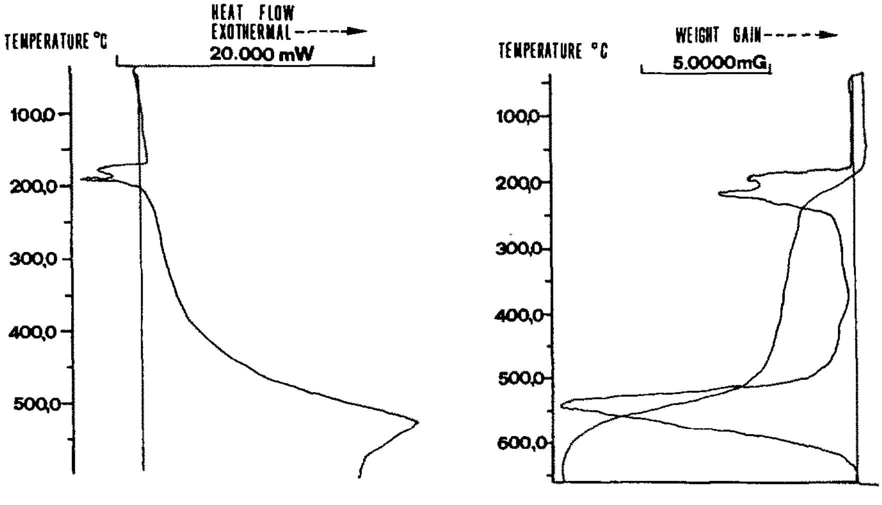

Fig. 1. TG and DSC curves of 6-chloropurine (6-ClPH).

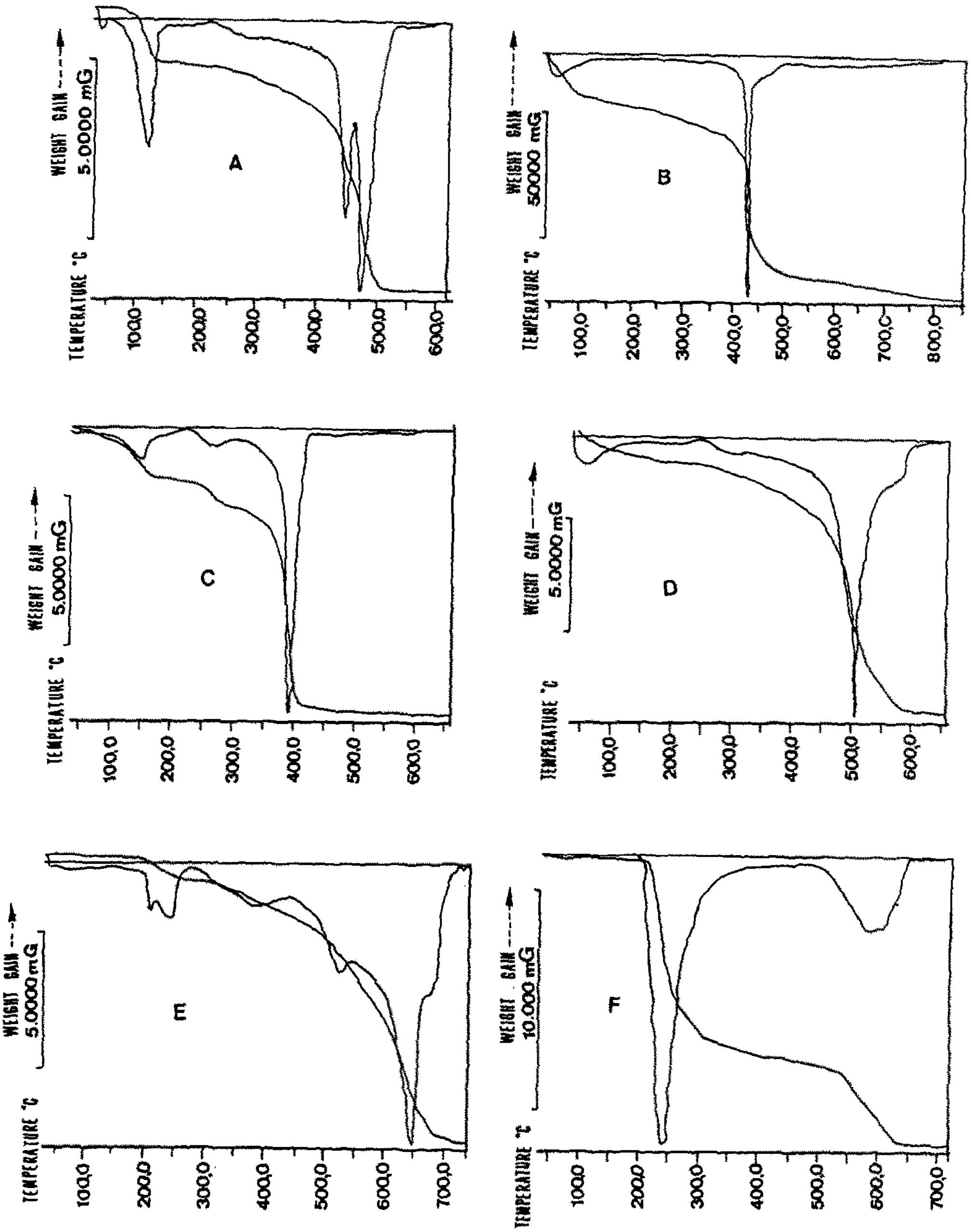

Fig. 2. TG curves of: A, $Co(C_5H_2ClN_4)_2 \cdot 4H_2O$; B, $Ni(C_5H_2ClN_4)_2 \cdot 3.5H_2O$; C, $Cu(C_5H_2ClN_4)_2 \cdot 4H_2O$; D, $Zn(C_5H_2ClN_4)_2 \cdot 1.5H_2O$; E, $Cd(C_5H_2ClN_4)_2 \cdot 1.5H_2O$; F, $Hg(C_5H_2ClN_4)Cl$.

Of the 6-ClPH complexes, only compound **VI** forms anhydrous crystals, whereas the other complexes are hydrated, as can be seen from the results of the elemental analyses (Table 1).

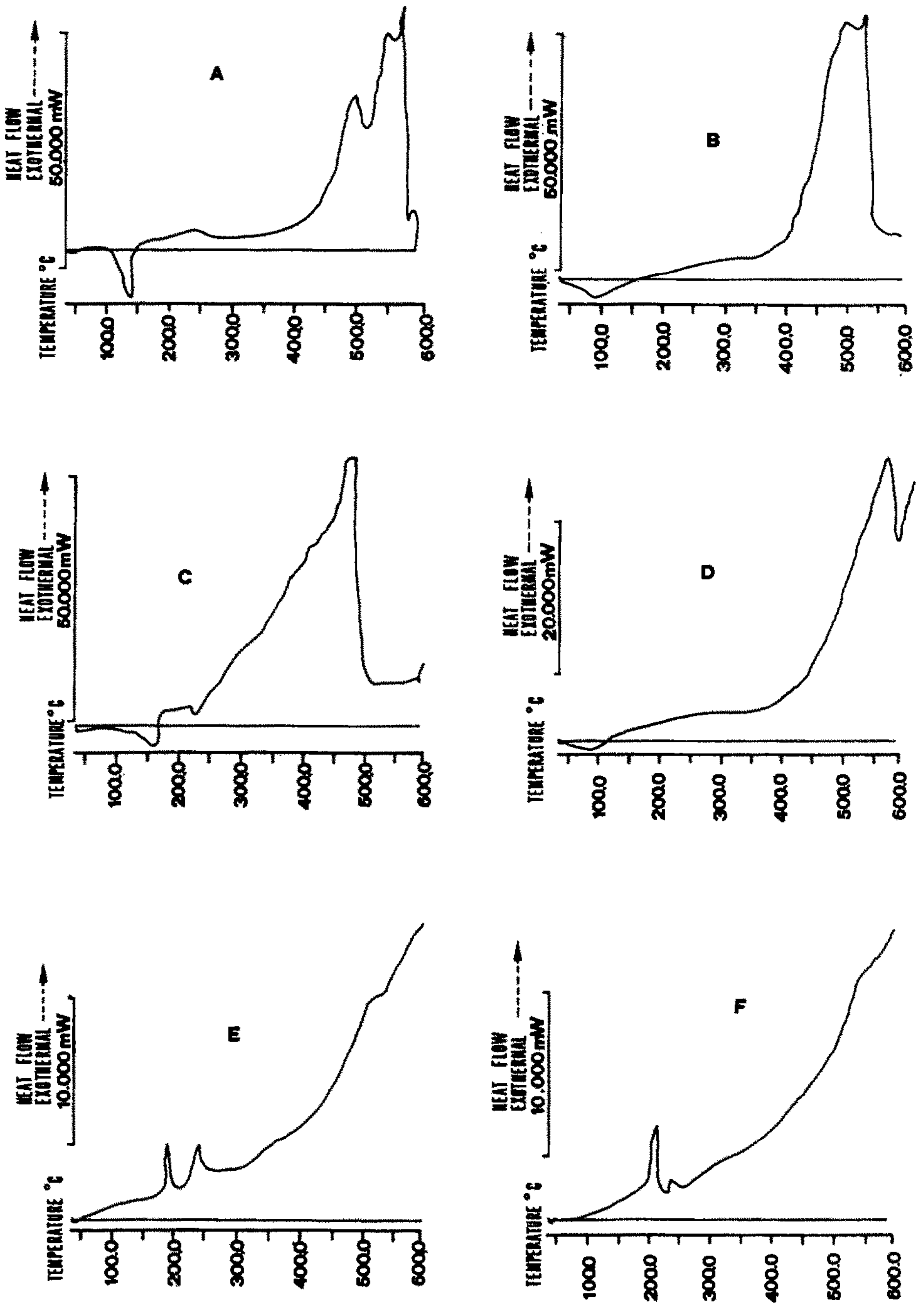

Fig. 3. DSC curves of: A, $Co(C_5H_2ClN_4)_2 \cdot 4H_2O$; B, $Ni(C_5H_2ClN_4)_2 \cdot 3.5H_2O$; C, $Cu(C_5H_2ClN_4)_2 \cdot 4H_2O$; D, $Zn(C_5H_2ClN_4)_2 \cdot 1.5H_2O$; E, $Cd(C_5H_2ClN_4)_2 \cdot 1.5H_2O$; F, $Hg(C_5H_2ClN_4)Cl$.

TABLE 2

TG assignations for the dehydration process

| Compound | Temperature range (°C) | Weight loss (%) | |
|---|---|---|---|
| | | Calc. | Found |
| $Co(C_5H_2ClN_4)_2 \cdot 4H_2O$ (I) | 70–160 | 16.44 | 16.27 |
| $Ni(C_5H_2ClN_4)_2 \cdot 3.5H_2O$ (II) | 50–140 | 14.69 | 14.90 |
| $Cu(C_5H_2ClN_4)_2 \cdot 4H_2O$ (III) | 50–180 | 16.26 | 15.57 |
| $Zn(C_5H_2ClN_4)_2 \cdot 1.5H_2O$ (IV) | 50–120 | 6.76 | 6.37 |
| $Cd(C_5H_2ClN_4)_2 \cdot 1.5H_2O$ (V) | 190–240 | 6.05 | 5.97 |

On heating these compounds, three processes can occur: dehydration, dehalogenation and pyrolitic decomposition. These can be discerned and studied from the corresponding TG and DSC curves (Figs. 2 and 3).

### *Dehydration processes*

Water is eliminated in the first step of the thermal decomposition of the hydrated complexes. The data for calculated and observed weight losses and the corresponding temperature ranges for the dehydration processes are given in Table 2. As can be observed, the experimental values for percentage weight-loss are in good agreement with those calculated for the total dehydration of the complexes mentioned above.

It can also be seen from Fig. 2 that the dehydration processes occur in a single step in the temperature range 50–180 °C, except for the Cd(II) complex. For this compound the presence of two overlapping weight-loss effects between 190 and 240 °C indicates the non-equivalence of the molecules of water, probably owing to different interactions of these water molecules in the complex. Furthermore, this compound **V**, and also compound **III**, both show high temperature values for the dehydration that suggest the existence of hydrogen bonds between the water molecules and the ligand [16,17].

Moreover, for all the complexes except **V**, the expected endothermic behaviour for the dehydration processes was observed in the DSC curves over the same temperature range (Fig. 3). The corresponding dehydration enthalpies have values between 16.7 kJ per mol $H_2O$ (**IV**) and 47.1 kJ per mol $H_2O$ (**I**). For compound **V**, the DSC curve shows an exothermic peak, the assignment of which is difficult. If it were due to water elimination alone, it would not be exothermic, but the temperature range is too low to correspond to pyrolitic degradation. Therefore, this exothermic peak could be explained as a combination of an endothermic peak corresponding to the dehydration and an exothermic peak of higher energy assigned to a structural change associated with the condensation process.

TABLE 3

TG assignations for the pyrolysis process

| Compound | Temperature range ( ° C) | Residue | Residue (%) | |
|---|---|---|---|---|
| | | | Calc. | Found |
| $Co(C_5H_2ClN_4)_2 \cdot 4H_2O$ (**I**) | 240–540 | CoO | 17.10 | 16.29 |
| $Ni(C_5H_2ClN_4)_2 \cdot 3.5H_2O$ (**II**) | 250–850 | NiO | 17.42 | 18.27 |
| $Cu(C_5H_2ClN_4)_2 \cdot 4H_2O$ (**III**) | 220–550 | CuO | 17.97 | 17.47 |
| $Zn(C_5H_2ClN_4)_2 \cdot 1.5H_2O$ (**IV**) | 250–650 | ZnO | 20.37 | 20.97 |
| $Cd(C_5H_2ClN_4)_2 \cdot 1.5H_2O$ (**V**) | 280–720 | CdO | 28.18 | 18.79 |
| $Hg(C_5H_2ClN_4)Cl$ (**VI**) | 300–650 | – | – | – |

### *Dehalogenation process*

The mercury complex (**VI**) is the only one in which chloride is present. The corresponding TG diagram shows a strong weight-loss effect, centred at 240 ° C, in which 69.3% of the initial sample is lost. This effect is assigned to the total dehalogenation and removal of $HgCl_2$ from the compound, in accordance with the calculated weight-loss (69.7%).

The DSC diagram shows an exothermic effect in the same temperature range, which suggests that the enthalpy of formation of $HgCl_2$ is higher than the corresponding enthalpy of pyrolysis, because if the above-mentioned effect were due to the dehalogenation only, it would not be exothermic.

### *Pyrolytic processes*

Once dehydrated, the compounds decompose in the 220–800 ° C temperature range. In the DSC plots (Fig. 3), one or two exothermic effects can be observed.

The final residues of the pyrolytic decomposition of the complexes were characterised by IR spectroscopy and are summarised in Table 3. In the case of complex **V**, the final residue (CdO) (18.8%) is lower than that calculated

TABLE 4

IR absorption bands ($cm^{-1}$)

| Compound | $\nu$(O–H) | $\nu$(N–H) | $\nu$(C=C) | $\nu$(C=N) | $\nu$(C–Cl) |
|---|---|---|---|---|---|
| 6-ClPH | – | 3101 | 1604 | 1550 | 671 |
| $Co(C_5H_2ClN_4)_2 \cdot 4H_2O$ (**I**) | 3418 | – | 1589 | 1537 | 661 |
| $Ni(C_5H_2ClN_4)_2 \cdot 3.5H_2O$ (**II**) | 3390 | – | 1592 | 1535 | 659 |
| $Cu(C_5H_2ClN_4)_2 \cdot 4H_2O$ (**III**) | 3400 | – | 1592 | 1560 | 656 |
| $Zn(C_5H_2ClN_4)_2 \cdot 1.5H_2O$ (**IV**) | 3408 | – | 1592 | 1544 | 657 |
| $Cd(C_5H_2ClN_4)_2 \cdot 1.5H_2O$ (**V**) | 3600, 3410 | – | 1592 | 1528 | 657 |
| $Hg(C_5H_2ClN_4)Cl$ (**VI**) | – | – | 1592 | 1544 | 648 |

(28.18%), owing to the partial sublimation of $CdCl_2$ in the 500–725°C range [18]. Likewise, the absence of a final residue in the pyrolysis of **VI** is due to the sublimation of $HgCl_2$. In the remaining complexes, the calculated and found residue values are in good agreement.

## *IR spectra*

The most significant IR data for the complexes are summarised in Table 4. The corresponding assignments have been made from literature data concerning the free ligand [19] and metal complexes of other purine derivatives.

The similarity in the IR spectra of the complexes suggests that the ligand exhibits the same coordination mode in all of them. In the 3600–3200 $cm^{-1}$ region, the IR spectra, except for that of complex **VI**, show bands assigned to $\nu$(O–H), indicating the presence of water molecules in the complexes. The $\nu$(N–H) band at 3101 $cm^{-1}$ for the free ligand is not observed in the complexes, indicating that anionic 6-ClP is coordinated through one of the imidazole-ring nitrogens. In addition, the band assigned to $\nu$(C–Cl) for the free ligand appears at a lower wavenumber in the IR spectra of the complexes which suggests that the exocyclic C6–Cl might also be involved in the coordination, so that 6-ClP probably acts as a bidentate ligand. This coordination mode has been found in other metal complexes of 6-substituted purines [20,21].

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