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Note

PREPARATION, CHARACTERISATION AND THERMAL STUDIES ON MIXED LIGAND COMPLEXES OF Ru(III) AND Pt(IV) WITH BIOLOGICALLY ACTIVE LIGANDS

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Mixed ligand complexes of ruthenium(III) and platinum(IV) with 6-amino-5-nitroso-2,4-pyrimidine diol and antipyrine have been synthesised in an aqueous medium and characterised by chemical analysis, electrical conductance, magnetic measurements, electronic and infrared spectral studies. The thermal behaviour of these complexes in a self-producing dynamic-air atmosphere has been investigated by thermogravimetric and derivative thermogravimetric methods. The intermediates obtained at the end of various thermal decomposition steps have been identified by chemical analysis and infrared spectral data of the residue obtained by isothermal heating of the complex at apparent temperatures. Kinetic parameters, such as apparent activation energy and order of reaction, have been calculated for the first step of the thermal decomposition reaction of both complexes, employing the graphical method of Coats and Redfern.

INTRODUCTION

Studies of the behaviour of mixed ligand complexes of compounds and their derivatives naturally occurring in living organisms with those given in the form of drugs can be of high biological interest. Pyrimidine derivatives and compounds in which the pyrimidine ring is part of a more complex system are widely distributed in living organisms. Antipyrine and its derivatives are widely used as pain relieving drugs. In the present studies, we have chosen 6-amino-5-nitroso-2,4-pyrimidine diol (ANP) as the primary ligand,

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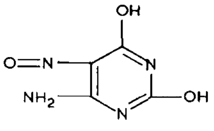
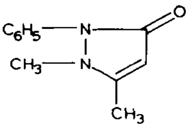
antipyrine (AP) as the secondary ligand. Their mixed ligand complexes with Ru(III) and Pt(IV) have been synthesised and characterised. The thermal behaviour of these complexes has also been investigated by using thermogravimetry (TG) and derivative thermogravimetric (DTG) techniques.



(ANP)



(AP)

EXPERIMENTAL

Materials

ANP was procured from Aldrich Chemical Company and E. Merck antipyrine was employed. Ruthenium chloride (Johnson Matthey) and platinum chloride (SISCO, Bombay) were used as received without further purification, nitrobenzene used for conductance measurements was purified by the method described by Fay and Lowry [1]. All other chemicals used were of analytical grade.

Preparation of the complexes

Aqueous solutions of metal ions (40 ml, 0.1 mol), ANP (80 ml, 0.2 mol) and AP (40 ml, 0.1 mol) were mixed and the reaction mixture was refluxed for 3 h. A dark brown precipitate appeared in the case of Ru(III) which was filtered and dried over P_3O_{10}. In the case of Pt(IV), the reaction mixture was concentrated after refluxing to one third of its original volume by the evaporation of water in air and then cooled in an ice bath for half an hour. The pinkish red crystals of the product were separated out. These were filtered and dried.

Analysis

Microanalyses of carbon, hydrogen and nitrogen contents were carried out in the Microanalytical Laboratories of Central Drug Research Institute, Lucknow. Ruthenium(III) and platinum(IV) were estimated by standard gravimetric methods [2]. Chlorine was determined by flushing the complex with $Na_2O_2 + NaOH$ (1 : 1 w/w) and then precipitating the chloride as AgCl.

Physical measurements

Infrared spectra of the complexes were recorded in the solid state (KBr pellets) in the region 4000–200 cm^{-1} with a Perkin-Elmer 621-grating spectrophotometer. Electronic spectra were taken in nujol mull on a Cary 14 spectrophotometer. Magnetic susceptibility measurements were carried out with a Gouy's balance using mercuric tetrathiocyanato cobaltate(II), $Hg[Co(CNS)_4]$, as calibrant. Conductance measurements were made at room temperature (25 ± 0.5°C) in nitrobenzene. TG and DTG curves were recorded on a Setaram G-70 thermoanalyser with a sample size of 20–35 mg, and a heating rate of 7 K min^{-1} in a self-producing air atmosphere.

RESULTS AND DISCUSSION

Characterisation

Analytical data and physical characteristics of the complexes are given in Table 1. The conductance measurement of the Ru(III) complex in $PhNO_2$ shows that it is essentially a non-electrolyte, while the result obtained for the Pt(IV) complex is suggestive of a 1 : 1 electrolytic nature.

Room-temperature magnetic moment measurements show that the Ru(III) complex is paramagnetic having a magnetic moment of 1.80 B.M., corresponding to one unpaired electron in this complex. The Pt(IV) complex is diamagnetic. These observations suggest them to be low-spin octahedral complexes. This is further supported by electronic spectral studies [3]. The Ru(III) complex exhibits three bands in the region 27 300–18 100 cm^{-1} and an intense charge-transfer band at 30 800 cm^{-1}. The Pt(IV) complex exhibits a *d–d* band at 20 804 cm^{-1}. Other bands are masked by an intense charge-transfer band appearing in the same region.

The infrared spectra of ANP show a strong band at 1460 cm^{-1} which may be assigned to the N–O stretching frequency [4]. On complex formation the intensity of this band diminishes and shifts towards a higher wavenumber

TABLE 1

Analytical data and physical characteristics

Complex	Found (calcd.) (%)					Molar conductance (ohm^{-1} cm^2 mol^{-1})	
	C	H	N	M	Cl		
$(ANP)_2$ Ru(AP)Cl	Brown	37.02 (35.82)	3.42 (3.14)	21.02 (21.99)	16.01 (15.88)	5.62 (5.88)	5.50
$(ANP)_2Pt(AP)/$ Cl Cl	Pinkish red	30.20 (29.76)	2.84 (2.61)	18.00 (18.27)	25.20 (25.47)	9.30 (9.27)	89.50

(1490 cm^{-1}), suggesting coordination of the nitroso group of ANP to the metal [5]. A high-intensity band at 1265 cm^{-1} in the free ANP may be assigned to the phenolic C–O stretching. In the complexes this band is shifted to a higher wavenumber (ca. 1310 cm^{-1}) suggesting that the hydroxy group of ANP in the 4th position takes part in the bond formation. This is further supported by the appearance of a new band in the complexes at ca. 670 cm^{-1} due to ν(M–O–C) vibrations [6–8]. In AP a strong band appears at 1660 cm^{-1} which may be assigned to ν(C=O) vibrations. This band is shifted towards the lower side in our complexes and is observed at around 1600 cm^{-1} indicating coordination of the carbonyl oxygen of the ligand to the metal. Similar observations were made by earlier workers [9–11].

Thermal analysis

TG and DTG curves of Ru(III) and Pt(IV) complexes in flowing air atmosphere are shown in Fig. 1.

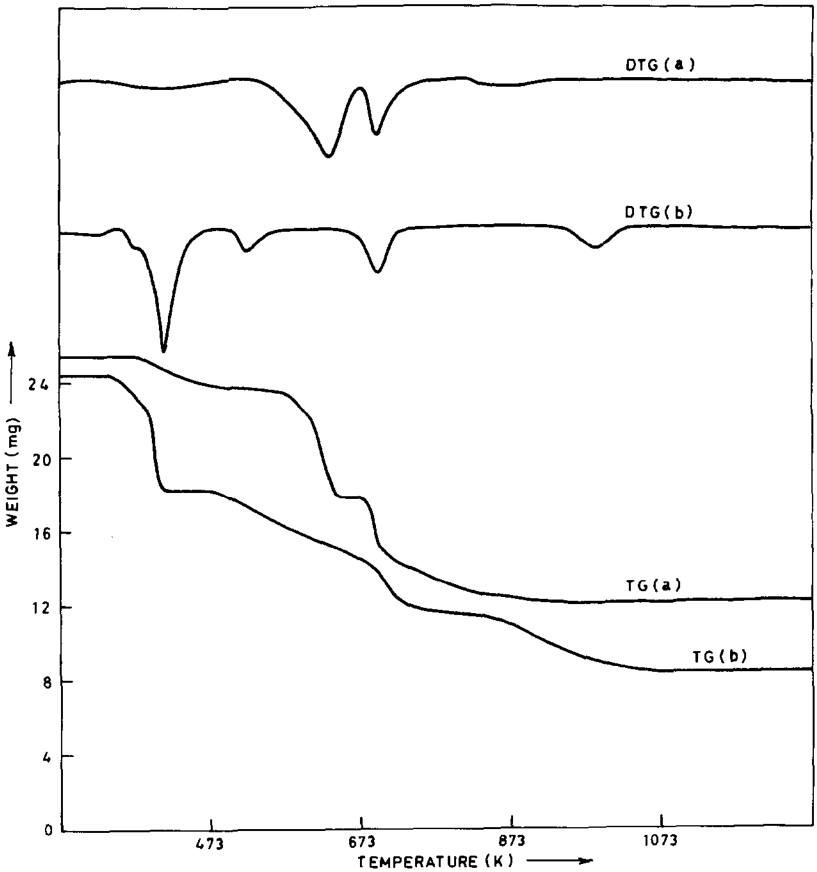


Fig. 1. TG and DTG curves of (a) Ru(III), (b) Pt(IV) complexes.

Decomposition of $(ANP)_2Ru(AP)Cl$

From the TG and DTG curves of $(ANP)_2Ru(AP)Cl$, it is evident that the complex shows a two-step decomposition. It is stable up to 373 K. Beyond this temperature it starts decomposing, the rate of decomposition is slow up to 573 K but then accelerates, resulting in the formation of an intermediate at 638 K. Analysis of the residue at this stage shows its composition to be $(ANP)_2RuCl$. The observed weight loss for this stage is 29.92% compared to the calculated value of 29.62% for one mole of antipyrine. Thus there is fairly good agreement between the two values. The intermediate $(ANP)_2RuCl$ can be isolated by heating $(ANP)_2Ru(AP)Cl$ isothermally at 650 K for 4 h. The loss of antipyrine ligand is indicated from the infrared spectra of the residue. The antipyrine free intermediate is stable up to 670 K when it starts decomposing with a maximum reaction rate at 693 K and finally results in the formation of a polymeric end product of apparent composition $[\{(ANP)Cl\}RuO]_n$ at 923 K. The polymeric intermediate is almost stable up to 1273 K and only a 2% weight loss is observed from the TG curve in the temperature range 923–1273 K. There is fairly good agreement in the observed weight loss of 22.84% against the calculated value of 23.17% for the second stage of decomposition. Based on the above information, the following decomposition scheme may be proposed for the decomposition of the Ru(III) complex.

$$\text{Step I: } (ANP)_2Ru(AP)Cl \xrightarrow{373-638\ K} (ANP)_2RuCl \qquad (1)$$

$$\text{Step II: } (ANP)_2RuCl \xrightarrow{670-923\ K} [\{(ANP)Cl\}RuO]_n \qquad (2)$$

Decomposition of $(ANP)_2Pt(AP)Cl_2$

The TG and DTG curves of the Pt(IV) complex show a three-step decomposition pattern. The complex is stable up to 333 K after which the first stage of decomposition starts which continues up to 413 K with a maximum rate at 408 K. The residue at this stage has the apparent composition $(ANP)_2PtCl_2$. The weight loss is 25.00% whereas the calculated value is 24.60%. The loss of antipyrine ligand can be seen from the infrared spectrum of the intermediate isolated by the isothermal heating of the complex at 440 K for 6 h. This intermediate is stable up to 473 K. Beyond this temperature the second stage of decomposition starts, which continues up to 723 K resulting in the formation of a polymeric intermediate $[(ANP)\cdot PtOCl_2]_n$ (weight loss: observed, 20.20%; calculated, 18.20%). The rate of reaction is fast initially, decreases and then again accelerates. The DTG curves show two peak maxima for this decomposition step at 523 and 698 K. The polymeric intermediate formed at this stage is highly unstable and could not be isolated by heating the complex isothermally. The last stage of decomposition is observed between 723 and 1073 K, with a maximum at 988 K, and the end product is identified as $PtOCl_2$. The observed weight loss for this stage is 20.96% which is in good agreement with the calculated value of 21.13%. The infrared spectrum of the end product, obtained by heating the complex isothermally, at 1073 K for 4 h compares with that of $PtOCl_2$. On the basis of these observations, a three-stage decomposition of the Pt(IV) complex may be proposed as follows

Step I: $[(ANP)_2Pt(AP)Cl]Cl \xrightarrow{333\text{-}413\ K} (ANP)_2PTCl_2$

Step II: $(ANP)_2PtCl_2 \xrightarrow{473\text{-}723\ K} [(ANP)PtOCl_2]_n$

Step III: $[(ANP)PtOCl_2]_n \xrightarrow{723\text{-}1073\ K} PtOCl_2$

The mechanisms proposed here for the thermal decomposition of Ru(III) and Pt(IV) complexes are tentative and are based on the results obtained from dynamic thermogravimetric and isothermal studies. Thermoanalytical methods, like TG, which are dynamic processes, are inadequate for determining the exact composition of intermediates. The composition of the residues isolated in isothermal experiments may not agree with the apparent composition assigned by mass loss measurements during thermal analysis.

Kinetic parameters, such as apparent activation energy and order of reaction, for the first thermal decomposition step of Ru(III) and Pt(IV) complexes have been determined by the graphical method of Coats and Redfern [12]. The plot of $-\log[-\log(1-\alpha)/T^2]$ vs. $1/T \times 10^3$ for $n = 1$

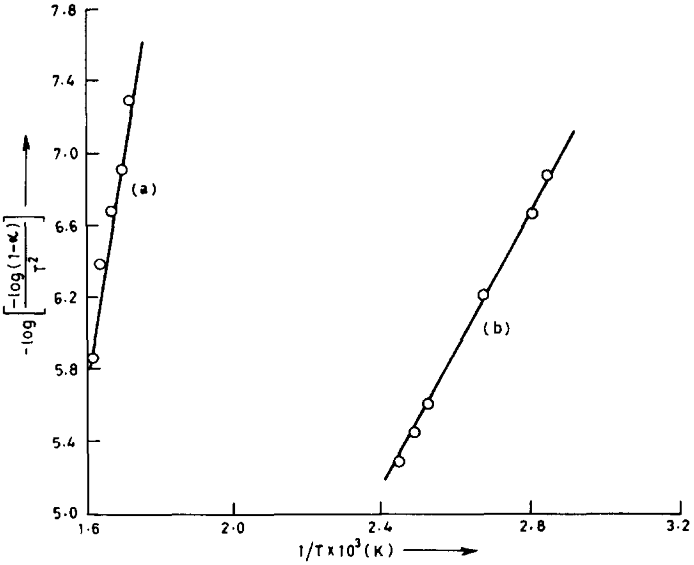


Fig. 2. Coats and Redfern linearisation curves of (a) Ru(III), (b) Pt(IV) complexes.

TABLE 2

Thermal analytical data of the complexes

Decomposition step	Temp. (K)	% weight loss		Activation energy E (kcal mol^{-1})	Order of reaction
		Obs.	Calcd.		
Decomposition of $(ANP)_2Ru(AP)Cl$					
Step I	373–638	29.92	29.62	61.95	1st
Step II	670–923	22.89	23.17		
Total % weight loss		52.76	52.79		
Decomposition of $(ANP)_2Pt(AP)Cl_2$					
Step I	333–413	25.00	24.60	17.89	1st
Step II	473–723	22.20	18.20		
Step III	723–1073	20.96	21.13		
Total % weight loss		66.16	65.18		

(where α is the fraction decomposed, T is the temperature in K and n is the apparent order of reaction) gives a straight line (Fig. 2) with a slope of $-E/2.303R$. The reason behind the calculation of kinetics for the first thermal decomposition step is exclusively thermal since the rate equation used is sensitive to the thermal properties of the sample and it is obvious that various thermal properties do not remain the same for the sample in the beginning and after first stage of decomposition. Hence, it is considered more accurate to calculate the kinetic parameters for the first stage decomposition reactions. The thermoanalytical data of the complexes are presented in Table 2.

CONCLUSION

It is evident from the thermoanalytical data that the Ru(III) complex is more stable than the Pt(IV) complex. The first stage of decomposition in both the complexes results in the loss of an AP molecule while in the second step the formation of a polymeric intermediate due to the partial decomposition of an ANP ligand is observed. The polymeric intermediate is almost stable in the case of Ru(III) up to 1273 K. However, in the case of the Pt(IV) complex, it is highly unstable and decomposes rapidly to $PtOCl_2$ in the next decomposition step. The order of reaction calculated for the first stage of decomposition, which results in the loss of an AP molecule, is found to be unity in both the complexes.

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