EFFECT OF SUBSTITUENTS ON THE STABILITY OF RHODIUM(III) COMPLEXES. I. METHYL AND SULPHUR SUBSTITUTED URACILS

JAMES R. LUSTY *

School of Chemistry, Robert Gordon's Institute of Technology, St. Andrew Street, Aberdeen AB1 1HG (Gt. Britain)

HARDY S.O. CHAN

Department of Chemistry, National University of Singapore, Kent Ridge 0511 (Singapore)

JAMES PEELING

Department of Chemistry, University of Petroleum and Minerals, Dhahran (Saudi Arabia)

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ABSTRACT

Complexes of rhodium(III) with the substituted nucleobases 6-methyluracil, 6-methyl-2-thiouracil and 2-thiouracil have been prepared. They have been subjected to thermal degradation studies and the pathway for decomposition has been correlated with their structure. The results are compared to other spectroscopic techniques using infrared and X-ray photoelectron spectroscopy. Comparative stabilities and substituent effects are discussed.

INTRODUCTION

The use of platinum complexes as antitumour agents has been established for some time [1,2]. Other group VIII transition elements have been used with some success, including some rhodium(III) complexes [3]. The interaction of platinum with uracil [4,5] and with some substituted uracils [6–8] has also received attention but apart from recent work on some thio-substituted derivitives [9,10] the interaction of uracil and substituted uracils with other metals of the second and third row transition block has been largely neglected. Base coordination to the metal will be strongly influenced by any ring substituents and this has been considered both in our laboratories and in published work elsewhere [11,12]. As part of our studies on base substituents we have looked at the effect on complex stability of sulphur and

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* Author to whom correspondence should be addressed.

methyl group substitution in a uracil ring. Previously we synthesised a series of complexes with platinum(II), palladium(II), iridium(III) and rhodium(III) with 6-methyl-2-thiouracil as a ligand [9]. We wish to report here the extension of that study and the use of thermal analysis as a collaborative technique. This approach has been used very successfully by us in recent studies on some xanthine complexes of platinum [13,14].

EXPERIMENTAL

The ligands 6-methyl-2-thiouracil (mtu), 6-methyluracil (mu) and 2-thiouracil (tu) were obtained commercially from Fluka Chemicals; rhodium trichloride was obtained from Johnson Matthey Chemicals and these starting materials were used without further purification. The complexes, [Rh(mtu)$_3$Cl$_3$], [Rh(mu)$_3$]Cl$_3$ and [Rh(tu)$_3$Cl$_3$] were prepared following the method described previously for the first complex [9]. The XPS were recorded on an AEI ES-200B spectrometer and the thermal analysis was conducted using a Perkin-Elmer TGS-1 thermal balance at $10°C$ min^{-1}, in static air. Infrared spectra were run using Perkin-Elmer 180B and 567 recording spectrophotometers.

RESULTS AND DISCUSSION

The prepared complexes and their analytical data are given in Table 1.

Thermal analysis

A tris chelating ligand complex with associated partially bound chlorine was previously advocated [9] for [Rh(mtu)$_3$Cl$_3$]. This type of loosely bound

TABLE 1

Analytical results

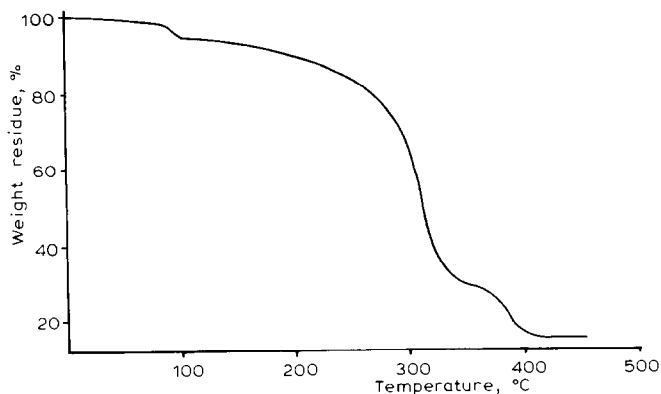| Complex formula	Found (calculated) (%)			Ligating atoms
	C	H	N	
[Rh(mtu)$_3$Cl$_3$]	28.1 (28.4)	2.84 (2.86)	13.0 (13.3)	N(3), C(2)=S
[Rh(mu)$_3$]Cl$_3$	30.5 (30.6)	3.09 (3.31)	14.1 (14.3)	N(1), C(2)=O
[Rh(tu)$_3$Cl$_3$] [a]	24.3 (24.3)	2.50 (2.04)	15.6 (14.2)	C(2)=S

[a] Sulphur 16.7% (16.2%).

Fig. 1. Thermogram for [Rh(mtu)$_3$Cl$_3$].

chlorine has been suggested by others for some thymine–ethylenediamine complexes of platinum [15] and we have recently found a similar behaviour in dithiouracil complexes of rhodium [10].

The thermogram of [Rh(mtu)$_3$Cl$_3$] is given in Fig. 1. It shows a three-stage decomposition pathway and clearly differs from the complex [Rh(mu)$_3$]Cl$_3$ (Fig. 2), which shows a sharp decomposition temperature at about 300°C. The initial loss (6.10%), in [Rh(mtu)$_3$Cl$_3$], corresponds to the partial loss of chlorine (one mole of chlorine per mole of complex would give a theoretical loss of 5.95%). This agrees with the evidence reported previously [9]. The major decomposition follows immediately and results in the removal of the methylthiouracil ligands and the remaining chlorine. Attempts to isolate the intermediate complex have so far proved unsuccessful. [Rh(mu)$_3$]Cl$_3$ does not show the same degradation pattern. Decomposition, although occurring at a similar temperature, is a single-stage process, without any prior chlorine
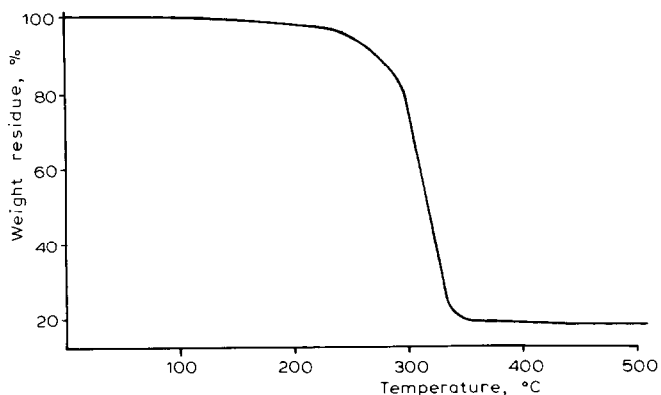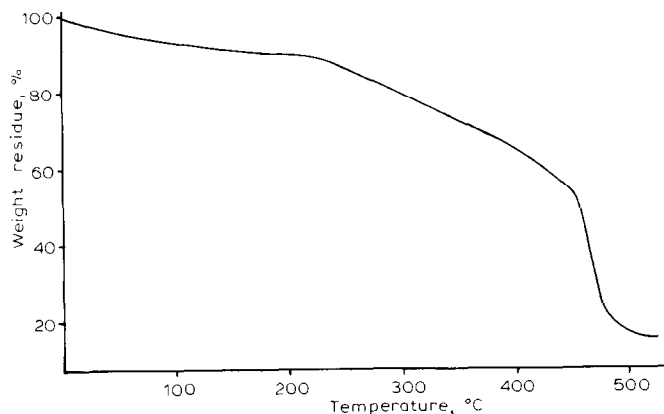

Fig. 2. Thermogram for [Rh(mu)$_3$]Cl$_3$.

Fig. 3. Thermogram for [Rh(tu)$_3$Cl$_3$].

elimination. The chlorine is present in the same form, either coordinated, with a monodentate uracil ligand or ionically, with the uracil ligands acting as a chelating species. From the infrared discussion to follow it is apparent that the chlorine is present in the ionic form. This was also shown by the rapid, quantitative precipitation of chlorine when this complex was treated with silver nitrate.

The decomposition of the complex with 2-thiouracil as the ligand (Fig. 3) showed a three-stage process. The initial loss of two moles of water occurred, followed by the loss of two moles of ligand per mole of the complex (actual weight loss 47.2%, theoretical loss 46.4%). The ligand is monodentate with the chorine bound to the metal to give a distorted octahedral complex. Of the three complexes studied this is the only one that exhibits monodentate ligand behaviour.

Spectroscopy

The infrared spectra for the 1800–1200 cm^{-1} region are shown in Fig. 4, together with the parent ligands. In the complex involving 6-methyl-2-thiouracil the formation of the iminol tautomer and coordination through the N(3) and the C(2)=S positions was previously demonstrated from the infrared spectrum (in particular the disappearance of the N(3)–H band, and the changes in the C=S bands), and from the XPS [9]. However, the infrared spectrum of tris(6-methyluracil)rhodium(III) chloride still shows a very distinctive band at 1420 cm^{-1}, due to δ(N(3)–H) and thus the N(3) position cannot be involved in bonding. However, the N(1)–H deformation mode at 1510 cm^{-1} has disappeared. This is similar to the behaviour for the platinum and palladium complexes of 6-methyl-2-thiouracil [9]. The iminol form is predicted, as ionisation of the thiouracil has not taken place. Similarly, a broadening of the O$_{1s}$ peak in the X-ray photoelectron spectrum
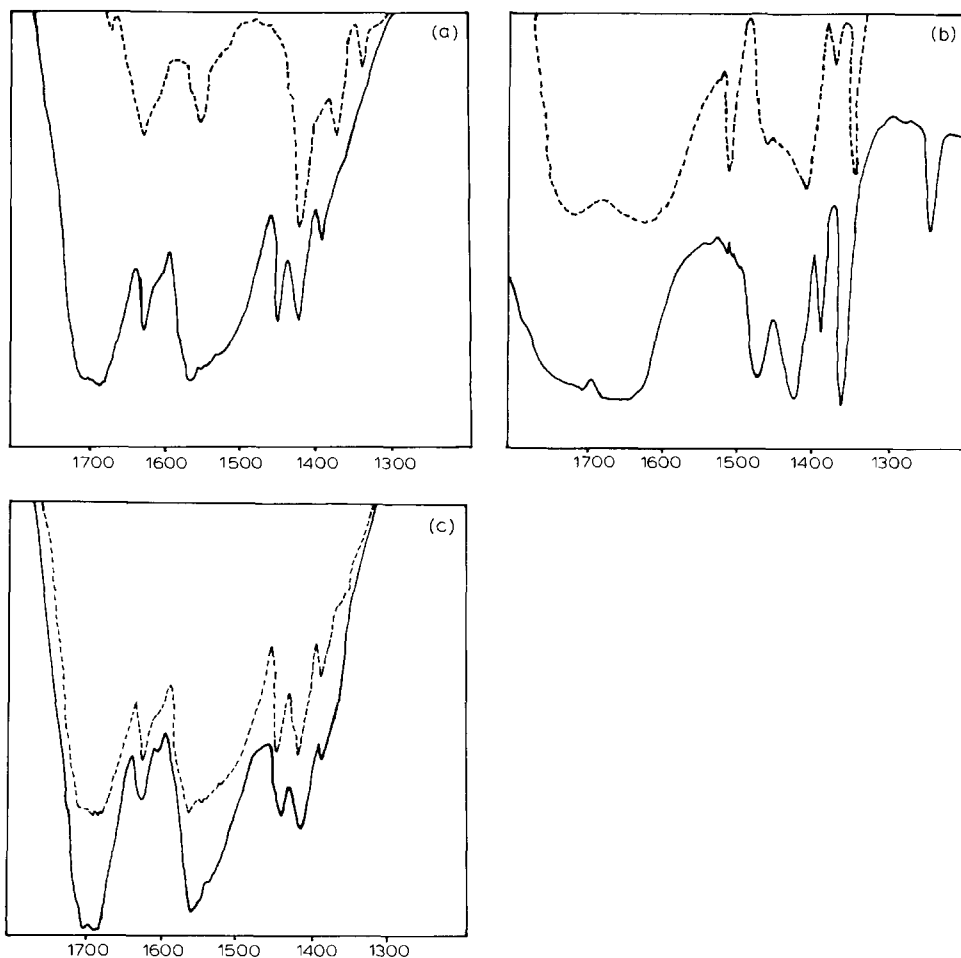
Fig. 4. Infrared spectra of the ligands and their complexes: (a) mtu and [Rh(mtu)$_3$Cl$_3$]; (b) mu and [Rh(mu)$_3$]Cl$_3$; (c) tu and [Rh(tu)$_3$Cl$_3$]; (— — — —) ligand; (———) complex.

of the anhydrous complex, compared to the sharper peak in the parent ligand, indicates the possible existence of the iminol form. The existence of two non-equivalent forms of nitrogen is confirmed from the XPS, by the observation of a non-centrosymmetric peak with a mean binding energy 0.4 eV above the parent ligand. This can be explained if one of the nitrogens present is coordinated. The carbonyl bands at 1720 and 1650 cm^{-1} are both reduced in intensity and the latter band, due to ν(C(4)=O), is split into two components. The ν(C(2)=O) band at 1720 cm^{-1} shows the greatest reduction and we have assumed this is an indication of coordination. The band at 1650 cm^{-1} is a composite band, consisting of both carbonyl and ν(C=C) components. The ligand is thus bound using the N(1) position and the C(2)=O position. We have not found any evidence from either the infrared

or the XPS to show that the chlorine is bound and, thus, the complex has been assigned as a cationic tris-chelating complex with ionic chloride.

The complex with 2-thiouracil is assigned as a tris(monodentate) trichloro complex on the basis of the infrared spectra, and the thermal analysis data presented earlier. The (C=S) bands were the only modes to show change and the N(1)–H band and the N(3)–H band showed no difference in their spectra. This is in contrast [16] to the platinum and palladium complexes which were shown to have bidentate ligand behaviour.

In conclusion it can be observed that the effect of sulphur on the coordination is to change the coordinating sites with rhodium. The use of sulphur as a ligand is expected and can be thought of in terms of hard and soft acid–base behaviour, with the second and third row transition metal ions generally preferring the softer bases as ligands, as demonstrated by sulphur.

The most likely form of coordination for uracil with a range of first row transition metals was thought to be the C(4)=O position [17], while complexes of platinum with uracil have been shown to use both the N(1) and the N(3) positons [4]. Both the nitrogens have been utilised in these rhodium(III) complexes, as well as the C(2)=O position, although we have not observed any evidence for C(4)=O coordination. The absence of the methyl group allows the chlorine to enter the coordination sphere of the metal, and its influence seems to be confined to a steric role.

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