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Complexes of 6-Methyl-2-thiouracil with Rhodium, Iridium, Platinum and Palladium

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Complexes of 6-methyl-2-thiouracil with rhodium iridium, platinum and palladium have been prepared. The infrared spectra of the complexes have been investigated, and the results compared to other pyrimidine-transition metal complexes. The prepared complexes consisted of either two or three moles of ligand coordinated to the metal ion, in square planar or octahedral symmetry. From the infrared it is apparent that the ligands have ambidentate behaviour. ESCA spectra have been obtained and preliminary results are presented as a method of investigating such complexes.

Introduction

Since the discovery that *cis*-dichlorodiammineplatinum(II) acted as an anticancer agent [1] there has been a great deal of interest in platinum complexes in particular, and group VIII transition metal complexes generally. A wide range of nucleic acid substituents has been used to produce complexes of medicinal interest. It has been found that 6-mercaptopurine is an excellent ligand to platinum, palladium [2] and copper [3]. Recently several metal complexes with this ligand have been reported [4] showing that sulphur coordinates preferentially, with the N(7) atom acting as a chelate on some occasions. Complexes with thiosubstituted pyridimidones have also been reported for some first row transition metals [5]. The thiouracils, 2- and 4-thiouracil and their 5X- and 6X-substituted derivatives have been used as ligands with a variety of transition metals [6–8], including some group VIII transition metals [7]. These ligands have several modes of coordination available to them, binding to the metal through either the N(1), S, N(3) or the carbonyl oxygen at C(4), or a combination of these. Khuller *et al.* advocated polymeric bidentate complexes in all but the monomeric square planar platinum(II) complex [6, 7], whereas other authors have preferred either discrete monodentate or bidentate complexes. The crystal structure of the octahedral Co(pyrimidine-2-thione)$_2$Cl$_2$ shows there to be considerable distortion involved in bidentate coordination [9]. Recent magnetic studies [10] on some 5X-substituted uracil copper(II) complexes supports bidentate coordination, in this case involving N(1) and C(2)=O positions. When the N(1) position is blocked with a methyl group coordination to platinum(II) occurs through the N(3) and C(4)=O and results in a dimeric bridging compound [11].

Because of the limited infrared data available on the thiouracil complexes we synthesised compounds with thiouracil as a ligand and compared them to similar uracil complexes. We report here the spectral study and also some preliminary infor-

TABLE I. Analytical Results.

Complex	Colour	Found (%)			Calculated (%)		
		C	H	N	C	H	N
Rh(L)$_3$Cl$_3$	orange	28.1	2.84	13.0	28.4	2.86	13.3
Ir(L)$_3$Cl$_3$	yellow	25.5	2.70	10.4	24.9	2.51	11.6
Pt(L$^-$)$_2$	yellow	25.9	3.2	12.7	25.1	2.10	11.8
Pd(L$^-$)$_2$	orange/brown	30.8	3.00	14.1	30.9	2.59	14.4

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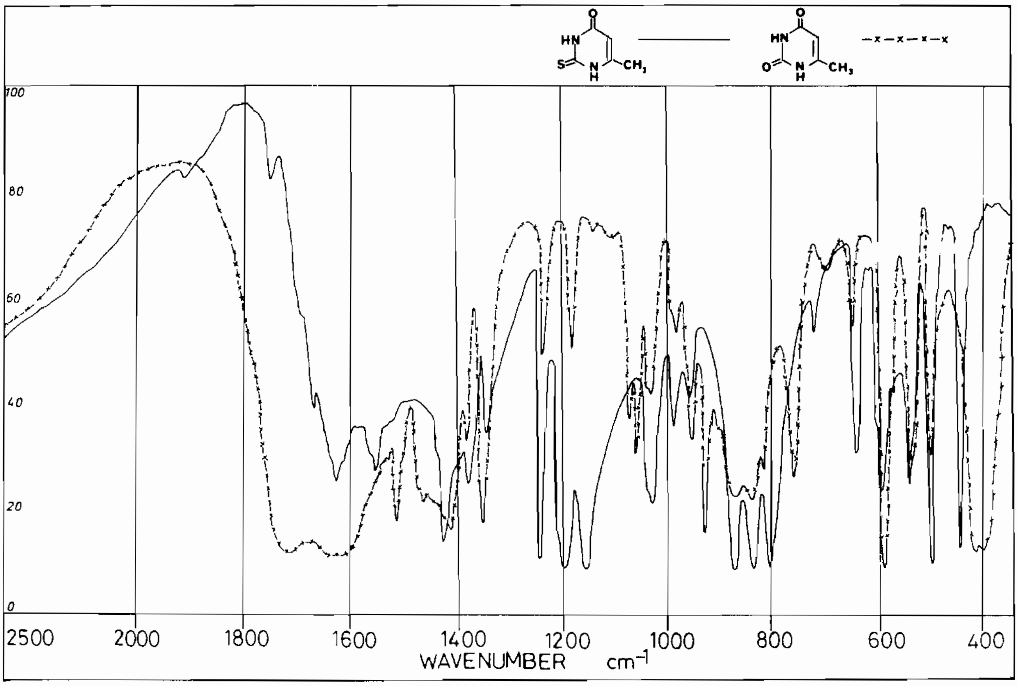


Fig. 1. Infrared spectra of 6-methyl-2-thiouracil and 6-methyluracil.

TABLE II. Infrared Spectra.

Assignment	6-methyl-2-thiouracil	$Rh(L)_3Cl_3$	$Ir(L)_3Cl_3$	$Pt(L^-)_2$	$Pd(L^-)_2$
ν(N–H) and	3100mb			3180m	3120m
ν(C–H)	3080m				2980w
ν(C(2)=O)	absent				
ν(C(4)=O)	1670m	1710sh	1710sh	1630s	1690w
and	1625s	1670sh	1675s		1665sh
ν(C=C)	1620sh	1648s	1650w		1632s
ν(C=S)	1560w	1570s	1565s	1560s	
(see text)	1550s	1555s	1555s	1550s	1548s
δ(N(1)–H)	1510w	1510vw	1510vw		
δ(N(3)–H)	1415s	1415w		1425s	1418s
					1400m
δ(C–H)	1380m	1380w	1395m	1385m	1375w
δ(C–H)	1190s	1190s	1190s	1195s	1193s
(C=S)	1160s	1168s	1170s	1165s	1165s
(see text)				1158s	
ν(C=S)	805s			802m	800m
	650s	650w		638w	
δ ring	590s	595m	610w	590s	590s
and	552s	550m	555m	552m	545m
δ(C=O)	508s	510m	510m	510s	510s
	450s	450s	452s	452s	450s
		362m	362m	365w	365w
	338s	335m	335m	335m	335w
ν(M–L)				310w	
	295m	295m	295m		
	270s	270m	270w	270s	
ν(M–L)	258m	260m			
	243s	243s	248s		
	220s	220s	220s		

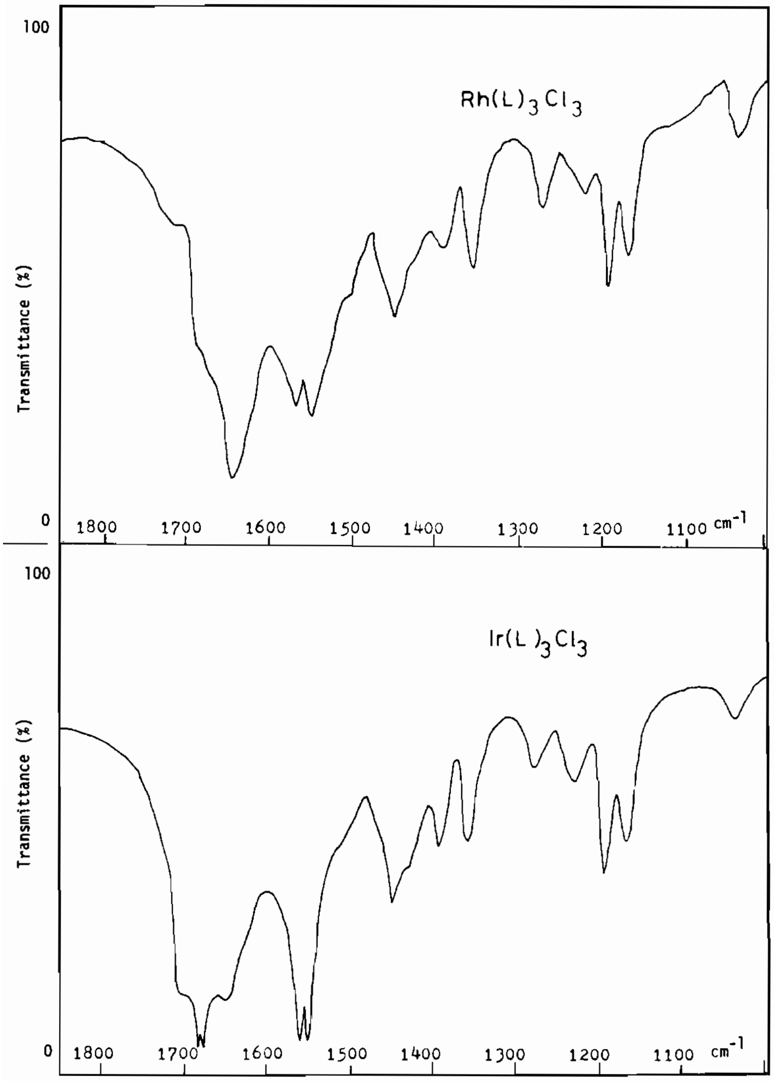


Fig. 2. Infrared spectra of the rhodium and iridium complexes.

mation concerning the ESCA of these complexes which has helped to determine the modes of coordination of the ligands.

Results and Discussion

A series of complexes using Rh(III), Ir(III), Pt(II) and Pd(II) have been prepared with the ligand 6-methyl-2-thiouracil. A complex with Rh(III) and 6-methyluracil had been synthesised previously and was used for comparison [12]. With the trivalent metal ions the ligand–metal ratio is 3:1 and it is 2:1 with platinum and palladium (Table I). Attempts to isolate complexes with other ratios, using the same preparative method, have proved unsuccessful. All the products involve some degree of bidentate coordination of the base. From the electronic spectra it is apparent that they involve either distorted octahedral (rhodium and iridium) or square planar symmetry (platinum and palladium). Samples were run in the infrared between 4000–400 cm^{-1} using nujol mulls and KBr plates or between 4000–180 cm^{-1} using CsI discs. The region 2500–400 cm^{-1} is shown for the free ligand and for 6-methyluracil in Fig. 1, and the region 1800–1000 cm^{-1} for the thiouracil complexes in Figs. 2 and 3. It is in this region that the carbonyl and thiocarbonyl stretches and N–H deformation modes occur. The major assignments are given in Table II although some ring modes have been omitted for clarity. Our assignments are in partial disagreement with some recently published copper(II) complexes [8] and the data published previously on the group VIII complexes [7]. Our assignments were obtained by a comparison of the infrared spectra of two bases, 6-methyl-2-thiouracil

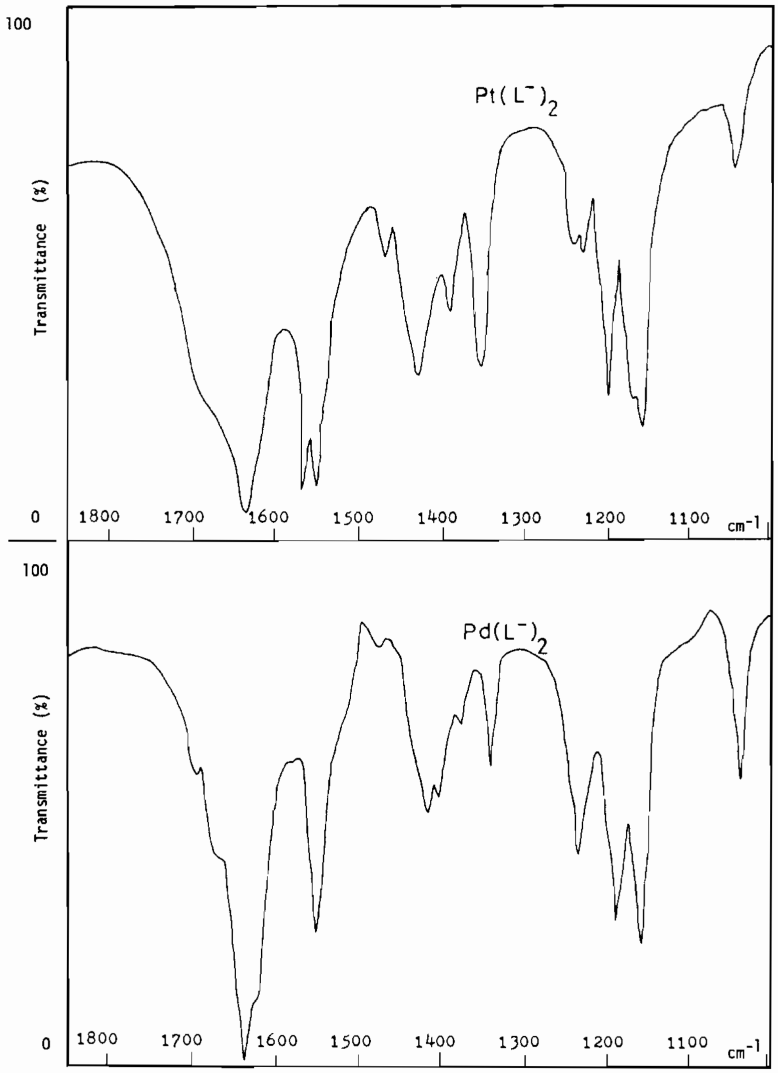


Fig. 3. Infrared spectra of the palladium and platinum complexes.

and 6-methyluracil, their complexes, and previously published spectral data on uracil [13] - and 2,4-dithiouracil [14]. The compounds give two distinct types of behaviour and will be discussed separately. Finally the ESCA spectra were recorded of these compounds and complemented the infrared data in showing that the complexes coordinated through different arrangements of atoms.

Rhodium and Iridium Complexes

On coordination the high frequency ν(N–H) band disappears. Bands at 3400 cm^{-1} could indicate water of crystallisation but none was apparent from the analytical results. The band at 1625 cm^{-1} in the free base due to ν(C=C) and ν(C(4)=O) shifts to higher frequency and the neighbouring nitrogen deformation mode, δ(N(3)–H) either disappears (iridium) or is very much reduced in intensity. This indicates nitrogen coordination. However, other changes occur and a study of the three thiocarbonyl bands of the ligands, at 1550 cm^{-1}, which shows considerable splitting, at 1160 cm^{-1}, which is a very strong band, and at 805 cm^{-1} indicate that sulphur is also involved in coordination. The ν(C=S) band at 805 cm^{-1} disappears in the complexes while that at 1160 cm^{-1} (having some ν(C–N) and ν(C=C) character [15]) is shifted to higher frequency by about 10 cm^{-1} and the intensity of the peak is reduced, compared to the neighbouring peak at 1190 cm^{-1}, which appears as the stronger peak in the free ligand. The centre of the band at 1550 cm^{-1} also moves to higher frequency. This implies some sulphur interaction with the metal. It is very difficult to attach much importance to the δ(N(1)–H) band as it is so weak (unlike the corresponding band in the 6-methyluracil complex). How-

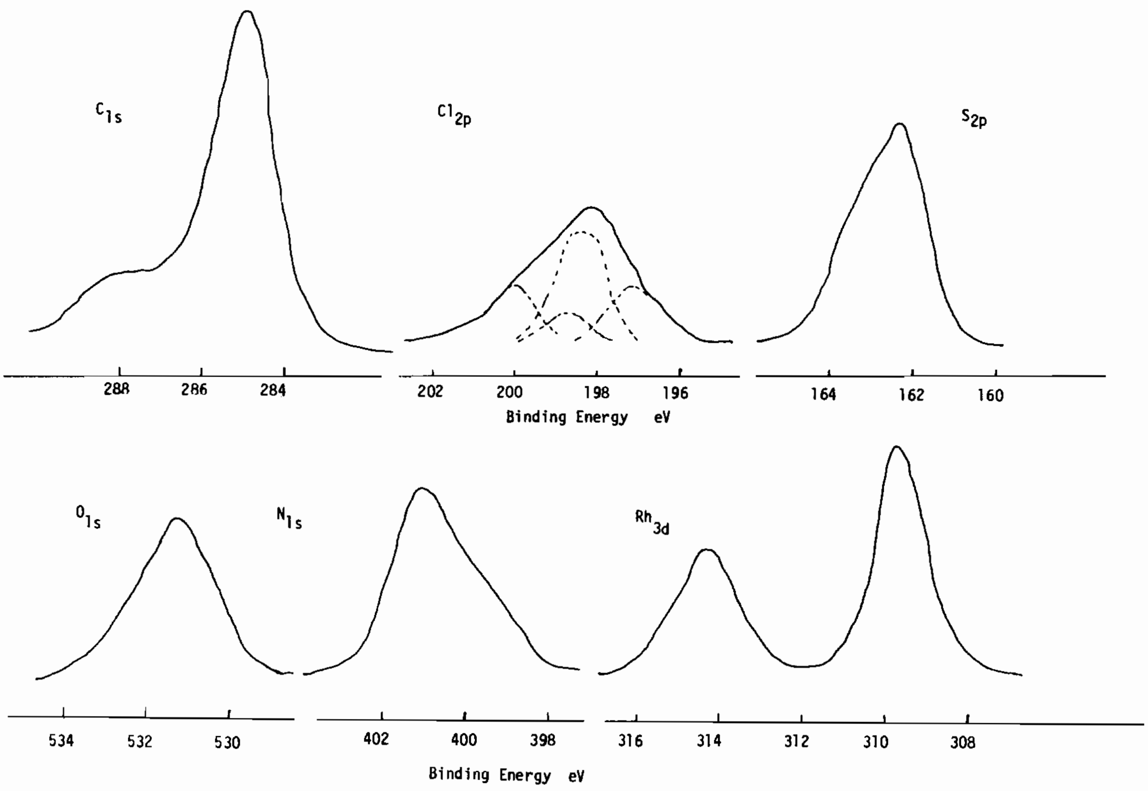
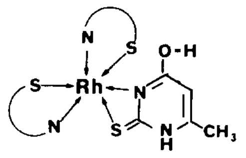


Fig. 4. ESCA spectrum of $Rh(L_3)Cl_3$.

ever in both complexes, unlike the platinum and palladium ones, it is still possible to observe this band with no apparent change in position or intensity. Total deprotonation of both nitrogen atoms is certainly not observed. Metal–ligand stretches at 258 cm^{-1} and 260 cm^{-1} have been assigned to ν(Rh–N) and ν(Ir–N) respectively. It would be easy to explain the structure as a tris(6-methyl-2-thiouracil)metal(III) chloride complex. However analysis by precipitation of the free chloride indicates that at least part of the chloride present is bound in some way. The ESCA spectra of these complexes (Fig. 4) gives a similar result, with very little shift recorded in the binding energy when compared to coordinated chlorines, in compounds such as $[Pt(NH_3)_2Cl_2]$. If deprotonation at N(3) has taken place, then consideration of the charges involved requires that the chlorine should not be present, unless the proton is relocated within the ring. Although this type of coordination without deprotonation is unusual it is not unique [2, 7]. The existence in solution of tautomeric forms of uracil and the thiouracil ions has been reported [16]. The ESCA spectrum shows a broad oxygen peak (Fig. 4), suggesting an O–H or O- - -H group as a possibility, as we observed in the infrared. Similarly the ratio of the peaks in the carbon band is unexpected when compared to the ligand. The occurrence of a C–OH could account for this behaviour. The absence of a band between 2650 cm^{-1} and 2550 cm^{-1} precludes th presence of a mercaptan tautomer. Two possibilities exist for the structure: a tris-ligand complex where the ligand is bidentate with the H–Cl molecules hydrogen bonded to the ligand, or a bidentate arrangement of the ligands in the hydroxy form with the chloride ions electrostatically held to this hydroxy group.

Platinum and Palladium Complexes

Coordination in these two complexes differs from the previous two in several ways. The infrared contains a band at 3180–3120 cm^{-1} (ν(N(3)–H) and the strong δ(N(3)–H) is still present but is split with components recorded above the original value of 1415 cm^{-1}. The absence of the δ(N(1)–H) band at 1510 cm^{-1} implies coordination through this atom. The thiocarbonyl bands at 1560 cm^{-1} and 1160 cm^{-1} show slightly smaller shifts than in the rhodium and iridium complexes. The band at 1160 cm^{-1} has a similar intensity to that observed in the free ligand, unlike the previous complexes. No tautomeric rearrangement is expected here as deprotonation at N(1) has taken place. Less change occurs as the ν(C–N) and ν(C=C) components of this band



[Rh(6-methyl-2-thiouracil)$_3$]

Fig. 5. Proposed structure for $Rh(L)_3Cl_3$.

should be similar in intensity to those in the free ligand. The band at 805 cm^{-1} is reduced in intensity and moves to lower frequency by several wavenumbers. Both ligands are ionised and the complexes may thus be designated as being square planar complexes involving coordination through the N(1) and C(2)=S. The ESCA spectra indicate that the sulphur is bound more strongly in these two complexes than in the rhodium and iridium ones. This is in accordance with the relative character of the metals, platinum and palladium being classified as type 'b' metals, preferring soft type 'b' ligands such as sulphur. Nitrogen, a type 'a' ligand, would be expected to coordinate to the harder transition metals such as rhodium(III). Sharper bands are also recorded for the oxygen and carbon peaks, indicating, we believe, that the ligand is present in the carbonyl form.

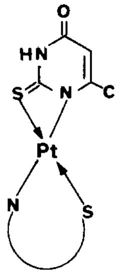
In conclusion, we have synthesised new complexes of the group VIII transition metals and characterised their modes of coordination. In the case of rhodium and iridium with 6-methyl-2-thiouracil the ligand acts as a bidentate chelate using the N(3) and C(2)=S positions (Fig. 5); with platinum and palladium the ligand forms a four membered ring using the N(1) and S atoms (Fig. 6). We have also reported assignments in the infrared which were not recorded or were reported erroneously.

Experimental

According to the methods reported in the literature *cis*-$[Pt(NH_3)_2Cl_2]$ and *trans*-$[Pd(NH_3)_2(NO_2)_2]$ were synthesised [17, 18]. The ligand was obtained commercially and used without further purification. Infrared spectra were recorded on a Perkin-Elmer 180B spectrophotometer. Microanalyses were carried out by the Analytical Services Laboratory, University of Petroleum and Minerals. The ESCA spectra were recorded on an AEI ES-200B.

[Rh(L)$_3$Cl$_3$] and [Ir(L)$_3$Cl$_3$]

To a solution of 20 mmol of the metal chloride $MCl \cdot 3H_2O$ in 25 cm^3 of acidified (HCl) ethanol, 60 mmol of the ligand, which had previously been suspended in 10 cm^3 ethanol was added. The solution was refluxed for 6 hours. On cooling the solution, orange and yellow crystals, respectively, precipitated out. They were filtered and washed with ice-cold ethanol and dried *in vacuo.*



[Pt(6-methyl-2-thiouracil)$_2$]

Fig. 6. Proposed structure for $Pt(L^-)_2$.

[Pt(L$^-$)$_2$] and [Pd(L)$_2$]

To a solution of the diammine complex in ethanol a 1:1 and 1:2 stoichiometric ratio of the ligand was added. The solution was refluxed for several hours before a precipitate occurred. The solution was filtered while hot and the compounds washed with cold ethanol and dried *in vacuo.* Further material was obtained by using a vacuum rotary evaporator to remove the excess solvent. Only complexes with a 1:2 ratio were formed.

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