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THERMAL STUDIES ON PLATINUM METAL COMPLEXES OF *N*-METHYLCYCLOHEXYL DITHIOCARBAMATE

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ABSTRACT

Platinum metal complexes of *N*-methylcyclohexyl dithiocarbamate of the type $[\mathrm{MecyhxNCS_2}]_n\mathrm{M}$ [cyhx = cyclohexyl; M = Pd, Pt ($n = 2$); Ru, Rh, Ir ($n = 3$); Os ($n = 4$)] have been synthesised. Spectral studies (IR and UV) indicate that the dithiocarbamate moiety is bidentate. From thermogravimetric (TG) curves, the order and activation energy of the thermal decomposition reaction have been elucidated. The variation of activation energy has been explained on the basis of hard and soft acid base (HSAB) theory. From differential thermal analysis (DTA) curves, the heat of reaction has been calculated.

INTRODUCTION

The dithiocarbamate functionality is known to exhibit many biochemical features [1]. Thus, many new ligands have been designed to test various hypotheses regarding biological properties, in particular the fungicidal and pesticidal activity of their metal complexes [2]. To investigate this effect, we synthesised some platinum metal complexes of *N*-methylcyclohexyl dithiocarbamate and studied their thermal characteristics. This followed directly from our previous investigation on the thermal behaviour of metal ion–biomolecule systems [3–5].

Yet another reason for the growing interest in studies of metal–dithiocarbamate complexes is to investigate the bonding mode of the ligand to the metal ion. The dithiocarbamate moiety can behave as both a monodentate and a bidentate ligand. The two bonding modes are distinguished by IR studies. The present complexes exhibit only one strong band at ca. 1000

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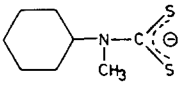
cm^{-1}, supporting the bidentate nature of the dithiocarbamate group, a doublet being expected in the case of monodentate behaviour [6].



In the UV region, the complexes show an intense band at ca. 39 000 cm^{-1} (log $\epsilon = 6.8$) arising due to the $\pi-\pi^*$ transitions of the N$\overset{...}{-}$C$\overset{...}{-}$S chromophore [7]. Another band which is expected to occur at ca. 31 200 cm^{-1}, and is associated with the inequivalence of C$\overset{...}{-}$S bonds, tends to disappear, showing that the dithiocarbamate ligand is bidentate [8].

It is thus evident from IR and UV studies that the *N*-methylcyclohexyl dithiocarbamate ligand shows S–S bidentate chelation. In this communication we report the results of TG and DTA interpretations for some platinum metal dithiocarbamate complexes.

EXPERIMENTAL

The following instruments were used: Shimadzu infrared spectrophotometer, IR-435, for IR spectra; Perkin–Elmer UV–visible spectrophotometer, model 554, for UV spectra; G-70 thermoanalyser, Setaram (Lyon, France), for TG studies up to 1173 K; Mettler DTA 2000 (Zurich, Switzerland) for DTA studies up to 673 K. Both TG and DTA studies were carried out in a dynamic nitrogen atmosphere, at a flow rate of 10^3 cm^3 min^{-1}, a heating rate of 7 ° C min^{-1} and a chart speed of 30 cm h^{-1}.

Platinum metal salts, $RuCl_3$, $RhCl_3$, $PdCl_2$, $IrCl_3$, $(NH_4)_2OsCl_6$ and K_2PtCl_4, were purchased from Fluka AG, Switzerland. Sodium *N*-methylcyclohexyl dithiocarbamate was prepared by the method of Gilman and Blatt [9].

The metal complexes were prepared by adding an aqueous solution of the appropriate metal salt to an aqueous solution of the ligand in stoichiometric proportions and stirring the mixture for ca. 15 min at 0–5 ° C. In the case of the platinum(II) complex, however, the contents were warmed on a water bath for 15 min. The precipitate so obtained was washed with cold water and aqueous ethanol and recrystallised from acetone solution. The osmium(IV) complex was obtained by the reaction of $(NH_4)_2OsCl_6$ and the ligand in a 1 : 5 molar ratio in aqueous methanol after a reaction time of 3 h.

RESULTS

The TG and DTA curves are shown in Figs. 1 and 2 respectively.

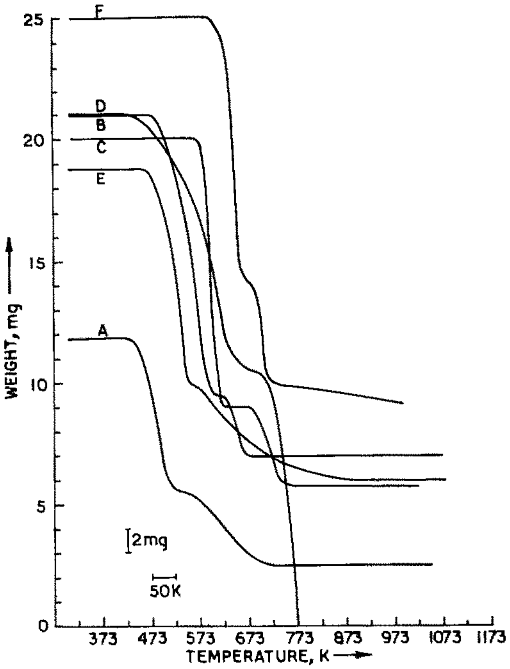


Fig. 1. TG curves for (A) Ru^{III}, (B) Rh^{III}, (C) Pd^{II}, (D) Os^{IV}, (E) Ir^{III} and (F) Pt^{II} dithiocarbamate complexes.

[MecyhxNCS$_2$]$_3$Ru

The complex is thermally stable up to 448 K and undergoes decomposition beyond this temperature, as indicated by the first weight loss step in the TG curve. The weight loss at 553 K corresponds to the formation of Ru_2S_3. Beyond 573 K, continuous weight loss in the TG curve has been observed up to 763 K, which corresponds to the decomposition of Ru_2S_3 to non-stoichiometric sulphides.

The DTA profile shows two endothermic peaks at 483 K and 518 K, corresponding to the decomposition of the complex to form Ru_2S_3. The endothermic thermal effect at 593 K corresponds to the decomposition of Ru_2S_3.

[MecyhxNCS$_2$]$_3$Rh

The weight loss in the TG curve commences at 473 K and shows a break at 603 K, corresponding to the formation of Rh_2S_3. Further weight loss up to 673 K corresponds to the decomposition of Rh_2S_3. There is no weight loss beyond 673, but the composition does not correspond to the formation of metallic rhodium. It is inferred that the non-stoichiometric metal sulphides are possibly the end products. The DTA curve shows two endothermic

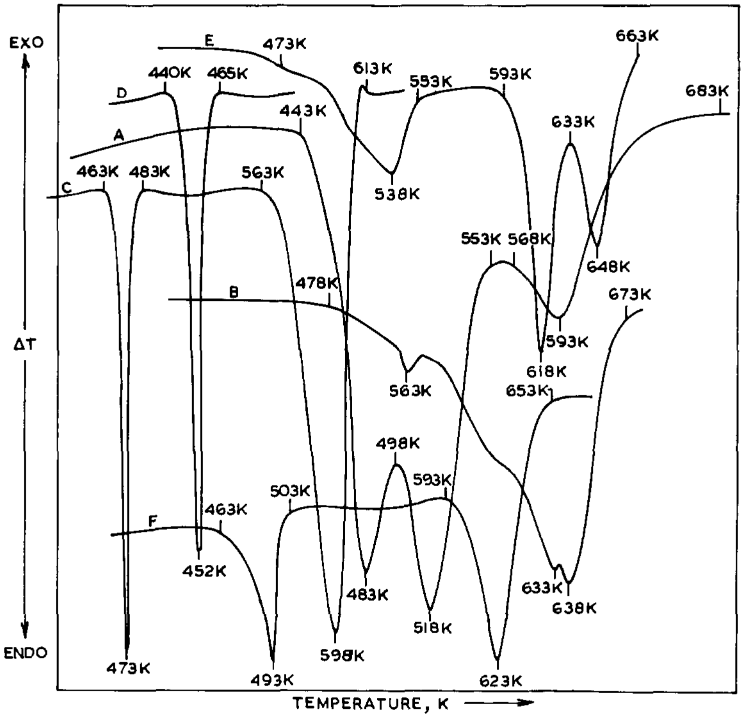


Fig. 2. DTA curves for (A) Ru^{III}, (B) Rh^{III}, (C) Pd^{II}, (D) Os^{IV}, (E) Ir^{III} and (F) Pt^{II} dithiocarbamate complexes.

peaks, at 563 K and 638 K. The former corresponds to the decomposition of the complex to Ru_2S_3 and the latter to the decomposition of the sulphide.

[MecyhxNCS$_2$]$_2$Pd

The TG curve indicates that the mass change begins at 463 K and continues up to 618 K. The weight loss corresponds to the formation of $Pd(SCN)_2$. The next decomposition step occurs in the temperature range 673–748 K and corresponds to the formation of PdS.

The DTA profile shows two sharp endothermic thermal effects. The first, at 473 K, corresponds to the melting of the complex, while the second, at 598 K, corresponds to the decomposition of the complex to $Pd(SCN)_2$.

[MecyhxNCS$_2$]$_4$Os

The TG of this complex reveals a weight loss in the temperature range 424–673 K, corresponding to the formation of Os_2S_3. Above 673 K, Os_2S_3 slowly volatilizes. At 773 K, the volatilization is complete and the crucible of the thermobalance is empty.

The DTA curve shows a sharp endothermic peak with $T_{max} = 452$ K, corresponding to the decomposition of the complex to Os_2S_3.

$[MecyhxNCS_2]_3Ir$

The complex is thermally stable up to 463 K. The weight loss in the temperature range 465–553 K corresponds to the decomposition of the complex to Ir_2S_3. After a small break, the TG curve shows continuous weight loss up to 873 K. This step, however, does not correspond to the formation of metallic iridium. The non-stoichiometric sulphides are probably formed.

The DTA profile shows an endothermic peak at 538 K, corresponding to the decomposition of the complex to Ir_2S_3. The thermal degradation of the latter is indicated by two endothermic peaks at 618 K and 648 K.

$[MecyhxNCS_2]_2Pt$

The TG curve shows an initial weight loss in the temperature range 463–658 K, corresponding to the decomposition of the complex to $Pt(SCN)_2$. This is followed by another weight loss in the temperature range 673–728 K, due to the thermal decomposition of $Pt(SCN)_2$ to PtS. Beyond 728 K, PtS slowly decomposes to metallic platinum.

The DTA curve shows two endothermic thermal effects, at 493 K and 623 K. The former corresponds to the melting of the complex, and the latter to its decomposition to $Pt(SCN)_2$.

DISCUSSION

The results of TG and DTA evaluations are presented in Table 1. The TG studies reveal that the Ru^{III}, Rh^{III}, Os^{IV} and Ir^{III} complexes yield the respective metal sulphides, Ru_2S_3, Rh_2S_3, Os_2S_3 and Ir_2S_3, at the end of the first decomposition step. Subsequently, the TG curves show little arrest, followed by continuous weight loss in each case; Os_2S_3 is completely volatile and leaves the crucible empty, while Ru_2S_3, Rh_2S_3 and Ir_2S_3 each lose a significant amount of sulphur as the temperature is raised. However, even at 1173 K the pure metals are not obtained. This is attributed either to the incomplete decomposition of these sulphides or to the formation of non-stoichiometric sulphides. The first step decomposition of Pd^{II} and Pt^{II} complexes results in the formation of the respective thiocyanates, $Pd(SCN)_2$ and $Pt(SCN)_2$. The former decomposes to PdS, the latter to PtS.

From the TG curves, the order n and activation energy E_a of the thermal decomposition reaction have been elucidated by the method of Coats and

TABLE 1

Thermal data

Complex	TG			DTA	
	Temp. range (K)	n	E_a (kJ mol^{-1})	T_{max} (K)	ΔH (kJ mol^{-1})
$[MecyhxNCS_2]_3Ru$	448–553	1	391	483, 518	59.87
	573–763	–	–	593	–
$[MecyhxNCS_2]_3Rh$	473–603	1	382	563	53.19
	620–673	–	–	638	–
$[MecyhxNCS_2]_2Pd$	463–618	1	857	473	36.54
	673–748	–	–	598	–
$[MecyhxNCS_2]_4Os$	424–673	1	211	452	31.53
	690–773	–	–	–	–
$[MecyhxNCS_2]_3Ir$	465–553	1	419	538	23.73
	593–873	–	–	618, 648	–
$[MecyhxNCS_2]_2Pt$	463–658	1	1314	493	21.31
	673–728	–	–	623	–

Redfern [10]. The linearisation curves are shown in Fig. 3. The order of reaction in each case is unity.

The E_a values of the Ru^{III}, Rh^{III} and Ir^{III} complexes are quite close to each other. This results from a similarity in the ionic radii of these metal

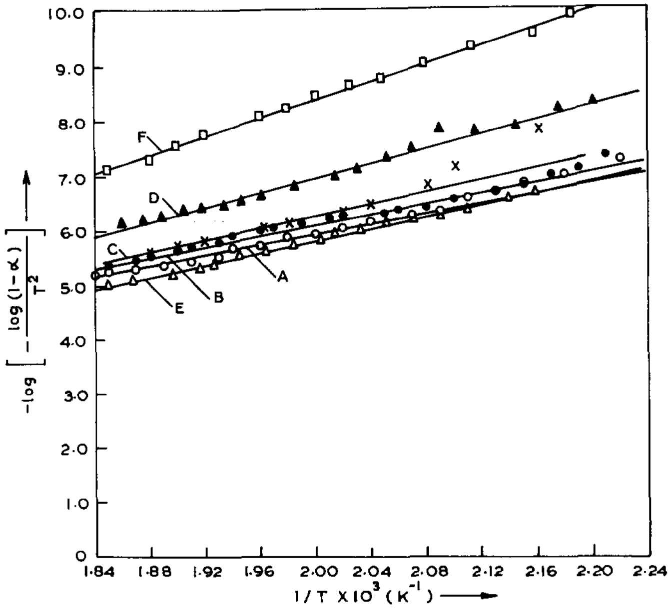


Fig. 3. Linearisation curves for (A) Ru^{III}, (B) Rh^{III}, (C) Pd^{II}, (D) Os^{IV}, (E) Ir^{III} and (F) Pt^{II} dithiocarbamate complexes.

ions (ca. 0.60 Å) [11]. The metal–ligand interactions are thus of comparable strength and the complexes require nearly equal activation energy for thermal degradation.

The higher charge on Os^{IV} makes it strongly polarising and hard. Since the sulphur donor ligands are known to be soft, the metal–ligand interactions in case of the osmium complex are quite weak; hence the exceptionally low value of E_a.

The Pd^{II} and Pt^{II} ions, because of their smaller formal charges, are soft in nature and are strongly bound to the dithiocarbamate ligand. The thermal decomposition, therefore, involves exceptionally high values of E_a. The smaller size of Pt^{II} (0.60 Å) as compared to Pd^{II} (0.64 Å) permits a closer approach of the ligand to the Pt^{II} ion. Hence the E_a value for the Pt^{II} complex is higher than that of Pd^{II} analogue.

The TG data are supplemented by DTA studies. All the thermal effects on DTA curves are endothermic in nature. The heat of reaction ΔH [12] has been calculated for the first thermal effect for each complex except for the Pd^{II} and Pt^{II} analogues. For the latter cases, the first thermal effect corresponds to the melting of the complexes. Hence the ΔH value was calculated for the second thermal effect. The temperature dependent calibration coefficient was obtained from the Currell equation [13].

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