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THERMOGRAVIMETRIC STUDY OF SOME NEW RHODIUM(III) AND RHODIUM(I) COMPLEXES CONTAINING HETEROCYCLIC TELLURIUM LIGANDS

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ABSTRACT

The thermal stability of some new rhodium(III) and rhodium(I) complexes containing heterocyclic tellurium ligands, namely, $[RhCl_3(C_4H_8Te)_3]$ (**1**), $[RhCl_3(C_4H_8OTe)_3]$ (**2**), $[RhCl_3(C_8H_5ClTe)_3]$ (**3**), $[RhCl_3(C_{10}H_{12}Te)_3]$ (**4**), $[RhCl_3(CO)(C_4H_8Te)_2]$ (**5**), $[RhCl_3(C_4H_8TeI_2)_3]$ (**6**), $[RhCl(COD)(C_4H_8Te)]$ (**7**) and $[RhCl(COD)(C_4H_8OTe)]$ (**8**) have been studied by thermogravimetric analysis. Complexes **1**–**6** lost two heterocyclic tellurium ligands in one or two stages depending on the nature of the ligands. Complexes **7** and **8** lost the heterocyclic tellurium ligand, forming the dimeric compound $[(COD)RhCl]_2$.

INTRODUCTION

There is a noticeable growth in the current interest in the chemistry of ligands containing tellurium as coordinating atom [1,2], yet relatively few papers have been published describing the chemistry of rhodium complexes containing tellurium ligands [1,3,4].

During an earlier research programme, a new series of rhodium(III) and rhodium(I) complexes containing heterocyclic tellurium compounds as ligands were synthesised and characterised [5] by various spectroscopic techniques and elemental analyses.

Here we report the thermal stability, decomposion and transformation of these new rhodium–tellurium complexes between ambient temperature and 600 ° C, by means of TG and DTG, in the hope of using them as catalysts for the hydrogenation of alkenes or as stabilisers for synthetic polymers [6].

EXPERIMENTAL

Materials

The rhodium–tellurium complexes used in this study were: *mer*-trichlorotris(1-telluracyclopentane)rhodium(III) (**1**), *mer*-trichlorotris(1-oxa-4-telluracyclohexane)rhodium(III) (**2**), *mer*-trichlorotris(3-chloro-4,5-benzotellurophene)rhodium(III) (**3**), *mer*-trichlorotris(5,6-dimethyl-1,3-dihydro-2-telluraindene)rhodium(III) (**4**), Carbonyltrichlorobis(1-telluracyclopentane) rhodium(III) (**5**), *mer*-trichlorotris(1,1-diiodo-1-telluracyclopentane)rhodium(III) (**6**), Chloro(η^4-1,5-cyclooctadiene)(1-telluracyclopentane)rhodium(I) (**7**) and Chloro(η^4-1,5-cyclooctadiene)(1-oxa-4-telluracyclohexane)rhodium(I) (**8**).

Compounds **1**–**7** were synthesised and characterised as previously reported [5] while compound **8** has been synthesised and characterised by Yousif [7].

Thermogravimetric analysis

The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were recorded on a Stanton Redcroft model 760 TG thermobalance equipped with a three-pen strip-chart recorder for the simultaneous recording of TG, DTG and temperature. The instrument was precalibrated with standard materials. All measurements were carried out under nitrogen atmosphere (flow rate 50 ml min^{-1}) and against standard α-Al_2O_3. The analyses were performed by heating the sample (weighing 2.4–4.0 mg) at a steady heating rate of 20°C min^{-1} until the sample was substantially decomposed. Typical thermograms are shown in Figs. 1 and 2.

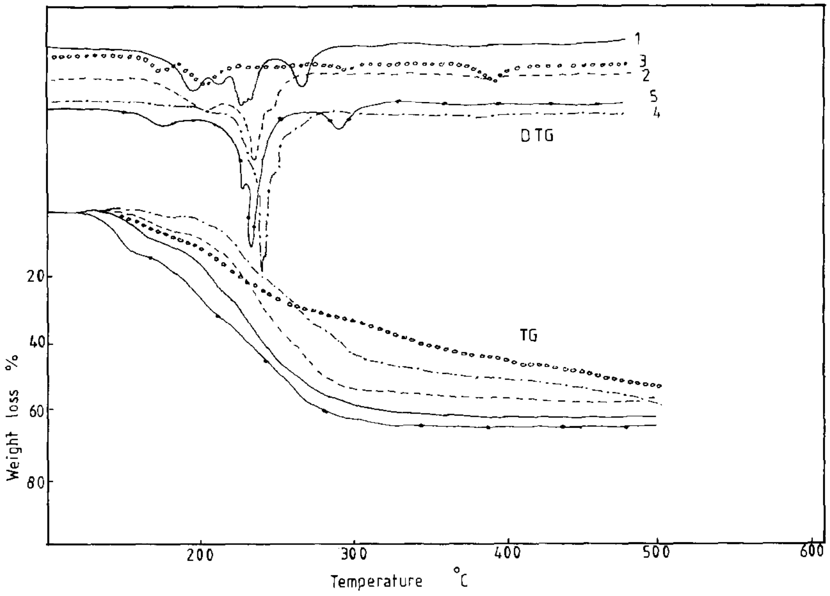


Fig. 1. Thermogravimetric curves (DTG and TG) for: ———, complex **1**; — — —, complex **2**; ○○○, complex **3**; ·—·—·, complex **4**; and ●——●, complex **5**.

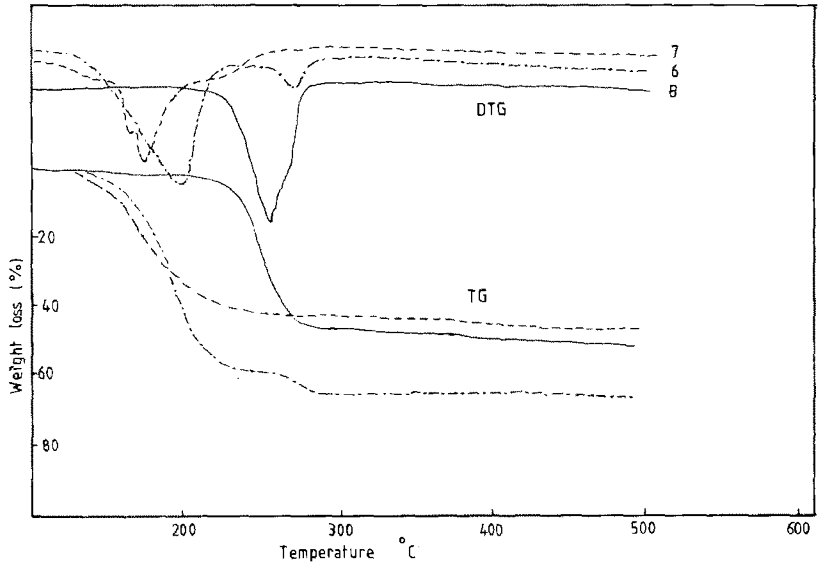


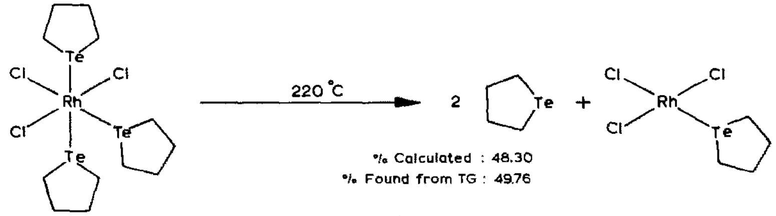
Fig. 2. Thermogravimetric curves (DTG and TG) for: –·–·–, complex **6**; — — —, complex **7**; and ———, complex **8**.

RESULTS AND DISCUSSION

The thermogravimetric curves for the octahedral complexes **1**, **2**, **3** and **4** (Fig. 1) show that these complexes lost two heterocyclic tellurium ligands to give the expected square-planar complexes, as it is well-known that octahedral complexes can lose two of their ligands from the axial position (d_{z^2}) [8]. As can be seen from Fig. 1, the two ligands of complexes **1**–**4** were lost in one or two steps depending on the nature of the heterocyclic tellurium ligands.

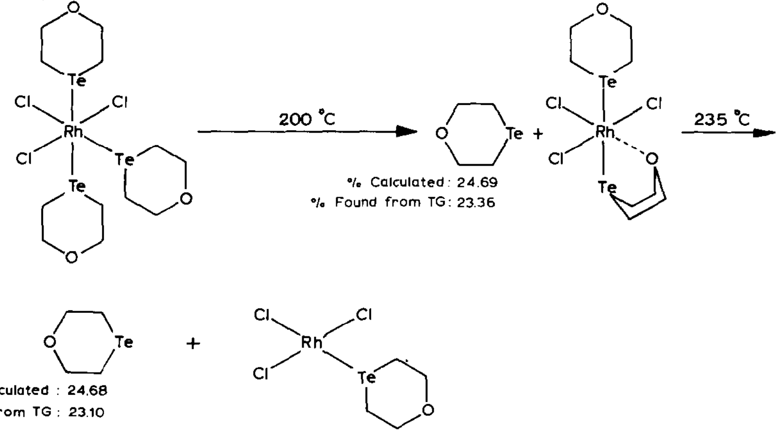
According to the thermogravimetric calculations, the following schemes are those expected for the thermal decomposion of complexes **1**–**4**.

Complex **1**



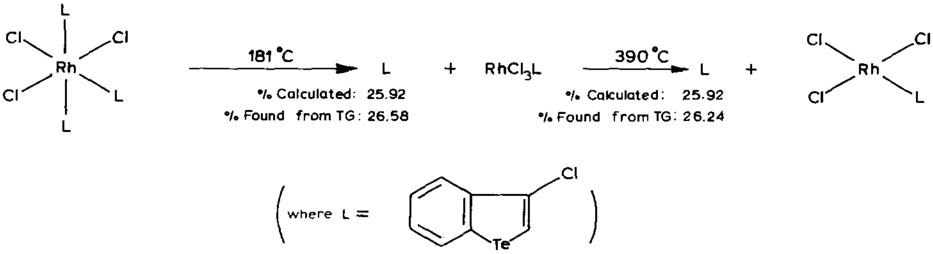
% Calculated : 48.30
% Found from TG : 49.76

Complex **2**



On heating complex **2**, two main overlapping peaks were observed on the TG curve (Fig. 1). This could be attributed to the ability of the ligand (C_4H_8OTe) to act as a bidentate ligand and to thus stablise the intermediate complex through the oxygen atom. The proposed intermediate is not unique, as the analogous 1,4-oxaselenan coordinates via both O and Se atoms as a bridge ligand [9].

Complex **3**

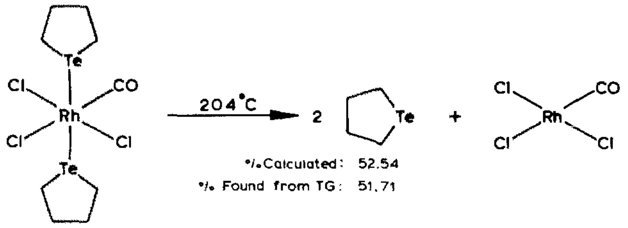


The coordinated ligand, C_8H_5ClTe, can also stabilise the proposed intermediate through the olefinic bond during the first loss at 181° C. The second peak was observed on the TG curve at 390 ° C, as can be seen in Fig. 1. One decomposition peak at 214° C was observed on the DTG curve for complex **4**, leaving the expected square-planar complex (see Fig. 1).

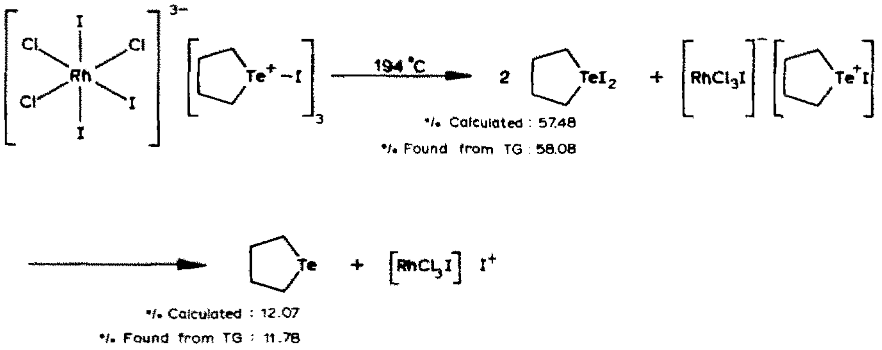
Complex 5

One decomposition peak at 204° C was observed for complex **5**. Our previous work [5] indicated that both heterocyclic tellurium ligands are in *trans* positions. This result was expected due to the back-donation of the CO ligand, as can be seen in the scheme.

Complex **5**



Complex **6**

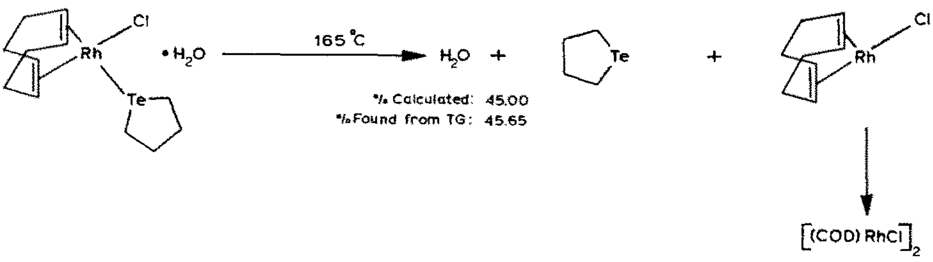


Complex **6** merits special mention: $[RhCl_3I_3]^{3-}[C_4H_8Te^+{-}I]_3$ was presumably formed [5] in solid state by halogen-exchange reactions of dihaloheterocyclic tellurium compounds [10,11]. Thus two decomposition peaks were observed, as can be seen in Fig. 2, at 194 and 271°C respectively. The second peak indicates the loss of the cyclic telluride and formation of the square-planar anion ($[RhCl_3I]^-$ I^+).

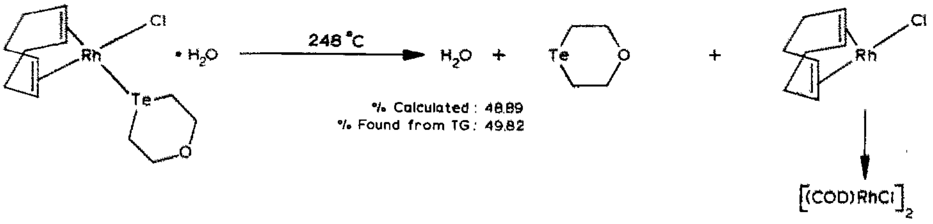
Complexes 7 and 8

The thermogravimetric calculations indicate that complexes **7** and **8** are bonded to one molecule of water and one decomposition peak was observed for each complex at 165 and 248°C respectively. The unstable three-coordinate intermediate could be dimerised to give $[(COD)RhCl]_2$, as shown in the following schemes

Complex **7**



Complex 8



The product, $[(COD)RhCl]_2$, was collected during thermolysis and identified by its melting point and its IR spectrum.

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