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CORRELATION OF THERMAL STABILITY WITH STRUCTURES FOR SOME METAL COMPLEXES

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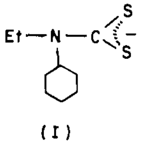
ABSTRACT

Thermogravimetric studies have been carried out for a number of complexes of the type $MCu(dtc)_4$[dtc = *N*-ethylcyclohexyldithiocarbamate (I); M = Zn(II), Cd(II), Hg(II)], $(\eta^5\text{-}C_5H_5)_2M'Cl(L)$(II) [L = benzylpenicillin; M′ = Ti(IV), Zr(IV)] and $[(\eta^5\text{-}R)_2M'L']^+[dtz]^-$(III) [HL′ = oxine; dtz = phenyldithiocarbazate ($C_6H_5NHNHCS_2$); R = cyclopentadienyl (C_5H_5), indenyl (C_9H_7)]. From TG curves, the order and apparent activation energy for the thermal decomposition reaction have been elucidated, and the various thermal stabilities have been correlated with some structural aspects of the complexes concerned.



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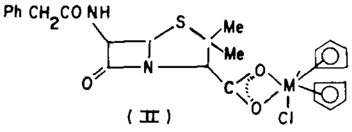

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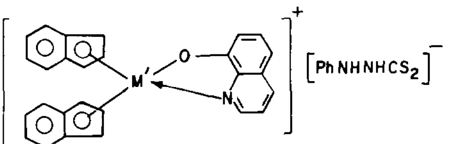

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INTRODUCTION

The diverse applications of thermal analysis have contributed to advances made in the fields of explosives, polymers, soil studies, space research, agrochemicals, organometallics, etc. [1]. In this paper an attempt is made to explain the variation in thermal stability of some metal complexes in terms of their structural parameters. Both ionic and nonionic complexes of transition and non-transition metals were selected for the present investigation. The thermal decomposition reaction for the nonionic complexes exhibits first-order kinetics, while for the ionic complexes, the order of thermal reaction is 0.9.

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EXPERIMENTAL

TG curves were recorded in air at a heating rate of 8° min^{-1} using a Setaram G-70 thermoanalyser (Lyon, France). Sodium *N*-ethylcyclohexyldithiocarbamate was prepared by the method of Gilman and Blatt [2], while phenylhydrazinium phenyldithiocarbazate was synthesised using the method of Anthoni [3]. $(\eta^5\text{-}C_9H_7)_2TiCl_2$ and $(\eta^5\text{-}C_9H_7)_2ZrCl_2$ were prepared by a standard method [4]. $(\eta^5\text{-}C_5H_5)_2TiCl_2$ was purchased from Fluka AG, Switzerland, while $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ was procured from Alfa Inorganics, Ventron, USA.

Preparation of the $MCu(dtc)_4$ complexes

The complexes were prepared by gradual addition of $Cu(NO_3)_2$ solution (1 mol) in 50 ml of an acetone: water mixture (80:20 v/v) to a 50 ml solution of sodium N-ethylcyclohexyldithiocarbamate (4 mol) in the same solvent mixture with vigorous stirring at room temperature. After 10 min a solution of $M(NO_3)_2$ (1 mol, M = Zn, Cd, Hg) in the same solvent mixture was added. The brown-coloured complexes precipitated out; they were filtered immediately, washed with water followed by acetone and finally dried.

Preparation of the $(\eta^5\text{-}C_5H_5)_2M'Cl(L)$ complexes

The potassium salt of benzylpenicillin was stirred with equimolar quantities of $(\eta^5\text{-}C_5H_5)_2M'Cl_2$ [M' = Ti(IV), Zr(IV)] in THF. After about 7 h the solution was filtered, and from the filtrate the solvent was evaporated under vacuum at room temperature, so as to reduce the volume of the filtrate to about one-quarter of the original. Petroleum ether was added to the concentrated filtrate and the mixture allowed to stand overnight. The yellow or brown products thus obtained were washed with petroleum ether; they were then recrystallised from an acetone solution by the addition of petroleum ether.

Preparation of the $[(\eta^5\text{-}R)_2M'L']^+[dtz]^-$ complexes

An aqueous solution of $[(\eta^5\text{-}R)_2M'L']^+Cl^-$ [HL' = oxine; R = C_5H_5, C_9H_7; M' = Ti(IV), Zr(IV)] was obtained by stirring an aqueous solution of $(\eta^5\text{-}R)_2M'Cl_2$ with a slight excess of oxine in about 100 ml of double-distilled water. After about 2 h the contents were filtered and the aqueous solution was shaken with about 25 ml of benzene. The aqueous phase was collected and to it a suspension of phenylhydrazinium phenyldithiocarbazate in water was slowly added. Ionic complexes of composition $[(\eta^5\text{-}R)_2M'L']^+[dtz]^-$ (dtz = $C_6H_5NHNHCS_2$) were obtained as green precipitates. These were filtered and washed with water, followed by petroleum ether. The complexes were reprecipitated from acetone solution by the addition of petroleum ether.

RESULTS

ZnCu(dtc)$_4$

From the TG curve it was observed that the mass change begins at 493 K and continues up to 593 K. The weight loss in this temperature range corresponds to the formation of a mixture of ZnO and CuO. The observed and calculated weight losses for this step are 80% and 81.6%, respectively.

CdCu(dtc)$_4$

The TG curve reveals a sudden weight loss in the temperature range 483–583 K. The observed weight loss of 80% corresponds to the formation of a mixture of CdO and CuO for which the calculated weight loss is 78.8%.

HgCu(dtc)$_4$

The TG curve indicates that the decomposition begins at 453 K and continues up to 673 K. The 71.4% weight loss over this temperature range corresponds to the formation of HgO and CuO. The calculated weight loss for this step is 70.7%. At temperatures greater than 793 K the HgO thus formed slowly volatilizes and at about 1223 K volatilization is complete. At this temperature CuO remains as the only product of thermal degradation.

$(\eta^5\text{-}C_5H_5)_2TiCl(L)$

The thermal degradation begins at 433 K and continues up to 1133 K. The weight loss in this temperature range corresponds to the formation of TiO_2. The observed and calculated weight losses for this step are 81% and 83.8%, respectively.

$(\eta^5\text{-}C_5H_5)_2ZrCl(L)$

The TG curve records a mass change of 76.5% in the 413–1033 K temperature range. This corresponds to the formation of ZrO_2, for which the theoretically calculated weight loss is 79.1%.

$[(\eta^5\text{-}C_5H_5)_2TiL']^+[dtz]^-$

From the TG curve, it is observed that this complex is thermally stable up to 333 K. Beyond this temperature, the TG curve shows a weight loss up to

363 K, which corresponds to the formation of the $[(\eta^5\text{-}C_5H_5)_2TiL']^+[SCN]^-$ complex. The observed weight loss is 25% which is in close agreement with the calculated value of 24.7%. The second decomposition step begins at 393 K and continues up to 493 K, registering a further weight loss of 36.8% corresponding to the formation of $(\eta^5\text{-}C_5H_5)_2Ti(CN)_2$, for which the calculated weight loss is 39.5%. At 523 K, TiO_2 begins to form and remains stable beyond 813 K.

$[(\eta^5\text{-}C_5H_5)_2ZrL']^+[dtz]^-$

From the TG curve it is observed that the first decomposition begins at 350 K, and that at 383 K $[(\eta^5\text{-}C_5H_5)_2ZrL']^+[SCN]^-$ is formed. The observed and calculated weight losses for this step are 21.4% and 22.8%, respectively. The second decomposition step begins at 403 K and continues up to 503 K, registering a further weight loss of 63.6%. The most plausible compound formed at the end of this step is $ZrO(CN)_2$, for which the theoretical weight loss is 62.3%. $ZrO(CN)_2$ volatilizes beyond 593 K.

$[(\eta^5\text{-}C_9H_7)_2TiL']^+[dtz]^-$

The TG curve indicates that the decomposition begins at 363 K, and that at 403 K the $[(\eta^5\text{-}C_9H_7)_2TiL']^+[SCN]^-$ complex is formed. The observed and calculated weight losses for this step are 21% and 20.6%, respectively. In the second step thermal degradation begins at 433 K and continues to 993 K, recording a further weight loss of 86.6%. This corresponds to the formation of TiO_2, for which the theoretical weight loss is 83.3%.

$[(\eta^5\text{-}C_9H_7)_2ZrL']^+[dtz]^-$

This complex is stable up to 443 K. The first step of the thermal degradation ends at 493 K. The theoretical and observed weight loss of 19.2% corresponds to the formation of $[(\eta^5\text{-}C_9H_7)_2ZrL']^+[SCN]^-$. The decomposition of the latter complex begins at 533 K and continues to 1133 K; the further weight loss of 76.2% corresponds to the formation of ZrO_2. The theoretical weight loss for this step is 76.5%.

DISCUSSION

From the TG curves, the order (n) and activation energy (E_a) of the thermal decomposition reaction have been elucidated using the method of Coats and Redfern [5]: the data are presented in Table 1. The linearization curves for $MCu(dtc)_4$, $(\eta^5\text{-}C_5H_5)_2M'Cl(L)$, $[(\eta^5\text{-}C_5H_5)_2M'L']^+[dtz]^-$ and $[(\eta^5\text{-}C_9H_7)_2M'L']^+[dtz]^-$ are shown in Figs. 1–4, respectively. The order of

TABLE 1

Thermal data

Complex	Temperature range (K)	n	E_a (kcal mol^{-1})
ZnCu(dtc)$_4$	493– 593	1	40.04
CdCu(dtc)$_4$	483– 583	1	36.60
HgCu(dtc)$_4$	453– 673	1	30.50
(η^5-C$_5$H$_5$)$_2$TiCl(L)	433–1133	1	9.15
(η^5-C$_5$H$_5$)$_2$ZrCl(L)	413–1033	1	5.72
[(η^5-C$_5$H$_5$)$_2$TiL′]$^+$[dtz]$^-$	333– 363	0.9	6.40
[(η^5-C$_5$H$_5$)$_2$ZrL′]$^+$[dtz]$^-$	350– 383	0.9	9.15
[(η^5-C$_9$H$_7$)$_2$TiL′]$^+$[dtz]$^-$	363– 403	0.9	11.18
[(η^5-C$_9$H$_7$)$_2$ZrL′]$^+$[dtz]$^-$	443– 493	0.9	14.23

reaction is one for the MCu(dtc)$_4$ and (η^5-C$_5$H$_5$)$_2$M′Cl(L) complexes, and 0.9 for the [(η^5-R)$_2$M′L′]$^+$[dtz]$^-$ derivatives.

A comparison of the activation energy data for thermal degradation of the MCu(dtc)$_4$ complexes reveals that the E_a values follow the order ZnCu(dtc)$_4$ > CdCu(dtc)$_4$ > HgCu(dtc)$_4$. This may be explained on the basis of the increasing size of the M(II) ions: Zn(II) < Cd(II) < Hg(II). In the case of the HgCu(dtc)$_4$ complex, the larger size of the Hg(II) ion prohibits a closer approach of the ligands to the metal ions, making the metal–ligand interactions comparatively weaker. This makes thermal degradation relatively easy and the reaction involves a lower value of E_a. For the ZnCu(dtc)$_4$ complex, the smaller size of the Zn(II) ion permits a closer approach of the

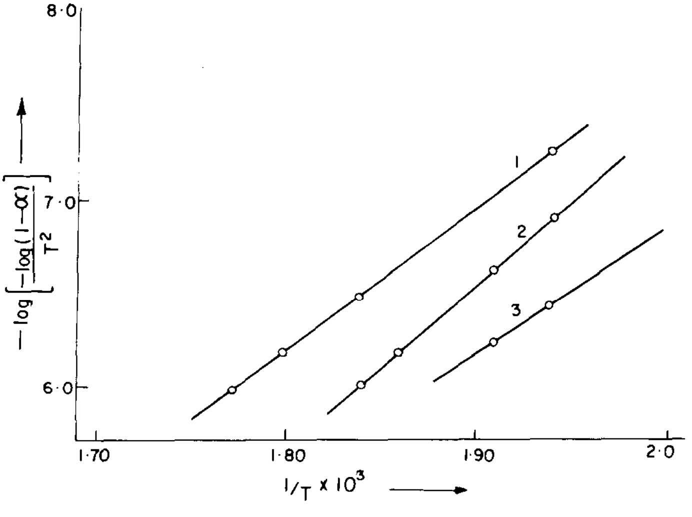

Fig. 1. Linearization curves: 1, ZnCu(dtc)$_4$; 2, CdCu(dtc)$_4$; 3, HgCu(dtc)$_4$.

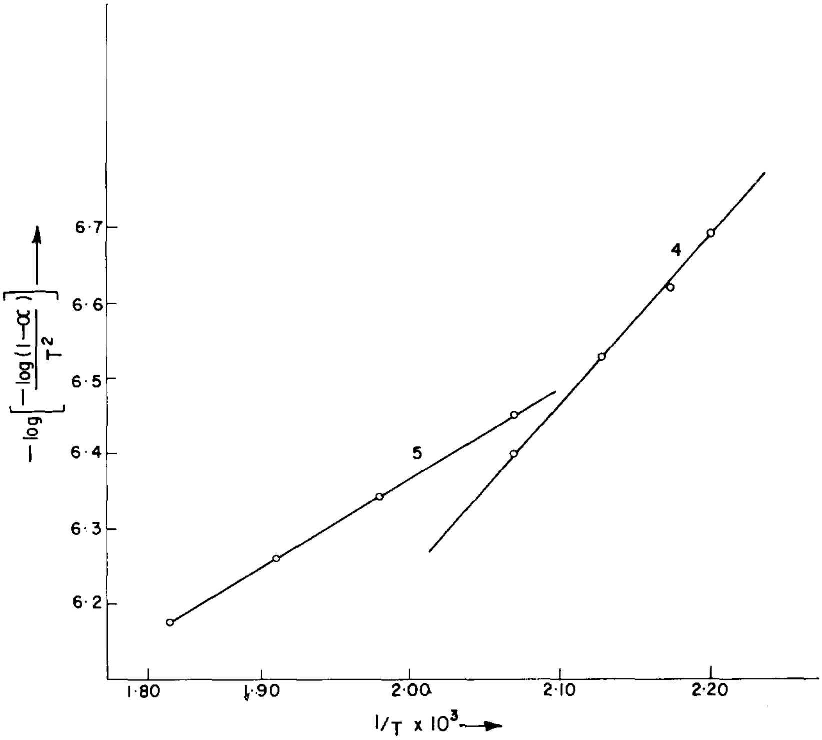

Fig. 2. Linearization curves: 4, $(\eta^5\text{-}C_5H_5)_2TiCl(L)$; 5, $(\eta^5\text{-}C_5H_5)_2ZrCl(L)$.

ligands to the metal ions, leading to a stronger metal–ligand interaction. Thus the thermal reaction involves a higher value of E_a.

The same patterns holds good for the $(\eta^5\text{-}C_5H_5)_2M'Cl(L)$ complexes. The benzylpenicillin ligand interacts more strongly with the Ti(IV) ion than with the Zr(IV) ion, due to the smaller size of the former. Hence, more energy is required to bring about the thermal degradation of the $(\eta^5\text{-}C_5H_5)_2TiCl(L)$ complex, leading to a higher value of E_a as compared with that for the corresponding zirconium derivative.

This rule, however, breaks down in the case of the $[(\eta^5\text{-}R)_2M'L']^+[dtz]^-$ derivatives. The titanium complex $[(\eta^5\text{-}R)_2TiL']^+[dtz]^-$ has a lower value of E_a than the zirconium analogue $[(\eta^5\text{-}R)_2ZrL']^+[dtz]^-$. Moreover, the thermal reaction of the cyclopentadienyl compounds $[(\eta^5\text{-}C_5H_5)_2M'L']^+[dtz]^-$ involves a lower activation energy than that of the corresponding indenyl derivatives $[(\eta^5\text{-}C_9H_7)_2M'L']^+[dtz]^-$. In an earlier communication [6] we studied the thermal reaction of structurally similar complexes of the type $[(\eta^5\text{-}R)_2HfL]^+HgCl_3^-$ [$R = C_5H_5$, C_9H_7, HL = oxine]. A comparison of the activation energy data revealed that the decomposition of the $[(\eta^5\text{-}C_9H_7)_2HfL]^+HgCl_3^-$ complex, as against the $[(\eta^5\text{-}C_5H_5)_2HfL]^+HgCl_3^-$ analogue, involved a lower value of E_a. This was attributed to steric reasons. The

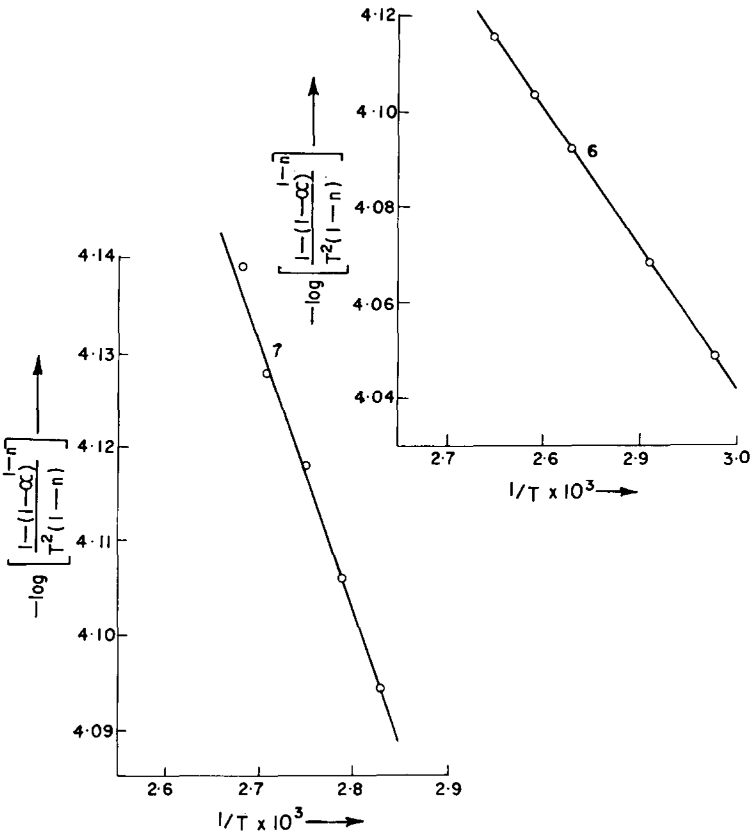

Fig. 3. Linearization curves: 6, $[(\eta^5\text{-}C_5H_5)TiL']^+[dtz]^-$; 7, $[(\eta^5\text{-}C_5H_5)_2ZrL']^+[dtz]^-$.

C_9H_7–Hf bond is broken more easily than the C_5H_5–Hf bond because of the steric repulsion arising from the bulkier indenyl group, thus making the cleavage relatively more spontaneous. The reverse trend is observed in the present complexes.

The higher thermal stability of the zirconium complexes $[(\eta^5\text{-}R)_2ZrL']^+[dtz]^-$ as compared with the titanium complexes $[(\eta^5\text{-}R)_2TiL']^+[dtz]^-$, and of the indenyl derivatives $[(\eta^5\text{-}C_9H_7)_2M'L']^+[dtz]^-$ as compared with their cyclopentadienyl analogues, $[(\eta^5\text{-}C_5H_5)_2M'L']^+[dtz]^-$, illustrates the stabilization of larger cations by larger anions, since this gives rise to a higher lattice energy. Thus, the larger dithiocarbazate anion stabilizes the larger $[(\eta^5\text{-}R)_2ZrL']^+$ cation more than the smaller $[(\eta^5\text{-}R)_2TiL']^+$ cation. Conversely, the titanium complexes have a greater tendency to form the complexes $[(\eta^5\text{-}R)_2TiL']^+[SCN]^-$, since the smaller thiocyanate anion can effectively stabilize the smaller $[(\eta^5\text{-}R)_2TiL']^+$ cation. Hence the thermal degradation of the titanium complex involves a lower value of E_a than does the corresponding complex of zirconium. Similarly, since the complex cations $[(\eta^5\text{-}C_9H_7)_2M'L']^+$ are larger in size than the cations $[(\eta^5\text{-}C_5H_5)_2M'L']^+$,

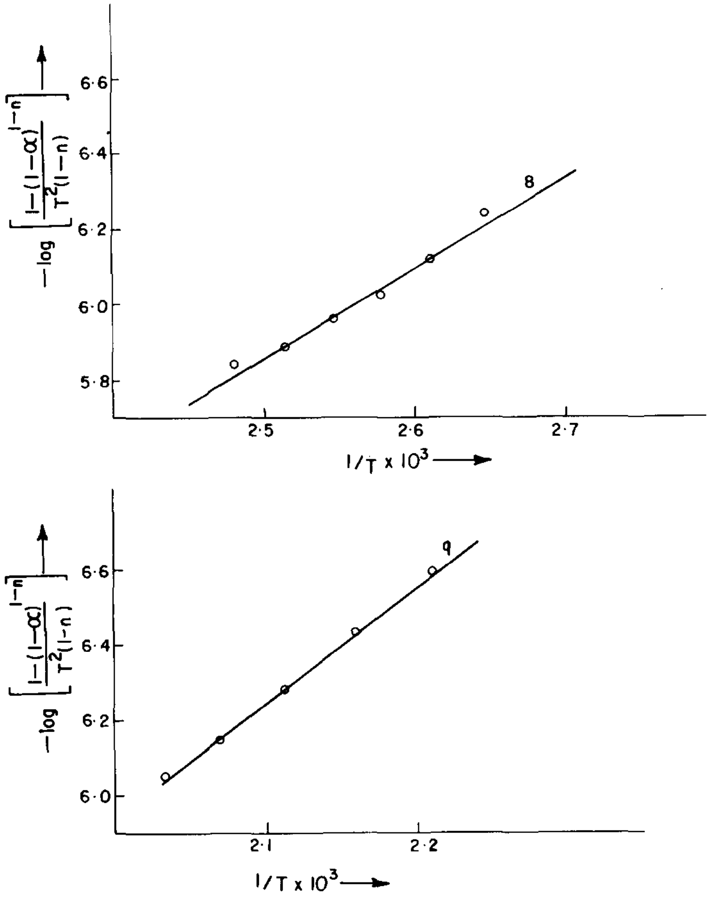

Fig. 4. Linearization curves: 8, $[(\eta^5\text{-}C_9H_7)_2TiL']^+[dtz]^-$; 9, $[(\eta^5\text{-}C_9H_7)_2ZrL']^+[dtz]^-$.

the indenyl derivatives are thermally more stable than their cyclopentadienyl analogues. Hence the former undergo thermal transformation with a higher value of E_a.

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