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THERMAL DEGRADATION OF TERNARY AND BINARY COMPLEXES OF ANTHRANILIC ACID AND LEUCINE WITH TRANSITION METAL IONS.

BY

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ABSTRACT

Thermogravimetric (TGA) and differential thermal analysis (DTA) for binary complexes of anthranilic acid and leucine with transition metal ions (copper,cobalt,nickel, and cadmium) were carried out. It was found that, irrespective of the metal ions used, the weight loss observed on heating is more or less similar for respective similar complexes.

A proposed physical mechanism of weight loss is put forward for both binary and ternary compounds. The mechanism follows the natural sequence of bond breaking and bond formation caused by the increase in potential thermal energy.

Binary complexes are found to suffer less weight loss than ternary complexes. The mechanism proposed for both types agrees to a reasonable extent with the observed experimental results.

INTRODUCTION

There have been several studies [1-5] concerned with transition metal complexes of anthranilic acid. Only brief attention has been directed to mixed ligand complexes of this acid or its derivatives [6-8]. In view of our interst in mixed ligand complexes [9-11] and also in view of the fact that the mixed ligand complexes play an important role in many naturally occurring biological process [12] , we undertook a study of the synthesis and characterisation of some transition metal mixed ligand complexes of anthranilic acid with leucine. In the last few years, great interest has been shown in the thermal analysis of phase transition. Several studies of these were based on the use of thermogravimettric (TGA) and differential thermal analysis (DTA) [13-15].

EXPERIMENTAL

2.1) PREPARATION OF THE COMPLEXES.

The preparation of the complexes followed essentially the following procedure : a solution of anthranilic acid (8m mole) in 20m mole hot water was added to a 20m mole hot solution of the respactive metal chloride ($Nicl_2$.

$6H_2O$, $CO\ cl_2 . 6H_2O$ or $Cu\ cl_2 . 2H_2O$) (4m mole) in water. The PH was adjusted at 7-8 using ammonia solution where a precipitation of the binary complexes occurs; the mixture was refluxed for about one hour. A solution (4m mole) of leucine in 30m mole water was than added dropwise at continuous stirring to the mixture; an immediate change of colour was observed . The reaction mixture was refluxed for one hour and the product was filtered, washed with warm water and dried.

2.2) PHYSICAL MEASUREMENT.

a) Thermogravimetric measurement were performed with a Heraeus TGA 500 thermo-balance using a Pt-Rh-Pt temperature sensor. The modern thermo-balance consists of the following component parts: recording balance, furnace, furnace temperature programmer or controller, and recorder, either of strip-chart or x-y function type.

The thermo-balance instrument permits the continuous weighing of a sample as a function of temperature. The sample may be heated or cooled at rates from 5-10 K/min and it may be isothermally maintained at a fixed temperature. The 60mg samples were placed in a platinum crucible. The heating rate was 10K/min. Dry nitrogen flew over the samples at a rate of 15m/min and the chamber cooling water flow rate was 10l/hour.

b) Differential thermal analysis (DTA) was performed with a Heraeus DTA 500 analyser using a Ni-Cr-Ni temperature sensor. A typical DTA apparatus consists of :

- a furnace or heating device.
- a sampls holder.
- a low - level dc amplifier.
- a differential temperature detector.
- a furnace temperature programmer.
- a recorder. and,
- control equipment for maintaining a suitable atmosphere in the furnace and sample holder.

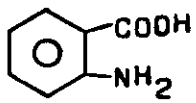
Many modifications of this basic design have been made,but all instruments measure the differential temperature of the sample as a function of temperature or time (assuming that the temperature rise is linear with time). The 45 mg sample was contained in a glass tube in the DTA cell. A heating rate of 5 K/min was used.

RESULTS AND DISCUSSIONS

The complexes under investigation were obtained from the reaction of anthranilic acid complexes with leucine according to the following equation :

$$M(Anth)_2 + BH \longrightarrow M(Anth)\ (B) + Anth\ H$$

$$M = CO^{+2},\ Ni^{+2},\ Cu^{+2}$$

Anth H = 

$$BH = (CH_3)_2CHCH_2\ \overset{CHCOOH}{\underset{NH_2}{|}}$$

Thermal degradation of binary and ternary complexes of anthranilic acid and leucine with transition metals according to the above equations might be analysed considering a simple approach of bond energy exchange. Bond breaking and formation may occur if the energy given to the molecule (in the form of heat or quatum energy) equals to or slightly exceeds the bond energy difference. A higher energy bond may be formed in a moleculs using the first exothermic bond breaking by the extra energy supplied to the molecule while heating. It might be as well happens that the higher energy bond does not form depending on the molecule environment and the existance or absence of catalytic materials. In our compounds there are a number of bonds having a variety of energies [16], these are listed in table (1). Thermal analysis (TGA) and (DTA) carried out on single and double ligands with Ni, Co, Cu and Cd listed in table(2), show different weight loss depending on whether single or double ligands are involved in the structure. thermal energy per mol of certain molecule can be expressed as:

$$E_{th} = n. \ K, \ T.N$$

where K is Boltzmann constant, T, is the absolute temperature and N, is the Avogadros number. The factor , n, is of the order 3 (for 3 degrees of freedom) but it might take higher values for some molcules depending on atomic size, being large for smaller atoms. This is not again a

general rule, because the bond formed will modify this factor. The thermal energyvalues calculated using the above equation are found to agree fairly well with the bond energy difference that causes newly formed bonds. This happend at relatively lower temperature where the compound is in stable condition. At higher temperature the higher energy bond does not form .

In both M(Anth)(Leuc) and $M(Anth)_2$ where M denotes the metal and Anth = Anthranilate, and Leuc = Leucinate, the weakest bond is the C-N bond, which breaks first, followed by the C-C bond as shown in table (1). The C-C bond may be formed if formed compound is stable, otherwise it may break after formation . These two bonds initiate the overall thermal decomposition of the structure. The initial loss of weight for both compounds is due to the water coordination evaporation followed by the resulting evolution of gasses after the C-C and C-N bond breaking.

In both structures, this however occur at different temperatures threshold which we believe to be caused by different temperatures threshold which we believe to be caused by different contents of water molecules, and its effect of the stability of the structure at room temperature during preparation. The different divalent metals used might also be responsible for this observed shift in the threshold of chemical decomposition according to the

difference in thermal ionization energies of the outermost electrons.

The thermal behaviour of the complexes was studied over the temperature range from room temperature up to 900K. The mixed ligand complexes of leucinate exhibit a great thermal stability . The TGA thermograms of the complexes consist of a number of decomposition steps, which have corresponding endothermic peaks in the DTA curves as shown as in figures (2,1).

Figure (1) illustrates the TGA and DTA thermogrames of M(Anth)(Leuc) where M is the divalent metal ions such as Cu, Co, and Ni. Figure (1a) contains Cu(Anth)(Leuc) with two endothermic and one exothermic peaks at about 550°K , 630°K , and at 630°K respectively. Figure (1b) illustrates Co(Anth)(Leuc) with only one endothermic peak at 600°K and one exthermic peak at 650°K. Figure (1c) shows the curves of Ni (Anth)(Leuc) with two endothermic peaks at 725°K and 800°K .

The overall reduction in sample weight is about 75% at temperature 840°K for Cu, for Co is 68% and for Ni slightly less of about 66% . This weight loss was observed to occur on a more or less distinct steps (clear in Cu compound) .

Secondly the M $(Anth)_2$ compounds exhibit a different trend in DTA and TGA measurement as shown in figure (2). Figure (2a) illustrates the DTA and TGA curves for $Cd(Anth)_2$ with two endothermic peaks at 690°K. Two exothermic peaks

are shown at about 750°K and 900°K . Figure (2b) shows two endothermic peaks at 562°K and 590°K and one endothermic peak at 850°K for $Co(Anth)_2$. Figure (2c) contains TGA and DTA curves for $Ni(Anth)_2$ with only one endothermic peak at 650°K on the DTA curve. The reduction in sample weight is about 55% for $Ni(Anth)_2$ and $Co(Anth)_2$ and slightly less of about 48% for Cd $(Anth)_2$. We conclude that the final residue in these compounds is larger than were observed in the first compounds containing leucinate molecules.

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FIGURE CAPTION

Figure (1): TGA and DTA thermogrames of:

a) Cu (Anth)(Leuc)

b) Co (Anth)(Leuc)

c) Ni (Anth)(Leuc)

Figure (2): TGA and DTA thermogrames of:

a) Cd $(Anth)_2$

b) Co $(Anth)_2$

c) Ni $(Anth)_2$

table(1)

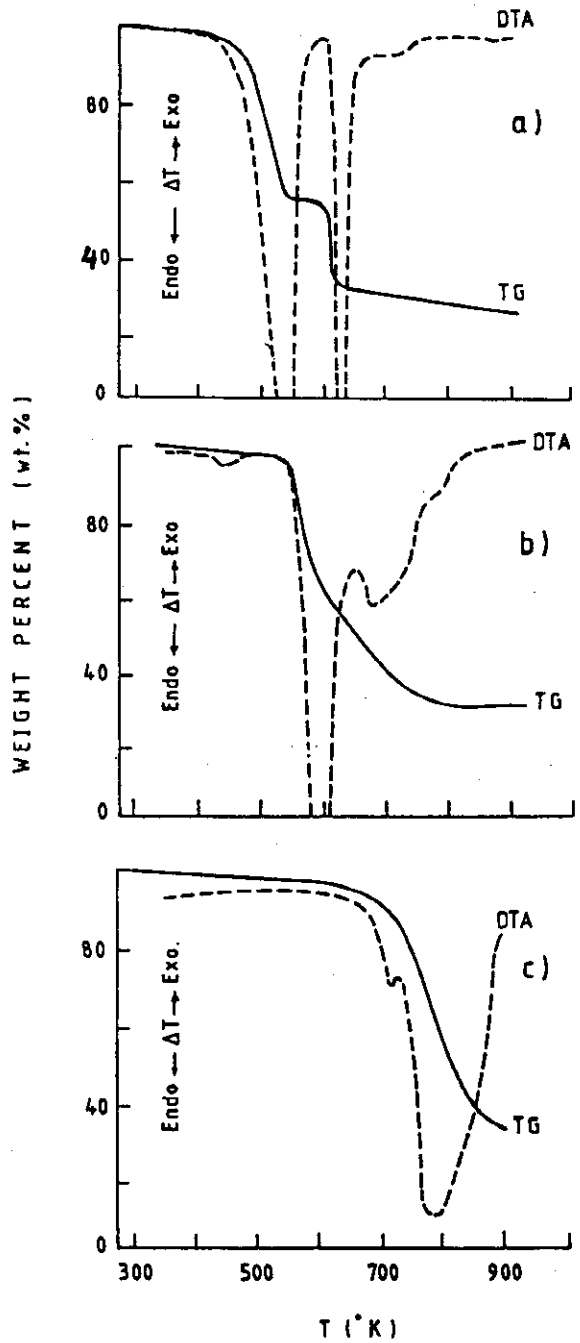
Bond energies of different molecules

Bond	Bond Energy (KT/mole)
C-N	3o4
C-C	345
C=C	61o
C-H	413
C-O	358
C=O	749
N-H	391
N-N	163

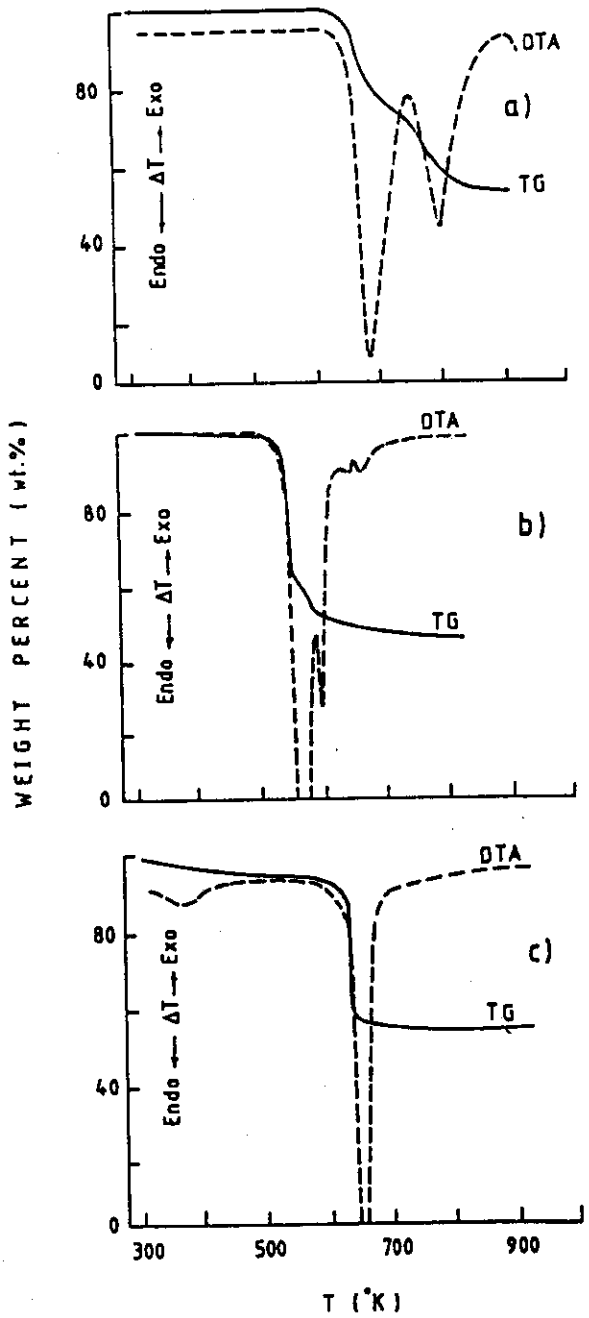
table (2)

List of the tested compounds

No.	Compound
1	Cu(Anth)(leuc). 2 H_2O
2	Co(Anth)(leuc). 4 H_2O
3	Ni(Anth)(leuc)
4	Cd$(Anth)_2$
5	Co$(Anth)_2$. H_2O
6	Ni$(Anth)_2$. H_2O


DTA
a)
TG
Endo ← ΔT → Exo
80
40
0
DTA
b)
TG
Endo ← ΔT → Exo
80
40
0
DTA
c)
TG
Endo ← ΔT → Exo.
80
40
0
300
500
700
900
T (°K)
WEIGHT PERCENT (wt.%)

Figure(1)


DTA
TG
a)
b)
c)
Endo ← ΔT → Exo
WEIGHT PERCENT (wt.%)
0
40
80
300
500
700
900
T (°K)

Figure(2)

التحلل الحرارى للمركبات الثنائية والثلاثية لحمض الانثرانيليك والليوسين مع أيونات المعادن الانتقالية

سمير العطوى ـ محمد الشباسى ـ عصام الرافعى ـ محمد على أحمد

أجريت قياسات نقص الوزن بالحرارة (TGA) وكذا معدل تغيير التحلل بالحرارة (DTA) للمركبات الثنائية لحمض الانثرانيليك والليوسين مع أيونات المعادن الأنتقالية (النحاس ، الكوبلت ، النيكل والكادميوم وقد وجد أنه بصرف النظر عن المعدن المستخدم ، فائه الفقد فى الوزن الملاحظ عند التسخين لا يتغير كثيرا للمركبات المتناظرة.

وقد أقترح من الناحية الفيزيائية نظام لتفسير النقص فى الوزن لكل من المركبات الثنائية والثلاثية . ويتبع هذا النظام التدرج الطبيعى لكسر وتكوين الروابط الناتجة من زيادة الطاقة الحرارية الكامنه.

وقد وجد أن المركبات الثنائية تعانى نقصا أقل فى الوزن من المركبات الثلاثية والنظام المقترح لكل من هذين النوعين يتفق الى حد ما مع النتائج العلمية التى أجرت.