Study of Thermal Stability of Tetraphenanthroporphyrazine and SomeMetal Complexes By Thermogravimetric Analysis .

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Abstract:

The thermal stability of previously prepared tetraphenanthroporphyrazine ($TPPH_2$) and its complexes with VO(IV) , Co(II) , Cu(II) , Zn(II) , Mg(II) , Ca (II) ions were studied by thermogravimetric analysis (TG & DTG) at temperature range (20-1000^{o}C). The results indicated that these compounds have a high thermal stability comparable to those of phthalocyanine compounds (PC) and higher than those of hemiporphyrazine compounds (HP) . In general metal complexes were more stable than parent ligand . Data of magnetic susceptibility and electrical conductivity were also obtained as further support for the studied compoundes .

Keywords: Tetraphenanthroporphyrazine , Thermal stability of porphyrazines

دراسة الاستقرارية الحرارية للتترافينانثروبورفرازين وبعض معقداتها الفلزية بواسطة التحليل الحراري الوزني

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الخلاصة:

شخصت الاستقرارية الحرارية لحلقة التترافينانثروبورفرازين ($TPPH_2$) ومعقداتها الفلزية مع الايونات Cu(II) VO(IV), Co(II), Zn(II), Ca (II), Mg(II) المحضرة سابقا من خلال دراسة التحليل الحراري الوزني (TG & DTG) في مدى درجات الحرارة (20–1000^{o}م) بينت النتائج ان هذه المركبات تمتلك استقرارية حرارية عالية مقاربة لمركبات الفثالوسيانين (PC) واكثر استقرارية من مركبات الهيميبورفرازين (HP) بصورة عامة كانت المعقدات الفلزية اكثر استقرارية من الليكاند.اجريت قياسات الحساسية المغناطيسية والتوصيلية الكهربائية وكانت النتائج متفقة مع الصيغ التركيبية المقترحة للمركبات المدروسة .

Introduction:

There are some unique properties related to porphyrazines and hemiporphyrazines that make them important candidates in different fields of applications other than being used as synthetic models to study the biochemical activities of naturally occuring compounds such as chlorophyll and hemine in catalysis and electron transfer reactions[1- 4]. Because of their strong colour , high stability towards heat and light , very low solubility and conductive properties , these compounds have been well recommended as colouring agents, photostibilizers, photosensitizers , semiconductors , sensors, detectors , electrophotographic materials and as catalysts [5- 10]

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There have been a growing interest to search for materials that are thermally stable and increase thermal stability of polymers , in addition their role in improving viscosity and conductivity of polymers. Phthalocyanines have been proved to be suitable candidats for such purposes [11]

In this work we are studying the thermal properties of another porphyrazine derivative namely tetraphenanthroporphyrazine (TPPH$_2$) (figure-1) and its metal complexes in comparison with some corresponding phthalocyanines through thermal behaviors by TG and DTG at high temperature. The thermal behavior of some Phthalocyanines have been studied earlier[12].The ligand and its sodium complex have been used as photosensitizers[13] , but to our knowledge no report have been published on thermal stability of these compounds except that they were reported earlier to have higher sublimation temperatures than Phthalocyanines [14]

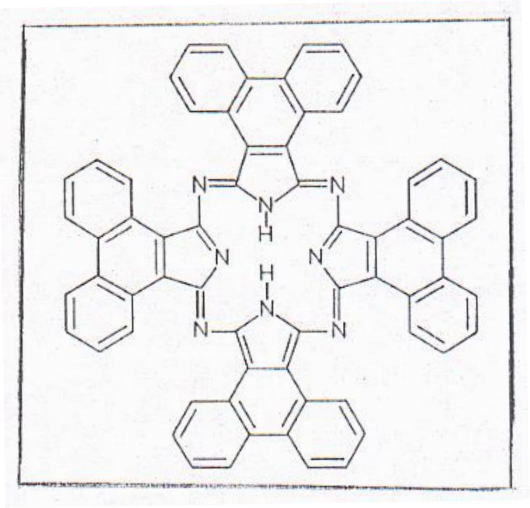

Figure 1- Tetraphenanthroporphyrazine (TPPH$_2$)

EXPERIMENTAL

Materials and Methods:

All solvents were purified and distilled prior to use [15] TPP and its metal complexes with Ca(II) , Mg(II) , Zn(II) , Cu(II) , Co(II) and VO(IV) were synthesized and purified according to methods described earleair [14]. Prior to use , TPPH$_2$ was purified successively by soxhlet extraction using dimethylformamide , ethanol , acetone and chloroform . The Cu(II) , VO(IV) complexes were purified by soxhlet extraction with ethanol acetone and chloroform .

Apparatus

Thermogravimetric Analysis were performed under anhydrous N$_2$ and the temperature rate was 20 ^{o}C . min^{-1} by Perkin – Elmer 7 Series Thermal Analysis System for TPPH$_2$ and its Co(II) complex and by Stanton Rodcorft TG.760 Series for the other complexes . Measurements were calibrated and corrected to nearest whole no. using calibration curves of changes in millivolts against temperature. Magnetic susceptibilities were measured at room temperature, using Magnetic Balance , Model MSB – MK1 .Specific conductivities in pyridine (10^{-3} M) were determined at room temperature by using Elektr - Leitfahigkeit Conductivity Meter .

Results and Discussion:

Results of CHN , UV –Visible , IR spectra , atomic absorption and single crystal X– ray diffraction of TPPH$_2$ and its metal complexes were reported earlier [14].In continuation of analytical work we found that measurement of magnetic moment (μ_{eff}) of soild complexes and conductivity in pyridine (10^{-3} M) were also necessary .

Table -1 describes results obtained from the measurement of magnetic susceptibility at room temperature of complexes together with the suggested geometries . μ_{eff} of [TPP Co $(H_2O)_2$] is 5.3 B.M. This value indicates that this complex is octahedral high spin [16- 18].The copper complex [TPP Cu (H_2O)] . 0.3 H_2O . 0.05 C_2H_5OH was found penta coordinate paramagnetic and the magnetic moment was 2.7 B.M. agrees with that reported in the literature [16].

The vanadium complex [TPP VO (H_2O)] . 0.2 C_2H_5OH was penta coordinate paramagnetic and μ_{eff} was 2.7 B.M . The Zn(II) , Ca(II) and Mg(II) complexes were diamagnetic which is attributed to full valence shells. The μ_{eff} of Co(II) , Ca(II) , VO(IV) complexes are larger than spin only (table 1), which is attributed due to orbital contribution [19].As in the case of metal phthalocyanines the coordination of ligands such as H_2O with the metal ion does not change the spin state of the parent complexes because of the coplanarity of these complexes [20,21]. On the other hand axial ligation with metal hemiporpherazines changes the spin state because of the non equivalent M-N bonds and low symmetry of these macrocycles. Metal ion in metal hemiporphyrazines lies out of plane of macrocyclic ring and binding with axial ligands makes metal ion lie in the plane of macrocyclic ring and hence changes the spin state [16].

Conductivity measurement in pyridine showed that the complexes were non electrolyte (table-1).

Table 1 - The results of molar conductivity and magnetic susceptibility measurements of TPP metal complexes.

Compounds	Molar conductivity $\times10^{-3}$ $S.cm^2.mol^{-1}$	μ_S B.M.	μ_{S+L} B.M.	μ_{eff} B.M.
[TPP VO (H_2O)] 0.1 C_2H_5OH	7.69	1.73	3.00	2.7
[TPP Co $(H_2O)_2$]	6.52	3.87	5.19	5.3
[TPPCu(H_2O)] 0.3 H_2O. 0.05 C_2H_5OH	8.40	1.73	3.00	2.7
[TPP Zn (H_2O)]	2.55	-	-	Diamagnetic
[TPP Ca $(H_2O)_2$]	3.59	-	-	Diamagnetic
[TPP Mg] 0.2 H_2O	2.30	-	-	Diamagnetic

Thermal decomposition of TPP and its metal complexes were studied and explained [22] by TG and DTG under anhydrous nitrogen atmosphere at temperature range 20- 1000°C . Results indicated that metal complexes have higher thermal stability than the parent ligand . After loss of solvent molecules ,VO(IV), Co(II), Cu(II), Zn(II), Ca(II), Mg(II) complexes Fig.(3,4,5) were found stable up to 580 , 490 , 484 , 456 , 450 and 366°C respectively while the ligand was less stable and started to decompose at 290 °C . Thermogram of $TPPH_2$ (Fig.2) showed a little weight loss in the initial stage up to 168 °C and was attributed to DMF molecules trapped in the crystal lattice table -2 . VO(IV) , Cu(II) and Mg(II) complexes exhibited loss of other solvent molecules such as water and ethanol at temperature range (80 - 120 °C) . All complexes except Mg(II) complex showed affinity towards coordination with H_2O molecules which were lost at higher temperature (145 - 350 °C) table -2. Such behaviors were similar to those of phthalocyanines and hemiporphyrazines in their affinity to coordinate with H_2O , HX and N-bases [23] . The VO(IV) complex was stable up to 580 °C . At temperature range 580-761 °C the oxygen released from the complex attacked C-N bond . Consequently the structure broke down with evolution of CO molecule . This observation agrees with the thermal behavior of VOPC reported in the literature [12]. Co(II) complex was stable up to 490 °C figure-2 a but above this temperature the decomposition rate was very high that weight loss reached (78.44 %)at 1000 °C. On the other hand weight loss exhibited by VO(IV), Cu(II), Zn(II), Mg(II), Ca(II) complexes and the ligand were 24.89 , 33. 33 , 30.83 , 50.00 , 60.05 , and 53.54 % respectively at 1000 °C (table -2) . This leads to the conclusion that the thermal stability of compounds decreased in the order VO(IV) > Co(II)

> Cu(II) > Zn(II) > Mg(II) > Ca(II) > $TPPH_2$ which indicates that the transition element complex were more stable than alkaline earth metals complexes . These results may be attributed to the importance of electrons available in the unfilled d- orbitals of transition metals which are more available and have higher affinity towards coordination with the ligand donor atoms .

The above mentioned results were close to those of metal phthalocyanines [24]. This may be expected because the latters have the same tetraaza nitrogens which combines four pyrrole rings and hence the bond distance M-N and coplanarity [14, 16] of metal phthalocyanine may be close to that of metal TPP . Hemiporphyrazins however have less thermal stabilities than phthalocyanines and tetraphenanthroporphyrazine (TPP) , this may be partly attributed to non equivalent of M-N bond length related to non-equivalent isoindole and pyridine nitrogens and to less aromaticity of macrocycles [16, 23, 25] . Therefore the coplanarity and stability of hemiporphyrazin compounds were less than those of phthalocyanines and TPP .

Other factors such as ionic radius , effective nuclear charge , crystal field stabilization energy (CFSE) , thermodynamic parameters , polarity and basicity of ligand may also influence stabilities of these complexes [26]. These factors will be studied in future work .

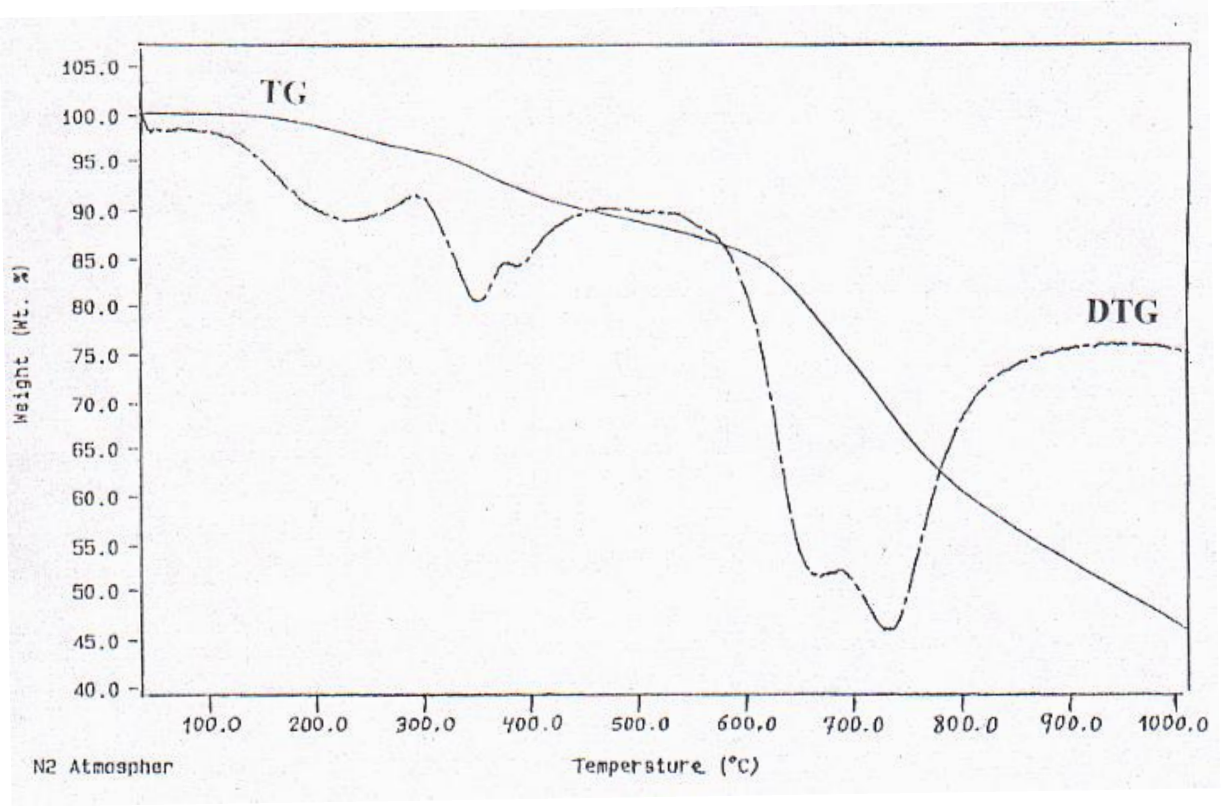

Figure 2- TG and DTG thermograph of [$TPPH_2$] 0.1 DMF

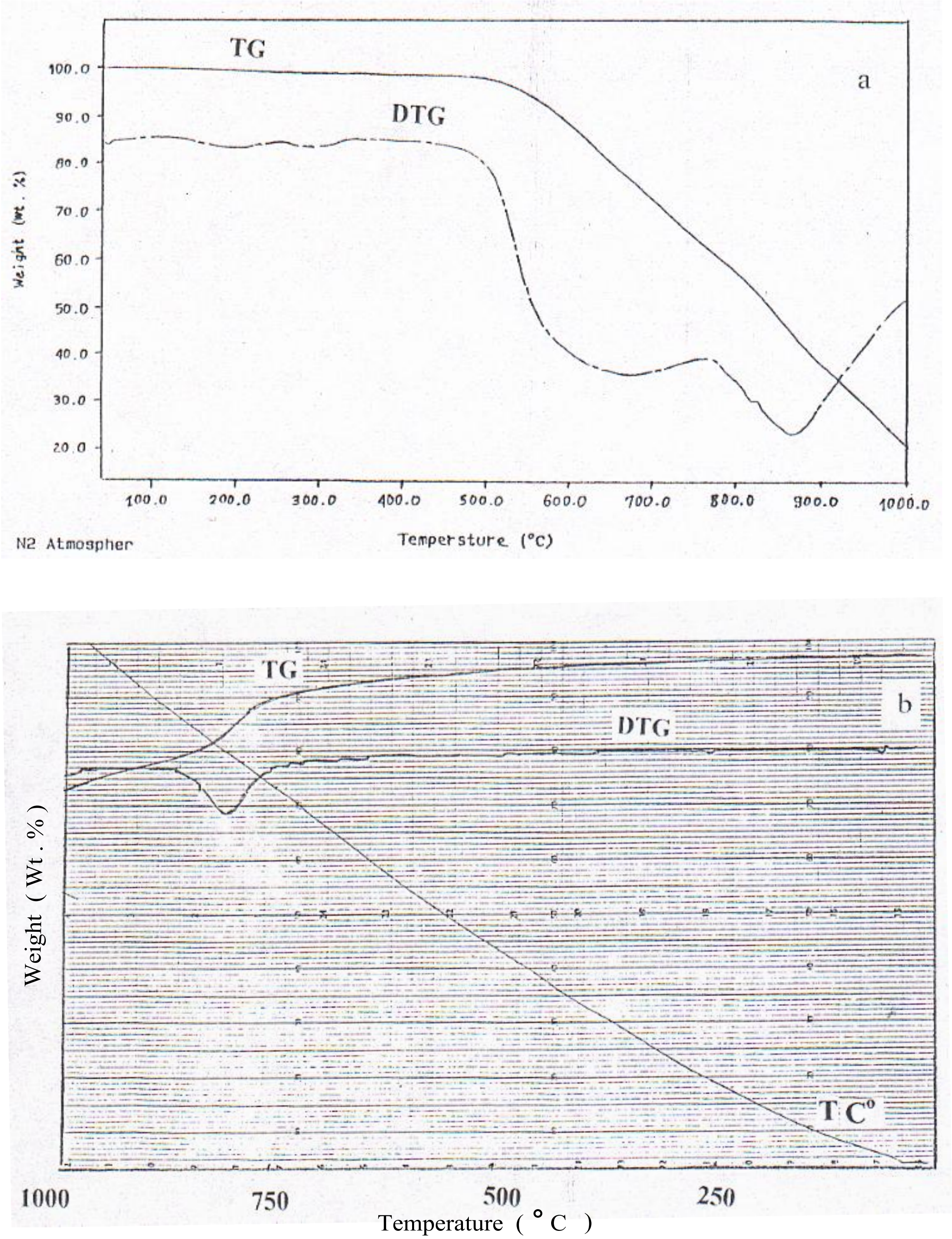

Figure 3 -TG and DTG thermograph of a - [TPPCo(H_2O)] b - [TPPVO(H_2O)] 0.1C_2H_5OH.

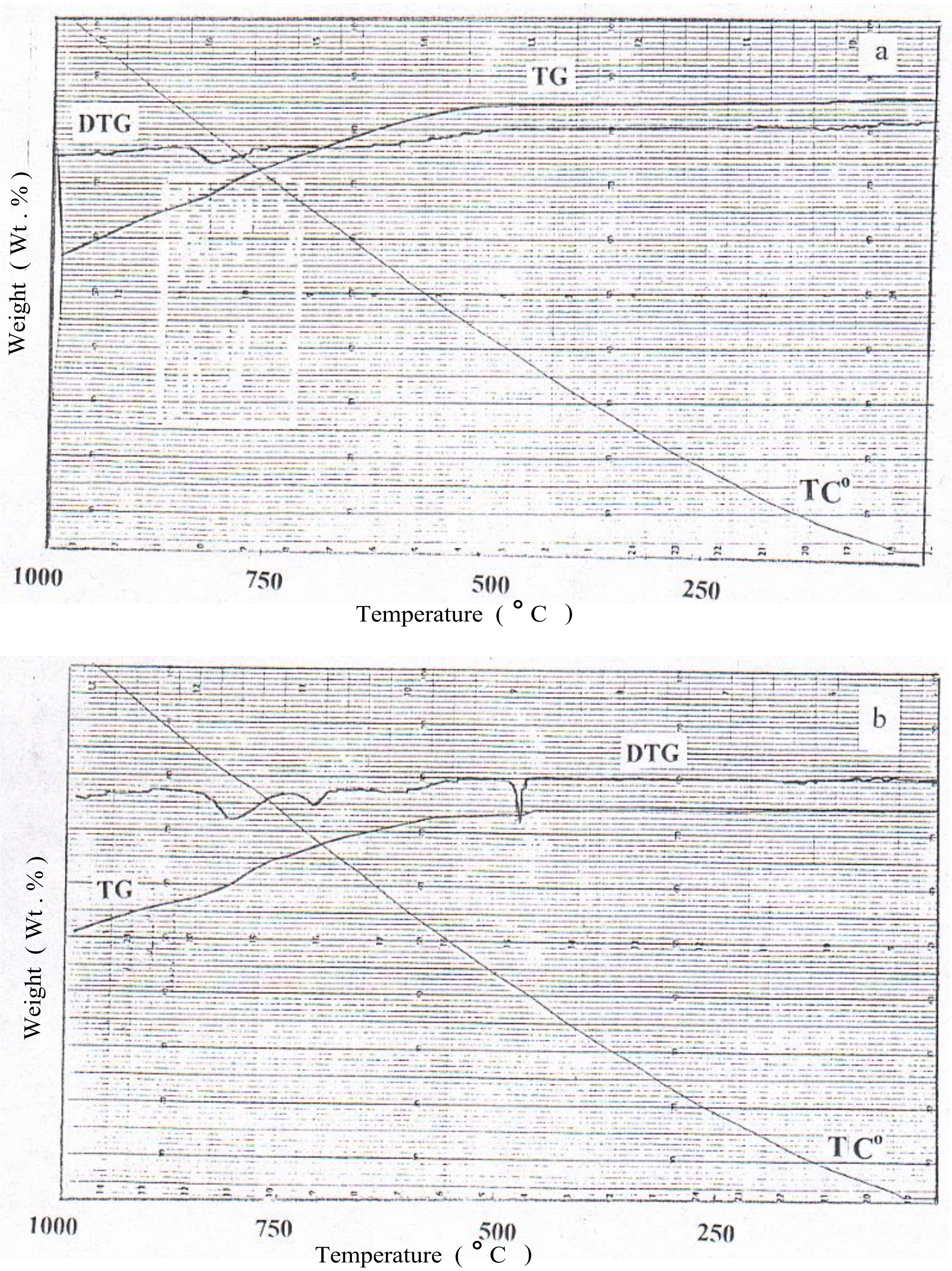

Figure 4- TG and DTG thermograph of a - [TPPCu(H_2O)]0.3 H_2O. 0.05 C_2H_5OH b -[TPPZn(H_2O)]

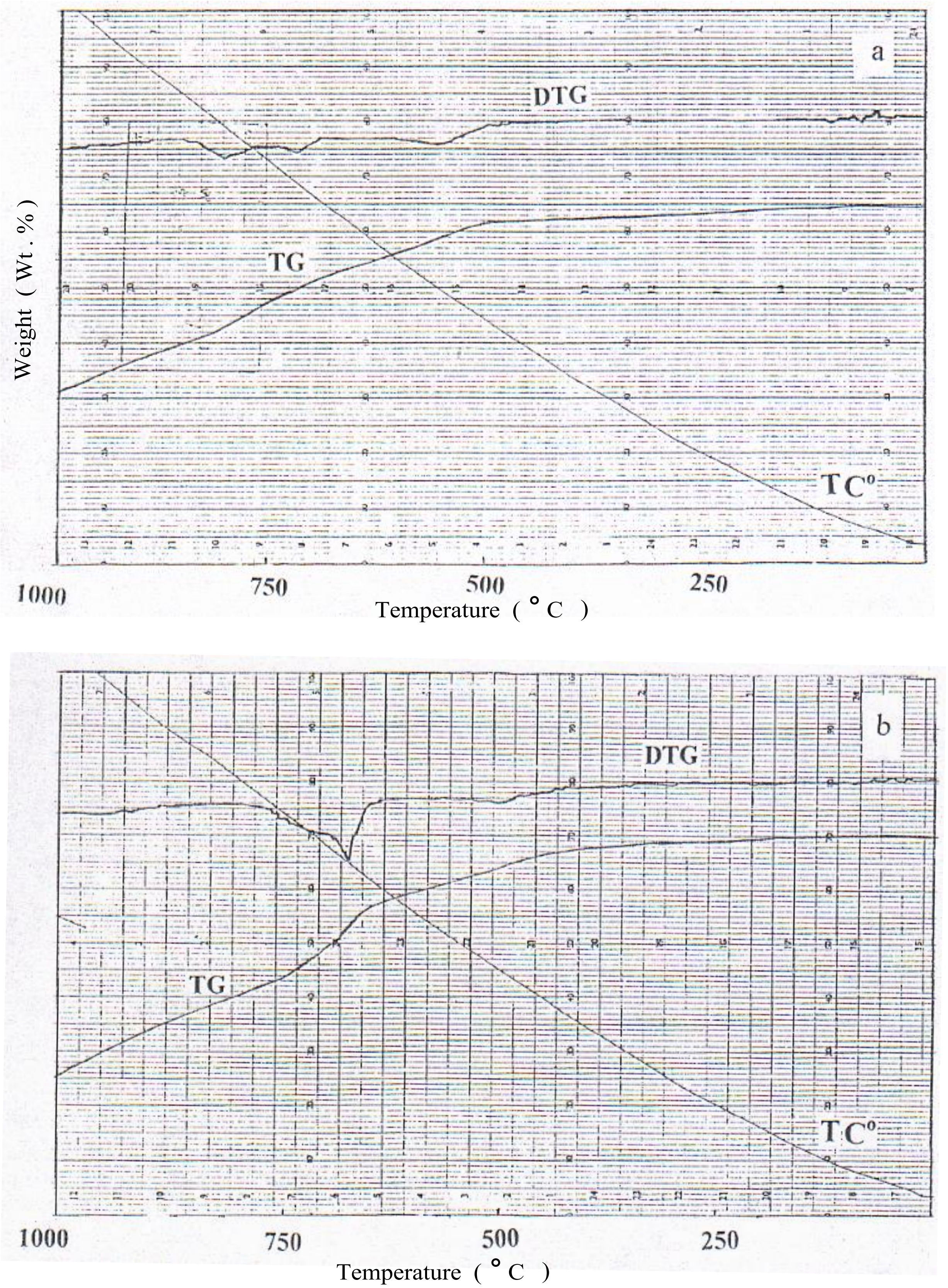

Figure 5-TG and DTG thermograph of a - [TPPMg] $0.2H_2O$, b- [TPPCa$(H_2O)_2$]

Table 2- The results of thermogravimetric analysis for the $TPPH_2$ and its VO(IV) ,Co(II),Cu(II),Zn(II),Ca(II) and Mg(II) complexes

Stable phase	Temperature rang of decomposition ^oC	DTG Decomposition peaks ^oC	% weight loss found (Calc.)
$[C_{64}H_{34}N_8]$ 0.1 DMF			
↓ -0.1 DMF	35 – 168	-	0.55 (0.79)
↓ $-CN_2H$	168 – 328	225	4.16 (4.45)
↓ - CN	328 – 393	350 , 390	3.33 (2.82)
↓ $-C_2NH$ -CN	393 – 620	-	6.38 (7.05)
↓ $-C_2N_2$ -CN $-C_{12}H_6$	620 – 793	673 , 733	25.25 (24.74)
↓ $-C_2H_2$ $-C_8H_4$	793 – 1000	-	13.87 (13.67)
$2C_{14}H_8 + C_6H_4$			46.46 (46.45)
$[C_{64}H_{32}N_8VO(H_2O)]$ 0.1 C_2H_5OH			
↓ -0.1 C_2H_5OH	20 –163	87	0.40 (0.45)
↓ $-H_2O$	163 – 478	248	1.86 (1.79)
↓ -CN -CO	478 – 761	717 – 734	6.17 (5.39)
↓ -CN $-C_2N_3$	761 – 827	804	9.27 (9.18)
↓ $-C_2N_2$ $-C_2$	827 – 1000	-	7.19 (7.58)
$3C_{14}H_8 + C_{12}H_8 + VCN$			75.11 (75.57)

Stable phase	Temperature rang of decomposition °C	DTG Decomposition peaks °C	% weight loss found (Calc)
$[C_{64}H_{32}N_8Co(H_2O)_2]$			
↓ $- H_2O$	59 – 218	192	0.76 (1.78)
↓ $- H_2O$	218 – 490	290	0.76 (1.78)
↓ - 2CN	490 – 559	-	4.81 (5.16)
↓ -2CN $-C_2N_3$ $-C_{15}H_8$ $-C_4$	559 – 800	666	36.15 (35.15)
↓ $-C_{14}H_8$ $-C_{12}H_8$ $- C_2$	800 – 1000	870	35.95 (34.95)
$C_{10}H_8 + CoCN$			21.55 (21.14)
$[C_{64}H_{32}N_8Cu(H_2O)]0.3H_2O.0.05C_2H_5OH$			
↓ $-0.05\ C_2H_5OH$	20 – 98	80	0.23 (0.23)
↓ $-0.3\ H_2O$	98 –145	118	0.59 (0.53)
↓ $- H_2O$	145 – 484	192	0.81 (1.79)
↓ - CN	484 – 575	531	3.38 (2.59)
↓ - 2CN $-2C_2N_2$	575 – 804	791	16.32 (15.58)
↓ $- C_{10}H_5$	804 – 1000	919	12.00 (12.38)
$3C_{14}H_8 + C_4H_4 + C_4CN$			66.67 (66.87)

Stable phase	Temperature rang of decomposition °C	DTG Decomposition peaks °C	% weight loss found (Calc.)
$[C_{64}H_{32}N_8Zn(H_2O)]$			
↓ - H_2o	20 – 456	163	0.93 (1.80)
↓ - CN	456 – 566	470	1.75 (2.60)
↓ - 2C N	566 – 688	598	5.36 (5.22)
↓ - C_2N	688 – 762	712	4.82 (3.80)
↓ - C_3N_3	762 – 814	803	8.31 (7.83)
↓ - C_8H_4	814 - 1000	-	9.66 (10.04)
$3C_{14}H_8 + C_5H_4 + ZnCN$			69.17 (68.65)
$[C_{64}H_{32}N_8\ Mg]$. $0.2H_2O$			
↓ - $0.2H_2O$	20 – 133	107	0.46 (0.38)
↓ -2CN	133 – 498	415	4.64 (5.52)
↓ - C_2N - CN	498 – 572	548	6.20 (6.80)
↓ - C_2N_3 - C_9H_4	572 – 774	708	19.04 (18.93)
↓ -$C_{14}H_8$	774 - 1000	796	19.66 (18.72)
$2C_{14}H_8 + C_5H_4 + MgCN$			50.00 (49.61)

Stable phase	Temperature rang of decomposition °C	DTG Decomposition peaks °C	% weight loss found (Calc.)
$[C_{64}H_{32}N_8Ca(H_2O)_2]$			
- H_2O	20 – 204	145	0.86 (1.82)
- H_2O	204 – 308	215	0.85 (1.82)
- C N	308 – 452	390	3.14 (2.63)
- C_2N_3 - C_2N_2 - CN	455 – 652	508	13.98 (14.57)
- C_9H_4 - C_5H	652 – 747	680	18.40 (17.50)
- C_3H_3 - $C_{14}H_8$	747 - 1000	921	22.82 (21.75)
$2C_6H_4 + C_{14}H_8 +$ Ca CN			39.95 (39.88)

Conclusion

The results obtained in this study indicate that $TPPH_2$ and its metal complexes have higher thermal stability compared with phthalocyanine compounds (PC) and hemiporphyrazine compounds(HP) and this is attributed to their rigid structures and the bonding nature between the metal ions and nitrogen atoms of the macrocyclic ring .

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