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Thermal studies of cobalt, iron and tin metalloporphyrins

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Abstract A free-base tetraphenyl porphyrin (TPP) and its corresponding metalloporphyrins (MTPP) where M = Co, Fe and Sn were synthesized and characterized by UV–visible spectroscopy, FTIR and ^{1}Hnmr spectroscopy. Thermal studies of these porphyrins were carried out in synthetic air from room temperature to 800 °C using thermal analyser. The residues of MTPP after thermal treatment were qualitatively analysed, which showed the presence of corresponding metal oxides. Further, the above MTPP were subjected to thermogravimetry–evolved gas and mass spectrometry (TG–EGA–MS) analysis for the detailed information about evolved gases at their corresponding decomposition temperatures. This information may be used to predict the probable mechanism for ring opening of the macromolecular porphyrins.

Keywords Metalloporphyrins · Thermogravimetry · Thermal behaviour · Evolved gas analysis · Mass spectrometry

Introduction

The synthetic porphyrins are important because they are structurally related to biologically important compounds like heme, chlorophyll, vitamin B_{12}, cytochrome, etc. They act as radiation sensitizers or protecting agents against radiation [1]. The catalytic activity of porphyrins in many reactions, their role as pigments and dyes, semiconductors, photoconductors, analytical reagents as well in photodynamic therapy exhibits their versatility. In the years to come they would be also employed in molecular switches, active elements of biosensors, elements of selective electrodes, nonlinear optical materials and as parts of electrochromic displays [2].

The synthetic porphyrins such as free-base tetraphenyl porphyrin (TPP), CoTPP, FeTPPCl and $SnTPPCl_2$ were synthesized to know their thermal behaviour in synthetic air and followed by thermogravimetry–evolved gas and mass spectrometry (TG–EGA–MS) analysis. This exercise has given the valuable information about the thermal stabilities of respective porphyrins and their decomposition.

Experimental

The free-base TPP was synthesized by suitable method [3]. Equimolar quantities of AR grade pyrrole and benzaldehyde were refluxed in propionic acid for half an hour. The reaction mixture was cooled and washed with hot methanol followed by hot water. The shiny purple crystals of TPP were then subjected to purification by dry column chromatography using silica gel (100–200 mesh) as stationary phase and $CHCl_3$ as mobile phase. The recovered purified TPP showed approximately 90% yield and the purity of which was checked by thin layer chromatography (TLC) using petroleum ether and chloroform (80:20%) and was found to be highly pure.

The above-purified TPP was used to synthesize CoTPP, FeTPPCl and $SnTPPCl_2$ by suitable method [4]. The purification method employed for these metalloporphyrins (MTPP) was dry column chromatography with silica gel (100–200 mesh) as stationary phase and mobile phase was modified by introducing gradient elution. In the case of CoTPP the mobile phase used was petroleum ether and chloroform (50:50%) and for FeTPPCl and $SnTPPCl_2$,

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methanol and chloroform (50:50%), respectively. The purity of the MTPP was checked on TLC plate and running in a mobile phase of petroleum ether and chloroform (80:20%) and was found to be satisfactory.

UV–visible spectra were recorded on Shimadzu visible spectrophotometer (model uv/2450 uv) using 10^{-4} and 10^{-5} M concentrations for each porphyrin. Infra red analysis of solid porphyrins were carried out using Shimadzu IR spectrometer (model prestige/21 FTIR). ^{1}Hnmr spectra were recorded using Varian 300 MHz model. TG–DSC measurements were recorded in synthetic air and argon atmosphere from room temperature to 800 °C using NETZSCH-Geratebau Gmbh Thermal Analyser (STA 409 PC) to find out thermal stability and decomposition temperature at different stages. The TG–EGA–MS results were recorded in argon atmosphere from room temperature to 900 °C. For detection of the gases evolved from the sample, the mass spectrometer was calibrated for some desired gases as expected from the structural information of the particular porphyrin. The temperature of the delivery tube which carries respective gases to the mass spectrometer was maintained below 125 °C.

Results and discussion

The porphyrins TPP, CoTPP, FeTPPCl and $SnTPPCl_2$ were characterized by UV–visible spectrometry [5–8]. Since, the molar extinction coefficient values of porphyrins is high, very small quantity of the sample is required to prepare the solution for spectrophotometry. At present, the concentrations of the solutions used were 10^{-4} and 10^{-5} M for Q-band and soret band, respectively. In free-base porphyrin like TPP the characteristic band 647 nm is present whereas after metallation the number of bands is reduced to minimum due to comparatively more molecular symmetry. Table 1 shows the characteristic absorption bands in soret and visible region for selected porphyrins.

The porphyrins in solid state were then subjected to characterization by FTIR measurements. In TPP a characteristic N–H stretching vibration at 3300 cm^{-1} is seen, which disappears after the insertion of a metal in MTPP. The above results are in good agreement with the literature values [7, 9]. Figure 1 shows IR spectrum of FeTPPCl as a representative compound in the selected porphyrin series.

^{1}Hnmr spectroscopy was further used to characterize the above porphyrins [10–13]. Figure 2 shows ^{1}Hnmr spectra of CoTPP as a representative sample of paramagnetic porphyrins. In CoTPP, it is seen that all types of proton signals are shifted to the maximum low field values with broadening of the resonance signals. Table 1 shows the proton NMR chemical shifts for β-pyrrole protons for the selected porphyrins.

TG–DSC measurements

Thermal studies of the porphyrins were conducted using thermogravimetry and differential scanning calorimetry in synthetic air from room temperature to 800 °C. Some reports also highlight the importance and relevance of thermal studies to macromolecules for kinetic and thermodynamic studies [14, 15].

Figure 3 shows the TG–DSC of TPP. It starts decomposing after 400 °C and the TG curve shows the mass loss up to 20% in first stage, and remaining 80% in next stage. Thus, it is seen that, TPP undergoes complete mass loss and no residue was left in the crucible. Further, from DSC curve it is clear that, TPP decomposes into four stages, i.e. at 432, 472, 546 and 719 °C, respectively. This decomposition may be due to rupture of pyrrole and phenyl rings. This shows that TPP is thermally stable up to 400 °C.

The CoTPP in synthetic air first shows gradual mass loss without any important thermal event but after this it shows sharp mass loss in two stages up to 76%. Thus, total mass loss for CoTPP at 800 °C is 87% as seen in Fig. 4. When the residue after thermal measurement was qualitatively analysed, it showed the presence of Co^{2+}, and hence confirmed the formation of metal oxide as an end product. The DSC curve in the above figure shows decomposition of CoTPP in four different stages at 413, 435, 502 and 574 °C, respectively.

Figure 5 shows the TG–DSC plot of FeTPPCl in synthetic air; it shows thermal stability up to 380 °C and then it loses mass up to 80% at 580 °C. The DSC curve of

Table 1 UV–visible absorption peaks and proton NMR chemical shifts

S. No.	Porphyrin	Absorption bands (in nm)					Chemical shift in ‘δ’ ppm for β-pyrrole protons
		Soret band	Q bands				
1	TPP	416	515	549	590	647	8.84
2	CoTPP	410	528				15.9
3	FeTPPCl	416	509	572	609		7.7
4	$SnTPPCl_2$	426	524	561	606	627	9.18

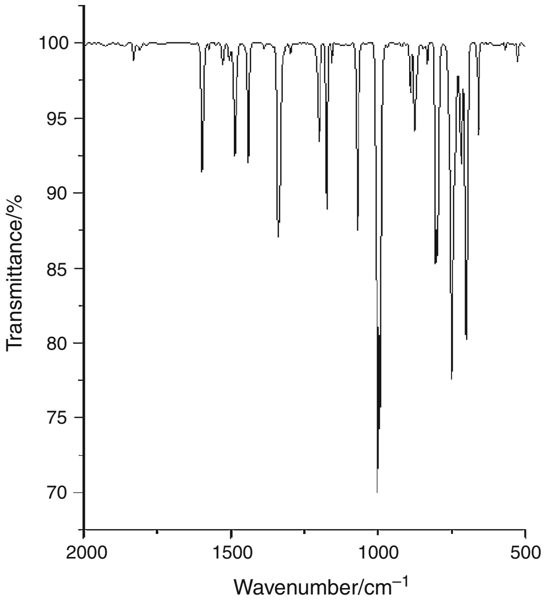

Fig. 1 FTIR spectra of FeTPPCl

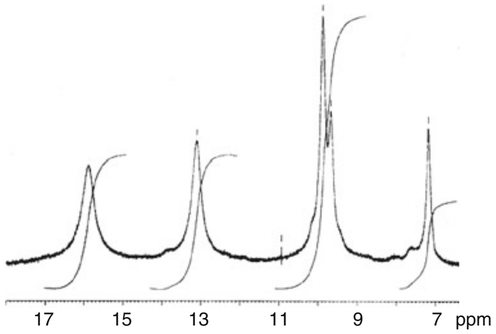

Fig. 2 Proton NMR of CoTPP

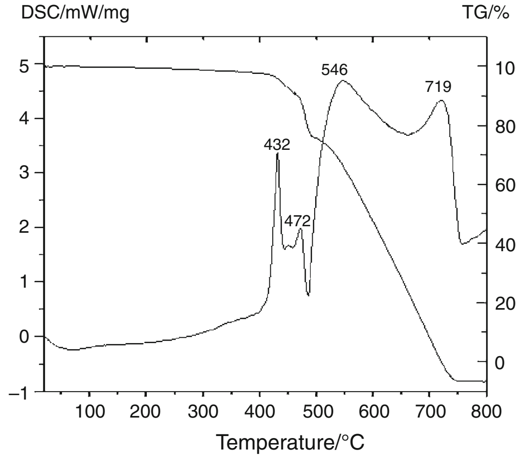

Fig. 3 TG–DSC curve of TPP

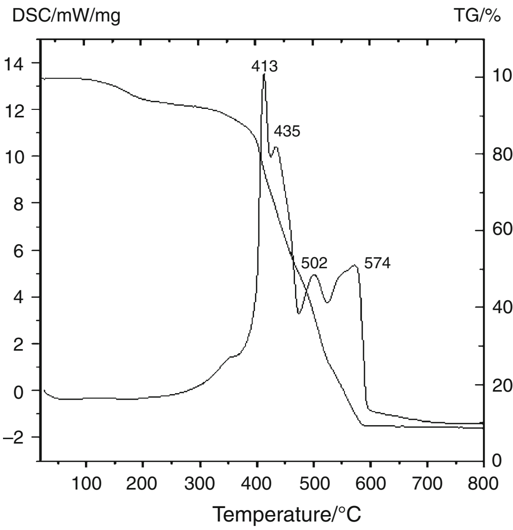

Fig. 4 TG–DSC curve of CoTPP

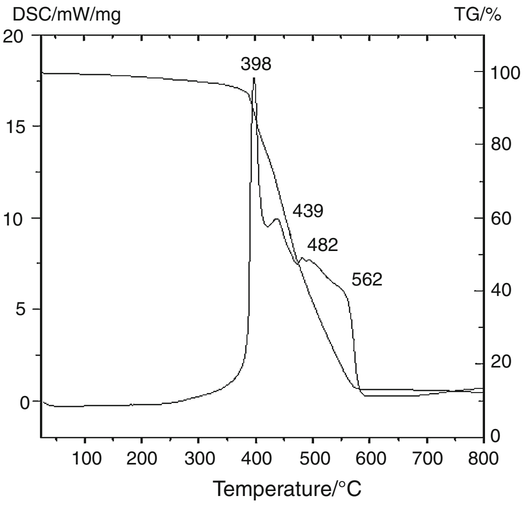

Fig. 5 TG–DSC curve of FeTPPCl

FeTPPCl shows four decomposition temperatures at 398, 439, 482 and 562 °C as is seen in the figure.

Figure 6 shows the TG–DSC results of $SnTPPCl_2$ in synthetic air. The TG curve shows loss of adsorbed moisture at 68 °C. Further, gradual loss in mass without any specific thermal event followed by sharp loss in mass up to 600 °C is observed and then no more mass loss. The DSC curve shows two decomposition temperatures at 489 and 515 °C, respectively. Thus, $SnTPPCl_2$ is thermally stable up to 440 °C.

The thermal stability of above porphyrins can be explained with help of X-ray diffraction studies. The TPP, a free-base porphyrin, is having rectangular geometry with D_{2h} symmetry, and it has shown 432 °C as first decomposition temperature. When TPP is metallated, the porphinato plane of four nitrogen atoms with Co^{2+} shows square planar

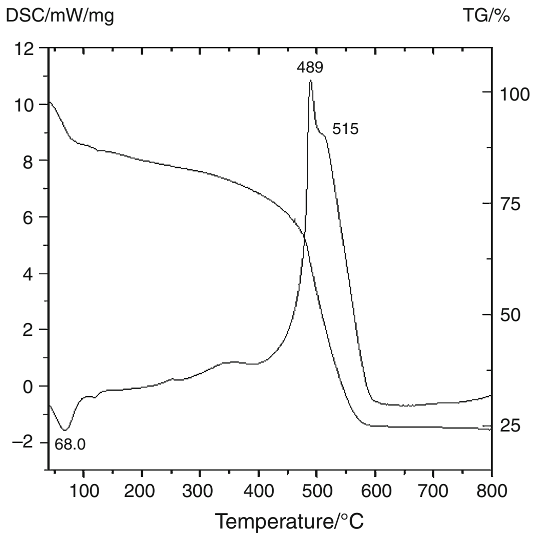

Fig. 6 TG–DSC curve of $SnTPPCl_2$

geometry with D_{4h} symmetry. Thus, when symmetry changes from D_{2h} to D_{4h}, stability of the compound should increase but square plane formed by CoTPP is not a perfect square but it is a ruffled square plane which decreases the thermal stability of CoTPP in comparison with TPP (432 °C), and it showed first decomposition temperature at 413 °C. When Fe was substituted in the porphyrin ring to form FeTPPCl, the geometry of a five coordinated compound is square pyramidal with C_{4v} symmetry. In this case, the central Fe atom is displaced from porphinato plane by 0.38 Å. Thus, the plane of four nitrogens with metal Fe is ruffled. Due to this reason the stability of a compound is expected to be less than TPP and CoTPP. This is seen by the first decomposition temperature of FeTPPCl at 398 °C. In $SnTPPCl_2$, there are two Cl atoms below and above the porphinato plane bonded to centrally located Sn. Here, as per X-ray analysis the stretching of Sn above and below the plane by two Cl atoms is equally compensated. Therefore, there is no displacement of Sn from the centre of the porphinato plane and exhibits octahedral geometry with D_{4h} symmetry. Thus, compound is expected to be most stable in the selected series of porphyrins. This is disclosed by the first decomposition temperature of $SnTPPCl_2$ at 489 °C which is higher of all. From above results it is evident that the thermal stability of the chosen series of porphyrins is in the following order $SnTPPCl_2 > TPP > CoTPP > FeTPPCl$, which is in accordance with their molecular geometries as revealed by X-ray diffraction studies.

TG–EGA–MS studies

This study involves conducting thermogravimetry and consequently number of evolved gases or organic species which are recorded by mass spectrometer within a selected temperature range. Therefore, depending upon the structure of the chosen compound, the mass spectrometer is calibrated for corresponding gases or organic species. In this case, there is every possibility that due to condensation some of the gases or species in the delivery tube may not be recorded even though they are present. TG–EGA–MS studies of CoTPP and FeTPPCl were conducted in argon atmosphere from room temperature to 900 °C.

Figure 7 shows the TG–EGA–MS diagram of CoTPP in argon. The evolved gases/species are H_2, CH_2/N and C_2H_4/N_2. It is also seen that, H_2 evolves at 475 to 750 °C, CH_2/N evolves within a range 650–750 °C and C_2H_4/N_2 evolves at around 725 °C. From these thermal events it gives an idea about the opening and fragmentation of porphyrin and phenyl ring. It is seen from Fig. 7 that there are two peaks during evolution of hydrogen at 475 and 750 °C, respectively. The first peak may be due to rupture of bonds between carbon and pyrrole protons whereas the second peak may be due to phenyl protons. Compared to phenyl ring, pyrrole ring is less aromatic and it being heterocyclic ring can be easily ruptured. This makes pyrrole proton to detach first followed by phenyl protons. Immediately after this, it is seen that with the further rise in temperature there is presence of CH_2/N and C_2H_4/N_2 species which strengthens the opening of pyrrole and phenyl rings. Thus EGA–MS analysis is helpful in giving mechanism of rupture of the porphyrin macro cycle sequentially.

Figure 8 shows TG–EGA–MS of FeTPPCl. The EGA–MS curves show presence of H_2, CH_2/N, C_2H_4/N_2 and HCl. The careful observation of the Fig. 8 indicates evolution of H_2 from 500 to 725 °C, CH_2/N at around 725 °C and C_2H_4/N_2 at around 750 °C. It is seen that after 400 °C, HCl is found to be present but signal obtained is feeble. This

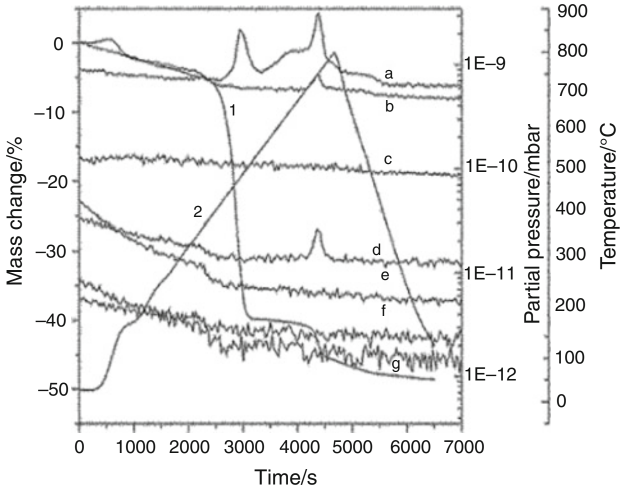

Fig. 7 TG–EGA–MS of CoTPP, (*1*) TG curve, (*2*) Temperature curve, (*a*) H_2, (*b*) C_2H_4/N_2, (*c*) NH_3, (*d*) C_2H_2/N, (*e*) C_2H_2, (*f*) C_2H_6 and (*g*) C_6H_5

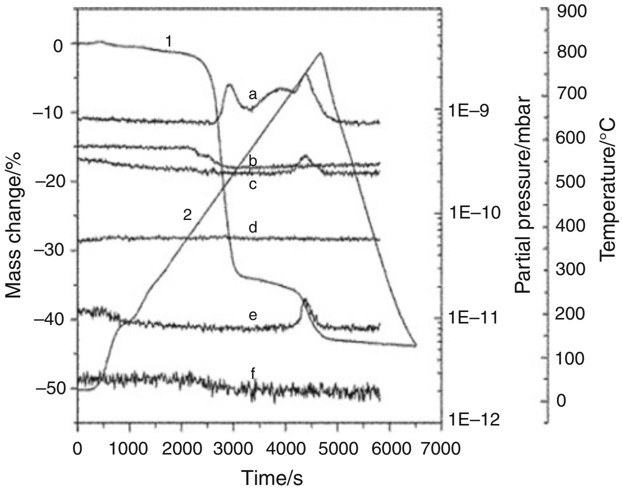

Fig. 8 TG–EGA–MS of FeTPPCl, (*1*) TG curve, (*2*) Temperature curve, (*a*) H_2, (*b*) HCl, (*c*) C_2H_4/N_2, (*d*) NH_3, (*e*) CH_2/N and (*f*) C_2H_2

explains that even though Cl being axial ligand to the central Fe gets detached first from the square pyramidal geometry and combines with hydrogen to give HCl. Further, the porphyrin ring opens up as mentioned for CoTPP.

Conclusions

The porphyrins found to be thermally stable up to around 400 °C. The free-base TPP showed complete loss in mass in TG–DSC measurements due to absence of metal. The MTPP did not show complete loss in mass due to presence of respective metal oxides. The TG–EGA–MS analysis has thrown light on the evolution of gases and different organic species depending upon the structure of the respective porphyrins. In the above-selected porphyrins, it is seen that the evolution of gases or species such as H_2 (2), CH_2/N (14) and C_2H_2/N_2 (28) is common to all porphyrins. Therefore, this gives the information about the sequence of cleavage of the porphyrin ring during the course of thermal analysis.

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