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Thermal behavior of tetrapyrrole derivatives and their mixed complexes

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ABSTRACT

The thermal properties of CoPc and ZnPc (Pc = phthalocyanine) and ZnTPP (TPP = tetraphenylporphyrin), pyrazine adducts and heterotriads [CoPc(pyz)ZnTPP(pyz)CoPc] and [ZnTPP(pyz)CoPc(pyz)ZnTPP] were investigated using TGA and DSC. The thermal stability of axial coordination was investigated for adduct complexes and it increased in the order $\mathrm{ZnPc(pyz)_2} < \mathrm{ZnTPP(pyz)_2} \approx \mathrm{CoPc(pyz)_2}$. The phthalocyanine–porphyrin mixed complexes decompose in several steps; the initial step corresponds to the degradation of the spacer ligand. It was shown that the breakdown mechanism of phthalocyanine macrocycle was affected by the triad formation.

1. Introduction

Metallophthalocyanines (MPc) and metalloporphyrins (MP) have unique physical and chemical properties [1–3]. Since their discovery until current days, these compounds have been extensively studied and have found applications in different ways, such as dyes or pigments, catalysts, semiconductors and electrochromic devices, among others [4,5]. The main applications of these compounds are related to π-electron conjugated system, thermal and chemical stability allied to the self-organization capability [6–11]. Combining the individual properties of these two complexes in the same structure by assembling a supramolecular structure can lead to the development of new materials with potential applications such as solar cells or photochromic devices.

The synthesis and investigation of such supramolecular assemblies have been stimulated lately. However, the knowledge of the properties of each macrocycle as individual components of supramolecular unit is relevant to understand the overall system. The reported information on thermal stability of these complexes is limited and few articles report the thermal properties of MPc or MP complexes [12].

Supramolecular assemblies, so far with promising results, are very recent and have received more attention concerning the electronic properties than thermal stability. The effect of peripheral functional groups or spacer ligands on the thermal stability has not been fully investigated.

In this paper, we report the study of the thermal characteristics of tetrapyrrole complexes (CoPc, ZnPc and ZnTPP), adducts ($\mathrm{CoPc(pyz)_2}$, $\mathrm{ZnPc(pyz)_2}$ and $\mathrm{ZnTPP(pyz)_2}$) and heterotriads formed by CoPc and ZnTPP having pyrazine (pyz) as spacer ligand, depicted in the Fig. 1, using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

2. Experimental

2.1. Synthesis of complexes, adducts and mixed complexes

ZnPc and CoPc were synthesized according to procedure described in the literature [13]. The purification procedure was adapted to avoid the use of solvents with high donor capabilities. The purification was carried out by washing with ethanol and methanol followed by Soxhlet extraction with acetone. Tetraphenylporphyrin ligand was prepared by reaction of pyrrol and benzaldehyde under reflux in acetic acid solution. The product was washed with methanol. ZnTPP was obtained as described by Rothermund and Menotti [14]. The crude product was purified chromatografically on aluminium oxide column using a 1:1 methanol/dichloromethane mixture as eluent.

Adduct complexes were obtained and purified for all three macrocycles, by fusion of pyrazine ligand, in excess, over the macrocycle complexes, as described by Schneider and Hanack [15]. The purity was verified by thin layer chromatography and elemental analysis.

Mixed porphyrin–phthalocyanine triads of CoPc and ZnTPP were obtained in two different macrocycle sequences. The syntheses were carried out by mixing free complexes and adduct in a 2:1 molar ratio, in dichloroethane solution. The solution was placed

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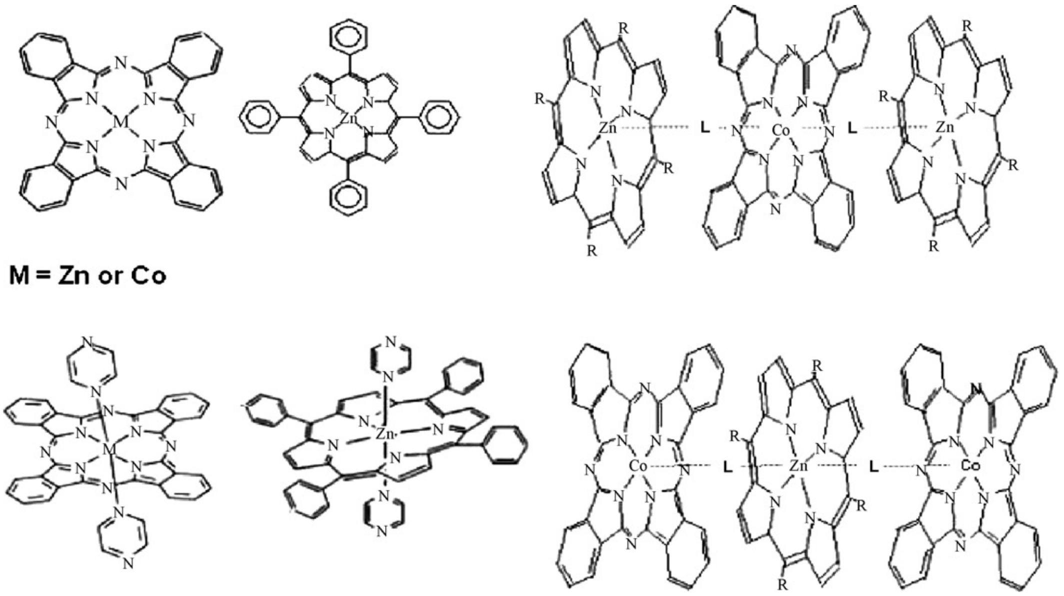

Fig. 1. Molecular structure of tetrapyrrole derivatives and mixed complexes: methallophthalocyanine MPc, Zinctetraphenylporphyrin ZnTPP; bispyrazinemethallophthalocyanine MPc(L)$_2$, zincbispyrazinetetraphenylporphyrin ZnTPP(L)$_2$; ZnTPP(L)CoPc(L)ZnTPP and CoPc(L)ZnTPP(L)CoPc (L = pyrazine and R = phenyl).

to react light protected at room temperature, until a powdery solid was formed. The solid was separated by centrifugation. The liquid residue was treated by solvent evaporation and purified by washing with ethanol. The triads ZnTPP(pyz)CoPc(pyz)ZnTPP and CoPc(pyz)ZnTPP(pyz)CoPc were obtained from precipitate and ethanol solution, respectively. The triads were characterized by infrared and UV–visible spectroscopy and elemental analysis. Anal. Calcd. for $C_{128}CoH_{80}N_{20}Zn_2$,: %: C, 73.6; H, 3.9; N,13.4. Found, %: C, 72.9; H, 3.7; N, 13.6 and Anal. Calcd. for $C_{116}Co_2H_{68}N_{24}Zn$, %: C, 70.2; H, 3.5; N, 16.8. Found, %: C, 70.3; H, 3.5; N, 16.1.

2.2. Instrumentation

Thermal stability was investigated by TGA and DSC. Thermogravimetric measurements were carried out on 2050 TGA TA instruments, under nitrogen flow, with heating rate of 10 °C/min, from 25 to 900 °C. Differential scanning calorimetry was performed using a Q100 DSC TA Instruments in the temperature range of −50 to 450 °C with a heating rate of 10 °C/min.

3. Results and discussion

ZnPc was synthesized and used to compare with ZnTPP and CoPc derivatives. ZnPc macrocycle was stable upto 416 °C and CoPc to 356 °C (Fig. 2a). Both metallophthalocyanines exhibit high thermal stability as described in literature [16,17], however ZnPc onset temperature suggests that zinc complex has higher stability. Nevertheless, the DTG peak temperature has not shown significant differences between the two phthalocyanine complexes.

The onset temperature suggests that the stability follows the order: ZnPc > ZnTPP > CoPc, however DTG temperature indicates that the ZnTPP is less stable than MPc parent. It may be due to different thermal decomposition reaction rates.

CoPc showed 4.4% weight loss between 234 and 356 °C with DTG peak at 310 °C, not observed for ZnPc complex. ZnTPP also showed a weight loss (2.5%) between 125 and 375 °C without apparent DTG peak. This first-stage weight loss was due to loss of adsorbed solvent molecules.

Differential scanning calorimetry was also performed. Fig. 2b shows the DSC curves for CoPc, ZnPc and ZnTPP. CoPc showed three endothermic peaks at 75, 255 and 286 °C, ZnPc showed several endothermic peaks and ZnTPP showed two endothermic peaks at 218 and 333 °C (Table 1). The endothermic peaks at ca. 75 °C for metallophthalocyanine and the exothermic peak at 54 °C for the metalloporphyrin complexes can be related to desolvation process of small solvent molecules weakly bound, although weight loss was not observed at these temperatures on TG curve as observed by Lebedeva and co-workers [18,19] for crystal solvates.

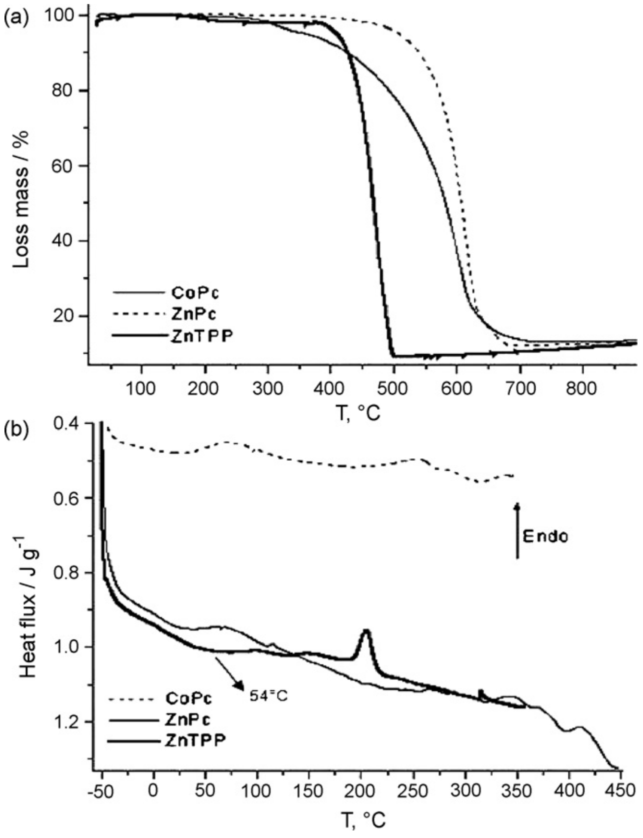

Fig. 2. TG (a) and DSC (b) curves of CoPc, ZnPc and ZnTPP complexes.

Table 1
Thermal decomposition data.

Compounds	Temperature range (°C)	DTG peak (°C)	Mass loss calculated (%)	Mass loss found (%)	DSC peak endothermic (°C)	DSC peak exothermic (°C)	Tentative assignment[a]
CoPc	234–356	310		4.4	75; 255; 286		
	356–654	599	82.3	82.0			Pc ring
ZnPc	416–692	606	86.6	86.9	72; 317; 349; 369; 412		Pc ring
ZnTPP	125–375	–		2.5	218; 333	54	
	375–496	465	88.6	88.8			TPP ring
$CoPc(pyz)_2$	120–248	186	11.4	11.5	54; 178		pyz
	293–654	602	74.7	74.0	325; 340		pyz and Pc ring
$ZnPc(pyz)_2$	33–88	51 and 76	4.2	4.3	69; 117; 129		Partial pyz
	427–630	596	83.1	83.0		284	Residual pyz and Pc ring
$ZnTPP(pyz)_2$	113–224	163 and 226	3.7	3.7	182; 208	54, 174	Partial pyz
	334–503	476	88.5	88.8	310	283	Residual pyz and TPP ring
ZnTPP(pyz)CoPc(pyz)ZnTPP	137–180	165	4.0	4.5			pyz
	320–483	469	67.2	67.1			2TPP ring: pyz and partial PC ring
	483–543	526	18.4	18.4			Pc ring
CoPc(pyz)ZnTPP(pyz)CoPc	95–217	–	5.8	5.8			pyz ring
	217–318	–	5.7	5.6			pyz ring
	318–492	478	70.6	70.5			TPP ring and partial Pc ring
	492–538	515	8.1	8.1			Pc ring

[a] The assignments are estimated using the minimal formula calculated by the weight loss.

Caminiti and co-workers [20] reported a phase transition for CoPc from α to βform using energy dispersive X-ray diffraction (EDXD) and DSC. The authors observed an intraphase polymorphic transition from 185 to 270 °C and evaluated the induction time at different temperatures. In the Fig. 2b an endothermic peak can be observed at 255 °C on the DSC curve. It may be due to the nucleation of an intraphase polymorphic transition from α to β-form as observed by Caminiti and coworkers. ZnPc DSC curve exhibits several peaks between 317 and 413 °C, with no weight loss associated at TG curve. The peaks at 349, 369 and 408 °C may be related to ZnPc intraphase polymorphous transitions followed by the initial decomposition of the macrocycle. The ZnTPP DSC curve showed an intraphase polymorphic transition at 218 °C [21]. The intraphase transition was observed for all three macrocycles, however this process happens at lower temperature to the porphyrin derivative.

Lebedeva and co-workers [19] have investigated the formation of crystal solvates with benzene and pyridine. The authors have shown that the thermodynamic stability of the interaction between $Zn(t\text{-}Bu)_4Pc$ and electron-donor ligands was ruled by the strength of the σ-bond metal-macroring. In order to investigate the coordination capabilities of the macrocycles, adducts with pyrazine ligand were prepared.

The axial coordination of pyrazine ligand resulted in a distinct profile to $CoPc(pyz)_2$ TG curve compared to CoPc complex (Fig. 3a). A weight loss between 120 and 248 °C (DTG peak at 186 °C) is observed, this temperature range is higher than pyrazine melting point or solvent desolvation and corresponds to partial loss of pyrazine ligands. The residual pyrazine ligand, still bound to the macrocycle complex, goes through decomposition from 293 to 654 °C (DTG peak: 602 °C) together with macrocycle ring. This process is better observed on DSC curve. Four endothermic peaks can be observed at $CoPc(pyz)_2$ DSC curve (Fig. 3b). The first endothermic peak at 54 °C is associated with desolvation process, not observed on TG curve. The second endothermic peak at 178 °C is consistent with the partial loss of the first pyrazine ligand coordinated to the metal ion, estimated by weight loss on TG curve. Endothermic peaks at 325 and 340 °C were observed at DSC curve, even though; the TG curve shows only a major thermal process from 293 to 654 °C. These two DSC peaks indicate that the remaining pyrazine ligand loss occurs before the macrocycle decomposition.

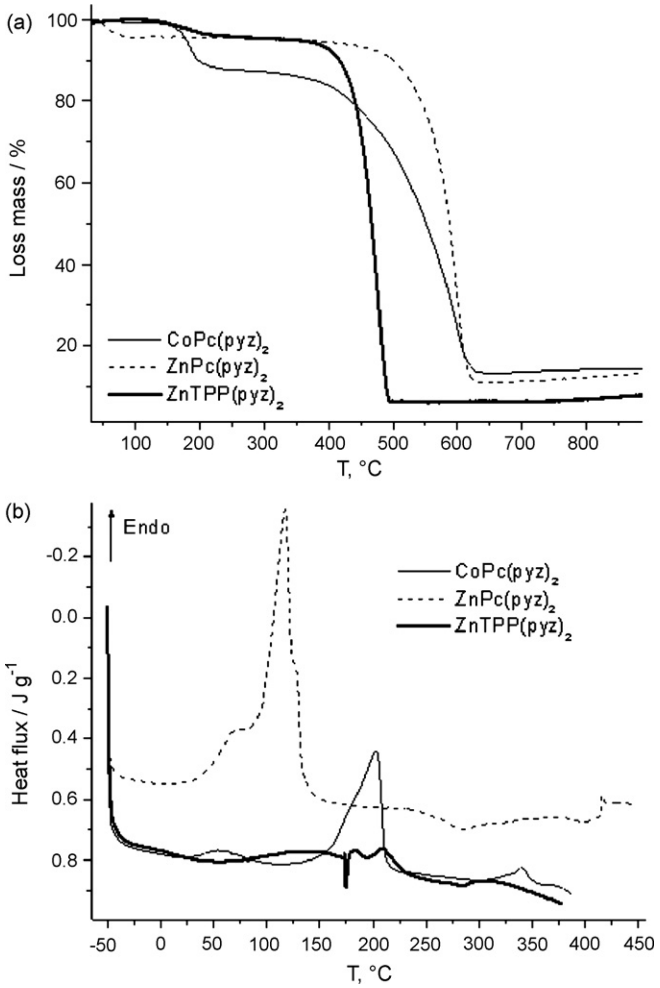

Fig. 3. TG (a) and DSC (b) curves of $CoPc(pyz)_2$, $ZnPc(pyz)_2$ and $ZnTPP(pyz)_2$.

TG curves for ZnPc(pyz)$_2$ and ZnTPP(pyz)$_2$ displayed slight differences on the thermal behavior compared to ZnPc and ZnTPP complexes. The major difference was related to weight loss of 4.3% for ZnPc(pyz)$_2$ between 33 and 88 °C and 3.7% between 113 and 224 °C for ZnTPP. These weight losses correspond to the partial fragmentation of the pyrazine ring. In both adducts the decomposition of the residual pyrazine ring seems to occur together with macrocycle ring (TPP or Pc). The loss of axial ligand seems to go through similar breakdown mechanism for both zinc adducts. The higher fragmentation temperature of pyrazine ligand for ZnTPP adduct (DTG peak at 166 °C) indicates a stronger interaction between the axial ligand and metallic center in the porphyrin derivative, which indicates that the macrocycle ligand has a significant role in the degradation process of the axial ligand.

The DSC curves showed a distinct behavior for adducts. ZnPc adduct exhibited three endothermic peaks from 50 to 150 °C not observed in the DSC curve of ZnPc. The endothermic peaks were observed at 69, 117 and 129 °C. The first peak at lower temperature can be assigned to the cleavage of the pyrazine ligand. The endothermic peaks at higher temperature (117 and 129 °C) and an exothermic peak at 284 °C may be related to the phase transition or residue rearrangements, which occur after the decomposition of the pyrazine ligand. ZnTPP(pyz)$_2$ DSC curve showed three endothermic peaks at 182, 208 and 310 °C and three exothermic peaks at 54, 174 and 283 °C. At 174 °C was observed an intraphase transition followed by the partial fragmentation of pyrazine ligand at 182 °C. The peak at 283 °C is related to rearrangements on the solid after the ligand loss followed by the degradation of the residual pyrazine fragments at 310 °C.

ZnTPP and CoPc adducts exhibited similar behavior concerning the temperature range for axial ligand decomposition. Although the metal ion and macrocycle ligand and breakdown mechanism are quite different, the loss of axial ligand occurs at similar temperature. When the same metal ion is coordinated to pyrazine ligand (ZnTPP(pyz)$_2$ and ZnPc(pyz)$_2$) similar breakdown mechanism was observed at different temperature ranges. The results indicate that the charge density on the metal ion, exerted by the macrocycle ligand or d configuration of metal ion, affects the thermal stability of the axial ligand.

Mixed porphyrin–phthalocyanine complexes of CoPc and ZnTPP were obtained having pyrazine ligand as spacer. Two different macrocycle sequences were isolated, ZnTPP(pyz)CoPc(pyz)ZnTPP and CoPc(pyz)ZnTPP(pyz)CoPc. The triad thermal stability was investigated through thermogravimetric analysis.

Fig. 4 shows the thermograms for both triads. The triad ZnTPP(pyz)CoPc(pyz)ZnTPP exhibits a weight loss of 4.7% at temperature range between 130 and 180 °C (DTG peak at 165 °C). This temperature is very similar to the temperature for partial fragmentation of pyrazine ligand observed for ZnTPP adduct. The thermal degradation of the macrocycles occurred at two well-defined temperature ranges. The first one occurs from 320 to 483 °C (with 67% weight loss, DTG peak at 469 °C) and another from 483 to 543 °C (18% at 526 °C). The first DTG peak is consistent with thermal degradation of the ZnTPP macrocycle, however, the second DTG peak occurred at lower temperature than the correlated temperature for CoPc macrocycle ring decomposition. The combined temperature ranges for the decomposition of isolated macrocycles are broader compared to the triad indicating that the formation of mixed complexes has an effect on the decomposition mechanism of the macrorings.

The CoPc(pyz)ZnTPP(pyz)CoPc triad showed a distinct thermal behavior regarding the spacer ligand decomposition. Two slight slopes with not-well-defined DTG peaks were observed at temperature ranges from 95 to 217 °C and 217 to 318 °C, with weight loss of 5.8 and 5.6%, respectively (Fig. 4). These weight losses correspond to pyrazine ligand degradation. The macrocycle degradation also occurred in two steps: one from 318 to 492 °C (DTG peak at 478 °C) and another from 492 to 538 °C (DTG peak at 515°). The overall temperature ranges for the macrocycle decomposition for both triads were similar. The first DTG peak at 478 °C occurred at similar temperature for degradation of the ZnTPP adduct macroring with partial decomposition of Pc macroring, while the remaining Pc residue goes through decomposition at 515 °C.

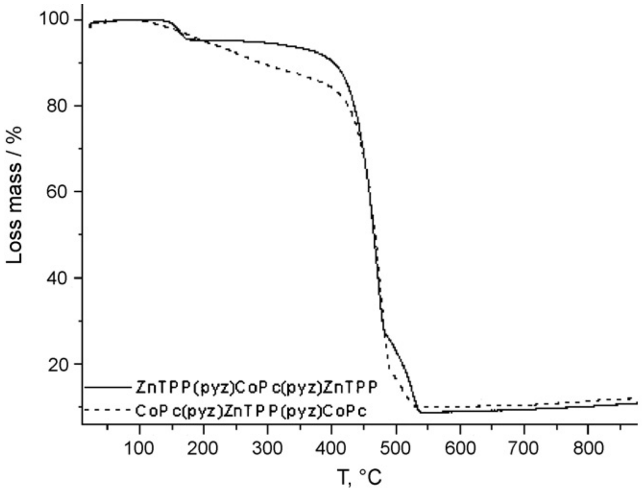

Fig. 4. TG curves of mixed complexes CoPc(pyz)ZnTPP(pyz)CoPc and ZnTPP(pyz)CoPc(pyz)ZnTPP.

4. Conclusions

The thermal properties of tetrapyrrole derivatives were investigated using TGA and DSC. DTG temperatures to macrocycle decomposition for CoPc and ZnPc were higher compared to ZnTPP derivative. The axial coordination stability decreases in the order CoPc(pyz)$_2$ $\approx$ ZnTPP(pyz)$_2$ > ZnPc(pyz)$_2$. The thermal decomposition of the CoPc adduct goes through different breakdown mechanisms than zinc adducts as shown by TG curves. The thermal stability of axial ligand was determined by the macrocyle ligand and coordinated metal ion. Phthalocyanine–porphyrin mixed complexes were synthesized and the thermal stability of two macrocycle sequences was investigated. The macrocycle sequence triads showed an effect on the temperature range for the breakdown of the spacer ligand and macrocycles cleavage, but always closer to the breakdown temperature of the ZnTPP unit. The TPP macrocycle breakdown temperature is not affected by the triad formation, however the decomposition of Pc ring occurs at lower temperature than the isolated complex.

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