

Spectral and thermal investigations of porphyrin and phthalocyanine nanomaterials

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Macroheterocyclic compounds, such as metal porphyrins and phthalocyanines, have unique physical and chemical properties and have potential applications in many areas such as in medicine[1]. New structures of porphyrins and phthalocyanines can form a new base for nanotechnology. The effects of peripheral functional groups or spacer ligands on the thermal stability has not been fully investigated. Some metallo- porphyrins and metallo-phthalocyanines (TPP, TPPTiCl₂, TPPWCl₄, PcSiCl₂, PcTiCl₂, and PcWCl₄) have been investigated in this paper using thermal analysis (TGA/DTG), infrared spectroscopy Fourier-transformed (FT-IR), fluorescence and UV-VIS absorption spectra. Thermogravimetry (TG) have been used to examine the thermochemistry, to study the thermal stability and thermal decomposition of the new complexes of porphyrins and phthalocyanines. The composition of these compounds were determined from the TGA curves.

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1. Introduction

Porphyrins (P) and phthalocyanine (Pc), either as free bases or metallocomplexes have been intensively studied during last few years because of their electrical and optical properties as well as their chemical and thermal stability. One of the most important properties of the porphyrin and phthalocyanine molecules is their ability to coordinate to metal ions, yielding stable intercomplex salts. Stable complexes of metallo-porphyrins and complexes of metallo- phthalocyanines results from formation of four equivalent σ bonds $N \rightarrow M$ [2]. Both of them have a planar macrocycle with an 18 π -electron system and large applications due to their unique optical, electronic, catalytic and structural properties.

Metallo-phthalocyanines (MPc) and metallo-porphyrins (MTPP) have unique physical and chemical properties. The main application of these compounds are related to π -electron conjugated system, thermal and chemical stability allied to the self-organization capability.

In this work, the stability of metallophthalocyanine has been studied through thermogravimetry analysis, FT-IR analysis, Fluorescence analysis, UV-VIS analysis.

2. Experimental

2.1. Materials and methods

Porphyrins are tetrapyrrolic pigments, Fig. 1, with four pyrrole subunits joined together by four methine bridges to give a cyclic molecule. With a highly conjugated skeleton, porphyrins have a characteristic ultra-

violet visible (UV-VIS) spectrum. The spectrum typically consists of an intense, narrow absorption band at around 400 nm, known as the Soret or B band, followed by four longer wavelength (450–700 nm), weaker absorptions (free-base porphyrins) referred to as the Q bands.

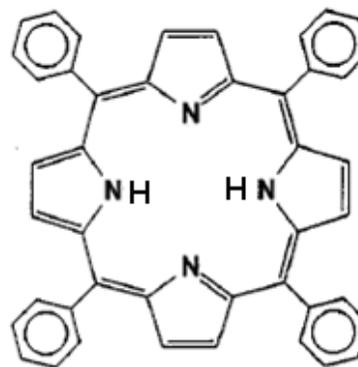


Fig. 1. Chemical structures of tetraphenylporphyrin TPP

Phthalocyanines are azaporphyrins consisting of four benzoindole nuclei connected by nitrogen bridges in a 16-membered ring of alternating carbon and nitrogen atoms around a central metal atoms which form stable chelates with metal cations (dia or paramagnetic ion). The molecule consists of the central metal atom (Si, Ti or W), which is surrounded by four nitrogen atoms—pyrrole; four other nitrogen atoms—bridging aza; 32 carbon atoms—the pyrrole and the benzene ones. (Fig. 2) [3].

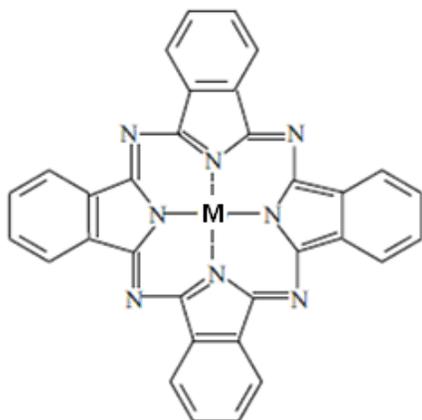


Fig. 2. Chemical structures of metallo-phthalocyanines

In general, phthalocyanines have UV-Vis absorption spectra with intense $\pi-\pi^*$ transitions, usually referred to as Q bands in the range 660-700 nm with higher energy vibration associated components in the range 600-660 nm. Also phthalocyanines have Soret B band in the range 420-320 nm, N band around 330-285 nm and an L-band at 270-230 nm [4].

Infrared spectra were measured using an FT-IR spectrometer coupled to a PC with analysis software. The samples were done in diamond ATR unit (attenuated total reflection), bonded into a tungsten carbide mount, impermeable non-allowing the lenses system condensation, KRS5 lenses - applications placed in the holder directly in the IR laser beam. ATR spectroscopy usually requires little to no sample preparation.

The samples were analyzed by Spectrofluorimeter Jasco FP 6500.

The UV-VIS spectra have been recorded in DMSO solvent, by using a SPECORD M400 Carl Zeiss Jena, equipped with a double beam microprocessor.

The TG curves of the samples were performed on a thermogravimetric analyzer Mettler Toledo sistem TGA/SDTA 851^e under nitrogen atmosphere (99.999%) from 25 to 900 °C, in Al₂O₃ crucibles (70 μ L). The heating rate was 10⁰ C /min and the flow rate of nitrogen was 80 mL /min. The TG equipment was calibrated by indium and aluminium pills.

3. Results and discussion

Infrared spectra were measured using an FT-IR spectrometer coupled to a PC with analysis software. The samples were done in diamond ATR unit (attenuated total reflection), bonded into a tungsten carbide mount, impermeable non-allowing the lenses system condensation, KRS5 lenses - applications placed in the holder directly in the IR laser beam. ATR spectroscopy usually requires little to no sample preparation.

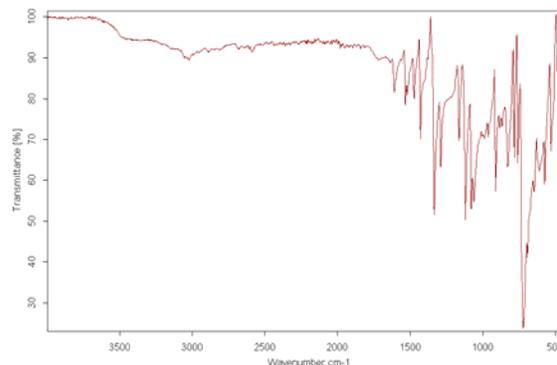


Fig. 3. IR spectra of PcSiCl₂

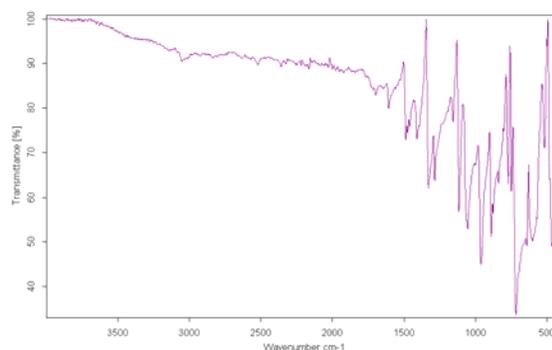


Fig. 4. IR spectra of PcTiCl₂

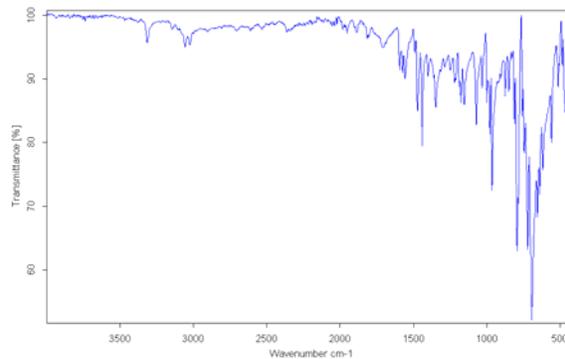


Fig.5. IR spectra of TPP.

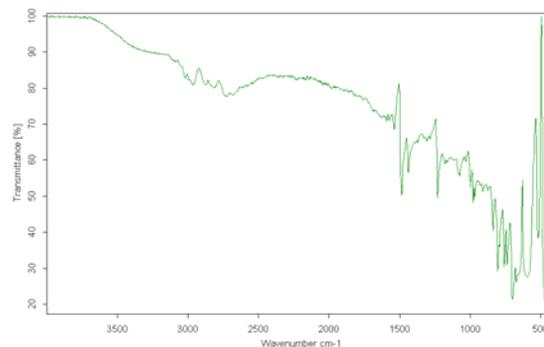
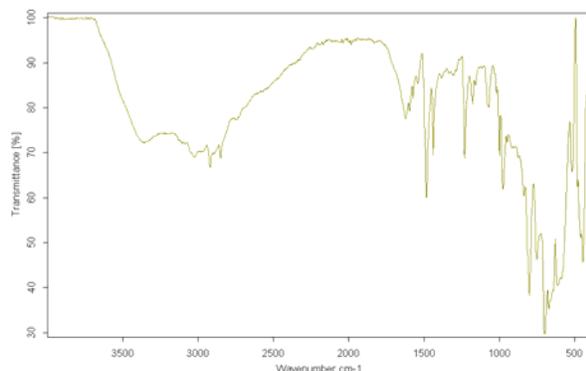


Fig. 6. IR spectra of TPPTiCl₂

Fig. 7. IR spectra of TPPWCl₄Table 1. Vibration frequencies (cm⁻¹) in IR spectra of MPcCl₂

PcSiCl ₂	PcTiCl ₂	Identification
3041	3050	ν _{C-H} (arom.)
1637	1637	ν (C=C)
1609	1605	ν (C=C)
1559	1542	ν (C=C)
1532	1524	ν (-N=)
1472	1488	ν (isoindole)
1429	1428	ν (isoindole)
1378	1393	ν (pyrrole and nitrogen mesoatoms)
1334	1330	ν (pyrrole)
1163	1157	δ _{C-H} (in-plane + isoindole)
1119	1118	Isoindole totally symm.
1061	1064	δ _{C-H} (in-plane+ isoindole)
1005	1001	δ _{N-H} (in-plane)
961	962	Benzene totally symm.
883	885	δ (isoindole + nitrogen mesoatoms)
783	790	δ _{C-H} (out-of-plane)
759	760	δ (Pc rings)
722	739	δ _{C-H} (out-of-plane)

For phthalocyanines, IR spectra reflect changes in the configuration of phthalocyanine macrocycles due to the introduction or substitution of a template metal (Table 1 Figures 3,4).

The IR spectra of aromatic condensed benzene rings of metal phthalocyanines include the most extensive set of stretching and bending vibration bands: stretching vibrations of C–H bonds (3046–3060 cm⁻¹) of relatively low intensity and skeletal C–C vibrations (1580–1610 cm⁻¹) with intensities varying from moderate to very low. The frequency of 1580 cm⁻¹ is caused by stretching vibrations of the C–C bond condensed with the pyrrole cycle. Intense vibrations in the region of 947 cm⁻¹ are totally symmetric stretching vibrations of C–C bonds of the aromatic ring. Plane bending vibrations of C–H are in the ranges of 1283–1289, 1158–1167, 1091–1096, and 1033–1060 cm⁻¹; their intensity, as a rule, varies from moderate to low.

Out-of-plane bending vibrations of C–H bonds of metal phthalocyanines appear in the range of 720–780 cm⁻¹.

A high-intensity band at 1500–1530 cm⁻¹ corresponds to vibrations of nitrogen bridging atoms (mesoatoms –N=). Stretching vibrations of isoindole fragments (including vibrations of the pyrrole and benzene residues) manifest themselves in the range of 1420–1480 cm⁻¹; the band intensity varies from low to very high. Vibrations of the –C=C–N= group (pyrrole fragment and nitrogen mesoatoms) appear as a low intensity band at 1396–1407 cm⁻¹ and a very strong (characteristic of all phthalocyanines) band at 1320–1365 cm⁻¹. Strong totally symmetric vibrations of isoindole fragments are in the range of 1112–1120 cm⁻¹.

Table 2. Vibration frequencies (cm⁻¹) in IR spectra of MTPP

TPP	TPPTiCl ₂	TPPWCl ₄	Identification
3438	-	-	ν _{N-H}
3313	-	-	δ _{N-H} associated
3055	3050	3050	ν (C-H)
3022	3018	3025	ν (C-H)
2901	-	2918	ν (C-H)
2813	2847	2849	ν (C-H)
1594	1591	1595	ν (C-H)
1574	1573	1573	ν (C=N)
1557	1537	1541	ν (C=NH)
1472	1485	1484	ν (C=N)
1441	1437	1440	ν (C=N)
1400	-	-	ν (C-H) pyrrole
1032	1029	1030	δ _{C-C}
1000	999	1001	δ _{C-H}
964	966	977	δ _{C-H}
874	875	876	γ _{C-C}
812	805	801	γ _{C-H}
785	792	752	γ _{C-H}

Table 2 and Figures 5-7 shows the most relevant results extracted from the IR spectra of the MTPP. IR spectra of TPP show the presence of the characteristic bands of ν_{N-H} in the spectral range 3314–3528 cm⁻¹.

Thus, two bands corresponding to the ν_{N-H}: the first one, well individualized in the area 3448–3430 cm⁻¹, which can be attributed to ν_{N-H} elongation vibrations; the second one, less intense, in the 3316–3314 cm⁻¹ range, corresponding to the stretching vibrations, ν_{N-H} associated were present.

Other four bands observed in the higher wavenumber region (3053 cm⁻¹ – 2849 cm⁻¹) to the stretching vibrational motion of C–H bond of the porphyrin ring. The bands at 1594–1608 cm⁻¹ and 1573–1582 cm⁻¹ can be assign to C–N stretching vibrations.

The samples were analyzed by Spectrofluorimeter Jasco FP 6500; the results are shown in Table 3 and Table 4.

Table 3. The emission bands of the metallo-phthalocyanines samples in the DMSO solutions, excited at $\lambda_{exc}=620$ nm

PcSiCl ₂		PcTiCl ₂	
λ_{em} (nm)	I	λ_{em} (nm)	I
678	673	627	18
		693	115

Table 4. The emission bands of the metallo-porphyrins samples in the DMSO solutions, excited at $\lambda_{exc}=620$ nm

TPP		TPPTiCl ₂		TPPWCl ₄	
λ_{em} (nm)	I	λ_{em} (nm)	I	λ_{em} (nm)	I
		612	64		
656	432	653	241	652	173
711	38	711	27	710	22

Phthalocyanines have UV-Vis absorption spectra with intense p-p* transitions, usually referred to as Q bands in the range 660-700 nm with higher energy vibration associated components in the range 600-660 nm. Also phthalocyanines have Soret B band in the range 420-320 nm, N band around 330-285 nm and an L-band at 270-230 nm.

With a highly conjugated skeleton, porphyrins have a characteristic ultra-violet visible (UV-VIS) spectrum. The spectrum typically consists of an intense, narrow absorption band at around 400 nm, known as the Soret or B band, followed by four longer wavelength (450-700 nm), weaker absorptions (free-base porphyrins) referred to as the Q bands.

The optical absorption of thermally evaporated tetraphenylporphyrin (TPP) in the UV-VIS region have been studied. The absorption spectra recorded in the UV-VIS region showed different absorption bands, Q-band region consist of four bands in the region 500-720nm, namely the Soret (B) at region 360-490nm, and two other bands labeled N and M in UV region.

Table 5. Maximum values of the wavelength, λ (nm), of the absorption bands of the UV-VIS spectra of the metal complexes in DMSO

Compounds	Soret λ (nm)	Q bands			
		IV	III	II	I
PcTiCl ₂	300				690
PcSiCl ₂	300		610	670	710
TPP	418	510	540	600	640
TPPTiCl ₂	410			600	620
TPPWCl ₄	410			600	645

The TG curves of the PcWCl₄, PcTiCl₂, PcSiCl₂, TPP, TPPTiCl₂ and TPPWCl₄ were performed on a thermogravimetric analyzer Mettler Toledo sistem TGA/SDTA 851^e under nitrogen atmosphere (99.999%) from 25 to 900 °C, in Al₂O₃ crucibles (70 μ L). The heating rate was 10⁰ C /min and the flow rate of nitrogen was 80 mL /min. The TG equipment was calibrated by indium and aluminium pills.

Metal complexes derived from phthalocyanine are fairly stable to thermal and oxidative decomposition, and parameters of that process depend on the number, position, and on the presence of other substituents.

The effect of peripheral functional groups or spacer ligands on the thermal stability has not been fully investigated [5].

Table 6. Thermal decomposition data

Compounds	Temp. range (°C)	Mass loss calculated (%)	Mass loss found (%)	Tentative assingment
PcWCl ₄	25-280	19,9	25,1	Pc ring
	280-900	31,74	39,18	
PcTiCl ₂	25-350	4,05	4,03	Pc ring
	350-900	65,7	54,5	
PcSiCl ₂	250-900	43,6	38,5	Pc ring
TPP	230-900	45,32	47,3	TPP ring
TPPWCl ₄	25-380	7,1	7,3	TPP ring
	380-900	43,6	40,7	
TPPTiCl ₂	25-350	15	15,9	TPP ring
	350-900	39,1	32,3	

One of the most important properties of the phthalocyanine molecules is their ability to coordinate to metal ions, yielding stable intercomplex salts. It is well known that phthalocyanine unit is resistant to thermal oxidation [5].

The thermal oxidation of the porphyrins and phthalocyanines occurs in several steps involving the oxidation of peripheral substituents, accompanied by some macrocycle breaks, and metals oxidation to higher oxides [2].

Metal complexes derived from phthalocyanine are fairly stable to thermal and oxidative decomposition, and parameters of that process depend on the number, position, and on the presence of other substituents [5].

The decomposition consists of two stages for PcWCl₄, PcTiCl₂, TPPTiCl₂, TPPWCl₄ and only one stage for PcSiCl₂ and TPP (Table 6).

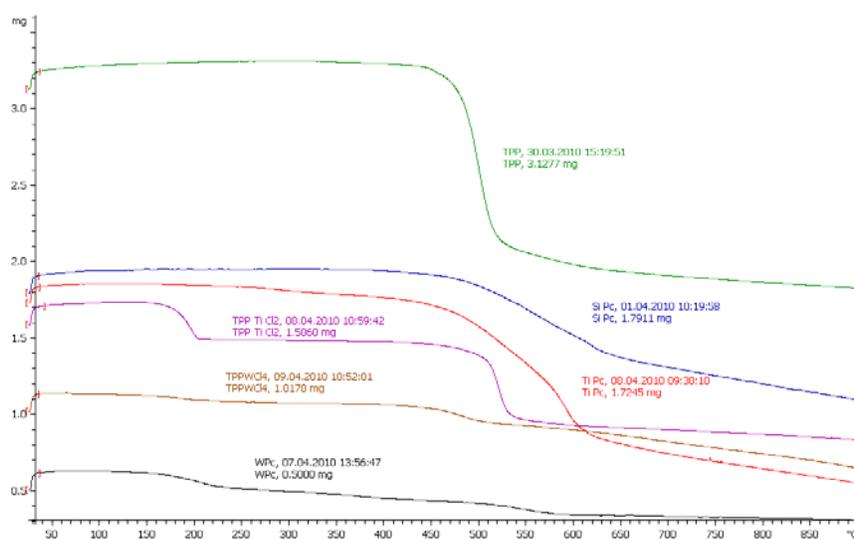


Fig. 8. TGA curves of ($PcSiCl_2$, $PcTiCl_2$, $PcWCl_4$, TPP, $TPPTiCl_2$, $TPPWCl_4$)

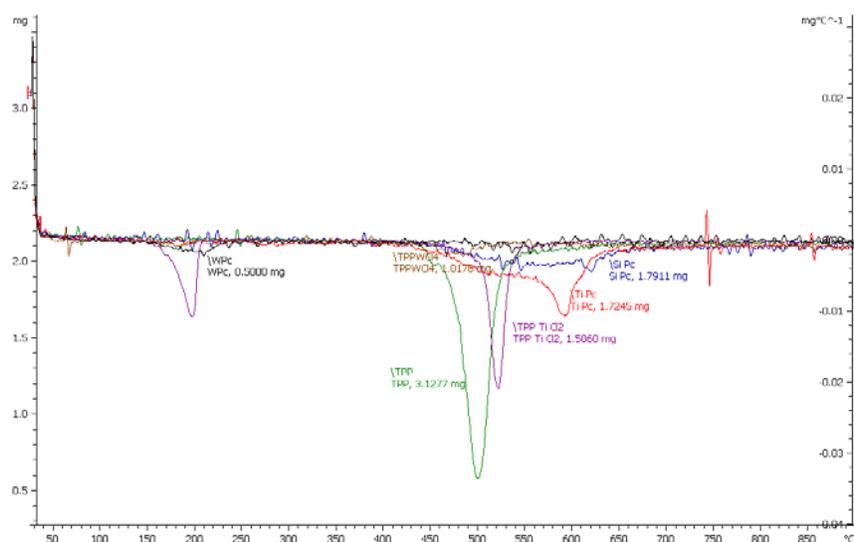


Fig. 9. DTG curves of ($PcSiCl_2$, $PcTiCl_2$, $PcWCl_4$, TPP, $TPPTiCl_2$, $TPPWCl_4$)

All the samples exhibit high thermal stability as described in literature, however $PcSiCl_2$ onset temperature suggests that this complex has higher stability. (Figure 9)

4. Conclusions

In this work, the stability the metalloporphyrins and metallophthalocyanines has been studied through thermogravimetry analysis, FT-IR analysis, Fluorescence analysis and UV-VIS analysis. Thermal properties of the metalloporphyrins and metallophthalocyanines were investigated by TGA/DTG methods, trying to appreciate the thermal stability of these compounds.

Acknowledgments

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References

- [1] S.-F. Pop, R.-M. Ion, M. Neagu, C. Constantin, Journal of Materials Science and Engineering USA, 4, 3,(2010)

- [2] S.-F. Pop, R.-M. Ion, J. Int. Res. Pub., Issue Materials, Methods & Technologies, **4**(2), 112 (2010).
- [3] V. V. Maslyuk, V. Y. Aristov, O. V. Molodtsova, D.V. Vyalikh, V.M. Zhilin, Y.A. Ossipyan, T. Bredow, I. Mertig, M. Knupfer, Appl Phys A **94**, 485 (2009).
- [4] R. Bonnett, Chem. Soc. Rev. **24**, 19 (1995)
- [5] S.-F. Pop, R.-M.Ion, J. Optoelectron. Adv. Mater. **12**(9), 1976 (2010).

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