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# Triazolephthalocyanine *versus* phthalocyanine nickel(II) and copper(II) complexes: a thermogravimetric stability study

**Valter Stefani,*[a] Beatriz Cabezón,[b] Elton L. G. Denardin,[a] Dimitrios Samios*[a] and Tomás Torres*[b]**

[a]*Laboratório de Instrumentação e Dinâmica Molecular, Instituto de Química/UFRGS, Av. Bento Gonçalves, 9500 CEP: 91501-970 Porto Alegre, RS, Brazil.*
*E-mail: dsamios@if.ufrgs.br; vstefani@iq.ufrgs.br*
[b]*Departamento de Quimica Orgánica (C-I), Facultad de Ciencias, Universidad Autónoma de Madrid, 28049 Madrid, Spain. E-mail: tomas.torres@uam.es*

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Several nickel(II) and copper(II) complexes of triazolephthalocyanine and phthalocyanine, bearing different substituents and substitution patterns, have been synthesised and studied by standard thermogravimetric techniques in order to evaluate their thermal stability and related molecular parameters. The overall thermodegradation processes have been analysed in the partial degradation processes. The comparison of thermal stability has been made in terms of partial degradation fitting parameters: maximum degradation rate ($R_{\max}$), maximum degradation rate temperature ($T_{R\max}$), degradation temperature range which is related to the half-width at half-height values ($\Gamma$); and conventional kinetic parameters: activation energy ($E_a$), pre-exponential factor (ln $A$) and reaction order ($n$); obtained by Barrett methods. The Ni(II) and Cu(II) phthalocyanine and triazolephthalocyanine complexes display high thermostability. The degradation processes and the corresponding maximum degradation rate temperature depend upon the complexed metal and the number, nature and position of the peripheral groups. The replacement of nickel by copper in unsubstituted metallophthalocyanines increases the degradation temperature, while the same change in triazolephthalocyanine complexes decreases this temperature. The effect of the side group and the kinetic behaviour have been studied. The compensation effect between pre-exponential factor $A$ and activation energy $E_a$ is confirmed.

## Introduction

Phthalocyanines,[1,2] and related compounds with well-defined specific physical and chemical properties, are considered promising targets for the construction of organic molecular materials. Their unusual properties, such as thermal stability, semiconductor behaviour[1,2] and intense non-linear optical responses,[3–6] allied to their chemical versatility and intrinsic capacity for self-assembly to provide supramolecular systems,[7–11] suggest a wide range of potential technological applications for phthalocyanines in materials science.

Triazolephthalocyanines (Tpc)[1] are isoelectronic core-modified phthalocyanines in which one isoindole ring has been formally replaced by a 1,2,4-triazole subunit. Two synthetic approaches can be employed to prepare these intrinsically unsymmetrical phthalocyanine analogues: a statistical procedure[13] affording Tpc's with the same kind of substitution in all three isoindole subunits, and the stepwise route[14] that provides Tpc's with a differently substituted isoindole opposite to the triazole moiety. These unsymmetrical macrocycles can be organised in Langmuir–Blodgett films[15,16] and have shown liquid-crystal behaviour,[17] semiconducting properties[18] and remarkable second and third order non-linear optical properties.[19]

A high thermal stability is generally considered an intrinsic property of these materials due to the studies carried out on unsubstituted phthalocyanines.[20,21] Unfortunately, few studies on the thermal properties of substituted derivatives have been described.[20]

In this paper, considering the importance of phthalocyanine derivatives, we report for the first time a thermogravimetric study of a series of metallotriazolephthalocyanines (MTpc) and compare the results with appropriate metallophthalocyanines (MPc). The aim of this work is to acquire knowledge of the thermal behaviour and the thermal stability of these new compounds.

Well-developed thermogravimetric analysis (TG) techniques[22] are widely used in order to study the thermal stability of materials[23,24] through the analysis[25] of the overall thermal degradation process[26–28] in terms of kinetic behaviour[29] and chemical structure and composition.[30] Quantitative and comparative analysis of the TG results can be used in order to determine the causes of the demonstrated thermal behaviour and relate it to the molecular structure. The chemical parameters studied here are related to the replacement of Ni(II) by Cu(II) in the inner cavity of the Pc and Tpc macrocycles as well as the presence of different side groups in the studied compounds.

## Experimental

### Materials and methods

Compounds **1a**,[14] **2a**,[14] **2b**,[19] **5**,[31] **6**,[32] **7**[33] and **9**[34] were prepared following literature procedures. Compounds **4a,b** and **8** were purchased from Aldrich Chemical Co. and used as received without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. UV/Vis and IR spectra were recorded on Perkin-Elmer Model Lambda 6 and PU 9716 Philips spectrometers, respectively. Melting points were determined on a Büchi melting-point apparatus and are uncorrected. Fast atom bombardment mass spectra (FAB-MS) were obtained from a VG AutoSpec spectrometer. Samples of the compounds were

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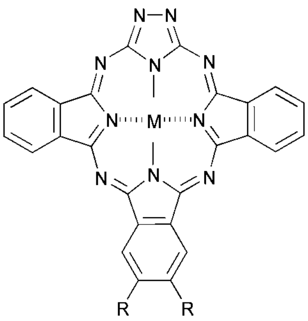
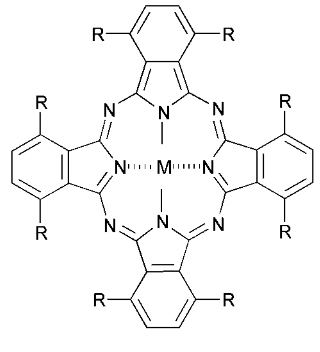


**1a** R = H, M = Ni
**1b** R = H, M = Cu
**2a** R = H, $OC_8H_{17}$, M = Ni
**2b** R = H, $OC_8H_{17}$, M = Cu
**3** R = $OC_{12}H_{25}$, M = Cu



**4a** R = H, M = Ni
**4b** R = H, M = Cu
**5** R = $OC_8H_{17}$, M = Ni
**6** R = $C_8H_{17}$, M = Ni

dissolved in a small volume of 3-nitrobenzyl alcohol and loaded onto a stainless steel probe tip. Microanalyses were performed by the Universidad Autónoma de Madrid University Microanalytical Service.

### Stepwise procedure for the preparation of 7,12:21,24-diimine-5,26:14,19-dinitriletribenzo[f,k,p][1,2,4,9,14,19]-hexaazacycloeicosanate(2−)-*N*$^{27}$,*N*$^{28}$,*N*$^{29}$,*N*$^{30}$-copper(II) (1b, 3)

A mixture of **7**[33] (0.20 g, 0.56 mmol), $Cu(OAc)_2$ (0.11 g, 0.56 mmol) and the corresponding 1,3-diiminoisoindoline (**8** or **9**) (1.13 mmol) in 2-ethoxyethanol (15 ml) was stirred at 55 °C for 2 d. After filtration, the raw material was triturated successively with methanol and 2-ethoxyethanol at reflux temperature and then the residue was repeatedly extracted with dichloromethane in the case of compound **3**, or with 1-chloronaphthalene in the case of **1b**. Finally, after vacuum evaporation of the solvent, the residue was washed with methanol and filtered. Compound **3** can also be purified by column chromatography on silica gel (dichloromethane–methanol 10 : 1).

Data for **1b**: Yield: 42%; mp >250 °C; FAB-MS (3-NOBA, TFA): $m/z = 527$, 529 $[(M+H)^+$, 100%]; UV/Vis (TFA): $\lambda_{max}$ (log $\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$) = 257 (4.46), 280 sh, 360 sh, 378 (4.35), 509 (3.75), 543 nm (3.45); IR (KBr): $\nu = 3600$–3200 (O–H), 1659, 1581, 1504, 1467, 1421 (C=N), 1396, 1314, 1287, 1188, 1085, 1019, 765, 748, 722 cm$^{-1}$ (C–H); Anal. calc. for $C_{26}H_{12}N_{10}Cu$. 2 $H_2O$: C, 55.37; H, 2.86; N, 24.83. Found: C, 55.13; H, 3.18; N, 24.75%.

Data for **3**: Yield: 22%; mp >250 °C; FAB-MS (3-NOBA, DCM): $m/z = 560$, 562 $[(M-2\cdot C_{12}H_{24}+H)^+$, 50%], 896, 898 $[(M+H)^+$, 100%]; UV/Vis ($CHCl_3$): $\lambda_{max}$ (log $\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$) = 246 (4.58), 289 (4.55), 305 (4.57), 387 (4.87), 520 sh, 541 (4.23), 582 (4.25), 637 nm (4.52); IR (KBr): $\nu = 3600$–3200 (O–H), 2924, 2855, 1595, 1496, 1473 (C=N), 1420, 1366, 1336, 1290, 1198, 1115, 1099, 1076, 756 cm$^{-1}$ (C–H); Anal. calc. for $C_{50}H_{60}N_{10}O_2Cu$. $H_2O$: C, 65.66; H, 6.83; N, 15.31. Found: C, 65.81; H, 6.61; N, 15.64%.

All the compounds have similar particle forms. They look like cylindrical rods (small fibers) of approximately 10 μm length and around 1 μm in diameter. Many of the particles are aggregates of the small fibers.

### TG studies

All compounds were analysed using Perkin-Elmer model 04 TGA equipment and the analysis was carried out using samples of approximately 3 mg in weight at a heating rate of 10 °C min$^{-1}$.

In order to compare and facilitate the understanding of the results, compounds have been classified. Two main groups of products can be distinguished according to the transition metal complexed in the inner cavity of the macrocycle (Cu or Ni). In addition to the molecular composition, the structure of the core and the side chain groups were considered suitable criteria to define subdivisions (Table 1).

In Table 1, groups I and II are characterised by the same central complexed metal (Ni). In the same way, the complexed metal in the compounds of group III is Cu. Groups I, II and III permit evaluation and comparison in terms of the chemical composition of the phthalocyanine systems.

The other three groups (IV, V and VI) consist of couples of the same organic ligand with a different central metal, Ni or Cu respectively. Group IV includes two triazolephthalocyanines peripherally substituted with one octyloxy group while groups V and VI compare two unsubstituted metal complexes of phthalocyanine and triazolephthalocyanine, respectively.

## Results and discussion

### Synthesis

Copper(II) triazolephthalocyanines **1b** and **3** were synthesised by treatment of equimolar amounts of 1,3-bis[(3′-imino-1′-isoindolinylidene)amino]-1,2,4-triazole (**7**) with copper(II) acetate and the appropriate 1,3-diiminoisoindoline **8**/**9** in 2-ethoxyethanol at 50 °C for two days (Scheme 1). Compound **3**, bearing aliphatic chains on the isoindole ring opposite to the triazole subunit, is readily soluble in apolar organic solvents, allowing its purification by column chromatography. Both compounds have been fully characterised by elemental analysis and FAB-MS, IR and UV/Vis techniques.

### TG analysis

In order to analyse the obtained thermograms, the least squares fit of multigaussian functions was used. The well-known Marquard algorithm for multifunctional fits permitted us to analyse the overall degradation process in the partial processes. The experimental results of the differential thermogravimetry together with the obtained fit results are illustrated in Fig. 1 and 2. Each of the partial degradation processes was evaluated according to Barrett's[35] method, where the *i* degradation process ($Nr_i$) is approximated by eqn. (1).

$$\frac{d\alpha_i}{dt} = A_i e^{(-E_i/RT)}(1-\alpha_i)^n \qquad (1)$$

In eqn. (1), *i* refers to the partial degradation process *Nr*, $\alpha_i$ is the conversion factor given by eqn. (2) as the ratio of the partial mass loss $\Delta m^i{}_{T,t}$ until the time *t* caused by the specific process *i*,

**Table 1** Pattern groups of studied compounds

| Compound | Formula | Groups | | | |
|---|---|---|---|---|---|
| | | I | | V | |
| **4a** | $C_{32}H_{16}N_8Ni$ | **4a** | | **4a** | |
| **5** | $C_{96}H_{144}N_8O_8Ni$ | **5** | | | |
| **6** | $C_{96}H_{144}N_8Ni$ | **6** | | | |
| | | II | | | VI |
| **1a** | $C_{26}H_{12}N_{10}Ni$ | **1a** | IV | | **1a** |
| **2a** | $C_{34}H_{28}N_{10}ONi$ | **2a** | **2a** | | |
| | | III | | | |
| **3** | $C_{50}H_{60}N_{10}O_2Cu$ | **3** | | | |
| **1b** | $C_{26}H_{12}N_{10}Cu$ | **1b** | | | **1b** |
| **2b** | $C_{34}H_{28}N_{10}OCu$ | **2b** | **2b** | | |
| **4b** | $C_{32}H_{16}N_8Cu$ | | | **4b** | |

divided by the total mass loss related to the same degradation process $Nr_i$.

$$\alpha=\frac{\Delta m^i_{T,t}}{\Delta m^i_{\mathrm{tot}}} \qquad (2)$$

$A$, $E$ and $n$ are the well-known Arrhenius kinetic parameters, pre-exponential frequency factor, activation energy, and reaction order, respectively.

Table 2 shows the fitting results in terms of partial degradation process number ($Nr$), maximum degradation rate ($R_{\max}$), maximum degradation rate temperature ($T_{R\max}$) and corresponding half-width at half-height ($\Gamma$) together with the kinetic parameters ln $A$, $E_a$ and $n$.

The evaluation and comparison of the results displayed in Table 2 according to the total number of partial degradation processes allows the following general observations to be made (see also Fig. 1 and 2). Five of the nine compounds studied, **1a,b**, **2a** and **4a,b**, show a one-step degradation. All of them correspond to peripherally unsubstituted phthalocyanines or triazolephthalocyanines, except **2a**, which contains one octyloxy side chain. They demonstrate comparable degradation behaviour with a relatively high maximum degradation rate ($R_{\max}<-0.5$ %$m$ °C$^{-1}$), comparable activation energy and pre-exponential values ($E_a$: 223–291 kJ mol$^{-1}$, ln $A$: 31–45), and the same reaction order ($n=1.5$).

The behaviour of complex **4a** (Fig. 2) is extremely pronounced through the very small half-width at half-height $\Gamma$, the extremely high values of $R_{\max}$ ($-2.407$ %$m$ °C$^{-1}$), $E_a$ (679 kJ mol$^{-1}$), ln $A$ (107) and $n$ (1.8). These results, which correspond to the highest values obtained in this study, indicate "explosion-like" degradation behaviour or a very fast chain mechanism reaction. In other words, a very fast solid–gas decomposition process.

Compounds **2b**, **3** (Fig. 1) and **5** (Fig. 2) show a two-step degradation process. All of them have in common the presence of alkoxy chains in the isoindole subunits that compose the macrocycles, though they have different chain lengths and numbers of substituents. The three compounds were demonstrated to be thermostable until approximately 420 °C. However, the number of side chain groups affects the thermal stability and the thermodegradation characteristics of the compounds. Complex **5**, with eight octyloxy moieties, shows $T_{R\max}=443$ °C and $\Gamma=25.7$ °C, while the parameters of **3**, which has two dodecyloxy chains, increase to $T_{R\max}=479$ °C and $\Gamma=68$ °C. Compound **2b**, with only one octyloxy group, displays even higher values: $T_{R\max}=481$ °C and $\Gamma=132$ °C (Table 2).

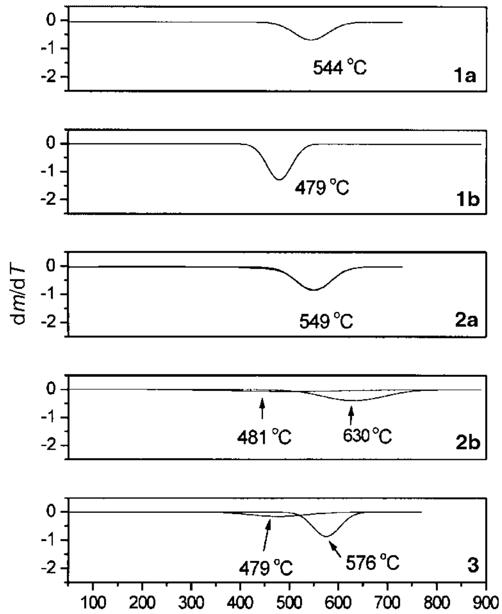
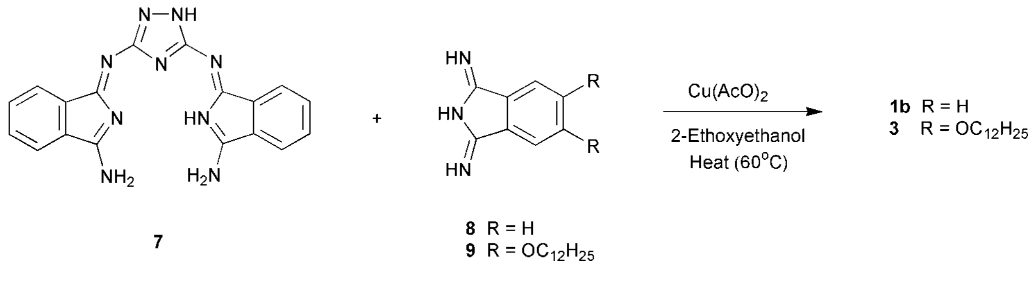


**Fig. 1** Fits of the experimental differential thermogravimetric curves of triazolephthalocyanine compounds **1–3**.

Finally, compound **6** (Fig. 2) exhibits unpredictable behaviour. The TG analysis of **6** shows four thermal degradation processes. The first, of relatively low intensity ($R_{\max}=-0.07$ %$m$ °C$^{-1}$), indicates an unusual thermal sensitivity at *ca.* 209 °C, which is a very low degradation temperature for MPc. A second degradation process is observed near 310 °C. This degradation temperature is again relatively low. The third and fourth degradation processes show temperatures of maximum degradation equal to 436 and 538 °C, respectively. The kinetic parameters of these processes are comparable with other processes in the same temperature region. The third process of **6** and the first process of **3** show practically the same $E_a$, ln $A$ and $n$ values. The same is valid for the fourth process of **6**, the unique degradation processes of **1a** and **2a**, and the second degradation process of **5**. This observation leads us to conclude that thermal degradation starts with the oxidation of the alkyl chain side groups and that the octyl group is more thermally sensitive than octyloxy.

The thermal degradation behaviour of the studied compounds can be better elucidated in terms of the divisions defined in Table 1.

Group I includes the nickel(II) phthalocyaninates **4a**, **5** and **6** with different side chain groups. While the unsubstituted nickel(II) phthalocyaninate (**4a**) presents only one very fast and



**Scheme 1** Synthesis of copper(II) triazolephthalocyanines.

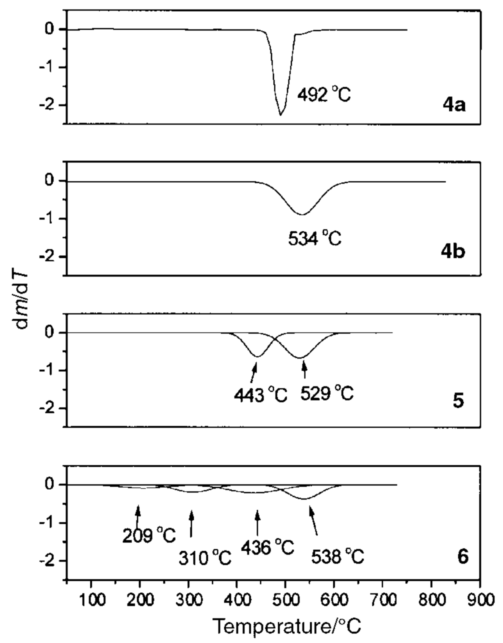


**Fig. 2** Fits of the experimental differential thermogravimetric curves of phthalocyanine compounds **4–6**.

intensive degradation process at a relatively high temperature (Fig. 2), the introduction of eight octyloxy groups results in the observation of two degradation processes for **5**, one at 443 °C and the second at 529 °C (Fig. 2). Both processes are slower than that of **4a**. A trace of the explosive character of **4a** remains in the first degradation process of **5** (very small $\Gamma$, and very high $E_a$, ln $A$ and $n$ values). Nevertheless, the addition of eight octyl side groups in the phthalocyanine ring leads to total loss of the explosive character, as study of the four degradation processes of **6** reveals. Additionally, the presence of the alkyl groups causes an extreme decrease in the degradation temperature of the material. Compound **4a** is practically thermostable till 470 °C ($T_{R\mathrm{max}} = 492$ °C, $\Gamma = 16$ °C) whereas compound **6** becomes thermosensitive at 170 °C ($T_{R\mathrm{max}} = 209$ °C, $\Gamma = 60$ °C).

Group II includes the nickel compounds **1a** and **2a**. As the fitting and the kinetic parameters show (Table 2), the triazolephthalocyanines display very high thermal stability up to approximately 500 °C. The introduction of one alkoxy group in the Tpc ring causes a small shift of the $T_{R\mathrm{max}}$ value from 544 up to 549 °C (Fig. 1). However, the characteristics of the substance remain almost unchanged.

The copper triazolephthalocyanines **1b**, **2b** and **3** constitute group III. The introduction of one octyloxy side chain in the triazolephthalocyanine core (compound **2b**) modifies the thermal behaviour of the material by comparison with copper(II) phthalocyaninate **1b**, which shows only one degradation process. Two degradation processes are present for **2b**: the first occurs at almost the same temperature as that of **1b** ($T_{R\mathrm{max}} = 481$ °C). The second degradation happens at higher temperature ($T_{R\mathrm{max}} = 630$ °C), in fact the highest temperature observed for a degradation process in this study. The presence of two dodecyloxy side groups in product **3** produces a behaviour similar to that of one octyloxy side chain. Compound **3** demonstrates two degradation processes with $T_{R\mathrm{max}} = 479$ and 576 °C, for the first and second processes, respectively. Comparing the fitting and kinetic parameters of compounds **1b**, **2b** and **3**, we can conclude that the introduction of alkoxy chains in the periphery of the Tpc core causes a shift to higher degradation temperature, followed by a significant slowing of the degradation velocity.

The other three groups (IV, V, VI) allow the comparison of the same phthalocyanines with a different central metal.

Group IV, that includes compounds **2a** and **2b**, shows that the presence of the $-OC_8H_{17}$ group is related to a double degradation process in the case of the Cu complex, while the Ni complex is less sensitive and continues to demonstrate only one process.

The comparative analysis of the thermo-oxidative character of compounds **4a,b** (group V) confirms that the Ni complex **4a** has an "explosive" character (very small $\Gamma$, 16 °C) at the temperature $T_{R\mathrm{max}} = 492$ °C. The substitution of Ni by Cu shifts the $T_{R\mathrm{max}}$ to 534 °C and additionally slows down the degradation process (Fig. 2).

Opposite behaviour is observed for group VI (**1a,b**). In this case, the triazolephthalocyaninate copper(II) displays a faster and intensive $\Gamma$ degradation process compared to nickel(II) triazolephthalocyaninate. The substitution of Cu by Ni results in a shift from $T_{R\mathrm{max}} = 479$ to 544 °C followed by a strong degradation velocity slow down (Fig. 1).

Coming back to the high activation energy of the compound **4a**, we have to evaluate the parameters which affect the kinetics of the studied processes. As already mentioned above, all the compounds studied here demonstrated similar particle form and size. The remaining question is: "Do the processes studied here belong to the same family of physico-chemical processes, or are they divided into two or more categories with different causes?".

According to Budrugeac and Segal,[36] in the case of heterogeneous solid–gas decomposition, the relationship

**Table 2** Fitting results of thermogravimetric derivative curves and the corresponding kinetic parameters obtained by Barrett's method[a]

| Compound | $Nr$ | $T_{R\mathrm{max}}$/°C | $\Gamma$/°C | $R_{\mathrm{max}}$/%$m$ °C$^{-1}$ | $E_a$/kJ mol$^{-1}$ | $r$ | ln $A$ | $n$ |
|---|---|---|---|---|---|---|---|---|
| **4a** | 1 | 492 | 15.89 | −2.41 | 679±24 | 0.990 | 107±4 | 1.8 |
| **5** | 1 | 443 | 25.74 | −0.50 | 318±9 | 0.991 | 53±1 | 1.6 |
| | 2 | 529 | 35.56 | −0.53 | 272±6 | 0.990 | 40±1 | 1.4 |
| **6** | 1 | 209 | 60.33 | −0.07 | 33±1 | 0.998 | 6.1±0.1 | 1.1 |
| | 2 | 310 | 43.72 | −0.16 | 92±2 | 0.995 | 17.4±0.5 | 1.3 |
| | 3 | 436 | 63.83 | −0.18 | 94±2 | 0.995 | 15.4±0.3 | 1.4 |
| | 4 | 538 | 38.52 | −0.30 | 246±5 | 0.992 | 35±1 | 1.4 |
| **1a** | 2 | 544 | 43.51 | −0.53 | 223±4 | 0.993 | 31±1 | 1.5 |
| **2a** | 1 | 549 | 41.1 | −0.84 | 250±7 | 0.992 | 35±1 | 1.5 |
| **3** | 1 | 479 | 67.59 | −0.12 | 95±1 | 0.997 | 13.5±0.5 | 1.3 |
| | 2 | 576 | 32.14 | −0.69 | 369±9 | 0.992 | 52±1 | 1.7 |
| **1b** | 1 | 479 | 29.38 | −1.29 | 291±8 | 0.991 | 45±1 | 1.5 |
| **2b** | 1 | 481 | 131.84 | −0.05 | 28.0±0.5 | 0.998 | 1.5±0.1 | 1.0 |
| | 2 | 630 | 74.34 | −0.32 | 130±2 | 0.996 | 15.3±0.3 | 1.3 |
| **4b** | 1 | 534 | 39.37 | −0.88 | 245±5 | 0.991 | 35±1 | 1.5 |

[a] $Nr$ = Degradation process number, $T_{R\mathrm{max}}$ = maximum degradation rate temperature, $\Gamma$ = degradation temperature range which is related to the half-width at half-height values, $R_{\mathrm{max}}$ = maximum degradation rate (d$m$/d$T$), $r$ = correlation factor, $n$ = reaction order.

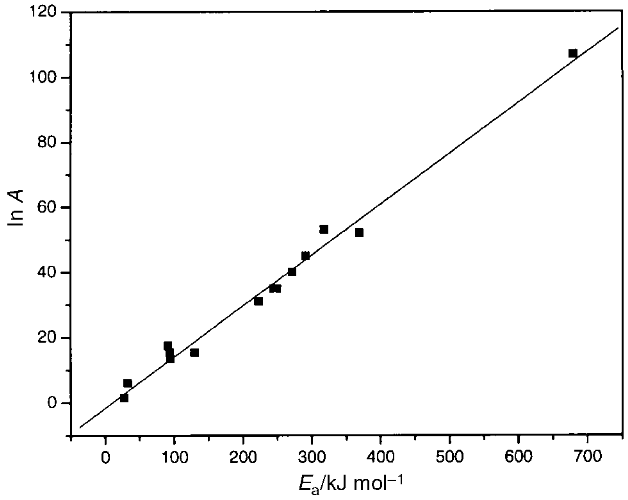


**Fig. 3** The plot ln $A$ *vs.* $E_a$ for compounds **1–6**.

$$\ln A = a + bE \qquad (3)$$

is valid, where $A$ is the pre-exponential factor and $E$ is the activation energy of the process. Eqn. (3) is valid independent of the isothermal or nonisothermal decomposition process. However, the physical meaning of the constants $a$ and $b$ is related to the compensation effect. In the case of isothermal conditions, they relate to the dependence of the activation parameters on the temperature and under nonisothermal conditions, they depend on the degree of conversion.

In Fig. 3 the obtained values of ln $A$ for all decomposition processes are plotted against corresponding activation energies $E_a$. It is observed that all compounds, independent of whether Ni or Cu is the central metal, fit the same linear function given $\ln A = 1.6013 + 0.1564E_a$ with correlation factor $r = 0.994$.

Fig. 3 constitutes clear evidence that the thermal degradation processes of all the nickel(II) and copper(II) triazolephthalocyanine and phthalocyanine complexes studied here, independent of side groups and complexed metal, belong to the same family and obey the same compensation effect. In this way, the high kinetic parameter values of compound **4a** may be related to the high symmetry of the compound, the substitution of the side groups by hydrogen and the presence of Cu as the central complexed metal.

## Conclusion

Both Ni(II) and Cu(II) complexes of phthalocyanine and triazolephthalocyanine are highly thermostable compounds, with degradation temperatures of *ca.* 450 °C.

The presence of Ni or Cu in the inner cavity of the macrocycle affects the thermostability properties of the complex. Surprisingly, this variation shows opposite behaviour when the macrocyclic host is a phthalocyanine compared to a triazolephthalocyanine. While the substitution of nickel by copper in a phthalocyaninate complex increases the degradation temperature, the same change in a triazolephthalocyaninate complex decreases this temperature.

The influence due to the presence of side groups in phthalocyanine-like complexes can be summarised as followed:

(1) the introduction of one octyloxy chain in the copper(II) triazolephthalocyaninates (**1b**, **2b**) causes the appearance of two very slow degradation processes with equal or higher $T_{R\max}$. Nevertheless, the same change in the nickel(II) triazolephthalocyaninates does not affect significantly the thermostability of the compound.

(2) in the case of the nickel(II) phthalocyaninate **4a**, the formal introduction of eight alkoxy groups causes the appearance of two slower degradation processes, one with a lower $T_{R\max}$ and the other with a higher one, compared to the unsubstituted complex **4a**. In that case, the introduction of side groups hardly decreases the thermostability of the material.

(3) However, the presence of alkyl chains (**6**) causes a very strong alteration to the thermostability of the material. Four degradation processes appear, three of them at lower temperatures, reducing the materials stability limit from *ca.* 450 °C in the unsubstituted complex to *ca.* 170 °C.

(4) All the observed degradation processes obey the heterogeneous solid–gas decomposition processes described by the equation $\ln A = a + bE_a$, where $A$ is the pre-exponential factor, $E_a$ the activation energy and, in this special case, $a = 1.6013$ and $b = 0.1564$.

In conclusion, in this paper, we have shown that triazolephthalocyanines are thermally very stable Pc analogues. This fact, together with their relevant physical properties,[37] make them attractive building blocks for the construction of molecular materials.

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