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# COMPARATIVE SELF-ASSEMBLY AND EQUILIBRIUM STUDIES OF Pd(II) COORDINATION OF β-OCTASUBSTITUTED OCTYLTHIO- AND DODECYLTHIO-DERIVATISED PHTHALOCYANINES

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## ABSTRACT

β-Octasubstitutedoctylthio-derivatised and dodecylthio-derivatised Phthalocyanines were investigated for Pd(II) coordination at room temperature. The effects of the chain length on number of bound Pd(II) ions, the binding process, structure of the final complexes and the equilibrium constants of coordination were also explored. The number of Pd(II) ions bound was 3 for all the molecules showing no contribution from chain length. There was a direct correlation among the carbon chain length, equilibrium constants and extent of loss of symmetry of the final structures. The longer chain length Phthalocyanine showed the higher equilibrium constant of 2.0 x $10^{13}$ $dm^3$ $mol^{-1}$ with a spectrum showing the more symmetrical final complex.

**Keywords:** Thio-derivatised, Phthalocyanines, Coordination, Equilibrium, Symmetry. Palladium.

## INTRODCUTION

Coordination studies of important metal ions by a wide range of ligands have been conducted because of the implications of these reactions in chemical and biochemical systems. Chemical interactions between metal ions like Ca(II), Mg(II), Pt(II), Pd(II), Ru(II) and Au(II) with varieties of natural ligands and their mimics have received a lot of attentions (Ivanova and Mayer-Figge, 2005; Ivanova *et al.*, 2005;Ivanova, 2007; Koleva *et al.*, 2007; Koleva *et al.*, 2008a; Koleva *et al.*, 2008b) because of their significance in *in-vivo* processes and synthesis of many metal complexes with potentials for deployment in diverse areas of practical applications .

Platinum group metal complexes, particularly those of Platinum and Palladium, are of great scientific importance because these complexes have proved to be efficient reagents, good phosphorescent compounds and catalysts for various important processes. Therefore, a lot of ligands have been combined with this class of metals as means to cater for wide lines of ends. These ligand-metal reactions have been initiated under various conditions, all or most of which involve the application of heat. Production of these complexes under room temperature and pressure is a rare a phenomenon. Phthalocyanines, especially those bearing the thio-functionality, are been investigated as ligands for self-assembly interactions with some of these metal ions (Bilgin *et al.*, 2006; Meryem *et al.*, 2006; Kandaz *et al*., 2007).

Phthalocyanines (Pcs), a versatile macrocycle, demonstrate an array of solid-state properties that make them notable examples of adaptable functional organic materials. They have attracted a great deal of attention due to their high chemical inertness, thermal stability, intense color and diverse chemistry associated with the extensive delocalized 18-π electron system of the Pc ring. The sulfur atoms, when thio-substituents are present in Pcs, can coordinate with soft metals such as silver(I), palladium(II) and platinum(II) with its lone pairs of electrons at room conditions.

A considerable amount of work has been done in this area and significant roles of molecular framework of phthalocyanines on Pd(II) assembly have been demonstrated. Tetra substituted alkylthio-derivatised metallophthalocyanines (MPcs) have been investigated but the coordinations were hampered by aggregation because of wide inter-substituent gap that allowed ligand-metal-ligand interactions (Bilgin *et al.*, 2006; Meryem *et al.*, 2006; Kandaz *et al.*, 2007). Octa substituted alkythio-derivatised phthalocyanines, because of their shorter inter-substituents distance, produced much better results in this area. The point of attachment of the substituents to the ring (α or β) and their relative orientation in space influenced the ease of coordination for the same reason with α-substituted analogues coordinating more Pd ions (Ogunbayo and Nyokong, 2009).

The trends observed in these works produced metal-complex assembly with no significant barriers, thereby showing potential for application in design of efficient micro sensing technique and chemo dosimeter and sometimes affording specific thermodynamically favoured self-assembled complexes at ordinary conditions.The resulting complexes could be of interest in areas such as phosphorescent sensor design and photothermal therapy on one hand and photocatalysis of chemical reactions and Photodynamic therapy (PDT) on the other, depending on how the open shell nature of multiple Pd(II) ions affect the life-time of excited states ($S_n$ and $T_n$) of the final complexes. The deployment of polynuclear metal complexes in the electrochemical reduction of oxygen and oxidation of alcohol towards fuel cell development has also been widely reported.

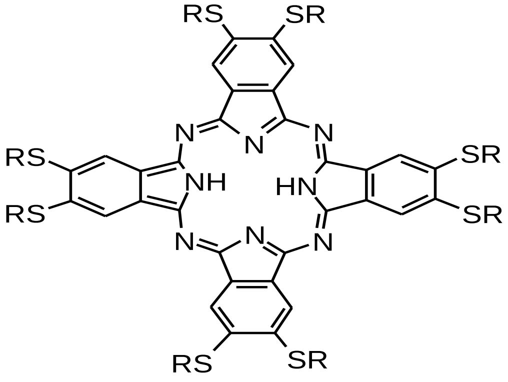
The alkylthio functionalized phthalocyanine ligands used so far have demonstrated molecular recognition for Pd(II), Ag(II) and Pt(II) that allowed its spontaneous coordination **(**Gürol *et al*, 1994; Kandaz *et al*, 2007; Ogunbayo and Nyokong, 2009; Ogunbayo et al, 2016; Yarasir *et al*, 2008). A previous work done in this area concentrated on the detail of the assembly processes for both peripheral and non-peripheral thio-substituted phthalocyanines and metallophthalocyanines (Ogunbayo and Nyokong, 2009), while another focused on the effect of the chain length of the thio-substituents on the assembly process of the non-peripherally substituted Pc and the equilibrium position (Ogunbayo et al, 2016). The hallmark of this work is the effect of the chain length of the thio-substituents on the assembly process of the peripherally thio-substituted Pc and the equilibrium position of the reaction which might serve, among others, as an indicator of the ease of metal ions recovery, if the molecules are deployed for Pd (II) ion metal sensing, extraction and chemodosimetry applications.

## MATERIALS AND METHODS

### Materials and equipment

2,3,9,10,16,17,23,24,-octakis (octylthio) phthalocyanine (**1**) and 2,3,9,10,16,17,23,24, octakis (dodecylthio) phthalocyanine (**2**) (**Figure 1**) were synthesized according to literature

(Ogunbayo and Nyokong, 2010). Dichloromethane (DCM) and palladium (II) chloride were purchased from Sigma-Aldrich. Ethanol was purchased from Merck. UV-Vis spectra were recorded on a Cary 500 UV/Vis/NIR spectrophotometer.



**1: R = $C_8H_{17}$**

**2: R = $C_{12}H_{25}$**

**Figure 1:** Strcuture of 2,3,9,10,16,17,23,24,-octakis(octylthio)phthalocyanine (**1**) and 2,3,9,10,16,17,23,24, octakis(dodecylthio)phthalocyanine (**2**)

### Palladium ions Assembly and Equilibrium Studies

For all studies, $PdCl_2$ was dissolved in ethanol and the Pcs in DCM. In order to minimize dilution effects, $PdCl_2$ stock solution (0.1 M) were added in microliters to the 2 mL of the Pc solution. For binding and kinetic studies, gradual addition of $PdCl_2$ solution was done and response monitored from spectroscopic changes. Varying amount of $PdCl_2$ stock solution was added to a fixed concentration ($5 \times 10^{-6}$ M) of the Pc derivatives to form various $PdCl_2$ concentrations (from $2 \times 10^{-5}$ to $2 \times 10^{-4}$ M), and the absorbance changes accompanying each addition monitored.

The steady increase in absorbance at the $\lambda_{max}$ of Pd bound Pc (product) with increase in Pd (II) ion concentration was noted and used in the determination of the binding constant, as well as number of bound Pd (II) ions, according to equation 1(Ogunbayo and Nyokong, 2009).

$$log\left[\frac{(A_{eq}-A_o)}{(A_\infty-A_{eq})}\right] = \log K + n\ log[Pd^{2+}] \quad (1)$$

Where $A_{eq}$ is the equilibrium absorbance of the Pd-bound Pc (product). This was the final absorbance of the product after each addition of $PdCl_2$ solution to the reaction. $A_o$, is the initial absorbance, before any $PdCl_2$ addition, at the wavelength at which the product was monitored; and $A_\infty$ is the maximum attainable absorbance of the product taken when further addition of $PdCl_2$ to the reaction mixture no longer resulted in spectral changes. K is the binding constant, while n is the number of bound $Pd^{2+}$ ions.

## RESULTS AND DISCUSSIONS

### Pd(II) ion Assembly

The original spectra of the two molecules **1**(Pc-$S(C_8H_{17})_8$) and **2** (Pc-$S(C_{12}H_{25})_8$) are shown in Figure 2. The similarity of the spectra means the length of chain has no effect on the spectra (Ogunbayo and Nyokong, 2010).

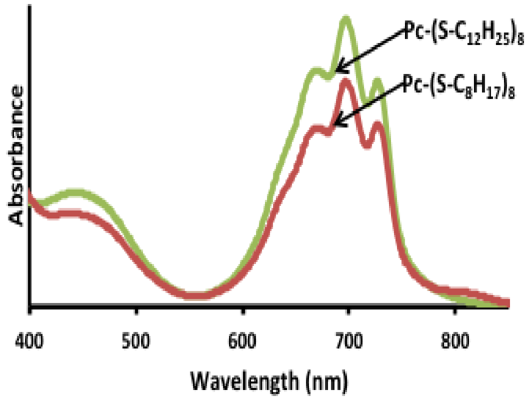


**Figure 2:** UV-Vis spectra of **1**(Pc-$S(C_8H_{17})_8$) and **2**(Pc-$S(C_{12}H_{25})_8$)in DCM

The Q band, which is the band for $S_0 \rightarrow S_1$ transitions, of the ligands were split since there was no metal in the cavity.The spectra generated on the addition of Pd(II) ions to Pc **1** are shown in Figure 3. The absorption spectra of the Pc before the addition of Pd(II) ions are shown in black in all the figures and the final spectra in green. Titration of **1** with Pd(II) ions caused the gradual disappearance of the peaks at 707 nm and 736 nm with simultaneous gain of prominence by the peak around 719 nm (Figure 3a). This could only be due to insertion of metal into the cavity of the Pc, because the final spectrum was comparable to that of metallated phthalocyanines (Figure 3c). The spectral changes could not be due to symmetric substitution of the Pd ions on the ring since a split Q band would still be observed if this was the case.

Additional Pd(II) ions resulted in broadening of the 719 nm peak with a peak appearing at 706 nm and the original peak at 719 nm was blue-shifted to around 697 nm. Along with this was the reduction of the intensity of the peak at 664 nm (Figure 3b). The blue shift was due to the engagement of the lone pair of electron on sulphur by a new peripherally bound Pd(II) on the Pc, reducing the mesomeric effect of sulphur lone pairs on the electron density in the ring. The broadening of the peak could be due to loss of symmetry due to uneven attachment of a Pd(II) ion to a side of the phthalocyanine ring.

Further addition of the ions led to the reduction of the broadening of the peak and appearance of another peak around 740 nm (Figure 3c). The spectral changes, the split of the Q-band, in Figure 3c gave the impression of another form of loss of symmetry, but might be due to the attachment of another Pd(II) ion.  A simultaneous blue shift of the Q-band, with reduction in broadening, would be an ideal observation, since the mesomeric contribution from the lone-pair donating sulphur would be eliminated. But this was not the case, probably because the broadening, due to loss of symmetry, masked such shift. These changes could all together be interpreted to mean a change in symmetry on the attachment of the second peripheral Palladium. No further changes were observed on further addition of the ions.

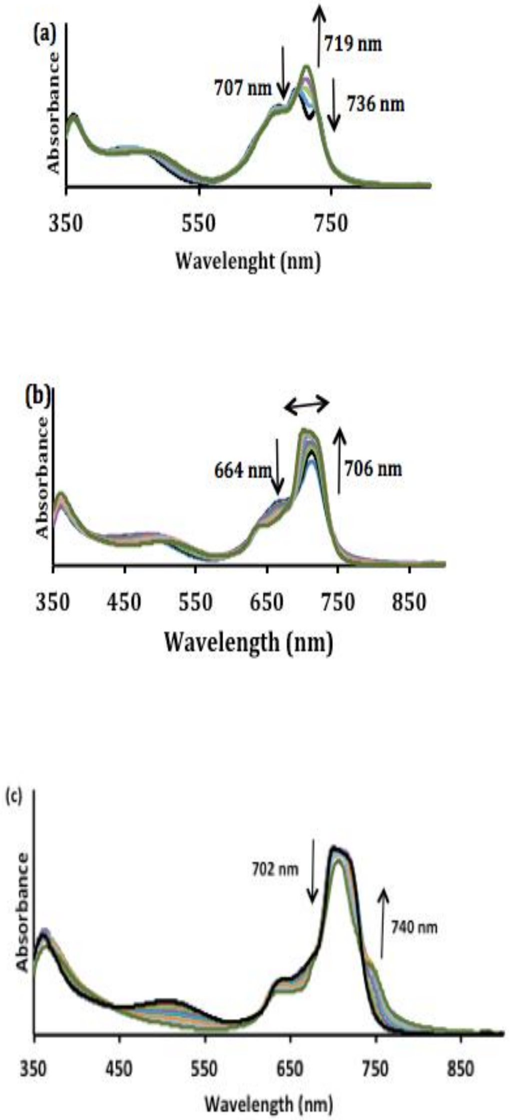


**Figure 3:** UV–Vis spectral changes observed on addition of $PdCl_2$ in ethanol to **1** in DCM**. (a)** $Pd^{2+}$ion insertion into the cavity (b) First peripheral $Pd^{2+}$ ion attachment (c) Second peripheral $Pd^{2+}$ ion attachment

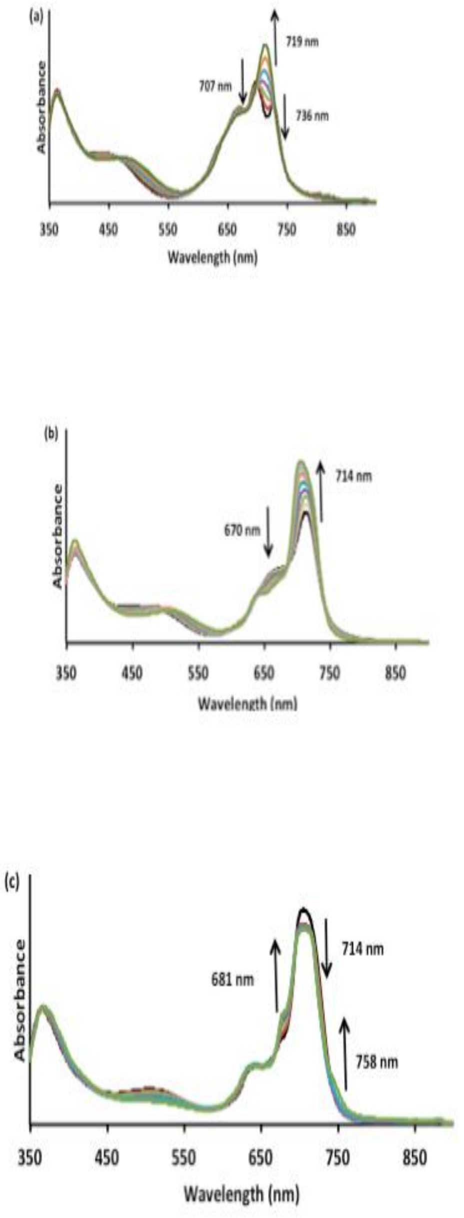


**Figure 4:** UV–Vis spectral changes observed on addition of $PdCl_2$ in ethanol to **2** in DCM**. (a)** $Pd^{2+}$ on insertion into the cavity (b) First peripheral $Pd^{2+}$ ion attachment (c) Second peripheral $Pd^{2+}$ ion attachment .

For Pc **2**, the processes apparently took the same form as **1**, with the insertion of metal into the cavity of the phthalocyanine observed through the reduction in the intensity of the split peaks around 707 nm and 736 nm and appearance of a new one in the middle at around 719 nm (Figure 4a), representing a transition to a planar configuration of metallated phthalocyanine (Ogunbayo and Nyokong, 2010). Further addition of Pd(II) ions led to spectral changes shown in Figure 4b. The broadening of the Q-band observed in **1** (Figure 3b**)** was also observed here, but this happened through increase in absorbance at around 714 nm. The final shape suggests loss of symmetry, due to attachment of the first peripheral Pd(II) ions. In Figure 4c, the increase in absorbance noticed at 740 nm in **1** was observed around 758 nm but with less prominence. Instead of a decrease in absorbance, observed in **1** around 702 nm, an increase in absorbance around 681 nm was noticed in **2**. This difference most likely means a different symmetry configuration from what was noticed in **1** on attachment of the second Palladium ion.

## Equilibrium Studies

Using equation 1, a plot of $\log\{(A_{eq}-A_o)/(A_\infty - A_{eq})\}$ versus $\log[Pd^{2+}]$, Figure 5, shows that the binding gave an equilibrium constant of $K = 1.25 \times 10^{12}\ dm^3\ mol^{-1}$ and n of 3 for **1** (Figure 5a). This shows that the number of Palladium ions coordinated to ligand **1** was 3.

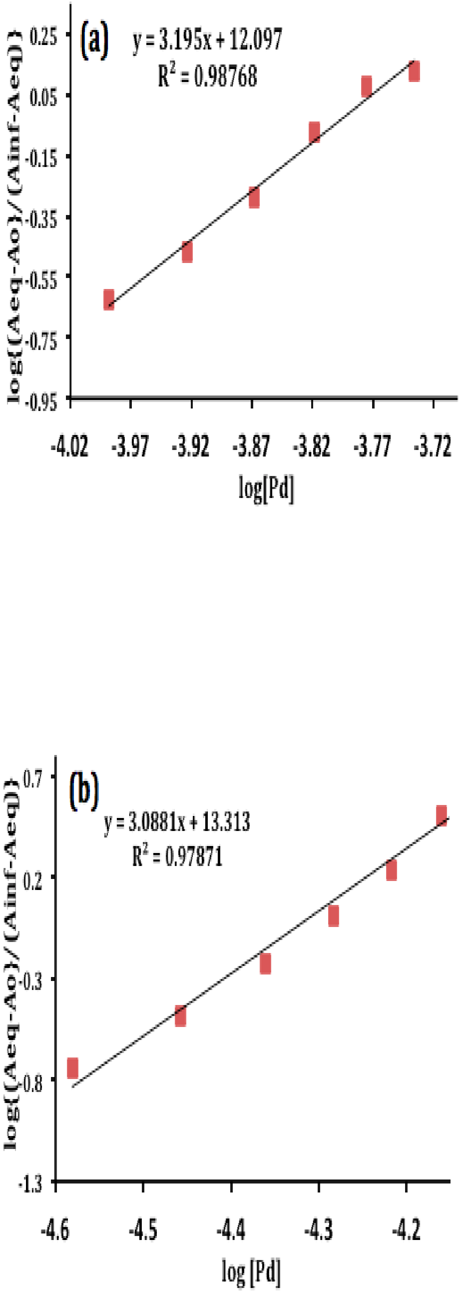


**Figure 5:** A plot of log{($A_{eq}$-$A_o$)/($A_\infty$ - $A_{eq}$)} versus log[$Pd^{2+}$] for (a) **1** (b) **2** in DCM

This same number was obtained for octapentylthio substituted metal-free phthalocyanines (Ogunbayo and Nyokong**,** 2009), showing that increase in the number of carbon in the substituent chain from five to eight did not affect the number of bound Pd(II), though the symmetry and equilibrium constants are different. For ligand **2**, the same plot gave an equilibrium constant of 2.0 x $10^{13}$ $dm^3$ $mol^{-1}$ (Figure 5b) and n value of 3, represented by scheme **1**.

$$H_2Pc \xrightarrow{3Pd(II)} Pc(Pd)_2$$

**Scheme 1**. Overall Process involved in Pd(II) coordination to the ligands

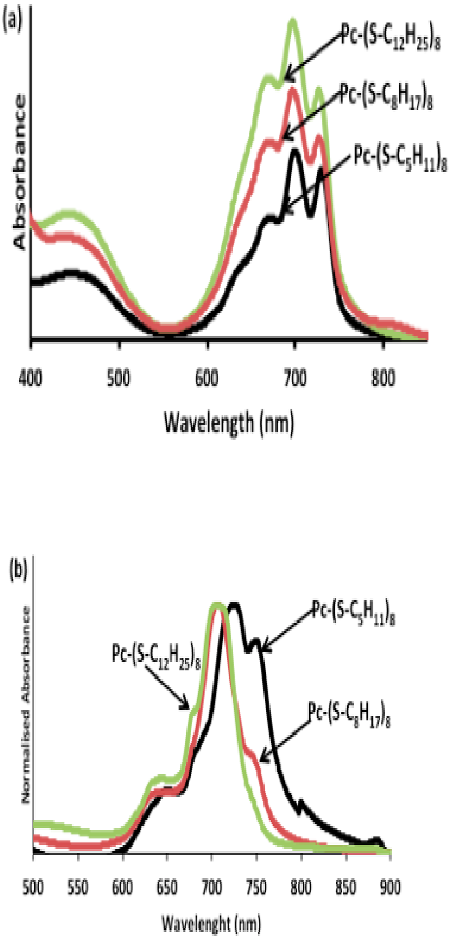


**Figure 6:** Comparison of UV-Vis spectra of (a) Initial Pc **1**, **2** and their 5-carbon chain analogue from previous work (Ogunbayo and Nyokong**,** 2009) (b) final Pd-Pc assembly of **1**, **2** and their 5-carbon chain analogue from previous work

(Ogunbayo and Nyokong**,** 2009).

The numbers of Pd(II) ions bound to a molecule of phthalocyanine were the same for the two phthalocyanine ligands under investigation in this work. The same number of Pd(II) was coordinated to similar analogue with a shorter carbon chain (penthylthio-derivatised) in our previous work (Ogunbayo and Nyokong**,** 2009) suggesting the number of Pd(II) ions coordinated was not affected by the length of the chain. However, the final spectra of the three complexes as shown in Figure 6b and their equilibrium constants showed that the chain lengths had interesting effect on the final structures and strength of the interactions between the ligands and the Pd(II) ions.

For the purpose of clear comparison, the original spectra of the two phthalocynaines in this work and that of the molecule from our previous work are overlaid (Figure 6a), with absorbance normalized for clear visibility. The same overlay was done for the final spectra (Figure 6b). The spectra of these three meta-free phthalocynaines are the same, showing that the length of the chain had no effect on the spectra of the molecules before coordination (Figure 6a). But the final spectra of their corresponding complexes, shown in Figure 6b, showed that the final complexes, in spite of their coordination to the same number of Pd(II) ions (Figure 5), do not have the same structure. This could be deduced from the obvious differences in their respective spectra, in spite of the similarity in the original spectra.

The spectra, due to the split nature of the Q-band, showed loss of symmetry in the three final complexes. However, the extent of the split and the relative intensities of the two peak for each of the complexes and their positions showed that the loss of symmetry were of different forms, with structural influence coming from the length of the carbon chain. This is also consistent with the values of equilibrium constants, which increased with increase in the length of the carbon chain.

The pentylthio-derivatised Pc has the lowest equilibrium constant of 5.7 x $10^{10}$ $dm^3$ $mol^{-1}$ (Ogunbayo and Nyokong**,** 2009) and the spectrum of its complex showed the most pronounced loss of symmetry (Figure 6b). The octylthio-derivatised Pc and the dodecylthio analogue have equilibrium constants of 1.25 x $10^{12}$ $dm^3$ $mol^{-1}$ and 2.0 x $10^{13}$ $dm^3$ $mol^{-1}$ respectively. Interestingly, their spectra showed less pronounced loss of symmetry, compared to their pentylthio analogue, with the dodecylthio analogue displaying the least loss of symmetry along with the highest equilibrium constant.

It's clear that one of the three Pd(II) ions is in the cavity for the three Pcs but the relative positions of the two on the periphery is obviously dictated by the chain length. This is inferred from the comparison of the spectra that represent the completion of the metal insertion into the cavity (Figures. 3a and 4a) and coordination of the first metal onto the periphery (Figures. 3b and 4b). The comparison shows that the structures are similar after insertion of palladium into the cavity. The major divergence in behavior started on attachment of the first metal onto the periphery, showing that the symmetry started getting affected by the first peripheral metal. This would help inform the position of the second one.

The correlation between chain length on one hand and equilibrium constants and extent of the loss of symmetry on the other might be seen as counter-intuitive since longer chain would be expected to disrupt molecular symmetry. But in this case it means that the longer the length of the chain the better the symmetry restoration of the final complex and the more the equilibrium position favors the complex formation.

## CONCLUSION

Pd(II) ion coordination studies of β-Octasubstituted octyl and dodecylthio-derivatised phthalocynaines were carried out with particular attention to the effect of their chain lengths on the coordination process and the equilibrium constants of the reactions. The results obtained from an earlier work on five carbon-chain thio-substituent $H_2Pc$, β-Octasubstituted pentylthio-derivatised Phthalocyanine was included, to allow a trend to be charted on the effect of chain lengths on the binding sequence, equilibrium constants and symmetry of the final complexes.A trend was established between the chain length and equilibrium constant of the reactions with longest chain showing the highest equilibrium constant. This same trend was demonstrated in the symmetry of the final complexes with the shortest chain phthalocyanine showing the most pronounced loss of symmetry.This trend is evidence that symmetrical multinuclear complexes are best designed using long chain ligands. In addition the longer the chain length, the more the thio-derivatised phthalocyanines become unsuitable for Pd(II) ions extraction and dosimetry.

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