

New congeners of molecular phthalocyanine with benzoquinones derivatives

E.H. EL-MOSSALAMY^{1*} and H.M. ARAFA²

¹Department of Chemistry, Faculty of Science, King Abdul Aziz University, P.O. Box 80203, Jeddah - 21589 (Saudi Arabia).

²Department of Chemistry, Faculty of Girls Education, Tabouk University, P.O. Box 741, Tabouk - 71491 (Saudi Arabia).

(Received: April 02, 2009; Accepted: June 03, 2009)

ABSTRACT

The charge transfer complexes between phthalocyanine as a donor and benzoquinone derivatives as acceptors viz., 2,3-dichloro-5,6-dicyano-1,4- benzoquinone (DDQ), p-chloranil (CHL) and chloranilic acid (CHLA) were synthesis and investigated by using some modern techniques such as; ICP and Nujol mull technique using spectrophotometer, that after identification and using synthesis and spectral methods, like elemental analysis, IR and ¹H NMR and melting point. Absorption fine structure spectroscopy with the high spatial resolution of X-ray microscopy. Linear Dichroism (LD), the anisotropic absorption of linearly polarised radiation by an oriented molecule, was observed in CT spectra. LD-NEXAFS offers excellent sensitivity to molecular orientation, and can be used to characterise molecular order in materials at high spatial resolution. Also the imaging surface of complexes was confirmed using optical microscope, electron microscope (scanning SEM, transmission TEM). Metal ions under study (Pt, Fe and Hf) were measured in milligrams per liter. Absorption spectrum was measured using suspension method using paraffin oil to study the electronic transitions for CT complexes. Analyses indicate the particle sizes of CT complex in the range of 65-85 nm.

Key words: Nanophthalocyanine, Charge transfer, ICP, SEM, TEM using benzoquinone.

INTRODUCTION

The novel tetrasubstituted metal-free phthalocyanine and metallophthalocyanines **7**, bearing four 13-membered diazadithia macrocycle moieties at peripheral positions were synthesized by cyclotetramerization of the corresponding phthalonitrile derivative in a multi-step reaction sequence. The metal-free phthalocyanine was synthesized by microwave irradiation of the corresponding dicyano compound in 2-(dimethylamino)ethanol for 10 min. The new compounds were characterized by IR, ¹H NMR, ¹³C NMR, UV Vis, elemental analysis and MS spectral data¹.

The synthesis, characterization and voltammetric and spectroelectrochemical properties

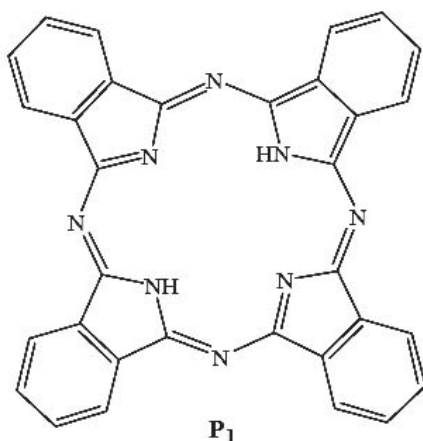
of newly synthesized lead phthalocyanines bearing tetra-(1,1-(dicarbopenthoxy)-2-(4-biphenyl)-ethyl), tetra-(1,1-(dicarbopenthoxy)-2-(1-naphthyl)-ethyl and tetra-(1,1,2-(tricarbo-pentoxoethyl)) substituents have been presented in this work for the first time. The characterization of the complexes was made by elemental analysis, ¹H NMR, FT-IR, UV Vis and MalDI-TOF. The solution redox properties and spectroelectrochemical investigation of the complexes are studied using various electrochemical techniques in DCM on a platinum electrode².

The infrared spectra of phthalocyanine and (Mg⁺², Mn⁺², Fe⁺², Co⁺², Zn⁺² and Pb⁺²) phthalocyanines were investigated using FTIR in the range from (4000-400 cm⁻¹), as halide discs. The absorption bands of phthalocyanines were

compared with the spectral data of phthalocyanine and discussed in relation to its structure. TG analysis curves show that, the main degradation step follows first order kinetics. The minor and major decomposition temperature and also the activation energy of the main degradation step was calculated and discussed. This study focuses on the correlation existing between the structure and the continuous dark conductivity in compacted powder³.

EXPERIMENTAL

Acceptors used in this study are 2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ)(A₁), chloranil (CHL)(A₂) and chloranilic acid (CHLA)(A₃), (All acceptors of Across). The molecular formula of the phthalocyanine (P₁) is the following:



Charge transfer compounds were prepared by 1:1 and 1:2 (D: A) in ethanol as solvent. Elemental analyses (EA) were performed in the King Abdul Aziz university. The elemental analyses data of the solid compound and its complexes along with melting point are given in Table (1). On interaction between CT compound and platinum (IV) in ethanol. The analysis verifies Schiff base (P₁) having the following molecular formula: C₃₂H₁₈N₈.

RESULTS AND DISCUSSION

Infrared absorption and ¹H NMR spectra

The IR spectra of the prepared solid CT molecular complexes were measured in KBr pellets

with a shimadzu IR- Spectrophotometer, given in Table (2). IR spectrum shows that there is a clear divergence in position of azomethine group in Schiff base (P₁) before and after the addition of acceptors and metal ions.

When comparing the values of vibration frequencies functional groups in P₁ before and after the addition of metal ions and the acceptors to show that there is a clear difference in position of these groups before and after the addition to different compositional form which has clearly demonstrated how molecular structure proposed for this compound.

The ¹H NMR spectra of solid CT molecular compound and its complexes were measured in DMSO. The chemical shifts in ppm for all peaks observed in the spectra are given in Table (2). All the observed peaks in the spectra of the individual components are also present in the complexes spectra suggesting their formation. The proton of azomethine group in P₁ is assigned at 3.5740 ppm, while its emerged in complexes at 3.9111, 4.1147 ppm. which confirm that there is a clear divergence in position of azomethine group in Schiff base (P₁) before and after the addition of acceptors and metal ions to it. The proton of five membered of P₁ is assigned at 8.1080 ppm. and at 8.2500 ppm. in its complexes.

Differential scanning calorimetry (DSC)

The DSC curves of four heating rate (a= 5, 7, 10 and 15oC/min.) between T_o C and heat flow which shown in figure (1) was obtained for a compound of Schiff base (P₁) was concluded following a temperature: glacial temperature (T_g), melting temperature (T_m), critical temperature (T_p) and crystalline temperature (T_c).

Crystallization energy EC of P₁ was calculated by using methods of each of all: Ozawa⁴, Coats Redfern and Sestak⁵ and Ozawa and Chen⁶.

Fig. 2 shows that the relationship between lnα and ln(-ln(1-x)) of P₁ at four heating rate (a= 5, 7, 10 and 15oC/min.) according the following equation:

$$\ln[-\ln(1-x)] - n \ln \alpha - \frac{(1.052mE_c)}{RT} \quad \dots(1)$$

Where α is heating rate and EC is crystallization energy. EC of P₁ which obtained after drawing the relationship between $\ln \alpha$ and $\ln(-\ln(1-x))$ according equation (1) (Ozawa method) [4] are given in Table (3) which showed that the EC of

P₁ is equal 2.065 kJ/mol⁻¹ and this indicate that the decomposition of this compound is three dimensional. And the relationship between $\ln(-\ln(1-x))$ against $10^3/T$ (K⁻¹) for P₁ which obtained at four heating rate ($\alpha= 5-15^\circ\text{C}$) according equation (1).

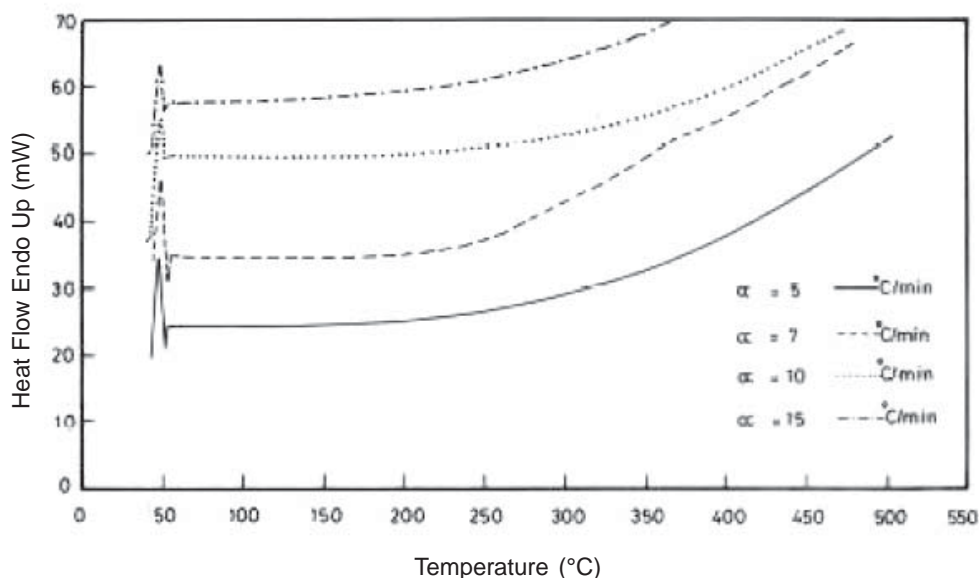


Fig. 1: DSC curve of Schiff base compound P₁ at four heating rate ($\alpha=$ A:5, B: 7, C: 10 and D: 15°C)

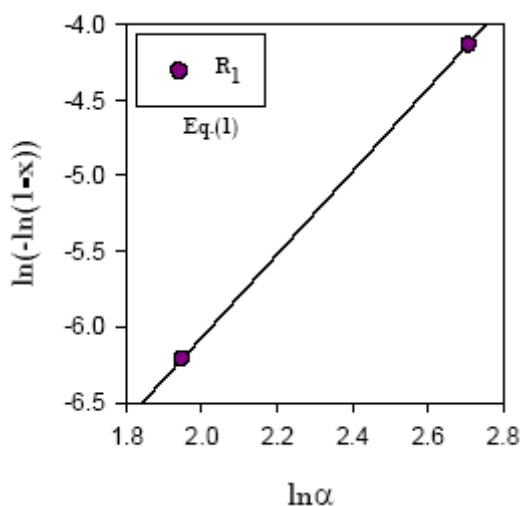


Fig. 2: Plot of $\ln \alpha$ against $\ln(-\ln(1-x))$ of P₁ at four heating rate ($\alpha= 5, 7, 10$ and 15°C) according Ozawa method

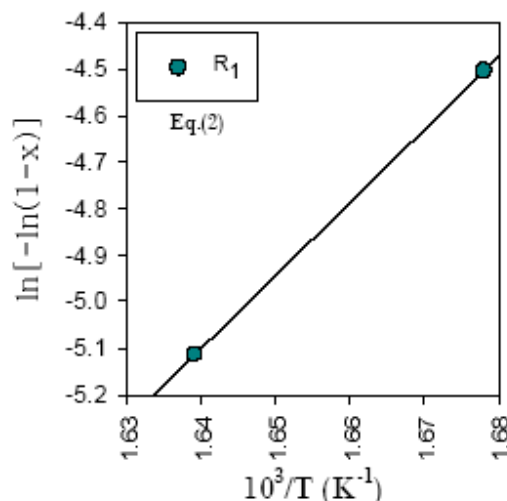


Fig. 3: Plot of $\ln(-\ln(1-x))$ against $10^3/T$ K⁻¹ of P₁ at four heating rate ($\alpha= 5, 7, 10$ and 15°C) according Redfern and Sestak method

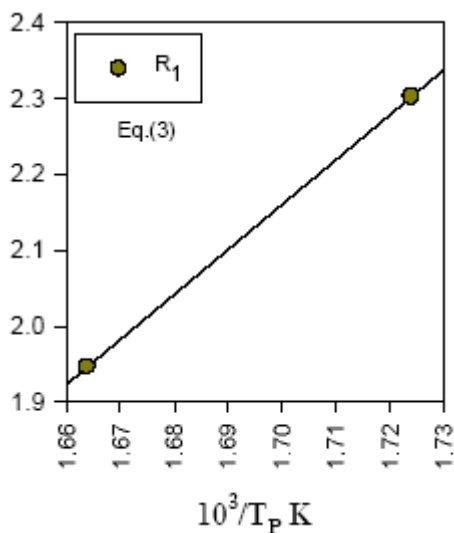


Fig 4: Plot of $\ln a$ against $10^3/TP \text{ K}^{-1}$ of P_1 at four heating rate ($\alpha = 5, 7, 10$ and 15°C) according Ozawa and Chen method

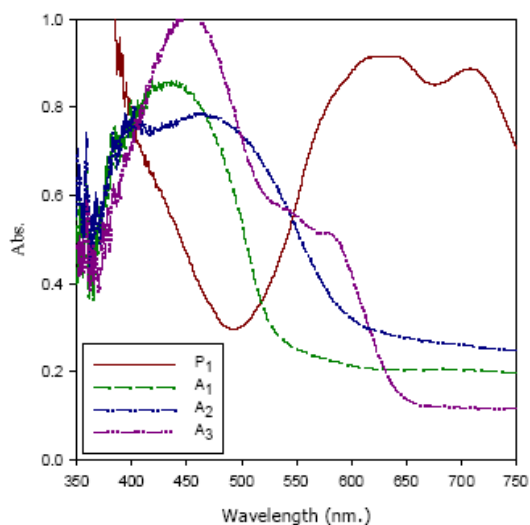


Fig. 5: Absorption spectrum of P_1 (donor) and acceptors which measured at 25°C

Crystallization energy of P_1 which obtained after drawing the relationship which shown in figure (3) between $\ln(\ln(1-x))$ against $1000/T \text{ K}^{-1}$ according equation (1) (Coats Redfern and Sestak method) [5] are given in Table (3) which showed that the average of EC for P_1 is equal $8.606 \text{ kJ/mol}^{-1}$. Crystallization energy of P_1 which obtained after draw the relationship which shown in figure (4) between $\ln a$ against $1000/TP \text{ K}^{-1}$, according equation (1)

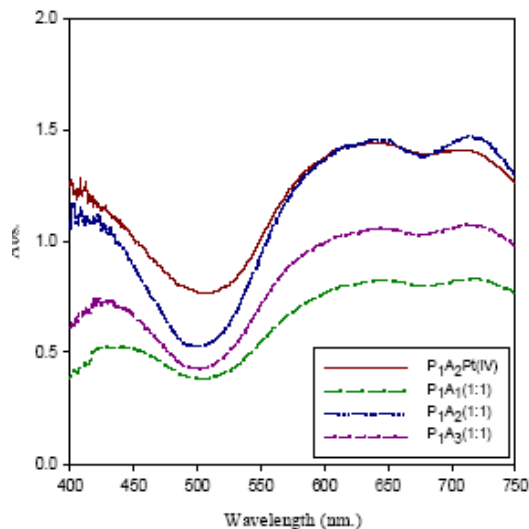


Fig. 6: Absorption spectrum of P_1 with all acceptors under study which prepared 1:1

(Ozawa and Chen method) [6] that the average of EC for P_1 is equal $46.786 \text{ kJ/mol}^{-1}$ where $m=n=1$.

Measuring the absorption spectrum for CT compounds using suspension method by paraffin oil (Nujol mull).

Electron absorption spectrum of CT compounds were measured at a wavelength in the range between 400-750 nm and then calculated the electron energy transition, which identified the symbol ECT by using the following Briegleb relation [7].

$$E_{CT} = I_P - (E_A + C) \quad \dots(2)$$

Where IP is ionization potential of donor compounds, EA is electron affinity of acceptor compounds and C is Coulombic force, which can be calculated by the following values of ECT experimental.

$$E_{CT} = \frac{1243.6}{\lambda(nm)} \quad \dots(3)$$

The IP values can be calculated through the use of the following:

Table 1: Analytical data and melting point of phthalocyanine and its complexes

| Comp. | %C | | %H | | %N | | %M ^{z+} | | Melting point (°C) |
|--------------------------------------|-------|-------|-------|-------|-------|-------|------------------|----------|--------------------|
| | Calc. | Found | Calc. | Found | Calc. | Found | Calc. | Found | |
| P ₁ | 6.219 | 6.321 | 3.498 | 3.465 | 1.555 | 1.602 | - | - | Above 350.0 |
| P ₁ A ₂ Pt(IV) | 3.711 | 3.804 | 1.856 | 1.868 | 0.781 | 0.795 | 1023.98 | 3282.169 | |

Table 2: The IR-spectra and 1H NMR signals of the CT molecular compounds under investigation and its complex which prepared from it

| Comp. | ν_{OH} (Cm ⁻¹) | $\nu_{\text{C-H}}$ (Cm ⁻¹) | $\nu_{\text{CH=N}}$ (Cm ⁻¹) | $\nu_{\text{C=C}}$ (Cm ⁻¹) | $\nu_{\text{N-M}}$ (Cm ⁻¹) | $\nu_{\text{CH=N}}$ (Cm ⁻¹) | δ_{Ar} | $\delta_{\text{Five Me.}}$ | δ_{OH} |
|--------------------------------------|---------------------------------------|--|---|--|--|---|----------------------|----------------------------|----------------------|
| P ₁ | 3272.5, 3594.7, 3840.7 | 2855.9 3042.5 | 1603.8 | 1494.1 | - | 3.5740 | - | 8.1080 | - |
| P ₁ A ₂ Pt(IV) | 3259.6, 3745.4 | 2842.6, 3043.7 | 1624.5 | 1464.8 | 741.2 | 3.9111 4.1147 | - | 8.2500 | - |

Table 3: Glacial temperature (T_g), melting temperature (T_m), critical temperature (T_p) and crystalline temperature (T_c) and crystallization energy of P₁ which was calculated by three methods having four heating rates

| Comp. | α (°C) | T _g (°C) | T _m (°C) | T _p (°C) | T _c (°C) | EC kJ/mol ⁻¹ | | |
|----------------|---------------|---------------------|---------------------|---------------------|---------------------|-------------------------|--------------------------|----------------|
| | | | | | | Ozawa eq | Coast Redfern Sestak eq. | Ozawa -Chen eq |
| P ₁ | 5 | 52.0 | 51.0 | 41.0 | 46.0 | | | |
| | 7 | 52.0 | 51.0 | 41.0, 350.0 | 46.0, 365.0 | 2.065 | 8.606 | 46.786 |
| | 10 | 53.0 | 52.0 | 42.0 | 49.0 | | | |
| | 15 | 53.0 | 52.0 | 42.0, 340.0 | 49.0, 345.0 | | | |

Table 4: Values of the average of ionization potential for donor and acceptors which calculated at the highest wavelength them

| Comp. | $\lambda_{\text{cm}} \times 10^{-7}$ | Mean I _p × 10 ¹⁴ |
|----------------|--------------------------------------|--|
| R ₁ | 713.588 | 3.27 |
| A ₁ | 455.541 | 5.13 |
| A ₂ | 508.311 | 4.60 |
| A ₃ | 583.245 | 4.01 |

$$I_p = a + b u_o \quad \dots(4)$$

Where is a=4.390, 5.156, 5.110, b=0.857, 0.778, 0.701 and u_o is transition energy from HOMO to LUMO (π - π^*), which confirms that when it is prepared in thin layer (film) of the article which is in solid state by using other material will be installed during the transition electronic center suspense account allows various physical parameters of CT compounds.

Table 5: Values of each all: potential ionization potential average, electron transition energy and Coulombic force of CT compounds which prepared 1:1 D:A and its complex at highest wavelength

| Comp. | $\lambda_{cm} \times 10^{-7}$ | Mean $I_p \times 10^{14}$ | E_{CT} (eV) | $C_1 (\times 10^{14})$ | $C_2 (\times 10^{14})$ | $C_3 (\times 10^{14})$ |
|---------------------------------------|-------------------------------|---------------------------|---------------|------------------------|------------------------|------------------------|
| R ₁ -A ₁ (1:1) | 724.604 | 3.22 | 1.710 | 3.22 | - | - |
| R ₁ -A ₂ (1:1) | 723.681 | 3.23 | 1.713 | - | 3.23 | - |
| R ₁ -A ₃ (1:1) | 723.351 | 3.23 | 1.714 | - | - | 3.23 |
| R ₁ -A ₂ Pt(IV) | 716.227 | 3.26 | 1.731 | - | 3.26 | - |

Table 6: Values of each of all: metal ions concentration average of P₁ with A₂ as acceptor and metal ion Pt(IV), percentage of metal ion weight to sample weight, SD and RSD

| Comp. | Metal | λ (nm) | Mean (mg/L) | (Wt/Wt)% | SD | RSD% |
|---------------------------------------|-------|----------------|-------------|----------|--------|------|
| R ₁ -A ₂ Pt(IV) | Fe | - | - | - | - | - |
| | Hf | - | - | - | - | - |
| | Pt | 265.945 | 127.742 | 6.5643 | 0.5087 | 0.40 |

Absorption spectrum of Schiff base (R1) and acceptors under study were measured at wavelength range between 350-750 nm after preparing in paraffin oil as solvent as shown in figure (4) and from them IP values were calculated and noted in Table (4).

The absorption spectrum of solid charge transfer compound, prepared by 1:1 donor: acceptor in addition to CT complex which has been containing the Pt (IV) in paraffin oil. It has been observed in the spectrum that there are new bands unprecedented emerging in single donor or acceptor although appearance it at highest a wavelength that is the electronic transfer occur in a new direction than it was a single compound. As further noted that there was a band or two bands show absorption in the absorption spectrum of compound CT, one shows a result of excited CT band at high a wavelength, it identifies hydrogen bonds (H-bond) or specify the transition proton (Proton-transfer) i.e. theirs occur transitions of $n-\pi^*$ and its the possibility because there is not migration proton in it. While the another bands which it show as a result excited CT bands at less wavelength occur as a result to transitions of $\pi-\pi^*$ where the electron is transfer from electron cloud of vinyl group to benzoquinones cycle of acceptors.

The figure (5) shows that the absorption spectrum of CT compound (P1A1) which prepared 1:1 and CT complex (P1A2 Pt(IV)). The values of IP, f_n , E_{CT} , f_n and C were calculated of CT compounds and noted in Table (5).

One of the most important applications of this technology that can be calculated electronic affinity of the acceptor, through a linear relationship between (ECT) (eV) against IP and from intercept can be calculated electronic affinity of compound have electrons acquisition by known amount of the Coulombic force [8] where that:

$$\text{Intercept} = - (E_A + C) \quad \dots(5)$$

According of (2) equation where the slope is equal one

Inductively coupled plasma (ICP)

Inductively coupled by optical emission technique of following metal ions: Pt, Fe and Hf of the most important and accurate techniques used to estimate the metal ion regardless of the status of oxidation. The metal was estimated in the sample measured in mille grams per liter that after digest it in concentrated nitric acid as shown in the Table

(6), which also include the percentage of the calculated weight of metal ion grams estimated to total weight of the sample (gram) and learn to be metal ion proportion internally multiplied by the per cent (Wt/Wt) %, and stresses the values that have been obtained in entering health expectation of a composite metal ion grantor and

the federation with the future composition of the complex compound $[(DM)^{-8} \dots A^{+8}]$. To avoid potential sampling error of measurement samples were taken during the monitoring of standard deviation (SD) and the relative standard deviation (RSD) of the samples and measured values also shown in the Table (6).

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