

Synthesis , Characterization and Molar Conductivity Study for Platinum(II) Phthalocyanine Complex and its Derivatives

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Abstract :

 A new complexes of platinum (II) phthalocyanine and its derivatives have been prepared , These complexes have been characterized by IR , U.V-visible spectroscopy and molar conductivity measurements . The molar conductivities have been measured in dimethylsulfoxide (DMSO), methylene chloride (CH₂Cl₂) and acetonitrile (CH₂CN) solvents at room temperature at 10^{-3} M. Conductivity measurements for all prepared complexes shows that complees behave as weak electrolytes in DMSO, CH₃CN and CH₂Cl₂ solvents in the range 10^{-5} . 10⁻³ M when plotting Λ_m vs. \sqrt{c} . The conductance data were analyzed by Krauss equation to determine the molar conductivity in infinitely dilution $(Λ₀)$ and dissociation constant (K_d) to determine the stability of these complexes. The effect of variation in the two parameter (Λ_0) and (K_d) were fully investigated.

1. Introduction

One of the most thermally stable systems of coordination complexes known is metallo phthalocyanines family ⁽¹⁾. Various attempts have been made to prepared metallo phthalocyanine and its analogues complexes with several metals such as copper and iron $(2,3)$, there is another method which might be easier reaction of phthalic anhydride or its analogues with excess of urea in presence of ammonium chloride and ammonium molybdate hydrate $(4,5)$. The metals reported in these complexes are cobalt , copper , chromium and iron , but up to data platinum phthalocyanine complexes have not been repoted $(6-8)$.

 Metallo phthalocyanine and their analogues have been investigated in detail for many years , especially with regard to their properties as dyestuffs , pigments and paints . In the last decate phthalocyanine and metallo phthalocyanine exhibit singular and unconventional physical properties interesting for applications in materials science $(9-11)$. Thus, in addition to basic research , the interest in phthalocyanines and metallo phthalocyanines have been recently expanding among others into applied fields such as photovoltaies , optical data storge , laser dyes , liquid crystals , chemical sensors and photosensitizers for photodynamic therapy $(11-13)$. Because of there are no investigations for platinum phthalocyanine and its derivatives , so our aim of this paper was synthesis , characterization and molar conductivity study of new complexes for platinum (II) phthalocyanine and its derivatives which might be very interesting in further studies especially in optical , sensors technology and laser dyes fields .

2. Experimental

 Acetyl chloride , ammonium chloride , ammonium molybdate tetrahydrate , phthalic anhydride , platinum metal , phosphorus penta chloride , sodium sulphide . 9-hydrate were purchased from Aldrich chemical company.

 K_2 PtCl₄ was prepared from platinum metal by literature procedure (14) . Propanoic acid was converted to propanoyl chloride by treatment with 1 equivalent of $PCl₄$ ⁽¹⁵⁾. Infrared spectra were measured as HBr disk on a FT-IR spectrophotometer Shimadzu model 8400 S in the range 4000-200 cm⁻¹. U.V-visible spectra were recorded on a Thermospectronic Helios α V 4.60 using N,N-dimethylformamide as solvent in the range 200-800 nm . Conductivity measurements were made with a konduktoskop modle 365 B . The cell fitted with platinum electrodes , was calibrated with 1 mmol.dm⁻³ aqueous potassium chloride solution . The solutions of platinum complexes were studied in a concentration range 10^{-5} - 10^{-3} M mol.dm⁻³ at room temperature the cell constant was found to be 0.785 cm⁻¹. The solvents DMSO, CH₂Cl₂ and CH₃CN were used as received without any further purification. Typical backgrounds conductivity for DMSO, CH_2Cl_2 and CH_3CN were 1.8, 1.5 and 1.4 μ ohm⁻¹ cm⁻² mol⁻¹ respectively. Melting points were determined on a Gallenkamp melting point apparatus .

3.Synthesis

Preparation of nitro phtalic acid(5)

3-and 4- nitrophtalic acids were prepared by nitration of phthalic anhydride as following :-

Phtalic anhydride (50g, 5 mole) was dissolved in 50ml of conc. Sulphuric acid at 75° C, then 21 ml of fuming nitric acid was added with vigorous stirring at 90° C . 15 ml of sulphuric acid was added dropwise for 1 hr, then 90 ml of nitric acid was added at 90°C with vigorous stirring for 3 hrs .After cooling, the mixture was filtered to remove the excess of nitric acid and sulphuric acid . The crude product washed several times with distilled water . Pale yellow

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powder were obtained m.p 220 $^{\circ}$ C (lit. 220 $^{\circ}$ C) yield 40%. The washing distilled water was collected and concentrated, 4-nitro phtalic acid was extracted from the washing water by treating with diethyl ether several times , collected and evaporated to form yellow powder m.p 165°C (lit. 165-166°C) yield 35%.

Preparation of nitro phtalic anhydrided(16)

3-and 4-nitro phthalic acid (0.1 mole) was added to acetic anhydride (20 g , 0.19 mole) and the mixture was refluxed for 1 hr . After cooling , the mixture was filtered and the solid product washed several times with absolute ethanol yield 90% .

Preparation of sodium polysulfide(5)

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Sodium sulphide (Na₂S_x) was prepared by dissolving sodium sulphide . 9-hydrate Na₂S.9H₂O (20 g, 0.08 mole) in 75 ml of distilled water . Then sulphur powder (5g , 0.15 mole) was added to this solution with vigorous stirring for 1 hr.

Preparation of complex[1] : platinum (II) phthalocyanine

 K2PtCl4 (3.32 gm , 8 mmole) , phtalic anhydride (4.73 g , 32 mmole) , ammonium molybdate tetrahydride (0.2 g) m ammonium chloride (0.5 g , 9 mmole) and excess of urea (30g , 0.5 mole) were grounded and placed in 250 ml round bottom flask containing 100 ml of nitrobenzene . The temperature of the stirred reaction mixture was increase gradually to 185^oC and maintained it for 5 hr. The hot mixture was filtered and the precipitate washed with ethanol repeatedly to remove the nitrobenzene . The solid product was dried and added to 200 ml of 1 N HCl and then refluxed for 1 hr , cooled to room temperature and filtered . The solid precipitate added to 200 ml of 1 N NaOH and reflux the solution for 1 hr , filtered and washing with distilled water to obtain brown crystals of platinum (II) phthalocyanine yield 85% . The complex $[2]$: platinum (II) -3,3`,3``,3``. tetranitrophtalocyanine and complex $[3]$: platinum (II) -4,4`,4``,4``. tetranitrophthalocyanine were synthesized in the same procedure with 3-nitrophthalic anhydride and 4-nitrophthalic anhydride respectively .

Preparation of complex [4] : platinum (II) – 3,3`,3``,3```-tetraaminophthalocyanine

 To a suspension of complex [2] (8.87 g , 10 mmole) in 45 ml of water added to (9.6 g , 40 mmole) of sodium polysulphide in 25 ml of distilled water in 20°C. The mixture was stirred at 20°C with vigorous stirring for 24 hrs. After cooling , the mixture was added to 50 ml of 1N HCl and stirred for 30 min . Then the solid precipitate was collected by centrifuge . The collected precipitated was added to 50ml of 1 N NaOH and stirred for 30 min . The result solid was collected by centrifuge and washing with distilled water. Pale brown solid of platinum (II) – 3,3`,3``,3``. tetraaminophthalocyanine was obtained yield 87% .

Preparation of complex [6] : platinum (II) – 3,3`,3``,3```-tetraacetamido phthalocyanine

 (7.67 g , 10 mmole) of complex [4] was suspension in 250 ml of pyridine then (3.14 g , 40 mmole) of acetyl chloride was added. The mixture reaction was stirred at $45{\text -}50^{\circ}\text{C}$ with vigorous stirring for 2 hrs. After cooling, the mixture filtered off , the solid crude was washed by water , absolute ethanol and acetone respectively . The complex [6] : platinum (II) – 3,3`,3``,3```-tetraacetamidophthalocyanine obtained as a pale brown crystals (yield 75%). The complex [7] : platinum -4,4`,4``,4```- tetraacetamidophthalocyanine was prepared in the same manner by reaction complex [5] with acetyl chloride (yield 71%) . Complex [8] : platinum (II) 4,4`,4``,4```- tetraacetamidophthalocyanine were prepared in same procedure of complex [6] and [7] respectively with propanoyl chloride .

4- Results and Discussion

 Nine complexes of platinum (II) phtalocyanine and their derivatives have prepared Figure (1.2) illustrate the prepared complexes [1]-[9] .

Figures (1,2) : The suggested structure of prepared complexes [1]-[9]

 The complex [1] , platinum (II) phthalocyanine , was prepared by reacting phthalic anhydride with excess of urea in presence of ammonium chloride and ammonium molybdate . 9-hydrate in nitrobenzene as solvent , while complex [2] : platinum (II) – 3,3`,3``,3```- tetraaminophthalocyanine and complex [3] : platinum (II) – 4,4`,4``,4`` tetraaminohthalocyanine were prepared in the same procedure but with 3- or 4- nitrophthalic anhydride respectively , which are prepared in situ from nitration of phthalic anhydride by HNO_3 and H_2SO_4 . The catalyst ammonium molbadate -9-hydrate is very important in preparative method in increasing the yields of complexes , reducing reaction time and decreasing the reaction temperature (17). The complexes [2] and [3] were prepared by nitration of phthalic anhydride by $HNO₃$ and $H₂SO₄$ but can not by direct nitration of platinum (II) phthalocyanine because these complexes have higher stability against these reagents . complexes [2] and [3] react with sodium polysulphide to reduction the nitro groups to amines groups to afford complex [4], platinum (II) $3,3^{\prime},3^{\prime\prime},3^{\prime\prime\prime}$ - tetraaminophthalocyanine, and complex [5] , platinum (II) -4,4`,4``,4```- tetraaminophthalocyanine respectively . The complexes [4] and [5] were converted to complex $[6]$, platinum (II)- 3,3`,3``,3```- tetraaminophthalocyanine and complex $[8]$, platinum (II)- 3,3`,3``,3``. tetrapropylamidophthalocyanine when reacted with acetyl chloride respectively , while complex [7] , platinum - $4,4^{\prime},4^{\prime\prime},4^{\prime\prime}$ tetrapropylamidophthalocyanine and complex [9], platinum (II) - $4,4^{\prime},4^{\prime\prime},4^{\prime\prime}$ tetrapropylamidophthalocyanine where prepared by reacting complexes [4] and [5] with propanoyl chloride (prepared in situ by reacting PCl₅ with propanoic acid) respectively. Preparative methods of these complexes are shown in scheme (1) . All prepared complexes can not be purified by recrystalization method because the insoluble in most organic and inorganic solvents. The purification of the prepared complexes was carried out by dissolving in acids as H_2SO_4 and HCl then with NaOH⁽¹⁸⁾. Generally, the prepared complexes are insoluble in water and ethanol and not sensitive to hydrolysis but can be dissolved in DMSO, DMF, CH_2Cl_2 , CH_3CN . The colour of prepared complexes are brown to dark brown. The prepared complexes were decomposed the temperature range $(300-348)$ °C. The high thermo – stability of prepared complexes can be attributed to the aromatic system of phthalocyanine molecule with highly resonance structure . The platinum (II) ion fitting with space inside phthalocyanine molecule also enhance this thermal stability . The melting points (decomposition) , yields and colour for all complexes are shown in table(1) .

Scheme (1) : prepared methods of the prepared complexes [1]-[9]

 The IR data of these complexes display characteristic bands at certain frequencies , Figures (3.4) show the IR spectra of [2] and [5] complexes respectively as examples while Table (2) summarized the important vibration bands of the prepared complexes. The observed vibration bands are similar to these in the literature and typical representive of IR spectra for metallo phthalocyanines complexes (22) .

All complexes showed two weak bands due to (Pt-N) stretching in the range 520-574 cm^{-1 (19)} this indicate that all the prepared complexes in cis form adopting D4h point group .The IR spectra show a strong band in the range 1591-1595 cm⁻¹ due to $v(C=C)$ stretching, while $v(C=N)$ appears in the range 1680-1692 cm⁻¹. The aromatic C-H stretching, $v(C=C)$ stretching band appeared in range 3029-3090 cm^{-1 (20)}. In all spectra of prepared complexes, there are several bands ranged 1150-700 cm⁻¹ assigned to the phthalocyanine skeletal vibrations. The IR spectra of complexes [2] and [3], figure (4) as example show two vibration bands, the first in range 1540-1542 cm⁻¹ due to a symmetrical stretching of NO₂ groups, while the other can be assigned symmetrical stretching of NO₂ groups ranged 1350-1356 cm⁻¹. The IR spectra of complexes [4] and [5], figure (5) show two bands in the range 3410-3415 cm⁻¹ attributed to N-H stretching of NH₂ groups, while the bending band of N-H appeared in 1620 cm⁻¹. The complexes [6]-[9] showed N-H stretching of amide groups in the range 3330-3335 cm⁻¹ while C=O of amide groups 1675-1693 cm⁻¹. Also, the complexes [6]-[9] , figure (6) as example, show medium bands in the range 2920-2926 cm⁻¹ due to aliphatic C-H stretching band (20) .

Table (2) : important functional groups for IR spectra for the prepared complexes [1]-[9] in cm-1

The U.V-visible data of all prepared complexes recorded in the range 200-800 nm using DMF as solvent . Figure (5,6) show spectra of complexes [1]and [3] respectively as examples and the electronic transitions of the prepared complexes [1]-[9] are summarized in the table (3) . Three electronic transitions are observed in all spectra [1]-[9] . The the first transition was observed in the range (625-665 nm) with $C(193-256 \text{ nm}) \text{ M}^{-1}$.cm⁻¹ which is can be attributed to a Q-band , which assigned to $a_{1u} \rightarrow$ eg⁽²¹⁾. The second band which observed in the range (345-365 nm) with ϵ ranged (175-230) M^{-1} cm⁻¹ can be attributed to a B-band, which assigned to $a_{2u} \rightarrow eg$ transition, while the third transition must be d-d transitions in the range (298-305 nm) with ϵ ranged (59.6-92) M^{-1} cm^{-1 (22)}. The Q-band in these complexes were observed to be red shifted when comparison complex [1] with complexes which contain amino and amide groups of complexes [4]-[9] while be equal with complexes [2] and [3] approximately . Also , there are red shifted in Q-band when replacement amino groups, complexes [4] and [5] with amido groups, complexes [6]-[9]. The red shifted in Qbands may be due to decrease in energy between various $\pi \rightarrow \pi^*$ transitions of the phthalocyanine ring and increasing in periphery of complexes . The same observations were found in B-bands of complexes .

Table (3) : U.V-visible data of complexes [1]-[9] at 10² M in DMF solvent

 The molar conductivity measurements have been carried out for all synthesized complexes [1]-[9] in different solvents : dimethyl sulfoxide (DMSO), methylene chloride (CH₂Cl₂) and acetonitrile (CH₃CN) at 10^{-3} M concentration at room temperature , Table (4) are summarized the molar conductivity data of the prepared complexes in different solvents. The molar conductivity (Λ_m) was calculated from equation $(1)^{(23)}$, where c is the molar concentration and k is the specific conductivity.

$$
\Lambda_m = K/C \quad \dots \dots \dots \dots \dots \dots \dots \quad (1)
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The molar conductivities values are in the range $(22{\text -}80)$ ohm⁻¹cm⁻¹mol⁻¹ which are below the (118-131) ohm⁻¹cm⁻¹ 1 mol^{-1} range which are display low molar conductivity to consider 1:1 electrolytes (24) .

a : units of ohm⁻¹cm⁻¹mol⁻¹ b: measured at 10^{-3} mol dm⁻³

Table (4) : molar conductivity data for the prepared complexes [1]-[9] in different solvents at room temperature

The molar conductivities in CH₂Cl₂ are higher than their values in DMSO and CH₃CN with corresponding complex . These differences may be attributed to that the DMSO and CH₃CN molecules can be adducted with platinum (II) center by coordination from sulphur and nitrogen atoms respectively, but this coordination does not occur in CH_2Cl_2 , also these differences may be due to the viscosity and dielectric constants of these solvents .

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 The molar conductivities of each complex in different solvents at room temperature have been measure and found to be within in the range 10⁻⁵-10⁻³ M. Plotting Λ_m versus \sqrt{c} show, clearly, that these complexes are weak electrolytes in DMSO, CH₃CN and CH₂Cl₂ solvents. Figure (7) shows the electrochemical behavior of complex [1] in different solvents. To determine the stability of these complexes in different solvents, the dissociation constant (K_d) and molar conductivity in infinitely dilution (zero concentration) (Λ_0) were calculated by Krauss equation , equation (2)

CΛm = Kd(Λo) 2 (1/Λm) - KdΛo ………………. (2)

When plotting $C\Lambda_m$ versus $1/\Lambda_m$ gives slope equal to $K_d (\Lambda_o)^2$ and when

C $\Lambda_m = 0$, $1/\Lambda_m = 1/\Lambda_o$. complex [2] is given as example, figure (6) showed C Λ_m versus $1/\Lambda_m$ curve in different solvents . Table (5) show these measured parameters for all prepared complexes in different solvents . The K_d values represent the stability of these complexes which can be arrange to decreasing K_d magnitudes . When the complex is fixed, generally, the complex in CH_2Cl_2 solvent are more stability than in CH_3CN solvent, also the complexes in CH3CN solvent are more stability than complex in DMSO solvent with the corresponding complex . The comparison of molar conductivity in infinity dilution of complex with corresponding complex in another solvent , the complexes in CH_2Cl_2 solvent have higher molar conductivity in infinitely dilution compared with CH_3CN solvent, also complex in CH₃CN has higher Λ_0 compared to same complex in DMSO solvent. This have been attributed to coordinate two DMSO molecules with platinum(II) ion by sulpher atom to form six coordinate complexes .Also , $CH₃CN$ molecules can be adduct with platinum (II) ion in the same manner . This observation do not happened in CH₃Cl₂ solvent . On the other hand, the Λ_0 was observed that complexes which have NH₂ groups, complexes [4] and [5], have higher Λ_0 compared with complexes which have amide groups, complexes [6]-[9], and complexes [6]-[9] have more Λ_0 than complexes which have nitro groups, complexes [2] and [3]. complex [1] have the least Λ_{o} . This observations have been attributed to these groups which have higher limited ionic conductivity .

Table (5) : showed molar conductivity at infinitely dilution (Λo**) and dissociation constant (Kd) in different solvents**

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