2-aminoethylthiol Substituted Cobalt and Manganese Phthalocyanines: Spectroscopic and Electrochemical Investigations

Owolabi M. Bankole

Department of Chemical Sciences, Adekunele Ajasin University, Akungba-Akoko, Ondo State, Nigeria

Abstract

Spectroscopic and electrochemical properties of 4-(2-aminoethylthio phthalocyanato complexes of cobalt (complex **3**) and manganese (complex **4**) are investigated in this work. The UV-Vis spectral properties of the complexes were typical of the nature of central metal (cobalt versus manganese) phthalocyanine. The Q-band of manganese 4-(2-aminoethylthio) phthalocyanine is red shifted with respect to cobalt manganese 4-(2-aminoethylthio) phthalocyanine. Solution electrochemistry of complex **3** showed three distinctly resolved redox processes attributed to $Co^I Pc^{-2}/Co^I Pc^{-3}$ ($E_{1/2} = -1.40\,V$ vs. AgCl), $Co^{II} Pc^{-2}/Co^I Pc^{-2}$ ($E_{1/2} = -0.275$ V vs. AgCl) and $Co^{III} Pc^{-2}/Co^{II} Pc^{-2}$ ($E_{1/2} = +0.64\,V$ vs. AgCl). No ring based oxidation was observed in complex **3**. Complex **4** showed both ring-based oxidation, attributed to $Mn^{III} Pc^{-1}/Mn^{III} Pc^{-2}$ ($E_{1/2} = +0.86\,V$ vs. AgCl) and ring-based reduction associated with $Mn^{II} Pc^{-2}/Mn^{II} Pc^{-3}$ ($E_{1/2} = -0.80\,V$ vs. AgCl), with the normal metal reduction, $Mn^{III} Pc^{-2}/Mn^{II} Pc^{-2}$ ($E_{1/2} = -0.07\,V$ vs. AgCl). The cathodic to anodic differences (E) of redox processes observed for **4** are $180\,mV$ and $130\,mV$, while the cathodic to anodic peak difference (E) for **3** are $290\,mV$ and $210\,mV$ at processes **I** and **II**. By virtue of this, manganese 4-(2-aminoethylthio) phthalocyanine complex has better electron transfer processes than the cobalt analogue.

Keywords: Phthalocyanine, electrochemistry, spectroscopic, Manganese phthalocyanine, cobalt phthalocyanine.

Introduction

Phthalocyanines are macrocyclic compounds that are structurally related to other macrocylic pigments such as porphyrins. The main structural differences between phthalocyanines and porphyrins are [1]; (i) the presence of four isoindole subunits in phthalocyanine complex have been replaced by pyrrole units in porphyrin; (ii) presence of four nitrogen atoms at the four meso positions of phthalocyanines while the pyrrole units in porphyrin are connected via carbon atoms.

Metallophthalocyanines have shown to be extremely versatile materials with state-of-the-art applications in electro catalysis and electro analysis [1-3]. They are employed as electrocatalysts when incorporate on electrode surfaces by acting as electron transfer mediators [1-3] for various applications including as sensors, electrochromic devices, semiconductors, nonlinear optics [4-9], photosensitizers, molecular electronics, photocatalysis [10-12]. As electrocatalysts, the majority of Metallophthalocyanine (MPc) complexes involve a change in oxidation state of the central metal.

Physical, spectroscopic and electrochemical properties of phthalocyanines depend largely on the nature and position of the substituents on MPc rings, axial ligations and nature of the central transition metals [13]. Fine-tuning the spectroscopic and electrochemical properties of Pcs can be achieved by varying the central metal atoms in the cavity of the Pc ring for improved functionalities [14-17]. Electrochemical behaviors of phthalocyanines containing electroactive central metals, such as cobalt [14,15,17] and manganese [18-20], have been reported. Their improved electron transfer processes are well documented [14-20]. Hence, phthalocyanine derivatives of Co and Mn are good candidates for the development of smart electrochemical sensors and other electrocatalysis applications [21-24]. The choice of 2-aminoethanethiol substituents for the studied complexes in this work was due to good spectroscopic, photochemical and enhanced electrochemical behaviors of sulfur-substituted phthalocyanines [25-27]. Hence, 4-(2-aminoethyl) thiol peripherally substituted Pc complexes containing Co and Mn analogues were employed in this work. This present work describes the spectroscopic and electrochemical properties of 2-aminoethylthiol substituted cobalt (**3**) and manganese (**4**) phthalocyanine complexes.

In this work, we show the importance of the aminoethanethiol groups on phthalocyanine complexes as potential electrocatalytic materials. Comparative studies on the spectroscopic and electrochemical of the two synthesized complexes are therefore reported for the first time in this work.

2. Experimental
2.1 Materials
Potassium carbonate, cobalt (II) chloride, manganese (II) acetate and dichloromethane (DCM) and 2-

aminoethanethiol hydrochloride was obtained from Sigma-Aldrich. Dimethylformamide (DMF), dimethyl sulphoxide (DMSO), methanol, ethanol, silica gel 60 (0.04-0.063 mm) (for column chromatography) were purchased from Merck. Tetrabutylammonium tetrafluoroborate ($TBABF_4$) (electrolyte for electrochemical experiments involving MPc complexes), 4-nitrophthalonitrile was obtained from Chemsavers. All solvents were distilled before use and all other reagents were of analytical grade and were used as received from the suppliers without further purification.

2.2 Instrumentation
Various spectroscopic techniques were employed for characterization of the synthesized phthalonitrile and MPc complexes. Ground state electronic absorption spectra were recorded on a Cary 500 UV-Vis-NIR spectrometer. IR spectra (KBr pellets) were recorded on a Perkin-Elmer spectrum 2000 FTIR spectrometer. ^{1}H NMR spectra were obtained using a Bruker AVANCE 300 MHz NMR spectrometer in DMSO-d_6. Elemental analyses were done using a Vario-Elementar Microcube ELIII, while mass spectra data were collected on a Bruker AutoFLEX III Smart-beam TOF/TOF mass spectrometer using a-cyano-4-hydrocinnamic acid as the matrix in the positive ion mode.

Electrochemical data were obtained using BioAnalytical systems (BAS) model 100B/W Electrochemical Workstation, or using the Autolab potentiostat PGSTAT 30 (Eco Chemie, Utretch, The Netherlands) using the General Purpose Electrochemical System data processing software (GPES, software version 4.9) or Advanced Electrochemical System (Princeton Applied Research) PAR-STAT 2273 equipment.

For all electrochemical experiments, a conventional three-electrode system was used. The working electrode was bare glassy carbon; silver-silver chloride wire and platinum wire were used as pseudo reference and auxiliary (counter) electrodes respectively.

The potential response of the $Ag|AgCl$ pseudo-reference electrode was less than the $Ag|AgCl$ (3 M KCl) by $0.015 \pm 0.003V$. Prior to use, the electrode surface was polished with alumina on a Buehler felt pad and rinsed with excess Millipore water. Electrochemical experiments involving MPc complexes were performed in freshly distilled DMF, containing $TBABF_4$ as supporting electrolyte. All electrochemical experiments were carried out in nitrogen saturated solutions.

2.3 Synthesis
2.3.1 4-(2-aminoethylthio) phthalonitrile (2), Scheme 1
The phthalonitrile precursor (**2**), **Scheme 1**, for the preparation of the aminoethane thio-substituted Pcs (**3 and 4**) was prepared following the literature procedure of 4-Propy-2-ynyloxy-phthalonitrile [**28**]. Briefly, a mixture of 4-nitrophthalonitrile **1** (1.0 g, 5.866mmol) and 2-aminoethanethiol hydrochloride (0.667 g, 5.866mmol) was stirred in anhydrous DMF (50 ml) under nitrogen atmosphere. After stirring for 15 minutes, finely ground anhydrous K_2CO_3 (9.61 g, 17.38 mmol) was added portion-wise during a 2 h period, after which the reaction mixture was allowed to stir for 48 h at room temperature. The crude product was poured into ice (250 g). The precipitate was filtered off, washed several times with water, until the filtrate was neutral. The pure product obtained was air dried. Yield of the product is 0.6485g (46%). IR (KBr) obtained for **2** is as follows; v_{max}/cm^{-1}: 3232.85-3358.18 (N-H), 3095.85 (Ar-C-H), 2931.9 (CH$_2$), 2231.71 (C≡N), 1654.98, 1581.68, 1533.46, 1431.23, 1342.5, 1220.98, 1192.05, 1126.47, 1192.05, 1126.47, 1070.53, 906.57, 871.85, 835.21, 713.69, 669.32, 599.88, 524.66, 418.57. MS, m/z: calcd 203.05; found 203.11 [M]$^+$. Anal. for C$_{10}$H$_9$N$_3$S %: calcd C 59.09, H 4.46, N 20.67, S 15.78; found C 58.98, H 4.61, N 20.17, S 15.29. ^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm): 7.78 (Ar-H,s, 1H), 7.71 (Ar-H,d, 1H), 7.40 (Ar-H,d, 1H), 3.12 (CH$_2$, t, 2H), 2.81 (CH$_2$, m, 2H), 2.20-2.66 (CNH$_2$, t, 2H).
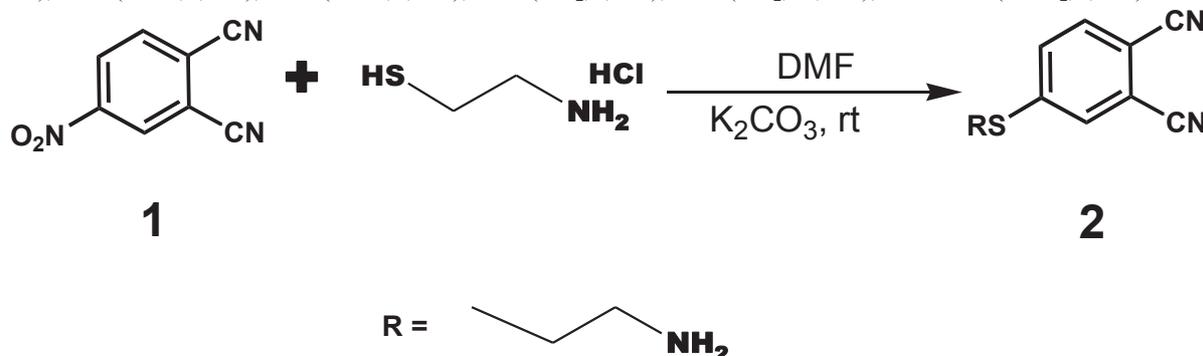
Scheme 1: Synthetic pathway for the synthesis of 4-(2-aminoethythio) phthalonitrile (**2**).

2.3.2 4-(2-aminoethylthio) phthalocyanine Cobalt (II), 3, Scheme 2
A mixture of compound **2** (0.05 g, 0.246 mmol), cobalt (II) chloride (0.032 g, 0.246 mmol), n-pentanol (5 mL) and DBU (0.5 mL) were refluxed for 20 h under nitrogen atmosphere. At the completion of the reaction, the

crude deep green product was precipitated with excess MeOH:H$_2$O (1:1) and purified by using column chromatography with neutral alumina as column material and DCM/MeOH (10:1) as eluent. The pure compound **3** was obtained as green solid. Yield: 0.08 g (38%). UV-Vis (DMF): λ_{max} (nm) (log ε): 693 (5.3), 628 (4.8), 478 (4.2); IR (KBr) ν_{max}/cm^{-1}; 3232.85-3358.18 (N-H), 3095.85 (Ar-C-H), 2966-2799 (CH2), 686 (C-S-C), 1619, 1572, 1508, 1462, 1384, 1318, 1239, 1113, 919, 739. MS, m/z: calcd 871.14; found 872.44 [M+H]$^+$. Anal. for C$_{40}$H$_{36}$N$_{12}$S$_4$Co %: calcd C 55.10, H 4.16, N 19.28, S 14.71; found C 55.80, H 4.82, N 18.96, S 14.22. ^{1}H NMR (300 MHz, DMSO-d$_6$), δ (ppm): 8.46 (Pc-H, 4H, m), 8.27, 7.95-7.71 (Pc-H, 8H, m), 3.12-2.56 (ethyl-H, 16H, m), 2.91-2.84 (CNH$_2$, t, 8H).
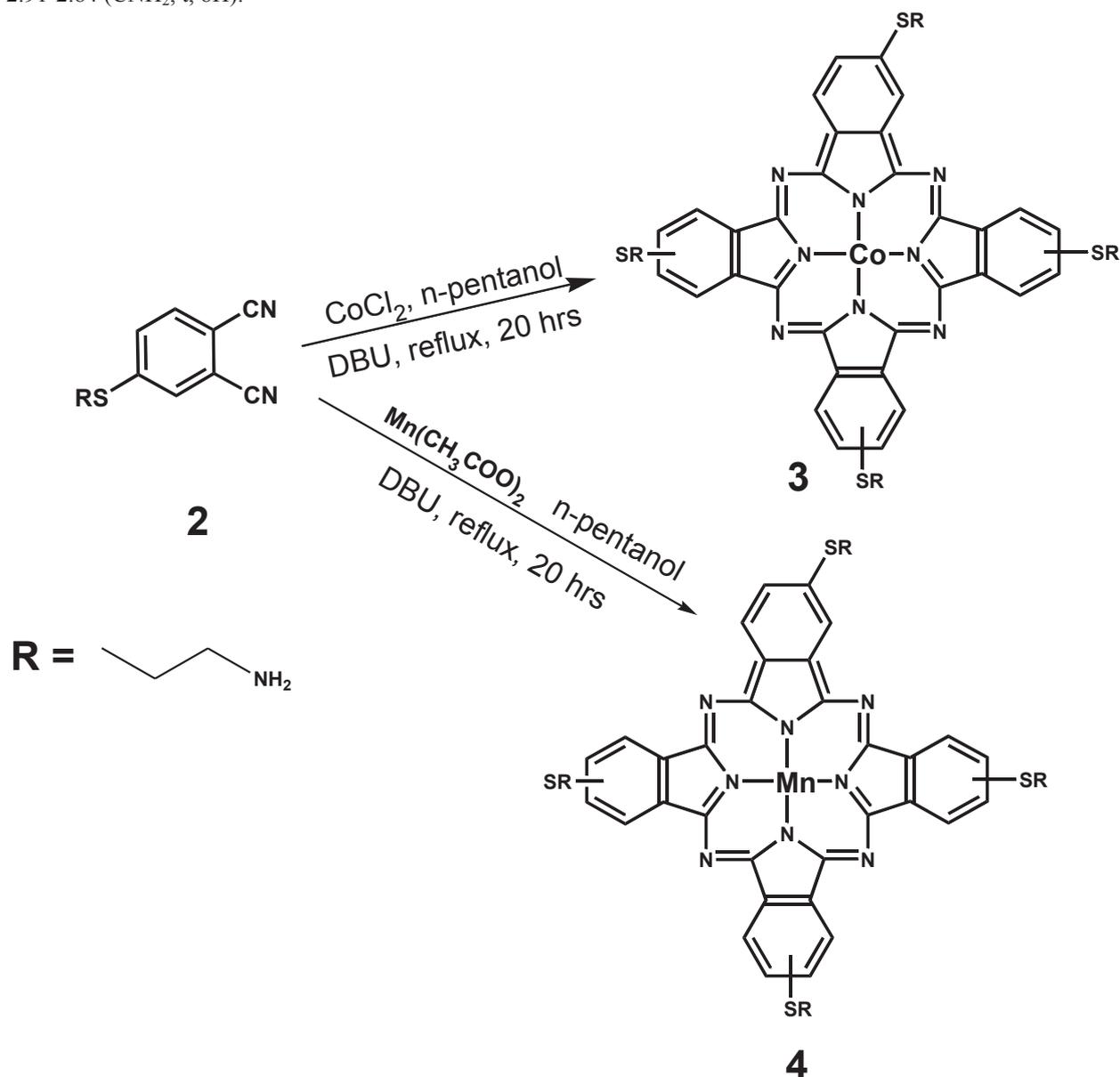
Scheme 2. *Synthetic pathway for the formation of 4-(2-aminoethylthio) phthalocyanine Cobalt (II), 3, and Manganese (III), 4.*

2.3.3 4-(2-aminoethylthio) phthalocyanine Manganese (III), 4, Scheme 2

The synthesis of compounds **4** and **3** were similar, except that **4** required the use of manganese acetate as metal salt in place of cobalt II chloride. Purification was achieved using column chromatography with neutral alumina as column material and DCM/MeOH (10:1) as eluent. Yield: 0.08 g (38.09%). UV-Vis (DMF): λ_{max} (nm) (log ε): 768 (5.4), 690 (4.8), 511 (4.5), 477 (4.5), 357 (5.1); IR (KBr) ν_{max}/cm^{-1}; 3191-3067 (Ar-C-H), 1064 689 (C-S-C), Mn-O stretch (877 cm^{-1}), 1763, 1716, 1374, 1308, 1236, 1109. Anal. Calc. for C$_{40}$H$_{36}$N$_{12}$S$_4$Mn: C 55.35, H 4.18, N 19.36, S 14.78; Found: C 55.26, H 4.90, N 18.98, S 14.88. MS (MALDI-TOF) m/z: Calcd. 867.14; Found: 868.02 [M+H]$^+$. ^{1}H NMR (300 MHz, DMSO-d$_6$), δ (ppm): 8.28 (Pc-H, 4H, m), 8.17, 7.91-7.62 (Pc-H, 8H, m), 3.03-2.76 (ethyl-H, 16H, m), 2.40-2.14 (CNH$_2$, t, 8H).

3. Results and Discussions

3.1. Synthesis and characterization

Synthetic pathway for the preparation of the precursor **2** to complexes **3** and **4** is represented in **Scheme 1**. The precursor was prepared via based-catalyzed nucleophilic aromatic displacement reactions [29,30]. Cyclotetramerization process of **2** occurred in the presence of $CoCl_2$ and $Mn(CH_3COO)_2$ to form the proposed complexes: **3** and **4** respectively. Complexes **3** and **4** were purified using column chromatography on alumina. The pure products were obtained in satisfactorily high yields and characterized by FTIR, elemental analysis, UV-Vis, ^{1}H NMR spectroscopies and MALDI-TOF. The characterization results obtained were in good agreements with the proposed structures shown in the **Scheme 2**. The compounds are effortlessly soluble in in organic solvents such as DMF, DCM, THF and DMSO.

3.2 Spectroscopic Properties

Molecular ion peaks of 872.44 $[M + H]^+$ and 868.02 $[M + H]^+$ were respectively observed for complexes **3** and **4**. These masses are definitive and truly represented the molecular weights of the proposed structures. Fragmentation of m/z peaks as $[M + nH]^+$ are in order, and have been previously reported in the literature [31]. Elemental analyses of the complexes gave percentage C, N and S values that were within 1% in all cases, which are within acceptable range for metallophthalocyanine complexes. ^{1}H NMR spectra confirmed the purity and the expected structures of the synthesized complexes. ^{1}H NMR spectra of the two complexes are very similar, except for the two central metals in the Pc cavities.

FTIR spectrum of phthalonitrile **2** shows characteristics split peaks at 3365.9 cm^{-1} and 3255 cm^{-1} attributable to N-H stretch of amine (NH_2), other notable IR spectrum observed in **2** is 2231.71 cm^{-1} due to C≡N. Formation of complexes **3** and **4** (**Figure 1**) were confirmed by the disappearance of prominent nitrile (C≡N) band of compound **2**. The split absorption signals around 3340-3202 cm^{-1} are consistent in the spectrum of the phthalonitrile as well as the synthesized molecules **3** and **4**. The positions of the other absorption peaks for the synthesized complexes in the infrared spectra were all in agreement with the proposed structures and literature data [32,33].
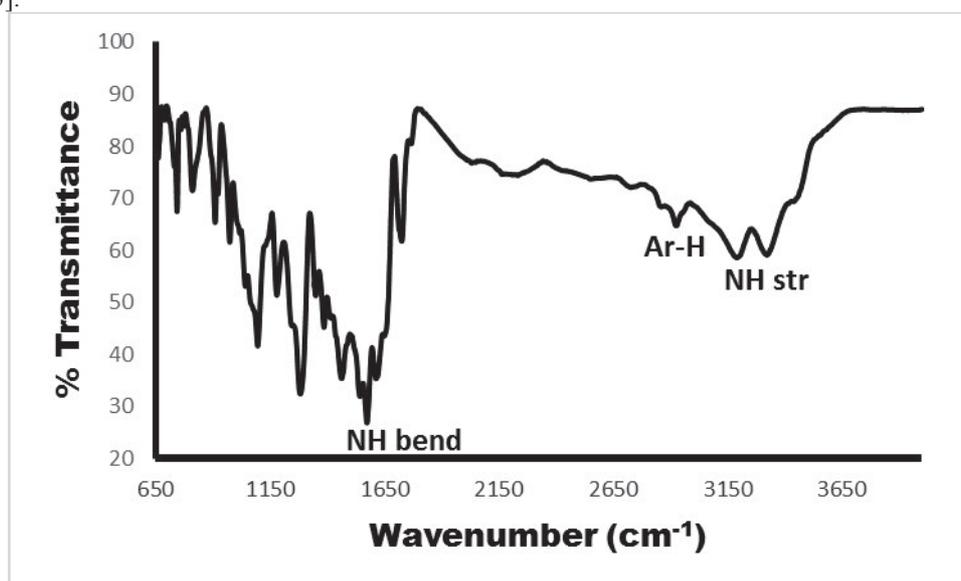
Figure 1: FTIR spectrum representative of compound **4**

The electronic absorption spectra of cobalt and manganese phthalocyanines showed monomeric behaviour in DMF (**Figure 2**); this is evidenced by single Q band for both complexes, typical of metallated phthalocyanines [34], with D_{4h} symmetry. The Q-bands of **3** and **4** were observed at 673 nm and 768 nm, respectively. Manganese analogue was red-shifted compared to that of cobalt analogue. The shift to higher wavelength of Q-band in compound **4** is characteristics of manganese phthalocyanines (MnPcs). This explained why MnPcs have purple colour in most cases. The position of Q-band absorption phthalocyanine complexes can be influenced by the nature of central metal, solvent, point of substitution of substituents and nature of the substituents on Pc rings [35,36]. Any of these parameters can as well be used to tune the photophysical and electrochemical properties of phthalocyanines for improved activities. Summary of absorption band maxima of complexes **3** and **4** are shown in **Table 1** below.

Table 1: Summary of absorption band maxima of Manganese 4-(2-aminoethylthio) phthalocyanine and Cobalt 4-(2-aminoethylthio) phthalocyanine complexes.

Complex	Q-band/nm	Vibrionic band/nm	Charge Transfer Band/nm	B-band/nm	Solvent
3	673	608	400	350	DMF
4	768	687	506 and 466	356	DMF
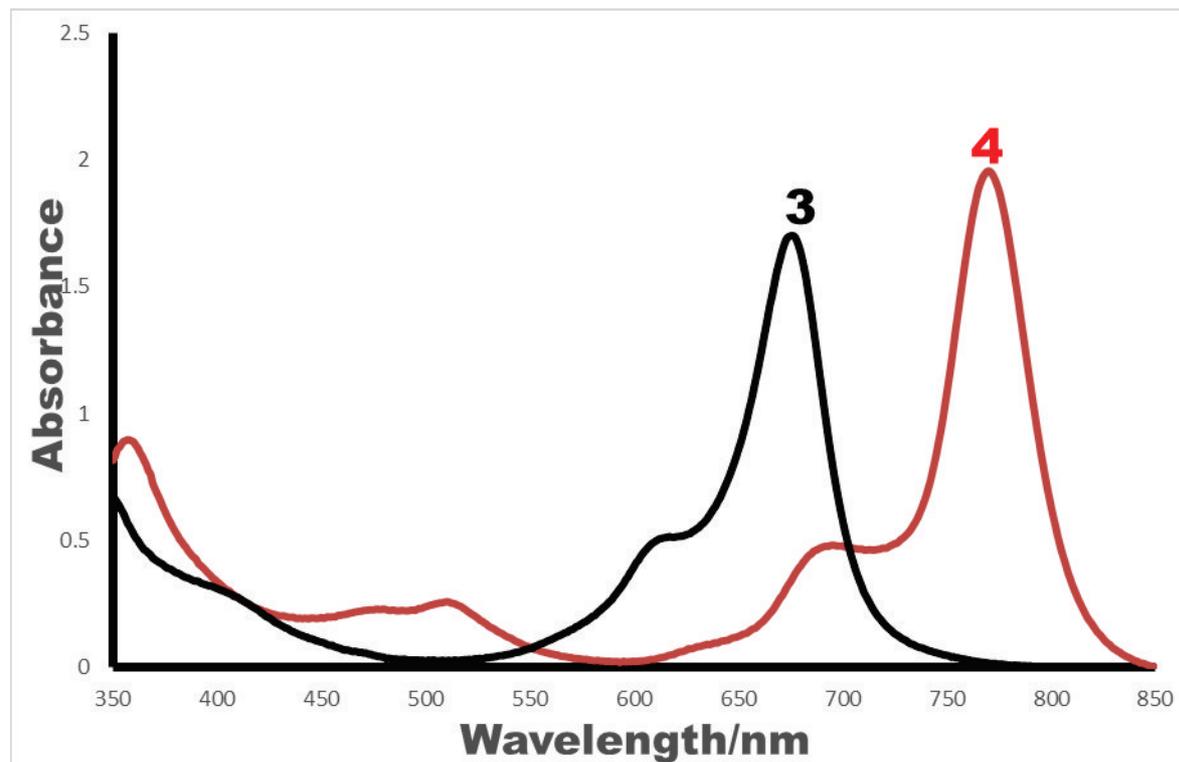
Figure 2: UV-Vis spectra of complexes **3** (2.41×10^{-6} M) and **4** (2.42×10^{-6} M) in DMF.

3.3 Electrochemical Properties of Cobalt and Manganese 4-(2-aminoethylthio) phthalocyanine

3.3.1 Cobalt 4-(2-aminoethylthio) phthalocyanine complexes, 3

Figure 3 shows cyclic voltammetry profile of 1×10^{-4} M of cobalt 4-(2-aminoethylthio) phthalocyanine complex, in freshly distilled, dried DMF, containing 0.1 M TBABF$_4$ (supporting electrolyte). Three distinctly defined redox processes can be identified as follows;

Process I: The process I has a half wave potential ($E_{1/2} = -1.40$ V vs. Ag|AgCl) and the potential peak difference (ΔE_p) is 290 mV. The process is a quasi-reversible process due to the weak return peaks and is usually assigned to ring reduction, $Co^I Pc^{-2}/Co^I Pc^{-3}$ couple.

Process II: The cathodic to anodic peak current (I_a/I_c) ratio is near unity, but quasi-reversible, because of peak to peak separation (ΔE) of 210 mV. This process is usually assigned to metal reduction, $Co^{II} Pc^{-2}/Co^I Pc^{-2}$ ($E_{1/2} = -0.275$ V vs. Ag|AgCl).

Process III: this process is assigned to metal oxidation, $Co^{III} Pc^{-2}/Co^{II} Pc^{-2}$ ($E_{1/2} = +0.64$ V vs. Ag|AgCl). This process is virtually irreversible due to the absence of return peak. No ring oxidation was observed as shown in the **figure 3** below. This may be explained in terms of the electron-releasing nature of the sulfur-containing substituents on the ring [37,38]. Since Co^{III} can be observed in coordinating solvents [39], its metal oxidation is expected [40].
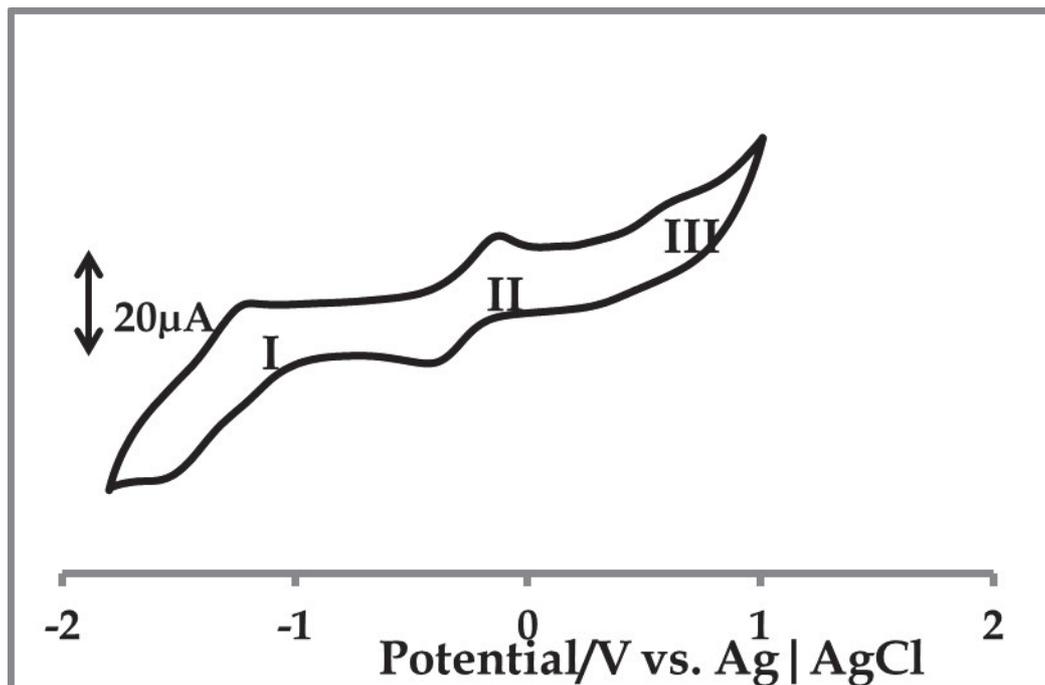
Figure 3: Cyclic voltammetry profiles of $1 \times 10^{-4} \, M$ of cobalt 4-(2-aminoethylthio) phthalocyanine in freshly distilled DMF containing 0.1 M TBABF$_4$ supporting electrolyte. Scan rate: $100 \, mVs^{-1}$.

The mechanism occurring in the processes **I, II** and **III** for of cobalt 4-(2-aminoethylthio) phthalocyanine in DMF are shown in **Figure 4** below:

$$Co^{I}Pc^{-2} \quad + \quad e^{-} \quad \longrightarrow \quad Co^{I}Pc^{-3} \qquad \textbf{(Process I)}$$

$$Co^{II}Pc^{-2} \quad + \quad e^{-} \quad \longrightarrow \quad Co^{I}Pc^{-2} \qquad \textbf{(Process II)}$$

$$Co^{II}Pc^{-2} \quad + \quad e^{-} \quad \longrightarrow \quad Co^{III}Pc^{-2} \qquad \textbf{(Process III)}$$

Figure 4: Redox processes I, II and III for Cobalt 4-(2-aminoethylthio) phthalocyanine complex

3.3.2 Manganese 4-(2-aminoethylthio) phthalocyanine complex, 4

Figure 5 shows cyclic voltammetry of 1×10^{-4} M of manganese 4-(2-aminoethylthio phthalocyanine complex, in freshly distilled, dried DMF, containing 0.1 M TBABF$_4$ (supporting electrolyte). Three distinctly defined redox processes can be identified as follows;

Process I: The half wave potential ($E_{1/2} = -0.80 \, V \, vs. Ag|AgCl$) and the potential peak difference (ΔE_p) is $180 \, mV$. The process **I** is a quasi-reversible with weak anodic component and large peak separation ($180 \, mV$). This process is usually assigned to ring reduction, $Mn^{II}Pc^{-2}/Mn^{II}Pc^{-3}$ couple. The cathodic to anodic peak current (I_a/I_c) ratio is 0.096. The split observed in the voltammogram of process **I** could be due to aggregation [41] since peripherally substituted ligand have a stronger tendency to aggregate in the solvent [42-44].

Process II: the anodic peak potential (E_{pa}) and cathodic peak potential (E_{pc}) in process II are $0.02V$ and $-0.15V$ respectively. The cathodic to anodic peak current (I_a/I_c) ratio is near unity (0.87), but quasi-reversible, because of peak to peak separation (ΔE) of 130 mV. This process is usually assigned to metal reduction, Mn^{III}Pc^{-2}/Mn^{II}Pc^{-2} ($E_{1/2} = -0.07 \, V \, vs. Ag|AgCl$).

Process III: this process is assigned to weak ring-based oxidation, Mn^{III}Pc^{-1}/Mn^{III}Pc^{-2} ($E_{1/2} = +0.86 \, V \, vs. Ag|AgCl$) consistent with literature [37,44,45]. This process is virtually irreversible due to the absence of return peak.
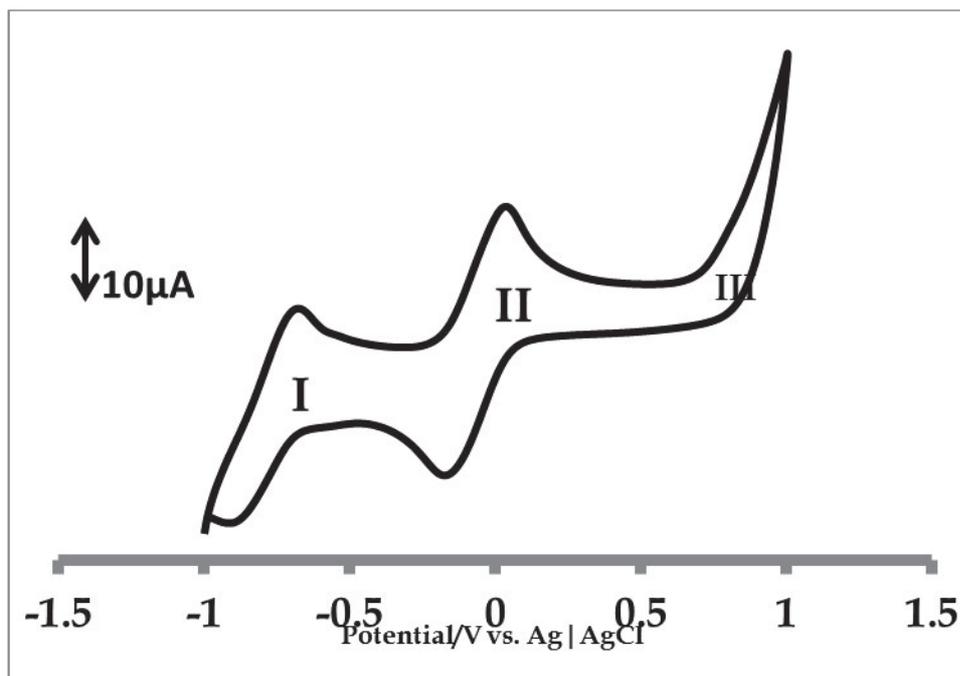
Figure 5: Cyclic voltammetry profiles of $1 \times 10^{-4} M$ of Manganese 4-(2-aminoethylthio) phthalocyanine complex in freshly distilled DMF containing 0.1 M TBABF$_4$ supporting electrolyte. Scan rate: $100\ mVs^{-1}$.

The redox processes **I, II** and **III** for manganese 4-(2-aminoethylthio) phthalocyanine complex are shown in **Figure 6**;

$$Mn^{II}Pc^{-2} + e^- \longrightarrow Mn^{II}Pc^{-3} \quad (Process\ I)$$

$$Mn^{III}Pc^{-2} + e^- \longrightarrow Mn^{II}Pc^{-2} \quad (Process\ II)$$

$$Mn^{III}Pc^{-1} \longrightarrow Mn^{III}Pc^{-2} + e^- \quad (Process\ III)$$
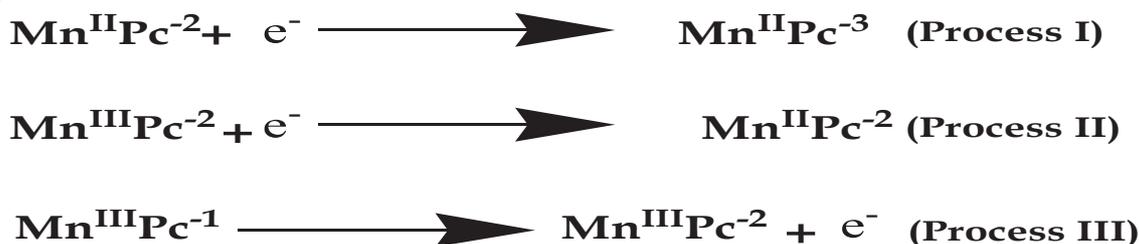
Figure 6: Redox processes I, II and III for Manganese 4-(2-aminoethylthio) phthalocyanine complex.

Table 2: Summary of half wave potential ($E_{1/2}$) data of MnPc and CoPc complexes in DMF, in $V\ vs.\ Ag|AgCl$.

Complex	$M^I Pc^{-2}/M^I Pc^{-3}$	$M^{II} Pc^{-2}/M^I Pc^{-2}$	$M^{II} Pc^{-2}/M^{II} Pc^{-3}$	$M^{III} Pc^{-2}/M^{II} Pc^{-2}$	$M^{III} Pc^{-1}/M^{III} Pc^{-2}$
3	-1.40 V	-0.275 V		+0.64 V	
4			-0.80 V	-0.07 V	+0.86 V

3 = Cobalt 4-(2-aminoethylthio) phthalocyanine, **4** = Manganese 4-(2-aminoethylthio) phthalocyanine.

The more positive the value of half wave potential ($E_{1/2}$) of an electroactive specie, the easier it gets to be reduced during cyclic voltammetry techniques. From the above (**Table 2**), process III of manganese 4-(2-aminoethylthio) phthalocyanine has higher positive value of half wave potential ($+0.86$ V) than that of cobalt 4-(2-aminoethylthio) phthalocyanine ($+0.64$ V), hence, reduction in process III of MnPc is energetically feasible than in process III of CoPc.

The processes I (-1.40 V) and II (-0.275 V) of cobalt 4-(2-aminoethylthio) phthalocyanine are more negative than that of manganese 4-(2-aminoethylthio) phthalocyanine. By virtue of this, oxidation processes I and II in cobalt 4-(2-aminoethylthio) phthalocyanine are more energetically feasible than that of manganese 4-(2-aminoethylthio) phthalocyanine.

4 Conclusions

The synthesis, spectroscopic and electrochemical properties of cobalt and manganese phthalocyanine complexes have been investigated. The effect of central transition metals; (cobalt versus manganese) was evident on their ground state absorption behaviours as seen in the UV-Vis spectra. The observed Q-band of manganese 4-(2-aminoethylthio) phthalocyanine (**4**) was red shifted with respect to cobalt 4-(2-aminoethylthio) phthalocyanine

(**3**). The detailed structural characterizations of the complexes were in good agreements with the expected results. Both manganese and cobalt phthalocyanine complexes synthesized showed interesting electrochemical properties consistent with that reported for **3** and **4** complexes. The cathodic to anodic peak differences (ΔE) of redox processes observed for **4** are 180 mV and 130 mV, while the cathodic to anodic peak differences ((ΔE) for **3** are $290 \text{ mV and } 210 \text{ mV}$ at processes **I** and **II.** By virtue of this, manganese phthalocyanine (**4**) has the best electron transfer processes than cobalt phthalocyanine (**3**) due to relatively smaller cathodic to anodic peak differences (ΔE) of the observed redox processes. The sluggish electron transfer processes in **3** are due to the relatively larger cathodic to anodic peak differences.

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