Polyhedron 29 (2010) 1257-1270

Contents lists available at ScienceDirect

Polyhedron



Syntheses and investigation of the effects of position and nature of substituent on the spectral, electrochemical and spectroelectrochemical properties of new cobalt phthalocyanine complexes

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ARTICLE INFO

Article history: Received 19 August 2009 Accepted 4 January 2010 Available online 11 January 2010

Keywords: Cobalt Diethylaminoethanethiol phthalocyanine Benzylmercapto phthalocyanine Cyclic voltammetry Spectroelectrochemisrty

ABSTRACT

The syntheses of new cobalt phthalocyanine (CoPc) complexes, tetra-substituted with diethylaminoethanethio at the peripheral (complex **3a**) and non-peripheral (complex **3b**) positions, and with benzylmercapto at the non-peripheral position (complex **5**), are reported. The effects of the nature and position of substituent on the spectral, electrochemical and spectroelectrochemical properties of these complexes are investigated. Solution electrochemistry of complex **3a** showed three distinctly resolved redox processes attributed to $\text{Co}^{IIP}\text{c}^{-2}/\text{Co}^{IP}\text{c}^{-2}$ ($E_{k_2} = +0.64 \text{ V}$ versus Ag|AgCl), $\text{Co}^{II}\text{P}\text{c}^{-2}/\text{Co}^{IP}\text{c}^{-2}$ ($E_{k_2} = -0.24 \text{ V}$ versus Ag|AgCl) and $\text{Co}^{IP}\text{c}^{-2}/\text{Co}^{IP}\text{c}^{-3}$ ($E_{k_2} = -1.26 \text{ V}$ versus Ag|AgCl) species. No ring oxidation was observed in complex **3a**. Complex **3b** showed both ring-based oxidation, attributed to $\text{Co}^{IIP}\text{c}^{-1}/\text{Co}^{IIP}\text{c}^{-2}$ ($E_{k_2} = -1.26 \text{ V}$ versus Ag|AgCl) species. No ring oxidation was observed in complex **3a**. Complex **3b** showed both ring-based reduction associated with $\text{Co}^{IP}\text{c}^{-2}/\text{Co}^{IP}\text{c}^{-3}$ species ($E_{k_2} = -1.46 \text{ V}$ versus Ag|AgCl), with the normal metal-based redox processes in CoPc complexes: $\text{Co}^{IIP}\text{c}^{-2}/\text{Co}^{IP}\text{c}^{-2}$ ($E_p = +0.41 \text{ V}$ versus Ag|AgCl) and $\text{Co}^{IP}\text{c}^{-2}/\text{Co}^{IP}\text{c}^{-2}$ ($E_{k_2} = -0.38 \text{ V}$ versus Ag|AgCl). Solution electrochemistry of complex **5** showed the same type and number of species observed in complex **3a**: $\text{Co}^{IIP}\text{c}^{-2}/\text{Co}^{IP}\text{c}^{-2}$ ($E_p = +0.59 \text{ V}$ versus Ag|AgCl), $\text{co}^{IIP}\text{c}^{-2}/\text{Co}^{IP}\text{c}^{-2}$ ($E_{k_2} = -0.26 \text{ V}$ versus Ag|AgCl) and $\text{Co}^{IP}\text{c}^{-2}/\text{Co}^{IP}\text{c}^{-2}$ ($E_{k_2} = -1.39 \text{ V}$ versus Ag|AgCl) species. These processes were confirmed using spectroelectrochemistry.

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1. Introduction

Metallophthalocyanine (MPc) complexes are some of the most researched molecules in modern chemistry. The extensive research interest generated by these macrocycles stems from their versatility, which is underscored by their wide range of applications. These applications include their uses in electronic devices, as gas sensors, as photosensitizers, in non-linear optics, in electrochromic devices and in Langmuir–Blodgett films [1,2]. Metallophthalocyanine complexes containing electroactive metals, such as cobalt, iron and other transition metals have also been extensively studied because of their electrocatalytic properties towards many analytes [3,4]. Importantly, the properties of these complexes can be tuned in order to meet specific qualities, suitable for their applications, by varying the central metal, the nature and position (peripheral and non-peripheral) of the substituent.

Cobalt phthalocyanine (CoPc) complexes are the most intensively studied phthalocyanines [4–7] because of their potential use as electrocatalysts and for the design of electrochemical sensors; which is anchored on the interesting coordination chemistry of cobalt. Cobalt exhibits three oxidation states: Co^I, Co^{II} and Co^{III}. Col does not bind any axial ligand; hence exist essentially in a square planar environment. Co^{II} does bind axial ligands but with low affinity, which suggests Co^{II} may exhibits coordination number of (i) four (square planar), (ii) five (penta-coordinate) and rarely (iii) six (hexa-coordinate). Co^{III} has high affinity for axial ligands and is usually stabilized by two axial ligands; hence exist predominantly in an octahedral environment. Axial ligation has direct effect on the solution electrochemistry of CoPc complexes. Co^IPc and Co^{ll}Pc species can be observed in both coordinating and noncoordinating solvents but Co^{III}Pc species is only observed in coordinating solvents, such as dimethyl sulphoxide (DMSO), dimethylformamide (DMF) and pyridine [8]. These solvents bind, as axial ligands, to two of the six coordination sites on Co^{III}, offering some form of stability to this oxidation state, hence the possibility of observing Co^{III}Pc species in the presence of these solvents. Apart from metal-based processes, redox activities can also be observed on the ring in CoPc complexes. The formation of Co^{III}Pc species is usually followed by the first ring oxidation (formation of Co^{III}Pc⁻¹ species); while the first ring reduction is preceded by the formation of Co^IPc species.





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^{0277-5387/\$ -} see front matter \odot 2010 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2010.01.004

The focus of the present study is to report the synthesis and investigate the effects of the nature and position of substituent on both the spectral, electrochemical and spectroelectrochemical qualities of new CoPc complexes tetra-substituted with diethylaminoethanethio (peripherally: complex 3a and non-peripheral: complex **3b**) and benzylmercapto (non-peripherally: complex **5**) substituents. The presence of these substituents makes these complexes good candidates in the formation of thin films, either by electrochemical polymerization or self-assembly technique, thus facilitating their use as electrocatalysts and in the development of electrochemical sensors. The synthesis of CoPc peripherally octa-substituted with diethylaminoethanethio has been reported [9]. This work reports on the peripherally (**3a**) and non-peripherally (3b) tetra-substituted CoPc derivatives. The synthesis of CoPc peripherally tetra-substituted with benzylmercapto (6) has also been reported [10]. This work reports on the non-peripheral substitution with benzvlmercapto (5).

2. Experimental

2.1. Materials

Potassium carbonate, cobalt chloride, 2-(diethylaminoethanethiol) hydrochloride and 2-diethylaminoethanol were obtained from Sigma–Aldrich. Benzylmercapto thiol was obtained from Fluka. Tetrabutylammonium tetrafluoroborate (TBABF₄) (Aldrich) was used as the electrolyte for electrochemical experiments. Aluminum oxide, WN-3: neutral and Silica Gel 60 (0.04–0.063 mm), for column chromatography, were purchased from Sigma–Aldrich and Merck, respectively. Dimethylformamide (DMF), dichloromethane (DCM) and dimethyl sulphoxide (DMSO) were obtained from Merck. DMF, DMSO, DCM, methanol and ethanol were distilled before use.

2.2. Electrochemical studies

All electrochemical experiments were performed using Autolab potentiostat PGSTAT 302 (Eco Chemie, Utrecht, The Netherlands) driven by the general purpose Electrochemical System data processing software (GPES, software version 4.9). Square wave voltammetric analysis was carried out at a frequency of 10 Hz, amplitude: 50 mV and step potential: 5 mV. A conventional three-electrode system was used. The working electrode was a bare glassy carbon electrode (GCE), Ag|AgCl wire and platinum wire were used as the pseudo reference and auxiliary electrodes, respectively. The potential response of the Ag|AgCl pseudo-reference electrode was less than the Ag|AgCl (3M KCl) by 0.015 \pm 0.003 V. Prior to use, the electrode surface was polished with alumina on a Buehler felt pad and rinsed with excess millipore water. All electrochemical experiments were performed in freshly distilled dry DMF containing TBABF₄ as supporting electrolyte.

Spectroelectrochemical data were obtained using a home-made optically transparent thin-layer electrochemical (OTTLE) cell which was connected to a Bioanalytical Systems (BAS) CV 27 voltammograph.

2.3. Equipment

UV–Vis spectra were recorded on Cary 50 UV–Vis/NIR spectrophotometer. IR (KBr discs) was recorded on Bruker Vertex 70-Ram II spectrophotometer. Elemental analysis was performed using Vario Elementar Microcube EL111. ¹H nuclear magnetic resonance (¹H NMR, 400 MHz) was obtained in CDCl₃ using Bruker EMX 400 NMR spectrometer.

2.4. Synthesis

2.4.1. 4-(2-Diethylaminoethanethiol) phthalonitrile (**2a**) and 3-(2diethylaminoethanethiol) phthalonitrile (**2b**)

4-Nitrophthalonitrile (compound 1a, Scheme 1a) and 3nitrophthalonitrile (compound 1b, Scheme 1b), were synthesized according to reported procedure [11]. Compound 2a was synthesized using the method reported for the synthesis of 1,2-bis-(diethvlaminoethanethiol)-4,5-dicyanobenzene with [12] some modifications as follows: compound **1a** (3.05 g, 17.6 mmol) was dissolved in anhydrous DMF (150 ml) under nitrogen and 2-diethylaminoethanethiol hydrochloride (9 g, 53.0 mmol) was added. After stirring for 10 min, finely ground anhydrous K₂CO₃ (29.3 g, 212.0 mmol) was added in portions over 2 h with stirring. The reaction mixture was stirred at room temperature for 48 h under nitrogen. Then the solution was poured into ice (900 g). The precipitate was filtered off, washed with water, until the filtrate was neutral. The product was then dried in air. Yield: 3.42 g (75%). IR (KBr) v_{max}/cm⁻¹: 3084–3018 (Ar–C–H), 2968–2807 (CH₂), 2229 (CN), 1582, 1542, 1471, 1384, 1289, 1225, 1198, 1142, 1072, 987, 906, 825, 732, 609, 521. ¹H NMR (CDCl₃) δ = 7.66–7.54 (m, 3H, Ar–H), 3.15-312 (t, 2H, SCH₂), 2.80-2.77 (t, 2H, NCH₂), 2.62-2.57 (qnt, 4H, CH₂C), 1.07–1.03 (t, 6H, CH₃) ppm.

Compound **2b**, Scheme 1b, was synthesized following the method described above for compound **2a**, using 3-nitrophthalonitrile (compound **1b**) in place of 4-nitrophthalonitrile (compound **1a**). Yield: 2.74 g (60%). IR (KBr) v_{max}/cm^{-1} : 2969–2814 (CH₂), 2229 (v_{CN}), 1565, 1520, 1445, 1372, 1290, 1231, 1193, 1133, 1065, 1029, 987, 855, 787, 730, 547, 439. ¹H NMR (CDCl₃) δ = 7.73–7.56 (m, 3H, Ar–H), 3.22–3.19 (t, 2H, SCH₂), 2.82–2.79 (t, 2H, NCH₂), 2.61–2.58 (dd, 4H, CH₂C), 1.06–1.02 (t, 6H, CH₃) ppm.

2.4.2. 3-(Benzylmercapto) phthalonitrile (4)

Compound **4** was synthesized (Scheme 2) following the procedure reported for 4-(benzylmercapto) phthalonitrile [10] with some modifications as follows: compound **1b** (6 g, 34.68 mmol) was dissolved in anhydrous DMSO (50 ml) under nitrogen and benzylmercapto thiol (5.55 g, 45 mmol) was added. After stirring strongly for 20 min, finely ground anhydrous K₂CO₃ (15 g, 108.7 mmol) was added in portions over 2 h with stirring. The reaction mixture was stirred at room temperature for 12 h under nitrogen. Thereafter, the crude product was precipitated out from the reaction mixture with ice (600 g). The precipitate was filtered off, washed with water, until the filtrate was neutral. The product was crystallized twice from ethanol and dried in air. Yield: 1.91 g (22%). IR (KBr) v_{max}/cm⁻¹: 3067–3031 (Ar–C–H), 2936–2852 (CH₂), 2226 (v_{CN}), 1961, 1561, 1500, 1447, 1289, 1187, 1155, 1066, 1030, 911, 854, 785, 709, 589, 555, 483, 434. ¹H NMR (CDCl₃) δ = 7.62–7.55 (m, 3H, S–Ar–H), 7.36–7.30 (m, 5H, C–Ar–H), 4.31 (s, 2H, CH₂) ppm.

2.4.3. Cobalt tetrakis-(2-diethylaminoethanethiol) phthalocyanines: **3a** (peripheral) and **3b** (non-peripheral)

Complexes **3a** (Scheme 1a) and **3b** (Scheme 1b) were synthesized following the method reported for the octa-substituted analogue [12] with some modifications.

2.4.3.1. Complex **3a**, Scheme 1a. A mixture of compound **2a** (0.40 g, 1.54 mmol) and cobalt(II) chloride (0.049 g, 0.38 mmol) was refluxed in 2-(diethylaminoethanol) (1.2 ml) for 12 h under nitrogen. Thereafter, the mixture was cooled to room temperature and treated with excess MeOH:H₂O (1:1) to precipitate the crude deep blue product. The product was filtered and dried in air. Purification was achieved using column chromatography with neutral alumina as column material and DCM/MeOH (10:1) as eluent. Yield: 1.08 g (64%). Anal. Calc. for C₅₆H₆₈N₁₂S₄Co·CH₂Cl₂: C, 56.95; H, 5.76; N,



Scheme 1a. Synthetic pathway for the formation of complex 3a.

14.23; S, 10.85. Found: C, 56.87; H, 5.78; N, 13.89; S, 11.25%. UV–Vis (DMF): λ_{max} (nm) (log ε): 675 (5.6), 615 (5.1), 406 (4.8), 352 (5.1); IR (KBr) ν_{max}/cm^{-1} ; 2965–2800 (CH₂), 1601, 1519, 1449, 1393, 1312, 1143, 1091, 930, 815, 771, 748, 689.

2.4.3.2. Complex **3b**, Scheme 1b. Complex **3b** was synthesized (Scheme 1b) and purified following the same method described for complex **3a**, using compound **2b** (0.40 g, 1.54 mmol) as the starting material in place of **2a**. Yield: 1.01 g (60%). Anal. Calc. for C₅₆H₆₈N₁₂S₄Co: C, 61.37; H, 6.21; N, 15.34; S, 11.69. Found: C, 60.96; H, 6.31; N, 14.80; S, 12.11%;. UV–Vis (DMF): λ_{max} (nm) (log ε): 693 (5.3), 628 (4.8), 478 (4.2); IR (KBr) ν_{max} /cm⁻¹; 2966–2799 (CH₂), 1619, 1572, 1514, 1462, 1384, 1318, 1239, 1113, 919, 739, 595.

2.4.4. Cobalt tetrakis-(benzylmercapto) phthalocyanine **5** (non-peripheral), Scheme 2

Complex **5** was synthesized following the method reported for the peripheral derivative [10] with some modifications. A mixture of compound **4** (0.6 g, 1.85 mmol) and cobalt(II) chloride (0.063 g, 0.49 mmol) was refluxed in 2-(diethylaminoethanol) (3 ml) for 6 h under nitrogen. The deep green crude product was precipitated, after cooling, in excess methanol. The precipitate was filtered and dried in air. Purification was performed using column chromatography with Silica Gel as column material and CHCl₃/MeOH (10:1) as eluent. Yield: 1.06 g, (42%). *Anal.* Calc. for C₆₀H₄₀N₈S₄Co·CH₂Cl₂: C, 62.93; H, 3.50; N, 9.79; S, 11.19. Found: C, 62.61; H, 3.91; N, 9.42; S, 10.68%. UV–Vis (DMF): λ_{max} (nm) (log ε): 692 (5.5), 355 (5.3); IR (KBr) ν_{max} /cm⁻¹; 3059 (*w*, Ar–C–H), 2920 (*w*, CH₂) 1584, 1448, 1318, 1241, 1114, 746, 702.

3. Results and discussion

3.1. Synthesis and spectral characterization

The synthetic routes for complexes **3a**, **3b** and **5** are shown in Schemes 1 and 2. The phthalonitriles, compounds **2a**, **2b** and **4** were obtained via a based-catalyzed (K_2CO_3) nucleophilic aromatic substitution reaction. Cyclotetramerization of **2a**, **2b** and **4** occurred in the presence of CoCl₂ to form the desired complexes:



Scheme 1b. Synthetic pathway for the formation of complex 3b.

3a, **3b** and **5**, respectively. Purifications of **3a** and **3b** were accomplished using column chromatography on alumina while that of **5** was performed on Silica Gel. The complexes were soluble in solvents such as DMF, DCM and DMSO.

Characterizations of the complexes were carried out using IR and UV–Vis spectroscopies as well as elemental analysis. The formation of complexes **3a**, **3b** and **5** was confirmed by the disappearance of the sharp C \equiv N vibration at 2229, 2229 and 2226 cm⁻¹ of **2a**, **2b** and **4**, respectively.

Fig. 1 shows the UV–Vis spectra of complexes **3a**, **3b** and **5** $(3.82 \times 10^{-6} \text{ M})$ in DMF. The effects of the nature and position of substituent on the spectral qualities of these complexes are clearly observable. The position and nature of substituent impact both hypochromic and bathochromic effects on the spectral properties of these complexes. The shift in spectra and changes in absorption behavior have been explained in terms of conformational distortion caused by the stress of the substituents in MPcs complexes [13] and have also been attributed to coordination of certain ligands to the central metal and enlargement of the π -system of the Pc [14–16]. They can also be attributed to aggregation in MPcs.

Complex **3a**, (peripheral), shows Q-band absorption at 675 nm in DMF, while that of complex **3b**, (non-peripheral) was observed at 693 nm, hence the latter was red-shifted compared to that of complex **3a**. Usually, non-peripheral substitution in MPc complexes imposes some measure of steric limitation on these macrocycles, leading to conformational distortion of the Pc skeleton, resulting in change in absorbance and shift in the position of Q- band. The degree of steric limitation is closely related to the complexity of the substituents. In the present study, a red-shift in Qband, characteristic of non-peripherally substituted MPcs complexes, was observed for complex **3b** compared to complex **3a** (Fig. 1). The Q-band of complex **5** (692 nm) was also red-shifted (bathochromic effect) compared to that of the recently reported peripheral analogue (674 nm) [10]. However, the position of Qband in complex **3b** (693 nm), Fig. 1, was similar to that of complex **5** (692 nm).

The spectra in Fig. 1 are relatively broad suggesting aggregation. Fig. 2a $(1.28-8.96 \times 10^{-6} \text{ M})$, 2b $(1.27-8.89 \times 10^{-6} \text{ M})$ and 2c $(1.27-5.72 \times 10^{-6} \text{ M})$ shows the effect of changing concentration on the spectra of complexes **3a**, **3b** and **5**, respectively. Beer's law was obeyed within the range of concentration investigated for all the complexes.

3.2. Cyclic and square wave voltammetry studies

3.2.1. Complex **3a**

Fig. 3a and b shows, respectively, the square wave and cyclic voltammetry profiles of 1×10^{-3} M of complex **3a** in freshly distilled dry DMF containing 0.1 M TBABF₄ as supporting electrolyte. Three distinctly defined redox processes (labeled **I**, **II** and **III**) can be observed. Process **III** (Fig. 3b) is assigned to metal oxidation, $Co^{III}Pc^{-2}/Co^{II}Pc^{-2}$ ($E_{\frac{1}{2}} = +0.64$ V versus Ag|AgCl), Table 1 in accordance with literature [8]. Metal oxidation is expected, since this species is usually observed in coordinating solvents [8]. This pro-



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(Published before [10])

Scheme 2. Synthetic pathway for the formation of complex 5.



Fig. 1. UV–Vis spectral of $3.82\times10^{-6}\,\text{M}$ of complexes 3a,3b and 5 in DMF.

cess is virtually irreversible. The irreversibility of oxidation processes of sulfur containing MPc processes is well documented [17,18] hence the irreversibility of process **III** is not surprising. Process **II** is assigned to metal reduction, $Co^{II}Pc^{-2}/Co^{I}Pc^{-2}(E_{\nu_2} = -0.24 \text{ V versus Ag}|\text{AgCI})$. It has cathodic to anodic peak current ratio of near unity, but quasi-reversible in that peak



Fig. 2. Effect of changing concentration on the UV–Vis spectra of (a) complex **3a** ($1.28-8.6 \times 10^{-6}$ M), (b) complex **3b** ($1.27-8.89 \times 10^{-6}$ M) and (c) complex **5** ($1.27-5.72 \times 10^{-6}$ M). Inset: Plot of absorbance vs. concentration. Solvent = DMF.

to peak separation (ΔE) of 161 mV was obtained (ΔE for ferrocene was 90 mV within the same potential window with the same scan rate (100 mVs⁻¹ versus Ag|AgCl)). Reversibility did not improve at shorter potential window. Process I is assigned to ring reduction, Co¹Pc⁻²/Co¹Pc⁻³ ($E_{1/2} = -1.26$ V versus Ag|AgCl). This process was also quasi-reversible with ΔE value of 151 mV, although with

cathodic to anodic current ratio of near unity. Spectroelectrochemistry is used below to confirm these processes.

3.2.2. Complex 3b

Electrochemical properties of complex **3b** were slightly different from that of complex **3a**. Effect of the position of substituent



Fig. 3. (a) Square wave and (b) cyclic voltammetry profiles of 1×10^{-3} M of complex **3a** in freshly distilled DMF containing 0.1 M TBABF₄ supporting electrolyte. Step potential: 5 mV, amplitude: 50 mV vs. Ag|AgCl, frequency: 10 Hz. Scan rate: 100 m Vs⁻¹ vs. Ag|AgCl.

Table 1

Summary of peak and half wave potentials, in volt vs. Ag|AgCl, of the new complexes in comparison with that of previously reported thio derivatised CoPc complexes. Values were recorded in DMF containing TBABF₄ unless otherwise stated.

Complex ^a	Co ^I Pc ⁻³ /Co ^I Pc ⁻²	Co ^{II} Pc ⁻² /Co ^I Pc ⁻²	Co ^{III} Pc ⁻² /Co ^{II} Pc ⁻²	Co ^{III} Pc ⁻¹ /Co ^{III} Pc ⁻²	Reference ^b
3a	-1.26	-0.24	+0.64		TW
3b	-1.46	-0.38	+0.41	+0.86	TW
5	-1.39	-0.26	+0.59		TW
6	-1.41	-0.38	+ 0.42	+0.89	10
CoOBMPc ^c	-0.58	-0.096	+0.72	+1.16	22
CoTDMPc ^d		-0.46	+0.44	+0.66	10

^a TDMPc = tetra dodecylmercapto phthalocyanine (peripheral) and OBMPc = octa benzylmercapto phthalocyanine (peripheral).

^b TW = this work.

^c Values recorded in DMF using tetrabutylammonium perchlorate instead of TBABF4.

^d Values recorded in dichloromethane (instead of DMF) using TBABF4.

on the electrochemical properties of complex **3b** was obvious when compared to that of complex **3a**. As discussed previously, non-peripheral positions are sterically crowded positions that may impose some conformational stress on MPc complexes. Fig. 4a and b shows, respectively, the square wave and cyclic voltammetry profiles of 1×10^{-3} M of complex **3b** in freshly distilled

dry DMF containing 0.1 M TBABF₄. Two irreversible oxidations, (process **III** and **IV**) are observed. Process **III** at E_p = +0.41 V versus Ag|AgCl is assigned to a metal based oxidation: Co^{III}Pc⁻²/Co^{II}Pc⁻² and process **IV** at E_p = +0.86 V versus Ag|AgCl to ring based oxidation: Co^{III}Pc⁻¹/Co^{III}Pc⁻². The larger currents for **IV** are due to the ring based Pc ring oxidation and the oxidation of the substituents



Fig. 4. (a) Square wave and (b) cyclic voltammetry profiles of 1×10^{-3} M of complex **3b** in freshly distilled DMF containing 0.1 M TBABF₄ supporting electrolyte. Step potential: 5 mV, amplitude: 50 mV vs. Ag|AgCl, frequency: 10 Hz. Scan rate: 100 m Vs⁻¹ vs. Ag|AgCl.

as is typical of sulfur containing MPc complexes [17,18]. Two reduction processes (I and II) were observed. The metal reduction process II (at $E_{\nu_2} = -0.38$ V versus Ag|AgCl) is reversible with ΔE value of 81 mV and cathodic to anodic peak current ratio of near unity, and is assigned to Co^{II}Pc⁻²/Co^IPc⁻². Process I at $E_{\nu_2} = -1.46$ V versus Ag|AgCl is then assigned to ring reduction (Co^IPc⁻²/Co^IPc⁻³) as is typical of CoPc complexes in DMF solutions. This couple was quasi-reversible with ΔE value of 110 mV.

The more sensitive square wave voltammetry technique showed other peaks whose origin may be due to aggregated species at the concentrations used for cyclic voltammtery [8]. The redox processes in **3b** were confirmed using spectroelectrochemistry.

Ring-based reduction (Pc^{-2}/Pc^{-3}) occurred at -1.26 V and -1.46 V (versus Ag|AgCl) in complexes **3a** and **3b**, respectively, while metal-based reductions (Co^{II}/Co^{I}) was observed at -0.24 V and -0.38 V in complexes **3a** and **3b**, respectively, thus showing that peripheral substitution **(3a)** results in easier reduction than non-peripheral substitution **(3b)**, while oxidation is easier for non-peripheral derivative **(3b)** as Table 1 shows. The ease of oxidation in **3b** could be a result of conformational distortion, induced by non-peripheral substitution.

The metal-based oxidation (Co^{III}/Co^{II}) , the only oxidative process observed in complex **3a**, was observed at +0.64 V and +0.41 V (versus Ag|AgCl) in complexes **3a** and **3b**, respectively.

The absence of ring oxidation in complex **3a** (Fig. 3b) underscores the limitation imposed on the complex with respect to undergoing oxidative processes. These observations were expected, since nonperipheral substitution makes the electron-donating substituent closer to the ring relative to peripheral substitution, thus increasing the electron-donating tendency of the substituent, making complex **3b** more susceptible to oxidation than complex **3a**. This suggestion was corroborated by results obtained from spectroelectrochemical studies, discussed later in this work.

3.2.3. Complex 5

Fig. 5a and b, respectively, shows the square wave and cyclic voltammetry profiles of 1×10^{-3} M of complex **5** in freshly distilled dry DMF containing 0.1 M TBABF₄. Electrochemical properties of complex **5** were not substantially different from that of complex **3a**. The major difference was the extent of reversibility of the redox processes. Three distinct redox processes were observed in complex **5** as was the case for **3a**. Like complex **3a**, no ring-based oxidation was observed in complex **5**. Although, complex **5** is non-peripherally substituted, like complex **3b**, the electron-withdrawing nature of the phenyl group of the benzylmercapto substituent favored reduction processes at the expense of oxidation, Table 1. Process **III** was an irreversible (and weak) process, and is assigned to metal oxidation, Co^{III}Pc⁻²/



Fig. 5. (a) Square wave and (b) cyclic voltammetry profiles of 1×10^{-3} M of complex **5** in freshly distilled DMF containing 0.1 M TBABF₄ supporting electrolyte. Step potential: 5 mV, amplitude: 50 mV vs. Ag|AgCl, frequency: 10 Hz. Scan rate: 100 m Vs⁻¹ vs. Ag|AgCl.

Co^{II}Pc⁻²(E_p = +0.59 V versus Ag|AgCl). This process was also energetically less feasible, as it was with complex **3a**, when compared to complex **3b** (Ep = +0.41 V versus Ag|AgC. Process **II**, Co^{II}Pc⁻²/Co^IPc⁻² ($E_{\frac{1}{2}}$ = -0.26 V versus Ag|AgCl), was quasi-reversible, although with a cathodic to anodic peak current ratio of near unity, but a peak separation larger than 90 mV for ferrocene. Process **I**, Co^{II}Pc⁻²/Co^IPc⁻³ ($E_{\frac{1}{2}}$ = -1.39 V versus Ag|AgCl), was also quasi-reversible. The quasi-reversibility of the processes suggests sluggish electron transfer in all cases.

3.3. Spectroelectrochemical studies

3.3.1. Complex 3a

The spectral changes observed on the application of potential slightly more negative of that of process II ($E_{i_2} = -0.24$ V versus Ag|AgCl, Fig. 3b) are shown in Fig. 6a. The presence of split Q-band in the starting spectrum was an indication of aggregation, as result of the concentration used for controlled electrolysis. The peak at about 628 nm is due to the aggregate while that at 672 nm is the monomeric peak. The wavelength of the Q-band of the peak associated with the monomer is slightly lower than that observed for the complex in Fig. 1 (675 nm) due to the effects of the electrolyte. Upon reduction at potentials of process II, a red-shift in Q-band of the monomeric peak (from 672 to

710 nm), with increased intensity, was observed. Considerable disaggregation of the complex was also noticed upon reduction, as evident from the narrowing of the absorption bands. Also there was emergence of a new intense peak at 474 nm during reduction. New peaks with intense signal between 400 and 500 nm are typical of the formation of Co^IPc species [19]. The shift in Q-band without decrease in intensity is a signature of metalbased reduction in MPc complexes. Hence, spectral changes shown in Fig. 6a are a confirmation of the reduction of Co^{II} to Co¹, corroborating the assignment of process II, in Fig. 3b, to Co^{II}Pc⁻²/Co^IPc⁻² species. Also clear isobestic points, observed at 556 and 691 nm, indicated that the process is a clean reduction involving two species. However, the first scan does not fall within the isosbestic point due to disaggregation during reduction. About 85% of the original spectrum was regenerated on the application of zero potential, showing some measure of reversibility of the process. The number of electron transferred was calculated to be approximately 1, using Eq. (1):

$$Q = nFVC \tag{1}$$

where *n*, F, V and C are the number of electrons transferred, Faraday's constant, volume and concentration of the electroactive species, respectively. Further reduction of the species formed in Fig. 6a, at potential more negative of process I ($E_{V_2} = -1.26$ V versus



Fig. 6. UV–Vis spectral changes observed for complex **3a** during controlled potential electrolysis at (a) -0.3 V (process **I**), (b) -1.4 V (process **I**) and **(c)** +0.7 V (process **III**) vs. Ag|AgCl. Dotted line in (a) and (c) (spectrum before electrolysis), dashed line (spectrum after electrolysis). Electrolyte = DMF containing 0.1 M TBABF₄. The final spectrum in (a) is the starting spectrum in (b).

Ag|AgCl, Fig. 3b) resulted in the spectral changes shown in Fig. 6b. Decrease in intensity of the new Q-band with shift in position of the band at 474–478 nm was noticed. Also there was formation of

new bands at 555 and 585 nm. Emergence of new bands in the 500–600 nm region is characteristic of ring-based reduction and the formation of Pc^{-3} species [20]. Hence, the spectral changes ob-

served in Fig. 6b confirmed the assignment of process I (in Fig. 3b) to $Co^{1}Pc^{-2}/Co^{1}Pc^{-3}$ species.

The spectral changes in Fig. 6c were obtained on the application of potential more positive of process **III** ($E_{1/2} = +0.64$ V versus Ag|AgCl, Fig. 3b). The starting spectrum has a split Q-band as observed in Fig. 6a. This can be attributed to aggregation as discussed earlier. The higher energy peak (628 nm) is due to the aggregate while the lower energy peak (672 nm) is associated with the monomer. Upon oxidation, there was increase in intensity of the Q-band due to the monomer and shift in position from 672 to 677 nm. These spectral changes are consistent with the oxidation of Co^{II} to Co^{III} pcc⁻²/Co^{II} pc⁻² couple. However, the minimal shift in position and slight change in intensity of the Q-band in Fig. 6c underline the difficulty, highlighted previously, with which oxidative processes occurred in complex **3a**.

3.3.2. Complex **3b**

Fig. 7a shows the spectral changes observed on the application of potential more negative of process II ($E_{V_2} = -0.38$ V versus

Ag|AgCl, Fig. 4b). The Q-band of the starting spectrum (694 nm) is similar to that of the spectrum of complex 3b (693 nm) in Fig. 1, showing minimal effects of the electrolyte which was observed for 3a. Reduction resulted in shift of the Q-band from 694 to 712 nm with constant intensity. There was also the emergence of new intense band at 473 nm. Presence of new intense peaks between 400 and 500 nm region typifies the formation of Co^IPc species, as discussed previously [19]. The shift in Q-band without change in intensity is characteristic of metal-based reduction in MPc complexes. Thus, the spectral changes noticed in Fig. 7a confirms the assignment of process II (Fig. 4b) to $Co^{II}Pc^{-2}/Co^{I}Pc^{-2}$ species. Clear isobestic points, noticed at 570 and 705 nm, showed that process **II** (Fig. 4b) is a clean reduction involving two species. Regeneration of over 90% of the starting spectrum, on the application of zero potential, confirmed the reversibility of the process. The number of electron transferred was calculated to be approximately 1 using Eq. (1). The species obtained in Fig. 7a was further reduced (Fig. 7b) on the application of potential more negative of that of couple I ($E_{\frac{1}{2}}$ = -1.46 V versus Ag|AgCl, Fig. 4b). There was a decrease in intensity of the new Q-band and emergence of new



Fig. 7. UV–Vis spectral changes observed for complex **3b** during controlled potential electrolysis at (a) -0.45 V (process **II**), (b) -1.5 V (process **I**), (c) +0.5 V (process **III**) and (d) +0.9 V (process **IV**) vs. Ag|AgCl. Dotted line in (a) (spectrum before electrolysis), dashed line (spectrum after electrolysis). Electrolyte = DMF containing 0.1 M TBABF₄. The final spectra in (a) and (c) are the starting spectra in (b) and (d) respectively.



band (570 nm) between 500 and 600 nm region. These spectral changes are consistent with the formation of Pc^{-3} species, as discussed previously [20]. This confirms the assignment of couple I (Fig. 4b) to $Co^{1}Pc^{-2}/Co^{1}Pc^{-3}$ species.

Application of potential more positive of process III (Ep = +0.41 V versus Ag|AgCl, Fig. 4b) resulted in the spectral changes shown in Fig. 7c. There was red-shifting of the Q-band of the starting spectrum (from 694 to 702 nm), with increased intensity, upon oxidation. These spectral changes are consistent with the oxidation of Co^{II} to Co^{III}. Hence, confirming the assignment of process **III** (Fig. 4b) to Co^{III}Pc⁻²/Co^{II}Pc⁻² species. The well defined spectral changes observed for this process, relative to that for the corresponding process in complex 3a (Fig. 6c), corroborate the previous suggestion that complex **3b** was more susceptible to oxidative process than complex **3a**. Further oxidations are expected to occur on the ring by virtue of the nature of CoPcs [18]. However, application of potential more positive of process IV (Ep = +0.86 V versus Ag|AgCl, Fig. 4b) resulted in the spectral changes shown in Fig. 7d. A decrease in Q-band intensity, without any appreciable increase in intensity around the 500 nm region, was observed. Increased intensity around the 500 nm region is characteristic of ring oxidation in MPc [18]. Hence, spectral changes observed in Fig. 7d may have suggested degradation of the complex as reported previously for other thiol derivatised MPc complexes [21,22]. Nonetheless, the assignment of process **IV** to $Co^{III}Pc^{-1}/Co^{III}Pc^{-2}$ was consistent with the nature of CoPc complexes (Table 1)

3.3.3. Complex 5

The spectral changes observed on the application of potential more negative of process II ($E_{\frac{1}{2}}$ = -0.26 V versus Ag|AgCl, Fig. 5b) is shown in Fig. 8a. The starting spectrum is the same as that shown for complex 5 in Fig. 1. The band around 628 nm is associated with vibronic transition but complicated by slight aggregation tendency. The main Q-band at 692 nm was red-shifted upon reduction (692-707 nm) without decrease in intensity. Also, there was the appearance of new peak, with increased intensity, at 473 nm. Presence of new peak with increased intensity in the 400-500 nm region is a signature of Co^IPc [19], as observed for Figs. 6a and 7a. The shift in Q-band, with the same intensity, is in agreement with metal-based reduction in MPc. Therefore, the spectral changes observed in Fig. 8a confirmed the assignment of process II (Fig. 5b) to Co^{II}Pc⁻²/Co^IPc⁻² species. Clear isobestic point at 572 and 700 nm showed that the process was a clean reduction, involving two species. The number of electron transfer was obtained to be approximately 1 using Eq. (1). Less than 70% of



Fig. 8. UV–Vis spectral changes observed for complex **5** during controlled potential electrolysis at (a) –0.35 V (process II), (b) –1.45 V (process I) and (c) +0.65 V (process III) vs. Ag|AgCl. Dotted line (spectrum before electrolysis), dashed line (spectrum after electrolysis). Electrolyte = DMF containing 0.1 M TBABF₄. The final spectrum in (a) is the starting spectrum in (b).

the original spectrum was regenerated on the application of zero potential. Although, this shows some measure of reversibility, it does testifies to the sluggish nature of electron transfer process in this complex, relative to that of the corresponding process in complexes **3a** and **3b**. The spectral changes are also not as resolved as that observed for the corresponding process in complex **3a**

(Fig. 6a) and complex **3b** (Fig. 7a), which shows that electron transfer processes are better in these complexes than in complex **5**. Further reduction of the species obtained in Fig. 8a occurred on the application of potential more negative of process **I** ($E_{V_2} = -1.39$ V versus Ag|AgCl, Fig. 5b) resulting in spectral changes shown in Fig. 8b. There was a decrease in the absorbance of the new Q-band, emergence of new band between 500 and 600 nm region and shift in position of the peak at 473 to 477 nm. These spectral changes are characteristic of Pc⁻³ species [20]. This confirms the assignment of process **I** (Fig. 5b) to Co^IPc⁻²/Co^IPc⁻³ species.

Application of a potential more positive of process **III** (*Ep* = +0.59 V versus Ag|AgCl, Fig. 5b) gave the spectral changes shown in Fig. 8c. An increase in absorbance and shift in position of the Q-band (692 to 697 nm) of the starting spectrum were observed. Although, these changes are minimal, they are characteristic of the oxidation of Co^{III} to Co^{III}. This confirms the assignment of process **III** (Fig. 5b) to Co^{III}Pc⁻²/Co^{II}Pc⁻² species. The minimal spectral changes noticed in Fig. 8c is a testimony to the reluctance of the complex, like complex **3a**, to undergo oxidative process, as explained previously.

4. Conclusion

The syntheses of new cobalt phthalocyanine complexes are reported. Their spectral, electrochemical and spectroelectrochemical properties have been extensively investigated. The Q-band of complex 3b was red-shifted, with lower intensity, relative to that of complex **3a**. This was attributed to conformational changes arising from non-peripheral substitution. The Q-band of complex 5, like that of complex 3b, was also red-shifted and of lower intensity with respect to that of complex **3a**. Change in the nature of substituent (diethylaminoethanethio versus benzylmercapto) did not significantly affect the position of Q-band. All the complexes showed interesting electrochemical properties consistent with that of CoPc complexes. However, oxidative processes were energetically more feasible in complex 3b while complexes 3a and 5 were more receptive to reductive processes. Complex 3b has the best electron transfer processes by virtue of relatively smallest cathodic to anodic peak differences of the observed redox processes, while complexes 3a and 5 showed a rather sluggish electron transfer processes, evident from relatively larger cathodic to anodic peak differences. Electrochemical properties were markedly affected by the nature of substituent. Spectroelectrochemical investigation confirmed the assigned processes in these complexes. The spectral changes noticed were in agreement with that of CoPc complexes and they corroborated the observed electrochemical identities of the new complexes.

Acknowledgements

This work was supported by the Department of Science and Technology (DST) and National Research Foundation (NRF) of South Africa through DST/NRF South African Research Chairs Initiative for Professor of Medicinal Chemistry and Nanotechnology and Rhodes University.

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