Inorganica Chimica Acta 363 (2010) 3662–3669

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Synthesis and electrochemical characterisation of new tantalum (V) alkythio phthalocyanines

Vongani Chauke, Tebello Nyokong *

Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa

ARTICLE INFO

Article history:
Received 16 November 2009
Received in revised form 7 April 2010
Accepted 5 May 2010
Available online 12 May 2010

Keywords:
Tantalum phthalocyanine
Cyclic voltammetry
Spectroelectrochemistry
Adsorption
Alkyl thio

ABSTRACT

The synthesis and electrochemical characterisation of octa-pentylthio (**4a**) and octa-octylthio (**4b**) – phthalocyaninato tantalum (III) hydroxide are hereby reported. These TaPc complexes absorb in the near infrared region (~800 nm in dichloromethane). They show good solubility in most common solvents especially non-viscous solvents such as dichloromethane and chloroform. NMR, mass and infrared spectroscopy and elemental analysis confirmed the structures and purity of the synthesised complexes. The cyclic voltammograms (CVs) showed reversible reduction couples and irreversible oxidation peaks. The latter exhibited adsorption behavior. The reduction processes were observed at −0.74 and −1.13 V (versus Ag|AgCl) for **4a**, and −0.67, −1.02 and −1.48 V (versus Ag|AgCl) for **4b**. Spectroelectrochemistry confirmed one metal reduction, with the rest of the redox processes being centered on the phthalocyanine ring.

1. Introduction

Metallophthlocyanines (MPcs) have attracted a lot of attention for many years since their discovery in the early 1900s. Their remarkable properties that include flexibility, chemical and thermal stabilities, semiconductivity and photoconductivity [1,2] have been of great interest in research. Traditionally, phthalocyanines (Pcs) have been used as dyes and pigments. Currently, the focus of research on MPc complexes is directed to applications in material science [3–5]. These include Pcs as liquid crystals [6–8], Langmuir–Blodgetts films [9–11], electrochemical sensors [12–14] and fuel cells [15]. Phthalocyanines with sulfur substituents generally absorb in the near infrared (NIR) region [16]. Pcs absorbing in the NIR region to match the 780 and 830 nm semiconductor lasers are used for optical data storage (ODS) whilst for security applications, Pcs employed cover the 700–1000 nm region [16–18]. Thiol substituted MPcs may be used to modify gold electrode surfaces for sensor applications [19–21], where there is a spontaneous formation of SAMs due to the strong gold–sulfur interactions. Thus the synthesis of thio derivatized Pc complexes is of importance for many practical applications.

Even though MPc complexes containing transition metals have been extensively studied, very little is known about tantalum phthalocyanines due to synthetic challenges. The difficulty arises from the fact that Ta–N distances in TaPc are ~2.17 Å (compared to Fe–N of 1.93 Å in FePc) [22,23], while the phthalocyanine cavity has an N–N distance of 3.96 Å [22], making it difficult for Ta to fit into the Pc cavity.

This results in highly unsymmetrical MPcs that are somewhat unstable. The synthesis and X-ray crystal structure of an unsubstituted TaPc have been reported before [23], and the electrochemical behavior of unsubstituted TaPc has been reported by our group [24]. Ring substituted TaPc derivatives are unknown and are reported here for the first time.

This work reports on the syntheses of non peripherally alkylthiol substituted TaPc complexes. MPcs with electron donating substituents, in particular sulfur substituted MPcs often show interesting electrochemistry that involves the central metal, the Pc ring and the substituents on the Pc ring. This has therefore motivated the study in this work.

2. Experimental

2.1. Materials

Acetone, tantalum (V) butoxide, dimethylsulfoxide (DMSO), 1-pentanethiol, 1-octanethiol, tantalum butoxide, 1,8-diazabicyclo{5.4.0}-undec-7-ene (DBU) and 1-pentanol were purchased from Sigma–Aldrich. Potassium carbonate, ammonium ferrous sulfate, deuterated chloroform ($CDCl_3$), 2,3-dicyanohydroquinone (**1**), *p*-toluenesulfonylchloride, tetrahydrofuran (THF), toluene, chloroform and dichloromethane (DCM) were procured from Merck. Tetrabutylammonium tetrafluoroborate ($TBABF_4$) was purchased from Sigma–Aldrich.

* Corresponding author. Tel.: +27 46 603 8260; fax: +27 46 622 5109.
E-mail address: T.nyokong@ru.ac.za (T. Nyokong).

0020-1693/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2010.05.003

2.2. Equipment

Column chromatography was performed on silica gel 60 (0.04–0.063 mm) and preparative thin layer chromatography was performed on silica gel 60 P F_{254}. Ground state electronic absorption spectra were performed on a Varian Cary 500 UV–Vis–NIR spectrophotometer, infrared spectra (KBr pellets) on Perkin–Elmer Spectrum 2000 FT-IR Spectrometer and ^{1}H nuclear magnetic resonance signals on a Bruker EMX 400 NMR spectrometer. Elemental analysis was performed at Rhodes University using a Vario-Elementar Microcube ELIII. MALDI-TOF mass spectrometry was carried out at the University of Stellenbosch using an ABI Voyager DE-STR MALDI-TOF instrument.

2.3. Electrochemical methods

Cyclic (CV) and square wave (SWV) voltammetry 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, Eco Chemie), using a conventional three-electrode system. A glassy carbon electrode (GCE, 3.0 mm diameter) was used as the working electrode. Silver–silver chloride (Ag|AgCl) and platinum wire were used as pseudo-reference and counter electrodes, respectively. Electrochemical experiments were performed in dry DCM containing $TBABF_4$ as the supporting electrolyte. Prior to scans, the working electrode was polished with alumina paste on a Buehler felt pad. This was followed by washing with de-ionised water. Spectroelectrochemical data was recorded using an optically transparent thin-layer electrochemical (OTTLE) cell which was connected to a Bioanalytical System (BAS) CV 27 voltammograph.

2.4. Synthesis

A procedure similar to that reported in literature [25,26] was employed for the synthesis of phthalonitriles (**2** and **3**) with slight alterations as follows.

2.4.1. 3,6-Bis(4′-methylphenylsulfonyloxy) phthalonitrile (*2*), Scheme 1

p-Toluenesulfonyl chloride (10.32 g, 27 mmol) was added to a mixture of 2,3-dicyanohydroquinone (**1**) (4.04 g, 12.5 mmol) and potassium carbonate (13.8 g, 50 mmol) in acetone (15 ml). The mixture was refluxed for 2 h. Thin layer chromatography (TLC) was performed to determine the consumption of 2,3-dicyanohydroquinone. The mixture was cooled to room temperature, poured to water (40 ml) and stirred for 1 h in water. The light brown product was filtered and oven dried to give 2. Yield: 9.51 g (79%) IR [(KBr) ν_{max}/cm^{-1}]: 3432, 3239, 3085, 2243, 2226 (CN), 1504, 1449, 1315, 1279, 1204, 1174, 1142, 1021, 1004, 979, 934, 847, 749, 694, 638, 614.

2.4.2. 3,6-Di(pentylthio)-4,5-dicyanobenzene (*3a*), Scheme 1

1-Pentanethiol (2.39 g, 22.9 mmol) was dissolved in DMSO under a nitrogen atmosphere and 3,6-bis(4′-methylphenylsulfonyloxy) phthalonitrile (**2**) (4.30 g, 9.18 mmol) was added. The mixture was stirred for 15 min and finely ground anhydrous potassium carbonate (5.07 g, 36.7 mmol) was added in portions for 2 h while stirring. The mixture was stirred under a nitrogen atmosphere for a further 12 h. Water was added and the aqueous phase extracted using chloroform (3 × 50 ml). The extracts were further treated with 5% sodium carbonate solution (2 × 250 ml). The solution was further treated with water (2 × 250 ml) and the solvent was evaporated off using a rotavapor. The product **3a** was recrystallised from ethanol. Yield: 2.19 g (71.7%). IR [(KBr)ν_{max}/cm^{-1}]: 3084, 2951, 2930, 2864, 2378(S–C), 2225(C≡N), 1444, 1283, 1202, 1181, 1173, 1145, 877, 847, 827, 725, 547, 447.

^{1}H NMR ($CDCl_3$): δ, ppm 7.49 (2-H, s, Ar–H), 2.99–3.02 (4-H, t, –CH_2), 1.63–1.71 (4-H, m, –CH_2), 1.37–1.46 (4-H, m, –CH_2), 1.28–1.36 (4-H, m, –CH_2), 0.88–0.91 (6-H, t, –CH_3).

2.4.3. 3,6-Di(octylthio)-4,5-dicyanobenzene (*3b*), Scheme 1

Synthesis and purification of **3b** were similar to that of compound **3a**, except 1-octanethiol was used instead of 1-pentane thiol. The amounts of reagents employed were: 1-octanethiol (2.39 g, 16.3 mmol), 3,6-bis(4′-methylphenylsulfonyloxy) phthalonitrile (**2**) (4.30 g, 9.18 mmol), ground anhydrous potassium carbonate (5.07 g, 36.7 mmol). Yield: 1.79 g, (58.1%). IR [(KBr)ν_{max}/cm^{-1}]: 2920, 2850, 2388(S–C), 2225(C≡N), 2023, 1637, 1466, 1422, 1204, 1143, 1032.

^{1}H NMR ($CDCl_3$): δ, ppm 7.40 (2-H, s, Ar–H), 2.98–3.10 (4-H, t, –CH_2), 1.62–1.75 (4-H, m, –CH_2), 1.61–1.50 (4-H-broad m, –CH_2), 1.40–1.52 (4-H, m, –CH_2), 1.21–1.38 (18-H, m, –$CH_2CH_2CH_3$).

2.4.4. 1,4,8,11,15,18,22,25-Octapentylthiophthalocyaninato tantalum (V) butoxide (*4a*, $(OH)_3TaOPTPc$), Scheme 1

3,6-Dipentylthiophthalonitrile (**3a**) (0.8 g, 1.20 mmol) in 1-pentanol (7.0 ml) was refluxed under a nitrogen atmosphere and tantalum (V) butoxide (0.138 g, 0.34 mmol) was added. After the addition of DBU (0.30 ml, 0.86 mmol), the reaction was continued for 6 h. The mixture was cooled and column chromatography over silica was done with $CHCl_3$ as eluent. Yield: 0.25 g (42%). UV–Vis (DCM): λ_{max} (nm) ($\log \varepsilon$) 276(6.36) 348(5.62) 722(5.44) 814 (5.81). IR [(KBr) ν_{max}/cm^{-1}]: 3290 (OH), 2922, 2852, 2350, 1561, 1459, 1361, 1310, 1279, 1156, 109, 932, 908(Ta–O), 750 (C–S–C). ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 7.65 (8H, s, Ar–H), 3.20 (16H, broad s, S-*CH_2*), 1.89 (16H, quintuplet, *CH_2*), 1.61 (16H, quintuplet, *CH_2*), 1.50 (16H, sextuplet, *CH_2*), 1.0 (24H, t, *CH_3*). *Anal.* Calc. $C_{72}H_{99}N_8S_8O_3Ta$: C, 55.36; H, 6.38; N, 7.17. Found: C, 55.45; H, 7.21; N, 7.92%. MALDI-TOF MS *m/z*: Calcd: 1561.52 amu. Found: (M−Ta) 1330 amu.

2.4.5. 1,4,8,11,15,18,22,25-Octaoctylthiophthalocyaninato tantalum (V) butoxide (*4b*, $(OH)_3TaOOTPc$), Scheme 1

Synthesis and purification of **4b** were similar to that of compound **4a**, except **3b** was employed instead of **3a**. The amounts of reagents employed were: 3,6-dioctylthiophthalonitrile (**3b**) (0.81 g, 1.20 mmol, 1-pentanol (∼8 ml), tantalum (V) butoxide (0.139 g, 0.34 mmol), DBU (0.30 ml, 0.86 mmol). Yield 0.31 (48%). UV–Vis (DCM): λ_{max} (nm) ($\log \varepsilon$) 416(3.82) 662(4.00) 609(3.73) 717 (4.41), 814 (5.76). IR [(KBr) ν_{max}/cm^{-1}]: 3419 (OH), 2955, 2920, 2850, 2538, 2400, 1637, 1563, 1432, 1368, 1312, 1281, 1223, 1181, 1142, 1091, 1031, 910, (Ta–O), 867, 787, 751 (C–S–C), 720. ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 7.51 (8H, s, Ar–H), 3.2 (16H, broad s, S-*CH_2*), 1.90 (32H, quintuplet, *CH_2*), 1.79 (32H, quintuplet, *CH_2*), 1.05 (56H, sextuplet, *$CH_2CH_2CH_3$*). *Anal.* Calc. $C_{96}H_{147}N_8S_8O_3Ta$: C, 60.72; H, 7.80; N, 5.90. Found: C, 60.92; H, 8.41; N, 6.42%. MALDI-TOF MS *m/z*: Calcd: 1898.16 amu. Found: (M−Ta) 1666.5 amu.

3. Results and discussion

3.1. Synthesis and characterisation

Scheme 1 gives the synthesis pathways for the TaPc complexes discussed in this work. 3,6-Bis(4′-methylphenylsulfonyloxy) phthalonitrile (**2**), was used to prepare 3,6-disubstituted phthalonitrile derivatives (**3a** and **3b**), through base-catalysed nucleophilic aromatic displacement. The reactions were carried out in DMSO at room temperature and gave yields of 71.7% for **3a** and 58.1%