

This article was downloaded by:

On: 27 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

Preparation of Octakis (methylthio)octaethylphthalocyaninato Titanium (IV) Benzenedichalcogenolates

Takeshi Kimura^a; Arata Yamamoto^a; Toshiharu Namauo^a

^a Center for Instrumental Analysis, Iwate University, Iwate, Japan

Online publication date: 27 May 2010

To cite this Article Kimura, Takeshi , Yamamoto, Arata and Namauo, Toshiharu(2010) 'Preparation of Octakis (methylthio)octaethylphthalocyaninato Titanium (IV) Benzenedichalcogenolates', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 185: 5, 1008 – 1013

To link to this Article: DOI: 10.1080/10426501003772144

URL: <http://dx.doi.org/10.1080/10426501003772144>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

PREPARATION OF OCTAKIS (METHYLTHIO)OCTAETHYLPHTHALOCYANINATO TITANIUM (IV) BENZENEDICHALCOGENOLATES

Takeshi Kimura, Arata Yamamoto, and Toshiharu Namao

Center for Instrumental Analysis, Iwate University, Iwate, Japan

Octakis(methylthio)octaethylphthalocyaninato titanium (IV) oxide (PcSMeTiO) was prepared from octakis(methylthio)octaethylphthalocyanine (PcSMe) upon treatment with titanium (IV) tetrabutoxide in DMF at 130°C. The reaction of PcSMeTiO with benzenedithiol or benzenediselenol produced octakis(methylthio)octaethylphthalocyaninato titanium (IV) benzenedichalcogenolates (4a,b) bearing titanium–sulfur or titanium–selenium bonds.

Keywords Phthalocyanine; S ligand; Se ligand; titanium

INTRODUCTION

Tetraazaporphyrins and related compounds have a variety of actual and potential applications in many fields such as dyes, pigments, catalysts, new functional materials, and sensitizers for photodynamic therapy.^{1,2} Among the great number of tetraazaporphyrins, phthalocyanines connecting one or two axial coordinating groups on the central metal atom have attracted much attention because the molecules could be applied to electrochromic displays, field-effect transistors, nonlinear optical materials, and dye-sensitized solar cells.³ Recently, Hanack and colleagues reported phthalocyaninato titanium (IV) complexes as compounds that have axial coordinating groups connected with titanium–oxygen or titanium–sulfur bonds,⁴ while Kobayashi and colleagues synthesized a mutually perpendicular phthalocyanine pentamer and related derivatives.⁵ These products were prepared by the ligand exchange reaction of tetra-*t*-butylphthalocyaninato titanium (IV) oxide with *o*-catechols, *o*-benzenedithiol, tetrahydroxy-*p*-benzoquinone, and octahydroxyphthalocyanine. In contrast, we reported the double-decker phthalocyanine, which was obtained by the reaction of two molecules of octakis(methylthio)octaethylphthalocyaninato titanium (IV) oxide (PcSMeTiO) with benzene-1,2,4,5-tetrathiol.⁶ To construct a new type of phthalocyanines with an axial ligand, PcSMeTiO was reacted with 3,6-diethyl-4,5-dibromobenzene-1,2-dithiol (**3a**) or 3,6-diethyl-4,5-dibromobenzene-1,2-diselenol (**3b**). This article reports the preparation

Received 26 November 2008; accepted 17 December 2008.

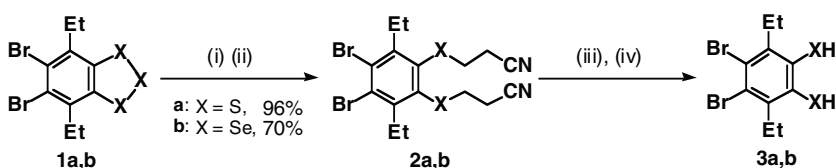
Dedicated to Professor Naomichi Furukawa on the occasion of his 70th birthday.

Address correspondence to Takeshi Kimura, Center for Instrumental Analysis, Iwate University, Morioka, Iwate 020-8551, Japan. E-mail: kimura@iwate-u.ac.jp

and electrochemical property of octakis(methylthio)octaethylphthalocyaninato titanium (IV) diethyldibromobenzenedichalcogenolates (**4a,b**).

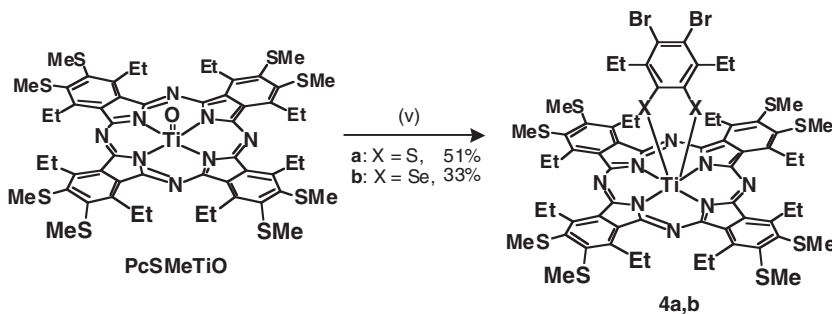
RESULTS AND DISCUSSION

5,6-Dibromo-4,7-diethylbenzotrithalcohenoles (**1a,b**) were converted into 1,2-bis(2-cyanoethylchalcogeno)-4,5-dibromo-3,6-diethylbenzenes (**2a,b**) in 96% and 70% yields, respectively, upon treatment with NaBH_4 and then 2-cyanoethyl bromide (Scheme 1).⁷



Scheme 1 (i) NaBH_4 , K_2CO_3 , THF/MeOH; (ii) $\text{BrCH}_2\text{CH}_2\text{CN}$; (iii) CsOH , THF/MeOH; (iv) HCl

The treatment of octakis(methylthio)octaethylphthalocyanine (PcSMe) with titanium (IV) tetrabutoxide by the procedure reported previously produced PcSMeTiO .⁶ To prepare benzenedithiol (**3a**) as a bidentate sulfur ligand, **2a** was reacted with CsOH in THF/MeOH under Ar (Scheme 1).^{8,9} The reaction mixture was acidified with concentrated HCl to generate **3a**. The prepared solution was transferred to the reactor containing PcSMeTiO , and the reaction mixture was stirred for 24 h (Scheme 2). After workup and purification with silica gel column chromatography and Bio-beads column chromatography, phthalocyanine (**4a**) with benzenedithiolate as the axial ligand was obtained in 51% yield.



Scheme 2 (v) **3a** or **3b**, THF/MeOH.

In the ^1H NMR spectrum, **4a** showed the signals of the ethyl and methylthio groups connected to the phthalocyanine core at $\delta = 1.60$ (t), 2.72 (s), and 4.68–5.00 (m) ppm. These chemical shifts are slightly upper field compared with those of PcSMeTiO : $\delta = 1.74$ (t), 2.78 (s), 4.94 and 5.02 (dq) ppm. The signals for the ethyl group of benzenedithiolate were observed at $\delta = 0.23$ (t) and 1.81 (q) ppm, which are higher magnetic field than those of **2a**: $\delta = 1.29$ (t) and 3.28 (q) ppm. These results could show that the benzene ring lies on the phthalocyanine plane and is strongly affected in the magnetic shielding range of the macrocycle. When ^{13}C NMR of **4a** was measured, the four signals for the phthalocyanine

skeleton, the five signals for the ethyl and the methylthio groups, and three signals for the coordinating benzene ring appeared in the following spectrum: $\delta = 11.5, 16.4, 22.7, 25.4, 30.0, 124.9, 132.9, 136.4, 146.7, 146.8, 147.9, 151.4$ ppm. Since the signals for PcSMeTiO were observed at $\delta = 16.8, 22.3, 25.2, 134.0, 146.8, 147.1, 151.8$ ppm, the signals for **4a** at 11.5, 30.0, 124.9, 136.4, 147.9 ppm might be the carbon of benzenedithiolate. It appears that the phthalocyanine skeleton of **4a** is a C₄ symmetric structure in the NMR time scale at 25°C, though benzenedithiolate coordinates to the central titanium atom. Furthermore, the FABMS spectrum of **4a** showed the corresponding molecular ion peak at $m/z = 1504.13$ [M^+].

The similar treatment of PcSMeTiO with **3b** produced phthalocyanine (**4b**) with benzenediselenolate in 33% yield. The ¹H NMR and ¹³C NMR spectra of **4b** were similar to those of **4a**. The ⁷⁷Se NMR spectrum showed the signal at $\delta = 448.5$ ppm, which is a much higher magnetic field than that of the bis(cyclopentadienyl)benzodiselenatitanole derivatives.¹⁰ The FABMS spectrum of **4b** exhibited the molecular ion peak at $m/z = 1600.13$ [M^+].

In the UV-vis spectra measured in CHCl₃, the Q band absorptions of **4a** and **4b** were observed at $\lambda_{\max} = 763.5$ and 765.5 nm, respectively, which were wider bandwidth and slightly longer wavelengths than that of PcSMeTiO ($\lambda_{\max} = 760$ nm). The bandwidth of the Q band absorption of the free-base phthalocyanine, PcSMe, is more enlarged than that of PcSMeTiO because of the proton alternation between the central pyrrolic nitrogen atoms. Although the phthalocyanine skeleton of **4a** and **4b** is the C₄ symmetry, the coordination of benzenedichalcogenolate to the central titanium atom in the axial direction could have made the symmetry of the π -electronic system decrease from C₄ to C₂, which resulted in the broadening of the Q band absorption of **4a** and **4b** compared with that of PcSMeTiO.

The electrochemical properties of **4a** and **4b** were examined by cyclic voltammetry using Ag/AgNO₃ as a reference electrode (measured in CH₂Cl₂, scan rate: 100 mV/s). The cyclic voltammogram of **4a** contained one irreversible oxidation ($E_p = 0.87$ V) and three quasi-reversible reduction potentials ($E_{1/2} = -1.73, -1.06$, and -0.76 V). Compound (**4b**) showed the irreversible oxidation potential at $E_p = 0.85$ V while the quasi-reversible reduction potentials were observed at $E_{1/2} = -1.78, -1.04$, and -0.75 V. As shown in Table I, it appeared that the oxidation and reduction potentials of **4a** and **4b** are higher than those of PcSMe and PcSMeTiO.

Table I Redox potentials (vs. Ag/AgNO₃)

Compounds	E _{1/2} [V]					ΔE (V)
	3rd reduction	2nd reduction	1st reduction	1st oxidation	2nd oxidation	
PcSMe ^a	—	−1.41	−1.08	0.52	0.91	1.60
PcSMeTiO ^a	—	−1.14	−0.80	0.68	1.13 ^c	1.48
4a ^b	−1.73 ^d	−1.06 ^d	−0.76 ^d	0.87 ^c	—	1.63
4b ^b	−1.78 ^d	−1.04 ^d	−0.75 ^d	0.85 ^c	—	1.60

^aScan rate: 200 mV/s.

^bScan rate: 100 mV/s.

^cIrreversible (E_p /V).

^dQuasi reversible.

ΔE is the difference between the first oxidation potential and the first reduction potential.

EXPERIMENTAL

NMR spectra were measured with a Bruker AC-400 spectrometer at 25°C. Mass spectra were obtained using a JEOL JMS-700 mass spectrometer. UV-vis spectra were recorded with a JASCO Ubest V-570 spectrometer. A Hokuto Denko Co. Model HAB-151 apparatus was employed for measuring oxidation potentials. Elemental analysis was performed using a Yanako MT-5 analyzer. Bio-beads (SX-1) for column chromatography were purchased from Nippon Bio-Rad Laboratories.

Oxidation Potentials

All measurements were performed by cyclic voltammetry, using Ag/AgNO₃ (0.01 mol/l) as a reference electrode (scan rate: 100 mV/s or 200 mV/s). A solution of *n*-Bu₄NClO₄ in CH₂Cl₂ (0.1 mol/l) was used as an electrolyte. The oxidation potential of ferrocene was observed at $E_{1/2} = 0.09$ V by the apparatus without any correction.

Materials

Compounds (**1a**), (**1b**), (**2a**), PcSMe, and PcSMeTiO were prepared using a method described previously.^{6,7}

1,2-Bis(2-cyanoethylseleno)-4,5-dibromodiethylbenzene (**2b**)

To a solution of **1b** (1.604 g, 3 mmol) and K₂CO₃ (831 mg, 6 mmol) in THF (20 ml)/MeOH (10 ml), NaBH₄ (347 mg, 9.1 mmol) was added under Ar, and the solution was stirred for 30 min. 3-Bromopropionitrile (0.97 ml, 12 mmol) was added to the solution. After stirring for 6 h and acidification with HCl, the solvent was evaporated, and the product was extracted with CHCl₃. The solvent was evaporated, and the residue was purified by column chromatography (Wakogel C-400, *n*-hexane:CHCl₃ = 1:1) to produce **2b** in 70% yield (1.182 g); colorless crystals; mp 83–86°C; ¹H NMR (400 MHz, CDCl₃) δ = 1.18 (t, *J* = 7.4 Hz, 6H), 2.71 (t, *J* = 7.2 Hz, 4H), 3.20 (t, *J* = 7.2 Hz, 4H), 3.43 (q, *J* = 7.4 Hz, 4H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ = 14.3, 18.7, 26.2, 36.2, 118.3, 130.3, 137.7, 149.5 ppm; ⁷⁷Se NMR (76 MHz, CDCl₃) δ = 325.2 ppm; HRMS Calcd for C₁₆H₁₈⁷⁹Br₂N₂⁸⁰Se₂, 555.8167. Found (*m/z*) 555.8167 (M⁺).

Generation of 3,6-Diethyl-4,5-dibromobenzene-1,2-dithiol (**3a**)

Compound (**2a**) (156.5 mg, 0.342 mmol) and CsOH (517.6 mg, 3.45 mmol) were placed in a glass reactor under Ar. THF (5 mL) and MeOH (5 mL) were added to the reactor, and the solution was stirred for 2 h. Concentrated HCl (0.29 mL) was added to the solution to generate the corresponding dithiol (**3a**).

Generation of 3,6-Diethyl-4,5-dibromobenzene-1,2-diselenol (**3b**)

Compound (**2b**) (98.4 mg, 0.177 mmol) and CsOH (263.8 mg, 1.76 mmol) were placed in a glass reactor under Ar. THF (5 mL) and MeOH (5 mL) were added to the reactor, and the solution was stirred for 2 h. Concentrated HCl (0.14 mL) in methanol (6.9 mL) was added to the solution to generate the corresponding diselenol (**3b**).

Octakis(methylthio)octaethylphthalocyaninato Titanium (IV) Benzenedithiolate (4a)

The solution of **3a**, prepared as described above, was transferred by syringe to the reactor containing PcSMeTiO (97.4 mg, 0.0845 mmol) under Ar. The solution was stirred for 24 h, and the solvent was evaporated. The residue was purified by column chromatography (Wakogel C-300HG, *n*-hexane: CHCl_3 = 1:1 and CHCl_3) and (Bio-beads, CHCl_3) to produce **4a** in 51% yield (65.2 mg); dark green powder, mp > 300°C; ^1H NMR (400 MHz, CDCl_3) δ = 0.23 (t, J = 7.2 Hz, 6H, CH_3), 1.60 (t, J = 7.2 Hz, 24H, CH_3), 1.81 (q, 4H, CH_2), 2.72 (s, 24H, SCH_3), 4.68–5.00 (m, 16H, CH_2) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ = 11.5, 16.4, 22.7, 25.4, 30.0, 124.9, 132.9, 136.4, 146.7, 146.8, 147.9, 151.4 ppm; UV-vis (CHCl_3) λ_{max} = 763.5 nm; FAB MS (m/z) 1504.13 [M^+]; Anal. Calcd for $\text{C}_{66}\text{H}_{74}\text{Br}_2\text{N}_8\text{S}_{10}\text{Ti}$: C, 52.58; H, 4.95; N, 7.43. Found: C, 52.36; H, 5.09; N, 6.53.

Octakis(methylthio)octaethylphthalocyaninato Titanium (IV) Benzenediselenoolate (4b)

Compound (**4b**) was prepared in 33% yield by the procedure as described above; dark green powder, mp 225°C; ^1H NMR (400 MHz, CDCl_3) δ = 0.29 (t, J = 7.4 Hz, 6H, CH_3), 1.59 (t, J = 7.2 Hz, 24H, CH_3), 1.93 (q, 4H, CH_2), 2.74 (s, 24H, SCH_3), 4.60–4.99 (m, 16H, CH_2) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ = 11.7, 16.4, 22.7, 25.4, 29.7, 125.2, 132.9, 139.5, 146.6, 146.8, 148.5, 151.2 ppm; ^{77}Se NMR (76 MHz, CDCl_3) δ = 448.5 ppm; UV-vis (CHCl_3) λ_{max} = 765.5 nm; FAB MS (m/z) 1600.13 [M^+].

REFERENCES

1. (a) K. M. Kadish, K. M. Smith, and R. Guilard, *The Porphyrin Handbook* (Academic Press, San Diego, 2003), Vols. 15–20; (b) C. C. Leznoff and A. B. P. Lever, *Phthalocyanines: Properties and Applications* (VCH, New York, 1989–1996), Vols. 1–4.
2. (a) D. Wöhrle, O. Suvorova, R. Gerdes, O. Bartels, L. Lapok, N. Baziakina, S. Makarov, and A. Slodek, *J. Porphyrins Phthalocyanines*, **8**, 1020 (2004); (b) G. de la Torre, P. Vázquez, F. Agulló-López, and T. Torres, *Chem. Rev.*, **104**, 3723 (2004); (c) G. de la Torre, C. G. Claessens, and T. Torres, *Chem. Commun.*, 2000 (2007).
3. (a) A. Morandeira, I. López-Duarte, M. V. Martínez-Díaz, B. O'Regan, C. Shuttle, N. A. Haji-Zainulabidin, T. Torres, E. Palomares, and J. R. Durrant, *J. Am. Chem. Soc.*, **129**, 9250 (2007); (b) L. Matín-Gomis, K. Ohkubo, F. Fernández-Lázaro, S. Fukuzumi, and Á. Sastre-Santos, *Org. Lett.*, **9**, 3441 (2007); (c) B. C. O'Regan, I. López-Duarte, M. V. Martínez-Díaz, A. Forneli, J. Albero, A. Moranderia, E. Palomares, T. Torres, and J. R. Durrant, *J. Am. Chem. Soc.*, **130**, 2906 (2008).
4. (a) M. Barthel, and M. Hanack, *J. Porphyrins Phthalocyanines*, **4**, 635, (2000); (b) M. Barthel, D. Dini, S. Vagin, and M. Hanack, *Eur. J. Org. Chem.*, 3756, (2002).
5. (a) N. Kobayashi and A. Muranaka, *Chem. Commun.*, 1855 (2000); (b) A. Muranaka, M. Okuda, N. Kobayashi, K. Somers, and A. Ceulemans, *J. Am. Chem. Soc.*, **126**, 4596 (2004); (c) A. Muranaka, K. Yoshida, T. Shoji, N. Moriichi, S. Masumoto, T. Kanda, Y. Ohtake, and N. Kobayashi, *Org. Lett.*, **8**, 2447 (2006).
6. T. Kimura, J. Kumasaka, and T. Namauo, *Eur. J. Org. Chem.*, 5079 (2008).
7. (a) T. Kimura, A. Yomogita, T. Matsutani, T. Suzuki, I. Tanaka, Y. Kawai, Y. Takaguchi, T. Wakahara, and T. Akasaka, *J. Org. Chem.*, **69**, 4716 (2004); (b) T. Kimura, T. Suzuki, Y. Takaguchi, A. Yomogita, T. Wakahara, and T. Akasaka, *Eur. J. Org. Chem.*, 1262, (2006); (c) T.

- Kimura, N. Kanota, K. Matsui, I. Tanaka, T. Tsuboi, Y. Takaguchi, A. Yomogita, T. Wakahara, S. Kuwahara, F. Nagatsugi, and T. Akasaka, *Inorg. Chem.*, **47**, 3577 (2008).
8. When sodium methoxide was used in the reaction of bis(2-cyanoethylthio)-3,6-diethylbenzenes instead of CsOH, the deprotection did not complete under the reaction conditions.
 9. The protecting group was removed as 2-cyanoethanol.
 10. N. Nagahora, S. Ogawa, S. Yoshimura, Y. Kawai, and R. Sato, *Bull. Chem. Soc. Jpn.*, **76**, 1043 (2003).