Metallophthalocyanin–ocenes: scandium phthalocyanines with an η5-bound Cp ring

Journal Name

COMMUNICATION

Metallophthalocyanin-ocenes: scandium phthalocyanines with an η^5-bound Cp ring

Rachel H. Platel,[a] Thiago Teixeira Tasso,[b] Wen Zhou,[a] Taniyuki Furuyama,[b] Nagao Kobayashi*[b] and Daniel B. Leznoff*[a]

**A series of new scandium complexes supported by the phthalocyanine (Pc) ligand have been prepared and structurally characterized. Reaction of $ScCl_3$ with phthalonitrile affords a mixture of PcScCl (1) and unreacted $ScCl_3$, which upon addition of $LiCH(SiMe_3)_2$ yields THF-soluble $PcSc(\mu-Cl_2)Li(THF)_2$ (2). Metathesis with NaCp or LiCp* generates $PcSc(\eta^5-C_5H_5)$ and $PcSc(\eta^5-C_5Me_5)$, respectively, which represent the first examples of η^5-Cp metal phthalocyanines where the Cp fragment sandwiches the metal centre.**

Since their discovery in 1934, metal phthalocyanines (MPcs) have received considerable attention. Their intense colour, low solubility and high chemical and thermal stability make them excellent dyes and suitable candidates for a range of materials applications.[1] Late transition-metal Pc chemistry is very well-developed, where the metals generally lie in the hole of the Pc core. Given this position of the metal, the marriage of PcM fragments with the archetypical cyclopentadienyl ligand (Cp) has been limited to utilizing one of their isoindole benzene rings of phthalocyanine[2] or subphthalocyanine[3] to form π-complexes; there are no examples of PcM complexes that form a sandwich-type "sitting-atop" system. In comparison, most porphyrin complexes incorporating MCp-fragments also utilize one of the four pyrrole rings of porphyrins as binding sites;[4] there are only a few examples of "sitting-atop" octaaethylporphyrin,[5] teteraphenylporphyrin,[6] alkylated porphycene,[7] and triarylated corrole complexes[8] with η^5-Cp units bound to the central metal, and these tend to use early-TM centres which usually lie above the plane of the macrocycle. In general, analogous early-transition metal phthalocyanine complexes are greatly under-developed - most focus on Pc_2M systems.[9] For example, there are only a few reported scandium(III) phthalocyanine complexes, including Pc_2Sc-based systems, PcSc(acetate) and a smattering of substituted ScPcX systems.[9, 10] In this communication, we report the first X-ray structure of a PcSc complex and the synthesis, structure, and optical properties of Cp- and pentamethylcyclopentadienyl (Cp*)-scandium sitting-atop Pc complexes - the first "metallophthalocyanin-ocenes".

The synthesis of PcScCl was targeted using an adapted procedure for the synthesis of PcYCl,[11] in which $ScCl_3$ was added to 8 equiv. of phthalonitrile at 180 °C in 1-chloronaphthalene, followed by heating at 260 °C for 6 h (Scheme 1). After filtration, a dark blue powder of PcScCl (1) was obtained in good yield.
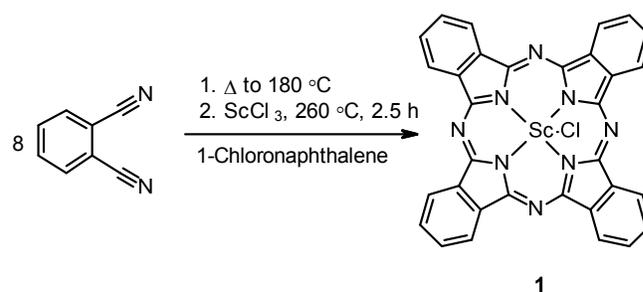
Scheme 1: Synthesis of 1.

The UV-vis spectrum of 1 in THF contains the characteristic absorptions for a PcM complex: a single Q-band at 674 nm and a Soret band at 347 nm. No sign of aggregation was observed in the concentration used for the measurements (4x □ □ □□ □M), as confirmed by the Beer-Lambert plot (Figure S1). Also, the MALDI-TOF MS of 1 shows a strong signal at m/z 592, corresponding to $[PcScCl]^+$. However, 1 was contaminated with approx. 15% of unreacted $ScCl_3$ and the two materials could not be separated due to their inherent

insolubility in most organic solvents. In an effort to obtain a soluble, pure material a THF-suspension of the mixture was treated with 1 equiv. of $LiCH(SiMe_3)_2$; the solubility of the material increased dramatically, yielding a bright turquoise solution. The UV-vis spectrum is identical to that of **1** and the ^1H NMR spectrum of this product (**2**) in THF-d_8 has peaks at δ = 9.53 and 8.24 ppm of equal integration, assigned to the two phthalocyanine ring protons. However, no resonances assignable to a Sc-alkyl moiety were observed; recrystallization from THF/hexanes yielded dark blue/purple crystals, revealing **2** to be $PcSc(\mu\text{-}Cl)_2Li(THF)_2$ (Scheme 2, Figure 1).
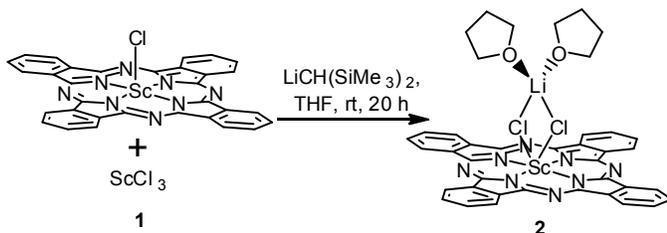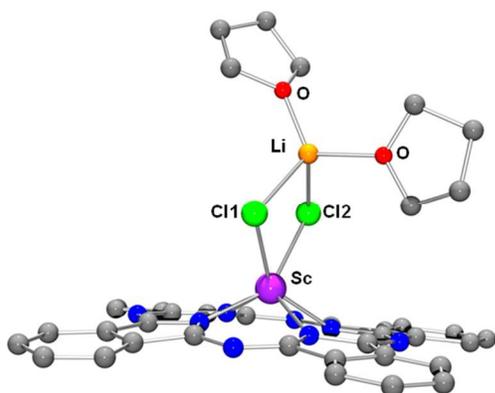
Scheme 2: Synthesis of **2**.

Figure 1: Molecular structure and numbering scheme of **2** (thermal ellipsoids shown at 30% probability). Hydrogen atoms are omitted for clarity. The Pc-N bound to Sc are N1, 3, 5 and 7. Selected bond lengths (Å) and angles (˚): Sc − Cl(1) 2.5330(15), Sc − Cl(2) 2.5293(17), Sc − N(1) 2.164(4), Sc − N(3) 2.177(4), Sc − N(5) 2.159(4), Sc − N(7) 2.192(4).

In the solid-state structure of **2**, the scandium centre is coordinated by the four Pc-nitrogen donors, with two chlorides bound *cis*; these are also bound to a lithium cation. The scandium centre is displaced by 0.93 Å from the mean plane of the Pc-nitrogen donors. The Pc ligand remains reasonably planar, although there is some slight unsymmetrical doming to accommodate the metal, with the side of the molecule containing N(1) and N(7) more distorted than that containing N(3) and N(5). The Sc − Cl bonds of 2.5330(15) and 2.5293(17) Å are comparable to other scandium chloride-lithium chloride adducts, including the 2.557(3) and 2.545(3) Å in $PhC(NSiMe_3)_2Sc(\mu\text{-}Cl)_2Li(TMEDA)$[12] and 2.496(1) and 2.509(1) Å in *rac*-IpSc(µ-Cl)$_2$Li(THF)$_2$[13] (Ip = $Me_2Si\{[C_5H_2\text{-}2,4\text{-}CHMe_2]_2\}$). The $Sc(\mu\text{-}Cl)_2$ core is butterflied, with a Sc − Cl(1) – Li – Cl(2) torsion angle of 14.5 °.

Compound **2** likely arises from the reaction of PcScCl with LiCl, formed *in situ* by the reaction of $LiCH(SiMe_3)_2$ with the residual $ScCl_3$. With this in mind, reaction with other lithium salts ($LiCH_2SiMe_3$, $LiN(SiMe_3)_2$) and with LiCl directly was

attempted. However, with $LiCH_2SiMe_3$, although a small amount of **2** was evident in the ^1H NMR spectrum, the major product was a different, unidentified material. With $LiN(SiMe_3)_2$ the major product was unreacted PcScCl, while with LiCl, no reaction occurred, probably due to the limited solubility of both reactants.

The solubility of **2** in THF opened the door to targeting organometallic-type PcSc complexes; the use of LiCl "ate"-type complexes to form salt-free metal-alkyls has been reported.[14] However, attempts to alkylate **2** using various alkyllithium or Grignard reagents gave mixtures of products that could not be conclusively characterized, but the observation of complex ^1H NMR spectra suggested that deprotonation of the ring-Pc could be occurring. As an alternative approach, protonolysis reactions between PcH_2 and homoleptic scandium $Sc[CH_2SiMe_3]_3(THF)_2$, $Sc[CH(SiMe_3)_2]_3(THF)_2$, $Sc[N(SiMe_3)_2]_3$ and $Sc[O\text{-}2,6\text{-}(CH_3)_2C_6H_3]_3$ complexes were attempted. In all cases, the absorption spectra of the crude reaction mixtures contained only a split Q-band, indicating that no metal-Pc species had been formed.

On the other hand, addition of 1 equiv. of the less basic NaCp or LiCp* in THF gave, after workup, deep blue powders characterized as PcScCp (**3**) and PcScCp* (**4**), respectively (Scheme 3).
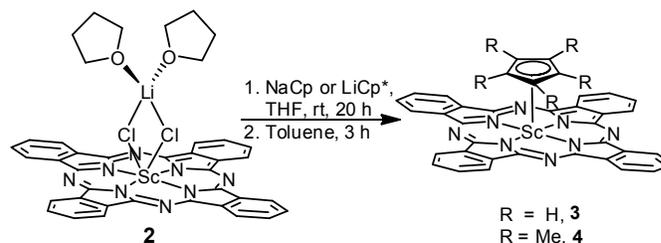
Scheme 3: Synthesis of **3** and **4**.

The ^1H NMR spectra of **3** and **4** in toluene-d_8 are considerably simpler than the spectra of the crude material (prior to workup) in THF-d_8. They both contain two resonances in the aromatic region, assigned to the Pc ring protons. The cyclopentadienyl protons are shifted several ppm upfield compared to their usual ranges; specifically, a singlet at δ 2.63 for the Cp-*H* in **3** and a singlet at δ -0.24 for the Cp-C*H*$_3$ in **4**. This is consistent with these protons being subjected to strong ring currents from the phthalocyanine core; a similar effect was observed in related $(OEP)Sc(\eta^5\text{-}Cp)$ derivatives.[5]
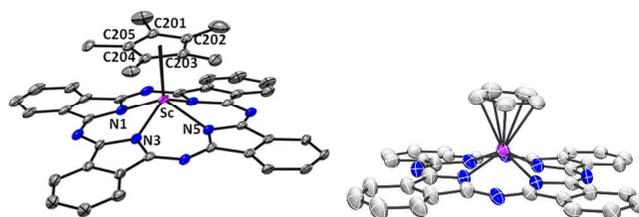
Figure 2: Molecular structures and numbering schemes of **3** (left) and **4** (right); thermal ellipsoids shown at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (˚). Compound **3**: Sc − N$_{av}$ 2.127(7), Sc − C$_{av}$ 2.432(9) to 2.468(9), Sc − Cp$_{centroid}$ 2.144(9) and 2.156(9). Compound **4**: Sc − N$_{av}$ 2.166(4), Sc − C 2.462(5) to 2.495(4), Sc − Cp$_{centroid}$ 2.174(5) and 2.185(5).

Crystals of compounds **3** and **4** were grown from a THF/hexanes mixture. The molecular structures (Figure 2) clearly reveal an η^5-bound Cp-type ligand in both complexes. To our knowledge, these represent the first examples of any PcM-bound Cp where the Cp fragment sandwiches the metal centre to yield "metallophthalocyanin-ocene" complexes, although CpM moieties have been previously ligated to the peripheral rings of Pc and subphthalocyanine molecules.[3]

As in **2**, there is little variation in the Sc – N_{Pc} lengths , with Sc – N distances measuring 2.127(7) (average) and 2.166(4) Å respectively for **3** and **4** (each contains two crystallographically independent, but structurally similar molecules). The Sc centre sits slightly lower in the central core than in **2** at 0.875 Å (**3**) and 0.898 Å (**4**), but are higher than the 0.80 Å in (OEP)ScCp.[3] The Cp and Cp* rings are nearly perfectly η^5-coordinated, with Sc – C distances between 2.432(8) and 2.468(9) Å in **3** and 2.462(5) to 2.495(4) Å in **4**. The Pc ligand domes to accommodate the Sc centre, with two opposite pyrrole rings in **4** angled down by 7.3 ° and 4.7 ° with respect to the N_4-plane; the pyrrole rings containing N(8) are only domed by 1.7 °; similar values are seen in **3**.

In order to probe the electronic structure of this metallophthalocyanin-ocene, the electronic and MCD spectra of **1**, **3**, and **4** were obtained (Figure 3). The Q and Soret bands of PcScCl appear at 674 and 347 nm in THF, respectively. The MCD spectrum shows dispersion-type Faraday *A*-terms corresponding to both peaks, supporting experimentally that the excited state is orbitally degenerate, like a typical monomeric D_{4h} symmetry metalated Pcs. A larger MCD intensity in the Q band than in the Soret band indicates that the angular momentum change in the Q transitions is larger than that in the Soret transitions. In addition, a minus-to-plus MCD sign pattern in ascending energy suggests that the energy difference between the HOMO and HOMO-1 (ΔHOMO) is larger than that between the LUMO and LUMO+1 (ΔLUMO).[15] These absorption features are almost the same as those of more typical PcM complexes (M = Ni, Cu, Zn, *etc*.), indicating that the axial chloride ligand marginally affects the electronic nature of **1**. For **3** and **4**, the sharp Q bands appear at 676 and 678 nm, respectively, shifting slightly to longer wavelength[16] from that of PcScCl, and the dispersion-type Faraday *A* MCD terms were also observed correspondingly in the MCD spectra, suggesting that π coordination to the Sc centre minimally affects the Q band region. Coordination of the Cp ligands, however, produced a slight increase in the absorbance at longer wavelength side of the Soret band. Since the absorption band of Cp appears in the UV region,[17] this increase of absorbance was assigned to a interaction between the phthalocyanine and the Cp ligand.

In order to enhance the interpretation of the electronic absorption spectra, MO calculations were performed for **1** and **3** at the B3LYP/6-31G* level. Calculated stick absorption spectra are attached at the bottom of Figure 3 (and listed in Table S1), and the MO energy levels and iso-surface plots of selected frontier MOs of **3** are shown in Figure 4. The calculated transitions in the Q-band region (619 and 602 nm) are composed of the HOMO, LUMO and LUMO+1, which are localized on the Pc ring and the contribution of the axial ligands was found to be small in these orbitals. In the Soret band region of **3**, four transitions were calculated at 339 and 331 nm. These transitions are complex and assigned mainly from HOMO-4, -9, -10, and -11 to LUMO and LUMO+1 transitions. The HOMO-10 delocalizes in the Pc ring and Sc centre, and the HOMO-9 and HOMO-11 localize in the lone pair of nitrogen atoms at the

meso-position of Pc, whereas the HOMO-4 is an a_{2u}-like orbital derived from Gouterman's "four orbital" theory.[18] The contribution of these four orbitals (HOMO-4, HOMO, LUMO, and LUMO+1) is large in both the Q and Soret band regions, indicating that these bands can be explained as typical metalated Pcs. On the other hand, the weak transition of PcScCp was calculated at 424 nm, though no bands were found in this region of the calculated spectrum of **1**. This band contains transitions from the HOMO-2 and HOMO-1 to LUMO and LUMO+1. The HOMO-2 and HOMO-1 are nearly degenerate and these orbitals are delocalized over both Pc and Cp ligand. Therefore, this calculated transition at 424 nm can be assigned to a charge-transfer (CT) transition from the Cp to the Pc so that the shoulder at the longer wavelength side of the Soret band of **3** appears to show the direct interaction with Cp ligand.
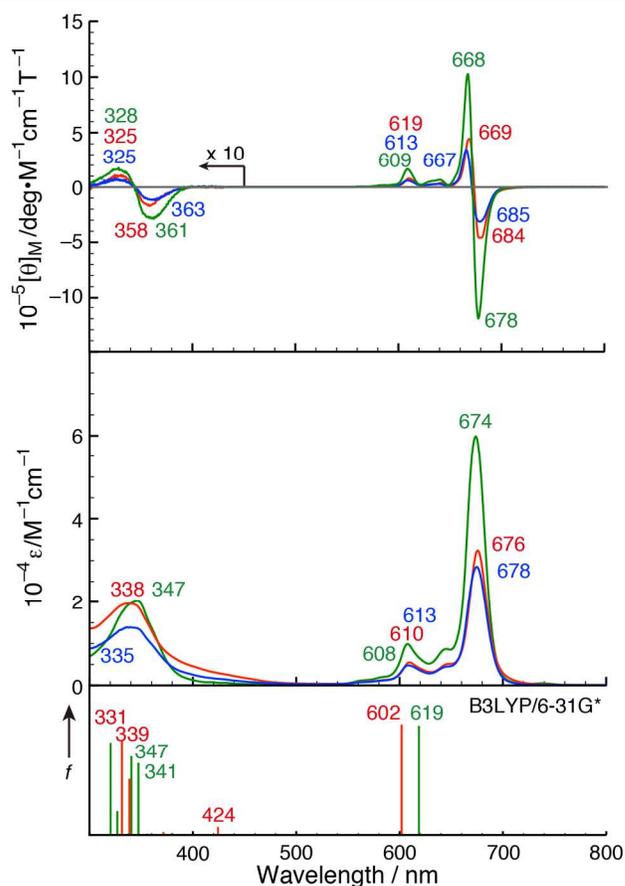

Figure 3. Electronic absorption (middle) and magnetic circular dichroism (top) spectra of **1** (green), **3** (red) and **4** (blue). The concentrations for absorption measurements were ca. 4 x 10⁻⁵ M. In the theoretical absorption spectra (bottom) of **1** and **3**, the solid lines are those calculated by the TD-DFT method.

In summary, we have prepared a series of the first structurally characterized PcScX compounds and the first metallophthalocyanin-ocene complexes (i.e., a PcM complex with an η^5-Cp ligand), thereby merging these two classical types of ligands into one complex. Formation of an axially functionalized LiCl-ate complex dramatically increases the solubility of the starting PcScCl system, allowing further transformations to proceed; this could be a general route to accessing soluble new unsubstituted PcM complexes. In view of the broad applications of PcM complexes and coupled with

the potential for redox activity in the Pc ligand, these molecules open a new avenue for metallophthalocyanine chemistry.
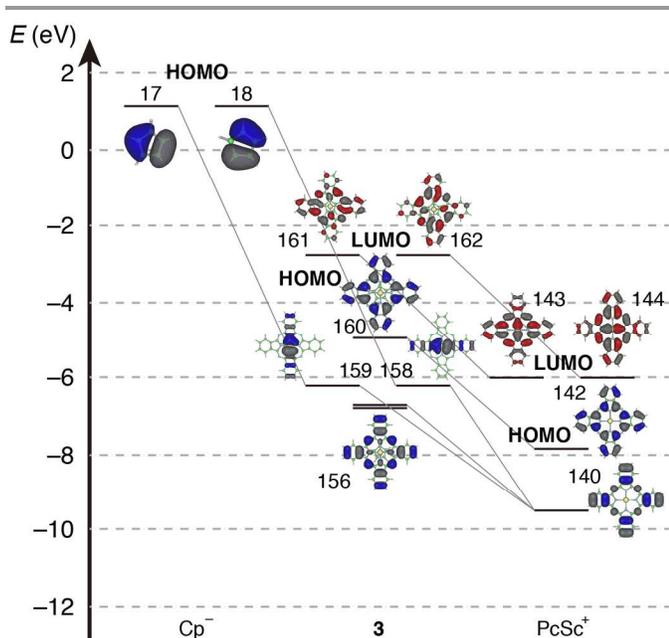

Figure 4. Partial molecular energy diagram and orbitals of PcScCp (**3**), Cp⁻, and PcSc⁺ calculated by B3LYP/6-31G*.

Notes and references

[a] Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, BC, Canada V5A 1S6. E-mail: dleznoff@sfu.ca Tel: +1 778 782 4887

[b] Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan. E-mail: nagaok@m.tohoku.ac.jp; Tel: +81 22 795 7719

† Electronic Supplementary Information (ESI) available: Crystallographic data for **2**, **3** and **4** in cif format (CCDC Deposition # 1038111-1038113, experimental synthetic and characterization details, and table of calculated excitation wavelength and oscillator strength for the components of the Q and Soret bands of **2** and **3**.

1   (a) The Porphyrin Handbook, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego, United States, 2003; (b) Handbook of Porphyrin Science, ed. K. M. Kadish, K. M. Smith and R. Guilard, World Scientific Publishing, Singapore, 2010.

2   S. M. Contakes, S. T. Beatty, K. K. Dailey, T. M. Rauchfuss and D. Fenske, Organometallics 2000, **19**, 4767-4774.

3   E. Caballero, J. Fernandez-Ariza, V. M. Lynch, C. Romero-Nieto, M. S. Rodriguez-Morgade, J. N. Sessler, D. M. Guldi and T. Torres, Angew. Chem. Int. Ed. 2012, **51**, 11337-11342.

4   L. Guesta and J. L. Sessler, Chem. Soc. Rev. 2009, **38**, 2716-2729.

5   J. Arnold and G. C. Hoffman, J. Am. Chem. Soc. 1990, **112**, 8620-8621.

6   H. –J. Kim, S. Jung, Y. M. Jeon, D. Whang and K. Kim, Chem. Commun. **1997**, 2201-2202.

7   L. Guesta, E. Kamas, V. M. Lynch, P. Chen, J. Shen, K. M. Kadish, K. Ohkubo, S. Fukuzumi and J. L. Sessler, J. Am. Chem. Soc. 2009, **131**, 13538-13547.

8   H. L. Buckley, W. A. Chomitz, B. Koszarna, M. Tasior, D. T. Gryko, P. J. Brothers and J. Arnold, Chem. Commun. 2012, **48**, 10766-10768.

9   (a) H. Hückstädt, A. Tutaβ, M. Göldner, U. Cornelissen and H. Homborg, Z. Anorg. Allg. Chem., 2001, **627**, 485-497.

10 L.A. Lapkina, S.G. Sakharov, N.Y. Konstantinov, V.E. Larchenko, Y.G. Gorbunova, A.Y. Tsivadze, Russ. J. Inorg. Chem., 2007, **52**, 1758-1768; I.S. Kirin, P.N. Moskalev, Zh. Noerg. Khim., 1971, **16**, 3179. One reported attempt to prepare PcScCl (**1**), by reaction of phthalonitrile and $ScCl_3$ in refluxing 1-chloronaphthalene for 4 – 6 hr, was deemed unsuccessful due to the exclusive observation of the $[PcH_2]^+$ ion (and no [PcSc]-fragment) in the mass spectrum of the product (I. S. Kirin and N. P. Moskalev, Russ. J. Inorg. Chem. 1971, **16**, 1687-1688); The only reported synthesis has very limited characterization data (K. Varmuza, G. Moresch and A. Meller, Monatsh. Chem. 1974, **105**, 327-333).

11 A. Tutaβ, M. Göldner, H. Hückstädt, U. Cornelissen and H. Homborg, Z. Anorg. Allg. Chem., 2001, **627**, 2323-2336.

12 J. R. Hagadorn and J. Arnold, Organometallics, 1996, **15**, 984-991.

13 J. C. Yoder, M. W. Day and J. E. Bercaw, Organometallics, 1998, **17**, 4946-4958.

14 K. C. Jantunen, F. Haftbaradaran, M. J. Katz, R. J. Batchelor, G. Schatte and D. B. Leznoff, Dalton Trans. 2005, 3083-3091.

15 (a) J. Mack, M. J. Stillman and N. Kobayashi, Coord. Chem. Rev. 2007, **251**, 429-453. (b) N. Kobayashi, A. Muranaka, and J. Mack, Circular Dichroism and Magnetic Circular Dichroism Spectroscopy for Organic Chemists, Royal Society of Chemistry, London, 2011.

16 This slight shift to longer wavelength can be explained as the result of exciton interaction between the Pc ligand and Cp or Cp* ring (N. Kobayashi, A. Muranaka and K. Ishii, Inorg. Chem. 2000, **39**, 2256-2257).

17 L. W. Pickett, E. Paddock and E. Sackter, J. Am. Chem. Soc. 1941, **63**, 1073-1077.

18 M. Gouterman, in The Porphyrins; ed. D. Dolphin, Academic Press, New York, 1978; Vol. III, Part A. p. 1.