[6] UV/Vis (CH_2Cl_2, $-80\,^{\circ}C$) λ_{max} (ε, $[M^{-1}cm^{-1}]$) 414 (14000), 316 nm (13000); EPR (CH_2Cl_2, 9.4 GHz, $-154\,^{\circ}C$): silent; Resonance Raman (frozen CH_2Cl_2 solution, $-154\,^{\circ}C$, $\lambda_{ex} = 457.9$ nm, only ^{18}O-sensitive peaks reported) 600 ($^{18}O_2$: 582, 574) cm^{-1}.

[7] X-ray crystal structure analysis of $[([D_{28}]i Pr_4dtne)Cu_2(\mu\text{-}O)_2](SbF_6)_2 \cdot 3\,CH_2Cl_2$: brown needle ($0.75 \times 0.16 \times 0.16$ mm); $C_{29}H_{34}D_{28}Cl_6Cu_2F_{12}N_6O_2Sb_2$, $M_r = 1366.35$, triclinic, space group $P\bar{1}$, $a = 9.8046(1)$, $b = 14.3591(2)$, $c = 18.4060(2)$ Å, $\alpha = 93.921(1)$, $\beta = 103.611(1)$, $\gamma = 102.646(1)^{\circ}$, $V = 2437.70(5)$ Å^3, $Z = 2$ at 173(2) K; $\rho_{calcd} = 1.864\ g\,cm^{-3}$; $2\theta_{max} = 49.98^{\circ}$; $Mo_{K\alpha}$ radiation. Data were collected using a Siemens SMART system and the structure was solved by direct methods. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed at calculated positions and refined as riding atoms with individual isotropic displacement parameters. Full-matrix least squares refinement on F^2 using SHELXTL V5.0 converged with final $R1 = 0.0544$ and $wR2 = 0.1318$ based on 8216 reflections $[I > 2\sigma(I)]$ and 602 variable parameters (max/min residual electron density 1.207/-0.952 e Å^{-3}). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-133. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. code +(1223) 336-033; e-mail: deposit@chemcrys.cam.ac.uk).

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Synthesis and Structure of the First Molecular Thulium(II) Complex: $[TmI_2(MeOCH_2CH_2OMe)_3]$**

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and William J. Evans*

A significant part of the emerging importance of 4f element chemistry involves complexes in which the lanthanide metal is in the +II oxidation state.[1] For example, $[SmI_2(thf)_x]$ is now a frequently used reducing reagent in organic synthesis,[2] the solvated metallocenes $[(C_5R_5)_2LnL_x]$ (Ln = Sm, Eu, Yb; R = Me, H; L = ethers) display an extensive and often unique organometallic chemistry,[3] the unsolvated metallocenes $[(C_5Me_5)_2Ln]$[4] have stimulated theoretical studies[5] due to their unusual bent structure, and divalent chalcogenide complexes are of interest as precursors to materials with interesting optical, electronic, and magnetic properties.[6]

To date this important divalent 4f element chemistry has involved only three metals, Sm^{II}, Eu^{II}, and Yb^{II}. Divalent ions can be formed for all of the metals in the 4f series by high-temperature reduction of the halides with the metal[7] or by radiolysis of trivalent metal ions trapped in crystalline lattices,[8] but these insoluble and dilute systems are generally only characterized by spectroscopic means. The large reduction potentials[9] (-2.3 to -2.9 V Ln^{III}/Ln^{II}) for 4f elements other than Eu, Yb, and Sm make these other divalent metals difficult to isolate as molecular species. Two exceptions are in the literature $[\{K(monoglyme)\}_2\{(C_8H_8)_2Ce\}]$[10] (monoglyme = diethyleneglycolmonoethyl ether) and $[\{(C_5Me_5)_2NdCl_2\}\{K(thf)_n\}_2]$,[11] but neither of these species have been fully characterized by X-ray crystallography.

We report here the first crystal structure analysis of a molecular complex of a divalent 4f element other than Eu, Sm, and Yb. This was done with thulium, which has the most stable divalent oxidation state after Eu, Yb, and Sm ($Tm^{III}/Tm^{II} = -2.3$ V vs NHE).[9a] The thulium diiodide **1** (dme = dimethoxyethane), was synthesized by reduction of TmI_3 with thulium metal in refluxing DME. Repeated treatment of the solid reactants with DME, followed by removal of DME under vacuum ultimately gave a 54% yield of **1** as an air-sensitive malachite-green crystalline solid. In the solid state and in solution, **1** slowly decomposes at room temperature to give a colorless solid and gaseous products. Decomposition is noticeably accelerated by sunlight which will completely decolorize a 1 mM solution of **1** in one hour.

$[TmI_2(dme)_3]$ **1**

Elemental analysis on **1** was consistent with three DME molecules per TmI_2 unit. This was confirmed by an X-ray crystal structure analysis (Figure 1).[12] The unit cell contains two independent molecules that have similar bonding parameters.

The thulium atom in $[TmI_2(dme)_3]$ (**1**) is seven-coordinate; two DME ligands are chelating and one is monodentate. This is a rare example of a complex containing a monodenate DME

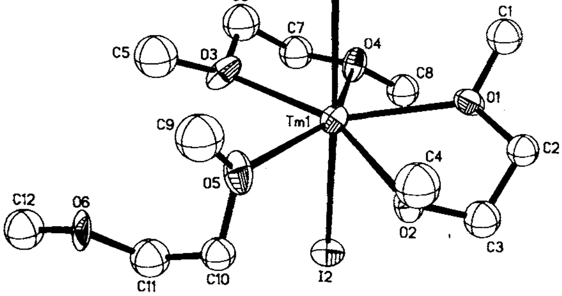

Figure 1. Thermal ellipsoid plot of one of the independent $[TmI_2(dme)_3]$ molecules in the unit cell of **1** (ellipsoids drawn at the 50% probability level). Selected bond lengths [Å] and angles [°]: Tm1–O5 2.47(2), Tm1–O1 2.48(2), Tm1–O2 2.489(14), Tm1–O3 2.50(2), Tm1–O4 2.50(2), Tm1–I1 3.141(2), Tm1–I2 3.186(2); O5-Tm1-O2 73.3(5), O1-Tm1-O2 65.8(5), O5-Tm1-O3 80.1(5), O1-Tm1-O4 75.9(5), O3-Tm1-O4 67.9(5), O5-Tm1-I1 92.3(4), O1-Tm1-I1 83.4(4), O3-Tm1-I1 83.8(4), O4-Tm1-I1 91.8(4), O5-Tm1-I2 91.2(4), O1-Tm1-I2 97.7(4), O2-Tm1-I2 84.6(4), O3-Tm1-I2 91.5(4), O4-Tm1-I2 82.4(4), I1-Tm1-I2 173.68(6).

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ligand.[13] The pentagonal-bipyramidal structure of **1** is similar to those of the solvated divalent samarium diiodide complexes **2**–**4**.[14] In all of these complexes, the halide ligands are in the

$[SmI_2(thf)_5]$ **2** $[SmI_2(dme)(thf)_3]$ **3** $[SmI_2(dme)_2(thf)]$ **4**

axial positions and oxygen donor atoms are at the equatorial sites. The average I-Tm-I angle (174.3(5)°) in **1** is similar to the I-Sm-I angles in **3** and **4** (178.8(1)°). The I-Tm-O angles range from 79.7(4) to 102.8(3)° and thus deviate from the angle expected in a perfect pentagonal bipyramid (90°). The corresponding I-Sm-O angles in **3** and **4** range from 79.2(1) to 100.6(1)°. The range of O-Tm-O angles for adjacent donor atoms (65.8(3)–80.5(5)°) is also similar to the corresponding range of O-Sm-O angles (63.6(1)-80.2(2)°) in **3** and **4**, and differs from the ideal angle of 72° because some of these angles involve a single chelating ligand and some are between ligands.

Previous data[14, 15] suggested that $[LnZ_2(solvate)_x]$ complexes, in which Z is an anionic ligand, favored $x = 5$ and a pentagonal-bipyramidal structure. The structure of **1** strongly supports these findings, since one DME molecule remains monodentate rather than binding as a bidentate ligand to form an eight-coordinate complex. Another alternative which is not observed is a six-coordinate bis(dme) complex.

In comparison with the metal–iodide distances in the samarium(II) complexes **3** and **4**, the average Tm–I distance (3.16(2) Å) in **1** is in the range expected for a Tm^{II} complex. The Sm–I distances in **3** and **4** are 3.231(1)–3.246(1) Å, and the ionic radius of samarium is about 0.13 Å larger than that of thulium.[16] The range of Tm–O distances (2.456(13)–2.546(14) Å) for the two independent molecules in the unit cell is wider than the range observed for Sm^{II}–O(dme) distances (2.595(5)–2.646(4) Å) in **3** and **4**, but again these distances are consistent with the presence of Tm^{II} after the difference in radius (0.13 Å) is taken into consideration.

The Tm^{II}–O distances in **1** are significantly different from the distances found in Tm^{III} complexes. For example, Tm^{III}–O(thf) distances of 2.353(3) and 2.315(3) Å have been reported in eight-coordinate $[(C_8H_8)Tm\{PhC(NSiMe_3)_2\}(thf)]$[17] and five-coordinate $[Tm\{P(SiMe_3)_2\}_3(thf)_2]$,[18] respectively. No Tm^{III}–I distances are available for comparison, but Tm^{III}–Cl distances ranging from 2.585(4) to 2.667(2) Å are found in the eight-coordinate complexes $[TmCl_2(OH_2)_2([12]crown\text{-}4)]Cl$[19] and $[TmCl(terpy)(OH_2)_4]Cl_2 \cdot 3H_2O$ (terpy = 2,2′:6′,2″-terpyridine).[20] Assuming that metal–chloride distances are typically 0.31–0.42 Å shorter than metal–iodide distances,[16, 21] analogous Tm^{III}–I distances would be in the range 2.89–3.09 Å which is substantially shorter than those observed in **1**.

The UV/Vis spectrum of **1** is similar to that of a solution of TmI_2 in THF prepared by heating TmI_3 with thulium metal in a welded tantalum crucible under argon at 800 °C.[22] The measured effective magnetic moment of **1** (4.53 μ_B (293 K)) matches the value of 4.5 μ_B calculated for a $4f^{13}$ electron configuration[23] and found for isoelectronic Yb^{III} complexes.[24] This value differs significantly from Tm^{III} magnetic moments which are typically 7.1–7.5 μ_B.[24]

These data unequivocally establish the existence of a new soluble divalent 4f element system whose chemistry can be explored. The high reactivity of this complex suggests that a rich chemistry can be developed.

Experimental Section

All manipulations were carried out under the exclusion of oxygen and moisture using vacuum line techniques. Thulium filings (6.2 g, 36 mmol), iodine (5.0 g, 19.7 mmol), and DME (20 mL) were stirred for 48 h under vacuum at room temperature. The TmI_3 that precipitated was washed with DME (5 × 70 mL) to remove unconverted iodine. The remaining mixture of Tm and TmI_3 was treated with DME (80 mL), and the mixture was heated to reflux and stirred until the solution turned green (approximately 30–45 minutes). The green solution was decanted from the solid Tm/TmI_3 mixture. DME was transferred from the solution by condensation under vacuum back to the remaining Tm and TmI_3. The mixture was again heated to reflux and stirred until the solution turned green. The operation was repeated six times. Final removal of solvent from the deep green solution by condensation under vacuum at room temperature produced malachite-green crystalline solids which were recrystallized from DME at −10 °C to yield **1** (7.3 g, 54%). X-ray quality crystals were grown from DME at −38 °C. The crystals decompose without melting on heating at 100 °C and are soluble in DME to the extent of 0.1 g mL^{-1}. IR (KBr): $\tilde{\nu}$ = 2929 s, 2879 m, 2829 w, 1453 s, 1409 w, 1364 w, 1284 w, 1239 w, 1189 m, 1095 s, 1055 s, 1030 s, 861 s, 811 w, 547 w, 482 w cm^{-1}. UV/Vis (1.15×10^{-3} M in DME, 20 °C, $\lambda_{max}(\varepsilon)$): 298 (700), 416 (250) , 562 (90), 624 (80) nm. Anal. calcd for $C_{12}H_{30}O_6I_2Tm$: I 36.62, Tm 24.37; found: I 36.28, Tm 23.58. Magnetic susceptibility (293 K) $\chi_M = 8741 \times 10^{-6}$, $\mu_{eff} = 4.5\ \mu_B$.

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[12] **1** crystallizes in the space group $P\bar{1}$ with $a = 13.007(2)$, $b = 14.122(2)$, $c = 14.553(2)$ Å, $\alpha = 109.412(10)$, $\beta = 106.069(10)$, $\gamma = 109.744(13)°$, $V = 2133.0(6)$ Å^3, and $\rho_{calcd} = 2.158$ g cm^{-3} for $Z = 4$ at 158 K. Least squares refinement of the model based on 4368 independent reflections converged to a final $wR2 = 0.1294$. (In comparison for refinement on F, $R1 = 0.0572$ for those 2990 data with $F > 4.0\sigma(F)$). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-146. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. code +(1223) 336-033; e-mail: deposit@chemcrys.cam.ac.uk).

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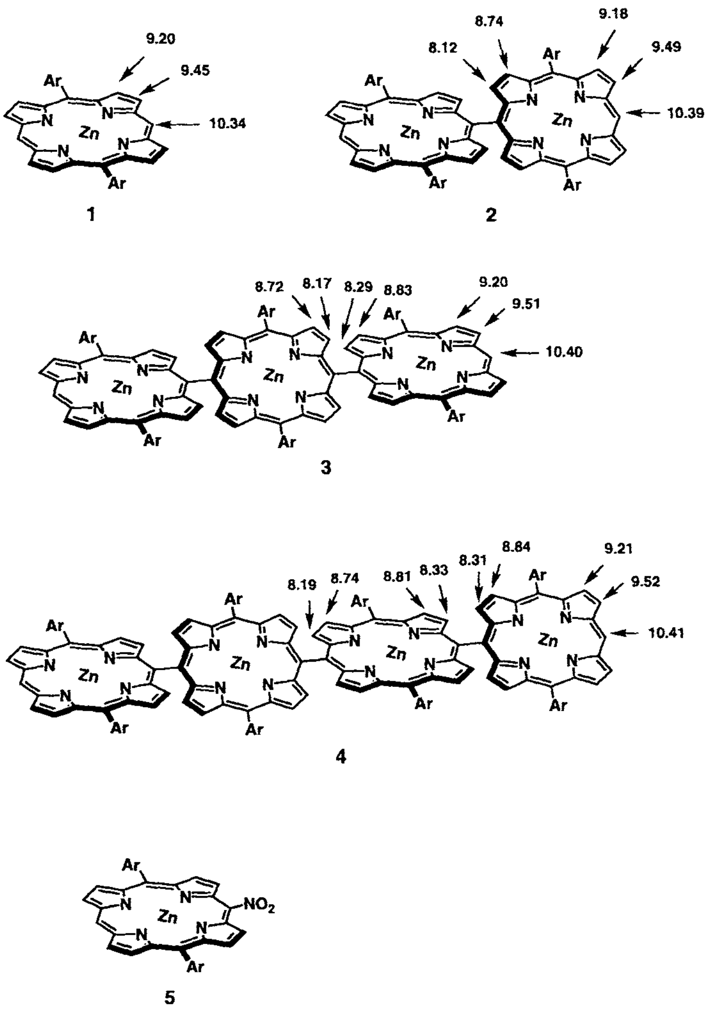
meso,meso-Linked Porphyrin Arrays**

Atsuhiro Osuka* and Hitoshi Shimidzu

Owing to the central importance of multiporphyrin assemblies in photosynthetic reaction centers and light-harvesting antenna complexes, considerable attention has been focused on the development of covalently linked porphyrin arrays as effective biomimetic models. Systematic studies on these models will aid also in the development of new photonic materials and molecular devices.[1-6] In these model studies a variety of bridges that connect porphyrin chromophores have been examined in their abilities to facilitate electron and photon connectivity or to perturb the spectral properties of the porphyrin chromophores. As an extension, a bridgeless, directly coupled porphyrin array may be a fascinating, ultimate candidate for exploring novel connectivity.

Here we report on a novel, very facile oxidative coupling reaction of zinc(II) 5,15-di(3,5-di-*tert*-butylphenyl)porphyrin (**1**) to give porphyrin dimer **2** and porphyrin trimer **3** as the first example of *meso,meso*-coupled multiporphyrins. Treatment of a chloroform solution of **1** with $AgPF_6$ (0.5 equiv) dissolved in acetonitrile for 5 h gave **2** and **3**; NMR analysis revealed the distribution of products: **1** (47%), **2** (27%), and **3** (4%). Although these products were difficult to separate over standard silica gel columns, they were separated by size exclusion chromatography,[7] by which the products are eluted in the order of molecular weight: first, higher oligomers and trace amounts of tetramer **4** > **3** > **2** > **1**. The yields of isolated compounds were 25% for **2** and 4% for **3**, based on the amount of **1** used. Reaction of **2** under analogous conditions (0.5 equiv $AgPF_6$) gave **4** in 23% yield. The regioselectivty of the coupling was quite high.[8]

Compounds **2**-**4** were fully characterized by ^1H NMR spectroscopy (500 MHz) and FAB mass spectrometry. ^1H NMR analysis revealed the presence of one *meso*- and two, four, six, and eight β-protons in **1**-**4**, respectively (Scheme 1). In the spectrum of **2** the signals of the inner β-protons are shifted upfield by $\Delta\delta = 1.33$ and 0.46 ppm relative to those of **1**, reflecting the ring current effect of the second porphyrin ring, while the signals of the outer β-protons appear nearly at the same chemical shifts. Similar features are observed for **3** and **4**. These data, analyzed in terms of the ring current model, suggest an approximate perpendicular arrangement of the neighboring porphyrins.



Scheme 1. Structures of **1**-**5**. NMR chemical shifts of the *meso*- and β-protons ($CDCl_3$) are indicated. Ar = 3,5-tBu$_2$C$_6$H$_3$.

$AgClO_4$ and $AgBF_4$ were similarly effective in this coupling, but the use of $AgNO_2$ led to *meso*-nitration, giving **5** almost quantitatively. The coupling reaction was accelerated by addition of I_2; under these conditions the reaction was complete within 5-10 min.[9] In the I_2-promoted reactions use of one or more equivalents of the Ag^I salt and I_2 led to lower yields of **2** and **3**, under otherwise the same reaction conditions.[10] Most probably, the initial generation of radical cation $\mathbf{1}^{\cdot +}$ followed by nucleophilic attack by a molecule of neutral **1** results in the formation of **2**, in analogy to the related *meso*-substitution reaction of porphyrins.[11] Thus, the nitrite ion traps $\mathbf{1}^{\cdot +}$ to give **5** in the reaction of $AgNO_2$, and an excess of strong oxidant (I_2/Ag^I salt) converts a large portion of **1** to $\mathbf{1}^{\cdot +}$, thereby suppressing the formation of **2**. The concurrent formation of **2** and **3** can be explained by the fact that **1** and **2** have nearly the same oxidation potentials.[12, 13] Consistent with this mechanism, treatment of a chloroform solution of **1** with tris(4-bromophenyl)aminium hexachloroantimonate, a typical one-electron oxidizing agent, provided **2** (8%) and **3** (2%).

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