

Synthesis and Structures of Porphyrin Complexes of Scandium: $\text{ClSc(TTP)} \cdot 2(\text{C}_{10}\text{H}_7\text{Cl})$ and $\text{O[Sc(TTP)]}_2 \cdot 6\text{THF}$

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Abstract

A facile, high yield metallation procedure is reported for the insertion of Sc into $\text{H}_2(\text{TTP})$ (TTP = dianion of *meso*-tetratolylporphyrin) using anhydrous ScCl_3 . Single crystal X-ray structures are reported for $\text{ClSc(TTP)} \cdot 2(\text{C}_{10}\text{H}_7\text{Cl})$ (**1**) and $\text{O[Sc(TTP)]}_2 \cdot 6\text{THF}$ (**2**). Compound **1**: space group $P2_1/c$ with $a = 19.850(17)$, $b = 28.822(24)$, $c = 9.954(9)$ Å, $\beta = 95.71(7)^\circ$, $Z = 4$; 2: space group $P2/n$, $a = 16.952(9)$, $b = 16.737(5)$, $c = 19.93(1)$ Å, $\beta = 112.56(5)^\circ$, $Z = 4$. Compounds **1** and **2** both had large amounts of poorly ordered solvents in the lattice which resulted in rather high R factors in the range of 12–14%. In **1**, the Sc is five-coordinate (4N and 1Cl) and is centered 0.68 Å above the plane defined by the four porphyrin nitrogens. For **2**, the Sc is 0.82 Å from the plane and contains a non-linear μ -oxide bridge with a Sc–O–Sc angle of $109(3)^\circ$, but with essentially coplanar porphyrin rings.

Introduction

The biscyclopentadienide complexes of the early transition elements, such as scandium, are highly reactive and undergo a large variety of reactions [1, 2]. Many of these compounds have two $2e^-$ ligands in addition to the two cyclopentadienide ligands giving electron counts of $16e^-$ for the metal atom. We report here that it is possible to prepare even more electron deficient species using porphyrin ligands in place of the cyclopentadienide ligands. This paper discusses the synthesis and structures of two $10e^-$ species, $\text{ClSc(TTP)} \cdot 2(\text{C}_{10}\text{H}_7\text{Cl})$ (**1**) and $\text{O[Sc(TTP)]}_2 \cdot 6\text{THF}$ (**2**).

In comparison to the porphyrin complexes of transition elements such as Fe and Mn, there is a paucity of data, particularly structural data, for porphyrins containing the early transition metals. Literature is available reporting the synthesis, and at least visible or infrared absorption data, for Sc [3, 5, 6a], Y [4, 5], La [5], Zr [3b, 3c, 5, 6, 7a], Hf [6c, 7] and Ti

[8]. Compounds **1** and **2** are apparently the first structurally characterized Sc porphyrin complexes.

Experimental

All operations were performed in a glove box under a helium atmosphere unless noted otherwise.

Materials

Pyrrole (Lancaster Synthesis) and 1-chloronaphthalene (Aldrich) were distilled under vacuum before use. Toluene (Burdick and Jackson, (B + J)) was distilled from sodium/benzophenone and stored in the glove box. Propionic acid (Lancaster), *p*-tolualdehyde (Lancaster), methanol (B + J), pentane (B + J) and scandium(III) chloride (Cerac) were used as received. *meso*-tetratolylporphyrin, $\text{H}_2(\text{TTP})$, was synthesized and purified according to Adler *et al.* [9].

Physical Measurements

IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer as CsI or KI pellets. Visible absorption spectra were taken of methylene chloride or toluene solutions on either a Hewlett-Packard 8451A, or Perkin-Elmer 330 spectrophotometer.

Scandium Tetratolylporphyrin Chloride, ClSc(TTP)

$\text{H}_2(\text{TTP})$ (1.1 g) and scandium(III) chloride (1 g; 4 equivalents) were added to 1-chloronaphthalene (13 ml) in a Schlenk flask. The flask was sealed with a stopcock adapter, brought out of the box and heated to reflux for 30 min under an N_2 purge**. The mixture turns violet by the end of the reaction, and completion of the reaction is confirmed by the visible absorption spectrum (see Table I). The product mixture is then cooled to room temperature, degassed on the vacuum line, taken back into the glove box and filtered (fine frit). This filtration should be done as soon as the reaction is cooled or the product may begin to precipitate onto the excess ScCl_3 . Upon setting 2–3 h, lustrous purple crystals

**The N_2 purge outlet is bubbled through oil, then water with blue litmus paper in it. A color change to red indicates the reaction is proceeding.

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TABLE I. Absorption Wavelengths (nm) for H₂(TTP), ClSc(TTP) and O[Sc(TTP)]₂^a

Compound	Soret band ^b	500–700 nm region ^b				Relative intensities
		IV	III	II	I	
H ₂ (TTP) ^c	420	515	552	592	649	IV > III > II > I
ClSc(TTP) ^c	422	518	556	596		III > II > IV
O[Sc(TTP)] ₂ ^d	414	516	550	592		III > II > IV

^aThe shape and position of these bands strongly resemble those found for lanthanide, Th and Y complexes [4] as well as other Sc porphyrins [6a]. It has been reported that the μ -oxo species of Sc dissociate largely or totally in solution. Therefore, it is not clear if these spectra are of the binuclear μ -oxo species or of mononuclear porphyrins [6a, 11]. ^bDetermined by λ of peak width/2 at 1/2 height. ^cIn CH₂Cl₂. ^dIn toluene.

TABLE II. IR Frequencies (cm⁻¹) for major peaks^a of H₂(TTP), ClSc(TTP) and O[Sc(TTP)]₂

Compound	
H ₂ (TTP)	3310, 1465, 1350, 1215s, 1180s, 960, 795–775b, 730, 530sh, 520
ClSc(TTP)	1480, 1331s, 1205s, 1182s, 1000s ^b , 800 ^b , 727s, 523s, 417s
μ -oxo-(ScTTP) ₂	1490, 1334s, 1205s, 1185s, 1000s ^b , 800s ^b , 730, 715sh, 525

^aPeaks of >50% relative absorption; s = sharp, b = broad, sh = shoulder. ^bHighest intensity peaks (nearly 100% absorption).

form in the filtrate. The crystals are filtered (coarse frit) washed quickly with 1 ml fresh 1-chloronaphthalene then with pentane (4 × 15 ml). The solid is then dried on the vacuum line. Yield = 800 mg (65% based on H₂(TTP)). IR: strong Sc–Cl peak occurs at 417 cm⁻¹ (see Table II)*.

μ -Oxo-(bis-scandium tetratolylporphyrin), O[Sc(TTP)]₂

A solution of ClSc(TTP) in CH₂Cl₂ (500 mg/4 ml) is filtered (fine frit), taken out of the glove box, and stirred with 1 ml H₂O for 1 min (a purple solid forms). Next, 4 N NaOH (1 ml) and methanol (1 ml) are added and the mixture is allowed to stir overnight. The visible spectrum confirms conversion from the chloride to the μ -oxo dimer (see Table I). The purple solid is then filtered (fine frit) washed with water (3 × 2 ml) and methanol (3 × 2 ml). The solid is then dried on the vacuum line. IR: Sc–O shoulder occurs at 715 cm⁻¹ [5] (see Table II).

X-ray Crystallography

The crystal data for compounds 1 and 2 are summarized in Table III. Both of these compounds contained relatively large amounts of disordered solvate molecules which we were unable to model completely satisfactorily which resulted in rather high final *R* factors.

*Peaks at (in order of decreasing intensity) 770 > 971 > 667 > 830 > 542 cm⁻¹ indicate incomplete removal of 1-chloronaphthalene. If this occurs, repeated trituration in and filtration from pentane (4 × 3 ml for 500 mg product), then drying under vacuum at 80 °C will remove the 1-chloronaphthalene.

C₄₈H₃₆N₄ScCl·2(C₁₀H₇Cl) (1)

Based on the systematic absences of: $0k0: k = 2n + 1$ and $h0l: l = 2n + 1$, as well as the successful refinement of the structure, the space group was determined to be *P*2₁/*c* (#14). The unit cell constants and orientation matrix were obtained from a least-squares refinement of 15 reflections in the range $9.5^\circ < \theta < 11.5^\circ$. The linear absorption coefficient for Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) was 28.1 cm⁻¹ and no absorption correction was made.

The structure was solved by direct methods. The Sc and Cl atoms were refined anisotropically and the remaining non-hydrogen atoms refined isotropically. Hydrogen atoms were not included in the refinement. There were two solvent regions in the lattice which could not be completely resolved. In each site a prominent 1-chloronaphthalene molecule could be located but yielded distorted molecules and non-positive definite atoms upon attempted least-squares refinement. The positional parameters for the most reasonable model were fixed for the final least-squares cycles and the isotropic temperature factors allowed to vary. The largest peak on the final difference map had a height of 0.86 e/ \AA^3 .

C₉₆H₇₂N₈Sc₂O·6THF (2)

Based on a statistical analysis of the intensity distribution, and the successful refinement of the structure, the space group was determined to be *P*2/*n* (#13). Cell constants were obtained from 24 reflections in the range $3^\circ < \theta < 8^\circ$. The absorption coefficient for Mo K α radiation ($\lambda = 0.7107 \text{ \AA}$) was 1.98 cm⁻¹ and no absorption correction was applied.

TABLE III. Crystallographic Data

	1	2
Formula	C ₄₈ H ₃₆ N ₄ ScCl·2(C ₁₀ H ₇ Cl)	C ₄₈ H ₃₆ N ₄ ScO _{0.5} ·3(C ₄ H ₈ O)
Formula weight	1074.5	946.1
<i>a</i> (Å)	19.650(17)	16.97(9)
<i>b</i> (Å)	28.822(24)	16.737(5)
<i>c</i> (Å)	9.954(9)	19.91(1)
β (°)	95.71(7)	112.56(5)
<i>V</i> (Å ³)	5610(9)	5223(9)
<i>Z</i>	4	4
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2/ <i>n</i>
<i>D</i> _{calc} (g cm ⁻³)	1.272	1.20
Radiation, diffractometer	Cu K α , Rigaku AFC 6-R rotating anode	Mo K α , Enraf-Nonius CAD-4
Crystal size (mm)	0.30 × 0.20 × 0.20	0.20 × 0.20 × 0.15
Temperature (°C)	23	-90
Scan mode	ω -2 θ	ω -2 θ
2 θ limits (°)	5-120	5-46
Absorption coefficient (cm ⁻¹)	28.1	1.98
No. reflections collected	6641	7555
No. unique reflections	6041	7258
No. unique data with <i>I</i> > 3 σ (<i>I</i>)	1341	1601
No. variables	316	237
<i>R</i> = $\Sigma(F_o - F_c)/\Sigma F_o $	0.123	0.142
Largest Δ/ρ	0.61	0.03

TABLE IV. Fractional Coordinates for Sc and Proximate Ligand Atoms and *B*_{eq}

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
1				
Sc1	0.2565(4)	0.0028(3)	0.3964(7)	3.6(4)
Cl1	0.1956(6)	0.0183(4)	0.1891(10)	6.6(7)
N1	0.1902(15)	-0.0342(11)	0.5237(28)	3.4(7)
N2	0.2405(14)	0.0597(10)	0.5327(26)	3.1(7)
N3	0.3582(14)	0.0318(10)	0.3921(26)	3.2(8)
N4	0.3093(15)	-0.0632(10)	0.3784(28)	3.1(7)
2				
Sc1	0.2184(4)	0.0344(4)	0.1584(4)	1.8(1)
O1	1/4	-0.038(4)	1/4	1(1)
O2	1/4	0.104(3)	1/4	1(1)
N1	0.309(2)	-0.030(2)	0.122(1)	1.7(6)
N2	0.271(1)	0.138(2)	0.120(1)	1.2(6)
N3	0.097(2)	0.101(2)	0.108(1)	1.8(6)
N4	0.138(2)	-0.065(2)	0.107(1)	2.1(6)

The structure was solved by the Patterson method and the positional and isotropic thermal parameters for the non-hydrogen atoms were refined. Of the three THF solvates in the asymmetric unit, one was ordered and its positional and thermal parameters were refined while the positional parameters for the most reasonable model for the other two THF molecules were fixed and were assigned isotropic thermal

parameters of *B* = 20.0. The hydrogen atoms were not included in the refinement. The largest peak on the final difference map had a height of 0.99 e/Å³ and was located 1.89 Å from the Sc. The *x*, *y* and *z* coordinates for the metals and their proximate ligand atoms are given in Table IV.

Results and Discussion

The synthesis of the scandium chloride complex of tetratolylporphyrin, ClSc(TTP), is easily accomplished by simply heating the free base porphyrin with anhydrous ScCl₃ in 1-chloronaphthalene in an N₂ stream. Upon filtration to remove the excess ScCl₃, the 1-chloronaphthalene solvate, ClSc(TTP)·2(C₁₀H₇Cl) (1) crystallizes from the solution as large purple crystals. These crystals were used directly for the X-ray structure analysis.

The structure of ClSc(TTP) is shown in Fig. 1. The Sc atom is five-coordinate which gives an electron count of only 10e⁻ for the Sc in this complex. The Sc atom assumes a position that is 0.68 Å above the least-squares plane containing the four N atoms. The four Sc-N distances are equal within experimental error at 2.17(3), 2.17(3), 2.18(3) and 2.18(3) Å. The Sc-Cl distance in 1 is 2.32(1) Å which is much shorter than the Sc to bridging Cl distances in solid state compounds like ScCl (2.591 Å) [12], Sc₅Cl₈ (2.53 to 2.67 Å) [13], ScCl₃ (2.58 Å) [14] or

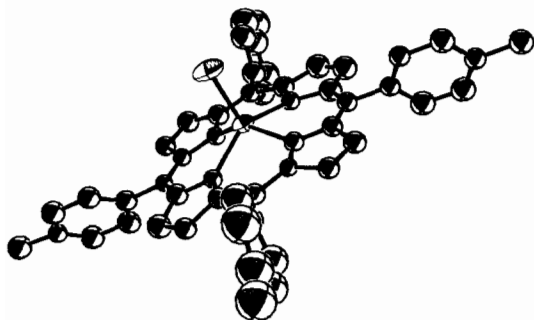


Fig. 1. Structure of 1.

$[(C_5H_5)_2ScCl)_2$ (2.575 Å) [15]. The Sc–Cl distance in **1** is also shorter than the terminal Sc–Cl distances in $(THF)_3ScCl_3$ (avg. = 2.41 Å) [16]. The four Cl–Sc–N angles are equal within experimental error at $107.6(8)^\circ$, $108.4(8)^\circ$, $107.6(8)^\circ$ and $109.0(8)^\circ$ giving the Sc atom a square pyramidal geometry which to our knowledge, has not been observed previously.

The $ClSc(TTP)$ molecule apparently maintains the square pyramidal geometry in solution as the 1H NMR spectrum shows the four protons on the phenyl rings to be inequivalent. The 1H NMR spectrum of $ClSc(TTP)$ is markedly different in THF *versus* benzene solution. The spectrum recorded in C_6D_6 displays resonances at δ 2.41 (s, toluene methyls), 7.30, 7.96 and 8.04 (m, phenyl), and 9.16 ppm (s, β -pyrrole). The spectrum recorded in $THF-d_6$, however, displays resonances at δ 2.68 (s, toluene methyl), 7.57, 8.00, 8.21 (m, phenyl) and 8.91 ppm (s, β -pyrrole). The significant chemical shift differences observed in this case may be an indication that THF is coordinating to the scandium.

The reaction of $Li[C_5(CH_3)_5]$ with $ClSc(TTP)$ was briefly investigated by 1H NMR spectroscopy. When a purple solution of $ClSc(TTP)$ in THF is treated with one equivalent of $Li[C_5(CH_3)_5]$, the solution turns orange and a solid separates from solution. Filtration and redissolution of the sparingly soluble solid in toluene- d_8 gave an orange solution and a 1H NMR spectrum consistent with $[(C_5(CH_3)_5)Sc(TTP)]$. The 1H NMR spectrum of $[C_5(CH_3)_5]Sc(TTP)$ displays porphyrin resonances at δ 2.46 (s, toluene methyl), δ 7.25, 7.45, 7.78 and 8.60 (all d, $J_{H,H} = 8$ Hz, phenyl) and δ 9.00 ppm (s, β -pyrrole). The $C_5(CH_3)_5$ resonance is found at δ -0.42 ppm, a chemical shift approximately 2 ppm to higher field than would be expected for a $C_5(CH_3)_5$ -Sc complex. Presumably, this chemical shift is due to $C_5(CH_3)_5$ methyl experiencing the porphyrin ring current inducing a higher degree of shielding and thus a higher field chemical shift.

When a sample of the material formulated above as $[C_5(CH_3)_5]Sc(TTP)$ was recrystallized from boiling THF/toluene, large red crystals separated from the solution upon cooling. The single crystal X-ray struc-

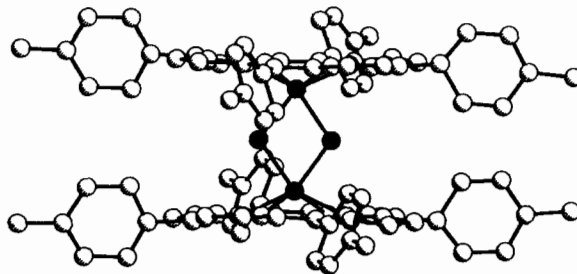


Fig. 2. Structure of 2.

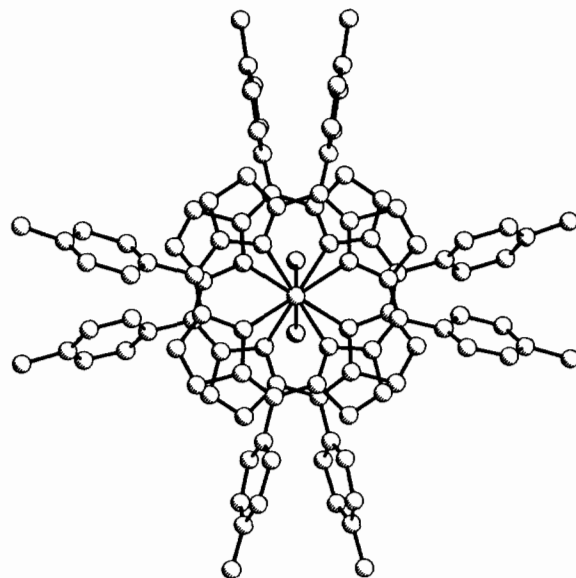


Fig. 3. Structure of 2 viewed down the Sc–Sc vectors.

ture of this material was determined but this analysis showed that the crystals were not $[C_5(CH_3)_5]Sc(TTP)$ but instead a μ -oxo bridged Sc porphyrin dimer, $O[Sc(TTP)]_2 \cdot 6THF$ (**2**). The source of the O atom is not known but possibilities include the THF solvent or traces of adventitious water.

The structure of $O[Sc(TTP)]_2 \cdot 6THF$ is shown in Fig. 2. Figure 3 shows the structure viewed down the Sc–Sc vector. The bridging oxygen is symmetrically disordered over two sites at 50% occupancy for each site as shown in Fig. 2. The two oxygen sites both lie on a crystallographic two-fold axis which relates the two halves of the dimer. As in **1**, the Sc atoms are above the least-squares plane of the four porphyrin nitrogen atoms, in this case by 0.82 Å. The four Sc–N distances are equivalent within the rather large experimental errors for this structure at 2.15(3), 2.21(3), 2.21(3) and 2.21(3) Å which are similar to Sc–N distances in $ClSc(TTP)$ (**1**). The distance between the Sc atom and the two oxygen atom positions are equal within experimental error at 2.06(3) and 2.09(3) Å. Unlike the nearly linear oxide bridge in $O[Fe(TPP)]_2$ (175°) [17] the μ -oxide bridge in **2**

has a tetrahedral angle about the oxygen (Sc—O—Sc = 109(3)° and 111(3)° for the two half O atom positions). The bis- μ -oxide of Zr(TTP) also has non-linear oxide bridges [18].

Conclusions

Free base tetraarylporphyrins are easily metallated with ScCl₃ in high yield in refluxing 1-chloronaphthalene to give the five-coordinate, square pyramidal ClSc(TTP) complex with a very short Sc—Cl bond. The μ -oxide of Sc(TTP) has a non-linear oxide bridge and both compounds contain Sc coordinated above the plane of the porphyrin rings.

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