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Structure and Characterization of the First Metal Complex of Dithiaporphyrin: $Ru(S_2TTP)Cl_2$

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Introduction

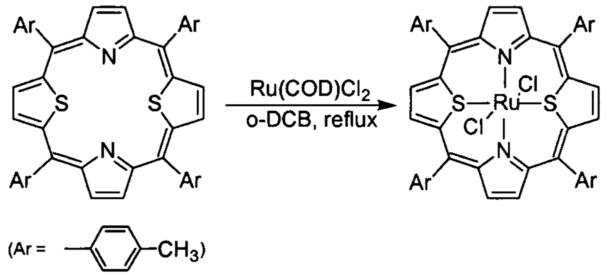
Core-modified porphyrins have one or more internal nitrogens substituted with other heteroatoms.[1] These compounds exhibit special electronic structures and different core geometries. It has been demonstrated that core-modified porphyrins can stabilize unusual metal oxidation states.[2] Core-modified porphyrins also provide a systematic way to explore the effects of core size and ring distortion on the metal affinity. Recently, the nickel thiaporphyrin complex has been applied to model cofactor F_{430}.[3] The most recent report demonstrated that, with red-shifted Q bands, dithiaporphyrin and diselenaporphyrin are better photosensitizers for photodynamic therapy than tetraphenylporphyrin.[4]

The synthesis and characterization of core-modified porphyrins are well documented in the literature pioneered by Broadhurst, Grigg, and Johnson[5] in 1971; however, limited information is available for the preparation of metal complexes of disubstituted heteroporphyrins, in particularly, dithiaporphyrin.[6] The weaker coordinating ability of the thiophene moiety and smaller core size are considered to hinder the formation of dithiaporphyrin complexes. Inspired by recent progress[7] on the coordination chemistry of core-modified porphyrins, we have explored suitable conditions for the preparation of a dithiaporphyrin metal complex. Here we report on the air stable ruthenium dithiaporphyrin complex, $Ru(S_2TTP)Cl_2$.

Results and Discussion

When dithiaporphyrin was reacted with 5 equiv of Ru(COD)Cl_2 in *o*-dichlorobenzene at reflux, the dithiaporphyrin complex, $Ru(S_2TTP)Cl_2{\cdot}2CH_2Cl_2$ (**1**), was isolated as a black solid after recrystallization from CH_2Cl_2/hexanes (yield 52%) (Scheme 1). Using Ru(COD)Cl_2 as the metal source is essential as other widely used starting materials, such as triruthenium dodecacarbonyl,[8] failed to produce the desired product. Compound **1** is air stable in solid form and solution. It has good solubility in CH_2Cl_2 and moderate solubility in toluene. A porphyrin-type UV−vis spectrum is found (Figure S1 in Supporting Information), with a maximum Soret band at 468 nm, which is red-shifted 32 nm compared with 436 nm[9] for the free base S_2TTP. The Q bands at 563, 594, and 810 nm are also significantly red-shifted compared with the free base. The bathochromic shift might be a reflection of the dithiaporphyrin ring distortion during the metalation.

Scheme 1



The ^1H NMR spectrum in $CDCl_3$ gives broad resonances at room temperature (Figure 1A) and indicates that the rotations of the tolyl groups are facile. The sharp singlet peaks at 8.51 and 7.48 ppm at 298 K are assigned as β-thiophenic and β-pyrrolic protons, respectively. This pattern is consistent with one pyrrole and one thiophene resonance from the effective symmetry, D_{2h}. The symmetrically equivalent meso tolyl rings give broad resonances at 8.12, 7.48, 7.29, and 7.28 ppm at room temperature and resolve into four doublets upon cooling to 223 K (Figure 1B). The temperature dependent ^1H NMR spectra suggest that at room temperature the tolyl groups are at dynamic exchange processes while at low temperature the rotation of the tolyl groups are slow so that all resonances are narrow. A similar phenomenon was reported in the ^1H NMR spectra of a thiaporphyrin palladium complex, Pd^{II}(SDPDTP)Cl[10] (SDPDTP: 5,10-diphenyl-15,20-ditolyl-21-thiaporphyrin). The ease of rotation of the phenyl rings could be ascribed to the tilting of the thiophene rings.

Compound **1** crystallized in the centrosymmetric triclinic space group *P*−1, with two molecules and four solvated CH_2Cl_2 in the unit cell. Both ruthenium atoms sit at special positions and generate half of the molecule from symmetry. The ORTEP representation of an independent molecule of **1** is shown in Figure 2A, while the important bond lengths and angles are presented in Table 1.

Both thiophenes coordinate to ruthenium in a pyramidal side-on fashion (Figure 2B). The geometry of sulfur resembles those of the thiaporphyrin and η^1-thiophene complexes. The bond distance of 2.251(1) Å for the Ru(1)−S(1) bond is slightly shorter than an average of 2.367 Å for ruthenium thiophene

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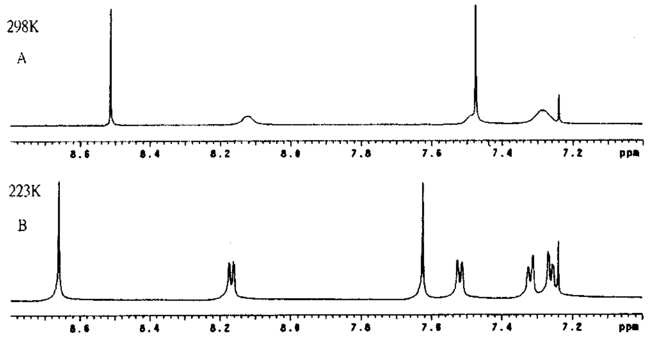

Figure 1. Room temperature (A) and 223 K (B) ^{1}H NMR spectra of Ru(S$_2$TTP)Cl$_2$.

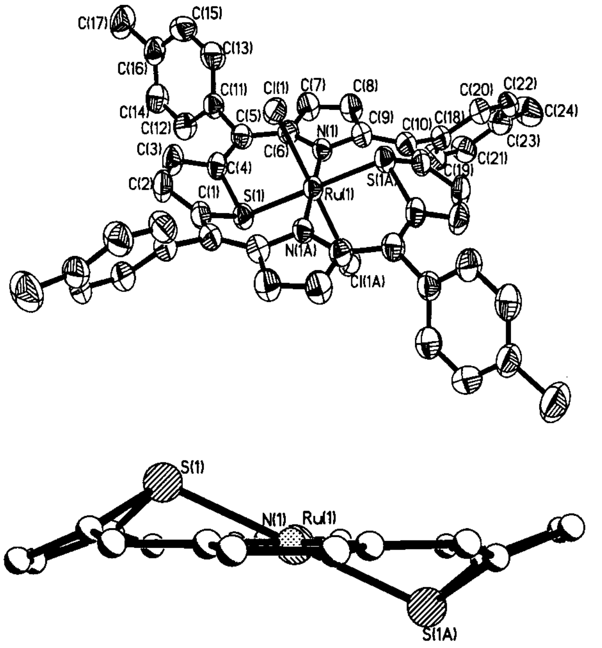

Figure 2. (A) ORTEP diagram (50% probability) for one of the two independent molecules (molecule Ru(1)) in the solid-state structure of Ru(S$_2$TTP)Cl$_2$. (B) Side view of molecule Ru(1) in the solid-state structure of Ru(S$_2$TTP)Cl$_2$ (tolyl groups and hydrogens were omitted for clarity).

Table 1. Selected Bond Distances (Å) and Angles (deg) for Ru(S$_2$TTP)Cl$_2$·2CH$_2$Cl$_2$

Bond Lengths (Å)			
Ru(1)−N(1)	2.082(3)	Ru(1)−Cl(1)	2.3993(11)
Ru(1)−S(1)	2.2506(10)	S(1)−C(4)	1.750(5)
S(1)−C(1)	1.755(4)	N(1)−C(6)	1.394(5)
Bond Angles (deg)			
N(1)−Ru(1)−Cl(1)	88.49(9)	S(1)−Ru(1)−Cl(1)	89.25(4)
N(1)−Ru(1)−S(1A)	89.78(9)	N(1)−Ru(1)−S(1)	90.22(9)
C(4)−S(1)−C(1)	91.8(2)	C(4)−S(1)−Ru(1)	108.07(14)
C(1)−S(1)−Ru(1)	108.21(14)	C(9)−N(1)−C(6)	106.6(3)
C(9)−N(1)−Ru(1)	127.3(3)	C(6)−N(1)−Ru(1)	125.9(3)

complexes,[11] but this is comparable to the corresponding distances in the palladium[10] (2.208(5) Å) or rhodium thiaporphyrin complex[12] (2.232(3) Å). The bond distances of Ru(1)−N(1) 2.082(3) Å and Ru(1)−Cl(1) 2.399(1) Å are both in the ranges of normal Ru(II) porphyrin complexes.[13]

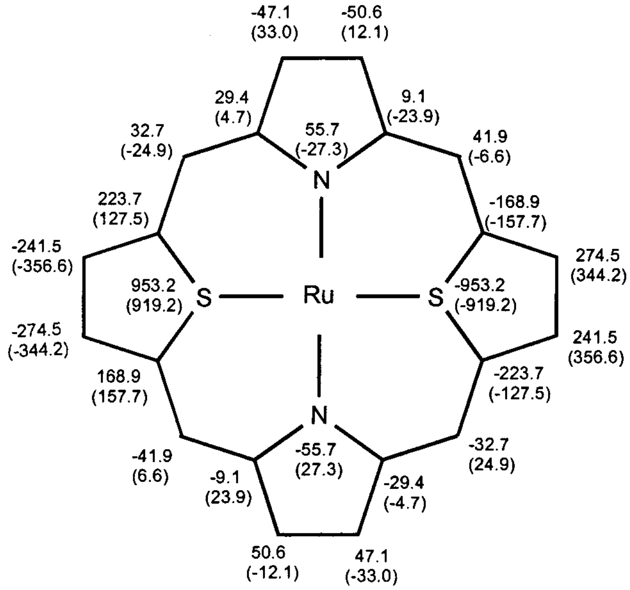

Figure 3. Deviation of atoms (in 0.001 Å) of molecule Ru(1) from the mean plane in the crystal structure of Ru(S$_2$TTP)Cl$_2$. The deviations of the second independent molecule, Ru(2), are placed in parentheses.

To accommodate ruthenium in a small dithiaporphyrin core, compound **1** displays a severely distorted dithiaporphyrin ring with two thiophene rings tilted away from the mean porphyrin plane. The distances and angles around the dithiaporphyrin core are close to the literature values for a free base dithiaporphyrin[14] and reflect that the ring distortion does not significantly affect the conjugate system of the dithiaporphyrin core. The deviation of atoms from the mean plane defined by two pyrrolic rings and four methine carbons is shown in Figure 3. The pyrrole rings are planar with mean deviation of 0.038 Å, which is much smaller than the mean deviation of 0.373 Å found for the thiophene rings. Interestingly, the α carbons of the thiophene rings deviate 0.17 and 0.22 Å from the mean plane, which might be attributed to the steric constrains from the axial ligands. The thiophene rings are not planar, with a dihedral angle of 12.7° between the planes C(1)−C(2)−C(3)−C(4) and C(1)−S(1)−C(4). The angle between plane C(1)−S(1)−C(4) and the Ru−S(1) bond is 116.6°, and the sulfur atom deviates 0.95 Å from the mean plane. The chlorides tilt 26° from the normal of the mean plane, leaning toward thiophene rings. The ruthenium metal sits in the mean plane with a regular octahedral coordinating geometry.

The cyclic voltammogram of compound **1** in methylene chloride is shown in Figure S2 in Supporting Information. One oxidation and two reduction steps are visible at potentials varying between +1.0 and −1.4 V. The free base S$_2$TPP was reported to have an oxidation potential at 1.18 V and two reduction potentials at −0.94 and −1.21 V.[15] Although metals may attenuate the redox potentials through the inductive effect, the first oxidation potential of 0.35 V and the first reduction potential of −0.71 V are located in a range not accessible for dithiaporphyrin centered process and are assigned to be the metal based Ru(II)/Ru(III) and Ru(II)/Ru(I) couple, respectively. Further spectroelectrochemical studies are required to understand the origination of the second reduction potential in compound **1**. However, the potential of −1.09 V is close to the first

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(11) The average of eight complexes found in the Cambridge Structural Database.

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reduction potential of dithiaporphyrin, and the process is temporarily assigned as the formation of the dithiaporphyrin anionic radical.

Ruthenium porphyrins are widely used as alternatives for iron porphyrins to model biological systems.[16] They also play important roles as catalysts in the area of small molecular catalysis.[17] The availability of the dithiaporphyrin complex provides a new direction in exploring ruthenium porphyrin chemistry. We have found that other five or six coordinated complexes can be prepared using compound **1** as the starting material. The unique chemistry of dithiaporphyrin complexes is currently under intensive study.

Experimental Section

Manipulations, reactions, and transfers of samples were conducted under nitrogen according to standard Schlenk techniques. For inert-atmosphere operation, solvents were dried, distilled, and degassed using standard techniques.[18] Pyrrole was freshly distilled from calcium hydride before use. Otherwise, all starting materials were obtained commercially and used without further purification. UV−vis spectra were recorded on a Hewlett−Packard 8453 spectrophotometer. Infrared spectra were recorded using KBr pellets on a Bio-Rad Model FTS-185 spectrophotometer. All cyclic voltammetric experiments were performed with a BAS-100W potentiostat. The cell consisted of a platinum bottom working electrode, a platinum wire auxiliary electrode, and a Ag/AgNO$_3$/CH$_3$CN reference electrode, with 0.1 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte in dichloromethane. The reported potential values are referenced to the SCE using the internal ferrocene/ferrocenium couple (0.22 V versus SCE) as the calibrator. ^{1}H NMR spectra were obtained on a Varian Unity Inova-600 spectrometer, while the ^{13}C NMR spectra were recorded on a Bruker Model AC 200 spectrometer. Analyses of carbon, hydrogen, and nitrogen were obtained with a CHN analyzer (Heraeus).

2,5-bis(tolylhydroxymethyl)thiophene,[19] tetratolyl-21,23-dithiaporphyrin[9] (S$_2$TTP), and di-μ-dichloro(η^4-1,5-cyclooctadiene)ruthenium-(II)[20] (Ru(COD)Cl$_2$) were prepared according to the methods reported in the literature.

Dichloro(*meso*-tetra-*p*-tolyl-21,23-dithiaporphyrinato) Ruthenium-(II), Ru(S$_2$TTP)Cl$_2$ (1). A 250 mL Schlenk flask fitted with a condenser was charged with Ru(COD)Cl$_2$ (397 mg, 1.42 mmol) and tetratolyl-21,23-dithiaporphyrin (200 mg, 0.284 mmol) in 50 mL of *o*-dichlorobenzene. The solution was degassed with nitrogen for 30 min and then heated at reflux under nitrogen. The reaction progress was monitored using UV−vis spectroscopy. After 5 h, the solution was cooled to room temperature and filtered through Celite. The solvent was removed under vacuum. The crude material was redissolved in a minimum amount of dichloromethane. The solution was purified by passing it through a patch of silica gel eluted with CH$_2$Cl$_2$/hexane (4:1). The brown solution was collected, concentrated to dryness, and then recrystallized from CH$_2$Cl$_2$/hexane to afford compound **1** as a black crystalline solid (0.126 g, 52%). ^{1}H NMR (600 MHz, 25 °C, CDCl$_3$, ppm): 8.51 (s, 4H, H_β), 8.12 (broad, 4H), 7.48 (broad, 4H), 7.48 (s, 4H, H_β), 7.29 (broad, 4H), 7.28 (broad, 4H), 2.53 (s, 16H, CH$_3$). ^{13}C NMR (50 MHz, 25 °C, CDCl$_3$, ppm): 164.0, 161.8, 145.4, 139.8, 139.6, 137.4, 135.2, 133.2, 129.4, 22.1. UV−vis (CH$_2$Cl$_2$) $\lambda_{\max}$ nm (log ϵ): 353 (4.46), 435 (4.56, sh), 468 (Soret) (4.75), 563 (4.00, sh), 594 (4.04), 810 (3.80). Elemental Anal. Calcd. (found) for RuC$_{48}$H$_{36}$N$_2$S$_2$Cl$_2$·0.6CH$_2$Cl$_2$: C, 62.91 (62.15); H, 4.01 (4.25); N, 3.02 (3.42). Crystals suitable for single-crystal X-ray diffraction were obtained by vapor phase diffusion of a dichloromethane/hexane solution.

Table 2. Crystallographic Data of Ru(S$_2$TTP)Cl$_2$·2CH$_2$Cl$_2$

	1
empirical formula	C$_{50}$H$_{40}$Cl$_6$N$_2$RuS$_2$
fw	1046.73
cryst syst	triclinic
space group	$P-1$
λ, Å (Mo, Ká)	0.71073
a, Å	11.1025(9)
b, Å	15.1884(12)
c, Å	15.3086(13)
α, deg	86.326(2)
β, deg	71.225(2)
λ, deg	73.912(2)
V, Å^3	2347.5(3)
Z	2
d_{calcd}, g cm^{-1}	1.481
μ, mm^{-1}	0.802
T, K	293(2)
R	0.0510^a
R_{WF}^2	0.1170^b
GOF	1.031

^{a} $R = \sum|(F_o - F_c)|/\sum F_o$. ^{b} $R_{\text{WF}}^2 = \{\sum w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]\}^{1/2}$.

Crystallography. The crystallographic data of compound **1** is summarized in Table 2 and in the Supporting Information. The crystal of compound **1** chosen for X-ray diffraction studies measured 0.48 × 0.10 × 0.07 mm. The crystal was mounted onto a glass fiber. Diffraction measurements were carried out at 295(2) K on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å) and θ between 1.40 and 27.55°. Least-squares refinement of the positional and anisotropic thermal parameters for the contribution of all non-hydrogen atoms and fixed hydrogen atoms was based on F^2. A SADABS[21] absorption correction was made. The SHELXTL[22] structural refinement program was employed.

Acknowledgment. We thank the National Science Council (Taiwan) for support of this work.

Supporting Information Available: X-ray crystallographic file, UV−vis spectrum, and cyclic voltammogram of Ru(S$_2$TTP)Cl$_2$ (CIF and PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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