

# Synthesis and Crystal Structure of the Rhenium(I) Tricarbonyl Complex of 5,10,15,20-Tetra-*p*-tolyl-21,23-dithiaporphyrin

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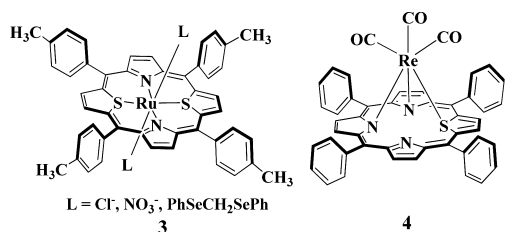
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## Supporting Information

**ABSTRACT:** The hexacoordinated rhenium(I) complex of 5,10,15,20-tetra-*p*-tolyl-21,23-dithiaporphyrin was synthesized, and the crystal structure analysis revealed the unusual binding mode of rhenium(I) to two thiophene sulfur atoms and one of the pyrrole nitrogen atoms of the porphyrin macrocycle.

Thiaporphyrins such as 5,10,15,20-tetra-*p*-tolyl-21-monothiaporphyrin (**1**; STTPH) and 5,10,15,20-tetra-*p*-tolyl-21,23-dithiaporphyrin (**2**; S<sub>2</sub>TTP) resulting from the replacement of one and two pyrrole ring(s), respectively, of the regular porphyrins (N<sub>4</sub> core) with thiophene(s) possess very interesting properties in terms of both their aromatic character and their ability to bind metal ions.<sup>1</sup> Porphyrins are versatile coordinating ligands and form complexes with almost all metals in the periodic table. On the other hand, thiaporphyrins have limited coordinating ability for the following reasons: (1) the presence of a large sulfur atom shrinks the core size of thiaporphyrins, and 21,23-dithiaporphyrin has a smaller core size than 21-monothiaporphyrin; (2) the thiophene sulfur atom has poor coordinating ability in thiaporphyrins.<sup>2</sup> A perusal of the literature reveals that so far there are only nine metal complexes of 21-thiaporphyrin<sup>3,4</sup> and only one metal complex of 21,23-dithiaporphyrin<sup>5</sup> was reported in the literature. Thus, 21,23-dithiaporphyrin does not prefer to form a metal complex like 21-thiaporphyrin. However, Hung and co-workers successfully synthesized a neutral hexacoordinated ruthenium(II) complex of S<sub>2</sub>TTP having two Cl<sup>-</sup> (**3a**) or two NO<sub>3</sub><sup>-</sup> (**3b**) ions as axial ligands as well as a novel unprecedented ruthenium(0) complex of S<sub>2</sub>TTP having two bis(phenylseleno) methanes (**3c**) as axial ligands.<sup>5</sup> Recently, we succeeded in preparing the Re(CO)<sub>3</sub> complex of *meso*-5,10,15,20-tetraphenyl-21-monothiaporphyrin (**4**; Chart 1), and crystal structure analysis showed that Re(CO)<sub>3</sub> binds to two pyrrole nitrogen atoms and one thiophene sulfur

## Chart 1

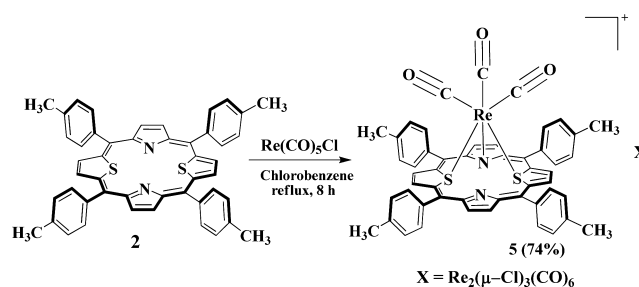


atom<sup>4a</sup> instead of three pyrrole nitrogen atoms, which it generally prefers, as established in the literature with porphyrins.<sup>4b-c</sup>

This inspired us to test rhenium(I) insertion into 21,23-dithiaporphyrin. We continuously tried over a period of time to synthesize the Re(CO)<sub>3</sub> complex of S<sub>2</sub>TTP (**5**) by changing metal precursors and reaction conditions. Unlike 21-thiaporphyrin, which has one ionizable proton to form the rhenium(I) complex, 21,23-dithiaporphyrin does not have an ionizable proton to readily bind the rhenium(I) ion. When we attempted to synthesize **5** by refluxing S<sub>2</sub>TTP with Re(CO)<sub>5</sub>Cl in 1,2-dichlorobenzene, the reaction worked but the yield was very poor because of arduous purification. We screened various reaction conditions, and here we report our successful method for the synthesis of **5** under slightly modified reaction conditions. The crystal structure obtained for **5** showed that Re(CO)<sub>3</sub> binds to two thiophene sulfur atoms and one pyrrole nitrogen atom and the macrocycle is highly distorted. This is the first example where two thiophene sulfur atoms and one pyrrole nitrogen atom of the 21,23-dithiaporphyrin ring is areinvolved in binding with the metal ion.

The reaction of S<sub>2</sub>TTP with 1.1 equiv of Re(CO)<sub>5</sub>Cl in chlorobenzene at reflux temperature for 8 h resulted in precipitation of the desired complex **5** (Scheme 1). The crude

## Scheme 1. Synthesis of Compound 5



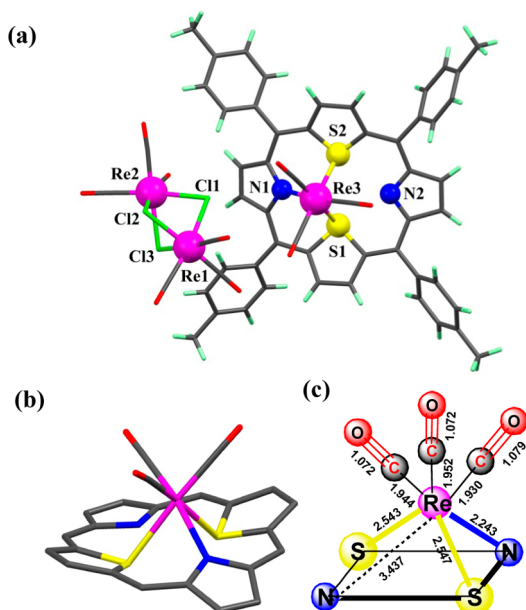
solid was washed several times with a mixture of CH<sub>2</sub>Cl<sub>2</sub> and petroleum ether (1:1) and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/*n*-pentane to afford the desired complex **5** as green crystals in 74% yield. High-resolution mass spectrometry analysis showed a molecular ion peak at *m/z* 976.1798 [(M + 1)<sup>+</sup>], which indicated the formation of **5**.

Coordination of a rhenium(I) ion with 21,23-dithiaporphyrin in **5** was unambiguously confirmed by single-crystal X-ray crystallography. Compound **5** was crystallized via slow diffusion

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of *n*-pentane into dichloromethane for over a period of 2 days. The crystal structure of **5** is shown in Figure 1 along with the



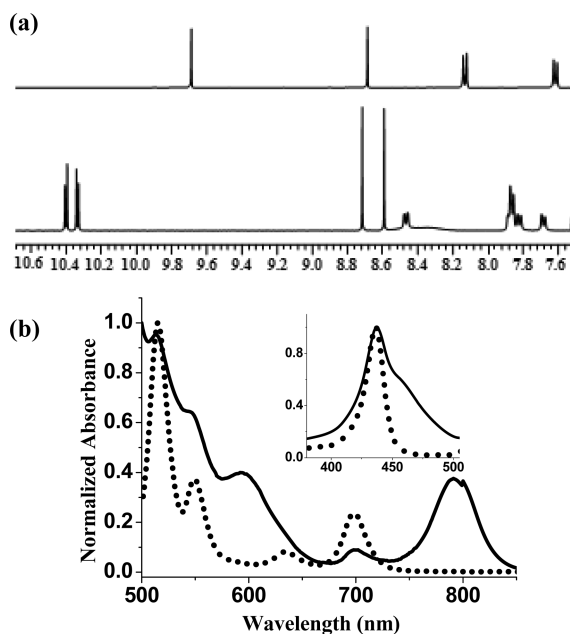
**Figure 1.** Single-crystal X-ray structure of **5**: (a) perspective view; (b) side view of **5** showing the distorted macrocyclic ring (*meso*-aryl rings, hydrogen atoms, and the counteranion are omitted for clarity); (c) simplified geometrical representation of **5** showing the coordination features around the central rhenium(I) ion.

coordination sphere and the bond lengths involving the rhenium(I) ion. The single-crystal X-ray structure of hexacoordinated rhenium(I) complex **5** obtained here is compared with the reported analogous hexacoordinated ruthenium(II) complex of  $S_2$ TTP (**3a**)<sup>5b</sup> and also with the  $Re(CO)_3$  complex of 21-thiaporphyrin (**4**). **3a**, **4**, and **5** were found to be crystallized in the triclinic space group  $P\bar{1}$ . **5** is cationic with a counteranion  $Re_2(\mu-Cl)_3(CO)_6$ , whereas **3a** and **4** are neutral.

As is clear from Figure 1, in **5**, the rhenium(I) metal ion is coordinated to one of the two pyrrole nitrogen atoms and, surprisingly, to both thiophene sulfur atoms of 21,23-dithiaporphyrin, leaving one pyrrole nitrogen atom uncoordinated. This observation is in agreement with recently reported **4** in which rhenium(I) is bound to two pyrrolic nitrogen atoms and one thiophene sulfur atom, leaving the third pyrrolic nitrogen atom uncoordinated. However, in **3a**, the ruthenium(II) ion is coordinated to both pyrrole nitrogen and thiophene sulfur atoms. Similar to **4**, in **5**, the other three coordinating sites of rhenium(I) are occupied by three carbonyl groups, whereas in **3a**, the hexacoordination geometry is satisfied with two trans-axial chloride ligands. In **5**, being a 5d transition-metal ion and larger in size, the rhenium(I) ion coordinates to 21,23-dithiaporphyrin by sitting on top of the porphyrin plane, and the rhenium(I) ion is placed at 1.729 Å above the plane defined by three coordinating atoms of 21,23-dithiaporphyrin (N1–S1–S2 plane). Because of the presence of two large sulfur atoms in the 21,23-dithiaporphyrin core, this displacement of the rhenium(I) ion from the porphyrin plane is significantly longer in **5** than in **4** (~1.51 Å).<sup>4</sup> The rhenium(I) ion is not positioned directly over the center of the macrocycle but is set to one side such that the rhenium(I) ion is in the midst of three coordinating atoms in **5**, as observed in **4**. However, in **3a**, the central ruthenium(II) ion is in the same plane defined by four

coordinating atoms of 21,23-dithiaporphyrin (N1–S1–N2–S2 plane) and placed in the middle of the plane without any displacement. In **5**, like **4**, the two thiophene sulfur atoms and one pyrrole nitrogen atom bend to coordinate with the rhenium(I) ion, whereas in **3a**, the two thiophene sulfur atoms bend in the opposite direction to the same extent, but two pyrrole nitrogen atoms remain in the same plane to coordinate with the ruthenium(II) ion. In **5**, the coordinated thiophene sulfur atoms S1 and S2 and pyrrole nitrogen atom N2 are significantly deviated (~0.21, 0.25, and 0.31 Å, respectively) compared to noncoordinated pyrrole nitrogen atom N1 (~0.17 Å) from the mean plane defined by 24-porphyrin-core atoms. In **4**, the two coordinated pyrrole nitrogen atoms N1 and N2 are deviated by ~0.40 and ~0.24 Å, respectively, thiophene sulfur atom S1 is deviated by ~0.16 Å, and the noncoordinated pyrrole nitrogen atom N3 is deviated by only ~0.12 Å from the mean 24-atom plane.<sup>4a</sup> However, in **3a**, the thiophene sulfur atoms S1 and S2 are significantly deviated (~0.93 Å each) compared to the negligible displacement of pyrrole nitrogen atoms N1 and N2 (~0.02 Å each) from the mean plane. Furthermore, in **5**, both Re–N (coordinated N) and average Re–S distances (2.24 and 2.54 Å, respectively) are significantly longer than those observed in **3a** (2.08 and 2.25 Å, respectively), but these are in the same range as that observed for the  $Re(CO)_3$  complex of 21-thiaporphyrin **4**.<sup>4</sup> The noncoordinated Re–N distance in **5** is much longer (3.437 Å) than that found in the rhenium(I) complex of 21-thiaporphyrin **4** (3.243 Å). Interestingly, the S1–S2 distance (3.152 Å) is much shorter in **5** compared to that in **3a** (4.498 Å). However, the N1–N2 distance is longer in **5** (4.703 Å) than in **3a** (4.498 Å). The carbonyl groups are aligned with the respective Re–N and Re–S bonds in **5**, as noted previously for **4**. The three Re–CO distances (av. 1.94 Å) are slightly longer, whereas the three Re–O distances (av. 1.09 Å) are slightly shorter in **5** compared to the  $Re(CO)_3$  complex of 21-thiaporphyrin **4** (av. 1.90 and 1.16 Å, respectively).<sup>4</sup> Furthermore, in **5**, the *meso*-tolyl groups, which are trans to each other, are oriented in the opposite direction with respect to each other by crossing the mean macrocycle plane like in **4**, whereas in **3a**, the *trans-meso*-phenyl groups are oriented in the same direction. The more coplanar nature of the *meso*-tolyl groups with the porphyrin ring in **4** and **5** compared to that in **3a** is revealed from the average dihedral angles between the *meso*-tolyl groups and the mean macrocycle plane, which are quite less in **4** and **5**. Interestingly, in compound **5**, the four average dihedral angles between the *meso*-tolyl groups and the mean macrocycle plane are not equal (41.7°, 45.3°, 55.7°, and 68.4°) as observed in **4** (48.7°, 59.2°, 68.5°, and 77.9°), but in **3a**, the average dihedral angles for the pair of *trans-meso* tolyl groups are exactly same (51.5° and 62.4° for each pair). Thus, crystal structure analysis clearly showed that the 21,23-dithiaporphyrin macrocycle is significantly distorted to bind the  $Re(CO)_3$  unit in **5**, as noted in **4**.

**5** was further characterized by NMR and absorption techniques. A comparison of <sup>1</sup>H NMR spectra of **5** with its corresponding free base **2** is shown in Figure 2a. The free base **2** shows one singlet at 9.69 ppm for four thiophene protons, one singlet at 8.69 ppm for four pyrrole protons, and two sets of aryl signals at 8.14 and 7.62 ppm. In **5**, the four thiophene protons are significantly downfield shifted and appear as two doublets at 10.40 and 10.33 ppm; the four pyrrole protons appear as two singlets at 8.71 and 8.59 ppm, and the *meso*-aryl protons appear as five sets of resonances in the 8.47–7.67 ppm region. The *meso*-tolyl –CH<sub>3</sub> protons also appear as two singlets at 2.79 and 2.76



**Figure 2.** (a) Comparison of  $^1\text{H}$  NMR spectra of **2** (top) with **5** (bottom) in the selected region recorded in  $\text{CDCl}_3$  and (b) absorption spectra of **5** (solid line) along with  $\text{S}_2\text{TTP}$  (dashed line) recorded in  $\text{CH}_2\text{Cl}_2$ .

ppm, reflecting the unsymmetric nature of **5**. The absorption spectrum of **5** shows five broad ill-defined Q bands at 515, 545, 595, 700, and 792 nm and one broad Soret band at 438 nm with a shoulder at 453 nm (Figure 2b). **5** is very weakly fluorescent.

In conclusion, we synthesized the rhenium(I) complex of 21,23-dithiaporphyrin in which the rhenium(I) ion was coordinated to one pyrrolic nitrogen atom and two thiophene sulfur atoms of the porphyrin ring and three carbonyl groups, as revealed by X-ray structural analysis. This is the first unusual binding mode of the 21,23-dithiaporphyrin unit toward a metal ion. The 21,23-dithiaporphyrin unit was significantly distorted upon binding with the  $\text{Re}(\text{CO})_3$  unit. The rhenium(I) complex of 21,23-dithiaporphyrin shows interesting features that need to be further investigated.

## ■ ASSOCIATED CONTENT

### Supporting Information

X-ray crystallographic data in CIF format and experimental, spectral, and crystallographic data of compound **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Sessler, J. L.; Gebauer, A.; Vogel, E. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; Academic Press: San Diego, 2000; Vol. 2, pp 1–49.
- (2) Latos-Grazynski, L.; Lisowski, J.; Szterenber, L.; Olmstead, M. M.; Balch, A. L. *J. Org. Chem.* **1991**, *56*, 4043.
- (3) (a) Latos-Grazynski, L.; Lisowski, J.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1989**, *28*, 1183. (b) Latos-Grazynski, L.; Lisowski, J.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 4428. (c) Lisowski, J.; Grzeszczuk, M.; Latos-Grazynski, L. *Inorg. Chim. Acta* **1989**, *161*, 153. (d) Chmielewski, J. P.; Grzeszczuk, M.; Latos-Grazynski, L.; Lisowski, J. *Inorg. Chem.* **1989**, *28*, 3546. (e) Latos-Grazynski, L.; Lisowski, J.; Chmielewski, J. P.; Grzeszczuk, M.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1994**, *33*, 192. (f) Latos-Grazynski, L.; Lisowski, J.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1989**, *28*, 3328. (g) Latos-Grazynski, L.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1989**, *28*, 4065. (h) Gebauer, A.; Schmidt, J. A. R.; Arnold, J. *Inorg. Chem.* **2000**, *39*, 3424. (i) Tung, J.-Y.; Liao, B.-C.; Elango, S.; Chen, J.-H.; Hsieh, H.-Y.; Liao, F.-L.; Wang, S.-L.; Hwang, L.-P. *Inorg. Chem. Commun.* **2002**, *5*, 150. (j) Pandian, R. P.; Chandrashekar, T. K. *Inorg. Chem.* **1994**, *33*, 3317. (k) Chuang, C.-H.; Ou, C.-K.; Liu, S.-T.; Kumar, A.; Ching, W.-M.; Chiang, P.-C.; dela Rosa, M. A. C.; Hung, C.-H. *Inorg. Chem.* **2011**, *50*, 11947.
- (4) (a) Ghosh, A.; Ravikanth, M. *Inorg. Chem.* **2012**, *51*, 6700. (b) Cullen, D. L.; Meyer, E. F.; Srivastava, T. S.; Tsutsui, M. *J. Am. Chem. Soc.* **1972**, *94*, 7603. (c) Tsutsui, M.; Hrun, C.-P. *J. Am. Chem. Soc.* **1974**, *96*, 2638. (d) Srivastava, T. S.; Hrun, C.-P.; Tsutsui, M. *J. Chem. Soc., Chem. Commun.* **1974**, 447. (e) Tsutsui, M.; Hrun, C.-P.; Ostfeld, D.; Srivastava, T. S.; Cullen, D. L.; Meyer, E. F., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 3952.
- (5) (a) Hung, C.-H.; Ou, C.-K.; Lee, G.-H.; Peng, S.-M. *Inorg. Chem.* **2001**, *40*, 6845. (b) Chuang, C.-H.; Ou, C.-K.; Liu, S.-T.; Kumar, A.; Ching, W.-M.; Chiang, P.-C.; dela Rosa, M. A. C.; Hung, C.-H. *Inorg. Chem.* **2011**, *50*, 11947.