7922 *Inorg. Chem.* **1996,** *35,* 7922−7923

A Bis-Capped Cofacial Metallodiporphyrin: Synthesis and Electrochemistry of a Molecule Containing Two Coaxial Metal−Metal Multiple Bonds in Close Proximity

James P. Collman* and H. T. Fish

Department of Chemistry, Stanford University
Stanford, California 94305

Received July 27, 1995

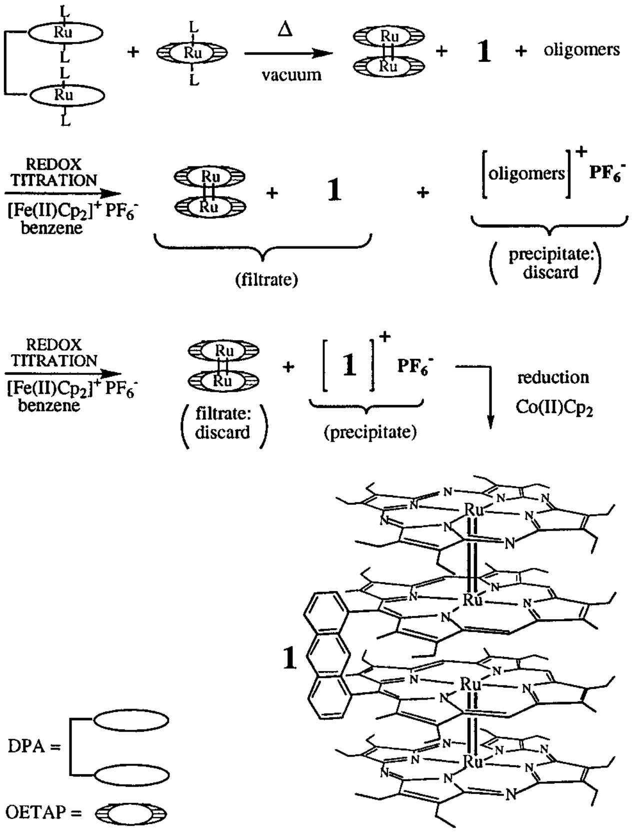
A general synthetic scheme has been developed to produce and characterize an array of metalloporphyrin dimers containing discrete metal−metal multiple bonds between a number of 4d and 5d transition metals.[1] These include homometallic and both intertriad and intratriad heterometallic dimers.[2] Bridged complexes containing metal−metal multiple bonds have also been prepared employing cofacial diporphyrins.[3] Intramolecular homo and hetero metal−metal bonds have been formed involving group 8 metal derivatives of a 1,8-biphenylene-bridged cofacial diporphyrin. The increased interporphyrin distance characteristic of analogous 1,8-anthracene bridged compounds favors intermolecular metal−metal bond formation and concomitant oligomerization.[3a]

Reported here are the synthesis and characterization of an unprecedented, tetrameric porphyrin complex, **1**, which contains two coaxial metal−metal multiple bonds separated by an anthracene bridge. Complex **1** consists of an anthracene-bridged, cofacial, bis-ruthenium diporphyrin, $Ru_2(DPA)$,[4] multiply bonded above and below to ruthenium tetraazaporphyrin monomers, Ru(OETAP). The construction of complex **1** allows one to probe the possible redox interactions of two, collinear, multiple metal−metal bonds in close proximity to one another. Complex **1** is reminiscent of Chisholm's tetranuclear Mo and W carboxylate complexes involving M−M quadruple bonds covalently linked via an anthracene 1,8-dicarboxylate bridge.[5]

Experimental Section

Materials and General Procedures. The starting materials, $Ru_2(DPA)(pyridine)_4$ and $Ru(OETAP)(pyridine)_2$ were prepared according to published methods, as were the cobaltocene, ferrocene, and ferrocenium hexafluorophosphate used in redox titrations and electrochemical analyses. All solvents were purified according to conventional methods and handled in a glovebox under a dry argon atmosphere.

Scheme 1. Synthesis and Isolation of **1**, [(OETAP)Ru=Ru(DPA)Ru=Ru(OETAP)]



Physical Measurements. ^1H NMR spectra were recorded on a Varian XL-400 Fourier transform spectrometer using toluene-d_8 as a solvent. UV−vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer with 2 nm resolution. All electrochemical measurements were performed in a glovebox under argon and were obtained using a computer-controlled PAR 273A potentiostat/galvanostat. Cyclic voltammetry was performed in freshly distilled THF with 0.2 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte. Both the working and auxillary electrodes were made of platinum, and a Ag/AgCl electrode served as a quasi-reference. The redox potentials were collected vs the ferrocene/ferrocenium redox couple observed at 0.339 V vs Ag/AgCl, and are reported vs NHE—which is assumed to be −0.197 V vs Ag/AgCl.

Preparation of the Porphyrin Tetramer. Synthesis and isolation of **1** was accomplished using a modified literature procedure (Scheme 1).[2a] $Ru_2(DPA)(pyridine)_4$ (19.5 mg) and 4 equiv of $Ru(OETAP)(pyridine)_2$ (37.6 mg) were colyophilized from benzene. The amorphous solid was then subjected to vacuum (10^{-5} Torr) and plunged into a silicon oil bath at 250 °C. After 3 h, the reaction mixture was cooled to room temperature and transferred to an argon-filled glovebox where subsequent isolation of the desired product was undertaken.

The reaction mixture was taken up in toluene and filtered in order to remove insoluble oligomers of $Ru_2(DPA)$. The filtrate was dried under vacuum and the residue combined with other samples prepared in an identical manner. The relative yields of the remaining pyrolysis products were determined from the integration of the ^1H NMR spectrum of this mixture. Isolation of **1** from the $[Ru(OETAP)]_2$ and other minor impurities was effected by a series of redox titrations (Scheme 1) in accordance with reported methods.[2a]

---

(1) (a) Collman, J. P.; Barnes, C. E.; Collins, T. J.; Brothers, P. J.; Gallucci, J.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 7030. (b) Collman, J. P.; Barnes, C. E.; Swepston, P. N.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 3500. (c) Collman, J. P.; Barnes, C. E.; Woo, L. K. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 7684. (d) Collman, J. P.; Garner, J. M.; Woo, L. K. *J. Am. Chem. Soc.* **1989**, *111*, 8141.

(2) (a) Collman, J. P.; Arnold, H. J.; Fitzgerald, J. P.; Weissman, K. J. *J. Am. Chem. Soc.* **1993**, *115*, 9309. (b) Arnold, H. J.; Collman, J. P.; Marchon, J. M.; Maldivi, P.; Yee, G. T.; Miller, J. S. *J. Am. Chem. Soc.*, submitted for publication. (c) Collman, J. P.; Arnold, H. J.; Weissman, K. J.; Burton, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 9761.

(3) (a) Collman, J. P.; Kim, K.; Garner, J. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1711. (b) Collman, J. P.; Garner, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 166.

(4) The following abbreviations are used throughout this note. DPA is the tetraanion of 1,8-bis{5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethyl)-porphyrinyl]anthracene. OEP and OETAP are the dianions of octaethyl porphyrin and octaethyl tetraazaporphyrin respectively. Cp is the cyclopentadienyl anion.

(5) Cayton, R. H.; Chisholm, M. H.; Huffman, J. C.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1991**, *113*, 8709.

S0020-1669(95)00940-2 CCC: $12.00

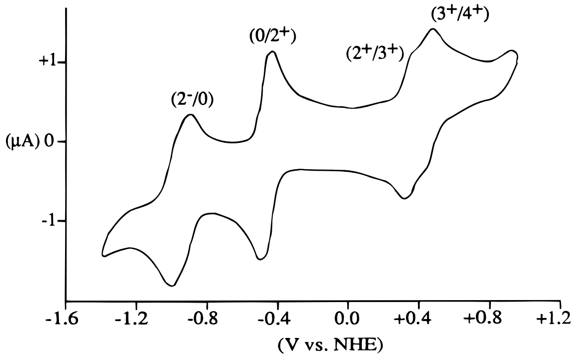


Figure 1. CV of **1** vs NHE[6] in 0.20 M tetrabutyl ammonium hexafluorophosphate in THF, scan rate: 50 mV s^{-1}. Molecular oxidation states are shown in parentheses.

Selected Spectroscopic Data for 1. UV/vis (toluene) λ_{max} (nm) 390; Soret, 520. ^1H NMR (toluene-d_8, 20 °C): δ 33.53 (m, 16H), 31.06 (s, 12H), 27.94 (s, 12H), 21.63 (m, 4H), 20.73 (m, 4H), 17.75 (m, 16H), 15.86 (s, 2H), 12.19 (s, 4H), 12.12 (d, 2H), 11.29 (m, 4H), 9.97 (s, 1H), 9.79 (d, 2H), 9.09 (dd, 2H), 8.76 (m, 4H), 3.03 (t, 12H), 2.60 (t, 12H), 2.51 (t, 48H).

Results and Discussion

Compound **1** exhibits a sharp, paramagnetically shifted ^1H NMR spectrum, the chemical shifts of which are very similar to the analogous mixed porphyrin dimer, [(OETAP)Ru═Ru(OEP)]. All observed signal positions, splittings and integrations are assigned. Addition of pyridine to **1** ruptures the metal−metal bonds and results in clean formation of the starting materials, Ru(OETAP)(pyridine)$_2$ and Ru$_2$(DPA)(pyridine)$_4$, in an exact ratio of 2:1.

Results of cyclic voltammetry (Figure 1)[6] indicate three reversible oxidation waves. The first 2-electron oxidation is followed by two 1-electron waves. This redox behavior indicates that a mixed valence complex is not readily generated. To confirm this, 1 equiv of ferrocenium, an efficient, outer-sphere one electron oxidant, was added to **1** in benzene. The precipitate which formed was isolated, and its visible spectrum showed no sign of the broad charge transfer band expected from a mixed valence complex. The original benzene solution was analyzed and found to contain only ferrocene and approximately half the original amount of **1.** Presumably, the oxidation product is the dication of **1,** though no thorough characterization was performed. This evidence indicates that the mixed valence compound of **1** is unstable with respect to conproportionation.

A MO diagram appropriate for flat, metalloporphyrin homodimers was developed by Cotton,[7] and is similar to that independently conceived by Figgis and Martin.[8] The scheme reasonably assumes that only metal d electrons participate in metal−metal bonding, and that the dimers exist in a staggered (D_{4d} symmetry) geometry. This simple bonding model has been used to predict the bond orders and spin states of metalloporphyrin dimers. The predictions have proven remarkably consistent with a wide range of experimental studies done on these molecules in a variety of oxidation states. Recently, Collman et al. demonstrated the applicability of the model to a heteroporphyrin dimer, (OEP)Ru═Ru(OETAP), a simple analogue of compound **1**.[2a]

When the metal−metal bond scheme of Figgis and Cotton is employed, the ^1H NMR and electrochemical data indicate that the complex contains two metal−metal double bonds which perturb each other very little. The length of the anthracene bridge apparently precludes significant interaction between the two metal−metal bonds in the mixed valence state, and the bonds can be considered independent of one another; thus, the 2-electron wave in the CV of **1** represents simultaneous removal of a single electron from each of its constituent metal−metal bonds. Significant perturbation of these two bonds by one another should have resulted in two 1-electron oxidations instead of the observed 2-electron transformation. The redox behavior of **1** is not completely surprising. Ru$_2$(DPA)(py)$_4$ exhibits a similar 2-electron oxidation, however, it was thought that removal of the pyridine ligands and replacement by a metal−metal bond−thus constraining two *coordinatively unsaturated* Ru(II) centers in close proximity−might allow increased communication between the constituent metals of the (DPA) moiety via their open coordination sites.

Acknowledgment. We thank the National Science Foundation for generous financial support and Jonathan Kendall for supplying H$_2$OETAP.

IC950940Y

---

[6] Redox potentials were collected vs observed ferrocene/ferrocenium redox couple at 0.339 V vs Ag/AgCl. Redox couples are reported vs NHE, which is assumed to be −0.197 V vs Ag/AgCl.

(7) (a) Cotton, F. A.; Curtis, N. F.; Harris, C. B.; Johnson, B. F. G.; Lippard, S. J.; Mague, J. T.; Robinson, W. R.; Wood, J. S. *Science* **1964**, *145*, 1305. (b) Cotton, F. A.; Curtis, N. F.; Johnson, B. F. G.; Robinson, W. R. *Inorg. Chem.* **1965**, *4*, 326. (c) Cotton, F. A.; Harris, C. B. *Inorg. Chem.*, **1965**, *4*, 330. (d) Cotton, F. A. *Inorg. Chem.* **1965**, *4*, 334.

(8) Figgis, B. N.; Martin, R. L. *J. Chem. Soc.* **1956**, 3837.