Note

Metalloporphyrin as a ligand in organometallic complexes: Synthesis and characterization of a nickel(II) porphyrin complex of 1,5-cyclooctadienedichlororuthenium(II)

Mannar R. Maurya [a], L. Keith Woo [b],*

[a] *Indian Institute of Technology Roorkee, Roorkee 247 667, India*
[b] *Departments of Chemistry, Iowa State University, Gilman Hall, Ames, IA 50011-3111, USA*

Abstract

A method for the synthesis of dinuclear metal complexes has been developed which utilizes the multichelating porphyrin ligand, α,α-5,15-bis(*o*-nicotinoylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin, H_2[DPE]-(py)$_2$ (*di*[*o*-nicotinoy*l*phenyl]*e*tiopor-phyrin). In addition to the porphyrin site, the two terminal pyridyl groups of the ligand serve as an additional chelate. The two metal binding sites are chemically different and can be used to bind different metal centers. The versatility of this ligand is demonstrated by fabricating a heterobimetallic complex, [Ni(DPE)-(py$_2$)]Ru(COD)Cl$_2$, composed of a porphyrin coordination complex linked to an organometallic fragment.
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1. Introduction

Multinuclear transition metal complexes are widely studied as biomimetic models for enzyme active sites [1]. Examples that contain a porphyrin fragment are particularly relevant to the class of enzymes known as cytochrome *c* oxidases [2]. These are the terminal enzymes in the electron transfer cascade, mediating the four-electron reduction of O_2 to water. By employing dinuclear metal complexes containing multichelating porphyrin ligands, considerable progress has been made in understanding structure–function relationships in enzyme active sites [3]. Moreover, multimetal complexes have strong prospects for generating unusual characteristics [4]. Particularly intriguing is the possibility of generating new properties or reactivities that cannot be produced by the individual metal complexes alone. These include opportunities for unusual electronic, magnetic, catalytic and redox properties and providing new models for charge transfer, electron transport, etc.

Fabrication of discrete multinuclear complexes relies heavily on ligand design. In addressing this issue, we developed difunctionalized porphyrin macrocycles that are capable of chelating more than one metal. These versatile ligands are useful for preparing a variety of di- and trinuclear coordination complexes [5] as well as for forming monolayers at gold [6]. The framework of our ligand is based upon α,α-bis(*o*-aminophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin or *di*[*o*-aminophenyl]*e*tioporphyrin (H_2[DPE]) that was originally prepared by Young and Chang [7]. In extending our work, we have used a difunctionalized porphyrin ligand to link a coordination complex with an organometallic fragment. The results of this work are reported here.

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* Corresponding author. Tel.: +1 515 294 5854; fax: +1 515 294 9623.

E-mail address: kwoo@iastate.edu (L.K. Woo).

2. Results and discussion

The structure and schematic representation of the binucleating porphyrin $[H_2(DPE)]$-$(py)_2$ is shown below (Fig. 1). Metallation of this porphyrin with Ni(II) was achieved by treatment with nickel acetate as described previously [5a]. This mononuclear complex behaves as a bidentate ligand. Thus, treatment of $Ru(\eta^4$-$C_8H_{12})$-$Cl_2(CH_3CN)_2$ with equimolar amounts of $[Ni(DPE)]$-$(py)_2$ in refluxing $CHCl_3$ led to the formation of the organometallic binuclear species $[Ni(DPE)]$-$(py)_2Ru$-$(\eta^4$-$C_8H_{12})Cl_2$. The complex $[H_2(DPE)]$-$(py)_2Ru$-$(\eta^4$-$C_8H_{12})Cl_2$ was also isolated in a manner identical to that for the binuclear complex by substituting $[H_2(DPE)]$-$(py)_2$ for $[Ni(DPE)]$-$(py)_2$. Systematic formation of these complexes is presented in Scheme 1. While dinuclear complex **2** can also be obtained by treating complex **1** with nickel acetate, synthesis via $[Ni(DPE)]$-$(py)_2$ resulted in purer product with better yields. Complex **2** is robust as a solid and in solution. However, $[H_2DPE]$-$(py)_2Ru(\eta^4$-$C_8H_{12})Cl_2$ slowly decomposed in solution to free porphyrin and unidentified paramagnetic products.

The UV–vis spectrum of mononuclear complex **1** exhibits a soret band at 410 nm and four visible bands at 510, 542, 576, and 628 nm, identical to that of the free base porphyrin. The presence of three resonances at 3.86, 2.67, and 2.01 ppm in the ^1H NMR spectrum indicates η^4-coordination of COD. The appearance of only a single band in the far-IR spectrum at 338 cm^{-1} demonstrates the *trans*-chloride configuration at Ru. In addition, bands at 634 and 468 cm^{-1} lie in the coordinated pyridyl in-plane and out-of-plane deformation
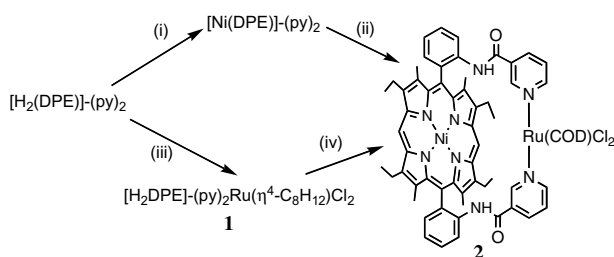
region [8]. IR and NMR spectral data strongly support the coordination of pyridine nitrogens to ruthenium of the $Ru(\eta^4$-$C_8H_{12})Cl_2$ group, while the UV–vis and ^1H NMR spectra indicate that complex **1** contains an unmetallated porphyrin. For example, the upfield proton singlet at -2.13 ppm is diagnostic of the internal N–H protons of the porphyrin. Thus, no insertion of ruthenium into the N_4–porphyrin chelate occurs despite the presence of labile ligands on $Ru(\eta^4$-$C_8H_{12})Cl_2$. This is not unusual as Ru(II) is d^6, low spin and insertion into the porphyrin binding site typically requires reaction temperatures above 80 °C [9].

The far-IR spectrum of the dinuclear complex **2** shows two peaks at 638 and 466 cm^{-1} assignable to in-plane and out-of-plane pyridine ring deformations [8]. These bands are shifted to higher frequencies than for those of free pyridines and reflect the metal coordination of these ligands. Complex **2** exhibits only a single band in CH_2Cl_2 solution as well as in mulls at 346 cm^{-1}, consistent with Ru–Cl stretches due to a *trans*-geometry.

The ^1H NMR spectrum of the dinuclear complex **2** shows distinctive changes in its proton resonances relative to those of the mononuclear $Ru(\eta^4$-$C_8H_{12})Cl_2$-$(CH_3CN)_2$ [10] and $[Ni(DPE)]$-$(py)_2$ species [11]. The absence of signals due to bound CH_3CN in **2** indicate the replacement of the coordinated acetonitriles by pyridine nitrogens of the binucleating ligand. The mononuclear complex $Ru(\eta^4$-$C_8H_{12})Cl_2(CH_3CN)_2$ exhibits three proton resonances at 4.27, 2.40 and 2.03 ppm due to olefinic hydrogens and *exo* and *endo* methylene protons of COD, respectively. The general up-field shift of the COD proton signals to 3.81, 2.99, and 1.84 ppm in complex **2** reflect the position of the Ru fragment above the porphyrin, within the cone of deshielding due to the ring current. The pyridyl proton resonances also reveal conformational changes of the chelate appendages upon binding to Ru. For example, in $[Ni(DPE)]$-$(py)_2$, the $H_{4'}$ and $H_{5'}$ protons (see Fig. 1) resonate at 6.83 and 6.59 ppm. In complex **2**, these signals shift down field to 7.10 and 6.89 ppm, respectively. Thus, prior to binding to Ru, the pyridyl groups are generally positioned with the N atom facing away from the porphyrin normal, placing $H_{4'}$ and $H_{5'}$ over the ring current. On chelation to Ru (Fig. 2), the pyridyl groups must rotate to
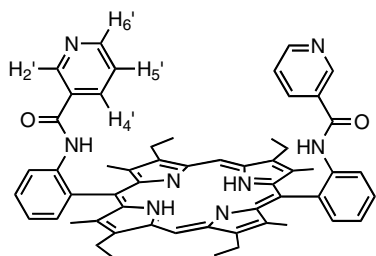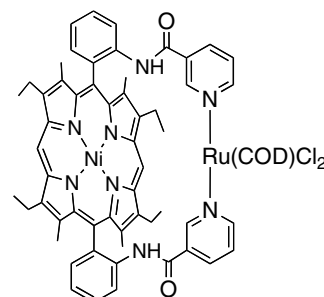

Fig. 1. Structural representation of the ligand $[H_2(DPE)]$-$(py)_2$ with numbering convention for pyridyl hydrogens.

Scheme 1. (i) and (iv) Ni(CH$_3$COO)$_2$; (ii) and (iii) Ru(η^4-C$_8$H$_{12}$)Cl$_2$(CH$_3$CN)$_2$.

Fig. 2. Structural representation of [Ni(DPE)]-(py)$_2$Ru(COD)Cl$_2$.

allow the N-donors to bind to Ru, placing $H_{4'}$ and $H_{5'}$ further away from the shielding cone of the porphyrin ring current.

3. Conclusion

The [H_2(DPE)]-py$_2$ ligand is a versatile chelate with two unique metal binding sites. Heterobinuclear complexes can be prepared in a designed fashion by metallating each site selectively and sequentially. By using chemical control, we have prepared a novel binuclear complex that consists of a coordination complex linked to an organometallic compound. With labile ligands bound to the organometallic fragment, it should be possible to elicit metal mediated processes in which a single substrate can interact simultaneously with both metals of the heterobimetallic complex.

4. Experimental

All commercial chemicals were used without further purification. CHCl$_3$ was dried over molecular sieves for several days and degassed before use. All reactions were carried out under an atmosphere of purified nitrogen. Synthesis of α,α-5,15-bis(o-nicotinamidophenyl)2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin, [H_2(DPE)]-(py)$_2$, and its Ni(II) complex were accomplished by the literature procedures [5c]. The method of Albers et al. [12] was used to prepare Ru(η^4-C$_8$H$_{12}$)Cl$_2$(CH$_3$CN)$_2$.

IR spectra were recorded as nujol mulls or in CH$_2$Cl$_2$ on an IBM IR-98 Fourier transform infrared spectrometer. Visible spectra were obtained in CHCl$_3$ at ambient temperature on a HP 8452A diode array spectrophotometer. ^{1}H NMR spectra were recorded in CDCl$_3$ on a Nicolet NIC 300 spectrometer and chemical shifts (in ppm) are reported relative to residual proton impurities in CDCl$_3$ (7.24 ppm).

4.1. [H_2(DPE)]-(py)$_2$Ru(η^4-C$_8$H$_{12}$)Cl$_2$ (**1**)

A mixture of Ru(η^4-C$_8$H$_{12}$)Cl$_2$(CH$_3$CN)$_2$ (42 mg, 0.11 mmol) and [H_2(DPE)]-(py)$_2$ (87 mg, 0.10 mmol) in 15 mL CHCl$_3$ was heated at reflux for 8 h while stirring. After evaporating the solvent to dryness, 2 mL CHCl$_3$ and 8 mL hexanes were added and the mixture was cooled to −10 °C for 5 h. The precipitated brown solid was filtered, washed with hexanes and dried in vacuo at 80 °C. Yield: 60 mg (51%). UV–vis (CHCl$_3$): 410 (soret), 510, 542, 576, 628 nm. ^{1}H NMR (CDCl$_3$): 10.16 (s, 2H, *meso*-H), 9.03 (d, 2H, aryl), 8.81 (d, 2H, 2′-py), 8.54 (d, 2H, 4′-py), 7.87 (m, 6H, aryl and NH), 7.70 (t, 2H, aryl), 6.81 (m, 2H, 6′-py), 6.66 (s, 2H, 5′-py), 4.08 (m, 12H, C*H*$_2$CH$_3$), 3.88 (m, 4H, =CH,

COD), 2.67 (m, 4H, *exo*-CH$_2$, COD), 2.52 (s, 12H, CH$_3$), 2.01 (m, 4H, *endo*-CH$_2$), 1.76 (t, 12H, CH$_2$C*H*$_3$), −2.13 (s, 2H, pyrrole-NH). IR (CH$_2$Cl$_2$): v(NH), 3395; v(CO), 1685; δ(Ru–py), 634, 468; v(Ru–Cl), 338 cm^{-1}.

4.2. [Ni(DPE)]-(py)$_2$Ru(η^4-C$_8$H$_{12}$)Cl$_2$ (**2**)

A solution of Ru(η^4-C$_8$H$_{12}$)Cl$_2$(CH$_3$CN)$_2$ (42 mg, 0.11 mmol) in 5 mL CHCl$_3$ was added to a stirred solution of Ni(DPE)-(py)$_2$ (93 mg, 0.10 mmol) in 10 mL CHCl$_3$. The reaction mixture was heated at reflux for 8 h. After concentrating the solvent to 2 mL, 10 mL of hexanes was added and the mixture was cooled to −10 °C for 18 h. A dark-red crystalline solid was filtered, washed with hexanes and dried in vacuo at 100 ° C for 5 h. Yield: 92 mg (75%). UV–vis (CHCl$_3$): 410 (soret), 530, 566 nm. ^{1}H NMR (CDCl$_3$): 9.48 (s, 2H, *meso*-H), 9.21 (d, 2H, aryl), 8.75 (d, 2H, 2′-py), 8.29 (d, 2H, 6′-py), 7.79 (m, 4H, aryl), 7.69 (s, 2H, NH), 7.61 (m, 2H, aryl), 7.10 (s, 2H, 4′-py), 6.89 (t, 2H, 5′-py), 3.81 (m, 4H, =CH, COD), 3.64 (m, 8H, C*H*$_2$CH$_3$), 2.99 (m, 4H, *exo*-CH$_2$, COD), 2.30 (s, 12H, CH$_3$), 1.84 (m, 4H, *endo*-CH$_2$ COD), 1.63 (t, 12H, CH$_2$CH$_3$). IR (mull): v(NH), 3379; v(CO), 1688, δ(Ru–py), 638, 466; v(Ru–Cl), 346 cm^{-1}. Anal. Calc. for C$_{66}$H$_{64}$N$_8$O$_2$Cl$_2$NiRu · H$_2$O: C, 62.71; H, 5.39; N, 9.14%. Found: C, 62.89; H, 5.18; N, 9.04%.

References

[1] L. Que, A.E. True, Prog. Inorg. Chem. 90 (1990) 97.
[2] T.P. Thrash, L.J. Wilson, Inorg. Chem. 40 (2001) 4556.
[3] J.P. Collman, R. Boulatov, C.J. Sunderland, in: K.M. Kadish, R.M. Smith, R. Guilard (Eds.), The Porphyrin Handbook, Wiley, New York, 2003, p. 279 (Chapter 46).
[4] L.F. Lindoy, Adv. Inorg. Chem. 45 (1998) 75.
[5] (a) L.K. Woo, M.R. Maurya, C.J. Tolppi, R.A. Jacobson, S. Yang, E. Rose, Inorg. Chim. Acta 182 (1991) 41;
(b) L.K. Woo, M.R. Maurya, Inorg. Chem. 30 (1991) 4671;
(c) L.K. Woo, M.R. Maurya, R.A. Jacobson, S. Yang, S.L. Ringrose, Inorg. Chem. 31 (1992) 913;
(d) L.K. Woo, M.R. Maurya, R.A. Jacobson, S. Yang, S.L. Ringrose, Inorg. Chim. Acta 193 (1992) 143.
[6] J. Zak, H. Yuan, M.-K. Ho, L.K. Woo, M.D. Porter, Langmuir 9 (1993) 2772.
[7] R. Young, C.K. Chang, J. Am. Chem. Soc. 107 (1985) 898.
[8] (a) K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, fifth ed., Wiley, New York, 1997, Part B, p. 24;
(b) R.J.H. Clark, C.S. Williams, Inorg. Chem. 4 (1965) 350.
[9] (a) J.W. Buchler, in: D. Dolphin (Ed.), The Porphyrins, vol. 1, Academic Press, New York, 1978, p. 406 (Chapter 10);

(b) J.K.M. Sanders, N. Bampos, Z. Clyde-Watson, S.L. Darling, J.C. Hawley, C.C. Mak, S.J. Webb, in: K.M. Kadish, R.M. Smith, R. Guilard (Eds.), The Porphyrin Handbook, vol. 3, Wiley, New York, 2000, p. 19 (Chapter 15).

[10] ^{1}H NMR of [Ru(η^4-C$_8$H$_{12}$)Cl$_2$(CH$_3$CN)$_2$] in CDCl$_3$: 4.27 (m, 4H, =CH, COD), 2.61 (s, 6H, CH$_3$CN), 2.40 (m, 4H, *exo*-CH$_2$, COD), 2.03 (pseudo q, 4H, *endo*-CH$_2$, COD).

[11] H NMR of Ni(DPE)-(py)$_2$ (CDCl$_3$): 9.48 (s, 2H, meso), 8.91 (d, 2H, 2′-py), 8.24 (s, 2H, NH), 8.20 (m, 2H, aryl), 8.14 (d, 2H, 6′-py), 7.81 (m, 2H, aryl), 7.39 (m, 4H, aryl), 6.83 (m, 2H, 4′-py), 6.59 (m, 2H, 5′-py), 3.66 (m, 8H, CH$_2$CH$_3$), 2.31 (s, 12H, CH$_3$), 1.55 (t, 12H, CH$_2$CH$_3$).

[12] M.O. Albers, T.V. Ashworth, H.E. Oosthuizen, E. Singleton, Inorg. Synth. 26 (1989) 68.