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Note

Synthesis, characterization, and X-ray crystal structure of a trimetallic diporphyrin complex

L. Keith Woo*,†, Mannar R. Maurya,
Robert A. Jacobson* and Sharon L. Ringrose
Ames Laboratory and Department of Chemistry, Iowa State University, Ames, IA 50011 (USA)

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Abstract

Treatment of two equivalents of *cis*-5,15-bis(*o*-[2-nicotinoylamido]phenyl-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrinato nickel(II), [Ni(DPE)-(NH-CO-py)$_2$], with [M(DMSO)$_4$](ClO$_4$)$_2$ in methanol produces trinuclear complexes, [Ni(DPE)-(NH-CO-py)$_2$]$_2$M(ClO$_4$)$_2$ where M is Pd or Pt. The trinuclear Ni$_2$Pd complex crystallizes from CHCl$_3$ to yield an octasolvate. An X-ray structure determination for [NiO$_2$N$_8$C$_{56}$H$_{52}$]$_2$Pd(ClO$_4$)$_2$·8HCCl$_3$ was carried out. Crystal data are as follows: monoclinic, $P2_1/n$ (No. 14), $a=14.378(7)$, $b=23.413(6)$, $c=21.140(6)$ Å, $\beta=105.30(3)°$, $V=6865(4)$ Å^3, $Z=2$, $R=0.076$ and $R_w=0.082$.

Introduction

We have recently developed difunctionalized porphyrin ligands which are capable of chelating more than one metal ion [1]. These versatile ligands are useful for preparing a variety of mono-, di- and trimetal coordination complexes which have well-defined binding sites in adjacent positions [2, 3]. A recent X-ray diffraction study on a bimetallic Cu–Pt porphyrin complex indicates that these multimetallic species can have unusual structural properties [2]. We report herein the single-crystal X-ray structure solution for a heterotrimetallic Ni$_2$–Pd bis-porphyrin complex. The ligand used in this complex, H$_2$(DPE)-(NH-CO-py)$_2$, is shown in Fig. 1.

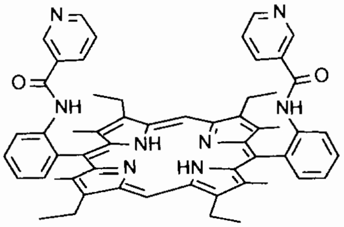

Fig. 1. Structural representation of the porphyrin ligand, H$_2$(DPE)-(NH-CO-py)$_2$, used in this work.

Experimental

General

All solvents and metal salts used in the synthesis were of analytical grade. Synthesis of Ni(DPE)-(NH-CO-py)$_2$ was accomplished by the literature procedure [1]. The palladium and platinum complexes, [M(DMSO)$_4$](ClO$_4$)$_2$, were prepared as reported [4].

Synthesis of [Ni(DPE)-(NH-CO-py)$_2$]$_2$Pd(ClO$_4$)$_2$

A 15 ml CHCl$_3$ solution of Ni(DPE)-(NH-CO-py)$_2$ (100 mg, 0.1079 mmol) was added to [Pd(DMSO)$_4$](ClO$_4$)$_2$ (40 mg, 0.060 mmol) which was dissolved in CH$_3$OH (2 ml) and H$_2$O (3 drops). After heating the reaction mixture at reflux for 24 h, the solution was cooled to 10 °C for 4 h. A pink solid (55 mg, 23%) was isolated by filtration, washed with methanol, and dried under reduced pressure. Analytically pure material was prepared as the CHCl$_3$ solvate by recrystallization from CHCl$_3$/hexanes. *Anal.* Calc. for C$_{112}$H$_{104}$N$_{16}$O$_{12}$Ni$_2$Pd·CHCl$_3$: C, 59.50; H, 4.61; N, 9.83. Found: C, 59.09; H, 4.64; N, 9.53%. UV–Vis (CH$_2$Cl$_2$): 408 (Soret), 532, 570 nm. ^{1}H NMR (CDCl$_3$): 9.36 (2H, *meso* H); 8.52 (m), 8.37 (m), 8.05 (m), 7.65 (m) aromatic protons; 5.6 (m), 5.48 (s); 3.65 (br m, CH$_2$); 2.40 (br), 2.31 (br) β-CH$_3$; 1.65 (br), 1.52 (br) CH$_3$.

Synthesis of [Ni(DPE)-(NH-CO-py)$_2$]$_2$Pt(ClO$_4$)$_2$

A solution of Ni(DPE)-(NH-CO-py)$_2$ (50 mg, 0.054 mmol) in CHCl$_3$ (7 ml) and methanol (3 ml) was added to [Pt(DMSO)$_4$](ClO$_4$)$_2$ (20 mg, 0.026 mmol) which was dissolved in 2 ml of methanol. After heating the reaction mixture at reflux for 24 h, the solvent was removed under reduced pressure. Recrystallization from CHCl$_3$/hexane at 10 °C produced a purple solid (55 mg, 44%) after filtering, washing with hexane, and drying *in vacuo*. UV–Vis (CHCl$_3$): 412 (Soret), 530, 566 nm. ^{1}H NMR

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*Authors to whom correspondence should be addressed.
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($CDCl_3$): 9.50 (s, 2H, *meso* H), 8.62 (d, 2H, H_3-aryl), 8.33 (br, py), 8.23 (br, py), 7.89 (t, 2H, H_4-aryl), 7.82 (d, 2H, H_6-aryl), 7.85 (t, 2H, H_5-aryl), 7.33 (br m, py), 5.01 (br, 2H, NH), 3.60 (m, 8H, CH_2), 1.47 (t, 12H, CH_3). *Anal.* Calc. for $C_{112}H_{104}N_{16}O_{12}Ni_2Pt \cdot 1/2CHCl_3$: C, 58.50; H, 4.53; N, 9.71. Found: C, 58.34; H, 4.54; N, 9.44%.

X-ray crystal structure determination

A purple platelet crystal of $[NiO_2N_8C_{56}H_{52}]_2$-$Pd(ClO_4)_2 \cdot 8HCCl_3$ having approximate dimensions of 0.36×0.36×0.10 mm was mounted in a glass capillary. All measurements were made on a Rigaku AFC6R diffractometer with graphite monochromated Mo Kα radiation and a 12KW rotating anode generator. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 17 carefully centered reflections in the range $12.49 < 2\theta < 15.23°$. Based on the systematic absences of $h0l$: $h+l \neq 2n$ and $0k0$: $k \neq 2n$ and the successful solution and refinement of the structure, the space group was determined to be $P2_1/n$ (No. 14).

The data (h, $\pm k$, $\pm l$) were collected at a temperature of -50 ± 1 °C using the ω scan technique to a maximum 2θ value of 50.1°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.42° with a take-off angle of 6.0°. Scans of $(1.05 + 0.30 \tan \theta)°$ were made at a speed of 16.0°/min (in omega). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 2 rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 400.0 mm.

The structure was determined by Patterson superposition methods and refined to a final residual of 0.076. The majority of non-hydrogen atoms were refined anisotropically with the exception of several atoms in solvent molecules. Hydrogen atom positions were calculated. The solvent molecules exhibited a fairly high degree of libration/disorder which contributed to an unusually rapid decrease in intensity with increasing sin θ.

Results and discussion

Preparation of trinuclear species generally leads to the formation of triangular complexes [5]. However, when rigid, planar ligand systems are employed, it is possible to design linear arrays of multi-metallic complexes. For this purpose, we recently attached nicotinamido (py-C(O)-NH) appendages to the α,α'-*ortho*-positions of diphenyletioporphyrin, H_2DPE to produce a multi-chelating ligand system, $H_2(DPE)$-$(NH$-CO-$py)_2$. It is possible to insert a single metal ion such as Ni(II), Cu(II) or Zn(II) into the porphyrin binding site to generate mono-metallic complexes, M(DPE)-$(NH$-CO-$py)_2$. We have also demonstrated that a second metal (e.g. Pd(II), Pt(II) etc) could be subsequently introduced to produce a binuclear assembly, M(DPE)-$(NH$-CO-$py)_2M'Cl_2$, in a controlled manner. In a formal sense, displacement of the two chloride ligands in this binuclear species with the nicotinamido appendages of an additional M(DPE)-$(NH$-CO-$py)_2$, should yield a linear trimetallic array of metal ions. In practice, these trinuclear complexes are readily prepared by treating two equivalents of M(DPE)-$(NH$-CO-$py)_2$ with one equivalent of $[M'(DMSO)](ClO_4)_2$ in a one-pot reaction. For example, when 0.054 mmol of Ni(DPE)-$(NH$-CO-$py)_2$ and 0.027 mmol of $[Pt(DMSO)_4](ClO_4)_2$ are heated in a refluxing solution of $CHCl_3$ and MeOH, formation of $[Ni(DPE)$-$(NH$-CO-$py)_2]_2Pt(ClO_4)_2$ is observed. ^1H NMR is a useful tool for characterizing this diamagnetic product. Particularly diagnostic is the signal arising from the *meso*-proton of the porphyrin framework. In the dinuclear complex Ni(DPE)-$(NH$-CO-$py)_2PtCl_2$, this signal occurs as a singlet at 9.43 ppm. In the trinuclear Ni_2–Pt product, the corresponding resonance appears as a singlet at 9.50 ppm

In a similar manner, a palladium analog, $[Ni(DPE)$-$(NH$-CO-$py)_2]_2Pd(ClO_4)_2$ can be prepared. The diagnostic *meso*-proton signal for this complex occurs at 9.36 ppm. A single-crystal X-ray diffraction analysis on this complex confirmed the assigned composition.

Crystal structure of $[Ni(DPE)$-$(NH$-CO-$py)_2]_2Pd(ClO_4)_2$

Pertinent crystallographic parameters are given in Table 1. The asymmetric unit contains half of a formula unit. The molecular structure and atom numbering scheme are shown in Fig. 2 and Table 2 lists selected bond distances and angles. The average dihedral angle between the mean planes of adjacent pyrrole rings is 26.6° and indicates that the porphyrin core of this complex is distorted in an S_4-ruffling mode similar to that observed for the tetragonal form of octaethylporphyrinato nickel(II) [6]. In addition, the *meso* carbons are alternately displaced above and below the mean porphyrin plane by an average of 0.55(6) Å. The Ni environment is essentially square planar with N–Ni–N bond angles ranging from 88.3(6) to 92.0(6). The largest displacement of a pyrrole nitrogen from the best least-squares NiN_4 plane is 0.08(1) Å. The Ni–N distances are typical of those reported for other Ni porphyrin complexes [7, 8].

TABLE 1. Crystallographic parameters for [Ni(DPE)-(NH-C(O)-py)$_2$]$_2$Pd(ClO$_4$)$_2$

Empirical formula	[NiO$_2$N$_8$C$_{56}$H$_{52}$]$_2$Pd(ClO$_4$)$_2$ 8HCCl$_3$
Formula weight	3115.88
Crystal system	monoclinic
a (Å)	14.378(7)
b (Å)	23.413(6)
c (Å)	21.140(6)
β (°)	105.30(3)
V (Å^3)	6865(4)
Z value	2
D_{calc} (g/cm^3)	1.507
F(000)	3168
μ(Mo Kα) (cm^{-1})	9.72
Corrections	Lorentz–polarization absorption decay
(transmission factors)	(0.91–1.00)
No. observations ($I > 3.00\sigma(I)$)	3273 (only 221 with $2\theta > 40°$)
No. variables	769
Residuals: R, R_w^{a}	0.076, 0.082
Goodness of fit indicator	2.49
Max shift/error in final cycle	1.52
Maximum peak in final difference map (e$^-$/Å^3)	0.84
Minimum peak in final difference map (e$^-$/Å^3)	−0.68

$^a R = \Sigma \| F_o \| - | F_c \| / \Sigma | F_o |$, $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}$.

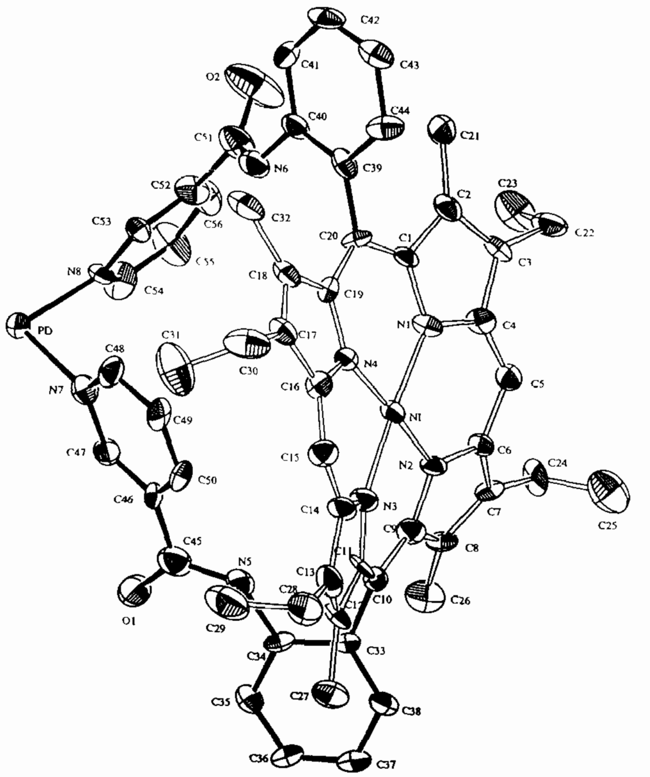

Fig. 2. Molecular structure and atom numbering scheme for the dication [Ni(DPE)-(NH-CO-py)$_2$]$_2$Pd. Ellipsoids are drawn at a 30% probability level. The Pd atom lies on an inversion center and only half of the complex is shown.

TABLE 2. Selected intramolecular distances (Å) and angles (°) involving the non-hydrogen atoms

Pd–N7	2.01(2)	C3–C4	1.44(2)
Pd–N8	2.02(2)	C3–C22	1.47(2)
Ni–N1	1.94(1)	C4–C5	1.40(2)
Ni–N2	1.94(1)	C5–C6	1.39(2)
Ni–N3	1.93(1)	C19–C20	1.39(2)
Ni–N4	1.91(1)	C20–C39	1.48(2)
O1–C45	1.18(2)	C22–C23	1.55(3)
O2–C51	1.23(2)	C39–C40	1.36(2)
N1–C1	1.39(2)	C39–C44	1.42(2)
N1–C4	1.38(2)	C40–C41	1.40(2)
N6–C40	1.44(2)	C41–C42	1.38(3)
N6–C51	1.35(2)	C42–C43	1.36(3)
N8–C53	1.32(2)	C43–C44	1.43(3)
N8–C54	1.36(2)	C51–C52	1.50(3)
C1–C2	1.47(2)	C52–C53	1.37(2)
C1–C20	1.37(2)	C52–C56	1.33(3)
C2–C3	1.42(2)	C54–C55	1.33(3)
C2–C21	1.50(2)	C55–C56	1.40(3)
N7–Pd–N7	180.00	C3–C4–C5	123(2)
N7–Pd–N8	91.3(6)	C4–C5–C6	128(2)
N7–Pd–N8	88.7(6)	C20–C39–C40	123(2)
N7–Pd–N8	88.7(6)	C20–C39–C44	119(2)
N7–Pd–N8	91.3(6)	C1–C20–C19	122(2)
N8–Pd–N8	180.00	C1–C20–C39	116(2)
N1–Ni–N2	92.0(7)	C19–C20–C39	121(2)
N1–Ni–N3	176.5(6)	C3–C22–C23	115(2)
N1–Ni–N4	88.3(6)	N6–C51–C52	117(2)
N2–Ni–N3	88.6(7)	C51–C52–C53	125(2)
N2–Ni–N4	175.0(6)	C51–C52–C56	117(2)
N3–Ni–N4	91.3(7)	C53–C52–C56	118(2)
Ni–N1–C1	128(1)	N8–C53–C52	123(2)
Ni–N1–C4	124(1)	N8–C54–C55	125(2)
C1–N1–C4	107(2)	C40–C39–C44	118(2)
Pd–N8–C53	120(1)	N6–C40–C39	117(2)
Pd–N8–C54	123(1)	N6–C40–C41	123(2)
C53–N8–C54	117(2)	C39–C40–C41	120(2)
N1–C1–C2	108(2)	C40–C41–C42	124(2)
N1–C1–C20	125(2)	C41–C42–C43	117(2)
C2–C1–C20	127(2)	C42–C43–C44	121(2)
C1–C2–C3	107(2)	C39–C44–C43	121(2)
C1–C2–C21	131(2)	O2–C51–N6	123(2)
C3–C2–C21	122(2)	O2–C51–C52	120(2)
C2–C3–C4	105(2)	C54–C55–C56	115(2)
C2–C3–C22	128(2)	C52–C56–C55	123(2)
C4–C3–C22	126(2)		
N1–C4–C3	112(2)		
N1–C4–C5	125(2)		

e.s.d.s in the least significant figure are given in parentheses.

The Pd(II) coordination sphere shows nearly ideal square planar geometry. The N(7)–Pd–N(8) bond angle is 91.3(6)°. Furthermore, the Pd–N bond distances are 2.01(2) Å. The dihedral angles between the PdN$_4$ plane and the pyridyl rings are 74.2 and 92.9°. These structural features are similar to those observed for a Pd(II)(NC$_5$H$_4$-p-Cl)$_4$ complex [9]. The Ni$_2$Pd trinuclear fragment consists of three linked square planar complexes. The intermolecular dihedral angle between NiN$_4$

and PdN_4 planes is 67.2°. This leads to a long non-bonded Ni–Pd distance of 7.718(3) Å.

Conclusions

With the use of rationally designed multi-chelating ligands, we have devised a general method for the preparation of linear arrays of transition metal complexes. These macrocyclic ligand systems allow the synthesis of trimetallic diporphyrin complexes As shown in the single-crystal X-ray structure, these novel molecules contain two distinct, contiguous pockets. This feature may lead to new avenues for catalysis and/or molecular recognition.

Supplementary material

Tables (33 pages) of anisotropic thermal parameters, intramolecular bond angles involving hydrogen atoms, torsion angles and least-squares planes, positional parameters, full listing of bond lengths and bond angles, and listing of observed and calculated structure factors (23 pages) are available from the authors.

Acknowledgements

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