

A comparison of two structural forms of α,α -5,15-bis(*o*-nicotinoylamidophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrinato nickel(II)

L. Keith Woo*, Mannar R. Maurya, Robert A. Jacobson*, Shumei Yang and Sharon L. Ringrose

Ames Laboratory and Department of Chemistry, Iowa State University, Ames, IA 50011 (USA)

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Abstract

The structure of α,α -5,15-bis(*o*-nicotinoylamidophenyl)-2,8,12-18-tetraethyl-3,7,13,17-tetramethylporphyrinato nickel(II), [Ni(DPE)]-(py)₂ has been determined by single-crystal X-ray diffraction analysis. [Ni(DPE)]-(py)₂·H₂O crystallizes from wet DMF/CH₃OH with one water molecule solvate, C₅₆H₅₄N₈O₃Ni in the space group *P*2₁/*n* with *a* = 14.240(2), *b* = 25.418(4), *c* = 14.725(5) Å, β = 117.20(6)°, *V* = 4740(4) Å³, *Z* = 4, *R* = 0.0807 and *R*_w = 0.1072.

Introduction

Ni(II) tetrapyrrole and related porphyrin complexes are of great interest as models for Factor 430 (F430), a Ni(II) corphin found in methyl coenzyme M reductase [1]. Of fundamental importance are the variations in structures that the macrocycle ligands in these complexes can exhibit. Recent studies indicate that conformational variations in porphyrin complexes control chemical properties as well as reaction sites [2, 3]. In addition, substituents in adjacent *meso*-carbon and β -pyrrolic positions apparently induce large porphyrin distortions to minimize steric interactions [3]. We have been investigating a series of porphyrin ligands which bear alkyl substituents at all β -pyrrolic positions and aryl groups at two of the *meso*-positions [4, 5]. Recently we reported the synthesis and structural characterization of a nickel(II) complex of α,α -5,15-bis(*o*-nicotinoylamidophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin, [Ni(DPE)]-(py)₂·2CHCl₃, 1·2CHCl₃ [5]. When this complex is crystallized from a different solvent a new structural form is obtained, [Ni(DPE)]-(py)₂·H₂O, 1·H₂O. A structural comparison of these two forms is discussed here.

Experimental

Commercial reagents were used as received, without further purification. [Ni(DPE)]-(py)₂ was prepared fol-

lowing literature procedures [5]. Crystals of [Ni(DPE)]-(py)₂·H₂O were grown by slow evaporation of a wet DMSO/CH₃OH solution.

Structural determination

Crystals of the compound tended to be poorly diffracting with relatively broad peaks. After numerous attempts, a crystal of somewhat better quality was found for use in the structure determination. A purple prism having approximate dimensions of 0.45 × 0.35 × 0.30 mm was mounted on a glass fiber using epoxy cement and attached to a standard goniometer head. All measurements were made on a Rigaku AFC6R diffractometer with graphite monochromated Mo K α radiation (0.71069 Å) and a 12 KW rotating anode generator. The data were collected at a temperature of -50 ± 1 °C using the ω scan technique to a maximum of 2 θ value of 55.1°. The cell constants and an orientation matrix for data collection were obtained from a least-squares refinement of 25 reflections in the range 12.43 < 2 θ < 15.13°. The unit cell was found to be monoclinic with dimensions *a* = 14.240(2), *b* = 25.418(4), *c* = 14.725(5) Å, β = 117.20(6)°. A total of 22 091 intensities was measured, and 5635 unique 'observed' reflection having *I* > 3 σ (*I*) were used in the structure determination and refinement. The intensities of three representative reflections were monitored periodically throughout the data collection and showed no decay. An empirical absorption correction, based on azimuthal scans of several reflections, was applied, and the data were corrected for Lorentz and polarization effects.

*Authors to whom correspondence should be addressed.

TABLE 1. Crystal data for $[\text{Ni}(\text{DPE})](\text{py})_2 \cdot \text{H}_2\text{O}^a$

Empirical formula	$\text{NiO}_3\text{N}_8\text{C}_{56}\text{H}_{54}$
Formula weight	945.79
Crystal system	monoclinic
a (Å)	14.240(2)
b (Å)	25.418(4)
c (Å)	14.725(5)
β (°)	117.20(6)
V (Å ³)	4740(4)
Space group	$P2_1/n$ (No. 14)
Z value	4
ρ_{calc} (g/cm ³)	1.325
Temperature (°C)	-50
Radiation (Å)	Mo K α (0.71069)
μ (cm ⁻¹)	4.62
Scan type	ω
$2\theta_{\text{max}}$	54.9°
N_{collect}	22091
N_{obs}	5645
$N_{\text{variables}}$	613
R (%)	8.07
R_w (%)	10.72
Max. peak (ED. Map) ($\bar{e}/\text{Å}^3$)	0.98

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

Four molecules per cell were indicated by density considerations. Based on the packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P2_1/n$. The position of Ni was located from the three-dimensional Patterson map. The positions of all other non-hydrogen atoms were located from electron density maps obtained after inclusion of the nickel atom, including one water molecule. Hydrogen positions were calculated and refined isotropically. Full-matrix least-squares refinement of positional and thermal parameters led to convergence with a final unweighted R factor of 0.081 and a weighted R factor of 0.107. Neutral atom scattering factors were taken from the literature [6], and corrections for anomalous dispersion effects were included [7]; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer [8]. All calculations were done using the TEXSAN crystallographic software package [9], and a molecular diagram was drawn using ORTEP [10]. Pertinent crystallographic parameters are shown in Table 1.

Results and discussion

The molecular structure and atom numbering scheme of $[\text{Ni}(\text{DPE})](\text{py})_2 \cdot \text{H}_2\text{O} \cdot \text{H}_2\text{O}$, $1 \cdot \text{H}_2\text{O}$, are shown in Fig. 1. Table 2 presents a listing of fractional coordinates and Table 3 lists selected bond distances and angles. Figure 2 shows an analogous ORTEP for $[\text{Ni}(\text{DPE})](\text{py})_2 \cdot 2\text{CHCl}_3 \cdot 1 \cdot 2\text{CHCl}_3$ [5]. The porphyrin skeletons in both structures have bond lengths and angles which

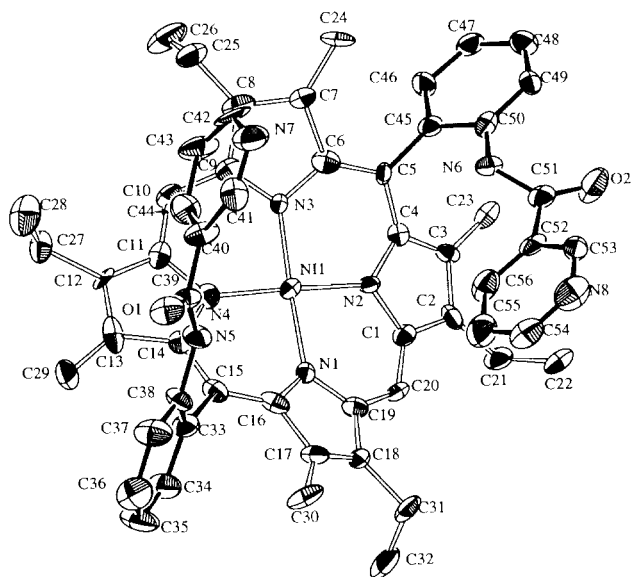


Fig. 1. Molecular structure and atom numbering scheme for $[\text{Ni}(\text{DPE})](\text{py})_2 \cdot \text{H}_2\text{O} \cdot \text{H}_2\text{O} \cdot \text{H}_2\text{O}$, $1 \cdot \text{H}_2\text{O}$.

are very similar to those in other crystallographically characterized Ni(II) porphyrin complexes [11]. For example, in both structures, Ni–Ni–N bond angles range from 88.5(1) to 91.9(1)° and the Ni is 0.11 Å out of the N₄ plane. In addition, both molecules show a similar extent of S₄-ruffling. For example the angles between adjacent pyrrole rings in $1 \cdot \text{H}_2\text{O}$ average 29.7° and the *meso*-carbon atoms are displaced alternately above and below the mean porphyrin plane by +0.55 to -0.39 Å. In $[\text{Ni}(\text{DPE})](\text{py})_2 \cdot 2\text{CHCl}_3$ the dihedral angle between pyrrole planes averages 28.6° and the *meso*-carbon atom displacement ranges from +0.57 to -0.52 Å.

The most unusual difference exhibited by the two structures of $[\text{Ni}(\text{DPE})](\text{py})_2$ is the manner in which the S₄-ruffling occurs. In $1 \cdot \text{H}_2\text{O}$, the *meso*-carbons bearing the aryl groups are displaced above the porphyrin plane towards the pyridyl groups by 0.55(1) and 0.48(1) Å. The corresponding *meso*-carbons in the CHCl₃-solvate structure, $1 \cdot 2\text{CHCl}_3$, are displaced below the porphyrin plane by -0.524(4) and -0.452(4) Å. The nature of the S₄-ruffling in $1 \cdot \text{H}_2\text{O}$ places the two pyridine appendages slightly closer together than in the CHCl₃-solvated structure. No significant interactions between appendages in the same molecule of $1 \cdot \text{H}_2\text{O}$ appear to exist as the closest approach involves atoms C40 and C55 at 6.82(3) Å. In contrast, the closest contact between the appendages in one molecule of $1 \cdot 2\text{CHCl}_3$ occurs between C48 and C56 (10.45(2) Å). Hydrogen bonding appears to occur between the carbonyl oxygen of one molecule of $1 \cdot \text{H}_2\text{O}$ and the amide NH of an adjacent molecule as indicated by the O1–N6

TABLE 2. Positional parameters and B_{eq} for $[\text{Ni}(\text{DPE})](\text{py})_2 \cdot \text{H}_2\text{O}$

Atom	x	y	z	B_{eq}
Ni1	0.4447(1)	0.32771(5)	0.3408(1)	1.75(5)
O1	0.7782(6)	0.5006(3)	0.7379(6)	3.3(4)
O2	0.1366(7)	0.4780(4)	-0.0928(7)	4.7(4)
N1	0.5756(6)	0.3307(3)	0.3305(6)	1.6(3)
N2	0.3619(6)	0.3273(4)	0.1936(6)	1.8(3)
N3	0.3170(6)	0.3344(3)	0.3528(6)	1.5(3)
N4	0.5250(7)	0.3190(4)	0.4845(7)	2.3(4)
N5	0.7233(8)	0.4334(4)	0.6219(7)	2.8(4)
N6	0.1706(7)	0.4472(3)	0.0675(7)	2.3(4)
N7	0.452(1)	0.5452(4)	0.5988(9)	4.1(5)
N8	0.428(1)	0.5610(4)	0.047(1)	4.5(6)
C1	0.3999(9)	0.3134(4)	0.1244(8)	2.1(4)
C2	0.314(1)	0.3046(4)	0.0247(9)	2.6(5)
C3	0.2216(8)	0.3160(4)	0.0311(9)	2.0(4)
C4	0.2538(8)	0.3320(4)	0.1353(8)	1.8(4)
C5	0.1864(8)	0.3538(4)	0.1734(8)	1.8(4)
C6	0.223(1)	0.3562(4)	0.2804(9)	2.2(5)
C7	0.152(1)	0.3705(5)	0.326(1)	2.8(5)
C8	0.203(1)	0.3488(5)	0.424(1)	3.4(6)
C9	0.3003(9)	0.3290(5)	0.4356(8)	2.3(4)
C10	0.3794(9)	0.3085(4)	0.5289(9)	2.4(5)
C11	0.485(1)	0.3040(4)	0.5510(8)	2.1(4)
C12	0.567(1)	0.2932(4)	0.6485(8)	1.8(4)
C13	0.662(1)	0.3033(4)	0.6498(9)	2.8(5)
C14	0.6314(9)	0.3219(4)	0.5457(8)	1.9(4)
C15	0.7026(9)	0.3409(4)	0.5086(9)	2.4(5)
C16	0.6728(9)	0.3467(4)	0.407(1)	2.3(5)
C17	0.741(1)	0.3623(5)	0.359(1)	2.9(5)
C18	0.6870(9)	0.3472(4)	0.2618(8)	2.2(4)
C19	0.5851(8)	0.3290(5)	0.2430(8)	2.2(4)
C20	0.5046(8)	0.3155(4)	0.1491(8)	1.8(4)
C21	0.325(1)	0.2896(5)	-0.0685(9)	3.0(5)
C22	0.321(1)	0.3365(6)	-0.134(1)	4.3(6)
C23	0.112(1)	0.3097(4)	-0.0543(9)	2.7(5)
C24	0.052(1)	0.4030(5)	0.283(1)	3.1(5)
C25	0.161(1)	0.3480(5)	0.500(1)	3.9(6)
C26	0.099(1)	0.2972(6)	0.491(1)	5.1(7)
C27	0.554(1)	0.2768(5)	0.7423(9)	3.2(5)
C28	0.565(1)	0.3240(6)	0.812(1)	4.7(6)
C29	0.770(1)	0.2980(5)	0.737(1)	3.6(6)
C30	0.846(1)	0.3877(5)	0.409(1)	3.9(6)
C31	0.729(1)	0.3495(5)	0.1831(9)	3.2(5)
C32	0.792(1)	0.3022(6)	0.189(1)	5.0(7)
C33	0.809(1)	0.3587(5)	0.5869(9)	2.8(5)
C34	0.901(1)	0.3308(5)	0.609(1)	3.5(5)
C35	0.999(1)	0.3473(6)	0.676(1)	4.4(6)
C36	1.009(1)	0.3954(6)	0.728(1)	4.8(7)
C37	0.922(1)	0.4247(5)	0.711(1)	3.8(6)
C38	0.821(1)	0.4073(4)	0.6414(9)	2.5(5)
C39	0.7110(9)	0.4743(4)	0.6741(9)	2.2(4)
C40	0.595(1)	0.4824(5)	0.643(1)	3.1(5)
C41	0.553(1)	0.5340(4)	0.627(1)	3.3(5)
C42	0.392(1)	0.5053(6)	0.591(1)	4.5(7)
C43	0.423(1)	0.4523(5)	0.607(1)	4.4(7)
C44	0.525(1)	0.4408(4)	0.629(1)	3.4(6)
C45	0.0828(9)	0.3739(4)	0.0982(8)	2.1(4)
C46	-0.010(1)	0.3466(5)	0.0767(9)	2.9(5)
C47	-0.105(1)	0.3624(5)	-0.000(1)	2.9(5)
C48	-0.114(1)	0.4061(5)	-0.058(1)	3.2(5)
C49	-0.021(1)	0.4348(4)	-0.0344(8)	2.3(5)
C50	0.075(1)	0.4199(4)	0.0393(9)	2.3(5)
C51	0.199(1)	0.4722(4)	-0.001(1)	2.7(5)
C52	0.310(1)	0.4905(4)	0.0432(9)	2.6(5)
C53	0.328(1)	0.5404(4)	0.0130(9)	2.8(5)
C54	0.507(1)	0.5309(6)	0.108(1)	4.2(7)
C55	0.494(1)	0.4815(5)	0.144(1)	4.2(6)
C56	0.393(1)	0.4620(5)	0.109(1)	3.3(5)
O3	0.196(2)	0.498(1)	0.739(2)	12(2)

TABLE 3. Selected intramolecular distances (Å) and bond angles (°) involving the non-hydrogen atoms of the porphyrin skeleton for $1 \cdot \text{H}_2\text{O}^a$

Distances (Å)			
Ni-N1	1.94(1)	C7-C24	1.53(2)
Ni-N2	1.93(1)	C8-C9	1.42(3)
Ni-N3	1.92(1)	C8-C25	1.51(3)
Ni-N4	1.92(1)	C9-C10	1.42(2)
N1-C16	1.38(2)	C10-C11	1.40(3)
N1-C19	1.37(2)	C11-C12	1.39(2)
N2-C1	1.40(2)	C12-C13	1.39(3)
N2-C4	1.38(2)	C12-C27	1.51(3)
N3-C6	1.39(2)	C13-C14	1.47(2)
N3-C9	1.35(2)	C13-C29	1.46(2)
N4-C11	1.41(3)	C14-C15	1.41(3)
N4-C14	1.36(2)	C15-C16	1.38(3)
C1-C2	1.45(2)	C15-C33	1.51(2)
C1-C20	1.35(2)	C16-C17	1.51(3)
C2-C3	1.38(3)	C17-C18	1.29(2)
C2-C21	1.49(3)	C17-C30	1.51(2)
C3-C4	1.45(2)	C18-C19	1.44(2)
C3-C23	1.50(2)	C18-C31	1.52(3)
C4-C5	1.43(3)	C19-C20	1.37(2)
C5-C6	1.42(2)	C21-C22	1.52(3)
C5-C45	1.48(2)	C25-C26	1.55(3)
C6-C7	1.50(3)	C27-C28	1.52(3)
C7-C8	1.41(2)	C31-C32	1.49(3)
Angles (°)			
N1-Ni-N2	91.1(5)	C4-C5-C6	119(1)
Ni-Ni-N3	173.9(5)	C4-C5-C45	118(1)
N1-Ni-N4	88.7(6)	C6-C5-C45	123(2)
N2-Ni-N3	89.3(5)	N3-C6-C5	124(2)
N2-Ni-N4	171.7(5)	N3-C6-C7	112(1)
N3-Ni-N4	91.8(6)	C5-C6-C7	122(1)
Ni-N1-C16	125(1)	C6-C7-C8	102(1)
Ni-N1-C19	126.5(8)	C6-C7-C24	131(2)
C16-N1-C19	107(1)	C8-C7-C24	127(2)
Ni-N2-C1	125.6(9)	C7-C8-C9	108(2)
Ni-N2-C4	128(1)	C7-C8-C25	125(2)
C1-N2-C4	105(1)	C9-C8-C25	127(1)
Ni-N3-C6	126(1)	N3-C9-C8	114(1)
Ni-N3-C9	129.1(8)	N3-C9-C10	122(2)
C6-N3-C9	104(1)	C8-C9-C10	124(2)
Ni-N4-C11	126(1)	C9-C10-C11	124(2)
Ni-N4-C14	132(1)	N4-C11-C10	123(1)
N2-C1-C2	110(1)	N4-C11-C12	111(2)
N2-C1-C20	123(1)	C10-C11-C12	124(2)
C2-C1-C20	126(2)	C11-C12-C13	110(2)
C1-C2-C3	106(2)	C11-C12-C27	127(2)
C1-C2-C21	125(2)	C13-C12-C27	123(1)
C3-C2-C21	128(1)	C12-C13-C14	102(1)
C2-C3-C4	107(1)	C12-C13-C29	129(2)
C2-C3-C23	124(2)	C14-C13-C29	130(2)
C4-C3-C23	129(2)	N4-C14-C13	114(2)
N2-C4-C3	111(1)	N4-C14-C15	121(1)
N2-C4-C5	124(1)	C13-C14-C15	126(1)
C3-C4-C5	125(1)	C14-C15-C16	123(1)
C14-C15-C33	116(2)	N1-C19-C20	124(2)
C16-C15-C33	121(2)	C18-C19-C20	127(2)
N1-C16-C15	124(2)	C1-C20-C19	126(2)
N1-C16-C17	107(1)	C2-C21-C22	113(1)
C15-C16-C17	128(1)	C8-C25-C26	111(2)
C16-C17-C18	107(2)	C12-C27-C28	111(1)
C16-C17-C30	127(2)	C18-C31-C32	112(2)
C18-C17-C30	127(2)	C15-C33-C34	119(1)
C17-C18-C19	109(2)	C15-C33-C38	122(1)
C17-C18-C31	126(2)	C5-C45-C46	120(1)
C19-C18-C31	125(1)	C5-C45-C50	121(1)
N1-C19-C18	109(1)		

^ae.s.d.s in the least significant figure are given in parentheses.

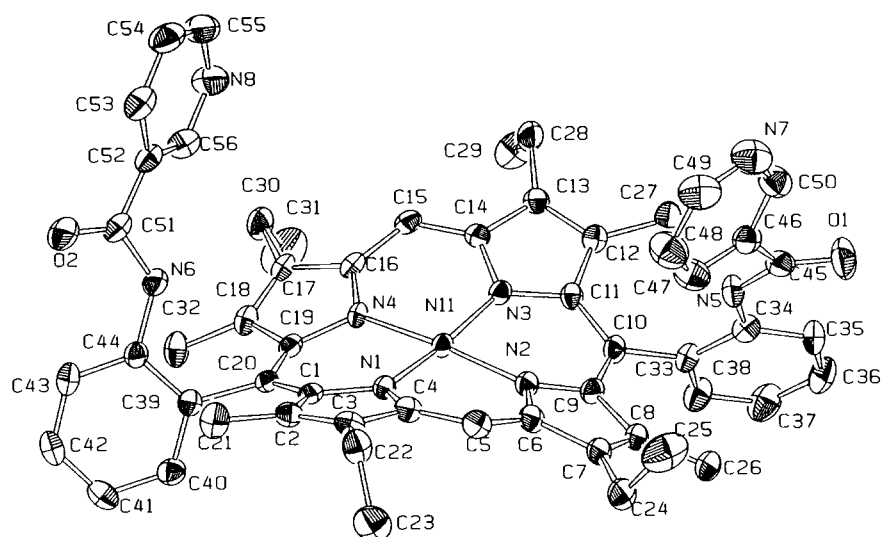


Fig. 2. Molecular structure and atom numbering scheme for $[\text{Ni}(\text{DPE})](\text{py})_2 \cdot 2\text{CHCl}_3, 1 \cdot 2\text{CHCl}_3$. Note that the atom numbering differs from that of $1 \cdot \text{H}_2\text{O}$.

distance of 2.93(1) Å. In addition, the water molecule appears to hydrogen bond to carbonyl oxygen O2 with an O2–O3 contact of 3.00(2) Å. In $1 \cdot 2\text{CHCl}_3$, no unreasonably short intermolecular distances are present. The shortest contact is 3.15(1) Å between O2 and the carbon of a chloroform.

Finally, an interesting comparison can be made with the structures of Zn complexes of octamethyltetraphenylporphyrin (OMTPP) and octaethyltetraphenylporphyrin (OETPP). Zn(OMTPP) and Zn(OETPP) are two of the most highly distorted porphyrin complexes known [2]. The high degree of S_4 -ruffling in these complexes is attributed to steric interactions between *meso*-phenyl groups and β -pyrrolic alkyl substituents. In these highly substituted porphyrin ligands, the phenyl groups rotate into the macrocycle plane to minimize contacts with the pyrrole substituents. Consequently, the pyrrole β -carbons exhibit the greatest excursion (± 1.18 Å) from the mean porphyrin plane while the *meso*-carbons show very little displacement (± 0.16 Å) from the same plane. Although the porphyrin ligands crystallographically characterized here also contain *meso*-aryl and β -pyrrolic alkyl groups, the major difference is the presence of an *ortho*-substituent on the aryl rings. As a result, the aryl rings in $1 \cdot \text{H}_2\text{O}$ and $1 \cdot 2\text{CHCl}_3$ do not rotate into the macrocycle plane. The dihedral angles between the mean porphyrin plane and the aryl rings range from 54 to 68° and are similar to those observed for other tetraarylporphyrins. In addition, the S_4 -ruffling in $[\text{Ni}(\text{DPE})](\text{py})_2$ is less severe and very similar to that of the β -only substituted tetragonal Ni(OEP) complex [11a]. In the two forms of $[\text{Ni}(\text{DPE})](\text{py})_2$ discussed here, the manner in which the S_4 -ruffling occurs appears to be very sensitive to

the type of solvate molecules present. Thus, the issue of porphyrin distortions remain a very complex function of metal, substituents and solvate molecules.

Supplementary material

Text detailing the data collection and listings of atomic coordinates, thermal parameters, bond distances and angles, least-squares planes, and calculated and observed structure factors (40 pages) are available from the authors.

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