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The Structure of Nitro-5,10,15,20-tetraphenylporphyrinato-(piperidine)cobalt(III)

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The structure of synthetic nitro-5,10,15,20-tetraphenylporphyrinato(piperidine)cobalt(III) has been determined by X-ray diffraction method. The results revealed that the porphyrin plane is markedly distorted to nonplanar due to the steric interaction between the axial piperidine and the porphyrin core.

Nitrosyl(5,10,15,20-tetraphenylporphyrinato)cobalt(II) ([$\mathrm{Co^{II}}$(tpp)(NO)])1) reacts with molecular oxygen in the presence of piperidine to nitro-5,10,15,20-tetraphenylporphyrinato(piperidine)cobalt(III) ([$\mathrm{Co^{III}}$(tpp)(pip)(NO_2)], **1**).2) The structure of **1** has been determined by X-ray diffraction method.

Complex **1** is obtained from [$\mathrm{Co^{II}}$(tpp)(NO)], piperidine, and O_2 gas at a pressure of 1 atm in 1,2-dichloroethane. The crude **1** is dissolved in a mixture of dichloromethane and methyl alcohole, and recrystallized by slow evaporation of the solvent at room temperature. The X-ray structural determination of **1** was done at room temperature using graphite monochromated Cu Kα radiation.3) The crystal data: $C_{49}H_{39}CoN_6O_2$, M=802.2; orthorhombic; space group $P2_12_12_1$; a=18.642(16), b=19.644(18), c=10.568(8) Å; V=3870 $Å^3$; Z=4; Dc=1.376 g/cm^3. The final R factor was 0.068 for 2303 independent reflections.

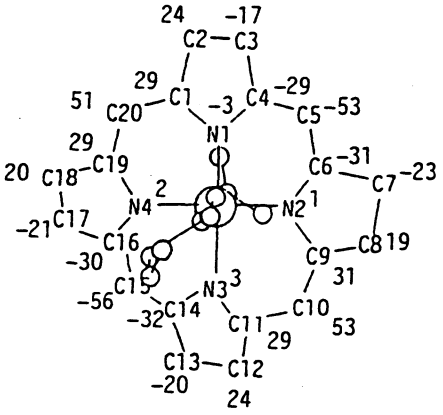

Fig. 1. The numbering scheme employed for atoms of the porphyrin core of **1**. Phenyl groups and hydrogen atoms are omitted. Piperidine and NO_2 group are shown with small circles. The figurs shown with atoms are perpendicular displacements ($\times 10^2$ Å) of atoms from the least-squares mean plane of 24 atom porphyrin core. (-) stands for the NO_2 group side.

The numbering scheme for atoms of the porphyrin core and the coordination geometry about the Co(III) of **1** are shown in Fig. 1 and Fig. 2, respectively. Some important distances and angles are shown in Table 1. The average equatorial Co-N distance is 1.953(9) Å. The axial Co-N5 is 2.044(10) and Co-N6 is 1.897(11) Å.

Piperidine takes a chair form and is coordinated to Co lying its ring plane perpendicular to the porphyrin ring. The distance between H atom linked to N5 (HN5 in Fig. 2) and N3 is 2.43 Å. This is short enough for the steric interaction between

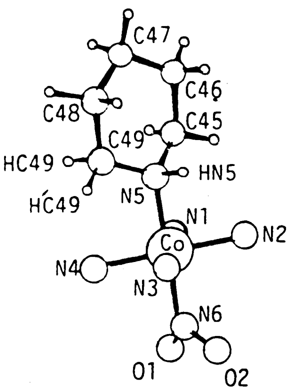

Fig. 2. Coordination geometry about the Co(III) of **1**.

Table 1. Some important distances (Å) and angles (°) in **1**

Co-N1	1.947 (9)
Co-N2	1.955 (9)
Co-N3	1.960 (8)
Co-N4	1.951 (9)
Co-N5	2.044(10)
Co-N6	1.897(11)
N6-O1	1.182(14)
N6-O2	1.207(14)
HN5-N3	2.431
N1-Co-N2	89.8 (4)
N1-Co-N4	90.0 (4)
N2-Co-N3	90.3 (4)
N3-Co-N4	89.8 (4)
N1-Co-N3	179.2 (4)
N2-Co-N4	178.2 (4)
N2-Co-N5	86.4 (4)
N1-Co-N6	90.9 (4)
N2-Co-N6	91.5 (4)
O1-N6-O2	115.4(11)

The figure in parentheses is the estimated standard deviation.

piperidine and porphyrin core to occur. As seen in Figs. 1 and 3, the porphyrin core is folded to form a shallow ditch and piperidine lies along the ditch. Some other short distances (Å) between atoms of piperidine and the porphyrin core are as follows: HN5-N2, 2.54; HN5-C11 (Figs. 1 and 2), 2.60; HN5-C10, 2.63; HN5-C9, 2.66; H'C49-N3, 2.66; H'C49-N4, 2.73; H'C49-C14, 2.87; H'C49-C16, 2.90; HC49-N4, 2.73; HC49-C19, 2.80. This steric interaction due to the close approach of piperidine to Co(III) gives **1** the characteristic molecular structure as follows. (a) The porphyrin core is distorted markedly to nonplanar as is shown in Fig. 3. The perpendicular displacements of atoms from the least-squares mean plane of porphyrin core are also shown in Fig. 1. The maximum displacement of atom is 0.558(9) Å at C15 and the average displacement is 0.262 Å. (b) The Co-N5 distance (2.044(10)) is longer than the Co-$N_{3,5\text{-lut}}$ (2.036(4) Å) in $[\mathrm{Co^{III}(tpp)(3,5\text{-}lut)(NO_2)}]$ reported by Scheidt et al. ($N_{3,5\text{-lut}}$ stands for N atom of 3,5-lutidine).[4] Thus **1** may be more unstable than expected from the basicity (pKa value) of piperidine.[5]

This sort of steric effect of piperidine in the six coordinate porphyrinatocobalt(III) is already known in the formation reaction of the dioxygen adduct of cobalt protoporphyrin IX dimethyl ester in toluene solution.[6] But only two reports for $[\mathrm{Co^{III}(tpp)(pip)_2}]^+$ [7] anf for **1** have shown the clear evidences by X-ray analysis data for the steric interactions between the axial piperidine and porphyrin core.

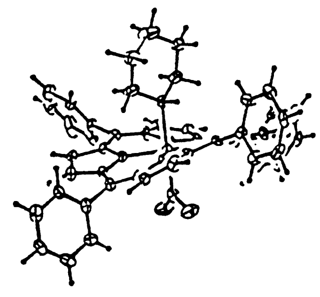

Fig. 3. Computer-drawn model of **1**.

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