

Bridged Dinitrogen Complexes of Iron and Chromium Porphyrins

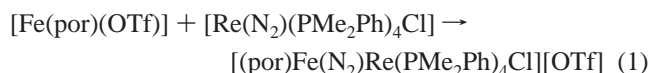
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Dinitrogen complexes of transition metals have attracted much attention due to their important roles in biological and abiological nitrogen fixation processes.¹ Of relevance to mechanisms of metal-mediated nitrogen fixation are dinuclear complexes containing μ - η^1 : η^1 -dinitrogen ligands, which depending on the extent of metal–nitrogen π bonding may be classified into three types, namely, dinitrogen (N_2)⁰ (**A**), diazenido(2-) (N_2)²⁻ (**B**), or hydrazido(4-) (N_2)⁴⁻ (**C**) ligand.^{1,2} Cummins and co-workers demonstrated that mononuclear molybdenum tris-amide complexes are capable of splitting dinitrogen via dinitrogen-bridged dimolybdenum intermediates.³ On the other hand, dinuclear μ - η^1 : η^1 -dinitrogen complexes are formed by coupling reactions of nitrido–osmium complexes, which may be viewed as a microscopic reverse of metal-assisted $N\equiv N$ cleavage.⁴ Although terminal dinitrogen complexes of metalloporphyrins are well documented, there are relatively few examples of analogous complexes with bridged dinitrogen ligands.⁵ Collman and co-workers reported that metal-bound ammonia can be converted to a bridged dinitrogen in a diruthenium complex of a cofacial diporphyrin via the bridged hydrazine and diazene intermediates, demonstrating the potential of metalloporphyrins as catalysts for dinitrogen reduction.⁶ This prompted us to study the bonding and structure of bridged dinitrogen complexes of metalloporphyrins. Heterometallic μ -dinitrogen complexes are generally synthesized by the reactions of terminal dinitrogen complexes with another Lewis acidic metal center such as titanium(IV) and molybdenum(IV).⁷ In this connection, we set out to investigate the reactions between a rhenium(I) dinitrogen complex and metalloporphyrins. We here report on the isolation and molecular structure of the first heterometallic bridged dinitrogen complexes containing iron(III) and chromium(III) porphyrins.

Treatment of [Fe(por)(OTf)] [por = octaethylporphyrinate OEP or tetra(*p*-tolyl)porphyrinate TTP] with 1 equiv of [Re(N_2)(PMe₂-Ph)₄Cl]⁸ led to formation of the dinitrogen-bridged Fe/Re complexes [(por)Fe(N_2)Re(PMe₂Ph)₄Cl][OTf] (por = OEP **1** or TTP **2**) characterized by UV/vis and IR spectroscopies (eq 1).⁹



No reactions were found between [Fe(por)Cl] and [Re(N_2)(PMe₂-Ph)₄Cl], suggesting that dissociation of the labile triflate ligand from the iron porphyrin is crucial for the formation of the bridged dinitrogen complexes. The KBr FT-IR spectra of **1** and **2** feature the N–N stretching modes at ca. 1803 and 1820 cm⁻¹, respectively, which are obviously lower than that for [Re(N_2)(PMe₂-Ph)₄Cl] (1920 cm⁻¹), indicating that the N–N triple bond in N_2 is weakened upon coordination to Fe(III). The ν_{NN} for **1** and **2** are, however, lower than those for reported dinitrogen complexes of metalloporphyrins, e.g., 2112 cm⁻¹ for [Ru₂DPB(*Im)₂](μ - N_2) (DPB = diporphyrinatobiphenylene tetraanion, *Im = 1-*tert*-butyl-5-phenylimidazole)⁶ and 2030 cm⁻¹ for [Os(OEP)(N_2)-(THF)].¹⁰ As revealed by UV/vis spectroscopy, [Fe(por)(OTf)] reacted with [Re(N_2)(PMe₂Ph)₄Cl] cleanly to give dinitrogen complexes. Upon addition of [Re(N_2)(PMe₂Ph)₄Cl] to a toluene solution of [Fe(OEP)(OTf)], the Soret band for [Fe(OEP)(OTf)] at 371 nm gradually dropped in intensity and concomitantly a new Soret band at 447 nm attributable to **1** appeared (Figure 1). The formation constant for **1** in toluene solution at 25 °C was determined spectrophotometrically to be ca. 410 ± 40 M⁻¹.¹¹ A slightly smaller formation constant (240 ± 25 M⁻¹) was found for **2** due to the larger steric bulk and/or lower basicity of TTP compared with that for OEP. Complex **1** is air stable both in the solid state and in toluene solution but decomposes gradually in chlorinated solvents to give uncharacterized products including [Fe(OEP)Cl]. The measured room-temperature magnetic moment of ca. 4.4 μ_{B} for **1** is consistent with the admixed intermediate-spin state of Fe(III) ($S = 3/2, 5/2$), which is normal for iron(III) porphyrins containing weakly coordinating axial ligands.¹² As suggested by Reed and Guiset, the chemical shift for the pyrrolic protons in [Fe(TPP)X] (TPP = tetraphenylporphyrinate) is very

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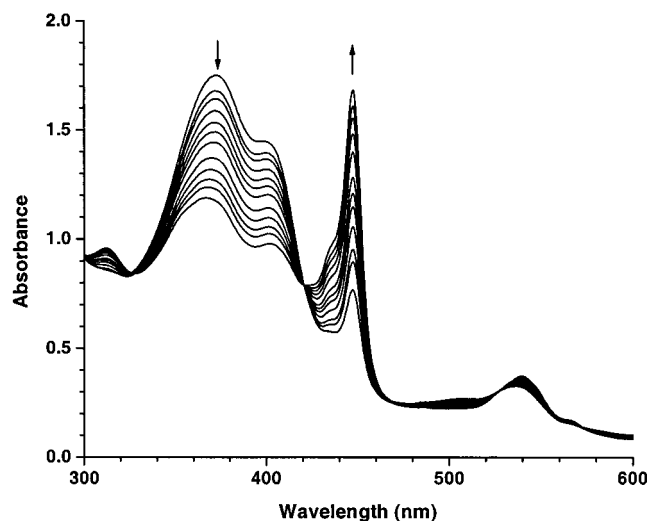


Figure 1. Optical spectral trace for the reaction between [Fe(OEP)(OTf)] and [Re(N₂)(PMe₂Ph)₄Cl] in toluene at room temperature. Time interval = 10 min.

sensitive to the nature of the axial ligand X.¹³ The observation of a pyrrolic resonant signal at $\delta -3.23$ in the ¹H NMR spectrum of **2** is consistent with the weak field strength of the bridged dinitrogen ligand.¹³ The solid-state structure of **1** has been unambiguously established by X-ray crystallography.¹⁴ Figure 2 shows a perspective view of the cation [(OEP)Fe(N₂)Re(PMe₂Ph)₄Cl]⁺. To our knowledge, this is the first crystal structure of a bridged dinitrogen complex of metalloporphyrin. The geometries around Re and Fe are pseudooctahedral and square-pyramidal, respectively, with the dinitrogen binding to Re and Fe in a $\mu-\eta^1:\eta^1$ fashion. The displacement of Fe from the N₄ mean plane (0.418 Å) and average Fe–N(pyrrole) distance [2.06(1) Å] are normal for intermediate-spin iron(III) porphyrins.¹⁵ The Re–N [1.832(10) Å] and N–N bond lengths [1.17(1) Å] are comparable to those in [(MeO)Cl₄Mo(N₂)Re(PMe₂Ph)₄Cl] [1.815(15) and 1.18(3) Å, respectively].^{7c} The Fe–N(dinitrogen) bond length of 1.93(1) Å is obviously longer than that in the iron(III) diazenide complex {[N₃N]Mo(N₂)₃Fe} (average distance of 1.84 Å, [N₃N]³⁻ = [(Me₃SiNCH₂CH₂)₃N]³⁻)¹⁶ but is comparable to that for low-spin [Fe(TPP)(N₃)] [1.953(5) Å].¹⁷ Like previously reported M(N₂)Re complexes,⁷ the Fe–N–N–Re linkage in **1** is essentially linear [Fe(1)–N(2)–N(1) and N(2)–N(1)–Re(1) bond angles being 170(1) and 177(1)°, respectively] with a π delocalized system. The relatively long Fe–N₂ π interaction in **1**, if there is any, should

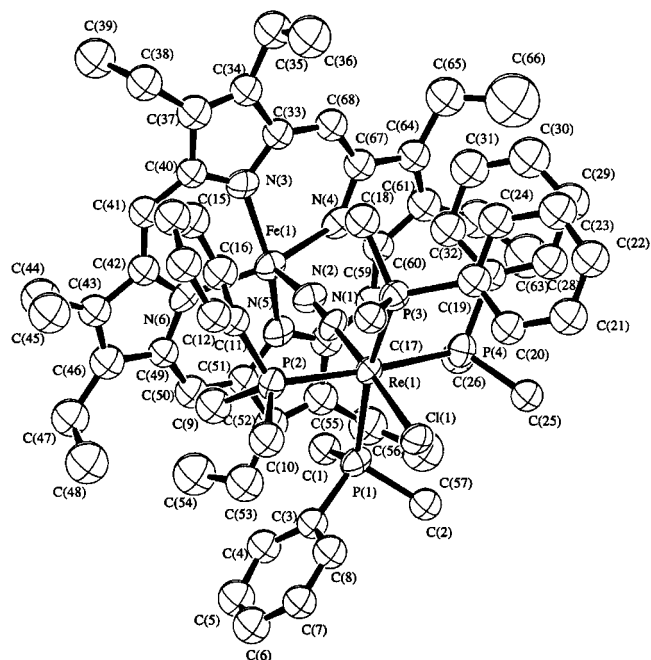


Figure 2. Perspective view of the cation [(OEP)Fe(N₂)Re(PMe₂Ph)₄Cl]⁺. Important bond lengths (Å) and angles (deg): Re(1)–N(1) 1.832(10), Fe(1)–N(2) 1.93(1), N(1)–N(2) 1.17(1); Re(1)–N(1)–N(2) 177(1), Fe(1)–N(2)–N(1) 170(1).

be weak, consistent with the observed magnetic and IR data. The bonding in **1** is therefore considered as intermediate between types **A** and **B** (vide infra).

Similarly, treatment of [Cr(OEP)(OTf)] with [Re(N₂)(PMe₂Ph)₄Cl] afforded the dinitrogen-bridged Cr/Re complex [(OEP)Cr(N₂)Re(PMe₂Ph)₄Cl][OTf] **3**, which exhibits the Soret band at 467 nm and the IR ν_{NN} at 1887 cm⁻¹. The ν_{NN} for **3** is similar to that for [CrCl₃(N₂){Re(PMe₂Ph)₄}(THF)₂] (1860 cm⁻¹)¹⁸ but is higher than those for **1** and **2**, indicating that the N–N bond in the Cr(III) complexes is stronger than those in the Fe(III) complexes. This perhaps is a reflection of weaker Cr(III)–N₂ interaction compared with the Fe(III)–N₂ counterpart. Accordingly the formation constant for **3** (140 ± 15 M⁻¹) was found to be smaller than that for **1**.

In summary, the first $\mu-\eta^1:\eta^1$ -dinitrogen complexes of iron(III) and chromium(III) porphyrins were synthesized and characterized. Iron(III) porphyrins appear to be stronger acceptors for the dinitrogen ligand than the analogous chromium porphyrin. The study of activation of the dinitrogen ligand in this new type of bimetallic dinitrogen complexes is underway.

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Supporting Information Available: Syntheses of complexes **1–3** and listings of final atomic coordinates, anisotropic displacement parameters, and bond lengths and angles of **1**·2CH₂Cl₂. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(13) High-spin iron(III) porphyrins with axial donor ligands exhibit downfield shifts for pyrrolic resonance whereas species approaching a pure intermediate state have upfield shifts (see ref 12).

(14) Crystal data for **1**·2CH₂Cl₂: formula C₇₁H₉₂Cl₅F₃FeN₆O₃P₄Re, fw 1709.82, monoclinic, space group *P*2₁/*a*, *a* = 21.405(7) Å, *b* = 18.896(4) Å, *c* = 21.55(1) Å, β = 116.24(2)°, *V* = 7814(4) Å³, *Z* = 4, ρ_{calcd} = 1.452 g cm⁻³, $\mu(\text{Mo K}\alpha)$ = 20.67 cm⁻¹. *R*(*R*_w) = 0.081(0.087) for 6980 reflections with *I* > 1.50 σ (*I*) and 430 variable parameters.

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