Ligand-Bridged Heterobimetallic Polymers: Silver(I)−Benzothiadiazole−Nickel Porphyrin Cation−Benzothiadiazole Arrays

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Porphyrin π cation radicals incorporating high oxidation states of Fe, Mn, Cr, and Ru catalyze epoxidations, hydroxylations, and oxidations of alkenes, alkanes, and other organic substrates.[1] Ni(III) tetraaza complexes catalyze similar oxidations,[2] and Ni(III) tetrapyrroles (factor 430) have been invoked in the catalytic cycle of methanogenic bacteria.[3] Porphyrins with elegantly designed superstructures have also been synthesized[4] in attempts to construct regiospecific catalysts that mimic the many biological processes mediated by porphyrins.[5]

We recently investigated a series of *meso*-tetraphenylporphyrins in which the introduction of pyrrole β substituents forces the molecules to adopt severely distorted saddle conformations, e.g. 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin: OETPP. The macrocycle distortions not only alter the physical and chemical properties of the molecules[6] but also exert significant geometric effects. We demonstrate here that the combination of saddle distortions and peripheral substituents forms superstructural "trenches" that impose specific orientations on ligands: crystallographic results establish that, in a hexacoordinated oxidized NiOETPP complex, the axial ligands are forced to align perpendicular to each other and along opposite porphyrin nitrogen axes. In addition, we describe the novel bimetallic polymer that results from the oxidation of NiOETPP by $AgClO_4$ in the presence of the bidentate ligand 2,1,3-benzothiadiazole (BTD).[7]

In CH_2Cl_2, Ni^{II}OETPP is readily oxidized[6a] with $AgClO_4$ to a radical which displays an isotropic EPR signal centered at $g = 2$ characteristic of a π cation radical at both 300 and 110 K. Upon addition of BTD, the EPR signal at 110 K is converted quantitatively to a new axial spectrum with $g_\perp = 2.272$ and $g_\parallel = 2.069$. The latter signal is typical of hexacoordinated Ni(III) species in a tetragonally elongated octahedral environment with one unpaired electron in the d_{z^2} orbital.[8] (The EPR spectra are included in the Supporting Information.)

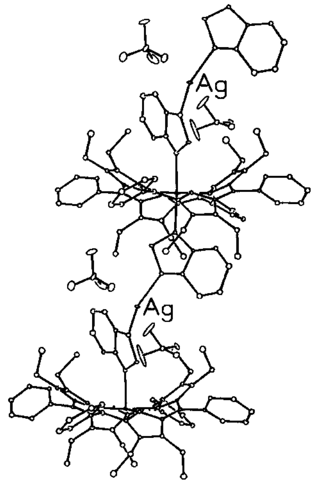

Figure 1. Structure of the polymeric aggregate of NiOETPP-$(BTD)_2{}^+ClO_4{}^-$ linked via silver ions. The two $ClO_4{}^-$ counterions of the porphyrin and silver cations flank the latter. Thermal ellipsoids are reduced to 5% probability for clarity.

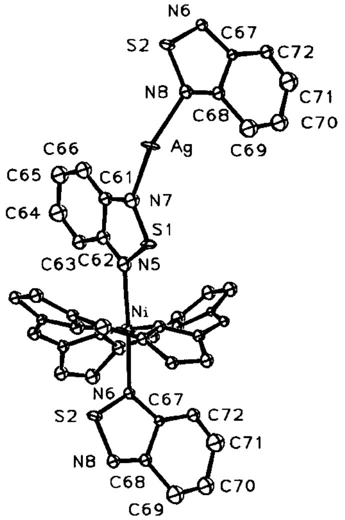

Figure 2. Molecular structure of a fragment of polymeric [−BTD−NiOETPP$^+$−BTD−Ag$^+$−]. The $ClO_4{}^-$ counterions and peripheral ethyl and phenyl substituents on the porphyrin are omitted for clarity. Thermal ellipsoids enclose 30% probability. Selected bond distances: average Ni−N$_{porphyrin}$ = 2.00(2) Å, Ni−N$_{axial}$ = 2.23 (2)Å, Ag−N = 2.31 (2)Å.

An X-ray structure of the ligated oxidized porphyrin[9] confirms the octahedral environment deduced from the EPR results and establishes that the porphyrin superstructure does indeed control the orientation of the axial ligands[10] (Figures 1 and 2). The Ni is coordinated by two BTDs with Ni−N distances of 2.23(2) and 2.00(2) Å to the BTD and porphyrin nitrogens, respectively. The ligands align along the axes defined by opposite pyrrole nitrogens at a dihedral angle of 81° to each other. Surprisingly,

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the saddle conformation of the parent NiOETPP[6a] is retained in the ligated species with the β carbons displaced an average of 1.31 Å above and below the mean plane of the porphyrin.

Additional noteworthy features are evident in the crystal structure. BTD was chosen as a ligand because its high oxidation potential[11] would prevent it from reducing the oxidized porphyrin and because it can function as a bidentate ligand[12] that might provide potential binding sites for substrates. As is obvious from Figures 1 and 2, the BTDs not only ligate to the Ni of the porphyrin but also bind to a silver ion to form bimetallic *polymeric* chains composed of $[-Ag^+-BTD-NiP^+-BTD-]$ units with two perchlorate anions to balance the charges of the silver and porphyrin cations. (The $AgClO_4$ was present in excess in the preparative oxidation of NiOETPP.) At 300 K, powdered samples of $[NiOETPP(BTD)_2Ag]^{2+}(ClO_4^-)_2$ exhibit a powder pattern EPR signal at $g_\perp = 2.298$ and $g_\| = 2.075$ similar to the axial signal in frozen solution described above.

The EPR spectra and the Ni−N distances of the oxidized porphyrin warrant further comment. The EPR data are certainly characteristic of a hexacoordinated Ni(III) with one unpaired electron in the d_{z^2} orbital.[8] However, the Ni−N distances within the oxidized porphyrin are typical of those observed in several hexacoordinated *high-spin* Ni(II) porphyrin derivatives.[13] Thus, they do not reflect the Ni−N bond contraction expected on oxidation of hexacoordinated Ni(II) to Ni(III) complexes in which the $d_{x^2-y^2}$ orbital is no longer occupied.[14] To reconcile the crystallographic and EPR data, we suggest that the ligated oxidized porphyrin is actually a high-spin Ni(II) porphyrin π cation, i.e. a three spin system: $d^1_{x^2-y^2}$, $d^1_{z^2}$, π^1, in which the electron in the $d_{x^2-y^2}$ orbital of the high-spin Ni(II) is antiferromagnetically coupled to the unpaired electron of the porphyrin π radical, leaving *one* unpaired electron in the Ni d_{z^2} orbital; i.e., the complex is a *pseudo* Ni(III) species. A similar antiferromagnetic coupling is observed in the corresponding $Cu^{II}OETPP^+ClO_4^-$ π radical.[6b] In that case, the single electron in the Cu(II) $d_{x^2-y^2}$ orbital pairs with that in the porphyrin to yield a diamagnetic complex. In both the Cu and Ni cases, mixing of the metal and π orbitals is favored by the nonplanar conformations of the porphyrins.[6b]

In summary, we find that oxidized NiOETPP binds two nitrogenous axial ligands that are forced to align perpendicular to each other in superstructural trenches formed by the saddle conformation of the molecule and its peripheral substituents. OETPPs thus provide simple synthetic avenues for controlling the orientations of axial ligands[15] and for constructing regiospecific pockets at porphyrin catalytic sites. The bidentate BTD further allows the incorporation of potential substrate binding sites. In addition, BTD offers the possibility of constructing new one-dimensional porphyrin polymers of interest in materials science[16] as evidenced by the novel bimetallic polymer composed of $[-Ag^+-BTD-NiP^+-BTD-]$ subunits reported here.

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Supporting Information Available: EPR spectra, additional structural diagrams, and listings of experimental crystallographic details, atomic coordinates, bond distances, and bond angles (14 pages). See any current masthead page for ordering information and Internet access instructions.

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(9) $(NiOETPP(BTD)_2{}^+)(Ag^+)(2ClO_4^-)_2\cdot 2CH_2Cl_2$ was prepared by oxidation of NiOETPP with $AgClO_4$ in CH_2Cl_2 followed by addition of BTD. The compound crystallized from CH_2Cl_2/pentane in space group $P1$ with $a = 12.994(7)$ Å, $b = 13.634(4)$ Å, $c = 12.801(7)$ Å, $\alpha = 101.49(4)°$, $\beta = 114.98(4)°$, $\gamma = 105.42(4)°$, $V = 1852(2)$ Å^3, and $Z = 1$. Data were collected at 298 K on an Enraf-Nonius CAD4 diffractometer with Cu Kα radiation. A total of 5417 reflections $(h,\pm k,\pm l)$ were measured with 4948 unique reflections and 4059 with $F_o > 4\sigma(F_o)$. Refinement yielded $R_F = 0.103$ and $R_{wF} = 0.113$. (Additional details are available in the Supporting Information.)

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