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Evidence for the Existence of an Imidazole Bridge between a Nickel Schiff Base and Co(TPP)

GREG BREWER and EKK SINN

Dept. of Chemistry, McCormick Rd., University of Virginia, Charlottesville, Va. 22901, U.S.A.

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The interest in imidazole as a bridging group has seen a great deal of synthetic interest since the discovery of such a group in the enzyme system superoxide dismutase [1]. A number of compounds have been prepared in which the imidazole acts a bridging group between two identical metals as in the case of manganese [2], nickel [3], and copper [4]. Imidazole can also link dissimilar metals as in a Co(III)–Cu(II) compound [5] and in several Cu(II)–Fe(II) examples [6]. The interest in the latter type of complexes centers around attempts to model the magnetic properties of certain naturally occurring metalloenzymes. One such enzyme system which has generated considerable interest is cytochrome c oxidase for which one postulate has a heme iron linked to Cu(II) by an imidazole group [7]. Attempts at preparing model compounds for this system have met with a limited degree of success [8].

Our interest in this area has centered on linking a divalent first row transition element to a metal porphyrin via an imidazole (Im) group. Our synthetic strategy revolved around the assymetric Schiff base complex, **I**, which contains a deprotonated imidazole, capable of bonding, via its outer nitrogen, to a metal porphyrin, **III** (Fig. 1). The advantage of this approach is that once imidazole binding to the metal porphyrin is established, it can be concluded that the binuclear complex has been formed since the divalent metal is already bound in the Schiff base environment. The structural identity of our metal complex and its ability to serve as an imidazole bridge were determined by crystallographic investigation on the copper ligand complex(I) and its adduct with Cu(HFA)$_2$ (**II**). Line drawings of these molecules, based on their ORTEP plots are shown in Fig. 1 along with the postulated structure of the present binuclear (**III**). The details of these structures were reported previously [9]. We now report solution and solid state ESR data for the existence of an imidazole bridge in the adduct of Co(TPP) and our nickel Schiff base complex.

Experimental

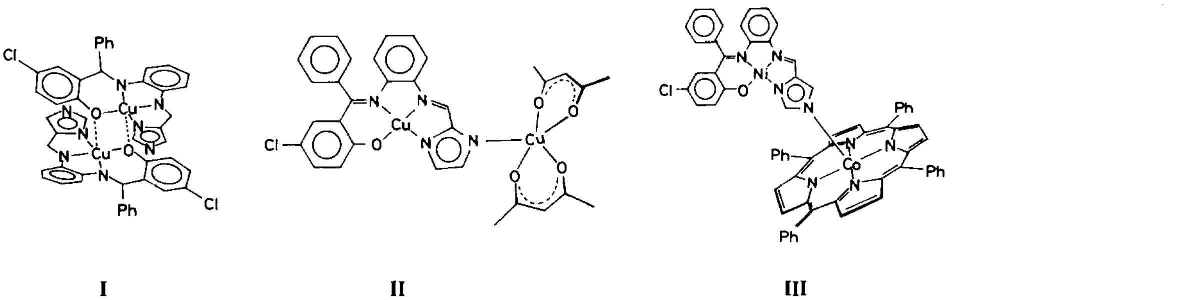
Preparation of the Complexes

The nickel Schiff base complex, Ni[CBP-PHEN-4-CHO-Im], was prepared as described previously [9] (see Fig. 2). Cobalt tetraphenylporphyrin, Co(TPP), was prepared by the method of Adler [10]. The binuclear adduct was prepared by refluxing equimolar amounts of the nickel Schiff base and Co(TPP) in toluene for one hour. The solution was hot filtered and on evaporation yielded the product. Elemental analyses were performed by Galbraith laboratories. Ni[CBP-PHEN-4-CHO-Im]·1.5H$_2$O requires 57.14% C, 3.73% H, 11.60% N. Found: 57.36% C, 5.42% H, 11.49% N. Ni[CBP-PHEN–4-CHO-Im]–Co(TPP) requires 72.02% C, 4.79% H, 9.08% N. Found: 71.09% C, 4.04% H, 9.61% N.

ESR Measurements

All ESR spectra were recorded on a Varian E-109 spectrometer at 9 GHz and 100 mW of power. The temperature was maintained by a Varian variable temperature controller using nitrogen as the flow gas.

Solution measurements were done in freshly distilled toluene. The samples were made up and sealed on a vacuum line to insure that the solutions were oxygen free.



I II III

Fig. 1. Line drawings of complexes. **I** parent copper imidazole system. **II** adduct with Cu(HFA)$_2$. **III** adduct of nickel complex with Co(TPP).

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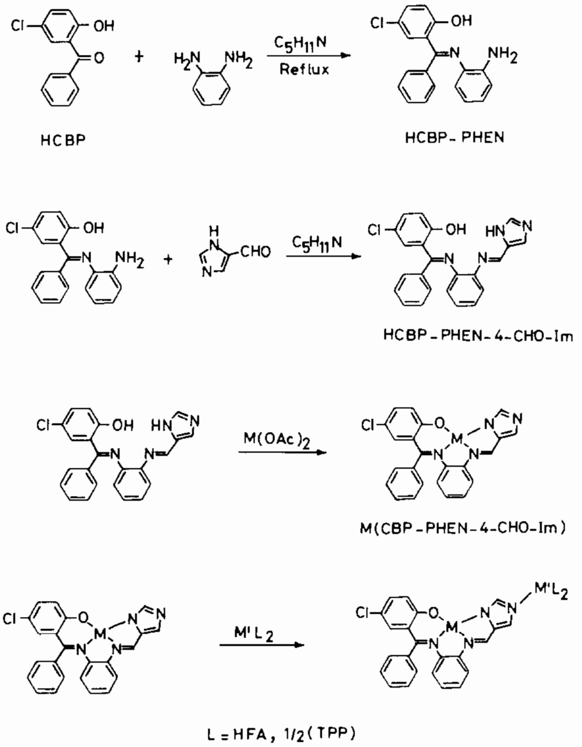

Fig. 2. Reaction scheme to prepare imidazole bridged binuclears.

Results and Discussion

ESR spectroscopy provides a good method for the investigation of axial ligation of cobalt porphyrins. The lone unpaired electron in the low spin d^7 configuration resides in the d_{z^2} orbital and is thus very sensitive to changes in axial ligation. Cobalt(II) porphyrins exhibit three distinct types of spectra [11] represented by **(I)** free Co(TPP) in which $g_{\parallel} = 1.8$ and $g_{\perp} = 3.3$, **(II)** five coordinated Lewis base adducts in which $g_{\parallel} = 2.002$ and $g_{\perp} = 2.3$, and **(III)** axial base adducts in the presence of molecular oxygen in which $g_{\parallel} = 2.07$ and $g_{\perp} = 2.002$. Type III also exhibits greatly diminished ^{59}Co hyperfine couplings in sharp contrast to the other types of complexes.

Nickel Schiff base adducts with Co(TPP) were used in this study because planar nickel(II) is ESR silent. The effects of axial ligation can then be observed in the ESR spectra of Co(TPP) without any complications from another paramagnetic metal. The frozen solution spectrum of Ni[CBP-PHEN-4-CHO-Im] with Co(TPP) is shown in Fig. 3a. This spectrum is very similar in appearance to those reported previously for the N–CH_3 imidazole and pyridine adducts of Co(p-OCH_3TPP) [12]. Note that the $g_{\perp}$ value has shifted from 3.3 in free Co(TPP) [13] to 2.3 in the present example. This is exactly what is expected on the formation of a Type II five coordinate axial adduct of Co(TPP) as postulated in Fig. 1.

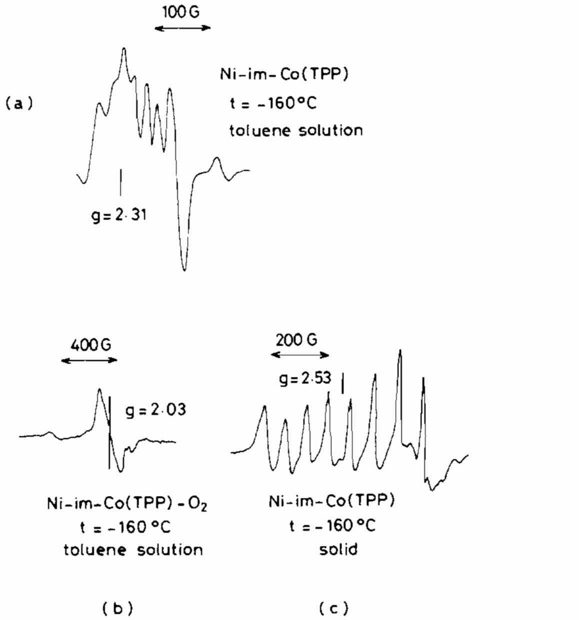

Fig. 3. ESR spectra of Ni[CBP-PHEN-4-CHO-Im]–Co(TPP).

This Type II spectrum is transformed to a Type III pattern on exposing the solution to oxygen. The spectral change is shown in Fig. 3b. The important features of this spectrum are that $g_{\perp}$ has decreased from 2.3 in the absence of air to ~2.0 in the presence of air and that the extent of hyperfine splitting has also dropped considerably. Both of these facts are consistent with the formation of a six coordinate adduct with one axial site being occupied by a Lewis base and the remaining site by molecular oxygen [12]. The unpaired electron density resides mainly on the oxygen which accounts for the sharp decrease in $g_{\perp}$ to roughly the free electron value and also for the decrease in the hyperfine splitting. This interpretation also accounts for the fact that this complex exhibits a spectrum at much higher temperatures than do the five coordinate adducts in accordance with the longer electron spin relaxation times for oxygen.

The spectrum of the solid adduct is shown in Fig. 3c. In this case the effect of axial ligation is to shift $g_{\perp}$ from 3.3 to 2.5. The hyperfine information is also clearly visible in this spectrum. This shows that the complex exhibits no reactivity with oxygen in the solid state.

The conclusion of this study is that the nickel Schiff base complex, Ni[CBP-PHEN-4-CHO-Im], forms a five coordinate imidazole bridge adduct of Co(TPP) in both solution and solid state. This is based on the similarity of the ESR spectral changes caused by our complex to those of imidazole and pyridine reported previously and also on the proven ability of this ligand to serve as an imidazole bridge (see Fig. 1). Structural investigation of this compound is in progress but has been hindered by the quality of the crystals. Further work done on this system and the related adduct of the copper Schiff base complex with Fe(TPP)Cl will allow a comparison of the magnetic data of these systems to that of cytochrome oxidase. Such a comparison may aid in the evaluation of the existence of an imidazole bridge in the enzyme system.

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