Synthesis and Reactivity of Copper(II) and Nickel(II) Imidazolate Complexes containing Unsymmetrical Tetradentate Schiff's Bases

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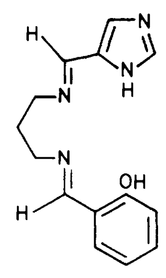
Copper(II) and nickel(II) imidazolate complexes containing unsymmetrical tetradentate Schiff's bases, prepared by the reaction of imidazolecarbaldehydes with the mono-Schiff's base from salicylaldehyde and 1,3-diaminopropane, react with metalloporphyrins to yield imidazolate-bridged bi- and tri-nuclear complexes.

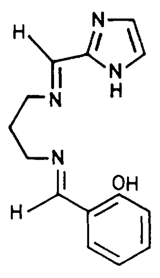
Recent interest in the design, synthesis, and characterization of unsymmetrical tetradentate Schiff's base complexes[1—4] has been prompted by the belief that systematic investigations of these complexes may shed light on the nature of complexes of biological interest in which the metal is in an unsymmetrical ligand environment. The lack of symmetry in synthetic examples can be achieved by the reaction of two different carbonyl compounds with a diamine.

The present communication reports the synthesis and chemical reactivity of copper(II) and nickel(II) complexes ML^1 and ML^2, of the tetradentate unsymmetrical Schiff's bases H_2L^1 and H_2L^2, in which an imidazolate is covalently bound to the Schiff's base framework, bound to the metal through one nitrogen, and capable of binding to another species through its rear-side nitrogen atom. These complexes provide a convenient synthetic route to a wide variety of imidazolate-bridged polynuclear species by reactions with metal-containing Lewis acids, such as metalloporphyrins. Imidazolate-bridged complexes of Cu^{II} and Fe^{III} are of interest as models of cytochrome c oxidase, in which strong antiferromagnetic coupling between Cu_U and haem a_3 of cytochrome c oxidase is thought to occur *via* a bridging imidazolate[5] or thiolate[6] ligand.

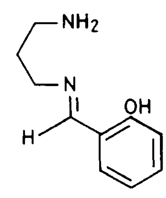
The unsymmetrical tetradentate Schiff's bases H_2L^1 and H_2L^2 were prepared by the reactions of imidazole-4(5)-carbaldehyde and imidazole-2-carbaldehyde, respectively, with HL^3, generated *in situ* by the reaction of its nickel complex,[7] $Ni(L^3)_2$, with dimethylglyoxime as described previously.[8] Reaction of H_2L^1 or H_2L^2 with 2 equiv. of triethylamine and one of metal acetate yields ML^1 and ML^2.



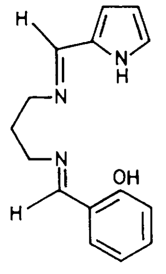
H_2L^1



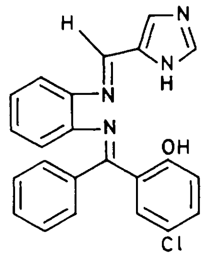
H_2L^2



HL^3



H_2L^4



H_2L^5

Alternatively, the nickel complexes can be prepared by the one-pot sequential reactions of NiL$^3{}_2$ with 2 equiv. of the aldehyde, 1 equiv. of nickel acetate, and 2 equiv. of triethylamine.

The new complexes have been characterized by magnetic susceptibility and i.r., u.v.–visible, and mass spectroscopic measurements. The u.v.–visible spectra consist of weak d–d transitions in the visible region as shoulders on intense u.v. absorptions. The i.r. spectra of all the compounds are similar, with strong absorption in the azomethine (HC=N) region (1620—1600 cm^{-1}) and no significant absorption above 3100 cm^{-1}. A molecular ion peak is observed in the fast atom bombardment mass spectra of the metal complexes of H_2L^1. The room-temperature magnetic moments of CuL^1 and CuL^2 are 1.90 and 1.71 B.M., respectively.

The rear-side nitrogen atom in the imidazole ring of H_2L^1 and H_2L^2 is readily available for bonding to metal-containing Lewis acids, as illustrated by the reaction of NiL^1 (Figure 1) or NiL^2 with Zn(tpp) in toluene (tpp = tetraphenylporphyrin dianion). The presence of isosbestic points and the overall spectral changes which are observed in the titration of Zn(tpp) with NiL^1 or NiL^2 clearly indicate that these complexes add axially to the zinc atom.[9] Binding by the imidazolate to give a Zn–imidazolate–Ni linkage is indicated since the structurally related NiL^4, which lacks a near-side nitrogen atom available for binding, does not react with Zn(tpp). CuL^1 and CuL^2 do not exhibit any reactivity toward Zn(tpp) in toluene. This observation may be explained by the formation of imidazolate-bridged species $(CuL^1)_x$ and $(CuL^2)_x$, in the solid state and in non-co-ordinating solvents, as reported for a copper complex of diethylenetriamine and imidazolate.[10] A structurally related complex, CuL^5, has been shown crystallographically to dimerize through its phenolic oxygen atom[11] but this does not prevent reaction with Zn(tpp)[9] since the rear-side nitrogen atom is free.

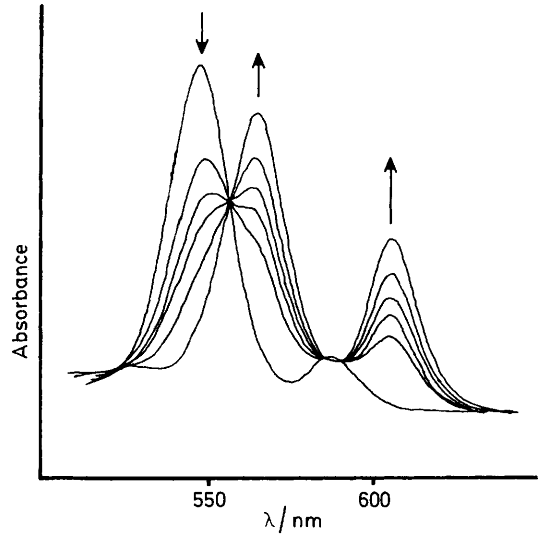


Figure 1. Spectral changes that accompany the reaction of Zn(tpp) with NiL^1 in toluene.

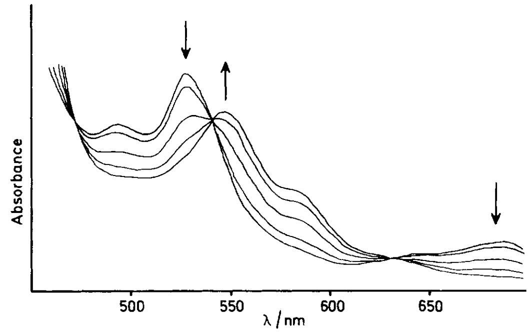


Figure 2. Spectral changes that accompany the reaction of [Fe(tpp)Cl] with CuL^1 in Me_2SO.

In contrast, both CuL^1 (Figure 2) and NiL^1 form the low-spin trinuclear bis-adduct [ML^1–Fe(tpp)–ML^1]$^+$, on reaction with [Fe(tpp)Cl] in the strongly co-ordinating solvent Me_2SO, as observed in the related reactions of [Fe(tpp)Cl] with 1-methylimidazole[12] and ML^5.[13] Full characterization of binuclear adducts of [Fe(tpp)Cl] with particular emphasis on the magnetic properties is the subject of current work. There is no evidence of bis-adduct formation in the reaction of CuL^2 or NiL^2 with [Fe(tpp)Cl]. Instead, an increase in intensity of the 529 nm band and a slight increase in the 600—700 nm region were observed. Similar observations were reported for the reaction of [Fe(tpp)Br] with 1-methylimidazole and were attributed to the formation of a monoadduct.[14] This observation may indicate that two molecules of ML^2 cannot approach within bonding distance of the low-spin iron without steric interference between the porphyrin and the proton on the imine carbon of ML^2. Steric control of axial ligation reactions of Fe^{III} porphyrins to give the mono-adduct rather than the bis-adduct has been observed[15] with [Fe(oep)]ClO$_4$ (oep is the dianion of octaethylporphyrin), where the porphyrin units form face-to-face dimers, but in general is not observed in the tpp series since thermodynamics favour production of the low-spin bis-adduct even with the sterically hindered 2-methylimidazole. It appears that the steric bulk of ML^2 is more effective than that of 2-methylimidazole in preventing bis-adduct formation. To our knowledge this is the first report of steric control in an axial ligation reaction of [Fe(tpp)Cl] which is effected by the use of a sterically hindered imidazole donor.

To summarize, isomeric imidazolate complexes have been prepared and characterized and can be used to form imidazolate-bridged species with metalloporphyrins, providing valuable systems with which to study the ability of imidazolate to serve as a bridge in models of biological molecules such as cytochrome c oxidase.

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