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Evaluation of the Formation Constant for an Imidazolate Bridged Binuclear Complex of Co(TPP)

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The ability of metalloporphyrins to form five- and six-coordinated species by adducting axial bases such as imidazole, pyridine or piperidine is well established. This complexation can be monitored by NMR, ESR and visible spectroscopy. The latter technique affords a facile method for the observation of a new species and a means of evaluating the equilibrium constant for adduct formation. In the case of cobalt porphyrins at room temperature, it has been shown that only one axial base reacts giving the five-coordinated adduct [1].

In the present study a copper Schiff base complex, Cu[CBP-PHEN-4-CHO-Im] (**I**), containing a deprotonated imidazole was reacted with cobalt tetraphenylporphyrin, Co(TPP), to yield a five-coordinated binuclear adduct (**II**) as shown in Fig. 1. The structure of **II** is postulated on the basis of the known structure of the adduct of **I** with copper(II) hexafluoroacetylacetonate [2] and on the strength of the similarity of the spectral changes, discussed below, that occur on addition of **I** or N-methylimidazole, N-CH_3Im, to Co(TPP). The latter adduct has also been structurally characterized [3]. The equilibrium constant for this reaction was measured, as well as that for the analogous reaction with N-CH_3Im in order that some comparison might bc made regarding the relative stability of the binuclear adduct.

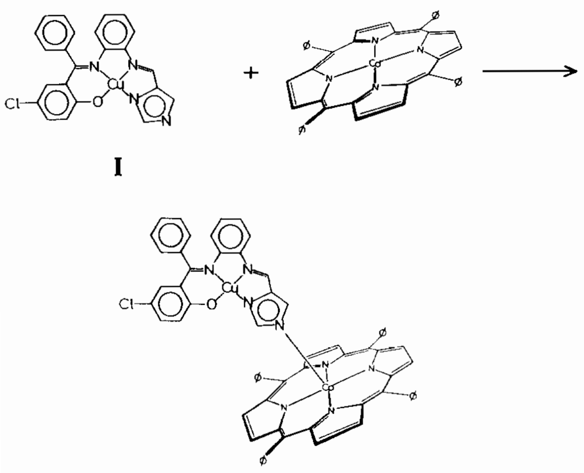

Fig. 1. Formation of the imidazolate bridged adduct.

Considerable interest has centered on the ability of imidazolate to serve as a bridge between metal atoms, as in the present example, since the discovery of an imidazolate bridge between copper and zinc in superoxide dismutase [4] and the postulation of such a bridge for the mammalian enzyme cytochrome c oxidase [5]. Structural studies of model compounds have confirmed the bridging role of imidazolate in both porphyrin [6] and non-porphyrin [7] environments. However, previous work on related imidazolate bridged binuclear complexes of metalloporphyrins [8] has not yielded formation constants.

Experimental

Reagents

Cu[CBP-PHEN-4-CHO-Im] was prepared by a literature procedure [9] and recrystallized from ethanol before use. N-methylimidazole and Co(TPP) were obtained from Aldrich Chemicals and Co(TPP) was stored with desiccant in the dark at 0 °C to prevent decomposition. Dry toluene was used for all spectral measurements.

Visible Spectra

Visible absorption measurements were obtained on a Perkin-Elmer Model 124 spectrophotometer equipped with a thermostatted cell compartment attached to a circulating constant temperature bath. A sample temperature of 20.7 °C was maintained during the measurements. The Co(TPP) absorption maximum at 529 nm was monitored for solutions of $\sim 4.5 \times 10^{-5}$ M Co(TPP) to which aliquots of N-CH_3Im or Cu[CBP-PHEN-4-CHO-Im] stock solutions werc added. Solutions were equilibrated for at least 20 min to insure that equilibrium was established. Equilibrium constants were evaluated by the method of Miller and Dorough [10] or, alternatively, by the method of Rose and Drago [11]. A correction for the weak absorbance of Cu[CBP-PHEN-4-CHO-Im] at 529 nm was accomplished with a calibration curve or by difference spectroscopy.

Results and Discussion

Evidence for axial ligation of bases to Co(TPP) is readily obtained by monitoring the changes in the visible absorption spectrum. On the formation of a five-coordinated adduct, the peak at 529 nm red shifts slightly and drops in intensity. Isosbestic points are observed at 518 and 538 nm (see Fig. 2) for

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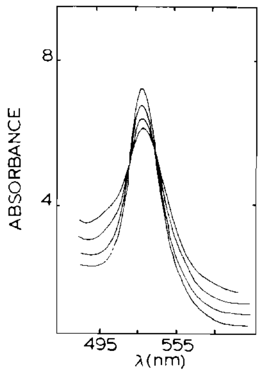

Fig. 2. Visible spectral changes observed upon addition of Cu[CBP-PHEN-4-CHO-Im] to Co(TPP) in toluene.

solutions which have identical concentrations of porphyrin but differing amounts of axial base. The spectral changes observed are nearly identical to those obtained with N-CH_3Im as the base and also for the Co(p-OCH_3)TPP pyridine complex [1]. An imidazolate bridged binuclear adduct is postulated in the present system due to the overall similarity of the spectral changes, the satisfactory evaluation of an equilibrium constant for a 1:1 adduct and related reactions employing this same copper complex.

An equilibrium constant of 5620 ± 180 M^{-1} was determined from the intersection point of a plot of K^{-1} *vs.* the extinction coefficient of the complex, by the method of Rose and Drago, as shown in Fig. 3. The present system is interpreted as a 1:1 complex since a plot of $\log[(A - A_0)/(A_\infty - A)]$ *vs.* $\log B$, where A_0 is the absorbance with no added base, A_∞ is the absorbance at a large excess of base, A is the absorbance of intermediate solutions, and B is the equilibrium concentration of Cu[CBP-PHEN-4-CHO-Im], gives a slope of 1.0 and K_2 values for other Co(TPP) amine complexes are known to be quite small [12].

The analogous reaction with N-CH_3Im yielded a K of 2700 M^{-1}, roughly half that for the reaction of Co(TPP) with Cu[CBP-PHEN-4-CHO-Im]. This could be due to a greater basicity of the Cu[CBP-PHEN-4-CHO-Im] complex or a more favorable energy match of the cobalt and imidazolate orbitals. It was previously noted that $\log K$ for the formation of a 1:1 adduct between Co(TPP) and an amine varies linearly with the pK_a of the conjugate acid of the amine for donors of the same type, imidazoles, pyridines and aliphatic amines, where steric effects are unimportant [1]. Steric effects should not be significant in the present comparison due to the fact that the nitrogen donor atom is removed from the steric bulk of the Cu[CBP-PHEN-4-CHO-Im] molecule. In fact, the substituents of the ring positions adjacent to the coordinating nitrogen are the same as in N-CH_3Im. The larger enthalpies of reaction of aromatic amines with cobalt porphyrins relative to aliphatic amines has been linked to the ability of the aromatic ring to serve as a π acceptor [1]. This ability is a function of the energy match between the metal d orbitals and the ligand π system, with imidazoles being better π acceptors than pyridines which are better π acceptors than aliphatic amines. Clearly this energy match will be distorted with Cu[CBP-PHEN-4-CHO-Im] relative to N-CH_3Im due to the fact that the imidazole is deprotonated and bound to another dipositive metal. The present data do not distinguish between these two effects.

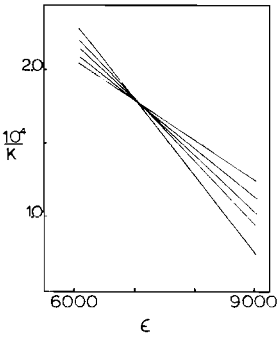

Fig. 3. Plot of K^{-1} *vs.* the extinction coefficient of the adduct for Co(TPP) + Cu[CBP-PHEN-4-CHO-Im] in toluene at 20.7 °C.

The analogous reaction with Ni[CBP-PHEN-4-CHO-Im] was not observed at room temperature in the same concentration range. This was unexpected since the complexes are identical except for the metals and since the nickel complex does react at liquid nitrogen temperature [13]. A somewhat different comparison was noted for the reaction of these bases with Zn(TPP) [14]. With zinc both bases reacted to form the five-coordinated species with nearly identical enthalpies, but the nickel complex yielded formation constants which were roughly 30% less than those of Cu[CBP-PHEN-4-CHO-Im]. The lower reactivity of the nickel complex may be due to either of the above effects.

The present results indicate that an imidazolate bridged heterobinuclear complex of Co(TPP) and Cu[CBP-PHEN-4-CHO-Im] is formed in solution, and, furthermore, that it forms with a greater K than does the N-CH_3Im adduct. Experiments designed to determine the extent of magnetic exchange and reactivity of other such imidazolate bridged metalloporphyrins may allow for a detailed investigation of the imidazolate bridged model of cytochrome c oxidase.

Acknowledgement

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References

1 F. A. Walker, *J. Am. Chem. Soc., 95,* 1150 (1973).

2 G. Brewer and E. Sinn, *186th National ACS Meeting,* Washington, D.C., 1983.

3 W. R. Scheidt, *J. Am. Chem. Soc., 96,* 90 (1974).

4 K. M. Beem, D. C. Richardson and K. M. Rajogopalan, *Biochemistry, 16,* 1930 (1977).

5 G. Palmer, G. T. Babcock and L. E. Vickery, *Proc. Nat. Acad. Sci. U.S.A., 73,* 2206 (1976).

6 J. T. Landrum, C. A. Reed, K. Hatano and W. R. Scheidt, *J. Am. Chem. Soc., 100,* 3232 (1978).

7 (a) W. H. Armstrong, A. Spool, G. C. Papaefthymiou, R. B. Frankel and S. J. Lippard, *J. Am. Chem. Soc., 106,* 3653 (1984); (b) W. M. Davis, J. C. Dewan and S. J. Lippard, *Inorg. Chem., 20,* 2928 (1981).

8 (a) T. Prosperi, *J. Chem. Soc., Chem. Commun.,* 196 (1979); (b) S. E. Dessens, C. L. Merrill, R. J. Saxton, R. L. Ilaria, J. W. Lindsey and L. J. Wilson, *J. Am. Chem. Soc., 104,* 4357 (1982).

9 R. Atkins, G. Brewer, E. Kokot, G. M. Mockler and E. Sinn, *Inorg. Chem., 24,* 127 (1985).

10 J. R. Miller and G. D. Dorough, *J. Am. Chem. Soc., 74,* 3977 (1952).

11 N. J. Rose and R. S. Drago, *J. Am. Chem. Soc., 81,* 6138 (1959).

12 F. A. Walker, *J. Am. Chem. Soc., 95,* 1154 (1973).

13 G. Brewer and E. Sinn, *Inorg. Chim. Acta., 87,* L41 (1984).

14 C. Brewer and G. Brewer, *189th National ACS Meeting,* Miami, Fl., 1985.