Inorganica Chimica Acta, 91 (1984) 247–250

Ligand and Carbon Monoxide Affinities of Iron(II) 'C_4-capped' Porphyrins

MAKOTO SHIMIZU, FRED BASOLO*
Department of Chemistry, Northwestern University, Evanston, Ill. 60201, USA
MARIA N. VALLEJO and JACK E. BALDWIN
The University, Oxford OX1 3QY, U.K.

Received August 25, 1983

Ligand and CO binding constants are reported for Fe(C_4-Cap) [1]. The results show that the CO affinities are Fe(C_2-Cap)(B) ≃ Fe(C_3-Cap)(B) > Fe(C_4-Cap)(B). Also the CO affinities are Fe(Cap)(1,5-DCIm) > Fe(Cap)(1,2-Me_2Im). These results are explained in terms of the possible steric factors involved.

Introduction

Whether or not the heme cavity, in the natural heme oxygen carriers, plays a major role in causing discrimination between the binding of O_2 and CO to hemoproteins is a question being actively investigated by the use of model iron(II) complexes [2–7]. It is suggested [8, 9] that the discrimination favoring O_2 over CO, relative to corresponding 'flat-open' iron(II) complexes, in hemoproteins is due to distal steric effects on the bonding of CO. Because of this steric hindrance, CO is unable to bind in its stable linear Fe–C–O fashion, so it binds less strongly than it would were it not distorted from its usual structure. In contrast, the distal steric effect does not disturb the binding of O_2 which forms a stable end-on bent structure of the moiety Fe–O–O.

We previously reported and compared [2] the O_2 and CO affinities of the iron(II) C_2- and C_3-capped porphyrins. Here we extend the study of CO affinities to the C_4-capped system, and also make use of the bulky 1,5-DCIm axial ligand.

Experimental

Reagents

Toluene was reagent grade and distilled under N_2 from sodium metal prior to use. 1,2-Me_2Im was dried over KOH, distilled under vacuum and stored under N_2 at 0 °C. 1.5-DCIm was synthesized by the method of Traylor and coworkers [3]. The N_2 gas was Matheson prepurified grade and was passed through a Redox column to remove residual O_2.

Gaseous carbon monoxide was Matheson Primary Standard 15.1 ppm, 190.3 ppm and 1.002% CO in N_2 for the measurements of CO binding constants.

Synthesis

The synthetic methods of Fe(C_2-Cap)Cl, Fe(C_3-Cap)Cl, and Fe(TPP)Cl were described in our previous paper [2]. Fe(C_4-Cap)Cl was obtained from Baldwin and coworkers.

Procedure

Base equilibrium measurements

The procedure used was described earlier [10]. For equilibria involving only a single ligand, B, there are two possible equilibrium expressions (eqns. 1 and 2):

$$\mathrm{Fe(Por)} + \mathrm{B} \overset{K^{B}}{\rightleftharpoons} \mathrm{Fe(Por)(B)} \tag{1}$$

$$\mathrm{Fe(Por)(B)} + \mathrm{B} \overset{K_B{}^{B}}{\rightleftharpoons} \mathrm{Fe(Por)(B)_2} \tag{2}$$

Data were treated in one of three different ways, depending on relative values of K^B and $K_B{}^B$, as described earlier [10].

Carbon monoxide affinity measurements

The procedure used was described in our previous paper [2]. The CO binding to five coordinate iron(II) porphyrin complexes is illustrated by eqn. 3:

$$\mathrm{Fe(Por)(B)} + \mathrm{CO} \overset{K_B{}^{CO}}{\rightleftharpoons} \mathrm{Fe(Por)(B)(CO)} \tag{3}$$

where

$$P_{1/2}{}^{CO} = \frac{1}{K_B{}^{CO}}$$

The Fe(Por)(B) solutions were prepared as described in the previous paper [2]. The base concentration was chosen to give greater than 99% of five-coordinate complex in the capped porphyrin systems, and 98% of that in the flat-open porphyrin system such as Fe(TPP)(1,2-Me_2Im). The concentrations of base

---

*Author to whom correspondence should be addressed.

0020-1693/84/$3.00

required were determined from the equilibrium constants K_B and $K_B{}^B$ (Table I).

Results

Table I contains data on the axial ligand and the CO affinities of some iron(II) capped porphyrins. Data for the corresponding Fe(TPP) are also included for comparison. Values of the equilibrium constants K^B (eqn. 1), for ligand (or base) addition to the complexes Fe(Por), in toluene, were estimated from titration spectra. Isosbestic points, after dilution corrections, were maintained throughout the titrations of Fe(Por) with ligand solutions (Fig. 1). It was not possible to obtain the value of K^B for the reaction of Fe(TPP) with 1,5-DCIm, because of the known behavior that $K^B \leqslant K_B{}^B$ for reactions of open-flat Fe(Por) with ligands unhindered near the coordinated nitrogen ligand atom.

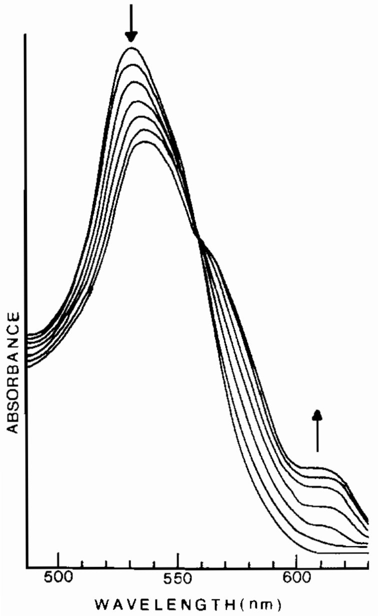


Fig. 1. Spectral changes occurring upon titration of 7.029 × 10^{-5} *M* toluene solution of Fe(C_4-Cap) with 0.2240 *M* 1,5-DCIm in toluene at 23.1 °C. The final base concentration is 1.12×10^{-2} *M*.

Spectrophotometric CO titrations of toluene solutions of Fe(Cap)(B) gave optical spectral changes, with isosbestic points, in accord with equilibria of the type represented by eqn. 3 (Fig. 2).

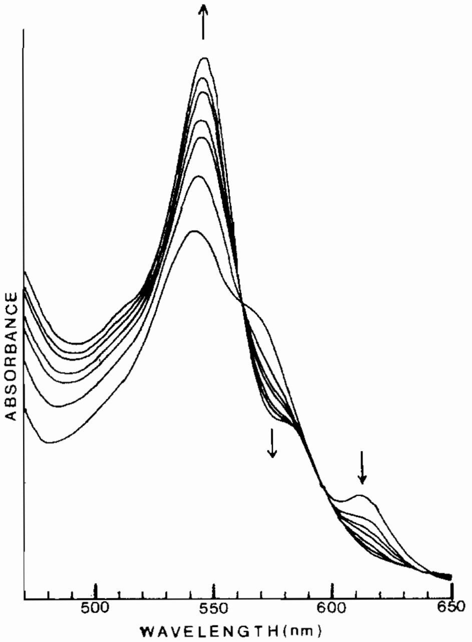


Fig. 2. Spectral changes occurring upon titration of a toluene solution of ~10^{-5} *M* in Fe(C_4-Cap)(1,5-DCIm), 0.1 *M* in 1,5-DCIm, with the following pressures of carbon monoxide at 25 °C; 0, 1.33×10^{-2}, 2.51×10^{-2}, 3.65×10^{-2}, 8.10×10^{-2}, 1.45×10^{-1} and 7.31 torr.

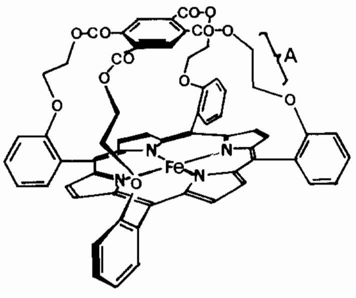
Discussion

Our previous papers report [2] studies on the binding of O_2 and of CO by five-coordinate iron(II) C_2- and C_3-capped porphyrins, (I).

TABLE I. Ligand and Carbon Monoxide Affinities of Some 'Capped' Iron(II) Porphyrins in Toluene.

Affinity	log $K^{B\,a}$		$P_{1/2}{}^{CO}$(torr)^b	
	1,2-Me_2Im	1,5-DCIm	1.0 *M* 1,2-Me_2Im	0.1 *M* 1,5-DcIM
Ligand	23.1 °C	23.1 °C	25 °C	25 °C
TPP	$4.43^{c,d}$	$\_^e$	$1.4 \times 10^{-1\,d,f}$	$\_^e$
C_2-Cap	3.06^d	3.17^d	$2.0 \times 10^{-1\,d}$	7.5×10^{-3}
C_3-Cap	3.61^d	3.00^d	$1.4 \times 10^{-1\,d}$	1.6×10^{-3}
C_4-Cap	3.39	2.99	4.1	2.1×10^{-2}

[a] Values reproducible within 0.05. [b] Values reproducible within 10%. [c] Log $K_B{}^B$ is 0.39 ± 0.10 at 23.1 °C. [d] Reference 2. [e] Since $K^B \leqslant K_B{}^B$, these values were not determined (see text). [f] Solution is 3.1×10^{-3} *M*, 1,2-Me^2Im in toluene.

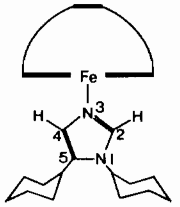


I

A, -$(CH_2-)_n$ n = 2 C_2-Cap
n = 3 C_3-Cap
n = 4 C_4-Cap

The results of these studies provided the first example (model or natural) of iron(II) complexes which discriminate against the binding of O_2 relative to CO. The weaker bonding of O_2 by Fe(Cap)(B) compared with Fe(TPP)(B) was attributed [2] to peripheral steric effects in the capped systems. In contrast, the similar binding of CO by Fe(Cap)(B) and by Fe(TPP)(B) was explained in terms of there being no central steric effect in the capped complexes. Other explanations [7, 11] have been given for these observations.

This paper reports the results of extending our previous studies on CO affinities to the C_4-capped system, in order to see if the trends found for the C_2- and C_3-capped iron(II) complexes continue. We also wanted to investigate the bulky ligand, 1,5-DCIm, because it was not expected to enter the cap of the C_2- and C_3-capped iron(II) complexes (II).

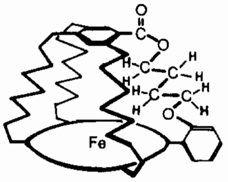


II

The data obtained are summarized in Table I.

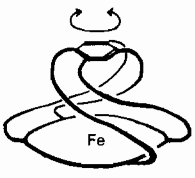
Values of log K^B for 1,5-DCIm show it behaves similar to other imidazole ligands in binding to iron(II) porphyrins, in spite of its large molecular size. This is true because the cyclohexyl groups are at the back of the ligand and do not impede coordination at the front. The bulky cyclohexyl groups should make it difficult for 1,5-DCIm to enter a cap to coordinate with Fe(Cap)(B), yet we find [12] that Fe(C_4-Cap)(1,5-DCIm)$_2$ forms at 0 °C. This suggests the C_4-cap is sufficiently flexible to scoot aside and allow a second 1,5-DCIm to coordinate.

The values of $P_{1/2}^{CO}$ (Table I) clearly show that (1) the CO affinity of Fe(C_4-Cap)(B) is less than that of the other iron(II) capped porphyrins, and (2) the CO affinities of Fe(Cap)(B) are larger for 1,5-DCIm than for corresponding 1,2-Me_2Im complexes. The first of these results can be explained in terms of central steric effects on the bonding of CO to give the linear moiety Fe–C–O. The affinities of Fe(C_4-Cap)(B) for both 1,2-Me_2Im and 1,5-DCIm are less than for the corresponding C_2- and C_3-cap complexes, which are similar to that of the flat-open Fe(TPP)(B). This sudden decrease in CO affinity of the C_4-Cap complex may be caused by its greater flexibility which allows it to achieve a squashed configuration, (III), more readily than do the C_2- and C_3-cap complexes. Studies [13] on shifts of the Soret bands of zinc capped porphyrins suggest a squashed structure for Zn(C_3-Cap). Since C_4-cap is expected to have even a greater tendency to do this, it follows that the linear Fe–C–O moiety would experience the greatest central steric effect in the C_4-cap complex. Models also indicate that Fe(C_4-Cap) can form a 'twisted' configuration, (IV),



III

Squashed structure.

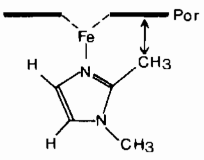


IV

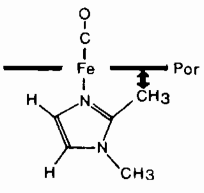
Twisted structure.

which could have a similar steric effect on Fe–C–O as does a squashed structure. Whichever structure occurs at C_4-cap, it can cause this system to have the experimentally observed sudden drop in CO affinity relative to C_2-cap and C_3-cap.

The lower CO affinities of the Fe(Cap)(1,2-Me_2Im) complexes, compared with corresponding Fe(Cap)(1,5-DCIm) complexes, may be due to the strain caused by the methyl group in the 2-position, (V).



V



VI

Addition of CO to form (VI) pulls the iron into the porphyrin plane, causing considerable strain in the complex and rendering it less stable. This results in the smaller affinity observed for 1,2-Me_2Im systems, relative to corresponding 1,5-DCIm systems. Note that the bulky ligand 1,5-DCIm has its bulk at the back of the molecule, but offers no steric strain at the front with the porphyrin plane, (II).

The interpretation of these new results in terms of central steric effects is in keeping with our earlier discussion [2]. This is not to dogmatically say that alternative explanations [3, 7, 11] should not be considered. As so often is true in science, the experimental facts are valid but explanations of the facts are speculations which can be modified or even discarded when more is learned about the systems. Surely these are systems where more study is warranted.

Acknowledgements

We thank the National Institutes of Health for support of this research. We also are grateful to Ube Industries Ltd. for support of M.S., their employee. We thank Professor T. G. Traylor for help with the synthesis of 1,5-DCIm.

References

1 Abbreviations: Por, dianion of porphyrin; C_2-cap, dianion of the C_2-capped porphyrin; C_3-cap, dianion of the C_3-capped porphyrin; C_4-cap, dianion of the C_4-capped porphyrin; TPP, dianion of meso-tetraphenylporphyrin; Im, imidazole; 1,2-Me_2Im, 1,2-dimethylimidazole; 1,5-DCIm; 1,5-dicyclohexylimidazole; B, monodentate ligand; $P_{1/2}^{CO}$ (= $(K_B^{CO})^{-1}$), the pressure at half saturation.

2 T. Hashimoto, R. L. Dyer, M. J. Crossley, J. E. Baldwin and F. Basolo, *J. Am. Chem. Soc., 104*, 2101 (1982); T. Hashimoto and F. Basolo, *Comments Inorg. Chem., 1*, 199 (1981), and references therein.

3 T. G. Traylor, D. Campbell, S. Tsuchiya, M. Mitchell and D. V. Stynes, *J. Am. Chem. Soc., 102*, 5939 (1980); T. G. Traylor, M. J. Mitchell, S. Tsuchiya, D. H. Campbell, D. V. Stynes and N. Koga, *J. Am. Chem. Soc., 103*, 5234 (1981).

4 A. R. Battersby and A. D. Hamilton, *J. Chem. Soc. Chem. Commun.*, 117 (1980).

5 D. H. Buch, L. L. Zimmer, J. J. Grybowski, D. J. Olszanshi, S. C. Jackels, R. C. Callahan and G. G. Christoph, *Proc. Natl. Acad. Sci., USA*, in press.

6 J. P. Collman, J. I. Brauman, T. J. Collins, B. L. Iverson and J. L. Sessler, *J. Am. Chem. Soc., 103*, 2450 (1981); J. P. Collman, J. I. Brauman, T. J. Collins, B. L. Iverson, G. Lang, R. B. Pettman, J. L. Sessler and M. A. Walters, *J. Am. Chem. Soc., 105*, 3038 (1983); J. P. Collman, J. I. Brauman, B. L. Iverson, J. L. Sessler, R. M. Morris and Q. H. Gibson, *J. Am. Chem. Soc., 105*, 3052 (1983).

7 G. B. Jameson and J. A. Ibers, *Comments Inorg. Chem., 2*, 97 (1983).

8 E. Antonini and M. Brunori, 'Hemoglobin and Myoglobin in their Reactions with Ligands', Elsevier, New York, 1971.

9 W. S. Caughy, *Ann. N.Y. Acad. Sci., 174*, 148 (1970); W. J. Wallace, J. A. Volpe, J. C. Maxwell, W. S. Caughy and S. Charache, *Biochem. Biophys. Res. Commun., 68*, 1379 (1976).

10 P. E. Ellis, J. E. Linard, T. Szymanski, R. D. Jones, J. R. Budge and F. Basolo, *J. Am. Chem. Soc., 102*, 1889 (1980).

11 N. J. Clayden, G. R. Moore, R. J. P. Williams and J. E. Baldwin, *J. Chem. Soc., Perkin Trans., 2*, 1693 (1982).

12 M. Shimizu and F. Basolo, *Inorg. Chim. Acta, Bioinorg.*, in press.

13 P. N. Venkatasubramanian and F. Basolo, *J. Indian Chem. Soc., 59*, 1288 (1982).