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Preliminary communication

N-ACYL ISOCYANIDE COMPLEXES OF DEUTEROPORPHYRINIRON(II): SPECTROSCOPIC STUDIES (IR AND ^{13}C NMR) OF THE *cis* LIGAND EFFECT IN HAEMES

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Summary

New deuteroporphyriniron(II) *N*-acyl isocyanide complexes have been prepared in order to study the sensitivity of the *N*-functionalized isocyanide to the *cis* -porphyrin effect.

The binding of alkyl isocyanides by metalloporphyrins and haemoproteins is a subject of considerable current interest [1]. It has been reported, remarkably that ethyl isocyanide appears to be a more sensitive probe than carbon monoxide for haemoglobin ^{13}C NMR studies [2]. However, although the alkyl isocyanides are very sensitive to the steric environment of the haeme, the electronic effect caused by porphyrin modification in models systems is rather small [3]. For instance, variation of porphyrin from TPP to OEP* did not cause any significant difference in the ^{13}C shift upon coordination of EtN ^{13}C [4]. We recently reported that *N*-acyl isocyanide (RC(=O)NC, R = Ph, t-Bu) ligands are more sensitive than alkyl isocyanides to variations in the axial base in $TPPFe^{II}(CNCOR)(base)$ derivatives [5]. In order to provide information on the *cis* electronic effect on *N*-acyl isocyanide binding, we have synthesised deuteroporphyriniron(II) *N*-acyl isocyanide complexes. The spectroscopic properties of these new complexes are discussed in comparison with those of $TPPFe^{II}$ adducts.

Ferrous deuteroporphyrin dimethyl ester ($DPDMEFe^{II}$ was prepared as previously described [6]. Addition of an excess of *N*-benzoyl isocyanide (3—4 equivalents) [7] in CH_2Cl_2 (10 cm^3) to 100 mg of $DPDMEFe^{II}$ (0.16 mmol)

*TPP = meso-tetraphenylporphyrinate; OEP = octaethylporphyrinate; DPDME = deuteroporphyrinate dimethyl ester.

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at 25°C under nitrogen results in rapid formation of DPDMEFe^{II}(CNCOPh)$_2$, readily identified by its IR spectrum in solution (ν(CN) 2016 cm^{-1}). This bis-adduct is precipitated by addition of pentane (yield: 85%). The electronic spectrum of DPDMEFe^{II}(CNCOPh)$_2$ exhibits λ_{max} at 415 nm ($\epsilon = 2.1 \times 10^5\ M^{-1}\ cm^{-1}$) and 534 nm ($\epsilon = 0.2 \times 10^5$) in toluene. The preparation of DPDMEFe(CNCOt-bu)$_2$ is achieved similarly using *N*-pivaloyl isocyanide [7] instead of CNCOPh (yield: 72%). Mixed hexacoordinated derivatives have been synthesised with *N*-acyl isocyanide and nitrogen bases as axial ligands. For example, addition of one equivalent of pyridine in CH_2Cl_2 (10 cm^3, 20°C, under nitrogen) to 80 mg of DPDMEFe(CNCOPh)$_2$ (0.09 mmol) led to formation of DPDMMEFe(CNCOPh)(Py), which was precipited by pentane addition yield: 89%, λ_{max} at 411 nm ($\epsilon = 2.7 \times 10^5$), 523 nm ($\epsilon = 0.44 \times 10^5$) in toluene. IR results are summarized in Table 1.

TABLE 1

ISOCYANIDE STRETCHING FREQUENCIES OF FERROUS PORPHYRIN COMPLEXES [a]

L	DPDMEFe(L)$_2$ [b]	DPDMEFe(L)(Py) [b]	TPPFe(L)$_2$ [c]	TPPFe(L)(Py) [c]
CNCOPh	2016	1955	2040	1980
CNCO-t-bu	2020	—	2045	—

[a] Nujol, ν in cm^{-1}. [b] This work. [c] Ref. 6.

The data suggest that the observed isocyanide stretching frequencies are importantly influenced by the electronic nature of the substituent on the periphery of the porphyrin ring. Thus, *N*-acyl isocyanide ligands bonded to DPDMEFe^{II} have lower C≡N stretching frequencies than do those in TPPFe^{II}-(CNCOR)$_2$. As expected, the more electron donating is a porphyrin the lower is the ν(CN) frequency. A significant shift ($\Delta\nu \simeq 25$ cm^{-1}) is also observed with mixed ligand species (P'Fe(CNCOPh)(Py); P' = DPDME and TPP). The effect of changes in the groups attached to the porphyrin ring has been also studied by examination of the chemical shift of the bound ^{13}CNCOPh. This, for example, DPDMEFe^{II}(^{13}CNCOPh)(Py) and TPPFe^{II}(^{13}CNCOPh)(Py) each show a single sharp resonance at 190.4 and 186 ppm, respectively downfield from external tetramethylsilane (CD_2Cl_2, 25°C). The *cis*-porphyrin effect similarly influences the stability of the Fe—CNCOR bond. The half-lives of the P'Fe(CNCOPh)$_2$ complexes ($2 \times 10^{-5}\ M$) in toluene under argon depend on the nature of the porphyrin (P'); they decrease from 4 h to < 1 min when going from P' = DPDME to P' = TPP. This is consistent with previous observations on porphyriniron carbonyl derivatives (porphyrin-Fe(CO)(Py)) in which the CO binding is stronger with the more hasic the deuteroporphyrin dimethyl ester [8]. Similar studies have been carried out on artificial haemoglobin containing modified haeme. However, no unambigous conclusion has been obtained in the relationship between the electronic effects of the porphyrin ring and the affinities of various ligands (O_2, CO) [9]. It is evident that use of *N*-acyl isocyanide ligands could be valuable for investigation of the *cis* effect in porphyrin chemistry.

References

1 P.I. Reisberg and J.S. Olson, J. Biol. Chem., 255 (1980) 4151; F. Stetzkowski, R. Banerjee, J.Y. Lallemand, B. Cendrier and D. Mansuy, Biochimie, 62 (1980) 795.
2 D. Mansuy, J. Thillet, B. Cendrier, J.Y. Lallemand and J.C. Chottard, Biochem. Biophys. Res. Comm., 83 (1978) 217.
3 W.S. Caughey, C.H. Barlow, D.H. O'Keele and M.C. O'Toole, Ann. N.Y. Acad. Sci., (1973) 296.
4 I. Morishima, T. Hayashi, T. Inubushi and T. Yonezawa, J. Chem. Soc. Chem., Commun., (1979) 483.
5 M. Le Plouzennec, A. Bondon and G. Simonneaux, Inorg. Chem., 23 (1984) 4398.
6 D. Brault and M. Rougee, Biochem., 13 (1974) 4591.
7 G. Hofle and B. Lange, Angew. Chem. Int. Ed. Engl., 16 (1977) 262.
8 D.V. Stynes, H.C. Stynes, B.R. James and J.A. Ibers, J. Am. Chem. Soc., 95 (1973) 4087.
9 R. Makino and I. Yamazaki, Arch. Biochem. Biophys., 165 (1974) 485; D.W. Seybert, K. Moffat, Q.H. Gibson and C.K. Chang, J. Biol. Chem., 252 (1977) 4225.