Notes

Contribution from the Institute of Chemistry,
University of Wrocław, 50 383 Wrocław, Poland

Proton Nuclear Magnetic Resonance Studies of Chloro(*N*-methyl-5,10,15,20-tetraphenylporphinato)cobalt(II) and Chloro(*N*-methyloctaethylporphinato)cobalt(II) Complexes

Lechosław Latos-Grażyński

Received August 24, 1984

The geometric and electronic constraints associated with alkylation of one of the pyrrole nitrogens are responsible for the essential differences in the properties of metal ion complexes of *N*-alkylporphyrins as compared to those of their non-methylated counterparts.[1–6]

^{1}H NMR spectroscopy is widely used for the characterization of metalloporphyrins.[7–9] Metal complexes of porphyrins have been employed with some success to mimic the spectroscopic properties of hemoproteins.[10]

The interest in high-spin Co(II)–*N*-alkylporphyrin complexes does not arise from their occurrence in natural systems but, rather, from spectroscopic considerations.

The possible application of ^{1}H NMR spectroscopy to elucidate a mechanism for the formation of N-alkylated porphyrins (green pigments) during the cytochrome P-450 destruction[11] may benefit from model studies using a variety of different metal ions as other mechanistic deductions involving regular metalloporphyrins have utilized several different metal ions.[7]

^{1}H NMR spectra of chloro(*N*-methyl-5,10,15,20-tetraphenylporphinato)cobalt(II) (**1**) and chloro(*N*-methyloctaethylporphinato)cobalt(II) (**2**) (Figure 1) clearly demonstrate a lack of fourfold symmetry, and the number of resonances is consistent with the presence of a mirror plane intersecting the chloride and the alkylated and opposite nitrogen atoms. The pattern of the spectrum of **1** with three downfield and one upfield pyrrole resonance is important, since it seems to be very characteristic for paramagnetic *N*-alkylporphyrin metal ion complexes.[5,6]

The full assignments of the resonances of **1** and **2** are presented in Figure 1 and are based on selective deuteration ((N-CH_3TPP-d_8)CoCl and (N-CH_3OEP-*meso*-d_4)CoCl) and use of complexes with Cl substituting phenyl positions[12] along with line width and intensity analysis.

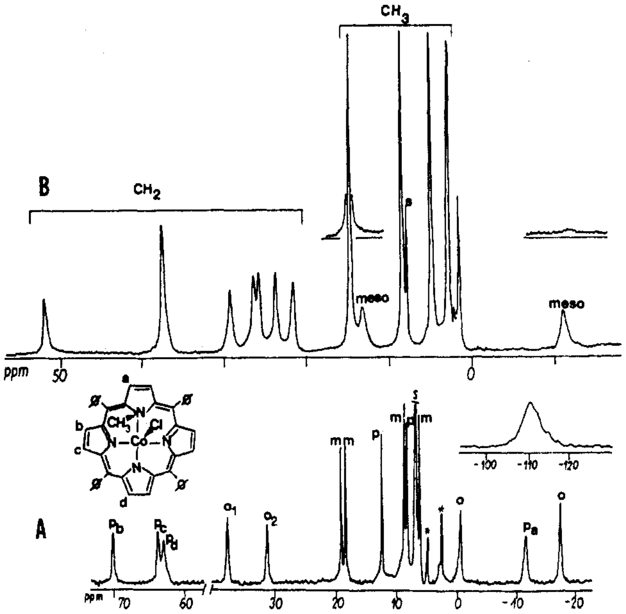

Figure 1. 100-MHz ^{1}H NMR spectra of (A) (N-CH_3TPP)CoCl (CD_2Cl_2, −80 °C; N-CH_3 resonance shown in the insert) and (B) (N-CH_3OEP)CoCl ($CDCl_3$, −60 °C, inserts present changes due to the meso deuteration). Abbreviations: p_x, pyrrole; o, ortho; m, meta; p, para.

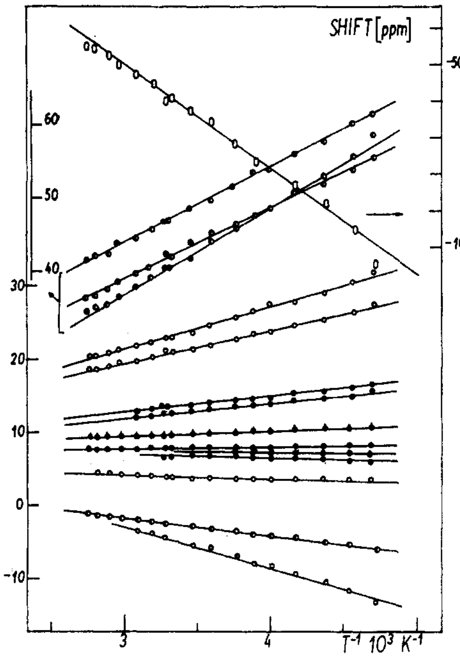

Figure 2. Plot of the temperature dependencies of the shifts of (N-CH_3TPP)CoCl in $CDCl_3$: (open circles) ortho; (solid circles) meta; (solid circles with "tail") para; (long ovals) N-CH_3; (half-filled circles) pyrrole.

---

[1] Anderson, O. P.; Lavallee, D. K. *J. Am. Chem. Soc.* **1977**, *99*, 1404.

[2] Anderson, O. P.; Lavallee, D. K. *J. Am. Chem. Soc.* **1976**, *98*, 4670.

[3] Anderson, O. P.; Lavallee, D. K. *Inorg. Chem.* **1977**, *16*, 1634.

[4] Lavallee, D. K.; Kopelove, A. B. *J. Am. Chem. Soc.* **1978**, *100*, 3025.

[5] Latos-Grażyński, L.; Cheng, R.-J.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1981**, *103*, 4270.

[6] Balch, A. L.; Chan, Y.-W.; Johnson, R.; La Mar, G. N.; Renner, M. W. *Inorg. Chim. Acta* **1983**, *79*, 175.

[7] La Mar, G. N.; Walker, F. A. "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IVB, p 61.

[8] Goff, H. M. *Phys. Bioinorg. Chem. Ser.* **1983**, *No. 1*, 237.

[9] Goff, H. M.; Phillippi, M. A.; Boersma, A. D.; Hansen, A. P. *Adv. Chem. Ser.* **1982**, *No. 201*, 357.

[10] (a) Latos-Grażyński, L.; La Mar, G. N.; Balch, A. L. *Adv. Chem. Ser.* **1982**, *No. 201*, 661. (b) Lar Mar, G. N.; de Ropp, J. S.; Latos-Grażyński, L.; Balch, A. L.; Johnson, R. B.; Smith, K. M.; Parish, D. W.; Cheng, R.-J. *J. Am. Chem. Soc.* **1983**, *105*, 782.

[11] (a) DeMatteis, F.; Jackson, A. H.; Gibbs, A. H.; Rao, K. R. N.; Atton, A.; Weerasinghe, S.; Hollands, C. *FEBS Lett.* **1982**, *142*, 44. (b) DeMatteis, F.; Hollands, C.; Gibbs, A. H.; DeSa, N.; Rizzardini, M.; *FEBS Lett.* **1982**, *145*, 87. (c) Oritz de Montellano, P. R.; Beilan, H. S.; Kunze, K. L. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 1490. (d) DeMatteis, F.; Gibbs, A. H.; Jackson, A. H.; Weerasinghe, S. *FEBS Lett.* **1980**, *119*, 109. (e) Oritz de Montellano, P. R.; Kunze, K. L.; Mico, B. A. *Mol. Pharmacol.* **1980**, *18*, 602.

[12] The synthesis of N-CH_3TPP-d_8 and N-CH_3OEP-*meso*-d_4 and Co(II) insertion have been carried out as previously described.[1,13–17]

[13] Adler, A. D.; Longo, R. F.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.

[14] Barnett, G. H.; Hudson, M. F.; Smith, K. M. *Tetrahedron Lett.* **1973**, 2887.

0020-1669/85/1324-1104$01.50/0

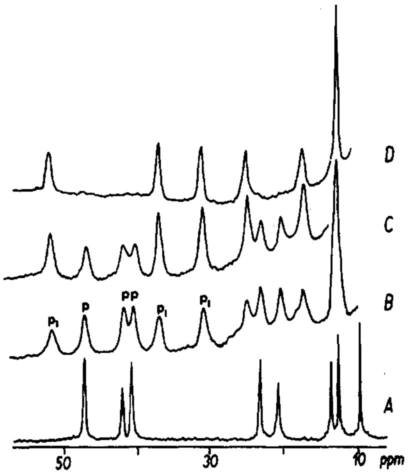

Figure 3. Titration of (N-CH_3TPP)CoCl with 1-methylimidazole (solvent $CDCl_3$, concentration of complex 12.8 mM, 25 °C). Concentration of 1-methylimidazole: (A) 0; (B) 0.45 M; (C) 0.6 M; (D) 2 M. Abbreviations: p, pyrrole resonances of **1**; p_1, pyrrole resonances of **3**. The remaining part of the spectrum is obscured by 1-MeIm resonances.

The plots of shift vs. T^{-1} for **1** (Figure 2) and **2** present a noticeable deviation from Curie law, particularly for pyrrole and NCH_3 resonances (extrapolated intercepts for pyrroles are 3.09, −8.3, 0.1, and −3.2 ppm and 41.5 ppm for NCH_3). This clearly implies the existence of thermal equilibrium between closely situated electronic states of high-spin Co(II).[1,18] The methylated nitrogen is approximately sp^3 hybridized;[1] therefore only a σ delocalization mechanism is available for the N-methyl group. For this type of delocalization one would expect to observe a large downfield shift[19] for the methyl resonance. The observed large upfield shift of the N-methyl group is consistent only with a predominant dipolar contribution to the isotropic shift.

When axial symmetry geometric factors are used to account roughly for dipolar shifts of the phenyl resonances, good linear correlations with isotropic shifts are achieved for several different orientations of the main magnetic axis. Therefore, its exact orientation remains unknown and the separation of the dipolar and contact shifts will require further detailed study of the magnetic tensor orientation and components.

The experimental line width ratios 1:1.18:1.14:1.25 (−60 °C) for H_b:H_c:H_d:H_a protons respectively are slightly different from those theoretically predicted on the basis of the dominating dipolar contribution to the relaxation mechanism,[7] i.e. 1:1.08:1.123:1.25 (r^{-6} values were calculated from the crystallographic data[1]). However, the considerably large differences between experimental and theoretical values have been observed at 20 °C. Due to the specific orientational dependence of the magnetic susceptibility tensor, an angular dependence of T_1 and T_2 can account for the difference.[21,22] This angular dependence is usually neglected for regular porphyrins as all pyrrole protons have a similar orientation with respect to the main magnetic axis. The tentative assignment of pyrrole resonances is presented in Figure 1.

The thermodynamic parameters for rotation of the phenyl groups of **1** were determined by ^{1}H NMR. Similar $\Delta G^{\ddagger}$ values for both (nonequivalent by geometry) sets of phenyl groups were determined on the basis of ln (line width) $= f(T^{-1})$ analysis.[23] The following values have been found ($CDCl_3$ solution): o_1 proton, $\Delta H^{\ddagger} = 9.0 \mp 0.4$ kcal, $\Delta S^{\ddagger}/R = -13.2 \mp 0.6$, $\Delta G^{\ddagger}_{298} = 16.9 \mp 0.8$ kcal; o_2 proton, $\Delta H^{\ddagger} = 11.4 \mp 0.6$ kcal, $\Delta S^{\ddagger}/R = -8.5 \mp 1.0$, $\Delta G^{\ddagger}_{298} = 16.5 \mp 1.3$ kcal. The measured values are similar to those reported previously for a large variety of non-N-substituted tetraphenylporphyrins and their complexes (*meso*-tetrakis(o-hydroxyphenyl)porphyrin,[24] $\Delta G^{\ddagger}_{298} = 24$ kcal; (TPP)Ni^{II}, $\Delta G^{\ddagger}_{463} > 26$ kcal;[25] TPP complexes of ruthenium, titanyl, and indium,[26] $\Delta H^{\ddagger} = 11.2$–$17.5$ kcal, $\Delta S^{\ddagger}/R = -3.7$ to -12.4, $\Delta G^{\ddagger}_{298} = 14.3$–$18.6$ kcal). The different positions of phenyls with respect to the N-methyl-substituted pyrrole ring are probably responsible for differences in the respective $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values.

The addition of 1-methylimidazole to **1** resulted in the formation of a new set of resonances corresponding to the five-coordinate species (N-CH_3TPP)Co^{II}(1-MeIm) (**3**) (Figure 3). The stability constant calculated from the pyrrole intensity ratio analysis equals 2.1 M (25 °C, $CDCl_3$), which remains in good agreement with reported values for other high-spin Co(II) complexes.[27,28] The resonances of the coordinated 1-MeIm have not been observed due to the fast exchange with uncoordinated ligands.

The identity of observed pyrrole resonances has been confirmed by the spectrum of (N-CH_3TPP-d_8)Co(1-MeIm). The spread of pyrrole resonances increases upon 1-MeIm coordination probably due to the preferred orientation of the 1-MeIm plane, which leads to preferential π spin density distribution.[31]

Other paramagnetic complexes with less pronounced dipolar contributions are being studied in order to elucidate the spin density distribution and spin-transfer mechanism.

Acknowledgment. This work was supported by the Polish Academy of Sciences (MR I.9 project).

Registry No. **1**, 51552-52-4; **2**, 94499-87-3; **3**, 94499-88-4; 1-MeIm, 616-47-7.

---

(15) Boersma, A. D.; Goff, H. M. *Inorg. Chem.* **1982**, *21*, 476.
(16) Bonnet, R.; Gale, I. A. D.; Stephenson, G. F. *J. Chem. Soc. C* **1967**, 1169.
(17) Smith, K. M., Ed. "Porphyrins and Metalloporphyrins"; Elsvier: New York, 1975; p 816.
(18) McGarvey, B. R. *J. Chem. Phys.* **1970**, *53*, 86.
(19) (N-CH_3TPP)FeCl[6] and (N-CH_3TPP)NiCl[20] demonstrated the N-CH_3 resonance at 149 ppm (−50 °C) and 177.8 ppm (−60 °C), respectively.
(20) Latos-Grażyński, L., submitted for publication.
(21) Sternlicht, H. *J. Chem. Phys.* **1965**, *43*, 2250.
(22) Sternlicht, H.; Schulman, R. G.; Anderson, E. *J. Chem. Phys.* **1965**, *43*, 3133.
(23) Satterlee, J. D.; La Mar, G. N.; Bold, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 1088.
(24) Gottwald, L. K.; Ullman, E. F. *Tetrahedron Lett.* **1969**, 3071.
(25) Walker, F. A. *Tetrahedron Lett.* **1971**, 4949.
(26) (a) Eaton, S. S.; Eaton, G. R. *J. Am. Chem. Soc.* **1975**, *97*, 3660. (b) Eaton, S. S.; Eaton, G. R. *J. Am. Chem. Soc.* **1977**, *99*, 6594.
(27) Chmielewski, P. Ph.D. Thesis, University of Wrocław, 1984.
(28) One has to note that UV spectra of N-alkylporphinato complexes are barely sensitive to the ligation state of the metal ion.[29] NMR and ESR spectroscopy make it possible to study such equilibria.[30]
(29) Lavallee, D. K. *Bioinorg. Chem.* **1976**, *6*, 219.
(30) Latos-Grażyński, L.; Jezierski, A. *Inorg. Chim. Acta*, in press.
(31) Walker, F. A.; Buehler, J.; West, J. T.; Hinds, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 6923.

Contribution from the Department of Chemistry,
The University, Southampton SO9 5NH, U.K.

Coordination Chemistry of Higher Oxidation States. 12.[1] Synthesis and Complexes of the Bis(phosphine) 1,2-Bis(dimethylphosphino)-3,4,5,6-tetrafluorobenzene, o-$C_6F_4(PMe_2)_2$

Simon J. Higgins and William Levason*

Received July 11, 1984

Recent studies[2-5] have shown that ligands of the type o-$C_6H_4(EMe_2)(E'Me_2)$ (E, E′ = P, As, Sb) (L–L) are particularly effective at stabilizing high formal oxidation states of the transition

---

(1) Part 11: Gary, L. R.; Higgins, S. L.; Levason, W.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1984**, 1433.
(2) Warren, L. F.; Bennett, M. A. *Inorg. Chem.* **1976**, *15*, 3126.
(3) Gray, L. R.; Gulliver, D. J.; Levason, W.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1983**, 133.
(4) Gray, L. R.; Higgins, S. J.; Levason, W.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1984**, 459.
(5) Higgins, S. J.; Levason, W., unpublished work.

0020-1669/85/1324-1105$01.50/0 © 1985 American Chemical Society