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Zinc–Porphyrin Phosphonate Coordination: Structural Control through a Zinc Phosphoryl–Oxygen Interaction

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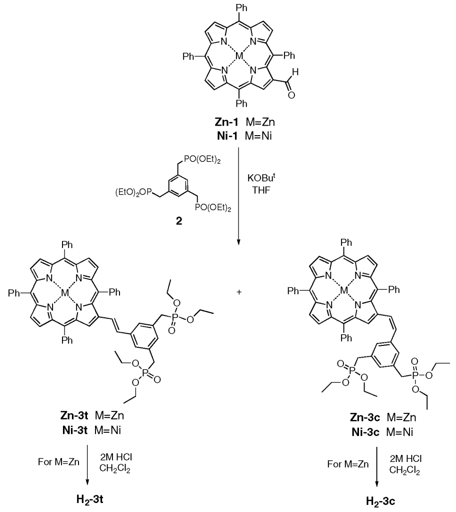
Inter- and intramolecular zinc–porphyrin phosphonate coordination in the cis and trans isomers of zinc tetraphenylporphyrinstyryldiphosphonate is reported, demonstrating the potential of the zinc phosphoryl–oxygen interaction for structural control.

Wittig reactions between zinc porphyrin aldehydes and phosphonium salts are part of a strategy developed in our laboratory toward the synthesis of functionalized porphyrin monomers and arrays for use in photovoltaic devices.[1] While we have shown that tris(benzylphosphonium) salts can be used in this regard, the intermediate porphyrin phosphonium salts are prone to hydrolysis, leading to difficulties in isolating the porphyrin arrays.[2] Consequently, we have investigated the potential of phosphonate chemistry for porphyrin array syntheses, an approach that not only has the advantage of providing more readily isolatable products but also typically produces only trans double bonds, obviating the need for the sometimes problematic isomerization procedures.[3]

Scheme 1. Synthesis of Free Base and Metalated Porphyrinstyryldiphosphonates



The reaction between zinc tetraphenylporphyrincarboxaldehyde (**Zn-1**) and 1,3,5-tris(diethoxyphosphorylmethyl)benzene[4] (**2**) surprisingly produced an isomeric mixture of the cis (30%) and trans (70%) isomers of zinc tetraphenylporphyrinstyryldiphosphonate (**Zn-3**) at room temperature, which were able to be separated after careful chromatography (Scheme 1). The proportion of the cis isomer increases to 40% upon carrying out the reaction at −60 °C, and no cis isomer is produced at a reaction temperature of 67 °C. The ^{1}H NMR spectra of the two isomers of **Zn-3** in CDCl$_3$ are shown in Figure 1, and the chemical shifts are listed in Table 1. In the cis isomer, the resonances associated with the protons attached to the arylphosphonate group (H$_{c-g}$) are all shifted to high field with respect to those of the trans isomer. The concentration dependence of the chemical shifts is also markedly different in the two isomers. Upon a decrease in the concentration of **Zn-3t**, significant shifts to low fields are observed. For the methyl resonance of the phosphonate group, for example, a tenfold decrease in the concentration results in a downfield shift of 0.21 ppm. For **Zn-3c**, the corresponding downfield shift is only 0.02 ppm.

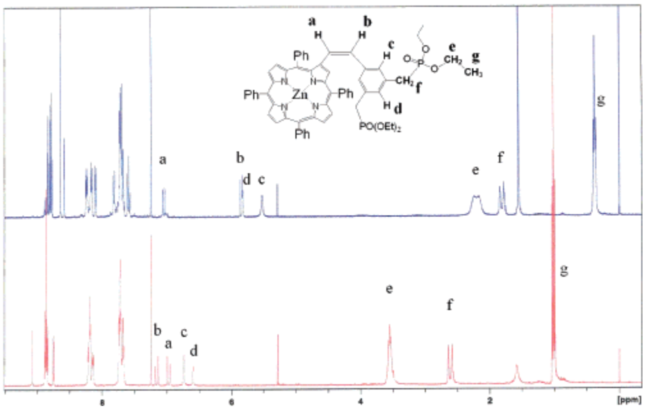


Figure 1. 400 MHz ^{1}H NMR spectra of 10^{-2} mol L^{-1} solutions of **Zn-3c** (upper trace) and **Zn-3t** (lower trace) in CDCl$_3$ at 25 °C.

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(1) Campbell, W. M.; Burrell, A. K.; Officer, D. L.; Jolley, K. W. *Coord. Chem. Rev.* **2004**, *248*, 1363−1379.

(2) Burrell, A. K.; Officer, D. L. *Synlett* **1998**, *12*, 1297−1307.

(3) Lawrence, N. J. In *Preparation of Alkenes: A Practical Approach*; Harwood, L. M., Moody, C. J., Eds.; Oxford University Press: Oxford, U.K., 1996; pp 19−58.

(4) Meier, H.; Lehmann, M.; Kolb, U. *Chem.*−*Eur. J.* **2000**, *6*, 2462−2469.

10.1021/ic070344r CCC: $37.00

Table 1. ^{1}H NMR (400 MHz) Chemical Shifts (ppm from Tetramethylsilane) of 10^{-2} M Solutions in Deuterochloroform at 25 °C[a]

	a	b	c	d	e	f	g
Zn-3t	6.98	7.16	6.74	6.60	3.55	2.61	1.02
Zn-3c	7.05	5.86	5.53	5.83	2.21	1.81	0.38
Ni-3t	6.86	7.10	6.98	7.11	4.06	3.15	1.30
Ni-3c	6.33	6.16	7.14	7.06	3.70	2.89	0.93
H_2-3t	7.01	7.28	7.07	7.16	4.08	3.19	1.30
H_2-3c	6.44	6.30	7.10	7.03	3.65	2.81	0.87

[a] Column headings refer to proton labels given in Figure 1.

Such significant differences cannot be explained in terms of the different geometries of the two isomers alone. The analogous chemical shifts of the free base trans derivative **H_2-3t**, which was prepared by demetalation of **Zn-3t** (Scheme 1), do not show a concentration dependence. In addition, the chemical shift differences between **H_2-3t** and **H_2-3c** (also prepared by demetalation) are significantly smaller than those of the zinc analogues (Table 1). Moreover, the chemical shifts of the nickel derivatives **Ni-3c** and **Ni-3t** are also concentration-independent, and their chemical shifts are similar to those of their corresponding free base (Table 1).

Consequently, coordination of the phosphoryl group to zinc, either inter- or intramolecularly, must be involved. In **Zn-3t**, the molecule exists as a planar conjugated system[5] and the phosphoryl O atoms are distant from the Zn atom, thus ruling out the possibility of intramolecular coordination. Any coordination must, therefore, be intermolecular such that the phosphoryl O atom of one molecule is coordinated to the Zn atom of a neighboring porphyrin moiety. Such a coordination brings phosphonate protons into the shielding zone of the porphyrin core, and the shift to high fields of the phosphonate protons with increasing concentration of **Zn-3t** can therefore be understood in terms of an increase in the ratio of coordinated to uncoordinated groups. An intermolecular polyether O−Zn^{II} interaction is the basis for dimerization of zinc porphyrins in the solid state.[6] In addition, there are a number of reports of zinc phosphonate anion−oxygen coordination in inorganic complexes,[7−10] and the first example of an intermolecular phosphonate ester P−O−Zn coordination that involves a zinc porphyrin was reported during the preparation of this manuscript.[11] There is also a report of a phosphoryl oxygen coordination to zinc(II) in dichlorobis(triphenylphosphine oxide)zinc(II).[12]

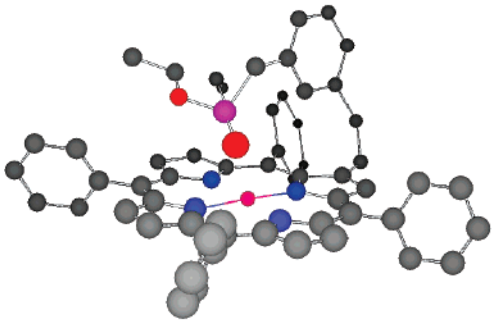

Figure 2. Computer-simulated possible structure of **Zn-3c**. For the purpose of clarity, the second phosphonate group is not shown.

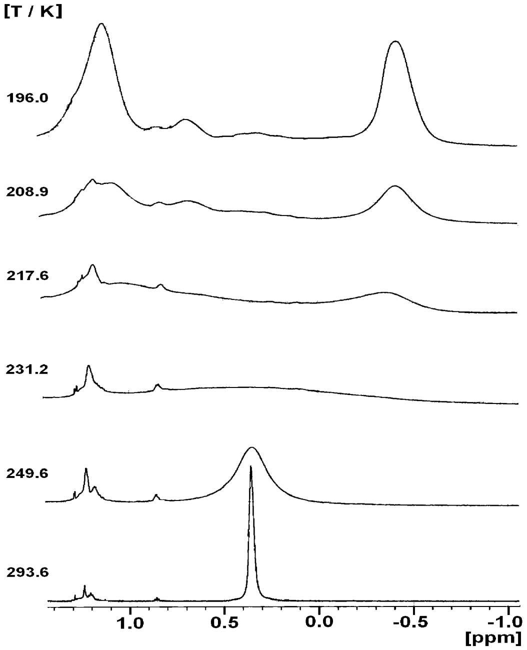

Figure 3. Temperature dependence of the appearance of proton-decoupled 700 MHz ^{1}H NMR spectra of the phosphonate CH_3 protons of **Zn-3c**.

In the cis isomer **Zn-3c**, steric interference between the β-pyrrolic substituent and triphenylphosphine (TPP) pushes the styryl group out of the plane of the porphyrin ring and enables one of the phosphonate O atoms to undergo intramolecular coordination to the central Zn atom, as shown in Figure 2. The protons associated with this phosphonate will experience a shielding effect as a result of ring currents in the porphyrin plane.[13,14] Because, in Figure 1, only one set of phosphonate chemical shifts is observed, the chemical shifts must represent the weighted average value of the two sets of protons as a result of fast exchange between coordinated and uncoordinated phosphonate groups. The line widths of the phosphonate proton resonances of **Zn-3c** at 25 °C are larger than the corresponding resonances in **Zn-3t** and are strongly temperature-dependent, as shown in Figure 3 for the methyl phosphonate protons (H_g). On cooling, the peak at 0.38 ppm (average of four methyl groups) splits into two peaks of equal intensity attributable

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(5) Bonfantini, E. E.; Burrell, A. K.; Officer, D. L.; Read, D. C. W.; McDonald, M. R.; Cocks, P. A.; Gordon, K. C. *Inorg. Chem.* **1997**, *36*, 6270−6278.

(6) Langford, S. J.; Woodward, C. P. *Polyhedron* **2007**, *26*, 338−343.

(7) Lei, C.; Mao, J.-G.; Sun, Y.-Q.; Zeng, H.-Y.; Clearfield, A. *Inorg. Chem.* **2003**, *42*, 6157−6159.

(8) Poojary, D. M.; Zhang, B.; Clearfield, A. *J. Am. Chem. Soc.* **1997**, *119*, 12550−12559.

(9) Poojary, D. M.; Zhang, B.; Clearfield, A. *Chem. Mater.* **1999**, *11*, 421−426.

(10) Yang, B.-P.; Mao, J.-G.; Sun, Y.-Q.; Zhao, H.-H.; Clearfield, A. *Eur. J. Inorg. Chem.* **2003**, 4211−4217.

(11) Matano, Y.; Matsumoto, K.; Terasaka, Y.; Hotta, H.; Yasuyuki, A.; Ito, O.; Shiro, M.; Sasamori, T.; Tokito, N.; Imahori, H. *Chem.*−*Eur. J.* **2007**, *13*, 891−901.

(12) Rose, J. P.; Lalancette, R. A.; Potenza, J. A.; Schugar, H. J. *Acta Crystallogr.* **1980**, *B36*, 2409−2411.

(13) Abraham, R. J.; Medforth, C. J.; Smith, K. M.; Goff, D. A.; Simpson, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 4786−4791.

(14) Cross, K. J.; Crossley, M. *Aust. J. Chem.* **1992**, *45*, 991−1004.

Table 2. Temperature Dependence of the Exchange Rate τ^{-1} between Coordinated and Uncoordinated Phosphonate Sites in **Zn-3c**

T/K	208.9	217.6	231.2	249.6	293.6
τ^{-1}/s^{-1}	8.30×10^2	1.59×10^3	5.99×10^3	3.32×10^4	8.29×10^5

to the coordinated (−0.40 ppm) and uncoordinated (1.16 ppm) phosphonates.

In order to determine the activation energy for the exchange process, the rates of exchange between bound and unbound sites in **Zn-3c**, given in Table 2, were obtained by fitting those portions of the spectra shown in Figure 3 that did not overlap with other resonances to the Gutowsky−Holm equations for uncoupled two-site exchange.[15] The large frequency difference between the two sites enabled a wide temperature range to be sampled, and within this range exchange effects dominate. The best-fit lifetimes were insensitive to changes in both the nonexchange chemical shift (1090 Hz, obtained from the spectrum at 196 K) and the value of T_2* [0.025 s, obtained from the spectrum (not shown) at 332 K]. The rate data were fitted to the Arrhenius equation, giving an activation energy E_a of 42.2(1.3) kJ mol^{-1} and a preexponential factor A of 2.5×10^{13} s^{-1}. The value of the activation energy is an order of magnitude smaller than that of typical covalent bond energies and roughly twice that of hydrogen-bonded energies.

That coordination occurs through the P═O bond was confirmed by separate experiments in which a deuterochloroform solution of zinc tetraphenylporphyrin (ZnTPP) was titrated into deuterochloroform solutions of triisopropylphosphite, triphenylphosphine oxide, and diisopropylbenzylphosphonate (Figure 4). Large and practically identical ^{31}P NMR shifts to high field were observed with increasing ZnTPP concentration in both the triphenylphosphine oxide and diisopropylbenzylphosphonate titrations, strongly suggesting that coordination occurs between the Zn and O atoms of the P═O bond. The best-fit K values at 25 °C, obtained from assuming a fast-exchange equilibrium between a ligand and a 1:1 complex, are 32 and 24 for the triphenylphosphine oxide and the diisopropylbenzylphosphonate complexes, respectively, values that are similar to those reported for the coordination of oxygen donor ligands to ZnTPP.[16]

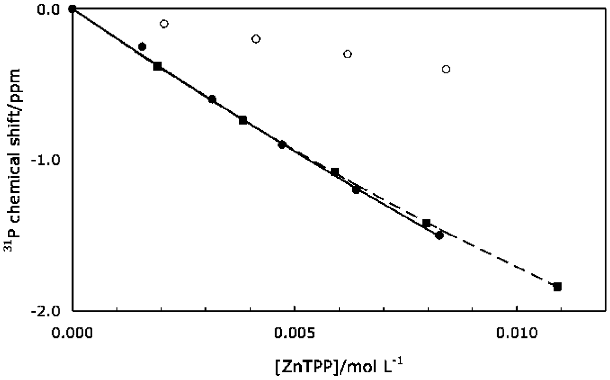

Figure 4. Plot of ^{31}P NMR chemical shifts of triisopropylphosphite (open circles), triphenylphosphine oxide (squares), and diisopropylbenzylphosphonate (closed circles), measured relative to the chemical shifts of the pure ligands, upon titration of ZnTPP into respectively 8.64×10^{-3}, 8.98×10^{-3}, and 8.58×10^{-3} M solutions of the ligands in $CDCl_3$ at 25 °C. The dotted and solid lines are best fits to respectively the triphenylphosphine oxide and diisopropylbenzylphosphonate data, assuming a 1:1 ligand/ZnTPP complex (see the text).

In conclusion, the experiments reported here support the notion that coordination of the tris(phosphonate) to **Zn-1** prior to the Wittig reaction affords a syn conformation of the oxaphosphane intermediate, leading to an increased yield of the cis isomer **Zn-3c**. This demonstrates, for the first time, structural control of a porphyrin derivative through an interaction between a phosphoryl oxygen and zinc and suggests that such interactions may be useful for the supramolecular assembly of porphyrin arrays. We are currently investigating this possibility.

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Supporting Information Available: Synthesis and characterization of **M-3c** and **M-3t**, where **M** = **H$_2$**, **Ni**, and **Zn**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.

(16) Nardo, J. V.; Dawson, J. H. *Inorg. Chim. Acta* **1986**, *123*, 9−13.