Phosphorus complex of corrole

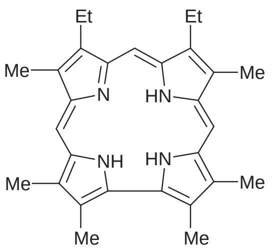
Roberto Paolesse,*[a] Tristano Boschi,[a] Silvia Licoccia,[a] Richard G. Khoury[b] and Kevin M. Smith[b]†

[a] *Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Roma, 00133, Italy*
[b] *Department of Chemistry, University of California, Davis, CA 95616, USA*

Reaction of 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole (1) with $POCl_3$ in pyridine affords the first non-metal derivative of corrole; in this compound, 2, the phosphorus is in a pentavalent state and is different from analogous complexes of porphyrins.

Non-porphyrin polypyrrolic macrocycles represent a novel field of research which has experienced impressive expansion in the last few years.[1] These compounds are particularly intriguing for both theoretical and experimental reasons. For example, they can enable studies of the way in which skeletal variations influence the aromaticity and the chemical properties of the macrocycles, thereby opening potential applications of these molecules in different fields, ranging from catalysis to biomedical sciences.

Among porphyrin analogues, corrole (*e.g.* **1**) was one of the first examples to be reported in the literature; it was synthesized more than 30 years ago by Johnson and Kay during their attempts to approach the corrin nucleus of vitamin B_{12}.[2] But recent investigations using the corrole macrocycle have revealed interesting differences in its coordination behavior compared with the analogous porphyrin complexes. Corrole, for example, is able to stabilize high oxidation states for coordinated metals, and to retain a planar conformation even when the peripheral positions are fully substituted.[1a,b] Despite these interesting properties, the coordination chemistry of corrole is substantially limited to the first row transition metals; expansion of the so-called 'periodic table' of metallocorrolates should allow researchers to study, in more detail, the coordination behavior of this macrocycle. In particular, coordination of phosphorus can be intriguing due to the non-metal character of this element and because it is, in its pentavalent state, the smallest ion so far coordinated to a porphyrin.[3] Herein we report the synthesis and characterization of the first example of a phosphorus corrole derivative.



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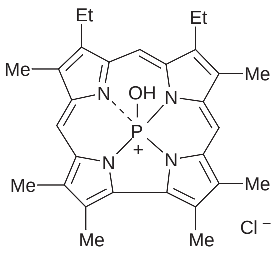

2

Reaction of 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole (**1**; H_3EMC)[2] with $POCl_3$ in pyridine at room temperature showed an immediate spectrophotometric change, with the formation of the spectrum of the characteristic corrole monocation.[4] When the mixture was heated at reflux the optical spectrum quickly changed (indicating the formation of a complex), with the complete disappearance of the absorbance characteristic of the corrole; Fig. 1 shows the optical spectra of the corrole monocation and the phosphorus complex. Evaporation of the solvent and recrystallization from CH_2Cl_2–hexane afforded a purple powder. In complexes with porphyrins, phosphorus has been reported to be hexacoordinated in a +V oxidation state;[3] in the case of octaethylporphyrin a transient +III state has been reported to be an intermediate during the metallation reaction.[3] In the present case of corrole, the electronic absorption spectrum is similar to those of other main group metallocorrolates.[5] By analogy with porphyrins it can be classified as 'normal',[6] thereby indicating the presence of the +V oxidation state for the coordinated phosphorus.

The ^1H NMR spectrum of the phosphorus corrole was also typical of a metallocorrolate, with the absence of internal NH resonances and the expected pattern for peripheral substituents. ^{31}P NMR spectroscopy showed a resonance for coordinated phosphorus at -102.5 ppm (relative to external H_3PO_4), which is significantly different from phosphorus complexes of porphyrins in which the phosphorus signal is at *ca.* -200 ppm.[7] This feature indicated that the diamagnetic ring current effect is less influential in determining the phosphorus resonance in the corrole derivative compared with porphyrin complexes. This difference can be attributed to two major factors: (i) the diminished aromatic character of corrole relative to porphyrin, and/or (ii) a different coordination geometry of phosphorus in the corrole complex. Both ^1H and ^{13}C NMR spectra ruled out the first hypothesis because resonances of the corrole derivative have almost the same chemical shifts as do the analogous porphyrinates.[8] A different coordination geometry seems more likely because the EI mass spectrum of the corrole complex showed a molecular peak at *m/z* 483, indicating the presence of only one ligand at an axial position. Analogous phosphorus porphyrinates are hexacoordinated.[3]

X-Ray characterization‡ performed on a single crystal of the phosphorus corrolate **2** allowed its unambiguous structural identification. The molecular structure is shown in Fig. 2. The phosphorus atom exhibits pentacoordinated geometry, lying more than 0.4 Å out of the mean corrole plane toward the oxygen atom of the axial hydroxy group. The P–O bond distance of 1.531 Å can be attributed to a single bond and is similar to the observed P–O distance in an analogous porphyrin complex.[3] The P–N bond lengths average 1.80 Å. These lengths

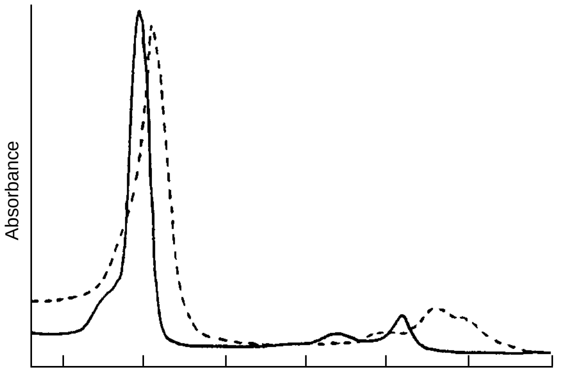

Fig. 1 Optical spectra, in CH_2Cl_2, of $[H_4EMC]^+$ (– – –), and [(EMC)-P(OH)]Cl (**2**), (——)

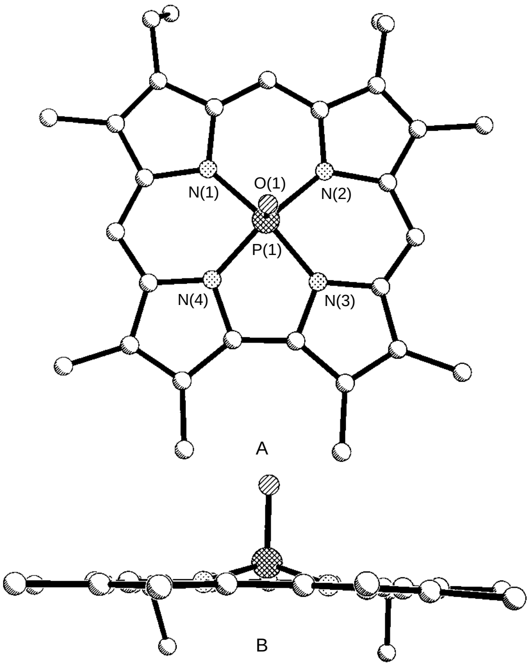

Fig. 2 Molecular structure‡ of [(EMC)P(OH)]Cl (**2**). A, top view; B, edge on view. The chloride counterion is omitted.

are shorter than those measured in any other metal complexes of this macrocycle[1a,b] and are not equivalent, as usual for metallocorrolates. Contrary to the situation in porphyrin derivatives the phosphorus corrolate macrocycle is almost planar, the mean plane deviation of the 23 core atoms being 0.0245 Å. The cationic nature of the macrocycle is confirmed by the presence of a chloride counterion.

The phosphorus complex reported herein is the first non-metal derivative of corrole; moreover, it represents a further example of different coordinative behavior of this macrocycle compared with the analogous and more ubiquitous porphyrin macrocycle. We are presently investigating the axial chemistry of this complex, and these studies will be the subject of a full paper.

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Notes and References

† E-mail: kmsmith@ucdavis.edu

‡ *Crystal Data* for **2** ($C_{29}H_{32}N_4PO$)(H_2O)(Cl): Crystals of **2** were grown from a mixture of CH_2Cl_2 and *c*-C_6H_6. A single parallel-piped crystal was selected with dimensions 0.20 × 0.14 × 0.10 mm. The unit cell was triclinic, space group $P\bar{1}$ with cell dimensions a = 11.038(3), b = 11.749(3), c = 12.031(3) Å, α = 96.50(2), β = 101.77(2), γ = 116.40(2)°, V = 1330.7(6) Å^3 and Z = 2 (M = 537.02, ρ_{calc} = 1.340 g cm^{-3}, μ = 2.112 mm^{-1}). Of 3778 reflections measured, 3513 were independent and 3054 had $I > 2\sigma$ (R_{int} = 0.044); number of parameters = 343. Final R factors were $R1$ = 0.0543 (based on observed data) and w$R2$ = 0.1957 (based on all data). CCDC 182/832.

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