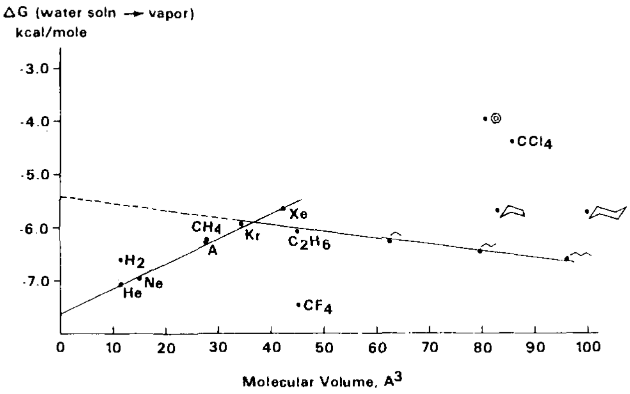

Figure 2.

this factor plays a role both in water and in octanol. In the latter case, however, it is less significant.

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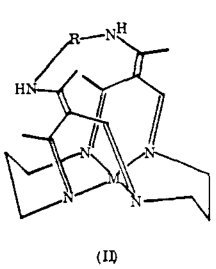
Totally Synthetic Heme Protein Models Based on Complexes with Superstructure Ligands

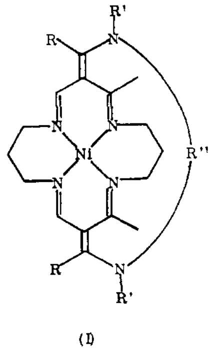
Sir:

Heme proteins perform many functions and yet all contain an iron porphyrin prosthetic group. The main part of the ligand field varies only slightly from species to species while the function varies greatly. Thus the protein is of similar importance to the heme in determining the specific function of the heme protein. We are concerned with the design and synthesis of complexes whose ligands have appropriate superstructures[1] to facilitate their emulation of various protein complexes.

Structure I summarizes a new family of superstructure complexes containing bicyclic ligands,[2] which might facilitate a variety of functions. However, we concentrate here on providing a single protected site, a "dry cave", near one of the metal coordination positions (structure II). Many different bridge groups can be built into the structure, including -(CH$_2$)$_n$ (n = 3-7), *m*- and *p*-xylyl, durenyl, substituted anthracenes, and groups containing heteroatoms. The bridge group is most important in determining the size and shape of the cavity. The groups R bracket the entrance to the dry cave and influence both its size and accessibility. To date R can be H-, CH$_3$-, CH$_3$(CH$_2$)$_n$-, *i*-C$_3$H$_7$-, or C$_6$H$_5$-. The group R′ affects the electron density at the metal ion.



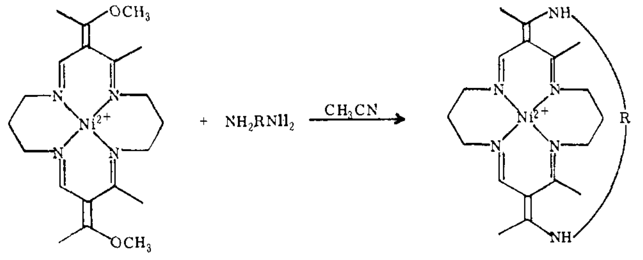
(II)



(I)

These studies are inspired by the elegant porphyrin chemistry of Professors Baldwin,[3] Collman,[4] Traylor,[5] and Battersby[6] and their associates. We see two advantages to the new substances reported here. Since these totally synthetic species involve ligand structures that are different from the porphyrins, the reproducing of natural function with them cannot be construed as deriving from the natural prosthetic group. Also, it is quite easy to vary components of these new structures so that the effects of a range of structural parameters are readily studied.

The synthetic strategy for the preparation of I is based on an unusual intermediate (structure III, eq 1). The vinyl carbon atom to which the methoxy group is attached readily undergoes addition-elimination reactions; the functional group is closely analogous to an ester group. Amines are excellent nucleophiles for this reagent and the stable products resemble carboxylic amides in their chemical properties. From the crystal structure,[7] III has a saddle shape (similar to structure II) and the two vinyl functions react with diamines under conditions of modest dilution forming I in high yield, usually >60%.



(III) (1)

The preparation of 2,11,20,26-tetramethyl-3,10,14,18,21,25-hexaazatricyclo[10.7.7.2^{5,8}]octacosa-1,5,7,11,13,18,20,25,27-nonaene(N$_4$)nickel(II) hexafluorophosphate, {Ni[*p*-xylyl(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$]}(PF$_6$)$_2$, proceeded as indicated in eq 1. α,α′-Diamino-*p*-xylene was prepared by the Gabriel synthesis.[8] The diamine (1.1 g, 8.1 mmol) dissolved in 500 mL of acetonitrile was added dropwise to 5.72 g (8.1 mmol) of {Ni[(MeOEthi)$_2$Me$_2$[16]tetraeneN$_4$]}(PF$_6$)$_2$ (III) dissolved in 500 mL of acetonitrile. The color changed from yellow-green to orange upon addition of the diamine. The solution was reduced in volume to 30 mL and then passed through a column (4-cm diameter, 15-cm length) packed with alumina under acetonitrile. The solvent was evaporated and methanol (200 ml) was added. The yellow crystalline product was isolated by filtration: yield, 3.6 g (57%). Anal. Calcd for $NiC_{26}H_{36}N_6P_2F_{12}$: C, 39.97; H, 4.65; N, 10.76. Found: C, 39.74; H, 4.70; N, 10.64.

The nickel(II) complex having a *p*-xylyl bridging group (R″) (R = CH$_3$ and R′ = H), ($NiN_6C_{26}H_{36}$)(PF$_6$)$_2$, was subjected to complete X-ray structure determination: space group, $Pmn2_1$; a = 11.621 (5), b = 8.471 (2), c = 16.117 (4) Å; $\alpha = \beta = \gamma = 90.00°$; $Z = 2$; $\lambda_{MoK\bar{\alpha}}$ = 0.71069 Å; T = 20 (1) °C; μ = 10.78 cm^{-1}; ρ_{obsd} = 1.61 (2), ρ_{calcd} = 1.63; $\omega = 2\theta$ scan technique for all reflections of positive *hkl* having $2\theta \leqslant 65°$; 2505 independent reflections of which 2255 had intensities $>3\sigma(F)$ above background. The solution was by the heavy-atom Patterson technique and standard Fourier and least-squares methods were used in refinement. The disorder in one PF$_6^-$ ion was satisfactorily treated by refining the coordinates, orientations, and occupancy factors of three rigid, partial-occupancy PF$_6^-$ groups. Hydrogen atom contributions were included in the least-squares calculations. The final disagreement indices are R = 0.055, R_w = 0.099, and GOF = 3.2.

The most striking features relate to the configuration and

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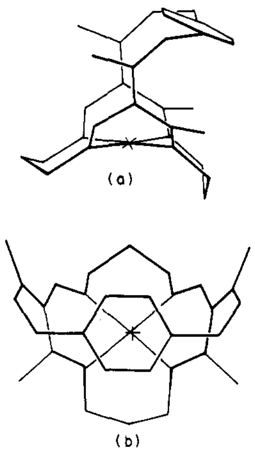


Figure 1. (a) Side view of the Ni(II) complex (I) where the bridge is a *p*-xylyl group. (b) Top view looking perpendicular to the xylyl ring at the nickel atom.

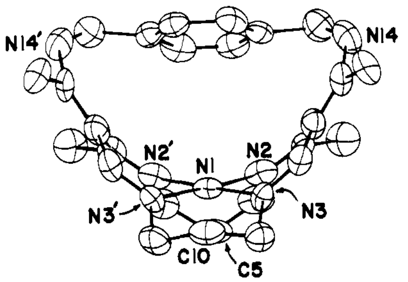
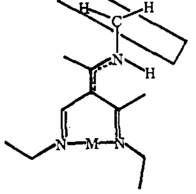


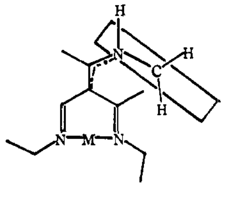
Figure 2. ORTEP diagram of the Ni(II) complex looking into the "dry cave".

conformation of the ligand (Figures 1 and 2). It clearly forms a hydrophobic cavity or "dry cave" in the vicinity of a vacant metal coordination site. The center of the *p*-xylyl group is displaced 2.6 Å to one side of the nickel and is tilted ~ 23° with respect to the coordination plane (Figure 1a), thus effectively forming both the roof and back of the cave but leaving a wide opening (~3.6 by 2.5 Å) at its mouth. The cavity is 6.78 Å wide (between nonbridghead vinyl carbons) and varies from 4.55 to 4.27 Å (rear) in height (Figure 2). The interior walls consist almost entirely of filled π orbitals, causing the cavity to be intrinsically hydrophobic—a "dry cave".

The double bonds in the parent macrocycle (N-2=C-6 and N-3=C-8) are localized so that C-6—C-7 and C-7—C-8 are essentially single bonds (Figure 3). In contrast, the bridging nitrogens are involved in delocalized π bonding, i.e., between N-14—C-12 and C-7=C-12. This causes N-14 to be planar and sp^2 hybridized and produces a form of geometrical isomerism that we have also characterized thoroughly for a number of these nickel complexes.[9] As shown in structures IV and V, the bridge may either rise directly above the N-14 atoms (lid-on isomer, structure IV) or project rearward from N-14 (lid-off isomer, structure V). The structure described here is that of a lid-off isomer.



(IV)



(V)

The characteristic saddle shape of the parent macrocycle requires the two saturated chelate rings to extend away from the dry cave. One of these has the favored chair conformation but the other adopts the boat shape (Figure 1a), presumably because of steric requirements of the bridging moiety. The coordination sphere about the nickel atom is approximately square planar with distances of the usual magnitude (Figure 3).

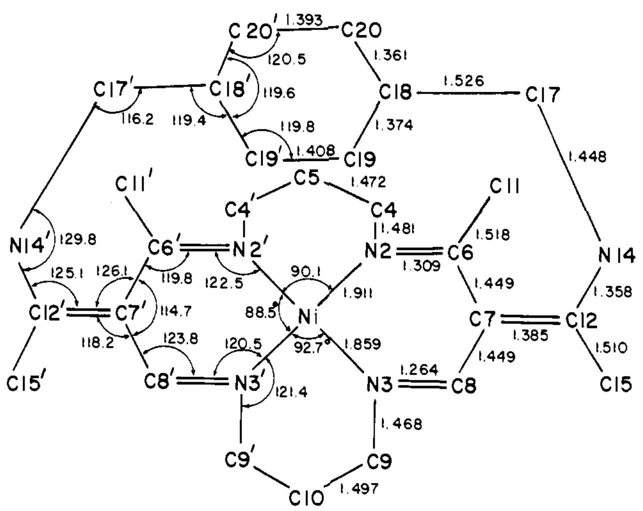


Figure 3. Bond distances and angles. The halves of the molecule are related by a crystallographic mirror plane through Ni, C-5 and C-10, bisecting the *p*-xylyl bridging group. Estimated standard errors in the metal–nitrogen distances are 0.005 Å (0.1° for the angles), while for the C–C and C–N bonds the esds average 0.007 Å (0.3°).

The complexes of these new ligands with other metal ions are under investigation. As would be expected, the dry cave site confers useful capabilities on the metal ion.[10]

References and Notes

(1) Recent synthetic developments in these and other laboratories employ the addition to ligands of components that may be viewed as serving roles analogous to the superstructures of ships; i.e., as the superstructure is altered the function of the species changes.
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(10) These studies were partially supported by the National Science Foundation.

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Palladium(0) Catalyzed Reaction of 1,3-Diene Epoxides. A Useful Method for the Site-Specific Oxygenation of 1,3-Dienes

Sir:

The site-specific oxygenation of unsaturated carbon skeletons is one of the most fundamental tasks in synthetic organic chemistry. We here describe three types of oxygenative transformations of 1,3-dienes, A–C. The type A reaction is formally viewed as an ene-type reaction caused by oxygen