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The N_2O_2 Porphyrinogen Skeleton: Access to a Novel Class of Coordinatively Unsaturated Transition Metal Ions

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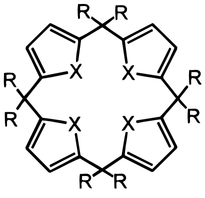
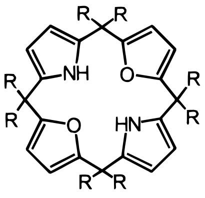
The porphyrinogen skeleton, which is stable when fully alkylated,[1,2] provides a variety of tridimensional binding cavities for metal ions. The binding peculiarities depend on (i) the sp^3 *meso* carbons whereby the bonding to the metal can vary from η^1 to η^5 [1] and (ii) the nature of the heteroatoms, allowing one to tune the binding ability of the cavity.

meso-Octaalkylporphyrinogen skeletons are known with different sets of heteroatoms;[3] two of them, **1**[1,2] and **2**,[3,4] will be considered here as reference compounds. The former was recently exploited in its tetraanionic form as a strong binder of a variety of early and late transition metals because of its special redox properties.[1,2] The *meso*-octaalkylporphyrinogen **2** has been largely unable to bind any cation because of the electrophilic nature of the furan oxygens.[4b,d,e] The binding properties of **1** and **2** allowed us to design a cavity which would strongly bind atoms in a linear arrangement, using the NH moieties, while the two oxygens would have the role of weakly binding spectators, as illustrated by the *meso*-octaalkyldioxaporphyrinogen $R_8O_2N_2H_2$, **3**.

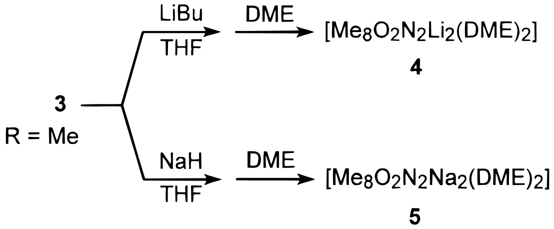


R_8X_4
X = NH, **1**; X = O, **2**

The core of **3** seems particularly appropriate for protecting a linear dicoordinate unsaturated metal ion in the presence of weakly binding electron-poor oxygens. The synthesis of **3** (R = Me) was performed using an improved published procedure based on the conversion of furan to pyrrole.[5] The metal complexation by **3**[6] was achieved via its lithium or sodium derivative,[7] which can engage in metathesis reactions with metal halides.



$R_8O_2N_2H_2$, **3**



(1)

The structure and the most relevant structural parameters of **5**[8] are shown in Figure 1. The planar rhombic Na_2O_2 array forms a dihedral angle of 86.01° with the N_2O_2 core, and each sodium cation has a tetrahedral coordination. The dioxapor-

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(6) Procedure for **3**: See Supporting Information.

(7) Procedure for **5**: **3** (5.0 g, 11.6 mmol) and NaH (0.72 g, 30.0 mmol) were combined in THF (100 mL). The orange solution was refluxed overnight and excess NaH then removed by filtration. The solvent was evaporated and the resulting solid triturated with *n*-hexane (100 mL) to give a beige solid, which was then filtered off and dried in vacuo (82%). Anal. Calcd for **5**·THF, $C_{28}H_{32}N_2Na_2O_2{\cdot}C_4H_8O$: C, 70.31; H, 7.38; N, 5.12. Found: C, 70.25; H. 7.40; N, 5.09. ^1H NMR (C_5D_5N, 298 K): δ 6.45 (s, 4 H, C_4H_2O), 5.70 (s, 4 H, C_4H_2N), 3.64 (m, 4 H, THF), 1.77 (s, 24 H, CH_3), 1.60 (m, 4 H, THF). White crystals suitable for X-ray analysis were obtained by recrystallization from DME. Anal. Calcd for **5**·2DME, $C_{28}H_{32}N_2Na_2O_2{\cdot}C_8H_{20}O_4$: C, 70.31; H, 7.38; N, 5.12. Found: C, 70.25; H, 7.40; N, 5.09. ^1H NMR (C_5D_5N, 298 K): δ 6.45 (s, 4 H, C_4H_2O), 5.70 (s, 4 H, C_4H_2N), 3.64 (m, 4 H, DME), 1.77 (s, 24 H, CH_3), 1.60 (m, 4 H, DME).

(8) Crystal data for **5**·2DME: $C_{36}H_{52}N_2Na_2O_6$, $M = 654.8$, monoclinic, space group $P2_1/n$, $a = 11.688(2)$ Å, $b = 12.300(2)$ Å, $c = 12.585(2)$ Å, $\beta = 97.41(1)°$, $V = 1794.1(5)$ Å^3, $Z = 2$, $D_{\mathrm{calcd}} = 1.212$ g/cm^3, $F(000) = 704$, λ(Cu Kα) = 1.541 78 Å, μ(Cu Kα) = 8.32 cm^{-1}, crystal dimensions 0.23 × 0.29 × 0.52 mm. The structure was solved using SHELX86 and anisotropically refined for all the non-hydrogen atoms. For 1466 unique observed reflections [$I > 2\sigma(I)$] collected at $T = 295$ K ($6 < 2\theta < 140°$), the current R is 0.056 ($R_{2w} = 0.136$). For details see the Supporting Information.

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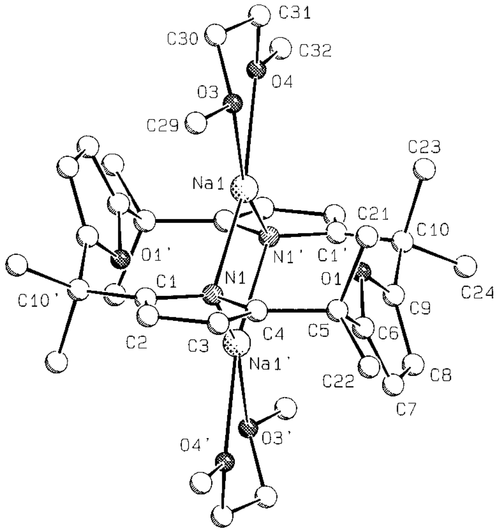
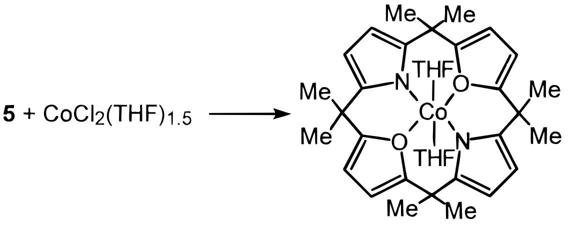


Figure 1. SCHAKAL view of complex **5**. Selected bond distances (Å) and angles (deg): Na1−N1 = 2.595(5), Na1−N1′ = 2.518(5), Na1−O3 = 2.391(5), Na1−O4 = 2.389(4); N1−Na1−N1′ = 108.3(1), O4−Na1−N1′ = 89.8(1), O4−Na1−N1 = 161.1(2), O3−Na1−N1′ = 158.9(2), O3−Na1−N1 = 92.8(1), O3−Na1−O4 = 69.2(1), Na1−N1−Na1′ = 71.6(1). Prime denotes a transformation of −*x*, 1 − *y*, 1 − *z*.

phyrinogen skeleton has a chair (or flattened partial cone) conformation, with the two pyrroles coplanar with the N_2O_2 core [dihedral angle 175.7(1)°], while the two up and down furans form a dihedral angle of 111.6(1)°. Such a conformation favors a η^5-furan−sodium interaction [Na···O1′, 2.877(4) Å; Na···C6′, 3.067(6); Na···C7′, 3.328(6); Na···C8′, 3.352(6); Na···C9′, 3.105(5) Å] according to the anticipated absence of a significant Na···O interaction.

Reaction of either **4** or **5** with metal halides gave the corresponding transition metal derivatives, as exemplified in reaction 2.



(2)

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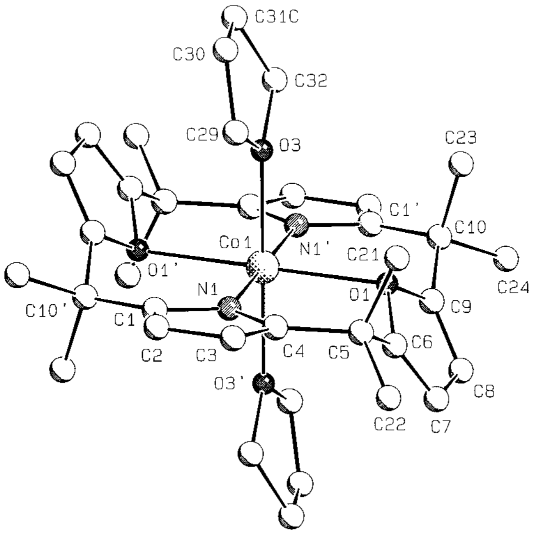

Figure 2. SCHAKAL view of molecule A in complex **6**. Selected bond distances (Å) and angles (deg): Co1−N1 = 2.041(5), Co1−O1 = 2.302(4), Co1−O3 = 2.242(5); O1−Co1−O1′ = 180(−), O3−Co1−N1 = 88.2(2), O3−Co1−O1 = 90.6(2), O1−Co1−N1′ = 90.2(2), O1−Co1−N1 = 89.8(2), N1−Co1−N1′ = 180(−). Disorder involving C31 has been omitted for clarity. Prime denotes a transformation of 1 − *x*, 1 − *y*, −*z*.

Crystals of **6**[9] contain two differently solvated forms (see Supporting Information), though only that shown in Figure 2 is commented on here.[10] The conformation of the dioxaporphyrinogen, as expressed by the two dihedral angles mentioned above [170.3(2)° and 124.3(2)° in **6**] is very close to that of **5**. Such a conformation results from a very weak Co−O(furane) interaction occurring at a longer distance [Co1−O1, 2.302(4) Å] than the Co−THF bond [Co1−O3, 2.242(5) Å]. The N_2O_2 set masks a dicoordinate cobalt in the cavity. The reactivity of low coordinated metals bonded to the dioxaporphyrinogen skeleton is under investigation along with the use of **3** in combination with early transition metals.

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Supporting Information Available: Text presenting the preparation of **3** and X-ray experimental details and crystal data for **5** and **6**, tables giving crystal data and summaries of the structure determinations, fractional atomic coordinates, thermal parameters, bond lengths, bond angles, and least-squares plane data for **5** and **6**, ORTEP drawings for **5** and **6**, and a SCHAKAL drawing of molecule B in complex **6** (22 pages). Ordering information is given on any current masthead page.

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[9] Procedure for **6**: **5** (1.76 g, 3.2 mmol) and $CoCl_2(THF)_{1.5}$ (0.76 g, 3.2 mmol) were dissolved in THF (100 mL); the resulting green solution was stirred at room temperature overnight and then refluxed for 1 h. The solvent was removed and the solid residue extracted with *n*-hexane (100 mL). Upon partial removal of *n*-hexane, a yellow solid precipitated (77%). Crystals suitable for X-ray analysis were grown in a diluted *n*-hexane solution. Anal. Calcd for **6**·THF, $C_{28}H_{32}CoN_2O_2 \cdot C_4H_8O$: C, 68.68; H, 7.34; N, 5.01. Found: C, 68.87; H, 7.34; N, 5.01. IR (Nujol), ν 1555, 1280, 1028 cm^{-1}.

[10] Crystal data for **6**: $C_{36}H_{48}CoN_2O_4 \cdot 2C_{34}H_{44}CoN_2O_{3.5}$, M = 1823.1, triclinic, space group $P\bar{1}$, a = 10.483(3) Å, b = 22.940(5) Å, c = 9.889(2) Å, α = 96.06(2)°, β = 95.96(2)°, γ = 94.39(2)°, V = 2342.8(10) $Å^3$, Z = 1, D_{calcd} = 1.292 g/cm^3, $F(000)$ = 971, λ(Mo Kα) = 0.710 69 Å, μ(Mo Kα) = 5.84 cm^{-1}, crystal dimensions 0.18 × 0.24 × 0.40 mm. The structure was solved by the heavy-atom method and anisotropically refined for all non-hydrogen atoms except for the disordered atoms. For 3869 unique observed reflections [$I > 2\sigma(I)$] collected at T = 295 K ($6 < 2\theta < 50°$), the current R is 0.053 (R_{2w} = 0.141). For details see the Supporting Information.