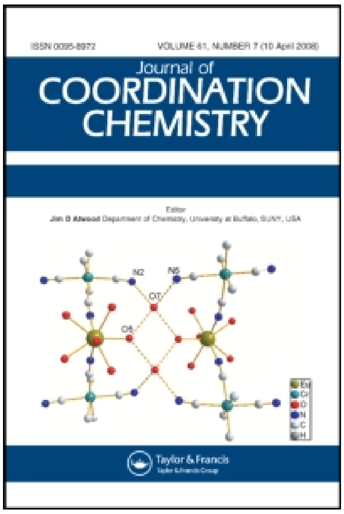

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Expanded Porphyrins: The Synthesis and Metal Binding Properties of Novel Tripyrrane-Containing Macrocycles

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EXPANDED PORPHYRINS: THE SYNTHESIS AND METAL BINDING PROPERTIES OF NOVEL TRIPYRRANE-CONTAINING MACROCYCLES

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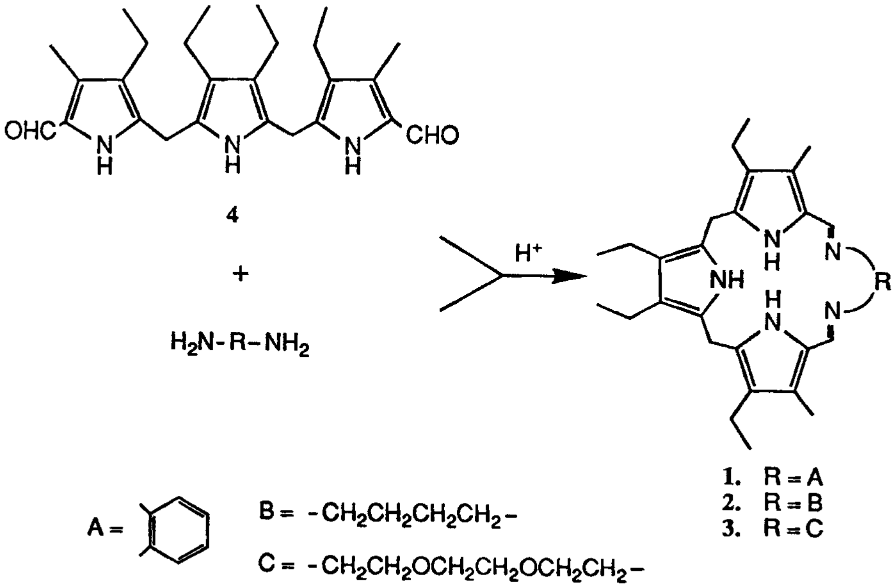
Abstract Novel tripyrrane macrocycles have been prepared by the Schiff base condensation of 2,5-bis-(3-ethyl-5-formyl-4-methyl-pyrrol-2-ylmethyl)-3,4-diethylpyrrole and simple diamines. The structurally characterized macrocycle **1** forms 1:1 complexes with both Rh(I) and Zn(II) cations in which the metal is coordinated only to the imine nitrogens. In the presence of Cd(II) and oxygen, however, compound **1** is oxidized to the aromatic pentadentate "expanded porphyrin" macrocycle **5**, into which the metal cation is fully complexed.

Keywords: Porphyrins, novel tripyrrane macrocycles, Schiff base condensation

Large polypyrrole macrocycles have been the subject of increasing attention in recent years. Most work with these systems has been concerned with exploring their physical, chemical, and structural properties.[1-5] Relatively little work has been devoted to exploring the metal binding behavior.[6-7] The coordination chemistry of pyrrole-containing nonporphyrin macrocycles, however, could prove intriguing: Unusual oxidation states, coordination geometries, or metal complexes might be stabilized in suitably designed systems. We present here the results of initial metal binding studies for our newly prepared tripyrrane-containing macrocycle **1**[8] and report the isolation of the "expanded porphyrin" **5** as its cadmium complex.

Recently, we developed a convenient synthesis of the tripyrrane-containing macrocycles, **1** and **2**[8] and have now extended this synthetic strategy to produce **3**.[9] Compounds **1-3** were prepared in up to 45% yield by the acid catalyzed Schiff base condensation of 2,5-bis-(3-ethyl-5-formyl-4-methyl-pyrrol-2-ylmethy)-3,4-diethylpyrrole (**4**)[8] with the appropriate diamine as shown in Scheme I. Somewhat higher yields have been obtained using an acid catalyzed, Pb^{2+} templated procedure.[8] It should be noted that compounds **1-3** are linked by saturated methylene bridges and hence display many of the properties expected for porphyrinogens.[10] They are, for instance, nearly colorless and are easily oxidized.



Scheme I

Depending on the choice of work up conditions, the macrocycles prepared by the above procedures are obtained as either the free-base or protonated forms. The latter are generally crystalline. This has allowed the X-ray structure of **1·HSCN** to be solved (Fig 1).[8] The nitrogen of the SCN^- counter anion is within hydrogen bonding distance of the various NH protons (three pyrroles and the protonated imine). A projection of the three dimensional structure onto the mean plane of the system gives an estimated center-to-nitrogen value of 2.5 Å for the nearly circular inner core. The cavity size of **1** thus appears to be larger than that of the free-base porphyrins for which corresponding distances of ca. 2.0 Å to 2.1 Å are observed.[11] Compound **1** is therefore expected to be an interesting system with which to explore the metal binding properties of pyrrole-containing, nonporphyrin macrocycles.

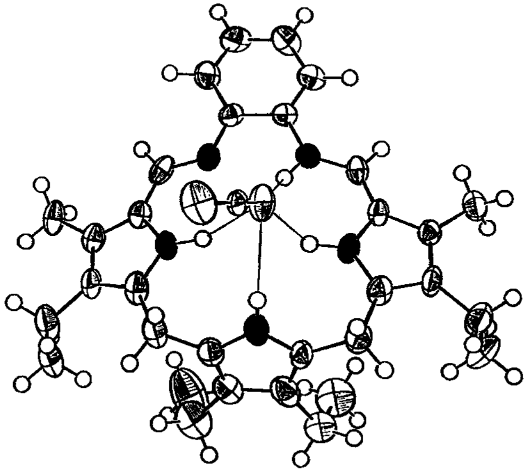


Figure 1 X-ray structure of **1·HSCN**

Treatment of the colorless macrocycle **1** with tetracarbonyl-μ-chlorodirhodium(I) in benzene followed by purification (recrystallization from dichloromethane-hexane) led to the isolation of a green microcrystalline material in 48% yield. On the basis of the available data,[9] this compound was characterized as a 1:1 Rh(I) complex **1·Rh(CO)$_2$Cl**. In making this assignment, the proton NMR spectrum was particularly diagnostic. All features for the Rh(I) complex are essentially identical to those of the starting ligand **1** except for those associated with the internal pyrrole NH protons. These are shifted upfield as compared to the free-base form of macrocycle **1**, with the degree of shift in these signals being greatest for the two imine substituted pyrroles (Table I). That these NH peaks are detected at all in the ^{1}H-NMR, however, is critical. It indicates that the Rh(I) fragment is bound in an η^2 fashion and suggests that the tripyrrane subunit does not participate in metal binding. An X-ray crystal structure determination is currently being attempted in an effort to support this analysis.

TABLE I Chemical shifts for pyrrole NH protons.

Compound	N-H Shifts in CDCl$_3$ (ppm)	
1	12.57	11.12
1·HSCN	11.53	9.79
1·Rh(CO)$_2$Cl	10.30	9.99
1·ZnCl$_2$	10.65	9.42
5·CdCl	-----	-----

When zinc chloride is reacted with compound **1**, a pink solid is obtained. The poor solubility of this material has hampered NMR and other analyses. As a result, a definitive structural assignment for this substance is not yet possible. CI mass spectrometry reveals a set of peaks which are consistent with a 1:1 zinc complex in which the zinc is bound in either a η^2 fashion to the two imines or in a η^4 fashion to an oxidized form of **1** in which one of the bridging methylenes has been converted to a methine. The observation of two peaks in the poorly resolved ^{1}H-NMR for the pyrrole NH protons (Table I), suggests that the first of these structures is correct. Importantly, the addition of pyridine causes the spectrum to revert to that of **1**. This suggests that the metal is no longer chelated and supports the structural assignment.

Markedly different behavior is observed when cadmium chloride is reacted with **1** under aerobic conditions. In this case, a strongly absorbing green material is isolated in 30% yield which displays properties consistent only with the structure shown in Fig. 2.[9] For instance, no pyrrole NH signals are observed in the ^{1}H-NMR and no signals are seen for the bridging methylene protons; rather, a new set of meso-like peaks for the bridging methine protons is observed at 11.30 ppm. Under the reaction conditions the macrocycle **1** is apparently oxidized to form the ***aromatic pentadentate*** ligand **5**, which is isolated in the form of its cadmium complex, **5·CdCl**. A more complete report of the fascinating properties of the novel "expanded porphyrin" macrocycle **5** will appear elsewhere.[12]

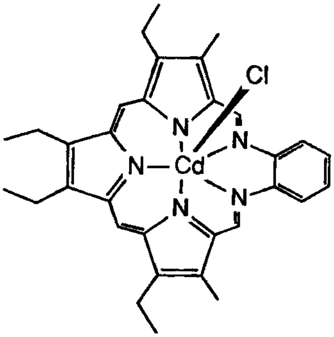


Figure 2 **5·CdCl**

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