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Serendipitous synthesis of trimetallic porphyrazine triads

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ABSTRACT

We report the synthesis and characterization of structurally unusual porphyrazine triads with three macrocycles bound to a central pyrazine core. These trimacrocyclic complexes were accidentally discovered during studies on the peripheral metallation of porphyrazinediamines. The crystal structure of the trizinc porphyrazine triad is described and the spectroscopic properties including electronic absorption spectra of this complex and the corresponding magnesium, free-base, and copper derivatives are reported.

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Porphyrinic arrays are of considerable importance as novel electronic and non-linear optical materials,[1–4] biomimetic models for photosynthesis, opto-electric devices, and light harvesting complexes.[5–19] Additionally, self-assemblies containing porphyrins with bipyridines, *trans*-$PdCl_2$ units, or ruthenium octahedra are of interest as molecular devices.[20–23] Binuclear metalloporphyrins and phthalocyanines linked by benzene ring fusion show intriguing redox and non-linear optical properties.[24–28] Previously, we have described the synthesis of a *trans*-benzo-fused hexaamino-porphyrazine dimer, which displayed a significant red-shift (100 nm) of the Q-band in the UV–vis spectrum.[29] We now report the synthesis and characterization of a new class of trimacrocyclic complexes with a central pyrazine core substituted with three diamino-porphyrazine units. These complexes were serendipitously discovered during our studies on porphyrazines as molecular scaffolds.[31–33]

Zinc porphyrazine **1a**[34] was deselenylated[35] and the resultant crude diamine **2a** was allowed to react with 2,6-pyridinedicarboxaldehyde and copper(II) chloride (Scheme 1). The expected fused porphyrazine–hexaazacrown–porphyrazine copper complex was not detected and instead a green dye (21%) with a molecular weight of 1928.4 [(M^+), MALDI-TOF] was isolated by chromatography. Alternative diporphyrazine multimetallic complexes were excluded on the basis of MS isotopic pattern analysis.[36]

An X-ray crystallographic structure determination revealed the structure to be trimer **3a** (Fig. 1). Although many bridged bis(porphyrinoids) are known, this new system has both porphyrazines that are in-plane and orthogonal relative to the central pyrazine. The Zn(1) and Zn(2) porphyrazine rings are essentially flat with the eight porphyrazine nitrogen atoms that are coplanar within ca. 0.03 and 0.05 Å, respectively, and are nearly coplanar with the central pyrazinium ring with the N_8 planes for the Zn(1) and Zn(2) porphyrazine rings oriented by ca. 2° and 3°, respectively, to the pyrazinium ring, which itself is coplanar to better than 0.01 Å. By contrast, the Zn(3) porphyrazine ring is both more distorted with the eight porphyrazine nitrogen atoms coplanar within only ca. 0.14 Å and oriented approximately orthogonally (ca. 76°) to the pyrazinium ring plane. The zinc center of one macrocycle was coordinated by an apical chloride ligand, whereas the other two possessed zinc centers axially coordinated by ethanol ligands. Bond lengths within the pyrazinium ring show the effect of the presence of the third porphyrazine ring on the bonding at the two nitrogen centers with the C–N distances at the three-coordinate nitrogen [1.357(3), 1.362(3) Å] being ca. 0.03 Å longer than those at its two-coordinate counterpart [1.328(3), 1.331(3) Å]. It is important to state that, although the solid-state structure indicates one chloride-coordinated zinc center, in solution, it is likely that this chloride is ionized and therefore the planar porphyrazine–pyrazine–porphyrazine dimeric unit should be symmetric.

We further examined the synthesis of porphyrazine **3a** from the crude diamine **2a** to probe the mechanism of its formation. Omission of both 2,6-pyridinedicarboxaldehyde and copper(II) chloride or reaction using excess (3 equiv) of copper(II) chloride failed to provide any complex **3a**. However, **3a** was obtained using sub-stoi-

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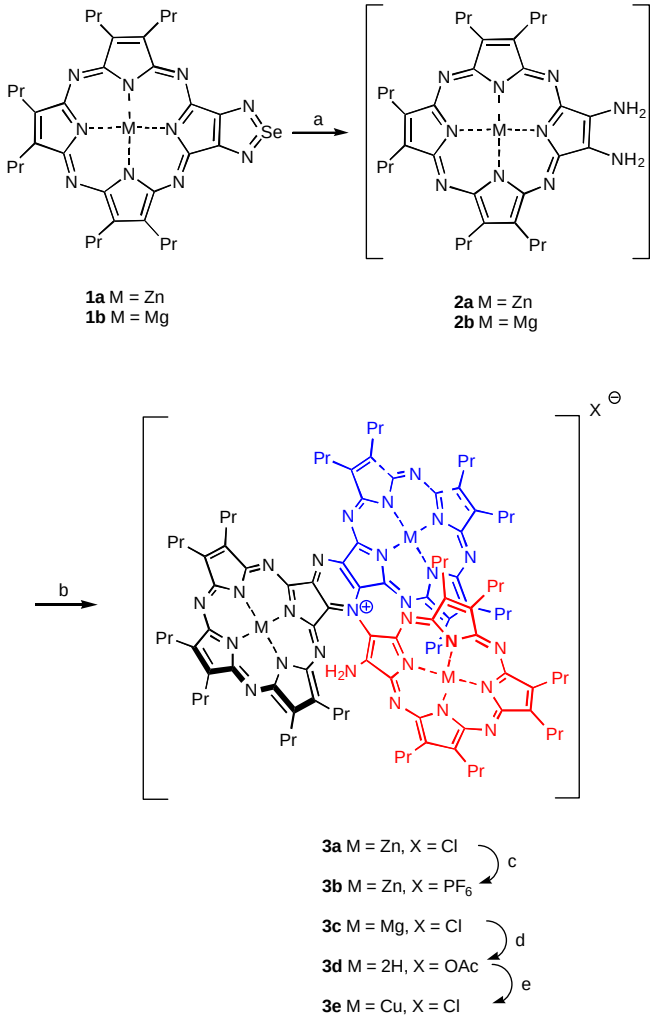


Scheme 1. Synthesis of triporphyrazines **3a** to **3e**. Reagents and conditions: (a) H_2S, pyridine, 25 °C; (b) 2,6-pyridinedicarboxaldehyde, $CuCl_2$, pyridine, 25 °C; (c) KPF_6, CH_2Cl_2, CH_3CN (1:1), 25 °C; (d) AcOH, CH_2Cl_2, 25 °C; (e) $CuCl_2$, PhCl, DMF, 100–115 °C.

chiometric quantities (0.3 equiv) of copper(II) chloride in the absence of 2,6-pyridinedicarboxaldehyde (21%) or using *iso*-amyl nitrite in toluene (7%). It is reasonable to suggest that complex **3a** is formed by dimerization of the porphyrazinediamine **2a** via tautomerism and a sequence of enamine-imine copper(II)-catalyzed condensation reactions (Scheme 2). It is possible that a copper(II)

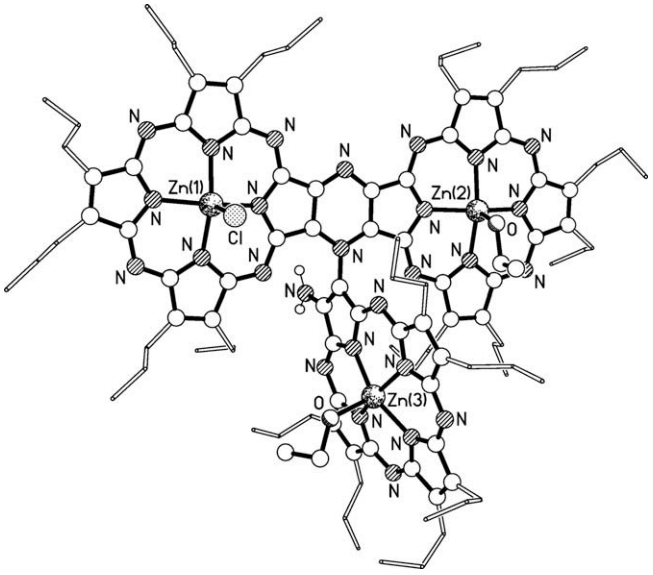
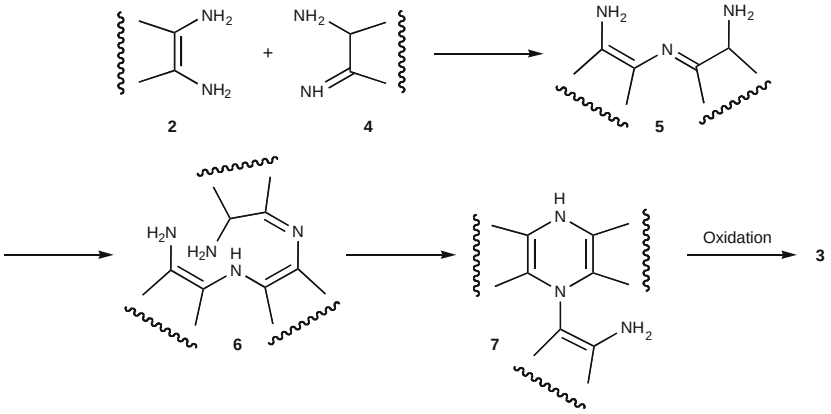


Figure 1. The molecular structure of the tri-zinc porphyrazine triad **3a**.

chloride-2,6-pyridinedicarboxaldehyde chelate is the active Lewis acid. Indeed, previous studies have determined such a complex to contain three-coordinate copper[37] and it is plausible that an analogous species is catalyzing the formation of the pyrazine ring system. Indeed, green crystals formed upon addition of copper(II) chloride to a solution of 2,6-pyridinedicarboxaldehyde in toluene and pyridine are consistent for a dipyridine complex, which was confirmed by unit cell determination (see Supplementary data).

Reaction of chloride **3a** with potassium hexafluorophosphate gave complex **3b**. Alternatively, condensation of magnesium porphyrazine **2b** with 2,6-pyridinedicarboxaldehyde and copper(II) chloride gave the magnesium complex **3c**. IR, MS, and UV–vis spectroscopy and comparison with the zinc complex **3a** were consistent with the structural assignments of complexes **3b** and **3c**. Additionally, demetallation of complex **3c** (74%) and remetallation of the resultant free-base **3d** with copper(II) chloride gave a triporphyrazine dicopper complex (37%), although the exact position of the two copper ions was not established. Further metallation of this crude product gave complex **3e** (65%).

With further material in hand we sought to investigate our hypothesis regarding ionization of the chloride-coordinated zinc center in solution. The ^1H NMR spectra of **3a**–**c** (see Supplementary data) however, were complex. We attribute this to the internal asymmetry of each unequivalent pz unit, coupled with several



Scheme 2. A possible mechanism for the synthesis of the complex **3**.

equilibrating complexes being present (chloride and solvent coordination). While the spectra were mostly measured in pyridine-d_5 solution in an attempt to minimize aggregation, this solvent possibly increased the problem of interconverting complexes. Indeed, despite anion exchange to the non-coordinating hexafluorophosphate counterion (**3a**–**b**), little improvement was visible in the spectra in pyridine-d_5. Switching to other solvents such as $CDCl_3$ did little to resolve the complex signals. A decrease in the complexity of the signals at 243 K, although accompanied by signal broadening, was observed in a variable temperature NMR study (see Supplementary data) of **3c** in pyridine-d_5. It is therefore highly likely that a number of coordinational equilibrium forms are competing at ambient temperature, complicating the NMR spectra of triads **3a**–**c**. Detailed NMR studies (see Supplementary data) at 243 K for triad **3c**, revealed differentiated signals for the propyl protons of the dimeric porphyrazine unit and the perpendicular unit, although the splitting of these signals was poorly resolved.

Another interesting feature of the NMR spectra was three broad resonances in the region of 0 to −1.5 ppm, which are atypical for metalloporphyrazines. Usually such signals are attributed to the ring protons in free-base porphyrazines.[30] After addition of D_2O to the triad **3c** in pyridine-d_5, the NMR signals in the region of 0 to −1.5 ppm were sharpened consistent with those resulting from water coordinating at the magnesium or zinc within the pz cavity. The variable temperature ^1H NMR spectra (see Supplementary data) further confirmed this, showing the disappearance of the signals in the region of 0 to −1.5 ppm at low temperature due to suppression of the rate of the coordinational equilibration.

The electronic absorption spectra of the macrocycles **3a**, **3b**, **3c**, and **3e** all exhibit a Soret (B) band between 342 and 350 nm and two broad Q-bands between 615 and 628 nm and 701 and 729 nm (see Supplementary data). There is also an additional peak between 573 and 588 nm, which has been assigned to n-π^* type transitions previously.[38] Although it is possible that the peaks around 620 nm and 720 nm are the result of a split Q-band due to the decrease in symmetry of the system,[39] it is more likely that they arise from two separate transitions; one from the fully conjugated, planar porphyrazine–pyrazine–porphyrazine unit and the other from the orthogonal, perpendicular porphyrazine ring. Previously, a dramatic red-shift of the Q-band has been observed for benzo-fused porphyrazine dimers.[29] Indeed, on comparison with a known copper-pyrazine porphyrazine,[40] the long-wavelength component of the Q-band for the metallated triads is red-shifted from 660 nm to around 720 nm. For the free-base triad **3d**, an extremely broad Q-band region is observed with maxima at 598 nm and 668 nm. Again, the broadening is most likely the result of overlapping transitions from the two orthogonal chromophores, coupled with the split Q-bands observed for the free-base macrocycles.[30] In addition, the zinc macrocycle **3a** also displays two fluorescence emissions at 430 nm and 628 nm (λ_{exc} 348 nm). A brief survey of the UV–vis spectra of complex **3b** in a variety of solvents revealed very little in the way of solvatochromic effects (see Supplementary data). The only significant change was found in pyridine, where the Q-band split disappeared and only one maximum at 621 nm was observed.

Preliminary static susceptibility measurements on complex **3e** show that exchange couplings among the three Cu(II) are weak, with exchange parameters, J_{ij}, of less than a few cm^{-1}. An X-band frozen-solution EPR spectrum (see Supplementary data) nonetheless shows a complicated pattern that extends over the field range, $0<\sim B_0<\sim 5500$ G, and is assigned to an overlap of signals from the spin-coupled manifolds with total spin, $S = 1/2, 1/2, 3/2$, which are formed by exchange among the three Cu^{II} ($S = 1/2$) ions.

In conclusion, copper(II)-catalyzed trimerization of porphyrazinediamines **2a** and **2b** gave the unusual novel porphyrazine triads **3a** and **3c**. The magnesium complex **3c** was easily converted into the corresponding free-base **3d** and copper **3e** derivatives. The electronic absorption spectra show complex Q-bands, which probably arise from overlapping transitions of the two orthogonal porphyrazine chromophores. We anticipate that these novel structures may show potential applications in electronic devices and molecular switches.

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Supplementary data

The experimental details, synthetic, spectroscopic data, and X-ray data for **3a**. The supplementary crystallographic data for **3a** (CCDC 288563) can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.06.120.

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