[6] For a previous experimental study of some labeled *n*-propanol/Fe^+ complexes, see: S. Karrass, T. Prüsse, K. Eller, H. Schwarz, *J. Am. Chem. Soc.* **1989**, *111*, 9018.

[7] The synthesis of the labeled propanols followed well-established preparative procedures. In brief, the [O-D]propanols were prepared by treatment of the corresponding sodium propanolates with D_2O. The [1,1-D_2]-, [2,2-D_3]-, [2,2,3,3,3-D_5]-, and [1,1,2,2,3,3,3-D_7]-*n*-propanols were made by reduction of the corresponding acids with $LiAlH_4$ or $LiAlD_4$, respectively. Catalytic reduction of unlabeled and [1-D_1]-prop-2-en-1-ol with deuterium afforded [2,3-D_2]- and [1,2,3-D_3]-*n*-propanols, respectively; the labeled allyl alcohol was made by reduction of acrolein with $LiAlD_4$. [3,3-D_2]- and [3,3,3-D_3]-*n*-propanols were prepared by Cu^I-catalyzed addition of the corresponding methyl Grignard reagents to ethylene oxide. Except the preparation of [1,1,1-D_3]isopropanol by addition of CD_3MgI to acetaldehyde, all labeled isopropanols were made by reduction of acetone, [D_6]acetone, 1,3-dichloroacetone, and [1,1,3,3-D_4]-1,3-dichloroacetone with $LiAlH_4$ or $LiAlD_4$, respectively.

[8] The experiments were performed with a modified VG ZAB/HF/AMD four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sectors) which has been described previously.[9] Briefly, propanol/Fe^+ complexes were generated by chemical ionization of a mixture of [$Fe(CO)_5$] and the corresponding propanol. The ions were accelerated to 8 keV kinetic energy and mass-selected by means of B(1)/E(1) at a resolution of $m/\Delta m \approx 3000$. Unimolecular fragmentations of metastable ions occurring in the field-free region preceding B(2) were recorded by scanning this sector. A total of 10 to 30 scans were averaged to improve the signal-to-noise-ratio, and the data are the averages of at least three independent measurements.

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[10] This criticism includes our own work, for example: a) S. Karrass, T. Prüsse, K. Eller, H. Schwarz, *J. Am. Chem. Soc.* **1989**, *111*, 9018; b) D. Schröder, W. Zummack, H. Schwarz, *J. Am. Chem. Soc.* **1994**, *116*, 5857; c) R. Wesendrup, C. A. Schalley, D. Schröder, H. Schwarz, *Organometallics* **1996**, *15*, 1435.

[11] The details of the algebraic formalisms used as well as a sensitivity analysis will be reported in a full article; they are available from Claudia.Trage@www.chem.tu-berlin.de.

[12] Note that secondary kinetic isotope effects need not be considered explicitly, because they are either inherently included in the analysis or cancel out in the H_2O/HDO ratios.

[13] Additional information, which will be presented in a full article, suggests that the C–O bond insertion **1**$\rightarrow$**2** is also quasi-irreversible for the metastable ions. This conclusion is further supported by the substantial barrier predicted for the insertion of Fe^+ into the C–O bond of methanol.[14]

[14] Y. Shiota, K. Yoshizawa, *J. Am. Chem. Soc.* **2000**, *122*, 12317, and references therein.

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[16] Review: J. M. Brown, *Angew. Chem.* **1987**, *99*, 169; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 190.

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A Novel Hemiporphyrazine Comprising Three Isoindolediimine and Three Thiadiazole Units**

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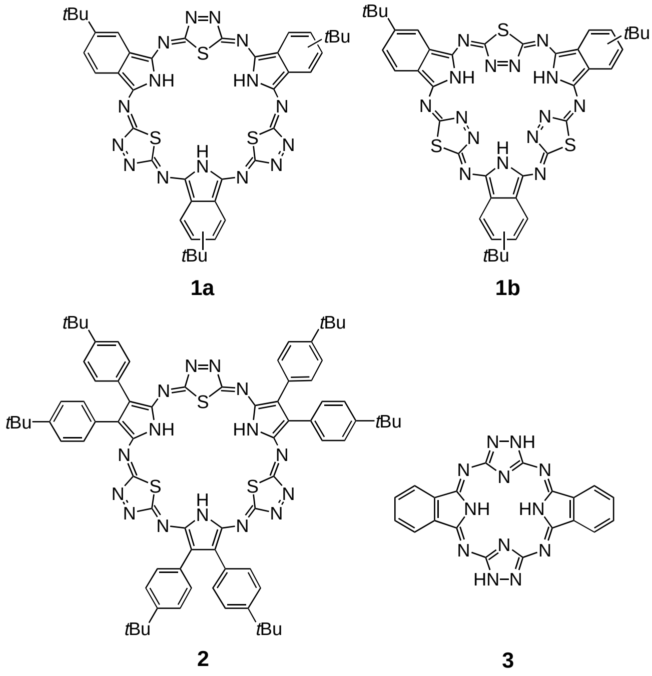
Large aromatic macrocyclic compounds such as porphyrins and phthalocyanines have attracted the interest of many chemists.[1, 2] In the phthalocyanine family, naphthalocyanines are important analogues and have been used in commercial fields such as read/write compact discs. Although not often used in practice, perhaps the next best known phthalocyanine analogues are hemiporphyrazines, which can be obtained by the condensation reaction of equimolar amounts of 1*H*-isoindole-1,3(2*H*)-diimines and 2,6-diaminopyridines.[3] Around a decade ago, a new member, synthesized from 1*H*-isoindole-1,3(2*H*)-diimines and 2,5-diamino-1,3,4-triazoles, was introduced into this family, and now such hemiporphyrazines are conventionally known as triazole hemiporphyrazine **3** (Scheme 1).[4] These compounds are cyclic tetramers



Scheme 1. Two possible structures **1a** and **1b** for the condensation products of 2,5-diamino-1,3,4-thiadiazole and 5-*tert*-butylisoindolediimine, and a possible structure for compound **2**. The triazole hemiporphyrazine structure is shown at the bottom right.

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consisting of two units each ("2+2"), and it has long been common knowledge that 2+2 type compounds are obtained from the above type of reaction. In contrast, here we report that the use of 2,5-diamino-1,3,4-thiadiazole (TDA) produces, as the exclusive cyclic products, the unusual cyclic hexamers **1a** and **1b**, each consisting of three isoindolediimine and three thiadiazole units (3+3) (Scheme 1). These may be termed thiadiazole superhemiporphyrazines, in keeping with the relationship between phthalocyanine and superphthalocyanine.

By analogy with the 2+2 synthesis of 1,2,4-triazole-containing hemiporphyrazines,[4] a mixture of equimolar amounts of TDA[5] and 5-*tert*-butyl-1*H*-isoindole-1,3(2*H*)-diimine was heated to reflux in butanol for 48 h to produce a deep red material, which was collected by filtration and washed with methanol. It was then extracted with hot chloroform, and the extract subjected to chromatography on a silica gel column, first with chloroform, then chloroform/methanol (8/2). The first, yellow-orange and the second, red fraction were collected and analyzed, together with an unresolved residue, by several spectroscopic methods. The second red fraction was an open-chain 2+2 oligomer containing terminal amino groups, while the residue consisted of open-chain *n*+*n* polymers. Surprisingly, the first fraction gave satisfactory data to substantiate the formation of 3+3 cyclic hexamers (26%; the final purification was carried out by gel-permeation chromatography (Bio-beads SX-2, Bio-rad)),[6] while no cyclic tetramer was detected. In a similar manner, the use of 3,4-bis(4-*tert*-butylphenyl)-3-pyrroline-2,5-diimine[7] in place of isoindolediimine produced a similar cyclic hexamer, namely, **2**.[6, 8] As a plausible explanation for the formation of the hexamer, we can consider the different covalent radii of sulfur (1.82 Å) and nitrogen (1.48 Å).[9] Sulfur atoms are larger than nitrogen atoms, and as a result, the estimated angle (calculation at the PM3 level[10]) between the two $C{-}N_{amino}$ bonds in TDA becomes 164°, as opposed to 140° in 2,5-diamino-1,3,4-triazole. Thus, if TDA is used as one of the two starting materials, it becomes more difficult to form a macrocycle from a smaller number of constituent units.

Figure 1 shows the electronic absorption and magnetic circular dichroism (MCD) spectra of **1**. In addition to two small absorption peaks at 499 and 471 nm, two intense main peaks appeared at 412 and 391 nm, and two bands of medium intensity were observed in the UV region. Compared with the spectrum of metal-free triazolehemiporphyrazine,[11] the two main peaks are shifted slightly to the red, while the intensity of the UV bands relative to that of the main bands is smaller, and the shape of the spectrum somewhat resembles those of [18]annulene derivatives.[12] The MCD spectrum gave many dispersion type curves (plausibly mostly Faraday *A* terms) corresponding to the absorption peaks. It is difficult to determine which of the two structures of **1** (i.e., **1a** and **1b** in Scheme 1) contributes more to the spectra, since semi-empirical calculations at the ZINDO/1[9] and AM1[13] levels produced both **1a** and **1b** as stable structures, although those using the PM3 Hamiltonian preferred the structure **1b**. In addition, ZINDO/S calculations at the ZINDO/1 level predicted similar spectra for structures **1a** and **1b**, which reproduced the experimental spectra.[8] Furthermore, the large Stokes shift of **1** (70 nm, 2465 cm^{-1}, not shown) indicates that **1** is a very flexible molecule. Accordingly, both **1a** and **1b** can be considered as structures of **1**.

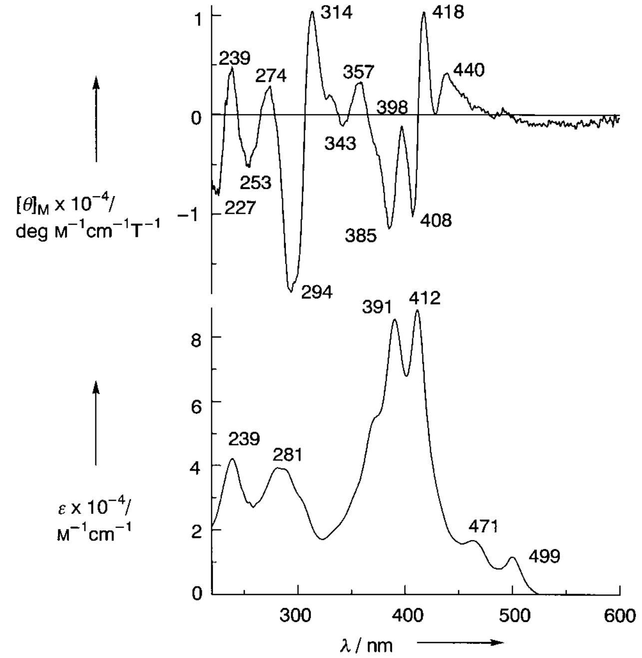

Figure 1. Electronic absorption (bottom) and MCD (top) spectra of **1** in THF.

Figure 2 shows the ESI-TOF mass and absorption spectra of the nickel complex of **1**, which was obtained by a nickel-insertion reaction in butanol.[6] The experimental distribution pattern of the mass spectrum agrees almost perfectly with that calculated for $[\mathbf{1}-3H+3Ni]$, and indicates that three nickel ions were incorporated into the skeleton of **1**. This is a phenomenon not seen in any porphyrinic compounds, including phthalocyanines and porphyrazines. The shape of the absorption spectrum differs greatly from that of **1** in Figure 1. The two very sharp, intense absorption peaks of **1** at 391 and 412 nm changed into two broad peaks of medium intensity, while the two medium-intensity peaks at 239 and 281 nm appear to have merged into a peak at 257 nm in $Ni_3\cdot\mathbf{1}$.

In conclusion, we have described the synthesis and some properties of unusual and relatively flexible 3+3 macrocycles obtained from condensation reactions between an isoindolediimine or 3,4-bis(4-*tert*-butylphenyl)-3-pyrroline-2,5-diimine and 2,5-diamino-1,3,4-thiadiazole as a new member of the phthalocyanine family. Superphthalocyanines have been prepared exclusively with uranium as a template,[14] and its size led to a superphthalocyanine structure composed of five isoindolediimine rings. Here, the wide angle between the two $C{-}N_{amino}$ bonds in diaminothiadiazole controls the size of the condensation product. Most interestingly, metal-insertion reactions led to the incorporation of three nickel or copper[8] atoms, and the resulting complexes exhibit totally different spectra from **1**. The details of the results of calculations, MCD and fluorescence spectroscopy, and electrochemistry will be reported in a full paper.

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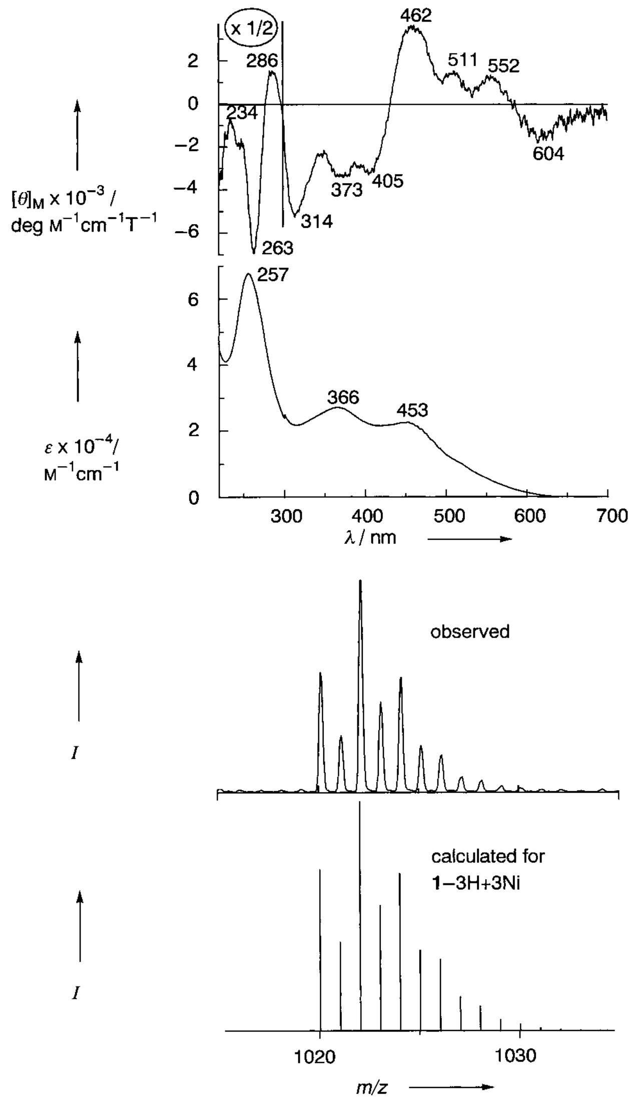

Figure 2. MCD (top) and electronic absorption (2nd from the top) spectra in THF and experimental (2nd from the bottom) and theoretical (bottom) ESI-MS spectra of $Ni_3 \cdot \mathbf{1}$.

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New Paradigms for Organic Catalysts: The First Organocatalytic Living Polymerization[**]

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In the last three decades, a significant effort has gone into the development of biodegradable polymers with the object of designing resorbable biomaterials and, more recently, for designing commodity thermoplastics from renewable resources. Aliphatic polyesters, particularly poly(lactide), combine biocompatibility and biodegradability with remarkable physical properties and possess the requisite thermal stability at the processing temperatures. Advances in organometallic chemistry in the design and synthesis of single-site metal catalysts for olefin,[1] ring opening metathesis,[2] and ring opening polymerization techniques[3] have enabled the preparation of well-defined functional polymeric materials with predictable molecular weights and narrow polydispersities. The ring-opening polymerization (ROP) of lactide has been accomplished with a variety of metal catalysts including aluminum, tin, zinc, and yttrium through a coordination–insertion mechanism.[4] Currently, considerable research is directed towards the preparation of organometallic compounds with tailored ligands that produced poly(lactides) with controlled stereochemistry and microstructure.[3, 5] However, there are few reports on the ROPs of lactides which do not use organometallic promoters.[6] Alternative strategies using only

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