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Contracted Porphyrinoids

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10-Heterocorroles: Ring-Contracted Porphyrinoids with Fine-Tuned Aromatic and Metal-Binding Properties**

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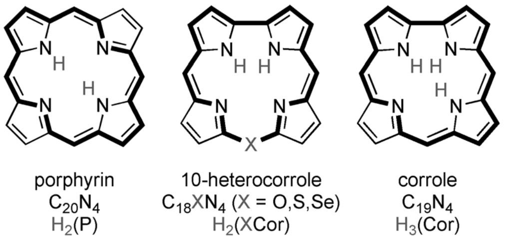
A current trend in porphyrinoid chemistry is the development of ring-contracted macrocycles and the study of their metal complexes.[1] Corroles clearly play a major role in this field, particularly with respect to species containing a porphyrin-like N_4 metal binding site.[2] However, many other non-contracted porphyrinoids, such as the porphyrin isomers and the azaporphyrins, are in fact also characterized by a smaller N_4 cavity.[3] Reports from coordination compounds of such macrocycles clearly prove the importance of the size of the metal binding site for spectacular results in terms of electronic structure,[4] small-molecule binding,[5] and catalysis.[6]

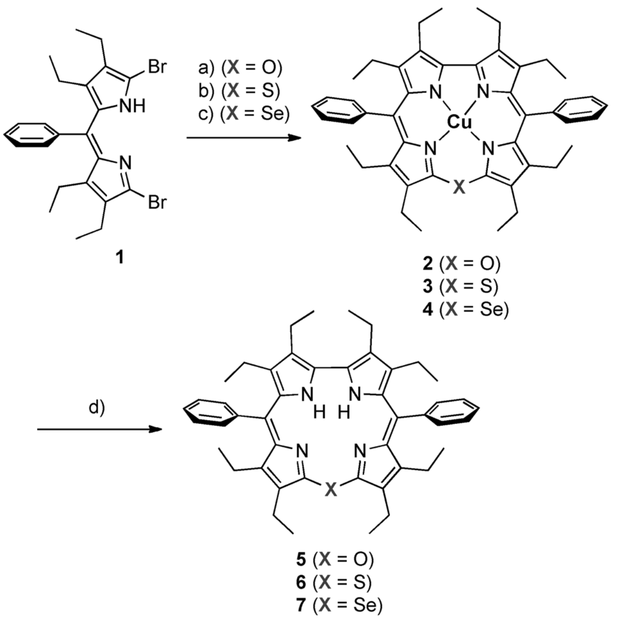
Conceptually, the class of 10-heterocorroles can be regarded as intermediate between porphyrins (dianionic ligand) and corroles (ring-contracted ligand; Scheme 1). 10-Heterocorroles with an oxygen, sulfur, or nitrogen atom in the backbone have been known for a long time,[7] and have recently gained renewed interest.[8] However, the literature procedures to synthesize these macrocycles are either long and cumbersome, or yield chelate complexes of Group 10 elements which cannot be demetalated without disintegration of the porphyrinoid ligand.



Scheme 1. 10-Heterocorroles $H_2(XCor)$ as hybrid structures from porphyrin and corrole frameworks (with the 18π main conjugation pathways shown in bold).

We are interested in free-base 10-heterocorroles with a Group 16 element (O, S, Se) in the backbone, as such ligands may allow a fine-tuning of the electronic properties of the transition metal through the size of the N_4 cavity. For this purpose, a general and efficient entry into this class of porphyrinoids (or better: corrinoids) was needed. We report here the successful syntheses and ligand properties of free-base 10-oxa-, 10-thia-, and 10-selenacorroles.

The known synthetic protocols leading to 10-heterocorroles are only of limited use for a general preparative entry into this class of porphyrinoids, as they either require a more than stoichiometric amount of supported palladium as a reagent, or a thioether precursor, the oxygen and selenium homologues of which are unavailable. To overcome these drawbacks we attempted to develop a metal-promoted two-step macrocyclization approach from α,ω-dibrominated dipyrrins such as **1** (Scheme 2). These precursors were first coupled to bromine-terminated linear tetrapyrrole copper(II) chelates by using a nBuLi/Cu^{II} protocol, and then cyclized in a second step to the desired copper(II) complexes such as **2**–**4**, by using different nucleophilic O, S, or Se transfer reagents, respectively. During the course of our investigations it



Scheme 2. Syntheses of 10-heterocorroles H_2L **5**–**7** via the copper(II) complexes **2**–**4**; a) $Cu(OAc)_2 \cdot H_2O$, wet DMF, 110°C, 15 min; b) $Cu(OAc)_2 \cdot H_2O$, DMF, 5 min, then $Na_2S \cdot 9H_2O$, 110°C, 15 min, then TFA, toluene, 110°C, 3 h; c) $Cu(OAc)_2 \cdot H_2O$, THF, 15 min, then KSeCN, 65°C, 12 h; d) $SnCl_2 \cdot 2H_2O$, HCl(aq), acetonitrile/dichloromethane, 15 min. TFA = trifluoroacetic acid.

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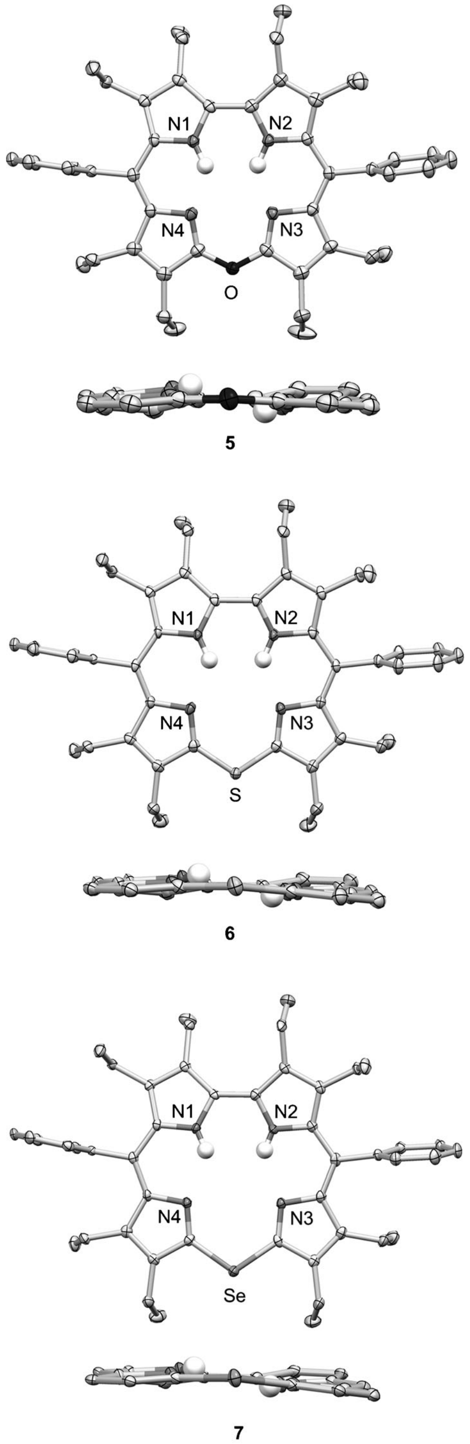
became apparent that the first step is not always necessary. In fact, heating the dipyrromethene **1** with copper(II) acetate in wet DMF for 15 minutes results in the formation of the copper–10-oxacorrole **2**, without the observation of any linear tetrapyrrole intermediate. After reductive demetalation with $SnCl_2 \cdot 2H_2O$/HCl in a mixture of acetonitrile and dichloromethane,[9] the desired 10-oxacorrole **5** was isolated as a pure compound in an overall yield of 39 % (Scheme 2). Treatment of **1** with copper acetate in DMF, followed by the addition of four equivalents of sodium sulfide, leads to the formation of several sulfur-containing macrocycles, as evident by mass spectrometry. Treatment of this mixture with additional copper acetate in a THF/methanol mixture, followed by trifluoroacetic acid in boiling toluene, and subsequent reductive demetalation results in the formation of the free-base 10-thiacorrole **6** as the exclusive product (16 % overall yield; Scheme 2). Potassium selenocyanate in THF was found to serve as the reagent of choice for the introduction of a selenium atom into the ligand backbone. The product mixture from the treatment of **1** with copper acetate and KSeCN can be purified by flash chromatography, and affords the pure copper chelate **4**. Chelate **4** is finally demetalated as above under reductive conditions to yield 42 % of the desired 10-selenacorrole **7**. All free-base compounds are obtained in analytical pure form after chromatography and recrystallization.

Mechanistically, the formation of the direct C–C bonds without any apparent reductive coupling appears particularly interesting. In the case of 10-thiacorrole, a thorough mechanistic and theoretic investigation of this process was recently published.[8d] According to these results, the reaction proceeds via the initial formation of a 5,15-dithiaporphyrin, from which the 10-thiacorrole is formed by sulfur extrusion. A similar reaction pathway also appears plausible for the formation of the 10-selenacorrole derivative **4**.

Crystallographic analyses of the 10-heterocorroles **5**–**7** have been undertaken, and the resulting molecular structures are presented in Figure 1. The measurements reveal basically planar macrocycles with small saddle-shaped distortions. This nonplanar conformation is accompanied by the binding of both inner hydrogen atoms at the bipyrrolic N-donor atoms, and attenuated by the sterically encumbered substitution pattern of the macrocycles. The C–C and C–N bonds within the five-membered rings clearly distinguish two pyrrolic and two pyrrolenine-like C_4N subunits through alternating bond lengths (see the Supporting Information). This feature is typically observed in tetrapyrrolic macrocycles, although, with the exception of corrphycene, a transoid arrangement of the NH moieties is predominant. The heteroatom X at the 10-position is bound almost symmetrically with C–X bond lengths of 1.360(2)/1.361(2) Å (**5**, X = O), 1.730(3)/1.739(3) Å (**6**, X = S), and 1.880(3)/1.887(3) Å (**7**, X = Se) in the ligand backbone, and the C-X-C angle at this position decreases from 125.0(1)° (**5**, X = O) to 112.8(1)° (**6**, X = S) to 110.3(1)° (**7**, X = Se), as expected. In combination, these changes result in a continuous increase in the size of the N_4 cavity from **5** to **6** to **7** (see below), and in a progressively trapezoid shape. Corroles also show a nonplanar macrocyclic structure because of the overcrowded center carrying three hydrogen atoms.[10]



5

6

7

Figure 1. Molecular structures of the free-base macrocycles **5**–**7** from single-crystal X-ray diffraction studies (top views, and front views without substituents). Thermal ellipsoids are set at 50 % probability. Carbon-bound hydrogen atoms are omitted for clarity.

The optical spectra of the 10-heterocorroles **5**–**7** show an unexpected feature. As depicted in Figure 2, the typical porphyrinoid spectrum, which is also found for corroles[11] and azacorroles,[7a] with a strong Soret band at about 400 nm and several weaker Q bands around 580 nm is only observed for the higher homologues **6** and **7**. For the 10-oxacorrole **5**,

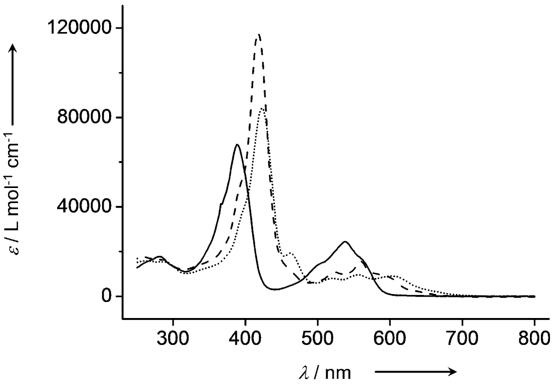


Figure 2. UV/Vis spectra (CH_2Cl_2) of the 10-heterocorroles **5** (X = O; ——), **6** (X = S; – – –), and **7** (X = Se; •••••).

however, the broadened bands and in particular the blue-shifted and relatively intense Q bands indicate diminished aromaticity and significant polyenic character, similar to linear tetrapyrrole metal chelates.[12] ^{1}H NMR spectroscopy is only of limited value for the characterization of **5**–**7** because of the high degree of substitution. For this reason the octaethyl-10-heterocorroles **5′**–**7′** were prepared by analogous reactions (see the Supporting Information), and the chemical shifts of the meso-situated as well as the N-bound protons were determined from these derivatives.

Table 1 presents the results from these measurements on **5′**–**7′**. The chemical shifts of both the NH protons and the meso protons are in agreement with the 10-thiacorrole **6′** being the compound with the highest degree of aromaticity, followed by the 10-selena derivative **7′** and the 10-oxacorrole **5′**. Interestingly, an analogous trend (S > Se > O) has long been known for the five-membered ring aromatic compounds furan, thiophene, and selenophene.[13] As the measured CH and NH resonances of **5′**–**7′** are also in good agreement with those predicted by GIAO NMR calculations[14] on the unsubstituted heterocorroles (Table 1; for details see the Supporting Information), we assume that the π conjugation of the macrocycle and thus the aromatic character increases in the order O ≪ Se < S. A similar conclusion has been drawn recently from NICS calculations on nickel complexes of meso-phenyl-10-oxacorrole and -thiacorrole, although the overall aromatic character appears to be more pronounced in the metal chelates.[1c,8d] As is apparent from recent publications, aromaticity in porphyrin and related nonbenzoid macrocycles is still an unsolved problem and a topic of current interest.[15] The fine-tuned aromatic behavior of the 10-heterocorroles described here may therefore be a welcome subject for future in-depth theoretical studies.

Table 1: Selected ^{1}H NMR chemical shifts δ (ppm) of the octaethyl derivatives **5′**–**7′** ($CDCl_3$, 200 MHz).[a]

Compound	H_2(OCor) **5′**	H_2(SCor) **6′**	H_2(SeCor) **7′**
meso-CH	8.28 (9.01)	8.91 (9.58)	8.55 (9.33)
NH	7.07 (6.80)	3.60 (4.19)	5.00 (5.08)

[a] Calculated values for unsubstitued 10-heterocorroles are shown in parentheses (GIAO, B3LYP/6-311+G(2d,p), $CHCl_3$).

The influence of the N_4 cavity size of the 10-heterocorroles **5**–**7** on the metal–ligand interaction was investigated for the copper complexes **2**–**4**. The optical spectra of the copper chelates suggest the same trend for the electronic properties of the ligands as for the free-base macrocycles, that is, the aromatic character increases in the order O ≪ Se < S (see the Supporting Information). Q-band EPR spectra of the three complexes (Figure 3), however, reveal an increasing rhombicity and the development of the A_{Cu} hyperfine interaction of the z component of the $\boldsymbol{g}$ tensor from 242 G (**2**, X = O) over 228 G (**3**, X = S) to 221 G (**4**, X = Se). These data clearly follow the order of the cavity size. Apparently, the metal properties are governed largely by the steric properties of the macrocycle cavity, and not (or to a much lesser extent) by the electronic properties of the ligand.

The special nature of 10-heterocorroles as ligands for metal complexes is particularly evident from a comparison of the N_4 cavity sizes[17] [7.05 Å^2 (**5**, X = O), 7.57 Å^2 (**6**, X = S), and 7.77 Å^2 (**7**, X = Se)] with those of the well-established corrole and of the porphyrin isomers.[18] For comparison, the respective values found in a series of octaethyl derivatives of porphyrin and its isomers are 8.50 Å^2 [porphyrin(1.1.1.1)], 8.27 Å^2 [corrphycene(2.1.0.1)], 8.23 Å^2 [hemiporphycene-(2.1.1.0)], 7.64 Å^2 [porphycene(2.0.2.0)], and 7.41 Å^2 for an octaalkylcorrole.[10,19] Iron and manganese complexes of the smallest of these ligands, that is, of porphycene and corrole, have so far provided the most spectacular results, such as non-innocent behavior,[20] stabilization of uncommon electronic states,[21] strong O_2 binding and CO discrimination,[22] and efficient O-transfer catalysis.[23] We expect the 10-heterocor-

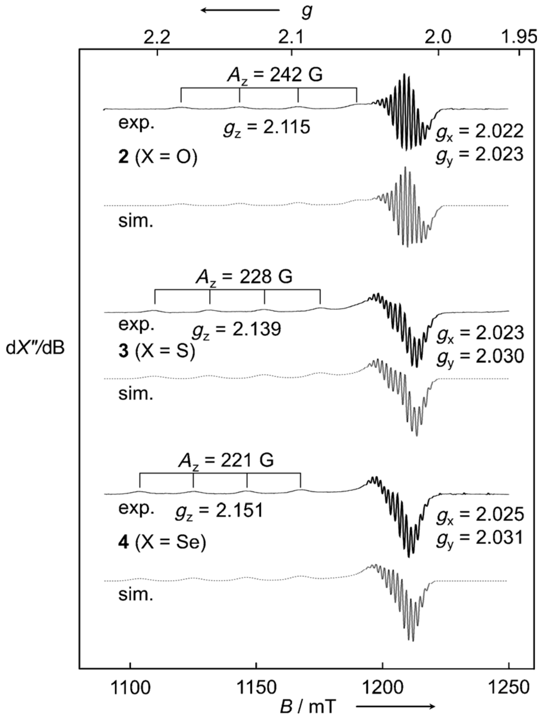


Figure 3. Q-band EPR spectra of copper–10-heterocorroles **2**–**4** in frozen toluene at 100 K (34.22 GHz, 80 mW/19 dB, modulation frequency: 100 kHz, modulation amplitude: 0.4 mT; ——) and simulated spectra (program hyperfinespectrum,[16] •••••).

roles with their even smaller cavities to provide an equally interesting and functional coordination chemistry, and we are now actively exploring this.

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