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New Porphyrinoids: Vanadyl(IV) Complexes of *meso*-Aryl-Substituted Corrphycene and 10-Oxocorrole Ligands

Martin Bröring,* Christian Hell, Frédérique Brégier, Olaf Burghaus, and Esther Cónsul Tejero

*Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerweinstrasse,
35043 Marburg, Germany*

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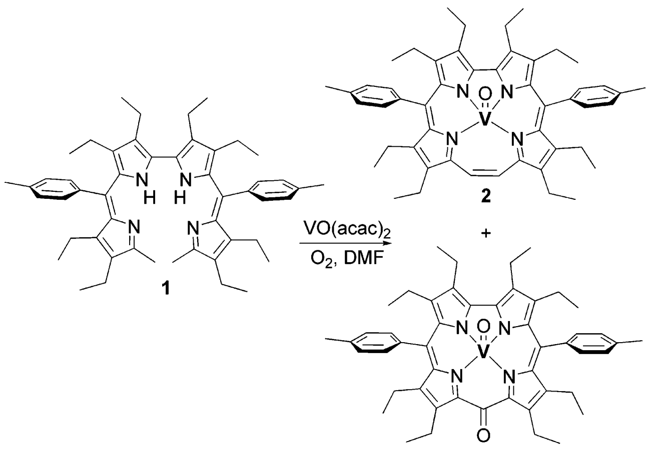
Rare vanadyl corrphycene and vanadyl 10-oxocorrole complexes were obtained via an oxidative macrocyclization process by the treatment of 6,6′-di-*p*-tolyl-2,2′-bidipyrrin with $VO(acac)_2$ in a hot dioxygen atmosphere. The geometric and electronic structures of the new porpyhrinoids were determined and showed the dependency of the spectral pattern from the aromaticity of the macrocyclic ligand.

The template synthesis of tetrapyrrolic macrocycles is an important concept in porphyrinoid chemistry.[1] Many porphyrins, chlorins, and related systems hardly available by any other means have been prepared by this method. Besides the parent biomacrocycles themselves, several important artificial porphyrinoids have also been reported to be formed from suitable open-chain precursors by a template approach.[2] As we have shown in the recent past, manganese and copper chelates of α,ω-dimethyl-2,2′-bidipyrrins like **1** (Scheme 1)[3] can act as such precursors, resulting in the formation of manganese corroles,[4] copper corroles, and copper 10-oxacorroles.[5] Screening further first-row transition-metal compounds for their ability to macrocyclize 2,2′-bidipyrrins, we have now found that only the vanadyl(IV) ion yields substantial amounts of macrocyclic products. We report here about the preparation, crystallographic characterization, and electronic structures of the products, namely, vanadyl(IV) corrphycene [(corrph)VO, **2**][6,7] and vanadyl(IV) 10-oxocorrole [(ocor)VO, **3**].[8]

Scheme 1. Formation of *meso*-Aryl-Substituted Vanadyl Corrphycene **2** and Vanadyl 10-Oxocorrole **3** from 2,2′-Bidipyrrin **1**



When a solution of di-*p*-tolyl-2,2′-bidipyrrin (**1**) in dry *N*,*N*-dimethylformamide is heated in the presence of excess $VO(acac)_2$, a ligand-exchange reaction and the partial formation of a vanadyl 2,2′-bidipyrrin complex occurs slowly, as indicated by in situ UV/vis spectra. The reaction does not go to completion, and the product is too labile to be isolated by chromatographical methods. Treatment of the hot solution with molecular dioxygen, however, results in a gradual color change from blueish-green to dark green over a period of 2

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* To whom correspondence should be addressed. E-mail: martin.broering@chemie.uni-marburg.de.

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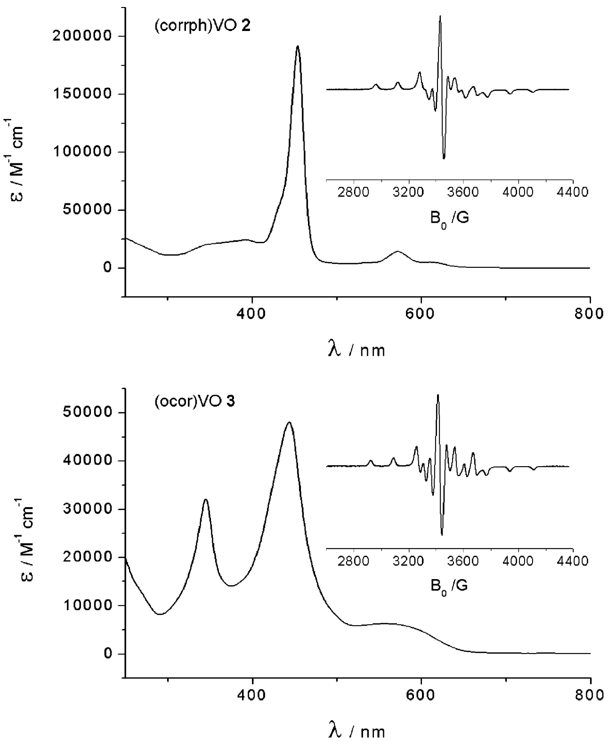

Figure 1. Comparison of UV/vis (CH_2Cl_2) and EPR spectra (CH_2Cl_2, 130 K; inset) of **2** (top) and **3** (bottom).

h. After an extractive workup, two new compounds, **2** and **3**, can be isolated from the reaction mixture by column chromatography. The novel corrphycene derivative **2** elutes first and is obtained in 12% yield after recrystallization, and the 10-oxocorrole chelate **3** forms in 2.4% yield. The assignments of the structures of **2** and **3** were concluded from combustion analyses and mass spectra.[9]

The electronic structures of **2** and **3** were examined by electron paramagnetic resonance (EPR) and UV/vis spectroscopy (Figure 1). X-band EPR spectra were taken in frozen CH_2Cl_2 at 130 K and confirmed the presence of a V^{IV} d^1 ion in both compounds. The values for **g** and **A** tensor components were obtained from a fitting routine to $g_1 = 1.9610$, $g_2 = 1.9820$, $g_3 = 1.9830$, $A_1 = 449$ MHz, $A_2 = 156$ MHz, and $A_3 = 126$ MHz for the corrphycene complex **2** and $g_1 = 1.9690$, $g_2 = 1.9865$, $g_3 = 1.9867$, $A_1 = 486$ MHz, $A_2 = 157$ MHz, and $A_3 = 157$ MHz for the 10-oxocorrole complex **3**. The spectra are only gradually distinct and prove to have very similar electronic structures for the VO $d_{xy}{}^1$ units in **2** and **3** despite the obvious differences in the size of the N,N,N,N coordination cavity. UV/vis spectra, on the other hand, reflect the electronic structure of the tetrapyrrolic ligand and are very different for **2** and **3**, as expected for an aromatic vs a nonaromatic compound.

2 and **3** could be obtained as blue and green blocks, respectively, by crystallization from dichloromethane/*n*-hexane mixtures and were investigated by single-crystal X-ray diffraction. Both species crystallize in the triclinic system, space group $P\bar{1}$, with $Z = 2$. **2** contains one molecule of dichloromethane per formula unit. Figures 2 and 3 show the molecular structures and give structural details.

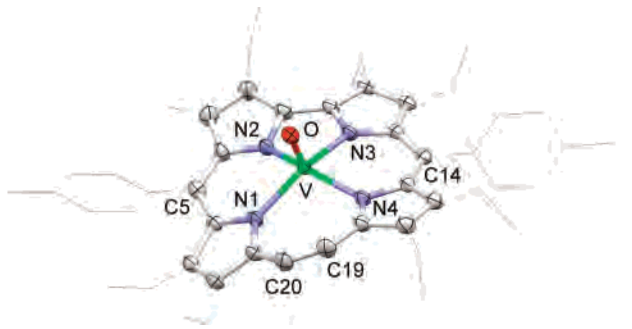

Figure 2. Molecular structure of **2** (ellipsoids are set at 50% probability; peripheral substituents are set as wire frame; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): V−N1 2.099(2), V−N2 2.039(3), V−N3 2.052(2), V−N4 2.100(2), V−O 1.587(2), C19−C20 1.370(5); N1−V−N2 83.09(10), N1−V−N3 146.81(10), N1−V−N4 103.52(10), N1−V−O 102.25(11), N2−V−N3 75.80(10), N2−V−N4 149.90(10), N2−V−O 106.02(11), N3−V−N4 83.92(10), N3−V−O 107.98(10), N4−V−O 101.23(11).

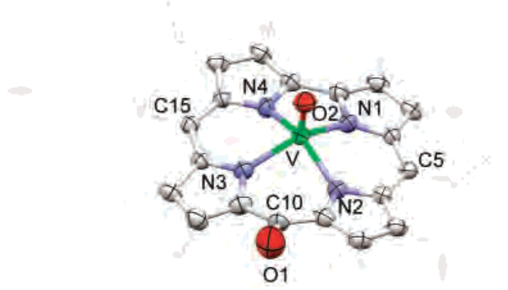

Figure 3. Molecular structure of **3** (ellipsoids are set at 50% probability; peripheral substituents are set as wire frame; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): V−N1 2.007(3), V−N2 2.013(3), V−N3 2.018(3), V−N4 2.015(3), V−O2 1.585(3), C10−O1 1.294(5); N1−V−N2 84.50(11), N1−V−N3 141.59(13), N1−V−N4 76.74(12), N1−V−O2 110.12(14), N2−V−N3 90.43(11), N2−V−N4 140.62(13), N2−V−O2 107.59(14), N3−V−N4 83.70(11), N3−V−O2 107.71(13), N4−V−O2 111.30(13).

In both complexes, the V^{IV} ion is found in a slightly distorted square-pyramidal coordination (τ parameter for **2**, 0.02; that for **3**, 0.05)[10] and with almost identical VO bond lengths of 1.587 and 1.585 Å, respectively. Because of the smaller cavity of **3**, the VN bonds are about 6 pm shorter for the oxocorrole derivative than for the corrphycene derivative, which shows bond lengths similar to those reported for vanadyl porphyrins (2.012−2.236 Å).[11] The doming of the vanadium ion in **2** of 0.503 Å is also in the same range as that for the porphyrin complexes (0.49−0.54 Å), while this value is much higher for oxocorrole **3** (0.658 Å).

The macrocyclic ligands of **2** and **3** both display strongly nonplanar distortion modes that can best be described by a saddle distortion with an overlay of a doming distortion.

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Because of the size of the vanadium central metal, the doming is more predominant for the smaller oxocorrole **3**, while the saddle is the major conformation of the corrphycene **2**. In both cases, the steric congestion introduced by the *meso*-aryl substituents enlarges the saddle distortion of the organic tetrapyrrole ligand backbone, and as a consequence of the pronounced additional doming of the ligand in **3**, the plane of the carbonyl functionality is tilted away from the mean-square N_4 plane by as much as 18.64°. These conformational details deviate largely from those found in vanadyl porphyrins, which display a simple and almost symmetric doming distortion only.

In summary, we have found a new VO-induced macrocyclization reaction for tetrapyrroles and reported the preparation and the structural and spectroscopic investigation of two rare porphyrinoid complexes of vanadium. Besides the ubiquitous geoporphyrins,[12] only a very small number of vanadium complexes of non-natural porphyrinoids has been described in detail so far.[13] This is even more surprising because vanadyl porphyrins have recently invoked renewed interest as possible drugs for the treatment of diabetes and cancer.[14] The advent of new vanadyl porphyrinoids thus provides new potential for the development of metal-based drugs.

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Supporting Information Available: Detailed syntheses, characterization, and X-ray crystallographic details (CIF) of compounds **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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