gel with CH_2Cl_2/*n*-hexane (1/5) as eluent yielded a yellow band of **1** (85.6 mg, 50 %) and an orange band of **2** (20 mg, 11 %).

1: Elemental analysis calcd for $C_{24}H_{60}Cu_8O_{12}P_6Se_{13}$: C 12.75, H 2.67; found: C 12.77, H 2.42; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 78.5$ (^1J(Se,P) = 674 Hz); ^1H NMR ($CDCl_3$, 25 °C): $\delta = 1.34$ (t, ^3J(H,H) = 7 Hz, 36 H; CH_3), 4.13 (m, 24 H; CH_3); positive-ion FAB-MS (nitrobenzyl alcohol): *m*/*z*: 2261.4 [M^+].

2: Elemental analysis calcd for $C_{32}H_{80}Cu_{12}O_{16}P_{10}Se_{22}$: C 10.89, H 2.28; found: C 10.99, H 2.35; $^{31}P\{^1H\}$ NMR ($CDCl_3$, −60 °C): $\delta = 134.0$ (^1J(P,Se) = 173.0, 347.8 Hz), 65.7 (^1J(Se,P) = 573, 660 Hz), 69.6 (^1J(Se,P) = 660, 729 Hz), 82.8 (^1J(Se,P) = 608, 677 Hz), 83.2 (^1J(Se,P) = 624, 712 Hz); ^1H NMR ($CDCl_3$, 25 °C): $\delta = 1.33$ (t, ^3J(H, H) = 7 Hz; CH_3), 1.40 (t, ^3J(H, H) = 7 Hz; CH_3), 4.09 (m; CH_2), 4.20 (m; CH_2).

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A Superoxovanadium(V) Complex Linking the Peroxide and Dioxygen Chemistry of Vanadium[**]

Harald Kelm and Hans-Jörg Krüger[*]

Dedicated to Professor Ernst G. Jäger
on the occasion of his 65th birthday

Within the one-electron redox chemistry of dioxygen species, the superoxide anion links the chemistry of molecular oxygen and peroxide. While peroxovanadium complexes are well established, superoxovanadium complexes are quite rare and have only been observed transiently by ESR spectroscopic methods as short-lived species in the reaction of vanadyl(IV) ions with hydrogen peroxide or in the reaction of metavanadate with mixtures of Ce^{4+}/H_2O_2 or Fe^{2+}/H_2O_2, using rapid-mixing flow techniques in the cavity of the ESR

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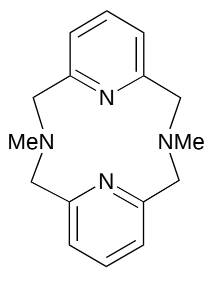
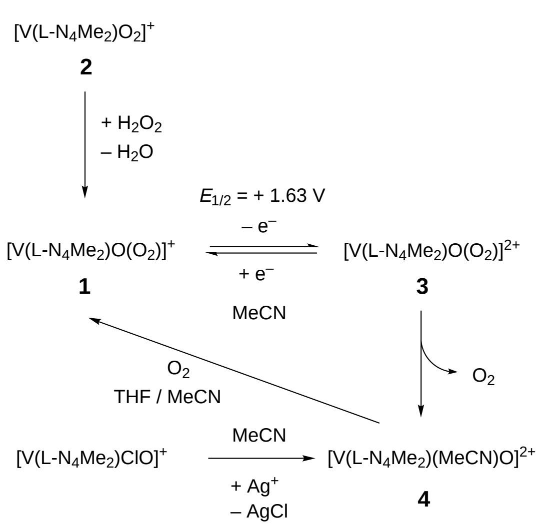
spectrometer.[1] The possible involvement of an oxosuperoxovanadium(v) intermediate has also been proposed, based solely on kinetic evidence, for the reaction of vanadyl(iv) or dioxovanadium(v) ions in hydrogen peroxide in the presence of various oxidizing reagents.[2] But in all these studies, the precise nature of the compounds involved in the reactions was not resolved. Here we describe for the first time the controlled preparation of an oxosuperoxovanadium(v) complex from a defined and well-characterized precursor complex by electrochemical means. Further, we provide evidence that this oxosuperoxovanadium(v) complex represents an important link between the dioxygen and peroxide chemistry of vanadium.



L–N_4Me_2

The starting point of our investigation is the red oxoperoxovanadium(v) complex $[V(L\text{-}N_4Me_2)O(O_2)]^+$ (**1**), which is obtained in 88 % yield from the reaction of the dioxovanadium(v) complex $[V(L\text{-}N_4Me_2)O_2]^+$ (**2**)[3] with 30 % aqueous hydrogen peroxide in acetonitrile (Scheme 1). X-ray structure analysis[4] reveals that the overall coordination environment of the vanadium ion in complex **1** (Figure 1) consists of the tetraazamacrocyclic ligand L-N_4Me_2, a terminal oxo, and a side-on-bound peroxo group. The O–O bond axis and the N_{amine}–N_{amine} axis are nearly colinear. The O–O bond length of 1.400 Å is consistent with the formulation of the O_2 unit as peroxo group and is at the lower range of the O–O distances commonly found in mononuclear oxoperoxovanadium(v) complexes (1.379–1.451 Å).[5–7] The coordination of the side-on-bound peroxo group and of the macrocycle L-N_4Me_2 is confirmed by ^1H NMR and IR spectroscopy. Thus, the ^1H NMR spectrum of the diamagnetic compound clearly demonstrates that, in solutions of complex **1**, the macrocyclic ligand remains coordinated through all its nitrogen donor atoms. Further, the presence of two AB and two AB_2 splitting patterns for the methylene and the pyridine ring protons in **1** are indicative of a C_s symmetry for the complex cation. On the basis of ^{18}O-isotope substitution experiments, the features at 953, 942, 580 and 569 cm^{-1} in the IR spectrum of **1** in acetonitrile are attributed to the V=O, O–O, and the two V–O_2 stretching vibrations, respectively. The visible region of the electronic absorption spectrum of **1** distinguishes itself from that of **2** only in the appearance of an absorption band at 443 nm that is responsible for the red color of the complex. The assignment of this band as a peroxo-to-vanadium ligand-to-metal charge transfer (LMCT) transition,[6, 8] as well as the previous assignments of the stretching vibrations, were confirmed by resonance Raman spectroscopy.



Scheme 1. Synthesis and reactions of **1**.

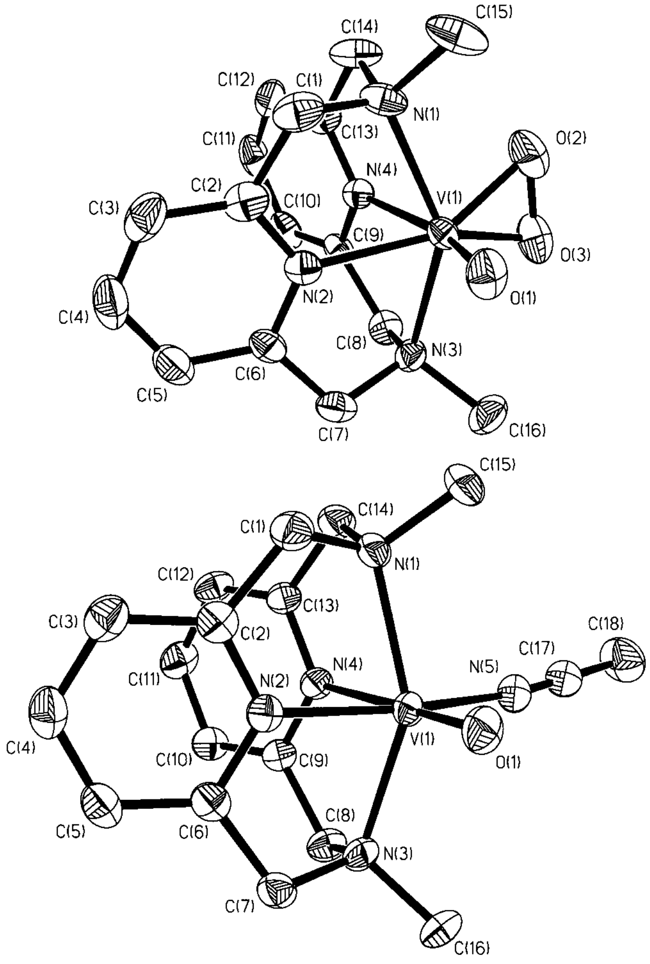


Figure 1. Perspective view of the complex cations $[V(L\text{-}N_4Me_2)O(O_2)]^+$ (**1**, top) and $[V(L\text{-}N_4Me_2)(MeCN)O]^{2+}$ (**4**, bottom) showing thermal ellipsoids at 50 % probability and the atom-numbering schemes. Selected bond lengths [Å] and angles [°]: **1**: V(1)-O(1) 1.613(2), V(1)-O(2) 1.851(3), V(1)-O(3) 1.847(3), V(1)-N(1) 2.204(4), V(1)-N(2) 2.155(3), V(1)-N(3) 2.216(3), V(1)-N(4) 2.159(3), O(2)-O(3) 1.400(5); O(2)-V(1)-O(3) 44.5(1), N(1)-V(1)-N(3) 143.9(1), N(2)-V(1)-N(4) 74.0(1); **4**: V(1)-O(1) 1.602(2), V(1)-N(1) 2.173(2), V(1)-N(2) 2.053(2), V(1)-N(3) 2.177(3), V(1)-N(4) 2.192(2), V(1)-N(5) 2.099(2); N(1)-V(1)-N(3) 148.11(7), N(2)-V(1)-N(4) 78.30(8).

Probably the most intriguing chemical property of **1** is revealed by its cyclic voltammogram. Thus, complex **1** is oxidized by one electron at 1.63 V versus SCE (1.20 V vs. Fc/Fc^+). At room temperature, the oxidative response approaches electrochemical quasi-reversibility at higher scan rates ($\Delta E = 97$ mV, $|i_{p,c}/i_{p,a}|$ 0.89 at 200 $mV\,s^{-1}$). Lowering the scan rates results in a decrease of the current ratio $|i_{p,c}/i_{p,a}|$ to about 0.50 at $10\,\mathrm{mV\,s^{-1}}$. At $-40\,^{\circ}\mathrm{C}$ the current ratio is improved, although the separation of the peak potentials ΔE is increased to 167 mV. Quantitative electrolysis of **1** at an applied potential of 1.80 V at $-40\,^{\circ}\mathrm{C}$ accounts for the transfer of $1.05\,e^-$ per molecule. Upon immediate re-reduction, approximately 79 % of the originally employed **1** is recovered. None of the starting material **1** is regained if the oxidation and the consecutive reduction are carried out at room temperature.

By performing the electrolysis at $-30\,^{\circ}\mathrm{C}$ in the cavity of an ESR spectrometer, the immediate oxidation product can be investigated. The solution ESR spectrum (Figure 2a) consists of a signal at $g_{\mathrm{iso}} = 2.0119$ that is split into eight lines with a hyperfine coupling constant $A^{\mathrm{V}}_{\mathrm{iso}}$ of $2.50 \times 10^{-4}\,\mathrm{cm^{-1}}$. The g value larger than 2.0 and the very small hyperfine coupling constant to the vanadium nucleus ($I = 7/2$) suggest the presence of a ligand radical bound to a vanadium ion. This result unambiguously proves that, during oxidation of **1**, the electron is removed from a molecular orbital on the peroxo ligand, resulting in the formation of the oxosuperoxovanadium(V) species (**3**) (Scheme 1). Somewhat similar ESR spectra were observed for the aforementioned short-lived species, using rapid-mixing flow techniques in the cavity of the ESR spectrometer.[1] However, in most of these investigations,[1a–c] a hydrogensuperoxide interacting with a vanadium(V) ion was proposed as the originator of the detected ESR spectrum. Considering that the oxidation of **1** is carried out in dry acetonitrile, the coordinated superoxide in **3** is judged to be deprotonated.

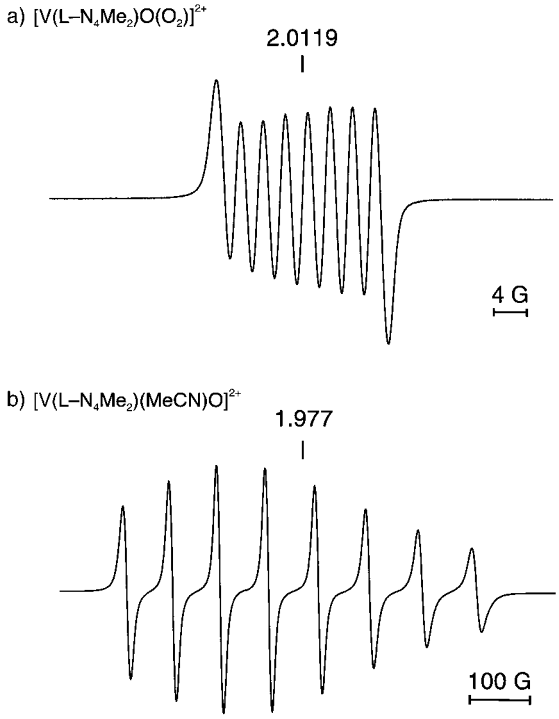


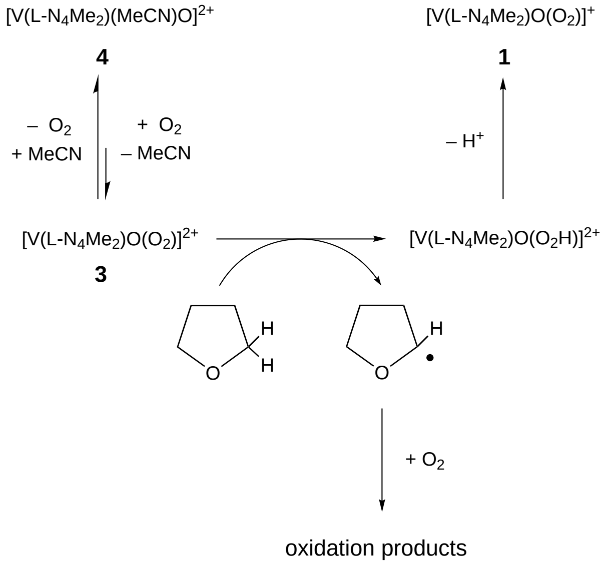
Figure 2. X-Band ESR spectra of a) a solution of $[\mathrm{V(L\text{-}N_4Me_2)O(O_2)}]^{2+}$ ions (**3**) electrochemically generated in MeCN (containing 0.2 M $\mathrm{NBu_4ClO_4}$ as electrolyte) at $-30\,^{\circ}\mathrm{C}$ in the ESR cavity and b) after raising the temperature to room temperature. (g_{iso} values are indicated).

No other ESR signal, except that attributed to complex **3**, is detected at $-30\,^{\circ}\mathrm{C}$. If a solution of **3** is exposed to temperatures higher than $-30\,^{\circ}\mathrm{C}$ for a very short time, then an ESR spectrum corresponding to the vanadyl(IV) complex $[\mathrm{V(L\text{-}N_4Me_2)(MeCN)O}](\mathrm{ClO_4})_2$ (**4**-$(\mathrm{ClO_4})_2$) can be observed. This complex was independently prepared from the vanadyl(IV) complex $[\mathrm{V(L\text{-}N_4Me_2)ClO}](\mathrm{ClO_4})$ by treatment with $\mathrm{AgClO_4 \cdot H_2O}$. The simulation of the solution spectrum of **4** yields an isotropic g value g_{iso} of 1.977 and a hyperfine coupling constant $A^{\mathrm{V}}_{\mathrm{iso}}$ of $92.8 \times 10^{-4}\,\mathrm{cm^{-1}}$ (Figure 2b). The ESR spectrum of the frozen solution (not shown) comprises an axial signal with g values $g_{\parallel} = 1.952$ and $g_{\perp} = 1.986$ and anisotropic hyperfine coupling constants $A^{\mathrm{V}}_{\parallel} = 161.3 \times 10^{-4}\,\mathrm{cm^{-1}}$ and $A^{\mathrm{V}}_{\perp} = 58.8 \times 10^{-4}\,\mathrm{cm^{-1}}$—all of which are typical for a vanadyl(IV) species.[3] The vanadyl(IV) species **4** is the direct decomposition product of the thermolabile superoxo complex **3**. The observation that the ESR spectrum of species **3** is not resumed upon cooling of the decomposition product, together with the coulometric results, indicates that the ESR spectrum of the vanadyl(IV) species does not correspond to a valence tautomeric (dioxygen)oxovanadium(IV) complex, but instead that a release of a dioxygen molecule occurs from the oxo(superoxo)vanadium(V) complex through an internal redox reaction yielding complex **4**. A similar decomposition reaction was proposed for the reaction of rather ill-defined vanadyl(IV) ions with hydrogen peroxide where by ESR spectroscopy an oxosuperoxovanadium(V) complex could be detected as the reaction intermediate and an evolution of molecular oxygen was observed.[1d] Further, it has been suggested that an oxosuperoxovanadium(V) intermediate reacts to give an uncoordinated dioxygen molecule and a vanadyl(IV) complex, solely on the basis of a kinetic study of the reaction of vanadyl(IV) or dioxovanadium(V) ions with hydrogen peroxide in the presence of various oxidizing reagents; also here there exists no spectroscopic characterization of the involved species.[2]

The question arises whether the oxygen release is reversible. Therefore the vanadyl(IV) complex **4**—a perspective view[4] of which is shown in Figure 1—was exposed to high pressures of molecular oxygen. No superoxo complex could be detected by ESR spectroscopy, indicating that the reversible equilibrium reaction (1) lies far on the side of the vanadyl(IV) complex. Therefore efforts were undertaken to trap the formed superoxovanadium(V) species by reducing it immediately to the stable peroxo complex. However, with conventional reducing reagents we were quite limited in raising the concentration of the reducing agents sufficiently in order to compete with the oxygen-release reaction; thus no formation of the peroxo complex was detected. In contrast, by

$$\underset{\mathbf{4}}{[\mathrm{V(L\text{-}N_4Me_2)(MeCN)O}]^{2+}} + \mathrm{O_2} \rightleftharpoons \underset{\mathbf{3}}{[\mathrm{V(L\text{-}N_4Me_2)O(O_2)}]^{2+}} + \mathrm{MeCN} \qquad (1)$$

utilizing an anhydrous acetonitrile–tetrahydrofuran mixture (v:v = 1:1) as solvent, a quantitative conversion of the vanadyl(IV) complex to the oxo(peroxo)vanadium(V) complex could be observed with molecular oxygen (yields of isolated product: 82%). Using $^{18}O_2$ results in the quantitative incorporation of ^{18}O atoms into the peroxo group.[9] We propose that the depicted equilibrium reaction (1) plays an essential role in this process because the very few oxosuperoxovanadium(V) complexes formed in this equilibrium abstract hydrogen atoms from tetrahydrofuran molecules, yielding oxohydroperoxovanadium(V) complexes that are subsequently deprotonated, thus rendering the oxoperoxovanadium(V) product (Scheme 2). Due to the presence of a large excess of tetrahydrofuran, the hydrogen atom abstraction reaction can compete with the oxygen release reaction. The tetrahydrofuryl radicals formed in this reaction react further with molecular oxygen in a radical chain reaction yielding three major oxidation products.[10] Recently, the first example of a direct formation of a vanadium(V) peroxide complex in the reaction of a vanadyl(IV) complex with molecular oxygen was described.[7, 11] Our results represent the second example of this rare type of reaction.



Scheme 2. Role of the equilibrium between **3** and **4** in the formation of the oxoperoxovanadium(V) product **1**.

In summary, we demonstrate for the first time a link between the dioxygen and the peroxide chemistry of vanadium through a superoxide complex for a well-defined system of mononuclear vanadium complexes. On the one hand, the vanadyl(IV) complex **4** can be converted by molecular oxygen in the presence of tetrahydrofuran to the corresponding oxoperoxovanadium(V) complex and, on the other hand, the oxoperoxovanadium(V) complex **1** can react to the vanadyl(IV) complex and molecular oxygen by a one-electron oxidation (Scheme 1). In both reactions an intermediary formed superoxo complex appears to be essential. In addition, we have shown that this relatively stable oxosuperoxovanadium(V) complex can be prepared by controlled synthetic means, thus allowing us the unique opportunity to investigate further the structural and electronic properties of such generally very unstable and therefore quite elusive species.[12]

Experimental Section

1-(BPh_4): A solution of $[V(L\text{-}N_4Me_2)O_2](BPh_4)$[3] (150 mg, 0.224 mmol) in acetonitrile (6 mL) was treated with 30% hydrogen peroxide solution (2 mL). The initially yellow solution was stirred for 4 h at 65 °C. After the addition of water (5 mL) to the resulting red solution at room temperature, the volume of the solution was reduced until precipitation of a red solid started to occur. A brief heating of the solution until the entire solid was again redissolved and subsequent storage of the solution at 0 °C for 1 d afforded analytically pure product (136 mg, 88%) as red crystalline material. Elemental analysis (%) calcd for $C_{40}H_{40}BN_4O_3V$: C 69.98, H 5.87, N 8.16; found: C 69.97, H 6.03, N 8.16; UV/Vis (acetonitrile): λ_{max} (ε_M) = 257 (9610), 263 (10500), 273 (sh, 3970), 443 nm (317); ^1H NMR (200 MHz, CD_3CN): $\delta = 3.69$ (s, 6H; CH_3), 4.37 ($J_{A,B} = 15.9$ Hz, 2H; CH_2), 4.68 ($J_{A,B} = 16.6$ Hz, 2H; CH_2), 4.86 ($J_{A,B} = 15.9$ Hz, 2H; CH_2), 5.23 ($J_{A,B} = 16.6$ Hz, 2H; CH_2), 6.75–7.1 (m, 14H; Ph-H and 3,5-py-H), 7.15–7.35 (m, 10H; Ph-H and 3,5-py-H), 7.56 (A-part, $J_{A,B2} = 7.88$ Hz, 1H; 4-py-H), 7.77 (A-part, $J_{A,B2} = 7.78$ Hz, 1H; 4-py-H); IR (KBr): $\tilde{\nu} = 1609$, 1581, 1479, 1457, 1445, 1427, 1382, 1029, 939, 881, 792, 735, 712, 704, 606, 566 cm^{-1} (strong bands only).

1-(ClO_4): A solution of $[V(L\text{-}N_4Me_2)(MeCN)O](ClO_4)_2$ (100 mg, 0.174 mmol) in absolute acetonitrile (5 mL) and absolute tetrahydrofuran (5 mL) was rapidly stirred for 3 d under an atmosphere of pure oxygen. The resulting red solution was evaporated to dryness and the residue was dissolved in acetonitrile (3 mL). Diffusion of diethyl ether into the solution afforded a red crystalline product (67 mg, 83%), which was filtered off, washed with diethyl ether, and dried in vacuo.

4-$(ClO_4)_2$: A solution of $[V(L\text{-}N_4Me_2)ClO](ClO_4)$[3] (107 mg, 0.228 mmol) and $AgClO_4 \cdot H_2O$ (52 mg, 0.230 mmol) in absolute ethanol (120 mL) was stirred for 3 d in the dark under an atmosphere of nitrogen. After the precipitated silver chloride was removed by filtration through celite, the residual solution was evaporated to dryness. The residue was dissolved in absolute acetonitrile. Diffusion of absolute diethyl ether into the solution rendered pure product as violet blocks, which were filtered off, washed with diethyl ether, and dried in vacuo (102 mg, 78%). Elemental analysis (%) calcd for $C_{18}H_{23}Cl_2N_5O_9V$: C 37.58, H 4.03, N 12.17; found: C 37.27, H 4.21, N 12.02; UV/Vis (acetonitrile): λ_{max} (ε_M) = 261 (7930), 266 (9480), 279 (sh, 1770), 541 (27), 652 nm (30); IR (KBr): $\tilde{\nu} = 2316$, 2288, 1612, 1582, 1483, 1454, 1382, 1169, 1094, 982, 880, 867, 809, 796, 624, 540 cm^{-1} (strong bands only).

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[4] Crystallographical data of **1**-(BPh_4): orthorhombic space group $Pna2_1$, $a = 23.111(24)$, $b = 15.807(7)$, $c = 9.275(3)$ Å, $V = 3388(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.346$ g cm^{-3}; $T = 153$ K; 5120 unique reflections (4223 reflections with $F_o > 4\sigma(F_o)$), $\mu(Mo_{K\alpha}) = 3.39$ cm^{-1}; 446 parameters (1 restraint); $R = 0.0427$ ($F_o > 4\sigma(F_o)$). Crystallographical data of **4**-$(ClO_4)_2$: monoclinic space group $P2_1/n$, $a = 8.545(2)$, $b = 17.267(15)$, $c = 16.757(7)$ Å, $\beta = 94.93(2)°$, $V = 2463(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.551$ g cm^{-3}; $T = 153$ K; 5675 unique reflections (4393 reflections with $F_o > 4\sigma(F_o)$), $\mu(Mo_{K\alpha}) = 6.77$ cm^{-1}; 323 parameters; $R = 0.0427$ ($F_o > 4\sigma(F_o)$). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-151355 (**1**-(BPh_4)) and CCDC-151356 (**4**-$(ClO_4)_2$). Copies of the data can be obtained free of charge on application to

CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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[9] In addition, the terminal oxide is enriched by approximately 50% with ^{18}O, presumably by an acid-catalyzed exchange with ^{18}O-enriched water produced in the oxidation of tetrahydrofuran.
[10] Of the three major oxidation products, two have been identified as 2-methyl-1,3-dioxane and γ-butyrolactone. The identity of the third product and the reaction mechanism of the oxidation reaction are under current investigation.
[11] Although not proposed, the reaction could proceed by a similar route via a superoxovanadium(V) intermediate. Here, however, in contrast to the reaction depicted in Scheme 2, the hydroxovanadyl(IV) species itself acts as reducing reagent, therefore rendering bis(oxo)vanadium(V) and oxoperoxovanadium(V) complexes in equimolar amounts.
[12] Preliminary ESR studies with partially ^{17}O-enriched superoxo complex have shown that at $-30\,^{\circ}C$ the superoxide unit is either symmetrically side-on-bound or that an end-on-bound superoxide undergoes a rapid rearrangement reaction, interchanging the bound and the unbound oxygen atoms faster than the ESR time scale.

Self-Assembly and Manipulation of Crown Ether Phthalocyanines at the Gel–Graphite Interface**

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The design, synthesis, and manipulation of supramolecular structures having well-defined geometries are great challenges. Such structures have possible applications in diverse fields such as materials science, molecular electronics, and sensor development.[1–3] The major source of inspiration for the generation of supramolecular architectures is the biological world.[4] On the other hand, new synthetic routes need to be developed that allow the constriction of molecular systems in such a way that the desired arrangements of components is obtained on the nanometer scale.[5, 6] Phthalocyanines (Pcs) constitute a widely investigated class of compounds which are interesting building blocks for the construction of supramolecular architectures.[7–11] Phthalocyanines have been self-assembled in solution and they can be deposited by using the Langmuir–Blodgett (LB) technique[9, 11] as well as by sublimation in ultra-high vacuum (UHV).[8, 12–14] The deposited assemblies have been visualized using scanning force microscopy (SFM)[11, 12] and scanning tunneling microscopy (STM).[13, 14]

Herein we report on the self-assembly and manipulation of monomeric Pcs from gels into layers at surfaces, studied by STM imaging. The Pcs (such as **1**) are functionalized with four benzocrown ether rings, which are each disubstituted with enantiomerically pure (*S*)-3,7-dimethyloctyl chains. The peculiar physicochemical properties of these chiral molecules arise from the fact that 1) they have an extended π-conjugated core which plays a key role in the charge-transfer properties of stacked Pcs; 2) they contain crown ethers which can host alkaline ions, and 3) they possess alkyl side chains which can induce a liquid crystalline behavior. In organic solvents **1** forms a gel in which helical fibers are present. The helicity of these fibers, which are composed of Pc stacks, can be tuned by the addition of alkaline ions, namely K^+.[15] The overall diameter of the fibers is equal to the diameter of the Pc discs with extended tails (6 nm), and the distance (d) between two Pc discs is 0.335 nm.

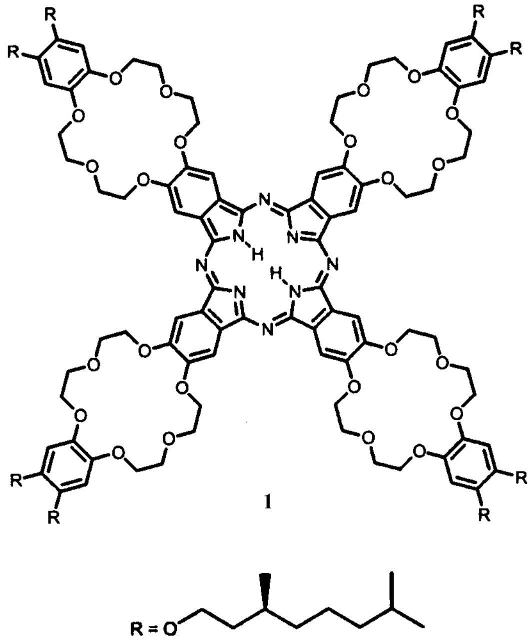

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Figure 1 shows sub-molecularly resolved STM images of the monomeric **1** moieties self-assembled at the interface between a gel and highly oriented pyrolitic graphite (HOPG). The molecular arrangement comprises two "face-on" phases (1 and 2 in Figure 1a), and one "edge-on" lamellar phase (3 and 4 in Figure 1a).

The "edge-on" lamellae, which are made up of π–π stacked Pcs (Figures 1b and 2) exhibit widths (w) of (4.7 ± 0.2) nm (Figure 1) and lengths up to hundreds of nanometers (image

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