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X-ray Structures of Mono- and Dinuclear Cu(II) Complexes of Novel Pyridine-Crown Ether Ligands

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Two novel pyridine-crown ether ligands, 1 and 2, have been synthesized by high-pressure additions of monoaza-15-crown-5 and diaza-18-crown-6, respectively, to 2-vinylpyridine. Treatment of ligand 1 with 1 equiv of Cu(ClO4)2·6H2O results in the formation of a mononuclear copper(II) complex 3, which crystallizes, as revealed by single-crystal X-ray diffraction, in the monoclinic space group P21/c (No. 14) with a = 8.4636(10) Å, b = 15.9125(5) Å, c = 19.373(4) Å, β = 110.341(16)°, V = 2446.3(1.0) Å3, and Z = 4. The structure refinement converged to R = 0.040 and Rw = 0.050. The copper(II) ion in 3 is surrounded by two crown ether oxygen atoms and two nitrogen atoms as well as by an oxygen atom of a methanol molecule which is bound in the crown ether ring. The geometry around the metal center is that of a distorted trigonal bipyramid. Addition of 1 equiv of Cu(ClO4)2·6H2O to ligand 2 yields a dinuclear Cu(II) complex (4), which coprecipitates with the bisprotonated ligand. The X-ray structure of 4·2HClO4 reveals a monoclinic space group C2/c (No. 15) with a = 26.4295(12) Å, b = 9.8275(4) Å, c = 26.8414(15) Å, β = 104.272(4)°, V = 6756.5(6) Å3, and Z = 4. The structure refinement converged to R = 0.078 and Rw = 0.071. Complex 4 consists of a dinuclear [Cu2(OH)2]2+ cation, with a perchlorate anion bound to it through a bifurcated hydrogen bond to the bridging hydroxo group. Each copper ion is 5-fold coordinated, viz. by two nitrogen and two oxygen atoms from the crown ether moiety and a bridging hydroxo group. Both copper ions have a trigonal bipyramidal environment. Ligand 2 is protonated on the amine functions present in the crown ether ring. Each proton forms a trifurcated H-bond with two crown ether oxygen atoms and a pyridine nitrogen. Complex formation in solution proceeds stepwise both for 3 and 4. At low Cu(II) to 1 ratios, two ligands molecules 1 coordinate to one Cu(II) ion. This intermediate reacts further at higher copper(II) concentrations to yield complex 3. Complex 4 is formed via a mononuclear copper(II) complex which is thought to have a structure similar to that of complex 3. Both 3 and 4 undergo irreversible oxidations in acetonitrile solution, at +0.04 and −0.36 V vs Fc/Fc+, respectively.

Introduction

As part of our program aimed at the design and synthesis of bimetallic oxidation catalysts, we recently reported on the reactivity of Cu(II)–crown ether pyrazole species.1 In alcoholic solution, these complexes are reduced to the corresponding Cu(I) complexes with concomitant oxidation of the alcohol to the aldehyde. In order to get further insight in the redox chemistry of this type of complexes, we decided to synthesise the crown ether–pyridine ligands 1 and 2 (Chart 1). These ligands differ in the number of nitrogen atoms present in the crown ether rings and are expected to give rise to different complexes with metal ions, e.g. copper ions. We report here on the details of the synthesis, crystal structures, and properties of the copper(II) complexes of the crown ether–pyridine ligands.

Experimental Section

Materials. All chemicals were obtained commercially. Solvents were dried and distilled prior to use, except methanol which was of HPLC-grade and used as received. Diethyl ether was distilled from sodium; dichloromethane and acetonitrile were distilled from calcium hydride. Dimethylformamide (DMF) was stored over 4 Å molecular sieves and distilled at reduced pressure. Acetonitrile used in the electrochemical measurements was deoxygenated by three repetitive freeze–pump–thaw cycles. 1,10-Diaza-4,7,13,16-tetraoxacyclooctadecane (2,2'-kryptofix) and 1-aza-4,7,10,13-tetraoxacyclododecane (monoaza-15-crown-5) were purchased from Merck. Cu(ClO4)2·6H2O was obtained from Janssen Chimica.

Preparation of the Ligands. 1-[2-(2-Pyridyl)ethyl]-1-aza-4,7,10,13-tetraoxacyclododecane (1). A solution of 1.057 g (4.8 mmol) monoaza-15-crown-5, 2.52 g (23.9 mmol) of 2-vinylpyridine, and 0.98 g (16.3 mmol) of acetic acid in 10 mL of methanol was transferred to a high-pressure Teflon capsule and kept at ambient temperature under a constant pressure of 15 kbar for 19 h. The color of the reaction mixture changed during this period from straw yellow to light red. The solvent was removed under reduced pressure, and the resulting purple-brown oil was dissolved in CH2Cl2 and washed (3 x) with a 15% aqueous NaOH solution. During this procedure, both layers turned brown. The organic layer was separated, dried (MgSO4), and concentrated in acetonitrile to yield a brown oil. This oil was subjected to column chromatography (silica gel, eluent CHCl3/MeOH/triethylamine, 89/10/1

Chart 1

sieves and distilled at reduced pressure. Acetonitrile used in the electrochemical measurements was deoxygenated by three repetitive freeze–pump–thaw cycles. 1,10-Diaza-4,7,13,16-tetraoxacyclododecane (2,2'-kryptofix) and 1-aza-4,7,10,13-tetraoxacyclododecane (monoaza-15-crown-5) were purchased from Merck. Cu(ClO4)2·6H2O was obtained from Janssen Chimica.

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Table 1. Crystallographic Data for 3

| a | 8.4636(10) Å | space group: P2_1/c (No. 14) |
| b | 15.912(5) Å |
| c | 19.373(4) Å | T = 150 K |
| \( \beta \) | 110.34(16) | \( \lambda = 0.71073 \) Å |
| V | 2446.3(1.0) Å³ |
| Z | 4 |
| \( R = 0.040^a \) |
| \( R_w = 0.050^a \) |

*s Definition of R factors: \( R = \sum |F_o| - |F_i| / \sum |F_o|; R_w = \left( \sum w\left| F_o \right|^2 - \sum \left| F_i \right|^2 \right) / \sum \left( w\left| F_o \right|^2 \right)^{1/2} \)

solutions were approximately \( 10^{-2} \) M in complex. The half-wave potential of a \( 10^{-3} \) M solution of ferrocene was measured under the same experimental conditions, yielding an \( E_{1/2} \) value of 0.050 V vs Fc//Fc.

**Crystal Structure Determination of 3.** A light-blue, tablet-shaped crystal (0.9 × 0.9 × 0.4 mm) was glued to the tip of a glass fiber and transferred into the cold nitrogen stream on an Enraf-Nonius CAD4-Turbo diffractometer rotating on anode. Accurate unit-cell parameters and an orientation matrix were determined by least-squares refinement of 25 well-centered reflections (SET4) in the range 11.6° \( < \theta < 14.1° \).

The unit-cell parameters were checked for the presence of higher lattice symmetry. * Crystal data and details on data collection and refinement are given in Table 1. Data were collected at 150 K in o2θ scan mode with scan angle \( \Delta \theta = 1.16 + 0.35 \tan \theta \). Intensity data of 6229 reflections were collected in the range 11.2° \( < \theta < 27.5° \), of which 5603 are independent. 4506 reflections with intensities above 2.5σ(0) level were used in the structure analysis. Data were corrected for Lp effects and for a linear zero of 2% for the three periodically measured reference reflections (222, 321, 345) during 14 h of X-ray exposure time. Standard deviations of the intensities as obtained by counting statistics were increased according to an analysis of the excess variance of the reference reflections: \( \sigma(0) = \sigma(0) + 0.0312^2 \). An empirical absorption/excitation correlation was applied (DEFABS, * correction range 0.880–1.143*). The structure was solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92,* Refinement on F was carried out by full-matrix least-squares techniques (SHELX76,*). Hydrogen atoms were included in the refinement on calculated positions (C–H = 0.98 Å) riding on their carrier atoms, except for the hydroxyl hydrogen of methanol, which was located on difference Fourier map and subsequently included in the refinement. The methyl group of methanol was refined as a rigid group. C(12) and C(13) are disordered over two positions. Weak bond constraints had to be introduced in order to derive a reasonable geometry. The minor components [site occupancy factor = 0.180(9)] of the disordered model were included in the refinement with an isotropic temperature factor; all other non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with one overall isotropic thermal parameter of 0.033(18)Å. Weights were introduced in the final refinement cycles. Convergence was reached at \( R = 0.040, R_w = 0.050, w = 1/\left| F_o \right|^2 \); and \( S = 1.38 \) for 341 parameters. A final difference Fourier map showed no residual density outside \(-0.53 + 0.95\) Å.

**Crystal Structure Determination of 4·2HClO₄.** A light-blue, rod-shaped crystal (0.15 × 0.23 × 0.73 mm) was sealed in a Lindemann-glass capillary and transferred to an Enraf-Nonius CAD4-F diffractometer. Final lattice parameters were determined by least-squares treatment of the setting angles (SET4) of 25 well-centered reflections in the range 9.0° \( < \theta < 14.2° \). Reduced-cell calculations did not indicate higher lattice symmetry. * Crystal data and details on data collection and refinement are presented in Table 2. Data were collected

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Table 2. Crystallographic Data for 2HClO₄ and 4

<table>
<thead>
<tr>
<th>chem formula:</th>
<th>[C₆H₅N₂O₃Cu]⁺</th>
<th>fw = 1588.62</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C₆H₅N₂O₃Cu][ClO₄]⁻</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| a = 26.4295(12) Å | space group: C2/c (No. 15) |
| b = 9.8275(4) Å | T = 22 °C |
| c = 26.8414(15) Å | λ = 0.710 73 Å |
| β = 104.272(4)° | Qₑ ≈ 1.562 g·cm⁻³ |
| V = 675.9(6) Å³ | μₑ₄ = 1.52 cm⁻¹ |
| Z = 4 | R = 0.078 |
|  | Rw = 0.071 |

* Definition of R factors: R = Σ|F₀| - |Fᵣ|/Σ|F₀|, Rw = (Σ|w(F₀)| - |Fᵣ|)/Σ|w(Fᵣ)|.11

at ambient temperature in o/2θ scan mode with scan angle Δθ = 0.72 + 0.35 tan θ°. From a total of 14 921 reflections in the range 0.78° < θ < 27.5° (7757 unique, R₀ = 0.066), 3370 satisfied the I > 2.5σ(I) criterion of observability. Data were corrected for Lp effects and for a linear decay of 11% of the three periodically measured reference reflections (224, 422, 422) during 180 h of X-ray exposure time. Standard deviations of the intensities as obtained by counting statistics were increased according to an analysis of the excess variance of the reference reflections: σ²(I) = σ²(I₀) + (0.03F)².4 An empirical absorption/extension correction was applied (DIFABS,9 correction range 0.670–1.138). The structure was solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92).6 Refinement on F was carried out by full-matrix least-squares techniques (SHELX76).7 Hydrogen atoms (including the amine hydrogen) were included in the refinement on calculated positions (C, N – H = 0.98 Å) riding on their carrier atoms, except for the hydroxyl hydrogen (H(36)), which was located on a difference Fourier map and subsequently included in the refinement. A bond length constraint (0.90(1) Å) was applied in order to prevent the atoms of the hydroxyl group from fusing. All non-hydrogen atoms were refined with anisotropic thermal parameters; the hydrogen atoms were refined with two overall isotropic thermal parameters with values of 0.166(14) and 0.052(5) Å² for the hydrogen atoms in the protonated ligand and the Cu(II) complex, respectively. The high thermal motion and the unusual anisotropy of the oxygen atoms of the perchlorate anion containing Cl(3) as well as of the carbon atoms C(20) and C(21) of the protonated ligand is indicative of some disorder. No satisfactory disorder models could be refined. Weights were introduced in the final refinement cycles. Convergence was reached at R = 0.078, Rₘ = 0.071, w = 1/σ²(F), and S = 5.88, for 437 parameters. A final difference Fourier map showed no residual density outside -0.78 and +0.71 e Å⁻³.

Neutral atom scattering factors were taken from Cromer and Mann,8 anomalous dispersion corrections from Cromer and Liberman.9 Geometrical calculations and illustrations were performed with PLATON.10 All calculations were performed on a DECstation 5000/125.

Results and Discussion

Synthesis. Ligands 1 and 2 were prepared by acid-catalyzed additions of monoaza-15-crown-5 and diaza-18-crown-6, respectively, to 2-vinylpyridine under high pressure (15 kbar). This type of reaction has been reported to take place at atmospheric pressure in a refluxing solvent.11,12 However, with 2-vinylpyridine and aza crown ethers, we hardly observed any product formation under such conditions. Most likely, this negative result is due to the electron-withdrawing effect of the oxygen atoms in the crown ether rings. Control reactions using dibutylamine instead of the aza crown ether as the starting material did lead to significant amounts of product at atmospheric pressure. Exposure of the free ligands 1 and 2 to temperatures exceeding 40 °C gave rise to a retro reaction, viz. the elimination of 2-vinylpyridine.

Addition of CuClO₄·2H₂O to a solution of the ligands 1 and 2 in methanol yielded the monocopper(II) complex 3 and the dicopper(II) complex 4, respectively. These were isolated as blue solids. It was observed that during the formation of 4 also the di-HClO₄ salt of 2 was formed. Crystals suitable for analysis by single-crystal X-ray diffraction were grown by allowing hexane to diffuse into methanolic solutions of the isolated solids. We have no indication that complexes 3 and 4 are thermally unstable under conditions where the free ligands 1 and 2 gave elimination of 2-vinylpyridine.

X-ray Structure of Methanolate-[1-[2-(2-pyridyl)ethyl]-aza-4,7,10,13-tetraoxacyclopentadecane]copper(II) Diperchlorate (3). The structure of the dication of 3 is shown in Figure 1. Positional parameters of the Cu complex are listed in Table 3; coordinates of the ClO₄⁻ counterions are given in the supplementary material. Selected bond distances and angles
are given in Table 4. Complex 3 contains a Cu(NO₃)₂ core which has a distorted trigonal bipyramidal geometry. The distortion from the idealized trigonal bipyramid (TPB) toward a square pyramid (SP) was calculated to be 49.4.¹ The ligand provides four donor atoms to the metal. The fifth coordination position is occupied by a methanol molecule. Interestingly, this methanol molecule forms a bifurcated hydrogen bond with the oxygen atoms O(2) and O(3) of the crown ether ring, which do not participate in the coordination of the copper ion. The basal plane of the Cu(II) coordination sphere in 3 is formed by the pyridine nitrogen N(1) at 1.999(3) Å and the oxygen atoms O(1) and O(4) of the crown ether ring at 2.049(2) and 2.268(3) Å, respectively. The apical positions are occupied by amine nitrogen N(2) at 1.992(2) Å, and oxygen atom O(5) of the methanol molecule at 1.962(2) Å.

X-ray Structure of [(Cu[N(H₂O)]₅][ClO₄]₂]*

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex 3

<table>
<thead>
<tr>
<th>Atom</th>
<th>Cu–O(5)</th>
<th>Cu–O(1)</th>
<th>Cu–N(1)</th>
<th>Cu–N(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1.962(2)</td>
<td>2.049(2)</td>
<td>1.999(3)</td>
<td>2.268(3)</td>
</tr>
<tr>
<td>O(5)</td>
<td>106.52(10)</td>
<td>97.85(10)</td>
<td>91.03(9)</td>
<td>80.11(9)</td>
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<tr>
<td>N(1)</td>
<td>155.13(11)</td>
<td>93.88(10)</td>
<td>82.31(9)</td>
<td>166.00(11)</td>
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<tr>
<td>N(2)</td>
<td>90.09(10)</td>
<td>97.32(10)</td>
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<td></td>
</tr>
</tbody>
</table>

Table 5. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters of the non-Hydrogen Atoms for the Bisprotonated Ligand 2

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq.) Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(4)</td>
<td>0.2472(4)</td>
<td>0.3515(14)</td>
<td>0.0942(4)</td>
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<tr>
<td>O(5)</td>
<td>0.2373(3)</td>
<td>0.4764(8)</td>
<td>0.0044(5)</td>
<td>0.098(4)</td>
</tr>
<tr>
<td>N(3)</td>
<td>0.3585(3)</td>
<td>0.2120(10)</td>
<td>0.0702(3)</td>
<td>0.073(5)</td>
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<tr>
<td>N(4)</td>
<td>0.2851(4)</td>
<td>0.0902(14)</td>
<td>0.1104(5)</td>
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<tr>
<td>C(14)</td>
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<td>0.083(5)</td>
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<tr>
<td>C(15)</td>
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<tr>
<td>C(16)</td>
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<td>0.1926(17)</td>
<td>0.0384(6)</td>
<td>0.105(7)</td>
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<td>C(17)</td>
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<tr>
<td>C(18)</td>
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<td>0.0863(5)</td>
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<tr>
<td>C(19)</td>
<td>0.3761(6)</td>
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<td>C(20)</td>
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<td>C(21)</td>
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<td>C(22)</td>
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<td>C(23)</td>
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<tr>
<td>C(25)</td>
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<td>0.5661(15)</td>
<td>0.0389(8)</td>
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<tr>
<td>C(26)</td>
<td>0.2378(6)</td>
<td>0.0171(18)</td>
<td>0.0817(6)</td>
<td>0.129(8)</td>
</tr>
</tbody>
</table>

¹ U(eq.) = one-third of the trace of the orthogonalized U.

Table 6. Bond Lengths (Å) for the Bisprotonated Ligand 2

<table>
<thead>
<tr>
<th>Atom</th>
<th>C(14)–C(15)</th>
<th>1.319(15)</th>
<th>N(4)–C(21)</th>
<th>1.50(3)</th>
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<tr>
<td>C(15)–C(16)</td>
<td>1.37(2)</td>
<td>N(4)–C(26)</td>
<td>1.48(2)</td>
<td>C(16)–C(17)</td>
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<tr>
<td>C(17)–C(18)</td>
<td>1.35(2)</td>
<td>O(4)–C(23)</td>
<td>1.40(2)</td>
<td>N(3)–C(18)</td>
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<tr>
<td>C(18)–C(19)</td>
<td>1.50(2)</td>
<td>O(5)–C(25)</td>
<td>1.43(2)</td>
<td>C(20)–N(4)</td>
</tr>
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</table>

Figure 2. PLUTON drawing of the protonated ligand 2. The molecule is situated at an inversion center. The ClO₄⁻ counterions have been omitted for clarity.

Table 7. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms for Complex 4

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq.) Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
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<td>O(1)</td>
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<td>0.0454(19)</td>
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<tr>
<td>O(2)</td>
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<td>0.0414(6)</td>
<td>0.3277(2)</td>
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<tr>
<td>O(3)</td>
<td>0.1165(8)</td>
<td>0.1223(8)</td>
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<tr>
<td>N(1)</td>
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<tr>
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<td>C(1)</td>
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<td>C(2)</td>
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¹ U(eq.) = one-third of the trace of the orthogonalized U.


The equatorial plane is formed by a pyridine nitrogen N(1) and an isobestic point appeared at 580 nm (see Figure 4). The perchlorate anion is hydrogen-bonded to a C104- ion. Both anions are situated at distances to Cu of 1.988(6), 2.287(6), and 2.069(6) Å, respectively. The apical positions are occupied by a crown ether group. The bond distances are all close to those found for 3. The Cu–Cu separation in complex 4 is 3.4592(15) Å. This distance is 0.56 Å larger than the Cu–Cu distance in a bis(α-hydroxyo)-bridged dinuclear Cu(II) complex which we characterized recently. In addition, a perchlorate anion is hydrogen bonded to the hydroxo proton H(36) (see Figure 3). The perchlorate oxygen atoms O(105) and O(105)b (= O105 [x, y, 1/2 - z]) interact with H(36) at a distance of 2.540(19) Å. The angle O(3) - H(36) - O(105) is 155.6(4)° and the O(105)-H(36)-O(105)b angle is 48.9(5)°.

Structures in Solution. The formation of complex 3 in acetonitrile was followed by monitoring the increase in the absorption of the d–d transition at 747 nm as a function of the Cu(II):l ratio. At low ratios (0–0.5), the increase in intensity was constant. At Cu(II):l > 0.5, the slope of the curve changed considerably less than that calculated for 3. The two cores in 4 share a hydroxo oxygen atom. The molecule has a 2-fold symmetry; the 2-fold rotation axis passes through the hydroxo group. The bond distances are all close to those found for 3. The equatorial plane is formed by a pyridine nitrogen N(1) and two crown ether oxygen atoms (O(1) and O(2)). These atoms have distances to Cu of 1.988(6), 2.287(6), and 2.069(6) Å, respectively. The apical positions are occupied by a crown ether nitrogen N(2) and the bridging hydroxo oxygen O(3) atom at distances to Cu of 2.021(8) and 1.887(3) Å, respectively. The Cu–Cu separation in complex 4 is 3.4592(15) Å. This distance is 0.56 Å larger than the Cu–Cu distance in a bis(α-hydroxyo)-bridged dinuclear Cu(II) complex which we characterized recently. In addition, a perchlorate anion is hydrogen bonded to the hydroxo proton H(36) (see Figure 3). The perchlorate oxygen atoms O(105) and O(105)b (= O105 [x, y, 1/2 - z]) interact with H(36) at a distance of 2.540(19) Å. The angle O(3) - H(36) - O(105) is 155.6(4)° and the O(105)-H(36)-O(105)b angle is 48.9(5)°.

Figure 4. UV–vis titration of ligand 1 with Cu(ClO4)2·6H2O: ratio Cu(II):1 (spectrum) = 0.5 (1), 0.7 (2), 0.9 (3), and 1.1 (4).

Figure 5. Proposed formation of complexes 3 (top) and 4 (bottom) in solution.

Figure 6. UV–vis titration of ligand 2 with Cu(ClO4)2·6H2O: ratio Cu(II):2 (spectrum) = 0.5 (1), 0.8 (2), 1.0 (3), 1.5 (4), 1.9 (5), and 2.1 (6). Figure 5, top). Since no methanol is present during the titration, a water molecule is thought to occupy the fifth coordination place at copper.

The formation of complex 4 in acetonitrile was also studied by UV–vis. The titration of ligand 2 with Cu(ClO4)2·6H2O revealed isobestic points at 410 and 562 nm in the region between 1 and 2 equiv of added Cu(II) (see Figure 6). A plot of the increase of absorption of the d–d transition at 734 nm versus the Cu(II)/2 ratio showed an inflection point at the value 1. These results suggest that a mononuclear Cu(II) complex is formed in the early stages of the reaction. This species reacts further to yield the dinuclear Cu(II) complex 4 (see Figure 5, bottom). It is likely that the mononuclear complex in solution has a structure comparable to that of the mononuclear complex 3, with a water molecule probably residing at one of the basal positions instead of a methanol molecule. Insertion of a second Cu(II) ion into this complex will then yield the dinuclear, aquo complex probably dissociates to give two complexes 3 (see Figure 5, bottom). Since no methanol is present during the titration, a water molecule is thought to occupy the fifth coordination place at copper.

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bridged dimer. In this dimer, it is favorable for the water molecule to be deprotonated, thus lowering the electrostatic repulsion between the Cu(II) centers. Oxygen atoms of the crown-ether ring may assist in the deprotonation reaction. The X-ray structure of complex 3 shows that such a neighboring group effect is feasible. Complex 4 displays in the UV−vis spectrum an absorption at 343 nm which is tentatively assigned to an O(H)→Cu charge transfer band.16,17

**Electrochemistry.** Complexes 3 and 4 were examined by cyclic voltammetry in acetonitrile to gain insight in their redox behavior. The former complex showed an irreversible wave with an $E_{1/2}$ (versus Fe/Fc+) for the Cu(II/I) couple of 0.04 V (see Figure 7, left). At fast scan rates (up to 5 V/s), no improvement of the cyclic voltammogram was observed, confirming the irreversible nature of the reduction. This problem is encountered more often in the electrochemistry of (bi)pyridine−Cu(II) complexes.18,19 As can be seen from Figure 7 (left), complex 3 is not stable under reducing conditions. The peak current decreases with every scan and is accompanied by a wave that grows in at $E_{1/2} = +0.65$ V. Clearly, this unidentified product results from the chemical reaction following the reduction of 3. At more negative potentials the Cu(I/0) wave was observed ($E_{1/2} = -0.72$ V, not shown in Figure 7).

Complex 4 is also reduced irreversibly, but at a considerably more negative potential than complex 3, viz. at $E_{1/2} = -0.36$ V (Cu(II) → Cu(I) and $-0.83$ V (Cu(I) → Cu(0)). Again, increasing the scan rate did not improve the reversibility of the system. As with complex 3, the reduction is accompanied by a chemical reaction (see Figure 7, right). The newly formed product oxidizes at a half-wave potential of ca 0.02 V and is therefore different from the product formed during the reduction of 3. Possibly, ligands 1 and 2 are not well suited for stabilizing the “soft” Cu(I) centers due to the coordination of the relatively hard crown ether oxygen atoms.20

**Concluding Remarks.** We have presented a new high pressure route for the synthesis of pyridine ligand systems that were not accessible before. A possible reaction path to the dinuclear hydroxo-bridged Cu(II) complex 4 is proposed, based on UV−vis titration studies and the X-ray structure of complex 3. Further work will include the synthesis and characterization of the Cu(I) analogues of 3 and 4 and the dioxygen binding and activation properties of these compounds.

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**Supplementary Material Available:** Further details of the structure determination, including atomic coordinates, bond lengths and angles, thermal parameters and a thermal motion ellipsoid plot for 3 and 2·2HClO₄·4 (11 pages). Ordering information is given on any current masthead page.