

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

Constantinus F. Martens,[†] Robertus J. M. Klein Gebbink,[†] Martinus C. Feiters,[†]
Huub Kooijman,[‡] Wilberth J. J. Smeets,[‡] Anthony L. Spek,[‡] and Roeland J. M. Nolte^{*‡}

Department of Organic Chemistry, NSR Center, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands, and Bijvoet Center for Biomolecular Research, Vakgroep Kristal- en Structuurchemie, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Received February 23, 1994[Ⓞ]

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 *P*2₁/*c* (No. 14) with *a* = 8.4636(10) Å, *b* = 15.912(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 *R*_w = 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 **2**. The X-ray structure of **4**·2HClO₄ reveals a monoclinic space group *C*2/*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 *R*_w = 0.071. Complex **4** consists of a dinuclear [Cu₂(OH)·2]³⁺ 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.

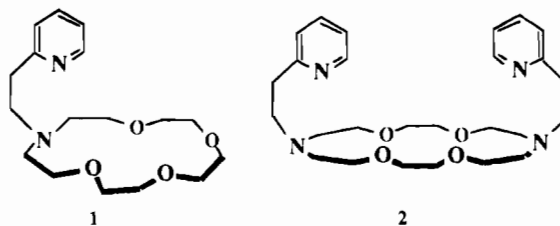
Introduction

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

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-tetraoxacyclooctadecane (2,2'-kryptofix) and 1-aza-4,7,10,13-tetraoxacyclopentadecane (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-tetraoxacyclopentadecane (**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×) with a 15% aqueous NaOH solution. During this procedure, both layers turned brown. The organic layer was separated, dried (MgSO₄), and concentrated *in vacuo* to yield a brown oil. This oil was subjected to column chromatography (silica gel, eluent CHCl₃/MeOH/triethylamine, 89/10/1

[†] University of Nijmegen.

[‡] Utrecht University.

[Ⓞ] Abstract published in *Advance ACS Abstracts*, October 15, 1994.

(1) Martens, C. F.; Schenning, A. P. H. J.; Klein Gebbink, R. J. M.; Feiters, M. C.; van der Linden, J. G. M.; Heck, J.; Nolte, R. J. M. *J. Chem. Soc., Chem. Commun.* **1993**, 88.

v/v) to give 1.07 g (70%) of 1 as an oil. R_f (TLC, silica 60H, eluent $\text{CHCl}_3/\text{MeOH}$, 9/1 v/v) = 0.15. Anal. Calcd for $\text{C}_{16}\text{H}_{28}\text{N}_2\text{O}_4$: C, 61.51; H, 9.03; N, 8.97. Found: C, 61.99; H, 8.77; N, 8.76. ^1H NMR (CDCl_3 , 90 MHz): δ 2.70–2.86 (m, 8 H, N- CH_2 , CH_2 -Py), 3.56 (m, 16 H, OCH_2), 6.94–7.24 (m, 2 H, Py- H), 7.49 (t of d, 1 H, Py- H), 8.41 (d, 1 H, Py- H). ^{13}C NMR (400 MHz, CDCl_3): δ 35.8 (CH_2 -Py), 54.4 ($\text{O}-\text{CH}_2\text{CH}_2$ -N), 56.6 (CH_2CH_2 -Py), 69.8, 70.0, 70.3, 70.8 (CH_2 -O), 120.9, 123.3, 136.1, 149.0, 160.4 (C of Py). IR (acetonitrile) 2960, 2862, (CH_2 stretch), 1634, 1592, 1570 (C=C, C=N), 1130 (C-O-C) cm^{-1} .

1,10-Bis[2-(2-pyridyl)ethyl]-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (2). A solution of 1.014 g (3.86 mmol) of 2,2'-kryptofix, 2.59 g (24.6 mmol) of 2-vinylpyridine, and 0.581 g (9.68 mmol) of acetic acid in 15 mL of methanol was transferred to a high-pressure Teflon capsule and kept at ambient temperatures under a constant pressure of 15 kbar for 60 h. The reaction mixture was worked up as described for compound 1. Yield: 663 mg (36.3%) of 2 as a yellow-brown, semi-solid material. R_f (TLC, silica 60H, eluent $\text{CHCl}_3/\text{MeOH}$ 9/1 v/v) = 0.14. Anal. Calcd for $\text{C}_{26}\text{H}_{40}\text{N}_4\text{O}_4$: C, 66.07; H, 8.53; N, 11.85. Found: C, 66.29; H, 8.67; N, 11.69. ^1H NMR (CDCl_3 , 100 MHz): δ 2.84 (m, 16 H, N- CH_2 , CH_2 -Py), 3.50 (m, 16 H, OCH_2), 6.92–7.11 (m, 4 H, Py- H), 7.48 (t of d, 2 H, Py- H), 8.40 (d, 2 H, Py- H). ^{13}C NMR (400 MHz, CDCl_3): δ 35.9 (CH_2 -Py), 53.8 ($\text{O}-\text{CH}_2\text{CH}_2$ -N), 55.7 (CH_2CH_2 -Py), 69.8 ($\text{O}-\text{CH}_2\text{CH}_2$ -O), 70.6 ($\text{O}-\text{CH}_2\text{CH}_2$ -N), 120.9, 123.2, 136.1, 149.1, 160.5 (C of Py). MS-FAB (m/z): 495 (2 + Na^+), 473 (2), 368 (2 - $\text{CH}_2\text{CH}_2\text{Py}$).

Preparation of the Complexes. Caution! Although we have experienced no difficulties with the perchlorate salts described, these should be regarded as potentially explosive and handled accordingly.²

[Cu·1·MeOH](ClO₄)₂ (3). To a solution of 196 mg (0.61 mmol) of 1, dissolved in 25 mL of methanol was added with stirring a solution of 224 mg (0.60 mmol) of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in 2 mL of methanol. The solution was stirred overnight, and the yellow-brown precipitate formed was filtered off. The resulting light green filtrate was concentrated *in vacuo*. Yield: 321 mg (90%) of a green solid. X-ray quality crystals were grown by slow diffusion of hexane into a methanolic solution of 3. Anal. Calcd for $\text{C}_{16}\text{H}_{28}\text{N}_2\text{O}_{12}\text{CuCl}_2\text{MeOH}$: C, 33.64; H, 5.31; N, 4.62. Found: C, 34.09; H, 4.54; N, 4.95. UV-vis (acetonitrile): 220, 259, 750 nm. MS-FAB (m/z): 486 (1·CuClO₄), 387 (1·Cu). IR (acetonitrile): 3240 (MeOH), 2872 (CH_2), 1610 (C=C, C=N), 1109, 625 (ClO_4^-) cm^{-1} .

[Cu₂·2·OH](ClO₄)₃ (4). A solution of 70 mg (0.19 mmol) of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in 2 mL of methanol was added dropwise to a stirred solution of 90 mg (0.19 mmol) of 2 in 20 mL of methanol. A turquoise precipitate was formed and filtered off; yield 104 mg (74%) of 4. Crystals, suitable for X-ray analysis, were obtained by slow diffusion of hexane into a methanolic solution of 4. Anal. Calcd for $\text{C}_{26}\text{H}_{40}\text{N}_4\text{O}_{17}\text{Cu}_2\text{Cl}_3 \cdot 4\text{HClO}_4$: C, 39.34; H, 5.21; N, 7.06. Found: C, 39.34; H, 5.20; N, 7.07. UV-vis (acetonitrile): 220, 257, 292, 343, 700 nm. MS-FAB (m/z): 815 (4 - ClO₄), 716 (4 - 2 ClO₄), 699 (4 - 2 ClO₄ - OH). IR (acetonitrile): 2886, 2834 (CH_2), 1611 (C=C, C=N), 1114, 625 (ClO_4^-) cm^{-1} . IR (KBr): 3417 (OH) cm^{-1} .

Physical Measurements. UV-vis spectra were recorded on a Perkin-Elmer Lambda 5 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker WH-90, a Bruker AC-100 or a Bruker WM-400 instrument. Chemical shifts are denoted in ppm relative to the internal standard tetramethylsilane. FAB-MS spectra were recorded on a VG 7070E instrument using 3-nitrobenzyl alcohol as the matrix. IR-spectra were recorded on a Perkin-Elmer 1720X instrument. Melting points were measured on a Reichert-Jung hot stage mounted on a microscope and are reported uncorrected. Conductivity measurements were carried out with a Schott Geräte CG 852 Konduktometer using 10^{-3} M solutions of the copper complexes in acetonitrile. Cyclic voltammetry experiments were performed with a PAR 173 potentiostat equipped with a PAR Model 176 I/E converter coupled to a PAR Model 175 universal programmer using a platinum auxiliary as well as working electrode and Ag^+/Ag (0.1 M AgNO_3) as reference electrode. All measurements were carried out in a glovebox under a dinitrogen atmosphere in acetonitrile solution with tetrabutylammonium hexafluorophosphate (TBAH) as the background electrolyte (0.1 M). The

Table 1. Crystallographic Data for 3

chem formula:	fw = 618.91
$[\text{C}_{18}\text{H}_{32}\text{N}_2\text{O}_5\text{Cu}](\text{ClO}_4)_2$	space group: $P2_1/c$ (No. 14)
$a = 8.4636(10)$ Å	$T = 150$ K
$b = 15.912(5)$ Å	$\lambda = 0.710$ 73 Å
$c = 19.373(4)$ Å	$\rho_{\text{calc}} = 1.680$ g/cm ³
$\beta = 110.341(16)$	$\mu_{\text{calc}} = 11.8$ cm ⁻¹
$V = 2446.3(1.0)$ Å ³	$R = 0.040^a$
$Z = 4$	$R_w = 0.050^a$

^a Definition of R factors: $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = [\sum (w||F_o| - |F_c||)^2 / \sum (w(F_o)^2)]^{1/2}$.

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 a $E_{1/2}$ value of 0.050 V.

Crystal Structure Determination of 3. A light-blue, tablet-shaped crystal ($0.9 \times 0.9 \times 0.4$ mm) was glued to the tip of a glass fiber and transferred into the cold nitrogen stream on an Enraf-Nonius CAD4-Turbo diffractometer on rotating anode. Accurate unit-cell parameters and an orientation matrix were determined by least-squares refinement of 25 well-centered reflections (SET4) in the range $11.6^\circ < \theta < 14.1^\circ$. The unit-cell parameters were checked for the presence of higher lattice symmetry.³ Crystal data and details on data collection and refinement are given in Table 1. Data were collected at 150 K in $\omega/2\theta$ scan mode with scan angle $\Delta\omega = 1.16 + 0.35 \tan \theta^\circ$. Intensity data of 6229 reflections were collected in the range $1.12^\circ < \theta < 27.50^\circ$, of which 5603 are independent. 4506 reflections with intensities above $2.5\sigma(I)$ level were used in the structure analysis. Data were corrected for L_p effects and for a linear decay of 2% of 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: $\sigma^2(I) = \sigma_{\text{cs}}^2(I) + (0.03I)^2$.⁴ An empirical absorption/extinction correlation was applied (DIFABS,⁵ correction range 0.880–1.143). 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 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 $0.033(18)$ Å². Weights were introduced in the final refinement cycles. Convergence was reached at $R = 0.040$, $R_w = 0.050$, $w = 1/[\sigma^2(F)]$, and $S = 1.58$, for 341 parameters. A final difference Fourier map showed no residual density outside -0.53 and $+0.95$ e Å⁻³.

Crystal Structure Determination of 4·2HClO₄. A light-blue, rod-shaped crystal ($0.15 \times 0.23 \times 0.73$ 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 $9.0^\circ < \theta < 14.2^\circ$. Reduced-cell calculations did not indicate higher lattice symmetry.³ Crystal data and details on data collection and refinement are presented in Table 2. Data were collected

- (3) Spek, A. L. *J. Appl. Crystallogr.* **1988**, *21*, 578.
- (4) McCandlish, L. E.; Stout, G. H.; Andrews, L. C. *Acta Crystallogr.* **1975**, *A31*, 245.
- (5) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.
- (6) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; García-Grandá, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF program system. Technical report of the Crystallography Laboratory; University of Nijmegen: Nijmegen The Netherlands, 1992.
- (7) Sheldrick G. M., SHELX76 Program for crystal structure determination. University of Cambridge, England, 1976.

Table 2. Crystallographic Data for 2·2HClO₄ and 4

chem formula: [C ₂₆ H ₄₁ N ₄ O ₅ Cu ₂] ⁺ [C ₂₆ H ₄₁ N ₄ O ₄] ⁻ 5[ClO ₄]	fw = 1588.62
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)°	ρ _{calc} = 1.562 g/cm ³
V = 6756.5(6) Å ³	μ _{calc} = 9.2 cm ⁻¹
Z = 4	R = 0.078 ^a
	R _w = 0.071 ^a

^a Definition of R factors: $R = \sum |F_o| - |F_c| / \sum |F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2] / \sum w(F_o^2)]^{1/2}$.

at ambient temperature in $\omega/2\theta$ scan mode with scan angle $\Delta\omega = 0.72 + 0.35 \tan \theta^\circ$. From a total of 14 921 reflections in the range $0.78^\circ < \theta < 27.5^\circ$ (7757 unique, $R_{int} = 0.066$), 3370 satisfied the $I > 2.5\sigma(I)$ 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: $\sigma^2(I) = \sigma_{\text{calc}}^2(I) + (0.03I)^2$.⁴ An empirical absorption/extinction correction was applied (DIFABS,⁵ 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 H(44)) 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 $R = 0.078$, $R_w = 0.071$, $w = 1/[\sigma^2(F)]$, and $S = 5.85$, for 437 parameters. A final difference Fourier map showed no residual density outside -0.78 and $+0.71 \text{ e } \text{Å}^{-3}$.

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

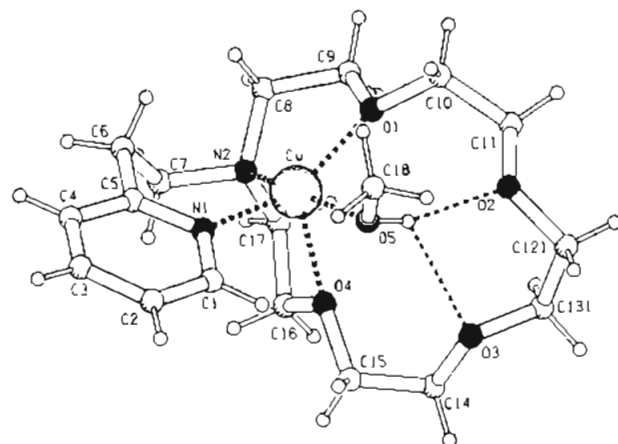


Figure 1. PLUTON¹⁰ drawing of complex **3**. The ClO₄⁻ counter ions have been omitted for clarity.

Table 3. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å²) for Complex **3** (Esd's in Parentheses)^a

atom	x	y	z	U(eq), Å ²
Cu	-0.09072(4)	-0.02183(2)	0.25207(2)	0.0157(1)
O(1)	0.0223(3)	0.04964(13)	0.34407(11)	0.0206(6)
O(2)	0.2017(3)	-0.10097(17)	0.43323(14)	0.0389(8)
O(3)	0.2930(3)	-0.17598(16)	0.32799(15)	0.0448(8)
O(4)	0.1171(3)	-0.06409(13)	0.21115(14)	0.0314(8)
O(5)	-0.0597(3)	-0.12392(13)	0.31211(12)	0.0220(6)
N(1)	-0.2859(3)	-0.06867(15)	0.16972(13)	0.0180(7)
N(2)	-0.0611(3)	0.08261(14)	0.20121(13)	0.0160(7)
C(1)	-0.3092(4)	-0.15206(19)	0.16398(18)	0.0247(9)
C(2)	-0.4532(4)	-0.1886(2)	0.11583(18)	0.0290(10)
C(3)	-0.5785(4)	-0.1373(2)	0.07122(18)	0.0298(10)
C(4)	-0.5525(4)	-0.0517(2)	0.07432(17)	0.0257(9)
C(5)	-0.4041(3)	-0.01827(19)	0.12387(15)	0.0190(8)
C(6)	-0.3708(4)	0.07446(18)	0.12659(16)	0.0213(8)
C(7)	-0.1939(4)	0.09512(18)	0.12756(16)	0.0201(8)
C(8)	-0.0663(4)	0.15286(17)	0.25069(16)	0.0198(8)
C(9)	0.0488(4)	0.13610(18)	0.32892(16)	0.0225(9)
C(10)	0.0636(4)	0.0316(2)	0.42177(16)	0.0266(9)
C(11)	0.2286(4)	-0.0144(3)	0.45418(18)	0.0379(13)
C(14)	0.3382(5)	-0.1622(2)	0.2639(3)	0.0430(13)
C(15)	0.1818(5)	-0.1450(2)	0.2018(2)	0.0356(11)
C(16)	0.1450(4)	-0.00145(19)	0.16493(19)	0.0255(9)
C(17)	0.1081(4)	0.08125(18)	0.19326(17)	0.0205(8)
C(18)	-0.1715(5)	-0.1583(2)	0.3468(2)	0.0337(11)
*C(121)	0.3467(5)	-0.1558(3)	0.4519(2)	0.0336(14)
*C(122)	0.3898(18)	-0.1089(13)	0.4576(11)	0.032(5)
*C(131)	0.4247(5)	-0.1515(3)	0.3931(2)	0.0335(14)
*C(132)	0.367(3)	-0.1920(13)	0.4141(8)	0.043(6)

^a U(eq) = one-third of the trace of the orthogonalized U. Starred atom sites have a Population less than 1.0.

temperatures exceeding 40 °C gave rise to a retro reaction, viz. the elimination of 2-vinylpyridine.

Addition of Cu(ClO₄)₂·6H₂O 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 (Methanolato){1-[2-(2-pyridyl)ethyl]-aza-4,7,10,13-tetraoxacyclotadecane}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

(8) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.

(9) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(10) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

(11) Karlin, K. D.; Hayes, J. C.; Gultneh, Y.; Cruse, R. W.; McKown, J. W.; Hutchinson, J. P.; Zubieta, J. *J. Am. Chem. Soc.* **1984**, *106*, 2121.

(12) Karlin, K. D.; Tyeklar, Z.; Farooq, A.; Haka, M. S.; Ghosh, P.; Cruse, R. W.; Gultneh, Y.; Hayes, J. C.; Toscano, P. J.; Zubieta, J. *Inorg. Chem.* **1992**, *31*, 1436.

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

Cu—O(5)	1.962(2)	Cu—O(1)	2.049(2)
Cu—N(1)	1.999(3)	Cu—O(4)	2.268(3)
Cu—N(2)	1.992(2)		
O(1)—Cu—O(4)	106.52(10)	O(4)—Cu—N(1)	97.85(10)
O(1)—Cu—O(5)	91.03(9)	O(4)—Cu—N(2)	80.11(9)
O(1)—Cu—N(1)	155.13(11)	O(5)—Cu—N(1)	93.88(10)
O(1)—Cu—N(2)	82.31(9)	O(5)—Cu—N(2)	166.00(11)
O(4)—Cu—O(5)	90.09(10)	N(1)—Cu—N(2)	97.32(10)

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

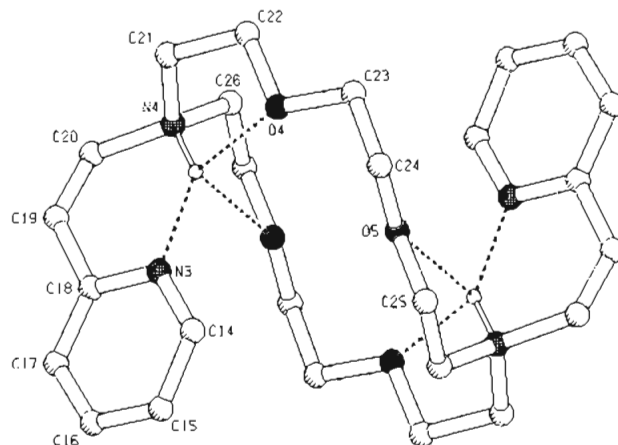
atom	x	y	z	U(eq), Å ²
O(4)	0.2472(4)	0.3515(14)	0.0942(4)	0.131(5)
O(5)	0.2373(3)	0.4764(8)	-0.0045(4)	0.098(4)
N(3)	0.3585(3)	0.2120(10)	0.0702(3)	0.073(3)
N(4)	0.2851(4)	0.0902(14)	0.1104(5)	0.128(6)
C(14)	0.3702(5)	0.3028(12)	0.0386(4)	0.083(5)
C(15)	0.4150(6)	0.2955(15)	0.0216(4)	0.095(6)
C(16)	0.4478(6)	0.1926(17)	0.0384(6)	0.105(7)
C(17)	0.4372(5)	0.0990(13)	0.0712(6)	0.100(6)
C(18)	0.3922(5)	0.1114(12)	0.0863(5)	0.078(5)
C(19)	0.3761(6)	0.0120(15)	0.1221(7)	0.156(9)
C(20)	0.3321(6)	0.001(2)	0.1294(8)	0.263(15)
C(21)	0.2725(9)	0.177(3)	0.1519(6)	0.221(18)
C(22)	0.2308(9)	0.278(2)	0.1316(7)	0.175(13)
C(23)	0.2103(7)	0.451(2)	0.0725(8)	0.162(11)
C(24)	0.2308(6)	0.5438(16)	0.0398(8)	0.147(9)
C(25)	0.2560(6)	0.5661(15)	-0.0380(8)	0.145(8)
C(26)	0.2378(6)	0.0171(18)	0.0817(6)	0.129(8)

^a U(eq) = one-third of the trace of the orthogonalized U.**Table 6.** Bond Lengths (Å) for the Bisprotonated Ligand 2

N(3)—C(14)	1.319(15)	N(4)—C(21)	1.50(3)
C(14)—C(15)	1.37(2)	N(4)—C(26)	1.48(2)
C(15)—C(16)	1.34(2)	C(21)—C(22)	1.48(3)
C(16)—C(17)	1.35(2)	C(22)—O(4)	1.39(2)
C(17)—C(18)	1.353(19)	O(4)—C(23)	1.40(2)
N(3)—C(18)	1.330(16)	C(23)—C(24)	1.46(3)
C(18)—C(19)	1.50(2)	C(24)—O(5)	1.41(2)
C(19)—C(20)	1.23(2)	O(5)—C(25)	1.43(2)
C(20)—N(4)	1.50(2)	C(25)—C(26)b	1.47(2)

are given in Table 4. Complex 3 contains a CuN₂O₃ core which has a distorted trigonal bipyramidal geometry. The distortion from the idealized trigonal bipyramid (TBP) toward a square pyramid (SP) was calculated to be 49.4%.¹³ 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 place 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 {1,10-Bis-[2-(2-pyridyl)ethyl]diaz-4,7,13,16-tetraoxacyclooctadecane}·2H₂O}·2ClO₄ [(2)·2H₂O}·2ClO₄). Positional parameters for [(2)·2H₂O}·2ClO₄ are given in Table 5; coordinates of the ClO₄⁻ counter ions are given in the supplementary material. Selected bond distances and angles are given in Table 6. The structure is presented in Figure 2. The bisprotonated ligand 2 was found to crystallize with its

**Figure 2.** PLUTON¹⁰ drawing of the protonated ligand 2. The molecule is situated at an inversion center. The ClO₄⁻ counter ions have been omitted for clarity.**Table 7.** Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms for Complex 4^a

atom	x	y	z	U(eq), Å ²
Cu	0.03410(4)	0.15518(10)	0.20266(4)	0.0386(3)
O(1)	0.1008(2)	0.0372(6)	0.2555(2)	0.0454(19)
O(2)	0.0322(2)	0.0414(6)	0.3277(2)	0.0437(19)
O(3)	0	0.2320(8)	1/4	0.044(3)
N(1)	0.0699(2)	0.3207(6)	0.1859(3)	0.037(2)
N(2)	0.0619(3)	0.0447(7)	0.1517(3)	0.044(3)
C(1)	0.1019(3)	0.4008(8)	0.2203(3)	0.047(3)
C(2)	0.1257(4)	0.5131(10)	0.2059(4)	0.061(4)
C(3)	0.1159(4)	0.5446(10)	0.1556(4)	0.061(4)
C(4)	0.0834(4)	0.4651(10)	0.1195(4)	0.058(4)
C(5)	0.0606(3)	0.3516(10)	0.1355(3)	0.047(3)
C(6)	0.0267(3)	0.2533(9)	0.0990(3)	0.049(3)
C(7)	0.0534(4)	0.1139(9)	0.1003(3)	0.057(4)
C(8)	0.1186(3)	0.0179(10)	0.1733(3)	0.056(4)
C(9)	0.1297(3)	-0.0389(10)	0.2268(3)	0.054(3)
C(10)	0.1163(3)	0.0046(10)	0.3091(3)	0.053(3)
C(11)	0.0853(3)	0.0891(9)	0.3364(3)	0.052(3)
C(12)	0.0254(3)	-0.0562(9)	0.3651(3)	0.055(3)
C(13)	0.0323(3)	-0.0868(9)	0.1464(3)	0.054(3)

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

dinuclear Cu(II) complex 4, ClO₄⁻ counterions, and a bridging hydroxy anion, in a 1:1:5:1 ratio. The amine nitrogen atoms in the crown ether ring are protonated with a nitrogen N(4) to proton H(44) distance of 0.981(18) Å. This amine proton is involved in an intra-molecule trifurcated¹⁴ hydrogen bond to N(3), O(4), and O(5) [$1/2 - x, 1/2 - y, \bar{z}$], with H···acceptor distances of 1.903(14), 2.382(18) and 2.497(16) Å, respectively. The N—H···acceptor angles amount to 138.8(1.2), 101.6(1.1), and 99.8(1.2)° for N(3), O(4) and O(5), respectively. The proton resides in a position that is very similar to the coordination sphere around the copper atoms in the dinuclear complex 4 (*vide infra*).

X-ray Structure of (μ-Hydroxo){1,10-bis-[2-(2-pyridyl)ethyl]diaz-4,7,13,16-tetraoxacyclooctadecane} di-copper(II) Triperchlorate (4). Positional parameters for the dinuclear cation are listed in Table 7; selected bond distances and angles for the dinuclear cation are given in Table 8. The structure of 4 is depicted in Figure 3. The coordination geometry around each copper(II) ion is similar to the geometry found in 3. Complex 4 contains two symmetry-related CuN₂O₃ cores in a distorted trigonal bipyramidal geometry. However, the percentage distortion from TBP to SP is 37.7, which is

(13) Holmes, R. R. *Prog. Inorg. Chem.*, 1984, 32, 119 and references therein.(14) Jeffrey, G. A.; Maluszynska, H.; Mitra, J. *Int. J. Biol. Macromol.* 1985, 7, 336.

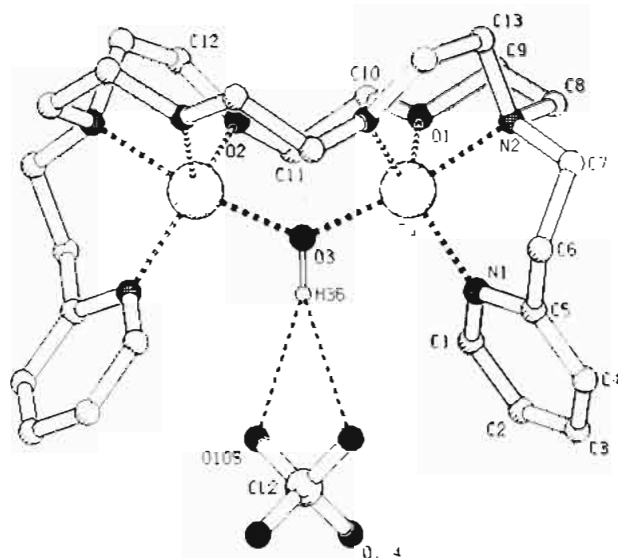


Figure 3. PLUTON¹⁰ drawing of complex 4. The bridging hydroxy anion is hydrogen-bonded to a ClO_4^- ion. Both anions are situated at a 2-fold rotation axis, running through O(3) and Cl(2). Nonbonded ClO_4^- counter ions have been omitted for clarity.

Table 8. Selected Bond Distances (Å) and Angles (deg) for Complex 4

Cu(1)–Cu(1)b	3.4592(15)	Cu(1)–N(2)	2.021(8)
Cu(1)–O(3)	1.887(3)	Cu(1)–O(2)b	2.069(6)
Cu(1)–N(1)	1.988(6)	Cu(1)–O(1)	2.287(6)
Cu(1)–O(3)–Cu(1)	132.8(4)	O(1)–Cu(1)–O(2)b	114.8(2)
N(2)–Cu(1)–O(3)	169.8(3)	O(1)–Cu(1)–N(1)	102.6(2)
N(2)–Cu(1)–O(1)	78.1(3)	O(2)b–Cu(1)–O(3)	89.0(2)
N(2)–Cu(1)–O(2)b	81.8(3)	O(2)b–Cu(1)–N(1)	139.2(3)
N(2)–Cu(1)–N(1)	90.8(3)	N(1)–Cu(1)–O(3)	99.1(3)
O(1)–Cu(1)–O(3)	102.02(18)		

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(μ -hydroxy)-bridged dinuclear Cu(II) complex which we characterized recently.¹⁵ 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)b 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):1 ratio. At low ratios (0–0.5), the increase in intensity was constant. At Cu(II):1 > 0.5, the slope of the curve changed and an isobestic point appeared at 580 nm (see Figure 4). Likely, first a complex is formed in which two ligands 1 coordinate a Cu(II) ion. At Cu(II):1 ratios exceeding 0.5, this complex probably dissociates to give two complexes 3 (see

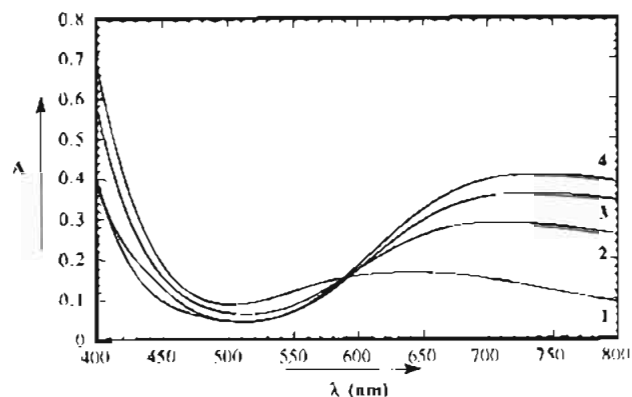


Figure 4. UV–vis titration of ligand 1 with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$: ratio Cu(II):1 (spectrum) = 0.5 (1), 0.7 (2), 0.9 (3), and 1.1 (4).

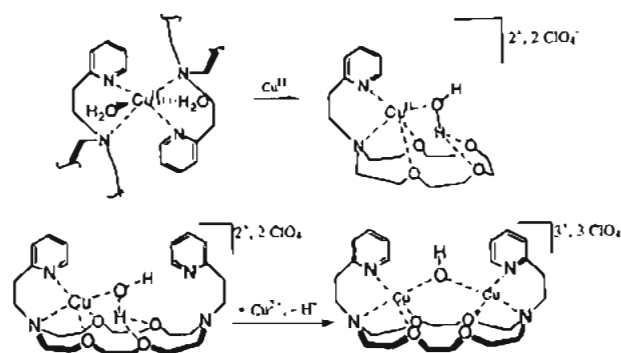


Figure 5. Proposed formation of complexes 3 (top) and 4 (bottom) in solution.

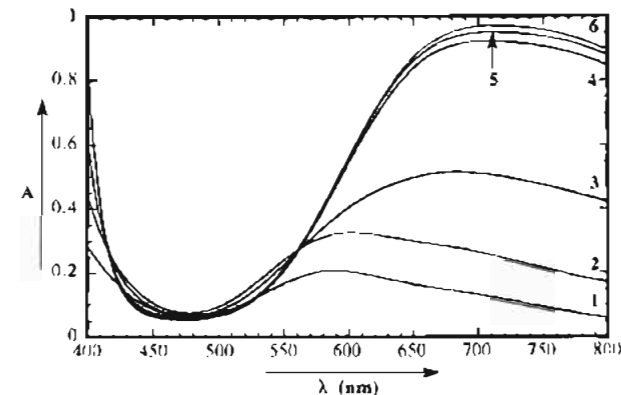


Figure 6. UV–vis titration of ligand 2 with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$: ratio Cu(II):2 (spectrum) = 0.5 (1), 0.8 (2), 1.0 (3), 1.5 (4), 1.9 (5), and 2.1 (6).

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 $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ 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

(15) Martens, C. F.; Schenning, A. P. H. J.; Feiters, M. C.; Heck, J.; Beurskens, G.; Beurskens, P. T.; Steinwender, E.; Nolte, R. J. M. *Inorg. Chem.* 1993, 32, 3029.

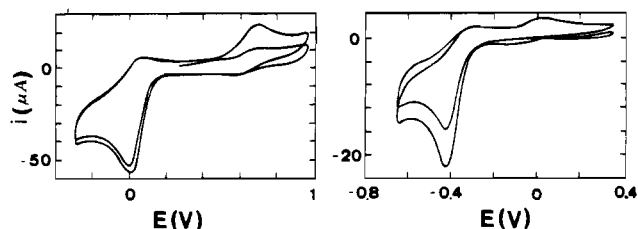


Figure 7. Cyclic voltammograms of complexes **3** (left, scan starts at 0.22 V in positive direction) and **4** (right, scan starts at 0.0 V in positive direction) in acetonitrile at a scan rate of 100 mV/s. Supporting electrolyte: 0.1 M Bu₄NPF₆.

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) to 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 Fc/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 uniden-

tified 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.

Acknowledgment. This work was supported by the Netherlands Foundation of Chemical Research (SON) with financial aid from the Netherlands Foundation for Scientific Research (NWO).

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.

- (16) Ishimura, Y. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3728.
 (17) Coughlin, P. K.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 1273.
 (18) Christou, G.; Perlepes, S. P.; Libby, E.; Folting, K.; Huffman, J. C.; Webb, R. J.; Hendrickson, D. N. *Inorg. Chem.* **1990**, *29*, 3657.

- (19) Yao, Y.; Perkovic, M. W.; Rillema, D. P.; Woods, C. *Inorg. Chem.* **1992**, *31*, 3956.
 (20) Huheey, J. E. *Inorganic Chemistry, Principles of Structure and Reactivity*; Harper International Edition: New York, 1978.