

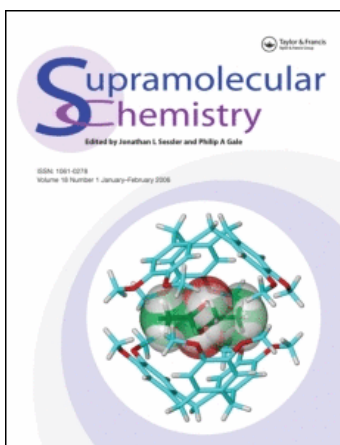
This article was downloaded by:

On: 29 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713649759>

Copper(II) Bipyridine and Crown Ether-Bipyridine Complexes: X-ray Structures, Characterization, and Properties as Histamine Receptors

To cite this Article (1996) 'Copper(II) Bipyridine and Crown Ether-Bipyridine Complexes: X-ray Structures, Characterization, and Properties as Histamine Receptors', *Supramolecular Chemistry*, 8: 1, 31 – 44

To link to this Article: DOI: 10.1080/10610279608233966

URL: <http://dx.doi.org/10.1080/10610279608233966>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Copper(II) Bipyridine and Crown Ether-Bipyridine Complexes: X-ray Structures, Characterization, and Properties as Histamine Receptors

C. F. MARTENS^a, A. P. H. J. SCHENNING^a, M. C. FEITERS^{a,*}, G. BEURSKENS^b, J. M. M. SMITS^b, P. T. BEURSKENS^b, W. J. J. SMEETS^c, A. L. SPEK^c, and R. J. M. NOLTE^a

Contribution from the University of Nijmegen: Department of Organic Chemistry, NSR-Centre^a, and the Department of Crystallography^b; University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands, and Utrecht University^c; Department of Crystal and Structural Chemistry, Bijvoet Centre for Biomolecular Research, Padualaan 8, 3584 CH Utrecht, The Netherlands.

(Received 25 October 1995; Revised 22 March 1996)

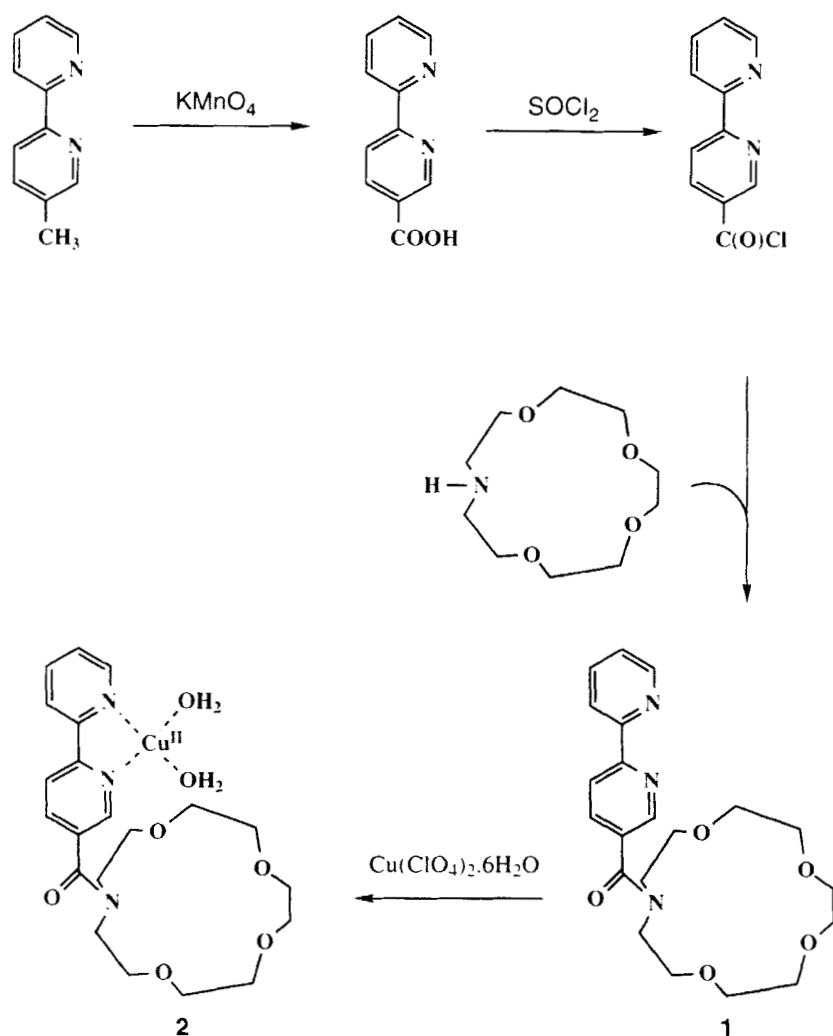
The synthesis and characterization, including the crystal structure, of the complex (**2**) of Cu(II) with the crown-ether bipyridine ligand, 1[5-2,2'-bipyridyl]carbonyl]-1-aza-4,7,10,13-tetraoxacyclopentadecane (**1**), are described. Compound **2**, C₂₇H₄₉N₃O₁₈Cl₂Cu, crystallizes in the triclinic space group P1 with cell constants $a = 10.160(1)$, $b = 13.014(1)$, $c = 15.934(2)$ Å, $\alpha = 74.18(1)^\circ$, $\beta = 84.83(1)^\circ$, $\gamma = 71.54(1)^\circ$, $V = 1923.0(4)$ Å³, $Z = 2$, $d_{\text{calc}} = 1.448$ g cm⁻³. The crystal structure was solved by vector search methods and refined by full-matrix least-squares on F² to $R = 0.086$ for 3163 observed reflections ($I > 2\sigma(I)$), 83 restraints and 390 parameters. The crystals contain two formula units per cell as a dimer, with each carbonyl oxygen of one monomer complex coordinating to the copper ion of the other. Each copper has elongated octahedral coordination geometry, with two nitrogens of one bipyridyl unit and four oxygens, viz. two water molecules, one perchlorate, and one carbonyl, as ligand donor atoms. There are no exchange interactions between the coppers as concluded from magnetic susceptibility measurements. Determination of the association constants of **2** with histamine.HCl and histamine.HClO₄ in ethanol yields values of 70 and 1000 M⁻¹, respectively. It is proposed that the imidazole and protonated amine group of histamine have binding interactions with the Cu(II) ion and the crown ether ring, respectively, of **2**. From

a solution of Cu(II) bipyridine complexes in the presence of both histamine and chloride, crystals of C₂₀H₁₆ClCuN₄ClO₄ with space group P2₁/c and cell constants $a = 10.7498(5)$, $b = 12.2394(7)$, $c = 16.9776(9)$ Å, $\beta = 112.248(4)$, $V = 2067.5(2)$ Å³, $Z = 4$, and $d_{\text{calc}} = 1.641$ g cm⁻³ were isolated. The structure was solved by heavy atom Patterson methods and refined to $R = 0.05$ for 2447 observed reflections and 344 parameters, without restraints. The Cu(II) ion in this complex, {Cu(bipyridine)₂Cl}ClO₄, which did not contain histamine, is five-coordinated, with 4 nitrogen donors of bipyridyl ligands and one chloride.

INTRODUCTION

Mono- and dinuclear copper complexes are interesting objects to study, for example as models to gain insight in the spectroscopic and catalytic properties of metallo-proteins.¹ We have previously reported models² for the oxygen activating multi-copper enzymes tyrosinase³ and dopamine-β-hydroxylase,⁴ which have the bio-

*Corresponding author.



SCHEME 1 Ligand synthesis and complex formation. Axial ligands and counterions in **2** have been omitted for clarity.

logical amines, tyrosine and dopamine, respectively, as substrates. We describe here the synthesis and characterization of the copper(II) complex **2** of a crown ether-bipyridine ligand system **1**,⁵ and its property as a histamine receptor (Scheme 1).

2,2'-Bipyridines are well-known ligands which usually form complexes with copper(II) in a 1:2 or 1:3 metal to ligand ratio,⁶ although a few complexes of 1:1 stoichiometry are known.⁷ The presence of a crown ether ring in **2** increases the steric bulk so that the formation of 1:1 complexes

is favoured. The coordination of Cu(II) by only one chelating ligand makes exchange reactions of the other monodentate ligands more likely. The ability of a crown ether ring to bind a protonated amine is well documented.⁸ Supramolecular complexes of metallo-hosts have previously been reported by us.² The metallohost presented here combines a copper(II) ion with a binding site for a protonated amine, and may be considered as a step towards the rational design of supramolecular catalytic systems which function according to the principles of metallo-enzymes.

RESULTS AND DISCUSSION

Synthesis of ligand 1. The synthesis of the ligand **1** is straightforward and outlined in Scheme 1. The starting compound 5-methyl-2,2'-bipyridine was prepared following a Kröhnke synthesis⁹ and was subsequently oxidized with potassium permanganate to 5-carboxy-2,2'-bipyridine.¹⁰ Reaction of the latter compound with thionyl chloride yielded 5-chlorocarbonyl-2,2'-bipyridine. This molecule was coupled to 13-aza-1,4,7,10-tetraoxacyclopentadecane to yield **1**.

Synthesis and description of the crystal structure of complex 2. Reaction of 1 equivalent of Cu-(ClO₄)₂·6H₂O with **1** in ethanol gave a clear

blue solution. Evaporation of the solvent and recrystallization from ethanol yielded a bright blue crystalline complex **2** of stoichiometry [Cu(II)·1.2H₂O·2ClO₄·3C₂H₅OH] (95% yield). An X-ray analysis was carried out to determine the structure of **2**. The crystal data and a summary of the structure solution and refinement are given in Table I, some interatomic distances in Table II, and data regarding hydrogen bonds in Table III. Figure 1 shows a drawing and the atomic numbering scheme for **2**. The crystallographic analysis shows that complex **2** has a 1:1 metal to ligand stoichiometry.

In the solid state, **2** actually is a dimer around a crystallographic center of symmetry: the cop-

TABLE I Crystal Data and Summary of Intensity Data Collection and Structure Solution and Refinement for Complex **2**, (Cu(II)·1.3CH₃CH₂OH·2ClO₄), and [Cu(bipyridine)₂Cl]ClO₄.

	Complex 2 (Cu(II)·1.3CH ₃ CH ₂ OH·2ClO ₄)	[Cu(bipyridine) ₂ Cl]ClO ₄
<i>Crystal data</i>		
Compound	C ₂₇ H ₁₉ N ₃ O ₁₈ Cl ₂ Cu	C ₂₀ H ₁₆ N ₄ O ₄ Cl ₂ Cu
Crystallization	EtOH/CH ₂ Cl ₂	EtOH
Formula weight	838.13	510.82
Crystal system	triclinic	monoclinic
Space group	P1	P2 ₁ /c
Cell constants	Least-squares fit for 25 reflections 9° < θ < 12°	Least-squares fit for 25 reflections: 10° < θ < 14°
a, Å	10.160(1)	10.7498(5)
b, Å	13.014(1)	12.2394(7)
c, Å	15.934(1)	16.9776(9)
α, °	74.18(1)	90
β, °	84.83(1)	112.248(4)
γ, °	71.54(1)	90
Cell volume, Å ³	1923.0(4)	2067.5(2)
Formula units/unit cell	2	4
D _{calc} , g cm ⁻³	1.448	1.641
μ, mm ⁻¹ (Mo Kα)	0.782	1.35
F(0 0 0), electrons	878	1036
<i>Intensity data collection</i>		
Diffractometer	Enraf-Nonius CAD-4	Enraf-Nonius CAD4T
Scan Mode	(ω-2θ)	(ω-2θ)
Temperature, K	298	298
Radiation, graphite monochromator	Mo Kα (λ = 0.71073 Å)	Mo Kα
Crystal dimensions, mm	0.50 × 0.29 × 0.18	0.05 × 0.25 × 0.25
Standard reflections	3, every 250 reflections	3, every hour
Decay of standards	0.97 – 1.02	none
Reflections measured	13567	10434
2θ-range, °	up to 25	4–55
range of h, k, l	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -18 ≤ l ≤ 18	-13 ≤ h ≤ 13, -15 ≤ k ≤ 0, -22 ≤ l ≤ 22

TABLE I (continued)

	Complex 2 (Cu(II)-1.3CH ₃ CH ₂ OH·2ClO ₄)	{Cu(bipyridine) ₂ Cl}ClO ₄
Corrections:		
Lorentz-polarization EMPABS ¹¹	0.98–1.03	
Reflections (observed)	6793 (2833, I > 3σ(I))	4732 (2447, F > 3σ(F _o))
	R _{merge} ^a 0.085 (0.048)	R _{av} 0.046
Computer programs ^b	local programs	
<i>Structure solution and refinement</i>		
Structure solution	Vector search methods ¹² using Cu-bipyridine as a model; three solvent molecules (EtOH) from Fourier map	Heavy atom Patterson methods
Computer programs	DIRDIF/ORIENT ¹³	DIRDIF/PATT ¹³
Structure refinement non-H atoms	Full-matrix least squares on F ² ; C(1) through C(12): isotropic split-up atoms: isotropic remaining atoms: anisotropic	anisotropic
H-atoms	H(301) on O(30), H(311) and H(312) on O(31) from Fourier map; isotropic remaining H-atoms: calculated positions, constrained isotropic	from difference density map, isotropic
Computer programs	SHELXL-93 ¹⁴	SHELXL-93 ¹⁴
Weights ¹⁴	0.110	w ⁻¹ = σ ² (F _o ²) + (0.0732F _o ²) ² + 0.64F _o ²
Shift/esd	less than 0.09	0
No. of restraints/parameters	83/390	0/344
Goodness-of-fit on F ²	1.035	1.004
R index	[I > 2σ(I)] R ₁ = 0.086	[I > 2σ(I)] R ₁ = 0.05
R indices (all data)	R ₁ = 0.180, wR ₂ = 0.232	R ₁ = 0.122, wR ₂ = 0.15
Largest diff. peak e.Å ⁻³	0.55 in the neighbourhood of the disordered ethanol	-0.51, 0.69

$$^a R_{\text{merge}} = \frac{\sum |F_o - \langle F_o \rangle|}{\sum F_o}$$

^busing neutral scattering factors and anomalous dispersion corrections¹⁵

per atom of one complex monomer is linked to the carbonyl oxygen of the related complex monomer (see Figure 2). The intra-dimer copper-copper distance Cu(1)...Cu(1') is 6.592(2) Å. Each of the copper centers is six-coordinated and surrounded by one bipyridyl unit, two wa-

ter molecules, one perchlorate oxygen, and a carbonyl oxygen atom of the related complex. The coordination geometry around copper is best described as an elongated octahedron. The basal plane of the copper coordination octahedron is formed by N(2), N(8) of the 2,2'-bipyridine

TABLE II Interatomic Distances (Å) and Angles (°) Relevant to the Coordination of the Copper Atom in 2.^a

Atoms	Distance	Atoms	Angle	Atoms	Angle
Cu(1)-N(2)	2.001(6)	N(2)-Cu(1)-O(29')	100.0(2)	O(30)-Cu(1)-O(29')	96.5(2)
Cu(1)-N(8)	1.986(6)	N(8)-Cu(1)-N(2)	81.2(2)	O(30)-Cu(1)-O(31)	91.3(2)
Cu(1)-O(30)	1.956(5)	N(8)-Cu(1)-O(29')	86.1(2)	O(31)-Cu(1)-N(8)	93.7(2)
Cu(1)-O(31)	1.980(5)	O(30)-Cu(1)-N(2)	93.5(2)	O(31)-Cu(1)-O(29')	85.4(2)
Cu(1)-O(29')	2.334(5)				
Cu(1)-O(32)	2.527(6)				

^aPrimed atom: -x, -y + 1, -z

TABLE III Hydrogen Bonds in the X-ray Structure of 2.^a

D	H	A	D - H	H...A	D...A	D - H...A
O(20A)		O(43A')			2.84(2)	
O(20A)		O(43B')			2.67(2)	
O(20B)		O(43A')			2.80(2)	
O(20B)		O(43B')			2.66(2)	
O(23A)		O(40)			2.49(2)	
O(23B)		O(40)			3.02(2)	
O(30)		O(43A')			2.59(2)	
O(30)		O(43B')			2.62(2)	
O(30)	H(301)	O(46)	1.05	1.76	2.65(1)	140
O(31)	H(311)	O(40)	0.97	1.87	2.64(1)	135
O(31)	H(312)	O(17)	1.05	1.90	2.74(1)	154
O(36A')		O(46)			3.08(2)	
O(36B)		O(46)			2.68(2)	
O(39B)		O(46)			3.03(2)	

^aD = donor atom, A = acceptor atom, primed atom: $-x, -y + 1, -z$; double primed atom: $-x, -y + 1, -z + 1$; Lengths in Å and angles in degrees.

ligand and O(30) and O(31) of the two water molecules (see Table II). The apical positions are occupied by a monodentate coordinating ClO_4^- anion (O(32)) and a carbonyl oxygen (O(29')). The second ClO_4^- anion is not within coordinating distance of the copper. The bond lengths (Table II) are well within the range of what is normally found for Cu(II)-bipyridine complexes.¹⁷ As many as seven hydrogen bonds to water and

ethanol are present in the structure (see Table III). As a result of the stabilizing effect of the hydrogen bonds the crown ether ring is partly unfolded. It has an elongated shape and lies more or less in the same plane as the bipyridine unit. The Cu-N and Cu-O distances in 2 match those determined for $[\text{Cu}(\text{bipy})(\text{H}_2\text{O})_4]^{2+}$ by EXAFS^{6d} (Table IV). The deviation in the axial bond lengths in the two complexes is probably

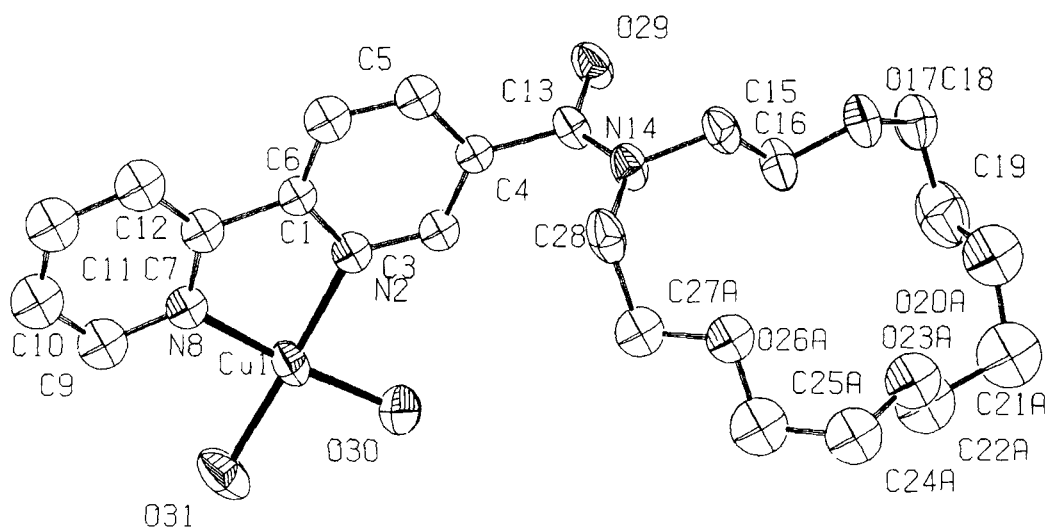


FIGURE 1 X-ray structure of complex 2 showing the crystallographic numbering scheme¹⁷. The axial coordinating carbonyl atom O(29'), the ethanol molecules O(40)-C(41)-C(42); O(43)-C(44)-C(45); O(46)-C(47)-C(48), and the perchlorate atoms Cl(2) with O(36) through O(39) have been omitted for clarity. From the coordinating perchlorate group the atoms O(33) through O(35) have also been omitted. Ellipsoids drawn at the 50% probability level.

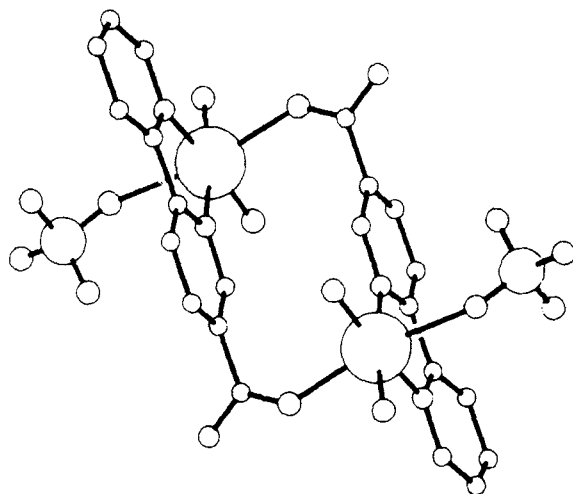


FIGURE 2 Drawing showing the copper(II) coordination sphere within the dimeric complex **2** and the connectivity between the dimeric units. The crown ether moieties, the non-coordinating perchlorate ions and the solvent ethanol molecules have been omitted for clarity.

the result of the fact that the O-donors in complex **2** (ClO_4^- and $\text{C}=\text{O}$) and in $[\text{Cu}(\text{bipy})(\text{H}_2\text{O})_4]^{2+}$ (water molecules) are different.

Magnetic properties. The crystals which we used for the analysis by X-ray crystallography were extremely hygroscopic and therefore not well suited for magnetic measurements. Powdering and subsequent drying at reduced pressure yielded a product (**2'**) in which ethanol was removed and four water molecules are present per copper as indicated by elemental analysis (see Experimental Section). A plot of $(X_M^{\text{corr}})^{-1}$ vs. T for **2'** is given in Figure 3. The data obey the Curie-Weiss law very well; least-square refine-

TABLE IV Comparison of the Bond Lengths in **2** with those in $[\text{Cu}(\text{bipy})(\text{H}_2\text{O})_4]^{2+}$.^a

2	Distance (Å)	$[\text{Cu}(\text{bipy})(\text{H}_2\text{O})_4]^{2+}$	Distance (Å)
Cu(1)-N(2)	2.001(6)	Cu-N	1.99
Cu(1)-N(8)	1.986(6)		
Cu(1)-O(30)	1.956(5)	Cu-O	1.97
Cu(1)-O(31)	1.980(5)		
Cu(1)-O(29')	2.334(5)	Cu-O	2.33
Cu(1)-O(32)	2.527(6)		

^aFrom ref. 6d, determined by EXAFS.

ment to the expression $X_M^{\text{corr}} = C/T$ gave $C = 0.4596$ (solid line in Figure 3). From this result, the g value can be calculated using the expression $C = Ng^2\beta^2/4k$, yielding $g = 2.21$, which is a typical value for Cu(II). The g-value and the observation of Curie-Weiss behaviour by **2'** indicate that exchange interactions between the copper centers are absent. This is in line with the expectation that neither a short Cu-Cu distance nor a superexchange pathway, conditions necessary to mediate spin-spin coupling¹⁸, are present in **2'**.

Conductivity and electrochemistry. In acetonitrile solution, **2'** behaves as a 2:1 electrolyte. The complex was examined with cyclic voltammetry but displayed no (electro)chemically reversible behaviour. This problem is more often encountered with (bi)pyridine-Cu(II) complexes.¹⁹⁻²¹ Possibly, the reduced form of this type of complexes is unstable, resulting in the decomposition of the compounds.

Complexation properties. Since the basal plane of **2** is formed by two strong N-ligands from the bipyridine-unit and two weak O-ligands from water it was expected that the latter ligands could be exchanged for other N-type ligands like imidazole. In addition, the crown-ether function could provide secondary stabilization if the imidazole ligand would possess a quaternary ammonium group. For these reasons we chose histamine.HX (Hs.HX, X = Cl^- or ClO_4^-) as the guest for our complexation studies.

To see whether copper(II)-bipyridine complexes are able to coordinate additional ligands, we first titrated $\text{Cu}(\text{bipy})_2(\text{ClO}_4)_2$ with Hs.HCl. A plot of the absorbance versus the ratio Hs.HCl/Cu(II) revealed that 1 equivalent of Hs.HCl reacted per copper ($\Delta\epsilon$ at 720 nm, $224 \text{ M}^{-1}\cdot\text{cm}^{-1}$, $K_{\text{ass}}, 2150 \text{ M}^{-1}$). After one night, clear blue crystals could be isolated from the solution in the cuvette. X-ray crystallographic analysis (*vide infra*) proved that the copper in these crystals is five coordinated. However, instead of the

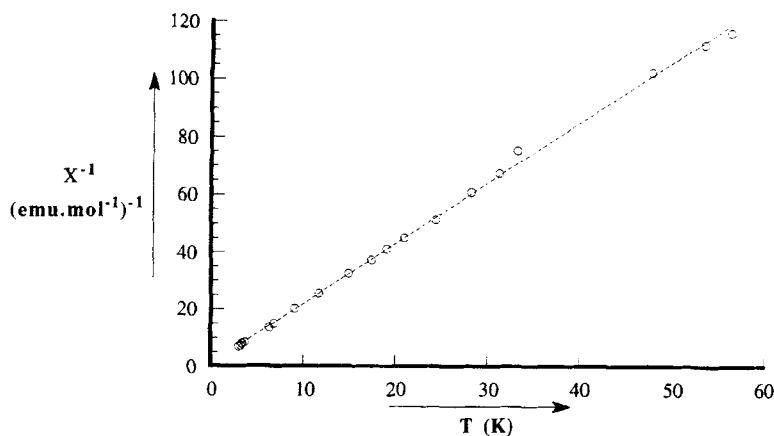


FIGURE 3 The inverse molar susceptibility as a function of the temperature.

imidazole moiety, a chloride atom (from Hs.HCl) has occupied the fifth coordination position at the copper center (see Figure 4). This complex is identical to that prepared in a different way by Hathaway and coworkers.²² From these results it must be concluded that, at least for bis(2,2'-bipyridyl)Cu(II) complexes, chloride is a better ligand than Hs. Steric hindrance and electrostatic repulsion may be the explanation for this.

A UV-vis titration of **2** with imidazole (Im) indicated that 2 equiv. of this ligand are bound, probably by substituting two coordinated water molecules. The 2Im_2 complex had λ_{max} 613 nm (ϵ $8.2 \cdot 10^3 \text{ l.mol}^{-1} \cdot \text{cm}^{-1}$). The spectra revealed an isosbestic point at 812 nm between 0–1 equivalent of added Im, but not above the ratio Cu:Im = 1. This leads us to the conclusion that preferably a 1:1 complex is formed which at higher ratios of Im to **2** is slowly converted into a 2:1 (Im:Cu) complex. The association constants were too high to be estimated by the UV-vis method.

For complexation of Hs.HCl with **2**, one may expect that electrostatic repulsion between the protonated amine and the Cu(II) center will result in a lowering of K_{ass} as compared to Im. Furthermore, the chloride ion may compete with the imidazole moiety for the binding to the copper ion since it has a high affinity for Cu(II). As

could be determined from a plot of the absorbance at 710 nm (λ_{max} , ϵ $1.1 \cdot 10^5 \text{ l.mol}^{-1} \cdot \text{cm}^{-1}$) versus the Hs/2 ratio, one equivalent of Hs.HCl is bound. A K_{ass} of 70 M^{-1} was found. That the Im moiety of Hs is coordinated to Cu(II) was indicated by the development of a dark green colour, typical for Cu(II) complexes with three N-donor ligands. The fact that Im and not Cl^- is responsible for this colour change was further confirmed by adding a saturated solution of

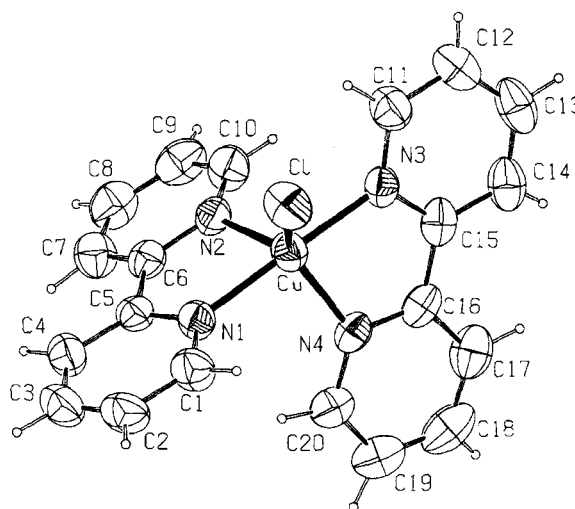


FIGURE 4 X-ray structure of the $[\text{Cu}(\text{bipy})_2\text{Cl}]\text{ClO}_4$ complex with the crystallographic numbering scheme.¹⁷ Ellipsoids drawn at the 50% probability level.



FIGURE 5 (left) Proposed binding of protonated histamine to **2'**. (right) Coordination polymer of **2'** and histamine.

NaCl to a solution of **2** in ethanol. In this case no colour change was observed. The ability of the histamine imidazole to compete more effectively with chloride ion for coordination to Cu(II) in **2** than in the control compound $\text{Cu}(\text{bipy})_2(\text{ClO}_4)_2$ is explained by the additional interaction of the histamine ammonium ion moiety with the crown ether in **2**.

We also carried out a titration of **2** with Hs.HClO₄. The change of counterion had a remarkable effect on the association constant, which increased to 1000 M^{-1} . Still, only one Hs-molecule was bound, and the resulting UV-vis spectrum was identical to that of the complex with Hs.HCl ($\lambda_{\text{max}} 710 \text{ nm}$, $\epsilon 1.1 \cdot 10^5 \text{ l.mol}^{-1} \cdot \text{cm}^{-1}$). In order to evaluate the binding properties of the crown ether moiety, a similar titration was carried out in the presence of Na⁺-ions. The latter ions are known to have a high affinity for 15-crown-5 and may occupy the crown ether ring, thereby blocking the second binding site for the protonated amine function of Hs. With 3 equivalents of NaClO₄ the K_{ass} was lowered to 750 M^{-1} , and the UV-vis spectrum of the complex had $\lambda_{\text{max}} 710 \text{ nm}$ ($\epsilon 9.2 \cdot 10^4 \text{ l.mol}^{-1} \cdot \text{cm}^{-1}$). We believe that this lower value of K_{ass} is mainly due to the competition between the Na⁺ ions and the protonated amine function of Hs. It should be noted, however, that this may not be the only reason. Fore-

most, the ionic strength of the solution is also drastically altered. Secondly, the electrostatic repulsion between **2** and the protonated Hs guest is increased when a cation is complexed in the crown ether ring. Nevertheless, the results lead us to propose a structure for the complex of **2** with Hs in which the imidazole group of the Hs guest coordinates to the Cu(II) ion of **2**, and the ammonium group is bound in the crown ether moiety of the same molecule of **2** (Figure 5, left).

The possible formation of polymeric species during the titrations cannot be ruled out completely. However, in order for this to happen the amine moiety must be deprotonated. This is not very likely under the present conditions. We tried to form a polymeric species deliberately by titrating **2** with the free base Hs. During this experiment, an insoluble blue precipitate was formed rapidly. Because of its insoluble nature, it is presumed to be a coordination polymer of Hs and **2** (Figure 5, right). This material was not further characterized. This result supports the idea that in the titrations with Hs.HX (X is Cl⁻ or ClO₄⁻) monomeric species are predominant.

Description of the structure of $\{\text{Cu}(\text{bipyridine})_2\text{Cl}\}\text{ClO}_4$. The structure of this complex is given in Fig. 4. Some interatomic distances are given in Table V. The monoclinic unit cell contains 4

TABLE V Interatomic Distances (Å) and Angles (°) Relevant to the Coordination of the Copper Atom in $\{\text{Cu}(\text{bipyridine})_2\text{Cl}\}\text{ClO}_4$.

Atoms	Distance	Atoms	Angle	Atoms	Angle
Cu-Cl	2.2610(14)	Cl-Cu-N(1)	92.04(11)	N(1)-Cu-N(3)	174.55(16)
Cu-N(1)	1.985(3)	Cl-Cu-N(2)	126.38(11)	N(1)-Cu-N(4)	96.26(14)
Cu-N(2)	2.134(4)	Cl-Cu-N(3)	93.41(11)	N(2)-Cu-N(3)	97.60(13)
Cu-N(3)	1.987(3)	Cl-Cu-N(4)	137.03(11)	N(2)-Cu-N(4)	96.60(14)
Cu-N(4)	2.071(4)	N(1)-Cu-N(2)	79.02(13)	N(3)-Cu-N(4)	79.80(14)

Cu(BiPy)₂Cl⁺ cations and 4 ClO₄⁻ anions. Interesting structural details reported by Hathaway and coworkers²² are confirmed in this study. In particular the Cu-N bond distance range, 1.985(3) – 2.134(4) Å is reproduced in detail. Quantitative analysis of the coordination around Cu shows it to be 32% on the Berry pseudo rotation path from trigonal pyramidal towards square pyramidal.²³

CONCLUSIONS

We have shown that it is possible to synthesize a well defined Cu(II) complex which contains a bipyridine ligand in a 1:1 metal to ligand ratio without the need for an additional strong, chelating anion or ligand. The structure of the complex has been determined by single-crystal X ray diffraction. The copper complex is able to bind imidazole and also mono-protonated histamine.²⁴ The latter molecule is bound with the help of a crown ether function tethered to the bipyridine ligand. The crown ether probably plays a role in stabilizing the protonated amine-function and thereby contributing to K_{ass}. It may be possible to improve the performance of the receptor by including a methylene group instead of the carbonyl linker between the aza crown ether and bipyridine moieties in **2**. This spacer would be more flexible and improve the complexing potential of the aza crown ether nitrogen.

MATERIALS AND METHODS

Instrumentation. UV-vis spectra were recorded on a Perkin-Elmer Lambda 5 spectrophotometer. Melting points were determined on a Reichert hot stage mounted to a microscope and are reported uncorrected. ¹H and ¹³C NMR spectra were recorded on a Bruker WH90 or a Bruker WM-400. FAB-MS spectra were recorded on a VG 7070E using 3-nitrobenzyl alcohol as a ma-

trix. IR-spectra were measured on a Perkin-Elmer 1720X. Conductivity measurements were carried out with a Schott Geräte CG 852 Konduktometer using 10⁻³ M solutions of the complex in acetonitrile. Variable-temperature magnetic susceptibility data were collected in the temperature range 4.2–270 K by using an Oxford Instruments Foner-type magnetometer, calibrated with a Ni-sample. A main solenoid field of 12000 G was employed. Temperatures were recorded with calibrated resistance thermocouples.

Materials. Cu(ClO₄)₂·6H₂O was purchased from Janssen Chimica. All solvents were dried and distilled prior to use. Purification of the synthesized compounds was performed by flash chromatography on silica (Merck kieselgel 60H). TLC analyses were performed on Merck Kieselgel 60 F₂₅₄ silica gel plates.

Warning! Although the perchlorate salts described here were not found to be shock sensitive, care should be taken in handling these compounds.²⁵

SYNTHESIS AND CHARACTERIZATION

5-Methyl-2,2'-bipyridine. This compound was synthesized as described in the literature.⁹

2,2'-Bipyridine-5-carboxylic acid. This compound was synthesized as described by Case¹⁰ for the preparation of 5,5'-dicarboxyl-2,2'-bipyridine.

5-Chlorocarbonyl-2,2'-bipyridine. A suspension of 300 mg (1.5 mmol) of 5-carboxyl-2,2'-bipyridine in 15 ml of SOCl₂ was refluxed under a dinitrogen atmosphere. The solid material dissolved completely after 30 min. of refluxing and stayed homogeneous. After 15 hrs. the excess of SOCl₂ was evaporated. The product was characterized by the disappearance of the OH-vibration at 3500 cm⁻¹.

1-[5-(2,2'-bipyridyl)carbonyl]-1-aza-4,7,10,13-tetraoxacyclopentadecane (**1**). To a solution of CH_2Cl_2 (50 ml) containing 516 mg of triethylamine (5.1 mmol) and 560 mg (2.55 mmol) of monoaza-15-crown-5 was added 573 mg (2.6 mmol) of 5-chlorocarbonyl-2,2'-bipyridine. This solution was stirred for 15 hrs. after which it was concentrated. The resulting oil was subjected to column chromatography (eluent 2% MeOH in CHCl_3) to yield **1** in 52% yield. Since 2,2'-bipyridine gives an intense red colour with Fe(II), an aqueous solution of FeSO_4 was used to identify the product on a TLC-plate. IR (KBr): 2864 (br, CH_2), 1632 ($\text{C}=\text{O}$), 1126 (C-O-C) cm^{-1} . ^1H NMR (CDCl_3): δ 3.6 and 3.8 (2 \times s, 20H, $\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$), 7.4 (m, 1H, pyH), 7.9 (m, 2H, pyH), 8.4 (m, 2H, pyH), 8.7 (m, 2H, pyH); ^{13}C NMR (CDCl_3 , assignment with the crystallographic numbering scheme, Fig. 1): δ 48.3 (N- CH_2), 69.0 (CH_2), 69.5 (CH_2), 70.3 (CH_2), 70.8 (CH_2), 120.5 (bipy-C12), 121.4 (bipy-C6), 124.1 (bipy-C9), 132.4 (bipy-C4), 135.7 (bipy-C11), 137.0 (bipy-C5), 147.3 (bipy-C10), 149.3 (bipy-C3), 155.4 (bipy-C1), 156.7 (bipy-C7), 169.8 ($\text{C}=\text{O}$).

Complex 2. Ligand **1** (200 mg, 0.5 mmol) was dissolved in 20 ml of ethanol. To this solution was added 182 mg (0.5 mmol) of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, dissolved in 5 ml of ethanol. The solution was refluxed for 30 min. and subsequently concentrated *in vacuo*. Recrystallization from ethanol yielded **2** as light blue crystals, which are very hygroscopic. In order to remove the ethanol molecules from the crystal lattice, the crystals were powdered and dried at reduced pressure for a prolonged period of time. This yielded a product (**2'**) in which four water molecules are present per copper as indicated by elemental analysis (see below). These water molecules could not be removed from the complex. Apparently, complex **2**, which contains only 2 water molecules, takes up 2 additional water molecules during powdering. These molecules are thought to displace the perchlorate and carbonyl oxygen atoms in the coordination sphere, yielding the monomeric species

2'. Comparison of the IR-spectra of the free ligand and the dried complex **2'** showed no shift in frequency of the $\text{C}=\text{O}$ vibration, which supports this explanation. IR (CsI): 2934 (CH_2), 1632 ($\text{C}=\text{O}$), 1471, 1446 ($\text{C}=\text{C}$, $\text{C}=\text{N}$), 1107, 625 (ClO_4) cm^{-1} . UV-vis in ethanol (λ_{max} nm; ϵ $1 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$): 705; 29. $\Lambda_{\text{M}} = 292 \text{ S} \cdot \text{cm}^2 \cdot \text{M}^{-1}$ (10^{-3} M in acetonitrile). FAB-MS: m/z 563 (56%, $1 \cdot \text{Cu}(\text{ClO}_4)^+$); 464 (100%, $1 \cdot \text{Cu}^+$). Anal. Calcd. for $\text{C}_{21}\text{H}_{27}\text{N}_3\text{O}_{13}\text{Cl}_2\text{Cu} \cdot 4\text{H}_2\text{O}$: C, 34.27; H, 4.79; N, 5.71. Found: C, 34.18; H, 4.70; N, 5.53.

Bis-bipyridylcopper(II) bisperchlorate. This compound was synthesized from 1 g (2.71 mmol) of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 846 mg (5.42 mmol) of 2,2'-bipyridine, and recrystallized from ethanol/water. Anal. calcd. for $\text{C}_{20}\text{H}_{16}\text{N}_4\text{O}_8\text{Cl}_2\text{Cu}$: C 41.79, H 2.81, N 9.75; found: C 41.76, H 2.78, N 9.62.

Crystals of $\{\text{Cu}(\text{bipyridine})_2\text{Cl}\}\text{ClO}_4$. Crystals of $\{\text{Cu}(\text{bipyridine})_2\text{Cl}\}\text{ClO}_4$ were obtained when the final solution of a UV-vis titration experiment (see below) of bis-bipyridylcopper(II) bisperchlorate with histamine.HCl was allowed to stand at room temperature for one night.

UV-vis titration experiments. In a typical procedure 2.5 ml of a stock solution containing 2.84×10^{-2} mmol of complex **2** in 5 ml of ethanol was transferred to a quartz cuvette (path length 1.000 cm) in a thermostatted compartment of a Perkin Elmer λ -5 UV-vis photospectrometer operated in the double beam mode. Subsequently, 10 μl aliquots of a stock solution containing 4.62×10^{-1} mmol Hs.HX in 5 ml of ethanol were added using a micropipette. The increase in the absorbance at 710 nm was measured and stored on a computer disk. Best fits through at least 20 data points were obtained using the computer program UV-fit. In order to check the validity of the method, the reverse experiment (titration of Hs.HX with complex **2**) was carried out as well. This procedure led to identical results.

Magnetic susceptibility measurements. For these measurements, a 30 mg sample of **2'** (of stoichiometry $\text{Cu}(\text{II}) \cdot 1 \cdot 4\text{H}_2\text{O} \cdot 2\text{ClO}_4$, see above) was

placed in a teflon cup with known magnetic susceptibility. The assembly was transferred to the magnetometer and cooled to approximately 4 K. In small steps, the temperature was increased and allowed to stabilize for several minutes before the magnetization was recorded.

X-ray structure determination of complex 2. The crystal data for complex 2 ($\text{Cu(II)} \cdot 1.3\text{CH}_3\text{CH}_2\text{OH} \cdot 2\text{ClO}_4$) and a summary of the data collection and the structure solution and refinement are given in Table I. The structure solution revealed the presence of three solvent ethanol molecules. The structure refinement was hampered by dis-

order expressed by some large displacement parameters. Thus, the positions of part of the crown ether chain, one perchlorate anion and one solvent molecule were split up to supply models for disorder (denoted A and B). The atomic positions were subjected to geometrically-restrained refinement which led to a reasonable hydrogen-bonding scheme (Table III). The atomic positional and vibrational parameters are given in Table VI. The crystallographic numbering scheme is given in Fig. 1 showing an ORTEP drawing of the complex cation; for clarity only the A atoms (occupance 0.56) of the disorder model are shown and hydrogen atoms as well as anions and solvent

TABLE VI Atomic Coordinates and Equivalent Isotropic Displacement Parameters for the Crystal Structure of 2. $U(\text{eq})$ is Defined as One Third of the Trace of the Orthogonalized Uij Tensor.

	x	y	z	$U(\text{eq}) (\text{\AA}^2, \times 100)$
Cu(1)	0.1802(1)	0.2948(1)	-0.0868(1)	4.3(1)
C(1)	0.2577(7)	0.3456(5)	0.0611(4)	3.5(2)
N(2)	0.1949(6)	0.3977(4)	-0.0174(4)	3.8(1)
C(3)	0.1536(7)	0.5112(5)	-0.0407(5)	3.8(2)
C(4)	0.1734(7)	0.5732(5)	0.0118(4)	3.3(2)
C(5)	0.2318(8)	0.5175(6)	0.0923(5)	4.7(2)
C(6)	0.2738(8)	0.4016(6)	0.1160(5)	5.2(2)
C(7)	0.3077(8)	0.2196(6)	0.0772(5)	4.3(2)
N(8)	0.2802(6)	0.1806(5)	0.0161(4)	4.1(1)
C(9)	0.3233(9)	0.0681(7)	0.0258(6)	5.9(2)
C(10)	0.3986(9)	-0.0028(8)	0.0979(6)	6.6(2)
C(11)	0.4270(9)	0.0355(7)	0.1592(6)	6.6(2)
C(12)	0.3811(9)	0.1540(7)	0.1501(6)	6.0(2)
C(13)	0.1250(7)	0.6997(5)	-0.0123(5)	3.7(2)
N(14)	0.2012(5)	0.7543(4)	-0.0655(4)	3.9(2)
C(15)	0.1613(8)	0.8773(5)	-0.0774(5)	4.5(2)
C(16)	0.0490(8)	0.9418(5)	-0.1427(5)	5.3(2)
O(17)	0.0198(5)	1.0566(4)	-0.1435(3)	5.0(1)
C(18)	-0.1103(8)	1.1269(6)	-0.1792(6)	5.7(2)
C(19)	-0.1232(10)	1.1344(8)	-0.2730(7)	8.0(3)
O(20A)*	-0.0107(24)	1.1773(20)	-0.3209(14)	8.4(12)
C(21A)*	0.0239(28)	1.1675(19)	-0.4115(16)	10.0(10)
C(22A)*	0.1132(23)	1.0488(17)	-0.4089(16)	8.5(7)
O(23A)*	0.2434(16)	1.0338(10)	-0.3725(8)	7.2(4)
C(24A)*	0.3499(19)	0.9414(12)	-0.3859(11)	7.5(6)
C(25A)*	0.3337(23)	0.8314(14)	-0.3375(11)	7.8(6)
O(26A)*	0.3287(14)	0.8216(9)	-0.2478(8)	5.3(4)
C(27A)*	0.3204(25)	0.7148(16)	-0.2024(10)	5.7(8)
O(20B)*	-0.0329(29)	1.1840(22)	-0.3231(14)	5.9(10)
C(21B)*	-0.0204(31)	0.1670(18)	-0.4087(15)	6.5(8)
C(22B)*	0.0534(27)	1.0493(19)	-0.4102(18)	8.3(9)
O(23B)*	0.1866(19)	1.0179(11)	-0.3738(9)	5.7(4)
C(24B)*	0.2628(24)	0.9082(18)	-0.3821(15)	8.3(8)
C(25B)*	0.3886(20)	0.8606(18)	-0.3282(12)	6.4(7)

TABLE VI (continued)

	x	y	z	U(eq) (Å ² , × 100)
O(26B)*	0.3649(17)	0.8294(11)	-0.2344(9)	4.8(5)
C(27B)*	0.3451(29)	0.7207(19)	-0.1965(12)	5.3(10)
C(28)	0.3328(7)	0.7005(6)	-0.1041(5)	5.2(2)
O(29)	0.0193(5)	0.7475(5)	0.0243(3)	4.7(1)
O(30)	0.0875(6)	0.4178(4)	-0.1845(3)	5.5(2)
O(31)	0.1931(6)	0.1830(4)	-1.527(4)	6.3(2)
Cl(1)	0.5142(2)	0.3375(2)	0.8593(2)	6.1(1)
O(32)	0.4071(6)	0.3027(6)	0.8366(4)	8.1(2)
O(33)	0.6101(8)	0.3424(7)	0.7919(6)	12.4(3)
O(34)	0.4614(8)	0.4388(6)	0.8835(7)	14.1(4)
O(35)	0.5832(9)	0.2534(7)	0.9322(5)	12.6(3)
Cl(2A)**	0.1593(14)	0.1867(8)	0.3392(7)	9.5(3)
O(36A)**	0.0559(24)	0.2375(16)	0.3966(13)	12.4(8)
O(37A)**	0.2395(20)	0.2545(17)	0.3116(15)	11.4(8)
O(38A)**	0.2273(25)	0.0749(15)	0.3677(15)	13.5(8)
O(39A)**	0.0855(29)	0.2045(29)	0.2506(17)	18.3(12)
Cl(2B)**	0.1040(10)	0.2099(6)	0.3131(6)	8.4(2)
O(36B)**	-0.0100(18)	0.2290(13)	0.3727(11)	10.8(6)
O(37B)**	0.2314(24)	0.2217(25)	0.3469(19)	17.9(12)
O(38B)**	0.1519(23)	0.0908(13)	0.3248(15)	13.9(7)
O(39B)**	0.0625(20)	0.2679(18)	0.2301(11)	13.1(7)
O(40)	0.3166(8)	0.1550(6)	0.6983(4)	9.7(2)
C(41)	0.3702(24)	0.2327(13)	0.6356(11)	18.6(9)
C(42)	0.4683(23)	0.1944(18)	0.5779(17)	25.4(13)
O(43A)***	0.0784(20)	0.6100(11)	0.2844(11)	6.8(5)
C(44A)***	0.1879(35)	0.5163(25)	0.3339(19)	13.6(13)
C(45A)***	0.1340(47)	0.4994(34)	0.4257(21)	20.1(20)
O(43B)***	0.0197(21)	0.6185(12)	0.3131(13)	7.9(6)
C(44B)***	0.1123(34)	0.5197(24)	0.3629(26)	13.5(13)
C(45B)***	0.2506(35)	0.5165(37)	0.3826(34)	21.1(22)
O(46)	0.1849(11)	0.5703(8)	0.7050(6)	13.1(3)
C(47)	0.2552(27)	0.5307(18)	0.6357(14)	20.9(10)
C(48)	0.3527(24)	0.5767(21)	0.5885(19)	23.9(12)
H(301)	0.1612	0.4606	-0.2083	11.3(36)
H(311)	0.2739	0.1783	-0.1903	13.8(46)
H(312)	0.1608	0.1249	-0.1489	10.2(36)

*occupancy factor 0.56/0.44, **occupancy factor 0.47/0.53, ***occupancy factor 0.51/0.49

molecules are omitted. Geometrical calculations and the ORTEP illustration were done with PLATON.¹⁶

X-ray structure determination of {Cu(bipyridine)}₂Cl/ClO₄. The crystal data and a summary of the data collection and the structure solution and refinement are given in Table I. The crystallographic numbering scheme is shown in Figure 4 and the positional parameters of non-hydrogen atoms are given in Table VII. Geometrical

calculations and the ORTEP illustration were done with PLATON.¹⁶ Full details may be obtained from one of the authors (A.L.S.).

Supplementary Material. Anisotropic displacement parameters, bond lengths and angles, hydrogen atom coordinates and isotropic displacement parameters for the crystal structure of complex 2 (5 pages), crystal data and details of the structure determination, final coordinates and equivalent isotropic thermal parameters of

TABLE VII Atomic Positional Parameters of Non-hydrogen Atoms and Ueq's ($\times 100$) with e.s.d.'s for the Crystal Structure of $\{\text{Cu}(\text{bipyridine})_2\text{Cl}\}\text{ClO}_4$.

Atom	x	y	z	U(eq) ($\text{\AA}^2 \times 100$)
Cu	0.12989(5)	0.04465(5)	0.36273(3)	4.47(2)
Cl	0.13785(13)	-0.13990(10)	0.36096(8)	6.32(4)
N(1)	-0.0238(3)	0.0489(3)	0.2514(2)	4.54(12)
N(2)	-0.0102(3)	0.1417(3)	0.3937(2)	4.37(12)
N(3)	0.2826(3)	0.0558(3)	0.4743(2)	4.42(12)
N(4)	0.2349(3)	0.1735(3)	0.3382(2)	4.59(12)
C(1)	-0.0235(6)	-0.068(5)	0.1820(3)	5.74(17)
C(2)	-0.1356(6)	-0.0089(5)	0.1079(3)	6.4(2)
C(3)	-0.2486(6)	0.0457(5)	0.1032(3)	6.21(17)
C(4)	-0.2481(5)	0.1026(4)	0.1733(3)	5.39(17)
C(5)	-0.1333(4)	0.1034(4)	0.2468(3)	4.31(12)
C(6)	-0.1219(4)	0.1632(4)	0.3250(3)	4.33(12)
C(7)	-0.2157(5)	0.2386(4)	0.3277(3)	5.89(17)
C(8)	-0.1922(6)	0.2935(5)	0.4032(4)	6.5(2)
C(9)	-0.0781(6)	0.2729(5)	0.4718(4)	6.5(2)
C(10)	0.0098(5)	0.1960(5)	0.4655(3)	5.61(17)
C(11)	0.2973(5)	-0.0092(5)	0.5419(3)	5.79(17)
C(12)	0.4084(6)	-0.0030(5)	0.6150(3)	6.20(17)
C(13)	0.5068(5)	0.0707(5)	0.6203(3)	6.54(19)
C(14)	0.4915(5)	0.1368(5)	0.5523(4)	6.1(2)
C(15)	0.3779(4)	0.1294(4)	0.4809(3)	4.85(16)
C(16)	0.3490(4)	0.1981(4)	0.4032(3)	4.67(14)
C(17)	0.4309(5)	0.2838(5)	0.3985(4)	6.67(19)
C(18)	0.3918(7)	0.3422(5)	0.3242(5)	7.5(3)
C(19)	0.2754(6)	0.3195(5)	0.2586(4)	6.6(2)
C(20)	0.1992(5)	0.2339(4)	0.2670(3)	5.58(17)
Cl(2)	0.35968(12)	0.10581(11)	0.13362(8)	5.82(4)
O(1)	0.2526(5)	0.1719(5)	0.0885(3)	13.2(2)
O(2)	0.4121(5)	0.0544(5)	0.0784(3)	12.6(2)
O(3)	0.4629(4)	0.1676(4)	0.1955(3)	9.62(19)
O(4)	0.3237(7)	0.0269(5)	0.1794(4)	15.6(3)

U(eq) = 1/3 of the trace of the orthogonalized U

the non-hydrogen atoms, hydrogen atom positions and isotropic thermal parameters, bond distances, bond angles, and torsion angles for the crystal structure of $\{\text{Cu}(\text{bipyridine})_2\text{Cl}\}\text{ClO}_4$ (20 pages).

Acknowledgements

The authors thank NWO, the Dutch Research Council, and its chemical branch, SON, for financial support (to C.F.M, W.J.J.S, and A.L.S.). Mr. C.J. Beers of the Department of Experimen-

tal Solid State Physics, University of Nijmegen, is acknowledged for assistance with the magnetic susceptibility measurements.

References

- [1] *Bio-inorganic Chemistry of Copper*, Karlin, K. D. and Tyeklár, Z. (Eds.) Chapman & Hall, New York, London, 1993
- [2] a Niele, F. G. M.; Martens, C. F.; Nolte, R. J. M.; *J. Am. Chem. Soc.* **1989**, 111, 2078
- [3] Lerch, K., *Life Chem. Reports* **1987**, 5, 221
- [4] Villafranca, J. J., in *Metal Ions in Biology* (Spiro, T. G., Ed.) Vol. III "Copper Proteins", John Wiley & Sons, New York, 1980, p. 263

- [5] Part of this work has been described in a preliminary form, cf. Martens, C. F.; Schenning, A. P. H. J.; Feiters, M. C.; Beurskens, G.; Beurskens, P. T.; Nolte, R. J. M., *Inorg. Chim. Acta* **1991**, 190, 163
- [6] a Hathaway, B. J.; Procter, I. M.; Slade, R. C.; Tomlinson, A. A. G.; *J. Chem. Soc. (A)* **1969**, 2219.
b Fereday, R.J.; Hodgson, P.; Tyagi, S.; Hathaway, B.J.; *J. Chem. Soc., Dalton Trans.* **1981**, 2070
c Onggo, D.; Craig, D.C.; Rae, A. D.; Goodwin, H.A.; *Aus. J. Chem.* **1991**, *44*, 219
- [7] a Nakai, H.; *Bull. Chem. Soc. Jpn.* **1977**, 50, 531
- [8] Cram, D. J.; Helgeson, R. C.; Peacock, S. C.; Kaplan, L. J.; Domeier, L. A.; Moreau, P.; Koga, K.; Mayer, J. M.; Chao, Y.; Siegel, M. G.; Hoffman, D. H.; Sogah, G. D. Y.; *J. Org. Chem.* **1978**, 43, 1930
- [9] Kröhnke, H.; *Synthesis* **1976**, 1
- [10] Case, F. H.; *J. Am. Chem. Soc.* **1948**, 68, 2574
- [11] North, A. C. T.; Philips, D. C.; Mathews, F. S.; *Acta Cryst.* **1968**, A24, 351
- [12] Beurskens, P. T.; Beurskens, G.; Strumpel, M.; Nordman, C. E.; *Patterson and Pattersons*, Glusker, J. P.; Patterson, B. K.; Rossi, M. Clarendon Press, Oxford, 1987
- [13] Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C.; *The DIRDIF program system, Technical Report of the Crystallographic Laboratory*, University of Nijmegen, The Netherlands, 1992
- [14] G. M. Sheldrick, *SHELXL-93, Program for crystal structure refinement*, University of Göttingen, Germany, 1993
- [15] *International Tables for X-ray Crystallography*, Vol. VI, Kynoch Press, Birmingham, 1974
- [16] Spek, A. L.; *Acta Cryst.* **1990**, A46, C34
- [17] Nakai, H.; *Bull. Chem. Soc. Jpn.* **1971**, 44, 2412
- [18] Mabbs, F. E.; Machin, D. J.; *Magnetism and Transition Metal Complexes*, Chapman & Hall, London, 1973
- [19] Klein Gebbink, R. J. M.; Martens, C. F.; van der Linden, J. G. M.; Kooijman, H.; Smeets, W. J. J.; Spek, A. L.; Feiters, M. C.; Nolte, R. J. M.; to be published
- [20] Christou, G.; Perlepes, S. P.; Libby, E.; Folting, K.; Huffman, J. C.; Webb, R. J.; Hendrickson, D. N.; *Inorg. Chem.* **1990**, 29, 3657
- [21] Yao, Y.; Perkovic, M. W.; Rillema, D. P.; Woods, C.; *Inorg. Chem.* **1992**, 31, 3956
- [22] Harrison, W. D.; Kennedy, D. M.; Power, M.; Sheahan, R.; Hathaway, B. J.; *J. Chem. Soc., Dalton Trans.* **1981**, 1556
- [23] Holmes, R. R.; *Inorg. Chem.* **1984**, 32, 119
- [24] Protonation occurs predominantly at the amino nitrogen. Some protonation also occurs at the imidazole nitrogen; however, the amount is too small to be detected by standard methods. See Noszál, B.; Rabenstein, D.; *J. Phys. Chem.* **1991**, 95, 4761
- [25] Wolsey, W. C.; *J. Chem. Educ.* **1973**, 50, A335