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LETTER

First example of a 1:1 copper(II)–2,2′-bipyridine complex

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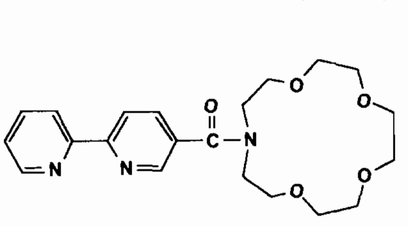
2,2′-Bipyridines are well-known ligands which form complexes with copper(II) in a 1:2 metal to ligand ratio [1–4]. As part of our program aimed at the development of host molecules which contain a metal center as well as a binding site (so called metallohosts [5]), we describe here a novel crown ether substituted 2,2′-bipyridine ligand (**1**). Ligand **1** forms an unusual 1:1 complex with copper(II) (**2**, Fig. 1).

Ligand **1** was synthesized by treating 1,4,7,10-tetraoxa-13-azacyclopentadecane [6] with 5′-chlorocarbonyl-2,2′-bipyridine [7, 8] in dichloromethane in the presence of triethylamine as a base. Column chromatography (silica 60H, eluent $CHCl_3$/MeOH 98/2 vol./vol.) yielded ligand **1** in 52% yield ($R_f = 0.6$ on silica 60H, $CHCl_3$/MeOH 9/1 vol./vol.).

Addition of 1 equiv. of $Cu(ClO_4)_2\cdot 6H_2O$ to **1** in ethanol gave a clear blue solution. Evaporation of the solvent and recrystallization from ethanol yielded metallohost **2** as blue crystals (95% yield). The stoicheiometry of the complex was $[Cu(\mathbf{1})](ClO_4)_2\cdot(C_2H_6OH)_3\cdot(H_2O)_2$.



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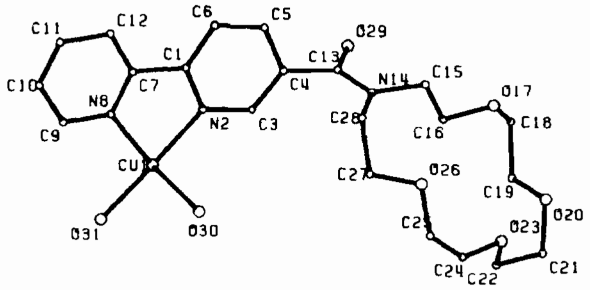

Fig. 1. Drawing of complex **2**. The solvent molecules, hydrogen atoms, anions and axial ligands are omitted for clarity.

The UV–Vis spectrum of **2** showed an absorption band at 705 nm ($\epsilon = 29$ mol l^{-1}). In the mass spectrometer (matrix glycerol or nitrobenzylalcohol) **2** was partly reduced to the copper(I) state. The most intense peaks were found at m/z 563 ($M-ClO_4$) and m/z 464 ($M-2ClO_4$). Cyclic voltammetry on complex **2** in CH_3CN revealed a quasi-reversible Cu^{II}/Cu^{I} reduction wave at $E_{1/2}$ -0.12 V versus Fc/Fc^+. In acetonitrile solution **2** behaved as a 2:1 electrolyte ($\Lambda_m = 292$ μS/cm, 10^{-3} M solution) [9].

An X-ray analysis was carried out to determine the exact structure of complex **2**.

Crystal data for **2**: $C_{27}H_{45}N_3O_{18}Cl_2Cu$, space group $P\bar{1}$, $a = 10.160(1)$, $b = 13.014(1)$, $c = 15.934(2)$ Å, $\alpha = 74.18(1)$, $\beta = 84.83(1)$, $\gamma = 71.54(1)°$, $V = 1923.0(4)$ Å^3, $Z = 2$. The structure was solved by automated vector search methods using 2586 observed reflection intensities and refined to $R = 0.065$.

Figure 1 shows a drawing of complex **2**. The copper center is six coordinated and surrounded by one bipyridyl unit, two water molecules, one perchlorate oxygen, and a carbonyl oxygen atom of a neighbouring complex. In the solid state **2** is actually a dimer: two copper atoms around a crystallographic center of symmetry are bridged by the two carbonyl oxygen atoms. The coordination geometry around copper is best described by an elongated octahedron. The usual copper to oxygen and nitrogen distances are found [10].

The basal plane of the copper coordination octahedron is formed by N(2) and N(8) of the 2,2′-bipyridine ligand and O(30) and O(31) of the two water molecules. The apical positions are occupied by a monodentate coordinating ClO_4 anion and a carbonyl oxygen. As many as seven hydrogen bonds to water and ethanol are present in the structure. As a result of the stabilizing effect of the hydrogen bonds the crown ether ring is partly unfolded. It

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has an elongated shape and lies more or less in the same plane as the bipyridine unit.

To our knowledge compound **2** is the first example of a 1:1 copper(II)–2,2′-bipyridine complex*. We are currently studying the complexation properties of metallohost **2**. Preliminary experiments indicate that guest molecules can be bound in the crown ether ring of **2** and at its metal centre, e.g. histamine · $HClO_4$ (1:1 complex UV–Vis λ_{max} (ϵ) 715 nm (146), K_{ass} 10^3 M; 1:2 (host:guest) complex K_{ass} 25 M). Details will be presented in a full paper [10].

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*In one paper the isolation of a 1:1 Cu(II)–2,2′-bipyridine complex is mentioned. No details were given, however, see ref. 1. Spectroscopic (EXAFS/UV–Vis) evidence for a 1:1 complex of Cu(II) and bipyridine was recently presented in ref. 4.

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