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# Macrocyclic dioxadiaza from the reaction of the (1,8-diamino-3,6-dioxaoctane)copper(II) cation with formaldehyde and the carbon acids nitroethane or diethylmalonate

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## Abstract

New square-planar copper(II) complexes of 13-membered dioxa diaza macrocyclic ligands, (12-methyl-12-nitro-4,7-dioxa-1,10-diazacyclotridecane)copper(II), $[Cu(L_1)]^{2+}$; and (12,12-dicarboxyethyl-4,7-dioxa-1,10-diazacyclotridecane)copper(II), $[Cu(L_2)]^{2+}$; with perchlorate, hexafluorophosphate and tetrachlorozincate as counter ions have been prepared from the one-pot template condensation reaction of formaldehyde and 1,8-diamino-3,6-dioxaoctane with the carbon acids nitroalkane or diethylmalonate in the presence of the copper(II) ion. Elemental analyses, FTIR, UV–Vis, conductometric, cyclic voltametry and magnetic measurements have been used to characterize the copper(II) complexes of these dioxa diaza macrocycles.

*Keywords:* Copper(II); Template synthesis; 13-Membered macrocycle

## 1. Introduction

The coordination geometry and properties of most transition metal complexes with 14, 16 and 18-membered polyaza macrocyclic ligands have been studied [1–15]. However, 13-membered macrocyclic ligands containing two nitrogen and two oxygen atoms in the fully saturated macrocyclic framework have not been reported to date. We have been interested in the synthesis of various types of polyaza macrocyclic complexes from one-pot metal template condensation reactions. Metal template condensation reactions often provide selective routes toward products that are not obtainable in the absence of metal ions. The reactions are simple "one-pot reactions", cheap and high yielding. Metal template condensation reactions involving carbon acids nitroethane or diethylmalonate, and formaldehyde have been employed in the preparation of various saturated polyazamacrocyclic complexes as described [16–24]. In each case, the nitro group introduced into the new ligand from the nitroalkane carbon acid can be chemically or electrochemically reduced to a pendant amine. This produces a new class of macro monocyclic amine ligands, some of which are capable of penta or hexa-coordination by employing the pendant primary amine group as a donor atom [18b]. In addition to the chemistry based on nitroalkanes, it was of some interest to us to investigate similar condensation reactions with other carbon acids. While nitroethane is a strong carbon acid ($pK_a \sim 8.6$), it is apparent that other simple organic molecules may be sufficiently acidic to participate in similar reactions. We have noted that diethylmalonate is acidic ($pK_a \sim 13.3$) [25], and may be reactive. With the latter carbon acid there is the prospect of forming cyclic molecules with pendant acid groups.

In previous papers [26–28], we reported a series of Ni(II) and Cu(II) complexes with hexaazacyclohexade-

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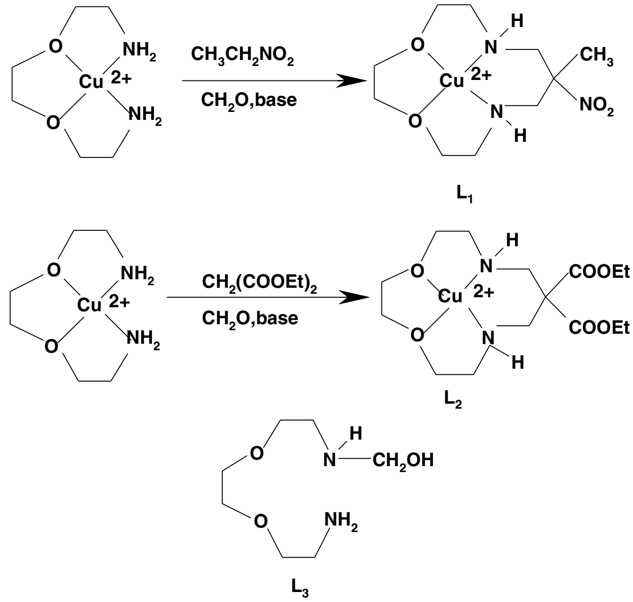

Scheme 1.

cane and decaazacyclooctadecane as ligands by the template condensation. In this paper, we report the synthesis, characterization and properties of new copper(II) complexes of (12-methyl-12-nitro-4,7-dioxa-1,10-diazacyclotridecane), $[Cu(L_1)]^{2+}$, and (12,12-dicarboxyethyl-4,7-dioxa-1,10-diazacyclotridecane), $[Cu(L_2)]^{2+}$, with perchlorate, hexafluorophosphate and tetrachlorozincate as counter ions. The mononuclear copper(II) complexes were prepared from the template condensation of (1,8-diamino-3,6-dioxaoctane), formaldehyde with the carbon acids nitroalkane or diethylmalonate in the presence of a metal ion (Scheme 1).

## 2. Experimental

### 2.1. Materials and measurements

*Safety note*. Perchlorate salts of transition metal complexes with organic ligands are often explosive and should be handled with caution. All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. For the spectroscopic measurements, water was distilled and organic solvents were purified according to the literature method [29]. Electronic absorption spectra were obtained with a Shimadzu UV–Vis scanning spectrophotometer (Model 2101 PC), FTIR (KBr, $cm^{-1}$) spectra with a Shimadzu Varian 4300 spectrophotometer and conductance measurements with a Metrohm Herisau conductometer E 518. The elemental analysis (carbon, hydrogen and nitrogen) of the complexes was obtained from a Carlo ERBA Model EA 1108 analyser. Magnetic moments were calculated from magnetic susceptibility data obtained using a Johnson Matthey MK-1 magnetic susceptibility balance. Atomic Absorption Spectra (AAS) were recorded on a Perkin–Elmer 4100–1319 spectrophotometer. The electrochemical data were obtained in acetonitrile with 0.1 M $(n\text{-Bu})_4NClO_4$ as the supporting electrolyte. The working electrode was a platinum disk, the auxiliary electrode was a coiled platinum wire and the reference electrode was $Ag/AgClO_4$ (0.1 M in $CH_3CN$), which showed +0.24 V versus SCE.

### 2.2. Preparation of (12-methyl-12-nitro-4, 7-dioxa-1, 10-diazacyclotridecane)copper(II) perchlorate, $[Cu(L_1)](ClO_4)_2$

1,8-Diamino-3,6-dioxaoctane (21.7 mmol, 3.22 g) was added to a solution of $Cu(NO_3)_2 \cdot 2.5H_2O$ (21.9 mmol, 5.19 g) in methanol (150 ml). The resulting blue solution was warmed to ca. 40 °C. Then nitroethane (21.9 mmol, 1.34 g), triethylamine (21.7 mmol, 2.2 g) and excess formaldehyde (12 ml, 36% aqueous, 1.57 mmol) were added. After heating for 60 min, the solution was diluted with a large volume of water, sorbed onto a column of SP-Sephadex C-25 ($Na^+$ form) resin (25 × 4 cm) and eluted with 0.2 $mol\,dm^{-3}$ $NaClO_4$. Only one major purple band was observed and collected, reduced in volume, and the product crystallized by slow evaporation. The complex was isolated as a blue-purple solid, further crystallization was achieved, but with some contamination from the electrolyte. *Anal.* Calc. for $C_{10}H_{21}Cl_2CuN_3O_{12}$: Cu, 12.46; C, 23.56; H, 4.15; N, 8.24%. Found: Cu, 12.34; C, 23.42; H, 4.04; N, 8.30%.

### 2.3. Preparation of (12-methyl-12-nitro-4,7-dioxa-1, 10-diazacyclotridecane)copper(II) tetrachlorozincate, $[Cu(L_1)][ZnCl_4]$

The perchlorate salt, $[Cu(L_1)](ClO_4)_2$, was dissolved in a small volume of water and an excess of zinc chloride was added, followed by acetone until the solution became turbid. The blue-purple product was collected after 24 h, washed with ethanol, and then recrystallized from hot methanol–propane-2-ol. *Anal.* Calc. for $C_{10}H_{21}Cl_4CuN_3O_4Zn$: Cu, 12.24; Zn, 12.8; C, 23.13; H, 4.05; N, 8.10%. Found: Cu, 12.09; Zn, 12.68; C, 23.02; H, 3.89; N, 8.25%.

### 2.4. Preparation of (12-methyl-12-nitro-4,7-dioxa-1, 10-diazacyclotridecane)copper(II) hexafluorophosphate, $[Cu(L_1)](PF_6)_2$

To an acetonitrile (50 ml) suspension of $[Cu(L_1)](ClO_4)_2$ (0.5 g) was added excess $NH_4PF_6$. $[Cu(L_1)](ClO_4)_2$ went into the solution, and white precipitates