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# Synthesis and structural characterization of a Cu(I) dimer of a tris(oxazoline) ligand

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## Abstract

The synthesis of a new tripodal tris(oxazoline) ligand, tris[4,4-dimethyl-2-(4,5-dihydrooxazolyl)]methylamine is described, and details of the X-ray crystal structure of its Cu(I) complex are presented. The complex crystallizes as a dimer in the triclinic space group $P\bar{1}$. Each Cu(I) ion is coordinated in a distorted trigonal geometry by two oxazoline groups from one tripod and a third oxazoline from the second ligand. The Cu(I)–Cu(I) distance is 5.7 Å. The CO adduct of the complex exhibits $\nu(CO) = 2066\ cm^{-1}$.

## Introduction

The development of new homogeneous transition metal catalysts designed to facilitate simple organic transformations in high yields with high degrees of enantioselection is an increasingly important goal. In recent years, attention has been focused on metal complexes incorporating oxazoline moieties as N-coordinating ligands [1]. The use of oxazolines in catalytic systems presents advantages over other nitrogen-containing ligands in that they are easily prepared. Furthermore, chiral oxazolines are readily available from optically pure amino alcohols.

For example, rhodium complexes of pyridinyl oxazolines have been found to catalyze the hydrosilation of ketones in high yields with up to 95% ee [2a-c]; a $C_2$-symmetric bis(oxazoline)–iridium complex catalyzes the hydrogenation of aryl alkyl ketones; and the palladium complex of the same ligand catalyzes nucleophilic allylic substitution reactions [3]. Additionally, Corey *et al.* have reported the use of a chiral bis(oxazolinyl)propane–iron(III) complex as a Diels-Alder catalyst [4].

Probably the most general application of oxazoline–metal catalysts has been in the cyclopropanation of alkenes. Masamune and co-workers first reported the use of bis(oxazoline)–Cu(II) complexes as highly efficient catalysts for asymmetric olefin cyclopropanation (up to 99% ee) with diazoacetates [5]. The Cu(I) complexes of bis(oxazoline) ligands have also been found to effect cyclopropanation reactions [3, 6–8].

Because oxazoline-ligated metal complexes possess desirable catalytic properties, we initiated a study aimed at extending the family of oxazoline ligands to include those possessing $C_3$ symmetry. Transition metal complexes of three-fold symmetric ligands are currently of interest because three equivalent open coordination sites can be obtained. Potentially such systems could provide highly stereocontrolled catalysis for reactions which proceed via octahedral intermediates. To this end, we now report the synthesis of the tripodal ligand tris[4,4-dimethyl-2-(4,5-dihydrooxazolyl)]methylamine (trioxma) and the X-ray crystal structure of its Cu(I) complex.

## Experimental

### General

All solvents and reagents are commercially available and were used without further purification. All procedures involving air sensitive compounds were performed under nitrogen in a Vacuum Atmospheres Drybox at less than 0.2 ppm $O_2$. $^1H$ NMR spectra (200 MHz) were recorded on a Bruker AC-200 spectrometer. Chemical shifts ($\delta$) are reported in ppm downfield from TMS. IR spectra were obtained using a Mattson-Polaris FT-IR spectrophotometer. Elemental analyses were performed by Atlantic Microlabs, Norcross, GA. Melting points were recorded with use of a Fisher-Johns melting point apparatus and are uncorrected.

### *Nitrilotriacetic acid trimethyl ester (1)*

A 1.0 l round-bottomed flask containing a magnetic stir bar and fitted with a reflux condenser was charged

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with 20.0 g (0.105 mol) of nitrilotriacetic acid, 500 ml MeOH and 10 ml conc. $H_2SO_4$. This mixture was allowed to reflux overnight. After cooling to r.t., the solution was made basic with saturated aqueous $NaHCO_3$. The MeOH was evaporated at reduced pressure, and the aqueous residue extracted with three, 200 ml portions of ether. The combined extracts were washed with water and brine and dried over $MgSO_4$. Filtration and evaporation of the solvent afforded 18.2 g (75%) of **1** as a colorless liquid which was used without further purification. $^1H$ NMR ($CDCl_3$): 3.68 (s, 6H, $CH_2$); 3.72 (s, 9H, $CO_2CH_3$).

### *Tris[4,4-dimethyl-2-(4,5-dihydrooxazolyl)]methylamine (trioxma) (2)*

To 250 ml of xylenes were added **1** (10.0 g, 42.9 mmol) and 2-amino-2-methyl-1-propanol (11.5 g, 129 mmol). The mixture was allowed to reflux for 2 days, after which time a Dean-Stark trap was applied and reflux continued for an additional 2 days with azeotropic removal of $H_2O$. After cooling, the xylenes were evaporated under reduced pressure, and the resulting dark residue dissolved in acetone and filtered through a pad of silica gel (60–200 mesh). Evaporation of the acetone afforded a dark brown residue that was distilled under vacuum to yield **2** (7.5 g, 50%) as a pale green oil, b.p. 158–161 °C (2 torr), which solidifies upon standing at −20 °C. $^1H$ NMR ($CDCl_3$: 1.28 (s, 18H, $CH_3$); 3.58 (s, 6H, O–$CH_2$); 3.96 (s, 6H, N–$CH_2$).

### *[Cu$^I$trioxma]$_2$[BF$_4$]$_2$ (3)*

In an inert atmosphere box, $[Cu^I(CH_3CN)_4]BF_4$ (0.54 g, 1.7 mmol) in 15 ml of dry, degassed MeOH was added to a stirred solution of trioxma **2** (0.60 g, 1.7 mmol) in 10 ml of MeOH. The resulting bright yellow solution was stirred at r.t. for 2 h. The MeOH was evaporated under vacuum and the resulting yellow solid was recrystallized from a minimum of hot MeOH to afford **3** (0.5 g, 59%) as colorless needles. *Anal.* Calc. for $C_{18}H_{30}CuN_4O_3BF_4$: C, 43.17; H, 6.04, N, 11.19. Found: C, 43.07; H, 6.07, N, 11.24%. IR (KBr) ($cm^{-1}$): 1061 $\nu(BF_4)$; 1665 $\nu(C{=}N)$. M.p. 220–225 °C (dec.).

### *X-ray crystallographic structure determination of 3*

Crystals of **3** suitable for X-ray analysis were grown by slow cooling of a hot methanolic solution of the complex. Crystallographic measurements were carried out using a Rigaku AFC-6S diffractometer and graphite monochromatized Mo K$\alpha$ radiation ($\lambda(K\alpha) = 0.71073$ Å) at −160 °C. Unit cell constants were derived from a least-squares refinement of 31 reflections in the range $35 < 2\theta < 41°$ (the $\theta$–$2\theta$ scan technique was used to record intensities). A stationary count for 0.1 of the scan time at each end of the peak was used to correct for background counts. Peaks were subjected to profile analysis and any portions of the scan not included in the peak were used to improve background estimates. The structure was refined using full-matrix least-squares techniques. The function minimized was $[\Sigma w(F_o - F_c)^2]^{0.5}$ with weights based on counter statistics. Calculations were performed using the NRCVAX system [9]. In the final cycles of refinement, all non-hydrogen atoms were given anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions 0.96 Å from the atom to which they are bonded and assigned isotropic thermal parameters based on the thermal parameters of that atom. There is a water of solvation which is included with 50% occupancy. Crystal data are given in Table 1.

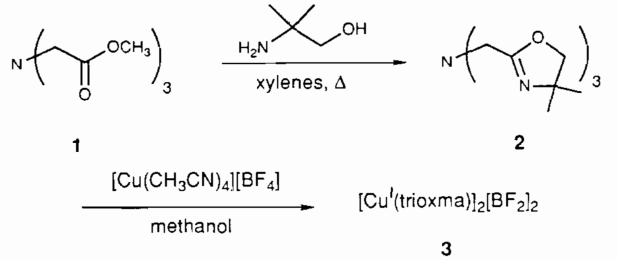
TABLE 1. Crystallographic data for $[Cu^I(trioxma)]_2[BF_4]_2$

| | |
|---|---|
| Formula | $C_{18}H_{31}CuBF_4N_4O_{3.5}$ |
| Temperature (°C) | −160 |
| Crystal size (mm) | 0.40 × 0.15 × 0.15 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| $a$ (Å) | 9.1935(22) |
| $b$ (Å) | 11.166(4) |
| $c$ (Å) | 12.656(4) |
| $\alpha$ (°) | 103.86(3) |
| $\beta$ (°) | 109.586(23) |
| $\gamma$ (°) | 91.983(24) |
| Volume (Å$^3$) | 1179.0(6) |
| $Z$ | 2 |
| Formula weight | 509.81 |
| $\rho_{calc}$ (Mg/m$^3$) | 1.436 |
| $\mu$ (mm$^{-1}$) | 0.99 |
| Transmission factors | 0.821–0.843 |
| Reflections collected | 4181 |
| Unique reflections | 4141 |
| Reflections of $I > 2.5\sigma(I)$ | 3537 |
| $R$ (all reflections) | 0.061 |
| $R_w$ (all reflections) | 0.072 |
| $R$ (obs. reflections) | 0.052 |
| $R_w$ (obs. reflections) | 0.070 |
| No. parameters | 290 |
| Maximum shift/sigma | 0.003 |
| Maximum residual electron density (e/Å$^3$) | 0.91 |
| Minimum residual electron density (e/Å$^3$) | −0.91 |

## Results and discussion

### *Synthesis*

The synthesis of tris[4,4-dimethyl-2-(4,5-dihydrooxazolyl)]methylamine (trioxma) is shown in Scheme 1. Nitrilotriacetic acid undergoes acid catalyzed esterification to afford the trimethyl ester **1** in 75% yield. Formation of the triamide and ring closure to the tris(oxazoline) tripod were accomplished in one pot by prolonged refluxing of the triester with 3 equiv. of



Scheme 1.

2-amino-2-methyl-1-propanol in xylenes. The tripod **2** was eventually isolated as a pale green oil in 50% yield after vacuum distillation. Addition of $[Cu^I(CH_3CN)_4]BF_4$ to a methanolic solution of **2** under $N_2$ afforded, after recrystallization, a 59% yield of colorless needles of $[Cu^I(trioxma)]_2[BF_4]_2$ (**3**).

In the solid state this complex is stable in air for months but in solution it rapidly oxidizes to a green Cu(II) species. Complex **3** reacts with carbon monoxide in nitromethane to give a carbonyl derivative with $\nu(CO) = 2066\ cm^{-1}$. Based on our previous work, this complex is most likely a four-coordinate CO adduct having three nitrogen donors in the coordination sphere [10].

### *Solid state structure of $[Cu^I(trioxma)]_2[BF_4]_2$ (3)*

The X-ray crystal structure of the cation **3** is shown in Fig. 1 [11]. The crystal belongs to the triclinic space group $P\bar{1}$. Selected bond distances and angles are given in Table 2.

Trioxma was designed to act as a tetradentate, tripodal ligand like tris(2-pyridinylmethyl)amine. However, as Fig. 1 shows, **3** crystallizes as a three-coordinate Cu(I) dimer utilizing two trioxma ligands. Each Cu(I) is ligated by two oxazoline groups from one ligand and one oxazoline from a second ligand. The Cu–Cu distance is 5.724 Å and the dimer sits on a crystallographic center of inversion. The geometry about the Cu(I) ions can best be described as distorted trigonal, and they sit 0.08 Å out of the plane defined by the three ligating nitrogen atoms. Two N–Cu–N angles are roughly equivalent (105 and 108°) with the third N–Cu–N angle considerably larger (146°). The Cu–N distances of approximately 2.0 Å are in accordance with those observed for other oxazoline–Cu complexes [8, 12, 13]. The tertiary amine nitrogen (N29) is definitely too far removed from the Cu(I) ion (2.7 Å) to engage in a bonding interaction.

Thus, rather than forming a unique mononuclear tris(oxazolinylmethyl)amine complex as we had hoped, the ligand **2** yields a three-coordinate Cu(I) dimer. The

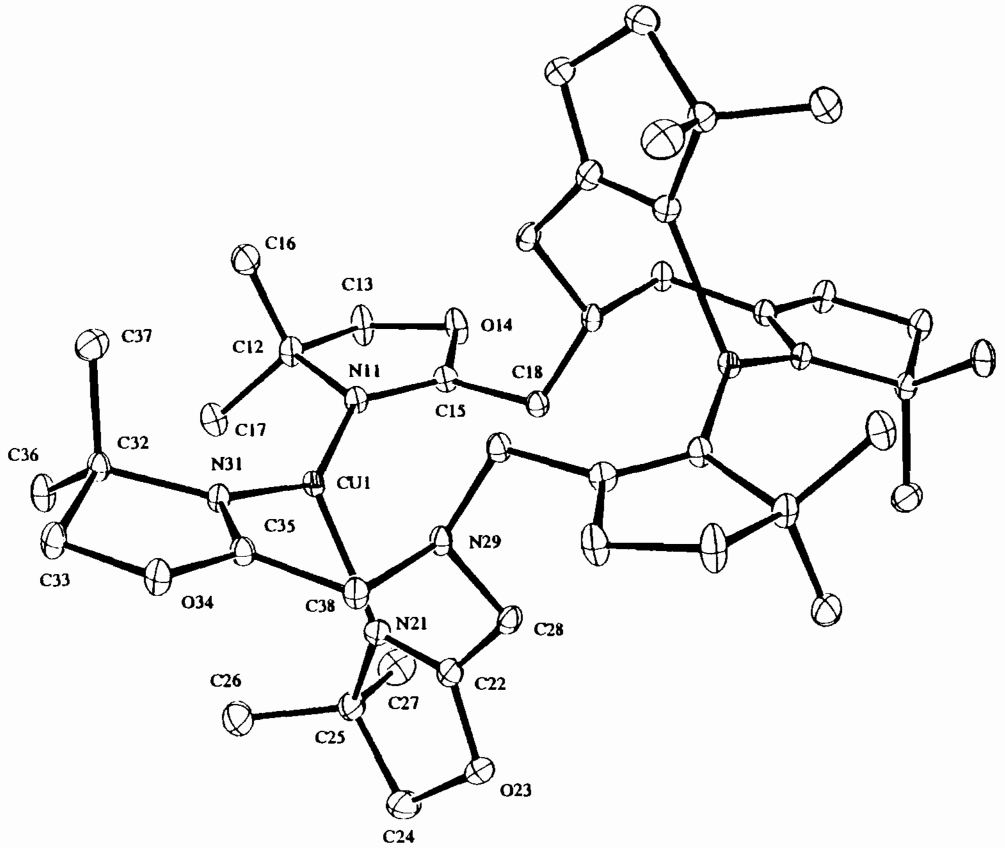


Fig. 1. Structure of the $[Cu(trioxma)]_2^{2+}$ cation showing 30% thermal ellipsoids. The compound sits on an inversion center and the Cu–Cu distance is 5.724 Å.

TABLE 2. Selected bond distances and angles for $[Cu^I(trioxma)]_2[BF_4]_2$

| | | | |
|---|---|---|---|
| Distances (Å) | | | |
| Cu1–N11 | 1.957(3) | C35–C38 | 1.503(5) |
| Cu1–N31 | 1.948(3) | N31–C35 | 1.277(5) |
| Cu1–N21 | 2.122(3) | N31–C32 | 1.506(5) |
| Cu1–N29 | 2.735(3) | C35–O34 | 1.342(4) |
| N29–C28 | 1.464(5) | C33–O34 | 1.456(5) |
| N29–C38 | 1.476(5) | C32–C33 | 1.535(5) |
| Cu1–C15 | 2.904(4) | C32–C37 | 1.522(6) |
| Cu1–Cu1′ | 5.724(3) | C32–C36 | 1.524(6) |
| Angles (°) | | | |
| N11–Cu1–N21 | 108.05(13) | C28–N29–C38 | 111.8(3) |
| N11–Cu1–N31 | 146.26(13) | C32–N31–C35 | 106.7(3) |
| N21–Cu1–N31 | 105.17(13) | N31–C32–C33 | 101.7(3) |
| N21–Cu1–N29 | 69.40(11) | N31–C43–C36 | 110.9(3) |
| Cu1–N31–C32 | 129.15(23) | N31–C32–C37 | 108.2(3) |
| Cu1–N31–C35 | 123.7(3) | C33–C32–C36 | 112.4(3) |
| N11–Cu1–N29 | 125.33(11) | C33–C32–C37 | 111.8(3) |
| N29–Cu1–N31 | 72.47(11) | C36–C32–C37 | 111.5(3) |
| Cu1–N21–C22 | 123.5(3) | C32–C33–O34 | 104.8(3) |
| Cu1–N21–C25 | 129.31(24) | C33–O34–C35 | 105.3(3) |
| Cu1–N11–C12 | 126.64(23) | N31–C35–C38 | 126.8(3) |
| Cu1–N11–C15 | 107.4(3) | N29–C38–C35 | 111.3(3) |

absence of an interaction between the amine nitrogen atom and the Cu(I) ion most likely results from an insufficient 'bite' angle between the amine and imine nitrogen atoms. Furthermore, this results in the inability of the three oxazoline rings of a single tripod to coordinate the Cu(I) in a favorable planar array, thereby promoting formation of the observed dimer. Such a situation has been observed for other N-coordinating tripodal ligands [10, 14, 15].

Unfortunately, the inability of trioxma to form a copper(I) complex with three-fold symmetry limits its possible use as a catalyst in the sense in which it was intended. Other metal complexes may form discrete mononuclear species, a goal which is currently under investigation.

## Conclusion

The synthesis of trioxma illustrates a simple and inexpensive route to new tris(oxazoline) tripodal ligands. Variation of the aminopropanol reagent should allow facile synthesis of chiral analogs, if desired. The Cu(I) complex of trioxma (**3**) has been structurally characterized and found to form a symmetrical dimer in the solid state. While the structure of **3** is not unusual when compared to other N-coordinating tripodal Cu(I) complexes, it is noteworthy in that it is one of only a few oxazoline–metal complexes characterized by X-ray crystallography [2c, 8, 12, 13, 16]. The complex **3** can undergo further substitution, as shown by its ready formation of a CO adduct. Since several metal–oxazoline complexes have been shown to be effective catalysts, the synthesis of other tris(oxazoline) tripods and their utility as catalysts merits further study.

## Supplementary material

A full listing of all bond distances and angles as well as final atomic coordinates for **3** is available from the authors upon request.

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