



Synthesis and structure of a dinuclear copper complex of a bis(bidentate)triazenide ligand

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Abstract

The synthesis and characterization of a dinuclear copper(II) complex with a bis(bidentate) ligand is reported. The ligand is a functionalized 1,3-diaryl triazene substituted with carboxymethyl groups at the ortho positions of the aryl rings. Reaction of this ligand with $\text{Cu}_2(\text{OAc})_4 \cdot 2\text{H}_2\text{O}$ resulted in the formation of the $\text{Cu}_2(\text{OAc})_3(\text{triazenide})$ where the triazenide binds to each copper through one of the triazenide nitrogens and the carbonyl oxygen of the pendant esters. The structures of this dinuclear complex and of the ligand are reported. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Triazene; Triazenide; Acetate; Copper(II) complex; Dinuclear structure

1. Introduction

The enhanced performance of many heterogeneous catalysts over their homogeneous counterparts can often be attributed to the close proximity of metal centers in the solid state and the cooperative interactions that can take place between them [1,2]. While cooperativity in heterogeneous catalysts has been well documented, replication of these interactions in homogeneous systems has been difficult. However, notable advances in bimetallic hydroformylation catalysts [3–8] and asymmetric Lewis acid catalysis [9–19], as well as other areas [20–23], have been reported.

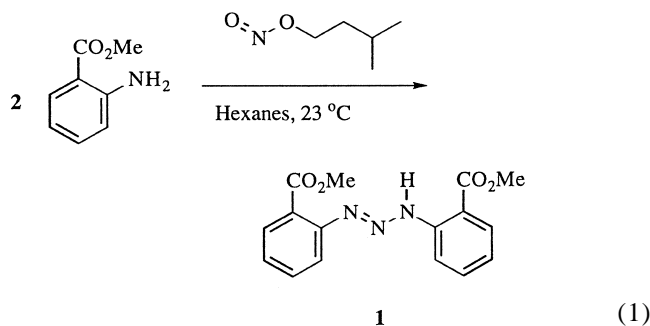
We are interested in the design and development of bis(bidentate) ligands to chelate two metal centers and hold them in close proximity [24–26]. Bridging ligands can not only position the metal centers for cooperative reactivity, they can also stabilize the resulting compounds. This strategy has been used very successfully in the synthesis of complexes containing metal–metal bonds [27,28]. Unbridged triple and quadruple metal–metal bonds are known for some bonding partners, however others require stabilization by ligands which bridge the metal centers and hold them together.

In our previous work, we prepared complexes of triazenide ligands bonded to main group elements [29,30].

Deprotonation of the triazene [31–33] gives the triazenide which readily binds to main group and transition metals. Ligands which are related to the triazenide are the carboxylate [34] and amidinate [35–37] ligands. The triazenide, amidinate, and carboxylate have been shown to bind in monodentate, bidentate and bridging fashions by X-ray crystallographic methods [34–39]. In this paper, we describe our use of bis(bidentate) ligand 1,3-bis(2-carboxymethyl)benzene triazene and its complex with copper(II).

2. Results and discussion

The ligand **1** was easily prepared in one step by the room temperature coupling of methyl anthranilate in hexanes using isoamyl nitrite according to the literature procedure (Eq. (1)) [40]. The yellow ligand **1** was readily crystallized from dichloromethane and hexane.



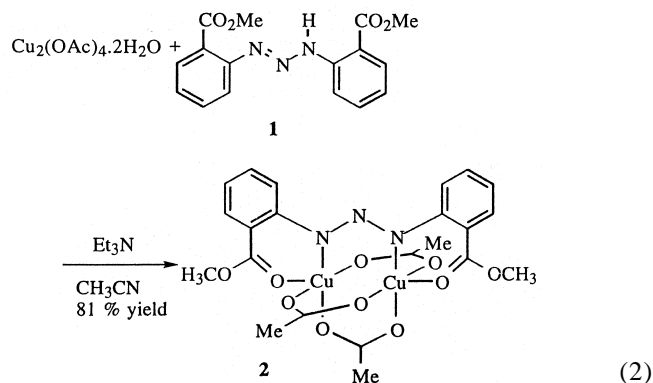
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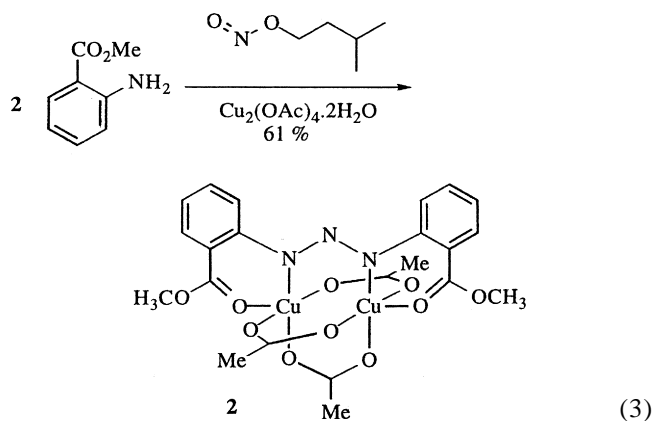
In order to demonstrate that compounds of the type of **1**

could act as bis(bidentate) ligands for dinuclear systems, we employed copper(II) in our initial experiments. Copper(II) was chosen for two reasons. Firstly, it is known that triazenide ligands readily bind to copper in a bridging fashion [41]. Secondly, dinuclear ‘paddle wheel’ type structures for copper(II) acetate are well known and very stable [34]. Furthermore, the $\text{Cu}_2(\text{OAc})_4$ core tends to bind two additional ligands in the axial positions which are along the Cu–Cu internuclear axis.

The copper(II) complex **2** was prepared by combining the ligand **1**, triethylamine, and copper(II) acetate in acetonitrile.



After stirring for 36 h the solution was dark green. Evaporation of the solvent and recrystallization from dichloromethane and hexanes gave crystals of **2** in 81% yield. The complex **2** was also synthesized in a one-pot procedure directly from methyl anthranilate (Eq. (3)), albeit in lower yield (61%). This procedure involved the in situ preparation of the ligand and coordination to the copper center.



The IR spectrum of **2** contained a strong absorption for the carbonyl group at 1694 cm^{-1} . In contrast, the $\text{C}=\text{O}$ stretching frequency of the diester **1** was 1728 cm^{-1} . This large shift in the $\text{C}=\text{O}$ stretching frequency of the ligand bound to copper indicated that the carbonyl oxygens were coordinated to the metal centers. No signals were observed when a solution of **2** was analyzed by ^1H and ^{13}C NMR spectrometry. Compounds of this type have been shown to

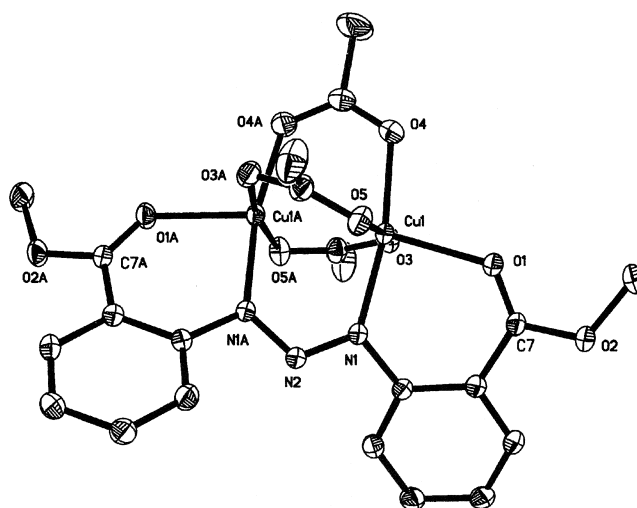


Fig. 1. An ORTEP diagram of **2**.

have a singlet ground state with a low-lying triplet state. The triplet state is partially populated at room temperature and the compounds are paramagnetic [42–44]. To elucidate the structure of **2**, X-ray quality crystals were grown from dichloromethane and hexanes. Data for an X-ray crystal structure were collected at room temperature and an ORTEP diagram of **2** is illustrated in Fig. 1. For purposes of comparison, an X-ray study of the ligand **1** was also undertaken. An ORTEP drawing of **1** is illustrated in Fig. 2. Selected bond distances and bond angles for **2** are in Table 1, and for **1** are in Table 2. X-ray structural data and collection parameters are in Table 3.

As illustrated in Fig. 1, the structure of **2** shows the triazenide ligand is bonded in a bis(bidentate) manner bridging the two copper centers. The triazenide has essentially replaced an acetate and the two axial water molecules in the structure of the hydrate $\text{Cu}_2(\text{OAc})_4 \cdot 2\text{H}_2\text{O}$. The molecule has a crystallographic C_2 -symmetry axis rendering many of the atoms symmetry equivalent. For example, N(1) and N(1A) are equivalent. The Cu(1)–N(1) distance in **2** is $1.991(2)\text{ \AA}$. The copper–nitrogen distance is similar to those found in copper(II) triazenide

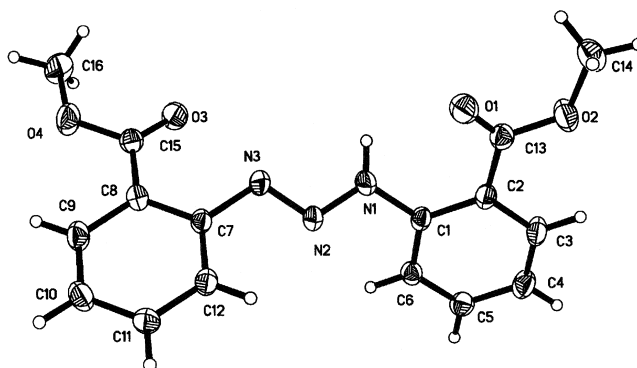


Fig. 2. An ORTEP drawing of **1**.

Table 1
Selected bond distances (Å) and angles (°) for compound **2**

Cu(1)–Cu(1A)	2.5316(6)
Cu(1)–O(1)	2.159(2)
Cu(1)–O(3)	1.947(2)
Cu(1)–O(4)	1.968(2)
Cu(1)–O(5)	1.977(2)
Cu(1)–N(1)	1.991(2)
N(1)–N(2)	1.279(2)
O(1)–C(7)	1.217(3)
O(2)–C(7)	1.324(3)
N(1)–N(2)–N(1A)	116.4(3)
O(1)–C(7)–O(2)	121.1(2)
O(1)–Cu(1)–Cu(1A)	171.31(5)
N(1)–Cu(1)–O(3)	89.06(8)
O(3)–Cu(1)–O(4)	88.30(9)
O(4)–Cu(1)–O(5)	89.19(9)
O(4)–Cu(1)–N(1)	168.53(8)
O(4)–Cu(1)–N(1)	168.53(8)

Table 2
Selected bond distances (Å) and angles (°) for ligand **1**

N(1)–N(2)	1.296(3)
N(2)–N(3)	1.293(3)
O(1)–C(13)	1.193(3)
O(2)–C(13)	1.334(3)
O(3)–C(15)	1.213(4)
O(4)–C(15)	1.350(3)
N(1)–N(2)–N(3)	113.6(2)
O(1)–C(13)–O(2)	122.8(2)
O(3)–C(15)–O(4)	121.0(4)

complexes $\text{Cu}_2(\text{dpt})_4$ (dpt=1,3-diphenyltriazenide) which range from 1.973 to 2.088 Å (average 2.020 Å) [41]. The Cu–O distances for the bridging acetates in **2** range from

Table 3
Crystal data and structure refinement parameters for **1** and **2**

Compound	1	2
Empirical formula	$\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_4$	$\text{C}_{22}\text{H}_2\text{Cu}_2\text{N}_3\text{O}_{10}$
FW	313.31	616.5
<i>a</i> (Å)	18.329(8)	8.8209(7)
<i>b</i> (Å)	13.160(3)	15.1062(12)
<i>c</i> (Å)	15.448(7)	19.421(2)
α (°)	90	90
β (°)	126.34(2)	102.147(6)
γ (°)	90	90
<i>V</i> (Å ³)	3002(2)	2529.9(4)
<i>Z</i>	8	4
Space group	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>T</i> (°C)	23	–86
Radiation, λ (Å)	Mo K α , 0.710373	Mo K α , 0.710373
ρ_{calcd} (g cm ^{–3})	1.387	1.621
μ (mm ^{–1})	0.102	0.1.74
Final <i>R</i> indices ^a	<i>R</i> 1=0.0541	<i>R</i> 1=0.0291
[<i>I</i> > 2 σ (<i>I</i>)]	<i>wR</i> 2=0.1511	<i>wR</i> 2=0.0782
<i>R</i> indices	<i>R</i> 1=0.0855	<i>R</i> 1=0.0340
(all data)	<i>wR</i> 2=0.8080	<i>wR</i> 2=0.0851

^a $R1 = \sum |F_o| - |F_c| / \sum |F_o|$; $wR2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2))]^{1/2}$.

1.968(2) to 1.977(2) Å. These distances are typical for bridging structures of this type [44].

Comparison of the structures of unbound triazene **1** and the triazenide ligand in **2** shows little variation of the bonding on coordination. The N(1)–N(2) and N(2)–N(3) bond distances in the triazene are 1.296(3) and 1.293(3) Å, respectively. It would be expected that the N–N bond distances would be dissimilar as a consequence of the different bond order between these atoms (Eq. (1)). However, in the structure of **1**, it is likely that the molecule is disordered with respect to the location of the hydrogen on N(1) or N(3) because the N(1)–N(2) and N(2)–N(3) distances are very close in length. In the copper complex **2**, the N(1)–N(2) bond distance is 1.297(2) Å which is, within experimental error, the same as in the unbound ligand. The N–N distances in $\text{Cu}_2(\text{dpt})_4$ were found to average 1.296 Å. The coordinated carbonyl oxygens in **2** are bonded with a Cu–O distance of 2.159(2) Å. These distances are similar to those of the $\text{Cu}_2(\text{OAc})_4 \cdot 2\text{L}$ complexes [44]. The N–N–N bond angle in the unbound ligand **1** was 113.6(2)° and in complex **2** was 116.4(3)°. Given the short Cu–carbonyl oxygen distances, it might be expected that the interaction of the copper with the carbonyl oxygen would induce notable changes in the bond distances in the ester, compared to the unbound ligand **1**. The carbonyl carbon–oxygen distance in **2** was found to measure 1.217(3) Å. In the ligand **1**, the distances were slightly shorter at 1.213(4) and 1.193(3) Å. In **1** the C–OMe distances are 1.334(3) and 1.350(3) Å, which is longer than the C–OMe distance found in the coordinated ligand of 1.324(3) Å. Coordination of **1** resulted in a change in the degree of twisting the ligand. The angles between the planes defined by the two aromatic rings of **1** and the two aromatic rings in **2** were 111.7 and 67.8°, respectively.

The Cu(1)–Cu(2) distance in **2** is 2.5316(6) Å. This Cu–Cu separation is typical of binuclear copper(II) compounds [44], although slightly longer than that found in $\text{Cu}_2(\text{dpt})_4$ (2.441 Å) [41].

In summary, the triazenide ligand **1** can bind in a bis(bidentate) fashion to copper(II). The ligand stabilizes the dimeric structure by chelating through the nitrogens and the carbonyl oxygens. Coordination of the ester carbonyl groups is easily identified by simply monitoring the C=O stretching frequency of the IR. We are currently exploring other systems with this ligand with the goal of applying the resultant complexes to catalysis.

3. Experimental

3.1. General

¹H NMR spectra were obtained on either the Varian Gemini 2000-BB 200 MHz Fourier transform spectrome-

ter. ^1H NMR spectra were recorded relative to residual protiated solvent. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were obtained at 50 MHz on the 200-MHz instruments, and chemical shifts were recorded relative to the solvent resonance. Chemical shifts are reported in units of parts per million downfield from tetramethylsilane and all coupling constants are reported in Hz. IR spectra were obtained on a Perkin-Elmer 1600 series spectrometer. Mass spectra were obtained on a Hewlett-Packard Model 5989 Series II mass spectrometer. Unless otherwise specified, all reagents were purchased from Aldrich Chemical Co. and used without further purification. Copper(II) acetate was purchased from Matheson, while 1,3-bis(2-carboxymethyl)benzene triazene was synthesized according to the literature procedure [40].

3.2. Synthesis and characterization of **2** from **1**

In air, 1,3-bis(2-carboxymethyl)benzene triazene (114 mg, 3.944×10^{-4} mol, 1.6 Equiv.) was dissolved in 3 ml of acetonitrile and stirred. To this orange solution was added triethylamine (59.7 mg, 5.91×10^{-4} mol, 1.5 Equiv.). A solution of $\text{Cu}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (96.6 mg, 2.24×10^{-4} mol, 1 Equiv.) in 2 ml of acetonitrile was slowly added and the solution stirred for 36 h at 25°C . The solvent was evaporated under reduced pressure and the green solid was washed with diethyl ether. Dichloromethane was added until most of the solid was dissolved and the solution was filtered. To the dark green solution was diffused hexane over a period of 1 week. Dark green crystals suitable for an X-ray structural determination formed and were isolated by decanting the solvent and washed with ether (121 mg, 2.05×10^{-4} mol, 81% based on $\text{Cu}_2(\text{OAc})_4 \cdot 2\text{H}_2\text{O}$), mp = $216\text{--}222^\circ\text{C}$ (with discoloration). IR (KBr): 2958, 1728, 1671, 1584, 772, 725 cm^{-1} ; no signals were observed in the ^1H NMR spectrum between 0–15 ppm or in ^{13}C NMR spectrum between 0–260 ppm; MS (*m/e*) 498, 497, 419, 347, 285, 244, 209, 194, 166, 120, 63.

3.3. Synthesis and characterization of **2** from methyl anthranilate

Methyl anthranilate (0.151 g, 1×10^{-3} mol, 1 Equiv.) was dissolved in 15 ml of methanol and stirred at 25°C . To this solution was added isoamyl nitrite (0.117 g, 1.00×10^{-3} mol, 1 Equiv.) followed by addition of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.3192 g, 1.60×10^{-3} mol, 1.6 Equiv.) as a solid. After stirring for 1 h all the $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ had dissolved and dark green reaction mixture was stirred for 2 days during which a precipitate formed. The solvent was removed under reduced pressure and the resulting solid dissolved in dichloromethane and filtered. The product was recrystallized by diffusion of pentane into a saturated solution of **2** in dichloromethane. Dark green crystals were obtained (0.188 g, 0.32×10^{-3} mol, 61%).

3.4. X-ray crystallographic procedures

Crystals were isolated from the mother liquor and were immersed in epoxy. A crystal was selected for the X-ray diffraction study and mounted on a quartz fiber and data were collected using a Siemens P4 diffractometer. Corrections for the effects of absorption anisotropy were made. Structure solutions were performed by direct methods and structure refinement was done with the programs SHELXS and SHELXL [45].

Supplementary data

Supplementary data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition numbers 1233386 for structure **1** and 1233387 for structure **2**.

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