



Versatile nuclearity in copper complexes with *ortho* functionalized 1,3-bis(aryl)triazenido ligands

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ARTICLE INFO

Article history:

Received 31 July 2009

Received in revised form 23 October 2009

Accepted 8 November 2009

Available online 17 November 2009

Dedicated to Prof. Jonathan R. Dilworth

Keywords:

Triazenido ligands

Copper(I)

Copper(II)

Polynuclear complexes

Coordination macrocycle

ABSTRACT

The synthesis, characterization and crystal structures of three new copper complexes derived from 1,3-bis(aryl)triazenido ligands bearing either a methoxycarbonyl, methylthio or a hydroxymethyl group in the *ortho* position of one of the aromatic rings are reported. In addition to the coordination of the triazenido fragment, the Lewis basic groups coordinate to the copper centers to form complexes with different nuclearity: {1-[2-(methoxycarbonyl)phenyl]-3-[4-methylphenyl]triazene and {1-[2-(methylthio)phenyl]-3-[4-methylphenyl]triazene form stable dinuclear and tetranuclear Cu(I) complexes, respectively. Reaction of {1-[2-(hydroxymethyl)phenyl]-3-[4-methylphenyl]triazene with either Cu(I) or Cu(II) results in a novel Cu(II) hexanuclear macrocyclic complex.

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1. Introduction

An approach toward the synthesis of complexes that exhibit new chemical and physical properties is the design of ligands that can be easily functionalized in order to modify the metal coordination sphere. A class of ligands that has attracted our attention are 1,3-bis(aryl)triazenides, since they exhibit a variety of bonding modes with distinct properties [1,2]. Triazenido ligands can bind through a single nitrogen to form monomeric complexes, through chelation to form bidentate complexes, or through bridging between two metal centers to form metallacycles or infinite coordination polymers (Fig. 1) [3,4]. 1,3-Bis(aryl)triazenido ligands (ArNNNAr^-) are “short-bite” ligands when compared with the more common (ArNCXAr^-) ($\text{X} = \text{N}, \text{O}, \text{S}$) analogues [5]. It can be expected that the incorporation of donor groups (X) at the *ortho* position of the 1,3-bis(aryl)triazenido ligands produces a markedly different coordination chemistry. Thus, we have turned our attention to the application of 1,3-bis(aryl)triazenido ligands bearing Lewis basic *ortho* substituents [6,7], expecting that they form additional chelate rings with the metal center and change their coordination environment. The coordination properties of border-

line or soft metals can be modulated by the choice of hard, but weakly coordinating groups such as the methoxycarbonyl [8–11] and the hydroxymethyl group [11], or the choice of softer, but more electron-donating substituents, such as the thiomethyl group [11]. These weakly coordinating groups can behave as hemilabile ligands [12], and allow for the generation of a free coordination site for substrate activation, thus providing complexes with potential catalytic applications.

In previous contributions we have reported the synthesis and structures of Cu(I) and Pd(I) complexes with such ligands. Both complexes are dinuclear with an almost planar 8-membered ring, which consists of two N_3 units and the metal centers (Fig. 2a) [9,11]. Triazenido ligands form also tetranuclear complexes with d^{10} metal ions, in which the metal centers are linked exclusively by the N_3^- fragments, thus forming a cage-like system (Fig. 2b) [13,14].

In this paper, we report on the synthesis and structure of copper complexes bearing 1,3-bis(aryl)triazenido ligands with a Lewis basic substituent in the *ortho* position of one of the aromatic rings (Fig. 3). Depending on the nature of the *ortho* substituent, these triazenes gave rise to dinuclear and tetranuclear copper(I) complexes, and a hexanuclear copper(II) complex. We are unaware of previously characterized macrocyclic hexanuclear copper complexes with triazenido ligands.

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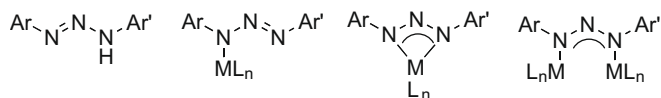


Fig. 1. A generic triazene and binding modes of triazenido ligands.

Since reports on catalytic applications of triazenido complexes are rather scarce [15–17], we were also interested in exploring the catalytic activity of our complexes. For this purpose, we selected the cyclopropanation of styrene with ethyl diazoacetate and examined the catalytic activity as a function of the complex nuclearity and S/C (substrate/catalyst ratio).

2. Experimental

2.1. General remarks

Reactions with copper(I) were performed under argon atmosphere, while those with copper(II) were realized under air. Unless otherwise specified all chemicals were purchased from Aldrich Chemical Co. and used without further purification. Copper(II) acetate was purchased from MCB, and copper(I) acetate was purchased from Strem. {1-[2-(methoxycarbonyl)phenyl]-3-[4-methylphenyl]}triazene (**1**) and {1-[2-(methylthio)phenyl]-3-[4-methylphenyl]}triazene (**2**) were synthesized according to previously reported procedures [11]. NMR spectra were recorded on Varian Gemini 200-BB FT equipment. ^1H NMR (200 MHz) and $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz) data are reported in ppm relative to Me_4Si as an internal standard. Coupling constants J are given in Hertz (Hz). IR spectra were recorded on a Perkin–Elmer 1605 FT-IR spectrophotometer. UV–vis absorption spectra were determined on a HP 8452A diode array spectrophotometer. Melting points were measured in a Gallenkamp apparatus and are uncorrected. EI mass spectra were obtained with a HP 5989 MS engine and HR-MS with an Agilent LCTOF(2006), a high resolution TOF analyzer with windows XP based OS and APCI/ESI ionization. Elemental analyses were performed at NuMega Resonance Labs (San Diego). Samples

for elemental analyses were dried at room temperature under vacuum for at least 24 h.

2.2. Ligands

2.2.1. {1-[2-(hydroxymethyl)phenyl]-3-[4-methylphenyl]}triazene (**3**)

2-Aminobenzyl alcohol (500 mg, 4.1 mmol, 1 equiv.) dissolved in water (5 mL) was mixed with 1 M HCl (5 mL, 12.3 mmol, 3 equiv.) at 0 °C, whereupon an aqueous solution (15%) of sodium nitrite (428 mg, 6.2 mmol, 1.5 equiv.) was added dropwise with stirring. Once the amine was dissolved, a 15% solution of *p*-toluidine in ethanol (439 mg, 4.1 mmol, 1 equiv.) was added at 0 °C, and the resulting solution stirred for 30 min. Then, the reaction mixture was neutralized with a 15% aqueous solution of NaOAc (32 mL) to give a yellow precipitate, which was filtered and dried over MgSO_4 . The product was purified by crystallization at –4 °C from a 9:1 ethyl acetate/hexane solvent mixture to obtain a yellow crystalline solid (459 mg, 1.9 mmol, 46%). Mp = 90–92 °C. IR (KBr): 3435, 3244, 2911, 1590, 1521, 1401, 1249, 1203, 1009, 813 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz, 25 °C): δ 7.66 (dd, J = 8.2, 1.2 Hz, 1H, Ar), 7.31 (dt, J = 8.6, 1.8 Hz, 3H, Ar), 7.17 (m, 3H, Ar), 7.06 (dt, J = 7.2, 1.2 Hz, 1H, Ar), 4.77 (s, 2H, $-\text{CH}_2-$), 2.33 (s, 3H, $\text{Ar}-\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 50 MHz, 25 °C): δ 135.8 ($\text{C}_{\text{Ar}}-\text{N}$), 134.8 ($\text{C}_{\text{Ar}}-\text{N}$), 129.8 (2 $\text{C}_{\text{Ar}}-\text{H}$), 129.6 ($\text{C}_{\text{Ar}}-\text{H}$), 129.0 ($\text{C}_{\text{Ar}}-\text{H}$), 128.9 ($\text{C}-\text{CH}_3$), 124.2 ($\text{C}_{\text{Ar}}-\text{H}$), 122.3 ($\text{C}-\text{CH}_2$), 118.7 ($\text{C}_{\text{Ar}}-\text{H}$), 117.7 ($\text{C}_{\text{Ar}}-\text{H}$), 115.9 ($\text{C}-\text{CH}_3$), 63.8 ($-\text{CH}_2-$), 21.0 ($\text{Ar}-\text{CH}_3$). EIMS [m/z (%): 241 (8) [$\text{M}]^+$, 119 (50) [$\text{M}^+-\text{N}_2(\text{C}_6\text{H}_4)\text{CH}_3$], 91 (100) [$\text{M}^+-\text{N}_3(\text{C}_6\text{H}_4)\text{CH}_2\text{OH}$].

2.3. Complexes

2.3.1. $[\text{Cu}\{\text{H}_3\text{C}-p-(\text{C}_6\text{H}_4)-\text{NNN}-(\text{C}_6\text{H}_4)-o-\text{COOCH}_3\}]_2$ (**4**)

{1-[2-(Methoxycarbonyl)phenyl]-3-[4-methylphenyl]}triazene (**1**) (149 mg, 0.555 mmol, 1 equiv.) was dissolved in CH_3CN (5 mL) and triethylamine (112 mg, 1.109 mmol, 2 equiv.) was added with stirring. Then, a solution of $\text{Cu}(\text{OAc})$ (68 mg, 0.555 mmol, 1 equiv.) in CH_3CN (5 mL) was slowly added and the mixture stirred for 10 min at room temperature. A red-orange precipitate formed, which was filtered to obtain a reddish microcrystalline air-stable

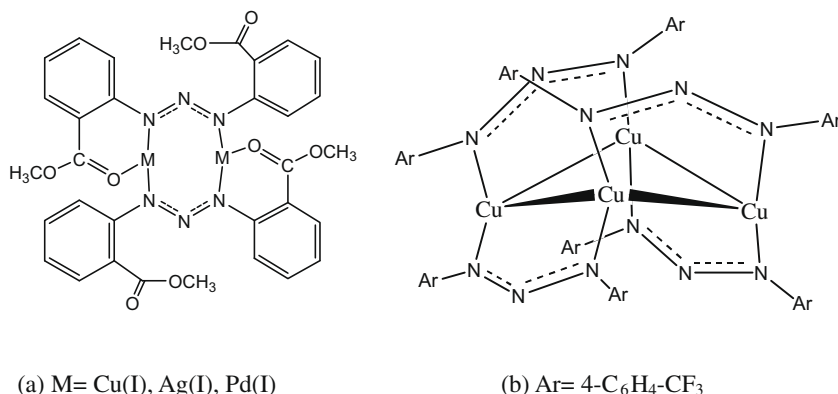


Fig. 2. With d^{10} metal ions triazenido ligands form (a) dinuclear and (b) tetranuclear complexes.

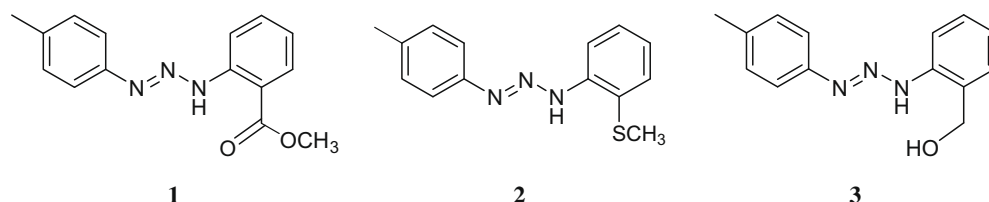


Fig. 3. Ortho functionalized triazenes **1–3** explored in this contribution for the formation of copper complexes.

solid. Recrystallization by vapor diffusion of hexane into a concentrated solution of the product in CH_2Cl_2 at room temperature gave red crystals, which were suitable for X-ray diffraction analysis (149 mg, 0.224 mmol, 81%). Mp = 200–205 °C. IR (KBr): 2952, 1676, 1562, 1476, 1357, 1200, 753 cm^{-1} . UV–vis (CH_2Cl_2 , 1.20×10^{-3} M): λ (ϵ) 222 (1017), 324 (3402), 394 (3300), 458 (3000), 486 nm ($2824 \text{ mL cm}^{-1} \text{ mol}^{-1}$). ^1H NMR (CDCl_3 , 200 MHz, 25 °C): δ 7.99–7.89 (m, 2H, Ar), 7.70–7.76 (m, 2H, Ar), 7.57–7.42 (m, 6H, Ar), 7.20–7.07 (m, 6H, Ar), 3.78 (s, 6H, $-\text{O}-\text{CH}_3$), 2.36 (s, 6H, Ar- CH_3). Anal. Calc. (%) for $\text{C}_{30}\text{H}_{28}\text{Cu}_2\text{N}_6\text{O}_4$: C: 54.29, H: 4.25, N: 12.66. Found: C: 54.50, H: 4.64, N: 12.91%. HRMS Calc. for $\text{C}_{30}\text{H}_{28}\text{Cu}_2\text{N}_6\text{O}_4$: 662.0764. Found: 662.0743.

2.3.2. $[\text{Cu}\{\text{H}_3\text{C}-p-(\text{C}_6\text{H}_4)-\text{NNN}-(\text{C}_6\text{H}_4)-o-\text{SCH}_3\}]_4$ (**5**)

Complex **5** was prepared in the same manner as **4** using triazene **2** to obtain a reddish microcrystalline solid that was first purified by column chromatography (florisil, CH_2Cl_2). Then, the product was crystallized by vapor diffusion of pentane into a concentrated solution of the product in CH_2Cl_2 at room temperature to give orange crystals suitable for X-ray diffraction analysis (34 mg, 0.054 mmol, 55%). Mp = 199–201 °C. IR (KBr): 2919, 1576, 1462, 1350, 1210, 819, 748 cm^{-1} . UV–vis (CH_2Cl_2 , 9.53×10^{-4} M): λ (ϵ) 272 (1421), 316 (4299), 398 (4215), 442 nm ($4081 \text{ mL cm}^{-1} \text{ mol}^{-1}$). ^1H NMR (CDCl_3 , 200 MHz, 25 °C): δ 7.84–6.88 (m, 16H, Ar), 2.37 (s, 3H, Ar- CH_3), 2.25 (s, 3H, $-\text{SCH}_3$), 2.24 (s, 3H, Ar- CH_3), 2.18 (s, 3H, $-\text{SCH}_3$). Anal. Calc. (%) for $\text{C}_{56}\text{H}_{56}\text{Cu}_4\text{N}_{12}\text{S}_4$: C: 52.57, H: 4.41, N: 13.14. Found: C: 52.40, H: 4.65, N: 13.22%. HRMS Calc. for $\text{C}_{56}\text{H}_{56}\text{Cu}_4\text{N}_{12}\text{S}_4$: 1279.5890. Found: 1280.0774.

2.3.3. $[\text{Cu}\{\text{H}_3\text{C}-p-(\text{C}_6\text{H}_4)-\text{NNN}-(\text{C}_6\text{H}_4)-o-\text{CH}_3\text{O}\}]_6$ (**6**)

Complex **6** was prepared in the same manner as **4** using ligand **3**, to obtain an amber green microcrystalline solid, which was purified by column chromatography (florisil, CH_2Cl_2). The resultant product was crystallized by vapor diffusion of pentane into a concentrated solution of the product in CH_2Cl_2 at room temperature to give amber-green crystals suitable for X-ray diffraction analysis (97 mg, 0.160 mmol, 68%). Mp > 300 °C. IR (KBr): 2919, 2832, 1598, 1578, 1504, 1370, 1215, 1034, 813, 754 cm^{-1} . UV–vis (CH_2Cl_2 , 3.90×10^{-4} M): λ (ϵ) 246 (3143), 334 (10030), 336 (9367), 390 nm ($8712 \text{ mL cm}^{-1} \text{ mol}^{-1}$). Anal. Calc. (%) for $\text{C}_{84}\text{H}_{78}\text{Cu}_6\text{N}_{18}\text{O}_6$: C: 55.53, H: 4.33, N: 13.88. Found: C: 55.92, H:

4.70, N: 14.03%. HRMS Calc. for $\text{C}_{84}\text{H}_{78}\text{Cu}_6\text{N}_{18}\text{O}_6$: 1812.2128. Found: 1812.2020.

2.3.4. X-ray crystallography

X-ray diffraction studies were performed on Bruker-APEX diffractometers equipped with a CCD area detector ($\lambda_{\text{Mo K}\alpha} = 0.71073 \text{ \AA}$, monochromator: graphite). Frames were collected at $T = 293 \text{ K}$ (compound **4**), $T = 291 \text{ K}$ (compound **5**) and $T = 100 \text{ K}$ (compound **6**) via ω -rotation at 10 s per frame (BRUKER-SMART) [18]. The measured intensities were reduced to F^2 and corrected for absorption with SADABS (BRUKER-SAINT-NT) [19]. Corrections were made for Lorentz and polarization effects. Structure solution, refinement and data output were carried out with the BRUKER SHELXTL-NT program package [20,21]. Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in geometrically calculated positions using a riding model. The crystal structure of compound **6** contains slightly disordered solvent molecules (pentane), of which one is localized on a special position ($\text{occ} = 0.50$). For their refinement DFIX, DANG, SIMU and DELU instructions were used to constrain bond lengths, bond angles and anisotropic displacement parameters.

A summary of selected crystallographic data and refinement parameters for the structural analyses is given in Table 1.

2.4. Catalytic reactions

2.4.1. General procedure

Under argon, 2.8 mL of a solution containing 114 mg of ethyl diazoacetate (1 mmol) in 1,2-dichloroethane were added during a time period of 6 h via a syringe pump to 2 mL of a solution of the catalyst and styrene (1 mL, 8.7 mmol) in 1,2-dichloroethane at 60 °C. After complete addition, the reaction mixture was stirred at 60 °C for a further 16 h to ensure complete reaction. The mixture was then cooled to room temperature, and purified through a short silica gel plug, whereupon the solvent and unreacted styrene were eliminated under reduced pressure. Yields were determined by GC (column β^{TM} -DEX 120, $30 \times 0.25 \text{ mm} \times 0.25 \text{ \mu m}$, column temperature 110 °C, isothermally).

3. Results and discussion

3.1. Syntheses and general characterization

3.1.1. Ligand **3**

Triazenes **1** and **2** were synthesized according to previously reported procedures [11], while triazene **3** was synthesized following a modified literature procedure, which consisted in the diazotization of 2-aminobenzyl alcohol with sodium nitrite, followed by coupling with *p*-toluidine [11]. Triazene **3** was isolated in 93% yield after crystallization from a 9:1 ethyl acetate/hexane solvent mixture at -4 °C .

The IR spectrum shows a broad band at 3435 cm^{-1} for the OH group and a single band at 3244 cm^{-1} for the NH group of the triazene fragment. The N_3 system gave a band at 1590 cm^{-1} . The ^1H NMR spectrum shows two singlets in the aliphatic region, one integrates for three protons at 2.33 ppm and is assigned to the *p*-tolyl methyl group; the second singlet at 4.77 ppm integrates for two protons and is assigned to the methylene group of the hydroxymethyl function. In the aromatic region there are four groups of signals in the region from 7.06 to 7.66 ppm, which integrate for 8 hydrogen atoms. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows a signal at 21.0 ppm for the *p*-tolyl methyl group, a signal at 63.8 ppm for the methylene group of the hydroxymethyl function and signals for 12 carbon atoms in the aromatic region (for assignment see Section 2). EIMS confirms the molecular weight (241) for triazene **3**.

Table 1

Crystallographic data and refinement parameters for compounds **4–6**.

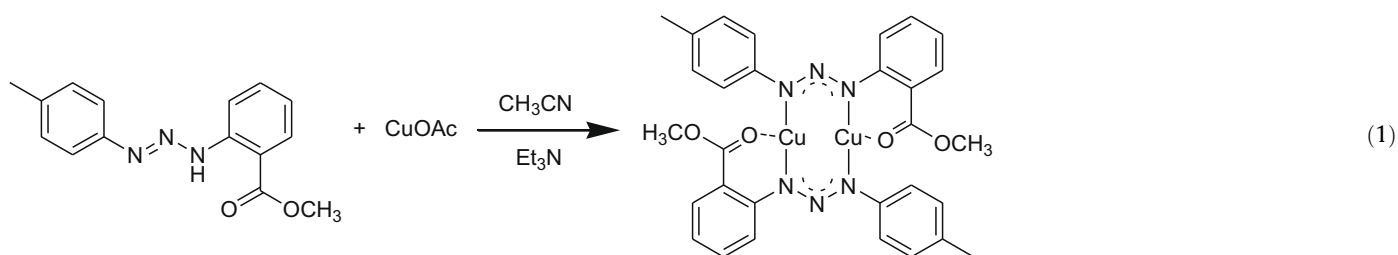
Compounds	4	5	6
Empirical formula	$\text{C}_{30}\text{H}_{28}\text{Cu}_2\text{N}_6\text{O}_4$	$\text{C}_{56}\text{H}_{56}\text{Cu}_4\text{N}_{12}\text{S}_4$	$\text{C}_{84}\text{H}_{78}\text{Cu}_6\text{N}_{18}\text{O}_6 \cdot 3\text{C}_5\text{H}_{12}$
Formula weight	663.66	1279.53	2033.32
Crystal system	Monoclinic	Triclinic	Tetragonal
Space group	$P2_1/c$	$P\bar{1}$	$P4_12_12$
<i>a</i> (Å)	4.030(1)	12.9948(8)	17.0900(12)
<i>b</i> (Å)	18.885(6)	14.5166(9)	17.0900(12)
<i>c</i> (Å)	18.184(5)	16.659(1)	33.542(3)
α (°)	90	70.141(1)	90
β (°)	91.641(6)	72.990(1)	90
γ (°)	90	75.873(1)	90
<i>V</i> (Å ³)	1383.4(7)	2789.5(3)	9796.7(14)
<i>Z</i>	2	2	4
ρ_{calc} (g cm^{-3})	1.593	1.523	1.379
<i>T</i> (K)	293(2)	291(2)	100(2)
λ (Å)	Mo K α 0.71073	Mo K α 0.71073	Mo K α 0.71073
μ (mm^{-1})	1.586	1.704	1.341
<i>R</i> (%) ^a	0.0947	0.0684	0.0471
<i>R_w</i> (%) ^b	0.1004	0.0765	0.1182

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $wR_2 = [\sum (w(F_o^2 - F_c^2))^2 / \sum (w(F_o^2))^2]^{1/2}$.

3.1.2. Copper complexes

Copper complexes **4–6** were prepared in dry acetonitrile by a combination of copper(I) acetate with the corresponding triazene (**1–3**) in the presence of triethylamine (see Eq. (1) for the synthesis of **4**, as an example). The products were isolated by filtration and purification was accomplished either by simple crystallization (**4**) or by column chromatography (florisil/dichloromethane) and subsequent crystallization (**5**, **6**) to provide analytically pure compounds in 81%, 55% and 68% yield, respectively. Compounds **4** and **5** were obtained in form of a reddish microcrystalline material, while compound **6** gave amber-green crystals. As shown by spectroscopic studies and X-ray diffraction analysis, these reactions lead to complexes with different coordination geometries and nuclearities. The nuclearity of the complexes is dependent on the nature of the *ortho* function within the triazenido ligand. Thus, from the methoxycarbonyl-functionalized ligand a dinuclear complex (**4**) was obtained, while the ligands with methylthio and hydroxymethyl substituents gave tetranuclear (complex **5**) and hexanuclear (complex **6**) species.



Copper(I), having a d^{10} configuration, is expected to exhibit diamagnetic behavior. Accordingly, complexes **4** and **5** are amenable to NMR analysis. However, we were surprised to find that complex **6** showed no signals in the ^1H NMR spectrum, which suggests a paramagnetic behavior, and the possibility that a Cu(II) complex had formed by an oxidation reaction. Although complex **6** was prepared under argon atmosphere, the Cu(I) product could not be isolated under such conditions; therefore crystallization was performed under air, which may have provided the oxidation conditions. Since the second ionization energy of copper is not excessive [22], deprotonation of the ligand to a dianionic species could have promoted the oxidation of copper(I) to form a more stable Cu(II) complex. Complex **6** was also obtained when the reaction of **3** was performed with copper(II) acetate in open air conditions.

The solid-state IR spectra of compounds **4–5** lack bands in the region for the triazene NH group, indicating the formation of a monoanionic tridentate ligand by deprotonation of the triazene precursor. In the case of compound **6** there is also no signal for the OH group, which indicates the formation of a neutral copper(II) complex in this case. This was confirmed by the absence of counterions in the X-ray structure. The IR spectrum of complex **4** exhibits a strong band for the carbonyl group at 1676 cm^{-1} , which is shifted to a wavenumber of lower energy when compared to the carbonyl group in the free triazene (1684 cm^{-1}), thus indicating coordination to the metal center. The ^1H NMR spectrum of **4** shows the characteristic signals for the methoxycarbonyl group at 3.78 ppm and the 4-methylphenyl function at 2.36 ppm; the aromatic hydrogens appear as a set of unresolved multiplets in the range 7.99–7.07 ppm integrating for 16 hydrogens.

The ^1H NMR spectrum of complex **5** shows two signals for the methylthio group, one at 2.25 ppm and one at 2.18 ppm. There are also two signals at 2.37 and 2.24 ppm for the methyl group

of the 4-methylphenyl function. The signal pattern in the aromatic region is complex and indicates the presence of four different aromatic rings. As shown by the X-ray diffraction analysis, this is due to different copper coordination modes: one part is tetracoordinated and the second has a coordination number of two (*vide infra*).

3.2. Description of the crystal structures

The molecular structures of **4–6** have been determined by X-ray diffraction and are shown in Figs. 4–6. The most relevant crystallographic data are summarized in Table 1. Selected bond lengths and angles are listed in Tables 2–4.

In compound **4** two copper atoms are bridged by two triazenido ligands, in which the carbonyl oxygen atoms of the pendent Lewis basic ester functions are coordinated to the copper centers. The absence of counterions indicates that the oxidation state of the starting metal complex has been preserved.

In the dimeric structure of the Cu(I) complex **4** each ligand bridges two metal centers (Fig. 4). This structure is therefore re-

lated to a series of Cu(I), Ag(I) and Pd(I) complexes containing unsubstituted bis(aryl)triazenido ligands, $[\text{Cu}(\text{PhNNNPh})]_2$ and $[\text{Ag}(\text{PhNNNPh})]_2$ [23,24], *ortho* functionalized triazenido ligands, $[\text{M}(\text{ArNNNAr})]_2$ ($\text{M} = \text{Cu(I)}$ and Ag(I) ; $\text{Ar} = o\text{-C}_6\text{H}_4\text{-COOCH}_3$) [9] and $[\text{Pd}(\text{ArNNNAr})]_2$, ($\text{Ar} = o\text{-C}_6\text{H}_4\text{-COOCH}_3$; $o\text{-C}_6\text{H}_4\text{-OMe}$) [11], and *ortho* functionalized amidinato ligands, $[\text{Ag}(\text{RNCPhNR})]_2$ ($\text{R} = o\text{-C}_6\text{H}_4\text{-COOCH}_3$, $o\text{-C}_6\text{H}_4\text{-SCH}_3$) [25]. Complex **4** has an almost planar 8-membered core formed by the two N_3 units and the copper centers (Fig. 4). The *trans* nitrogen atoms exhibit a N–Cu–N

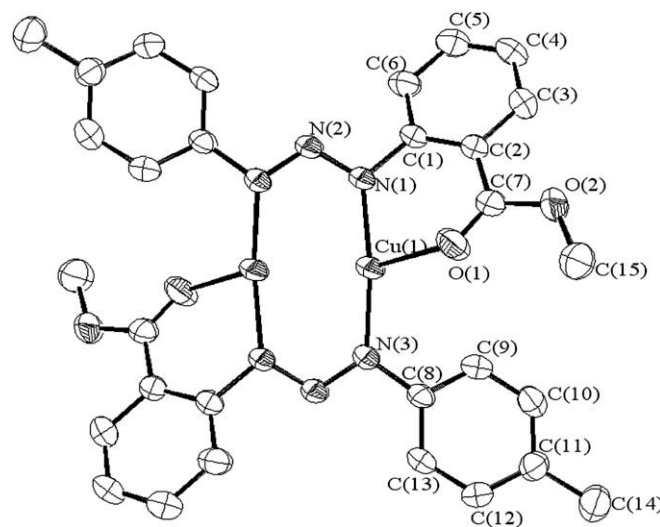


Fig. 4. ORTEP diagram showing the structure of compound **4** with thermal ellipsoids at the 50% probability level and the atom labeling scheme. Hydrogens are omitted for clarity.

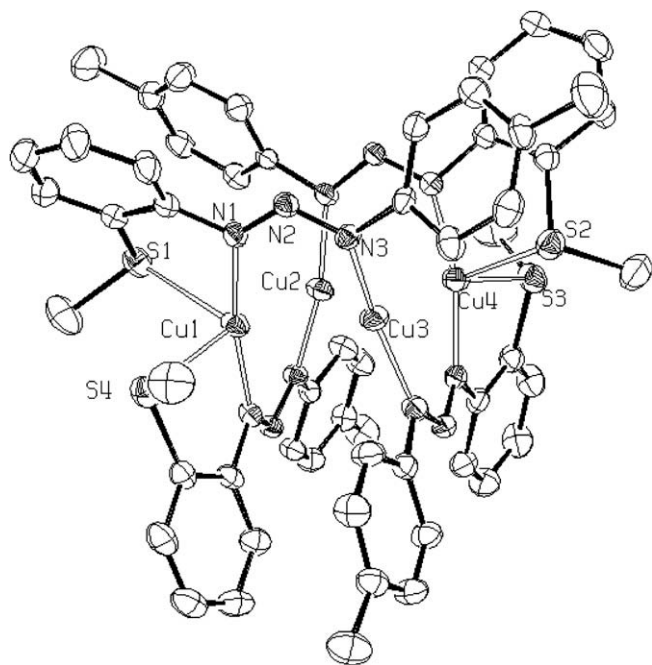


Fig. 5. ORTEP diagram showing the structure of compound **5** with thermal ellipsoids at the 50% probability level and the atom labeling scheme. Hydrogens are omitted for clarity.

bond angle of $169.80(13)^\circ$, indicating a small distortion from planarity of the Cu-triazenido framework due to the coordination of the carbonyl ester group. As in the Pd(I), Cu(I) and Ag(I) analogues, the coordinated carbonyl oxygens in **4** lie slightly above and below the planar core with Cu–Cu–O angle of $140.61(9)^\circ$. The Cu–N(1) and Cu–N(3) bond lengths in **4** are identical, $1.910(3)$ and $1.907(3)$ Å and the Cu··Cu distance, $2.4755(11)$ Å, is significantly shorter than the Cu··Cu distance found in copper metal (2.64 Å).

In the molecular structure of compound **5** four copper atoms are bridged by four alternating triazenido ligands. Additionally, the pendent Lewis basic thiomethyl groups are coordinated to the copper centers (Fig. 5). As in **4**, the absence of counterions indicates that the oxidation state of the starting copper(I) complex has been preserved.

The structure of complex **5** is similar to that of the tetranuclear Cu(I) and Ag(I) complexes $[\text{Cu}(\text{MeNNNMe})]_4$ [13], $[\text{Cu}(\text{F}_3\text{CC}_6\text{H}_4$

Table 2
Selected bond distances (Å) and angles ($^\circ$) for compound **4**.

Bond distances (Å)	
Cu(1)–N(3)	1.907(3)
Cu(1)–N(1)	1.910(3)
Cu(1)–O(1)	2.272(3)
Cu(1)–Cu(1)	2.4755(11)
N(1)–N(2)	1.310(4)
N(2)–N(3)	1.306(4)
C(1)–N(1)	1.437(5)
C(8)–N(3)	1.427(5)
C(7)–O(1)	1.216(5)
C(7)–O(2)	1.330(5)
C(15)–O(2)	1.433(5)
Bond angles ($^\circ$)	
N(1)–N(2)–N(3)	115.8(3)
N(1)–Cu(1)–N(3)	169.80(13)
Cu(1)–Cu(1)–N(1)	85.68(10)
Cu(1)–Cu(1)–N(3)	86.21(10)
Cu(1)–Cu(1)–O(1)	140.61(9)
O(1)–Cu(1)–N(1)	106.44(12)
O(1)–Cu(1)–N(3)	83.77(11)
N(1)–Cu(1)–N(3)	169.80(13)
N(2)–N(3)–C(8)	111.4(3)
N(2)–N(3)–Cu(1)	125.4(3)
Cu(1)–O(1)–C(7)	117.4(3)

$\text{NNNC}_6\text{H}_4\text{CF}_3)_4$ [14], and $[\text{Ag}(\text{H}_3\text{COC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{OCH}_3)]_4$ [26], in which four triazenido ligands are bound to four copper atoms forming a 16-membered folded-ring system with metal–nitrogen bondings (Fig. 5). Complex **5** contains a tetranuclear copper core. The Cu··Cu distances in complex **5** are $2.6702(6)$, $2.7029(7)$, $2.8006(6)$ and $2.6500(6)$ Å for Cu(1)–Cu(2), Cu(1)–Cu(3), Cu(2)–Cu(3) and Cu(3)–Cu(4), respectively, which are longer than the Cu··Cu distances found in $[\text{Cu}(\text{MeNNNMe})]_4$ at $2.66(1)$ Å [23], $[\text{Cu}(\text{F}_3\text{CC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{CF}_3)]_4$ at $2.579(1)$ Å [14] and in $[\text{Cu}(\text{FC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{F})]_4$ at $2.6070(9)$ Å [27]. Cu··Cu distances in **5** are in general above the range of weak bonding interactions [27]. Complex **5** contains two types of copper centers; assuming no Cu··Cu interactions, the first has a coordination number of 2 with two nitrogen atoms coordinated to the 14 electron copper(I) center, and the second has a coordination number of 4 with two nitrogen atoms and two sulfur atoms coordinated to an 18 electron metal center. Each of the four-coordinate copper centers is embedded in two chelate rings resulting from the coordination of one nitrogen atom and one sulfur atom from each of the bridging triazenido ligands. The Cu–S distances vary from $2.4751(11)$ to $2.5621(12)$ Å, and the

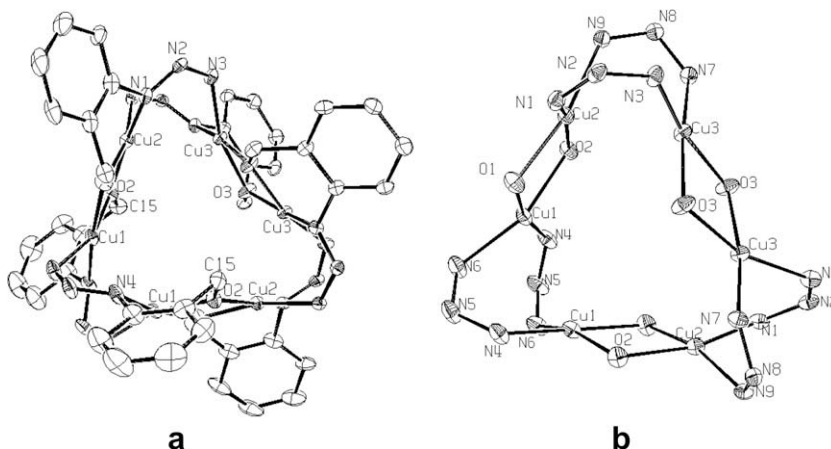


Fig. 6. (a) ORTEP diagram showing the structure of compound **6** with thermal ellipsoids at the 50% probability level and the atom labeling scheme. Hydrogens and methyl groups are omitted for clarity. (b) View of the hexanuclear core in complex **6**.

Table 3Selected bond distances (Å) and angles (°) for compound **5**.

Bond distances (Å)	
Cu(1)–N(1)	1.946(3)
Cu(1)–N(10)	1.918(3)
Cu(1)–S(1)	2.5621(12)
Cu(1)–S(4)	2.5161(11)
Cu(2)–N(6)	1.894(3)
Cu(2)–N(12)	1.901(3)
Cu(3)–N(3)	1.898(3)
Cu(3)–N(9)	1.905(3)
Cu(4)–N(4)	1.950(3)
Cu(4)–N(7)	1.937(3)
Cu(4)–S(2)	2.5112(11)
Cu(4)–S(3)	2.4751(11)
Cu(1)–Cu(2)	2.6702(6)
Cu(1)–Cu(3)	2.7029(7)
Cu(2)–Cu(3)	2.8006(6)
Cu(2)–Cu(4)	2.7340(6)
N(1)–N(2)	1.295(3)
N(2)–N(3)	1.294(3)
N(4)–N(5)	1.296(3)
N(5)–N(6)	1.297(3)
N(7)–N(8)	1.304(3)
N(8)–N(9)	1.304(3)
N(10)–N(11)	1.316(3)
N(11)–N(12)	1.300(3)
Bond angles (°)	
N(1)–Cu(1)–N(10)	168.75(12)
Cu(2)–Cu(1)–S(1)	121.70(3)
Cu(3)–Cu(1)–S(4)	163.92(3)
N(10)–Cu(1)–S(4)	83.30(8)
N(6)–Cu(2)–N(12)	157.29(12)
N(6)–Cu(2)–Cu(1)	106.64(8)
N(3)–Cu(3)–N(9)	156.14(12)
N(3)–Cu(3)–Cu(4)	109.77(8)
N(4)–Cu(4)–N(7)	165.37(11)
S(2)–Cu(4)–Cu(2)	146.18(3)
S(3)–Cu(4)–Cu(3)	164.67(3)
N(4)–Cu(4)–Cu(3)	92.28(8)
N(7)–Cu(4)–Cu(3)	81.16(8)
N(1)–N(2)–N(3)	115.4(3)
N(4)–N(5)–N(6)	115.5(3)
N(7)–N(8)–N(9)	115.0(3)
N(10)–N(11)–N(12)	114.9(3)
Cu(3)–Cu(4)–Cu(2)	62.663(17)
Cu(1)–Cu(2)–Cu(4)	166.33(2)
Cu(1)–Cu(3)–Cu(4)	118.13(2)
Cu(2)–Cu(4)–Cu(3)	62.663(17)
Cu(2)–Cu(1)–Cu(3)	62.825(17)
Cu(1)–Cu(2)–Cu(3)	59.159(16)
Cu(4)–Cu(2)–Cu(3)	57.200(16)

Table 4Selected bond distances (Å) and angles (°) for compound **6**.

Compound 6	
Bond distances (Å)	
Cu(1)–N(4)	1.966(4)
Cu(1)–N(6)	1.990(4)
Cu(2)–N(1)	1.947(4)
Cu(2)–N(9)	1.991(3)
Cu(3)–N(7)	1.948(3)
Cu(3)–N(3)	1.978(4)
Cu(1)–O(1)	1.916(3)
Cu(1)–O(2)	1.919(3)
Cu(2)–O(1)	1.921(3)
Cu(2)–O(2)	1.925(3)
Cu(3)–O(3)#1	1.917(3)
Cu(3)–O(3)	1.918(3)
Cu(1)–Cu(1)#1	2.9323(11)
Cu(1)–Cu(2)	3.0282(7)
Cu(2)–Cu(3)	2.7819(7)
Cu(3)–Cu(3)#1	2.9878(10)
N(1)–N(2)	1.307(5)
N(2)–N(3)	1.307(5)
N(4)–N(5)#1	1.291(6)
N(5)–N(6)	1.290(5)
N(5)–N(4)	1.291(6)
N(7)–N(8)	1.301(5)
N(8)–N(9)	1.289(5)
Bond angles (°)	
O(1)–Cu(1)–O(2)	75.89(12)
O(1)–Cu(1)–N(4)	167.84(14)
O(2)–Cu(1)–N(4)	92.89(14)
O(1)–Cu(1)–N(6)	96.06(15)
O(2)–Cu(1)–N(6)	160.91(16)
O(1)–Cu(2)–O(2)	75.61(12)
O(1)–Cu(2)–N(1)	89.98(14)
O(2)–Cu(2)–N(1)	164.14(14)
O(1)–Cu(2)–N(9)	165.18(14)
O(2)–Cu(2)–N(9)	99.99(13)
O(3)#1–Cu(3)–O(3)	76.96(14)
O(3)#1–Cu(3)–N(7)	167.27(14)
O(3)–Cu(3)–N(7)	90.56(13)
O(3)#1–Cu(3)–N(3)	93.86(14)
O(3)–Cu(3)–N(3)	161.78(14)
N(4)–Cu(1)–N(6)	96.04(16)
N(1)–Cu(2)–N(9)	95.59(15)
N(7)–Cu(3)–N(3)	98.84(14)
Cu(1)–O(1)–Cu(2)	104.3(5)
Cu(1)–O(2)–Cu(2)	103.9(5)
Cu(3)#1–O(3)–Cu(3)	102.3(5)

Symmetry transformations used to generate equivalent atoms: #1 $-y+1, -x+1, -z+3/2$.

Cu–N distances from 1.894(3) to 1.950(3) Å. The N–Cu–N bond angles are 156.14(12) and 157.29(12)° for the two-fold coordinated copper atoms, and 165.37(11) and 168.75(12)° for the four-fold coordinated copper atoms. The deviations from ideal linear and tetrahedral coordination geometries can be attributed to coordination requirements.

In complex **6** three-folded dinuclear units of the composition $\{[\text{Cu}(\text{ArNNNAr})]_2\}$ are bridged by the methoxy groups of the *ortho* functionalized triazenido ligands to form an overall hexanuclear macrocyclic complex (Fig. 6).

As already mentioned, the absence of counterions indicates that the copper centers have oxidation state 2+. Each metal center has a coordination number of 4, with a rather distorted square-planar geometry. The distortion is indicated by the deviations from the ideal angles of a square-planar geometry (180° and 90°) with the *trans* O–Cu–N bond angles in the range of 160.91(16)–167.27(14)°, and the *cis* O–Cu–O and N–Cu–N bond angles in the range of 75.61(12)–76.96(14)° and 95.59(15)–98.84(14)°, respectively. This should be due to ligand bond requirements upon for-

mation of the cycle (Table 4). The Cu···Cu distances in the range of 2.7819(7)–3.0282(7) Å are larger than in the dinuclear complex **4**, 2.4755(11) Å, and the tetranuclear complex **5**, 2.6702(6)–2.8006(6) Å. The Cu–N bond lengths vary from 1.947(4) to 1.991(3) Å and are also larger than the corresponding bond lengths in **4** (1.907(3)–1.910(3) Å) and in **5** (1.894(3)–1.950(3) Å). Cu–O bond lengths in **6** are in the range of 1.916(3)–1.925(3) Å and compare well with the tetranuclear alkoxo bridged triazenido complex $[\text{Cu}(\text{FC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{F})(\text{OCH}_3)]_4$ at 1.919(3)–1.926(3) Å [27]. Cu–O bond lengths in **6** are also similar to those in related hydroxo and alkoxo bridged copper complexes: tetrakis[(μ -hydroxo)(μ -sulfathiazolato)copper(II)]tetrakis(dimethylsulfoxide) at 1.901(9)–1.923(9) Å [28] and a tetranuclear complex formed by *N*-2-pyridylsalicylaldehyde at 1.965(6)–1.971(6) Å [29]. Cu–O–Cu angles in **6** are in the range 102.3(5)–104.3(5)°, slightly larger than the angles in the alkoxo bridged triazenido complex $[\text{Cu}(\text{FC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{F})(\text{OCH}_3)]_4$ at 102.0(1)° [27] and the copper complex of *N*-2-pyridylsalicylaldehyde at 102.9(3)° [29], due to structure requirements for a larger cycle.

Table 5Cyclopropanation of styrene with ethyl diazoacetate catalyzed by complexes **4–6**^a.

Entry	Catalyst	S/C ^b	Yield ^c	cis/trans ratio
1	4	100:1	32	38:62
2	4	100:0.1	25	36:64
3	5	100:1	72	30:70
4	5	100:0.1	75	33:67
5	6	100:1	88	30:70
6	6	100:0.1	89	34:66

^a At 60 °C.^{b,c} Relative to ethyl diazoacetate.

3.3. Catalysis

In a set of experiments to evaluate the potential catalytic activity of our complexes, cyclopropanation of styrene with ethyl diazoacetate (EDA) was performed as a function of the complex nuclearity and S/C (substrate/catalyst ratio) (Eq. (2)). The typical experimental procedure is described in Section 2 and the results are illustrated in Table 5.

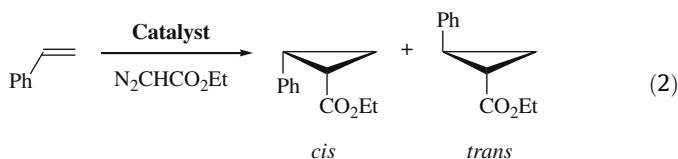


Table 5 shows that the overall yields vary from low to moderate, and are virtually independent of the S/C ratio. Interestingly, the yield increases as a function of the nuclearity of the copper complex, from dinuclear (32% and 25%) to tetranuclear (72% and 75%) and hexanuclear (88% and 89%), suggesting that some kind of metal cooperativity might occur in the catalytic process. The oxidation state of copper in the complexes does not seem to play an important role in this reaction. The *cis/trans* ratio of the cyclopropanation products are similar to those achieved with other copper complexes containing nitrogen donor ligands [30].

4. Conclusions

Reported herein are the structures of three new copper complexes (**4–6**), which have been derived from 1,3-bis(aryl)triazenido ligands bearing different Lewis basic groups in the *ortho* position of one of the aromatic rings. Due to the variation of the Lewis basicity and steric requirements of the varying coordinating functions, complexes with different nuclearity have been obtained. While the methoxycarbonyl group in **4** and the methylthio group in **5** stabilize copper in the 1+ oxidation state forming dinuclear and tetranuclear complexes, the methyleneoxy group in complex **6** seems to prefer oxidation state 2+ with the formation of a novel hexanuclear macrocyclic complex. Although the results from the evaluation of the catalytic activity of **4–6** are scanty, they do indicate that might be a dependence on the nuclearity of the complex, which may be relevant for the design of new catalysts for different chemical transformations.

Acknowledgements

This work was supported by Consejo Nacional de Ciencia y Tecnología (CONACyT) Grant 60467 and Consejo del Sistema Nacional de Educación Tecnológica (COSNET) Grant 486-02-P. The authors are indebted to Professor Patrick J. Walsh for fruitful comments on this research. Analytical support by Daniel Chávez is gratefully acknowledged. J.J.N.-E., G.R.-M., C.C.-A. and F.R.-A. thank CONACyT for graduate fellowships. C.C.-A. thanks ESET, LLC for complementary financial support.

Appendix A. Supplementary material

CCDC 741827, 741828 and 741829 contain the supplementary crystallographic data for **4**, **5** and **6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.11.014.

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