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Synthesis, characterization, and structure of dinuclear copper(I) and silver(I) complexes of *ortho*-functionalized 1,3-bis(aryl)triazenide ligands

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Abstract

The synthesis, characterization, and crystal structures of dinuclear copper(I) and silver(I) complexes with a functionalized 1,3-diaryl triazenide ligand are reported. The triazene ligand is substituted with carboxymethyl groups in the *ortho* positions of the aryl rings that can coordinate to electron deficient metals. Reaction of this ligand with Cu(OAc) and Ag(OAc) resulted in the formation of dinuclear complexes with an eight-membered ring core composed of the two triazenide ligands and two metals. In these complexes, only one carbonyl group of each triazenide ligand binds to the metal centers.

Keywords: Triazene; Triazenide; Copper(I) complex; Silver(I) complex; Dinuclear structure

1. Introduction

Cooperativity in heterogeneous catalysts can lead to greatly increased reactivity and catalyst lifetimes [1,2]. Such benefits are often ascribed to the interaction of metal centers held in close proximity in the solid state. Due to challenges associated with the study of heterogeneous catalysts, a long-standing goal in catalysis has been to develop homogeneous models for heterogeneous catalysts. The simplest model systems for heterogeneous catalysts are bimetallic complexes in which the two metal centers have a synergistic effect and exhibit reactivity not observed with the related mononuclear complexes. Recent advances in catalysis using bimetallic complexes with cooperative interactions have been made in asymmetric hydroformylation [3–8], lanthanide/main group systems based on BINOL [9–11], asymmetric alkylation of aldehydes [12], and others [13–28].

Our interests have been in the synthesis and characterization of bimetallic complexes bearing triazenide ligands [29–31]. While such ligands are isoelectronic with amidinate [32,33] and carboxylate ligands [34], their chemistry has been considerably less explored. We recently demonstrated that the functionalized ligand 1,3-bis(2-carboxymethyl)benzene triazene (**1**), which is easily synthesized in one step from commercially available materials [35], enforces a dinuclear structure [31]. Reaction of **1** with $Cu_2(OAc)_4 \cdot 2H_2O$ in the presence of base resulted in the formation of **2** as shown in Eq. (1) [31].

Dinuclear complexes of this type are of considerable interest because of the controversy over whether a metal–metal bond exists in these systems [36] and because of their interesting photophysical properties

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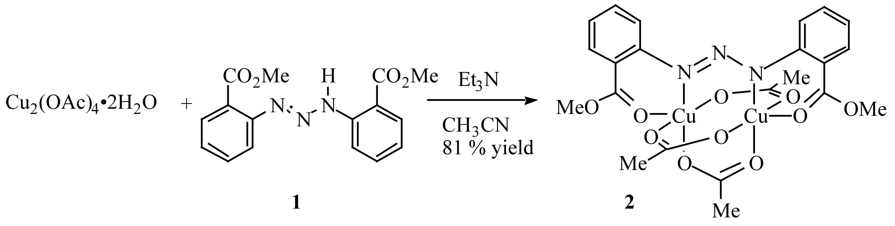
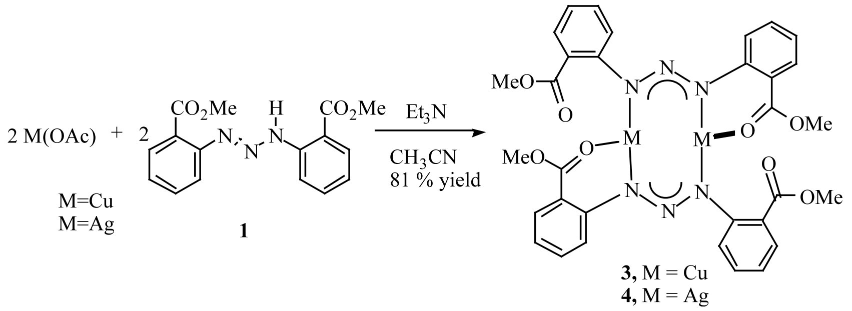


(1)

[37,38]. With this in mind, we set out to synthesize the Cu(I) and Ag(I) complexes of the ligand **1**. Herein we report the synthesis and structure of the dinuclear bis(triazenide) complexes of copper(I) and silver(I). In contrast to the Cu(II) structure of **2** (Eq. 1)) [31], where the ligand binds in a bis(bidentate) fashion, in the Cu(I) and Ag(I) complexes each ligand binds in a bidentate fashion to one metal and a monodentate fashion to the other in the solid state.

2. Results and discussion

The synthesis of copper and silver complexes of ligand **1** is shown in Eq. 2). Combination of a solution of copper(I) acetate in acetonitrile with a mixture of triazene **1** and triethylamine under a nitrogen atmosphere resulted in the formation of a red–brown microcrystaline compound, **3**. Solid **3** was isolated by filtration and found to be air-stable. Purification was accomplished using column chromatography on florisil in dichloromethane followed by crystallization to provide analytically pure **3** in 65% yield. The silver complex **4** was prepared in a similar fashion. An orange solution of **1** with triethylamine was combined with silver acetate in methanol. The reaction mixture was heated to 40 °C for 10 min and cooled to room temperature (r.t.). On standing, pale yellow crystals of **4** formed and were isolated in 94% yield by filtration.



(2)

X-ray quality crystals of the copper complex were grown from CH_2Cl_2 by slow evaporation of the solvent.

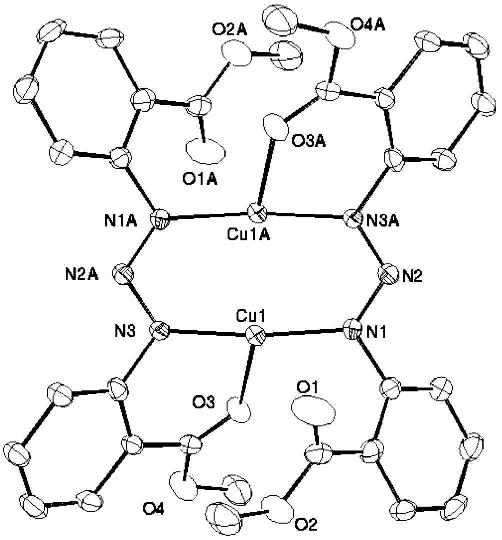


Fig. 1. Structure of **3**. Bond distances and angles are given in Table 1.

The structure was determined and an ORTEP diagram is illustrated in Fig. 1 with bond distances and angles displayed in Table 1. Details of the structure are compiled in Table 3. The structure consists of two copper centers bridged by two triazenide ligands. A single ester carbonyl group is coordinated to each copper center, with one ester of each ligand remaining unbound. The structure is similar to the Cu(I) dinuclear complex $[Cu(PhNNNPh)]_2$ (**5**) [37,39] and related to the tetrameric Cu(I) complex $[Cu(ArNNNAr)]_4$ (**6**, Fig. 2,

Table 1
Selected bond distances (Å) and angles (°) for complex **3**

Cu(1)–Cu(1A)	2.4289(12)
Cu(1)–N(1)	1.909(4)
Cu(1)–N(3)	1.905(4)
Cu(1)–O(3)	2.163(4)
C(15)–O(3)	1.205(6)
N(2)–N(3A)	1.312(5)
N(1)–N(2)	1.300(5)
C(13)–O(1)	1.183(6)
N(1)–N(2)–N(3A)	113.3(4)
Cu(1A)–Cu(1)–O(3)	145.00(12)
O(3)–C(15)–O(4)	120.4(5)
N(1)–Cu(1)–O(3)	102.2(2)
N(1)–Cu(1)–N(3)	169.8(2)
N(3)–Cu(1)–O(3)	87.9(2)
Cu(1A)–Cu(1)–N(1)	85.69(12)
Cu(1A)–Cu(1)–N(3)	86.56(12)

$Ar = 4\text{-}C_6H_4\text{–}CF_3$), in which each ligand bridges two different copper centers [40]. Both **3** and **5** have planar 8-member cores formed by the two N_3 units and the copper centers (Fig. 2). In **3** and **5** the N–Cu–N bond angles are 169.8° and 171.8°, respectively, indicating that there is only a small distortion in the Cu–triazene framework of **3** due to the coordination of the ester carbonyl group. The carbonyl oxygens of **3** lie above and below the planar core with a Cu–Cu–O angle of 145.0(1)°. The C–O distance of the coordinated carbonyl oxygen is slightly elongated (1.205(6) Å) with respect to the free carbonyl group (1.183(6) Å), as expected. The Cu–N(1) and Cu–N(3) distances in **3** are very similar at 1.909(4) and 1.905(4) Å, and can be compared to the Cu–N distance in **2** of 1.991(2) Å [31] and those in **5** of 1.898(18) and 1.939(18) Å [39]. The copper–nitrogen distances in **3** are shorter than those of the dinuclear copper(II) triazenide complex $Cu_2(PhNNNPh)_4$, which range from 1.973(6) to 2.088(6) Å (average 2.020 Å) [41]. In **6** the Cu–N distances are 1.882(7) and 1.883(6) Å [40]. The N–N distances in **3** of 1.300(5) and 1.312(5) Å are very close, as is often observed with triazenide ligands bound to late metals. The Cu–Cu distances in **3**, **5**, **6**, and **2** are 2.439(12), 2.451(8), 2.579(1), and 2.531(1) Å, all of which are shorter than Cu–Cu distances found in copper metal (2.64 Å).

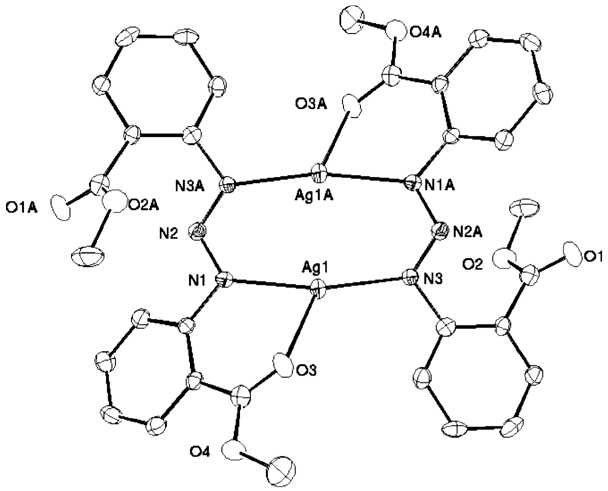
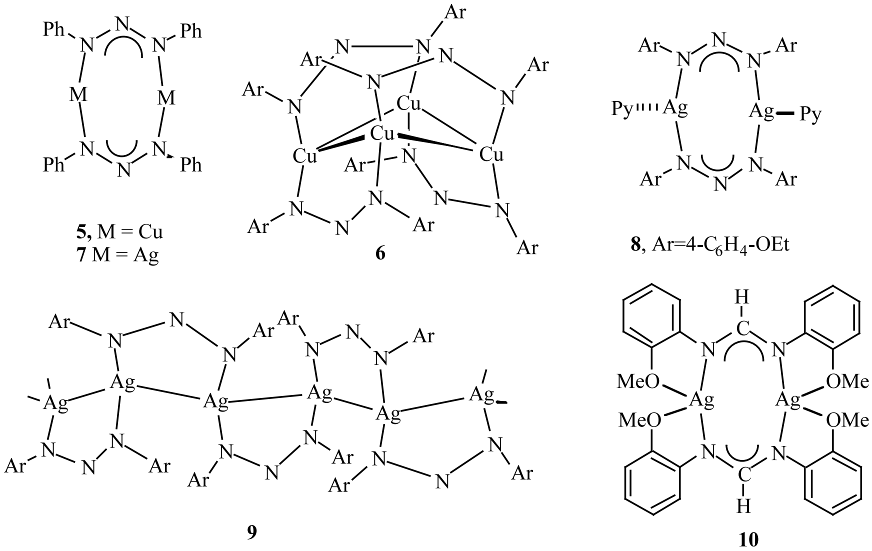


Fig. 3. Structure of **4**. Bond distances and angles are given in Table 2.

The silver(I) complex **4** also crystallized to form X-ray grade pale yellow crystals. A structure determination study was performed on one of these crystals and an ORTEP diagram is illustrated in Fig. 3. Selected bond lengths and angles are listed in Table 2 and crystallographic data are in Table 3. The structure of **4** has the same gross features as that of **3**. The eight-membered ring formed by the triazenide ligands and silver atoms is nearly planar, with the oxygen of the carbonyl above and below the plane of the ring [Ag–Ag–O = 134.0(2)°].



5, M = Cu
7 M = Ag

6

8, $Ar=4\text{-}C_6H_4\text{-}OEt$

9

10

Fig. 2. Structures of related triazenide and amidinate complexes.

Table 2
Selected bond distances (Å) and angles (°) for complex **4**

Ag(1)–Ag(1A)	2.704(2)
Ag(1)–N(3)	2.165(7)
Ag(1)–N(1)	2.203(7)
Ag(1)–O(3)	2.475(6)
C(13)–O(3)	1.222(10)
N(1)–N(2)	1.297(9)
N(2)–N(3A)	1.296(9)
C(15)–O(1)	1.205(11)
N(1)–N(2)–N(3A)	117.8(7)
Ag(1A)–Ag(1)–O(3)	134.0(2)
O(3)–C(13)–O(4)	120.8(9)
N(3)–Ag(1)–O(3)	113.6(2)
N(1)–Ag(1)–N(3)	167.2(3)
N(1)–Ag(1)–O(3)	75.0(2)
Ag(1A)–Ag(1)–N(3)	82.3(2)
Ag(1A)–Ag(1)–N(1)	84.9(2)

The structure is closely related to the silver triazenide complex $[Ag(Ph{-}NNN{-}Ph)]_2$ (**7** [42], Fig. 2) and the pyridine adduct $[(Py)Ag(Ar{-}NNN{-}Ar)]_2$ (**8**, Ar = 4-C_6H_4–OEt) [43] which have the same core structures. A polymeric derivative, **9**, in which each ligand bridges two different metals, has also been reported [40]. A related amidinate dinuclear (**10**), in which the amidinate ligand contains Lewis basic groups that coordinate to the silver has recently appeared in the literature [38,44]. The core structure of **10** is similar to **4** and **7** (Fig. 2). The Ag–N distances in **4** of 2.165(7) and 2.203(7) Å are slightly longer than those of **7** (2.155(3) and 2.144(4) Å) and those found in the polymeric structure **9** (2.121(6) and 2.104(7) Å). The Ag–Ag distances in **4**, **7**, **8**, and **9** are 2.704(2), 2.669(1), 2.726(1), and 2.834(1) Å, respectively.

Table 3
Crystal data and structure refinement parameters for **3** and **4**

Compound	3	4
Empirical formula	$C_{16}H_{14}CuN_3O_4$	$C_{16}H_{14}AgN_3O_4$
FW	375.84	420.17
a (Å)	16.579(3)	8.3983(8)
b (Å)	10.699(3)	15.9952(13)
c (Å)	17.567(3)	12.4553(11)
α (°)	90	90
β (°)	90	108.942
γ (°)	90	90
V (Å^3)	3115.9(11)	1582.5(2)
Z	8	4
Space group	*Pbca*	$P2_1/c$
T (°C)	21	21
Radiation, λ (Å)	Mo Kα, 0.710373	Mo Kα, 0.710373
D_{calc} (g cm^{-3})	1.602	1.764
μ (mm^{-1})	1.428	1.300
Final R indices [a] [$I > 2\sigma(I)$]	$R_1 = 0.0471$ $wR_2 = 0.0931$	$R_1 = 0.0622$ $wR_2 = 0.0988$
R indices (all data)	$R_1 = 0.1122$ $wR_2 = 0.1222$	$R_1 = 0.1415$ $wR_2 = 0.1285$

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

The pendent methoxy groups in the amidinate **10** are bonded to the silver with distances of 2.691(5)–2.894(6) Å. Although the Ag–O distances in **10** are long, they have been shown to provide thermal stability to the complex [44]. The Ag–O distance in **4** is considerably shorter at 2.475(6) Å and we believe that this interaction stabilizes the complex based on its high melting point (204–205 °C).

The strong IR stretch of carbonyl groups can provide information about the strength of the interaction of this group with metal centers. The interpretation of the IR data for compounds **1**–**4**, however, is not as straightforward as that involving simple dative ligands for two reasons: (1) on formation of a complex, the triazene must be deprotonated, which will result in a change in the C–O stretching frequency; (2) each ligand binds to two metal centers. The IR spectrum of the unbound diester **1** (CH_2Cl_2) contains strong absorptions for the carbonyl groups at 1725 and 1697 cm^{-1}. Compound **3** exhibits two stretches at 1714 and 1684 cm^{-1} in CH_2Cl_2 and at 1700 and 1671 cm^{-1} in KBr. In the KBr spectrum of **3**, we believe that one carbonyl oxygen is coordinated to copper and one is free, as observed in the solid state structure. Because of the similarity between the solution and solid state IR spectra, we propose that one of the carbonyl oxygens of each ligand is bonded in solution. For the purposes of comparison, the IR spectra of **2** (Eq. (1)) exhibited a single absorption for the carbonyl group at 1694 cm^{-1}. In the silver complex **4**, the carbonyl stretches were observed at 1727 and 1684 cm^{-1} (KBr) suggesting analogous behavior to **3**.

The copper and silver complexes **3** and **4** are diamagnetic and amenable to NMR analysis. The ^1H and $^{13}C\{^1H\}$ NMR spectra of both the copper and silver complexes are indicative of a single ligand environment with equivalent ester and aryl groups. The equivalence of the esters in solution could be explained if the coordinated ester and free ester exchange rapidly on the NMR time scale. In the hopes of understanding the solution structure, a sample of the copper dinuclear complex **3** was cooled to −80 °C in the probe of a 200 MHz NMR spectrometer. No significant changes in the spectra were observed under these conditions. The analogous experiment with the silver derivative **4** was not possible due to the sparing solubility of this compound in most solvents, including DMSO-d_6.

In summary, we have synthesized dinuclear copper(I) and silver(I) complexes of the functionalized triazenide ligand **1** and characterized these compounds by X-ray crystallography. IR data indicate that in solution, like the solid state structures, the metal has a single coordinated carbonyl oxygen. Variable temperature NMR experiments with the copper dinuclear **3** are consistent with a rapid exchange of the bound and unbound carbonyl oxygens.

We are currently preparing other novel triazene ligands and their transition metal complexes.

3. Experimental

3.1. Synthesis and characterization of **3**

Under an inert atmosphere, an acetonitrile solution of ligand **1** [35] (0.085 g, 0.272 mmol, 1 equiv.) and triethylamine (0.0412 g, 0.408 mmol, 1.5 equiv.) was added to a stirred acetonitrile solution of Cu(OAc) (0.050 g, 0.408 mmol, 1.5 equiv.). After mixing was complete, a brown precipitate formed. The reaction mixture was filtered to obtain a reddish brown microcrystalline solid, found to be air stable. The crude product was purified by column chromatography (florisil, CH_2Cl_2) and crystallized by slow evaporation from CH_2Cl_2. Yield (100.1 mg, 0.1333 mmol, 65.6%). M.p. = 239–241 °C; IR(KBr): 2947, 1700, 1671, 1340, 1307, 1256, 1204, 1080, 765 cm^{-1}; (CH_2Cl_2): 1714, 1684, 1596, 1568, 1477, 1437, 1341 cm^{-1}; ^1H NMR (500 MHz, CD_2Cl_2, 298 K): δ 7.80 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.3$ Hz, 1H), 7.55 (dd, $J_1 = 8.3$, $J_2 = 0.7$ Hz, 1H), 7.41 (dt, $J_1 = 8.4$ Hz, $J_2 = 1.5$ Hz, 1H), 7.08 (dt, $J_1 = 7.1$ Hz, $J_2 = 1.0$ Hz, 1H), 3.43 (s, 3H) ppm; ^1H NMR (200 MHz, CD_2Cl_2, 193K): δ 7.86 (d, $J = 7.7$ Hz, 1H), 7.58 (d, $J = 7.9$ Hz, 1H), 7.50 (t, $J = 7.5$ Hz, 1H), 7.16 (t, $J = 7.7$ Hz, 1H); 3.41 (s, 3H) ppm; ^{13}C NMR (CD_2Cl_2, 298 K): δ 169.4, 153.1, 133.6, 131.4, 124.3, 123.8, 121.7, 52.7 ppm; Elemental analysis Calc. for: $C_{16}H_{14}CuN_3O_4$: C, 51.13, H, 3.75, N, 11.18; Found: C, 50.74, H, 3.51, N, 11.07%.

3.2. Synthesis and characterization of **4**

In air, ligand **1** (0.187 g, 0.599 mmol, 1 equiv.) was dissolved in 10 ml CH_2Cl_2 and stirred. To this orange solution was added triethylamine (0.182 g, 1.797 mmol, 3 equiv.) and a solution of Ag(OAc) (0.100 g, 0.599 mmol, 1 equiv.) in methanol (10 ml). The reaction mixture was stirred for 10 min at 40 °C and allowed to cool to r.t. without stirring. After 24 h, pale yellow crystals formed (0.237 g, 0.283 mmol, 94% yield). M.p. = 204–205 °C. IR(KBr): 2949, 1727, 1684, 1347, 1307, 1256, 1189, 1157, 1080, 767 cm^{-1}; ^1H NMR [$(CD_3)_2SO$, 500 MHz, 298 K]: δ 7.58 (dd, $J_1 = 7.7$ Hz, $J_2 = 1.0$ Hz, 1H), 7.52 (dd, $J_1 = 8.1$ Hz, $J_2 = 1.2$ Hz, 1H), 7.48 (dt, $J_1 = 8.2$ Hz, $J_2 = 1.34$ Hz, 1H), 7.15 (dt, $J_1 = 7.6$ Hz, $J_2 = 1.5$ Hz, 1H), 3.58 (s, 3H) ppm; ^{13}C NMR [$(CD_3)_2SO$, 500 MHz, 298 K]: δ 168.6, 151.5, 131.5, 129.6, 123.4, 123.3, 123.2, 51.7 ppm; Elemental analysis Calc. for: $C_{16}H_{14}AgN_3O_4$: C, 45.74, H, 3.36, N, 10.00; Found: C, 45.35, H, 3.13, N, 9.87%.

4. Supplementary material

Crystallogrpahic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, for **3**: CCDC No. 187742; for **4**: CCDC No. 187741. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; email: deposit@ccdc.ac.uk or www: http://www.ccdc.cam.ac.uk).

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