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Synthesis and Structures of Dinuclear Copper(I) and Silver(I) 1,3-Bis-[(2-chloro)benzene]triazenide Complexes

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Abstract. In the presence of Et_3N, the reaction of 1,3-bis[(2-chloro)benzene]triazene (HL) with CuCl or $AgNO_3$ gives the triazenide complexes $\{Cu_2(L)_2\}$ (**1**) and $\{Ag_2(L)_2\}$ (**2**), respectively. The X-ray crystal structures of both complexes were obtained. The metal–metal distances (Cu···Cu and Ag···Ag) are 2.4974(5) and 2.7208(5) Å, respectively.

Introduction

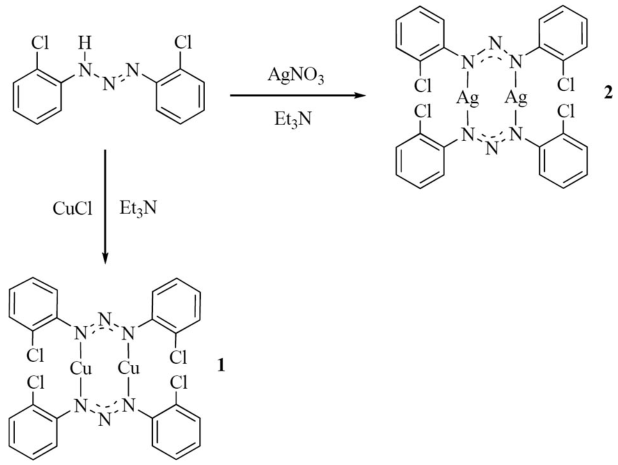
An approach toward the synthesis of complexes that exhibit new chemical and physical properties is the design of ligands that can be easily functionalized in order to modify the metal coordination sphere. Anionic, bridging, nitrogen bonded ligands, such as triazenides have attracted our attention, since they show a variety of bonding modes with distinct properties.[1–3] This versatile ligand has been employed in the synthesis of complexes of transition metals[4–9] and main group elements.[10,11] Additionally, triazenide ligands can stabilize late transition metal complexes showing only close metal–metal interaction[12] or containing metal–metal bonds.[13] In our previous work, we have prepared some polynuclear complexes with triazenide ligands.[14–16] On the basis of preliminary studies, we are interested in the synthesis and reactivity with transition metals of new triazenes.

In our lab, a triazene, namely 1,3-bis[(2-chloro)benzene]triazene (HL) was synthesized and characterized. In the presence of Et_3N, the reaction of HL and CuCl or $AgNO_3$ affords the triazenide complexes $\{Cu_2(L)_2\}$ (**1**) or $\{Ag_2(L)_2\}$ (**2**), respectively. In this paper, we present the synthesis and characterization of HL, as well as complexes **1** and **2** thereof.

Results and Discussion

Synthesis and Characterization

1,3-Bis[(2-chloro)benzene]triazene (HL) was synthesized by the reaction of 2-chloroaniline and sodium nitrite in 64 % yield. ^{1}H resonances are found at δ = 9.92 ppm for a singlet of triazene group hydrogen atom, and in the range of 7.70–7.10 ppm for the aromatic protons (Figure S1, Supporting Information). Scheme 1 shows the procedure for the synthesis of complexes **1** and **2**. Complex **1** was obtained as red crystals by the reaction of HL and CuCl in dichloromethane/acetonitrile in 43.1 % yield, and complex **2** was obtained as red crystals by the reaction of HL and $AgNO_3$ in dichloromethane/THF in 41.2 % yield.



Scheme 1. Schematic representation of the synthesis of complexes **1** and **2**.

The electronic spectra of HL, **1**, and **2** were recorded in CH_2Cl_2 (Figure S2; Supporting Information). HL exhibits two bands at 243 and 356 nm. Complex **1** exhibits four bands at 229, 268, 286, and 372 nm, and complex **2** shows two bands at 240 and 363 nm. Compared with that of HL (356 nm), the absorption maxima of the low-energy band of complex **1** (372 nm) and complex **2** (363 nm) are red-shifted to a longer-wavelength region. This is assignable to intraligand transitions of the L^- ligands, as well as a *M*→L MLCT transition from the *M*(I) ion (*M* = Cu or Ag) to the deprotonated ligand (L^-).

Copper(I) or silver(I), which has the d^{10} configuration, is expected to exhibit diamagnetic behavior. Accordingly, com-

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plexes **1** and **2** are amenable to NMR analysis. The ^{1}H NMR spectroscopic data in [D_2]methylene dichloride obtained for complexes **1** and **2** are consistent with a single-ligand environment. In the case of both the copper and silver products, ^{1}H NMR spectroscopy reveals a similar series of resonances. For complex **1**, ^{1}H resonances are found in the range of 7.68–7.07 ppm for the aromatic protons (Figure S3). In complex **2**, ^{1}H resonances are found in the range of 7.56–7.11 ppm for the aromatic protons (Figure S4).

Structural Analysis

Single crystal X-ray diffraction analysis of the two complexes reveal the solid-state structure of the complexes to be a di-copper complex [$Cu_2(L)_2$], and a di-silver complex [$Ag_2(L)_2$], respectively. Table 1 lists details of the crystal parameters, data collection and refinements for complexes **1** and **2**. Table 2 lists the selected bond lengths and angles for **1** and **2**.

Table 1. Crystallographic data for complexes **1** and **2**.

	1	2
Empirical formula	$C_{24}H_{16}Cu_2Cl_4N_6$	$C_{24}H_{16}Ag_2Cl_4N_6$
Formula weight	657.33	745.97
λ /Å	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a /Å	7.5565(7)	12.7951(17)
b /Å	9.0949(8)	7.3076(10)
c /Å	9.8671(9)	15.0536(15)
α /°	70.866(2)	90
β /°	87.653(2)	115.599(8)
γ /°	76.804(2)	90
V /Å^3	623.32(10)	1269.4(3)
Z	1	2
Dc /Mg·m^{-3}	1.751	1.952
F(000)	328	728
θ range for data collection /°	2.19 to 27.57	2.75 to 27.51
Reflections collected / unique	7688/2848	8344/2899
Data / restraints / parameters	2848/0/163	2899/0/163
Goodness-of-fit on F^2	1.023	0.999
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0282$ $wR_2 = 0.0662$	$R_1 = 0.0263$ $wR_2 = 0.0592$
R indices (all data)	$R_1 = 0.0415$ $wR_2 = 0.0716$	$R_1 = 0.0418$ $wR_2 = 0.0653$

The molecular structure of the complexes [$Cu_2(L)_2$], and [$Ag_2(L)_2$] are depicted in Figure 1 and Figure 2. The copper and silver complexes [$Cu_2(L)_2$] and [$Ag_2(L)_2$] are isotypic, and share many of the gross structural features of previously structurally characterized Cu^I, and Ag^I di-metallic systems[17–20] (Table 3), consisting of two central metal atoms bridged by two triazenide ligands in an μ,η^1,η^1-fashion, with approximately linear two coordinate arrangements [N(1)–Cu(1)–N(3#1): 171.00(7)° and N(1)–Ag(1)–N(3#1): 166.64(7)°, respectively], with the deviation caused by the metal atoms moving away from each other. The N–N–N angle in [$Ag_2(L)_2$] is 117.47(18)°, larger than that observed in [$Cu_2(L)_2$] [115.43(16)°], due to different sizes for silver and copper atoms.

Both complexes are formed by the two N3 ligands and the {*M*2} unit (*M* = Cu or Ag). The Cu–N and Ag–N bond lengths in both [$Cu_2(L)_2$] and [$Ag_2(L)_2$] are within the expected ranges for terminal *M*(I)–N bonds [Cu–N: 1.8966(16) Å and 1.8983(16) Å; Ag–N: 2.1666(18) Å and 2.1722(18) Å].[2,12,18] Similarly the N–N bond lengths within the triazenide ligands {N(1)–N(2): 1.302(2) Å, N(2)–N(3): 1.301(2) Å in [$Cu_2(L)_2$] and N(1)–N(2): 1.302(3) Å, N(2)–N(3): 1.294(3) Å in [$Ag_2(L)_2$]} are also comparable to those observed in related systems.[12,18] A significant point of interest in these dimeric Cu^I and Ag^I complexes is the presence of relatively short *M*···*M* intramolecular distances. In both complexes, the metal–metal distances [Cu(1)–Cu(1#): 2.4974(5) Å and Ag(1)–Ag(1#): 2.7208(5) Å] are significantly shorter than the sum of the van der Waals radii[21] of copper (1.40 Å) and silver (1.72 Å) and are directly comparable to related dimeric complexes listed in Table 3. It is not unusual for short metal–metal distances to be observed in complexes with bridging ligands. For this reason the presence of true metallophilic interactions is often dubious.

Table 2. Selected bond lengths /Å and angles /° for complexes **1** and **2**.

1			
Cu(1)–N(1)	1.8966(16)	Cu(1)–N(3)#1	1.8983(16)
Cu(1)–Cu(1)#1	2.4974(5)	N(1)–N(2)	1.302(2)
N(2)–N(3)	1.301(2)	N(3)–Cu(1)#1	1.8983(16)
N(1)–Cu(1)–N(3)#1	171.00(7)	N(1)–Cu(1)–Cu(1)#1	85.94(5)
N(3)#1–Cu(1)–Cu(1)#1	85.08(5)	N(1)–Cu(1)–Cl(2)#1	112.78(5)
N(3)#1–Cu(1)–Cl(2)#1	74.88(5)	Cu(1)#1–Cu(1)–Cl(2)#1	139.78(2)
N(2)–N(1)–Cu(1)	126.24(13)	C(1)–N(1)–Cu(1)	122.31(13)
N(3)–N(2)–N(1)	115.43(16)	N(2)–N(3)–Cu(1)#1	127.17(13)
2			
Ag(1)–N(3)#1	2.1666(18)	Ag(1)–N(2)	2.1722(18)
Ag(1)–Ag(1)#1	2.7208(5)	N(1)–N(2)	1.302(3)
N(2)–N(3)	1.294(3)	N(3)–Ag(1)#1	2.1666(18)
N(3)#1–Ag(1)–N(2)	166.64(7)	N(3)#1–Ag(1)–Ag(1)#1	83.02(5)
N(2)–Ag(1)–Ag(1)#1	83.69(5)	N(3)#1–Ag(1)–Cl(2)	121.02(6)
N(2)–Ag(1)–Cl(2)	71.28(6)	Ag(1)#1–Ag(1)–Cl(2)	142.84(3)
N(3)#1–Ag(1)–Cl(3)#1	69.12(6)	N(2)–Ag(1)–Cl(3)#1	120.72(6)
Ag(1)#1–Ag(1)–Cl(3)#1	136.12(3)	Cl(2)–Ag(1)–Cl(3)#1	80.98(3)
N(3)–N(1)–N(2)	117.47(18)		

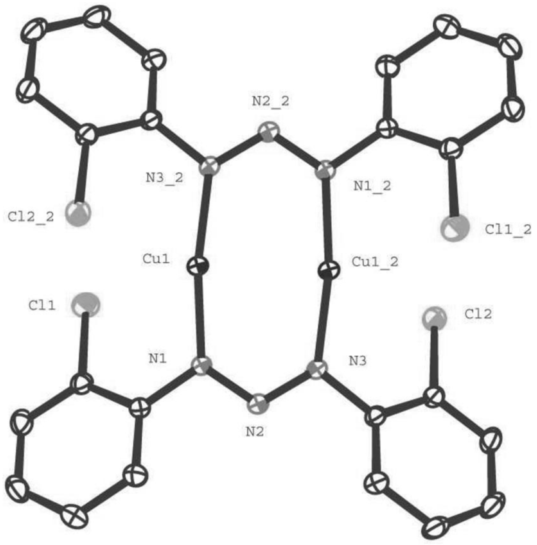

Figure 1. Molecular structure of $Cu^{I}_2(L)_2$ (**1**).

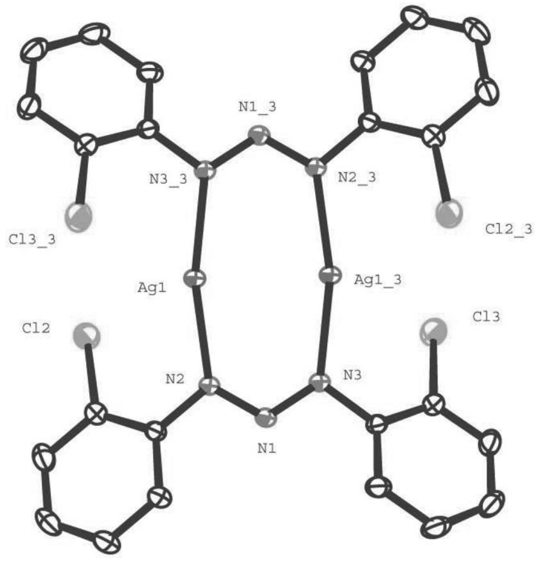

Figure 2. Molecular structure of $Ag^{I}_2(L)_2$ (**2**).

Table 3. Cu···Cu and Ag···Ag distances /Å in some bridged dinuclear Cu^{I} and Ag^{I} complexes.

Complex	*d*(*M*···*M*)	Reference
$[Cu_2(\mu\text{-Ph-NNN-Ph})_2]$	2.4405(10)	[17]
$[Cu_2(\mu\text{-}C_6H_3(i\text{Pr})_2\text{-NNN-}C_6H_3(i\text{Pr})_2)_2]$	2.4458(4)	[12]
$[Cu_2\{\mu\text{-}o\text{-}C_6H_4(CO_2Me)\text{-NNN-}o\text{-}C_6H_4\text{-}(CO_2Me)\}_2]$	2.4289(12)	[18]
$[Cu_2\{\mu\text{-}o\text{-}C_6H_4(Cl)\text{-NNN-}o\text{-}C_6H_4\text{-}(Cl)\}_2]$	2.4974(5)	this work
$[Ag_2(\mu\text{-Ph-NNN-Ph})_2]$	2.669(1)	[19]
$[Ag_2\{\mu\text{-MeOC}_6H_4\text{-NNNC}_6H_4\text{OMe}\}$	2.680(2)	[20]
$[Ag_2\{\mu\text{-}o\text{-}C_6H_4(Cl)\text{-NNN-}o\text{-}C_6H_4\text{-}(Cl)\}_2]$	2.7208(5)	this work

Conclusions

1,3-Bis[(2-chloro)benzene]triazene (HL) was synthesized by the reaction of 2-chloroaniline and sodium nitrite. Deprotonated HL can bridge central copper and silver atoms to give two dinuclear complexes **1** and **2**, which were characterized by X-ray crystallography and ^{1}H NMR spectra. We are currently preparing other new triazenide ligands and their transition metal complexes.

Experimental Section

Data were collected with a Bruker SMART CCD area detector using graphite monochromated Mo-*K* radiation (0.71073 Å) at room temperature. All empirical absorption corrections were applied by using the SADABS program.[22] The structures were solved by direct methods and the corresponding non-hydrogen atoms are refined anisotropically. All the hydrogen atoms of the ligands were placed in calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL computer program.[23]

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-876006 and CCDC-876007. (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Synthesis of 1,3-Bis[(2-chloro)benzene]triazene (HL): 2-Chloroaniline (10 mmol) in water (5 mL) was mixed with HCl (1 mol·L^{-1}, 30 mL, 30 mmol) at 0 °C. An aqueous solution (15 %) of sodium nitrite (15 mmol) was added dropwise with stirring. Once the amine was dissolved, a solution of 2-chloroaniline in ethanol (10 mmol) was added at 0 °C and the mixture was stirred for 3 h. The reaction mixture was neutralized with a 15 % aqueous of $NaCH_3CO_2$ (15 mL) to give an orange precipitate. The reaction mixture was filtered, and the solid was purified by crystallization at –4 °C from 9:1 ethyl acetate/*n*-hexane to obtain yellow crystals, which were collected and dried in vacuo (yield 1.7 g, 64 %). $C_{12}H_9Cl_2N_3$: calcd. C 54.16; H 3.41; N 15.79 %; found: C, 54.07; H, 3.39; N, 15.66 %. **^{1}H NMR** (CD_2Cl_2): δ = 9.92 (s, 1 H), 7.69 (d, *J* = 2.0 Hz, 2 H), 7.40 (d, *J* = 2.0 Hz, 2 H), 7.29 (t, *J* = 3.0 Hz, 2 H), 7.14 (t, *J* = 2 Hz, 2 H) ppm. **UV/Vis** [CH_2Cl_2, λ_{max} /nm (ε /L·mol^{-1}·cm^{-1})]: 243 (3.5×10^4), 356 (4.7×10^4).

Synthesis of $[Cu_2(L)_2]$ (1): To a solution, containing ligand (HL) (0.266 g, 1 mmol) and triethylamine (0.10 g, 1 mmol) in dichloromethane/acetonitrile (20 mL, 1:1), CuCl (0.10 g, 1 mmol) was added and the mixture was stirred for 15 min. The solution was allowed to slowly evaporate, affording red crystals, which were collected and dried in vacuo (yield 0.141 g, 43.1 %). $C_{24}H_{16}Cu_2Cl_4N_6$: calcd. C 43.85; H 2.45; N 12.79 %; found: C, 43.79; H, 2.48; N, 12.81 %. **^{1}H NMR** (CD_2Cl_2): δ = 7.67 (d, *J* = 2.0 Hz, 4 H), 7.38 (d, *J* = 2.0 Hz, 4 H), 7.28 (t, *J* = 2.0 Hz, 4 H), 7.09 (t, *J* = 2 Hz, 4 H) ppm. **UV/Vis** [CH_2Cl_2, λ_{max} /nm (ε /L·mol^{-1}·cm^{-1})]: 229 (6.2×10^4), 268 (5.6×10^4), 286 (5.3×10^4), 372 (7.2×10^4).

Synthesis of $[Ag_2(L)_2]$ (2): The procedure was performed in the same way as that for the synthesis of **1** except that CuCl was replaced with $AgNO_3$. Red crystals characterized as $[Ag_2(L)_2]$ **2** were obtained in 41.2 % (0.154g). $C_{24}H_{16}Ag_2Cl_4N_6$: calcd. C 38.64; H 2.16; N 11.27 %; found: C 38.61; H 2.18; N 11.31 %. **^{1}H NMR** (CD_2Cl_2): δ = 7.55 (d, *J* = 2.0 Hz, 4 H), 7.47 (d, *J* = 2.0 Hz, 4 H), 7.31 (t, *J* = 2.0 Hz, 4 H), 7.13 (t, *J* = 2 Hz, 4 H) ppm. **UV/Vis** [CH_2Cl_2, λ_{max}/nm (ε /L·mol^{-1}·cm^{-1})]: 240 (8.0×10^4), 363 (7.5×10^4).

Supporting Information (see footnote on the first page of this article): ^{1}H NMR and electronic spectra of the ligand and complexes **1** and **2**.

Acknowledgements

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