Journal of Organometallic Chemistry 696 (2011) 2820–2828

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Silver(I)-organic networks constructed with flexible silver-ethynide supramolecular synthon o-, m-, p-Cl–$C_6H_5OCH_2C{\equiv}C{\supset}Ag_n$ ($n = 4, 5$)

Bo Li [a], Shuang-Quan Zang [a,*], Can Ji [a], Thomas C.W. Mak [a,b,**]

[a] *Department of Chemistry, Zhengzhou University, Zhengzhou 450001, PR China*

[b] *Department of Chemistry and Center of Novel Functional Molecules, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR, PR China*

ARTICLE INFO

Article history:
Received 24 March 2011
Received in revised form
3 May 2011
Accepted 3 May 2011

Keywords:
Silver-organic coordination polymer
Ag···Cl interaction
Supramolecular synthon

ABSTRACT

A series of five silver coordination polymers [(AgL1)·$(AgCF_3COO)_5$·$(H_2O)_3$] (**1**), [$(AgL1)_2$·$(AgCF_3COO)_{11}$·$(H_2O)_6$] (**2**), [(AgL2)·$(AgCF_3COO)_3$·(H_2O)] (**3**), [(AgL3)·$(AgCF_3COO)_4$·$(CH_3CN)_2$] (**4**), and [(AgL3)·$(AgCF_3COO)_7$·$(CH_3CN)_2$·$(H_2O)_2$] (**5**) have been constructed from three flexible anionic ligands HL1, HL2, and HL3 (HL1 = 1-chloro-2-(prop-2-ynyloxy)benzene, HL2 = 1-chloro-3-(prop-2-ynyloxy)benzene, HL3 = 1-chloro-4-(prop-2-ynyloxy)benzene). In these compounds, the invariable appearance of the μ_4- and μ_5-ligation modes of the ethynide moiety affirms the general utility of the flexible silver-ethynide supramolecular synthon o-, m-, p-Cl–$C_6H_5OCH_2C{\equiv}C{\supset}Ag_n$ ($n = 4, 5$) in coordination network assembly. Among them, Ag···Cl interaction plays a vital role in assembling the supramolecular structures in complexes **1**–**3**.

1. Introduction

The design of new supramolecular synthons with multi-center binding sites for constructing new kinds of non-classical coordination/organometallic supramolecular architectures is receiving increasing attention [1–13]. Indeed, common weak intermolecular interactions such as hydrogen bonding [14–17] and $\pi\cdots\pi$ [18–21] have been employed as available cohesive forces in the consolidation of such supramolecular architectures. However, several other unconventional intermolecular interactions metal···halogen [22–28] argentophilic [29–37] remain largely unexplored. Though supramolecular structures held by the Ag···I–aryl interaction (Ag···I distance ranges from 2.719 to 3.357 Å) have been known for over a decade [23,38,39], the significance of analogous interactions involving the lighter halogens has been called into question until recent times, when examples are reported for both the Ag···Br–aryl (Ag···Br 3.179(5), 3.726(6) Å in {$[Ag_2(bppy)_3][Ag(bppy)_2][Ag(bppy)]_2PW_{11}Co(bppy)O_{39}$}·$2H_2O$, where bppy represents 5-(4-bromophenyl)-2-(4-pyridinyl)pyridine, and 3.186(6) Å in $Ag(Br_4C_6(OH)O)(Ph_3P)_2$) [25,26] and Ag···Cl–aryl interactions (3.184(5) Å in $Ag(Cl_4C_6(OH)O)(Ph_3P)_2$, 2.721(5), 2.739(5), 2.740(5), 2.770(5), 2.804(6) Å in *cyclo*-[{$Pt(C_6Cl_5)_2(\mu\text{-}OH)(\mu\text{-}Ag)$}$_4$], 3.287(2) Å in $2AgL^2$·$5AgCF_3COO$·$2CH_3CN$·H_2O, (L^2 = 3,4-dichlorophenylethynide), and 3.280(3) Å in AgL^5·$4AgCF_3COO$·$2CH_3CN$ (L^5 = 2-chlorophenylethynide)) [26,28,40].

Following our investigation of the coordination chemistry of silver ethynediide (Ag_2C_2) [41–43], we have conducted systematic studies on various complexes containing silver(I) 1,3-butadiynediide (Ag_2C_4) [44]. Furthermore, utilizing new metal–ligand supramolecular synthons of the type R–$C{\equiv}C{\supset}Ag_n$ (R = aryl or alkyl; $n = 4, 5$) [45,46] and $Ag_n{\subset}C{\equiv}C$–R–$C{\equiv}C{\supset}Ag_n$ (R = o-, m-, p-C_6H_4; $n = 4, 5$) [47], we have obtained a series of metal-organic networks stabilized by argentophilic and silver-ethynide (σ, π and mixed σ, π) interactions. Recently, we have explored the employment of several ligands with an ethynide ethynyl group attached to a phenyl, biphenyl, or naphthyl skeleton via a flexible –CH_2–O– link for the construction of MOFs consolidated by both silver(I)–ethynide and silver(I)–aromatic interactions [48–50]. By utilizing new metal–ligand supramolecular synthons of the type p-X–$C_6H_5OCH_2C{\equiv}C{\supset}Ag_n$ (X = I, Br; $n = 4, 5$) [51], we have obtained a series of metal-organic networks, which provides unequivocal evidence for the existence of the Ag···Br–aryl, Ag···I–aryl interactions. The change of substituent group of the phenyl ring may leads to a modification of the resulting coordination networks. As a continuation of our research, in this work, we systematically investigate the effect of the supramolecular synthon o-, m-, p-Cl–$C_6H_5OCH_2C{\equiv}C{\supset}Ag_n$ ($n = 4, 5$) to see whether non-covalent Ag···Cl–aryl interaction could be an effective and reliable tool in the context of metal-organic network assembly.

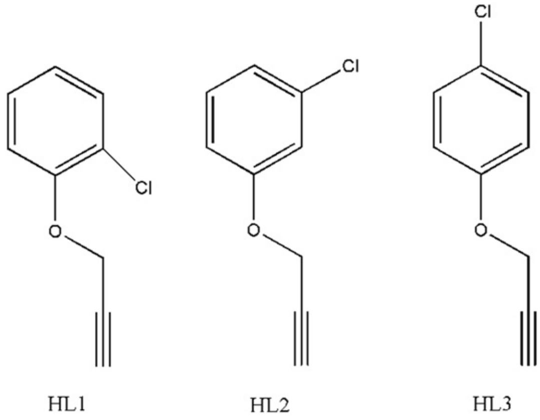
---

* Corresponding author. Tel.: +86 0371 67780136; fax: +86 371 6778 0136.

** Corresponding author. Department of Chemistry and Center of Novel Functional Molecules, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR, PR China. Tel.: +86 852 2609 6279; fax: +86 852 2603 5057.

E-mail addresses: zangsqzg@zzu.edu.cn (S.-Q. Zang), tcwmak@cuhk.edu.hk (T.C.W. Mak).

0022-328X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2011.05.002



Scheme 1. Structural formulas used as ligands in forming new silver(I)-ethynide complexes.

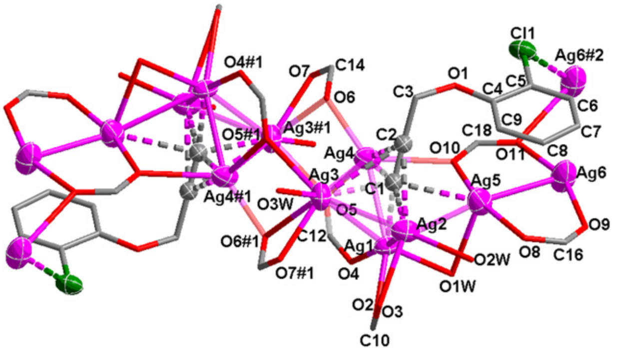


Fig. 1. Coordination mode of L1 in **1**. All hydrogen atoms and CF_3 groups are omitted for clarity. Selected bond lengths [Å]: C1≡C2 1.213(2), Ag1–C1 2.240(11), Ag2–C1 2.212(12), Ag2–C2 3.064(14), Ag3–C1 2.293(13), Ag3–C2 2.995(13), Ag4–C1 2.419(12), Ag4–C2 2.536(14), Ag5–C1 2.914(14), Ag6#2–Cl1 3.204(8), Ag1···Ag2 2.793(14), Ag1···Ag3 2.896(2), Ag1···Ag4 2.934(14), Ag1···Ag5 3.140(2), Ag2···Ag3 3.069(2), Ag3···Ag4 3.088(2), Ag5···Ag6 2.951(2). Symmetry codes: #1 $1 - x, 1 - y, 1 - z$; #2 $-x, 1 - y, -z$.

Herein we report the syntheses and structural characterization of five silver (I) complexes of three new ligands, which bearing terminal ethynide moieties attached via pendent arms to the *ortho*-, *meta*- and *para*-position of a chlorobenzene skeleton, respectively: $[(AgL1)\cdot(AgCF_3COO)_5\cdot(H_2O)_3]$ (**1**), $[(AgL1)_2\cdot(AgCF_3COO)_{11}\cdot(H_2O)_6]$ (**2**), $[(AgL2)\cdot(AgCF_3COO)_3\cdot(H_2O)]$ (**3**), $[(AgL3)\cdot(AgCF_3COO)_4\cdot(CH_3CN)_2]$ (**4**), and $[(AgL3)\cdot(AgCF_3COO)_7\cdot(CH_3CN)_2\cdot(H_2O)_2]$ (**5**), where HL1 = 1-chloro-2-(prop-2-ynyloxy)benzene, HL2 = 1-chloro-3-(prop-2-ynyloxy)benzene, and HL3 = 1-chloro-4-(prop-2-ynyloxy)benzene) (Scheme 1).

2. Experiments

2.1. Reagents

Commercially available 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, propargyl bromide (80% in toluene) and K_2CO_3 were used without further purification. Acetone, dichloromethane, ethyl acetate, *n*-hexane, acetonitrile and triethylamine were purified according to standard procedures. All synthetic reactions yielding organic ligands and polymeric starting materials were carried out under a nitrogen atmosphere.

Caution! Silver ethynide complexes are potentially explosive and should be handled in small amounts with extreme care.

2.1.1. Synthesis of 1-chloro-2-(prop-2-ynyloxy)benzene (HL1)

HL1 was synthesized according to the literature method [52]. Propargyl bromide (1.4 mL, 12.5 mmol) and K_2CO_3 (1.73 g, 12.5 mmol) were added to a solution of 2-chlorophenol (1.67 g, 10 mmol) in acetone (30 mL). The solution was heated under reflux for 24 h under nitrogen atmosphere. The precipitate was filtered off and the filtrate was evaporated to dryness to yield the crude product as a yellow oil. It was purified by chromatography on silica gel to afford pale yellow oil. Yield: 73%. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.71–7.19$ (4H, benzene); 4.68 (2H, OCH_2); 2.51 (1H, C≡CH). IR (Nujol): $\nu = 2108\ cm^{-1}$ (w, $\nu_{C\equiv C}$). *Anal.* Calc. for C_9H_7ClO (166.61): C 64.88; H 4.23. Found: C 64.81; H 4.29%.

1-Chloro-3-(prop-2-ynyloxy)benzene(HL2): HL2 was obtained by the above procedure except that 3-chlorophenol replaced 2-chlorophenol. Yield: 67%. ^1H NMR (300 MHz, $CDCl_3$):

Table 1
X-ray crystal data and structure refinement for compounds **1**–**5**.

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{19}H_{10}Ag_6ClF_{15}O_{14}$	$C_{40}H_{24}Ag_{13}Cl_2F_{33}O_{30}$	$C_{15}H_8Ag_4ClF_9O_8$	$C_{21}H_{12}Ag_5ClF_{12}N_2O_9$	$C_{27}H_{16}Ag_8ClF_{21}N_2O_{17}$
Formula weight	1429.94	3084.80	954.14	1239.13	1937.83
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.284(3)	11.2472(10)	9.9198(17)	8.9144(18)	11.324(2)
b (Å)	11.314(3)	16.8357(16)	10.7012(18)	14.203(3)	14.435(3)
c (Å)	15.299(4)	20.7545(19)	11.3863(19)	14.384(3)	17.583(3)
α (°)	90.267(5)	108.755(2)	82.885(3)	69.607(4)	66.531(3)
β (°)	101.694(6)	97.071(2)	87.013(3)	76.707(4)	74.435(3)
γ (°)	113.166(5)	93.784(2)	75.221(3)	85.448(4)	87.881(4)
V (Å^3)	1750.7(8)	3669.6(6)	1159.4(3)	1661.3(6)	2531.8(8)
Z	2	2	2	2	2
$Dcalc$ (g cm^{-3})	2.713	2.792	2.733	2.477	2.542
F(000)	1340	2892	896	1168	1820
Reflections collected	9518	20214	6330	9494	13911
Independent reflections	6135	12893	4064	6132	8876
R(int)	0.0419	0.0422	0.1003	0.0440	0.0795
Data/restraints/parameters	6135/1572/509	12893/102/1129	4064/58/353	6132/48/484	8876/221/745
GOF on F^2	1.064	1. 144	1.085	1.062	1.055
$R_1[(I > 2\sigma(I)]$	0.0828	0.0489	0.0609	0.0462	0.0622
$wR_2[(I > 2\sigma(I)]$	0.2418	0.1376	0.1748	0.1215	0.1697
R_1 (all data)	0.0913	0.0595	0.0646	0.0523	0.0823
wR_2 (all data)	0.2506	0.1439	0.1797	0.1258	0.1821
Max/min (e Å^{-3})	2.265 and −1.861	2.380 and −1.554	1.953 and −1.628	1.336 and −1.116	2.555 and −1.509