Polyhedron 44 (2012) 138–142

Contents lists available at SciVerse ScienceDirect

Polyhedron

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

Synthesis, characterization and crystal structures of Hg^{II} complexes with asymmetric ortho-functionalized 1,3-bis(aryl)triazenide ligands

Mohammad Kazem Rofouei [a,*], Jafar Attar Gharamaleki [a], Mohammad Reza Melardi [b], Seyed Mahdi Hosseini [a], Fatemeh Hosseinzadeh [a], Mitra Peyman [b], Atefeh Ghannadan [b], Behrouz Notash [c], Giuseppe Bruno [d], Hadi Amiri Rudbari [d]

[a] Faculty of Chemistry, Tarbiat Moallem University, Tehran, Iran
[b] Department of Chemistry, Islamic Azad University, Karaj Branch, Karaj, Iran
[c] Department of Chemistry, Shahid Beheshti University, G. C., Evin, Tehran 1983963113, Iran
[d] Dipartimento di Chimica Inorganica, Universita di Messina, Messina, Italy

ARTICLE INFO

Article history:
Received 28 March 2012
Accepted 19 June 2012
Available online 28 June 2012

Keywords:
Mercury(II)
Triazene
X-ray crystal structure
$\pi\cdots\pi$ Stacking
C–H$\cdots\pi$ interaction

ABSTRACT

The synthesis of two $[Hg(L1)_2]$ and $[Hg(L2)_2]$ complexes using asymmetric triazenes as ligands are reported. The triazene ligands are substituted with cyano and chloride groups in the *ortho* positions of the aryl rings (where HL1 and HL2 are 1-(2-ethoxyphenyl)-3-(2-cyanophenyl)triazene and 1-(2-ethoxyphenyl)-3-(2-chlorophenyl) triazene, respectively). These complexes were prepared by the reaction of corresponding triazenes with $Hg(NO_3)_2$ and were characterized by FT-IR, NMR, elemental and single crystal X-ray analyses. Both triazene ligands were found to deprotonate on coordination and act as tridentate chelating ligands forming distorted N_4O_2 octahedral geometry around Hg^{II} atoms. Hydrogen bonds, $\pi\cdots\pi$ and C–H$\cdots\pi$ stacking interactions help to the stabilization of the resulted frameworks.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Hydrogen-bonding and other types of non-covalent interactions like $\pi\cdots\pi$ and C–H$\cdots\pi$ stacking interactions play an important role in the building of supramolecular systems [1,2]. Aryl triazenes have been studied over several years for their interesting structural, anticancer, and reactivity properties [3–10]. Triazene compounds characterized by having a diazoamino group (–N=NNH–) commonly adopt a *trans* configuration in the solid state. As ligands, the N=NNH moieties can show different types of coordination in metal complexes. They can be monodentate, (N1,N3)-chelating towards one metal atom or (N1,N3)-bridging over two metal atoms [11], toward wide variety of metal transition complexes [12,13]. In these compounds secondary bonds, or interactions, such as hydrogen bonds and metal·π-aryl interactions, can play an important role in their structural stability [14,15]. In recent years, we have been involved in the complexation of transition metal ions with several triazene compounds as ligands. Starting from different bis(diaryl) symmetric and asymmetric-substituted triazenide as ligand. Recently, we have shown that several complexes of Hg^{II} have a remarkable ability to self-assemble in different manners through metal–η^2–η^2-arene π-interactions and non-classical C–H$\cdots$O hydrogen bonding. We have previously reported the synthesis of [1,3-bis(2-methoxyphenyl)]triazene [16], [1,3-bis(2-ethoxyphenyl)]triazene [17] and [1,3-bis(2-cyanophenyl)]triazene [18] molecules that can act as ligands. Also, we have published the Hg(II) complexes with [1,3-bis(2-methoxyphenyl)]triazene by using $HgCl_2$ [19], $HgBr_2$ [20], $Hg(CH_3COO)_2$ and $Hg(SCN)_2$ [21] salts as starting materials. More recently, a Hg(II) complex with [1,3-bis(2-ethoxyphenyl)]triazene as ligand is reported in which $Hg(NO_3)_2$ is used as starting salt [22]. To investigate the effect of the substituted derivatives on coordination behavior of the triazene ligands, we have introduced ortho-, meta- and para-bis(phenyltriazene)benzenes (and substituted derivatives), with two triazene groups in one molecule as ligands. In this work we studied the complexation of 1-(2-ethoxyphenyl)-3-(2-chlorophenyl)triazene and 1-(2-ethoxyphenyl)-3-(2-cyanophenyl)triazene) with nitrate salt of Hg^{II} ion in aqueous solution, in order to investigate the stoichiometry of the resulting mercury(II) complexes.

2. Experimental

2.1. Materials and physical techniques

All chemicals were of analytical grade and were used as commercially obtained without further purification. IR spectra in the frequency range of 4000–400 cm^{-1} were recorded using

---

[*] Corresponding author. Tel.: +98 2188848949; fax: +98 2188820993.
E-mail address: rofouei@tmu.ac.ir (M.K. Rofouei).

0277-5387/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.poly.2012.06.045

Perkin–Elmer RXI spectrometer using KBr disks. Elemental analysis was carried out using a Perkin–Elmer 2400(II) CHNS/O analyzer. Melting points were measured on a Barnstead Electrothermal 9200 apparatus.

2.1.1. Synthesis of [(EtOPhNHNNPhCN)], [HL1]

A 100 ml flask was charged with 10 g of ice and 15 ml of water and then cooled to 273 K in an ice-bath. To this was added 2 mmol (0.24 g) of 2-aminobenzonitrile and 2 mmol of hydrochloric acid (36.5%) and 2 ml of water. To this solution was then added a solution containing $NaNO_2$ (0.32 g) in 3 ml of water during a 15 min period. The *p*H of the solution was then adjusted at 6 by adding a solution containing 1 g of sodium acetate in 10 ml of water. After mixing for 15 min, the obtained solution was added to a solution of 2 mmol (0.26 ml) of *o*-phenetidine and 2 ml of methanol and 4 ml of water. After mixing for 24 h, the yellow-orange precipitate was filtered off and dried. Our attempt to crystallize this compound was unsuccessful. m.p.: 121–123 °C. IR (KBr): $\nu(\text{cm}^{-1})$: 3331, 2223, 1602, 1513, 1478, 1470, 1437 , 1313, 1275, 1231, 1119, 1040, 927, 770, 735, 603. ^{1}H NMR (300 MHz, d_6-DMSO): 1.38 (3H, CH_3), 4.13 (2H, CH_2), 6.90–7.85 (8H, aromatic), 12 (1H, NH). ^{13}C NMR (300 MHz, d_6-DMSO): 14.5, 64.0, 102.2–145.5 ppm. Elemental *Anal.* calc. for $C_{15}H_{14}N_4O$: C, 67.66; H, 5.26; N, 21.05. Found: C, 67.38; H, 4.26; N, 20.65%.

*2.1.2. Synthesis of [(EtOPhNHNNPhCl)] [HL2], (**1**)*

This ligand was also prepared by the same method as described above with this difference that *o*-chlorobenzenamine (0.1 mol, 10.54 ml) was used as starting material. Also, recrystallization was performed by *n*-hexane. m.p.: 73–75 °C. IR (KBr): $\nu(\text{cm}^{-1})$: 3336, 3067, 1600, 1530, 1467, 1437, 1410 , 1306, 1259, 1212, 1119, 1045, 1035, 746, 732, 719. ^{1}H NMR (300 MHz, d_6-DMSO): 1.38 (3H, CH_3), 4.12 (2H, CH_2), 6.92–7.61 (8H, aromatic), 11.72 (1H, NH). ^{13}C NMR (300 MHz, d_6-DMSO): 14.7, 64.1, 112.8–146.5 ppm. Elemental *Anal.* calc. for $C_{14}H_{14}N_3OCl$: C, 60.98; H, 5.12; N, 15.24. Found: C, 61.04; H, 5.0; N, 15.29%.

*2.1.3. Synthesis of [Hg^{II}(EtOPhNNNPhCN)$_2$], [Hg(L1)$_2$], (**2**)*

The complex was prepared by mixing 0.27 g (1 mmol) of [1-(2-ethoxyphenyl)-3-(2-cyanophenyl)triazene) in 10 ml of anhydrous methanol with 0.27 g (1 mmol) of mercury(II) nitrate in 10 ml of anhydrous methanol. After being mixed for an hour, a yellow precipitate was obtained. The resultant precipitate after filtration and washing was dissolved in THF. Yellow needle-like crystals suitable for X-ray analysis of the complex (**2**) were obtained by slow evaporation of the solvent in 2 weeks.

$C_{30}H_{26}HgN_8O_2$ (731.18); m.p.: 219–221 °C. IR (KBr): $\nu(\text{cm}^{-1})$: 3069, 2977 , 2220, 1589, 1494, 1477, 1372, 1333, 1291, 1275, 1218, 1161, 1120, 1038, 918, 743, 734, 672. ^{1}H NMR (300 MHz, d_6-DMSO): 1.16 (3H, CH_3), 4.10 (2H, CH_2), 7.00–7.81 (8H, aromatic). ^{13}C NMR 300 MHz, d_6-DMSO): 14.0, 64.5, 104.8–151.4 ppm. Elemental *Anal.* calc. for $C_{30}H_{26}HgN_8O_2$: C, 49.31; H, 3.56; N, 15.34. Found: C, 49.60; H, 3.38; N, 15.26%.

*2.1.4. Synthesis of [Hg^{II}(EtOPhNNNPhCl)$_2$], [Hg(L2)$_2$], (**3**)*

To a yellow solution prepared by dissolving 0.29 g (1 mmol) of 1-(2-ethoxyphenyl)-3-(2-chlorophenyl)triazene in 40 ml of anhydrous methanol, 0.16 g (0.5 mmol) of mercury(II) nitrate dissolved in 5 ml of anhydrous methanol were added. After 1/2 h stirring, an orange precipitate was formed. It was then filtered off, washed with methanol and dried in vacuum. The solid was dissolved in 20 ml THF. Orange-red plate like crystals suitable for X-ray analysis of the complex, were obtained by slow evaporation of the solvent within a week. IR (KBr): $\nu(\text{cm}^{-1})$: 2881, 1584, 1493, 1470, 1456, 1386, 1286, 1263, 1235, 121, 1196, 1121, 1035, 918, 759, 741, 735. ^{1}H NMR (300 MHz, d_6-DMSO): 1.17 (3H, CH_3), 4.06 (2H, CH_2), 6.99–7.73 (8H, aromatic). ^{13}C NMR (300 MHz, d_6-DMSO): 14.1, 64.3, 113.0–150.5 ppm. Elemental *Anal.* calc. for $C_{28}H_{26}Cl_2HgN_6O_2$: C, 44.84; H, 3.49; N, 11.2. Found: C, 45.18; H, 3.51; N, 11.12%.

3. Crystallography

Crystallography measurements were made using a Bruker APEX2 CCD diffractometer for compounds (2) and (3), and also

Table 1
Crystal data for the compounds (**1**)–(**3**).

	1	**2**	**3**
Empirical formula	$C_{14}H_{14}ClN_3O$	$C_{30}H_{26}HgN_8O_2$	$C_{28}H_{26}Cl_2HgN_6O_2$
Formula weight	275.73	731.18	750.04
T (K)	298	293	293
λ (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$C2/c$
Unit cell dimensions			
a (Å)	14.688 (3)	7.9472 (3)	22.497 (4)
b (Å)	4.4064 (9)	8.6812 (3)	9.049 (2)
c (Å)	22.337 (8)	20.7136 (7)	14.746 (3)
α (Å)		91.245 (2)	
β (Å)	111.46 (2)	92.970 (2)	108.89 (2)
γ (Å)		91.811 (2)	
V (Å^3)	1345.5 (6)	1426.03 (9)	2840.2 (10)
Z	4	2	4
D_{calc} (Mg m^{-3})	1.361	1.703	1.754
Absorption coefficient (mm^{-1})	0.279	4.439	5.646
F(000)	576	716	1464
θ Range for data collection (°)	1.96–29.22	0.98–30.06	2.68–30.30
Index ranges	$-20 \leqslant h \leqslant 20, -6 \leqslant k \leqslant 5, -28 \leqslant l \leqslant 30$	$-11 \leqslant h \leqslant 11, -12 \leqslant k \leqslant 12, -29 \leqslant l \leqslant 29$	$-31 \leqslant h \leqslant 31, -12 \leqslant k \leqslant 12, -20 \leqslant l \leqslant 20$
Reflections collected/unique (R_{int})	13923/3595 (0.0905)	57106/8309 (0.052)	58699/4223 (0.031)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3595 / 0 / 177	8309 / 0 / 370	4223 / 0 / 177
Goodness-of-fit on F^2	1.134	1.14	1.019
Final $R[I > 2\sigma(I)]$	$R1 = 0.0742$, $wR2 = 0.1335$	$R1 = 0.0654$, $wR2 = 0.1665$	$R1 = 0.0242$, $wR2 = 0.0718$
R indices (all data)	$R1 = 0.1346$, $wR2 = 0.1553$	$R1 = 0.0748$, $wR2 = 0.1702$	$R1 = 0.0273$, $wR2 = 0.0737$
Largest differences in peak and hole (e A^{-3})	0.231 and −0.184	2.89 and −4.32	0.89 and −1.36

Download English Version:

https://daneshyari.com/en/article/1334734

Download Persian Version:

https://daneshyari.com/article/1334734

Daneshyari.com