Polyhedron 28 (2009) 1205–1210

Contents lists available at ScienceDirect

Polyhedron

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

Mercury(I) complexes with bidentate iminopyridine ligands: Synthesis, spectral characterization and structural analysis

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ARTICLE INFO

Article history:
Received 10 January 2009
Accepted 4 February 2009
Available online 3 March 2009

Keywords:
Mercury(I) complexes
2-Pyridinecarbaldehyde
Diimine ligands
Crystal structures

ABSTRACT

Four mercury(I) complexes, $[L^2HgHgL^2](NO_3)_2$ (L^2 = (4-fluorophenyl)pyridin-2-ylmethyleneamine, **1**; (4-chlorophenyl)pyridin-2-ylmethyleneamine, **2**; (4-bromophenyl)pyridin-2-ylmethyleneamine, **3** and (4-iodophenyl)pyridin-2-ylmethyleneamine, **4**) have been synthesized and characterized by CHN analysis, IR and UV–Vis spectroscopy. The crystal structures of **1** and **3** were determined by single crystal X-ray spectroscopy. These complexes contain the Hg_2^{2+} moiety with a mercury–mercury bonded core, in which one diimine ligand is coordinated to each mercury atom. The Hg atoms have an additional axial interaction with the oxygen atom of the NO_3^- anion in both complexes. Complex **1** shows a step in the Hg–Hg bond due to the parallel configuration of the planar ligands. However, the ligand planes in the complex **3** are nearly planar and these planes are approximately perpendicular to each other. Supramolecular structures were built in both complexes via π–π stacking of the diimine ligands.

1. Introduction

The crystal chemistry of mercury(I)–nitrogen complexes with the characteristic Hg_2^{2+} dumbbell is more or less singular [1–3]. These complexes can be divided into systems with $[L^1HgHgL^1]^{2+}$, $[HgHgL^2]^{2+}$, $[L^2HgHgL^2]^{2+}$ and $[(L^2)_2HgHg(L^2)_2]^{2+}$ cations (L^1 and L^2 are mono- and bidentate nitrogen donor ligands, respectively). The ligands such as pyridine and its derivatives form linear or near-linear complexes of the type $[L^1HgHgL^1]^{2+}$ [4–12]. An $[HgHgL^2]^{2+}$ element is present in the asymmetric complex $Hg_2(phen)(NO_3)_2$, in which the bidentate phenanthroline ligand is bound to one of the Hg centers [12]. An $[L^2HgHgL^2]^{2+}$ kernel is observed for $Hg_2(phen)_2(NO_3)_2$ [9,13], $[Hg_2(4\text{-benzylpyridine})_4](ClO_4)_2$ [14] and $[Hg_2(naphthyridine)_2](ClO_4)_2$ [15]. The $[L^2HgHgL^2]^{2+}$ core forms a nearly planar geometry with the bis-bidentate pyrazolyl-pyridine ligand [16]. The complex $[Hg_2(phen)_4](OTf)_2$, in which eight N-donor atoms are coordinated to the dimercury(I) dumbbell, is a single example containing the $[(L^2)_2HgHg(L^2)_2]^{2+}$ moiety [13]. Mercury(I) complexes with nitrogen ligands generally appear to be unstable, although there are a few exceptions (for example, the above noted complexes). This apparent instability has been attributed to the tendency of such ligands to induce dismutation of the mercury(I) ion due to the relatively greater stability of the corresponding mercury(II) complexes. π-Acceptor ligands such as pyridine and phenanthroline are known to form stable mercury(I) complexes [4]. Iminopyridine ligands stabilizing low valent metal redox-states seem to be good candidates for such studies and were used for the synthesis of Cu(I) and Re(I) complexes [17,18]. According to this view, we describe the synthesis and structural characterization of Hg(I) complexes of the type $[L^2HgHgL^2]^{2+}$ in which L^2 is an unsymmetrical bidentate iminopyridine ligand (Fig. 1).

2. Experimental

2.1. General

All chemicals were reagent grade and were used as received. The solvents used for the reactions were purified by literature methods [19]. The ligands (4-fluorophenyl)pyridin-2-ylmethyl-ene-amine, **A**, (4-chlorophenyl)pyridin-2-ylmethyleneamine, **B**, (4-bromophenyl)pyridin-2-ylmethyleneamine, **C** and (4-iodophenyl)pyridin-2-ylmethyleneamine, **D** were prepared according to reported procedures [20].

Elemental analyses were performed using a Heraeus CHN-O-RAPID elemental analyzer. Infrared spectra were recorded on a Bruker Tensor 27 instrument. Electronic absorption spectra were recorded on a JASCO V-570 spectrophotometer; $\lambda_{max}(\log\varepsilon)$.

2.2. Syntheses

2.2.1. Synthesis of $[Hg_2(A)_2](NO_3)_2$ (**1**)

A solution of mercury(I) nitrate dihydrate (280 mg, 0.5 mmol) in absolute methanol (10 ml) was added to a solution of **A**

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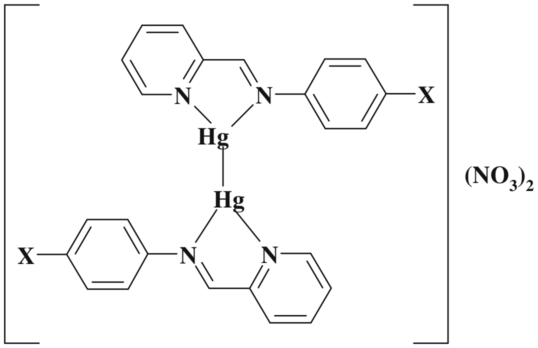
doi:10.1016/j.poly.2009.02.020



Complex	X
1	F
2	Cl
3	Br
4	I

Fig. 1. Chemical formula of Hg(I) complexes **1–4**.

Table 1
Crystal data and structure refinements for **1** and **3**.

Complex	**1**	**3**
Empirical formula	$C_{24}H_{18}F_2Hg_2N_6O_6$	$C_{24}H_{18}Br_2Hg_2N_6O_6$
Formula weight	925.62	1047.44
Temperature (K)	150(1)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$
a (Å)	7.2680(2)	35.571(1)
b (Å)	8.8507(2)	7.1888(2)
c (Å)	10.202(2)	26.781(8)
α (°)	97.52(3)	90
β (°)	97.19(3)	129.554(1)
γ (°)	102.04(3)	90
V (A^3)	628.4(2)	5280(3)
Z	1	8
Density (g cm^{-3})	2.446	2.635
μ (mm^{-1})	12.270	14.696
F(000)	430	3856
Crystal size (mm^3)	0.14 × 0.11 × 0.03	0.23 × 0.12 × 0.11
θ range for data collection (°)	2.88–27.47.	1.48–30.03
Index ranges	$-9 \leqslant h \leqslant 9$, $-11 \leqslant k \leqslant 11$, $-12 \leqslant l \leqslant 13$	$-49 \leqslant h \leqslant 50$, $-10 \leqslant k \leqslant 10$, $-37 \leqslant l \leqslant 37$
Reflections collected	5778	32124
Independent reflections [R_{int}]	2832 [0.0788]	7667 [0.0917]
Completeness to θ = 27.47°	98.1%	99.4%
Absorption correction	semi-empirical from equivalents	semi-empirical from equivalents
Maximum and minimum transmission	0.696 and 0.313	0.1948 and 0.1331
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/ parameters	2832/0/181	7667/0/361
Goodness-of-fit (GOF) on F^2	1.055	0.990
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0577, wR_2 = 0.1404	R_1 = 0.0427, wR_2 = 0.0712
R indices (all data)	R_1 = 0.0739, wR_2 = 0.1518	R_1 = 0.0908, wR_2 = 0.0837
Largest difference in peak and hole (e Å^{-3})	4.521 and −4.235	2.518 and −2.406

(200 mg, 1 mmol) in methanol (10 ml). The resulting precipitate that formed immediately was dissolved in hot absolute methanol (20 ml). The filtered solution was cooled in the dark, giving the complex as light yellow needles, which were washed successively with ice-cooled absolute methanol (5 ml) and ether (25 ml), and dried in a vacuum desiccator overnight. Yield: 92%. *Anal.* Calc. for $C_{24}H_{18}F_2Hg_2N_6O_6$: C, 31.14; H, 1.96; N, 9.08. Found: C, 31.17; H, 1.95; N, 9.05%. UV–Vis: $\lambda(\log\varepsilon)$ (DMSO): 243(4.11), 275(3.92), 295(3.91). IR (KBr/ν, cm^{-1}): 1596 (C═N).

2.2.2. Synthesis of $[Hg_2(B)_2](NO_3)_2$ (2)

This complex was prepared by a procedure similar to that for **1** using 21.7 mg (0.1 mmol) of **B**. Light yellow crystals were collected by filtration and dried in *vacuo*. Yield: 93%. *Anal.* Calc. for $C_{24}H_{18}Cl_2Hg_2N_6O_6$: C, 30.07; H, 1.89; N, 8.77. Found: C, 30.09; H, 1.87; N, 8.74%. UV–Vis: $\lambda(\log\varepsilon)$ (DMSO): 240(4.21), 273(3.84), 297(3.71). IR (KBr/ν, cm^{-1}): 1601 (C═N).

2.2.3. Synthesis of $[Hg_2(C)_2](NO_3)_2$ (3)

This complex was prepared by a procedure similar to that for **1** using 26.1 mg (0.1 mmol) of **C**. Light yellow crystals were collected by filtration and dried in *vacuo*. Yield: 86%. *Anal.* Calc. for $C_{24}H_{18}Br_2Hg_2N_6O_6$: C, 27.52; H, 1.73; N, 8.02. Found: C, 27.50; H, 1.72; N, 8.05%. UV–Vis: $\lambda(\log\varepsilon)$ (DMSO): 239(4.23), 269(3.86), 298(3.86). IR (KBr/ν, cm^{-1}): 1599 (C═N).

2.2.4. Synthesis of $[Hg_2(D)_2](NO_3)_2$ (4)

This complex was prepared by a procedure similar to that for **1** using 30.8 mg (0.1 mmol) of **D**. Light yellow crystals were collected by filtration and dried in *vacuo*. Yield: 89%. *Anal.* Calc. for $C_{24}H_{18}Hg_2I_2N_6O_6$: C, 25.25; H, 1.59; N, 7.36. Found: C, 25.28; H, 1.56; N, 7.34%. UV–Vis: $\lambda(\log\varepsilon)$ (DMSO): 238(4.20), 272(3.81), 296(3.95). IR (KBr/ν, cm^{-1}): 1602 (C═N).

2.3. X-ray analyses

Crystals of **1** and **3**, which were suitable for X-ray crystallography, were obtained as described above. A summary of the key crystallographic information is given in Table 1. Diffraction data for **1** was collected on a Bruker–Nonius Kappa-CCD diffractometer using monochromated Mo Kα radiation and measured using a combination of ϕ scans and ω scans with κ offsets to fill the Ewald sphere. The data was processed using the Denzo-SMN package [21]. Absorption corrections were carried out using SORTAV [22]. The structure was solved and refined using SHELXTL V6.1 [23] for full-matrix least-squares refinement based on F^2. All H-atoms were included in calculated positions and allowed to refine in a riding-motion approximation with U_{iso} tied to the carrier atom. Diffraction data for **3** collected on a Bruker SMART APEX2 CCD area detector using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Preliminary orientation matrices were obtained from the first frames using APEX2 [24]. The structures were solved using direct methods and refined by the full-matrix least-squares method on F^2 data using SHELXTL [25]. All H-atoms were geometrically positioned and refined using a riding model with d (C–H) = 0.93 Å, $U_{iso} = 1.2U_{eq}(C)$.

3. Results and discussion

3.1. Synthesis and spectral properties

The mercury(I) complexes were prepared by reacting equimolar quantities of mercury(I) nitrate and the ligands in methanol. These complexes are light yellow solids, which are insoluble in chloroform, methanol, ethanol and acetone, and are stable under ambient conditions. While most mercury(I) complexes containing nitrogen donor ligands undergo disproportionation reactions, some imines are known to form stable mercury(I) complexes [4,13]. The existence of stable iminopyridine complexes of mercury(I), which have