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Crystal structures and Hirshfeld surface analysis calculations of mercury(II) complexes with a diiminopyridine ligand

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ABSTRACT

The reaction of a diiminopyridine ligand, *N,N′*-bis(phenyl(pyridin-2-yl)methylene)propane-1,3-diamine (L), with mercury(II) salts gave two complexes namely $[Hg(L)Cl]\cdot 0.5[Hg_2Cl_6]$ (**1**) and $[Hg(L)(\mu\text{-}I)HgI_3]$ (**2**), which were characterized by XRD, NMR and FTIR. The crystal structure of **1** consists of discrete units of $[Hg(L)Cl]^+$cations and $[Hg_2C1_6]^{2-}$ anions in the ratio 2:1. The coordination of mercury in the cation is approximately square pyramidal (sp), the metal center is chelated in a tetradentate manner by the ligand and further coordinated by one chlorine atom. In **2** the packing can be described as units of μ-I-connected square pyramidal (sp) and tetrahedral Hg complexes. The sp coordination around the metal atom is defined by the N_4 donor set of the ligand and one bridging iodide. The hydrogen–chlorine donor–accepter interactions in **1** stabilize an infinite 1-D chain; however, such interactions were not observed in **2**. Analysis of their Hirshfeld surfaces indicates that the molecules in **1** and **2** are packed predominately by means of van der Waals forces, 'edge to face' aromatic ring packing and weak C–H··X donor-acceptor interactions.

1. Introduction

Self-assembly of small building blocks into polymeric molecular frameworks, have evoked much research interest, owing to their suitability in applications such as: microelectronics, nonlinear optics, molecular selection, ion exchange and catalysis [1–7]. One particularly attractive method for preparation of these complexes is through use of dynamic coordination chemistry. It employs labile metal centers and bridging ligands that form the primary structural unit, which in combination with weak non-covalent interactions, leads them to organize into supramolecular assemblies [8].

Hg(II) can take on a variety of coordination geometries such as: linear, octahedral and distorted hexagonal bipyramid arrangements. Severe distortions from ideal coordination geometry take place as observed in many crystal structures reported to date [9,10]. The ability to attach a variety of functionalities to several positions on diiminopyridine framework allows ligands to be readily tailored to promote desired geometries for the construction of coordination complexes [11–13] of particular interest.

As a part of ongoing efforts in the development of metal complexes with diiminopyridines [14] the reactions of Hg(II) salts with N,N′-bis(phenyl(pyridin-2-yl)methylene)propane-1,3-diamine (L) (Scheme 1) are investigated. The preparation, physicochemical characterization and the X-ray crystal structures of the cationic and neutral mercury complexes are reported in this paper.

2. Experimental

2.1. Materials

The solvents and reagents used in these studies were obtained from commercial sources and were used as received.

Caution! Mercury and its compounds are toxic [15].

2.2. Physical measurements

FT-IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer on solid state samples.

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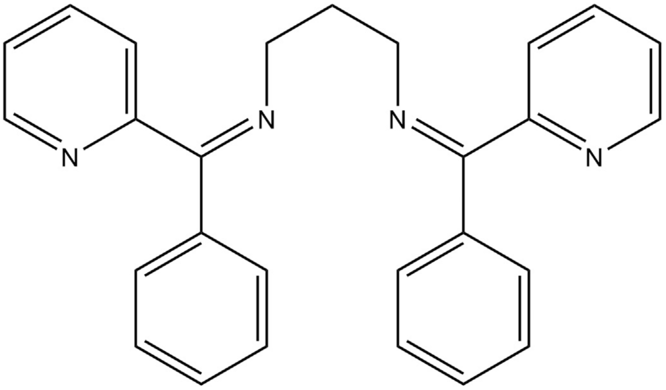

Scheme 1. Molecular structure ligand L.

^{1}H NMR and ^{13}C NMR spectra were recorded on Varian Mercury Plus 400 spectrometer in $CDCl_3$ and DMSO-δ_6 at ambient temperature using 5 mm sample tubes spinning at 20 Hz. ^{1}H spectra were recorded using a 45° excitation pulse, as 16 transients, over an acquisition time of 2 s, with a recycle delay of 1 s. 64 k data points were collected using a spectral window of 8.8 kHz. All chemical shifts are reported with respect to TMS as the primary reference.

Microanalyses were carried out using a Heraeus CHNO Rapid analyzer.

2.3. X-ray crystallography

X-ray data for the complexes were collected at 100 K on a Bruker AXS SMART APEX CCD diffractometer, using Mo K_α radiation ($K_\alpha = 0.71073$ Å) in the ω-scan mode. All structures were determined using direct methods and refined by full-matrix least-squares procedures using the SHELXTL [16]. All the hydrogen atoms were fixed in calculated positions. Structure visualizations were prepared by using DIAMOND software [17]. Crystallographic data and details of the data collection and structure refinements are listed in Table 1.

2.4. Hirshfeld surface analysis

Hirshfeld-surface (HS) analysis has recently become a popular method for the analysis of X-ray structures to investigate detailed aspects of molecular packing; for instance: polymorphism, solvatomorphism [18], and other aspects of supramolecular arrangement [19]. This is due to its complementary character to traditional structure viewing, where interactions are not examined in isolation but rather within the context of the whole system. Additionally, color-mapping of functions describing specific properties of the HS (*e.g.*d_{norm}, shape index) allows for intuitive recognition and visual analysis of interactions between molecules [20]. All contact distances to the Hirshfeld surface (d_i, d_e) can be summarized in the form of two-dimensional histograms (2-D fingerprint plots), whose shapes are characteristic for certain close-contact environments [21]. It is of equal significance that each 2-D fingerprint plot can be split into respective close contacts, and their contributions can be expressed in terms of a percentage share [22].

Hirshfeld surface and 2-D fingerprint calculations were performed using the Crystal Explorer package *ver.* 3.1 [23]. Crystal structures were imported from CIF files. By default, H–X bond lengths were set to neutron values (C–H = 1.083 Å, O–H = 0.983 Å, N–H = 1.009 Å). Hirshfeld surfaces were generated for complex molecules using high resolution and mapped with the d_{norm} or shape index functions. 2-D fingerprint plots were prepared with the use of the same software.

2.5. Synthesis of ligand

N,N′-bis(phenyl(pyridin-2-yl)methylene)propane-1,3-diamine (L) was synthesized according to the published procedure [24].

2.6. Synthesis of $[Hg(L)Cl]\cdot 0.5[Hg_2Cl_6]$ (**1**)

N,N′-bis(phenyl(pyridin-2-yl)methylene)propane-1,3-diamine (0.5 mmol) and mercury(II) chloride (0.5 mmol) were placed in the main arm of a branched tube. Methanol was carefully added to fill the arms. The tube was sealed and immersed in an oil bath at 60 °C while the branched arm was kept at ambient temperature. After 4 days, colorless crystals were isolated in the cooler arm and filtered off, washed subsequently with acetone and ether, and dried in air. Yield: 75%. Elemental composition for $C_{27}H_{24}Cl_4Hg_2N_4$ is predicted as C, 34.23; H, 2.55; N, 5.91% and was found to be C, 34.36; H, 2.42; N, 5.31%.

FTIR of $[Hg(L)Cl]\cdot 0.5[Hg_2Cl_6]$ in KBr.

ν (cm^{-1})	Intensity	Assignment
669	Strong	δ_{CH} (oop) mono-Ar
765	Medium	δ_{CH} (β-ring) 2-pyridine
1006	Medium	δ_{CH}
1309	Medium	δ_{CH}
1431	Medium	ν_{C-C} (skeletal)Pyr
1582	Medium	ν_{N-C} (skeletal) Pyr
1626	Medium	$\nu_{C=N}$ (immine)
2904	Weak	ν_{C-H} sp^3
2936	Weak	ν_{C-H} sp^3
3063	Weak	ν_{C-H} sp^2

400 MHz ^{1}H NMR of $[Hg(L)Cl]\cdot 0.5[Hg_2Cl_6]$ in DMSO-δ_6.

δ (ppm)	Muliplicity (integral)	Assignment
1.841–1.858	ddddq[1](2H)	$C_{(2)}H_2$ -propane
2.761–2.792	dddq[2] (4H)	$C_{(1,3)}H_2$-propane
7.070–7.104	ddd (2H)	H_4-pyridine
7.238–7.264	m[3] (H)	$H_{2,6}$-phenyl
7.330–7.385	m[4] (7H)	$H_{3,4,5}$-phenyl
7.542–7.585	td (2H)	H_3-pyridine
7.716–7.737	dm (4H)[5]	H_2-pyridine
8.533–8.550	dm (2H)	H_5-pyridine

[1] AB-quartet of d (*large, J = 10–13 Hz*) of d *medium, J = 5–9 Hz*) of d (*small, J = 0–4 Hz*) of d (*small*). [2] AB quartet of d (*small*) of d (*large*) of d (*medium*). [3] AA′ part of a strongly coupled AA′BB′C. [4] BB′C part of a strongly coupled AA′BB′C of phenyl. [5] Integrations are not quantitative due to T_1(^{1}H) differences in pyridine ring.

100 MHz $^{13}C\{^1H\}$ of $[Hg(L)Cl]\cdot 0.5[Hg_2Cl_6]$ in DMSO-δ_6.

δ (ppm)	Assignment
27.43	$C_{(2)}$ -propane
41.26	$C_{(1,3)}$-propane
75.50	C=N
121.65	C_4-pyridine
121.92	C_2-pyridine
127.05	*Para*-C-benzene
127.54	*Meta*-C-benzene
128.44	*Ortho*-C-benzene
136.70	C_3-pyridine
143.70	*Ipso*-C-benzene
148.83	C_5-pyridine
163.71	*Ipso*-C_1-pyridine

2.7. Synthesis of $[Hg(L)\ (\mu\text{-}I)HgI_3]$ (**2**)

This compound was prepared using similar method to **1** using *N,N′*-bis(phenyl(pyridin-2-yl)methylene)propane-1,3-diamine and mercury(II) iodide. Yield: 70%. Predicted elemental composition for $C_{27}H_{24}Hg_2I_4N_4$ is predicted to beC, 24.69; H, 1.84; N, 4.27% and was found to be C, 24.64; H, 1.55; N, 4.39%.