Journal of Molecular Structure 1103 (2016) 265–270

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

The interplay of thiophilic and hydrogen bonding interactions in the supramolecular architecture of phenylmercury 4-hydroxypiperidine dithiocarbamate

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ARTICLE INFO

Article history:
Received 16 June 2015
Received in revised form
3 August 2015
Accepted 1 October 2015
Available online 9 October 2015

Keywords:
Dithiocarbamate
Mercury
Weak interaction
ab initio
AIM

ABSTRACT

A new phenylmercury(II) dithiocarbamate complex [PhHg($S_2CN(CH_2)_4CH(OH)$)], (**1**) has been synthesized and characterized by elemental analyses, IR, ^1H and ^{13}C NMR spectroscopy and X-ray crystallography. The crystal structure of **1** shows a linear arrangement at the Hg(II) centre of the molecule through bonding of the sulphur atom of the dithiocarbamate ligand and the carbon atom of the aromatic ring. Weak intermolecular thiophilic Hg···S interactions lead to a "head-to-tail" dimer and the presence of a hydroxyl group at the periphery of piperidine moiety generates a 1D-chain network through intermolecular O···H interactions. The nature of weak intra- and intermolecular Hg···S, H···S and intermolecular O···H interactions have been assessed with the help of *ab initio* calculations and atoms-in-molecules (AIM) approach.

1. Introduction

A considerable amount of interest is concentrated on the functionalization of the aliphatic and aromatic substituents in the dithiocarbamate chemistry [1–17]. This permits to develop the complicated architectures and this in turn has potential to give rise to tuneable physical properties [1–17]. But still the main problem the crystal engineers are facing is the reasonable assembly of molecules into three dimensional arrangements which are capable of controlling wide range of intermolecular interactions.

Organomercury(II) compounds continue to attract attention owing to their importance in the preparation of other organometallics [18–27], as intermediates in organic chemistry [18] and their relevance to mercury detoxification [19]. Organomercury(II) dithiocarbamates have been found to be extremely versatile groups in the construction of supramolecular arrays [28–35], exhibit photoluminescence properties [29,30] and are also used as dyes for solar energy harvesting in dye-sensitized solar cells (DSSCs) [31,35].

The earlier investigation on phenylmercury(II) dithiocarbamate complexes revealed that the bulkiness of the pendant group in the ligands play important role in the construction of the supramolecular architecture through Hg…S interactions [28]. Alcock termed such contacts as "secondary interactions" [36–39]. Organomercury(II) dithiocarbamates having an $-NH_2$ group in the periphery of the dithiocarbamate ligand have been reported [28], but because of the steric restrictions, the compounds have not exhibited intermolecular Hg…N secondary interactions. Recently we had reported the organomercury(II) dithiocarabamates displaying weak Hg…N secondary interactions alongwith the Hg…S interaction and their nature was addressed using quantum chemical calculations [40]. Additionally the role of weak Hg…N secondary interactions alongwith the Hg…S interaction was also investigated in controlling the photoluminescent properties [40].

With these viewpoints and in the quest of new type of secondary interactions in organomercury(II) dithiocarbamates and to generate the new supramolecular motifs herein we report the

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http://dx.doi.org/10.1016/j.molstruc.2015.10.001

synthesis, characterization and X-ray structures of a new phenylmercury(II) dithiocarbamate containing –OH group at the periphery of the dithiocarbamate ligand. The magnitude of intermolecular interaction energies in supramolecular motifs have been estimated at the MP2 level of theory and the intra-as well as the intermolecular interactions have been validated using atoms-in-molecules (AIM) theory.

2. Experimental details

2.1. General considerations

All chemicals were of analytical grade obtained from commercial sources and used without further purification. The solvents were purified in accordance with the standard methods.

IR as KBr pellet was recorded on Varian 3100 FTIR spectrophotometer. The FT-IR experiment was performed under ambient conditions. A total of 30 scans were accumulated for the spectrum to obtain a reasonable signal to noise ratio with a spectral resolution of 10 $cm^{-1.}$ The ^{1}H and ^{13}C NMR spectra in DMSO-d_6 were recorded on a and JEOL AL300 FTNMR spectrometer. Chemical shifts were reported in parts per million using TMS as internal standard. Elemental analysis was performed on Exeter analytical Inc "Model CE-440 CHN analyzer".

2.2. Synthesis of [$PhHg(S_2CN(CH_2)_4CH(OH)$] (**1**)

4-hydroxypiperidine (0.101 g, 1 mmol) was dissolved in 15 mL of anhydrous THF and to it was added NaOH (0.040 g, 1 mmol) dissolved in 0.5 mL of water. The mixture was stirred for 10 min and then CS_2 (0.114 g, 1.5 mmol) was added. The mixture was stirred for an additional 30 min until the colour of the solution became yellow. To the resulting solution phenylmercury(II) acetate (0.335 g, 1 mmol) dissolved in dichloromethane (15 mL) was added dropwise and the solution was additionally stirred for another 1 h. The resulting solution was filtered and evaporated at room temperature to obtain a white coloured powder of [$PhHg(S_2CN(CH_2)_4CH(OH)$].

[$PhHg(S_2CN(CH_2)_4CH(OH)$] (**1**) (0.377 g, yield 83%); m.p. 187 °C. ^{1}H NMR (DMSO-d_6, δ): 7.39–1.18 (m, 5H, C_6H_5), 4.90 (s, 1H, –OH), 4.23 (s, 4H, $-CH_2$), 3.84 (s, 4H, $-CH_2$), 3.56 (s, 1H, –CH). ^{13}C NMR ($CDCl_3$, δ): 199.7 ($-NCS_2$), 155.6, 138.2, 137.2, 128.3, 127.9, 127.7 (C_6H_5), 64.8, 47.9, 33.8 (piperidine). ν_{max}(KBr)/cm^{-1} 3705 (–OH), 1433 (C=N), 967 (C=S), 851 (C–S). Anal. Calc. for $C_{12}H_{15}HgNOS_2$: C, 31.75; H, 3.33; N, 3.09. Found: C, 31.90; H, 3.28; N, 3.16%.

2.3. X-ray crystallography

Intensity data for **1** were collected at 150(2) K on an Agilent Xcalibur diffractometer using graphite monochromated Mo-Kα radiation $\lambda = 0.71073$ Å. Unit cell determination, data collection and data reduction were performed with CrysAlisPro [41]. The structure was solved by direct methods (SIR97) [42] and refined by a full-matrix least-squares procedure based on F^2 [43]. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were located at calculated positions and refined using a riding model. All hetero hydrogen atoms have been located in the difference Fourier map and were refined with bond lengths restraints. The asymmetric unit consists of half a dimeric Hg complex and one $CHCl_3$ solvent molecule which is located about a two fold axis and therefore disordered with occupation factor of 50%. Two solvent molecule atoms C21 and CL2 had to be refined with ADP restraints. The OH group in the main molecule is disordered over two sites in the ratio 1:1. Bond length restraints were applied for O1, O1A and H1, H1A. Additionally, H1 had to be refined riding on its parent atom as the ADP became negative. There is one large peak 2.3 Å from Hg which is an artefact.

Crystal Data: $C_{25}H_{31}C_{l3}Hg_2N_2O_2S_4$, M = 1027.29, Monoclinic, I2/a, a = 9.1909(3) Å, b = 11.9357(5) Å, c = 31.0086(13) Å, $\beta = 97.783(4)^\circ$, V = 3370.3(2) $Å^3$, Z = 4, D_{calc} = 2.025 mg m^{-3}, F(000) = 1944, crystal size 0.120 × 0.040 × 0.036 mm, reflections collected 14388, independent reflections 3802 [$R_{(int)}$ = 0.0489], Final indices [$I > 2\sigma(I)$] $R_1 = 0.0509$ $wR_2 = 0.1208$, R indices (all data) $R_1 = 0.0612$, $wR_2 = 0.1260$, gof 1.133, Largest difference peak and hole 5.204 and −1.739 e $Å^{-3}$.

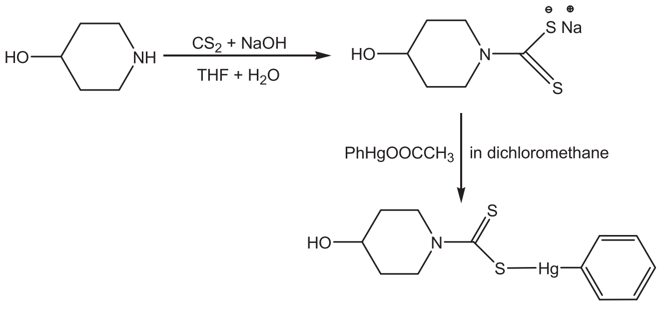
2.4. Computational details

Molecular geometries were optimized at the level of density functional theory (DFT) using the B3LYP exchange-correlation functional [44]. The split valence basis sets, 6-31G** were used at all C, N, O, S and H atom centres. Stephens, Basch, Krauss ECP triple-split basis set, CEP-121G was used for the Hg atom. Vibrational analysis was performed at the same level as geometry optimization. Potential energy distribution along internal coordinates was calculated by VEDA 4 software [45]. Internal coordinate system recommended by Pulay et al. was used for the assignment of vibrational modes [46]. The molecular electrostatic potential surfaces for monomer as well as the dimer have been generated using the same level of theory. The crystal structure of **1** was used as a starting point for all geometry optimizations. The intermolecular interaction energies have been estimated at the MP2 level of theory. For the interaction energy calculations, the Hg…S distances have been fixed for the dimer while all other degrees of freedom were relaxed in the geometry optimization. The stabilization energies for dimeric motif involving the two molecules (ΔE_{dimer}) were calculated from the formula $\Delta E_{dimer} = E_{dimer} - (2 \times E_{monomer})$. $E_{monomer}$ was calculated by optimizing a single molecule at the same level of theory. The intermolecular interaction strengths are significantly weaker than either ionic or covalent bonding, therefore it was essential to do basis set superposition error (BSSE) corrections. The BSSE corrections in the interaction energies were done using Boys-Bernardi scheme. In this paper all the interaction energies have been reported after BSSE correction [47]. All computational experiments have been performed using the Gaussian 03 programme [48].

3. Results and discussion

3.1. Synthesis

Complex [$PhHg(S_2CN(CH_2)_4CH(OH)$] (**1**) was obtained by the addition of stoichiometric amount of phenylmercuric acetate to sodium 4-piperidinoldithiocarbamate in a mixture of THF, water and dichloromethane (Scheme 1). Complex **1** was air stable and moderately soluble in DMSO, methanol, acetone, dichloromethane



Scheme 1. Synthesis of the complex **1**.