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КРАТКИЕ СООБЩЕНИЯ

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HYDROTHERMAL SYNTHESIS OF A NANO-ROD MERCURY(II) METAL-LIGAND COORDINATION COMPOUND

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A novel nano-rod mercury(II) coordination compound [Hg (BINH)I_2] (**1**), (BINH is the abbreviation of benzylideneisonicotinohydrazide) is synthesized by a hydrothermal method that produces the coordination compound at a nanosize level. The new nanostructure is characterized by scanning electron microscopy, powder X-ray diffraction, elemental analysis, and IR spectroscopy. Compound **1** was structurally characterized by single crystal X-ray diffraction and the single-crystal structure of this complex shows that each mercury(II) center is four-coordinated with two N-donor atoms from tow BINH ligands and tow iodo anions. Self-assembly of this complexes is pereformed by CH$\cdots$I and π—π stacking interactions. The supramolecular features in these complexes are controlled by weak directional intermolecular interactions.

Keywords: Hg(II), metal-ligand, nano-rod, hydrothermal.

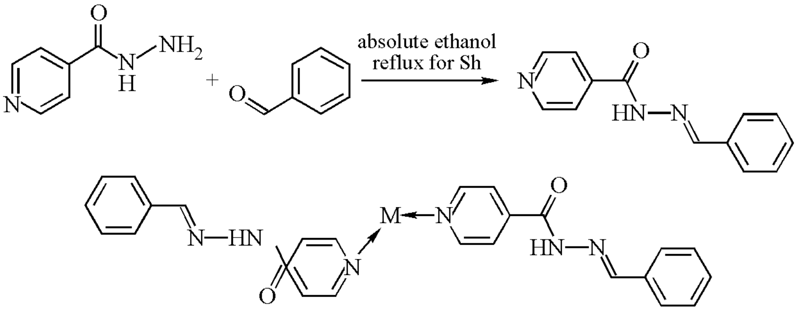
Introduction. Metal coordination polymers have been studied widely since they represent an important interface between synthetic chemistry and materials science, having specific structures, properties not found in mononuclear compounds. The synthesis of metal coordination polymers is often guided by the quest to understand how molecules can be organized and how functions can be achieved. Many attempts have been made to prepare a variety of transition metal complexes using different spacers, and their structures and properties have been physically and chemically determined [1—15]. In contrast to coordination polymers of transition metal ions, the formation of polymers with heavy metal ions such as mercury(II) seems to be surprisingly sparse, and, despite the attractive properties of mercury(II) compounds in terms of their potential applications in paper industry, paints, cosmetics, preservatives, thermometers, manometers, fluorescent lamps and mercury batteries [6] (although somehow limited due to its toxicity), there have been until recently only very few reports on Hg(II) complexes with e.g. rigid or flexible organic nitrogen donor-based ligands. In the literatures, the reported several Hg(II) based organic/inorganic polymers based on N,N′-bidentate ligands, such as 4,4′-bipyridine (bipy), *trans*-1,2-bis(4-pyridyl)ethene (bpe), 1,2-bis(4-pyridyl)ethane (bpa), and 1,2-bis(4-pyridyl) propane (bpp) [16—18].

The organic part of a coordination compounds exhibits interesting effects on the self-assembly of coordination compounds. Aromatic ligands can act as hydrogen-bonding acceptors or donors, and also can provide recognition sites for π—π stacking interactions to form interesting supramolecular structures when coordinating to metal ions. The d^{10} metal complexes and coordination compounds have attracted extensive interest in recent years since they exhibit appealing structures [19—25].

This work stems from our interest in the study of coordination behaviors of Hg(II) with the benzylideneisonicotinohydrazide Schiff-base ligand. The structural chemistry of the ligand is especially interesting due to its one functional coordination mode (Scheme 1).

Actually herein, we report a nano-rod mercury(II) coordination compound, prepared by a hydrothermal method with benzylideneisonicotinohydrazide Schiff-base ligands: {[Hg(BINH)I_2] (**1**), (BINH is the abbreviation of benzylideneisonicotinohydrazide).

Experimental. Physical property measurements. The BINH ligand prepared (Scheme 1) according to the literature procedures in air atmosphere [26] was used without further purification.



Scheme 1. Scheme for the preparation of the BINH ligand

All reagents and solvents for the synthesis and analysis were commercially available and used as received. Infrared spectra were recorded in KBr pellets using a Perkin-Elmer 883-IR spectrophotometer and on a Nicolet 520 FTIR spectrophotometer. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 II elemental analyzer. Powder X-ray diffraction (XRD) measurements were performed using an X′pert diffractometer manufactured by the Panalytical Company, with monochromatized CuK_α radiation. The crystallite sizes of selected samples were estimated using the Scherrer formula. The morphology of materials was examined by a scanning electron microscope SEM (Hitachi S-4200). Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Crystallographic data were collected at 298 K with the Oxford Xcalibur CCD area detector diffractometer, using graphite monochromated MoK_α ($\lambda = 0.71069$ Å) radiation. Data reduction and absorption correction were performed using CrysAlis RED 1.171.26 (Oxford Diffraction). The structure of the samples were analyzed by direct methods using SIR2004 [27] and refined by full-matrix least squares using SHELX-97 [28]. Hydrogen atoms were generated at specific position using SHELX-97 [28]. The results for publication were prepared using SHELXTL [28] and ORTEPIII [29].

Preparation of [Hg(BINH)I_2]. To prepare the nano-structure of [Hg(BINH)I_2] (**1**) by the hydrothermal procedure, mercury(II) iodide (0.45 g, 1 mmol) and BINH (0.22 g, 1 mmol) were dissolved in 15 ml of H_2O. The solution was charged into a Teflon-lined stainless steel autoclave and heated at 150 °C for 48 h. After the autoclave was rapidly cooled to room temperature, the product was filtered, dried, and characterized.

Product **1**: m.p. = 200 °C. Analysis: Found; C: 33.20, H: 2.80, N: 8.90 %. calcd. for $C_{26}H_{26}HgI_2N_6O_4$: C: 33.19, H: 2.79, N: 8.93 %).

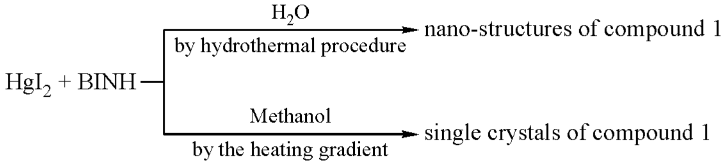
IR (selected bands; in cm^{-1}): 756 (*m*, C—H), 1448 (*s*, C=N_{imine}), 1478 (*m*), 1528 (m), 1568 (*s*, C=$C_{aromaic}$ and C=$N_{aromaic}$), 1655 (*vs*, C=O), 3027 (*w*, C—$H_{aromatic}$) [28].

Isolated single crystals of this compound were prepared by the branch tube [30] method: mercury(II) iodide (0.45 g, 1 mmol) was placed in one arm of a branched tube and BINH (0.22 g, 1 mmol) in another. Methanol was then carefully added to fill both arms, the tube was sealed, and the ligand-containing arm was immersed in a bath at 60 °C, while another was left at ambient temperature. After 6 days, crystals (m.p. 198 °C) suitable for an X-ray structure determination formed in the arm at ambient temperature. They were then filtered off, washed with acetone and ether, and air dried. Yield: 77 %.

Product **1**: m.p. = 198 °C. Analysis: Found; C: 33.20, H: 2.85, N: 8.95 %. calcd. for $C_{26}H_{26}HgI_2N_6O_4$: C: 33.19, H: 2.79, N: 8.93 %).

IR (selected bands; in cm^{-1}): 755 (*m*, C—H), 1450 (*s*, $C{=}N_{imine}$), 1478 (*m*), 1530 (m), 1568 (*s*, $C{=}C_{aromaic}$ and $C{=}N_{aromaic}$), 1655 (*vs*, C=O), 3025 (*w*, $C{—}H_{aromatic}$) [31].

Results and discussion. Using two different routes, the reaction between the BINH ligands and mercury(II) iodide produced the title compound $[Hg(BINH)I_2]$ (**1**). Scheme 2 gives an overview of the methods used for the synthesis of $[Hg(BINH)I_2]$ (**1**) using two different routes.



Scheme 2. Materials produced and synthetic methods

The elemental analysis data and IR spectra of the nano-structures and the single crystal material are indistinguishable. The IR spectra of the nano-structures and the single crystal materials show the characteristic absorption bands for the BINH ligand. The relatively weak absorption bands at around 3025 cm^{-1} are due to the C—H modes involving the aromatic ring hydrogen atoms. The absorption band with a strong intensity in the frequency range 1470—1570 cm^{-1} corresponds to aromatic ring vibrations of the BINH ligand. The absorption bands with a strong intensity at 1450 cm^{-1} correspond to C=N of the imine group of the BINH ligands [31].

The acceptable match, with very slight differences in peak positions, observed between the simulated and experimental powder XRD patterns indicates that the nano-structure sample is a single crystalline phase identical to that obtained by single crystal diffraction. The significant broadening of the peaks of the nano-rod structure indicates that the particles are of nanometer dimensions. The average size of the particles was estimated by the Scherrer formula, $D = 0.891\lambda/\beta\cos\theta$, where D is the average grain size, λ is the X-ray wavelength (1.5418 Å), θ is the diffraction angle, and β is the full-width at half maximum of an observed peak. The obtained value is D = 50 nm.

Fig. 1 shows the nano-rods that observed by scanning electron microscopy. The morphology of compound **1** prepared by the hydrothermal procedure (Fig. 1) are the rods with a diameter of about 70—140 nm.

The structure of complex **1** was determined by X-ray crystallography. The crystallographic data are summarized in Table 1, and selected bond lengths and bond angles are shown in Table 2.

An ORTEP view of complex **1** is shown in Fig. 2. The mercury atoms are linked by two nitrogen atoms of two BINH ligands and two iodo anions. The Hg atom is surrounded by an I_2N_2 coordination sphere.

There are CH···I interactions amongst the weak interactions (I1···H17—C17 with a distance of 3.180 Å, I1···H125—C25 with a distance of 3.646 Å) and O···HC interactions (O1···H2A—C2A with a distance of 2.365 Å, O1···H7A—C7A with a distance of 2.595 Å, O2w···H18A—C18A with a distance of 2.367 Å, O2w···H20A—C20A with a distance of 2.647 Å) whose values suggest relatively strong interactions within this class of weak non-covalent contacts [32]. There are π—π stacking interactions between the aromatic rings of the BINH ligands belonging to the neighboring units in compound **1**. The py groups of BINH are almost parallel and this parallel array of the planes of the aromatic moieties indicates that these inter-

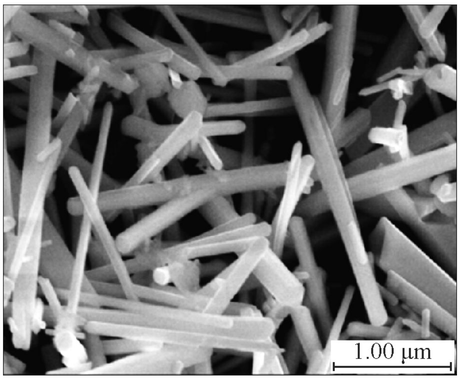


Fig. 1. SEM photographs of $[Hg(BINH)I_2]$ (**1**) nano-rods

Table 1

Crystal data and structure refinement for [Hg(BINH)I_2] (**1**)

Empirical formula	$C_{26}H_{26}HgI_2N_6O_4$
Formula weight	940.92
Temperature, K	566(2)
Wavelength, Å	0.71073
Crystal system	Orthorhombic
Space group	$Pna2_1$
Unit cell dimensions, Å, deg.	$a = 48.8234(8)$, $b = 4.68570(10)$, $c = 12.7286(2)$, $\alpha = \beta = \gamma = 90.00$
Volume, $Å^3$	2911.94(9)
Z	4
Density (calculated), Mg/m^3	2.146
Absorption coefficient, mm^{-1}	7.448
$F(000)$	1768
Crystal size, mm	0.30×0.10×0.06
θ range for data collection, deg.	74 to 51.98
Index ranges	$-60 \le h \le 41$, $-5 \le k \le 5$, $-15 \le l \le 11$
Reflections collected / independent	11246 / 4753 [R(int) = 0.0302]
Data / restraints / parameters	4753 / 31 / 155
Goodness-of-fit on F^2	1.115
Final R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0794$, $wR_2 = 0.2030$
Final R indexes [all data]	$R_1 = 0.0802$, $wR_2 = 0.2040$

Table 2

Selected bond lengths [Å] *and angles* [deg.] *for* [Hg(BINH)I_2] (**1**)

Hg1—N1	2.525(9)	N1Hg1N4	112.0(4)	N1Hg1I1	96.0(2)
Hg1—N4	2.533(9)	N1Hg1I2	97.4(3)	I2Hg1I1	156.23(5)
Hg1—I1	2.625(2)	N4Hg1I1	97.8(2)	N4Hg1I1	95.3(2)
Hg1—I2	2.664(2)				

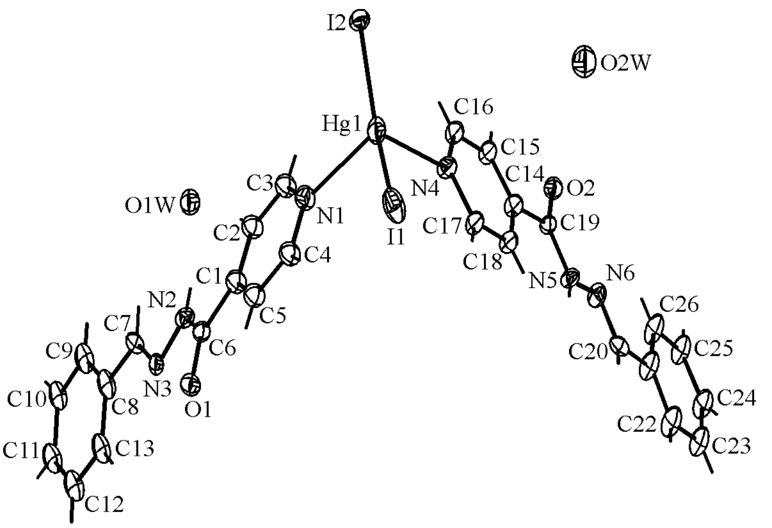
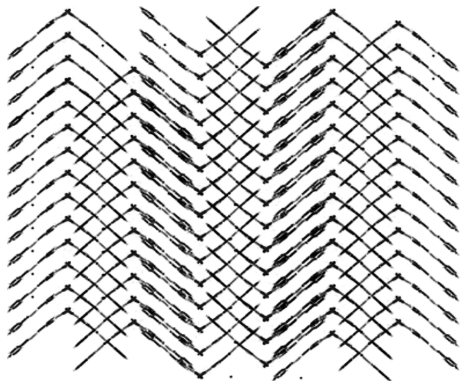


Fig. 2. ORTEP view of [Hg (BINH)I_2] complex (**1**)

Fig. 3. Packing of 1D chains to form 2D supramolecular layers *via* intermolecular interactions



actions are of the face-to-face π-stacking type [33] (Fig. 3). The centroid—centroid distance of py groups is 3.461 Å and 3.572 Å, and the angle between the ring normal and the centroid vectors is 0.70° and 0.68°.

Conclusions. In this work, a novel mercury(II) iodide coordination compound containing the BINH ligand was described together with a hydrothermal preparation of nanostructures of this coordination compound. The crystal structure of the complex has also been determined. The mercury atoms were linked by two nitrogen atoms of tow "BINH" ligand and two iodo anions and the Hg atom surrounded by an I_2N_2 coordination sphere. The ability of weak interactions to control the packing of molecular moieties to generate different patterns suggested their importance in crystal engineering. It is obviously clear that such weak interactions are prolific in molecular assemblies providing both directionality and flexibility in the crystal structure. Weak interaction distances in this compound were smaller than the sum of the van der Waals radii, indicating a preferred influence on the overall crystal packing.

Supplementary material. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-876701 for [Hg (BINH)I_2] (**1**). Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44-1223-336033; E-mail: de-posit@ccdc.cam.ac.uk].

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