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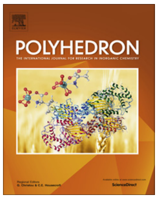

On the zinc(II) and mercury(II) compounds with Schiff-base *N*-(*p*-anisoyl)-2-oxo-1-naphthylideneamine. Tautomerism of the ligand and polymerization of mercury compound *via* Hg···I contact

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ABSTRACT

A series of novel complexes, dihalo-bis(*N*-*p*-anisoyl-2-oxo-1-naphthylideneamine-*O*)zinc(II) (**1**, **2**, **3**) and di-μ-halo-bis[halo(*N*-*p*-anisoyl-2-oxo-1-naphthylideneamine-*O*)mercury(II)] (**4**, **5**, **6**), of the general formulae $[ZnX_2(LH)_2]$ and $[HgX_2(LH)]$, X = Cl, Br, I, have been prepared. The crystal structure of **1** reveals the four-co-ordinated zinc center by two halogen atoms and two oxygen atoms from neutral monodentate Schiff-base ligand in the form of distorted tetrahedron. Mercury atom in the asymmetric unit of mercury adduct **6** is co-ordinated with two iodine atoms and one oxygen atom from neutral monodentate Schiff-base ligand. The $HgI_2(LH)$ moieties are linked into 1D polymeric chains via Hg···I contacts.

The UV–Vis spectra of the adducts obtained in the ethanolic solution as well as the results of the ^{1}H and ^{13}C NMR measurements performed in d_6-dmso indicate that adducts undergo the decomposition after dissolving.

1. Introduction

Schiff-bases derived from 2-hydroxy-1-naphthaldehyde have been, and they still are a subject of interest of the chemists during the last several decades. These compounds, as well as other Schiff-bases derived from *o*-hydroxy aromatic aldehydes, exhibit strong OH···N or NH···O intramolecular hydrogen bonding, which results in formation of six-membered ring, and may exist in enol-imine or/and keto-amine tautomeric as well as zwitter-ionic form (Scheme 1) [1]. Interconversions between mentioned forms are well known in solid-state, solutions, vapor, and Langmuir-Bladgett films [2]. Due to such structural properties, *o*-hydroxy aromatic aldehyde based Schiff-bases show thermo-, photo- and solvatochromic effects which are a direct consequence of an intramolecular proton (hydron) transfer between O and N site accompanied by the existence of an intramolecular hydrogen bond [3].

The compounds in question, *i.e.* Schiff-bases of the 2-hydroxy-1-naphthaldimine type show great complexation ability toward metal ions. Metal complexes with 2-hydroxy-1-naphthaldimines still attract attention of the chemists worldwide due to their various properties, *e.g.* structural characteristics in the metal co-ordination sphere [4], biological activities [5,6], colori-/fluorimetric properties, *etc.* [7,8].

According to the Cambridge Structural Database [9] there is no 12th group metal compounds with the Schiff-base *N*-(*p*-anisoyl)-2-oxo-1-naphthylideneamine that have been structurally characterized. Further survey of the CSDB reveals that there is a certain number of the metal compounds involving the above mentioned ligand. More precisely, there are a few tin complexes prepared and determined by Teoh and co-workers [10–12] and Zhang and co-workers as well [13]. Belhadj Lachachi and co-workers have recently researched preparation pathways and structural characteristics of a series of platinum organometalic complexes derived from various 2-hydroxy-1-naphthaldimine Schiff-bases including *N*-(*p*-anisoyl)-2-oxo-1-naphthylideneamine [14]. On the other hand, according to our best knowledge, there are only few zinc (II) and mercury(II) complexes with the Schiff-bases of the 2-hydroxy-1-naphthaldimine type that are structurally [15–19] or only spectroscopically characterized [20].

Analyzing the metal complexes with the Schiff-bases, the tautomeric properties of those ligands have to be taken into account. Therefore, it should be mentioned here that it is known that tautomeric equilibrium of the Schiff-bases derived from 2-hydroxy-1-naphthaldehyde is usually shifted toward the keto-amine tautomeric form (Scheme 1) in the solid-state [21–23] as

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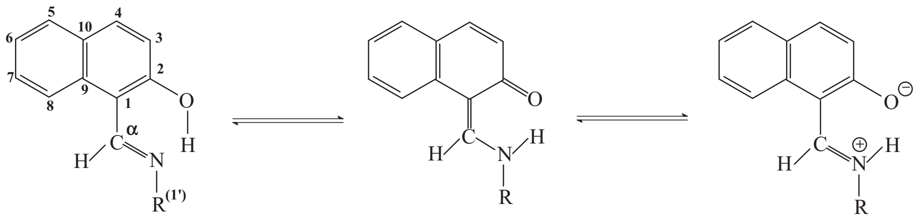

Scheme 1. Tautomeric equilibrium of the Schiff-bases derived from 2-hydroxy-1-naphthaldehyde.

well as in solution [24]. Also, there are some examples of the structures of this type of the Schiff-bases which tautomeric equilibrium lies on the enol-imine side [25].

So, with the aim to make more complete the co-ordination chemistry of the 12th group metals with the Schiff-bases, we undertook the investigation of the zinc(II) and mercury(II) halides with the *N*-(*p*-anisoyl)-2-oxo-1-naphthylideneamine. This paper reports the preparation, IR, NMR and UV characterization and thermal studies on a series of the 1:2 complexes of zinc(II) halides as well as on a series of the 1:1 complexes of mercury(II) halides with the above mentioned Schiff-base. This investigation takes a part in our work [17–19] on the 12th group metal compounds with the biologically important ligands, as the Schiff-bases are [24].

2. Materials and methods

All reagents used were purchased from Aldrich, solvents from Kemika-Zagreb and were used without further purification. C, H, and N analysis was provided by the Analytical Services Laboratory of the Ruđer Bošković Institute. The IR spectra of all mentioned compounds were recorded in a Perkin Elmer FT Spectrum RX I in the range 4000–450 cm^{-1} as KBr discs. The UV–Vis spectra were recorded using a Varian Cary 300 operating in the range 190–900 nm. The ^1H and ^{13}C NMR spectra were recorded in a Bruker AV-600 spectrometer, at 20 °C. All chemical shifts, in parts per million (ppm), are referred to TMS. Digital resolution was 0.32 Hz per point. ^{13}C NMR spectra were recorded by APT technique. The thermal measurements were performed using a simultaneous TGA-DTA analyzer (*TA Instruments*, SDT Model 2960). The samples were placed in small aluminium oxide sample pans. The TGA and DTA curves were obtained by placing the samples of about 2–5 mg in mass, in open sample pans, with a heating rate of 10 °C/min and argon (purity above 99.996%) pouring at a flow rate of 50 ml/min. The SDT was calibrated with indium.

2.1. Preparation of the ligand and basic analytical data

[annapH]. The preparation of the ligand *N*-(*p*-anisoyl)-2-oxo-1-naphthylideneamine was performed by conventional condensation method. *Anal.* Chemical analysis: found (required for $C_{18}H_{15}NO_2$) C, 77.5 (78.0); H, 5.65 (5.45); N, 5.08 (5.35)%. Selected IR-max (KBr disc, cm^{-1}): 1621vs (C=O), 1539m-s (C=C), 1210m-s (C–N), 1175m-s (Ar C=O).

UV–Vis absorptions (EtOH): λ_{max}/nm (ε/$dm^3\ mol^{-1}\ cm^{-1}$) 235 (25500), 323 (7400), 339 (7000) and 445 (9370). ^1H NMR peaks (d_6-dmso): 15.94 (N*H*, 1H, d), 9.55 (*H*-α, 1H, d), 6.94–8.42 (Ar–*H*, 10H, m). Selected ^{13}C NMR peaks (d_6-dmso): 154.39 (C-α), 108.68 (C-1), 168.82 (C-2), 137.46 (C-1′).

2.2. Preparation of the adducts and basic analytical data

The ethanolic solutions of the corresponding metal(II) halides and the Schiff-base in 1:2 (**1**–**3**) or 1:1 (**4**–**6**) molar ratio were mixed and refluxed for some time (*n.b.* the preparation of **5** is the exception). The reaction mixture was then left to stand for two days. The compounds were filtered off, washed with ethanol and dried in vacuo. After it were allowed to stand for a few days, the filtrates of **1** and **6** yielded the crystals of good quality for X-ray diffraction experiment.

[$ZnCl_2(annapH)_2$] (1). Reaction time: 0.5 h. Color: yellow-orange. Yield: 95%. *Anal.* found (required for $C_{36}H_{30}Cl_2N_2O_4Zn$): C, 62.52 (62.58); H, 4.68 (4.38); N, 3.87 (4.06); Zn, 9.85 (9.46)%. Selected IR-max (KBr disc, cm^{-1}): 3427br, w (N–H), 1627vs (C=O), 1548s (C=C), 1216m-s (C–N), 455w-m (M–O).

[$ZnBr_2(annapH)_2$] (2). Reaction time: 2 h. Color: yellow-orange. Yield: 94%. *Anal.* found (required for $C_{36}H_{30}Br_2N_2O_4Zn$): C, 55.38 (55.44); H, 4.09 (3.88); N, 3.49 (3.59); Zn, 8.52 (8.32)%. Selected IR-max (KBr discs, cm^{-1}): 3445br, w (N–H), 1623vs (C=O), 1548m-s (C=C), 1215m-s (C–N), 451w-m (M–O).

[$ZnI_2(annapH)_2$] (3). Reaction time: 2 h. Color: yellow-orange. Yield: 86%. *Anal.* found (required for $C_{36}H_{30}I_2N_2O_4Zn$): C, 49.35 (49.48); H, 3.62 (3.46); N, 2.92 (3.21); Zn, 7.40 (7.48)%. Selected IR-max (KBr discs, cm^{-1}): 3420br, w-m (N–H), 1626vs (C=O), 1548m-s (C=C), 1216m-s (C–N), 455w-m (M–O).

[$HgCl_2(annapH)$] (4). Reaction time: 10 h. Color: yellow. Yield: 76%. *Anal.* found (required for $C_{18}H_{15}Cl_2NO_2Hg$): C, 39.63 (39.98); H, 2.91 (2.77); N, 2.42 (2.59); Hg, 37.38 (37.10)%. Selected IR-max (KBr discs, cm^{-1}): 3447br, w-m (N–H), 1620vs (C=O), 1548m-s (C=C), 1216w (C–N), <450 (M–O).

[$HgBr_2(annapH)$] (5). Reaction time: the product immediately precipitated. Color: yellow. Yield: 70%. *Anal.* found (required for $C_{18}H_{15}Br_2NO_2Hg$): C, 34.34 (34.40); H, 2.83 (2.38); N, 2.09 (2.23); Hg, 32.20 (31.86)%. Selected IR-max (KBr discs, cm^{-1}): 3453br, w-m (N–H), 1619vs (C=O), 1548m-s (C=C), 1215w (C–N), <450 (M–O).

[$HgI_2(annapH)$] (6). Reaction time: 4 h. Color: orange. Yield: 89%. *Anal.* found (required for $C_{18}H_{15}I_2NO_2Hg$): C, 29.42 (29.88); H, 1.78 (2.07); N, 1.77 (1.94); Hg, 28.21 (27.72)%. Selected IR-max (KBr discs, cm^{-1}): 3446br, w-m (N–H), 1626vs (C=O), 1548m-s (C=C), 1213w (C–N), <450 (M–O).

2.3. Single-crystal X-ray diffraction experiment

The general and crystallographic data for complexes **1** and **6** are listed in Table 1. Diffraction measurements were made on an Oxford Xcalibur diffractometer, equipped with a CCD area detector, using Mo Kα radiation (λ = 0.71073 Å) at temperature of 296(2) K. Structures were solved by direct methods, all non-hydrogen atoms were refined anisotropically based on F^2 by weighted full-matrix least squares. Programs SHELXT-2014 [26] and SIR2014 [27] integrated in the WinGX v. 2014.1.v [28] software system were used to solve structures. Program SHELXL-2014 [26] was used to refine structures. Hydrogen atoms belonging to C_{sp2} and C_{sp3} carbon atoms were placed in geometrically idealized positions and they were constrained to ride on their parent atoms using the appropriate SHELXL-2014 [26] HFIX instructions. The positions of hydrogen atoms belonging to the nitrogen atoms N11 and N21 in complex **1** were determined from difference Fourier syntheses and their