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Synthesis and structure of new Schiff base derivatives obtained from 2-(formylphenyl)mercury bromide

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ABSTRACT

Reactions of (2-formylphenyl)mercury(II) bromide **10** with primary amines give *mono*-, *bis*- and *tris*-Schiff base derivatives (**11**–**18**). Structures of the synthesized compounds show the presence of five-membered intramolecular Hg···N interaction. Luminescence studies of the compounds have been performed. Attempts to use the synthesized compounds for binding neutral donor molecules or fluoride ions were unsuccessful.

1. Introduction

Arylmercury chlorides with in-built donor atoms, capable of forming 5-membered rings, have been extensively studied due to; (i) their applications in the synthesis of other organometallic compounds via transmetallation [1–9], (ii) observation of chirality due to mercury as a stereocentre [10,11], and (iii) luminescence properties [12]. *o*-Mercurated compounds with in-built N-donor functionalized aromatic ligands are known to exhibit Hg···N secondary interactions. The typical examples of *o*-mercurated halides with 5-membered Hg···N interactions include (Fig. 1); (2-(pyridin-2-yl)phenyl)mercury(II) chloride (**1**) [13], (2-(phenyldiazenyl)phenyl)mercury(II) chloride (**2**) [14], [2-(dimethylaminomethyl) phenyl]mercury(II) chloride (**3**) [15], (2-((dimethylamino) ethyl)phenyl)mercury(II) chloride (**4**) [15], *o*-mercurated ferrocenyl amines (**6**) [16–18], and imines (**7**) [19] etc. Although scores of organomercury halides having Hg···N intramolecular interaction are known in the literature, a search in Cambridge Crystallographic Database reveals that the structurally characterized bromide analogs are rare.

The intramolecular Hg···N/O interactions are generally weak. In some of these intramolecularly coordinated compounds, the mercury atom is out of plane i.e. slightly pyramidal and becomes chiral [10]. Our group has been interested in the study of weak Hg···N/O/Hg interactions and has investigated these by structural and theoretical studies [20–22]. We thought it worthwhile to systematically investigate the nature of Hg···N intramolecular interactions in a series of mono-, bis- and tris- Schiff base derivatives derived from 2-(formylphenyl)mercury bromide and also probe the presence/absence of mercury as a stereocentre. The bis- and tris-Lewis acidic arylmercury bromides can also serve as suitable hosts for binding anions. In this paper we report the first isolation of an intramolecularly coordinated arylmercury bromide in enantiomerically pure form, which is chiral without a chiral center. We also report on the nature of Hg···N interaction in the synthesized compounds.

2. Results and discussion

2.1. Synthesis

Precursors **8** and **9** were prepared from 2-bromobenzaldehyde by following the literature procedure. (Scheme 1) [23,24]. The reaction of the intermediate, (2-(1,3-dioxolan-2-yl)phenyl)magnesium bromide obtained from **8** with 1 equivalent of $HgBr_2$ yielded **9**, which on subsequent reaction with *p*-toluenesulfonic acid monohydrate, gave **10**. The synthesis of the mono-Lewis acidic Schiff bases **11**–**14** was accomplished by the condensation reactions of **10**

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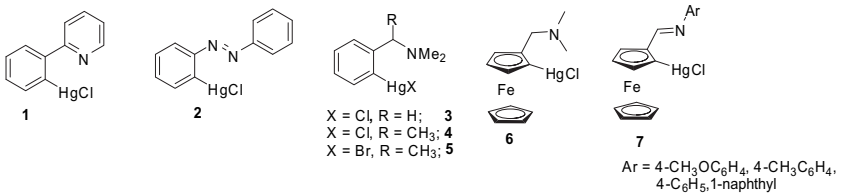
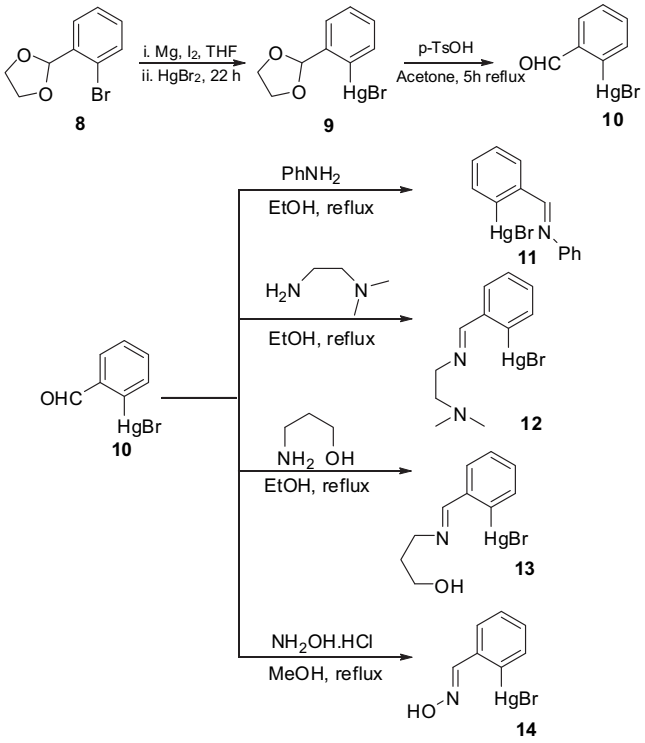
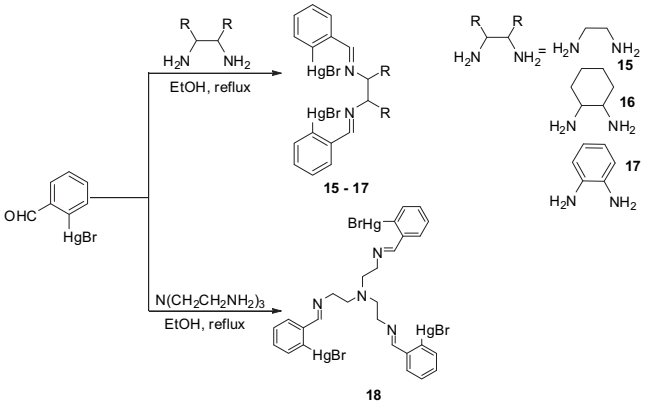


Fig. 1. Representative examples of *o*-mercurated halides.



Scheme 1. Synthesis of compounds **11**–**14**.

with various monoamines (Scheme 1). Similarly, refluxing **10** with diamines and triamine led to the formation of a series of bis- and tris-Lewis acidic Schiff bases (**15**–**18**) (Scheme 2). Except the bis-Lewis acid derivative **17**, which is yellow in colour, the other derivatives were obtained as off-white solids. The Schiff bases obtained are sparingly soluble in chloroform, acetone, DMSO and insoluble in alcohol. All the compounds are air- and moisture stable for weeks both in the solid state as well as in solution.



Scheme 2. Synthesis of compounds **15**–**18**.

2.2. Molecular structures of **10, 11, 12, 13, 17** and **18**

The molecular structure of **10** is depicted in Fig. 2a. Compound **10** crystallizes in $P2_1/c$ space group. The coordination geometry around mercury is T-shaped with C1—Hg—Br bond angle being 177.8(3)° (Table 1). The intramolecular Hg···O distance is 2.820(9) Å. This is close to the value 2.824(7) Å reported for the corresponding chloro- analog of **10** [25]. It is interesting to note that the Hg atom in **10** exhibits both intermolecular as well as intramolecular interactions with oxygen atom of the aldehydic group. The intermolecular Hg···O distance (2.943(9) Å) is shorter than the sum of the van der Waals radii of mercury (1.73—2.05 Å) [13,26,27] and oxygen (1.52 Å) [28]. This intermolecular interaction leads to expansion along the *c* axis to give a one dimensional wavy network of Hg—O bonds (Fig. 2b).

Compound **11** crystallizes in orthorhombic crystal system with $P2_12_12_1$ chiral space group (Fig. 3). The coordination geometry around Hg is T-shaped with C1—Hg—Br bond angle of 176.6(4)° (Table 1). The slight deviation of C1—Hg—Br bond angle from linearity can be attributed to the stronger secondary interaction of the imine nitrogen with mercury. The Hg···N distance of 2.685(12) Å is significantly less than sum of the van der Waals radii of mercury (1.73—2.05 Å) [13,26,27] and nitrogen (1.55 Å) [28], however, considerably longer than the sum of their covalent radii (2.03 Å) [29]. It is also worth noting that the Hg···N distance of 2.685(12) Å is shorter than that observed in [2-(dimethylaminomethyl)phenyl] mercury(II) chloride (2.764(6) Å) [15], and 2-chloromercuro-1-[(4-methoxyphenylimino)methyl] ferrocene (2.897(2) Å) [19].

In similar compounds, chirality has been observed due to mercury being a stereocentre where mercury is out of the plane of surrounding attached atoms [10]. However, for compound **11**, it is not the case and the mercury atom is coplanar with the atoms bonded to it. However, the phenyl ring bonded to N is not planar with the rest of the molecule and this conformation results in axial chirality. The phenyl ring bonded to N has a twist angle of 13.1° from the rest of the molecule. This twist is due to the a strong intramolecular coordination of the imine N to Hg. Due to this, the N atom is not in the plane with the N-phenyl ring of the molecule. The molecule has "P" chirality.

The molecular structure of compound **12** is shown in Fig. 4. It is interesting to note that compound **12** exists as dimer in the solid state that gives rise to a 10-membered macrocyclic structure. The mercury atoms in the macrocyclic structure are 4-coordinated and have a distorted tetrahedral geometry. The expected linearity of C—Hg—Br bond angle is lost and it has a value of 163.66(16)°. This deviation from linearity is highest in the series. This significant deviation from the linearity is due to coordination of the terminal nitrogen of one unit of the dimer with the mercury atom (N2···Hg# and N2#···Hg) of the other half of the dimer. Also it is noteworthy that the intermolecular Hg···N2# distance of (2.658(5) Å) is shorter than the intramolecular Hg···N1 distance of 2.776(6) Å in **12** (Table 2).