



Synthesis and characterization of cobalt complexes with pentafluorophenylhydrazine: Nucleophilic attack of phenolic oxygen to pentafluorophenyl ring during condensation of two Schiff base ligands

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ABSTRACT

A new dinuclear complex of Co(III), [Co(L¹)(μ-N₃)(N₃)₂] (1) and a mononuclear complex of Co(II) [Co(L²)₂(N₃)₂] (2) were synthesized and characterized by elemental analyses, spectroscopic methods and X-ray diffraction analyses [L² is (E)-2-(1-(2-(perfluorophenyl)hydrazono)ethyl)pyridine and HL¹ is a ligand which formed by condensation of two molecules of the other Schiff base ligand HL¹ = (E)-2-((2-(perfluorophenyl)hydrazono)methyl)phenol]. In complex 1 the final ligand HL¹ was formed via nucleophilic attack of the NH group in one hydrazone to the azomethine moiety in another hydrazone and the subsequent SNAr reaction of the phenolic oxygen to pentafluorophenyl nucleus giving rise to Ph–O–Ph structure.

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1. Introduction

The chemistry of hydrazine and hydrazone based ligands and their transition metal complexes is involving a broad research field such as coordination chemistry, analytical chemistry, biochemistry and catalysis [1]. These ligands create various environments similar to biological systems by coordinating through oxygen and nitrogen atoms. Therefore, they are target molecules for mimicking the behaviors of several biological systems [2]. It is well known that the –NH₂ group of hydrazines, R–NH–NH₂, has a high reactivity in the condensation reaction with carbonyl group [3]. Moreover, after formation of Schiff base, the intact –NH– moiety may be involved in the nucleophilic reactions [4]. For example, this part of hydrazone ligands is able to attack C=O and C=N groups [5] or may be involved in further Schiff base condensation [6].

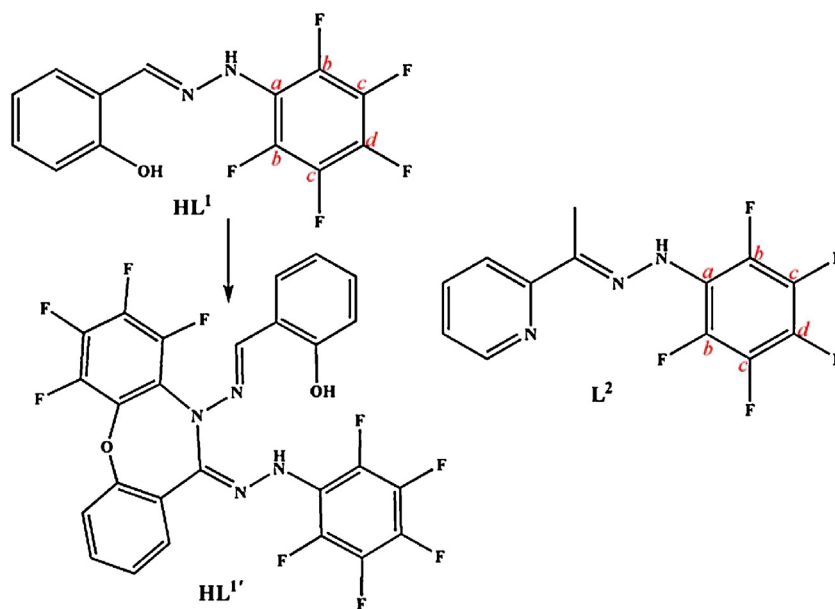
On the other hand, the synthesis of new compounds containing fluorine atom has become an important part of organic chemistry,

which may be attributed to the application of fluorine based materials in crystal engineering [7], biology [8] and material science [9]. Pentafluorobenzene derivatives, C₆F₅X, are highly reactive compounds toward nucleophilic attack. Various nucleophilic reagents (like ROH [10], RSH [11], and RNH₂ [12]) replace fluorine atom(s) in polyfluoroaromatic compounds.

Pentafluorophenylhydrazine (PFPH) is a ditopic compound: (i) it can act as a precursor for preparing hydrazine based ligands; (ii) due to the presence of pentafluorophenyl group, it is highly expected to be a suitable compound for study on reactions involving carbon-fluorine bond as the reaction site. PFPH has been successfully employed as reagent for determining low concentration of carbonyl compounds in the atmosphere [13] and drinking water [14]. Also, its derivatives have been used for the analysis of nabumetone and testosterone in human plasma [15]. Nevertheless, there is scarce study on coordination capability of PFPH derivatives and to the best of our knowledge, including search in the Cambridge Structural Database (CSD) [16], only three metal complexes with PFPH based ligands have been reported [17]. In this study, we report synthesis, characterization and crystal structures of two cobalt complexes of Schiff base ligands derived from PFPH (Scheme 1).

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Scheme 1. The structures of ligands used in this study.

2. Results and discussion

2.1. Syntheses of complexes and spectroscopy

The reaction of pentafluorophenylhydrazine with salicylaldehyde or 2-acetylpyridine in methanol gave the desired Schiff base ligands (HL^1 and L^2) with high yield and purity (Scheme 1). Elemental analyses and NMR spectra of ligands (Figs. S1 and S2) confirm their proposed structures. In 1H NMR spectrum of HL^1 the singlet peak at δ 8.34 ppm is due to azomethine ($CH=N$) hydrogen. In 1H NMR spectrum of L^2 the signal at δ 2.38 ppm is due to CH_3 group and the hydrogen of $N-H$ group is located at δ 9.04 ppm. For HL^1 , the peaks of $N-H$ and $O-H$ groups are located at δ 10.41 and 10.43 ppm, respectively. In both ligands four peaks between δ 7 and 8 ppm are due to aromatic hydrogen atoms. In ^{13}C NMR spectrum of ligands the signals of carbon atoms of pentafluorophenyl ring appear as seven multiplet peaks (due to $C-F$ coupling). In fact, six multiplet peaks are related to three types of carbon atoms directly connected to F atoms (see Figs. S1 and S2). The peaks of these three carbon atoms split to doublet peaks by $^1J_{CF} \approx 250$ Hz. The remaining multiplet peak (δ 121.4 ppm in HL^1 and δ 122.1 ppm in L^2) is related to carbon atom of pentafluorophenyl ring connected to $-NH-$ group (split by $^3J_{CF}$). Complexes $[Co(L^1)(\mu-N_3)(N_3)]_2$ (**1**) and $[Co(L^2)_2(N_3)_2]$ (**2**) were synthesized by the reaction of ligands, $CoSO_4 \cdot 7H_2O$ and NaN_3 with molar ratios of 1.0:1.0:2.0 in methanol. It was found that the structure of HL^1 is changed during the complexation and another ligand (L^1) is formed by coupling of two HL^1 ligands. Spectroscopic data confirm that the HL^1 is not formed by direct reaction of salicylaldehyde and pentafluorophenylhydrazine. In the IR spectrum of complex **1**, two very strong bands at 2067 and 2007 cm^{-1} are due to presence of two different EO-bridged and terminal azide ligands [18]. In complex **2** the stretching vibration of the azide group, $\nu(N_3)$, appears at 2064 cm^{-1} . The absorption bands at 1605 (**1**) and 1600 cm^{-1} (**2**), can be assigned to the imine $C=N$ stretching frequency of the coordinated ligands [19]. In both **1** and **2**, the broad peak at about 3400 cm^{-1} is due to $N-H$ group of coordinated ligands and indicates they are involved in hydrogen bonding [20].

2.2. X-ray structure of $[Co(L^1)(\mu-N_3)(N_3)]_2$ (**1**)

In order to define the coordination sphere conclusively, a single-crystal X-ray diffraction study was made. The crystal data and refinement parameters are presented in Table 1. The structure of complex **1** with atom numbering scheme is shown in Figs. 1 and S3 and selected bond lengths and angles are given in Table 2. The complex is centro-symmetric dimer lying in a special position, on an inversion center. Single crystal analysis indicates that the structure of the ligand coordinated to the Co(III) is quite different from the initially employed ligand. Probably, during the complexation, two molecules of Schiff base ligand (HL^1) were connected to each other resulting in another ligand (HL^1'). Although this reaction seems to be difficult, similar aggregate of hydrazine based ligand in the presence of manganese ion has been recently reported by Tang et al. [21]. Nucleophilic attack of NH group of $-NH-N=C$ moiety to $C=N$ group and formation of new $C=N$ bond (through nitrogen atom of $-NH-NC$ and azomethine carbon) has been earlier reported by Müller et al., too [22]. In the present study, during the complexation the $N-H$ moiety of one ligand attacks to the azomethine carbon atom of the second one, and consequently one H_2 molecule removes to form another $C=N$ group by this condensation (Scheme 2). During this reaction, the nucleophilic attack of phenolic oxygen of salicylidine group to the neighbored fluorine atom on pentafluorobenzene ring excretes fluoride anion and $Ph-O-Ph$ group together with seven-membered ring form (Fig. 2). The proposed mechanism of this reaction and formation of HL^1' is shown in Scheme 2.

In **1**, the environment of cobalt atom is a six-coordinated structure as a $CoON_5$ with oxygen and two nitrogen atoms provided by the Schiff base ligand, a nitrogen atom from terminal azide ligand and two nitrogen atoms from two $\mu_{1,1}$ -azide bridging groups. The overall geometry around cobalt(III) ion in complex **1** is best described as a distorted octahedral. Two cobalt(III) cations are linked by two end-on bridging azide groups giving rise to four-membered Co_2N_2 cyclic unit. In **1**, the Schiff base ligand forms equatorial plane together with the nitrogen atom from the inversion-related azide bridging ligand. The axial positions are occupied by the nitrogen atoms from two azide ligands: one terminal and one bridging N_3^- . Thus, each bridging azide is the

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