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## Molecular structure of mercury(II) thiocyanate complexes based on DFT calculations and experimental UV-electron spectroscopy and Raman studies



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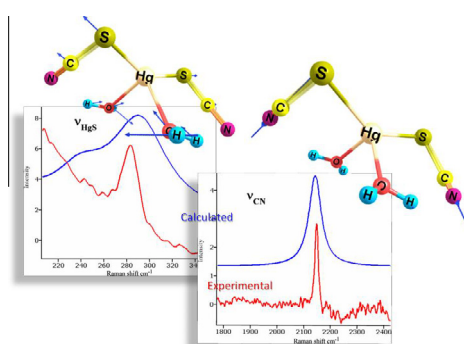
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### HIGHLIGHTS

- Raman and UV spectral studies of  $[\text{Hg}(\text{SCN})_n]^{2-n}$  complexes were performed.
- Vibrational frequencies and electronic spectra were calculated using DFT theory.
- The effect of solvation and  $\text{H}_2\text{O}/\text{D}_2\text{O}$  exchange on vibrational spectra was studied.
- Hg(II) was always four-coordinated with thiocyanate and (or) water ligands.

### GRAPHICAL ABSTRACT



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### ABSTRACT

In this work, we report a combined experimental and theoretical study on molecular structure, vibrational and electronic spectra of  $[\text{Hg}(\text{SCN})_n]^{2-n}$  complexes (where  $n = 2, 3, 4$ ) in the aqueous solution. Molecular modeling of the mercury(II) complexes were done by the density functional theory (DFT) method using B3LYP functional with Stuttgart relativistic ECP 78MWB basis set for Hg and 6-311++G(d,p) basis set for all other atoms. The effect of different solvation models with explicit (ligand) and/or implicit water environment upon its geometry, vibrational frequencies and UV spectrum have been studied. The influence of  $\text{H}_2\text{O}/\text{D}_2\text{O}$  exchange on the experimental and calculated vibrational frequencies of studied complexes has been established. The double-peak character of the  $\nu_{\text{Hg-S}}$  vibrational mode of the all analyzed mercury complexes and  $\nu_{\text{C=N}}$  mode of  $[\text{Hg}(\text{SCN})_3\text{H}_2\text{O}]^-$  complex, respectively, were proposed here for the first time. The formation of four-coordinated Hg(II) complexes with thiocyanate and (or) water ligands was verified.

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### Introduction

Mercury is one of the most important elements in the environment [1]. Mercury(II) compounds offer attractive properties in

terms of their potential applications in paper industry, paints, cosmetics, preservatives, thermometers, manometers, fluorescent lamps, and mercury batteries [2]. Mercury is capable to form complexes with many inorganic ligands and reagents [3]. A search in the Cambridge Structural Database shows 123 mercury(II) thiocyanate complexes and the most of these compounds are monomeric structures [2].

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Thiocyanate-containing metal complexes are considered to be the most investigated systems because of their diverse structures (linkage isomerism), applications in magnetic materials and luminescence properties [4]. In agreement with the HSAB (hard soft acid base) theory the  $\text{SCN}^-$  ion coordinates to hard acids (i.e.  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Na}^+$ ) through nitrogen atom, and the uncoordinated sulfur atom is involved in hydrogen bonds and sometimes involved in S–S interactions. If the transition metal center is soft acid (i.e.  $\text{Cd}^{2+}$ ,  $\text{Cu}^+$ ,  $\text{Hg}^{2+}$ ), then  $\text{SCN}^-$  ligand binds to central ion through sulfur atom. Different stretching modes of the thiocyanato ligand can generate various types of supramolecular structures with particular properties [5–8]. The geometry and coordination mode of  $\text{NCS}^-$  ion in 3d metal complexes is strongly influenced by the electronic and steric effects around the central ion [5]. However, the final bonding mode depends also on the metal charge, other coordinated ligands and steric effects [9]. Thiocyanato bridges play an important role in the magnetic exchange pathways between paramagnetic centers too [10]. Simultaneous presence of two different metal centers can potentially give rise to interesting physico-chemical properties and lead to attractive novel topologies and intriguing frameworks [11,12].

According to Schmidt et al. [13] powerful and sensitive analytical tools, which provide a wealth of information on the physical/structural and chemical composition of a sample without a priori knowledge, are vibrational spectroscopic techniques [13]. Dealing with the intrinsic view of molecule in the solution, it is well known that the spectroscopic and structure properties of molecules in solution are influenced by the solvation [14]. Since the first quantitative measurements were made, it has been clear that many types of solvent–solute interactions are possible in the solution. The onset of intramolecular interactions often leads to gross changes in band positions, intensity and shape, which can be explained in terms of changes in force constants, normal coordinates and electron redistribution due to the interaction [15,16]. However, because of extended vibrational coupling and the influence of ionization of ending groups, the interpretation of the vibrational spectrum is not straightforward, and in general cannot be accomplished without the high level of computational modeling [17].

In recent years, the density functional theory (DFT) has been favored as a tool for quantum chemistry because of its efficiency and accuracy with respect to the evaluation of a number of molecular properties and relative fastness in studying relatively large molecules [18–20]. During such quantum chemical calculations inclusion of both bulk effect and interaction with explicit water molecules improves the agreement with experimental results and is essential for the quantitative understanding of the solvent effects [21–24]. Kato et al. [25] found that the inclusion of explicit water molecules is a key factor for obtaining reliable computational results.

Mercury(II) complexes are of interest since they are widely found in the aqueous solutions employed for the determination of chloride ions in clinical and industrial laboratories [26] or obtained during mercury determination procedures using titrimetric analysis [27].

The quantum chemical studies of the mercury–thiocyanato complexes have been started in the last two decades. Fukushima et al. [7] reported the formation energies, geometry optimizations of the simple tetrahedral  $[\text{Hg}(\text{SCN})_4]^{2-}$  complex using only theoretical calculations. Šašić et al. [14,15] analyzed the influence of various solvents on Hg–S, C≡N and S–C vibrations of  $\text{Hg}(\text{SCN})_2$ ,  $[\text{Hg}(\text{SCN})_3]^-$ ,  $[\text{Hg}(\text{SCN})_4]^{2-}$  complexes using Raman analysis. Chillemi et al. [28] has tried to explain the structure and coordination of the pure hydrated Hg(II) complex in aqueous solution. Hofer et al. [29] also reported the results of the study of hydrated mercury(I)-dimer based on molecular dynamics. Additionally, Rosdahl et al. [30] performed the theoretical and vibrational spectroscopic study of the solvated mercury(I) dimer. The behavior of mercury

ions in some environments (i.e. biological, industrial) is not always clearly established at the molecular level. It is helpful to model the complexes and to determine how these ions may act *in vivo* with each other. It is well known that even slight geometrical distortions or slight modifications in complex structure can modify, enhance or inhibit their behavior and such knowledge is especially important. According to this, in this paper we present the molecular structures and the spectroscopic characterization of mercury(II) thiocyanate complexes in the aqueous media. The studies of the coordination features of  $[\text{Hg}(\text{SCN})_n]^{2-n}$  complexes (where  $n = 2, 3, 4$ ) using different solvation models are based on the comparison of the results of quantum chemical calculations and experimental Raman and UV spectra.

## Experiment

### Reagents

All chemicals were of analytical-reagent grade, purchased from Sigma Aldrich and used without further purification. Distilled water and heavy water were used throughout the present study as solvents. In order to avoid hydrolysis of standard  $\text{HgSO}_4$  solutions, both distilled water as well as heavy water was acidified with the least amount of concentrated sulfuric acid.

### Procedure

#### UV spectroscopic analysis

The solutions of  $[\text{Hg}(\text{SCN})_n]^{2-n}$  complexes with the metal(II)-ligand molar ratios of 1:2, 1:3 and 1:4, all in the level of  $10^{-4}$  M, were prepared by mixing the necessary volumes of the standard solutions of 0.02255 M  $\text{HgSO}_4$  and 0.1 M KSCN. Distilled water for the dilution of mixtures to a known volume was used. UV spectra of the samples were acquired on Lambda 35 UV spectrometer (PerkinElmer) using 2-mm quartz cuvette.

#### Raman spectroscopic analysis

The solutions of  $[\text{Hg}(\text{SCN})_3]^-$ ,  $[\text{Hg}(\text{SCN})_4]^{2-}$  complexes, both in the level of  $10^{-2}$  M, and solution of  $\text{Hg}(\text{SCN})_2$ , in the level of  $10^{-3}$  M, were prepared by mixing the necessary volumes of standard solutions of 0.02255 M  $\text{HgSO}_4$  and 0.5 M KSCN. Distilled water for the dilution of mixtures to a known volume was used.

For isotopic exchange analysis heavy water (deuterium oxide  $\text{D}_2\text{O}$ ) was used as a solvent for the preparation of  $\text{Hg}(\text{SCN})_2$ ,  $[\text{Hg}(\text{SCN})_3]^-$  and  $[\text{Hg}(\text{SCN})_4]^{2-}$  solutions, at the same concentration level.

Raman spectra were recorded using Echelle type spectrometer RamanFlex 400 (PerkinElmer, Inc.) equipped with thermoelectrically cooled ( $-50$  °C) CCD camera and fiber-optic cable for excitation and collection of the Raman spectra. The 785-nm beam of the diode laser was used as the excitation source. Spectra were collected with an integration time of 10 s. Each spectrum was recorded with accumulation of 30–50 scans, yielding total acquisition time of 300–500 s. The wavenumber axis was calibrated using the polystyrene standard (ASTM E 1840), yielding  $\pm 1$   $\text{cm}^{-1}$  absolute wavenumber accuracy for well defined narrow bands. Intensities were corrected by the NIST intensity standard (SRM 2241). The analysis of Raman spectra was made by subtracting the spectra of acidified distilled water and acidified heavy water from the spectra of each mixture of  $\text{Hg}^{2+}$  and  $\text{SCN}^-$  ions, respectively.

#### Quantum chemical calculations

All the calculations were performed using the Gaussian for Windows package version G03W [31]. The geometry optimization

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