

New metalorgano-chalcogenide compounds based on polymeric frameworks constructed by Se–Hg intermolecular interactions: Preparation, structural characterization, and Raman evaluation



Simone Finoto^a, Amilcar Machulek Junior^a, Anderson Rodrigues Lima Caires^a, Eduardo J. de Arruda^a, Gleison Antônio Casagrande^{a,*}, Cristiano Raminelli^b, L.H.C. Andrade^c, S.M. Lima^c

^aGrupo de Pesquisa em Síntese e Caracterização Molecular, Universidade Federal de Mato Grosso do Sul, Av. Senador Filinto Muller, 1555, Campo Grande, MS 79074-460, Brazil

^bDepartamento de Ciências Exatas e da Terra, Universidade Federal de São Paulo, Diadema, SP 09972-270, Brazil

^cUniversidade Estadual de Mato Grosso do Sul, Dourados, MS 79804-970, Brazil

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ABSTRACT

This study investigated the synthesis and structural characterization of two new polymeric frameworks based on metalorgano-chalcogenide materials. X-ray analyses revealed the frameworks of prepared compounds **1** and **2** to be polymeric chains achieved through Se–Hg intermolecular interactions. A detailed Raman evaluation of the compounds was performed, showing their synthetic precursors to constitute a safe and reproducible model for the assignment of the main vibrational modes of the molecules investigated. Complete characterization of **1** and **2** also included elemental analysis, IR spectroscopy, UV–Vis absorption data, and EDX analysis.

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1. Introduction

The preparation and characterization of molecules for use in technological applications has extensively contributed to the development of materials science [1]. Supramolecular arrangements [2,3], dimeric arrays [4,5], and noteworthy systems exhibiting hypervalent and charge-transfer properties [6,7] have been determined in solid state and are regarded as important structural features of derivatives of organo-chalcogenium halides (Se and Te). Nanosized materials based on II–VI metal chalcogenides are also receiving considerable attention because of their remarkable optical and luminescent properties [8–15] and possible applications to technological devices [16–20]. In this perspective, metalorganic chalcogenide chemistry plays an important role, providing strategies for the preparation of metal-chalcogenide nanoparticles, such as CdTe, HgTe, and ZnTe, from molecules that have structural metal–chalcogen bonds [21–24].

The application of organochalcogen materials containing II–VI and II–II'–VI central core units as single-source precursors to prepare binary and ternary nanomaterials with interesting optical properties has been described [25,26] in studies demonstrating the importance of this class of molecules for the controlled

preparation of nanocrystals within the 2–5 nm range, promoted by a hexadecylamine (HDA) solvent system. These experiments correlated with the hypothesis that metal-chalcogenide compounds act as “seeds” in the nucleation process involved in the preparation of nanomaterials. Fenske and co-workers have explained in detail the peculiarity of metal chalcogenide compounds—materials that exhibit properties on the border between molecules and materials [27]. Furthermore, chalcogenide clusters containing group-12 metals (Zn, Cd, Hg) in their structures can function as model compounds in spectroscopic studies of the corresponding nanoparticles (ME), since these clusters display a clear structural similarity with bulk materials. Finally, the use of chalcogenide clusters to prepare nanosized materials via lysothermal synthesis offers important advantages and higher synthetic control when compared with other methodologies not based on metal-organochalcogen clusters as precursors [25]. Progress in these investigations depends largely on the development of novel organochalcogen materials suitable for these purposes.

Motivated by the prospect of future application of these materials in the field of materials chemistry, our research group has investigated the synthesis and characterization of new metal-chalcogenide compounds that present interesting structural and spectroscopic features [28–30]. To contribute to the development of the metal-organochalcogen chemistry and expand the available literature, the present study reports the synthesis and structural

* Corresponding author. Tel.: +55 67 3445 3595.

E-mail address: gleisoncasag@gmail.com (G.A. Casagrande).

characterization, along with spectroscopic data and a detailed Raman analysis, of two novel metal-chalcogenide compounds based on polymeric frameworks constructed by Se–Hg intermolecular interactions.

2. Experimental

2.1. Chemicals and measurements

The starting materials – namely, $(\text{PhSe})_2$, $(4\text{-ClC}_6\text{H}_4\text{Se})_2$, and $(\text{PhSe})_2\text{Hg}$ – were prepared according to published methods [31,32]. Mercury(II) reactants, NaBH_4 , and solvents were obtained commercially (Aldrich or Sigma) and used without further purification. Elemental analyses (CHN) were performed using a Perkin–Elmer 2400 instrument. FT-IR spectra were acquired on a 4100 spectrophotometer (Jasco) using KBr pellets. The diffuse reflectance spectra of the samples were measured from pure solid using a Lambda 650 UV–Vis spectrophotometer (Perkin–Elmer). Raman measurements were carried out by exciting the samples under an Innova 308C Ar^+ laser (Coherent) at 514.5 nm. A confocal setup using lenses of 4 mm focal length was employed to focus the laser beam into the substrates and to detect SERS signals. Scattering light, filtered by an edge filter, was focused into an optical fiber coupled to an iHR 320 monochromator (Horiba Jobin Yvon), using a S3903-102Q PDA CCD (Sygnature Hamamatsu) for detection. All measurements were performed at room temperature. Melting points were determined using an Instruterm DF-3600 apparatus and employed uncorrected. EDX analyses were performed using a JSM-6380LV scanning electron microscopy (Jeol) equipped with a Noran System SIX energy-dispersive X-ray spectrometer (Thermo Scientific). X-ray data were collected using an Apex II CCD area detector diffractometer (Bruker) with graphite-monochromatized $\text{Mo K}\alpha$ radiation. The crystal structures of the compounds were solved by direct methods using *SHELXS* and refined with *SHELXL* [33]. All non-hydrogen atoms were localized from Fourier maps and refined with anisotropic displacement parameters. The hydrogen atoms were included at their theoretical ideal positions and treated with the “riding model” approximation, with $\text{C–H} = 0.93 \text{ \AA}$ (aryl) as an option in *SHELXL*. More detailed information on the structure determinations is given in Table S1.

2.2. Preparation of compounds 1 and 2

Polymeric compounds **1** and **2** were synthesized by modifying a published method [28].

2.2.1. Synthesis of $[(\text{PhSe})_7\text{Hg}_4(\text{SCN})\text{Py}]_n$ (**1**)

To a solution of 0.1794 g (0.35 mmol) of $(\text{PhSe})_2\text{Hg}$ in methanol:tetrahydrofuran (10 mL, 1:1), 0.0158 g (0.05 mmol) of $\text{Hg}(\text{SCN})_2$ was added. After 15 min, 2 mL of pyridine was added, followed by stirring at room temperature for 1 h. The resulting pale yellow solution was filtered into a 25 mL beaker and subjected to slow evaporation of the volatile solvents for one day, yielding yellow needles suitable for X-ray analysis. Properties: Yellow, air-stable crystalline substance; $\text{C}_{48}\text{H}_{40}\text{Hg}_4\text{N}_2\text{SSe}_7$ (FW. 2031.96). Yield: 0.0850 g of crystals (42%) based on the $(\text{PhSe})_2\text{Hg}$ used. M.p. 138–140 °C. Elemental analysis: Calc. (%): C, 28.35; H, 1.96; N, 1.37. Found: C, 27.81; H, 1.91; N, 1.31%. IR (KBr, ν/cm^{-1}) 3047 ($\nu_{\text{S–C–H}_{\text{arom.}}}$), 2105 ($\nu_{\text{S–C=N}}$), 1573, 1472, 1434 ($\nu_{\text{S=C}}$ and $\nu_{\text{S–C=N}}$), 1064, 1018 ($\delta_{\text{S–C–H}_{\text{arom.}}}$), 732, 686 ($\delta_{\text{S–C–H}_{\text{arom.}}}$ out-of-plane) [34,35]. EDX analysis: found (%): Hg (60.65), Se (39.35); structural analysis from X-ray data: Hg (57.80), Se (39.8).

2.2.2. Synthesis of $[(4\text{-ClC}_6\text{H}_4\text{Se})_2\text{Hg}]_n$ (**2**)

To a solution of $(4\text{-ClC}_6\text{H}_4\text{Se})_2$ (0.3820 g; 1.0 mmol) in methanol and chloroform (12 mL, 1:1), NaBH_4 (0.7562 g; 2.0 mmol) was

added until the solution became colorless. This was followed by dropwise addition of a solution of HgCl_2 (0.2715 g; 1.0 mmol) in methanol and H_2O (5 mL, 1.0:0.2). The resulting solution was stirred at room temperature for 1 h. The yellow solid obtained by filtration and was washed three times with ethanol, dried in a desiccator, and recrystallized in a tetrahydrofuran:methanol:pyridine solvent system (15 mL, 1:1:1), yielding yellow needles suitable for X-ray analysis. Properties: Yellow, air-stable crystalline substance; $\text{C}_{12}\text{H}_8\text{Cl}_2\text{HgSe}_2$ (FW. 581.59). Yield: 0.4950 g (85%) based on the $(4\text{-ClC}_6\text{H}_4\text{Se})_2$ used. M.p. 218–220 °C. Elemental analysis: Calc. (%): C, 24.78; H, 1.38. Found: C, 24.61; H, 1.31%. IR (KBr, ν/cm^{-1}) 3077 ($\nu_{\text{S–C–H}_{\text{arom.}}}$), 1558, 1384 ($\nu_{\text{S=C}}$), 1095, 1010 ($\delta_{\text{S–C–H}_{\text{arom.}}}$), 813 ($\delta_{\text{S–C–H}_{\text{arom.}}}$ out-of-plane), [34,35]. EDX analysis: found (%): Hg (52.68), Se (35.99); structural analysis from X-ray data: Hg (46.70), Se (36.70).

3. Results and discussion

3.1. Crystal structures of prepared compounds 1 and 2

In the past 10 years, a substantial expansion occurred in the literature on the synthesis of new metal-organochalcogen compounds, stimulated by the remarkable structural and optical features of this family of compounds, particularly in the solid state. However, few articles have reported the synthesis and structural characterization of metal-organochalcogen compounds based on polymeric structures constructed by Hg–Se intermolecular interactions [28,29,36,37]. The compounds described in the present study are representative examples of novel metal-organoselenium polymeric frameworks. X-ray measurements, selected bond distances, and bond angles are shown in Tables 1 and 2 (Supplementary information). Fig. 1 shows the discrete molecular structure of **1**.

The discrete molecular unit of **1** has an adamantanoid-like organization composed of six bridges of the $[\mu_2\text{-(Se)Ph}]^-$ type between the selenium atoms in the phenylselenolate anion and Hg(II) atoms. A pyridine molecule and a thiocyanate moiety complete the structure, which has neutral charge. Fig. 2 shows the polymeric organization achieved through an intermolecular bond – Hg2–Se1(#1), of 2.6934(13) Å – that connects the adamantanoid cages along the *c* crystallographic axis. Furthermore, Table 2 (Supplementary information) shows that the internal Se–Hg bond lengths of the adamantanoid units range from 2.5486(13) Å, for Se7–Hg4, to 2.7313(13) Å, for Se7–Hg2. Based on the models proposed by Addison [38] and Houser [39] to predict the coordination geometry involved in four- and five-coordinate systems, we

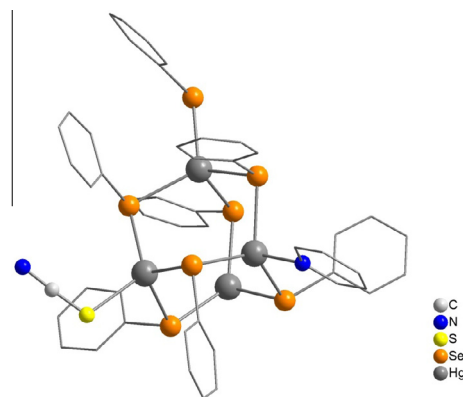


Fig. 1. Molecular structure of **1**. The adamantanoid organization of the structure has been achieved through phenylselenolate bridges of the $[\mu_2\text{-(Se)Ph}]^-$ type involving different Hg–Se bonds ranging from 2.7313(13) Å to 2.5486(13) Å. Hydrogen atoms have been omitted for clarity.

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