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A facile preparation of two new isostructural metal–organochalcogen clusters from simple starting materials: Sonochemical synthesis, X-ray structures and spectroscopic remarks

Maisy I.P.R. Modesto [a], Simone Finoto [a], Gleison Antônio Casagrande [a,*], Cristiano Raminelli [b], Ernesto Schulz Lang [c], Davi F. Back [c], Samuel Leite Oliveira [d], Marco Antônio U. Martines [d]

[a] Laboratório de Síntese e Caracterização Molecular, Universidade Federal da Grande Dourados, Rod. Dourados/Itahum, Km 12, 79.804-970 Dourados, MS, Brazil
[b] Departamento de Química, Universidade Federal de São Paulo, Campus Diadema, 09972-270 Diadema, SP, Brazil
[c] Departamento de Química, Universidade Federal de Santa Maria, 97.105-900 Santa Maria, RS, Brazil
[d] Grupo de Óptica e Fotônica, Universidade Federal de Mato Grosso do Sul, CP 549, 79070-900 Campo Grande, MS, Brazil

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ABSTRACT

In this work, the formation and characterisation of two new isostructural metal–organochalcogen clusters from simple starting materials was investigated. A sonochemical synthesis was performed in a one-pot procedure without the isolation of synthetic intermediates. This methodology offers a new approach to prepare cluster compounds, and this experiment led to the formation of $[(PhTe)_{12}Hg_8(S)X_2(Py)_2]\cdot Py$ (X = Br, I; Py = Pyridine) in good yield. The X-ray analyses reveal that the framework of the clusters contains a similar $[Hg_8(\mu_4\text{-}S)Te_{12}]$ core as the central unit. The sulphur atom present in the core of both structures has a tetrahedral coordination geometry achieved by four S–Hg(II) bonds. The complete characterisation of the synthesised materials also includes elemental analyses, IR spectroscopy and UV–Vis absorption data.

1. Introduction

Currently, development of the field of materials science and the search for new molecules to use in technologic applications are of great interest [1]. Investigations into the structural features of the derivatives of chalcogenium halides (Se and Te) in the solid state have revealed the involvement of these species in supramolecular arrangements [2,3], dimeric arrays [4,5] and interesting systems containing hypervalent and charge-transfer properties [6,7]. Nanomaterials based on II–VI metal chalcogenide are receiving considerable attention because of their remarkable optical and luminescent properties [8–15] and their possible applications in electronic devices, such as light-emitting devices, solar cells, lasers, printing of integrated circuits, biological detection devices and so forth [16–20]. From this perspective, the metalorganic chalcogenide chemistry plays an important role; for example, this chemistry offers interesting strategies for the preparation of metal–chalcogenide nanoparticles, such as CdTe, HgTe and ZnTe, from molecules that contain metal–chalcogen bonds in their structures [21–24]. The application of organochalcogen clusters containing II–VI and II–II′–VI central core units as single-source precursors to prepare binary and ternary nanomaterials with interesting optical properties was described previously in the literature [25,26]. These studies have demonstrated the importance of this class of molecules to controlled preparation of nanocrystals within the 2–5 nm range, promoted by a hexadecylamine (HDA) solvent system. These experiments are correlated with the hypothesis where the core units of the clusters act as a "seed" in the nucleation process involved in the preparation of the nanomaterials of interest. Fenske and co-workers have explained the present day importance of metal chalcogenide clusters; these compounds have been suggested to contain 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 corresponding nanoparticles (ME) once they displays a clear structural relationship to the bulk materials. Finally, the use of chalcogenide clusters to prepare nanosized materials via lyothermal synthesis offers major advantages and synthetic control when compared to other methodologies that do not use metal–organochalcogen clusters as precursors [25]. The progress of these investigations depends largely on the development of new organochalcogen materials suitable for these purposes. In this context, our research group, motivated by the future applications of these materials in the field of materials chemistry, has investigated the synthesis and characterisation of new clusters that present interesting structural and spectroscopic

* Corresponding author. Tel.: +55 67 3410 2091; fax: +55 67 3410 2072.
E-mail address: gleisoncasag@gmail.com (G.A. Casagrande).

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features [28–30]. To enrich the literature and to contribute to the development of the chemistry of metal–organochalcogen clusters derivatives, we present in this work the sonochemical synthesis, structural characterisation and spectroscopic remarks of two new isostructural organochalcogen clusters $[(PhTe)_{12}Hg_8(S)X_2(Py)_2]\cdot Py$ (X = Br, I; Py = Pyridine) containing $[Hg_8(\mu_4\text{-}S)Te_{12}]$ cores as central units.

2. Experimental

2.1. Chemicals and measurements

The starting materials (PhTeTePh and $(PhTe)_2Hg$) were prepared according to methods reported in the literature [31,32]. The mercury(II) halides and solvents were obtained commercially (Aldrich® or Sigma®) and used without further purification. The reactions were performed with a microtip probe connected to a 500 W Sonics Vibra-cell ultrasonic processor operating at 20 kHz at 20% of the maximum power output. Elemental analyses (CHN) were performed using a Perkin-Elmer 2400 analyser. FT-IR spectra were acquired on a JASCO-4100 spectrophotometer using KBr pellets, and the solution UV–Vis absorption spectra were acquired on a Cary 50 UV–Vis spectrophotometer using quartz cuvettes. The diffuse reflectance spectra of the samples were measured using a spectrometer (USB4000, Ocean Optics). A pulsed xenon lamp (PX-2, Ocean Optics) was used as the irradiation source. Samples were diluted in anhydrous KBr, and MgO powder was used as a reference (100% reflectance). All measurements were performed at room temperature. Melting points were determined using an Instruterm DF-3600 apparatus and are uncorrected. EDX analyses were performed using a scanning electron microscopy (JEOL JSM-6380LV) equipped with a Thermo Scientific Noran System SIX energy dispersive X-ray spectrometer. The X-ray data were collected using a Bruker APEX II CCD area-detector diffractometer with graphite-monochromatised Mo Kα radiation. The crystal structures of the clusters were solved by direct methods using the SHELX package [33]. All non-hydrogen atoms were refined with anisotropic displacement parameters, and the hydrogen atoms were included at their theoretical ideal positions. More detailed information about the structure determinations is given in Table 1.

2.2. Preparation of the clusters

The clusters were synthesised by sonication of the reaction media exploring a one-pot procedure in accordance with Scheme 1, proposed below:

Cluster **1**: In a 25 ml beaker, 0.1830 g (0,3 mmol) $(PhTe)_2Hg$ + 0.0360 g (0.1 mmol) $HgBr_2$ + 0.0040 g (0.05 mmol) thiourea were mixed. Afterwards, 6 ml DMSO + 6 ml methanol + 3 ml pyridine were added, and the solution was sonicated by an ultrasonic probe with a frequency of 20 kHz at room temperature for 5 min. The obtained solution was filtered, and after one day, prismatic yellow crystals were isolated from the solution. The same procedure was applied to prepare Cluster **2**. Cluster **1**: $C_{87}H_{75}Br_2Hg_8N_3S_1Te_{12}$ (Yield: 0.186 g (78%) based on the $(PhTe)_2Hg$ used; crystals decompose at 151–153 °C; *Anal.* Calc.: C, 23.27; H, 1.68; N, 0.94. Found: C, 22.85; H, 1.63; N, 0.89%; IR (KBr, ν/cm^{-1}) 3047 (ν_S-C–$H_{arom.}$), 1571, 1468, 1425 (ν_S-C=C and ν_S-C=N), 726, 685 (δ_s-C–$H_{arom.}$ out-of-plane) [34,35]; EDX found (%) Hg, Te, S, Br = 48.55, 45.95, 1.14, 4.36; structural analysis from X-ray data Hg, Te, S, Br = 48.22, 46.01, 0.96, 4.80; Cluster **2**: $C_{87}H_{75}Hg_8I_2N_3STe_{12}$ (Yield: 0.178 g (72%) based on the $(PhTe)_2Hg$ used; crystals decompose at 148–150 °C; *Anal.* Calc.: C, 22.79; H, 1.65; N, 0.92; Found: C, 22.63; H, 1.60; N, 0.88; IR (KBr, ν/cm^{-1}) 3042 (ν_S-C–$H_{arom.}$), 1567, 1469, 1431 (ν_S-C=C and ν_S-C=N), 726, 686 (δ_s-C–$H_{arom.}$ out-of-plane). EDX found (%) Hg, Te, S, I = 46.46, 45.45, 1.17, 6.92; structural analysis from X-ray data Hg, Te, S, I = 46.89, 44.74, 0.94, 7.40.

3. Results and discussion

3.1. Synthetic considerations

The preparative chemistry of binary and ternary metal–organochalcogen clusters is a subject that has attracted the attention of some research groups due to the remarkable structural and spectroscopic features that these molecules present in the solid

Table 1
Crystal data and structure refinement for the clusters.

	Cluster **1**	Cluster **2**
Empirical formula	$C_{87}H_{75}Br_2Hg_8N_3STe_{12}$	$C_{87}H_{75}Hg_8I_2N_3STe_{12}$
Formula weight	4490.30	4584.28
T (K)	293(2)	293(2)
Radiation; λ (Å)	Mo Kα; 0.71073	Mo Kα; 0.71073
Crystal system	monoclinic ($P2_1/c$)	monoclinic ($P2_1/c$)
Unit cell dimensions		
a (Å)	29.5202(2)	30.0591(15)
b (Å)	13.95040(10)	13.9742(6)
c (Å)	27.2233(2)	27.4368(13)
β (°)	112.128(10)	113.487(2)
V (Å^3)	10385.30(13)	10570.0(9)
Z/D_{calc} (g cm^{-3})	4/2.872	4/2.881
Absorption coefficient (mm^{-1})	15.913	15.463
F(000)	7872	8016
Crystal size (mm)	0.10 × 0.10 × 0.10	0.11 × 0.09 × 0.10
Range for data collection θ (°)	1.49–27.15	1.48–26.08
Index ranges	$-37 \leqslant h \leqslant 37$, $-17 \leqslant k \leqslant 17$, $-34 \leqslant l \leqslant 34$	$-11 \leqslant h \leqslant 11$, $-17 \leqslant k \leqslant 17$, $-31 \leqslant l \leqslant 33$
Reflections collected	94293	48138
Reflections unique	22965	8710
Completeness to θ maximum (%)	99.8	99.7
Absorption correction	Semi-empirical	Semi-empirical
Maximum and minimum transmission	0.2991 and 0.1618	0.4616 and 0.3361
Data/restraints/parameters	22965/0/905	8710/0/389
Goodness-of-fit (GOF) on F^2	1.100	1.076
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0488, wR_2 = 0.0795	R_1 = 0.0583, wR_2 = 0.1094
R indices (all data)	R_1 = 0.0889, wR_2 = 0.0885	R_1 = 0.1345, wR_2 = 0.1287
Largest difference in peak and hole (e Å^{-3})	2.161 and −0.915	1.009 and −0.856