

Synthesis and solid state characterization of two insoluble tetrathiometalates

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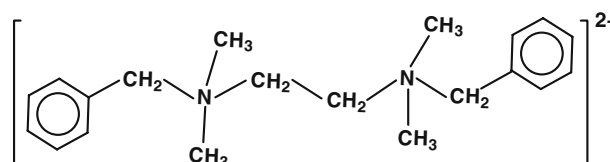
Abstract

The aqueous reaction of ammonium tetrathiometalates $(\text{NH}_4)_2[\text{MS}_4]$ ($\text{M} = \text{Mo}$ or W) with $(\text{dbtmen})\text{Br}_2 \cdot 2\text{H}_2\text{O}$ ($\text{dbtmen} = N,N'$ -dibenzyl- N,N,N',N' -tetramethylethylenediammonium dication) results in the formation of the highly insoluble compounds $(\text{dbtmen})[\text{MoS}_4]$ (1) and $(\text{dbtmen})[\text{WS}_4]$ (2) in near quantitative yields. Compounds (1) and (2) have been characterized by elemental analysis, spectroscopic methods, X-ray powder diffraction and TG–DTA. Both compounds exhibit nearly identical IR spectra and X-ray powder patterns. The compounds exhibit a single strong signal for the asymmetric M–S stretching vibration at 475 cm^{-1} in (1) and at 457 cm^{-1} in (2). Complex (2) is thermally more stable than the corresponding Mo analogue (1). Thermal decomposition products of (1) and (2) are carbon contaminated amorphous metal disulfides and are formulated as $\text{MoS}_{1.99}\text{C}_{2.06}\text{N}_{0.07}$ and $\text{WS}_{1.75}\text{C}_{3.02}$ based on elemental analysis of the residue.

Introduction

The chemistry of soluble metal sulfide complexes [1–3] is an area of frontier research in view of the use of metal sulfide materials in hydrodesulfurization catalysis (HDS) [4], and the importance of layered metal disulfides for the preparation of nanomaterials [5]. The use of metal sulfides in biological and industrial catalysis indicates that this area holds potential for continued theoretical and practical applications. Both MoS_2 or WS_2 can be directly synthesized from the elements at elevated temperatures, while the synthesis of MoS_2 by a metathesis reaction of MoCl_5 with Na_2S [6] or by the oxidative decarbonylation of $\text{Mo}(\text{CO})_6$ in the presence of H_2S has been reported [7]. The reported synthesis of MoS_2 by reacting $(\text{NH}_4)_2[\text{MoS}_4]$ with hydroxylamine [8], hydrazine [9], or more recently by the ultrasonic spray pyrolysis (USP) of aqueous $(\text{NH}_4)_2[\text{MoS}_4]$ on a silica template followed by thermal decomposition [4] is an important reason for the renewed interest in the chemistry of tetrathiomolybdates. The direct pyrolysis of bis(cetyltrimethylammonium)tetrathiotungstate has been shown to lead to the formation of bulk quantities of uniform WS_2 nanotubules [10], indicating the importance of organic ammonium salts in materials applications. Recently we have shown that tetraalkylammonium tetrathiomolybdates are useful precursors for the preparation of MoS_2 containing considerable amounts of C, with the C originating from the organic cation [11].

As part of an ongoing research programme aimed at the development of metal chalcogenide materials, we have investigated the synthesis and structural chemistry of several organic ammonium tetrathiometalates [12–25]. The structural studies are aimed at understanding the importance of weak N–H \cdots S interactions between the organic cation and the $[\text{MS}_4]^{2-}$ anions [18, 19]. It is to be noted that S \cdots H interactions are important in biology [26] but are not very well understood and hence addressed in recent theoretical investigations [27]. In our earlier work we have shown that the number and strength of N–H \cdots S bonds in organic ammonium tetrathiometalates affects the M–S bond distances. A similar observation has been reported by the Siemeling group in their recent work on piperidinium thiotungstates [28]. During the course of our structural investigations we were seeking organic ammonium tetrathiometalates, which do not exhibit H-bonding between the cation and anion as model compounds, for a comparative structural study. The tetrathiometalates $(\text{dbtmen})[\text{MoS}_4]$ (1) and $(\text{dbtmen})[\text{WS}_4]$ (2) ($\text{dbtmen} = N,N'$ -dibenzyl- N,N,N',N' -tetramethylethylenediammonium dication; Scheme 1)



Scheme 1.

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contain fully alkylated organic dications and hence cannot exhibit H-bonding interactions between the cation and anion. The synthesis and solid state characterization of (1) and (2) are described in this report. The high insolubility of (1) and (2) in several solvents precluded the preparation of crystals suitable for structure determination. However the thermal decomposition of (1) or (2) in an inert atmosphere results in the formation of carbon contaminated amorphous group VI metal disulfides, and the results of these investigations are described herein.

Experimental

Materials and methods

All the chemicals used in this study were of reagent grade and were used as received. $(\text{NH}_4)_2[\text{MS}_4]$ ($\text{M} = \text{Mo}$ or W) [29] and $(\text{dbtmen})\text{Br}_2 \cdot 2\text{H}_2\text{O}$ [30] were prepared by literature methods. The details of the instrumentation used in this work were the same as described in our earlier reports [16, 17].

Preparation of $(\text{dbtmen})[\text{MoS}_4]$ (1) and $(\text{dbtmen})[\text{WS}_4]$ (2)

An aqueous solution of $(\text{dbtmen})\text{Br}_2 \cdot 2\text{H}_2\text{O}$ (494 mg, 1 mmol) in H_2O (20 cm^3) was added to an aqueous solution (20 cm^3) of freshly prepared $(\text{NH}_4)_2[\text{MoS}_4]$ (260 mg, 1 mmol). This resulted in the immediate precipitation of the highly insoluble orange-red microcrystalline complex $(\text{dbtmen})[\text{MoS}_4]$ (1). The product was left undisturbed in the reaction mixture for *ca.* 1 h and then filtered off, washed with copious amounts of H_2O followed by isopropyl alcohol (15 cm^3) and Et_2O (20 cm^3), and then dried in air. Yield: 515 mg (98% based on Mo). The use of $(\text{NH}_4)_2[\text{WS}_4]$ (348 mg, 1 mmol) instead of $(\text{NH}_4)_2[\text{MoS}_4]$ in the above reaction resulted in the formation of the highly insoluble yellow complex $(\text{dbtmen})[\text{WS}_4]$ (2) in near quantitative yields. Found: C, 45.1; H, 5.6; N, 5.3; S, 23.3%. $\text{C}_{20}\text{H}_{30}\text{N}_2\text{MoS}_4$ calcd.: C, 45.95; H, 5.8; N, 5.4; S, 24.5%. IR data: 2982 (m), 1458 (s), 1216 (m), 1155 (m), 997 (m), 865 (s), 787 (s), 730 (s), 475 (s) (ν_3) cm^{-1} ; Raman data: 483 (m) (ν_3), 468 (m) (ν_3), 454 (s) (ν_1), 183 (m) (ν_4), 174 (m), 169 (m), 111 (m) cm^{-1} . Solid state u.v.-vis. data (in BaSO_4): 244, 321, 474 nm. Found: C, 38.5; H, 4.8; N, 4.5; S, 19.5%. $\text{C}_{20}\text{H}_{30}\text{N}_2\text{WS}_4$ calcd.: C, 39.3; H, 5.0; N, 4.6; S, 21.0%. IR data: 2984 (m), 1445 (s), 1355 (m), 1217 (s), 1155 (m), 997 (s), 864 (s), 786 (s), 730 (s), 706 (m), 619 (m), 584 (m), 457 (s) (ν_3); Raman data: 484 (w), 479 (s) (ν_1), 469 (m), 453 (m) (ν_3), 180 (s) (ν_4), 171 (s), 110 (m) cm^{-1} ; Solid state u.v.-vis. data (in BaSO_4): 283, 399 nm.

Results and discussion

Synthetic aspects

In earlier work we reacted organic amines with $(\text{NH}_4)_2[\text{MS}_4]$, leading to the formation of the less soluble organic ammonium tetrathiometalates [12–19]. Our synthetic strategy was based on the previously reported metathesis of $(\text{NEt}_4)\text{Cl}$ with $(\text{NH}_4)_2[\text{MS}_4]$ in acetonitrile [31] or the aqueous reaction of $(\text{NEt}_4)\text{OH}$ with $(\text{NH}_4)_2[\text{MS}_4]$, for the preparation of the tetraethylammonium salts [29]. For the synthesis of (1) and (2), $(\text{dbtmen})\text{Br}_2 \cdot 2\text{H}_2\text{O}$ [30] was used as the organic source. The reaction of $(\text{dbtmen})\text{Br}_2 \cdot 2\text{H}_2\text{O}$ with $(\text{NH}_4)_2[\text{MS}_4]$ ($\text{M} = \text{Mo}$ or W) instantaneously afforded the highly insoluble complexes $(\text{dbtmen})[\text{MoS}_4]$ (1) and $(\text{dbtmen})[\text{WS}_4]$ (2). The use of the analogous organic dichloride trihydrate (B.R. Srinivasan, submitted for publication) in the above reaction also leads to the formation of (1) and (2), indicating their facile formation. Alonso and coworkers have developed a synthetic methodology which involves the reaction of a quaternary ammonium halide and sodium hydroxide with $(\text{NH}_4)_2[\text{MS}_4]$ for the preparation of tetraalkylammonium MS_4 compounds [32]. It is interesting to note that the formation of (1) or (2) can be achieved without using NaOH and this can be attributed to the highly insoluble nature of the products. Increasing the pH of the reaction medium by adding NaOH does not have any effect on the formation of both complexes; however, under acidic conditions (1) and (2) are not stable and undergo decomposition as evidenced by color changes and the formation of black insoluble sulfides on acidification of the reaction mixture. Unlike the organic ammonium tetrathiometalates reported by us earlier, which dissolve in aqueous bases like ammonia or NaOH, DMF, DMSO, compounds (1) and (2) do not dissolve in any aqueous bases or organic solvent. Hence, they could not be recrystallized to give suitable crystals for a single crystal X-ray study. Our attempts to prepare single crystals of (1) or (2) by further diluting the initial reagent solutions were not successful. However the crystalline nature of both compounds can be readily evidenced from their X-ray powder patterns (Figure 1). Both compounds exhibit sharp reflections and the two diffractograms are nearly identical, indicating the isostructural nature of the two compounds. In addition, the large number of reflections as well as their positions indicates a low crystal symmetry. This observation is in accordance with our earlier structural work, where we observed that a pair of $[\text{MS}_4]^{2-}$ compounds linked to the same organic cation are generally isostructural [12–21]. Based on elemental analyses, the orange-red complex $(\text{dbtmen})[\text{MoS}_4]$ (1) and the yellow complex $(\text{dbtmen})[\text{WS}_4]$ (2) are formulated as $\text{C}_{20}\text{H}_{30}\text{N}_2\text{MoS}_4$ and $\text{C}_{20}\text{H}_{30}\text{N}_2\text{WS}_4$, respectively.

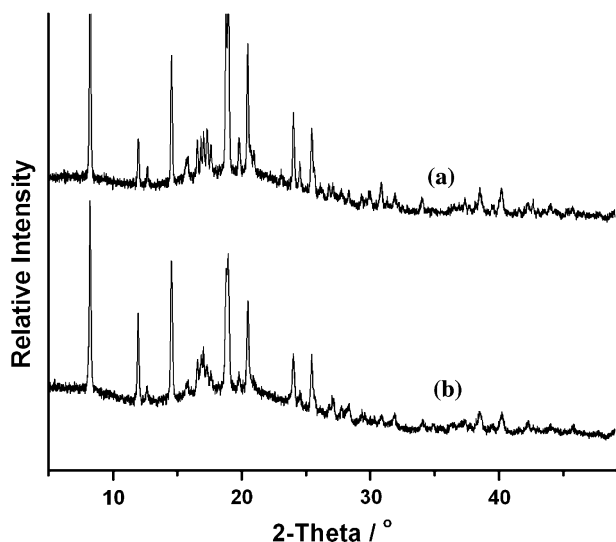


Fig. 1. X-ray powder diffractograms of (a) (dbtmen)[MoS₄] (1) and (b) (dbtmen)[WS₄] (2).

Spectral and thermal studies

The optical and vibrational spectra are quite useful to confirm the presence of both the [MS₄]²⁻ chromophore and the organic (dbtmen)²⁺ cation in (1) and (2). The solid state electronic spectra exhibit absorption maxima at 244, 321 and 474 nm [compound (1)] and at 283 and 399 nm [compound (2)], characteristic of the [MS₄]²⁻ moiety and readily assigned to the charge transfer transitions of the tetrahedral [MS₄]²⁻ chromophores [1]. The infrared spectra of (dbtmen)Br₂·2H₂O and of (1) and (2) exhibit several intense signals in the mid IR region, which can be assigned to the organic cation (dbtmen)²⁺. The IR spectra of (1) and its corresponding W analogue (2) are identical except that the signal below 500 cm⁻¹ in the tetrathiotungstate (2) is shifted to lower energies, in accordance with earlier reports [1, 33]. No intense signals below 500 cm⁻¹ are observed in the IR spectrum of the salt (dbtmen)Br₂·2H₂O, indicating that the low energy signals are due to the vibrations of the [MS₄]²⁻ units in (1) and (2). For the free tetrahedral [MS₄]²⁻ anion, four characteristic bands ν_1 (A₁), ν_2 (E), ν_3 (F₂), and ν_4 (F₂) are expected [33]. All the four bands are Raman active while ν_3 and ν_4 are IR active. In our earlier work we have shown that the strength and number of N-H...S interactions between an organic cation and the [MS₄]²⁻ anion can affect the MS₄ tetrahedron by elongating one or two of the M-S bonds and such distortions show up in the IR spectra in the form of extra signals, as observed for (pipH₂)[MS₄] (M = Mo or W; pip = piperazine) [16, 17] and (N-Me-enH₂)[WS₄] (N-Me-en = N-methylethylenediamine) [18]. However in (1) and (2), both N atoms of the cation (dbtmen)²⁺ are fully alkylated and hence there is no possibility of H-bonding interactions between the cation and anion. In accordance with this, compound (1) exhibits a single sharp signal at 475 cm⁻¹ while in (2) a strong

signal is observed at around 457 cm⁻¹, which can be assigned to the asymmetric stretching vibration (ν_3) of the M-S bond. The assignment of this signal to ν_3 gains credence from the Raman spectra, which show a weak signal for this vibration compared to an intense signal for the symmetric stretching vibration ν_1 , (Figures 2 and 3). The degenerate (ν_2 and ν_4) signals are observed in the Raman spectra around 180 cm⁻¹. The profile of the ν_3 signal in (1) and (2) indicates that the MS₄ tetrahedron is relatively less distorted compared to (pipH₂)[MS₄] [16, 17]. We are aware that this aspect of distortion can only be unambiguously verified from single crystal X-ray data and efforts are underway in our laboratories to prepare single crystals of (1) and (2) by the solvothermal route, another method which has also been used by us for the synthesis of several phase pure tetrathiometalates [34-40].

Thermal investigations were carried out in Ar atmosphere to understand the decomposition behavior of (1) and (2) and the composition of the final sulfide residues. The resulting TG-DTA curves are presented in Figures 4 and 5, respectively, and the thermal data of compounds (1) and (2) are presented in Table 1. On heating, compound (1) starts decomposing at around 140 °C, evidenced by a rapid mass drop in the TG curve. This process is accompanied by two closely related endothermic events at about 170 and 209 °C (Figure 4) and these events could not be resolved. The second endothermic peak is broader than the first, indicating a more complex thermal reaction. The peak temperature (T_{p1}) for (1) of 170 °C is in the range reported for tetrathiomolybdates containing fully alkylated ammonium cations [11, 41] like tetraheptylammonium (T_{p1} = 150°C), tetraoctylammonium (T_{p1} = 150°C), tetrapentylammonium (T_{p1} = 130°C), tetrahexylammonium (T_{p1} = 150°C) [42]. The small difference can be attributed to the differing cations. It is to be noted that (1) contains a dication (dbtmen)²⁺ unlike the monocations (R₄N)⁺ (R = alkyl) in the above complexes. With increasing temperature, the TG

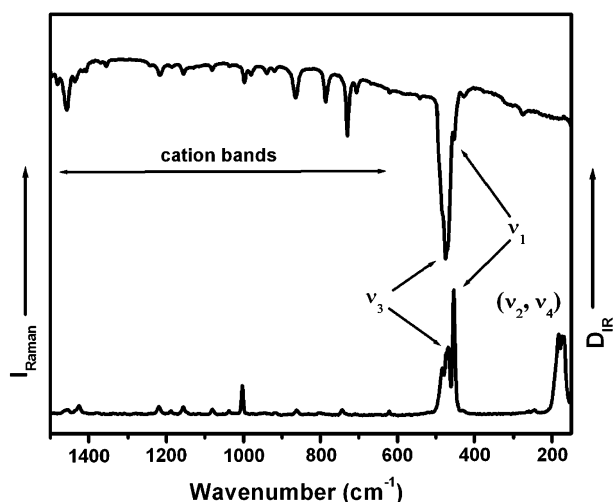


Fig. 2. IR-Raman spectra of (dbtmen)[MoS₄] (1).

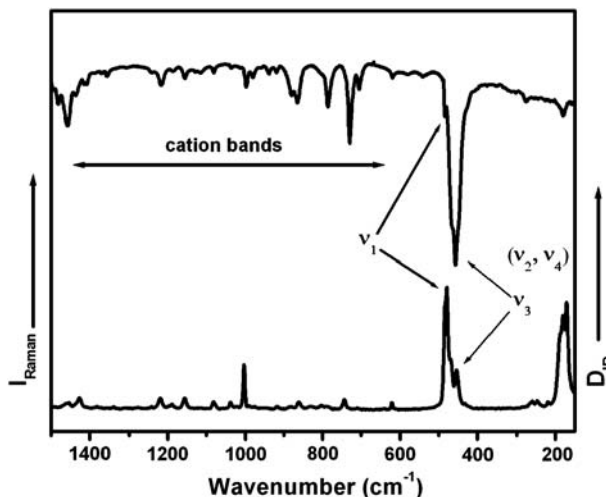


Fig. 3. IR-Raman spectra of (dbtmen)[WS₄] (2).

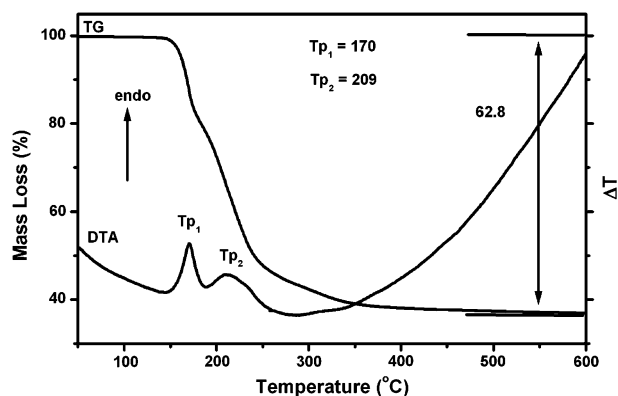


Fig. 4. TG-DTA curves for (dbtmen)[MoS₄] (1) (heating rate 4 °K/min in flowing Ar; *T_p* is peak temperature).

curve shows mass loss up to 400 °C, followed by a slight mass change up to 600 °C. The thermal reaction consisting of two endotherms can be attributed to the decomposition of (dbtmen)²⁺ as well as the thiometalate, although the exact nature of the intermediates cannot be commented on in the absence of a mass spectral study of the emitted fragments. The expected mass loss for the formation of MoS₃ is 64.3% and

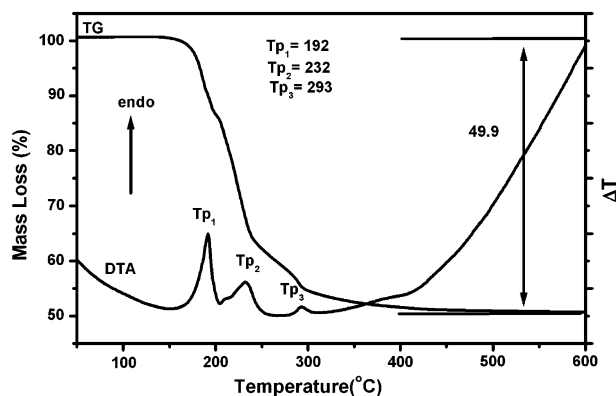


Fig. 5. TG-DTA curves for (dbtmen)[WS₄] (2) (heating rate 4 °K/min in flowing Ar; *T_p* is peak temperature).

Table 1. Thermal decomposition data for (1) and (2)

Details	(dbtmen) [MoS ₄] (1)	(dbtmen) [WS ₄] (2)
Onset temperature (°C)	142	152
<i>T</i> ₁ (°C)	170	192
<i>T</i> ₂ (°C)	209	232
Final temperature (°C)	600	600
Observed mass loss (%)	62.84	49.88
Observed residue (%)	37.16	50.12
Final composition of residue (considering only Mo, S, C and N)	MoS _{1.99} C _{2.06} N _{0.07}	WS _{1.75} C _{3.02}

69.4% for MoS₂. The X-ray powder pattern (Figure 6) of the residue exhibited only broad humps, indicating its amorphous nature. For compound 1 the observed experimental mass loss up to 600 °C is 62.8%. This value is close to that expected for the formation of MoS₃. It is known that MoS₃ is amorphous but unstable at high temperature, as it has been shown to change exothermically to MoS₂ at around 350 °C for ammonium tetrathiomolybdate [43]. In our recent work on thiometalates we have shown that organic ammonium tetrathiometalates decompose to sulfides containing C. The elemental analysis of the residue showed the presence of considerable amounts of C and N (13.3%, 0.6%) and based on this data the residue can be formulated as MoS_{1.99}C_{2.06}N_{0.07}. Thus the presence of C can account for the observed mass loss in the thermal decomposition of (1) and also the complex nature of the decomposition process. This is in accordance with our recent results of the thermal investigations of tetraalkylammonium MoS₄ compounds, which exhibit very complex processes involving structural phase transitions as well as emission of different organic fragments like disulfides, and amines [11].

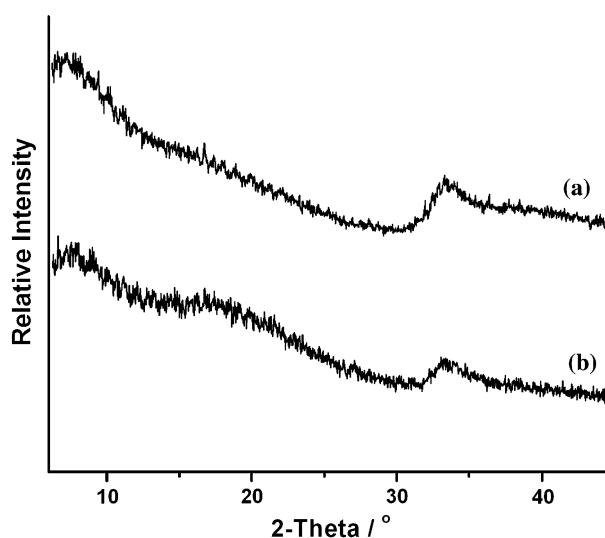


Fig. 6. X-ray powder diffractograms of (a) MoS_{1.99}C_{2.06}N_{0.07} and (b) WS_{1.75}C_{3.02} sulfides formed by *in situ* decomposition of (dbtmen)[MoS₄] (1) and (dbtmen)[WS₄] (2).

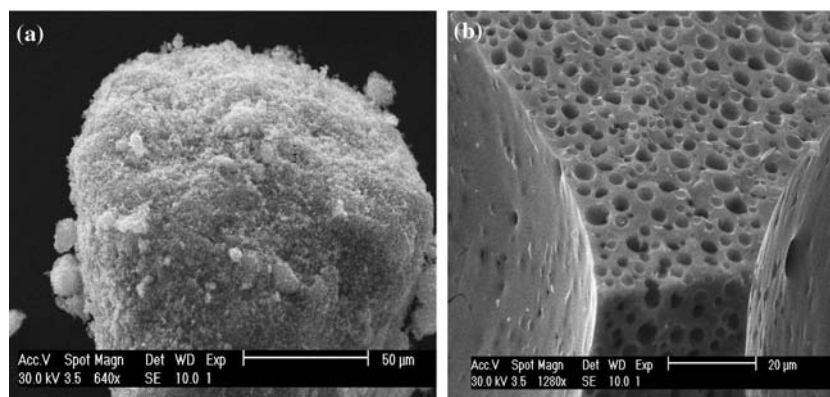


Fig. 7. Scanning electron micrographs of carbon contaminated MoS_2 and WS_2 residue obtained by the thermal decomposition of (a) $(\text{dbtmen})[\text{MoS}_4]$ (1) and (b) $(\text{dbtmen})[\text{WS}_4]$ (2).

Compound (2) decomposes in a similar way to (1), with the degradation starting at $\sim 150^\circ\text{C}$. The mass loss is accompanied by three endothermic events occurring at higher temperatures than for the corresponding Mo compound (1), as evidenced by signals in the DTA at 192, 232, and 293°C . This can be attributed to the nearly simultaneous decomposition of the organic cation and thiometalate although the exact nature of the intermediates cannot be confirmed in the absence of mass spectral data. The expected mass loss for the formation of WS_3 is 45.9% while the formation of WS_2 requires a mass loss of 40.7%. The experimental mass loss up to 600°C is 49.9% and an analysis of the amorphous residue (Figure 6) showed the presence of a similar C content (13.05%) as in the residue of (1). Based on analytical data the composition of the amorphous residue can be given as $\text{WS}_{1.75}\text{C}_{3.02}$. The formation of this carbon-contaminated residue is again indicative of a complex decomposition process, as observed for the Mo analogue.

The C-containing residues $\text{MoS}_{1.99}\text{C}_{2.06}\text{N}_{0.07}$ and $\text{WS}_{1.75}\text{C}_{3.02}$, were further investigated by electron microscopy (SEM) to study their morphological features. SEM images of the final materials are displayed in Figure 7. $\text{MoS}_{1.99}\text{C}_{2.06}\text{N}_{0.07}$ has a sponge-like morphology (Figure 7a) while $\text{WS}_{1.75}\text{C}_{3.02}$ has a porous structure with bubble-like cavities (Figure 7b), probably resulting from the elimination of organic byproducts during decomposition.

Conclusions

The highly insoluble complexes (1) and (2) can be readily synthesized by a simple cation exchange reaction between ammonium tetrathiometalate and the organic dication under aqueous conditions. The complexes analysed satisfactorily for the given formula. The presence of the organic cation as well as the tetrathiometalate anion was confirmed from the optical and vibrational spectra while the crystalline nature of (1) and (2) was evidenced from the powder

pattern. Compounds (1) and (2) can be thermally decomposed endothermically leading to the formation of amorphous carbon-contaminated metal disulfides.

Acknowledgements

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