

Thermal and Spectroscopic Investigations of Organic Ammonium Tetrathiotungstates

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Abstract

Ethylenediammonium tetrathiotungstate, (enH₂)[WS₄] **1**, 1,3-propanediammonium tetrathiotungstate (1,3-pnH₂)[WS₄] **2**, N,N,N',N'-tetramethylethylenediammonium tetrathiotungstate (tmenH₂)[WS₄] **3** and 1,4-dimethylpiperazinium tetrathiotungstate, (1,4-dmpH₂)[WS₄] **4** were prepared by reacting an aqueous solution of (NH₄)₂[WS₄] with the corresponding organic diamines. The complexes **1-4** were characterized by elemental analysis, IR, UV-Vis and TG-DTA methods. On heating, compounds **1**, **2** and **4** decompose in a single step while **3** decomposes in two closely related steps. Elemental analysis, X-ray and ESEM techniques have been used for the characterization of the final thermolysis products. The compounds **1-4** decompose at higher temperatures to form carbon contaminated amorphous tungsten disulfides.

Introduction

The use of (NH₄)₂[WS₄] as precursor for the soft synthesis of WS₂ nanotubes [1], has generated much interest in the chemistry of tetrathiotungstate. Recently it has been reported that the direct pyrolysis of bis(cetyltrimethylammonium) tetrathiotungstate leads to the formation of bulk quantities of uniform WS₂ nanotubules [2] indicating the emerging importance of organic ammonium salts of [WS₄]²⁻ in material applications. As part of our programme on the development of new metal sulfide materials we have structurally characterized several tetrathiotungstates [3-7]. The spectroscopic and thermal characterization of four organic ammonium tetrathiotungstates is described in this paper.

Experimental

Ethylenediamine (en), 1,3-propanediamine (1,3-pn), N,N,N',N'-tetramethylethylenediamine (tmen) and 1,4-dimethylpiperazine (1,4-dmp) were used in this work as obtained from commercial sources. The details of the instrumentation used in this investigation are described elsewhere [6]. Compounds **1-4** were synthesized by base promoted cation exchange method as described earlier [3-5].

Results and Discussion

Synthetic and spectroscopic details

The synthesis of the title compounds was readily accomplished in good yields by reacting $(\text{NH}_4)_2[\text{WS}_4]$ with the corresponding organic amine. All the complexes **1-4** analysed satisfactorily (Table 1). The complexes exhibit bands characteristic of $[\text{WS}_4]^{2-}$ chromophore at around 393, 277 and 221 nm in their UV-Visible spectra. The IR spectra of **1-4** exhibit several bands in mid IR region, which can be attributed to the absorptions of the organic cations. In all the complexes **1-4**, N-H stretching vibrations appear at around 3000 cm^{-1} as broad signals. The strong signal at 452 cm^{-1} in the IR spectrum of **1** can be assigned to the triply degenerate asymmetric stretching vibration (ν_3) of W=S bond while the weak band at 183 cm^{-1} can be assigned to (ν_4) mode. An intense signal at 475 cm^{-1} in the Raman spectrum of **1** can be the symmetric stretching vibration (ν_1) while the medium signal at 464 cm^{-1} arises due to asymmetric stretching vibration (ν_3). The weak signals at 195 and 183 cm^{-1} in the Raman spectrum can be assigned to (ν_2) and (ν_4) vibration modes. The IR and Raman spectra of **2-4** can be similarly explained (Table 1).

Thermal studies

The TG and DTA results of the complexes **1-4** are summarized in Table 2. The TG-DTA trace of complex **1** is displayed in Fig 1. The use of an organic ammonium cation like $(\text{enH}_2)^{2+}$ in **1** enhances the thermal stability of tetrathiotungstate as **1** starts decomposing at relatively at higher temperature (onset = $267\text{ }^\circ\text{C}$) accompanied with an endothermic signal at $290\text{ }^\circ\text{C}$ as compared to $(\text{NH}_4)_2[\text{WS}_4]$ which starts decomposing at $180\text{ }^\circ\text{C}$ [8]. The DTA event can be assigned for the simultaneous removal of en and H_2S . The expected mass loss (25.17 %) for the emission of en and H_2S is close to the observed mass loss (25 %) till 400°C . On further heating up to $500\text{ }^\circ\text{C}$, relatively very little mass loss (total mass loss = 26.65 %) is observed. The elemental analysis of the final residue indicated the presence of C&N (7.66 %). Based on this, the thermal decomposition product of **1** can be formulated as $\text{WS}_2\text{C}_{1.8}\text{N}_{0.5}$ and this is in agreement with the W:S ratio of 1:2 obtained from ESEM measurement. The residue showed no sharp peaks in its X-ray powder pattern, indicating amorphous phase of WS_2 . Complex **2** is thermally stable till 220°C above which, it starts decomposing accompanied by an endothermic peak at 267°C in DTA curve (Fig. 2). Complex **2** is thermally more stable as compared to the corresponding isosturctural Mo

analogue recently reported by us [7] which starts decomposing at 190°C. The elemental analysis of the final product showed the presence of C (5.17%) and N (2.07%) and the residue can be formulated as $WS_{2.1}C_{1.2}N_{0.4}$. This formulation is in good agreement with the results (W:S = 1: 1.9) from electron microscopy. The TG-DTA trace of complex **3** is depicted in Fig 3. Complex **3** is thermally stable upto 151 °C, followed by decomposition which is accompanied by three endo peaks at 190, 202 and 224 °C in DTA curve. Complex **3** is thermally more stable compared to the earlier reported Mo analogue [7], which decomposes at around 112°C. However **3** decomposes at lower temperature compared to $(NH_4)_2[WS_4]$ and can be attributed to the bulkiness of tmen. Upto 500 °C, about 35.94 % of mass loss is observed and this is in good agreement with formation of WS_3 . However, elemental analysis showed considerable amounts of C based on which the residue has been formulated as $WS_{2.2}C_{1.4}N_{0.3}$. This formulation gains further credence based on the electron microscopy result (W:S ratio ; 1:2). Complex **4** starts decomposing with a strong endo peak at 206 °C in its DTA curve, with an onset at around 182 °C (Fig. 4). The elemental analysis of the final residue showed considerable amount (7.82%) of C and N based on which the residue can be formulated as $WS_{2.2}C_{1.4}N_{0.4}$. The amount of carbon in the residue of **3** and **4** is same. The formulation of the residue as $WS_{2.2}C_{1.4}N_{0.4}$ is in accordance with the electron microscopy result which gave a W:S ratio very close to 1:2. The X-ray powder patterns of the decomposed products of **1-4** were featureless indicating the amorphous nature of disulfides.

Conclusions:

The organic ammonium tetrathiotungstates **1-4** were investigated by thermal and spectroscopic techniques. Complexes **1** and **2** are thermally more stable compared **3** and **4**, which contains bulkier cations. The thermal decomposition products of all the complexes are carbon contaminated amorphous tungsten sulfides.

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Table 1 Analytical and spectroscopic data for **1-4**

Compound	1	2	3	4
Analysis (%) Found (Calcd.)	C 6.46 (6.42), H 2.62 (2.70), N 7.38 (7.49), S 34.22 (34.27)	C 9.29 (9.29), H 3.20 (3.12), N 7.16 (7.22), S 32.82 (33.04)	C 16.79 (16.74) H 4.15 (4.22), N 6.55 (6.51), S 30.89 (29.80)	C 16.87 (16.82) H 3.69 (3.77) N 6.92 (6.54) S 30.02 (29.95)
UV-Vis data λ_{\max} in nm	393 (15452) 277 (18528) 221 (17340)	393(14489) 277(16619) 220 (16154)	393 (15076) 277(18221) 221(17090)	393 (15293) 277 (17048) 220(16473)
IR bands (cm^{-1})	3027(br),1570, 1528,1442,1429 1324,1297,1121 1297,1121,1081 1024,952,865,805 477(ν_1),452(ν_3) 213,183(ν_4),146 121	3048(br),1561 1482,1401,1327 1204,1098,935 752,483(ν_1),472 (ν_3),211,170(ν_4) 115	3009(br),1464, 1321,965,783, 479(ν_1),452(ν_3) 249,189(ν_4),51 122, 88	3007(br),1551 1475,1087 1018,909,734 498,470(ν_1) 457(ν_3),218 188(ν_4),150 113, 93
Raman bands (cm^{-1})	475, 464, 352, 195, 183, 118	479, 453, 196, 173	479, 464, 456, 193, 173	477, 448, 186 154

ϵ_{\max} values are in $\text{mol}^{-1} \text{l cm}^{-1}$ and are given in parentheses.

Table 2 Thermal data for 1-4

Compound	1	2	3	4
Heating rate,	4 K/min	4 K/min	4 K/min	4 K/min
Inert atmosphere	N ₂	N ₂	N ₂	N ₂
Final Temp (°C)	500	500	500	500
Onset Temp (°C)	267	220	151	182
DTA peaks (Tp)	290 endo	276 endo	190 endo	206 endo
		333 endo	202 endo	431 exo
			224 endo	
			395 exo	
Mass loss (%)	26.6	29.8	35.9	35.9
Final Residue	WS ₂ C _{1.2} N _{0.5}	WS _{2.1} C _{1.2} N _{0.4}	WS _{2.2} C _{1.4} N _{0.4}	WS _{2.2} C _{1.4} N _{0.3}
ESEM result	1.91	1.19	1.2	1.8

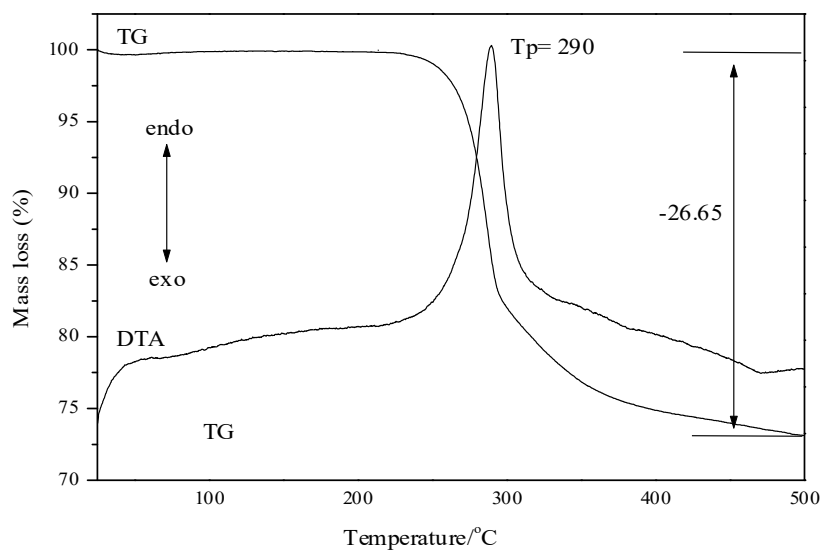


Fig 1 TG-DTA curves of (enH₂)[WS₄] **1**

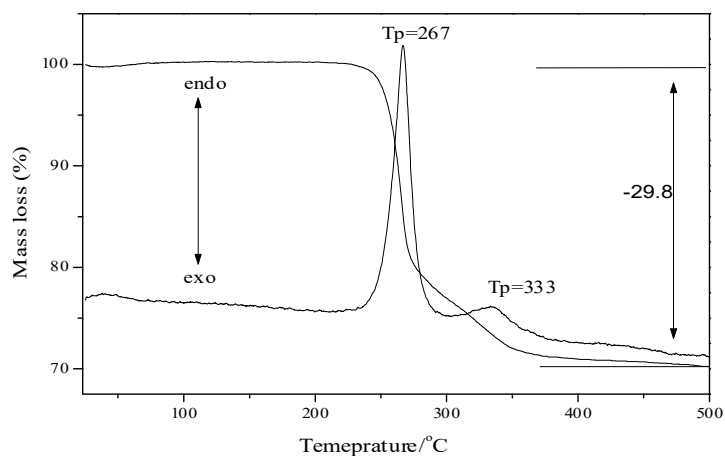


Fig 2 TG-DTA curves of (1,3-pnH₂)[WS₄] **2**

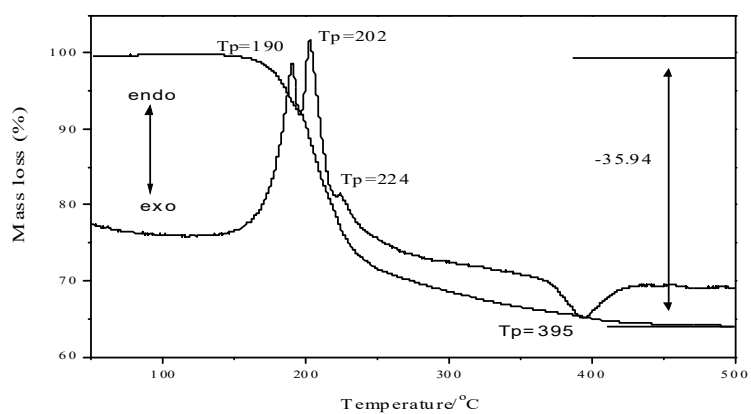


Fig 3 TG-DTA curves of (tmenH₂)[WS₄] **3**

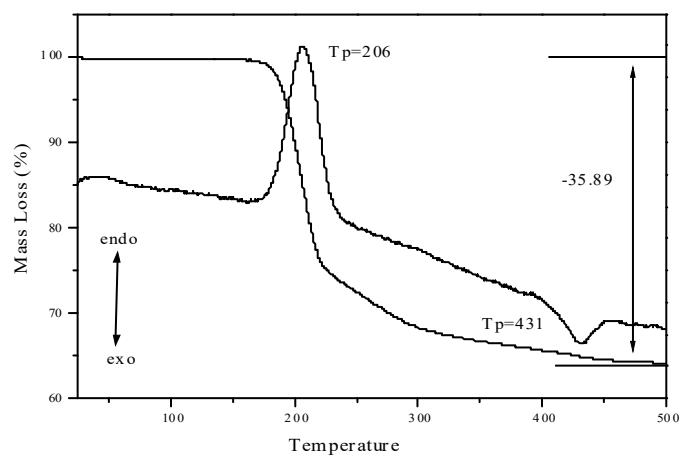


Fig 4 TG-DTA curves of (1,4-dmpH₂)[WS₄] **4**