

# Cation–anion interactions in bis( $\pm$ )*trans*-2-aminocyclohexylammonium tetrathiotungstate, 1,7-diazonia-4-aza-heptane tetrathiotungstate and 1,5-diazonia-9-aza-nonane tetrathiotungstate

Bikshandarkoil R. Srinivasan<sup>a,\*</sup>, Christian Näther<sup>b</sup>, Sunder N. Dhuri<sup>a</sup>, Wolfgang Bensch<sup>b</sup>

<sup>a</sup> Department of Chemistry, Goa University PO, Goa 403 206, India

<sup>b</sup> Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel, Olshausenstraße 40, D-24098 Kiel, Germany

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Dedicated to Prof. Dr. Y.S. Prahalad on the occasion of his 60th birthday.

## Abstract

The reaction of  $(\text{NH}_4)_2[\text{WS}_4]$  with ( $\pm$ )*trans*-1,2-diaminocyclohexane (*trans*-1,2-cn), bis(2-aminoethyl)amine (dien) and bis(3-amino-propyl)amine (dipn) leads to the formation of the organic ammonium tetrathiotungstates (*trans*-1,2-cnH)<sub>2</sub>[WS<sub>4</sub>] (**1**), (dienH<sub>2</sub>)[WS<sub>4</sub>] (**2**) and (dipnH<sub>2</sub>)[WS<sub>4</sub>] (**3**) [*trans*-1,2-cnH is ( $\pm$ )*trans*-2-aminocyclohexylammonium; dienH<sub>2</sub> is 1,7-diazonia-4-aza-heptane; dipnH<sub>2</sub> is 1,5-diazonia-9-aza-nonane] in good yields. The title complexes **1–3** react with  $[\text{Ni}(\text{en})_3]^{2+}$  (en = ethylenediamine) forming the highly insoluble complex  $[\text{Ni}(\text{en})_3][\text{WS}_4]$ . The structure of the complexes **1–3** can be described as consisting of tetrahedral  $[\text{WS}_4]^{2-}$  dianions which are linked to the monoprotonated cation of *trans*-1,2-cn in **1** and the diprotonated cations of dien and dipn in **2** and **3**, with the aid of weak hydrogen bonding interactions. The difference between the longest and the shortest W–S bond lengths  $\Delta$  is 0.0104, 0.0170 and 0.0173 Å in **1**, **2** and **3**, respectively. A comparative study of the structural features of several tetrathiotungstates is presented and the interactions between the organic cations and the tetrathiotungstate anions are discussed in terms of the magnitude of  $\Delta$ , the difference between the longest and the shortest W–S bond distances.

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## 1. Introduction

The chemistry of Mo/W–S complexes is currently a frontier area of research owing to the use of the group VI metal sulfides in hydrodesulfurization catalysis [1] and the importance of layered metal disulfides in nanomaterials [2]. The soluble sulfides of the group VI metals W and Mo [3–5] are a unique class of compounds with a wide range of metal to sulfur stoichiometries, metal oxidation states, coordination geometries and bonding modes of the sulfido ligands. The use of  $(\text{NH}_4)_2[\text{WS}_4]$  as a precursor for the soft

synthesis of WS<sub>2</sub> nanotubes [6,7] is an important reason for the current interest in the chemistry of tetrathiotungstate. Li and coworkers have reported that the direct pyrolysis of bis(cetyltrimethylammonium) tetrathiotungstate leads to the formation of bulk quantities of uniform WS<sub>2</sub> nanotubules [8], indicating the importance of organic ammonium salts of  $[\text{WS}_4]^{2-}$  in material applications. The simplest mononuclear W–S compound ammonium tetrathiotungstate  $(\text{NH}_4)_2[\text{WS}_4]$ , known from the days of Berzelius [9], has been used as a starting material for the synthesis of a variety of di-, tri- and polynuclear W–S complexes [3,4]. From a structural point of view, the acentric tetrahedral  $[\text{WS}_4]^{2-}$  unit can be used as a building block to create non-centrosymmetric materials by an appropriate

\* Corresponding author. Tel.: +91 832 2451345; fax: +91 832 2451184.  
E-mail address: [srini@unigoa.ac.in](mailto:srini@unigoa.ac.in) (B.R. Srinivasan).

choice of cation. The  $WS_4$  tetrahedron is flexible and can exist in a variety of structural environments as evidenced by the structural characterization of several  $[WS_4]^{2-}$  complexes with different counter ions [10–18]. In many of these compounds, the  $WS_4$  tetrahedron is slightly distorted with one or two of the W–S bonds elongated, which has been attributed to  $S \cdots H$  interactions between  $[WS_4]^{2-}$  and the organic ammonium cation. Our work with  $[WS_4]^{2-}$  has shown that organic amines can be used as cationic handles to distort the  $WS_4$  tetrahedron [17]. In order to understand the importance of H-bonding interactions in the structural chemistry of tetrathiotungstates, we are investigating the reactions of  $[WS_4]^{2-}$  with several amines, which differ in terms of their steric bulk and the number of potential donor H atoms. In the present work, we wish to describe the spectroscopic and structural characterization of three new tetrathiotungstates obtained by the reaction of  $(NH_4)_2[WS_4]$  with the cyclic diamine ( $\pm$ )*trans*-1,2-diaminocyclohexane (*trans*-1,2-cn) and the acyclic triamines bis-(2-aminoethyl)amine (dien) and bis(3-aminopropyl)amine (dipn). The title compounds constitute three additions to the growing list of structurally characterized tetrathiotungstates. The availability of structural information for several tetrathiotungstates permits us to make a comparative study of the structural features, the details of which are described in this paper.

## 2. Experimental

### 2.1. Materials and methods

The organic amines *trans*-1,2-cn, dien, dipn and the solvents were used as obtained from commercial sources with analytical purity.  $(NH_4)_2[WS_4]$  was prepared by a literature method [19]. The details of the instrumentation used for the elemental analysis, IR, Raman and UV–Vis spectroscopy are the same as described in our previous reports [16,17].

### 2.2. Synthesis of organic ammonium tetrathiotungstates 1–3

$(NH_4)_2[WS_4]$  (348 mg, 1 mmol) was dissolved in 15 mL of distilled water containing a few drops of aqueous ammonia, and filtered. To the clear yellow filtrate *trans*-1,2-cn (0.3 mL) was added in drops at room temperature and the reaction mixture was kept for crystallization. After a day, yellow blocks of compound **1** slowly crystallized. The crystals were isolated by filtration, washed well with ice-cold water (5 mL), isopropanol (10 mL) and ether (10 mL) and dried under vacuum. The yield of the product was 400 mg. The use of dipn and dien instead of (*trans*-1,2-cn) in the above procedure afforded complexes **2** and **3** in 60% yield. All the complexes are quite stable in air.

(*trans*-1,2-cnH) $_2[WS_4]$  **1**: *Anal.* Calc. for  $C_{12}H_{30}N_4WS_4$ : C, 26.57; H, 5.58; N, 10.33; S, 23.64. Found: C, 26.38; H, 5.49; N, 10.08; S, 22.65%.

IR data: 3309, 3239, 3095, 2939, 2856, 1581, 1498, 1443, 1398, 1229, 1126, 1002, 965, 847, 583, 521, 482 ( $\nu_1$ ), 465

( $\nu_3$ ), 429, 409, 329, 286, 214, 136, 102  $cm^{-1}$ ; Raman data: 481 ( $\nu_1$ ), 464 ( $\nu_3$ ), 193 ( $\nu_4$ ), 178, 168  $cm^{-1}$ .

UV–Vis data in nm ( $\epsilon$  in  $mol^{-1} l cm^{-1}$ ) 393 (18437), 277 (23802), 219 (24375).

(dienH) $_2[WS_4]$  **2**: *Anal.* Calc. for  $(C_4H_{15}N_3WS_4)$ : C, 11.51; H, 3.60; N, 10.07; S, 30.74. Found: C, 11.63; H, 3.52; N, 9.94; S, 28.15%.

IR data: 3243, 3054 (br), 1563, 1547, 1513, 1458, 1365, 1297, 1279, 1257, 1203, 1162, 1122, 1107, 1094, 1026, 980, 959, 933, 866, 824, 797, 789, 770, 750, 627, 479 ( $\nu_1$ ), 464 ( $\nu_3$ ), 443, 357, 324, 243, 185 ( $\nu_4$ ), 99  $cm^{-1}$ ; Raman data: 481 ( $\nu_1$ ), 460 ( $\nu_3$ ), 359, 188 ( $\nu_4$ )  $cm^{-1}$ .

UV–Vis data in nm ( $\epsilon$  in  $mol^{-1} l cm^{-1}$ ) 393 (15858), 280 (17459), 220 (19244).

(dipnH) $_2[WS_4]$  **3**: *Anal.* Calc. for  $(C_6H_{19}N_3WS_4)$ : C, 16.18; H, 4.30; N, 9.44; S, 28.80. Found: C, 16.36; H, 4.26; N, 9.933; S, 29.12%.

IR data: 3275, 3235, 2993, 1573, 1518, 1460, 1420, 1380, 1284, 1208, 1083, 1040, 989, 922, 868, 823, 755, 478 ( $\nu_1$ ), 461 ( $\nu_3$ ), 292, 258, 233, 188 ( $\nu_4$ )  $cm^{-1}$ ; Raman data: 477 ( $\nu_1$ ), 458 ( $\nu_3$ ), 188 ( $\nu_4$ )  $cm^{-1}$ .

UV–Vis data in nm ( $\epsilon$  in  $mol^{-1} l cm^{-1}$ ) 393 (12441), 277 (18114), 217 (21122).

### 2.3. Crystal structure determination

Intensity data were collected on a STOE Imaging Plate Diffraction System for compound **1** and on an AED-II four-circle diffractometer for compounds **2** and **3**, using graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ). The raw intensities were corrected for Lorentz, polarization effects. All structures were solved with direct methods using SHELXS-97 [20] and refinement was done against  $F^2$  using SHELXL-97 [21]. All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were located in the difference map but were positioned with idealized geometry and refined isotropically using a riding model. In compound **2** the N atom of dien is disordered due to symmetry. The structure can also be solved and refined in the non-centrosymmetric space group  $Pmn2_1$ . In this case no disorder is present but the absolute structure cannot be determined (Flack  $x$ -parameter 0.5) and strong correlation of the atomic coordinates of the symmetry related atoms occur. When the structure was checked for higher symmetry using Platon, the space group  $Pmmm$  was selected. Therefore this space group was chosen. Intensity data were additionally collected at low temperature (170 K) using a different crystal to check whether the disorder is dynamic or static in nature. However the disorder persists even at low temperature and no indications were found for a symmetry change. In the present contribution we describe only the room temperature data because the quality of the structure model was much better than that of the low temperature data set. The technical details of data acquisition and some selected refinement results are summarized in Table 1.

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