Journal of Alloys and Compounds 495 (2010) 131–137

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Spectroscopic and thermal characterization of tetrathiomolybdate-organic amine homologous systems

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ARTICLE INFO

Article history:
Received 10 November 2009
Received in revised form 19 January 2010
Accepted 21 January 2010
Available online 1 February 2010

Keywords:
Tetrathiomolybdates
Organic amines
Single crystals
Thermal properties

ABSTRACT

The homologous series of organic–inorganic hybrid single crystals (diethylenetriamine-H_2-MoS_4—**I**, triethylenetetramineH_2-MoS_4—**II** and 1,4-diazobicyclo-2,2,2-octaneH-NH_4-MoS_4—**III**) were prepared by passing hydrogen sulfide gas in the aqueous solution of ammonium heptamolybdate and their respective amines. These crystals were analysed using Fourier Transform-Infrared (FT-IR), UV–vis and ^{1}H NMR spectroscopy. The discrepancies in the bond angles and bond lengths have been theoretically explained in terms of hybridisation variations. The thermal analytical techniques such as TG/DTG and DSC were used to study thermal properties at high and low temperatures. DSC at low temperature suggested reversible solid–solid transitions and the respective ΔH, ΔS and ΔG have been derived. SEM analysis of the crystals showed the sedimented smooth layers of these sulfido-metallic crystals before heat treatment were converted into fine powder with tiny capillary pores in the bulk after thermal treatment.

1. Introduction

The importance of molybdenum–sulfur chemistry in industrial catalysis and bioinorganic chemistry has stimulated recent interest inducing broad research in these fields [1–4]. Many of the new sulfidometal complexes prepared and characterized, in the recent years, have revealed novel structures and bonding modes. The binary Mo–S anions such as $MoS_4{}^{2-}$, $Mo_2S_8{}^{2-}$, $Mo_2S_{12}{}^{2-}$, $Mo_3S_9{}^{2-}$, [5–7] have unusual stoichiometries, oxidation states and coordination geometries. A variety of structurally diverse Mo–S compounds have been synthesized using $[MoS_4]^{2-}$ precursor with the appropriate organic/inorganic precursors as a building block for the synthesis of several novel Mo–S inorganic complexes [8,9] and inorganic pathways [10]. The bioavailable Mo–S when enters the cell, is subsequently incorporated by complex biosynthetic machineries into metal cofactors [11,12]. All enzymes depend on molybdenum catalyze redox reactions by taking advantage of the versatile redox chemistry of the molybdenum [13]. In nature, two very different systems have been developed to control the redox state and catalytic power of molybdenum, which functions as an efficient catalyst in oxygen-transfer reactions. In either case, at least three S and two O atoms form ligand to molybdenum which is typical for molybdenum nitrogenase [14]. Moreover, the use of tetrathiomolybdate for the treatment of metastatic cancer has added an entire new dimension to the chemistry of these ions [15,16].

In this report, we have synthesized, spectroscopically and thermally characterized water soluble organic amine-$MoS_4{}^{2-}$ single crystals. We have also tried to explain the abnormalities in the bonding modes of these hybrid systems through fractional differences between sp^2 and sp^3 hybridisations. To the best of our knowledge, no reports on thermal treatment (at low temperature) of these systems are found. We have attempted to make this study on few of our crystals whose structure has been determined. Since it is very interesting to see how organic amine and inorganic $[MoS_4]^{2-}$ materials respond to thermal treatment, we hereby report the spectroscopic and analytical characterization of these single crystals for better understanding of the bonding modes and charge-transfer transitions between the coordinating amine and the thiochelate.

2. Experimental details

2.1. Preparation of (amine-MoS_4) single crystals [dienH_2-MoS_4 (*I*), trienH_2-MoS_4 (*II*) and 1,4-diazobicycloamineH-NH_4-MoS_4 (*III*)]

The detail experimental techniques have been described elsewhere [17–19]. In short, a steady stream of H_2S gas was passed through the aqueous ammonium heptamolybdate (3 g, E Merck) in water (30 cm^3) containing organic amine (8 cm^3 99% pure, E Merck) for 2 h at 50 °C. The immediate brown precipitate obtained was dissolved in continuous flow of H_2S gas. The resulting blood red solution was filtered and allowed to stand at 15 °C for 1 h. The crystals were filtered, washed with ice-cold water/isopropanol/petroleum ether and dried under vacuum. The yield after recrystallization in hot water (70–80 °C) was found to be 70–75%.

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doi:10.1016/j.jallcom.2010.01.101

2.2. Instrumentation

The IR spectra were recorded in the PerkinElmer RXI FT-IR spectrophotometer after pressing the samples with KBr. UV–vis spectrums were recorded using the PerkinElmer Lambda 3B UV-Visible spectrophotometer. The protons NMR spectral analyses of the organic amine based terathiomolybdates in D_2O were carried out using JEOL GSX-400 NMR instrument at swiping frequency of 400 Hz cm^{-1} at ambient temperature. TG and DSC analysis was performed in PerkinElmer thermal analyzer (TGA 7) in ambient air and NETZSCH DSC 204 instrument in nitrogen atmosphere. The furnace is supplied with a silver block assisted by a miniature-jacketed heater where the temperature is monitored periodically by a thermocouple integrated into the furnace wall. The sample chamber has two silver lids one for the sample and the other for reference. The instrument further comprised a cooling unit where there was a provision for liquid nitrogen, air and refrigeratory bath (circulatory) for the low temperature measurements. The sample $\approx$ 6.5 mg was closed in Al_2O_3 sample chamber and kept in the heating unit for thermal measurements. The X-ray diffraction patterns were obtained with a Phillips diffractometer using CuK_α radiation. The samples were then pressed on a glass plate with a well of depth 1 mm.

3. Results and discussion

3.1. Stability

The crystals **I**, **II** and **III** [Fig. 1(a)–(c)] were left in the open air and the blood red colour slowly changed to black in 15, 35 and 60 days respectively due to the exchange of sulfur with oxygen in the samples. It has been reported [20,21] that ammonium tetrathiomolybdate slowly decomposes in air by induced electron transfer process resulting in the formation of $[Mo_2O_2S_6]^{2-}$ species and the process is quite facile under room temperature. Therefore, the crystals had to be stored under N_2 atmosphere to avoid deterioration to facilitate their use at a latter time. The relative stability of **III** compared to those of **I** and **II** could be ascribed to the bonding of MoS_4^{2-} through rigid bicyclic amine with strong H-bonds [see Fig. 1(c)]. Though the hydrogen bonding networks were present in all the three crystals, the lower stabilities are suggested due to the flexibility of the linear amines in contrast to the rigidity accrued by cyclic amine.

3.2. Infrared spectroscopy

The FT-IR intense bands positions occurring at 3078.2, 3065.5 and 3057.2 cm^{-1}, for **I**, **II** and **III** are attributed to the $\nu(N–H)^+$ evidencing the molecular interactions between the organic and inorganic moieties (Fig. 2). It has also been observed that the terminal rather than the central N–H understandably participates in H-bonding. The ν(C–H) for all the three crystals occurred at 1446.5, 1441.1, and 1444.2 cm^{-1} respectively. The infrared bands at 1114.8, 1128.4, and 1045.6 cm^{-1} for **I**, **II** and **III** are attributed to ν(C–N) vibration of the amines. In the case of linear amines bending/stretching is easier than that in cyclic amine where the bending/stretching could result in angle strain to a considerable extent. For this reason the ν(C–N) frequency occurs at the higher region as compared to those of **I** and **II** obviously occurring at a lower region. The band at 474.5, 474.1 and 481.6 cm^{-1} for **I**, **II** and **III** could be attributed to the presence of ν(Mo=S) asymmetric vibration due to MoS_4^{2-}moiety. The infrared spectrum of $Mo_2S_4^{2+}$ core was reported to correspond to ν(Mo=S) at 523 $cm^{-1}$and a series of weaker bands between 496 and 296 cm^{-1} differing substantially from the infrared spectrum exhibited by $Mo_2S_{12}^{2-}$ anion [1,10]. Recently it has been reported that the ν(Mo–S) band for the doubly bridged and double cubane cluster complex of $[MoFe_3S_4]$ exhibits

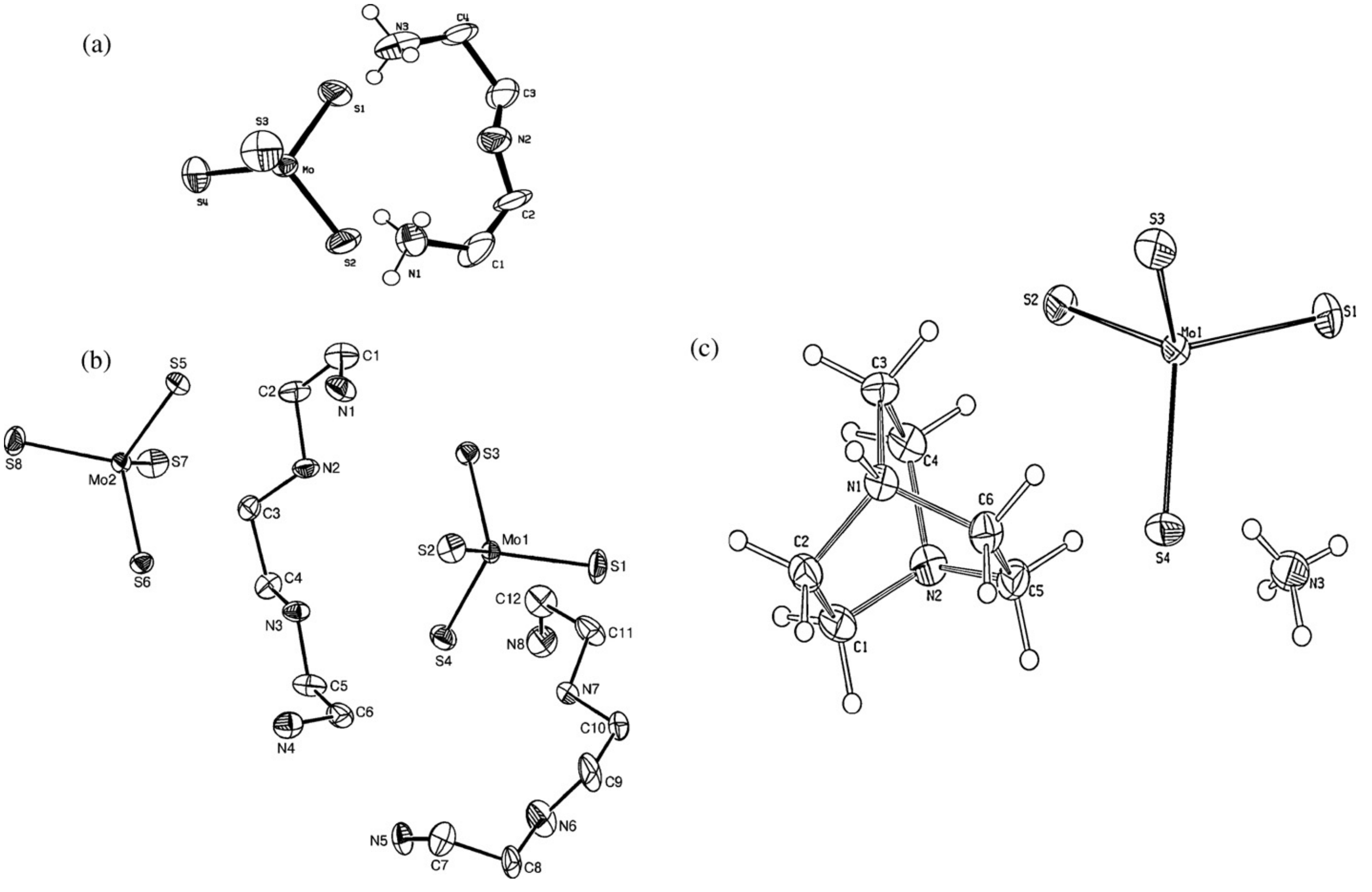

Fig. 1. ORTEP structures of (a) diprotonated diethylene triammonium tetrathiomolybdate $[dienH_2][MoS_4]$, (b) diprotonated triethylene tetraammonium tetrathiomolybdate $[trienH_2][MoS_4]$ and (c) Protonated 1,4-diazo-bicyclo-2,2,2-octane ammonium tetrathiomolybdate $[NH_4][DABCOH][MoS_4]$.