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Preparation and Properties of the Sodium Salt of Tetrathiomolybdate(VI), $Na_2MoS_4 \cdot 3.5H_2O$

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The thiomolybdate anions $MoO_xS_{4-x}^{2-}$, $x = 0–3$, are considered as active intermediates in the Cu–Mo antagonism that afflicts ruminants [1–3]. MoS_4^{2-} is also involved in the formation of the active site of nitrogenase [4]. These simple tetrahedral anions are of interest spectroscopically and their chemical properties are well documented [5, 6]. More recently $(NH_4)_2MoS_4$ has been shown to be an effective antidote against certain metal ions [7]. In this study replacement of NH_4^+ by Na^+ reduced the toxity (LD_{50} value) of the salt, this is of importance to current clinical trials of these salts. Although 'Na_2MoS_4' is commercially available it is invariably of low purity and mostly contains insoluble MoS_2 and MoS_3. There is no published method for the preparation of the Na^+ salt.

Interestingly, the use of large cations to obtain solid salts has led to the conclusion that these are necessary to stabilise the thiomolybdate ions [6].

We herein report a method of preparing the Na^+ salt of the MoS_4^{2-} anion together with its characterisation.

Experimental

Apparatus and Materials

IR spectra were obtained as KBr discs with a Perkin Elmer 683 spectrometer. UV/visible spectra of aqueous solutions were recorded on a Perkin Elmer 555 spectrophotometer. X-ray powder diffraction data were obtained using Ni-filtered Cu-K_α radiation from a Philips PW101 diffraction generator and either a Debye-Scherrer or a Gandolfi camera. Thermogravimetric analyses were made with an automatic Stanton-Redcroft TG750 TGA balance.

Reagents were of 'AnalaR' grade or equivalent, except for acetone and diethylether which were of 'standard Laboratory Reagent' grade. H_2S of 99.6% purity was obtained from BDH Ltd. All water was distilled and deionised before use.

Analyses

Sodium analysis was by flame photometry using a Corning 400 flame photometer calibrated against standard 'AnalaR' NaCl solutions (0–40 ppm). Molybdenum was determined gravimetrically as the oxinate complex [8]. A weighed quantity of the sodium salt was first decomposed by digestion with bromine water followed by nitric acid. The method was first tried with $(NH_4)_2MoS_4$ with entirely satisfactory results. The water content was determined by TGA, complete water loss being observed over the temperature range 80–160 °C.

Preparations

$(NH_4)_2MoS_4$

It was prepared by the method outlined by Mellor [9]. Ammonium paramolybdate (5 g) was dissolved in water (15 cm^3) and ammonia (0.88, 50 cm^3) added. A vigorous stream of H_2S was bubbled through the solution for *ca.* 20 min. The dark red solution on cooling to room temperature deposited red crystals of the product. The crystals were filtered, washed with ethanol and dried *in vacuo*. Yield *ca.* 80%.

$Na_2MoS_4 \cdot 3.5H_2O$

$(NH_4)_2MoS_4$ (5 g) was dissolved in an ice-cold aqueous NaOH solution (1.7 g, 20 cm^3). NH_3 and H_2O were then slowly removed by vacuum pumping for 3–4 h. The solid red residue was extracted with acetone (60 cm^3) and then diethylether (150 cm^3) added to the filtrate. Red crystals of the product formed, these were filtered, washed with ether (3 × 10 cm^3) and then dried *in vacuo*. Yield 3.5 g (55%). Analytical data from two different preparations are given in Table I and spectroscopic properties in Table II.

Results and Discussion

Preparations

The starting material $(NH_4)_2MoS_4$ is the easiest of the tetrathiomolybdate salts to prepare in high

TABLE I. Analytical Data.

	%Na	%Mo	%H_2O	Residual %
Preparation I	14.1	28.1	18.8	39.0
Preparation II	13.6	30.0	18.92	37.4
Calculated for $Na_2MoS_4 \cdot 3.5H_2O$	13.82	28.81	18.92	(%S 38.45)

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TABLE II. Spectroscopic Properties.

	$Na_2MoS_4 \cdot 3.5H_2O$	$(NH_4)_2MoS_4$
IR/cm^{-1}	3450 (broad)	–[a]
	1650 (weak)	–
	480 (strong)	480 (strong)
UV–Vis./nm	465 (12000)[b]	465 (11800)
	315 (16000)	315 (16600)
	240 (22700)	240 (24700)

[a] Absorptions due to NH_4^+ not shown. [b] Molar extinction coefficients in parentheses/L^3 mol^{-1} cm^{-1}.

yield and of good purity, our preparation followed the simpler procedure recommended earlier by Mellor [9] rather than that recently published by McDonald *et al.* [10]. The recommendation of heating to 50–60 °C in the latter procedure is not necessary since the reaction is exothermic. For obtaining the sodium salt from $(NH_4)_2MoS_4$ we followed the method suggested by McDonald *et al.* [10] for the synthesis of tetraalkylammonium salts, the reaction can be summarized as:

$$(NH_4)_2MoS_{4(aq)} + 2NaOH_{(aq)} = Na_2MoS_{4(aq)} + 2H_2O + 2NH_3\uparrow$$

The product, obtained as the 3.5 H_2O hydrate, is extremely water soluble and, in contrast to the K^+ and NH_4^+ salts, is also soluble in polar organic solvents. As with the other salts it must be stored over a dessicant otherwise decomposition to black insoluble sulphides occurs.

Whilst the K^+ salt can be prepared with care [3] directly from molybdate, this is not a suitable route for obtaining the Na^+ salt. The high basicity of the reaction medium resulted in decomposition during solvent removal. Neither could the Na^+ salt be precipitated by adding large excesses of organic solvents, it is too highly soluble. Attempts made at lower basicity were also unsuccessful, reaction proceeding mainly to the MoS_3^{2-} stage.

Characterisation

The spectroscopic properties of the MoS_4^{2-} ion are well documented [5, 6, 11]. Tables I and II show the Na^+ salt to have identical properties to that of the NH_4^+ salt. The 480 cm^{-1} band in the IR spectrum is assigned to ν(Mo–S). The other bands can be attributed to the presence of H_2O, this was confirmed by TGA which showed a weight loss over the range 80–160 °C corresponding to 3.5 (±0.1) mol H_2O. The X-ray powder diffraction patterns of the NH_4^+ and K^+ salts are identical and show them to have the same structure as β-K_2SO_4 [12]. The Na^+ salt is seen from Table III to have a different crystal structure.

TABLE III. X-Ray Powder Diffraction Data.

$(NH_4)_2MoS_4$		$Na_2MoS_4 \cdot 3.5H_2O$	
d-spacing/ 10^{-10} m	relative intensity/%	d-spacing/ 10^{-10} m	relative intensity/%
6.096	30	6.937	30
5.146	100	6.254	30
4.801	50	5.605	100
3.796	20	5.353	95
3.518	50	4.651	30
3.070	50	4.330	10
2.833	45	4.202	30
2.762	10	3.532	20
2.572	10	3.432	20
2.509	5	3.331	1
2.408	1	3.202	1
2.319	5	3.122	100
2.236	45	2.790	95
2.088	5	2.713	20
2.021	1	2.643	5
1.984	20	2.307	20
1.874	10	2.198	3
1.831	10	2.161	8
1.763	5	2.126	3
1.741	5	2.075	7
1.663	20	2.001	5
1.622	15	1.962	3

The differences in behaviour presumably reflect the influence of the smaller Na^+ ion. The suggestion [6] that the larger cations are necessary to stabilise the MoS_4^{2-} ion is in fact a reflection of the differences in solubilities of these salts rather than any differences in thermodynamic stability.

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