Note

STUDY OF AN ORDERED MIXED OXO SALT BY THERMAL AND VIBRATIONAL ANALYSIS: $(NH_4)_2H_3AsO_4SO_4$

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A great number of compounds possess two types of tetrahedral oxo ions in their framework, but these tetrahedra are generally distributed at random. In the literature only two examples exist of compounds which show an order between their isolated TO_4 tetrahedra [1,2]. One of these compounds, $(NH_4)_2H_3AsO_4SO_4$, presents the arsenate and sulphate oxo ions ordered in the lattice as $[H_3AsO_4SO_4]^{2-}$ groups, which are linked by two ammonium ions and form chains connected by hydrogen bonds [1]. The results of the comparison of this compound with some other $M_2H_3PO_4SO_4$ related mixed salts (where M = K, NH_4) [3], show that the order is responsible for the formation of a superstructure [1].

Information on the thermal treatment of ordered mixed oxo salts is not reported in the literature. For this reason, the thermal and vibrational behaviours of $(NH_4)_2H_3AsO_4SO_4$ have been analysed in this note in order to contribute to the knowledge of these ordered phases.

EXPERIMENTAL

Crystals of $(NH_4)_2H_3AsO_4SO_4$ were obtained from a stoichiometric solution of ammonium sulphate and arsenic acid. The solution was kept at room temperature and the crystals of the salt appeared by slow evaporation a few days later.

The purity of the sample was checked by microsopic and X-ray diffraction analyses.

Thermogravimetric and differential thermal analyses were carried out on a Rigaku thermoanalyser (type YLDG/CN 8002 L2) working under a constant flow of N_2 (0.4 l min^{-1}). The heating rate was $10°C$ min^{-1} and α-Al_2O_3 was used as DTA standard. The temperature was raised to $700°C$. Additional thermal analyses were carried out in a furnace using a Pt crucible. The different degradation steps were characterized by X-ray diffractometry and IR spectroscopy.

The IR spectra were recorded on a Perkin–Elmer 580B spectrophotometer using the KBr-pellet technique.

The Raman spectrum was obtained with a Spex-Ramalog 1403 double monochromator spectrometer, equipped with a Scamp data processor. The 514.5 nm line of an argon-ion laser was used for the excitation of the sample.

RESULTS AND DISCUSSION

Thermal behaviour

Typical TG and DTA curves are shown in Fig. 1. According to these results, a very complex thermal process occurs between 150 and 430°C.

In the first step of the pyrolysis, a loss of water leads to the formation of $(NH_4)_2SO_4$ which melts at 235°C (second endothermic peak). The As_2O_5 obtained is reduced to As_2O_3 losing O_2 in a further step at 295°C. The corresponding DTA signal is broad and not well defined. The following step is reached at 388°C. This last degradation process begins with an exothermic signal: the decrepitation of $(NH_4)_2SO_4$ [4]. However, a new endothermic process occurs abruptly. It corresponds to the As_2O_3 sublimation, which is observed as a very marked endothermic inflection at 420°C [4]. At this temperature, the thermolysis of the original sample is complete and the crucible is empty.
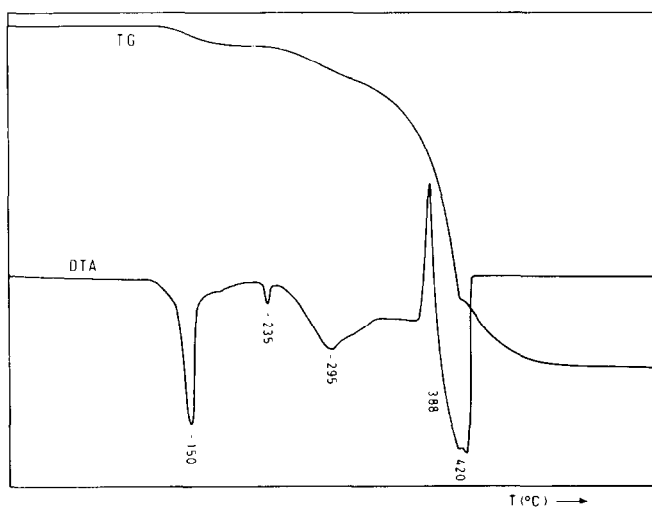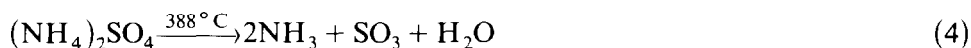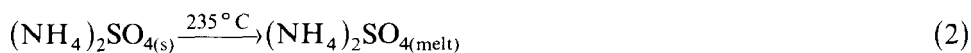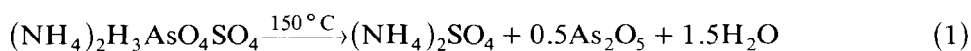

Fig. 1. TG and DTA curves of $(NH_4)_2H_3AsO_4SO_4$.

TABLE 1

Analysis of the thermal data of $(NH_4)_2H_3AsO_4SO_4$

T (°C)	Wt. loss (%)	Accumulative wt. loss (%)	Step	Theor. (%)	DTA signal
150	9.85	9.85	(1)	9.85	Endo
235	–	9.85	(2)	–	Endo
295	5.82	15.67	(3)	5.83	Endo
388	48.17	63.84	(4)	48.17	Exo
420	36.16	100	(5)	36.15	Endo

The experimental results allow the formulation of the following decomposition scheme, which shows that no solid residue remains above 430°C

$$(NH_4)_2H_3AsO_4SO_4 \xrightarrow{150°C} (NH_4)_2SO_4 + 0.5As_2O_5 + 1.5H_2O \tag{1}$$

$$(NH_4)_2SO_{4(s)} \xrightarrow{235°C} (NH_4)_2SO_{4(melt)} \tag{2}$$

$$0.5As_2O_5 \xrightarrow{295°C} 0.5As_2O_3 + 0.5O_2 \tag{3}$$

$$(NH_4)_2SO_4 \xrightarrow{388°C} 2NH_3 + SO_3 + H_2O \tag{4}$$

$$0.5As_2O_{3(s)} \xrightarrow{420°C} 0.5As_2O_{3(g)} \tag{5}$$

The quantitative evaluation of the thermogravimetric curve is given in Table 1.

Vibrational behaviour

IR and Raman spectra are very useful tools for studying the vibrational behaviour of mixed salts [5–7]. In this case the presence of two different types of oxo ions in the lattice is similar to that observed in numerous mixed salts. However, the existence of an internal order contributes to the good resolution of the spectra, which show very well-defined bands in both IR and Raman studies. Figure 2 shows the vibrational spectra of $(NH_4)_2H_3AsO_4SO_4$. Table 2 gives the assignment of all the observed bands.

For the analysed compound, for the space group $P2_1/c$, monoclinic system, and $Z = 4$, a lowering of the tetrahedral symmetry from T_d to C_1 is expected. However, in the AsO_4 group, the presence of the three long As–O $\cdots$ H bonds and the short As=O bond (1.703 and 1.634 Å, respectively) distorts the polyhedra slightly. This situation seems to indicate that this anion may probably have C_{3v} symmetry which can be corroborated by IR and Raman spectroscopies. For the SO_4 polyhedra, where four similar S–O distances are observed (between 1.466 and 1.484 Å), the lowering to C_1 symmetry can also be confirmed by these spectroscopic techniques.
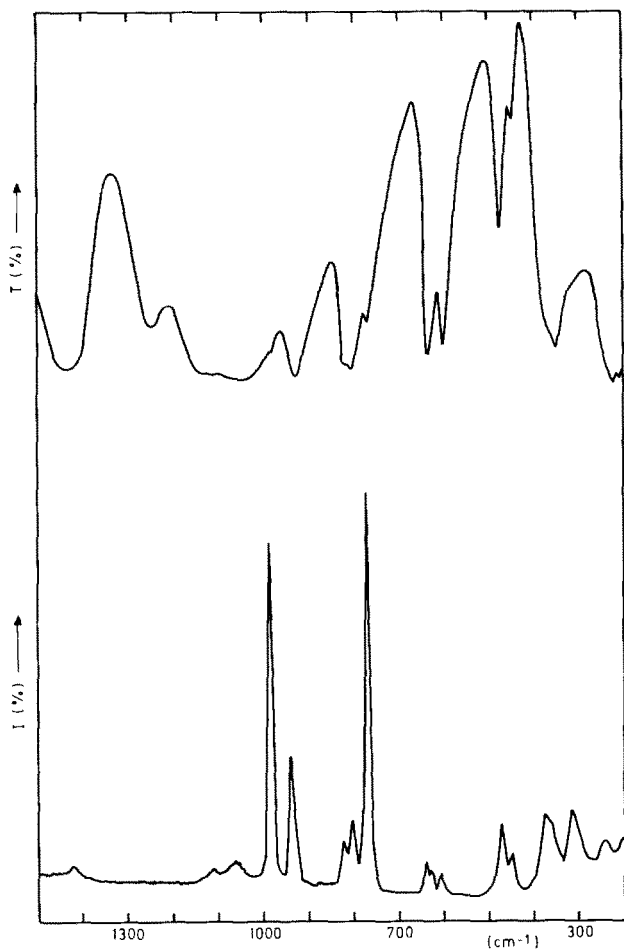
Fig. 2. $(NH_4)_2H_3AsO_4SO_4$ vibrational spectra: IR (top); Raman (bottom).

In relation to the As–O vibrations, the spectroscopic behaviour of the $[H_3AsO_4]$ group resembles that observed in the H_3AsO_4 acid which presents an intense band corresponding to the As=O double bond (923 cm^{-1}) [8,9]. In this study, the bands located at 933 and 930 cm^{-1} in the Raman and IR spectra, respectively, can be assigned to the As=O mode. The bands in the 850–750 cm^{-1} region are assigned to the symmetric and antisymmetric stretchings of the As–O $\cdots$ H bonds [8,9]. In this region three bands are observed at 772, 803 and 820 cm^{-1} in the IR spectrum and 766, 797 and 816 cm^{-1} in the Raman spectrum. The first band, in both spectra, corresponds to the symmetric stretching and the other two, to the antisymmetric stretching of the As–O $\cdots$ H bonds, confirming the proposition of the C_{3v} symmetry (see Table 3). This seems to indicate that the influence of the C_1 site symmetry is of no importance. A similar behaviour has been explained in the literature for the vibrational analysis of arsenic acid and its hydro-

TABLE 2

Assignment of the $(NH_4)_2H_3AsO_4SO_4$ vibrational frequencies

IR	Raman	Assignment
3150 vs	3048 vw (broad) ⎫	
3040 vs	⎬	$\nu(N-H)$
2940 m	⎭	
2322 m	2300 vw	$\nu(As-O-H)$
1408 vs	1412 vw	$\delta(NH_4)$
1250 m		
1122 vs	1106 vw ⎫	
1055 vs	1050 vw ⎭	$\nu_{as}(S-O)$
980 sh	978 vs	$\nu_s(S-O)$
930 s	933 m	$\nu(As=O)$
820 s	816 w ⎫	
803 s	797 m ⎭	$\nu_{as}(As-O\cdots H)$
772 m	766 vs	$\nu_s(As-O\cdots H)$
638 sh	633 w ⎫	
625 s	622 w ⎬	$\delta_{as}(S-O_4)$
605 s	598 w ⎭	
475 m	465 m ⎫	
450 m	443 w ⎭	$\delta_s(S-O_4)$
378 sh	368 m ⎫	
360 vs	358 sh ⎮	
338 sh	⎬	$\delta(As-O\cdots H)$
	309 m ⎮	$\nu(N-H\cdots O)$
	236 w ⎭	See text

genated AsO_4H^{2-} anion [8]. It is possible to observe all the expected bands in the S–O vibrations, considering that the S occupy general positions (see Table 3) [10–12].

Finally, the frequencies at the two ends of the spectra are well characterized. In the highest region, broad bands located at 3050 and 2650 cm^{-1} can be attributed to N–H stretching [13]. The band at 2250 cm^{-1} can be assigned to As–O–H stretching and the strong band at 1430 cm^{-1} to NH_4 bending. At the other extreme of the IR and Raman spectra the frequencies

TABLE 3

Correlation diagram for $(NH_4)_2H_3AsO_4SO_4$

Point group					Activity		
					Raman only	IR only	Raman and IR
T_d	$\nu_1(A_1)$	$\nu_2(E)$	$\nu_3(F_2)$	$\nu_4(F_2)$	(A_1+E)	–	$(2F_2)$
C_{3v}	(A_1)	(E)	(A_1+E)	(A_1+E)	–	–	$(3A_1+3E)$
C_1	(A)	$(2A)$	$(3A)$	$(3A)$	–	–	$(9A)$

below 250 cm^{-1} can be assigned to lattice vibrations. The band at 236 cm^{-1} in the Raman spectrum is probably due to stretching of the hydrogen bonds N–H $\cdots$ O.

In conclusion, it is important to note that the thermal behaviour is very interesting because it shows that no solid residue remains above 430°C. However, sulphate and arsenate salts are degraded, in general, at higher temperatures [4]. The symmetry of the oxo ions is lowered from the isolated polyhedra T_d symmetry by the vibrational spectroscopy. However, the C_1 site symmetry expected can only be confirmed for the SO$_4$ ions. In contrast, the AsO$_4$ groups remain with C_{3v} symmetry, indicating that the influence of the C_1 site symmetry is of no importance. For this reason, the TO$_4$ polyhedra show different symmetries in the same lattice.

ACKNOWLEDGEMENTS

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