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Studies on Some Telluro-Tungstomolybdates

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Ammonium telluro-tungstomolybdate $6(NH_4)_2O \cdot 2TeO_3 \cdot WO_3 \cdot 10MoO_3 \cdot 30H_2O$ and the corresponding salts with silver, strontium, barium, cerium, lead, iron and guanidine have been isolated, their properties studied and the composition determined by the analytical methods. IR spectra of ammonium and guanidine salts have been recorded and the characteristic peaks assigned. Thermal decomposition studies (TGA and DTA) of ammonium salt were made. Differential thermal analysis of ammonium salt was done in nitrogen atmosphere too.

Formation of heteropoly salts by tungsten and molybdenum is well known.(1) Tellurium has also been reported to form heteropoly salts with various elements such as molybdenum,(2) tungsten,(3) phosphorus, arsenic.(4)

The condensation reaction of telluric acid with tungstic acid was studied by Rosenheim and Traube.(5) Recently telluric-12 tungstic heteropoly acid(6) and its silver salt(7) was studied by Ganelina.

Formation of heteropoly salts of telluric acid with molybdic acid has been extensively studied.(8) A series of heterotrisalts containing tellurium, vanadium, molybdenum, tungsten, phosphorus has been studied in these laboratories(9-11) and the work is now extended to study the heterotrisalt formation of tellurium, tungsten and molybdenum.

The preparation, analysis and some properties of ammonium telluro-tungstomolybdate and its salts with silver, strontium, barium, cerium, lead, iron and guanidine are reported in this communication.

Experimental

All the chemicals used were of E. Merck or B. D. H. pure quality. Ammonium telluro-tungstomolybdate-telluric acid (4.6 g) and molybdic acid (21.6 g) were refluxed in ammoniacal medium for 6 hr. Five grams of tungstic acid dissolved in sufficient quantity of ammonium hydroxide was added to the above solution and refluxed for another 10 hr. The solution was then evaporated to a small bulk and kept in a refrigerator for crystallization. White crystalline ammonium telluro-tungstomolybdate was obtained which was recrystallized and analysed. The compound is stable at room temperature but decomposes on heating or treatment with acids. The analytical data are shown in Table 1.

Its silver, strontium, barium, cerium, lead, iron and guanidine salts were prepared by adding silver nitrate, strontium acetate, barium chloride, cerous nitrate, lead nitrate, ferric chloride and guanidine hydrochloride solutions to the ammonium salt solution in water.

Tellurium was estimated as metallic tellurium and ammonia as described earlier.(8) Tungstic and molybdic acids were separated by standard method. The other cations silver, strontium, barium, cerium, lead, iron were estimated by usual gravimetric methods and guanidine by microanalytical method. The results are recorded in Table 1.

IR spectra (KBr phase) of ammonium and guanidine salts were recorded on Perkin Elmer infracord in 2—15 μ region.

Thermogravimetric analysis of ammonium salt was carried out on a Stanton Thermobalance of 1 mg sensitivity. The sample of the size 150—170 mesh was heated at a uniform rate of 3°C/min. The loss in weight was obtained as the furnace temperature is increased and the temperature recorded automatically. The TGA curve of ammonium telluro-tungstomolybdate has been given in Fig. 1.

The DTA of the ammonium salt was carried out as reported in an earlier communication.(9) The heating was carried out in nitrogen atmosphere also.

Results and Discussion

Assignment of definite structure to the heteropoly acids and their salts encounters a great difficulty on account of the large size of the molecules involved. However, the composition of ammonium telluro-tungstomolybdate has been arrived at on the basis of analytical results. The stability of the

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1) "Gmelins Handbuch der Anorganischen Chemie," System-Nummer 54, Verlag Chemie GMBH, Berlin, p. 324: *ibid.*, System Nummer 53, p. 312.

2) *Ibid.*, System Nummer 53, p. 321.

3) *Ibid.*, System Nummer 54, p. 325.

4) R. F. Weinland and H. Prause, *Z. anorg. Chem.*, **28**, 45 (1901).

5) A. Rosenheim and A. Traube, *ibid.*, **91**, 75 (1915).

6) E. Sh. Ganelina, *Zhur. Neorg. Khim.*, **7**, 1570 (1962).

7) E. Sh. Ganelina and T. N. Reznikova, *ibid.*, **8**, 1891 (1963).

8) S. Prasad and K. C. Pathak, *J. Indian Chem. Soc.*, **42**, 373 (1965).

9) S. Prasad and K. C. Pathak, *ibid.*, **42**, 698 (1965); **43**, 348 (1966).

10) S. Prasad and K. C. Pathak, ThisBu lletin, **39**, 2666 (1966).

11) S. Prasad and K. C. Pathak, *Indian J. Chem.*, **5**, 14 (1967).

TABLE 1. ANALYTICAL DATA FOR THE

Tellurotungsto-molybdate	Formula	Colour
Ammonium	$6(NH_4)_2O\cdot 2TeO_3\cdot WO_3\cdot 10MoO_3\cdot 30H_2O$	White $(NH_4)_2O$:
Silver	$6Ag_2O\cdot 2TeO_3\cdot WO_3\cdot 10MoO_3\cdot 8H_2O$	Yellowish whits Ag_2O:
Strontium	$6SrO\cdot 2TeO_3\cdot WO_3\cdot 10MoO_3\cdot 12H_2O$	White SrO:
Barium	$6BaO\cdot 2TeO_3\cdot WO_3\cdot 10MoO_3\cdot 15H_2O$	White BaO:
Cerium	$2Ce_2O_3\cdot 2TeO_3\cdot WO_3\cdot 10MoO_3\cdot 10H_2O$	Yellowish white Ce_2O_3:
Lead	$6PbO\cdot 2TeO_3\cdot WO_3\cdot 10MoO_3\cdot 6H_2O$	White PbO:
Iron	$2Fe_2O_3\cdot 2TeO_3\cdot WO_3\cdot 10MoO_3\cdot 10H_2O$	Brownish violet Fe_2O_3:
Guanidine	$6(CN_3H_6)_2O\cdot 2TeO_3\cdot WO_3\cdot 10MoO_3\cdot 20H_2O$	White $(CN_3H_6)_2O$:

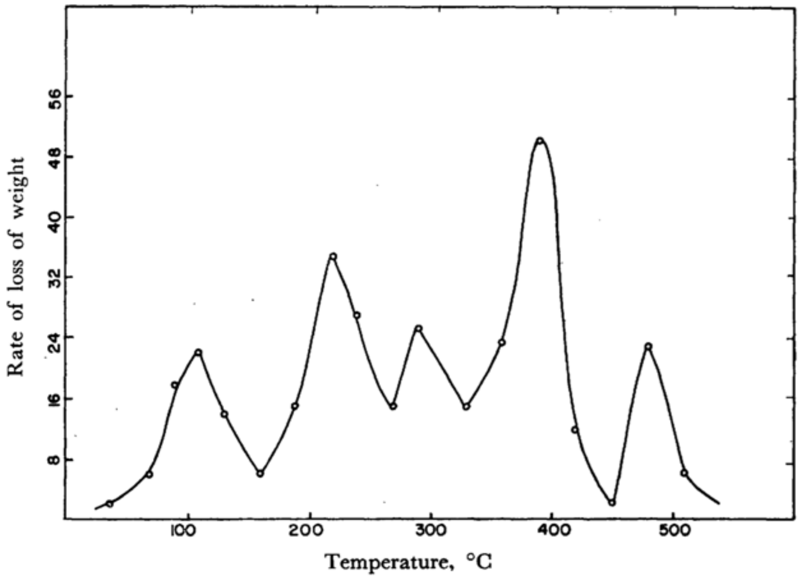

Fig. 1. TGA curve of ammonium telluro-tungstomolybdate.

anion has also been cenfirmed by passing freshly prepared solution of the ammonium salt through a cation exchange resin (Amberlite IR 120 in H+ form). The composition of the solution after passing through the resin remained the same although free acid could not be crystallized from the solution due to its highly soluble nature. The precipitated silver, strontium, barium, cerium, lead, iron and guanidine salts conform to the same formula except that the cationic part is replaced by the respective metals.

The TGA curve of ammonium telluro-tungstomolybdate (Fig. 1) shows the weight losses at 110, 222, 290, 390 and 480°C. The peaks upto 300°C are due to the dehydration of the compound which is in good agreement with the DTA curve (Fig. 2A) in which two endothermic peaks at 105 and 280°C are observed. After this temperature the decomposition of the compound occurs resulting in two peaks at 390 and 480°C.

The two endothermic peaks at 105 and 280°C in the DTA curve correspond to the dehydration of the compound. This clearly indicates that the water molecules are removed at two different temperatures, one at 105°C and the other at 280°C. The water molecules of crystallization are removed at 105°C and the water of constitution at a considerably higher temperature (280°C).

The characteristic exothermic peak at 380°C in DTA curve is either due to the oxidation or decomposition of ammonia at the surface of MoO_3 which acts as a ctalyst. The presence of exothermic peak due to the catalytic oxidation of ammonia has been observed by other workers while studying the thermal decomposition of ammonium molybdate[12] and ammonium vanadate[13]. The oxidation of ammonia in the last stage of decomposition has been suggested as a possible source of the exothermic heat. The nitrogen atmosphere

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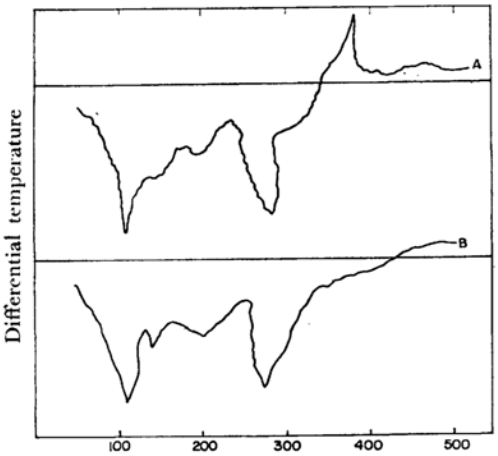
12) E. Ma, This Bulletin, **37**, 171 (1964).

13) M. Taniguchi and T. R. Ingraham, *Can. J. Chem.*, **42**, 2467 (1964).

VARIOUS TELLURO-TUNGSTOMOLYBDATES

Metallic oxide %		TeO_3 %		WO_3 %		MoO_3 %		H_2O %	
Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
10.68	10.86	12.60	12.22	7.82	8.07	50.42	50.06	17.68	18.79
39.88	39.07	10.01	9.87	6.38	6.52	39.82	40.44	3.91	4.05
21.30	21.74	12.58	12.27	7.99	8.11	50.88	50.30	7.25	7.55
28.02	28.64	11.18	10.93	7.08	7.22	45.54	44.79	8.18	8.41
23.32	22.96	12.04	12.28	8.32	8.11	49.86	50.32	6.46	6.29
39.24	38.60	10.28	10.13	6.48	6.68	40.95	41.48	3.04	3.11
12.90	12.67	13.62	13.93	9.31	9.20	57.32	57.06	6.85	7.14
25.10	25.52	10.72	10.98	7.16	7.25	45.48	44.99	11.54	11.26



Furnace temperature, °C

Fig. 2. Differential thermal analysis curves.
A. Ammonium telluro-tungstomolybdate
B. Ammonium telluro-tungstomolybdate in nitrogen

gives normal endothermic peaks (Fig. 2B) showing thereby that there is no oxidation of ammonia.

In IR spectra of ammonium and guanidine salts, the strong peaks at 3100 cm^{-1} and 3300 cm^{-1}, 1610 cm^{-1} and 1650 cm^{-1} respectively are due to the O–H stretch and O–H bending of water molecules present. In case of ammonium salt a strong peak at 1400 cm^{-1} is attributed to the characteristic deformation vibration of NH_4^+ ion [$\delta(NH_4)$], whereas a strong peak at 1550 cm^{-1} in case of guanidine salt is due to C=N stretch and N–H deformation of the guanidine molecule. The strong peak at 3300 cm^{-1} in case of guanidine salt may not be pure O–H stretch as it is being overlapped by N–H stretch vibrations of guanidine.

The vibrational bands appearing at 910 cm^{-1} in ammonium salt, 940 cm^{-1} and 880 cm^{-1} in guanidine salt may be due to mixed Mo–O and W–O vibrations. The regions of the absorption of the above vibrations are so close that in the compounds they overlap to a considerable extent to form broad bands. The argument may not be exactly valid since no discrete Mo–O or W–O modes of vibrations are present.

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