The Preparation of Heteropoly Salts of Selenium and Molybdenum

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Gibbs[1] and Péchard[2] seem to have been the first to observe the formation of heteropoly acids and their salts of selenium and molybdenum with different ratios of selenium dioxide and molybdenum trioxide. Rosenheim and Krause[3] prepared ammonium salt, $3(NH_4)_2O\cdot2SeO_2\cdot8MoO_3\cdot6H_2O$, by treating one mole of selenium dioxide with one mole of molybdenum trioxide; they also prepared another type of ammonium salt, $2(NH_4)_2O\cdot5SeO_2\cdot5MoO_3\cdot8H_2O$. Prandtl and Blochin[4] isolated ammonium salt ($2(NH_4)_2O\cdot2SeO_2\cdot5MoO_3\cdot3H_2O$), rubidium salt ($2Rb_2O\cdot2SeO_2\cdot5MoO_3\cdot5H_2O$), and also barium salt ($2BaO\cdot2SeO_2\cdot5MoO_3\cdot7H_2O$). By acidifying a boiling ammoniacal solution of selenium dioxide and molybdenum trioxide in a molar ratio of 1 : 6 with nitric acid, Prandtl, Blochin and Obpacher[5] obtained a compound with the composition of $(NH_4)_2O\cdot SeO_2\cdot6MoO_3\cdot4H_2O$.

The present communication will deal with the preparation of and the properties of two new ammonium molybdoselenites and their heavy metal salts, which have been confirmed by conductometric titrations.

Experimental and Results

All the chemicals used were of Merck's or B.D.H. quality of purity.

Ammonium Salt of Molybdoselenite, Type, I.—*Preparation.*—Seleneous acid and molybdic acid in the molar ratio of 1 : 4 were dissolved in aqueous ammonia and refluxed for 6 hr. at about 110°C. The clear solution thus obtained was evaporated to a small volume and then acidified with acetic acid to pH 3. On cooling, a white crystalline powder appeared; this was then recrystallized from water. It was analyzed after dried by successive washings with alcohol and finally by keeping it in a vacuum desiccator.

Analytical Results and Properties. — Found: $(NH_4)_2O$, 9.39; SeO_2, 13.82; MoO_3, 42.90; H_2O, 33.89. Calcd. for $3(NH_4)_2O\cdot2SeO_2\cdot5MoO_3\cdot30H_2O$: $(NH_4)_2O$, 9.62; SeO_2, 13.52; MoO_3, 44.10; H_2O, 32.76%.

It is a white crystalline powder stable at room temperature, but it decomposes when heated, giving a residue containing molybdenum trioxide and a small amount of selenium dioxide. It is soluble in water, and insoluble in alcohol, ether, benzene and nitrobenzene. Dilute nitric acid or dilute hydrochloric acid produces a slight change in color when boiled with this compound.

Silver Salt of Molybdoselenite, Type I. — A yellowish white compound was produced when silver nitrate was added to the ammonium salt solution.

Found: Ag_2O, 37.15; SeO_2, 11.09; MoO_3, 36.46; H_2O, 15.42. Calcd. for $3Ag_2O\cdot2SeO_2\cdot5MoO_3\cdot17H_2O$: Ag_2O, 36.6; SeO_2, 11.4; MoO_3, 37.14; H_2O, 15.83%.

Lead Salt of Molybdoselenite, Type I.—This salt was prepared by adding an aqueous solution of lead nitrate to the ammonium salt solution. It is dirty white in color.

Found: PbO, 42.1; SeO_2, 13.3; MoO_3, 40.2; H_2O, 3.4. Calcd. for $3PbO\cdot2SeO_2\cdot5MoO_3\cdot3H_2O$: PbO, 41.01; SeO_2, 13.09; MoO_3, 42.1; H_2O, 3.2%.

Ferric Salt of Molybdoselenite, Type I.—This is a powdery, yellow precipitate, insoluble in water and alcohol, formed when a dilute solution of ferric chloride is added in excess to the solution of the ammonium salt.

Found: Fe_2O_3, 10.09; SeO_2, 14.26; MoO_3, 45.6; H_2O, 27.5. Calcd. for $Fe_2O_3\cdot2SeO_2\cdot5MoO_3\cdot24H_2O$: Fe_2O_3, 10.4; SeO_2, 14.48; MoO_3, 46.9; H_2O, 28.4%.

Cerous Salt of Molybdoselenite, Type I.—A light yellow salt is obtained by adding a cerous nitrate solution to a dilute solution of the ammonium salt.

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1) W. Gibbs, *Ber.*, **18**, 1089 (1885).

2) M. E. Péchard, *Ann. chim. phys.*, (6) **30**, 395 (1893).

3) A. Rosenheim and L. Krause, *Z. anorg. u. allgem. Chem.*, **118**, 177 (1921).

4) W. Prandtl and W. von Blochin, ibid., **93**, 45 (1915).

5) W. Prandtl, W. von Blochin and H. Obpacher, ibid., **93**, 70 (1915).

TABLE I. COMPOSITIONS OF LEAD, FERRIC AND CEROUS MOLYBDOSELENITE, TYPE I, ESTIMATED BY CONDUCTIVITY TITRATIONS

Volume of titration mixture: 65 ml.
Temperature: 30±0.5°C

Molarity of ammonium salt	Molarity of titrant	Volume of titrant in ml.	Molar ratio ammonium salt : titrant
	Titration with lead nitrate		
6.738×10^{-5}	10.09×10^{-3}	0.64	1 : 2.94
10.107×10^{-5}	10.09×10^{-3}	0.97	1 : 2.96
13.476×10^{-5}	10.09×10^{-3}	1.30	1 : 2.94
16.845×10^{-5}	10.09×10^{-3}	1.59	1 : 2.94
20.214×10^{-5}	10.09×10^{-3}	1.94	1 : 2.95
	Titration with ferric chloride		
10.107×10^{-5}	10.15×10^{-3}	0.65	1 : 2.95
13.476×10^{-5}	10.15×10^{-3}	0.86	1 : 2.93
16.845×10^{-5}	10.15×10^{-3}	1.08	1 : 2.94
20.214×10^{-5}	10.15×10^{-3}	1.31	1 : 2.96
	Titration with cerous nitrate		
10.107×10^{-5}	10.28×10^{-3}	0.63	1 : 2.91
13.476×10^{-5}	10.28×10^{-3}	0.84	1 : 2.94
16.845×10^{-5}	10.28×10^{-3}	1.05	1 : 2.93

Found: Ce_2O_3, 23.31; SeO_2, 15.1; MoO_3, 48.94; H_2O, 10.7. Calcd. for $Ce_2O_3\cdot 2SeO_2\cdot 5MoO_3\cdot 9H_2O$: Ce_2O_3, 22.9; SeO_2, 15.5; MoO_3, 50.27; H_2O, 11.3%.

Ammonium Salt of Molybdoselenite, Type II.—This compound was prepared by dissolving seleneous acid and molybdic acid in a molar ratio of 1 : 4 in aqueous ammonia and by then acidifying the boiling solution with nitric acid. A yellow compound was precipitated. The compound is insoluble in water, alcohol, and ether, but soluble in dilute hydrochloric acid.

Found: $(NH_4)_2O$, 10.56; SeO_2, 10.18; MoO_3, 67.4; H_2O, 11.86. Calcd. for $4(NH_4)_2O\cdot 2SeO_2\cdot 9MoO_3\cdot 12H_2O$: $(NH_4)_2O$, 10.71; SeO_2, 11.43; MoO_3, 66.8; H_2O, 11.1%.

Conductometric Titrations.—0.01 M solutions of ammonium molybdoselenite, type I, and the titrants (i. e., silver nitrate, lead nitrate, ferric chloride and cerous nitrate), were prepared in conductivity water. The titrants were added from a micro buret in small amounts to different volumes of the ammonium salt solution (0.001 M) diluted to 65 ml., the mixture was stirred well, and the readings were recorded after allowing the precipitate to settle down. The end point was obtained graphically by plotting the volume of the titrant added against the conductance. The results are given in Table I.

Discussion

The compounds present great difficulty in determining their structure because of the large size of the molecule. However, the compositions of the salts have been determined on the basis of our analytical results, which have been proved further by conductometric titrations.

Conductometric titrations of the ammonium salt, type I, with the titrants with univalent, bivalent or trivalent cations have been carried out. In all the cases except silver nitrate, sharp breaks at the molar ratios of the ammonium salt to the titrant of 1 : 3 (divalent) and 1 : 2 (trivalent) cations lend support to the formation of the salts reported.

In the case of silver nitrate, apparently there is no formation of the salt at that particular dilution; this results in a regular increase in the conductance giving a straight line.

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