485. *Heteropoly-tungstic Acids and Heteropoly-tungstates. Part II. 11-Tungsto-aluminic, -chromic(III), and -manganic(III) Acids and their Salts.*

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Following the general methods outlined in Part I (preceding paper), three further 11-heteropoly-tungstic acids have been isolated, all with tervalent central ions. These are 11-tungsto-aluminic, -chromic(III), and -manganic(III) acid. The first two have been obtained in solid form, the third in solution only. From all three, salts have been prepared and characterised. A microscopical examination has been made of some of the salts to determine their principal optical constants. Some physical constants, including specific gravity and pH of aqueous solutions, have been noted.

By saturation of ammonium paratungstate solutions with aluminium hydroxide, Daniels (*J. Amer. Chem. Soc.*, 1908, **30**, 1846) obtained a colourless semi-transparent mass, assumed to be the ammonium salt of a tungstoaluminic acid, and from it prepared salts of metals by double decomposition. The free acid could not be isolated. Various heteropoly-tungstates of tervalent chromium and manganese, prepared by similar methods, have been described by Balke and Smith (*ibid.*, 1903, **25**, 1230), Daniels (*loc. cit.*), and Rogers and Smith (*ibid.*, 1904, **26**, 1745). These products were of variable composition, giving values of the ratio $R_2O_3 : WO_3$ between 1 : 9 and 1 : 12, and according to Rosenheim (Abegg's " Handbuch," Vol. 4, Part 1, p. 1050) they were not definite compounds. Of the corresponding molybdenum compounds, only 6-molybdo-aluminates and -chromates are known, no compounds of higher series being formed. Tervalent manganese does not appear to form molybdate complexes, but quadrivalent manganese does, giving apparently a series of 9-molybdomanganates (Friedheim and Keller, *Ber.*, 1906, **39**, 4301).

Since electrolytes are virtually absent in saturations of ammonium paratungstate with metallic hydroxides, there is nothing to prevent extensive peptisation, and the products obtained by Daniels *et al.* undoubtedly contained an excess of metallic hydroxide, accounting for the low values of the ratio $R_2O_3 : WO_3$. The ready peptisation of ferric hydroxide in saturations of sodium paratungstate (Part I) confirms this view. Rosenheim (*loc. cit.*) is therefore justified in assuming that these tungsto-aluminates, -chromates, and -manganates are not definite compounds.

The solubilities of the alkali 6-heteropoly-tungstates and -molybdates are usually sufficiently low to permit the preparation of well-defined crystalline specimens by direct saturation of boiling alkali paratungstate or paramolybdate solutions with the appropriate metal nitrate or chloride. In some cases, however, where a very insoluble double alkali metal–metal paratungstate is formed, indirect methods must be used. The alkali salts of heteropoly-acids of higher series containing metallic substituents are much more soluble, and it is difficult to obtain authentic specimens from the complex mother-liquors derived from saturations. The isolation of the free heteropoly-acids is thus most desirable.

The general methods of preparation have been set out in Part I. Boiling sodium para-tungstate solutions, with a pH >6.4, are capable of precipitating aluminium, chromium, and manganic hydroxides from salts of the metals. Saturation with aqueous solutions of aluminium

nitrate runs smoothly, with virtually no secondary precipitation, the stoicheiometric basis being the same as that used in the preparation of 11-tungstoferric(III) acid. The pH of the saturated mother-liquor is <4 and the ether addition compound of 11-tungstoaluminic acid can be isolated by extraction with ether and 6M-sulphuric acid. Saturation of boiling sodium paratungstate solutions with aqueous chromium nitrate proceeds smoothly at first, but in the later stages precipitation of a green sodium chromium tungstate (approximately of paratungstate type) takes place. The pH of the saturated mother-liquor is between 5 and 6, and attempts at extraction with ether and 6M-sulphuric acid lead only to extensive precipitation of tungstic acid. It is necessary to acidify the hot mother-liquor with dilute nitric acid until the pH has fallen to 3. After cooling, extraction with ether and 6M-sulphuric acid can be carried out, though some emulsification is usual. The ready hydrolysis of manganic salts makes the use of dilute solutions of these as saturating agents scarcely practicable. Three methods of preparation have been used to obtain the saturated mother-liquor from which 11-tungstomanganic(III) acid can be extracted : (1) Saturation of boiling sodium paratungstate solution with an excess of freshly prepared manganic hydroxide, dilute nitric acid being slowly added in 10% excess of that required to convert the paratungstate into metatungstate. (2) Addition of solid potassium hexacyanomanganate(III), slowly and in small amounts to a boiling sodium paratungstate solution; hydrolysis to manganic hydroxide takes place at once, and this is readily taken up by the paratungstate. Because of the alkaline hydrolysis products of the hexacyanomanganate the solution must be acidified while hot with dilute sulphuric acid to bring the pH below 4 before extraction of the 11-tungstomanganic(III) acid with ether and 6M-sulphuric acid. (3) The best method is saturation of boiling sodium paratungstate solutions with small successive portions of an intimate mixture of manganous sulphate and potassium persulphate; this is similar to Friedheim and Keller's method (*loc. cit.*) for the preparation of the molybdomanganates. Oxidation of Mn^{2+} to Mu^{3+} takes place *in situ*, and the decomposition products of the persulphate give a mother-liquor of pH <4, from which, after removal of suspended manganese oxides, 11-tungstomanganic acid can be extracted without difficulty by Drechsel's method.

For reasons stated in Part I, the ether addition compounds obtained by Drechsel's method contain, in addition to tungsto-aluminic, -chromic, or -manganic acid, substantial amounts of metatungstic acid. From the first two acids this can be removed by repeated evaporation of their aqueous solutions, followed by baking, but the stability of the third acid is too low to withstand this treatment, and the acid has been obtained only in aqueous solution.

Analysis of the free acids and their salts shows that they are of similar composition to 11-tungstoferric(III) acid, the value of $R_2O_3 : WO_3$ approximating to 1 : 22. The four acids may thus be formulated as $R_2O_3,22WO_3,aq.$ or $H_{10}[R_2W_{22}O_{74}],aq.$ The solubility of the acids in water is so high that only crystal aggregates can be obtained, though octahedral outlines appear on long keeping of concentrated solutions. Isomorphism is, however, shown by the salts, which vary in basicity between 8 and 10, and are all substantially hydrated. Tungsto-aluminic acid and its salts are colourless, the chromic acid and its salts pale green or, exceptionally, violet, and the manganic acid and its salts intensely deep red. The ammonium, potassium, and barium salts are readily soluble in water, and crystallise well, but usually effloresce when kept, breaking down into microcrystalline powders. Isomorphism is very marked with the potassium and barium salts. The guanidine and silver salts are much less soluble, giving only small but well-defined crystals.

A microscopic examination has been made of some of the salts to determine their principal optical constants. The colour of the tungstomanganates is dependent on the colour of the crystal sections, varying from a light yellow in very thin sections to a dark red. Similarly, the tungstochromates appear colourless in thin sections and light green in thicker, while the tungstoaluminates are colourless. Typically octahedral cleavage is shown by nearly all crystal fragments, triangular views being of most frequent occurrence, although occasionally rectangular or hexagonal views are presented. Ammonium tungstoaluminate is uniformly isotropic and is therefore cubic. Ammonium tungsto-chromate and -manganate appear to exist as at least two different crystalline hydrates, one of which is cubic. Ammonium tungstomanganate, when dehydrated over phosphoric acid, is also cubic, but when exposed to the atmosphere it gradually develops weak polarisation colours when observed in polarised light. Ammonium tungsto-ferrate behaves similarly, the more hydrated form in each case being only weakly birefringent, and of lower refractive index than the dehydrated form. The guanidine salts of all three acids crystallise in rectangular prisms, which generally lie on the microscope slide so that the plane of the bisectrix is inclined at only a small angle to the vertical, thus allowing their optical axial figures to be easily observed. The guanidine salts are uniformly biaxial negative in

character and are most probably of monoclinic symmetry. Silver tungstomanganate forms rectangular prisms, which extinguish parallel to their principal length. There are indications that several of the other salts prepared are of cubic symmetry, including barium tungstomanganate and potassium and cæsium tungstoaluminates, but owing to the tendency to efflorescence of the barium and potassium salts, especially when crushed, observation is difficult. Crushed crystal fragments were used in all cases except for the guanidine salts, which were of convenient size for microscopic examination as obtained directly from their mother-liquors. The refractivity of these heteropoly-salts is very high; only with ammonium tungsto-aluminate was the value below 1·7. The measurement thus required media of high refractive index, a saturated solution of the heavy-metal iodides (Sb, As, Sn, Bi) in methylene iodide being used for this purpose, dilution with more solvent being made as required.

<div align="center">EXPERIMENTAL.</div>

The starting material for the preparation of the acids was a solution of sodium paratungstate, obtained by adding 194·4 ml. of N-nitric acid to a solution of 56·12 g. of sodium tungstate dihydrate in 400 ml. of water.

Tungstoaluminic Acid.—To the boiling sodium paratungstate solution, mechanically stirred, was added, during 20—24 hours, a solution of 10 g. of hydrated aluminium nitrate in 500 ml. of water. Complete hydrolysis of the aluminium nitrate being assumed, this gives nitric acid 30% in excess of that required (60·8 ml. of N.) to convert the para- into meta-tungstate (cf. preceding paper, p. 2364). The precipitate formed with each drop of aluminium nitrate solution redissolved at once, and practically no permanent precipitate remained at the end of the saturation. The pH of the cold solution was below 4.

Tungstochromic Acid.—Under similar conditions, 8·1 g. of chromium nitrate nonahydrate in 500 ml of water gave rise to a pale green precipitate of a sodium chromium tungstate from an early stage; this partly redissolved at first but became permanent in the later stages. An average sample of this substance had the empirical formula $2Na_2O,Cr_2O_3,9WO_3,33H_2O$, and so was rather more basic than paratungstate. The pH of the cold solution was above 5, showing the presence of unchanged para-tungstate. To remove this, 50 ml. of 4N-nitric acid were slowly added to the hot solution, the final pH being below 4. In the hope that chromium would enter the paratungstate nucleus more readily when present in anionic form, $K_3Cr(CN)_6$ and K_3CrF_6 were used instead of chromium nitrate, but hydrolysis of these salts was very incomplete, and their use was less satisfactory.

Tungstomanganic Acid.—Three methods of preparation were used, the third being the best. (1) To the boiling paratungstate solution were added 10 g. of fresh manganic hydroxide, prepared according to Meyer and Nerlich (*Z. anorg. Chem.*, 1921, **116**, 125). To the mechanically stirred suspension were added during 20—24 hours 67 ml. of N-nitric acid (10% excess) made up to 500 ml. The dark red colour of tervalent manganese deepened gradually, but in at least half the preparations hydrolysis took place quite suddenly in the later stages, precipitating the tervalent manganese already taken up, and leaving only a pale yellow solution, containing small amounts of a sodium manganous paratungstate. (2) Similarly, on addition of 8 g. of $K_3Mn(CN)_6$ simultaneously with 120 ml. of N-nitric acid (to react with the alkaline hydrolysis products), the $K_3Mn(CN)_6$ was seen to be immediately hydrolysed, and the hydroxide was rapidly taken up by the paratungstate. Appreciable amounts of H_2MnO_3 remained at the end of saturation. (3) To avoid the necessity for acidification during saturation, Friedheim and Keller's method (*loc. cit.*) for the preparation of molybdomanganates was tried, an intimate mixture of manganese sulphate tetrahydrate (7 g.) and potassium persulphate (9 g.) being added under the usual conditions to the paratungstate. The deep red colour of Mn(III) became more intense as saturation proceeded. There was little secondary precipitation of H_2MnO_3, and the final pH, owing to hydrolysis of the persulphate ion, was below 4, no acidification being necessary.

The Free Acids.—On completion of the saturations, the solutions were concentrated to about 200 ml., cooled, and kept at 6° for 20—24 hours to allow any unchanged paratungstate (not necessarily absent at pH values <4) to separate. The solutions, after filtration, were cooled in ice, mechanically stirred, and, after the addition of 300—400 ml. of dry ether, acidified slowly with 400 ml. of 6M-sulphuric acid. With tungstochromic acid emulsification was frequent and could not be avoided.

The mixture, on being transferred to a separating funnel, formed three layers, the lowest being the ether addition compound of the heteropoly-acid, colourless in the case of tungstoaluminic acid, pale green with tungstochromic acid, and an intense dark red with tungstomanganic acid. These compounds were freed from entrained mother-liquor by dropping them through three successive portions of dry ether. They were finally run into water, and the ether was removed by an air current. The first two acids were finally isolated in solid form by evaporation to dryness, baking at 120—130°, extraction of the residue with water, and concentration *in vacuo* over sulphuric acid, as for tungstoferric acid. Tungstomanganic acid was too unstable to withstand this treatment, but its aqueous solution is comparatively stable and gives the corresponding salts without difficulty.

11-*Tungstoaluminic acid* is a colourless solid, very soluble in water, obtained only as crystal aggregates; it shows no definite break in the temperature–dehydration curve (Found : Al_2O_3, 1·66; WO_3, 84·70; H_2O, 14·31. $Al_2O_3,22WO_3,49H_2O$ requires Al_2O_3, 1·67; WO_3, 83·83; H_2O, 14·34%). Its apparent basicity was 10, as found by potentiometric titration with sodium hydroxide.*

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* This acid can be represented as $H_{10}[Al_2W_{22}O_{74}],44H_2O$, and the other acids and their salts can be formulated as if containing a similar complex ion.

Ammonium 11-*tungstoaluminate*, prepared from aqueous solutions of the free acid by saturation with ammonium nitrate, formed perfectly transparent colourless octahedra, readily soluble in water [Found : $(NH_4)_2O$, 3·12; Al_2O_3, 1·63; WO_3, 84·07; H_2O, 10·43. $4(NH_4)_2O,Al_2O_3,22WO_3,36H_2O$ requires $(NH_4)_2O$, 3·43; Al_2O_3, 1·68; WO_3, 84·20; H_2O, 10·69%]; d 4·848; n 1·4599; pH of an approx. 0·002M-solution, 3·50. The crystals were stable in air, but became opaque on long exposure. From the original nitrate-containing mother-liquor the salt separates as rectangular prisms, recrystallising from water as octahedra.

Guanidine 11-*tungstoaluminate* was prepared by addition of guanidine hydrochloride solution to a solution of the free acid. It separated as a microcrystalline solid, giving, on recrystallisation from water, colourless leaflets or small rectangular prisms [Found : $(CN_3H_6)_2O$, 10·37; Al_2O_3, 1·69; WO_3, 84·78; H_2O, 3·16. $5(CN_3H_6)_2O,Al_2O_3,22WO_3,11H_2O$ requires $(CN_3H_6)_2O$, 11·00; Al_2O_3, 1·67; WO_3, 83·79; H_2O, 3·55%]; d 4·145. It was sparingly soluble in water; pH of approx. 0·002M-solution, 4·72. Crystals of this salt are biaxial negative and of small optic axial angle. The highest refractive index observed exceeds 1·78; the lowest is 1·768.

Potassium 11-tungstoaluminate, prepared from concentrated aqueous solutions of potassium nitrate and the free acid, formed large colourless octahedra, d 5·45, fairly soluble in water, but relatively easily hydrolysed when its solution is heated. The crystals are efflorescent, rapidly breaking down to a white microcrystalline powder on exposure to air. The pH of an approx. 0·002M-solution was 4·72. A complete analysis was not obtained, but $Al_2O_3 : WO_3$ was determined as *ca.* 1 : 22.

The barium and the cæsium salt are less well defined. The former is very soluble in water, separating from concentrated solutions as a white microcrystalline powder; the latter crystallises as colourless opaque prisms, sparingly soluble in water. Solutions of both salts are readily hydrolysed on heating.

11-Tungstochromic(III) acid was a pale green solid, obtained only as crystal aggregates from concentrated aqueous solutions. It was very soluble in water. No satisfactory analysis has been obtained for this acid, though it forms well-defined salts.

Ammonium 11-*tungstochromate*(III), prepared from concentrated aqueous solutions of ammonium nitrate or chloride and the free acid, exists as at least two different stable hydrates. The lower hydrate forms large transparent violet octahedra, perfectly isotropic. The higher hydrate forms large green octahedra or rectangular prisms. These are uniaxial positive, and probably of tetragonal symmetry. The green hydrate has refractive indices $\omega = 1·775$, $\varepsilon = 1·736$; d 4·619; and the pH of a 0·002M-solution is 2·83. Both hydrates are very soluble in water and are fairly stable in air [Found : $(NH_4)_2O$, 3·07; Cr_2O_3, 2·44; WO_3, 82·10; H_2O, 12·39. Green $4(NH_4)_2O,Cr_2O_3,22WO_3,43H_2O$ requires $(NH_4)_2O$, 3·33; Cr_2O_3, 2·44; WO_3, 81·81; H_2O, 12·41%].

Barium 11-*tungstochromate*(III), prepared from concentrated aqueous solutions of the free acid and barium chloride, or by direct neutralisation of the free acid with barium carbonate, forms large pale green transparent octahedra, rapidly efflorescent, giving a pale green microcrystalline powder (Found : BaO, 12·01; Cr_2O_3, 2·27; WO_3, 74·98; H_2O, 11·36. $5BaO,Cr_2O_3,22WO_3,43H_2O$ requires BaO, 11·28; Cr_2O_3, 2·24; WO_3, 75·08; H_2O, 11·39%); d 4·519; pH of 0·002M-solution, 2·95.

Guanidine 11-*tungstochromate*(III) separates as a pale green microcrystalline powder when aqueous solutions of guanidine hydrochloride and the free acid are mixed. Recrystallisation from water, in which it is sparingly soluble, gives small pale green leaflets or rectangular prisms [Found : $(CN_3H_6)_2O$, 11·39; Cr_2O_3, 2·47; WO_3, 83·24; H_2O, 2·61. $5(CN_3H_6)_2O,Cr_2O_3,22WO_3,9H_2O$ requires $(CN_3H_6)_2O$, 11·01; Cr_2O_3, 2·50; WO_3, 83·83; H_2O, 2·66%]. All three refractive indices are greater than 1·7; small optic axial angle; d 4·284; pH of 0·002M-solution, 2·54.

Potassium 11-tungstochromate(III) was prepared from concentrated aqueous solutions of potassium nitrate or chloride and the free acid. It forms large pale green transparent octahedra, d 4·976, rapidly efflorescing to a microcrystalline powder. Its aqueous solutions are readily hydrolysed; pH of approx. 0·002M-solution, 2·88. No complete analysis was obtained but $Cr_2O_3 : WO_3$ was determined as about 1 : 22.

11-*Tungstomanganic*(III) *Acid.*—This acid was obtained only in admixture with metatungstic acid, but its aqueous solution was stable and was used for the preparation of salts. There is no reduction on exposure to daylight.

Ammonium salt. Prepared from concentrated solutions of ammonium nitrate and the free acid, chloride ions being excluded because of their reducing properties, this *salt* forms large transparent deep red (almost black) octahedra [Found : $(NH_4)_2O$, 3·44; Mn_2O_3, 2·44; WO_3, 80·21; H_2O, 13·75. $4(NH_4)_2O,Mn_2O_3,22WO_3,49H_2O$ requires $(NH_4)_2O$, 3·27; Mn_2O_3, 2·48; WO_3, 80·35; H_2O, 13·89%], d 3·844, very soluble in water (pH of 0·002M-solution, 5·02), and becoming opaque on exposure to the air. Dehydration over phosphoric oxide gives isotropic crystals, n 1·798. There is also a higher hydrate which is anisotropic, probably tetragonal, and of lower refractive index.

Barium salt. Prepared by direct neutralisation of aqueous solutions of the free acid with barium carbonate, this *salt* forms large deep red transparent octahedra (Found : BaO, 12·64; Mn_2O_3, 2·47; WO_3, 79·94; H_2O, 5·63. $5BaO,Mn_2O_3,22WO_3,20H_2O$ requires BaO, 12·00; Mn_2O_3, 2·47; WO_3, 79·89; H_2O, 5·63%), fairly stable in air. It is isotropic; d 4·178; n >1·7; pH of 0·002M-solution, 4·28.

Guanidine salt. This *salt* was prepared by mixing aqueous solutions of guanidine hydrochloride and the free acid. It is sparingly soluble, recrystallising from water as reddish-brown rectangular prisms, d 4·322 [Found : $(CN_3H_6)_2O$, 11·73; Mn_2O_3, 2·51; WO_3, 80·87; H_2O, 4·90. $5(CN_3H_6)_2O,Mn_2O_3,22WO_3,17H_2O$ requires $(CN_3H_6)_2O$, 10·74; Mn_2O_3, 2·53; WO_3, 81·81; H_2O, 4·90%]; pH of approx. 0·002M-solution, 4·49. Crystals of this salt are biaxial negative, and of small optical axial angle; the highest refractive index observed, γ, was 1·762, the lowest, α, being 1·728.

Silver salt. This was most probably of tetragonal symmetry; $n > 1.7$; d 5.828; pH of 0.002M-solution, 2.44. The ratio $Mn_2O_3 : WO_3$ was determined as approx. 1 : 22.

Potassium salt. Prepared from concentrated aqueous solutions of potassium nitrate and the free acid, this salt forms large, transparent, deep red octahedra, d 5.094, readily effloresing to give a reddish-brown microcrystalline powder. Aqueous solutions hydrolysed extensively on boiling; pH of 0.002M-solution, 4.47; $n > 1.7$. The ratio $Mn_2O_3 : WO_3$ was found to be approx. 1 : 22.

The more soluble salts separate very slowly from their mother-liquors, in some cases only after several weeks at 6°.

Refractive-index Measurements.—A suitable medium was obtained by dissolving 20 g. of iodoform, 10 g. of sulphur, 8 g. of AsI_3, 5 g. of BiI_3, 5 g. of SnI_2, and 4 g. each of As_2S_3 and Sb_2S_3 in 50 g. of methylene iodide, and filtering. This solution was diluted with methylene iodide as required. As the refractive indices to be measured, with the exception of that of ammonium 11-tungstoaluminate, were outside the range of the Abbé refractometer, they were measured indirectly by dilution of the liquid with benzene or carbon tetrachloride, the mixture rule being used to calculate the index required. These values were checked by direct measurement, using a cell made from a microscope slide with a 0.5″ diameter hole cut in it, the base being a cover-slip cemented to the lower side. This gave a depth of liquid within the working distance of the microscope high-power objective.

Analysis.—Barium was determined as sulphate by double decomposition with dilute sulphuric acid, the anions of the free acids being sufficiently stable to permit this. Aluminium was determined by precipitation as hydroxide after removal of tungsten as cinchonine tungstate, both being ignited to the respective oxides. Chromium was determined by oxidation to chromate in alkaline solution, reduction with excess of ferrous sulphate, and back-titration. Manganese was precipitated as oxide with hydrogen peroxide in alkaline solution, converted into sulphate and weighed as such. Reduction of the tungstomanganates in hydrochloric–hydrobromic acid solution, followed by distillation of the bromine into excess of potassium iodide and titration of the iodine set free, established the tervalent state of the manganese and gave a confirmatory value for the metal. Ammonia was determined by distillation into standard acid, and guanidine by the micro-Dumas method (J.C.). Water was determined by dehydration at progressively rising temperatures, finally by ignition. No breaks in the temperature–dehydration curves were obtained corresponding to lower hydrates, decomposition usually beginning above 160°.

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