526. *Heteropolytungstic Acids and Heteropolytungstates. Part III.** 12-*Tungstozincic Acid and its Salts, and Some* 12-*Tungsto*-3-*zincates.*

By Donald H. Brown and John A. Mair.

Zinc forms two heteropoly-acids with tungsten, a 3 : 12- and a 1 : 12-acid. The 3 : 12-acid was only identified through its salts, as the free acid was not isolated. The 1 : 12-acid was isolated, as were a number of its salts. The structure of cæsium 12-tungstozincate was shown to be similar to that of cæsium 12-tungstophosphate.

The methods of preparation of the heteropoly-acids of zinc and tungsten involve the addition of a zinc salt to a hot solution of sodium paratungstate or metatungstate. The salts of 12-tungsto-3-zincic acid, which have solubilities comparable with those of the corresponding normal paratungstates, are removed by fractional crystallisation. The 12-tungstozincic acid is extracted from the mother-liquors by the formation of the ether addition compound.[1]

The salts obtained of 12-tungsto-3-zincic acid showed different apparent basicities,

---

* Part II, *J.*, 1950, 2372.

[1] Drechsel, *Ber.*, 1887, **20**, 1452.

a maximum of nine being exhibited in the guanidine and nickel salts. When the salts were heated in a thermal balance no apparent break was observed in the curve of water lost versus temperature. Thus, presumably, the oxide lattice broke down before the salt was completely dehydrated. In an attempt to obtain the free acid, a solution of the sodium salt was passed through a cation-exchange resin saturated with hydrogen ions. The effluent was shown to contain a mixture of 12-tungstozincic acid and metatungstic acid. Both zinc and tungsten were retained in the column. The passage of the sodium salt solution down the column can be compared to a slow acidification. This was confirmed by slowly acidifying a solution of the sodium salt during 6 hours at about 90°. Again some 12-tungstozincic acid and some metatungstic acid were obtained.

From the original preparations the 12-tungstozincic acid was isolated as a yellow crystalline solid. Its solubility was comparable to that of metatungstic acid from which it was separated by baking on a steam-bath. Because of the low thermal stability of metatungstic acid it decomposed, giving tungstic acid and leaving as the only soluble product 12-tungstozincic acid. To determine the basicity of the acid, a sample was heated on the thermal balance. No break in the curve was observed, again probably because the oxide lattice broke down during dehydration. A solution of 12-tungstozincic acid, titrated potentiometrically against sodium hydroxide solution, gave a mean equivalent weight of 572. From the molecular weight of $ZnO,12WO_3,29H_2O$, for a six-basic acid, the equivalent weight is 565. These results are sufficiently close to suggest that the acid has a basicity not greater than six. This is confirmed in the majority of the salts prepared. 12-Tungstozincic acid was found, by displacement of toluene from a density bottle, to have a density of 4·14 g./c.c.

12-Tungstozincic acid and its salts resemble closely in chemical behaviour 12-tungstophosphoric acid and its salts. Keggin[2] and Santos[3] analysed the structures of 12-tungstophosphoric acid and cæsium 12-tungstophosphate. The cæsium salt of 12-tungstozincic acid was used for comparison as there always appeared to be slight decomposition, with subsequent formation of tungstic acid, from 12-tungstozincic acid itself. Powder photographs were taken with the specimen mounted in a fine Lindemann-glass tube. The structure was found to be cubic with a unit-cell length 11·86 Å. This value is close to that (11·83 Å) found by Santos for cæsium 12-tungstophosphate. The intensities were measured and found to agree with those calculated from a structure similar to that proposed for cæsium 12-tungstophosphate, but with zinc as the central atom.

EXPERIMENTAL

Two methods of preparation were used.

(1) Sodium tungstate dihydrate (56·2 g.), dissolved in water (400 ml.), was converted into the paratungstate by addition of N-nitric acid (198·6 ml.) and boiling the mixture. To the solution was added with stirring a solution of zinc nitrate (10 g.) in water (700 ml.) during 20 hr. The temperature of the paratungstate solution was kept about 80—90°. Higher temperatures caused partial hydrolysis of the products to zinc paratungstate.

(2) Sodium tungstate dihydrate (56·2 g.) in water (400 ml.) was converted into the metatungstate by boiling it with N-nitric acid (255·4 ml.). Zinc oxide (10 g.) was added during 5 days to the stirred metatungstate solution at about 80—90°.

The solutions obtained by either method were filtered hot, then concentrated slowly to about 150 ml. and set aside. Small white crystals separated, which recrystallised from water. The different methods of preparation gave salts with differing analyses but each yielded an ammonium salt of the same composition. The salts obtained appeared to be different sodium zinc salts of 12-tungsto-3-zincic acid.

The mother-liquors were extracted with ether and 12N-sulphuric acid. The ether addition compound formed was purified by dropping it through several portions of ether. On dilution

---

[2] Keggin, *Proc. Roy. Soc.*, 1934, *A*, **144**, 75.

[3] Santos, *ibid.*, 1935, *A*, **150**, 309.

with water, the ether separated and was removed by evaporation. The aqueous solution was evaporated to dryness on a steam-bath and the tungstic acid, formed by the decomposition of the metatungstic acid present, removed by filtration. The process was repeated until little tungstic acid was precipitated. The final aqueous extract was concentrated to small bulk, first on the steam-bath and then over concentrated sulphuric acid in a partial vacuum. Yellow crystals of 12-*tungstozincic acid* separated (Found: ZnO, 2·42; WO_3, 82·4; H_2O, 15·3. $ZnO,12WO_3,29H_2O$ requires ZnO, 2·42; WO_3, 82·2; H_2O, 15·4%).

Salts of 12-*Tungsto*-3-*zincic Acid.—Ammonium salt.* This *salt* was prepared by adding a hot saturated solution of ammonium chloride to a hot solution of sodium 12-tungsto-3-zincate. The solution was filtered hot and set aside. On cooling, colourless crystals separated which recrystallised from water [Found: NH_4, 4·1; ZnO, 7·3; WO_3, 80·7; H_2O, 6·0. $4(NH_4)_2O,3ZnO,12WO_3,11H_2O$ requires NH_4, 4·1; ZnO, 7·1; WO_3, 81·1; H_2O, 5·8%].

Nickel salt. The *nickel salt* was prepared by adding a hot saturated solution of nickel nitrate to a hot solution of the ammonium salt, filtering and cooling. Green crystals separated, which recrystallised from water (Found: NiO, 8·22; ZnO, 6·2; WO_3, 68·9; H_2O, 17·5. $4{\cdot}5NiO,3ZnO,12WO_3,39H_2O$ requires NiO, 8·3; ZnO, 6·1; WO_3, 68·4; H_2O, 17·3%).

Guanidine salt. This *salt* was prepared by adding 5% aqueous guanidine hydrochloride to a dilute solution of the ammonium salt. If the temperature was kept at about 80°, the precipitate was formed slowly. The resulting small colourless crystals were only slightly soluble in water [Found: CH_6N_3, 14·7; ZnO, 6·3; WO_3, 72·4; H_2O, 5·9; $4{\cdot}5(CH_6N_3)_2O,3ZnO,12WO_3,12{\cdot}5H_2O$ requires CH_6N_3, 14·8; ZnO, 6·3; WO_3, 72·0; H_2O, 5·8%].

Salts of 12-*Tungstozincic Acid.—Ammonium salt.* The *ammonium salt* was prepared by adding a hot concentrated solution of ammonium chloride to a hot concentrated solution of 12-tungstozincic acid, then filtering and cooling the mixture. The salt, which separated as colourless crystals, recrystallised rom water [Found: NH_4, 3·1; ZnO, 2·5; WO_3, 84·8; H_2O, 8·3. $3(NH_4)_2O,ZnO,12WO_3,15H_2O$ requires NH_4, 3·3; ZnO, 2·5; WO_3, 84·6; H_2O, 8·2%].

Barium salt. This *salt* was prepared by neutralising a solution of 12-tungstozincic acid with barium carbonate, then filtering and cooling the mixture. The salt separated as colourless crystals, which recrystallised from water (Found: BaO, 12·1; ZnO, 2·18; WO_3, 72·9; H_2O, 13·1. $3BaO,ZnO,12WO_3,28H_2O$ requires BaO, 12·0; ZnO, 2·12; WO_3, 72·7; H_2O, 13·2%).

Guanidine salt. This *salt* was prepared by adding 5% aqueous guanidine hydrochloride to a solution of 12-tungstozincic acid. Filtration and cooling gave white crystals which recrystallised from water [Found: CH_6N_3, 11·2; ZnO, 2·4; WO_3, 82·3; H_2O, 3·35. $3(CH_6N_3)_2O,ZnO,12WO_3,6H_2O$ requires CH_6N_3, 11·3; ZnO, 2·4; WO_3, 82·3; H_2O, 3·2%].

Analyses.—Barium was determined as the sulphate by precipitation with dilute sulphuric acid, the anion being stable enough to permit this. Zinc was determined by precipitation as the oxine derivative; nickel by precipitation with dimethylglyoxime; tungsten by precipitation with cinchonine hydrochloride and ignition to the oxide; ammonia by distillation into standard acid solution; water by ignition and difference; and guanidine by the micro-Dumas method.

The authors thank Mr. J. Cameron for the nitrogen microestimations. One of them (D. H. B.) is also indebted to the D.S.I.R. for a maintenance grant.

CHEMISTRY DEPARTMENT, THE UNIVERSITY, GLASGOW. [*Received, March 3rd,* 1958.]