774. *The Preparation, Properties, and Structure of 12-Tungstocupric*(II) *Acid.*

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A 12-heteropolytungstate with copper(II) as the central ion has been isolated and examined. It is difficult to prepare since an intermediate stage is readily hydrolysed by boiling water. Once isolated, it is stable to almost 250° without significant decomposition. The copper appears to exist in an undistorted tetrahedral environment.

Mixing an aqueous solution of sodium paratungstate with an aqueous solution of cupric nitrate or sulphate gives substantial yields of a blue-green, very sparingly soluble product whose composition varies with the temperature at which the preparation is carried out. At room temperature, the product approximates in composition to sodium cupric paratungstate $3Na_2O,2CuO,12WO_3,30H_2O$. Rosenheim[1] formulated this as a sodium 6-tungstocuprate $Na_3CuH_5[H_2(WO_4)_6],11\frac{1}{2}H_2O$, but the very small solubility in water and the persistence of the colour of the hydrated cupric ion suggest that this compound is a sodium cupric salt and not a true heteropolytungstate. At higher temperatures the composition of the product tends towards that of cupric paratungstate, $5CuO,12WO_3,33H_2O$, and above 70° this is almost the sole product. If the preparation is carried out at 60—70°, removal of the precipitated cupric paratungstate leaves a greenish-yellow mother-liquor from which extraction with ether and 12N-sulphuric acid gives the greenish-yellow ether addition compound of 12-tungstocupric(II) acid accompanied by varying amounts of the ether addition compound of metatungstic acid. From this mixture, 12-tungstocupric acid is obtained almost free from metatungstic acid by repeated evaporation of an aqueous solution to dryness, the low thermal stability of metatungstic acid leading to its almost complete decomposition to hydrated tungstic oxide.

12-Tungstocupric(II) acid resembles 12-tungstoferric[2] and 12-tungstozincic acid[3] in colour. Ammonium, potassium, guanidine, and barium 12-tungstocuprate are 6-basic and isomorphous with the corresponding 12-tungstoferrates and 12-tungstozincates, and the structures of the cæsium salts appear to be almost identical. The free tungstocupric(II) acid is very slowly decomposed by hydrogen sulphide but resists reduction by iodide ion to a tungstocupric(I) acid.

Experimental

Sodium tungstate (56·2 g.) in water (300 ml.) was converted into the para-salt by addition of N-nitric acid (194·4 ml.). This solution was treated with cupric nitrate solution (7·4 g. of hexahydrate in 300 ml.), dropwise, with stirring, at 60—70° during 4—6 hr., a blue-green precipitate being formed. Cooling and filtration gave a yellow-green solution. This was evaporated slowly at ~60° to 50 ml., more blue-green crystals separating. The filtered mother-liquor was kept at 6° until no further solid separated. Final filtration gave a solution of pH *ca.* 4·4. This was diluted to about 200 ml., and 200 ml. of ether were added. The solution was then stirred and acidified with 12N-sulphuric acid (400 ml.), added dropwise. The lowest of the three layers formed was the greenish-yellow ether addition compound of 12-tungstocupric(II) acid together with the ether addition compound of metatungstic acid. The mixture had a density *ca.* 2·1 and the average yield, in terms of sodium tungstate used, was around 30%. The ether addition compound was freed from entrained aqueous extraction-liquor by dropping it through successive portions of anhydrous ether. On dilution with water, the ether separated and was removed by an air current. The resulting aqueous solution of 12-tungstocupric and metatungstic acid was evaporated to dryness on the steam-bath, the residue was extracted with water and filtered off, and the process was repeated until very little further tungstic acid separated. The final aqueous extract, when concentrated to small volume, afforded yellow octahedra.

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[1] Rosenheim, *Z. anorg. Chem.*, 1916, **96**, 164.

[2] Brown and Mair, *J.*, 1962, 1512.

[3] Brown and Mair, *J.*, 1958, 2597.

Thermogravimetric analysis of this product was carried out on a Stanton thermogravimetric balance at a chart speed of 6 in./hr. The energies of activation for the loss of water and for the decomposition of the anion were calculated as described by Freeman and Carrol[4] for a system involving a solid decomposing into a solid and a gas. This involved plotting $\Delta(1/T)/\Delta \log x$ against $\Delta \log (-\mathrm{d}x/\mathrm{d}t)/\Delta \log x$, where T was the absolute temperature and x the number of molecules of water at temperature T. This plot gave a straight line with slope $-E/2{\cdot}3\boldsymbol{R}$, where E was the energy of activation.

The free acid and salts were analysed as follows. Barium was determined as sulphate by precipitation with dilute sulphuric acid, the anion being stable enough to permit this. Copper was determined by precipitation as the oxine derivative; tungsten by precipitation with cinchonine hydrochloride and ignition to the oxide; ammonia by distillation into standard acid solution; water by ignition and difference; potassium by difference; and guanidine by the micro-Dumas method.

Results.—Tungstocupric(II) acid is very soluble in water. Aqueous solutions are stable to strong acids but are decomposed by strong bases with the separation of cupric hydroxide. Thermal analysis of a sample of the free acid giving an empirical analysis for $CuO,12WO_3,30H_2O$, showed three regions where loss of weight occurred. The first (around 120°) involved $22H_2O$, the second (around 200°) $5H_2O$, and the third (around 250°) the remaining $3H_2O$. The energies of activation were 7, 21, and 48 kcal./mole, respectively. The last value is slightly less than those found for 12-tungstoferric(III) and 12-tungstozincic(II) acid, namely, 60 and 56 kcal./mole, although the other two former values are similar. In each case water was lost in accordance with a first-order reaction.

The *potassium salt* was prepared by saturating an aqueous solution of the acid with potassium chloride and recrystallising the precipitate from water (Found: K_2O, 7·9; CuO, 2·2; WO_3, 81·1; H_2O, 8·9. $3K_2O,CuO,12WO_3,18H_2O$ requires K_2O, 8·1; CuO, 2·3; WO_3, 80·2; H_2O, 9·35%). The *ammonium salt* was similarly prepared but by using ammonium chloride [Found: $(NH_4)_2O$, 4·6; CuO, 2·4; WO_3, 82·9; H_2O, 10·3. $3(NH_4)_2O,CuO,12WO_3,19H_2O$ requires $(NH_4)_2O$, 4·6; CuO, 2·4; WO_3, 82·8; H_2O, 10·2%]. The *guanidine salt* was prepared as above by using a 10% solution of guanidine hydrochloride [Found: $(CN_3H_6)_2O$, 12·0; CuO, 2·45; WO_3, 83·1; H_2O, 2·5. $3(CN_3H_6)_2O,CuO,12WO_3,5H_2O$ requires $(CN_3H_6)_2O$, 12·3; CuO, 2·4; WO_3, 82·8; H_2O, 2·6%]. The *barium salt* was prepared as above by using barium chloride (Found: BaO, 12·3; CuO, 2·1; WO_3, 75·7; H_2O, 10·0. $3BaO,CuO,12WO_3,20H_2O$ requires BaO, 12·4; CuO, 2·2; WO_3, 75·6; H_2O, 9,8%).

Lines and intensities for cæsium 12-tungstocuprate and 12-tungstoferrate.

$h^2 + k^2 + l^2$	Calc.	Cuprate Obs.	Ferrate Obs.
6	13·7	15	15
8	5·8	5	5
10	25·7	20	25
12	150·0	150	150
14	0·9	Abs.	Abs.
16	79·9	80	75
18	17·6	20	17
20	0·2	Abs.	Abs.
22	94·5	100	90
24	11·8	10	10
26	79·7	80	80
27	8·8	10	10
30	46·7	50	50
32	86·7	80	90
33	10·2	10	10
34	9·1	10	10
36	15·1	15	15
38	92·1	90	90
40	2·1	Abs.	Abs.
41	28·9	30	25
42	47·5	50	45
44	78·9	80	80
46	2·7	Abs.	Abs.
48	29·5	30	30
50	206·3	200	210

The structure of cæsium 12-tungstocuprate(II) was confirmed by X-ray powder photography. The specimen was mounted in a fine Lindemann glass tube and photographs were taken with Cu-K_α radiation. The structure was found to be cubic with a unit-cell length of 11·85 Å, very close to those of cæsium 12-tungstoferrate[2] (11·88 Å) and 12-tungstozincate[3] (11·86 Å). The intensities (cf. Table) agreed with those calculated from a structure similar to that proposed for cæsium 12-tungstophosphate[5] but with copper as the central ion. Comparative photographs of the four cæsium salts appeared almost identical.

[4] Freeman and Carrol, *J. Phys. Chem.*, 1958, **62**, 394.

[5] Santos, *Proc. Roy. Soc.*, 1935, *A*, **150**, 309.

DISCUSSION

These results suggest that tungstocupric(II) acid is a 12-tungsto-acid and that the central copper atom is bound tetrahedrally to four oxygen atoms. This is one of the few authenticated structures involving tetrahedrally bound bivalent copper. The mechanism of preparation probably involves two processes: polymerisation of the tungstate ions and transference of the copper from the distorted octahedral hydrate to the tetrahedral environment of the heteropoly-acid. The latter step involves considerable change in the crystal-field stabilisation energy. Dunitz and Orgel [6] have calculated that this would be about 15·2 kcal./mole and have suggested that this relatively large energy barrier is one reason for the lack of tetrahedral copper(II) complexes. In this case, the only possible co-ordination is tetrahedral, since the four oxygen atoms involved are held in position by being also co-ordinated each to three separate tungsten atoms in the lattice. Any alteration in the position of these atoms would be obvious in the *X*-ray powder photograph. Once isolated, 12-tungstocupric(II) acid is moderately stable. The difficulty in preparation, however, is probably due to this difference in crystal-field stabilisation energies. The polymerisation of the tungstate ions is facilitated by boiling of the solution. This, however, hydrolyses an unstable intermediate, probably the $[HCuW_6O_{21}]^{3-}$ ion or some similar ion, to give the more insoluble copper paratungstate. Once the complete sphere of WO_6 octahedra has been formed by the addition of the 12N-sulphuric acid, the 12-tungstocupric ion is more stable.

The spectrum of 12-tungstocupric acid in water shows a broad peak around 7000 cm.$^{-1}$. The normal $Cu(6H_2O)^{2+}$ ion gives a broad peak around 13,000 cm.$^{-1}$. The former value is slightly higher than that obtained by taking 4/9 of 13,000 = 5670, *i.e.*, the approximate value for a tetrahedral four-hydrate. However, similar types of result have been obtained with other 12-heteropolytungstates,[7] suggesting that the ligand field arising from the oxygen ions in the lattice is greater than for the corresponding hypothetical four-hydrates.

The authors thank Mr. A. G. Macdonald and Mr. T. E. Anderson for assistance in the early stages of this work.

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[*Received, March 16th*, 1962.]

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[6] Dunitz and Orgel, *J. Phys. and Chem. Solids*, 1957, **3**, 318.
[7] Brown, unpublished work.