852. *The Preparation, Properties, Structure, and Spectra of 12-Tungstomanganic*(IV) *Acid and its Stability Relative to Analogous 12-Heteropolytungstates.*

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The existence of a 12-heteropolytungstic acid with manganese(IV) as the central ion has been confirmed and the properties of the acid have been examined. The structure has been worked out from *X*-ray powder photographs and it appears to be a typical 12-heteropolytungstate. Study of the spectra has confirmed the tetrahedral environment of the manganese(IV). No 12-heteropolyacid with manganese(II) as the central ion could be prepared; possible reasons for this are discussed.

SEVERAL heteropolytungstates containing tervalent manganese have been claimed. Rogers and Smith[1] and Rosenheim and Schwer[2] prepared several compounds. In particular Mair and Waugh[3] isolated an unstable coloured acid which they identified through its salts as either a 1 : 11 or a 2 : 22 heteropolytungstate. Later work by Waugh and Singer,[4] using ultracentrifuge methods, suggested that 1 : 11 was the correct formulation. Just[5] prepared a compound $3Na_2O,MnO_2,5WO_2,18H_2O$ which is the only recorded heteropolytungstate containing manganese(IV). No heteropolytungstates containing manganese(II) have been claimed. The purpose of this work was to examine the possible formation of 12-heteropolytungstates, analogous to 12-tungstoferric(III) acid[6] but containing manganese as the central ion.

EXPERIMENTAL

A solution of sodium tungstate (56·2 g. in 300 ml. of water) was converted into the para-form by the addition of N-nitric acid (194·4 ml.). This boiling solution was treated with manganese sulphate (8 g.) in water (500 ml.), dropwise, with stirring, during 4—6 hr. The solution gradually became yellow-brown, and a pale brown precipitate was formed. This precipitate, on analysis was found to be sodium manganese paratungstate, and was rejected. The solution was then set aside for a day, filtered, treated with ether, then slowly acidified with 12N-sulphuric acid (400 ml.). The lowest of the three layers formed, the ether addition compound, was then purified by dropping it through two columns of ether; manganese was found not to be present in it.

The experiment was repeated, but this time 8 g. of manganese sulphate and 10 g. of

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[1] Rogers and Smith, *J. Amer. Chem. Soc.*, 1904, **26**, 1475.

[2] Rosenheim and Schwer, *Z. anorg. Chem.*, 1914, **89**, 235.

[3] Mair and Waugh, *J.*, 1950, 2372.

[4] Waugh and Singer, *Proc. Nat. Acad. Sci. U.S.A.*, 1952, **38**, 1027.

[5] Just, *Ber.*, 1903, **36**, 3619.

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

potassium persulphate in 500 ml. of water were added, a dark brown precipitate being formed. On cooling and filtering, a dark brown solution remained. This solution was unstable and decomposed slowly at room temperature. On addition of ether and 12N-sulphuric acid, the ether addition compound formed had a deep red-brown colour. On dilution with water, the ether separated and was removed in a current of air. The tungstomanganic acid formed was comparable in thermal stability with metatungstic acid and therefore purification by the thermal decomposition of metatungstic acid was not possible. The most effective purification was by fractional crystallisation of the salts.

Thermogravimetric analysis was carried out on a Stanton thermogravimetric balance at a chart speed of 6 in. per 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[7] for a system involving a solid decomposing into a solid and a gas.

An X-ray powder photograph of the cæsium salt was taken by mounting the specimen in a fine Lindemann glass tube and using Cu-K_α radiation. The intensities were measured by inspection. The spectra were taken on an Optika recording spectrophotometer.

The salts were analysed in the following manner. Manganese was precipitated with hydrogen peroxide, as the oxide, converted into the sulphate and weighed as such. The valency of the manganese in the complex was confirmed by dissolution in standard sodium oxalate solution, rapid acidification with concentrated sulphuric acid, boiling until colourless, filtration, and back-titration with permanganate. Tungsten was determined by precipitation with cinchonine hydrochloride and ignition to the oxide; ammonia by distillation into standard acid solution; water by difference; potassium by difference after drying; and guanidine by the micro-Dumas method.

Results.—Tungstomanganic acid is very soluble in water. The aqueous solutions are slowly decomposed by strong acids and rapidly decomposed by strong alkali. Thermal analysis of the free acid (containing a little metatungstic acid as impurity) showed only one region where loss of weight occurred—around 150°—and the energy of activation found was 15 kcal. mole^{-1}. 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 fractionally recrystallising the precipitate from water (Found: K_2O, 5·6; MnO, 2·5; WO_3, 81·5; H_2O, 10·7. $2K_2O,MnO_2,12WO_3,20H_2O$ requires K_2O, 5·5; MnO, 2·5; WO_3, 81·4; H_2O, 10·5%). The *ammonium salt* was prepared as above, but by using ammonium chloride [Found: $(NH_4)_2O$, 3·2; MnO, 2·5; WO_3, 81·5; H_2O, 12·8. $2(NH_4)_2O,MnO_2,12WO_3,25H_2O$ requires $(NH_4)_2O$, 3·0; MnO, 2·5; WO_3, 81·3; H_2O, 13·1%]. Analysis of the valency state of manganese in eight samples gave values of 85, 89, 94, 96, 96, and 97% of MnO_2, suggesting that the dominant species was Mn(IV) but that some manganese in lower valency state was also present.

From the X-ray powder photographs of cæsium tungstomanganate, the structure was found to be cubic with a unit cell length of 11·80 Å, very close to that of cæsium 12-tungstoferrate(III)[6] (11·88 Å). The intensities were calculated from a structure similar to that of the latter but with manganese as the central ion and were found to be close to the observed intensities. Lines and intensities are given in the Table along with those of cæsium 12-tungstoferrate.

Lines and intensities for cæsium 12-tungstomanganate(IV) and 12-tungstoferrate(III).

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

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

The spectrum of an aqueous solution of tungstomanganic(IV) acid showed fairly strong absorption over the visible region, a strong peak at 38,400 and a weak broad peak at 7000 cm.$^{-1}$ having extinction coefficients $9{\cdot}9 \times 10^4$ and 18, respectively.

DISCUSSION

The results indicate that tungstomanganic(IV) acid is a 12-acid. The intense red-brown colour and the analytical values suggest that, although manganese(IV) is the dominant species, another manganese ion of different valency is also present. Attempts to prepare 12-acids containing manganese(II) or manganese(VII) failed. Since manganese(V) and manganese(VI) are unstable in acid solution, the most likely second species is, therefore, manganese(III) but this could not be proved.

12-Tungstomanganic(IV) acid is less stable thermally than some 12-heteropolytungstates containing first-row transition metals as the central ion. Also metatungstic acid, the parent 12-acid, with no central ion, is unstable at room temperature. Thus the central ion plays an important part in stabilising the tungstate group.

From a consideration of the change in crystal-field stabilisation energy required on moving the metal ion from the approximately octahedral hydrate to the tetrahedral environment of the 12-heteropoly-acid, a certain pattern emerges. This can best be illustrated by the following table where Δ is the splitting energy.

No. of *d*-electrons	Octahedral stabilisation energy	Tetrahedral stabilisation energy	Central metal ion
1, 6	$-\frac{2}{5}\Delta$	$-\frac{3}{5}\Delta$	Co^{3+}
2, 7	$-\frac{4}{5}\Delta$	$-\frac{6}{5}\Delta$	Co^{2+}
3, 8	$-\frac{6}{5}\Delta$	$-\frac{4}{5}\Delta$	Mn^{4+}, Cr^{3+}, Ni^{2+}
4, 9	$-\frac{3}{5}\Delta$	$-\frac{2}{5}\Delta$	Cu^{2+}
0, 5, 10	0	0	Mn^{2+}, Fe^{3+}, Zn^{2+}

The value of Δ for a tervalent ion in a tetrahedral environment is around 9000 cm.$^{-1}$, and for a bivalent ion about 4500 cm.$^{-1}$. Therefore, it would be expected that for the tervalent central ions the order of stability should be $Fe^{3+} > Co^{3+} \gg Cr^{3+}$. Experimentally, 12-tungstoferrate(III) and 12-tungstocobaltate(III) ions are stable in aqueous solution, whereas 12-tungstochromate(III) acid is slowly hydrolysed by water. The thermal decomposition values for the solid free acids are approximately 390°, 370°, and 250°, respectively. For the bivalent central ions, the order of stability should be Mn^{2+} and $Zn^{2+} > Co^{2+} \gg Cu^{2+}$. Experimentally, apart from Mn^{2+}, this is also found to be the case, with 12-tungstocuprate(II) unstable in aqueous solution and with thermal decomposition values of 350°, 340°, and 250°, for Mn^{2+}, Zn^{2+}, and Co^{2+}, respectively. Ni^{2+}, which would be expected to form the least stable 12-acid, in fact can only be obtained as a 6-acid. Manganese(IV) is a d^3-ion and should give a 12-acid comparable in stability with that of chromium(III). The fact that it is much less stable is probably due to the smaller size of the ion (0·52 Å compared with 0·65 Å). Similarly, manganese(II) is a d^5-ion and should give a stable 12-acid. The fact that it does not could be due to its being larger than the other bivalent ions and possibly just outside the upper size limit for inclusion in 12-heteropolytungstates.

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