

The Nature and Properties of Manganese Violet

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A new method for the preparation of manganese violet is reported and the formula confirmed as manganese(III) ammonium pyrophosphate by wet analysis, X-ray powder diffraction, infrared spectroscopy, thin-layer chromatography, and magnetic measurements. The thermal decomposition has been studied and thermogravimetric curves obtained. Using the above techniques, the products have been identified as either manganese(II) trimetaphosphate, or a mixture of manganese(II) tri- and tetra-metaphosphates depending on the temperature and duration of heating.

MANGANESE VIOLET is a finely powdered pigment¹ with empirical formula $\text{MnNH}_4\text{P}_2\text{O}_7$. It is insoluble in organic solvents and in most ionic solvents. Manganese(III) has a strong tendency to form complexes, in which the +3 oxidation state is greatly stabilised. The bonding between Mn and phosphate has considerable covalent character, and the colour is due to the Mn being strongly

co-ordinated by phosphate or ammonia. Numerous examples of precipitated pyrophosphates are known,²⁻⁸ and these are frequently coloured amorphous powders. The salts $\text{NaMnP}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$, $\text{KMnP}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$, and $\text{NH}_4\text{MnP}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ are known,⁹ the first two being pale red and soluble in water, whilst the last is violet and insoluble. There is no conclusive proof that manganese violet is a pyrophosphate, and the formula could be

¹ Soc. Dyers and Colourists, Colour Index, 2nd edn., 1956, 3, 77742.

² A. Schwarzenberg, *Annalen*, 1848, 65, 133.

³ H. Beer, *Ann. Physik*, 1848, 75, 152.

⁴ T. Persos, *Ann. Chim. Phys.*, 1847, 20, 315.

⁵ T. Persos, *Annalen*, 1848, 65, 163.

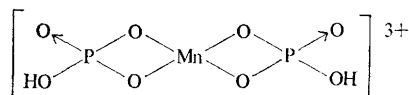
⁶ T. Fleitmann and W. Henneberg, *Annalen*, 1848, 65, 387.

⁷ H. Bassett, W. L. Bedwell, and J. B. Hutchinson, *J. Chem. Soc.*, 1936, 1412.

⁸ A. Rosenheim, *Z. anorg. Chem.*, 1926, 153, 126.

⁹ A. Rosenheim and T. Triantaphyllides, *Berichte*, 1915, 48, 582.

accounted for by an equimolecular mixture of ortho- and tri-polyphosphates, or by a complex such as ^{10,11}



When manganese violet is heated to about 500° it loses water and ammonia, though the products formed have not been identified, nor the mechanism investigated. We wished to confirm the structure, to identify the thermal decomposition products, and to suggest a mechanism for the changes.

EXPERIMENTAL

Preparation.—Manganese dioxide (10 g.) was mixed with phosphoric acid (12.5 g.; *d* 1.75) and ammonium dihydrogenphosphate (10.6 g.). The mixture was heated at 120° for ½ hr. until a 'melt' was obtained, and at 300° for a further 1 hr. An excess of water was added to the hot material, and the aqueous suspension was boiled for ½ hr. and filtered. The residue was washed with hot water and dried at 110–120°, and yielded *ca.* 20 g. of purple powder. Careful analysis was necessary as samples were sometimes found to contain MnO₂ or Mn₄(P₂O₇)₃.

Analysis.—Manganese violet reacted with dilute sulphuric acid to give a precipitate of manganese dioxide and a pink solution containing Mn²⁺ ions, due to disproportionation of Mn^{III}, and was soluble in conc. sulphuric acid to give a red solution. It was decomposed by sodium hydroxide with the evolution of ammonia, and by hydrochloric acid with the evolution of chlorine. A solution of sulphur dioxide in water dissolved the manganese violet but discharged the violet colour and reduced Mn^{III} to Mn²⁺. Because of its insolubility, the instability of the Mn³⁺ ion and mutual interferences of phosphates and manganese, analysis was difficult.

The ammonia content of manganese violet was determined by distillation with sodium hydroxide.¹² Manganese was determined in the manganese oxide produced by treatment with alkali¹³ and also by the bismuthate method¹⁴ on solutions in sulphurous and sulphuric acid. Phosphorus was estimated by the ammonium molybdate method¹² (Found: Mn 22.0; NH₄⁺ 6.86; P₂O₇⁴⁻ 71.1. Calc. for MnNH₄P₂O₇: Mn, 22.24; NH₄⁺ 7.26; P₂O₇⁴⁻, 70.5%).

Thermogravimetric Analysis.—On gentle heating, dry powdered samples of manganese violet changed colour from violet to blue, water being driven off. On cooling in air, the original colour was restored. Heating to higher temperatures liberated ammonia and left a white residue, which fused at red heat to a pale pink glass.

A Stanton recording thermobalance was used to follow the thermal decomposition up to 800°, using samples of about 0.2 gm. in a platinum crucible. A heating rate of 250° hr. was used in most cases, and temperatures were recorded to ±5°. The decomposition occurred in two stages, with a loss of about 3% of the total weight occurring between 150

and 340° corresponding with the formation of the blue colour, then a very sharp loss of 10% between 340 and 460°, leaving a white residue. On further heating this sintered to a pink glass about 800° without any appreciable weight loss.

Analysis of the strongly heated and the fused samples by the methods mentioned above, and also X-ray fluorescence analysis for Mn and P performed in a fused borax disc, were all in agreement with the formula for manganese metaphosphate [Mn(PO₃)₂]_n.

X-Ray Powder Diffraction.—X-Ray diffraction patterns were recorded using a Philips diffractometer and Cu-Kα radiation. Manganese violet and the heated samples all gave patterns which did not match any in the ASTM index,¹⁵ and all showed a considerable degree of amorphous character. The *d* spacings in Å and the relative intensities (in parentheses) of the lines are recorded:

Manganese ammonium pyrophosphate: 5.64 (100), 5.22 (25), 4.10 (95), 3.11 (20), 3.03 (50), 2.98 (25), 2.92 (55), 2.89 (75), 2.72 (20), 2.06 (15). Heated material-manganous metaphosphate: 6.19 (20), 5.77 (25), 4.65 (15), 4.31 (15), 3.75 (65), 3.44 (20), 3.22 (20), 3.15 (20), 3.07 (30), 3.05 (100), 2.93 (20), 2.77 (50), 2.48 (10).

Fused material-manganous metaphosphate: 3.07 (40), 3.05 (100), 2.91 (30).

Thin-layer Chromatography.—A thin-layer chromatographic technique¹⁶ with an acidic solvent on cellulose was used to study a solution of manganese violet in sulphurous acid, and on the soluble salts formed from manganese violet, the heated product and the fused product by metathesis with sodium sulphide. Manganese violet in sulphurous acid and the soluble product from metathesis both showed a large amount of pyrophosphate with a slight trace of orthophosphate (probably produced by hydrolysis). The heated residue showed major quantities of tri- and tetra-metaphosphates, and the fused sample a major amount of trimetaphosphate, together with traces of pyro- and orthophosphate.

Infrared Spectroscopy. Nujol mulls of manganese violet, the heated and the fused samples were prepared, and spectra obtained on a Unicam SP 200 instrument. These were compared with previous published data.¹⁷ The spectrum of manganese violet corresponded to that of a pyrophosphate, and the other two indicated the presence of metaphosphates.

Magnetic Measurements.—The magnetic susceptibility of manganese violet was found to be 5.2 B.M. compared with the value of 4.9 predicted for Mn³⁺. The moments of the heated and fused samples were 6.0 and 6.1 B.M., respectively, in good agreement with the value of 5.9 predicted for Mn²⁺.

DISCUSSION

Analysis, chromatography, infrared, and magnetic measurements confirm the formula of manganese violet as MnNH₄P₂O₇. Thermal decomposition occurs in two stages, the product from heating being a mixture of manganous tri- and tetra-metaphosphates, whilst the

¹⁰ J. I. Watters and I. M. Kolthoff, *J. Amer. Chem. Soc.*, 1948, **70**, 2455.

¹¹ J. I. Watters and I. M. Kolthoff, *Ind. Eng. Chem.*, 1943, **15**, 8.

¹² A. I. Vogel, 'Quantitative Inorganic Analysis,' 3rd edn., Longmans, London, 1962, pp. 254, 574.

¹³ W. G. Palmer, 'Experimental Inorganic Chemistry,' Cambridge University Press, Cambridge, 1962, p. 481.

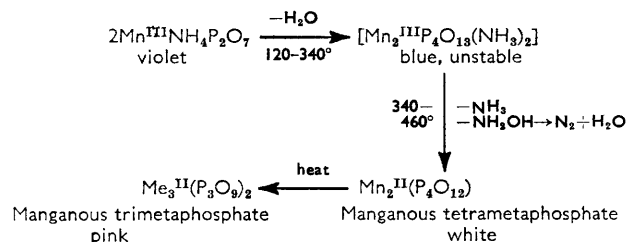
¹⁴ N. H. Furman, 'Standard Methods of Chemical Analysis,' vol. 1, 6th edn., Van Nostrand, London, 1962, p. 645.

¹⁵ ASTM Index of X-ray powder diffraction data, 1965.

¹⁶ D. Thorburn Burns and J. D. Lee, 'Studies in Inorganic Analysis. The identification of certain oxy salts of phosphorus,' *Microchim. Acta*, in the press.

¹⁷ D. E. C. Corbridge and E. J. Lowe, *J. Chem. Soc.*, 1953, 493.

fused product is manganous trimetaphosphate. The following scheme explains the observed analytical, physical, and thermogravimetric results.



It is postulated that the reduction of Mn^{III} to Mn^{II} is associated with the oxidation of ammonia to hydroxyl-

amine which then decomposes to nitrogen and water, or alternatively the ammonia is oxidised to nitrogen directly.

To confirm the evolution of nitrogen, some manganese violet was heated in a vacuum line and the evolved gases passed through two traps cooled in liquid nitrogen. The molecular weight of the remaining gas was measured by weighing a known volume at known temperature and pressure. The result obtained was 27.8, confirming that the gas was nitrogen.

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