148. *The Manganohalides of Pyridine and Quinoline.*

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COMPOUNDS of pyridinium halides with manganous halides are described by several authors. They include: (A) Compounds of type $MnX_2,2RHX$, or $(RH)_2MnX_4$, *viz.*, (I) $MnCl_2,2C_5H_5NHCl$ (Pincussohn, *Z. anorg. Chem.*, 1897, **14**, 388); (II) $MnCl_4,2C_5H_5N$ (*sic*; Reitzenstein, *ibid.*, 1898, **18**, 290); (III) $MnBr_2,2C_5H_5NHBr$ (Meyer and Best, *ibid.*, 1900, **22**, 182). (B) Compounds of type MnX_2,RHX, *viz.*, (IV) $MnCl_2,C_5H_5NHCl$ (Pincussohn, *loc. cit.*). No compounds of manganous halides and quinolinium halides have been described hitherto.

Reitzenstein described the compound (II) as *light green* and assigned to it the above formula mainly on the grounds that the more probable formula, $MnCl_2,2C_5H_5NHCl$, which fitted his analyses equally well, had already been allocated by Pincussohn to his *yellow* compound (I). Meyer and Best described their compound (III) as crystallising in *white* needles; moreover, they criticised Reitzenstein's formulation of his compound (II).

It appeared desirable to settle the formula of the compound (II), and to investigate the anomaly presented by the three different colours assigned to salts of similar composition; and it has now been shown (1) that the salt (II) is, in fact, $(C_5H_5NH)_2MnCl_4$, and is light green; (2) that Pincussohn's salt is an impure specimen of the salt (II), associated with a small amount of a pink *compound* $MnCl_2,C_5H_5NHCl,H_2O$ (V) (not previously described); (3) that Meyer and Best's salt (III) is also light green.

The green colour is apparently associated with the $MnCl_4''$ ion: a faint yellowish-green colour is developed when anhydrous manganous chloride is dissolved in concentrated hydrochloric acid, and is also perceptible when solutions of manganous chloride and lithium chloride are mixed and concentrated to a small bulk (Saunders, *Amer. Chem. J.*, 1892, **14**, 127). No green double salts of manganous chloride and inorganic chlorides have been prepared, though several pink hydrated salts of the type $R_2'MnCl_4$ have been made.

EXPERIMENTAL.

The compound $(C_5H_5NH)_2MnCl_4$ was prepared in four ways:

(1) By the method of Reitzenstein, who warmed freshly precipitated manganese dioxide with a solution of pyridine in concentrated hydrochloric acid, filtered, and evaporated the solution on the water-bath. The dark brown filtrate deposited pink crystals on cooling—a fact not mentioned by Reitzenstein. The mother-liquor when concentrated gave light green crystals, which were washed with alcohol and ether and dried in the desiccator (Found: Mn, 15·3; Cl, 39·8%).

(2) The above preparation was then carried out with manganous chloride in place of manganese dioxide, thus showing clearly that the manganese in Reitzenstein's compound could not be other than bivalent. The hydrated chloride (62·5 g.) was dissolved in 750 c.c. of concentrated hydrochloric acid and 50 g. of pyridine were added. The liquid was evaporated to 100 c.c., and the mass of pink needles was separated, washed with alcohol, and dried in a vacuum; this salt proved to be (V) (see below). The green filtrate was evaporated to 30 c.c., and the green needle-shaped crystals which separated on cooling were filtered off, washed with alcohol,

and dried in a vacuum desiccator [Found : Mn, 15·4; Cl, 39·3. Calc. for $(C_5H_5NH)_2MnCl_4$: Mn, 15·4; Cl, 39·7%].

(3) Pincussohn added " pure manganous chloride to an aqueous solution of pyridinium chloride," but gave no details. If the manganous chloride is hydrated, or if the solution of pyridinium chloride is not very concentrated, the pink salt (V) is obtained. On dissolving, with the aid of heat, anhydrous manganous chloride (1 mol.) in an aqueous solution of pyridinium chloride (3 mols.) saturated in the cold, light green needles, identical with (II), crystallised out. If the solution contained a little more water, a pale yellow product was obtained; this, when allowed to crystallise slowly (needles, 2—4 mm. long), was seen to contain pink and green crystals. Solutions containing both the pink and the green salt are yellowish, and doubtless Pincussohn's salt was contaminated with a little of the salt (V) : his analytical results are somewhat high in manganese and low in pyridine.

(4) By mixing hot solutions of dry pyridinium chloride and anhydrous manganous chloride in anhydrous alcohol, pale green needles are obtained on cooling. If water is present, the pink salt (V) is formed.

Pyridinium tetrachloromanganite forms light leaf-green needles which soften and melt at 152—155° (decomp.) and at higher temperatures lose pyridinium chloride; it is slightly deliquescent. Reitzenstein records that, when pressed between filter papers, frequently renewed, it is converted into a pink salt, which on the basis of its manganese content (19·23%), he formulated as $MnCl_2,2C_5H_5N$, but the author's analyses of the pink residue thus obtained and not further dried indicated that it was the moist compound (V) [Found : Mn, 19·6; Cl, 38·1. Calc. for $(C_5H_5NH)MnCl_3,H_2O$: Mn, 21·2; Cl, 41·0%. Calc. for $MnCl_2,2C_5H_5N$: Mn, 19·4; Cl, 25·0%]. Reitzenstein implies that chlorine is evolved in this process; but this is not so.

The tetrachloromanganite is exceedingly soluble in water. Reitzenstein states that it forms a colourless solution. With a little water, however, it gives a green solution which remains unchanged; more dilute solutions are very pale pink, probably as a result of the change of the $MnCl_4''$ ion into the $[MnCl_3H_2O]'$ ion. On evaporation of the more dilute solutions, the pink salt (V) crystallises out.

The chemical properties of the tetrachloromanganite are those of a manganous compound. No chlorine is lost when it is heated, and alkalis give a white precipitate of manganous hydroxide. The halogen in all these halides is completely and instantly precipitated by silver nitrate.

Pyridinium Tetrabromomanganite.—According to Meyer and Best (*loc. cit.*) this salt is formed when an alcoholic solution of pyridinium bromide is mixed with a solution of freshly precipitated manganese dioxide in alcoholic hydrobromic acid. A repetition of this work showed that, from the deep yellow-brown solution, light yellow crystals are formed, which on being washed with alcohol and ether become paler, but not white. Recrystallisation from alcohol, twice repeated, gave a green product, slightly more yellowish than the tetrachloromanganite.

Pyridinium tetrabromomanganite was also made by a process analogous to (3) above, a trihalogeno-salt not being obtained in this case, but only green crystals of the tetrabromo-salt (Found : Mn, 10·2; Br, 59·3. Calc. : Mn, 10·3; Br, 52·8%). Method (4) similarly gave the tetrabromomanganite. The salt resembles the tetrachloromanganite in most respects; it is slightly yellowish-green, it melts sharply without decomposition at 173°, and its solubility in alcohol is greater and in water less than that of the corresponding chlorine compound.

Attempts to prepare the double iodide were unsuccessful. Solutions of pyridinium iodide and manganous iodide, both in hydriodic acid and in alcohol, deposit only the constituent salts.

Compounds of the Type B.—Pincussohn (*loc. cit.*) evaporated to dryness an aqueous solution of equimolecular proportions of manganous chloride and pyridinium chloride, dried the residue, dissolved it in alcohol, and filtered. The crystals separating were dull pink and analysis showed them to be $(C_5H_5NH)MnCl_3$. The existence of this salt was confirmed; but, contrary to Pincussohn's statement, it does not crystallise unchanged from water, the crystals separating being *pyridinium trichloromanganite monohydrate* (V). This is readily obtained by crystallising equimolecular proportions of its components from water. It forms rose-pink needles, very soluble in water [Found : Mn, 21·2; Cl, 40·83. $(C_5H_5NH)MnCl_3,H_2O$ requires Mn, 21·2; Cl, 41·0%]. When heated, it effloresces and then loses pyridinium chloride, but does not melt. It is not deliquescent, but effloresces in the desiccator after some days.

Quinolinium Manganohalides.—*Quinolinium trichloromanganite* was made by method (2) above; pink tufts of fine hair-like crystals of the *dihydrate* separated copiously [Found : Mn, 17·0; Cl, 32·8. $(C_9H_7NH)MnCl_3,2H_2O$ requires Mn, 16·8; Cl, 32·5%]. The mother-liquor, on evaporation to a very small bulk, became green, and on cooling, formed a viscous mass;

on dilution with alcohol, this afforded light green leaflets. These were extracted with hot alcohol, and the extract on cooling deposited small green crystals of *quinolinium tetrachloromanganite* in poor yield [Found: Mn, 13·0; Cl, 31·2. $(C_9H_7NH)_2MnCl_4$ requires Mn, 12·0; Cl, 31·0%], slightly contaminated with the following compound.

The white residue from the alcohol extraction, when further washed with alcohol and dried, yielded *quinolinium trichloromanganite monohydrate* as a white powder faintly tinged pink [Found: Mn, 17·5; Cl, 34·4. $(C_9H_7NH)MnCl_3,H_2O$ requires Mn, 17·8; Cl, 34·4%].

Quinolinium tetrabromomanganite. This *salt* was obtained by crystallising a mixture of quinolinium bromide and anhydrous manganous bromide from alcohol; it was pale yellowish-green and rapidly became white in moist air but retained its colour in the desiccator [Found: Mn, 8·9; Br, 50·1. $(C_9H_7NH)_2MnBr_4$ requires Mn, 8·7; Br, 50·4%]. By crystallising a solution of manganous and pyridinium bromides in hydrobromic acid (*d* 1·5), a yellowish-pink *dihydrate* was obtained [Found: Mn, 8·2; Br, 48·2. $(C_9H_7NH)_2MnBr_4,2H_2O$ requires Mn, 8·2; Br, 47·7%].

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