157. *The Manganohalides of Pyridine.*

By W. S. Fyfe.

Dipyridinomanganous chloride combines with dry hydrogen chloride to form a green compound, previously formulated as $(PyH)_2MnCl_4$ and here reformulated as $H_2MnPy_2Cl_4$. The double salt $MnCl_2,PyHCl,H_2O$ has also been reformulated as the acid $H_2MnPyCl_3(OH)$. The potassium salts of these acids have been isolated.

A number of compounds of pyridine and manganous chloride have been described previously. Pincussohn (*Z. anorg. Chem.*, 1897, **14**, 388) gave details of a yellow compound, $MnCl_2,2PyHCl$, and a pink compound, $MnCl_2,PyHCl$, whilst Reitzenstein (*ibid.*, 1898, **18**, 290) described a green compound, $MnPy_2Cl_4$, and a pink salt, $MnPy_2Cl_2$. Meyer and Best (*ibid.*, 1900, **22**, 182) described the bromide, $MnBr_2,2PyHBr$. Taylor (*J.*, 1934, 699) revised this work and came to the following conclusions : (*a*) Pincussohn's yellow compound and Reitzenstein's green compound were identical and best formulated as $(PyH)_2MnCl_4$; (*b*) Pincussohn's pink compound was $MnCl_2,PyHCl,H_2O$; (*c*) Reitzenstein had reported that when the green compound, $MnPy_2Cl_4$, was pressed between filter papers the pink compound, $MnPy_2Cl_2$, was produced, chlorine being evolved in the change. Taylor proved that no loss of chlorine occurred and that the product was $MnCl_2,PyHCl,H_2O$; (*d*) the green colour of concentrated solutions was due to the $MnCl_4^{--}$ ion and the pink colour of more dilute solutions was due to the $(MnCl_3,H_2O)^{--}$ ion.

The present investigation indicates that, in the case of the green complex, the pyridine is bound to the manganese atom and is not present as the pyridinium ion. This compound has been reformulated as the complex dibasic acid, $H_2MnPy_2Cl_4$. The compound, $MnCl_2,PyHCl,H_2O$, described by Taylor, has also been reformulated as the acid, $H_2MnPyCl_3(OH)$. The identity of the pink salt, $MnPy_2Cl_2$, described by Reitzenstein has been confirmed, and a new salt, $MnPy_2Cl_2,2H_2O$, described.

EXPERIMENTAL.

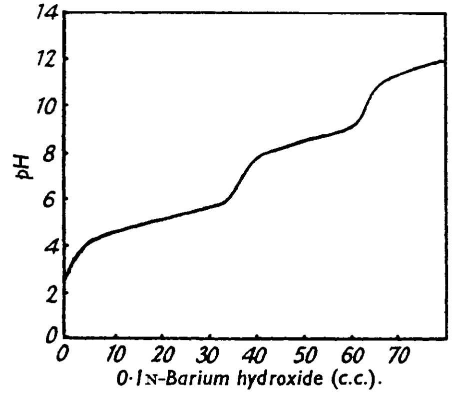
Dipyridinomanganous Chloride.—This compound is precipitated as fine pink needles on addition of pyridine to alcoholic solutions of manganous chloride. These can be washed in ether, vacuum dried, and recrystallised from alcohol (Found : Mn, 19·1; Cl, 25·2; N, 8·3. Calc. for $MnPy_2Cl_2$: Mn, 19·4; Cl, 25·0; N, 9·9%). Addition of pyridine to concentrated aqueous solutions of manganous chloride also precipitates this compound, which is also obtained when pyridine is added to a hot solution of manganous chloride in concentrated hydrochloric acid, but it then redissolves to form the green complex, $H_2MnPy_2Cl_4$.

All the chloride ions are precipitated in the cold by silver nitrate. The molar conductivities measured at 25° were :

Molar concentration	0·1	0·01	0·005	0·0025	0·0012
Conductivity (mhos)	164	191	216	250	280

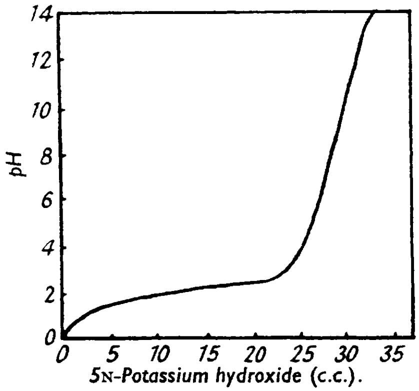
These measurements are in harmony with complete ionisation into $MnPy_2^{++}$ and $2Cl^-$. Freezing-point depressions in water gave a value of 68 for the molecular weight (Calc. for $MnPy_2Cl_2$: 284), *i.e.*, a van't Hoff's factor (*i*) of 4·2, indicating that the complex ion, $MnPy_2^{++}$, is also partly dissociated.

FIG. 1.



Neutralisation curve of 20 *c.c. of* $0·1M-H_2MnPy_2Cl_4$.

FIG. 2.



Neutralisation curve of 15 *c.c. of* $5M-H_2MnPy_2Cl_4$.

Dipyridinomanganous Chloride Dihydrate.—This compound crystallises in large white crystals from dilute solutions of manganous chloride and pyridine, and was originally found in the residues remaining after the crystallisation of $MnPy_2Cl_2$ (Found : Mn, 16·9; Cl, 22·1. $MnPy_2Cl_2,2H_2O$ requires Mn, 17·2; Cl, 22·2%). The *dihydrate* loses the two molecules of water on continued vacuum desiccation. It is not deliquescent but is readily soluble in water. Freezing-point and conductivity data are identical with those obtained for $MnPy_2Cl_2$, indicating that in solution the states of dipyridinomanganous chloride and its dihydrate are probably identical.

Hydrogen Tetrachlorodipyridinomanganate(II).—(*a*) This compound was prepared by Reitzenstein's method of adding pyridine to a solution of manganese dioxide in hydrochloric acid. On evaporation to dryness on a water-bath the green compound was obtained.

(*b*) The compound was similarly prepared from manganic oxide and trimanganese tetroxide.

(*c*) It can also be prepared by evaporating to dryness a solution of manganous chloride in hydrochloric acid and pyridine. Pale green crystals are obtained, and this material was used in physical measurements.

(*d*) The green material was also prepared by passing dry hydrogen chloride over dipyridinomanganous chloride, this change occurring very rapidly; the dihydrate does not change under these conditions.

Examination of the compounds, prepared in these different ways, by both analytical and optical methods indicated their identity (Found : Mn, 15·3; Cl, 39·6; N, 7·2. Calc. for $H_2MnPy_2Cl_4$: Mn, 15·4; Cl, 39·7; N, 7·8%). The apparent optic axial angle is 59° ± 2°; n_β 1·653 ± 0·002.

The material was purified by boiling in ether and chloroform, to remove traces of hydrogen chloride and pyridine hydrochloride. Recrystallisation from alcohol and water is not possible, and recrystallisation from pyridine produces dipyridinomanganous chloride, a change which gives some indication of the strength with which the hydrogen chloride is held in the lattice. The material was dried at about 1 mm.

A typical neutralisation curve for the complex is given in Fig. 1. In dilute solution a two-stage curve is obtained, the first stage corresponding to the neutralisation of the pyridinium ion and the second to the precipitation of manganous hydroxide. However, in concentrated solutions a one-stage curve, corresponding to the neutralisation of the acid, $H_2MnPy_2Cl_4$, is given (Fig. 2). In dilute solutions this material is extensively hydrolysed. Freezing-point depressions in aqueous solutions gave a value of 80 for the molecular weight (Calc. for $H_2MnPy_2Cl_4$: 357). This gives a value for *i* of 4·4. Molar conductivities measured at 20° were :

Molar concentration	5	0·5	0·1	0·01	0·001
Conductivity (mhos)	7	117	186	220	260

Preparation of $H_2MnPy_2Cl_4$ *from Manganese Dioxide and Manganous Chloride.*—Manganese dioxide dissolved in hydrochloric acid, in the presence of pyridine at 0°, formed at first a deep green solution and only slight amounts of chlorine were evolved even on warming the solution on a water-bath. It thus appeared that the deep green solution contained a complex ion of quadrivalent manganese. When the solution was evaporated to crystallisation little chlorine was evolved until near the crystallisation point when chlorine was liberated quantitatively : $MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$. At this stage the solution became a pale green and pale green crystals separated. The preparation of the green complex from manganous chloride was also studied, and no oxygen absorption, as occurs in the oxidation of the cobaltous amines, or hydrogen evolution was observed. It thus appears that the complex could not be other than one of the manganous ion.

Potassium Tetrachlorodipyridinomanganate(II).—This pink *salt* was precipitated when a green, concentrated solution of the acid was neutralised with concentrated potassium hydroxide. It is fairly soluble in water. If dilute solutions of the acid are used manganous hydroxide is precipitated (Found : Mn, 12·4; Cl, 33·0; Py, 38·0; K, 16·2. $K_2MnPy_2Cl_4$ requires Mn, 12·6; Cl, 32·8; Py, 36·6; K, 18·0%). The isolation of this material indicates that the green complex contains the $MnPy_2Cl_4^{--}$ ion.

Hydrogen Trichlorohydroxopyridinomanganate(II).—This compound was prepared by Reitzenstein by pressing the green complex between filter papers, and was erroneously recorded by him as $MnPy_2Cl_2$. It crystallises from dilute aqueous solutions of $H_2MnPy_2Cl_4$; pink crystals are obtained which can be washed in ether and chloroform. The *compound* crystallises as the monohydrate, and this molecule of water is lost on vacuum desiccation [Found, in vacuum-desiccated material : Mn, 21·1; Cl, 41·0. $H_2MnPyCl_3(OH)$ requires Mn, 21·1; Cl, 41·0%. Found in air-dried material : Mn, 19·5; Cl, 38·4. Calc. for $H_2MnPyCl_3(OH),H_2O$: Mn, 19·9; Cl, 38·6%]. It undergoes hydrolysis in dilute solutions as does $H_2MnPy_2Cl_4$, and repeated recrystallisations from water produce manganous chloride. By neutralising concentrated solutions of the pink acid with concentrated potassium hydroxide the potassium salt, $K_2MnPyCl_3(OH)$, was obtained.

In this series of compounds there is a steady drop in the β refractive index : $H_2MnPy_2Cl_4$, n_β 1·653; $H_2MnPyCl_3(OH)$, n_β 1·62; $MnCl_2,2H_2O$, n_β 1·59.

Ionic Migration Experiments.—These were conducted on a large number of the coloured solutions to obtained evidence as to whether the colour was in the anion or the cation. In the deep green solution from manganese dioxide in hydrochloric acid and pyridine and from manganous chloride in hydrochloric acid, and solutions of $H_2MnPy_2Cl_4$ the colour was associated with the anion.

Hydrogen Hexachlorodipyridinomanganate(IV).—The deep green solutions obtained at first from the solution of manganese dioxide in hydrochloric acid in the presence of pyridine most probably contain the quadrivalent complex acid, $H_2MnPy_2Cl_6$. This compound has been obtained in an impure condition by dissolving manganese dioxide in an ethereal solution of hydrogen chloride and pyridine. It separates as a green viscous liquid. All attempts to crystallise the material have led to its decomposition, and the formation of $H_2MnPy_2Cl_4$.

Nitrogen could not be determined satisfactorily by the Kjeldahl method ; the method used was to steam-distil the pyridine from a strongly alkaline solution of the complex, and titrate the pyridine with hydrochloric acid, using a pH-meter.

DISCUSSION.

There is no doubt that Reitzenstein's formulation of the green complex as $MnPy_2Cl_4$ is incorrect ; the compound does not contain quadrivalent manganese. Taylor formulated this complex as a pyridinium salt and doubtless much of the evidence from dilute solutions supports this view as the pyridinium ion is a product of the hydrolysis of the $MnPy_2Cl_4^{--}$ ion. However, the isolation of the alkali-metal salts supports the formulation of the green complex as the acid, $H_2MnPy_2Cl_4$. The very rapid entry of hydrogen chloride into the complex $MnPy_2Cl_2$ to form $H_2MnPy_2Cl_4$ when the gas is passed over the material, and its equally ready removal by washing it with pyridine, suggests that the hydrogen chloride molecule is co-ordinated and not taking part in the formation of a pyridinium ion. The addition of hydrogen chloride resembles the change of $PtCl_4$ to H_2PtCl_6 in which two molecules of hydrogen chloride are co-ordinately bound. This compound also is hydrolysed in water, losing hydrochloric acid. The complex dipyridinomanganous chloride contains two molecules of pyridine co-ordinated by the lone pair on the nitrogen to the manganese. The formation of the pyridinium salt $(PyH)_2MnCl_4$ by molecular rearrangement on exposure of the salt to hydrogen chloride would be improbable. Moreover, the hydrogen chloride is easily removed by treating the compound with pyridine. It is more probable that the chlorine atoms on the hydrogen chloride molecules fill up the remaining spaces in the lattice, donating their lone pairs and giving the manganous ion six-fold co-ordination. Freezing-point depressions do not support the presence of a three-ion salt and the stability in Kjeldahl nitrogen determinations is not to be expected from a pyridinium salt.

Two different structures have been proposed for dipyridinomanganous chloride; Cox, Shorter, Wardlaw, and Way (*J.*, **1937**, 1556) concluded that the structure was similar to that of dipyridinocobaltous chloride, which has a *trans*-planar configuration. Mellor and Coryell (*J. Amer. Chem. Soc.*, 1938, **60**, 1786) proposed an octahedral configuration from magnetic evidence. As the maximum co-ordination number of the manganous ion is six, it is not obvious, on the latter hypothesis, how water and hydrogen chloride could enter the lattice to give $MnPy_2Cl_2,2H_2O$ and $H_2MnPy_2Cl_4$.

Assuming the planar configuration, however, this addition could readily occur with the production of an octahedral configuration. It is noteworthy that hydrogen chloride has no effect on $MnPy_2Cl_2,2H_2O$, probably because there are no positions of entry for this molecule.

The instability of the green liquid, $H_2MnPy_2Cl_6$, is not unexpected on structural grounds, for in this compound the small quadrivalent manganese ion is in eight co-ordination.

Some evidence of the hydrolysis of the green acid in dilute solutions comes from the formation of the compounds $H_2MnPyCl_3(OH)$ and eventually $MnCl_2,2H_2O$ on continued recrystallisation. The change is essentially H–OH for H–Cl as occurs in the case of the platinic acids. As the complex ion is considerably dissociated the hydrogen chloride liberated will combine with any free pyridine from the dissociation $MnPy_2Cl_4^{--} = MnCl_4^{--} + 2Py$. The position of the pyridine molecule will then be taken by a water molecule. This change evidently at first goes only one stage, for $H_2MnPyCl_3(OH)$ can be isolated. A general scheme for the hydrolysis is :

$$H_2MnPy_2Cl_4 + 2HOH \longrightarrow H_2MnPyCl_3(OH),H_2O + PyHCl$$
$$H_2MnPyCl_3(OH),H_2O + 2H_2O \longrightarrow MnCl_2,4H_2O + PyHCl$$

The hydrolysis products and not the parent ions account for the properties of the dilute solutions. The freezing-point depressions indicate that in all cases the complex ions are considerably dissociated. Again the precipitation of the manganese ion by phosphate indicates that a considerable amount of the ion is present at equilibrium. The chloride ions are also readily precipitated from all the complexes. Magnetic measurements (Selwood, "Magnetochemistry," p. 153, Interscience Publishers, N.Y., 1943) show that all the complexes are paramagnetic and that no coupling of electrons has occurred; they are thus *normal* complexes on the Biltz classification. This is in agreement with their instability.

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