The Co-ordination Chemistry of Manganese. Part II.[1] Some Pentachloromanganates(III)

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The complexes M_2MnCl_5 (M = NMe_4, NMe_3H, Cs), M_2MnCl_5,H_2O (M = NH_4, K, Rb), and $[NMe_2H_2]_2MnCl_5,EtOH$ have been prepared and their properties compared with those of $[NEt_4]_2MnCl_5$ and $M'MnCl_5$ (M' = $phenH_2$, $bipyH_2$); $[NMeH_3]_2MnCl_5$ was difficult to isolate in a pure state. The complexes were characterised by magnetic measurements and by electronic and i.r. spectroscopy. All the complexes appear to be five-co-ordinate in acetone solution, and all except $[NMe_2H_2]_2MnCl_5,EtOH$ and ' $[NMeH_3]_2MnCl_5$ ' are structurally similar in the solid state.

Apart from the fluoro-complexes, the complex halides of manganese are principally those of oxidation state II.[2,3] Hexachloromanganates(IV) were prepared by Moews,[4] and there are a number of reports of chloro-complexes of manganese(III). Three examples of the hexachloromanganate(III) ion, $MnCl_6^{3-}$, are known,[1,5] the anion being stabilised by the large trivalent cations $M(pn)_3^{3+}$ or $Co(en)_3^{3+}$ (M = Rh, Co; pn = 1,2-diaminopropane, en = ethylenediamine). Alkali-metal pentachloromanganates(III) have been reported[6-9] but there is considerable doubt as to their formulation, both $M_2{}^{I}MnCl_5$ and $M_2{}^{I}MnCl_5,H_2O$ types being claimed. It is interesting to note that in the analogous fluoro-complexes, the NH_4^+, Na^+, and Li^+ compounds are of the type M^IMnF_5, whilst the K^+ and Cs^+ (Rb^+ salt unknown) are $M_2{}^{I}MnF_5,H_2O$.[3] A recent *X*-ray study of K_2MnF_5,H_2O[10] has shown that it does not contain discrete $[MnF_5,H_2O]^{2-}$ ions, but rather distorted MnF_6 octahedra with *trans*-fluorine bridges, the H_2O being unco-ordinated. There are only three well characterised examples of the $[MnCl_5]^{2-}$ ion in the literature, *viz.* $[NEt_4]_2[MnCl_5]$,[11] $[bipyH_2][MnCl_5]$, $[phenH_2][MnCl_5]$[12] (bipy = 2,2'-bipyridyl, phen = 1,10-phenanthroline). An *X*-ray structural investigation[13] of $[bipyH_2][MnCl_5]$ showed the $MnCl_5^{2-}$ group to exist as discrete units, with a distorted square pyramidal structure; a similar structure was proposed[14] for the NEt_4^+ and $phenH_2^{2+}$ salts on the basis of the similarity of their polarised crystal spectra.

EXPERIMENTAL

Manganese(III) complexes are unstable to light, especially in solution in organic solvents. The pentachloromanganates(III) are hydrolysed by moist air and decompose when kept at room temperature. Since some of the alkylammonium salts undergo considerable decomposition after 24 h *in vacuo* in the dark, all measurements were carried out on freshly prepared samples.

The compounds MnO(OH)[15] and $Ca(MnO_4)_2,4H_2O$[16] were prepared by literature methods; precipitated reagent grade MnO_2 (B.D.H.) was used (the granular form proved unsatisfactory). Before use, the alkylammonium chlorides were dried *in vacuo* at room temperature. All other materials were reagent grade or better, and were used without further purification.

The method of Goodwin and Sylva[12] was used to prepare $[bipyH_2][MnCl_5]$ and $[phenH_2][MnCl_5]$.

Other Complexes.—' *Purple solution.*' A rapid stream of dry hydrogen chloride was passed into a suspension of MnO_2 (20 g) in carbon tetrachloride (250 ml) at −10°. After 2 h the black solid was filtered off (G1 sinter), washed with carbon tetrachloride (2 × 50 ml), and extracted with diethyl ether at −20°. The deep purple solution obtained was filtered and used immediately.

The method of Gill,[11] somewhat modified, was used to prepare $[NEt_4]_2MnCl_5$: a dilute solution of NEt_4Cl in ethanol (*ca.* 2 g/150 ml) was added dropwise to an excess of the purple solution. Deep green $[NEt_4]_2MnCl_5$ precipitated immediately, addition of the NEt_4Cl solution being stopped when the colour of the ether solution had faded to a pale purple. The product was filtered off (G4 sinter), washed with ether (30 ml), and dried *in vacuo* (an excess of NEt_4Cl should be avoided (it tends to contaminate the product) and care should be taken not to suck air through the precipitate on the filter since this causes some hydrolysis). The yield was practically quantitative based on NEt_4Cl.

The $[NMe_4]_2MnCl_5$, $[NMe_3H]_2MnCl_5$, and $[NMe_2H_2]MnCl_5,EtOH$ complexes were prepared analogously.

Potassium aquopentachloromanganate(III), K_2MnCl_5,H_2O, was prepared from $Ca(MnO_4)_2$ a method similar to that used by Weinland and Dinklacker being used,[9] or from MnO_2 or MnO(OH); the most satisfactory method was that from MnO(OH):

(a) *From* $Ca(MnO_4)_2,4H_2O$. A solution of $Ca(MnO_4)_2,4H_2O$ (5 g) in the minimum of quantity of water, was added at 0° to concentrated hydrochloric acid (100 ml), saturated with hydrogen chloride, at 0°. After the initial violent reaction had subsided the dark solution was set aside at room temperature and was shaken from time to time during 2 h. Saturated potassium chloride solution (15 ml) was added to the mixture which was then cooled to 0° and saturated with

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hydrogen chloride. The solution was set aside for 30 min at 0° after which the dark precipitate was filtered off (G4 *sinter*), washed with saturated aqueous hydrochloric acid (5 ml), and dried *in vacuo* (yield 7 g, 76%).

(b) *From* MnO_2. Precipitated manganese dioxide (5 g) in concentrated hydrochloric acid (100 ml) was saturated with hydrogen chloride at −10° for 1 h. The dark solution was filtered through a precooled sinter (G1) and saturated potassium chloride solution (20 ml) was added to the filtrate; the mixture was worked-up as in (a) (yield 11 g, 60%).

(c) *From* MnO(OH). Powdered MnO(OH) (5 g) was added to concentrated hydrochloric acid, saturated with hydrogen chloride at 0°, and the mixture was shaken until most of it had dissolved. Any solid residue was filtered off (G3 sinter), saturated potassium chloride solution (20 ml) was added to the filtrate, and the mixture was worked-up as in (a) (yield 14 g, *ca.* 78%).

The ammonium, rubidium, and caesium salts were prepared by method (c). Attempts to prepare sodium, lithium, calcium, strontium, or barium salts failed. In each case saturation of the dark solution with hydrogen chloride precipitated a white solid, which proved to be metal chloride. Use of $[NMeH_3]Cl$ solution produced small yields of a red-brown solid, which formed a sticky solid when dried.

Bromo-complexes.—Attempts to prepare Mn^{III} bromo-complexes by methods analogous to those above failed. Addition of $Ca(MnO_4)_2$, MnO_2, or MnO(OH) to saturated aqueous hydrobromic acid, in the presence of various large cations (NEt_4^+, K^+, Cs^+) resulted in immediate liberation of bromine and the formation of orange-yellow solutions. Bromine was also formed on reaction of dry hydrogen bromide or acetyl bromide with manganese dioxide suspended in ether. By addition of MnO_2 to partially frozen saturated aqueous hydrobromic acid (−78°), a transient green-black colour was seen, but this disappeared rapidly when the cooling bath was removed.

Physical Methods.—Carbon, hydrogen, and nitrogen analyses were performed by the microanalytical service of this Department; chlorine was determined by the Volhard method,[17] manganese(III) iodometrically, and the alkali-metals gravimetrically as the tetraphenylborates.[18] I.r. spectra were measured in Nujol and hexachlorobutadiene mulls on a Perkin-Elmer 621 spectrophotometer; electronic spectra were recorded for acetone solutions on a Unicam SP 700 spectrophotometer, and solid reflectance spectra on a Beckman DK2A spectrophotometer using $BaSO_4$ as diluent. Magnetic susceptibilities were obtained by the Gouy method and corrected for diamagnetism by use of Pascal's constants.[19]

RESULTS

The ten pentachloromanganates(III) prepared are listed, along with their analytical data, in Table 1. The dark crystalline *NN'*-dihydrobipyridinium and *NN'*-dihydrophenanthrolinium salts, prepared by the published method,[12] gave a green streak when ground on filter paper. The amine salts were prepared by a modification of Gill's method.[11] A very deep purple solution, reputed [20,21] to contain $MnCl_3$, is obtained upon ether extraction of the black product from the reaction of dry hydrogen chloride with a suspension of manganese dioxide in carbon tetrachloride. Addition of an ethanolic solution of the appropriate alkylammonium chloride to this purple solution resulted in immediate precipitation of the pentachloromanganate(III). The green tetraethylammonium salt, $[NEt_4]_2MnCl_5$, is unchanged after several weeks in a vacuum desiccator in the dark, but $[NMe_4]_2MnCl_5$ and $[NMe_3H]_2MnCl_5$ are measurably (high C, H, low Cl analyses) decomposed after 24 h. With $[NMe_2H_2]Cl$ a brown compound, analysing as $[NMe_2H_2]_2MnCl_5$,EtOH was obtained; this, too, was unstable. We could not obtain a pure sample of $[NMeH_3]_2MnCl_5$ by this route, the brownish product always being high in carbon and hydrogen, and deficient in manganese(III); a microscopic examination of some samples showed the presence of some white crystals ($NMeH_3Cl$?) among the brown powder.

TABLE 1

Physical properties and analyses of the complexes

Compound	Colour	M.p. (°C)	χ_M (corr) [a]	μ_{eff} (B.M.)	Analyses (%) [g]					
					C	H	N	Mn	Cl	*M* [h]
$[bipyH_2]MnCl_5$	Green-black	160(d) [b]	10,093 [c]	4·88	30·5(30·8)	2·9(2·6)		14·2(14·1)	44·7(45·4)	
$[phenH_2]MnCl_5$	Green-black	155(d)	11,553 [c,d]	5·01	34·4(34·8)	2·8(2·4)		13·1(13·3)	43·1(42·8)	
$[NEt_4]_2MnCl_5$	Dark green	160(d)	10,740	5·01	39·6(39·0)	8·6(8·2)	5·6(5·7)	11·2(11·1)	36·0(36·0)	
$[NMe_4]_2MnCl_5$	Dark green	~100(d)	10,610	5·00	25·8(25·3)	6·7(6·4)	6·4(7·3)	14·8(14·4)	46·0(46·6)	
$[Me_3H]_2MnCl_5$	Olive green	~110(d)	10,905	5·06	19·8(20·4)	6·1(5·7)	7·1(7·9)	15·2(15·6)	50·5(50·4)	
$[NMe_2H_2]_2MnCl_5$,EtOH	Dark brown	85 [e]	8759	4·56	19·4(19·4)	6·6(6·0)	7·1(7·5)	14·4(14·8)	48·2(48·0)	
$[NH_4]_2MnCl_5,H_2O$	Dark purple	162(d) [f]	10,358	4·95		3·9(3·5)	9·9(9·8)	19·6(19·2)	61·5(62·1)	
$[K_2MnCl_5,H_2O$	Dark purple	168(d) [f]	10,265	4·94				17·0(16·8)	53·9(54·0)	24·5(23·7)
Rb_2MnCl_5,H_2O	Red-brown	160(d) [f]	10,123	4·93				13·1(13·0)	41·9(42·2)	39·0(40·6)
Cs_2MnCl_5	Black	~185(d)	9765	4·83				12·1(11·1)	36·5(35·6)	52·8(53·5)

[a] $\times 10^6$ c.g.s. units. [b] *d* = Decomposition. [c] Ref. 20. [d] At 270 K; all others determined at 293 K. [e] Melts to a green liquid. [f] All lose H_2O before melting. [g] Calc. figures in parentheses. [h] *M* = Alkali metal.

The ammonium and the alkali-metal (K, Rb, Cs) compounds were prepared by addition of a saturated aqueous solution of the appropriate chloride to a solution of manganese(III) in concentrated hydrochloric acid. The latter is best prepared by dissolution of powdered MnO(OH) in cold concentrated hydrochloric acid. The use of calcium permanganate or manganese dioxide is satisfactory only if carefully controlled, since the initial products from both these is a solution containing manganese(IV). Immediate addition of alkali chloride solution to this results in the formation of $M^I_2MnCl_6$ (M^I = NH_4, K, Rb, or Cs).[9] When these solu-

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[18] Ref. 17, p. 562.

[19] B. N. Figgis and J. Lewis in ' Modern Coordination Chemistry,' eds. J. Lewis and R. G. Wilkins, Interscience, New York, 1960, p. 403.

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tions containing manganese(IV) were saturated with hydrogen chloride and then set aside for 2—3 h reduction of Mn^{IV} to Mn^{III} occurred; addition of $M^{I}Cl$ to the solutions then gave pentachloromanganates(III). Since even with these precautions a few samples prepared in this way were found to give high chlorine analyses, and also to be high in oxidising power, presumably due to contamination with Mn^{IV}, the preparation from MnO(OH) is recommended. Both $[NH_4]_2MnCl_5,H_2O$ and K_2MnCl_5,H_2O are prepared as dark purple crystals, which could be ground to a red-brown powder, and gave a brown streak on filter paper. The red-brown crystalline Rb_2MnCl_5,H_2O was deep red-purple when powdered. The caesium salt was anhydrous and black. The alkali-metal salts decomposed only very slowly in the dark if protected from moisture, but decomposition was much faster in light. Attempts to isolate complexes with the smaller lithium or sodium cations, or with dipositive cations (Ca, Sr, Ba), were unsuccessful. Addition of solutions of the chlorides of these elements to the dark solution of MnO(OH) in concentrated hydrochloric acid, followed by saturation with hydrogen chloride, resulted only in precipitation of the metal chloride.

All the pentachloromanganates(III) decomposed with loss of chlorine when heated; they dissolved in concentrated hydrochloric acid to give deep green-black solutions, which became red-brown on dilution. The solubility of the alkali-metal salts in hydrochloric acid fell rapidly in the order $K \sim NH_4 \gg Rb > Cs$; water instantly decomposed them with formation of a red-brown solid—no doubt one of the higher oxides of manganese.

Bromo-complexes of manganese(III) could not be obtained. The reaction of MnO_2, $Ca(MnO_4)_2,4H_2O$, or MnO(OH) with concentrated aqueous hydrobromic acid resulted in liberation of bromine. The solutions produced were red-yellow because of dissolved bromine. Similarly a suspension of MnO_2 in carbon tetrachloride oxidised dry hydrogen bromide to bromine, ether extraction of the resulting solid producing a yellow solution, due, once again, to liberated bromine. Acetyl bromide did not react with an ether suspension of MnO_2 at low temperatures, whilst when heated or catalysed with $[NEt_4]_2MnCl_5$ or $Mn(OAc)_3$, a violent reaction accompanied by evolution of bromine occurred. Since any bromomanganate(III) species is expected to be dark, the absence of colour in these reactions is evidence for the absence of appreciable quantities of any such species.

DISCUSSION

Infrared Spectra.—All the complexes were insufficiently soluble in common solvents for solution i.r. spectral studies. The far-i.r. spectral bands (400—200 cm^{-1}), together with some other absorptions, are listed in Table 2.

TABLE 2

I.r. and electronic spectra of the complexes

Compound	400—200 cm^{-1} region	Other bands	Assignment	Solution (kk)	Reflectance (kk)
$[bipyH_2]MnCl_5$	350, ν 210			24·0, 17·4, ~13·2	25·0, 17·4, ~12·1
$[phenH_2]MnCl_5$	360, 220			24·7, 17·4, ~13·1	24·6, 17·5, ~11·9
$[NEt_4]_2MnCl_5$	333, 280, 260			23·8, 17·4, ~13·3	23·5, 16·0, ~11·3
$[NMe_4]_2MnCl_5$	360, 280			23·6, 17·6, ~12 9	23·2, 16·0, ~12·0
$[NMe_3H]_2MnCl_5$	280, 265, 235	2720, 2520, 2460	ν(NH)	24·0, 17·2, ~13·2	24·4, 16·0, ~12·1
$[NMe_2H_2]_2MnCk_5$,EtOH	280sh, 240sh, 220	~3400	(H_2O)	24·1, 17·3, ~13·2	24·4, 17·3, ~9·75
		2720, 2440, 2400	ν(NH)		
‘ $[NMeH_3]_2MnCl_5$ ’	340w, 280—200bv	~3400	(H_2O)	24·0, 17·7,~13·0	23·6, 17·7, ~10·5
		~3200	ν(NH)		
$[NH_4]_2MnCl_5,H_2O$	370, 350, ~200	~3400, 1610	(H_2O)	24·0, 17·4, ~13·1	24·3, 18·8, 16·4sh, ~13·3
		3160, 3040, 1400	(NH_4^+)		
K_2MnCl_5,H_2O	370, 350, ~200	~3400, ~1600	(H_2O)	23·9, 17·4, ~13·2	23·3, 18·2, ~12·7
Rb_2MnCl_5,H_2O	380, 355, ~200	~3400, 1620	(H_2O)	24·1, 17·2, ~13·3	23·2, 18·7, ~13·5
Cs_2MnCl_5	360, 340, 220			24·0, 17·5, ~13·2	23·5, 19·6sh, 17·0, ~14·0

The far-i.r. spectrum of $[bipyH_2]MnCl_5$, which is known to contain discrete $MnCl_5^{2-}$ ions, shows one broad strong ν(MnCl) vibration at 350 cm^{-1}, and a weaker absorption at *ca.* 210 cm^{-1}. The high frequency of the ν(MnCl) vibration is similar to that found for the $MnCl_6^{3-}$ ion [1,22] (*ca.* 340—360 cm^{-1}). The spectrum of $[phenH_2]MnCl_5$ is very similar. The spectra of the alkylammonium compounds in the 400—200 cm^{-1} region are unexpectedly complex. In the absence of Raman spectra, and bearing in mind the possibility of splitting of bands due to lattice effects and the strong Jahn–Teller distortion in the d^4 configuration, only tentative deductions can be made. Since bridging chlorines are expected to absorb at lower frequencies than terminal chlorines,[23] the bands below 300 cm^{-1} in the Et_4N^+ and Me_4N^+ complexes could possibly be due to the former. On the other hand it must be borne in mind that $[NMe_3H]_2MnCl_5$ shows no ν(MnCl) > 300 cm^{-1}; clearly, all the chlorines cannot be bridging in this complex. The spectra of M_2MnCl_5,H_2O ($M = K$, Rb, NH_4) and Cs_2MnCl_5 are very similar, suggesting similar structures, and that the water is present as lattice water and is not co-ordinated in the aquo-complexes.

Electronic Spectra.—The electronic spectra of high-spin manganese(III), a d^4 system subject to Jahn–Teller distortion, are imperfectly understood. Davis *et al.*[24] argued that the spectra of the pentachloromanganates(III) could be explained by assuming that the manganese achieved six-co-ordination by sharing axial ligands as in $[NH_4]_2MnF_5$.[25] The *X*-ray structure determination of $[bipyH_2]MnCl_5$, which showed [13] the manganese to be

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[25] D. R. Sears and J. L. Hoard, *J. Chem. Phys.*, 1969, **50**, 1066.

five-co-ordinate in a distorted square-pyramidal environment, resulted in a reassessment of the assignments. Bellitto *et al.*[14] concluded that the band at *ca.* 24 kK was due to charge-transfer transitions, and that the lower bands were *d–d* transitions. All the pentachloromanganates(III) studied in this work dissolve in acetone to give deep green solutions, which have very similar spectra (Table 2); the small differences may be due to slight decomposition. The similarity between the solution spectra and that of [bipyH_2]$MnCl_5$ in the solid state argues in favour of a similar five-co-ordinate distorted square pyramidal geometry for all these complexes in solution. Thus, assuming C_{4v} symmetry in solution the bands can be assigned to the transitions $^5A_2 \rightarrow {}^5A_1$ (*ca.* 13 kK), $^5A_2 \rightarrow {}^5B_1, {}^5B_2$ (*ca.* 17 kK), and charge transfer (*ca.* 24 kK). Because of the rapid decomposition of these complexes in solution attempts were not made to determine extinction coefficients. A typical solution spectrum, that of $[NEt_4]_2MnCl_5$, is shown in the Figure. The resemblance of this spectrum to that of manganese(III) in concentrated hydrochloric acid[26] (bands at 12·8, 17·7, 25·6 kK) is noteworthy, suggesting that the $MnCl_5^{2-}$ species is present in such solutions at low pH. The solid reflectance spectra are of two types. All but two complexes exhibit reflectance spectra which are very similar to the solution spectra and, more important, are similar to the solid spectrum of [bipyH_2]$MnCl_5$. Thus, all the complexes except $[NMe_2H_2]_2MnCl_5$,EtOH and ' $[NMeH_3]_2MnCl_5$ ' are five-co-ordinate in the solid state and in solution. The other two complexes have the low-energy band shifted to even lower frequencies, reminiscent of six-co-ordinate structures.[24] Davis *et al.*[24] have assigned a band *ca.* 10 kK to the $^5B_{1g} \rightarrow {}^5A_{1g}$ transition in D_{4h} symmetry. While a structure cannot be assigned to these complexes with any great degree of confidence, it is interesting to note that the spectral changes have occurred in complexes where the cation, [NMe_2H_2] or [$NMeH_3$], has a relatively small volume. This may mean the crystal-packing forces allows chlorine bridging or, in the case of $[NMe_2H_2]_2MnCl_5$,EtOH, even allows co-ordination of the ethanol molecule. However, it should also be noted that in the complexes containing even smaller cations (NH_4, K, Rb), although solvation occurs, the H_2O molecule does not co-ordinate.

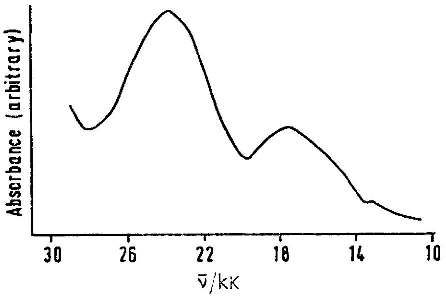

FIGURE Electronic spectrum of $[NEt_4]_2MnCl_5$ in acetone

Other Properties.—The equivalent conductance of $[NEt_4]_2MnCl_5$ is 168 Ω^{-1} cm^2 mol^{-1} in nitromethane, good evidence for a 2 : 1 electrolyte. The other pentachloromanganates(III) were either insufficiently soluble in the solvents tried (nitromethane, acetonitrile, and acetone), or decomposed so rapidly in solution that reproducible values could not be obtained.

Goodwin and Sylva[20] measured the susceptibilities of [phenH_2]$MnCl_5$ and [bipyH_2]$MnCl_5$ over a range of temperatures, and found them to be simple paramagnetics with θ values of −20 and −10 K, respectively. Gill[11] reported an ' approximately zero ' θ value for $[NEt_4]_2MnCl_5$. The magnetic moments of octahedral[27] or square pyramidal[20] manganese(III) complexes, in which no magnetic interaction occurs, approximate to the ' spin-only ' value for high spin d^4, *i.e.* 4·9 B.M. The alkylammonium complexes reported here have moments of *ca.* 5 B.M., whilst the alkali-metal complexes have lower moments, *ca.* 4·93 B.M. The Cs_2MnCl_5 complex has a moment of 4·83 B.M. which may be indicative of some small magnetic interaction. The pentafluoromanganates(III) of NH_4, Li, and Na, which are of the type M_2MnF_5, exhibit antiferromagnetism.[28] The effective magnetic moment of $[NMe_2H_2]_2MnCl_5$,EtOH was found to be 4·56 B.M.; we can offer no satisfactory explanation for this.

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