Contribution from the Department of Chemistry, University of Queensland, St. Lucia, Old. 4067, Australia, and Department of Chemistry, Queensland Institute of Technology, Brisbane, Queensland 4000, Australia

The Multidentate Chemistry of Manganese(II). II. Six and Eight Coordinate Compounds with Bidentate Ligands

B. Chiswell* and E.J. O'Reilly**

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The existence of colourless, pure manganese(II) complexes containing four molecules of 1:10-phenanthroline (phen) per manganese atom has been substantiated, and some new compounds of this type prepared to extend the range of known compounds to the following: $Mn(phen)_4X_2 . nH_2O$ (where X = a weakly or non-coordinating anion such as BPh_4, I or 2-bromocamphor-π-sulphonate; n = 2, 4 or 6 depending upon X). A number of yellow compounds possessing three or two molecules of phen per manganese atom have also been prepared for comparison with tetrakis-phen compounds, as have also the colourless complexes $M(phen)_4(ClO_4)_2 . nH_2O$ (where M = Sr, Ba or Pb; n = 0, 4 or 5). Two other bidentate ligands with rigid chelate rings, viz. o-phenylenediamine and 8-aminoquinoline, have also been shown to yield 8-coordinate tetrakis-ligand manganese(II) perchlorate complexes, as well as octahedral compounds of the types $[Mn(ligand)_3](ClO_4)_2$ and $[Mn(ligand)_2X_2]$, (where X = Cl or Br). On the other band, bidentate nitrogenous ligand with more flexible chelate rings have been shown to yield tris- and bis-ligand octahedral complexes of the types $[Mn(ligand)_3](ClO_4)_2$ and $[Mn(ligand)_2X_2]$ (where X = Cl or Br).

Introduction

Manganese(II) complexes of 1:10 phenanthroline (phen) have been known for a number of years. Thus, Brandt *et al.*[1] in 1954 mention the bis-, tris and tetrakis-phen manganese(II) compounds, while Broomhead and Dwyer[6] isolated $[MnphenCl_2]$ in 1961. The compound tetrakis-1:10-phenanthrolinemanganese(II) perchlorate, first reported by Pfeiffer and Werdelmann,[3] is of particular interest, as is also the $Mn(phen)_4$ (2-bromo-camphor-π-sulphonate)$_2$ complex.[4] Althought Brandt *et al.*[1] considered it to be unlikely for the manganese atom to be eight-cordinate, they did not suggest possible structures for these compounds.

In an infrared study in 1959, Schilt and Taylor[2] suggested that all the compounds of formula $M(phen)_4(ClO_4)_2 . nH_2O$ (where M = Sr, Ba, Pb or Mn; n = 0, 2 or 4) were eight-coordinate, with all four phenanthroline molecules acting in a bidentate capacity.

Eight-coordinate compounds of manganese(II) are not common. In 1963 some Russian authors[7] found that both 8-hydroxy- and 8-thioloquinoline formed compounds of the type $Mn(lig)_2(Hlig)_2$ (where Hlig = protonated ligand), in which all ligand groups acted as bidentate chelates.

More recently, Bodner and Hendricker[8] have reported that the bidentate, 1,8-naphthyridine, forms a tetrakis- compound with manganese(II) perchlorate, in which the manganese atom is coordinated to eight nitrogen atoms. The crystal structure[9] of the isomorphous $Fe(ligand)_4(ClO_4)_2$ compound substantiates this claim.

In all the above tetrakis- bidentate manganese(II) complexes, the ligand entity possesses a strictly rigid structure. This requires that if the nitrogen atom (or one of the nitrogen atoms) is coordinated, then the second donor atom must be wihin bonding proximity to the metal ion. To attempt to delineate the features which lead to the formation of compounds of this type, we have undertaken an investigation of (i) the manganese(II) complexes of 1:10-phenanthroline; (ii) the manganese(II) complexes of other nitrogenous bidentate ligands.

Results and Discussion

As reported by Pfeiffer and Werdelmann,[3] the tetraphen perchlorate complex can be prepared by mixing one molecular proportion of manganese(II) perchlorate in water with either two or four molecular proportions of 1:10-phenanthroline hydrate in methanol. In fact we have found that intermixture of one molecular proportion of any manganese(II) salt, with a range of molecular proportions of phen from 1 to 5, yields the compound $Mn(phen)_4(ClO_4)_2 . 4H_2O$, provided that bot excess perchlorate ion and water

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* Department of Chemistry, University of Queensland, St. Lucia, Qld. 4067, Australia. Present Address: University Chemical Laboratories, Lensfield Road, Cambridge, England.

** Department of Chemistry, Queensland Institute of Technology, Brisbane, Queensland 4000, Australia.

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are present. Thus treatment of any of the manganese-phen perchlorate salts described in this paper with perchlorate ion in aqueous solution, led to the deposition of this compound.

The colour of Mn(phen)$_4$(ClO$_4$)$_2$. nH$_2$O is of interest. Althought Pfeiffer and Werdelmann inconsistently describe the compound as being "yellowish needles" in one preparation and "nearly white" in another preparation, we have consistently found that the compound, when recrystallised from water, is a completely colourless powder. The inconsistency in the report of these workers may be in the fact that the "yellowish needles" description applies to the initial preparation of the compound. The colour of the compound obtained from the recrystallisation from water is not described. As the aqueous solution from which the tetrakis-compound is obtained is yellow, perhaps the yellow colour is due to the presence of solution on the crystals. Spectrophotometric evidence[5] indicates that the colour of the solution is due to the presence of [Mn(phen)$_3$]$^{2+}$. Attempts by Miller and Brandt[5] to salt this complex cation out of solution as the chloride salt, led to the deposition of [Mn(phen)$_2$Cl$_2$]. We have found that yellow crystals of [Mn(phen)$_3$](ClO$_4$)$_2$ are slowly deposited when the concentrated filtrate obtained after removal of the tetrakis-complex is allowed to stand for some days. It is of interest that no spectrophotometric evidence of the presence in aqueous solution of [Mn(phen)$_4$]$^{2+}$ could be obtained.[5]

Pfeiffer and Werdelmann[3] even further complicated the problem by recrystallising the tetrakis-compound from butanol as "glistening yellow rhomboids", and demonstrating that these crystals were soluble in alcohol, glacial acetic acid, pyridine and nitrobenzene, to yield bright yellow-coloured solutions. Presumably the analytical figure given by these workers refer to the water-recrystallised rather than the butanol-recrystallised product, as we have found that this latter product is [Mn(phen)$_3$](ClO$_4$)$_2$. H$_2$O.

A further problem of colour lies in the description by Pfeiffer and Tappermann[4] of the compound Mn(phen)$_4$(2-promocamphor-π-sulphonate)$_2$. 6H$_2$O as being "bright yellow". Our results show this compound, and the new tetrakis-phen iodide, tetraphenylborate and tetrafluoroborate to be colourless; the solutions from which they are obtained being yellow in colour.

All the known tris, bis- and mono-phen complexes of manganese(II) are yellow, and it would seem likely that such colour arises from metal-ligand charge transfer transitions, which come into operation upon complexation of the phen ligand to the metal atom. If this is the case, the colourless nature of the terakis-compounds indicates that the phen moieties are bonded in such a way that there is little delocalization of the π-electron system on the four ligand groups. The electronic spectra of the tetra-phen compounds of manganese(II) in aqueous solution could not be used to diagnose the actual ligands, as the yellow solution has been shown to possess [Mn(phen)$_3$]$^{2+}$ with no evidence of the tetrakis-complex.[5] Solid state reflectance spectra failed to reveal any clear peaks.

Thermogravimetric analysis of Mn(phen)$_4$(ClO$_4$) . 4H$_2$O is of interest. Schilt and Taylor[2] reported the preparation of Mn(phen)$_3$(ClO$_4$)$_2$ by heating the tetrakis-phen compound in vacuo over P$_2$O$_5$ at 185°; Pfeiffer and Werdelmann[4] report that the same treatment yields bright yellow Mn(phen)$_2$(ClO$_4$)$_2$.

We have found that freshly prepared Mn(phen)$_4$(ClO$_4$)$_2$. 4H$_2$O readily loses two water molecules when allowed to stand in air. The dihydrate then loses no further water in air over a period of two years. Thermogravimetric treatment of the colourless dihydrate indicates that two water molecules are lost at between 75 and 119°C to yield the colourless Mn(phen)$_4$(ClO$_4$)$_2$. At approximately 180°C, over a period of 25 min., a phenanthroline molecule is lost and a yellow powder, shown by analysis to be Mn(phen)$_3$(ClO$_4$)$_2$, is obtained. Further heating loss up compound indicated an indeterminate weight loss up to 300°C, at which point the compound exploded. We could obtain no evidence that the bis-phen complex was obtained by prolonged heating of the tetraphen compound at 180-190°C.

Schilt and Taylor[2] based their assignment of eight-coordination for the compounds M(phen)$_4$(ClO$_4$)$_2$. nH$_2$O (M = Mn, Pb, Sr or Ba) on the basis of infrared peaks in the regions 1510-1550 and 700-900 cm^{-1}. They claim that their results indicated no uncomplexed phen in all four compounds. We have also studied the infrared spectra of these and the other manganese compounds described in this paper. We find that the peak systems are exceedingly complex and very similar for all the phen compounds studied.

The infrared spectra indicate that in all the perchlorate compounds the anion is basically ionic, with the strong broad ν_3 band occurring at approx. 1100 cm^{-1}, and the weaker ν_1 band appearing at roughly 950 cm^{-1}.

Thermogravimetric analysis of colourless Sr(phen)$_4$(ClO$_4$)$_2$. 4H$_2$O indicates the loss of four water molecules at 55-80°C, and then no further weight loss until decomposition commences at approximately 200 °C. Colourless Pb(phen)$_4$(ClO$_4$)$_2$ demonstrates no weight loss upon heating until decomposition commences at approximately 200°C. These results may very tentatively be interpreted to indicate that whereas the tetrakis-phen manganese compound loses water then phen to yield the stable [Mn(phen)$_3$]$^{2+}$ complex, the strontium and lead compounds lose water (if present), but decompose upon further heating.

Although attempts to grow crystals of Mn(phen)$_4$(ClO$_4$)$_2$. 4H$_2$O have been unsuccessful, the corresponding strontium, barium and lead compounds are crystalline. However, X-ray powder patterns of the manganese compound are not identical to those of any of the three other compounds. Further attempts to obtain crystals of Mn(phen)$_4$(ClO$_4$)$_2$. 4H$_2$O for X-ray analysis are being undertaken.

Attemptes to prepare in solution the compound Mn(phen)$_2$(ClO$_4$)$_2$ mentioned by Pfeiffer and Werdelmann[4] yielded colourless Mn(phen)$_4$(ClO$_4$)$_2$. 4H$_2$O when Mn(ClO$_4$)$_2$ and phen were mixed in aqueous solution, or yellow [Mn(phen)$_2$XH$_2$O]ClO$_4$ when MnX$_2$ (X = Cl, Br or I) was treated with sodium perchlorate and phen in ethanol solutions. The interaction of MnX$_2$ (X = Cl, Br or I) with phen in ethanol solution led to the isolation, as expected, of the bis-phen complexes [Mn(phen)$_2$X$_2$].

In widening the scope of the study to see if other bidentate ligands could yield tetrakis-ligand manganese(II) complexes, we have studied only nitrogenous donors, although the Russian work would indicate that such complexes are not restricted to nitrogen donor-ligands.

The addition of a concentrated ethanolic solution of each of the ligands, *o*-phenylenediamine, 8-aminoquinoline, 1,3-propanediamine, ethylenediamine, 2-pyridylhydrazine and 2-aminoethylpyridine, (5 molecular proportions), to concentrated ethanolic solutions of manganese(II) perchlorate (1 molecular proportion) yielded a white precipitate in each case. In the case of the first two ligands, the compound had the formula, $Mn(ligand)_4(ClO_4)_2$, while for the other four ligands the tris-complex, $Mn(ligand)_3(ClO_4)_2$ was obtained.

Attempts to prepare complexes of manganese(II) perchlorate and 2-aminopyridine (potential 4-membered chelate ring) or 1,8-diaminonaphthalene (potential 6-membered chelate ring) were unsuccessful under similar conditions to the above preparations, even when carried out in an inert atmosphere. In each case, no white precipitate was obtained and upon concentration of the reaction solution, and standing, manganese dioxide gradually deposited.

On the other hand, 2,9-dimethyl-1:10-phenanthroline yielded a pale yellow bis-ligand complex of manganese(II) perchlorate, $Mn(ligand)_2(ClO_4)_2$.

Attempts to obtain tris-ligand compounds of *o*-phenylenediamine or 8-aminoquinoline, by evaporation of the yellow coloured solutions remaining after the tetrakis-complex had been filtered off, led to the slow formation of deprotonated complexes. These compounds were not tetrakis-ligand complexes, and will be reported at a later date. However, these tris-complexes were obtained by dissolving the corresponding tetrakis-compound in acetone or nitromethane, adding a drop of perchloric acid, and allowing the solution to evaporate slowly and deposit crystals of the required compound.

Infrared spectra indicate that in all the perchlorate compounds, the anion is basically ionic. In each case a single broad band is observed at approx. 1100 cm^{-1}, with a smaller peak at roughly 950 cm^{-1}. Attempts to confirm the ionic nature of the perchlorate in the tetrakis-compounds, by measurement of molar conductivities in nitromethane, are almost certainly invalid. All the compounds, $Mn(ligand)_n(ClO_4)_2$ (where $n = 3$ or 4), have values in the region of 160-180 r.o. in this solvent. However, as $Mn(ligand)_3(ClO_4)_2$ is the only moiety that can be obtained from solutions of the compounds in this solvent, it is doubtful if the tetrakis-compounds are present in solution. Nevertheless, these tris-compounds are clearly 1:2 electrolytes, and the similarity of the infrared spectra of tris- and tetrakis-compounds in the perchlorate band region would suggest that the latter compounds also possess ionic perchlorate groups.

Gibson and McKenzie[10] have noted that in multidentate ligands containing pyridine residues, the infrared peaks due to pyridyl ring vibrations appear at approx. 1610 and 1570 cm^{-1} in the free ligand, and at approx. 1590 and 1570 cm^{-1} when the pyridine residue is coordinated to a metal ion. The results of our studies, shown in the infrared spectra table, agree with their postulate, and suggest that in all the pyridine-containing complexes described, and in particular the compound $Mn(8\text{-aminoquinoline})_4(ClO_4)_2$, the pyridyl residue is coordinated.

It would appear likely that infrared evidence would be useful in deciding if all the primary amine groups in the complexes $Mn(ligand)_4(ClO_4)_2$, (ligand = *o*-phenylenediamine or 8-aminoquinoline), are bonded. Thus, Marks *et al.*[11] have claimed that in the *o*-phenylenediamine complexes, $Ni(ligand)_nX_2$ (where $n = 2, 3, 4$ or 6; X = monovalent anion), uncoordinated amine has NH stretch peaks at 3405-3380 cm^{-1} and CN peaks at 1282-1277 cm^{-1}, while coordinated amine has highest energy NH peaks at 3350-3290 cm^{-1} and CN peaks at 1260-1230 cm^{-1}. These workers have used this classification to adduce that for the compound in which $n = 4$ there are two bidentate and two monodentate ligands. However, work of Duff,[12] and the work reported here, would suggest that no such simple distinction between bonding and nonbonding amines in *o*-phenylenediamine (PDA) is possible. Infrared spectra by Marks *et al.*[11] and Duff[12] on the same compounds, viz. $Ni(PDA)_2Br_2$, $Ni(PDA)_3X_2$ (X = Br or NO_3), in at least two of the three compounds bear little resemblance. Furthermore, in the compounds $Ni(PDA)_3Cl_2$[12] and $Ni(PDA)_2(HSO_3)_2$ (M = Co or Ni),[13] Duff reports strong NH stretching peaks above 3405 cm^{-1}, which is the top limit set by Marks *et al.* for uncoordinated *o*-phenylenediamine.

The highest energy NH frequency of strong intensity, and the CN stretch frequency for some of the manganese(II) complexes of this work, are listed in the infrared spectra table. No conclusions can be made from these results, beyond the facile observation that the ligand NH and CN stretch vibrations change when the ligand is coordinated.

As was found for the tetrakis-phen compounds, the solid reflectance spectra of the $Mn(ligand)_4(ClO_4)_2$ complexes showed no features of significance.

The seven bidentate ligands, *o*-phenylenediamine, 8-aminoquinoline, 2-pyridylhydrazine, ethylenediamine, 1,3- propanediamine, 2-aminomethylpyridine and 2,9-dimethyl-1:10-phenanthroline, all yielded colourless to yellow octahedral compounds of the type $[Mn(ligand)_2X_2]$ (where Xy = Cl or Br), when an ethanolic solution of the ligand (5 molecular proportions) was added to manganese(II) chloride or bromide (1 molecular proportion) in ethanol. All these compounds exhibited virtually no conductivity in nitromethane solution.

Conclusions

The evidence clearly indicates that, although bidentate nitrogenous ligands with 5 or 6-membered chelate rings readily form octahedral compounds of the type $[Mn(ligand)_3](ClO_4)_2$ when reacted with manganese(II) perchlorate, or octahedral $[Mn(ligand)_2X_2]$, (where X = Cl or Br), when reacted with manganese(II) chloride or bromide, in situations in which the chelate ring is particularly rigid, tetrakis-bidentate complexes can be obtained in the presence of non- or weakly coordinating anions. Thus, the ligands

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Table I. Table of Compounds.

Compound	Colour		Analysis %				Method of Prepn.	Mag. Mmt. μ_{eff} in B.M.
			C	H	N	Mn		
(i) 1: 10-phenanthroline compounds								
$Mn(phen)_4(ClO_4)_2 \cdot 4H_2O$ [a]	white	Calc.	55.1	3.8	10.7	5.3	A_1	6.0
		Found	55.1	3.6	10.8	5.5		
$Mn(phen)_4(BF_4)_2 \cdot 2H_2O$	white	Calc.	57.1	3.6	10.6	5.4	A_1	5.9
		Found	56.8	3.7	10.6	5.4		
$Mn(phen)_4(BPh_4)_2 \cdot 2H_2O$	white	Calc.	71.7	6.0	8.9	4.4	L	6.0
		Found	71.4	6.2	8.9	4.2		
$Mn(phen)_4I_2 \cdot 4H_2O$ [b]	white	Calc.	52.3	3.6	—	5.0	A_1	6.0
		Found	52.8	3.5	—	4.7		
$Mn(phen)_4$(2-bromocamphor-π-sulphonate)$_2 \cdot 6H_2O$	white	Calc.	54.3	4.8	7.5	3.7	B	6.0
		Found	54.0	4.8	7.5	3.6		
$Sr(phen)_4(ClO_4)_2 \cdot 5H_2O$	white	Calc.	52.5	3.8	10.2	—	A_2	—
		Found	52.4	3.5	10.1	—		
$Ba(phen)_4(ClO_4)_2 \cdot 4H_2O$	white	Calc.	51.1	3.5	9.9	—	A_2	—
		Found	51.2	2.8	9.9	—		
$Pb(phen)_4(ClO_4)_2$	yellow	Calc.	51.2	2.8	9.9	—	A_2	—
		Found	51.3	2.8	9.8	—		
$Mn(phen)_3(ClO_4)_2 \cdot 2H_2O$	yellow	Calc.	54.4	3.0	10.6	—	C	5.9
		Found	54.3	3.2	10.5	—		
$Mn(phen)_3(ClO_4)_2 \cdot 1H_2O$	yellow	Calc.	53.2	3.2	10.3	6.8	D and E	5.9
		Found	53.2	3.4	10.4	6.8		
$Mn(phen)_3(BPh_4)_2$	yellow	Calc.	81.8	5.2	—	4.4	A_1	5.9
		Found	82.1	5.2	—	4.3		
$Mn(phen)_2Cl_2$	yellow	Calc.	59.3	3.3	—	11.3	E	6.0
		Found	59.3	3.4	—	11.5		
$Mn(phen)_2Br_2$	yellow	Calc.	50.1	2.8	9.7	9.5	E	6.0
		Found	50.1	2.8	9.1	9.4		
$Mn(phen)_2I_2$	yellow	Calc.	43.0	2.4	—	8.2	F	6.0
		Found	43.1	2.6	—	8.4		
$Mn(phen)_2(NO_2)_2$	yellow	Calc.	56.8	3.2	16.6	10.8	G	6.0
		Found	56.7	3.2	16.0	10.7		
$Mn(phen)_2(H_2O)Cl$	yellow	Calc.	50.1	3.2	9.9	9.7	H	5.9
		Found	50.0	3.3	9..7	9.8		
$Mn(phen)_2(H_2O)Br$	yellow	Calc.	48.6	3.0	—	9.3	J	5.9
		Found	48.4	3.0	—	9.3		
$Mn(phen)_2(H_2O)I$	yellow	Calc.	43.6	2.7	8.5	8.3	K	6.0
		Found	43.4	2.6	9.0	8.7		
(ii) Other compounds.								
$Mn(PDA)_4(ClO_4)_2$ [1]	white	Calc.	42.4	4.7	16.3	8.0	L	6.0
		Found	42.2	4.7	16.1	7.9		
$Mn(8\text{-}AQ)_4(ClO_4)_2$ [2]	white	Calc.	51.9	3.8	13.4	6.6	L	6.0
		Found	51.7	3.7	13.1	6.5		
$Mn(PDA)_3(ClO_4)_2$	white	Calc.	37.4	4.1	14.5	9.5	M	5.9
		Found	37.1	4.2	14.3	9.2		
$Mn(8\text{-}AQ)_3(ClO_4)_2$	white	Calc.	47.3	3.5	12.1	8.0	M	6.0
		Found	47.0	3.1	12.2	8.0		
$Mn(en)_3(ClO_4)_2$ [3]	white	Calc.	16.5	5.5	19.3	12.6	L	—
		Found	16.9	5.5	19.4	12.3		
$Mn(pn)_3(ClO_4)_2$[4]	white	Calc.	22.7	6.3	17.6	11.5	L	5.9
		Found	22.6	6.2	17.2	11.2		
$Mn(pyhy)_3(ClO_4)_2$ [5]	white	Calc.	30.9	3.6	21.6	9.5	L	6.1
		Found	30.9	3.8	21.9	9.0		
$Mn(apic)_3(ClO_4)_2$[6]	white	Calc.	37.3	4.1	14.5	9.5	L	—
		Found	37.1	4.0	14.3	9.4		
$Mn(PDA)_2Cl_2$	yellow	Calc.	43.2	4.7	16.2	16.0	L	—
		Found	42.9	4.7	16.0	15.7		
$Mn(PDA)_2Br_2$	yellow	Calc.	33.4	3.7	13.0	12.8	L	—
		Found	33.4	3.7	12.7	12.4		
$Mn(8\text{-}AQ)_2Br_2$	yellow	Calc.	52.0	3.9	13.3	13.2	L	6.0
		Found	52.0	3.6	13.4	13.3		
$Mn(8\text{-}AQ)_2Cl_2$	yellow	Calc.	42.8	3.2	11.1	10.9	L	—
		Found	43.0	3.4	11.0	11.0		
$Mn(en)_2Cl_2$	white	Calc.	19.6	6.5	22.8	22.3	L	—
		Found	19.4	6.2	22.4	22.0		
$Mn(pn)_2Br_2$	white	Calc.	19.8	5.5	15.9	15.2	L	5.9
		Found	19.6	5.5	16.2	15.4		
$Mn(pyhy)_2Br_2$	pale yellow	Calc.	27.8	3.2	19.4	12.7	L	—
		Found	28.1	3.0	19.0	12.7		
$Mn(apic)_2Br_2$	yellow	Calc.	33.4	3.7	13.0	12.8	L	5.9
		Found	33.6	3.7	13.0	12.8		

Table IV. (Continued)

$Mn(DMP)_2(ClO_4)_2$ [7]	yellow	Calc.	50.0	3.6	8.4	8.2	L	5.9
		Found	49.7	3.4	8.6	8.4		
$Mn(DMP)_2Cl_2$	pale yellow	Calc.	62.1	4.4	10.3	10.1	L	6.0
		Found	61.9	4.2	10.3	10.1		
$Mn(DMP)_2Br_2$	yellow	Calc.	54.3	3.8	8.9	8.7	L	—
		Found	54.3	3.4	8.5	8.7		

[a] Heating the freshly prepared compound at 100-105°C led to a 6.8% weight loss. Calculated weight loss for $4H_2O$ is 6.9%. When the compound is allowed to stand in air, two molecules of water are lost to give the dihydrate (Found: C, 56.8; H, 3.7; Mn, 5.5 Calc. C, 57.1; H, 3.6; Mn, 5.4%). [b] Weight loss at 110°C for 24 hr. was 6.6%. Calculated weight loss for $4H_2O$ is 6.5%.

Ligand abbreviations: [1] o-phenylenediamine; [2] 8-aminoquinoline; [3] ethylenediamine; [4] 1,3-propanediamine; [5] 2-pyridylhydrazine; [6] 2-aminomethylpyridine; [7] 2,9-dimethyl-1:10-phenanthroline.

Table II. Infrared Spectra Table (frequencies in cm^{-1}).

Compound	Free ligand	$Mn(ligand)_4(ClO_4)_2$	$Mn(ligand)_3(ClO_4)_2$	$Mn(ligand)_2Br_2$
(i) Pyridyl ring vibrations				
8-aminoquinoline	1591, 1570	1611, 1570	1610, 1570	1611, 1570
2-pyridylhydrazine	1588, 1571	—	1609, 1570	1609, 1571
2-aminomethylpyridine	1589, 1570	—	1609, 1571	1610, 1571
(ii) NH stretch vibrations				
o-phenylenediamine	3385	3345	3365	3360
8-aminoquinoline	3390	3335	3350	3360
2-pyridylhydrazine	3395	—	3345	3355
2-aminomethylpyridine	3380	—	3350	3360
(iii) CN stretch vibrations (in range 1290-1220 cm^{-1})				
o-phenylenediamine	1275	1253	1258	1260
8-aminoquinoline	1273	1250	1250	1255

1:10-phenanthroline, *o*-phenylenediamine and 8-aminoquinoline, in the presence of anions such as perchlorate or tetraphenylborate, yield these 8-coordinate compounds. On the other hand, ligand entities with less rigid chelate chains do not yield such compounds. It is of interest that although it is not possible to see how one of the nitrogen donors of 1:10 phenanthroline could be coordinated without the other nitrogen being within bonding distance of the metal, it is possible to make molecular models of both *o*-phenylenediamine and 8-aminoquinoline compounds in which only (one of) the amino-group(s) is coordinated.

In the case of 2,9-dimethyl-1:10-phenanthroline, only bis-ligand complexes can be obtained. Presumably the steric hindrance of the methyl groups prevents tris- or tetrakis-ligand complex formation.

Experimental Section

Preparation of Compounds. The physical properties of the complex compounds are listed in the tables. The code for the methods of preparation is as follows:

(A1) Preparations were carried out by the general method of Shilt and Taylor.[2] This entails interaction in aqueous solution of manganese(II) sulphate, 1:10-phenanthroline and an alkali metal or ammonium perchlorate, tetraphenylborate, tetrafluoroborate or iodide as required.

(A2) Preparations by the method of Schilt and Taylor.[2]

(B) Prepared by the method of Pfeiffer and Tappermann.[4]

(C) Heat treatment of $Mn(phen)_4(ClO_4)_2 . 2H_2O$ at 180°C for 25 min.

(D) Recrystallisation of the corresponding tetrakis-ligand compound from acetone, n-butanol or nitromethane.

(E) Interaction of the required manganese(II) salt and 1:10-phenanthroline in either 1:3 or 1:2 molecular proportions in either acetone or ethanol solutions.

(F) Sodium iodide (6 mmole) in warm ethanol (5 ml) was added to manganese(II) chloride in warm ethanol (5 ml). The precipitated sodium chloride was removed by filtration and 1:10-phenanthroline monohydrate (6 mmole) in warm ethanol (10 ml) was added. The greenish yellow crystalline precipitate obtained, was filtered, washed with ethanol and air dried. The same product was obtained when manganese(II) acetate (1 mmole), lithium iodide (50% excess) and 1:10-phenanthroline monohydrate (2 m mole) were reacted in warm ethanol.

(G) Manganese(II) sulphate (1 mmole) and 1:10-phenanthroline monohydrate (2 mmole) were dissolved in warm aqueous solution (50 ml) to which was added an excess of potassium nitrite in warm water

(10 ml). From the deep yellow solution a yellow solid was deposited which was filtered, washed with water and air dried.

(H) Sodium perchlorate (excess) in warm ethanol (5 ml) was added to manganese(II) chloride (2 mmole) in warm ethanol (5 ml.

The precipitated sodium chloride was removed by filtration and 1:10-phenanthroline (4 mmole) in warm ethanol (5 ml) was added. The pale yellow solution yielded a pale yellow precipitate which was filtered, washed with ethanol and air dried.

(J) Manganese(II) sulphate (1 mmole) and 1:10-phenanthroline monohydrate (2 mmole) were dissolved in warm aqueous solution (20 ml). On addition of excess sodium bromide, a yellow precipitate was obtained which was washed, air dried and dried over silica gel.

(K) Lithium iodide (excess) and manganese(II) perchlorate (1 mmole) were dissolved in warm acetone. This solution was added to the warmed solution of tetrakis-(1:10-phenanthroline)manganese(II) perchlorate (1 mmole) in acetone. A greenish yellow precipitate was obtained which was filtered, washed with acetone and air dried.

(L) A concentrated ethanolic solution of the ligand (5 molecular proportions) was added to a concentrated ethanolic solution of the required manganese(II) salt (1 molecular proportion) with stirring. The required product was precipitated towards the end of addition of ligand, and was removed by filtration.

(M) The corresponding tetrakis-ligand complex was dissolved in acetone or nitromethane, a drop of perchloric acid was added, and the solution allowed to slowly evaporate and deposit the required tris-complex.

Infrared Spectra. Were carried out on a Perkin-Elmer 457 Spectrophotometer using Nujol mulls and KBr discs.

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