The Multidentate Chemistry of Manganese(II). III. Complexes of Linear Quadridentate Nitrogenous Ligands

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Linear quadridentate nitrogenous ligands have been shown to yield three different types of Manganese(II) compound. Simple octahedral compounds of formulation $Mn(quad)X_2^*$ (where X = Cl, Br, ClO_4 or BPh_4) are obtained with most ligands. However, with sterically rigid ligands, compounds of the type $[Mn(quad)_2]X_2$ $(X = ClO_4 \text{ or } BPh_4$, possibly 8-coordinate) can also be prepared, while on the other hand with less rigid ligands, bridged dimers of the type $[Mn_2(quad)_3]X_4$ $(X = ClO_4 \text{ or } BPh_4)$ are also obtained.

Introduction

Lions and Martin¹ in 1958 reported the interaction of biacetyl and 2-pyridylhydrazine to yield the osazone Ib, and showed that it could function as a planar chelat-

 $R_{1} = R_{2} = R_{2}$ $H_{1} = R_{1} = R_{2} = R_{1}$ $I_{1} = R_{1} = R_{2} = R_{1}$ $I_{2} = R_{1} = R_{2} = R_{3}$ $I_{3} = R_{1} = R_{1} = R_{2} = CR_{3}$ $I_{3} = R_{1} = R_{1} = R_{2} = CR_{3}$ $I_{3} = R_{1} = R_{2} = R_{3}$ $I_{3} = R_{1} = R_{2} = R_{3}$

ing agent. Later workers² demonstrated that neutral divalent metal complexes of copper, nickel and palladium could readily be obtained by the removal in alkaline solution of the two hydrazine protons to yield intensely coloured compounds. More recent work on the metal complexes of ligands of type I has been undertaken by a number of workers.³

In the preparation of square planar manganese(II) compounds for oxygenation studies⁴, attempts were made to prepare the compounds [Mn(quad I)]X₂ (where X = Cl, Br, ClO₄ or BPh₄). Octahedral compounds could be isolated when MnX₂ · nH₂O was added

to any ligand I in ethanol for X = Cl or Br, but when $X = ClO_4$ or BPh₄, colourless complexes of formulation Mn(quad)₂X₂ were precipitated. This behaviour is reminiscent of similar results obtained in the preparation of [Mn(bidentate)₄]X₂ (X = ClO₄, BPh₄ or I; bidentate = 1,10-phenanthroline, *o*-phenylenediamine or 8-aminoquinoline)⁵. We have accordingly investigated the manganese(II) complexes of ligands of type I and of a series of linear nitrogenous quadridentates.

Results and Discussion

The ligands studied are shown I to X. It was found



that upon careful addition by titration of two molecular proportions of ligands I, II, IV and VIII in ethanol to one molecular proportion of $Mn(ClO_4)_2$ or Mn $(BPh_4)_2$ in water, the colourless bis-complexes [Mn $(quad)_2]X_2 \cdot nH_2O$ precipitated when the titration just

^{* (}quad) = abbreviation for quadridentate ligand; the number of the ligand is shown in specific cases.

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reached its end-point. Under the same conditions, the ligands III, V, VI, VII, IX and X all yielded the yellow complexes $[Mn_2 \ ligand_3]X_4 \cdot nH_2O$ at a titration ratio of 2 MnX₂ to 3 ligand. Mono-complexes, *viz*. Mn (quad)(ClO₄)₂ · nH₂O could be prepared for all ligands except I and IV by intermixing 1:1 molecular ratios of ligand and Mn(ClO₄)₂ in ethanol, and leaving the solutions to crystallise over several weeks. Similarly, yellow, orange or green mono-ligand halide complexes could be obtained for all ligands by this latter method of preparation. The compounds prepared are listed in the Table. Although all the perchlorate and tetraphenylborate compounds deposited with water of crystallisation, analytical figures are given for the anhydrous compounds obtained by drying over P₂O₅ at

Nitromethane solutions $(\sim 10^{-3}M)$ of all the perchlorate and tetraphenylborate salts exhibited conductivities typical of 1:2 electrolytes (see Table) calculated on the molecular weight basis of one manganese atom per formulation *viz*. [Mn(quad)_n]X₂ (where $n = 1, 1^{1/2}$ or 2; $X = ClO_4$ or BPh₄). This evidence of ionic nature of the compounds is supported by their solid mull infrared spectra. All the perchlorate compounds exhibit the strong broad ν_3 band at ~1100 cm⁻¹ and the weaker ν_1 band at ~950 cm⁻¹, typical of ionic perchlorate.⁶

All compounds possess normal magnetic moments for high spin d^5 manganese(II). No detail could be observed in the UV-visible spectra carried out on the $\sim 10^{-3}M$ nitromethane solutions. Higher concentrations of solution could not be obtained due to solubility problems. This problem also prevented NMR or solution molecular weight studies, while the ionic and/or explosive nature of the perchlorates and tetraphenylborates percludes their mass spectrometry. Solid state

Compound	Colour		Analysis						/1000	I.R. Pyridine Breathing
			С	н	N	Mn	Cl or Br	295K	(r.o)	(cm ⁻¹)
(i) Mnquad X_2										
Mn(quad Ia)Cl ₂	yellow	Calc.	39.3	3.3	22.9	15.0	19.4	5.94	7.0	1591 and
	•	found	39.1	3.3	22.7	14.8	19.0			1570
Mn(quad Ib)Br ₂	orange	Calc.	34.8	3.3	17.4	11.4	33.1	5.98	6.1	1591 and
	2	found	34.6	3.4	17.0	11.3	33.0			1570
Mn(quad Id)Cl ₂	yellow	Calc.	45.7	4.3	20.0	13.3	16.9	6.00	1.2	1591 and
		found	45.5	4.0	20.3	13.4	16.5			1572
Mn(quad II)Cl ₂	yellow	Calc.	46.2	3.8	15.4	15.1	19.5	6.01	2.0	1593 and
		found	46.4	3.5	15.0	15.0	19.0			1570
$Mn(quad II)(ClO_4)_2$	yellow	Calc.	34.1	2.8	11.4	11.2	14.4	6.00	87.1	1593 and
		found	34.3	2.8	11.4	11.5	14.1			1574
Mn(quad III)(ClO ₄) ₂	orange	Calc.	35.5	3.2	11.0	10.8	14.0	6.02	87.2	1590 and
		found	35.3	3.6	11.2	10.5	13.6			1570
Mn(quad V)(ClO ₄) ₂	green	Calc.	33.8	3.6	11.3	11.1	14.3	6.00	88.3	1595 and
		found	33.7	3.6	11.0	10.9	14.0			1575
Mn(quad V)Cl ₂	green	Calc.	45.7	4.9	15.2	14.9	19.3	5.99	4.1	1595 and
		found	45.5	4.9	15.4	14.3	19.0			1571
Mn(quad VI)(ClO ₄) ₂	green	Calc.	35.2	3.9	10.9	10.8	13.9	5.96	90.3	1592 and
		found	35.5	3.6	10.7	10.6	13.7			1573
Mn(quad VI)Br ₂	green	Calc.	38.2	4.2	11.9	11.7	34.0	5.98	1.1	1593 and
		found	38.0	4.2	11.8	11.8	33.6			1569
Mn(quad VII)(ClO ₄) ₂	green	Calc.	35.2	3.9	10.9	10.8	13.9	5.99	91.2	1591 and
		found	35.5	3.6	10.6	10.9	13.6			1567
Mn(quad VII)Cl ₂	green	Calc.	47.1	5.3	14.7	14.4	18.6	6.00	2.0	1592 and
		found	47.3	5.5	14.4	14.7	18.4			1571
$Mn(quad VIII)(ClO_4)_2$	yellow	Calc.	22.6	4.2	13.2	12.9	16.7	6.00	87.6	-
		found	22.6	4.3	13.0	12.7	17.0			_
Mn(quad IV)(ClO ₄) ₂	yellow	Calc.	26.5	4.9	12.4	12.1	15.7	6.01	88.4	-
		found	26.2	4.8	12.3	12.4	15.3			
Mn(quad IX)Cl ₂	yellow	Calc.	37.0	6.8	17.3	17.0	21.9	6.02	2.0	_
		found	36.9	6.9	17.1	17.0	21.8			_
$Mn(quad X)(ClO_4)_2$	yellow	Calc.	17.9	4.5	14.0	13.7	17.7	6.00	89.3	-
		found	17.7	4.3	13.6	13.4	17.5			-
Mn(quad X)Br ₂	yellow	Calc.	19.9	5.0	15.5	15.2	44.3	5.87	2.1	-
		found	19.7	5.0	15.1	15.0	44.0			

TABLE. Properties of Complexes.

Multidentate Complexes of Mn(II)

TABLE. (Cont.)

$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Compound	Colour		Analy	ysis				μ_{eff}	⊿ 1000 in MaNO	I.R. Pyridine
(ii) $[Mn_2(quad]_3]X_2$ $[Mn_2(quad III)_3](ClO_4)_4$ yellow Calc. 42.7 3.8 13.3 8.7 11.2 5.99 88.6 1594 and found 43.0 3.8 13.2 8.6 11.0 1566 $[Mn_2(quad III)_3](ClO_4)_4$ yellow Calc. 79.0 6.0 7.8 5.1 - 5.89 90.4 1589 and found 78.7 5.9 7.6 5.4 - 1575 $[Mn_2(quad V)_3](ClO_4)_4$ cream Calc. 78.6 6.5 7.8 5.1 - 5.96 93.1 1588 and found 40.6 4.4 13.7 8.6 11.0 1569 $[Mn_2(quad VI)_3](ClO_4)_4$ yellow Calc. 42.3 4.7 13.1 8.6 11.1 5.96 94.3 1589 and found 78.7 5.9 7.3 5.2 7.5 5.3 - 1570 $[Mn_2(quad VI)_3](ClO_4)_4$ yellow Calc. 42.3 4.7 13.1 8.6 11.1 5.96 94.3 1589 and found 78.0 6.0 15.2 10.0 12.9 5.99 87.6 - 600 89.1 - 1570 $[Mn_2(quad IX)_3](ClO_4)_4$ yellow Calc. 75.0 7.3 9.2 6.0 - 6.00 89.1 - 1570 $[Mn_2(quad X)_3](BPh_4)_4$ yellow Calc. 39.2 3.3 22.9 7.5 9.7 6.01 93.0 1592 and found 73.9 5.6 14.2 4.8 - 1570 $[Mn(quad Ia)_2](ClO_4)_2$ white Calc. 39.2 3.3 22.9 7.5 9.7 6.01 93.0 1592 and found 73.9 5.6 14.2 4.8 - 1570 $[Mn(quad Ia)_2](ClO_4)_2$ white Calc. 39.2 3.3 22.9 7.5 9.7 6.01 93.0 1592 and found 73.9 5.6 14.2 4.8 - 1570 $[Mn(quad Ia)_2](ClO_4)_2$ white Calc. 39.2 3.7 22.0 7.3 9.3 5.95 91.5 1592 and found 73.9 5.6 14.2 4.8 - 1570 $[Mn(quad Ia)_2](ClO_4)_2$ white Calc. 42.5 4.0 21.2 6.9 9.0 5.94 91.8 1590 and found 42.5 4.2 11.9 21.5 6.3 9.1 1575 $[Mn(quad Ia)_2](ClO_4)_2$ white Calc. 43.7 71.8 9.3 1.9 1.575 $[Mn(quad Id)_2](ClO_4)_2$ white Calc. 42.5 4.0 21.2 6.9 9.0 5.94 91.8 1590 and found 45.5 4.2 19.8 6.3 8.0 1576 $[Mn(quad Id)_2](ClO_4)_2$ white Calc. 45.6 4.3 19.9 6.5 8.4 5.99 87.7 1591 and found 45.5 4.2 19.8 6.3 8.0 1576 $[Mn(quad Id)_2](ClO_4)_2$ white Calc. 45.6 4.3 19.9 6.5 8.4 5.99 87.7 1591 and found 45.5 4.2 19.8 6.3 8.0 1576 $[Mn(quad Id)_2](ClO_4)_2$ white Calc. 45.6 4.3 19.9 6.5 8.4 5.99 87.7 1591 and found 45.5 4.2 19.8 6.3 8.0 1576 $[Mn(quad Id)_2](ClO_4)_2$ white Calc. 78.0 5.8 9.6 4.7 - 5.99 88.5 1593 and found 45.5 4.2 19.8 6.3 8.0 1570 $[Mn(quad Id)_2](ClO_4)_2$ white Calc. 78.0 5.8 9.6 4.7 - 5.99 88.5 1593 and found 45.2 3.4 13.5 6.7 8.6 7.8 5.98 89.7 1591 and				c	Н	N	Mn	Cl or Br	295K	(r.o)	(cm ⁻¹)
$ \begin{split} & \left[Mn_2(\operatorname{quad}\ III)_3(\operatorname{CIO}_4)_4 & \operatorname{yellow} & \operatorname{Calc}, \ 42.7 & 3.8 & 13.3 & 8.7 & 11.2 & 5.99 & 88.6 & 1594 \ \operatorname{and} \\ & \operatorname{found} \ 43.0 & 3.8 & 13.2 & 8.6 & 11.0 & 1566 \\ & \operatorname{Calc}, \ 70.0 & 6.0 & 7.8 & 5.1 & - & 5.89 & 90.4 & 1589 \ \operatorname{and} \\ & \operatorname{found} \ 78.7 & 5.9 & 7.6 & 5.4 & - & 1575 \\ & \left[Mn_2(\operatorname{quad}\ V)_3(\operatorname{CIO}_4)_4 & \operatorname{cream} & \operatorname{Calc}, \ 40.8 & 4.4 & 13.6 & 8.9 & 11.5 & 5.97 & 92.1 & 1589 \ \operatorname{and} \\ & \operatorname{found} \ 78.7 & 5.9 & 7.6 & 5.4 & - & 1570 \\ & \left[Mn_2(\operatorname{quad}\ VI)_3(\operatorname{CIO}_4)_4 & \operatorname{cream} & \operatorname{Calc}, \ 78.6 & 6.5 & 7.8 & 5.1 & - & 5.96 & 93.1 & 1588 \ \operatorname{and} \\ & \operatorname{found} \ 78.7 & 6.2 & 7.5 & 5.3 & - & 1570 \\ & \left[Mn_2(\operatorname{quad}\ VI)_3(\operatorname{CIO}_4)_4 & \operatorname{yellow} & \operatorname{Calc}, \ 78.6 & 6.1 & 5.2 & 7.5 & 5.3 & - & 1570 \\ & \left[Mn_2(\operatorname{quad}\ VI)_3(\operatorname{CIO}_4)_4 & \operatorname{yellow} & \operatorname{Calc}, \ 42.3 & 4.7 & 13.1 & 8.6 & 11.1 & 5.96 & 94.3 & 1589 \ \operatorname{and} \\ & \operatorname{found} \ 42.0 & 4.9 & 13.2 & 8.7 & 11.0 & 1570 \\ & \left[Mn_2(\operatorname{quad}\ IX)_3(\operatorname{CIO}_4)_4 & \operatorname{yellow} & \operatorname{Calc}, \ 75.0 & 7.3 & 9.2 & 6.0 & - & \\ & \operatorname{found} \ 42.0 & 4.9 & 13.2 & 8.7 & 11.0 & - & \\ & \operatorname{found} \ 32.4 & 6.0 & 15.4 & 10.3 & 12.9 & 5.99 & 87.6 & - \\ & \operatorname{found} \ 32.4 & 6.0 & 15.4 & 10.3 & 12.5 & & & & \\ & \left[Mn_2(\operatorname{quad}\ IX)_3(\operatorname{CIO}_4)_4 & \operatorname{yellow} & \operatorname{Calc}, \ 75.0 & 7.3 & 9.2 & 6.0 & - & \\ & \operatorname{found} \ 39.3 & 3.4 \ 22.6 & 7.2 & 9.3 & & & \\ & \left[Mn(\operatorname{quad}\ 1a)_2(\operatorname{CIO}_4)_2 & \operatorname{white} & \operatorname{Calc}, \ 37.5 & 5.1 & 4.3 & 4.7 & - & 5.86 & 91.7 & 1593 \ \operatorname{and} \\ & \operatorname{found} \ 39.3 & 3.4 \ 22.6 & 7.2 & 9.3 & & \\ & \left[Mn(\operatorname{quad}\ 1a)_2(\operatorname{CIO}_4)_2 & \operatorname{white} & \operatorname{Calc}, \ 37.5 & 5.1 \ 4.3 & 4.7 & - & 5.96 & 91.7 & 1593 \ \operatorname{and} \\ & \operatorname{found} \ 73.9 & 5.6 & 14.2 & 4.8 & - & \\ & \left[Mn(\operatorname{quad}\ 1b)_2(\operatorname{CIO}_4)_2 & \operatorname{white} & \operatorname{Calc}, \ 42.5 & 4.0 & 21.2 & 6.9 & 9.0 & 5.94 & 91.8 & 1590 \ \operatorname{and} \\ & \operatorname{found} \ 40.6 & 3.7 & 21.8 & 7.0 & 8.9 & \\ & \left[Mn(\operatorname{quad}\ 1b)_2(\operatorname{CIO}_4)_2 & \operatorname{white} & \operatorname{Calc}, \ 45.5 & 4.3 \ 19.9 & 6.5 & 8.4 & 5.99 & 87.7 & 1591 \ \operatorname{and} \\ & \operatorname{found} \ 40.6 & 3.7 & 21.8 & 7.0 & 8.9 & \\ & \left[Mn(\operatorname{quad}\ 1b)_2(\operatorname{CIO}_4)_2 & whit$	(ii) $[Mn_2(quad)_3]X_2$			_							
	$[Mn_2(quad III)_3](ClO_4)_4$	yellow	Calc.	42.7	3.8	13.3	8.7	11.2	5.99	88.6	1594 and
$ [Mn_2(quad M_1)_3(GPn_4)_4 = yellow Calc. 79.0 6.0 7.8 5.1 - 5.89 90.4 1588 and found 78.7 5.9 7.6 5.4 - 1575 [Mn_2(quad V1)_3](ClO_4)_4 cream Calc. 78.6 6.1 7.7 8.5 1.0 1569 [Mn_2(quad V1)_3](ClO_4)_4 vellow Calc. 40.8 4.4 13.6 8.9 11.5 5.97 92.1 1588 and found 78.3 6.2 7.5 5.3 - 5.96 93.1 15588 and found 78.3 6.2 7.5 5.3 - 1570 [Mn_2(quad V1)_3](ClO_4)_4 vellow Calc. 42.3 4.7 13.1 8.6 11.1 5.96 94.3 1589 and found 78.3 6.2 7.5 5.3 - 1570 [Mn_2(quad X1)_3](ClO_4)_4 vellow Calc. 75.0 7.3 9.2 6.0 - 6.00 89.1 - found 32.4 6.0 15.4 10.3 12.5 - 0.1 1570 [Mn_2(quad X)_3](BPh_4)_4 vellow Calc. 75.0 7.3 9.2 6.0 - 6.00 89.1 - found 74.7 7.2 9.0 5.8 100 12.9 5.99 87.6 - 1572 [Mn(quad la)_2](ClO_4)_2 vellow Calc. 75.0 7.3 9.2 6.0 - 6.01 93.0 1592 and found 74.7 7.2 9.0 5.8 1572 [Mn(quad la)_2](ClO_4)_2 white Calc. 73.7 5.5 14.3 4.7 - 5.86 91.7 1593 and found 73.9 5.6 14.2 4.8 - 1570 [Mn(quad la)_2](ClO_4)_2 white Calc. 73.7 5.5 14.3 4.7 - 5.86 91.7 1593 and found 73.9 5.6 14.2 4.8 - 1570 [Mn(quad la)_2](ClO_4)_2 white Calc. 73.7 5.5 14.3 4.7 - 5.86 91.7 1593 and found 73.9 5.6 14.2 4.8 - 1570 [Mn(quad la)_2](ClO_4)_2 white Calc. 40.9 3.7 22.0 7.3 9.3 5.95 91.5 1592 and found 42.1 3.9 21.5 6.3 9.1 5.5 1590 and found 42.1 3.9 21.5 6.3 9.1 5.5 5.5 1.590 and found 42.1 3.9 21.5 6.3 9.1 5.5 5.5 1.590 and found 42.1 3.9 21.5 6.3 9.1 5.5 5.5 1.590 and found 41.5 1.2 1.2 6.9 9.0 5.94 91.8 1590 and found 42.1 3.9 21.5 6.3 9.1 5.5 5.5 1.590 and found 41.5 1.2 1.2 6.9 9.0 5.94 91.8 1590 and found 42.1 3.9 21.5 6.3 9.1 5.5 5.5 1.590 and found 41.5 1.5 7.5 4.0 21.5 6.3 9.1 5.5 5.5 1.590 and found 41.5 1.5 7.5 4.2 1.8 7.0 8.9 15.5 1590 and found 41.5 1.5 7.5 4.0 21.5 6.3 9.1 5.5 5.5 1.590 and found 41.5 1.5 7.5 4.0 21.5 6.3 8.0 15.5 7.5 1.590 and found 41.5 1.5 7.5 4.0 21.5 6.3 8.0 15.5 7.5 1.591 and found 71.6 5.8 4.5 5.9 8.5 1.593 and found 71.6 5.7 9.5 9.5 9.5 1.591 and found 71.6 5.7 9.5 9.7 6.02 86.5 1590 and found 71.6 5.8 15.5 7.3 9.2 1570 [Mn(quad Il)_2](CIO_4)_2 white Calc. 42.0 3.8 15.5 7.7 3.9.2 1570 [Mn(quad Il)$	[Mn ₂ (quad III) ₃](BPh ₄) ₄		Cala	43.0	3.0	13.2	8.0 5 1	11.0	5 80	00.4	1500
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		yenow	Calc.	79.0	0.0	7.8	5.1	_	5.89	90.4	1589 and
$ [Mn_2(quad V_{J_3}](ClO_4)_4 & cream [Mn_2(quad VI)_3](ClO_4)_4 & cream [Mn_2(quad VI)_3](ClO_4)_4 & yellow Calc. 78.6 6.5 7.8 5.1 - 5.96 93.1 1588 and found 78.3 6.2 7.5 5.3 - 1570 [Mn_2(quad VI)_3](ClO_4)_4 & yellow Calc. 23. 4.7 13.1 8.6 11.1 5.96 94.3 1589 and found 42.0 4.9 13.2 8.7 11.0 1570 [Mn_2(quad IX)_3](ClO_4)_4 & yellow Calc. 32.6 6.0 15.2 10.0 12.9 5.99 87.6 - found 74.7 7.2 9.0 5.8 [Mn_2(quad X)_3](BPh_4)_4 & yellow Calc. 75.0 7.3 9.2 6.0 - found 74.7 7.2 9.0 5.8 [Mn(quad Ia)_2](ClO_4)_2 & white Calc. 73.7 5.5 14.3 4.7 - [Mn(quad Ia)_2](ClO_4)_2 & white Calc. 42.5 4.0 21.2 6.9 9.0 5.94 91.8 1592 and found 73.9 5.6 14.2 4.8 - [Mn(quad Ia)_2](ClO_4)_2 & white Calc. 42.5 4.0 21.2 6.9 9.0 5.94 91.8 1590 and found 73.9 5.6 14.2 4.8 - [Mn(quad Ia)_2](ClO_4)_2 & white Calc. 42.5 4.0 21.2 6.9 9.0 5.94 91.8 1590 and found 42.1 3.9 21.5 6.3 9.1 1575 [Mn(quad Id)_2](ClO_4)_2 & white Calc. 42.5 4.0 21.2 6.9 9.0 5.94 91.8 1590 and found 45.5 4.2 12.8 6.3 9.1 1575 [Mn(quad Id)_2](ClO_4)_2 & white Calc. 42.5 4.0 21.2 6.9 9.0 5.94 91.8 1590 and found 45.5 4.2 19.8 6.3 8.0 1575 [Mn(quad Id)_2](ClO_4)_2 & white Calc. 42.5 4.0 21.2 6.9 9.0 5.94 91.8 1590 and found 45.5 4.2 19.8 6.3 8.0 1575 [Mn(quad Id)_2](ClO_4)_2 & white Calc. 42.5 4.0 21.2 6.9 9.0 5.94 91.8 1590 and found 45.5 4.2 19.8 6.3 8.0 1576 [Mn(quad Id)_2](ClO_4)_2 & white Calc. 42.5 4.0 3.7 21.8 7.0 8.9 1576 [Mn(quad Id)_2](ClO_4)_2 & white Calc. 42.6 0.3 8 15.3 7.5 9.7 6.02 86.5 1592 and found 45.5 4.2 19.8 6.3 8.0 1576 [Mn(quad Il)_2](ClO_4)_2 & white Calc. 78.0 5.8 9.6 4.7 - 5.99 88.5 1593 and found 74.6 5.4 13.3 4.0 - 1570 [Mn(quad Il)_2](ClO_4)_2 & white Calc. 78.0 5.8 9.6 4.7 - 5.99 88.5 1593 and found 74.6 5.4 13.3 4.0 - 1570 [Mn(quad Il)_2](ClO_4)_2 & white Calc. 78.0 5.8 9.6 4.7 - 5.99 88.5 1593 and found 74.6 5.4 13.3 4.0 - 1570 [Mn(quad Il)_2](ClO_4)_2 & white Calc. 78.0 5.8 9.6 4.7 - 5.99 88.5 1593 and found 74.5 5.8 9.6 4.7 -$	$[M_{P} \pmod{V}] (C C)$		Cala	/0./	3.9	12.6	5.4 o n	-	5.07	02.1	15/5 1580 and
$ [Mn_2(quad VI)_3](BPh_4)_4 cream $	$[Mn_2(quad V)_3](ClO_4)_4$	cream	Calc.	40.6	4.4	13.0	0.9	11.5	5.97	92.1	1589 and
$ [Mn_2(quad VI)_3](SPn_4)_4 cream Calc. 70.6 0.5 7.8 5.1 - \qquad 5.96 93.1 \qquad 1588 and found fou$			Cala	40.0	4.4	13.7	8.0 5 1	11.0	5.06	02.1	1509
$ \begin{bmatrix} Mn_2(quad VII)_3 \\ (CIO_4)_4 & yellow \\ Calc. & 2.3 & 4.7 & 13.1 & 8.6 & 11.1 \\ found & 42.0 & 4.9 & 13.2 & 8.7 & 11.0 \\ Mn_2(quad IX)_3 \\ (CIO_4)_4 & yellow \\ Calc. & 32.6 & 6.0 & 15.2 & 10.0 & 12.9 \\ found & 32.4 & 6.0 & 15.4 & 10.3 & 12.5 \\ Mn_2(quad X)_3 \\ (BPh_4)_4 & yellow \\ Calc. & 75.0 & 7.3 & 9.2 & 6.0 & - \\ found & 74.7 & 7.2 & 9.0 & 5.8 & - \\ \end{bmatrix} $ $ \begin{bmatrix} Mn_2(quad X)_3 \\ (BPh_4)_4 \\ (quad Ia)_2 \\ (CIO_4)_2 \\ Mn(quad Ia)_2 \\ (CIO_4)_2 $	$[Mn_2(quad VI)_3](BPn_4)_4$	cream	Calc.	/8.0	0.3	7.8	5.1	_	5.90	93.1	1588 and
$ [Mn_2(quad VII)_3](CIO_4)_4 yellow Calc. 42.3 4.7 13.1 8.6 11.1 5.96 94.3 1589 \text{ and} \\ found 42.0 4.9 13.2 8.7 11.0 12.9 5.99 87.6 - \\ found 32.4 6.0 15.4 10.3 12.5 - \\ [Mn_2(quad IX)_3](BPh_4)_4 yellow Calc. 75.0 7.3 9.2 6.0 - \\ found 74.7 7.2 9.0 5.8 - \\ \hline (iii) [Mn(quad)_2]X_2 Mhite Calc. 39.2 3.3 22.9 7.5 9.7 6.01 93.0 1592 \text{ and} \\ found 39.3 3.4 22.6 7.2 9.3 1572 1593 \text{ and} \\ found 39.3 3.4 22.6 7.2 9.3 1572 1593 \text{ and} \\ found 39.3 3.4 22.6 7.2 9.3 1572 1593 \text{ and} \\ found 13.9 5.5 14.3 4.7 - \\ [Mn(quad Ia)_2](BPh_4)_2 white Calc. 73.7 5.5 14.3 4.7 - \\ found 73.9 5.6 4.2 4.8 - \\ found 42.1 3.9 21.5 6.3 9.1 1575 1592 \text{ and} \\ found 42.1 3.9 21.5 6.3 9.1 1575 1592 \text{ and} \\ found 40.6 3.7 21.8 7.0 8.9 1576 1592 \text{ and} \\ found 40.6 3.7 21.8 7.0 8.9 1576 1592 \text{ and} \\ found 40.5 3.7 5.5 4.4 4.3 - \\ found 40.6 3.7 21.8 7.0 8.9 1576 1592 \text{ and} \\ found 40.5 3.7 5.5 8.4 5.99 87.7 1591 \text{ and} \\ found 40.6 3.7 21.8 7.0 8.9 1576 1592 \text{ and} \\ found 40.6 3.7 21.8 7.0 8.9 1576 1592 \text{ and} \\ found 40.6 3.7 21.8 7.0 8.9 1576 1592 \text{ and} \\ found 40.6 3.7 21.8 7.0 8.9 1576 1592 \text{ and} \\ found 40.6 3.7 21.8 7.0 8.9 1576 1591 \text{ and} \\ found 40.6 3.8 15.3 7.5 9.7 6.02 86.5 1590 \text{ and} \\ found 40.6 3.8 15.3 7.5 9.7 6.02 86.5 1590 \text{ and} \\ found 40.2 3.8 15.3 7.5 9.7 6.02 86.5 1590 \text{ and} \\ found 40.0 3.8 15.3 7.5 9.7 6.02 86.5 1590 \text{ and} \\ found 6100 7.9 5.7 9.5 4.6 - 1574 1571$. 11	round	/8.3	0.2	1.5	5.3	-	5.04	04.0	1570
$ \begin{bmatrix} \text{Nn}_2(\text{quad IX})_3](\text{CIO}_4)_4 & \text{yellow} \\ \text{Calc.} & 32.6 & 6.0 & 15.2 & 10.0 & 12.9 \\ \text{found} & 32.4 & 6.0 & 15.4 & 10.3 & 12.5 \\ \text{IM}_2(\text{quad X})_3](\text{BPh}_4)_4 & \text{yellow} \\ \text{Calc.} & 75.0 & 7.3 & 9.2 & 6.0 & - & 6.00 & 89.1 \\ \text{found} & 74.7 & 7.2 & 9.0 & 5.8 & - & & - \\ \end{bmatrix} \\ \begin{bmatrix} \text{Mn}(\text{quad Ia})_2]\mathbf{X}_2 \\ \begin{bmatrix} \text{Mn}(\text{quad Ia})_2](\text{CIO}_4)_2 & \text{white} \\ \text{Calc.} & 39.2 & 3.3 & 22.9 & 7.5 & 9.7 \\ \text{found} & 39.3 & 3.4 & 22.6 & 7.2 & 9.3 \\ \text{found} & 39.3 & 3.4 & 22.6 & 7.2 & 9.3 \\ \end{bmatrix} \\ \begin{bmatrix} \text{Mn}(\text{quad Ia})_2](\text{BPh}_4)_2 & \text{white} \\ \text{Calc.} & 73.7 & 5.5 & 14.3 & 4.7 & - \\ \text{found} & 73.9 & 5.6 & 14.2 & 4.8 & - \\ \end{bmatrix} \\ \begin{bmatrix} \text{Mn}(\text{quad Ia})_2](\text{CIO}_4)_2 & \text{white} \\ \text{Calc.} & 42.5 & 4.0 & 21.2 & 6.9 & 9.0 \\ \text{found} & 37.9 & 5.6 & 14.2 & 4.8 & - \\ \end{bmatrix} \\ \begin{bmatrix} \text{Mn}(\text{quad Ib})_2](\text{CIO}_4)_2 & \text{white} \\ \text{Calc.} & 42.5 & 4.0 & 21.2 & 6.9 & 9.0 \\ \text{found} & 42.1 & 3.9 & 21.5 & 6.3 & 9.1 \\ \end{bmatrix} \\ \begin{bmatrix} \text{Mn}(\text{quad Ic})_2](\text{CIO}_4)_2 & \text{white} \\ \text{Calc.} & 42.6 & 1.3 & 9.2 & 5.8 & 5.95 \\ \text{Mn}(\text{quad Id})_2](\text{CIO}_4)_2 & \text{white} \\ \text{Calc.} & 45.6 & 4.3 & 19.9 & 6.5 & 8.4 \\ \text{found} & 40.6 & 3.7 & 21.8 & 7.0 & 8.9 \\ \end{bmatrix} \\ \begin{bmatrix} \text{Mn}(\text{quad Id})_2](\text{CIO}_4)_2 & \text{white} \\ \text{Calc.} & 45.6 & 4.3 & 19.9 & 6.5 & 8.4 \\ \text{found} & 45.5 & 4.2 & 19.8 & 6.3 & 8.0 \\ \end{bmatrix} \\ \begin{bmatrix} \text{Mn}(\text{quad Id})_2](\text{CIO}_4)_2 & \text{white} \\ \text{Calc.} & 45.6 & 4.3 & 19.9 & 6.5 & 8.4 \\ \text{found} & 46.2 & 3.8 & 15.3 & 7.5 & 9.7 \\ \end{bmatrix} \\ \begin{bmatrix} \text{Mn}(\text{quad Id})_2](\text{CIO}_4)_2 & \text{white} \\ \text{Calc.} & 46.0 & 3.8 & 15.3 & 7.5 & 9.7 \\ \text{found} & 46.2 & 3.8 & 15.3 & 7.5 & 9.7 \\ \end{bmatrix} \\ \begin{bmatrix} \text{Mn}(\text{quad II})_2](\text{CIO}_4)_2 & \text{white} \\ \text{Calc.} & 52.2 & 3.4 & 13.5 & 6.7 & 8.6 \\ \text{found} & 46.2 & 3.8 & 15.3 & 7.5 & 9.7 \\ \end{bmatrix} \\ \begin{bmatrix} \text{Mn}(\text{quad II})_2](\text{CIO}_4)_2 & \text{white} \\ \text{Calc.} & 52.2 & 3.4 & 13.5 & 6.7 & 8.6 \\ \text{found} & 52.3 & 3.4 & 13.5 & 6.7 & 8.6 \\ \end{bmatrix} \\ \begin{bmatrix} \text{Mn}(\text{quad II})_2](\text{CIO}_4)_2 & \text{white} \\ \end{bmatrix} \\ \begin{bmatrix} \text{Calc.} & 52.2 & 3.4 & 13.5 & 6.7 & 8.6 \\ \text{found} & 52.3 & 3.4 & 13.5 \\ \end{bmatrix} \\ \begin{bmatrix} \text{Mn}(\text{quad VIII})_2](\text{CIO}_4)_2 & \text{white} \\ \end{bmatrix} \\ \begin{bmatrix} \text{Calc.} & 52.2 & 3.4 & 1$	$[Mn_2(quad VII)_3](CIO_4)_4$	yellow	Calc.	42.3	4.7	13.1	8.6	11.1	5.96	94.3	1589 and
$ \begin{bmatrix} Mn_2(quad IX)_3 \\ [Mn_2(quad X)_3](CIO_4)_4 & yellow \\ found 32.4 & 6.0 & 15.2 & 10.0 & 12.9 & 5.99 & 87.6 \\ found 32.4 & 6.0 & 15.4 & 10.3 & 12.5 & - \\ found 32.4 & 6.0 & 15.4 & 10.3 & 12.5 & - \\ found 74.7 & 7.2 & 9.0 & 5.8 & - & - \\ \end{bmatrix} $			found	42.0	4.9	13.2	8.7	11.0			1570
$ \begin{bmatrix} Mn_2(quad X)_3](BPh_4)_4 & yellow & Calc. 75.0 7.3 9.2 6.0 - 6.00 & 89.1 - 6.00 & 89.1 - 6.00 & 89.1 - 6.00 & 89.1 & - 6.00 & 89.1 & - 6.00 & 89.1 & - 6.00 & 89.1 & - 6.00 & 89.1 & - 6.00 & 89.1 & - 6.00 & 89.1 & - 6.00 & 89.1 & - 6.00 & 89.1 & - 6.00 & 89.1 & - 6.00 & 15.7 & - 6.01 & 93.0 & 1592 and found 39.3 3.4 & 22.6 & 7.2 & 9.3 & - 5.86 & 91.7 & 1593 and found 73.9 & 5.6 & 14.2 & 4.8 & - & 1570 & - 5.86 & 91.7 & 1593 and found 42.1 & 3.9 & 21.5 & 6.3 & 9.1 & - 5.86 & 91.7 & 1593 and found 42.1 & 3.9 & 21.5 & 6.3 & 9.1 & - 5.70 & - 5.94 & 91.8 & 1590 and found 42.1 & 3.9 & 21.5 & 6.3 & 9.1 & - 5.70 & - 5.94 & 91.8 & 1590 and found 42.1 & 3.9 & 21.5 & 6.3 & 9.1 & - 5.76 & - 5.94 & 91.5 & 1592 and found 42.1 & 3.9 & 21.5 & 6.3 & 9.1 & - 5.76 & - 5.94 & - 5.99 & 87.7 & 1591 and found 40.6 & 3.7 & 21.8 & 7.0 & 8.9 & - 5.95 & 91.5 & 1592 and found 40.6 & 3.7 & 21.8 & 7.0 & 8.9 & - 5.76 & - 5.76 & - 5.76 & - 5.76 & - 5.76 & - 5.70 & - 5.70 & - 5.70 & - 5.70 & - 5.70 & - 5.99 & 87.7 & 1591 and found 42.5 & 4.2 & 19.8 & 6.3 & 8.0 & - 5.76 & - 5.70 & - 5.99 & 88.5 & 1593 and found 42.2 & 3.8 & 15.3 & 7.5 & 9.7 & 6.02 & 86.5 & 1590 and found 40.6 & 3.8 & 15.3 & 7.5 & 9.7 & 6.02 & 86.5 & 1590 and found found 42.2 & 3.8 & 15.3 & 7.5 & 9.7 & 6.02 & 86.5 & 1590 and found found 42.2 & 3.8 & 15.3 & 7.5 & 9.7 & 6.02 & 86.5 & 1590 and found found 40.2 & 3.8 & 15.3 & 7.5 & 9.7 & 6.02 & 86.5 & 1590 and found found 40.2 & 3.8 & 15.3 & 7.5 & 9.7 & 6.02 & 86.5 & 1590 and found found 77.9 & 5.7 & 9.5 & 4.6 & - & 1576 & - & 1576 & - & 1576 & - & 1576 & - & 1576 & - & 1576 & - & 1576 & - & - & 1576 & - & - & 1576 & - & - & - & - & - & - & - & - & - & $	$[Mn_2(quad IX)_3](ClO_4)_4$	yellow	Calc.	32.6	6.0	15.2	10.0	12.9	5.99	87.6	-
$ \begin{bmatrix} Mn_2(quad X)_3 \\ [Mn_2(quad X)_3 \\ [Mn_2(quad X)_3] \\ [Mn_2(quad $			found	32.4	6.0	15.4	10.3	12.5			-
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$[Mn_2(quad X)_3](BPh_4)_4$	yellow	Calc.	75.0	7.3	9.2	6.0	_	6.00	89.1	-
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			found	74.7	7.2	9.0	5.8	-			-
$ \begin{bmatrix} Mn(quad Ia)_2 \\ [(ClO_4)_2 \\ (Mn(quad Ib)_2 \\ [(ClO_4)_2 \\ (Mn(quad Ic)_2 \\ (ClO_4)_2 \\ (Mn(quad VIII)_2 \\ (ClO_4)_$	(iii) $[Mn(quad)_2]X_2$										
$ \begin{bmatrix} \text{Im}(\text{quad Ia})_2 (\text{BPh}_4)_2 & \text{white} & \text{Calc.} 73.7 & 5.5 & 14.3 & 4.7 & - & 5.86 & 91.7 & 1593 \text{ and} \\ & \text{found} & 73.9 & 5.6 & 14.2 & 4.8 & - & & 1570 \\ \hline [\text{Mn}(\text{quad Ib})_2](\text{CIO}_4)_2 & \text{white} & \text{Calc.} & 42.5 & 4.0 & 21.2 & 6.9 & 9.0 & 5.94 & 91.8 & 1590 \text{ and} \\ & \text{found} & 42.1 & 3.9 & 21.5 & 6.3 & 9.1 & & & 1575 \\ \hline [\text{Mn}(\text{quad Ic})_2](\text{CIO}_4)_2 & \text{white} & \text{Calc.} & 40.9 & 3.7 & 22.0 & 7.3 & 9.3 & 5.95 & 91.5 & 1592 \text{ and} \\ & \text{found} & 40.6 & 3.7 & 21.8 & 7.0 & 8.9 & & & 1576 \\ \hline [\text{Mn}(\text{quad Id})_2](\text{CIO}_4)_2 & \text{white} & \text{Calc.} & 45.6 & 4.3 & 19.9 & 6.5 & 8.4 & 5.99 & 87.7 & 1591 \text{ and} \\ & \text{found} & 45.5 & 4.2 & 19.8 & 6.3 & 8.0 & & & 1576 \\ \hline [\text{Mn}(\text{quad Id})_2](\text{CIO}_4)_2 & \text{white} & \text{Calc.} & 74.9 & 5.9 & 13.1 & 4.3 & - & 6.01 & 86.0 & 1589 \text{ and} \\ & \text{found} & 74.6 & 5.4 & 13.3 & 4.0 & - & & & 1570 \\ \hline [\text{Mn}(\text{quad II})_2](\text{CIO}_4)_2 & \text{white} & \text{Calc.} & 46.0 & 3.8 & 15.3 & 7.5 & 9.7 & 6.02 & 86.5 & 1590 \text{ and} \\ & \text{found} & 46.2 & 3.8 & 15.5 & 7.3 & 9.2 & & & 1570 \\ \hline [\text{Mn}(\text{quad II})_2](\text{CIO}_4)_2 & \text{white} & \text{Calc.} & 78.0 & 5.8 & 9.6 & 4.7 & - & 5.99 & 88.5 & 1593 \text{ and} \\ & \text{found} & 77.9 & 5.7 & 9.5 & 4.6 & - & & & 1574 \\ \hline [\text{Mn}(\text{quad IV})_2](\text{CIO}_4)_2 & \text{white} & \text{Calc.} & 52.2 & 3.4 & 13.5 & 6.7 & 8.6 & 5.98 & 89.7 & 1591 \text{ and} \\ & \text{found} & 52.3 & 3.4 & 13.5 & 6.7 & 8.6 & 5.98 & 89.7 & 1591 \text{ and} \\ & \text{found} & 52.3 & 3.4 & 13.5 & 6.3 & 8.1 & & & 1571 \\ \hline [\text{Mn}(\text{quad VIII})_2](\text{CIO}_4)_2 & \text{white} & \text{Calc.} & 32.3 & 6.1 & 18.8 & 9.2 & 11.9 & 5.91 & 92.3 & - & \\ & \text{found} & 32.2 & 6.4 & 18.5 & 9.0 & 11.5 & & - & & & & & & & & & & & & & & & & $	[Mn(quad Ia) ₂](ClO ₄) ₂	white	Calc.	39.2	3.3	22.9	7.5	9.7	6.01	93.0	1592 and
$ \begin{bmatrix} Mn(quad Ia)_2 \end{bmatrix} (BPh_4)_2 & \text{white} & Calc. 73.7 5.5 14.3 4.7 - 5.86 & 91.7 1593 \text{ and} \\ found 73.9 5.6 14.2 4.8 - 1570 \\ [Mn(quad Ib)_2] (CIO_4)_2 & \text{white} & Calc. 42.5 4.0 21.2 6.9 9.0 5.94 & 91.8 1590 \text{ and} \\ found 42.1 3.9 21.5 6.3 9.1 & 1575 \\ [Mn(quad Ic)_2] (CIO_4)_2 & \text{white} & Calc. 40.9 3.7 22.0 7.3 9.3 5.95 & 91.5 1592 \text{ and} \\ found 40.6 3.7 21.8 7.0 8.9 & 1576 \\ [Mn(quad Id)_2] (CIO_4)_2 & \text{white} & Calc. 45.6 4.3 19.9 6.5 8.4 5.99 & 87.7 1591 \text{ and} \\ found 45.5 4.2 19.8 6.3 8.0 & 1576 \\ [Mn(quad Id)_2] (BPh_4)_2 & \text{white} & Calc. 74.9 5.9 13.1 4.3 - 6.01 & 86.0 1589 \text{ and} \\ found 74.6 5.4 13.3 4.0 - 1570 \\ [Mn(quad II)_2] (CIO_4)_2 & \text{white} & Calc. 78.0 5.8 9.6 4.7 - 5.99 & 88.5 1590 \text{ and} \\ found 77.9 5.7 9.5 4.6 - 1570 \\ [Mn(quad IV)_2] (CIO_4)_2 & \text{white} & Calc. 52.2 3.4 13.5 6.7 8.6 5.98 & 89.7 1591 \text{ and} \\ found 52.3 3.4 13.5 6.3 8.1 & 1571 \\ [Mn(quad VIII)_2] (CIO_4)_2 & \text{white} & Calc. 32.3 6.1 18.8 9.2 11.9 5.91 92.3 - \\ found 32.2 6.4 18.5 9.0 11.5 & -1 \\ \end{bmatrix}$	(1		found	39.3	3.4	22.6	7.2	9.3			1572
$ \begin{bmatrix} \operatorname{Mn}(\operatorname{quad}\operatorname{Ib})_2 \end{bmatrix} (\operatorname{ClO}_4)_2 & \operatorname{white} & \operatorname{Calc.} 42.5 & 4.0 & 21.2 & 6.9 & 9.0 & 5.94 & 91.8 & 1590 \text{ and} \\ & found & 42.1 & 3.9 & 21.5 & 6.3 & 9.1 & 1575 \\ \begin{bmatrix} \operatorname{Mn}(\operatorname{quad}\operatorname{Ic})_2 \end{bmatrix} (\operatorname{ClO}_4)_2 & \operatorname{white} & \operatorname{Calc.} 40.9 & 3.7 & 22.0 & 7.3 & 9.3 & 5.95 & 91.5 & 1592 \text{ and} \\ & found & 40.6 & 3.7 & 21.8 & 7.0 & 8.9 & 1576 \\ \begin{bmatrix} \operatorname{Mn}(\operatorname{quad}\operatorname{Id})_2 \end{bmatrix} (\operatorname{ClO}_4)_2 & \operatorname{white} & \operatorname{Calc.} 45.6 & 4.3 & 19.9 & 6.5 & 8.4 & 5.99 & 87.7 & 1591 \text{ and} \\ & found & 45.5 & 4.2 & 19.8 & 6.3 & 8.0 & 1576 \\ \begin{bmatrix} \operatorname{Mn}(\operatorname{quad}\operatorname{Id})_2 \end{bmatrix} (\operatorname{ClO}_4)_2 & \operatorname{white} & \operatorname{Calc.} 74.9 & 5.9 & 13.1 & 4.3 & - & 6.01 & 86.0 & 1589 \text{ and} \\ & found & 74.6 & 5.4 & 13.3 & 4.0 & - & 1570 \\ \begin{bmatrix} \operatorname{Mn}(\operatorname{quad}\operatorname{II})_2 \end{bmatrix} (\operatorname{ClO}_4)_2 & \operatorname{white} & \operatorname{Calc.} 46.0 & 3.8 & 15.3 & 7.5 & 9.7 & 6.02 & 86.5 & 1590 \text{ and} \\ & found & 46.2 & 3.8 & 15.5 & 7.3 & 9.2 & 1570 \\ \begin{bmatrix} \operatorname{Mn}(\operatorname{quad}\operatorname{II})_2 \end{bmatrix} (\operatorname{ClO}_4)_2 & \operatorname{white} & \operatorname{Calc.} 78.0 & 5.8 & 9.6 & 4.7 & - & 5.99 & 88.5 & 1593 \text{ and} \\ & found & 77.9 & 5.7 & 9.5 & 4.6 & - & 1574 \\ \begin{bmatrix} \operatorname{Mn}(\operatorname{quad}\operatorname{IV})_2 \end{bmatrix} (\operatorname{ClO}_4)_2 & \operatorname{white} & \operatorname{Calc.} 52.2 & 3.4 & 13.5 & 6.7 & 8.6 & 5.98 & 89.7 & 1591 \text{ and} \\ & found & 52.3 & 3.4 & 13.5 & 6.3 & 8.1 & 1571 \\ \begin{bmatrix} \operatorname{Mn}(\operatorname{quad}\operatorname{VIII})_2 \end{bmatrix} (\operatorname{ClO}_4)_2 & \operatorname{white} & \operatorname{Calc.} 32.3 & 6.1 & 18.8 & 9.2 & 11.9 & 5.91 & 92.3 & - \\ & found & 32.2 & 6.4 & 18.5 & 9.0 & 11.5 & - \\ \end{bmatrix}$	[Mn(quad Ia) ₂](BPh ₄) ₂	white	Calc.	73.7	5.5	14.3	4.7	_	5.86	91.7	1593 and
$ \begin{bmatrix} Mn(quad Ib)_2] (CIO_4)_2 & white \\ Calc. 42.5 & 4.0 & 21.2 & 6.9 & 9.0 \\ found & 42.1 & 3.9 & 21.5 & 6.3 & 9.1 \\ Mn(quad Ic)_2] (CIO_4)_2 & white \\ Calc. 40.9 & 3.7 & 22.0 & 7.3 & 9.3 \\ found & 40.6 & 3.7 & 21.8 & 7.0 & 8.9 \\ Mn(quad Id)_2] (CIO_4)_2 & white \\ Calc. 45.6 & 4.3 & 19.9 & 6.5 & 8.4 \\ found & 45.5 & 4.2 & 19.8 & 6.3 & 8.0 \\ Mn(quad Id)_2] (BPh_4)_2 & white \\ Calc. 74.9 & 5.9 & 13.1 & 4.3 & - \\ found & 74.6 & 5.4 & 13.3 & 4.0 & - \\ found & 74.6 & 5.4 & 13.3 & 4.0 & - \\ Mn(quad II)_2] (CIO_4)_2 & white \\ Calc. 46.0 & 3.8 & 15.3 & 7.5 & 9.7 & 6.02 & 86.5 \\ Mn(quad II)_2] (CIO_4)_2 & white \\ Calc. 78.0 & 5.8 & 9.6 & 4.7 & - \\ Mn(quad II)_2] (BPh_4)_2 & white \\ Calc. 52.2 & 3.4 & 13.5 & 6.7 & 8.6 \\ Mn(quad IV)_2] (CIO_4)_2 & white \\ Calc. 32.3 & 6.1 & 18.8 & 9.2 & 11.9 \\ Mn(quad VIII)_2] (CIO_4)_2 & white \\ Calc. 32.3 & 6.1 & 18.8 & 9.2 & 11.9 \\ Mn(quad VIII)_2] (CIO_4)_2 & white \\ Calc. 32.3 & 6.1 & 18.8 & 9.2 & 11.9 \\ Mn(quad VIII)_2] (CIO_4)_2 & white \\ Calc. 32.3 & 6.1 & 18.8 & 9.2 & 11.9 \\ Mn(quad VIII)_2] (CIO_4)_2 & white \\ Calc. 32.3 & 6.1 & 18.8 & 9.2 & 11.9 \\ Mn(quad VIII)_2] (CIO_4)_2 & white \\ Calc. 32.3 & 6.1 & 18.8 & 9.2 & 11.9 \\ Mn(quad VIII)_2] (CIO_4)_2 & white \\ Calc. 32.3 & 6.1 & 18.8 & 9.2 & 11.9 \\ Mn(quad VIII)_2 \end{bmatrix} $			found	73.9	5.6	14.2	4.8	_			1570
$ \begin{bmatrix} \operatorname{Mn}(\operatorname{quad} \operatorname{Ic})_2 \\ [\operatorname{Mn}(\operatorname{quad} \operatorname{Ic})_2 \\ [\operatorname{ClO}_4)_2 \\ \text{white} \\ \begin{bmatrix} \operatorname{Calc.} 40.9 \\ \operatorname{found} 42.1 \\ \operatorname{Subd} 3.7 \\ 22.0 \\ \operatorname{found} 40.6 \\ \operatorname{Subd} 7.2 \\ 21.8 \\ \operatorname{Subd} 7.0 \\ \operatorname{Subd} 9.1 \\ \operatorname{Subd} 7.3 \\ 9.3 \\ \operatorname{Subd} 9.1 \\ \operatorname{Subd} 7.3 \\ 9.3 \\ \operatorname{Subd} 7.3 \\ 9.3 \\ \operatorname{Subd} 7.3 \\ 9.3 \\ \operatorname{Subd} 7.3 \\ $	[Mn(quad Ib) ₂](ClO ₄) ₂	white	Calc.	42.5	4.0	21.2	6.9	9.0	5.94	91.8	1590 and
$ \begin{bmatrix} Mn(quad Ic)_2] (ClO_4)_2 & \text{white} & Calc. 40.9 & 3.7 & 22.0 & 7.3 & 9.3 \\ found 40.6 & 3.7 & 21.8 & 7.0 & 8.9 \\ found 40.6 & 3.7 & 21.8 & 7.0 & 8.9 \\ found 40.6 & 3.7 & 21.8 & 7.0 & 8.9 \\ found 45.5 & 4.2 & 19.8 & 6.3 & 8.0 \\ \begin{bmatrix} Mn(quad Id)_2] (ClO_4)_2 & \text{white} & Calc. 74.9 & 5.9 & 13.1 & 4.3 & - \\ found 74.6 & 5.4 & 13.3 & 4.0 & - \\ found 74.6 & 5.4 & 13.3 & 4.0 & - \\ found 46.2 & 3.8 & 15.5 & 7.3 & 9.7 \\ \begin{bmatrix} Mn(quad II)_2] (ClO_4)_2 & \text{white} & Calc. 46.0 & 3.8 & 15.3 & 7.5 & 9.7 \\ found 46.2 & 3.8 & 15.5 & 7.3 & 9.2 \\ \begin{bmatrix} Mn(quad II)_2] (ClO_4)_2 & \text{white} & Calc. 78.0 & 5.8 & 9.6 & 4.7 & - \\ found 77.9 & 5.7 & 9.5 & 4.6 & - \\ \end{bmatrix} $			found	42.1	3.9	21.5	6.3	9.1	0171	210	1575
$ \begin{bmatrix} Mn(quad Id)_2 \\ (ClO_4)_2 \end{bmatrix} = Minte \begin{bmatrix} Calc. 45.6 \\ 3.7 \\ 21.8 \end{bmatrix} = \begin{bmatrix} 7.0 \\ 8.9 \end{bmatrix} = \begin{bmatrix} 7.0 \\$	[Mn(quad Ic)](ClO ₂).	white	Calc	40.9	37	22.0	73	93	5.95	91.5	1592 and
$ \begin{bmatrix} Mn(quad Id)_2](ClO_4)_2 & \text{white} & Calc. 45.6 & 4.3 & 19.9 & 6.5 & 8.4 & 5.99 & 87.7 & 1570 \\ found 45.5 & 4.2 & 19.8 & 6.3 & 8.0 & 1576 \\ [Mn(quad Id)_2](BPh_4)_2 & \text{white} & Calc. 74.9 & 5.9 & 13.1 & 4.3 & - & 6.01 & 86.0 & 1589 and \\ found 74.6 & 5.4 & 13.3 & 4.0 & - & 1570 \\ [Mn(quad II)_2](ClO_4)_2 & \text{white} & Calc. 46.0 & 3.8 & 15.3 & 7.5 & 9.7 & 6.02 & 86.5 & 1590 and \\ found 46.2 & 3.8 & 15.5 & 7.3 & 9.2 & 1570 \\ [Mn(quad II)_2](BPh_4)_2 & \text{white} & Calc. 78.0 & 5.8 & 9.6 & 4.7 & - & 5.99 & 88.5 & 1593 and \\ found 77.9 & 5.7 & 9.5 & 4.6 & - & 1574 \\ [Mn(quad IV)_2](ClO_4)_2 & \text{white} & Calc. 52.2 & 3.4 & 13.5 & 6.7 & 8.6 & 5.98 & 89.7 & 1591 and \\ found 52.3 & 3.4 & 13.5 & 6.3 & 8.1 & 1571 \\ [Mn(quad VIII)_2](ClO_4)_2 & \text{white} & Calc. 32.3 & 6.1 & 18.8 & 9.2 & 11.9 & 5.91 & 92.3 & - \\ found 32.2 & 6.4 & 18.5 & 9.0 & 11.5 & - \\ \end{bmatrix} $	[1111(quad 10)2](0104)2		found	40.6	37	21.8	7.0	89	0.00	71.5	1576
$ \begin{bmatrix} Mn(quad H)_2 \\ (ClO_4)_2 \end{bmatrix} = White \begin{bmatrix} Calc. 43.5 & 4.2 & 19.8 & 6.3 & 8.0 \\ found 45.5 & 4.2 & 19.8 & 6.3 & 8.0 \\ found 45.5 & 4.2 & 19.8 & 6.3 & 8.0 \\ found 74.6 & 5.4 & 13.3 & 4.0 \\ found 74.6 & 5.4 & 13.3 & 4.0 \\ found 74.6 & 5.4 & 13.3 & 4.0 \\ found 46.2 & 3.8 & 15.3 & 7.5 & 9.7 \\ found 46.2 & 3.8 & 15.5 & 7.3 & 9.2 \\ \begin{bmatrix} Mn(quad II)_2 \\ (ClO_4)_2 \end{bmatrix} \end{bmatrix} \\ \begin{bmatrix} ClO_4 \\ 2 \end{bmatrix} \\ White \begin{bmatrix} Calc. 78.0 & 5.8 & 9.6 & 4.7 \\ found 77.9 & 5.7 & 9.5 & 4.6 \\ found 77.9 & 5.7 & 9.5 & 4.6 \\ found 52.3 & 3.4 & 13.5 & 6.7 & 8.6 \\ found 52.3 & 3.4 & 13.5 & 6.3 & 8.1 \\ \begin{bmatrix} Mn(quad IV)_2 \\ (ClO_4)_2 \end{bmatrix} \end{bmatrix} \\ \begin{bmatrix} ClO_4 \\ 2 \end{bmatrix} \\ White \begin{bmatrix} Calc. 32.3 & 6.1 & 18.8 & 9.2 \\ found 32.2 & 6.4 & 18.5 & 9.0 \\ \end{bmatrix} \\ \begin{bmatrix} Mn(quad VIII)_2 \\ 2 \end{bmatrix} \\ \begin{bmatrix} ClO_4 \\ 2 \end{bmatrix} \\ \begin{bmatrix} Mn(quad VIII)_2 \\ 2 \end{bmatrix} \\ \begin{bmatrix} ClO_4 \\ 2 \end{bmatrix} \\ White \begin{bmatrix} Calc. 32.3 & 6.1 & 18.8 & 9.2 \\ 11.9 \end{bmatrix} \\ \begin{bmatrix} Mn(quad VIII)_2 \\ 2 \end{bmatrix} \\ \begin{bmatrix} ClO_4 \\ 2 \end{bmatrix} \\ White \begin{bmatrix} Calc. 32.3 & 6.1 & 18.8 & 9.2 \\ 11.9 \end{bmatrix} \\ \begin{bmatrix} Mn(quad VIII)_2 \\ 2 \end{bmatrix} \\ \begin{bmatrix} ClO_4 \\ 2 \end{bmatrix} \\ White \begin{bmatrix} Calc. 32.3 & 6.1 & 18.8 & 9.2 \\ 11.9 \end{bmatrix} \\ \begin{bmatrix} Mn(quad VIII)_2 \\ 2 \end{bmatrix} \\ \begin{bmatrix} ClO_4 \\ 2 \end{bmatrix} \\ White \begin{bmatrix} Calc. 32.3 & 6.1 & 18.8 & 9.2 \\ 11.9 \end{bmatrix} \\ \begin{bmatrix} Mn(quad VIII)_2 \\ 2 \end{bmatrix} \\ \begin{bmatrix} ClO_4 \\ 2 \end{bmatrix} \\ White \begin{bmatrix} Calc. 32.3 & 6.1 & 18.8 & 9.2 \\ 11.9 \end{bmatrix} \\ \begin{bmatrix} Mn(quad VIII)_2 \\ 2 \end{bmatrix} \\ \begin{bmatrix} ClO_4 \\ 2 \end{bmatrix} \\ White \begin{bmatrix} Calc. 32.3 & 6.1 & 18.8 & 9.2 \\ 11.9 \end{bmatrix} \\ \begin{bmatrix} Mn(quad VIII)_2 \\ 2 \end{bmatrix} \\ \begin{bmatrix} ClO_4 \\ 2 \end{bmatrix} \\ White \begin{bmatrix} Calc. 32.3 & 6.1 & 18.8 & 9.2 \\ 11.9 \end{bmatrix} \\ \begin{bmatrix} Mn(quad VIII)_2 \\ 2 \end{bmatrix} \\ \begin{bmatrix} ClO_4 \\ 2 \end{bmatrix} \\ White \begin{bmatrix} Calc. 32.3 & 6.1 & 18.8 & 9.2 \\ 11.9 \end{bmatrix} \\ \begin{bmatrix} Mn(quad VIII)_2 \\ 2 \end{bmatrix} \\ \begin{bmatrix} ClO_4 \\ 2 \end{bmatrix} \\ White \begin{bmatrix} Calc. 32.3 & 6.1 & 18.8 & 9.2 \\ 11.9 \end{bmatrix} \\ \begin{bmatrix} Mn(quad VIII)_2 \\ 2 \end{bmatrix} \\ \begin{bmatrix} Mn(quad $	$[Mn(quad Id)_2](ClO_4)_2$	white	Calc	45.6	43	100	6.5	84	5 99	877	1501 and
$ \begin{bmatrix} Mn(quad Id)_2](BPh_4)_2 & \text{white} & Calc. 74.9 & 5.9 & 13.1 & 4.3 & - & 6.01 & 86.0 & 1589 \text{ and} \\ found 74.6 & 5.4 & 13.3 & 4.0 & - & & 1570 \\ \hline [Mn(quad II)_2](CIO_4)_2 & \text{white} & Calc. 46.0 & 3.8 & 15.3 & 7.5 & 9.7 & 6.02 & 86.5 & 1590 \text{ and} \\ found 46.2 & 3.8 & 15.5 & 7.3 & 9.2 & & 1570 \\ \hline [Mn(quad II)_2](BPh_4)_2 & \text{white} & Calc. 78.0 & 5.8 & 9.6 & 4.7 & - & 5.99 & 88.5 & 1593 \text{ and} \\ found 77.9 & 5.7 & 9.5 & 4.6 & - & & 1574 \\ \hline [Mn(quad IV)_2](CIO_4)_2 & \text{white} & Calc. 52.2 & 3.4 & 13.5 & 6.7 & 8.6 & 5.98 & 89.7 & 1591 \text{ and} \\ found 52.3 & 3.4 & 13.5 & 6.3 & 8.1 & & 1571 \\ \hline [Mn(quad VIII)_2](CIO_4)_2 & \text{white} & Calc. 32.3 & 6.1 & 18.8 & 9.2 & 11.9 & 5.91 & 92.3 & - \\ found 32.2 & 6.4 & 18.5 & 9.0 & 11.5 & & - \\ \hline \end{bmatrix} $		white	found	45.5	4.2	10.9	63	8.0	5.77	07.7	1576
$ \begin{bmatrix} Mn(quad H)_2 \\ (ClO_4)_2 \\ (Mn(quad H)_2 \\ (Mn(quad H$	[Mn(quad Id) ₂](BPh ₄) ₂	white	Calc	74 9	5 0	13.1	A 3	0.0	6.01	86.0	1580 and
$ \begin{bmatrix} Mn(quad II)_2](ClO_4)_2 & \text{white} & Calc. 46.0 & 3.8 & 15.3 & 7.5 & 9.7 & 6.02 & 86.5 & 1570 \\ & found 46.2 & 3.8 & 15.5 & 7.3 & 9.2 & 1570 \\ & found 46.2 & 3.8 & 15.5 & 7.3 & 9.2 & 1570 \\ & found 77.9 & 5.7 & 9.5 & 4.6 & - & 1570 \\ & found 77.9 & 5.7 & 9.5 & 4.6 & - & 1574 \\ & found 77.9 & 5.7 & 9.5 & 4.6 & - & 1574 \\ & found 52.3 & 3.4 & 13.5 & 6.3 & 8.1 & 1571 \\ & [Mn(quad IV)_2](ClO_4)_2 & white & Calc. 52.2 & 3.4 & 13.5 & 6.3 & 8.1 & 1571 \\ & found 52.3 & 3.4 & 13.5 & 6.3 & 8.1 & 1571 \\ & [Mn(quad VIII)_2](ClO_4)_2 & white & Calc. 32.3 & 6.1 & 18.8 & 9.2 & 11.9 & 5.91 & 92.3 & - \\ & found & 32.2 & 6.4 & 18.5 & 9.0 & 11.5 & - \\ \end{bmatrix} $		white	found	74.6	5.1	13.1	4.5	_	0.01	80.0	1570
$ \begin{bmatrix} Mn(quad II)_2](ClO_4)_2 & white Calc. 46.0 5.8 15.5 7.3 9.2 & 1550 and found 46.2 3.8 15.5 7.3 9.2 & 1570 \\ \begin{bmatrix} Mn(quad II)_2](BPh_4)_2 & white Calc. 78.0 5.8 9.6 4.7 - 5.99 88.5 & 1593 and found 77.9 5.7 9.5 4.6 - 1574 \\ \begin{bmatrix} Mn(quad IV)_2](ClO_4)_2 & white Calc. 52.2 3.4 13.5 6.7 8.6 5.98 89.7 & 1591 and found 52.3 3.4 13.5 6.3 8.1 & 1571 \\ \begin{bmatrix} Mn(quad VIII)_2](ClO_4)_2 & white Calc. 32.3 6.1 18.8 9.2 11.9 5.91 92.3 - found 32.2 6.4 18.5 9.0 11.5 & - \\ \end{bmatrix} $	[Mn(quad II) ₂](ClO ₄) ₂	white	Cala	74.0 46.0	2.9	15.5	4.0	07	6.02	96 5	1570 1500 and
$ \begin{bmatrix} Mn(quad II)_2](BPh_4)_2 & \text{white} & Calc. 78.0 & 5.8 & 9.6 & 4.7 & - & 5.99 & 88.5 & 1593 \text{ and} \\ found 77.9 & 5.7 & 9.5 & 4.6 & - & & 1574 \\ \hline [Mn(quad IV)_2](ClO_4)_2 & \text{white} & Calc. 52.2 & 3.4 & 13.5 & 6.7 & 8.6 & 5.98 & 89.7 & 1591 \text{ and} \\ found 52.3 & 3.4 & 13.5 & 6.3 & 8.1 & & 1571 \\ \hline [Mn(quad VIII)_2](ClO_4)_2 & \text{white} & Calc. 32.3 & 6.1 & 18.8 & 9.2 & 11.9 & 5.91 & 92.3 & - \\ found 32.2 & 6.4 & 18.5 & 9.0 & 11.5 & & - \\ \hline \end{bmatrix} $		white	Calc.	40.0	3.0 2.0	15.5	7.5	9.7	0.02	80.5	1590 and 1570
$ [Mn(quad II)_2](ClO_4)_2 \text{white} Calc. 78.0 5.8 9.6 4.7 - 5.99 88.5 1593 \text{ and} \\ found 77.9 5.7 9.5 4.6 - 1574 1574 1574 1574 1574 1574 1574 1574 1574 1574 1574 1574 1574 1571 $	[Mar(and II)](DDL)		Colo	40.2	5.0	15.5	7.5	9.2	5.00	00 5	1570
$ [Mn(quad IV)_2](ClO_4)_2 \text{white} \begin{array}{ccccccccccccccccccccccccccccccccccc$	$[Mn(quad II)_2](BPh_4)_2$	white	Calc.	/8.0	5.8	9.6	4.7	-	5.99	88.5	1593 and
$ [Mn(quad IV)_2](ClO_4)_2 \text{white} Calc. 52.2 3.4 13.5 6.7 8.6 5.98 89.7 1591 \text{ and} \\ found 52.3 3.4 13.5 6.3 8.1 1571 $			round	//.9	5.7	9.5	4.0	-	5.00	00 7	15/4
$[Mn(quad VIII)_2](ClO_4)_2 white \begin{cases} found 52.3 & 3.4 & 13.5 & 6.3 & 8.1 \\ Calc. & 32.3 & 6.1 & 18.8 & 9.2 & 11.9 \\ found & 32.2 & 6.4 & 18.5 & 9.0 & 11.5 \\ \end{cases} \begin{array}{c} 5.91 & 92.3 & - \\ - & - & - \\ \end{array}$	$[Mn(quad IV)_2](ClO_4)_2$	white	Calc.	52.2	3.4	13.5	6.7	8.6	5.98	89.7	1591 and
$ [Mn(quad VIII)_2](CIO_4)_2 \text{white} Calc. 32.3 6.1 18.8 9.2 11.9 5.91 92.3 - \\ found 32.2 6.4 18.5 9.0 11.5 - \\ \end{array} $			found	52.3	3.4	13.5	6.3	8.1			1571
found 32.2 6.4 18.5 9.0 11.5 –	$[Mn(quad WIII)_2](ClO_4)_2$	white	Calc.	32.3	6.1	18.8	9.2	11.9	5.91	92.3	-
			found	32.2	6.4	18.5	9.0	11.5			-

electronic reflectance spectra of a range of the complexes of all types yielded no useable information.

The structures of the three classes of compound prepared, viz.: (i) MnquadX₂; X = Cl, Br, ClO₄orBPh₄; (ii)[Mn₂(quad)₃]X₄; X = ClO₄ or BPh₄; (iii)[Mn (quad)₂]X₂; X = ClO₄ or BPh₄ can be postulated in the following ways.

(i) Mnquad X_2 are normal octahedral complexes with the perchlorate and tetraphenylborate perhaps weakly bonded in the fifth and sixth octahedral sites in the solid, or with a solid packing array that allows weak interactions between atoms in coordinated ligands and manganese atoms in adjacent molecules.

(ii) $[Mn_2(quad)_3]X_4$ are probably dimers. Ligands such as II are known to bridge between metal atoms⁷.

The possible modes of bridging are numerous, but in general may be classified into various arrangements possessing a single, a double or a triple ligand bridge between adjacent manganese atoms. Molecular models indicate that ligands III, V, VI, VII and X can give single ligand bridge dimers, ligands IX and X double ligand bridge dimers, and ligands VI, VII and X triple ligand bridged dimers.

Of the four ligands which yield $[Mn(quad)_2]X_2$ complexes, models indicate that ligands IV and VIII would prefer to have all four donor nitrogens on the one metal atom. Ligand II can form a strained triple ligand bridge dimer as it does in $[Cu_2(quad II)_3](ClO_4)_4^7$, while ligand I can form a double bridge dimer as in [Ni (quad Id)]₂, but to do this it must strain to bond through N_1 , N_3 , N_5 and N_6 of I.³ Such behaviour cannot be exhibited by the structurally similar ligands II, IV and VIII.

(iii) Assuming that all the potential nitrogen donor atoms are bonded in $[Mn(quad)_2]X_2$, then these compounds are 8-coordinate. In this context it is of interest to note that the preparation of these compounds is very similar to that of the $[Mn(bidentate)_4]X_2$ compounds previously claimed to be 8-coordinate. Furthermore, the element of rigidity in structure, which appeared to be important for these bidentate ligands to give 8-coordinate species⁵, is also present in these quadridentate ligands (I, II, IV, and VIII). Any diminution of this rigidity allows the ligand to bridge, and in preference to 8-coordination one obtains octahedral bridged dimers.

Proof of 8-coordination is difficult to obtain outside of X-ray crystallography, and none of the compounds has yet been obtained in a crystalline form. However, the majority of the ligands possess terminal pyridine moieties. In each such case the free ligand has an infrared stretch at ~1610 cm⁻¹ and at ~1570 cm⁻¹ attributed to the pyridine breathing mode. Upon complexation, the peak at 1610 is lowered to approximately 1590 cm⁻¹. This behaviour is claimed⁸ to be typical of coordinated pyridine residues. Infrared study of the N–H stretch region for complexes of ligands possessing N–H bonds reveals only weak ill-defined peaks, and no meaningful information could be obtained from this source.

It is possible to construct molecular models of $[Mn (quad)_2]^{2+}$ in which ligands I, II, IV, and VIII are almost planar with their eight nitrogen donors bonded to a dodecahedral metal atom. On the other hand, all four ligands could readily yield complexes of the [Sn pc] (pc = phthalocyanine) type, with a square antiprismatic structure⁹. The colourless nature of these compounds, when the other types of complexes are yellow or deeper coloured, suggests that the ligand donors are weakly bonded with little disturbance of the ligand electronic structure. This, plus the fact that crystal field stabilisation energy is zero for any high spin d^5 stereochemistry, supports the contention that these are 8-coordinate structures.

Experimental

The Schiff-base ligands were prepared by normal methods (see for example reference 2) and recrystallised from aqueous ethanol. Ligands V, VI and VII were kindly supplied by Dr E. D. McKenzie of the University of Sheffield, England. The metal complexes were prepared in the following way:

$[Mn(quad)_2]X_2$ and $[Mn_2(quad)_3]X_4$

Aproximately 0.2*M* aqueous solutions of $Mn(ClO_4)_2$ and $Mn(BPh_4)_2$ were prepared and standardised by EDTA titration (back titration with standard CuSO₄ using PAN indicator). Accurate amounts of Mn(II)salt were then placed in a flask and titrated, with stirring, with an 0.2*M* ethanolic solution of the required ligand. The required complexes precipitated as fine deposits at one of the two stoichiometries. The complexes were dried over P₂O₅, under vacuum at 120°C.

$MnquadX_2$

These complexes were obtained by adding approximately one molecular equivalent of the required manganese(II) salt in ethanol to approximately one molecular equivalent of the required ligand also in ethanol. Crystals of the complexes deposited over a period of one to eight weeks. After being removed by filtration, the crystals were dried as above.

Instrumentation

Infrared spectra were recorded on a Perkin–Elmer-457 spectrometer using nujol mulls. Conductivities were measured using a Philoscope conductivity bridge and a dip-type platinum electrodes. Magnetic moments were obtained on either a Faraday or Gouy magnetic balance. Microanalyses were carried out in the Departments of Chemistry, University of Cambridge and University of Queensland microanalytical laboratories.

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