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

B. CHISWELL
Department of Chemistry, University of Queensland, St. Lucia, Q., 4067, Australia
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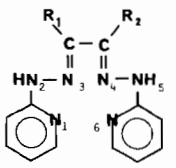
Linear quadridentate nitrogenous ligands have been shown to yield three different types of Manganese(II) compound. Simple octahedral compounds of formulation Mn(quad)X_2 (where X = Cl, Br, ClO_4 or BPh_4) are obtained with most ligands. However, with sterically rigid ligands, compounds of the type $[Mn(quad)_2]X_2$ (X = ClO_4 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 or BPh_4) are also obtained.*

Introduction

Lions and Martin[1] 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-



Ia : $R_1 = R_2 = H$
Ib : $R_1 = R_2 = CH_3$
Ic : $R_1 = H$; $R_2 = CH_3$
Id : R_1-C-C-R_2 in a cyclohexane ring

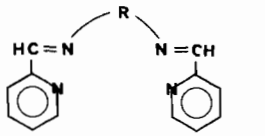
ing agent. Later workers[2] demonstrated that neutral divalent metal complexes of copper, nickel and palladium could readily be obtained by the removal in alkaline solution of the two hydrazine protons to yield intensely coloured compounds. More recent work on the metal complexes of ligands of type I has been undertaken by a number of workers.[3]

In the preparation of square planar manganese(II) compounds for oxygenation studies[4], attempts were made to prepare the compounds [Mn(quad I)]X_2 (where X = Cl, Br, ClO_4 or BPh_4). Octahedral compounds could be isolated when $MnX_2 \cdot nH_2O$ was added to any ligand I in ethanol for X = Cl or Br, but when X = ClO_4 or BPh_4, colourless complexes of formulation $Mn(quad)_2X_2$ were precipitated. This behaviour is reminiscent of similar results obtained in the preparation of $[Mn(bidentate)_4]X_2$ (X = ClO_4, BPh_4 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.

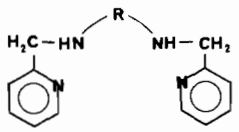
* (quad) = abbreviation for quadridentate ligand; the number of the ligand is shown in specific cases.

Results and Discussion

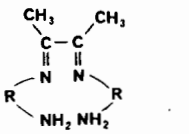
The ligands studied are shown I to X. It was found



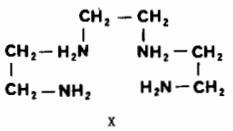
II : R = $-(CH_2)_2-$
III : R = $-(CH_2)_3-$
IV : R = o-phenylene ring



V : R = $-(CH_2)_2-$
VI : R = $-(CH_2)_3-$
VII : R = $-CH(CH_3)-CH_2-$



VIII : R = $-(CH_2)_2-$
IX : R = $-(CH_2)_3-$



X

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

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 MnX_2 to 3 ligand. Mono-complexes, *viz.* $Mn(quad)(ClO_4)_2 \cdot nH_2O$ could be prepared for all ligands except I and IV by intermixing 1:1 molecular ratios of ligand and $Mn(ClO_4)_2$ 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 P_2O_5 at 120° C.

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.* $[Mn(quad)_n]X_2$ (where n = 1, $1^1/_2$ or 2; X = ClO_4 or BPh_4). 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

TABLE. Properties of Complexes.

Compound	Colour		Analysis					μ_{eff} in B.M./ 295K	Λ1000 in $MeNO_2$ (r.o)	I.R. Pyridine Breathing (cm^{-1})
			C	H	N	Mn	Cl or Br			
(i) $MnquadX_2$										
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
		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. (Cont.)

Compound	Colour		Analysis					μ_{eff} in B.M./ 295K	Λ 1000 in $MeNO_2$ (r.o)	I.R. Pyridine Breathing (cm^{-1})
			C	H	N	Mn	Cl or Br			
(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
$[Mn_2(quad\ III)_3](BPh_4)_4$	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.	40.8	4.4	13.6	8.9	11.5	5.97	92.1	1589 and
		found	40.6	4.4	13.7	8.6	11.0			1569
$[Mn_2(quad\ VI)_3](BPh_4)_4$	cream	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
$[Mn_2(quad\ VII)_3](ClO_4)_4$	yellow	Calc.	42.3	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	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	–	6.00	89.1	–
		found	74.7	7.2	9.0	5.8	–			–
(iii) $[Mn(quad)_2]X_2$										
$[Mn(quad\ Ia)_2](ClO_4)_2$	white	Calc.	39.2	3.3	22.9	7.5	9.7	6.01	93.0	1592 and
		found	39.3	3.4	22.6	7.2	9.3			1572
$[Mn(quad\ Ia)_2](BPh_4)_2$	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
$[Mn(quad\ Ib)_2](ClO_4)_2$	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
$[Mn(quad\ Ic)_2](ClO_4)_2$	white	Calc.	40.9	3.7	22.0	7.3	9.3	5.95	91.5	1592 and
		found	40.6	3.7	21.8	7.0	8.9			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
$[Mn(quad\ Id)_2](BPh_4)_2$	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
$[Mn(quad\ II)_2](ClO_4)_2$	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
$[Mn(quad\ II)_2](BPh_4)_2$	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
$[Mn(quad\ IV)_2](ClO_4)_2$	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
$[Mn(quad\ VIII)_2](ClO_4)_2$	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) $MnquadX_2$; X = Cl, Br, ClO_4 or BPh_4; (ii) $[Mn_2(quad)_3]X_4$; X = ClO_4 or BPh_4; (iii) $[Mn(quad)_2]X_2$; X = ClO_4 or BPh_4 can be postulated in the following ways.

(i) $MnquadX_2$ 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 atoms[7]. 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 species[5], 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 claimed[8] 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 structure[9]. 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 $CuSO_4$ 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 P_2O_5, 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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