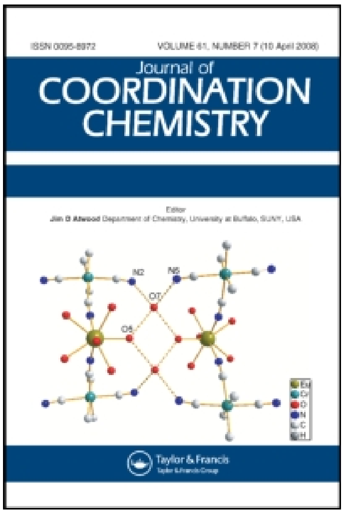

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Structural, Magnetic and Electrochemical Studies of a New Series of Macrocyclic Mononuclear and Binuclear Manganese(III) and Unusually Stable Manganese(II) Complexes

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To cite this Article Parimala, S. , Kandaswamy, M. , Nissa, M. Niloffar and Velmurugan, D.(2003) 'Structural, Magnetic and Electrochemical Studies of a New Series of Macrocyclic Mononuclear and Binuclear Manganese(III) and Unusually Stable Manganese(II) Complexes', Journal of Coordination Chemistry, 56: 4, 261 — 274

To link to this Article: DOI: 10.1080/0095897031000068996

URL: http://dx.doi.org/10.1080/0095897031000068996

J. Coord. Chem., 2003, Vol. 56, No. 4, pp. 261–274

STRUCTURAL, MAGNETIC AND ELECTROCHEMICAL STUDIES OF A NEW SERIES OF MACROCYCLIC MONONUCLEAR AND BINUCLEAR MANGANESE(III) AND UNUSUALLY STABLE MANGANESE(II) COMPLEXES

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(Received 7 June 2002; In final form 15 October 2002)

The synthesis of several mononuclear and binuclear manganese(III) complexes from 3,4:9,10-dibenzo-1,12[{*N*,*N*′-bis(4-methyl-1-oxa)-6,6′-formyl}-2-benzyldiaza]-5,8-dioxacyclotetradecane have been described. The X-ray crystal structure of the manganese(III) complex $[MnL^{2a}(H_2O)(ClO_4)]\cdot(ClO_4)_2\cdot3H_2O\cdot CH_3OH$ revealed a six coordinate manganese atom with octahedral geometry. All four phenyl rings were found to lie almost in one plane with the manganese atom slightly lifted from it due to Jahn-Teller distortion. Room temperature magnetic studies of the mononuclear complexes gave μ_{eff} values around 5 B.M. Electrochemical studies of mononuclear complexes showed irreversible reduction in the range -0.15 to -0.4 V for the Mn(III)/Mn(II) redox couple and *quasi*-reversible oxidation around $+0.8$ V for the Mn(III)/Mn(IV) species. Binuclear complexes showed two *quasi*-reversible reductions in the -0.3 and -0.7 V regions corresponding to Mn(III)Mn(III)/Mn(III)Mn(II) and Mn(III)Mn(II)/Mn(II)Mn(II) couples, respectively. The oxidation process showed two waves around $+0.6$ and $+0.9$ V; the former is due to the formation of a Mn(III)Mn(IV) complex and the latter to a Mn_2(IV,IV) complex (the latter showed more reversibility in the given scan time). Rare types of mono and binuclear manganese(II) complexes consisting of bridging phenolic oxygens were synthesized under special conditions. The complexes showed an ESR signal centred around 3200 G. Room temperature magnetic studies of the mononuclear manganese(II) complexes gave a μ_{eff} value of 6.1 B.M., close to the spin-only value for high spin Mn(II). Electrochemical studies of the mononuclear complex showed *quasi* reversible oxidation around 1 V and the binuclear complex showed unusual two, one-electron oxidations at high positive potentials (1.2 to 1.7 V).

Keywords: Macrocyclic complexes; Binuclear; Manganese (III); Manganese (II); Electrochemistry

INTRODUCTION

Manganese is involved in a number of redox functions [1] in living systems, as observed in water splitting by photosynthetic enzymes [2], disproportionation of H_2O_2 [3] (catalase activity) in microorganisms, and so on. These multielectron redox catalysts

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ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/0095897031000068996

produce the necessary reducing or oxidizing equivalents [4] for the enzymatic processes. The oxygen evolving centre (OEC) in photosystem(II) [5] of green plants and manganese catalase [6] has a binuclear centre or manganese aggregates of higher nuclearity in their active sites. EXAFS [7] analysis of the OEC suggests the presence of at least two or more short Mn···Mn distances, close to the intermetallic distance of a normal bis(μ-oxo) dimanganese core. Thus the strong interaction that is observed in these complexes can be expected to occur between manganese atoms present in the active site of metalloenzymes. In order to explore the interactions between the manganese metal ions, several model complexes have been prepared [8], whose ligand environments have been suitably designed. The simple, yet straightforward synthesis of Schiff base ligands and their binuclear or mononuclear manganese complexes dominate the literature of manganese coordination chemistry [9]. The synthetic access of the ligands has facilitated the design and synthesis of polydentate macrocycles [10]. Among the various classes of macrobicycles, there are only a few [11] that can accommodate two metal ions in close proximity. The lateral macrobicycles discussed in this context have different binding sites and mononuclear and binuclear manganese(III) complexes display unique and interesting redox properties. The synthesis and characterization of such a complex are reported in this communication. Though it is quite difficult to form stable Mn(II) complexes derived from a salen ligand containing bridging phenolic oxygens, we have synthesized stable mononuclear and binuclear Mn(II) complexes, obtained their EPR spectra and studied their magnetic and electrochemical behaviour.

EXPERIMENTAL SECTION

Chemicals

Chemicals of the highest purity that were commercially available were used as received. Manganese perchlorate hexahydrate was prepared from manganese carbonate and perchloric acid.

Physical Measurements

Elemental analyses were performed using a Heraeus CHN instrument. IR spectra were recorded with KBr pellets on a Shimadzu IR-408 spectrophotometer. Electronic spectra were recorded on a Hitachi 320 double beam spectrophotometer. Room temperature magnetic susceptibilities were measured using an E.G&G model 155 vibrating sample magnetometer. EPR spectra were recorded on a Bruker ER 200 spectrometer at room and liquid nitrogen temperatures. Cyclic voltammetric studies were performed at room temperature in DMF using a CHI 600A instrument. A three electrode cell assembly was used in which the working electrode was glassy carbon, the counter electrode was platinum and a saturated calomel electrode (SCE) was the reference. Tetrabutylammonium perchlorate (0.1M) was used as the supporting electrolyte. Complexes (10^{-3} M) were deoxygenated by purging with nitrogen.

Crystal Data Collection

The complex $[MnL^{2a}(H_2O)(ClO_4)](ClO_4)_2 \cdot 2H_2O$ synthesized was crystallized from acetonitrile–methanol by slow evaporation. A dark brown crystal of size

$0.34 \times 0.24 \times 0.20$ mm was used for intensity data collection. Data were collected on a Siemens smart CCD area detector diffractometer with MoKα radiation ($\lambda = 0.71073$ Å) using ω scan mode. The computer software SAINT was used for cell refinement. The θ range for data collection was from 1.64 to 25°; data were 97.4% complete. An absorption correction was applied to the data with the SADABS program with maximum and minimum effective transmission factors of 0.903 and 0.843, respectively. Out of 26 908 reflections, 8478 reflections were unique with $I \geq 2\sigma(I)$ and these were used for the structure analysis. Examination of systematic absences indicated the space group $P2_1/n$.

Structure Solution and Refinement

The structure was solved by direct methods using SHELXS-97 [12]. An E-map calculated for the most consistent phase set yielded the positions of all non-hydrogen atoms including the water molecules, perchlorate ions and lattice methanol. The trial structure was refined isotropically for a few cycles by full-matrix least-squares methods using SHELXL-97 [13]. Except for two oxygen atoms (O3C and O3D), all other non-hydrogen atoms were then subjected to anisotropic refinement for a few cycles. The R factor converged to 0.10 and at this stage all hydrogen atoms were fixed geometrically and allowed to ride on their parent atoms. At the final stage of refinement, the oxygen atoms (O3C and O3D) were included in the anisotropic refinement for only one cycle. The final R value was 0.0896. The final electro density map contains maximum and minimum peak heights of 1.389 and -0.606 eÅ^{-3}, respectively. The maximum peak is in the vicinity of the disordered perchlorate ion. Geometric parameter calculations were performed using PARST [14]. Crystallographic data for the complex have been deposited in the Cambridge Crystallographic Centre, deposition number 157513.

Synthesis of Precursor Ligands

3,4;9,10-Dibenzo-1,12[{N,N′-bis(4-methyl-1-oxa)-6,6′-formyl}-2-benzyldiaza]-5,8-di-oxacyclotetradecane (L^1)

To a stirred solution of 3-chloromethyl-5-methylsalicylaldehyde (3.68 g, 200 mM) in THF, a mixture of 3,4:9,10-dibenzo-1,12-diaza-5,8-dioxocyclotetradecane-1,11-diene [15,16] (2.98 g, 100 mM) and triethylamine (2.8 mL, 200 mM) was added dropwise and refluxed for 4 h. The reaction mixture was then diluted with water and the compound extracted with three portions of chloroform, and dried over magnesium sulphate. The compound was recrystallized from THF, M.P.: 164°C. ^{1}H NMR spectrum ($CDCl_3$, δ): 9.5(s, aldehyde), 6.8(m, aromatic), 3.7(s, benzylic methylene group), 4.1(s, methylene group attached to oxygen atom), 4.7(s, methylene group attached to nitrogen atom), 2.1(s, methyl group attached to the phenyl ring).

3,4;9,10-Dibenzo-1,12[{N,N′-bis(4-methyl-1-oxa)-6,6′-formyl}-2-benzyldiaza]-5,8-di-oxacyclopentadecane (L^2)

The compound was prepared by the method described above using 3,4:9,10-dibenzo-1,12-diaza-5,8-dioxocyclopentadecane-1,11-diene (3.12 g, 100 mM), M.P. 110°C. ^{1}H NMR spectra ($CDCl_3$, δ): 10.29(s, aldehyde), 7.2(m, aromatic), 4.5(s, methylene group attached to nitrogen atom), 3.8(s, methylene group attached to oxygen atom, 3.6(s, benzylic methylene group), 2.2(s, methyl group attached to the phenyl ring).

3,4;9,10-Dibenzo-1,12[{N,N′-bis(4-methyl-1-oxa)-6,6′-formyl}-2-benzyldiaza]-5,8-di-oxacyclohexadecane (L^3)

The compound was prepared by the procedure as described above from 3,4:9,10-dibenzo-1,12-diaza-5,8-dioxocyclohexadecane-1,11-diene (3.26 g, 100 mM), M.P. 160°C. ^{1}H NMR spectra ($CDCl_3$, δ): 10.3(s, aldehyde), 7(m, aromatic), 4.0(s, methylene group attached to nitrogen atom), 3.6(s, methylene group attached to oxygen atom), 3.3(s, benzylic methylene group), 2.1(s, methyl group attached to the phenyl ring).

Synthesis of Macrocyclic Mononuclear Manganese(III) Complexes

To a solution of compound (**L**^{1}) (0.594 g, 1 mM) in 50 mL of chloroform, manganese perchlorate hexahydrate (0.365 g, 1 mM) in 10–15 mL of methanol and the appropriate diamines (1,2-diaminoethane, 0.07 ml, 1 mM; 1,3-diaminopropane, 0.08 mL, 1 mM; 1,4-diaminobutane, 0.1 mL, 1 mM) in 10 mL of methanol were added and refluxed for 12 h. The dark brown complex obtained upon evaporation was recrystallized from acetonitrile.

$[MnL^{1a}(H_2O)(ClO_4)](ClO_4)_2 \cdot 2H_2O$

Anal. C, 44.23; H, 4.72; N, 5.29 (%). Calculated for $C_{38}H_{48}N_4O_{13}Cl_3Mn$: C, 44.45; H, 4.68; N, 5.45. IR [cm^{-1}]: ν(C=N), 1618; $\nu(ClO_4)$, 1090; λ_{max}/nm in acetonitrile: 305, 398, 550 (*d–d* band).

$[MnL^{1b}(H_2O)(ClO_4)](ClO_4)_2 \cdot 2H_2O$

Anal. C, 44.82; H, 4.73; N, 5.05. Calculated for $C_{39}H_{50}N_4O_{13}Cl_2Mn$: C, 44.77; H, 4.85; N, 5.22. IR: ν(C=N), 1625; $\nu(ClO_4)$, 1092; λ_{max}/nm in acetonitrile: 265, 400, 558.

$[MnL^{1c}(H_2O)(ClO_4)](ClO_4)_2 \cdot 2H_2O$

Anal. C, 45.56; H, 4.54; N, 5.42. Calculated for $C_{40}H_{52}N_4O_{13}Cl_2Mn$: C, 45.30; H, 4.97; N, 5.15. IR: ν(C=N), 1620; $\nu(ClO_4)$, 1095; λ_{max}/nm in acetonitrile: 268, 395, 565.

$[MnL^{2a}(H_2O)(ClO_4)](ClO_4)_2 \cdot 2H_2O$

The complex was synthesized by the method as described above from the precursor ligand **L**^{2} (0.606 g, 1 mM), manganese perchlorate hexahydrate (0.365 g, 1 mM) and the appropriate diamine. *Anal.* C, 44.23; H, 4.32; N, 5.53. Calculated for $C_{39}H_{50}N_4O_{13}Cl_2Mn$: C, 44.60; H, 4.83; N, 5.20. IR: ν(C=N), 1624; $\nu(ClO_4)$, 1089; λ_{max}/nm in acetonitrile: 282 393, 545.

$[MnL^{2b}(H_2O)(ClO_4)](ClO_4)_2 \cdot 2H_2O$

The complex crystallized as dark brown prisms suitable for X-ray diffraction studies. *Anal.* C, 45.85; H, 4.76; N, 5.56. Calculated for $C_{40}H_{52}N_4O_{13}Cl_2Mn$: C, 45.30; H, 4.97; N, 5.15. IR: ν(C=N), 1618; ν(ClO_4), 1087; λ_{max}/nm in acetonitrile: 272, 392, 557.

$[MnL^{2c}(H_2O)(ClO_4)](ClO_4)_2 \cdot 2H_2O$

Anal. C, 45.23; H, 4.86; N, 5.23. Calculated for $C_{41}H_{54}N_4O_{13}Cl_2Mn$: C, 45.84; H, 4.86; N, 5.09. IR: ν(C=N), 1622; ν(ClO_4), 1094; λ_{max}/nm in acetonitrile: 278, 388, 570.

$[MnL^{3a}(H_2O)(ClO_4)](ClO_4)_2 \cdot 2H_2O$

The complex was synthesized by the same method from the precursor ligand $\mathbf{L}^3$ (0.626 g, 1 mM), manganese perchlorate hexahydrate (0.365 g, 1 mM) and the appropriate diamine. *Anal.* C, 44.98; H, 5.02; N, 5.46. Calculated for $C_{40}H_{52}N_4O_{13}Cl_2Mn$: C, 45.30; H, 4.97; N, 5.15. IR: ν(C=N), 1625; ν(ClO_4), 1091; λ_{max}/nm in acetonitrile: 280, 390, 542.

$[MnL^{3b}(H_2O)(ClO_4)](ClO_4)_2 \cdot 2H_2O$

Anal. C, 45.96; H, 5.12; N, 5.24. Calculated for $C_{41}H_{54}N_4O_{13}Cl_2Mn$: C, 45.82; H, 5.09; N, 5.08. IR: ν(C=N), 1622; ν(ClO_4), 1087; λ_{max}/nm in acetonitrile: 276, 382, 555.

$[MnL^{3c}(H_2O)(ClO_4)](ClO_4)_2 \cdot 2H_2O$

Anal. C, 46.82; H, 5.08; N, 4.99. Calculated for $C_{42}H_{56}N_4O_{13}Cl_2Mn$: C, 46.32; H, 5.21; N, 5.03. IR: ν(C=N), 1620; ν(ClO_4), 1089; λ_{max}/nm in acetonitrile: 285, 392, 560.

Synthesis of Macrocyclic Binuclear Manganese(III) Complexes

$[Mn_2L^{1a}(CH_3COO)_2(ClO_4)_2] \cdot 2H_2O$

To a solution of $\mathbf{L}^1$ (0.594 g, 1 mM) in 50 mL of chloroform, manganese acetate dihydrate (0.258 g, 1 mM) in 50 mL of methanol was added and refluxed for 3 h. This was followed by addition of manganese perchlorate hexadrate (0.365 g, 1mM) in 15 mL of methanol and the diamine (1,2-diaminoethane, 0.07 mL, 1 mM; 1,3-diaminopropane, 0.08 mL, 1 mM; 1,4-diaminobutane, 0.1 mL, 1 mM) in 10 mL of methanol was added and refluxed for 6 h. The dark brown complex was recrystallized from acetonitrile. *Anal.* C, 40.35; H, 4.43; N, 4.62. Calculated for $C_{38}H_{48}N_4O_{13}Cl_2Mn$: C, 40.60; H, 4.23; N, 4.74. IR: ν(C=N), 1623; ν(ClO_4), 1087, 1118, ν(M–O–C=O), 1387; λ_{max}/nm in acetonitrile: 320, 370, 425, 550.

$[Mn_2L^{1b}(CH_3COO)_2(ClO_4)_2] \cdot 2H_2O$

Anal. C, 48.22; H, 5.14; N, 5.75. Calculated for $C_{39}H_{50}N_4O_{13}Cl_2Mn$: C, 41.17; H, 4.35; N, 4.68. IR: ν(C=N), 1620; ν(ClO_4), 1092, 1118, ν(M–O–C=O), 1382; λ_{max}/nm in acetonitrile: 322, 368, 420, 558.

$[Mn_2L^{1c}(CH_3COO)_2(ClO_4)_2]\cdot 2H_2O$

Anal. C, 41.82; H, 4.62; N, 4.65. Calculated for $C_{40}H_{52}N_4O_{13}Cl_2Mn_2$: C, 41.65; H, 4.46; N, 4.62. IR: ν(C=N), 1639; $\nu(ClO_4)$, 1092, 1115, ν(M–O–C=O), 1375; λ_{max}/nm in acetonitrile: 315, 365, 430, 565.

$[Mn_2L^{2a}(CH_3COO)_2(ClO_4)_2]\cdot 2H_2O$

The complex was synthesized from the precursor ligand $\mathbf{L}^2$ (0.606 g, 1 mM), manganese acetate dihydrate (0.258 g, 1 mM), manganese perchlorate hexahydrate (0.365 g, 1 mM) and the appropriate diamine as mentioned above. *Anal.* C, 41.28; H, 4.58; N, 4.44. Calculated for $C_{39}H_{50}N_4O_{13}Cl_2Mn_2$: C, 41.17; H, 4.35; N, 4.68. IR: ν(C=N), 1635; $\nu(ClO_4)$, 1091, 1110, ν(M–O–C=O), 1387; λ_{max}/nm in acetonitrile: 317, 363, 424, 562.

$[Mn_2L^{2b}(CH_3COO)_2(ClO_4)_2]\cdot 2H_2O$

Anal. C, 48.85; H, 5.32; N, 5.71. Calculated for $C_{40}H_{52}N_4O_{13}Cl_2NMn_2$: C, 41.65; H, 4.46; N, 4.62. IR: ν(C=N), 16.35; $\nu(ClO_4)$, 1091, 1112, ν(M–O–C=O), 1369; λ_{max}/nm in acetonitrile: 322, 364, 420, 579.

$[Mn_2L^{2c}(CH_3COO)_2(ClO_4)_2]\cdot 2H_2O$

Anal. C, 42.08; H, 4.63; N, 4.48. Calculated for $C_{41}H_{54}N_4O_{13}Cl_2Mn_2$: C, 42.12; H, 4.57; N, 4.57. IR: ν(C=N), 1635; $\nu(ClO_4)$, 1089, 1115, ν(M–O–C=O), 1386; λ_{max}/nm in acetonitrile: 320, 370, 422, 585.

$[Mn_2L^{3a}(CH_3COO)_2(ClO_4)_2]\cdot 2H_2O$

The complex was synthesized by the same method from ligand $\mathbf{L}^3$ (0.626 g, 1 mM). *Anal.* C, 41.62; H, 4.38; N, 4.60. Calculated for $C_{40}H_{52}N_4O_{13}Cl_2Mn_2$: C, 41.65; H, 4.46; N, 4.62. IR: ν(C=N), 1630; $\nu(ClO_4)$, 1092, 1118, ν(M–O–C=O), 1380; λ_{max}/nm in acetonitrile: 316, 365, 425, 555.

$[Mn_2L^{3b}(CH_3COO)_2(ClO_4)_2]\cdot 2H_2O$

Anal. C, 42.23; H, 4.37; N, 4.61. Calculated for $C_{40}H_{52}N_4O_{13}Cl_2Mn_2$: C, 42.12; H, 4.57; N, 4.57. IR: ν(C=N), 1638, $\nu(ClO_4)$, 1094, 1115, ν(M–O–C=O), 1392; λ_{max}/nm in acetonitrile: 319, 368, 423, 560.

$[Mn_2L^{3c}(CH_3COO)_2(ClO_4)_2]\cdot 2H_2O$

Anal. C, 42.50; H, 4.69; N, 4.57. Calculated for $C_{40}H_{52}N_4O_{13}Cl_2Mn_2$: C, 42.58; H, 4.67; N, 4.51. IR: ν(C=N), 1630; $\nu(ClO_4)$, 1090, 1116, ν(M–O–C=O), 1386; λ_{max}/nm in acetonitrile: 320, 366, 427, 568.

Synthesis of Manganese(II) Complexes

Mononuclear Mn(II) Complexes

[MnL^{1a}] To a solution of **L**^{1} (0.594 g, 1 mM) in about 50 mL of chloroform, manganese perchlorate hexahydrate (0.365 g, 1 mM) in 10–15 mL of methanol was added. The solution was deaerated by purging with nitrogen, a deaerated solution of 1,2-diaminoethane (0.07 mL, 1 mM) added, and the whole mixture refluxed under a continuous stream of nitrogen for 6 h. The resulting yellow complex was evaporated and dried under a stream of nitrogen.

[MnL^{2b}] The complex was synthesized by the above method from ligand **L**^{2} using 1,3-diaminopropane.

Binuclear Mn(II) Complex

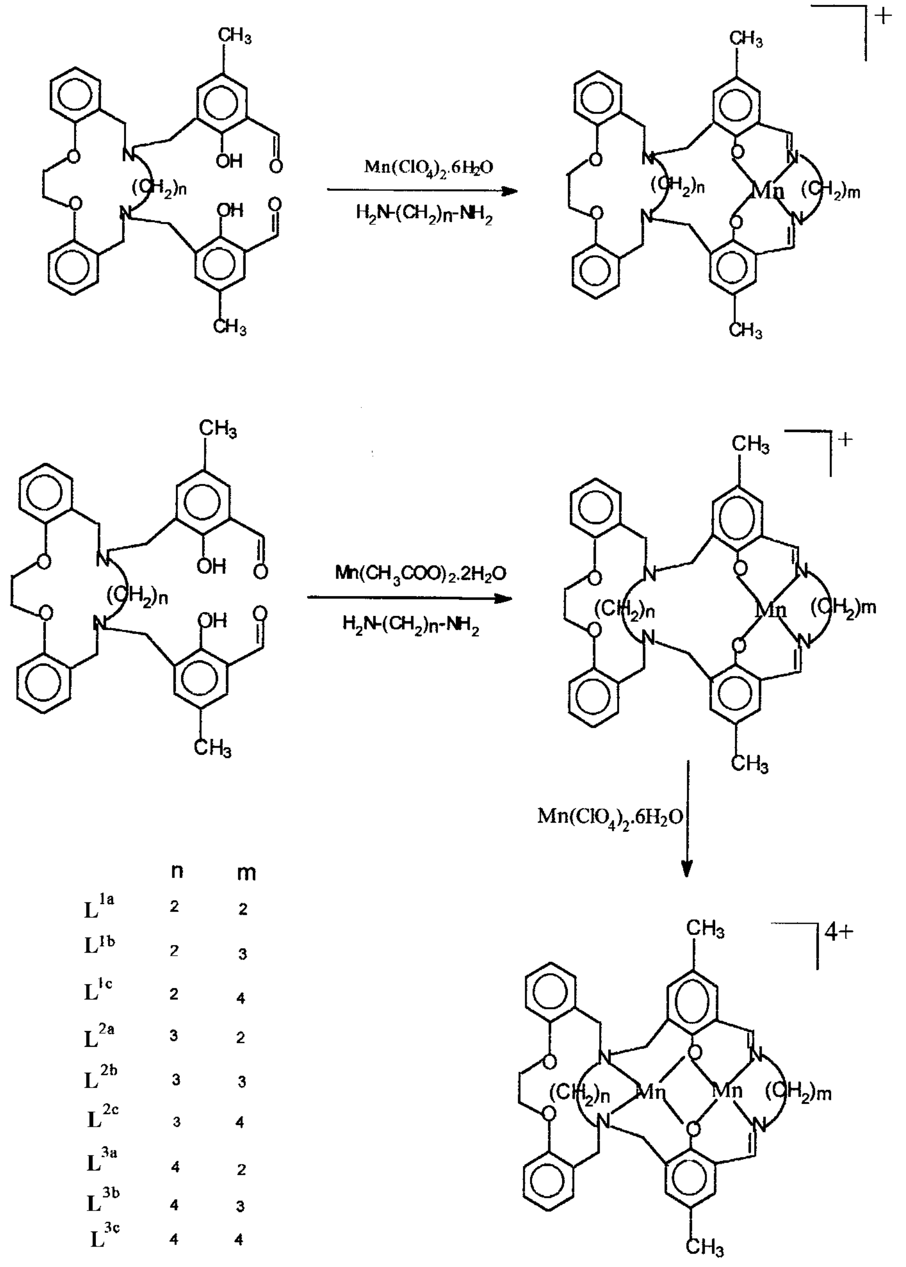
[Mn$_2$L^{2b}] The binuclear complex was synthesized by adopting the above method by reacting a 1:1:1:1 stoichiometric ratio of the ligand, metal acetate, metal perchlorate and 1,3-diaminopropane.

RESULTS AND DISCUSSION

The mononuclear macrocyclic complexes were synthesized from the precursor ligands using manganese perchlorate and appropriate diamines by the template method. $[MnL^{2a}(ClO_4)(H_2O)](ClO_4)_2 \cdot 2H_2O \cdot CH_3OH$ crystallized as dark brown prisms suitable for single crystal X-ray studies. Attempts to crystallize the binuclear manganese complexes proved to be futile. Unusually stable mononuclear Mn(II) complexes were synthesized by reacting a stoichiometric ratio of the ligand, metal perchlorate and the diamine. Binuclear manganese(II) complexes were synthesized using a unimolar ratio of the ligand, metal acetate, metal perchlorate and the diamine in a nitrogen atmosphere. The complexes are fairly stable but slowly changed to dark brown Mn(III) species when exposed to atmospheric oxygen over long periods. The Scheme shows the overall synthesis of mono and binuclear manganese complexes.

X-ray Structure of $[MnL^{2a}(ClO_4)(H_2O)](ClO_4)_2 \cdot 2H_2O \cdot CH_3OH$

Figure 1 shows an ORTEP III [17] diagram of the manganese complex with 20% probability ellipsoids. Selected geometrical parameters are given in Tables I and II. In the complex, the macrocycle provides four donors; two amine nitrogen atoms and two phenoxy oxygen atoms are coordinated in the equatorial plane at distances of 1.951(6), 1.975(5), 1.858(5) and 1.872(4) Å, respectively. The fifth and the sixth sites are occupied by water molecule O1W and a perchlorate oxygen atom O1A (Mn1–O1W = 2.237(5); Mn1–O1A = 2.513(5) Å). Coordination of the perchlorate ion is elongated and weak. Distortion towards the water molecule (O1W) is noted and this is the reason for the slight distortion of the square basal plane. In the macrocyclic ligand, atoms N18 and N39 are protonated. Oxygen atoms of the perchlorate groups and the oxygen atom of the methanol solvent molecule (O4W) have large displacement parameters. There is thermal disorder for C8 and O3D atoms and no



	n	m
L^{1a}	2	2
L^{1b}	2	3
L^{1c}	2	4
L^{2a}	3	2
L^{2b}	3	3
L^{2c}	3	4
L^{3a}	4	2
L^{3b}	4	3
L^{3c}	4	4

SCHEME

attempt was made to model the disorder. Bond lengths within the basal plane have a rather small range and may be influenced by the Jahn–Teller [18] effect; otherwise, bond lengths and angles are comparable with reported values [19].

Phenyl ring A makes angles of 52.3(3)°, 55.6(2)° and 59.9(3)°, respectively, with the Rings B, C and D. The angle between Rings B and C, B and D and C and D are 8.9(2)°,

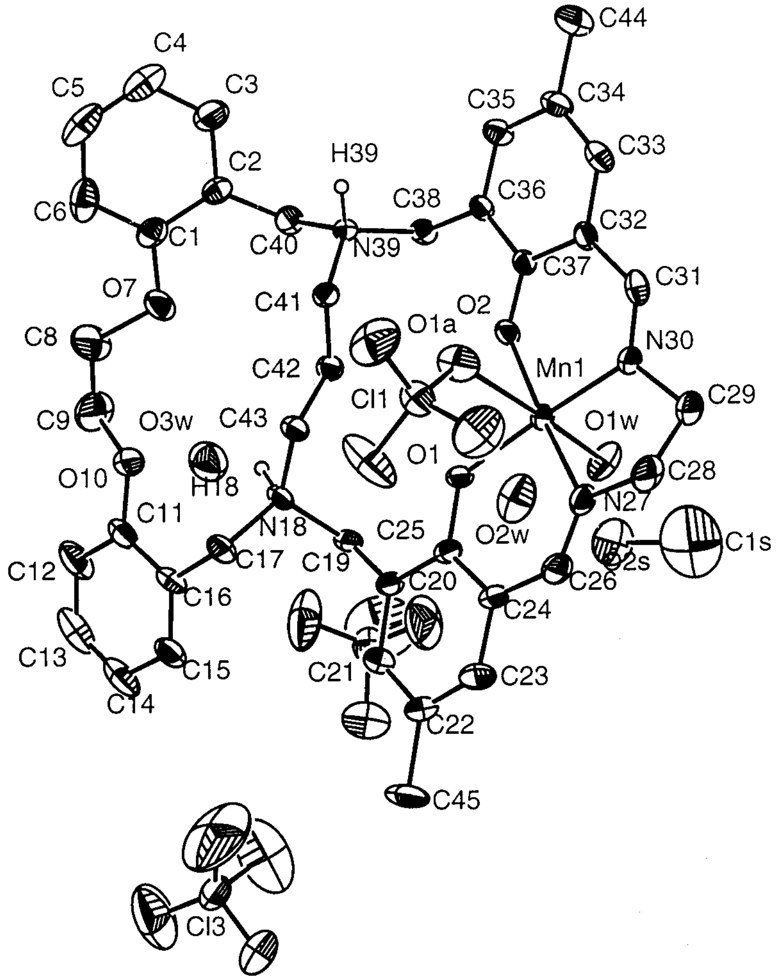


FIGURE 1 Perspective view of the complex salt $[MnL^{2a}(ClO_4)(H_2O)]$ $(ClO_4)_2 \cdot 2H_2O \cdot CH_3OH$, showing the atom numbering scheme. Cl_2 lies behind C21.

18.0(3)° and 9.1(2)°, respectively. Phenyl rings C and D and the manganese fragment containing the basal plane are nearly planar. Atom C42 deviates by about 0.233 Å above the plane (N39–C41–C42–C43–N18) and C41 deviates by about − 0.009 Å below the plane, making a W shape.

The manganese complex packs in such a way that solvent channels are formed around each symmetry-related molecule along the *b* axis. Several intramolecular C–H···O and intermolecular C–H···O and N–H···O interactions occur in the crystal. The coordinated water molecule O1W makes an intramolecular hydrogen bond with the free water molecule O2W. There are intermolecular hydrogen bonds between N18–H18···O3W and N39–H39···O2S, where the former is weaker than the latter. Most of the oxygen atoms of the perchlorate ions and the phenoxy oxygens O1 and O2 are involved in the inter- and intramolecular contacts with neighbouring molecules. The crystal packing is stabilized only through hydrogen bonding of solvent molecules.

TABLE I Crystal data and structure refinement for [Mn $\mathbf{L}^{2a}$]

Empirical formula	$C_{40}H_{45}Cl_3MnN_4O_{20}$
Formula weight	1063.1
Temperature	293(2) K
Wavelength	0.7107 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 13.6055(1)$ Å
	$b = 24.5662(4)$ Å
	$c = 15.0979(2)$ Å
	$\beta = 107.372(1)°$
Volume (Å^3)	4816.1(1)
Z	4
Density (calc) (Mg m^{-3})	1.466
Absorption coefficient (mm^{-1})	0.521
Absorption correction	SADABS
Maxi. and mini. transmission	0.9030 and 0.8428
F(000)	2196
Crystal size (mm)	0.34 × 0.24 × 0.20
Theta range for data collection	1.64 to 25.00°
Index ranges	$-12 \leq h \leq 16$
	$-28 \leq k \leq 29$
	$-17 \leq l \leq 12$
Reflections collected	26908
Independent reflections	8478
Observed reflections [$I \geq 2\sigma(I)$]	4393
Completeness to 2theta = 25.00	97.4%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8478/0/621
Goodness-of-fit on F^2	1.044
Final *R* indices [$I \geq 2\sigma(I)$]	$R1 = 0.0896$
	$wR2 = 0.2417$
R indices (all data)	$R1 = 0.1637$
	$wR2 = 0.2868$
Largest diff. peak and hole (eÅ^{-3})	1.389 and −0.6061

TABLE II Bond distances (Å) and angle (°) involving non-hydrogen atoms (e.s.ds are in parentheses)

Atoms	*Length*	*Atoms*	*Angles*
Mn(1)–O(1)	1.858(5)	O(1)–Mn(1)–O(2)	93.5(2)
Mn(1)–O(2)	1.872(4)	O(1)–Mn(1)–N(30)	173.0(2)
Mn(1)–N(30)	1.951(6)	O(2)–Mn(1)–N(30)	92.1(2)
Mn(1)–N(27)	1.975(5)	O(1)–Mn(1)–N(27)	92.7(2)
Mn(1)–O(1W)	2.237(5)	O(2)–Mn(1)–N(27)	171.0(2)
Mn(1)–O(1A)	2.513(5)	N(30)–Mn(1)–N(27)	81.4(2)
C(17)–N(18)	1.527(8)	O(1)–Mn(1)–O(1W)	88.5(2)
N(18)–C(43)	1.495(8)	O(2)–Mn(1)–O(1W)	93.7(2)
N(18)–C(19)	1.531(8)	N(30)–Mn(1)–O(1W)	95.4(2)
C(26)–N(27)	1.276(9)	N(27)–Mn(1)–O(1W)	93.1(2)
N(27)–C(28)	1.477(9)	O(1)–Mn(1)–O(1A)	88.0(2)
C(29)–N(30)	1.480(9)	O(2)–Mn(1)–O(1A)	82.7(2)
N(30)–C(31)	1.297(9)	N(30)–Mn(1)–O(1A)	88.5(2)
C(38)–N(39)	1.518(8)	N(27)–Mn(1)–O(1A)	90.9(2)
N(39)–C(40)	1.523(8)	O(1W)–Mn(1)–O(1A)	174.7(2)
N(39)–C(41)	1.519(8)	C(25)–O(1)–Mn(1)	129.4(4)
C(41)–C(42)	1.521(9)	C(37)–O(2)–Mn(1)	128.3(4)
C(42)–C(43)	1.536(9)	C(43)–N(18)–C(19)	116.9(5)
Cl(1)–O(1B)	1.402(7)	C(26)–N(27)–Mn(1)	124.8(5)
Cl(1)–O(1D)	1.414(6)	C(28)–N(27)–Mn(1)	114.1(5)
Cl(1)–O(1A)	1.433(5)	C(29)–N(30)–Mn(1)	115.1(5)
Cl(1)–O(1C)	1.444(7)	Cl(1)–O(1A)–Mn(1)	132.7(3)

IR and Electronic Spectra of the Mononuclear and Binuclear Complexes

IR spectra of mononuclear complexes show broad absorption in the region around 3423 cm^{-1} indicative of lattice water. A sharp, strong absorption around 1620 cm^{-1} is due to the azomethine (C=N) bond. Strong absorption for the aromatic rings occurs in the 1560 cm^{-1} region. Absorption at 1090 cm^{-1} is indicative of perchlorate anions. This peak is split, showing the weak coordination to the manganese atom. Binuclear manganese(III) complexes show strong absorption in the 1620 cm^{-1} region indicative of the formation of C=N by Schiff base condensation. A doublet at 1079 and 1118 cm^{-1} is due to the coordinated perchlorate ions. Strong absorption around 1385 cm^{-1} is due to the $M \cdots O–C=O$ group involving the unidentate acetate group. The ν(C=O) stretch of the unidentate acetate is found around 1665 cm^{-1}.

Electronic spectra show very weak *d–d* transitions in the visible region. A charge transfer band observed in the 425 nm region arises from ligand-to-metal charge transfer. Other azomethine and π–π* transitions are observed in the 300 and 370 nm regions. The *d–d* bands show a slight red shift with increasing chelate ring size.

Room Temperature Magnetic Studies

Room temperature magnetic studies of the mononuclear manganese(III) complexes give μ_{eff} values in the range 4.9–5.3 BM consistent with magnetically dilute, d^4, high spin manganese(III).

Room temperature moments for the mononuclear manganese(II) complex [MnL^{2b}] give μ_{eff} value of 6.1 BM, as expected for high spin, d^5 Mn(II).

EPR Spectra

X-band EPR spectra of the mononuclear complexes showed slight hyperfine splitting at 77 K. However, the splitting pattern was not observed for the same complex at room temperature and a single broad band was obtained. The X-band EPR spectrum of the binuclear Mn(II) complex [$Mn_2\mathbf{L}^{2b}$] gave a broad band centred at 3200 G at 77 K. This is attributed to the interaction of Mn(II)–Mn(II) centres through bridging phenolic oxygen atoms.

Electrochemistry of Mn(III) Complexes

Cyclic voltammetric data were obtained from 10^{-3} M DMF solutions at slow scan rates (0.05V/sec) over a potential range $+1.2$ to -1.2 V. Data are listed in Tables III to V. Mononuclear manganese(III) complexes show one electron redox process at cathodic and anodic potentials. The reduction of Mn(III) to Mn(II) was irreversible for most of the complexes and is observed in the range -0.14 to -0.38 V as expected for a Mn(III)Mn(II) couple [20–22]. However, complexes $Mn\mathbf{L}^{1a}$ and $Mn\mathbf{L}^{2b}$ show reversibility at $+0.1$ V. These two complexes appear to stabilize the lower oxidation state where the chelate ring sizes of both compartments are the same. Reduction potentials are influenced by distortions around the metal ion as a result of increasing chelate ring size [23]. Hence all three ligands $\mathbf{L}^1$, $\mathbf{L}^2$, $\mathbf{L}^3$ show an anodic shift of reduction potentials as the chelate ring size increases by addition of alkyl groups. The oxidation of Mn(III) to Mn(IV) is observed around $+0.8$ V in a *quasi*-reversible process. Though the Mn(IV)

TABLE III Cyclic voltammetric data for mononuclear manganese(III) complexes

Complexes	*Cathodic potential region* (V)	*Anodic potential region*			
		Ep_a (V)	Ep_c (V)	ΔEp (mV)	$E_{1/2}$ (V)
$[\mathrm{Mn}\mathbf{L}^{1a}]$	-0.38	$+0.86$	$+0.76$	100	$+0.81$
$[\mathrm{Mn}\mathbf{L}^{1b}]$	-0.34	$+0.84$	$+0.74$	100	$+0.79$
$[\mathrm{Mn}\mathbf{L}^{1c}]$	-0.32	$+0.84$	$+0.72$	120	$+0.78$
$[\mathrm{Mn}\mathbf{L}^{2a}]$	-0.26	$+0.85$	$+0.75$	100	$+0.80$
$[\mathrm{Mn}\mathbf{L}^{2b}]$	-0.14	$+0.83$	$+0.73$	100	$+0.78$
$[\mathrm{Mn}\mathbf{L}^{2c}]$	-0.10	$+0.87$	$+0.76$	112	$+0.81$
$[\mathrm{Mn}\mathbf{L}^{3a}]$	-0.37	$+0.86$	$+0.75$	112	$+0.81$
$[\mathrm{Mn}\mathbf{L}^{3b}]$	-0.28	$+0.87$	$+0.74$	132	$+0.81$
$[\mathrm{Mn}\mathbf{L}^{3c}]$	-0.25	$+0.85$	$+0.75$	100	$+0.80$

TABLE IV Electrochemical data for the reduction of binuclear manganese(III) complexes (V)

Complexes	Ep_c^1	Ep_a^1	ΔEp^1	$E_{1/2}^1$	Ep_c^2	Ep_a^2	ΔEp^2	$E_{1/2}^2$
$[\mathrm{Mn}_2\mathbf{L}^{1a}]$	-0.40	-0.15	250	-0.28	-0.70	-0.60	100	-0.65
$[\mathrm{Mn}_2\mathbf{L}^{1b}]$	-0.35	-0.08	270	-0.21	-0.70	-0.62	80	-0.66
$[\mathrm{Mn}_2\mathbf{L}^{1c}]$	-0.28	-0.05	230	-0.16	-0.70	-0.50	200	-0.60
$[\mathrm{Mn}_2\mathbf{L}^{2a}]$	-0.48	-0.20	280	-0.34	-0.80	-0.70	100	-0.75
$[\mathrm{Mn}_2\mathbf{L}^{2b}]$	-0.38	-0.20	180	-0.29	-0.80	-0.70	100	-0.75
$[\mathrm{Mn}_2\mathbf{L}^{2c}]$	-0.18	-0.05	230	-0.08	-0.70	-0.60	100	-0.65
$[\mathrm{Mn}_2\mathbf{L}^{3a}]$	-0.56	-0.15	410	-0.36	-1.35	-1.26	90	-1.31
$[\mathrm{Mn}_2\mathbf{L}^{3b}]$	-0.28	-0.01	270	-0.15	-1.00	-0.92	80	-0.96
$[\mathrm{Mn}_2\mathbf{L}^{3c}]$	-0.22	-0.05	170	-0.12	-0.75	-0.55	200	-0.65

TABLE V Electrochemical oxidation data for the binuclear manganese(III) complexes

Complexes	Ep_a^1/V	Ep_a^2/V	Ep_c^2/V	ΔEp^2/mV	$E_{1/2}^2$/V
$[\mathrm{Mn}_2\mathbf{L}^{1a}]$	$+0.62$	$+0.98$	$+0.78$	200	$+0.88$
$[\mathrm{Mn}_2\mathbf{L}^{1b}]$	$+0.56$	$+0.95$	$+0.75$	200	$+0.85$
$[\mathrm{Mn}_2\mathbf{L}^{1c}]$	$+0.60$	$+0.86$	$+0.72$	140	$+0.78$
$[\mathrm{Mn}_2\mathbf{L}^{2a}]$	$+0.58$	$+1.06$	$+0.80$	260	$+0.93$
$[\mathrm{Mn}_2\mathbf{L}^{2b}]$	$+0.48$	$+0.90$	$+0.75$	150	$+0.82$
$[\mathrm{Mn}_2\mathbf{L}^{2c}]$	$+0.58$	$+0.95$	$+0.78$	170	$+0.87$
$[\mathrm{Mn}_2\mathbf{L}^{3a}]$	$+0.60$	$+1.00$	$+0.76$	240	$+0.88$
$[\mathrm{Mn}_2\mathbf{L}^{3b}]$	$+0.62$	$+0.97$	$+0.75$	220	$+0.86$
$[\mathrm{Mn}_2\mathbf{L}^{3c}]$	$+0.65$	$+1.15$	$+0.90$	250	$+1.02$

is stabilized by the macrocyclic ligand, variation in chelate ring size does not influence the oxidation potential. In the case of mononuclear complexes, the macrocyclic ligand stabilizes the higher oxidation state Mn(IV) but not the lower oxidation state.

Binuclear manganese(III) complexes show two well-resolved *quasi*-reversible waves in the cathodic region. The first reduction potential is observed in the range -0.15 to -0.4 V due to the presence of Mn(III)Mn(III)/Mn(III)Mn(II) couple and is consistent with earlier reports [24–26], for binuclear complexes derived from Schiff base or cyclam ligands [27]. As the first Mn^{3+} is reduced to Mn^{2+}, the larger Mn^{2+} ion imparts electrostatic repulsion [28] between the metal ions and reduction occurs at higher negative potentials around − 0.7 to − 0.8 V. The second reduction is observed in the range − 0.7 to − 0.8 V and shows good reversibility, unlike most other such complexes. We attribute this process to the formation of Mn(II)Mn(II) species. Though the mononuclear complexes show irreversible reduction, the binuclear complexes show good *quasi*-reversibility. Intermetallic influences might be expected to account for the stability of the lower oxidation state. Similar to the mononuclear complexes, binuclear complexes also show the same trend of anodic shift of reduction potentials with increase in chelate ring size. Upon fixing the chelate ring size at the saturated donor atom compartment and varying the size of the other set, the anodic shift is observed for the first reduction potential, whereas the second reduction remains unaffected. This observation is rationalized by the fact that the metal ion in the unsaturated donor atom site is reduced first and is consistent with Mandal's [29] observations.

The oxidation process shows a poorly resolved wave around + 0.4 to + 0.6 V and a well resolved peak in the range + 0.9 to + 1.0 V. The former corresponds to the Mn(III)Mn(III)/Mn(III)Mn(IV) couple, as reported [30,31]. The latter corresponds to the Mn(III)Mn(IV)/Mn(IV)Mn(IV) couple and is consistent with earlier report [32]. The Mn_2(IV) species so formed is highly stable as observed in a well-resolved reduction of the corresponding complex during the reverse scan. The Mn(III)Mn(IV) species might have undergone fast oxidation to Mn_2(IV) in the time scale noted (25 to 100 mV/s) and thus the mixed valent complex Mn(III)Mn(IV) appears to be quite unstable. Continuous potential electrolysis at this potential showed that a one electron oxidation process occurs. The oxidation potentials decrease as the chelate ring size increases. Thus distortion in geometry favours oxidation. However, the shift is observed only in the second oxidation potential; the first oxidation potential remains unaffected.

Electrochemical Oxidation of Mn(II) Complexes

Cyclic voltammograms of the Mn(II) complexes (mononuclear) give *quasi*-reversible, one-electron oxidation of Mn(II) to Mn(III) in the potential region around + 1 V. Normally, Mn(II), complexes have high oxidation potentials as reported earlier [33]. The binuclear complex [Mn$\mathbf{L}^{2b}$] give a *quasi*-reversible, two step, one-electron oxidation. The first oxidation was observed at a potential of 1.3 V and the second at + 1.7 V. This is an unusually high positive potential. The electrochemical species formed are quite stable as it is evident from the fact that they show good reversibility. Hence these complexes have good prospects in the preparation of mixed valent complexes to serve as models for PSII.

In conclusion, we note that novel mononuclear and binuclear manganese(III) complexes have been synthesized, characterized and the structure of the mononuclear manganese(III) complex [Mn$\mathbf{L}^{2a}$] solved. Electrochemical studies of the mononuclear complex show irreversible one-electron processes for the formation of Mn(II) species and a *quasi*-reversible one-electron oxidation to Mn(IV). The binuclear complexes, however, show a *quasi*-reversible, single step, two-electron process for the formation of Mn_2(II) and Mn_2(IV) species. The Mn(II) complexes formed by the reduction of mononuclear Mn(III) complexes are quite unstable, whereas the binuclear complexes stabilize the lower oxidation state to a greater extent. Synthesis of fairly stable Mn(II) complexes reveal the possibility of preparing mixed valent complexes which could act as good photosystem II models.

Acknowledgment

S.P. thanks CSIR New Delhi for financial assistance.

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