DALTON
FULL PAPER

Synthesis, spectral and electrochemical properties of a new series of unsymmetrical bis(phenoxo) bridged macrocyclic binuclear manganese(III) complexes

Munasamy Marappan, Verigidusamy Narayanan and Muthusamy Kandaswamy *

Department of Inorganic Chemistry, University of Madras, Guindy Campus, Madras 600 025, India

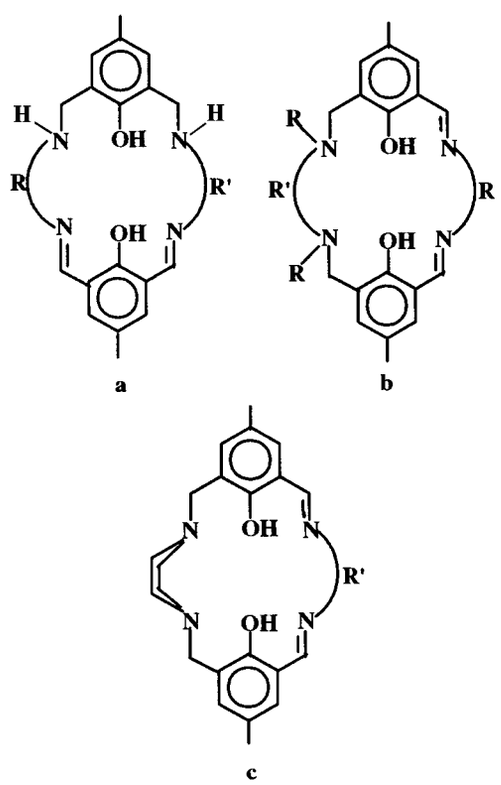
Received 21st July 1998, Accepted 22nd July 1998

A new series of binuclear bis(phenoxo) bridged manganese(III) complexes with dissimilar co-ordination environments have been prepared. The macrocyclic ligands have two different compartments, one has two unsaturated nitrogen and the other two saturated nitrogen donor atoms. The two phenoxide oxygens are common to both manganese(III) ions. Two reduction couples were observed for all the complexes in the negative potential region (0.00 to −1.60 V) [$Mn^{III}_2 \longrightarrow Mn^{II}Mn^{III} \longrightarrow Mn^{II}_2$]. The first one electron reduction is observed around −0.90 V and the second around −1.30 V. In the positive potential region (0.00 to +1.00 V) two oxidation couples are observed for all the complexes [$Mn^{III}_2 \longrightarrow Mn^{III}Mn^{IV} \longrightarrow Mn^{IV}_2$]. The first one electron oxidation is observed around +0.25 V and the second around +0.60 V. The first one electron reduction potential mainly depends upon the ring size, substituent at the *para* position to the phenoxide oxygen in the ligand system and axially bound halide ions. In the positive potential region the first one electron oxidation potential is less sensitive to ring size variation and varies with the axially bound halide ion.

Introduction

Nature prefers macrocyclic derivatives for many fundamental biological functions such as photosynthesis and transport of oxygen in mammalian and other respiratory systems.[1] Generally, such derivatives have higher thermodynamic and kinetic stability than acyclic ones.[2] Studies of the geometry around the metal center present in the active sites and its electronic and magnetic behaviour are highly cumbersome due to the fact that the metal ion is embedded in a biopolymer backbone.[3] Hence, the synthesis and studies of model systems are important and give more insight about the co-operative phenomena, electron transfer and magnetic interaction between metal centers.[4–6]

Symmetrical (Robson type) binuclear bis(phenoxo) bridged macrocyclic complexes have been synthesized and their electrochemical and magnetic properties studied in detail.[7–13] However, studies of unsymmetrical binuclear macrocyclic complexes are sparse.[13b,14–16] In macrocyclic systems the redox and magnetic exchange properties of metal centers are affected by the ring size, co-ordination sites and electronic effects such as substituents at the aromatic ring of the ligand system.[9,10,14,15] In continuation of our earlier work[17] on the binuclear copper complexes of unsymmetrical macrocyclic ligands, here we report the synthesis of new series of macrocyclic dimanganese(III) complexes using macrocyclic binucleating ligands of type **c** having different co-ordination environments. The redox behaviour of the phenoxo bridged manganese(III) ions in the macrocyclic ligand environment with respect to ring size variation, substituent at the *para* position and axially bound halide ions is discussed.



Experimental

Physical measurements

The elemental analyses C, H and N of the ligand and complexes were carried out using a Heraeus CHN rapid analyzer. The manganese contents of the complexes were determined by a Perkin-Elmer atomic absorption spectrophotometer (model 2380). Proton NMR spectra were recorded on a 90 MHz Varian spectrometer (model 390), mass spectra on a JMS-DX 303 HF spectrometer, infrared spectra as KBr discs on a Shimadzu IR-408 spectrometer and electronic spectra in dmf on a Hitachi-320 spectrophotometer. Conductivity measurements were carried out in dmf at 27 °C using a CM 82T conductivity bridge (Elcot pvt Ltd.) and cyclic voltammograms were recorded on an apparatus comprising a PAR model 175 universal programmer, model 176 current to voltage convertor,

model 179 coulometer (EG&G Ltd.) and Perkin-Elmer Hitachi model 057 X-Y recorder. For the electrochemical studies Ag–AgCl was used as the reference electrode and platinum foil was used as both working and counter electrodes, NBu_4ClO_4 as supporting electrolyte and dmf as the solvent. Cyclic voltammograms for each complex were recorded at 20, 50, 100 and 200 mV s^{-1} scan rates. Coulometric experiments were conducted at 100 mV higher potential after the first and second redox wave. Electron spin resonance spectra were recorded using a Bruker 200 DS spectrometer operating in X-band region with a microwave frequency of 9.7 GHz.

Materials

5-Methylsalicylaldehyde was prepared by following the literature method.[18] 5-Bromosalicylaldehyde was purchased from Fluka, tetrabutylammonium perchlorate (Fluka) was recrystallized from hot water and dmf (HPLC) was obtained from Qualigens and used as such. All other chemicals and solvents were of reagent grade and used as received.

Synthesis of precursor compounds

6,6′-Piperazine-1,4-diyldimethylenebis(4-methyl-2-formylphenol) **I** used for the synthesis of macrocyclic complexes was prepared by the reported procedure.[17,19]

6,6′-Piperazine-1,4-diyldimethylenebis(4-bromo-2-formylphenol) **II**. A mixture of piperazine (2.2 g, 0.025 mol), paraformaldehyde (1.8 g, 0.06 mol) and 5-bromosalicylaldehyde (10.2 g, 0.05 mol) in methanol–acetic acid (100 cm^3, 4 : 1 v/v) was stirred for 10 h at 60 °C and neutralized with a saturated solution of sodium carbonate after cooling to room temperature. Ethanol was removed by distillation and the residue extracted with chloroform. The pale yellow solid was recovered after removing the solvent by distillation and further purified by silica gel column chromatography using chloroform–light petroleum (bp 60–80 °C, 1 : 4 v/v) as the eluent. Yield 9 g (64%), mp 217 °C (Found: C, 46.32; H, 3.71; N, 12.75. Calc. for $C_{20}H_{20}Br_2N_2O_4$: C, 46.80; H, 3.90; N, 12.50%). ^1H NMR ($CDCl_3$): δ 1.8 (m, 8 H, piperazine CH_2), 3.60 (m, 4 H, benzylic CH_2), 7.0–7.4 (d, 4 H, aromatic CH) and 9.85 (s, 2 H, CHO). IR (KBr): 3450 (phenolic OH), 2840–2940 (N–CH_2), 1645–1650 (CHO) and 1450 cm^{-1} (aromatic skeleton).

Synthesis of complexes

$[Mn_2L_A^1Cl_2]Cl_2\cdot H_2O$ 1. The precursor compound **I** (1.90 g, 0.005 mol) was dissolved in chloroform (20 cm^3). One portion of $MnCl_2$ (0.985 g, 0.05 mol) in methanol (50 cm^3) was added. The resulting reaction mixture was refluxed for 30 min. Another portion of $MnCl_2$ (0.985 g, 0.05 mol) and 1,2-diaminoethane (0.30 g, 0.005 mol) in methanol (20 cm^3) were added and reflux continued for 1 h. During this period the mixture became dark brown. On slow evaporation of the solvent at room temperature a dark brown complex was obtained which was repeatedly washed with diethyl ether, dried and recrystallized from methanol. Yield: 3.0 g (73%) (Found: C, 43.37; H, 4.33; Mn, 15.69; N, 8.53. Calc. for $C_{24}H_{28}Mn_2N_4O_2\cdot H_2O$: C, 43.24; H, 4.20; Mn, 15.61; N, 8.41%). UV/VIS [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})] in dmf: 290 (10 700), 420 (6600) and 615 (170). Molar conductance (Λ_M/S cm^2 mol^{-1}) in dmf: 135.

Using the above procedure the following macrocyclic complexes have been synthesized by changing the precursor compounds, diamines and manganese(II) salts.

$[Mn_2L_A^2Cl_2]Cl_2\cdot 2H_2O\cdot MeOH$ 2. This complex was prepared using compound **I** (1.90 g, 0.005 mol), $MnCl_2$ (1.97 g, 0.01 mol) and 1,3-diaminopropane (0.37 g, 0.005 mol). Yield 2.8 g (70%) (Found: C, 42.85; H, 5.31; Mn, 14.32; N, 7.72. Calc. for $C_{25}H_{30}Cl_4Mn_2N_4O_2\cdot 2H_2O\cdot CH_3OH$: C, 42.73; H, 5.20; Mn, 14.25; N, 7.63%). UV/VIS [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})] in dmf: 280 (11 100), 400 (7200) and 620 (255). Molar conductance (Λ_M/S cm^2 mol^{-1}) in dmf: 130.

$[Mn_2L_A^3Cl_2]Cl_2\cdot 3H_2O$ 3. This complex was prepared from compound **I** (1.90 g, 0.005 mol), $MnCl_2$ (1.97 g, 0.01 mol) and 1,4-diaminopropane (0.43 ml, 0.005 mol). Yield 3.0 g (75%) (Found: C, 42.65; H, 5.17; Mn, 14.16; N, 7.59. Calc. for $C_{26}H_{32}Cl_4Mn_2N_4O_2\cdot 3H_2O$: C, 42.74; H, 5.21; Mn, 14.24; N, 7.67%). UV/VIS [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})] in dmf: 280 (10 850), 410 (8400) and 625 (170). Molar conductance (Λ_M/S cm^2 mol^{-1}) in dmf: 142.

$[Mn_2L_A^1Br_2]Br_2\cdot 2H_2O$ 4. This complex was prepared by the reaction of compound **I** (1.90 g, 0.005 mol), $MnBr_2$ (1.43 g, 0.005 mol), 1,2-diaminoethane (0.30 g, 0.005 mol) and $MnBr_2$ (1.43 g, 0.005 mol) in chloroform–methanol (150 cm^3, 1 : 4 v/v). Yield 3.5 g (70%) (Found: C, 34.17; H, 3.78; Mn, 11.77; N, 6.30. Calc. for $C_{24}H_{28}Br_4Mn_2N_4O_2\cdot 2H_2O$: C, 34.25; H, 3.88; Mn, 11.87; N, 6.39%). UV/VIS [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})] in dmf: 290 (11 700), 420 (7900) and 610 (175). Molar conductance (Λ_M/S cm^2 mol^{-1}) in dmf: 139.

$[Mn_2L_A^2Br_2]Br_2\cdot 2H_2O$ 5. This complex was prepared by the method used for **4**, 1,3-diaminopropane (0.37 g, 0.005 mol) being used in the place of 1,2-diaminoethane. Yield 3.5 g (73%) (Found: C, 33.66; H, 4.39; Mn, 11.30; N, 6.10. Calc. for $C_{25}H_{30}Br_4Mn_2N_4O_2\cdot 2H_2O$: C, 33.62; H, 4.31; Mn, 11.21; N, 6.03%). UV/VIS [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})] in dmf: 285 (10 600), 400 (8600) and 620 (205). Molar conductance (Λ_M/S cm^2 mol^{-1}) in dmf: 150.

$[Mn_2L_A^3Br_2]Br_2\cdot 4H_2O$ 6. Using the above method, 1,4-diaminobutane (0.43 g, 0.005 mol) was used in the place of 1,3-diaminopropane. Yield 3.9 g (79%) (Found: C, 36.42; H, 4.20; Mn, 11.78; N, 6.37. Calc. for $C_{26}H_{32}Br_4Mn_2N_4O_2\cdot 4H_2O$: C, 36.49; H, 4.28; Mn, 11.71; N, 6.31%). UV/VIS [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})] in dmf: 280 (11 100), 420 (8300) and 625 (225). Molar conductance (Λ_M/S cm^2 mol^{-1}) in dmf: 148.

$[Mn_2L_B^1Cl_2]Cl_2\cdot 2H_2O$ 7. This complex was prepared by the reaction of compound **II** (2.56 g, 0.005 mol), $MnCl_2$ (0.985 g, 0.005 mol), 1,2-diaminoethane (0.30 g, 0.005 mol) and $MnCl_2$ (0.985 g, 0.005 mol) in chloroform–methanol (200 cm^3, 1 : 4 v/v). Yield 3.2 g (80%) (Found: C, 32.38; H, 3.13; Mn, 12.70; N, 6.79. Calc. for $C_{22}H_{22}Br_2Cl_4Mn_2N_4O_2\cdot 2H_2O$: C, 32.43; H, 3.19; Mn, 12.78; N, 6.87%). UV/VIS [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})] in dmf: 290 (10 400), 390 (5600) and 600 (310). Molar conductance (Λ_M/S cm^2 mol^{-1}) in dmf: 125.

$[Mn_2L_B^2Cl_2]Cl_2\cdot 4H_2O$ 8. This complex was prepared by using the above method with 1,3-diaminopropane (0.37 g, 0.005 mol) in place of 1,2-diaminoethane. Yield 3.0 g (72%) (Found: C, 31.86; H, 3.65; Mn, 12.09; N, 6.54. Calc. for $C_{23}H_{24}Br_2Cl_4Mn_2N_4O_2\cdot 4H_2O$: C, 31.94; H, 3.70; Mn, 12.04; N, 6.48%). UV/VIS [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})] in dmf: 285 (10 780), 400 (5900) and 610 (240). Molar conductance (Λ_M/S cm^2 mol^{-1}) in dmf: 133.

$[Mn_2L_B^1Br_2]Br_2\cdot H_2O$ 9. This complex was prepared by the reaction of compound **II** (2.56 g, 0.005 mol), $MnBr_2$ (1.43 g, 0.005 mol), 1,2-diaminoethane (0.30 g, 0.005 mol) and $MnBr_2$ (1.43 g, 0.005 mol) in chloroform–methanol (200 cm^3, 1 : 4 v/v). Yield 4.75 g (82%) (Found: C, 27.14; H, 2.53; Mn, 11.72; N, 5.82. Calc. for $C_{22}H_{22}Br_6Mn_2N_4O_2\cdot H_2O$: C, 27.05; H, 2.46; Mn, 10.65; N, 5.73%). UV/VIS [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})] in dmf: 285 (10 900), 390 (7200) and 600 (270). Molar conductance (Λ_M/S cm^2 mol^{-1}) in dmf: 130.

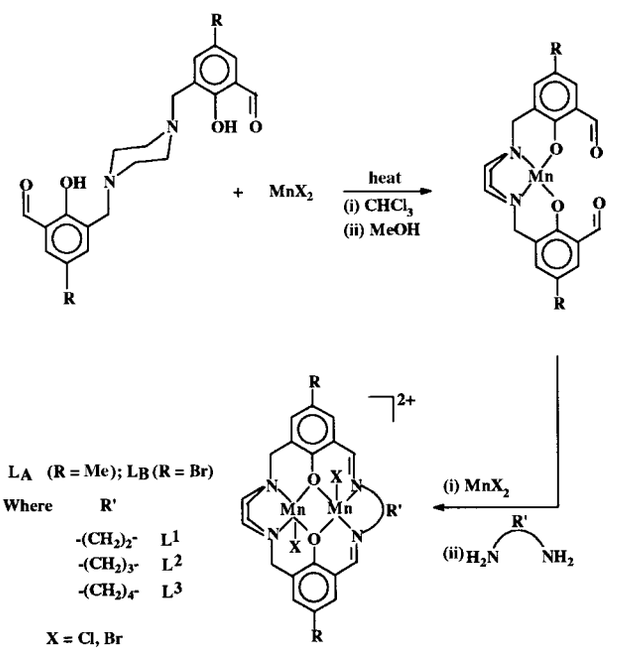
$[Mn_2L_B^2Br_2]Br_2\cdot 4H_2O$ 10. This complex was prepared by using the above method with 1,3-diaminopropane (0.37 g, 0.005

mol) in place of 1,2-diaminoethane. Yield 4.68 g (78%) (Found: C, 26.38; H, 3.00; Mn, 9.90; N, 5.30. Calc. for $C_{28}H_{24}Br_6Mn_2N_4O_2\cdot 4H_2O$: C, 26.44; H, 3.06; Mn, 9.96; N, 5.36%). UV/VIS [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})] in dmf: 285 (10 700), 405 (6400) and 610 (235). Molar conductance (Λ_M/S cm^2 mol^{-1}) in dmf: 127.

Results and discussion

Preparation of the complexes

The binuclear macrocyclic manganese(III) complexes were prepared from the respective precursor compounds, manganese(II) halide and diamines in a single-step procedure. Addition of 1 mol of manganese(II) chloride or bromide to the precursor compound in methanol–chloroform resulted in mononuclear complexes. Addition of another mol of manganese(II) chloride or bromide with appropriate diamines results in Schiff base condensation between the two formyl groups of the precursor compound and diamines (template condensation, Scheme 1). Owing to open air oxidation, the oxidation state of the manganese ion changed from +2 to +3.



Scheme 1 Preparation of macrocyclic complexes $[Mn_2L_A^{1-3}X_2]^{2+}$ and $[Mn_2L_B^{1-3}X_2]^{2+}$

Spectral and conductivity measurements

The formation of an imine group (C=N) in the macrocyclic complexes by Schiff base condensation between CHO and NH_2 is evidenced by the appearance of a strong peak at 1610–1620 cm^{-1}. The precursor compound shows a peak around 1650–1670 cm^{-1} due to the presence of a CHO group. A broad band around 3400 cm^{-1} suggests the presence of water molecules.

Electronic spectra of all the complexes were measured in dmf (HPLC grade) at 298 K (room temperature) in the range 270–750 nm. They are similar with weak bands in the visible region (600–640 nm) due to metal centered d–d transitions. Since the manganese(III) ion is readily oxidising, the ligand to metal charge transfer may obscure some of the metal centered d–d transitions.[20] Moderately intense charge-transfer bands appear in the visible region in the range 430–460 nm. These arise due to charge transfer from phenoxide oxygen to Mn^{III} and also to azomethine transitions.[21] A stronger peak in the range 280–290 nm is due to intraligand transitions (π–π^*). The d–d band shifts slightly to lower energy with increase in the chain length between the imine nitrogens. The distortion of the N_2O_2 plane

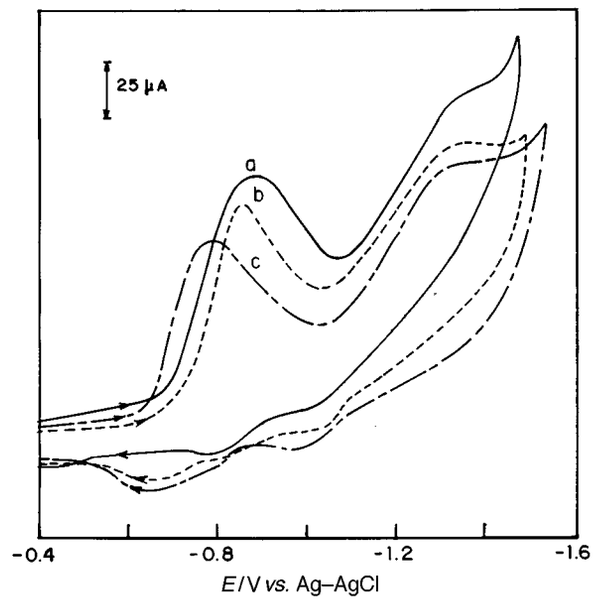


Fig. 1 Cyclic voltammograms for (a) $[Mn_2L_A^1Br_2]^{2+}$ **4**, (b) $[Mn_2L_A^2Br_2]^{2+}$ **5** and (c) $[Mn_2L_A^3Br_2]^{2+}$ **6** in the cathodic region; platinum electrodes, scan rate 50 mV s^{-1}, concentration 1×10^{-3} M in dmf.

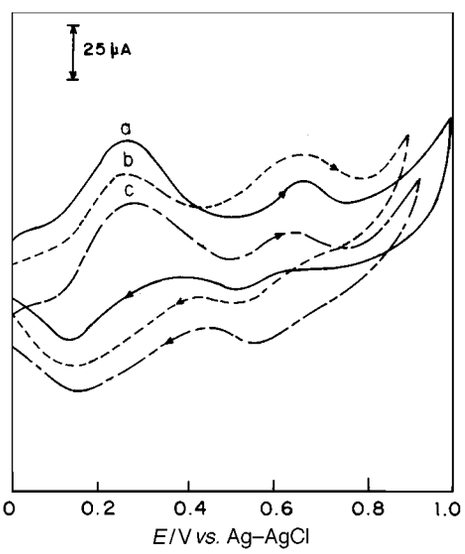


Fig. 2 Cyclic voltammograms for (a) $[Mn_2L_A^1Br_2]^{2+}$ **4**, (b) $[Mn_2L_A^2Br_2]^{2+}$ **5** and (c) $[Mn_2L_A^3Br_2]^{2+}$ **6** in the anodic region; details as in Fig. 1.

geometry around the metal center may increase with this increase.[22]

The EPR spectra of the complexes do not show any characteristic lines or hyperfine lines at both room temperature and 77 K,[23] suggesting that the oxidation state of the manganese ion is +3. The conductivity measurements reveal that the complexes have a dipositive charge.[24] From the electronic, EPR and conductivity studies, it can be inferred that each manganese ion in the complex is in the +3 oxidation state.

Cyclic voltammetry

The redox behaviour of the metal complexes was studied in the potential range +1.0 to −1.60 V. Fig. 1 shows typical cyclic voltammograms for **4**–**6** in the cathodic region and Fig. 2 those for the same complexes in the anodic region. The electrochemical data are summarized in Table 1. All the complexes show two reduction waves in the cathodic region at different potentials. During the reverse sweep the complexes exhibit two oxidation waves at different potentials. Coulometric studies confirmed that each reduction is associated with a single elec-

Table 1 Electrochemical data * of the complexes

Complex	Reduction (cathodic potential region)						Oxidation (anodic potential region)					
	$^1E_{pc}$	$^1E_{pa}$	ΔE_p^1	$^2E_{pc}$	$^2E_{pa}$	ΔE_p^2	$^1E_{pa}$	$^1E_{pc}$	ΔE_p^1	$^2E_{pa}$	$^2E_{pc}$	ΔE_p^2
1	−1.00	−0.30	700	−1.38	−0.93	450	+0.25	+0.04	210	+0.54	+0.40	140
2	−0.94	−0.32	620	−1.28	−1.02	260	+0.25	+0.08	150	+0.59	+0.46	130
3	−0.86	−0.42	440	−1.28	−1.06	220	+0.27	+0.10	170	+0.56	+0.45	110
4	−0.88	−0.77	110	−1.32	−1.07	250	+0.29	+0.13	160	+0.62	+0.50	120
5	−0.82	−0.66	160	−1.30	−1.06	240	+0.28	+0.14	140	+0.65	+0.53	120
6	−0.78	−0.65	130	−1.28	−1.04	240	+0.31	+0.14	170	+0.64	+0.54	100
7	−0.92	−0.32	600	−1.18	−1.00	180	+0.26	+0.12	140	+0.62	+0.52	100
8	−0.82	−0.16	660	−1.20	−0.92	280	+0.30	+0.14	200	+0.70	+0.54	160
9	−0.86	−0.72	140	−1.24	−0.96	280	+0.31	+0.11	200	+0.64	+0.54	100
10	−0.78	−0.36	420	−1.22	−0.80	420	+0.32	+0.20	120	+0.70	+0.58	120

* Potentials are given in V *vs.* Ag–AgCl; $\Delta E_p = E_{pc} - E_{pa}$ in mV. In dmf (concentration 1×10^{-3} M); supporting electrolyte NBu_4ClO_4 (0.1 M); scan rate 50 mV s^{-1}; platinum working electrode, platinum auxiliary electrode, Ag–AgCl reference electrode.

tron transfer process.[25] The ΔE_p value for most of the complexes for the first redox couple is more than 300 mV and for the second redox couple, is more than 200 mV. The higher ΔE_p value is due to the difference between the original complex and the reduced species. After the second reduction the complexes may undergo ligand replacement reaction and form new species. So the oxidation peak is not related to the corresponding reduction peak of the original complexes. Hence these reduction processes are not reversible. The same interpretation holds good for the redox process of the complexes in the anodic potential region. Therefore the reduction process may involve the following steps:† $Mn^{II}{}_2 \xleftarrow{+e} Mn^{II}Mn^{III} \xleftarrow{+e} Mn^{III}{}_2 \xrightarrow{-e} Mn^{III}Mn^{IV} \xrightarrow{-e} Mn^{IV}{}_2$. Electrochemically the mixed valence $Mn^{III}Mn^{II}$ and $Mn^{III}Mn^{IV}$ species can be produced from complex **1** by constant potential electrolysis at 100 mV higher than the first reduction and oxidation potentials. The mixed valence species was confirmed by ESR spectra. The $Mn^{III}Mn^{II}$ species gave a six-line pattern with hyperfine splitting corresponding to the presence of Mn^{2+}. The ESR spectrum of the $Mn^{III}Mn^{IV}$ species shows the presence of the manganese(IV) ion.

The synthesized macrocyclic ligands have two compartments: one has two unsaturated nitrogen (azomethine) and two phenoxide oxygen donor atoms for co-ordination and the other has two saturated nitrogen (piperazine) and two phenoxide oxygen donor atoms. The two phenoxide oxygen atoms are common to both the manganese(III) ions. Mandal *et al.*[26] have reported that the first one electron reduction potential is shifted towards more cathodic values with increase in the saturation of the azomethine linkage in macrocyclic systems. Hence it is reasonable to believe that in the macrocyclic complex the first one electron reduction occurs at the manganese(III) ion co-ordinated to unsaturated nitrogen atoms and second at the ion co-ordinated to the saturated nitrogen atoms.

From Table 1 it is observed that the first one electron reduction of the metal center is influenced mainly by the macrocyclic ring size. It shifts to more anodic values as the size increases. With increase in the chain length between the imine nitrogens, the degree of distortion of the N_2O_2 plane around the metal center increases. It is known that more distortion in the co-ordination geometry favours facile electrochemical reduction and hence anodic shift in the first reduction potential. This behaviour is consistent with earlier observations.[15b,27]

The second one electron reduction potential has less variation with increase in alkyl chain length. It takes place at the manganese(III) ion present in the piperazine compartment. The structural variation in the imine nitrogen compartment (variation in the chain length) has very little effect on the co-ordination geometry of the piperazine nitrogen compartment. Therefore it is reasonable to believe that the degree of geometrical distortion around the piperazine-co-ordinated Mn^{III} is less than that around the imine-co-ordinated Mn^{III}. So the second electron reduction is less sensitive to the variation in the alkyl chain length.[15b,17]

The complexes containing the electron withdrawing substituent Br at the *para* position to the phenoxide oxygen in the phenyl ring are reduced at lower negative potentials, compared with those containing the electron donating substituent CH_3. This is due to the electron withdrawing group decreasing the electron density at the Mn^{III}.[28] All the axial chloro complexes are reduced at higher cathodic potentials, than those of the axial bromo complexes. This may be due to the higher basicity of the chloride than the bromide ion.[20b,29]

The oxidation potential of the metal center is influenced by the axial halogen atom. The axial bromo complexes were oxidized at more positive potentials than those of the axial chloro complexes. Unlike the first reduction potential of the metal center, the first oxidation potential does not vary much with increase in the macrocyclic ring size. It takes place at the metal center present in the piperazine nitrogen compartment. The increase in the ring size may not have much influence on this compartment. The size of the oxidized ion, Mn^{IV}, is smaller than that of Mn^{III}. However, the size of the reduced ion Mn^{II} is greater than that of Mn^{III}. This increase may result in more stereochemical change around the metal center. Hence the first reduction potential varies considerably with the ring size.

Conclusion

The synthesized macrocyclic ligand complexes have two dissimilar saturated and unsaturated N_2O_2 compartments. The metal ion in the unsaturated compartment is reduced first. This is inferred from the change in the reduction potential with change in macrocyclic and chelate ring size in the unsaturated compartment. The metal ion present in the saturated compartment is oxidized first. This may be inferred from the fact that the change in ring size does not affect the first oxidation potential of the metal ion. This observation indicates that small changes in the electronic and structural co-ordination environment affect the redox potential of the complexes. It is evident that the function and reactivity of metalloenzymes vary with the co-ordination environment around the metal centre in the active sites.

Acknowledgements

M. M. acknowledges the Tamil Nadu Government for providing financial support for this research programme.

† The authors acknowledge a referee for his critical evaluation and suggestions in the electrochemical part.

References

1 P. K. Coughlin and S. J. Lippard, *J. Am. Chem. Soc.*, 1984, **106**, 2328; Y. Agnus, R. Louis, J. P. Gisselbrechi and R. Weiss, *J. Am. Chem. Soc.*, 1984, **106**, 93; D. Lusscau, J. M. Savariauli, P. C. Cassou and J. P. Tuchangues, *J. Chem. Soc.*, *Dalton Trans.*, 1988, 1225; H. Diril, H. R. Chang, X. Zhang, S. K. Larsen, J. A. Polenza, C. G. Pierpont, H. J. Schugar, S. S. Isted and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1987, **109**, 6207.

2 L. F. Lindoy, *The Chemistry of Macrocyclic Ligands*, Cambridge University Press, Cambridge, 1989.

3 D. Voet and J. G. Voet, *Biochemistry*, 2nd edn., Wiley, New York, 1995; E. Frieden, *Biochemistry of the Essential Trace and Ultratrace Elements*, Plenum, New York, 1984.

4 K. Weighardt, *Angew. Chem.*, *Int. Ed. Engl.*, 1989, **28**, 1153.

5 W. M. Coleman and L. T. Taylor, *Coord. Chem. Rev.*, 1980, **32**, 1.

6 V. L. Pecoraro, M. J. Baldwin and A. Gelasco, *Chem. Rev.*, 1994, **94**, 807.

7 R. Robson, *Inorg. Nucl. Chem. Lett.*, 1970, **6**, 125; N. F. Pilkington and R. Robson, *Aust. J. Chem.*, 1970, **23**, 2225.

8 P. Zanello, S. Tamburini, P. A. Vigato and G. A. Mazzochin, *Coord. Chem. Rev.*, 1987, **77**, 165.

9 H. Okawa and S. Kida, *Inorg. Nucl. Chem. Lett.*, 1971, **7**, 751; *Bull. Chem. Soc. Jpn.*, 1972, **45**, 1759.

10 M. Tadokoro, H. Okawa, N. Matumoto, M. Koikawa and S. Kida, *J. Chem. Soc.*, *Dalton Trans.*, 1991, 1657.

11 B. F. Hoskins, R. Robson and G. A. Williams, *Aust. J. Chem.*, 1975, **28**, 2593, 2607; *Inorg. Chim. Acta*, 1976, **16**, 121; A. W. Addison, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 899.

12 R. R. Gagne, C. A. Koval and T. J. Smith, *J. Am. Chem. Soc.*, 1977, **99**, 8367; R. R. Gagne, C. A. Koval, T. J. Smith and M. C. Cimolino, *J. Am. Chem. Soc.*, 1979, **101**, 4571; R. R. Gagne, C. L. Spiro, T. J. Smith, C. A. Hamann, W. R. Thies and A. K. Shiemke, *J. Am. Chem. Soc.*, 1981, **103**, 4073; C. L. Spiro, S. E. Lambert, T. J. Smith, E. N. Duesler, R. R. Gagne and D. N. Hendrickson, *Inorg. Chem.*, 1981, **20**, 1229; S. L Lambert and D. N. Hendrickson, *Inorg. Chem.*, 1979, **18**, 2683.

13 K. K. Nanda, R. Das, M. J. Newlands, R. Hynes, E. J. Gabe and K. Nag, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 897; R. Das, K. K. Nanda, K. Venkatasubramaniam, P. Paul and K. Nag, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 1253; K. K. Nanda, R. Das, K. Venkatasubramaniam and K. Nag, *Proc. Indian Acad. Sci.* (*Chem. Sci.*), 1994, **106**, 673.

14 M. Tadokora, H. Sakiyama, N. Matsumoto, M. Koikawa and S. Kida, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 313; H. Okawa, J. Nishio, M. Ohba, M. Tadokora, N. Matsumoto, M. Koikawa, S. Kida and D. E. Fenton, *Inorg. Chem.*, 1993, **32**, 2949; M. Yonemura, Y. Matsumuro, H. Furutachi, M. Ohba, H. Okwa and D. E. Fenton, *Inorg. Chem.*, 1997, **36**, 2711.

15 H. Okawa, M. Tadokora, Y. Aratake, M. Ohba, K. Shindo, M. Mitsumi, M. Koikawa, M. Tomono and D. E. Fenton, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 253.

16 J. Nishio, H. Okawa, S. Ohtsuka and M. Tomono, *Inorg. Chim. Acta*, 1994, **218**, 27; H. Furutachi and H. Okawa, *Inorg. Chem.*, 1997, **36**, 3911.

17 S. Karunakaran and M. Kandaswamy, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 1595.

18 J. C. Duff, *J. Chem. Soc.*, 1941, 547.

19 K. Gunasekaran, S. S. Sundra Raj, D. Velmurugan, K. K. Chacko, S. Karunakaran and M. Kandaswamy, *J. Chem. Crystallogr.*, 1994, **24**, 71.

20 (*a*) A. B. P. Lever, *Inorganic Electronic Spectroscopy*, 2nd edn., Elsevier, New York, 1984; (*b*) W. M. Coleman, R. T. Boggeses, J. W. Hughes and L. T. Taylor, *Inorg. Chem.*, 1981, **20**, 1253.

21 R. K. Boggeses, J. W. Hughes, W. M. Coleman and L. T. Taylor, *Inorg. Chim. Acta*, 1980, **38**, 183; M. Fujiwara, T. Matsushita and T. Shono, *Polyhedron*, 1985, **4**, 1895.

22 S. J. Gruber and C. M. Harris, *Inorg. Nucl. Chem.*, 1968, **30**, 1805; M. Honda, *Helv. Chim. Acta*, 1957, **40**, 27; R. L. Belford, *Mol. Phys.*, 1962, **5**, 251; L. Sacconi, *J. Chem. Soc.*, 1964, 276.

23 R. S. Drago, *Physical Methods in Chemistry*, Saunders College Publishing, Philadelphia, 1987.

24 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.

25 B. W. Rossister and J. F. Hamilton, *Physical Methods of Chemistry*, 2nd edn., Wiley, New York, 1985, vol. 2.

26 S. K. Mandal, L. K. Thompson, K. Nag, J. P. Charland and E. J. Gabe, *Inorg. Chem.*, 1987, **26**, 1391; *Can. J. Chem.*, 1987, **65**, 2815.

27 R. C. Long and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1983, **105**, 1513.

28 W. M. Coleman, R. T. Goehring, L. T. Taylor, J. G. Mason and R. K. Boggess, *J. Am. Chem. Soc.*, 1979, **101**, 2311.

29 S. Pal, M. M. Olmstead and W. H. Armstrong, *Inorg. Chem.*, 1995, **34**, 4708.

Paper 8/05712E