Synthesis and Crystal Structure of a Novel Binucleating Symmetrical μ-Bis(tetradentate) Schiff Base Ligand: Syntheses and Redox Properties of Dimanganese(III/III) Complexes

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A family of dinuclear manganese(III/III) complexes $[Mn_2^{III}(\mu\text{-}X)(\mu\text{-}L)(Y)_2](Z)_2$ (X = Cl, OMe, OEt; Y = H_2O; Z = Cl) (**6a**–**c**) of a new μ-bis(tetradentate) ligand, H_3L, derived from the stepwise Schiff base condensation of triethylenetetramine, acetylacetone, and salicylaldehyde has been reported for the first time. NMR spectral and single crystal X-ray structural characterizations of the ligand confirm the formation of a five-membered imidazolidine ring as a backbone to have a new type of doubly bridging binucleating ligand system. In methanol solutions both the $Mn^{III}Mn^{IV}/Mn^{III}Mn^{III}$ and $Mn^{II\text{-}I}Mn^{III}/Mn^{III}Mn^{II}$ couples are observable for the chloro-bridged complex with $E_{1/2}$ in the range of +0.49 to –0.13 V vs. saturated calomel electrode (SCE). The calculation of the comproportionation constant (K_c) from the $E_{1/2}$ values clearly point towards the role of the Mn–O(phenolate)–Mn core for thermodynamic stability of the parent dimanganese(III/III) complex.

Introduction

The field of binucleating ligands and their metal complexes has been receiving considerable attention in recent years.[1] These ligands can coordinate two of the same, or different, metal ions at a suitable predetermined distance to bind and activate a small molecule[2] between the metal centres. Such systems of transition metal complexes may be of interest in relating structures to interesting magnetic behaviours in homo- and hetero-dimetallic complexes,[3] and may mimic aspects of two-metal biosites in various proteins and enzymes.[4] Dinuclear complexes containing manganese centres in close proximity have been the subject of recent extensive investigations due to their involvement in a variety of important biochemical processes like catalytic disproportionation of H_2O_2 to H_2O and O_2 in Mn-catalase[5] and several others,[6] where the Mn_2^{III} unit is present as a redox core in the enzymatic cycle.[7] The Mn^{III}/Mn^{III} oxidation states are believed to participate in the catalytic cycle of Mn-catalase.[8] Furthermore, manganese model-compounds with Cl−Mn bonding have potential applications to the oxygen evolving complex (OEC) in Photosystem II (PSII).[9−13] Insight into the redox properties of Mn-catalase systems and the role of the Mn_2^{III} unit can be obtained from electrochemical studies of new synthetic dimanganese(III/III) complexes. Herein we describe a detailed synthetic account of the preparation of a novel binucleating ligand, its spectroscopic and X-ray structural characterisation, and synthesis of its dimanganese(III/III) complexes and their electron transfer properties.

Results and Discussion

The precursor hexadentate Schiff base ligand (**1**), formed from salicylaldehyde and triethylenetetramine, usually binds to a single metal ion in an octahedral (**2**) geometry, using two tridentate meridional (ONN) halves. However, incorporation of a seventh donor site (D) as a spacer bridging group inside this ligand framework, via an imidazolidine ring formation with a pendent salicylaldehyde group, resulted in a compartmentally fused μ-bis (tetradentate) ligand system (**3**). Here we report the synthesis and structural characterization of one such acyclic binucleating ligand and its binding property towards manganese(III) ions. This novel synthetic strategy for binucleating ligand systems is applicable to all meridionally spanning hexadentate ligands having an ethylenediamine backbone. A new symmetrical binucleating ligand, H_3L, having unsymmetrical compartments containing 1-methyl-3-oxobut-1-enyl end groups and its dimanganese(III/III) complexes are reported.

We have taken advantage of the known[14−19] imidazolidine ring formation reaction as shown in Scheme 1 to prepare the N_4O_3 Schiff base ligand. The ligand is potentially heptadentate, but has its chelating arms spread wide to allow bridging of two metal ions. Though free H_3L exits in the keto form (**4**) in the solid state, it can coordinate two metal ions in the enol form.[1a,20] The unsymmetrical "salenacac" (**5**)-winged ligand (**4**) could take up one metal ion in each wing and fold along the spacer backbone with the help of monoatomic (Cl or OR) exogenous bridging. Reaction of H_3L with $MnCl_2{\cdot}4H_2O$ in the absence or presence

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Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/eurjic or from the author.

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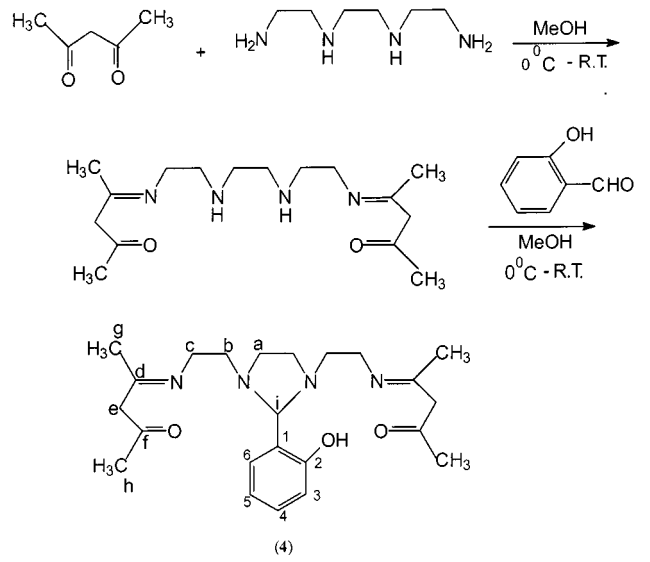
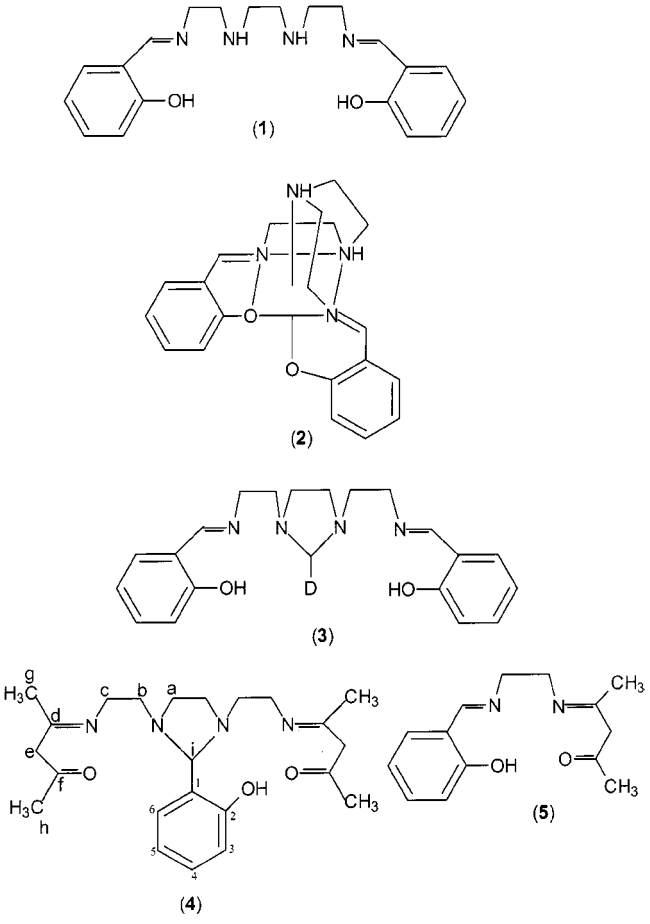
of NaOR (R = Me, Et) afforded complexes of the type $[Mn_2(\mu\text{-}L)(\mu\text{-}X)(H_2O)_2]Cl_2$ (X = Cl, OMe, OEt), where the potentially heptadentate ligand H_3L is coordinated as a μ-bis (tetradentate) N_2O_2-donor ligand with endogenous imidazolidine nitrogen and phenolic oxygen bridging.



Scheme 1



The complexation reaction in the presence of O_2 (from air) oxidizes all the Mn^{2+} centres to Mn^{3+}. During complex formation all the three protons from the phenol and enol functions are removed. The flexibility of the imidazolidine ring and the tendency of the manganese (III) centres to attain octahedral geometry appear to be the driving force for this overall non-planar arrangement of the complex. The potentially heptadentate, but functionally μ-bis (tetradentate), Schiff base ligand H_3L was prepared by a stepwise condensation reaction of trien with two equivalents of acetylacetone and salicylaldehyde in a 1:2:1 molar ratio in 78% yield (Scheme 1). The five-membered imidazolidine ring was formed at the ethylenediamine backbone with salicylaldehyde. The imidazolidine bridging-arm was therefore unique (compared to the other two ketoimine arms), as is clearly shown in the ^1H NMR spectra. ^1H and ^{13}C NMR spectral assignments for the H_3L were consistent with the proposed formulations. The infrared spectrum of the ligand showed peaks around 1605 cm^{-1}, which is characteristic of imine C=N functions. The phenolic OH resonance was observed as a broad signal at about δ = 10.7. This downfield signal can be explained by the intermolecular hydrogen bond of the phenolic OH with solvent ($CDCl_3$), water, or water of crystallization in the solid state (shown in the X-ray structure determination, vide infra). No enolic OH resonance was observed within the 20 ppm range, confirming the diketone form of H_3L in solution.

The molecular structure of H_3L was determined by X-ray crystallography. A view of the dinucleating ligand is shown in Figure 1, and selected bond lengths and angles are listed in Table 1. The ligand molecule is rendered quite rigid by the formation of a five-membered imidazolidine ring and by the presence of three very weak intermolecular hydrogen bonds with a water of crystallization [O(2)−H(2)···O(11) = 2.647 Å; O(11)−H(11A)···O(1) = 2.730 Å; O(11)−H(11B)···O(3) = 2.739 Å]. The water molecule in $H_3L{\cdot}H_2O$ sits comfortably, with the help of these hydrogen-bonding interactions, within the intermolecular hydrophilic pocket created by the keto and phenol functionalities of the ligand. Both N(1)−C(6)−C(7)−N(2) and N(3)−C(17)−C(18)−N(4) adopt gauche conformations [torsion angles: N(1)−C(6)−C(7)−N(2) = 57.5 (6) °; N(3)−C(17)−C(18)−N(4) = −55.5 (6) °]. The whole ligand structure resembles a big Y. Among the three intermolecular hydrogen bonds the bond length between phenolic hydrogen [H(2)] on one ligand molecule and oxygen [O(11)] of the water molecule is lowest 2.65 Å, and results in a highly ordered packing (Figure 2).

The molecular structure clearly shows two tetradentate non-planar compartments suitable for binding two of the same, or different, metal ions. The phenoxy hydrogen of the middle phenolate arm is not intramolecularly hydrogen bonded to one of the imidazolidine nitrogen as is the case with the H_3api ligand.[19] The observed >C=O distances of terminal acetylacetone arms are quite normal[21] for the purely keto tautomeric form in the crystalline state. The similar C−C distances within keto-imine framework also support this observation. The C=N distances also corre-

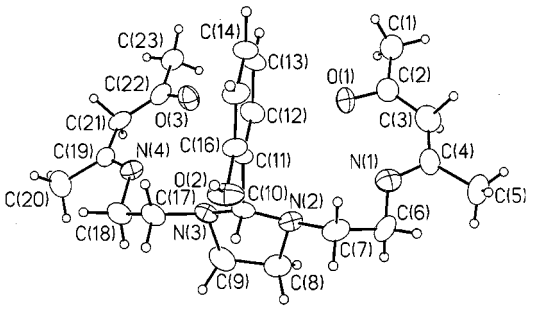


Figure 1. ORTEP plot and labelling scheme for H_3L; all atoms are shown as 50% probability ellipsoids; H atoms are omitted for clarity

Table 1. Selected bond lengths (Å) and angles (°) for $H_3L{\cdot}2H_2O$

O(1)−C(2)	1.273(6)	O(2)−C(16)	1.362(6)
O(3)−C(22)	1.256(6)	N(1)−C(4)	1.338(7)
N(1)−C(6)	1.441(7)	N(2)−C(10)	1.445(7)
N(2)−C(7)	1.453(7)	N(2)−C(8)	1.472(7)
N(3)−C(17)	1.438(6)	N(3)−C(9)	1.470(6)
N(4)−C(19)	1.483(7)	N(4)−C(18)	1.329(7)
C(1)−C(2)	1.480(7)	C(2)−C(3)	1.498(8)
C(3)−C(4)	1.382(8)	C(4)−C(5)	1.383(8)
C(6)−C(7)	1.501(8)	C(8)−C(9)	1.526(8)
C(4)−N(1)−C(6)	125.2(5)	C(10)−N(2)−C(7)	112.9(4)
C(10)−N(2)−C(8)	104.2(4)	C(7)−N(2)−C(8)	114.0(4)
C(17)−N(3)−C(9)	113.3(4)	C(10)−N(3)−C(9)	103.8(8)
C(19)−N(4)−C(18)	123.4(4)	O(1)−C(2)−C(3)	122.6(5)
O(1)−C(2)−C(1)	117.1(5)	C(3)−C(2)−C(1)	120.2(5)
C(2)−C(3)−C(4)	126.0(6)	N(1)−C(4)−C(3)	121.1(5)
N(1)−C(4)−C(5)	118.2(5)	C(3)−C(4)−C(5)	120.6(5)
N(1)−C(6)−C(7)	110.2(4)	N(2)−C(7)−C(6)	111.4(4)
N(2)−C(8)−C(9)	104.1(4)	N(3)−C(9)−C(8)	104.7(4)
N(2)−C(10)−N(3)	101.8(4)	N(2)−C(10)−C(11)	113.8(4)
N(3)−C(10)−C(11)	112.0(4)		

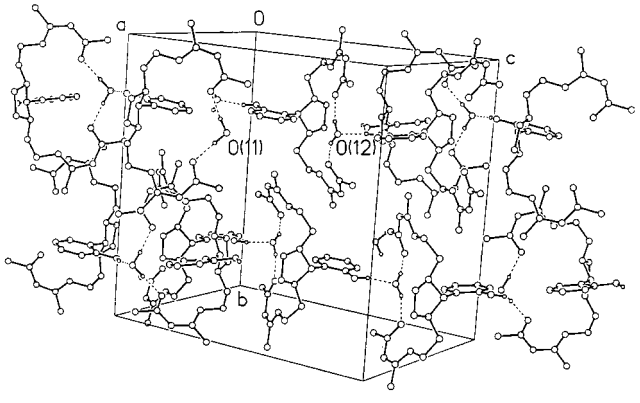
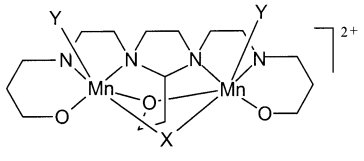


Figure 2. Packing diagram of the H_3L molecule showing hydrogen bonding with a water molecule

spond to a formal double bond.[19] The C−C and C−N distances within the imidazolidine ring are in the1.457−1.496 Å range.

Homodinuclear manganese(III) complexes with the formulation $[Mn_2^{III}(\mu\text{-}X)(\mu\text{-}L)(Y)_2](Z)_2$ (X = Cl, OMe, OEt; Y = H_2O; Z = Cl) (**6**) were prepared from reactions of Mn^{2+} with the ligand H_3L in presence and absence of bases (alkoxide), following oxidation by air. The homodinuclear complexes contain two manganese(III) ions, each coordinated by the N_2O_2 donor set of one half of the ligand. The phenolate O atom from the middle arm of the ligand acts as an endogenous bridge between the two metal centres. The exogenous alkoxide bridge and terminal Y groups complete the coordination sphere and the bi-octahedral structure. The binucleating ligand provides four donor points around each manganese(III) centre. We have so far been unable to synthesize any mononuclear complex of manganese(III) using H_3L. Those complexes could have been used as controls in comparing the change in spectral and magnetic behaviour through dinuclear complex formation. Single-crystal X-ray structure determination of a heterodinuclear assembly of copper(II)-zinc(II) inside the compartments of a similar type of ligand recently[22] established distorted square-pyramidal geometries around each metal centre. Microanalysis data for complexes **6a**−**c** (See Exp. Sect.) confirm their composition. The complexes are highly soluble in polar solvents such as methanol, dimethylformamide, and dimethyl sulfoxide, and are moderately soluble in non-polar solvents like dichloromethane and tetrahydrofuran.

The IR spectra of the complexes show strong C=N stretching frequencies of the imine functions at around 1612 cm^{-1}. The complexes have characteristic μ_2-bridging phenolic ν_{C-O} vibrations in the range 1509−1536 cm^{-1}. The terminal C−O and alkoxide bridging C−O stretching frequencies are observed at around 1295 and 1145 cm^{-1} respectively. The electronic spectra of the intimate dimanganese(III/III) complexes in methanol solutions show several intense absorptions in the near UV region (Table 2, Figure 3).



(**6**)

a : X = Cl

b : X = OMe

c : X = OEt

The moderately intense UV band near 360 nm is typical for the 2-hydroxyphenylimino chromophore.[23] The bands near 300 nm for the present complexes are due to the overlap of the azomethine transition with the charge-transfer band from bridging phenolic oxygen to the d-orbital of Mn^{III}. Absence of any inter-valence band in the 1170 nm region eliminates the possibility for a $Mn^{III}Mn^{II}$ species.[24]

In methanol solutions the complexes behave as 1:2 electrolytes (conductivity values, 180−210 $ohm^{-1}cm^2$ mol^{-1}).The complexes are paramagnetic and correspond to the trivalent states of the metals (high-spin d^4, S = 2) in these complexes. Magnetic studies of powdered samples of

Table 2. Electronic spectral and cyclic voltammetric data for $[Mn_2(\mu\text{-}L)(\mu\text{-}X)(H_2O)_2]Cl_2$

Compound	Electronic spectral data λ_{max}, nm (ε, $dm^3\ mol^{-1}\ cm^{-1}$)	Cyclic voltammetric data[a] $E_{1/2}$, V (ΔE_p, mV)
$[Mn_2(\mu\text{-}L)(\mu\text{-}Cl)(H_2O)_2](Cl)_2$	400 (2250), 340 (4500), 280 (10965), 232 (20305), 217 (20815)[b]	0.49 (90), −0.13[c]
$[Mn_2(\mu\text{-}L)(\mu\text{-}OMe)(H_2O)_2](Cl)_2$	390 (9525), 281 (18740), 235 (28580), 214 (29860)[b]	0.47 (115) [c]
$[Mn_2(\mu\text{-}L)(\mu\text{-}OEt)(H_2O)_2](Cl)_2$	383 (4555), 300 (16545), 240 (21650), 214 (26430)[c]	0.46 (100) [c]

[a] Supporting electrolyte TEAP: reference electrode SCE; $E_{1/2} = 0.5\ (E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively; $\Delta E_p = E_{pa} - E_{pc}$; scan rate 50 mV S^{-1}. – [b] In aqueous solution. – [c] In methanol solution.

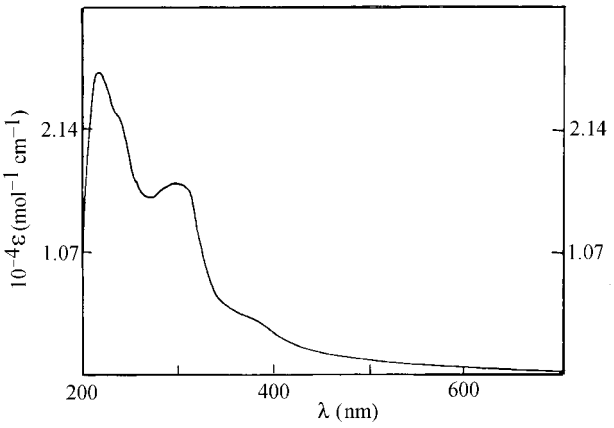


Figure 3. Electronic spectrum of $[Mn_2(\mu\text{-}L)(\mu\text{-}OEt)(H_2O)_2]Cl_2$ (**6c**) in DMF at 298 K

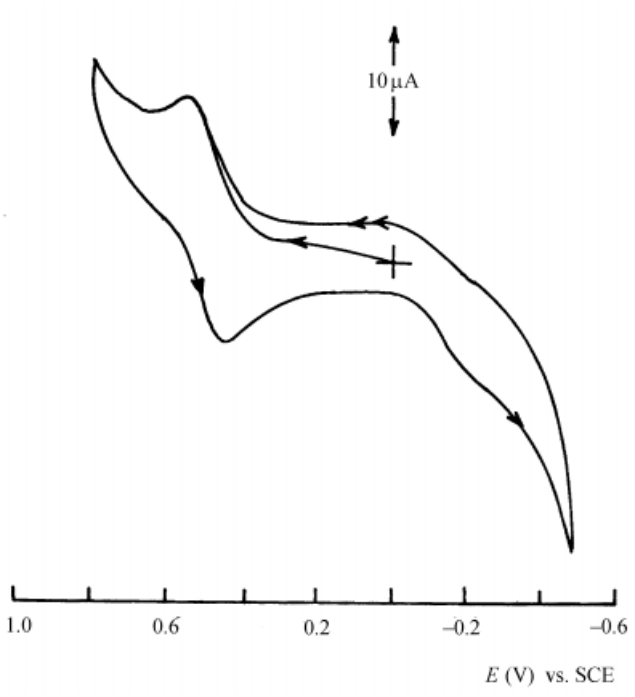


Figure 4. Cyclic voltammogram (scan rate 50 mVs^{-1}) of 10^{-3} M solutions of $[Mn_2(\mu\text{-}L)(\mu\text{-}Cl)(H_2O)_2]Cl_2$ (**6a**) in MeOH at a Pt electrode at 298 K

the complexes were carried out at room temperature using a Gouy balance. The room temperature magnetic moments (μ_{eff}) of the complexes were in the range of 4.24−4.39 μ_B per Mn at 298 K (total μ_{eff} 5.99−6.21 μ_B). The dependence of the room temperature magnetic moments on exogenous bridging is in the order Cl > OMe > OEt, clearly indicating the role of the single exogenous bridging group in varying the magnetic interactions.

The electron-transfer properties of complexes **6a**−**c** were studied in aqueous and methanol solutions by cyclic voltammetry (CV) using a platinum working-electrode. The complexes are electroactive with respect to the metal centres and exhibited two redox processes in the potential range +1.0 V *versus* a saturated calomel electrode (SCE) (tetraethylammonium perchlorate as supporting electrolyte, at 298 K). The chloro-bridged complex showed one oxidative and one reductive response on the positive and negative side of SCE, respectively (Figure 4).

The cathodic and anodic peak heights(i_{pc} and i_{pa}) are equal, and vary as the square root of the scan rate; E_{pc} and E_{pa} are virtually independent of the scan rate. The measured oxidation and reduction potentials were lower in aqueous solutions than in non-aqueous solutions. Both the processes are assumed to be metal-centred. The first quasi-reversible response on the positive side of SCE is due to the one-electron oxidation of Equation (1).

$$[Mn^{III}Mn^{IV}(\mu\text{-}L)(\mu\text{-}Cl)(H_2O)_2]^{3+} \rightleftarrows [Mn^{III}Mn^{III}(\mu\text{-}L)(\mu\text{-}Cl)(H_2O)_2]^{2+} \quad (1)$$

On further scan reversal on the negative side, the one-electron reductive couple in Equation (2) was observed.

$$[Mn^{III}Mn^{III}(\mu\text{-}L)(\mu\text{-}Cl)(H_2O)_2]^{2+} \rightleftarrows [Mn^{III}Mn^{II}(\mu\text{-}L)(\mu\text{-}Cl)(H_2O)_2]^{+} \quad (2)$$

Constant-potential coulometric- and cyclic-voltammetric current height (i_{pa}) data suggest the one-electron nature of these couples. From the separation of $E_{1/2}$ (oxidative response) and $E_{1/2}$ (reductive response) values for $[Mn_2(\mu\text{-}L)(\mu\text{-}Cl)(H_2O)_2]Cl_2$, the comproportionation constant (K_C at 298 K) of the reaction in Equation (3) was calculated to be 5.77×10^{10}, indicating that the Mn_2^{III} complex is considerably stabilized with respect to the $Mn^{III}Mn^{IV}$ and $Mn^{III}Mn^{II}$ species.

$$[Mn^{III}Mn^{IV}(\mu\text{-}L)(\mu\text{-}Cl)(H_2O)_2]^{3+} + [Mn^{III}Mn^{II}(\mu\text{-}L)(\mu\text{-}Cl)(H_2O)_2]^{+} \rightleftharpoons 2\,[Mn^{III}Mn^{III}(\mu\text{-}L)(\mu\text{-}Cl)(H_2O)_2]^{2+} \quad (3)$$

Thus, the cyclic voltammetric study gives an idea of the stability of the parent dimanganese(III/III) complexes with respect to disproportionation. A similar behaviour was reported for other binuclear manganese(III/III) complexes.[25] The reduction potential for $Mn_2^{III/IV}$ species is low compared to the other fully exogenous $(\mu\text{-O})(\mu\text{-OAc})_2$ triply bridged complexes.[26,27] The mixed-valence complexes are stable on the cyclic-voltammetric time scale. A reduction potential in acetonitrile of $E_{1/2} \approx +1.05$ V was measured for a functional model of Mn catalase possessing an alkoxo-bridged core structure.[28] The results described in this section indicate that the $Mn^{II}Mn^{III}$, Mn_2^{III} and $Mn^{III}Mn^{IV}$ oxidation states are accessible for complex **6a** in methanol.

Variation of the terminal arms of the ligand and the single exogenous bridging group to get different homo- and heterodinuclear complexes is currently under investigation. To suppress the deviation in redox potentials for successive electron transfers, charge neutralization within the complex, perhaps by proton release (from coordinated H_2O) or uptake of Cl^- (replacement of coordinated H_2O), might provide the requisite adjustment in redox potentials. Studies in that direction are also in progress.

Conclusion

It has been shown that the nitrogen-oxygen donor Schiff base ligand H_3L, with imidazolidine bridging groups, can be easily synthesized in high yields in a step-wise condensation reaction from the hexadentate precursor ligand with ethylenediamine back-bone. The ligand forms an interesting class of dimanganese complexes, and can serve as multi-electron reservoir showing stepwise electron transfer behaviour. The stability of the dimanganese(III/III) complexes of different but similar types of parent ligand such as H_3L could be compared with respect to the electrochemically generated $Mn^{III}Mn^{IV}$ and $Mn^{III}Mn^{II}$ species.

Experimental Section

Physical Measurements: Microanalyses (C, H N) were performed using a Perkin−Elmer 240 C elemental analyser. IR spectra were obtained on a Perkin−Elmer 883 spectrometer (200−4000 cm^{-1}) prepared as KBr pellets. Electronic spectra were recorded on a Shimadzu UV/Vis/NIR 3100 (190−3200 nm) (MeOH, 1 cm quartz cell) spectrometer. Magnetic susceptibilities were measured using a home built Gouy balance fitted with a polytronic DC power supply. Diamagnetic corrections for ligand susceptibilities were made using Pascal's constants. ^1H and ^{13}C NMR spectra were obtained on a Bruker AC 200 NMR spectrometer using TMS as the internal standard. Electrochemical measurements were made using a PAR model 173 potentiostat/galvanostat, 175 universal programmer, 178 electrometer, and 377-cell system. A planar Beckaman 39273 platinum-disk working-electrode, a platinum-wire auxiliary-electrode, and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. A digital series 2000 Omni Graphic recorder was used to trace the voltammograms. Electrochemical measurements were made under a dinitrogen atmosphere. All chemical data were collected at 298 K and are uncorrected for junction potentials. Solution electrical conductivity was measured using a Unitech type UI31C digital conductivity meter with a solute concentration of about 10^{-3}.

Materials: Triethylenetetramine (trien) was obtained from S.D. Fine Chem, India. Salicylaldehyde and 2,4-pentanedione were purchased from SRL, India and S.D. Fine Chem, India, respectively. All other chemicals and solvents were reagent grade materials and were used as received without further purification. Purification of methanol and preparation of tetraethylammonium perchlorate (TEAP) for electrochemical work was performed as reported in the literature.[29]

1,3-Bis[3-aza-3-(1-methyl-3-oxobut-1-enyl)-prop-3-en-1-yl]-2-(2-hydroxyphenyl)-1,3-imidazolidine (H_3L): A solution of trien (7.00 g, 47.8 mmol) in methanol (50 mL) was added to an ice-cold solution of acetylacetone (9.57 g, 95.6 mmol) in methanol (100 mL). The resulting pale-yellow solution was stirred for ca. 15 min. at 0 °C. The hexadentate precursor diketone is a yellow oily product and was not isolated for the synthesis of **4**. In the next step, a solution of salicylaldehyde (5.84 g, 47.8 mmol) in methanol (50 mL) was added to the previous solution of diketone. The yellow solution was then stirred, initially at 0 °C for 15 min., and finally at ambient temperature (30 °C) for 23 h. The solution was then evaporated to dryness to give a yellow crystalline compound. The product was isolated by filtration, washed with water and hexane, and finally dried in vacuo over fused $CaCl_2$ for a total yield of 15.46 g (78%), m.p. 85−87 °C. − $C_{23}H_{34}N_4O_3$ (414.55): calcd. C 66.64, H 8.27, N 13.52; found C 66.52, H 8.16, N 13.57. − MS (EI): *m/z* = 414 [M^+]. − IR (KBr): $\tilde{\nu}$ = 1605 cm^{-1} (vs, $\nu_{C=N}$), 1546, 1443 (s, $\nu_{C=C}$). − ^1H NMR (200 MHz, $CDCl_3$): δ = 1.76 (s, 6 H, g), 2.65 (m, 4 H, a), 2.77 (m, 8 H, b, c), 6.79 (m, 2 H, 3,5), 10.73(H, b, phenolic OH). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.55 (g), 28.65 (h), 42.17 (a), 50.95 (b), 52.04 (c), 89.33 (i), 95.62 (e), 116.87 (3), 118.82 (5), 120.34 (1), 130.35 (6), 130.80 (4), 158.03 (2), 162.70 (d), 194.99 (f).

Preparation of the Dimanganese(III/III) Complexes: All manipulations were carried out under aerobic conditions. Since many of the syntheses are similar, a detailed procedure is given only for a representative example.

$[Mn_2(\mu\text{-}L)(\mu\text{-}Cl)(H_2O)_2]Cl_2$: Solid $MnCl_2{\cdot}4H_2O$ (0.477 g, 2.41 mmol) was added in portions during 15 min. to a solution of H_3L (0.5 g, 1.206 mmol) in methanol (20 mL). The resulting brown solution was stirred with a magnetic stirrer in air for 1 h at ambient temperature for complete oxidation of all Mn^{2+} centres to Mn^{3+}. The solution was then evaporated to dryness to give a brown gummy mass. A solid brown powder was obtained from this mass after trituration with hexane, collection by filtration, washing thoroughly with a little cold water to remove the produced NaCl, and washing with hexane. The compound was finally dried in vacuo over P_4O_{10}. Yield 0.714 g (89%). − $C_{23}H_{35}Cl_3Mn_2N_4O_5$ (663.79): calcd. C 41.62, H 5.31, N 8.44, Mn 16.55; found C 41.55, H 5.28, N 8.50, Mn 16.59. − IR (KBr): $\tilde{\nu}$ = 3394 cm^{-1} (b), 1612 (vs), 1536 (s), 1441 (s), 1386 (s), 1298 (s).

$[Mn_2(\mu\text{-}L)(\mu\text{-}OMe)(H_2O)_2]Cl_2$: Solid $MnCl_2{\cdot}4H_2O$ (0.477 g, 2.41 mmol) was added in portions during 15 min. to a solution of H_3L (0.5 g, 1.206 mmol) and NaOMe (0.07 g, 1.30 mmol) in methanol (30 mL). The resulting brown solution was stirred with a magnetic stirrer in air for 1 h at ambient temperature. The solution was then evaporated to dryness to yield a brown gummy mass. A solid brown powder was obtained after trituration with hexane, collection by filtration and washing thoroughly with hexane. The compound was finally dried in vacuo over P_4O_{10}. Yield 0.692 g (87%). − $C_{24}H_{38}Cl_2Mn_2N_4O_6$ (659.37): calcd. C 43.72, H 5.81, N 8.49, Mn 16.66; found C 43.66, H 5.86, N 8.52, Mn 16.72. − IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1} (b), 1612 (vs), 1509 (s), 1440 (s), 1385 (s), 1296 (s).

$[Mn_2(\mu\text{-}L)(\mu\text{-}OEt)(H_2O)_2]Cl_2$: This compound was prepared following the above procedure, except that ethanol was used as solvent and stirring was continued for 1 h. − $C_{25}H_{40}Cl_2Mn_2N_4O_6$ (673.39): calcd. C 44.59, H 5.99, N 8.32, Mn 16.32; found C 44.51, H 6.01, N 8.37, Mn 16.41. − IR (KBr): $\tilde{\nu}$ = 3394 cm^{-1} (b), 1610 (vs), 1510 (s), 1438 (s), 1390 (s), 1296 (s).

X-ray Crystallography: Orange prismatic crystals of ligand **1** were obtained by slow diffusion of hexane into a dichloromethane solution of H_3L. Selected crystal data and data collection parameters are given in Table 3. The unit cell parameters were determined by the usual procedure of random searching followed by indexing. The plate-like yellow crystal selected for data collection was mounted at the end of a quartz fibre and covered with a thin layer of epoxy resin. Data were collected on an Enraf−Nonius CAD-4 diffractometer with PC control,[30] using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) by ω scans within the angular range 4.0−45.0°. The structure was solved by direct methods[31] in the monoclinic space group $P2_1/c$, which is the only space group in either the orthorhombic or monoclinic system consistent with the systematic absences found in the data. All non-hydrogen atoms were refined anisotropically. All data were used in the least-squares calculations[32] and the structure was refined to F_o^2. There was no significant residual electron density in a final difference Fourier map. The detailed experimental write-up and comments on the structure determination are given as Supplementary Material.

Table 3. Crystallographic data for $H_3L{\cdot}2H_2O$

Empirical formula	$C_{23}H_{34}N_4O_3{\cdot}H_2O$
M_r	432.56
System	Monoclinic
Space group	$P2_1/c$
a/Å	13.587(7)
b/Å	18.170(11)
c/Å	19.283(13)
β/°	90.09(8)
U/Å^3	4761(5)
Z	8
D_c/g cm^{-3}	1.207
Radiation(λ/Å)	Mo-K_α (0.71073), graphite monochromated
Crystal size/mm	0.59 × 0.34 × 0.15
T, °C	−123 ± 1
Scan method	ω-scans
θ Range for data collection/°	4.0−45.0
μ/cm^{-1}	8.3
Data, restraints, parameters	4400, 2, 582
R[a]	0.0624
R_w[b]	0.1626
Goodness of fit on F^2	1.007
Largest difference peak and trough/e Å^{-3}	0.37, −0.41
$(shift/e.s.d.)_{max}$	0.033

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. − [b] $R_w = \Sigma w(|F_o| - |Fc|)^2/\Sigma w(F_o)^2]^{1/2}$.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-152200. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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