Binuclear Metal Complexes. Part 55.[1] Dimanganese(II) and Mixed-valence Manganese(II,III) Complexes of 'Strati-bis' Schiff Bases with Two Salen-like † Donating Sites

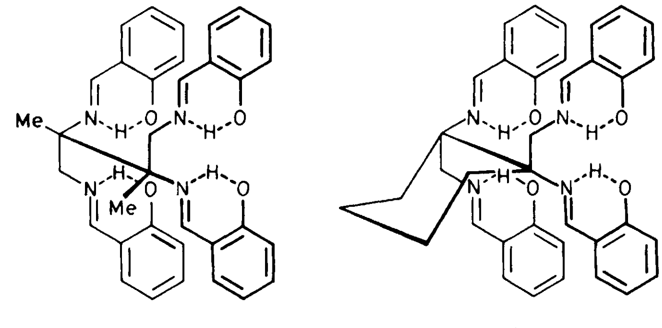
Hisashi Ōkawa,* Atsunori Honda, Masaaki Nakamura, and Sigeo Kida
Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki,Higashiku, Fukuoka 812, Japan

Dimanganese(II) complexes with 'strati-bis' (two planar metal ions in a face-to-face configuration in one molecule) Schiff bases, 2,3-dimethyl-1,2,3,4-tetrakis(salicylideneimino)butane (H_4L^1) and 1,2-bis(salicylideneimino)-1,2-bis(salicylideneiminomethyl)cyclohexane, have been examined. They are fairly stable to oxidation by molecular oxygen in the solid state, but they are air-oxidized in dichloromethane to mixed-valence Mn^{II}–Mn^{III} species. The mixed-valence complex with $(L^1)^{4-}$ has been isolated and characterized by electrochemical, magnetic, and spectroscopic methods. An antiferromagnetic spin-exchange interaction ($-J$ = 6.0 cm^{-1}) operates between the Mn^{II} and Mn^{III} ions. It shows the transition arising from the Mn^{III} site and a new transition at 7.7 × 10^3 cm^{-1}. The latter near-i.r. band has been assigned to the inter-valence transition based on the agreement of its half-bandwidth with the predicted value by Hush's theory and the solvent dependence of the band frequency. The delocalization parameter α is estimated to be 0.05, which corresponds to the class II type in the classification of Robin and Day.

'Strati-bis' metal complexes with two planar metal ions in a face-to-face configuration within a molecule have been the subject of recent studies because of interest in their physicochemical properties,[2–4] catalytic functions,[5] and use as models for the active sites of some biological dimetal systems.[6–8] Bis(porphyrin) metal complexes have been extensively investigated. On the other hand, less attention has been paid to the complexes of strati-bis Schiff bases with two 'salen-like' donating sites [H_2salen = ethylenebis(salicylideneimine)] although metal complexes with H_2salen and its homologues are sometimes useful models of the active site of coenzyme B_{12}[9,10] and oxygen carriers[11,12] in biological systems.

In previous papers,[13–16] we have shown that 2,3-dimethyl-1,2,3,4-tetrakis(salicylideneimino)butane (H_4L^1) and 1,2-bis(salicylideneimino)-1,2-bis(salicylideneiminomethyl)cyclohexane (H_4L^2) (Figure 1) form dimetal complexes of a strati-bis or stacked configuration with divalent and trivalent metal ions. The complexes were found to exhibit novel electronic, electrochemical, magnetic, and optical properties, compared with their relevant mononuclear complexes. Electrochemical features of the dicopper(II) and copper(II)–nickel(II) complexes are particularly of interest, since they are reduced at a relatively high potential to the Cu^I—Cu^{II} and Cu^I—Ni^{II} species, respectively, and the reduced species are considerably stable against oxidation by molecular oxygen.[13,14] The formation of mixed-valence species has been also suggested for the di-iron(II) and di-iron(III) homologues.[15] These characteristics may be rationalized in terms of electron delocalization over the molecule associated with the stacked configuration.

As an extension of these studies, we have synthesized the dimanganese(II) complexes [Mn_2L^1] and [Mn_2L^2] and examined their properties. It was found that the complexes are air-oxidized in dichloromethane solution to form mixed-valence manganese(II,III) complexes. Of these, the mixed-valence complex of $(L^1)^{4-}$ has been isolated and characterized by electrochemical, magnetic, and spectroscopic methods.



H_4L^1 H_4L^2

Figure 1. Structures of H_4L^1 and H_4L^2

Experimental

Preparations.—The ligands H_4L^1 and H_4L^2 were prepared by the method described previously.[13]

[Mn_2L^1]. A methanolic solution of H_4L^1 (0.5 g), manganese(II) acetate tetrahydrate (0.44 g), and NaOH pellets (0.15 g) was stirred at room temperature for 24 h under an atmosphere of nitrogen. Yellowish orange crystals thus deposited were collected by filtration, washed with a small amount of methanol, and dried *in vacuo*. Yield 0.3 g (Found: C, 59.8; H, 5.10; N, 7.85. Calc. for $C_{34}H_{30}Mn_2N_4O_4\cdot CH_3OH$: C, 60.0; H, 4.90; N, 8.00%).

[Mn_2L^2]. This complex was obtained as orange crystals by the reaction of H_4L^2 (0.2 g), manganese(II) acetate tetrahydrate (0.17 g), and NaOH pellets (0.05 g) in absolute methanol (20 cm^3). Yield 0.15 g (Found: C, 60.8; H, 5.20; N, 7.45. Calc. for $C_{36}H_{32}Mn_2N_4O_4\cdot 0.67\ CH_3OH$: C, 60.65; H, 5.15; N, 7.55%).

$Mn_2L^1(OH)(H_2O)$. A yellow solution of [Mn_2L^1] (0.1 g) in dichloromethane (15 cm^3) was exposed to air for 12 h. The solution turned deep red. The reaction mixture was placed in a desiccator and slowly concentrated to a small portion under reduced pressure to give almost black prisms. Yield 0.07 g (Found: C, 58.05; H, 4.80; N, 7.75. Calc. for $C_{34}H_{33}Mn_2N_4O_6$: C, 58.05; H, 4.70; N, 7.95%).

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† Salen = ethylenebis(salicylideneiminate).

Non-S.I. units employed: B.M. = 9.274 × 10^{-24} J T^{-1}; $\chi_{e.m.u.} = \frac{10^6}{4\pi}\chi_{S.I.}$.

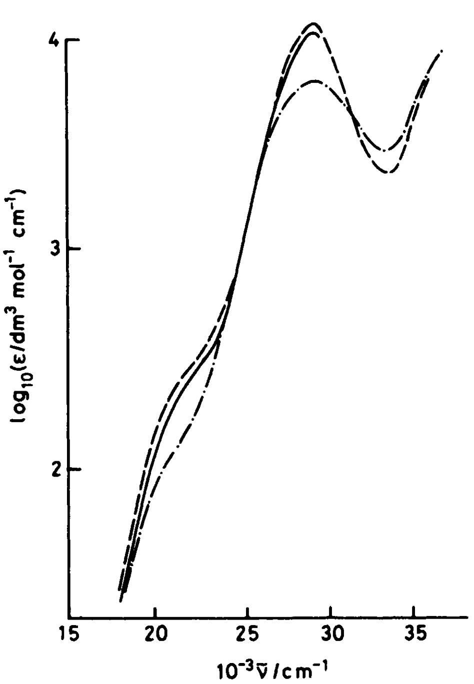

Figure 2. Electronic spectra of [Mn$_2$L^1] (———), [Mn$_2$L^2] (– – –), and [Mn(salpn)] (— · —) in CH$_2$Cl$_2$ under an N$_2$ atmosphere

Measurements.—Electronic spectra were recorded on a Shimadzu model MPS-5000 multi-purpose spectrophotometer. Infrared spectra were recorded on a Hitachi–Perkin-Elmer 225 grating i.r. spectrophotometer on KBr discs.

Magnetic susceptibilities were measured by the Faraday method. The apparatus was calibrated using Hg[Co(NCS)$_4$].[17] Effective magnetic moments were determined by the equation $\mu_{\text{eff.}} = 2.828\,(\chi_A T)^{\frac{1}{2}}$, where χ_A is the susceptibility of the constituent atoms corrected for diamagnetism using Pascal's constants. Temperature variations of magnetic susceptibility were measured with the same instrument from liquid-nitrogen temperature to 300 K with liquid nitrogen as the cryogenic material. Differential pulse polarograms and cyclic voltammograms were recorded on a Yanagimoto P-1000 voltammetric analyser in freshly distilled dichloromethane. The measurements were carried out with a three-electrode cell equipped with a glassy-carbon working electrode, a platinum-coil auxiliary electrode, and a calomel electrode as reference electrode. Tetrabutylammonium perchlorate (0.1 mol dm^{-3}) was added as the supporting electrolyte. All the potentials were normalized by the use of ferrocene as an internal standard.[18,19] Controlled-potential electrolyses were carried out with a Yanagimoto model VE-8 controlled-potential electrolyser.

Results and Discussion

In contrast with the general observation that manganese(II) complexes of salen-type ligands are very air sensitive and readily oxidized to higher oxidation states,[20] the dimanganese(II) complexes [Mn$_2$L^1] and [Mn$_2$L^2] are relatively insensitive to air in the solid state. They could be handled in air for 20—30 min without any change in appearance and weight, although prolonged exposure to air caused decomposition.

The inertness of the complexes to air enabled us to measure highly reliable magnetic susceptibilities. The magnetic moments of [Mn$_2$L^1] and [Mn$_2$L^2] at room temperature are 5.99 and 5.94 B.M. per metal ion, respectively, which fall in the range for normal high-spin manganese(II) complexes. It is known that [Mn(salen)] has a magnetic moment less than the spin-only value at room temperature and the moment decreases on lowering the temperature.[21] The magnetic behaviour of this complex is attributed to an antiferromagnetic spin-exchange interaction associated with dimerization through the phenolic oxygens, as demonstrated for [{Cu(salen)}$_2$],[22] [{Co(salen)}$_2$],[23,24] and [{Fe(salen)Cl}$_2$].[25] We have measured the magnetic susceptibilities of [Mn$_2$L^1] and [Mn$_2$L^2] in the range 78—300 K and found that the moments are practically independent of temperature. Thus, there is no appreciable magnetic exchange interaction in these complexes. The Dreiding model study suggests that the geometrical requirement of the ligands precludes the intramolecular linking of the MnN$_2$O$_2$ moieties through the phenolic oxygens, though they can stack on each other.

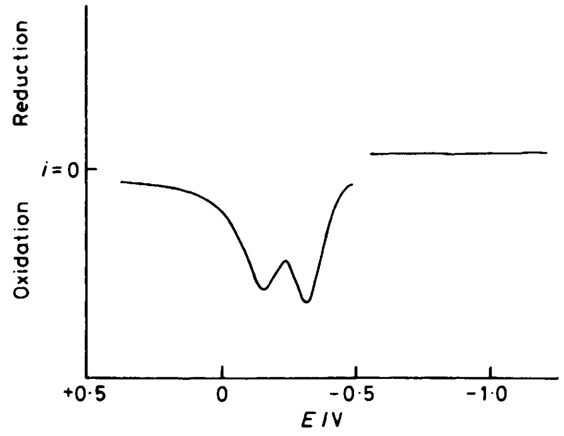

Figure 3. Differential pulse polarogram of [Mn$_2$L^1] (5 × 10^{-4} mol dm^{-3}); scan rate 0.01 V s^{-1}

Electronic spectra of the complexes measured in dichloromethane under anaerobic conditions (Figure 2) exhibit an intense band at 28.5 × 10^3 cm^{-1} and a shoulder near 21 × 10^3 cm^{-1}, both of which can be assigned to intra-ligand transitions. Indeed, these spectra closely resemble the spectrum of [Zn(salen)].[26] This fact and the absence of any appreciable absorption in the region below 20 × 10^3 cm^{-1} clearly demonstrate the electronic configuration of the manganese(II) ion to be of high-spin. This is consistent with the results from the magnetic measurements on solid samples. The electronic spectra were further examined in comparison with the spectrum of [propane-1,2-diylbis(salicylideneiminato)]manganese(II), [Mn(salpn)]. The adoption of [Mn(salpn)] instead of [Mn(salen)] as reference is due to the following reasons: (*i*) [Mn(salpn)] is readily soluble in dichloromethane while [Mn(salen)] is sparingly soluble, probably because of dimerization, and (*ii*) [Mn(salpn)] exactly corresponds to half of the [Mn$_2$L^1] molecule and hence is a better reference to it. The spectrum of [Mn(salpn)] is also included in Figure 2. The band of [Mn(salpn)] at 28.5 × 10^3 cm^{-1} has an intensity almost the same as that of the corresponding band of [Zn(salen)].[26] As is seen in Figure 2, the bands at 28.5 × 10^3 and 21 × 10^3 cm^{-1} of the dimanganese(II) complexes are more intense compared with those of [Mn(salpn)]. The increased intensities of the intra-ligand transition bands might be regarded as an indication of an interaction between the MnN$_2$O$_2$ moieties, though a detailed spectroscopic interpretation is not possible at present.

Differential pulse polarograms of the dimanganese(II) complexes each contain two oxidation waves near −0.15 and −0.3 V (Figure 3). Since the oxidation of the ligands does not occur

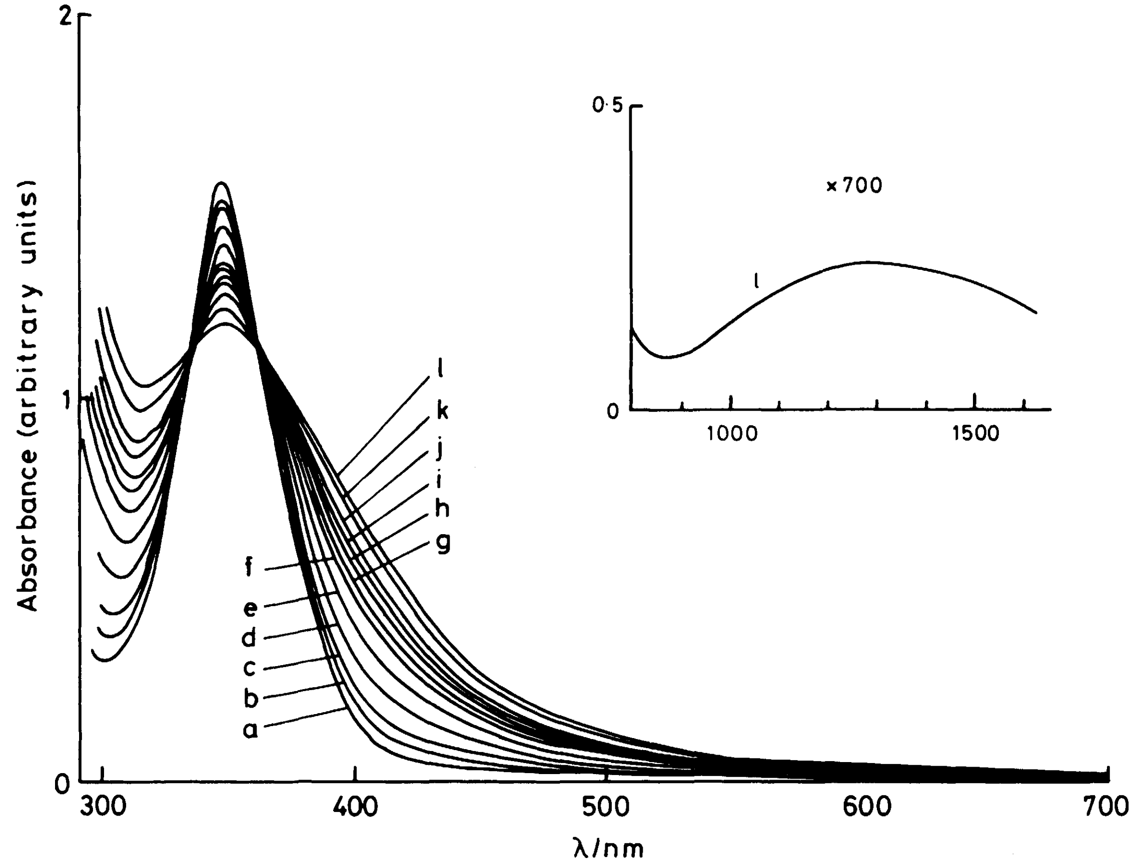

Figure 4. Electronic spectral changes for $[Mn_2L^1]$ (1.47×10^{-5} mol dm^{-3}) in CH_2Cl_2 after exposure to air. Exposure times: (a) 0, (b) 15, (c) 30, (d) 45, (e) 75, (f) 105, (g) 135, (h) 165, (i) 195, (j) 235, (k) 400, and (l) 600 min

up to +0.5 V, both waves can be attributed to the oxidation of manganese(II). It is already known that the dicopper(II),[13] copper(II)-nickel(II),[14] di-iron(II),[15] and di-iron(III) [15] complexes of $(L^1)^{4-}$ and $(L^2)^{4-}$ also exhibit two redox waves. For these complexes it has been shown that the stacked and the non-stacked species (with respect to the MN_2O_2 planes) are in an equilibrium in solution, and the redox reaction of the stacked species occurs at a higher potential compared with the non-stacked species. Thus, the observation of two oxidation waves leads us to an assumption that the dimanganese(II) complexes are also in equilibrium between the stacked and the non-stacked species in solution. The wave near −0.15 V can be assigned to the one-electron transfer process, Mn^{II}–$Mn^{II} \longrightarrow Mn^{II}$–$Mn^{III}$, of the stacked species, while the wave near −0.3 V to the two-electron transfer process, Mn^{II}–$Mn^{II} \longrightarrow Mn^{III}$–$Mn^{III}$, of the non-stacked species.

Despite the considerable inertness to molecular oxygen in the solid state, the dimanganese(II) complexes were gradually oxidised in dichloromethane in air forming a red solution. The oxidation has been followed spectrophotometrically for $[Mn_2L^1]$, and the results are given in Figure 4. The spectrum changed with the isosbestic points at 337 and 364 nm and finally exhibited absorption bands at 350, 606, and 1 300 nm (see also Figure 5). Similarly, the oxidized solution of $[Mn_2L^2]$ showed absorptions at 350, 590, and 1 300 nm.

From the oxidized solution of $[Mn_2L^1]$ reddish black prisms were isolated. On the other hand, we were unsuccessful in isolating a pure oxidation product from $[Mn_2L^2]$. From the analytical results, the oxidized product may be formulated as $Mn_2L^1(OH)(H_2O)$, $Mn_2L^1(O)(H_2O)$, or $Mn_2L^1(OH)_2$. Its i.r. spectrum is practically the same as that of $[Mn_2L^1]$ except for bands at *ca.* 3 500 and 600 cm^{-1}. The former can be assigned to the O–H vibration. The latter band may be assigned to the Mn–O stretching mode, indicating the co-ordination of hydroxy- or oxo-anion to the metal.[27,28]

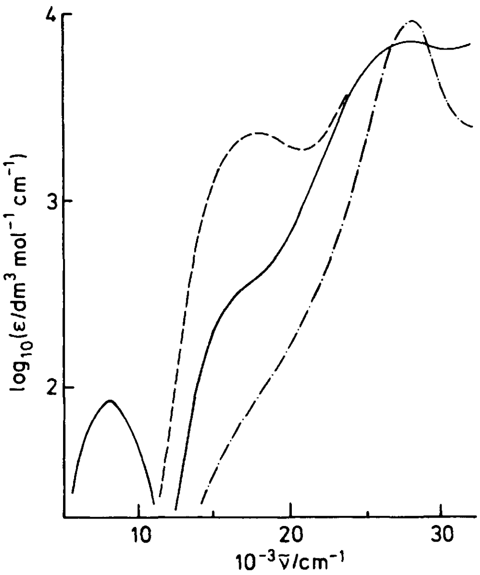

Figure 5. Electronic spectra in CH_2Cl_2 of $Mn_2L^1(OH)(H_2O)$ (———), its oxidized solution at 0 V (– – –), and its reduced solution at −1.30 V (— · —)

Table 1. Temperature variations of magnetic susceptibility and magnetic moment of $Mn_2L^1(OH)(H_2O)$

T/K	$10^2\chi_M$/e.m.u. mol^{-1}	$\mu_{eff.}$*/B.M.
87.4	4.665	5.71
93.0	4.549	5.82
103.5	4.361	6.00
113.2	4.190	6.16
126.9	3.928	6.31
139.5	3.865	6.41
153.3	3.447	6.50
166.3	3.251	6.68
179.2	3.074	6.64
193.5	2.892	6.69
207.7	2.739	6.75
221.1	2.612	6.80
234.2	2.502	6.85
247.8	2.397	6.89
261.3	2.291	6.92
273.0	2.213	6.95
285.6	2.121	6.96
298.5	2.048	6.99

* Magnetic moment per two manganese ions.

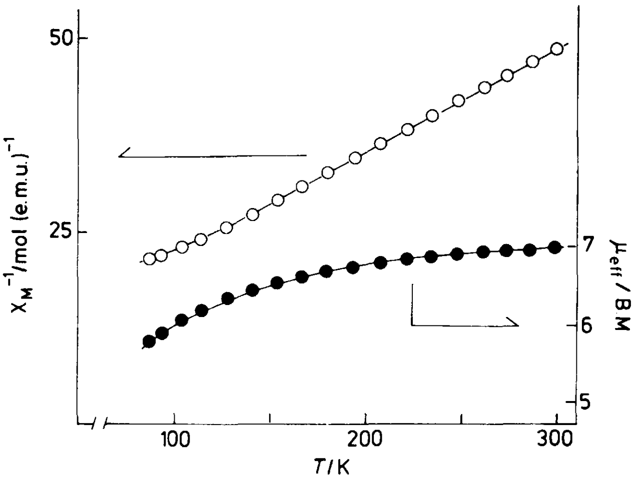

Figure 6. Temperature variations of inverse magnetic susceptibility and magnetic moment per molecule for the oxidized species. The solid curves are drawn based on the theoretical expression for the ($S = \frac{5}{2}$)–($S = 2$) system with the parameters $g = 1.98$ and $-J = 6.0$ cm^{-1}

In order to determine the oxidation states of the metal ions in the oxidized species, magnetic susceptibilities were measured in the range from 77 K to room temperature. The magnetic moment per molecule of the oxidised species is 7.0 B.M. at room temperature and decreases on lowering the temperature (Table 1). This suggests the existence of an antiferromagnetic spin-exchange interaction within the molecule. First it was attempted to interpret the cryomagnetic property in terms of the Van Vleck equation for the ($S = 2$)–($S = 2$) system based on the Heisenberg model, equation (1), where χ_A is the susceptibility per metal ion and other symbols have their usual meanings. A tolerably good agreement between the experimental and theoretical susceptibilities was achieved over the temperature range, with the magnetic parameters $g = 2.18$ and $J = -4.45$ cm^{-1}. However, such a large g value is quite unreasonable for a manganese(III) ion, because manganese(III) complexes are generally known to have a magnetic moment close to the spin-only value and thence a g value very close to 2.0.[29] Indeed, the g values for well characterized binuclear manganese(III) complexes with Schiff bases derived from salicylaldehydes and 3-aminopropanol are nearly 2.0.[30]

$$\chi_A = \left(\frac{Ng^2\beta^2}{kT}\right)\left(\frac{30\exp(20J/kT) + 14\exp(12J/kT) + 5\exp(6J/kT) + \exp(2J/kT)}{9\exp(20J/kT) + 7\exp(12J/kT) + 5\exp(6J/kT) + 3\exp(2J/kT) + 1}\right) + N\alpha \qquad (1)$$

In the Mn^{II}–Mn^{III} case, assuming that both metal ions are of high spin, the magnetic susceptibility per two metal ions is given by equation (2). As is seen in Figure 6, the experimental data can be well simulated by equation (2) with a reasonable g value of 1.97 and an exchange integral J of -6.0 cm^{-1}. In the evaluation of these parameters we have neglected the temperature-independent paramagnetism $N\alpha$, since it is generally small and is estimated to be *ca.* 1% (or less) of the total susceptibility at room temperature. Based on these magnetic investigations we may conclude that the oxidized species is a novel Mn^{II}–Mn^{III} mixed-valence complex of formula $Mn_2L^1(OH)(H_2O)$.

$$\chi_M = \left(\frac{Ng^2\beta^2}{kT}\right)\left(\frac{165\exp(24J/kT) + 84\exp(15J/kT) + 35\exp(8J/kT) + 10\exp(3J/kT) + 1}{5\exp(24J/kT) + 4\exp(15J/kT) + 3\exp(8J/kT) + 2\exp(3J/kT) + 1}\right) + N\alpha \qquad (2)$$

It is noteworthy that an appreciably strong antiferromagnetic spin-exchange interaction operates in this complex, while there is practically no interaction in the dimanganese(II) complexes. Previous studies have revealed a very weak ferromagnetic spin-exchange interaction in dicopper(II) complexes[13] and no magnetic interaction in di-iron(II) and di-iron(III) complexes [15] of $(L^1)^{4-}$ and $(L^2)^{4-}$. These facts suggest that direct spin-exchange is negligibly small even when the complexes adopt the stacked configuration. Thus, it is reasonable to assume that the antiferromagnetic interaction in $Mn_2L^1(OH)(H_2O)$ is of a superexchange mechanism through the hydroxy bridge. Based on considerations of the Dreiding model, a molecular structure with an Mn–O(H)–Mn bridge can be readily constructed where two MnN_2O_2 moieties are arrayed nearly parallel to each other with an interplanar distance of 3.3—3.5 Å. It is unclear, however, at present if the water molecule is co-ordinated to the metal or included in the crystal lattice.

It has been confirmed that $Mn_2L^1(OH)(H_2O)$ shows electrochemical behaviour essentially the same as that of oxidized solutions of $[Mn_2L^1]$ and $[Mn_2L^2]$. The differential pulse polarogram of $Mn_2L^1(OH)(H_2O)$ is given in Figure 7, which involves an oxidation wave at -0.26 V and a reduction wave at -0.77 V. When measured by cyclic voltammetry, both redox processes are found to be quasi-reversible, the difference between the cathodic and anodic peaks being 100 mV for the first couple and 90 mV for the second couple (Figure 8). We tentatively assign the wave at -0.26 V to the one-electron transfer process, Mn^{II}–$Mn^{III} \longrightarrow Mn^{III}$–$Mn^{III}$, and that at -0.77 V to Mn^{II}–$Mn^{III} \longrightarrow Mn^{II}$–$Mn^{II}$.

In order to verify this, controlled-potential electrolysis has been carried out for $Mn_2(L^1)(OH)(H_2O)$ and the electronic spectra of the electrolyzed solutions have been measured. Figure 5 shows the absorption spectra of the solution oxidized at 0 V and that reduced at -1.30 V. The former is a deep blue solution and exhibits an absorption at 18×10^3 cm^{-1} charac-

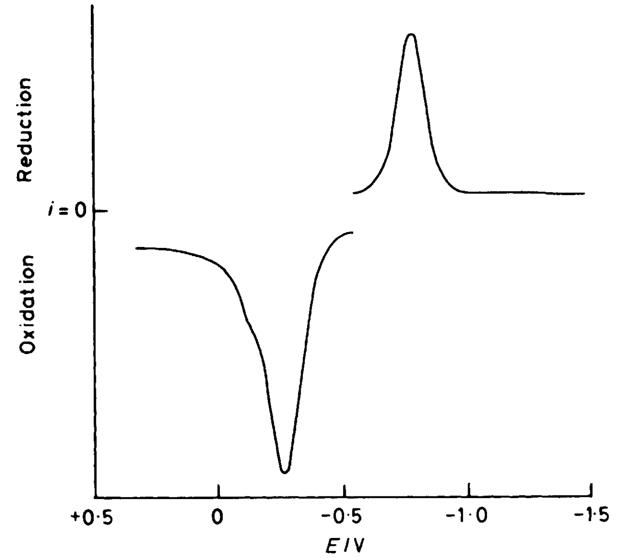

Figure 7. Differential pulse polarogram of $Mn_2L^1(OH)(H_2O)$ (6×10^{-4} mol dm^{-3}); scan rate 0.01 V s^{-1}

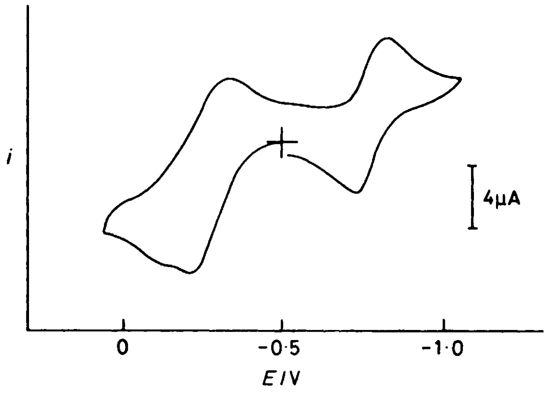

Figure 8. Cyclic voltammogram of $Mn_2L^1(OH)(H_2O)$ (6×10^{-4} mol dm^{-3}); scan rate 0.042 V s^{-1}

teristic of the manganese(III) complexes with salen-like Schiff bases.[31,32] The latter is a yellow solution and its electronic spectrum is very similar to that of $[Mn_2L^1]$ given in Figure 2. All of these facts clearly indicate a one-electron transfer for both processes, equation (3).

$$[\mathrm{Mn^{III}{}_2L^1(OH)(H_2O)}]^+ \overset{-0.26\ \mathrm{V}}{\rightleftharpoons} \mathrm{Mn^{II}Mn^{III}L^1(OH)(H_2O)} \overset{-0.77\ \mathrm{V}}{\rightleftharpoons} [\mathrm{Mn^{II}{}_2(L^1)(OH)(H_2O)}]^- \quad (3)$$

From a comparison of the spectrum of $Mn_2L^1(OH)(H_2O)$ with the spectra of its electrolyzed solutions, it is evident that the near-i.r. band (7.7×10^3 cm^{-1}) is characteristic of the mixed-valence complex. As far as we know, such a low-frequency band has not been observed for manganese(II) nor manganese(III) complexes with salen-like Schiff bases. Thus, we assign this band to the inter-valence transition between manganese(II) and manganese(III) ions.

Table 2. Solvent effects on the near-i.r. band of $Mn_2L^1(OH)(H_2O)$

Solvent	$(1/n^2) - (1/D)$	$10^{-3}\ \tilde{\nu}_{\max.}$/cm^{-1}
CH_3CN	0.53	7.8
NN-Dimethylformamide	0.46	7.8
CH_2Cl_2	0.38	7.7
C_6H_6	0	7.5

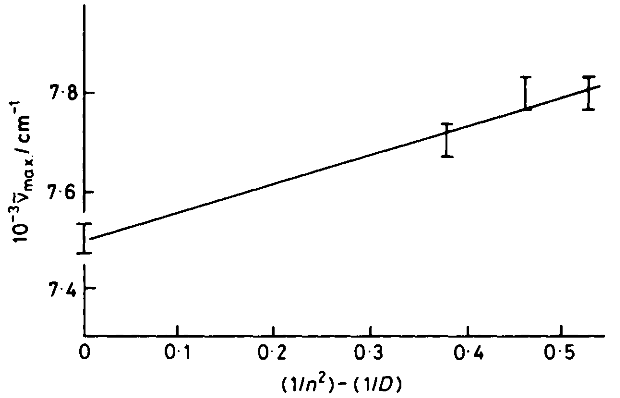

Figure 9. Plot of $\tilde{\nu}_{max.}$ *vs.* $(1/n^2) - (1/D)$ for $Mn_2L^1(OH)(H_2O)$

Hush[33] has predicted that the half-bandwidth, $\Delta\tilde{\nu}_{\frac{1}{2}}$, is equal to $(2.31\tilde{\nu}_{\max.})^{\frac{1}{2}}$. The half-width observed for the above near-i.r. band is *ca.* 4 400 cm^{-1}, which compares with the calculated value (4 500 cm^{-1}) from Hush's equation. The agreement with Hush's prediction is quite satisfactory compared with that for the mixed-valence complexes so far characterized.[34]

According to Hush's theory,[33] the energy of an inter-valence transfer band should vary with solvent according to $(1/n^2) - (1/D)$, where n is the refractive index and D the dielectric constant of the solvent. Thus, the near-i.r. band of the mixed-valence complex has been examined on changing the solvent; the results are given in Table 2. A plot of $\tilde{\nu}_{\max.}$ *vs.* $(1/n^2) - (1/D)$ is shown in Figure 9. Only small shifts are observed for the present complex probably because of the short metal–metal distance (*ca.* 3.3 Å: this was estimated from the Dreiding model); electron transfer in this complex entails a much smaller dipole moment change than in ruthenium complexes with a large metal–metal distance (*ca.* 7 Å).[35–37] Despite the very limited range of solvents used, the trend in the shift of the near-i.r. band agrees well with Hush's theory. All of these facts add strong support for the assignment of the near-i.r. band to the inter-valence transition.

According to Hush,[33] the delocalization coefficient, α^2, a measure of mixing of oxidation states, can be calculated from equation (4), where r is the distance between the metal ions

$$\alpha^2 = \frac{(4.25 \times 10^{-4})\varepsilon_{\max.}\Delta\tilde{\nu}_{\frac{1}{2}}}{\tilde{\nu}_{\max.}\, r^2} \quad (4)$$

(in Å) and other terms have their usual significance. For the present mixed-valence complex, the value of α^2 (*ca.* 0.0025) is obtained using $r = 3.3$ Å, $\tilde{\nu}_{\max.} = 7\,700$ cm^{-1}, $\varepsilon_{\max.} = 95$ dm^3 mol^{-1} cm^{-1}, and $\Delta\tilde{\nu}_{\frac{1}{2}} = 4\,400$ cm^{-1}. Thus, $Mn_2L^1(OH)(H_2O)$ belongs to the class II type in the classification of Robin and Day.[38] This is consistent with the fact that the spectrum contains both the absorption of manganese(III) (16.5×10^3 cm^{-1}) and the inter-valence absorption.

The present study has shown (*i*) that the strati-bis Schiff bases, $(L^1)^{4-}$ and $(L^2)^{4-}$, stabilize the lower oxidation states of manganese probably due to the intra-molecular stacking of the two co-ordination planes, and (*ii*) that the air-oxidized products of $[Mn_2L^1]$ and $[Mn_2L^2]$ are novel Mn^{II}–Mn^{III} mixed-valence class II complexes.[38]

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