# Fixation of Sulphur Dioxide by Manganese(II)-Schiff Base Complexes: Thermal Stability of these Adducts and the Possible Conversion of the Coordinated $SO_2$ to Sulphate

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**Abstract.** A series of manganese(II) complexes of general formula $MnL^n(H_2O)_m$ (where $H_2L^n$ are substituted N,N′-bis(salicylidene)-1,2-diimino-2,2-dimethylethane) have been prepared by electrochemical synthesis and characterized by analytical and spectroscopic techniques, magnetism and by studying their redox reversibility character by cyclic and normal pulse voltammetry. The reactivity of these complexes with sulphur dioxide has been investigated in the solid state and in toluene slurries at room temperature. The studies of the reversibility of the reaction (desorption studies) by thermogravimetrical analysis (TGD) have shown a different behaviour among the $SO_2$-adducts (from irreversible to totally reversible fixing), pointing to different $SO_2$ binding modes. Thus, adducts **10**, **12** and **14**, kept the $SO_2$ after TGD, signifying S−bridged $SO_2$ binding mode, while TGD for **8**, **9** and **13** revealed the lability of their $SO_2$, attributable to ligand bound $SO_2$ coordination. The manganese(II) precursor **4** is that one which has the ability of reversily fixing a major quantity of $SO_2$ and undergoes the sulphato reaction to form **11** also.

**Keywords:** Manganese; Schiff bases; Electrochemical synthesis; Sulphur dioxide

## Introduction

The study of the coordination chemistry of sulphur dioxide presents an increase interest because it is an extremely versatile ligand with a plentiful variety of coordination modes. Depending on the binding mode, the $SO_2$ is more or less activated and shows different reaction behaviour [1−3]. The understanding of this behaviour is crucial to the study of the linkage of this ligand with transition metals as a possible way to remove $SO_2$ from gas streams.

The emissions of sulphur dioxide to the atmosphere are becoming not only a growing environmental problem, which causes the acid rain (responsible from the damage of forests to the deterioration of buildings and historical monuments), but also a serious human health threat. Thus, recent epidemiologic studies have found an association between human mortality and $SO_2$ pollution among city populations [4]. $SO_2$ removal from flue gas is then an attractive research challenge that explains our interest in the binding of sulphur dioxide to transition metal complexes with the aim of developing systems for reversible coordination of this pollutant. So $SO_2$ could be recovered and used for other purposes, e.g., $H_2SO_4$ production [5, 6]. In our previous investigations on the binding of sulphur dioxide we have found reversible binding by series of $Mn^{II}$, $Fe^{II}$, $Co^{II}$ and $Cu^{II}$ complexes [6−8].

In this paper we report the reactivity of a series of new manganese(II)-Schiff base complexes towards $SO_2$ (see Scheme 1). Seven substituted N,N′-bis(salicylidene)-1,2-diimino-2,2-dimethylethane ($H_2L^n$) have been prepared by reacting the appropriately-substituted aldehyde with 1,2-diamino-2-methylpropane. It is well-known that this type of tetradentate ONNO Schiff base ligands tightly coordinates the manganese ion in a square-planar geometry, yielding much stable complexes [9]. These manganese-Schiff base complexes appear as suitable systems to bind $SO_2$ without decomposition [10, 11].

## Results and Discussion

### *Synthesis and characterization of complexes*

The reaction of the seven cited Schiff bases $H_2L^n$ with a manganese plate in an electrochemical cell yields a series of complexes **1-7** (see Scheme 1) with formulae $MnL^n(H_2O)_m$ [12]. The electrochemical efficiency of the cell, around 0.5 mol $F^{-1}$, is in accordance with the following mechanism of the reaction:

Cathode: $H_2L + 2e^- \rightarrow H_2(g) + L^{2-}$

Anode: $L^{2-} + Mn \rightarrow MnL + 2e^-$

This synthetic procedure allowed us to obtain these neutral complexes with high purity and in very good yield

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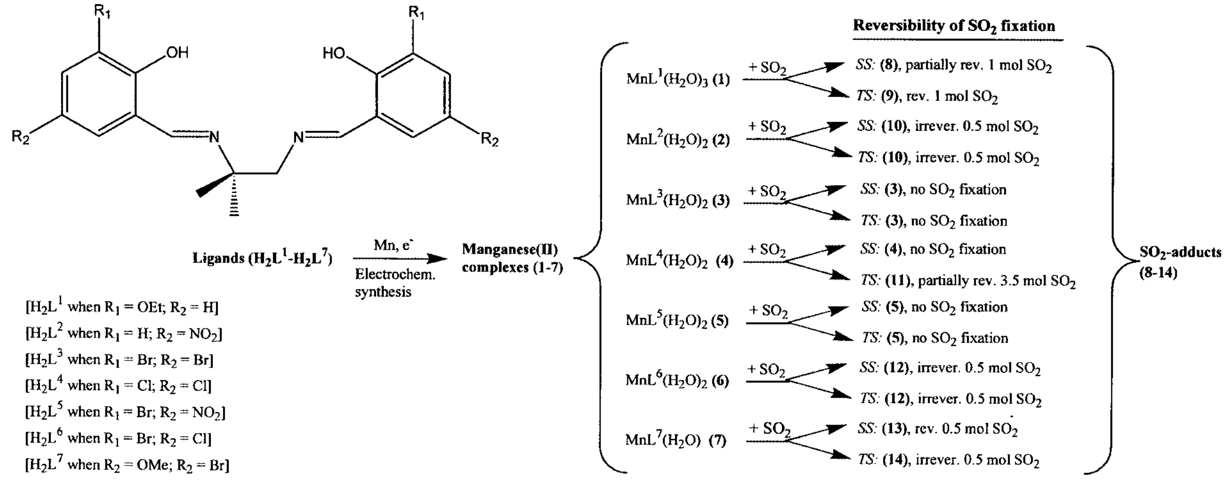

**Scheme 1** Structure of the ligands employed in the current study ($H_2L^1$-$H_2L^7$), and the resulting empirical formulae for the manganese(II) complexes (**1**-**7**), indicating the amount of reversible/irreversible $SO_2$ fixed by each one both in solid state (SS) and in toluene slurries (TS).

(Table 1). All these complexes seem to be air and thermal stable, melting above 300 °C without decomposition. Most of them are insoluble or sparingly soluble in water and common organic solvents, but soluble in polar coordinating solvents such as DMF, DMSO and pyridine.

The IR spectra of the complexes (Table 1) show a strong band between 1619 and 1637 $cm^{-1}$ attributable to $\nu(C{=}N)$. This band appears 4-12 $cm^{-1}$ shifted to lower frequency with respect to the free ligand. Moreover the $\nu(C{-}O)$ band is also shifted 7-42 $cm^{-1}$ to higher frequency with respect to the free ligand. This behaviour is compatible with the participation of both imine nitrogen and phenolic oxygen atoms in the coordination to the manganese ion, illustrating the dianionic and tetradentate character of these ligands in the complexes, as we have found earlier [13−15].

The FAB mass spectra show, in all cases, a peak due to the fragment $[MnL]^+$, which thus further corroborate coordination of these ligands to the metal atom. But other minor peaks, attributable to dimeric fragments $[Mn_2L_2]^+$, can be also detected in some cases.

Magnetic measurements were performed at room temperature for the complexes with diamagnetic corrections. Their magnetic moments are close to those expected for magnetically dilute $Mn^{II}$ ions, confirming the oxidation state II for the central atom and, therefore, that the ligands act as dianionics.

The electrochemical behaviour of the complexes in DMF solution was studied by cyclic and normal pulse voltammetry. The oxidation state +II for the manganese ions are confirmed by NPV, as they exhibited anodic and cathodic currents when the initial potentials were more positive than the wave voltage range. However, when the initial potentials were more negative than the wave voltage range, only an anodic current was observed. This behaviour suggests that only the reduced form of the implied redox system $Mn^{II}$-$Mn^{III}$ is present in solution, as we have previously reported [13].

A one-electron reduction-oxidation wave is observed by cyclic voltammetry for each complex except **1**, which suffers an irreversible one-electron oxidation process $[Mn^{II}] \rightarrow [Mn^{III}]$. The electron donor character of the ethoxy substituent in the phenyl ring of $H_2L^1$ determines the greater tendency of **1** to stabilise manganese(III). On the contrary those ligands with electron withdrawing groups (e.g. $NO_2$) seem to stabilise better the manganese(II) oxidation state and compounds with such ligands present higher oxidation potentials (0.422-0.495 V).

Most of the complexes (**2**-**7**) show both reduction and oxidation waves, which can be defined as quasi-reversible electrochemical behaviours (Fig. 1). Nevertheless the peak to peak separation is slightly longer than in other series of manganese(II) complexes derived from tetradentate Schiff

**Table 1** Elemental analysis, mass spectrometry (FAB), IR spectroscopy, magnetic moments at room temperature and voltammetric data for the complexes **1**-**7**.

| Complex | Colour | Found (Calcd.) (%) % N | % C | % H | FAB | IR spectra[b)] ($cm^{-1}$) $\nu(C{=}N)$ | $\nu(C{-}O)$ | μ (BM) | Redox potentials[c)] (V) Eox | Ered |
|---|---|---|---|---|---|---|---|---|---|---|
| $MnL^1(H_2O)_3$, **1** | brown | 6.0 (5.7) | 53.5 (53.7) | 6.3 (6.5) | 435 (870)[a)] | 1621 vs (1627) | 1299 s (1272) | 5.5 | −0.141 | [d)] |
| $MnL^2(H_2O)_2$, **2** | ochre | 11.6 (11.8) | 45.5 (45.5) | 3.9 (4.2) | 439 | 1637 s (1641) | 1340 s (1330) | 5.9 | 0.422 | 0.097 |
| $MnL^3(H_2O)_2$, **3** | brown | 3.6 (3.7) | 29.0 (28.8) | 2.2 (2.3) | 664 | 1633 vs (1645) | 1296 s (1274) | 5.7 | 0.096 | −0.112 |
| $MnL^4(H_2O)_2$, **4** | ochre | 5.5 (5.4) | 41.6 (41.3) | 3.3 (3.4) | 488 | 1622 vs (1627) | 1302 s (1293) | 5.8 | 0.092 | 0.002 |
| $MnL^5(H_2O)_2$, **5** | ochre | 8.6 (8.8) | 34.3 (34.1) | 2.9 (2.8) | 596 | 1635 s (1640) | 1335 s (1328) | 5.9 | 0.495 | 0.148 |
| $MnL^6(H_2O)_2$, **6** | ochre | 4.8 (4.6) | 35.2 (35.3) | 2.8 (2.9) | 417 | 1619 vs (1631) | 1299 s (1290) | 6.0 | 0.104 | −0.122 |
| $MnL^7(H_2O)$, **7** | brown | 5.0 (4.8) | 41.0 (41.0) | 4.0 (3.8) | 566 | 1625 vs (1632) | 1300 s (1258) | 5.6 | −0.062 | −0.332 |

[a)] fragment $[MnL]^+$, in parentheses $[Mn_2L_2]^+$; [b)] vs = very strong; s = strong; free ligand bands in parentheses; [c)] at scan rate 0.02 V $s^{-1}$; [d)] not observed.

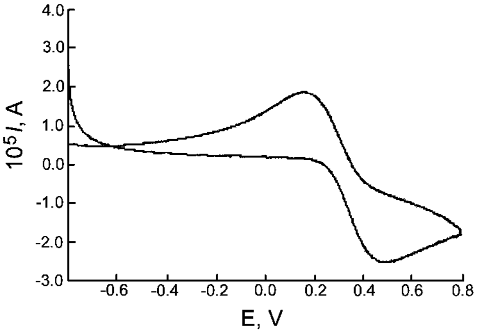

**Fig. 1** Cyclic voltammetry for **5** at a scan rate of 0.02 V $s^{-1}$.

base ligands [14, 16], highlighting a poorer reversible character for the present complexes.

Comparison of the electrochemical behaviour under stationary conditions with other series of monomeric manganese-Schiff base complexes [15, 16] shows lower current intensities for the present work compounds. The current intensity obeys the Randles-Sevcik equation [17], and all factors in this equation are similar for all the complexes, except for the diffusion coefficient of each. This behaviour could be attributed to a probably dimeric or polymeric structure of complexes **1-7**, which in fact present current intensities comparable to other polymeric manganese-Schiff base complexes [11, 18, 19].

### *Reactivity towards $SO_2$*

The reactivity of the manganese(II) complexes **1-7** towards sulphur dioxide at room temperature has been studied in the solid state (SS) and in toluene slurries (TS). The new $SO_2$-adducts were characterised by elemental analysis, IR spectroscopy, FAB spectrometry, desorption studies (see Table 2) and by comparison with other well-characterised systems [20−26]. A comparative study between the $SO_2$ adducts obtained from the solid state (**8**, **10**, **12**, **13**) and from toluene slurries (**9, 10, 11, 12**, **14**) shows that the metal precursor complexes can bind a greater quantity of sulphur dioxide in toluene slurry.

On the other hand, manganese precursors that incorporate Schiff bases with electron-donor groups on the phenyl rings were among those capable of fixing a larger quantity of $SO_2$. In contrast, electron-withdrawing substituents on the Schiff base phenyl rings do not favour the ability to bind $SO_2$. Such behaviour can be explained as a charge balance that starts when electron-withdrawing substituents provoke deficitary-charge rings, which subsequently accept charge from the phenoxy and imine groups. As result of this balance, the electronegativity of these last groups, which coordinate the manganese ion, decreases. The resulting lower basic character of these complexes restricts the ability to bind $SO_2$. Thus, for example, no $SO_2$-adduct was obtained after the interaction of $SO_2$ with precursors **3** or **5**.

The mass spectrometry analysis confirms the stability of the entity Mn-Schiff base, which always resists the reaction of the precursors towards $SO_2$. In this way, FAB mass spectra show molecular ions due to $[MnL]^+$ fragments, corroborating the fact that these Schiff bases are still coordinated to the manganese ion.

Comparative IR studies show remarkable changes in the spectra of the initial manganese complexes after exposure to $SO_2$, except for those that do not bind any gas (complexes **3**, **4** and **5** in solid state, and **3** and **5** in toluene slurry medium). Although *Kubas* [27] has tried to correlate the S−O stretching frequencies with the coordination mode of the sulphur dioxide in adducts of $SO_2$, it is immediately clear that overlaps between the IR regions for each mode do occur, so this technique cannot unequivocally provide bonding assignment and must be used in conjunction with other data. $SO_2$ lability studies are generally a good criterion to distinguish between some of these bonding modes, because $SO_2$ adducts with $\eta^1$−S pyramidal and ligand bound are labile and they lose sulphur dioxide easily, whereas desorption does not occur when sulphur dioxide is $\eta^1$−S planar or S−bridged. A positive way to allow us confirming the reversible or irreversible character of the $SO_2$ coordination is the investigation of the resulting products after the thermogravimetrical desorption studies of the $SO_2$-adducts by elemental analyses and IR spectra.

We can then propose $SO_2$ acting as S−bridged for compounds **10**, **12** and **14**, because on the one hand they clearly show the typical $\nu_s(SO_2)$ stretching frequencies for this bonding mode (1085-925 $cm^{-1}$), and on the other hand IR spectra recorded after the desorption studies showed no disappearance of these bands, which is indicative of a distinctive irreversible S−bridged $SO_2$ coordination. The fraction-

**Table 2** $SO_2$ lability by TGD and analytical, IR and MS data for the found adducts after interaction of the precursors with $SO_2$.

| Adducts formed | Medium[a)] | Found (Calcd.) | | | | FAB[b)] | IR spectra ($cm^{-1}$) | TGD[c)] |
|---|---|---|---|---|---|---|---|---|
| | | % N | % C | % H | % S | | | |
| $MnL^1\mathbf{(SO_2)}(H_2O)_2$, **8** | SS | 5.3 (5.2) | 48.9 (49.2) | 6.0 (5.6) | 5.9 (6.0) | 435 | $\nu_{as}(SO_2)$ 1121 [25] | Part. rev. |
| $MnL^1\mathbf{(SO_2)}(H_2O)_2$, **9** | TS | 5.3 (5.2) | 48.9 (49.2) | 5.8 (5.6) | 5.7 (6.0) | 435 | $\nu_{as}(SO_2)$ 1206, $\nu_s(SO_2)$ 1120 [25] | Rev. |
| $MnL^2\mathbf{(SO_2)_{0.5}}(H_2O)_2$, **10** | SS or TS | 11.0 (11.0) | 42.6 (42.6) | 4.0 (3.9) | 2.9 (3.1) | 439 | $\nu_s(SO_2)$ 1022 {S−bridge} | Irrever. |
| $MnL^4\mathbf{(SO_2)_{1.5}(HSO_4)_2}(H_2O)$, **11** | TS | 3.4 (3.5) | 27.2 (27.1) | 2.5 (2.3) | 13.9 (14.1) | 488 | $\nu(SO_4)$ 1113, 1001, 931, 616 {Sulphate} | Part. rev. |
| $MnL^6\mathbf{(SO_2)_{0.5}}(H_2O)$, **12** | SS or TS | 4.6 (4.5) | 34.9 (34.5) | 3.0 (2.6) | 2.4 (2.6) | 575 | $\nu_s(SO_2)$ 1034 {S−bridge} | Irrever. |
| $MnL^7\mathbf{(SO_2)_{0.5}}(H_2O)$, **13** | SS | 4.8 (4.5) | 38.7 (38.9) | 4.0 (3.6) | 2.6 (2.6) | 596 | $\nu_s(SO_2)$ 1092 {ligand bound} | Rev. |
| $MnL^7\mathbf{(SO_2)_{0.5}}(H_2O)$, **14** | TS | 5.0 (4.5) | 38.6 (38.9) | 4.0 (3.6) | 2.0 (2.6) | 596 | $\nu_s(SO_2)$ 1038 {S−bridge} | Irrever. |

[a)] Reaction medium: SS = Solid state; TS = Toluene slurry; [b)] fragment $[MnL]^+$, [c)] TGD: Thermogravimetrical desorption studies: Rev. = reversible; Part. rev. = partially reversible; Irrever. = irreversible

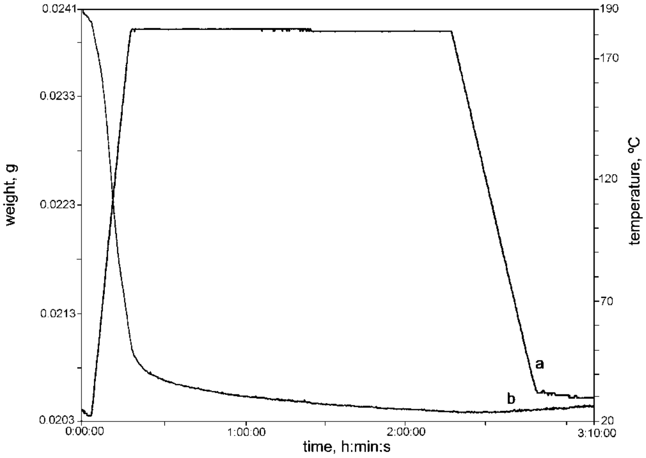

**Fig. 2** Desorption thermogramme for **9**: a) represents the temperature and b) the curve of the variation of mass versus temperature and time, showing a loss of about 15 %.

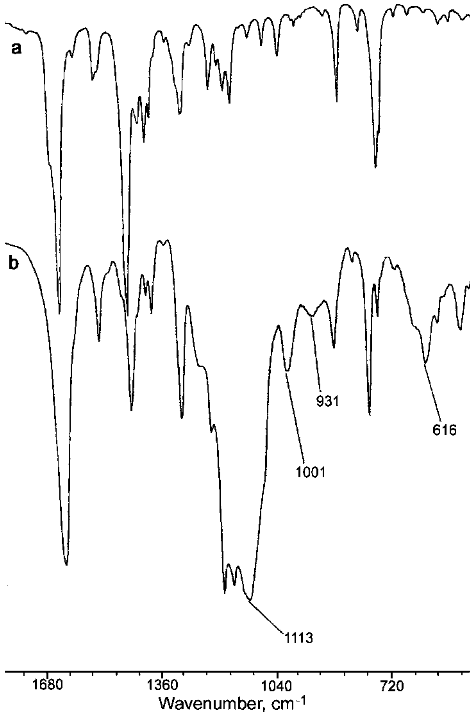

**Fig. 3** a) IR spectrum of **4**, and b) IR absorption bands for hydrogensulphate group in **11** after exposition of **4** to $SO_2$ in toluene slurry.

ary stoichiometry of the $SO_2$ adducts, deduced from the analytical data in Table 2, is also indicative of their polymeric nature.

A parallel comparative study establishes a second shared pattern for adducts **8**, **9** and **13**, which presents IR bands attributable to ligand bound $SO_2$ coordination, characterized by a reversible character. Thermogravimetrical desorption studies point to such assignment (Fig. 2), although **8** only present a partially reversible behaviour, which may mean the presence of another different coordination mode in this adduct that we are unable to establish in an unequivocally way. But the experimental data does allow rejection of the $\eta^1{-}S$ pyramidal binding mode for these three adducts because they are air stable and none of them undergo the sulphato reaction. The so-called sulphato reaction takes place with $SO_2$ adducts containing $\eta^1{-}S$ pyramidal group [27].

A particular case study is **11**, which merits further discussion, because it really suffers the sulphato reaction and also binds $SO_2$ in a reversible way. The manganese(II) complex **4** does not fix any $SO_2$ in solid state but its exposition to $SO_2$ in toluene slurry medium is able to bind 3.5 molecules of $SO_2$, two of them evolute through the sulphato reaction with, apparently, the hydrated water molecules because all the processes were done under inert atmosphere with Schlenk techniques. The resulting product, **11**, keeps 1.5 molecules of $SO_2$, but it also presents two hydrogensulphate groups, according with the elemental analysis, the IR spectroscopy, and the magnetic moment of 3.9 B. M., which is attributable to $Mn^{IV}$. The hydrogensulphate groups are easily identifiable by $\nu(HSO_4)$ frequencies [28] at 1113, 1001, 931 and 616 $cm^{-1}$ (Fig. 3), indicating the loss of the tetrahedral symmetry of the sulphate anion. This sulphate reaction involves a previous $\eta^1{-}S$ pyramidal coordination mode, with an acid behaviour through the sulphur atom, that is quite unusual in first row transition metal complexes, in contrast with the adducts of second and third row transition metals, because *d* orbitals of the first transition series have lower energies than those of the second and third rows, ensuing higher stability of their HOMO orbitals, which do not favours a charge transfer to an acidic $SO_2$.

On the other hand, it is well known that transition metals catalyse the oxidation of sulphur dioxide in the atmosphere [29]. This oxidation has been observed in a large number of reactions studied in solution with $Mn^{II}$, $Fe^{III}$, $Co^{II}$, $Cu^{II}$ and $Zn^{II}$ complexes, where $HSO_4^-$ and/or $SO_4^{2-}$ were found [6−8, 23].

## Conclusions

Studies on the reactivity of manganese(II)-Schiff base complexes towards $SO_2$ demonstrate that those are suitable precursors to study the interaction with this noxious gas because: a) most of the complexes absorb $SO_2(g)$ in a manner that could be connected with the basicity of the complexes (that indeed could be modulated by the choice of the substituents on the phenyl rings of the Schiff base); b) the manganese-Schiff base entity seems to be stable towards $SO_2$, fixing the molecule/s without decomposition; c) the redox properties of the manganese-Schiff base systems would allow in some cases their catalysis of the oxidation of sulphur dioxide to sulphate or hydrogensulphate.

Manganese(II) complex **4** arises as a particular interesting precursor to fix $SO_2$ in an important quantity. The gas is, in this case, coordinated through $\eta^1{-}S$ pyramidal coordination mode, which involves both reversibility and the possibility of undergoing the sulphato reaction.

However, we have also found different $SO_2$ binding modes among the present series of adducts, proposing S−bridging for **10**, **12** and **14**, and ligand bound for **8**, **9** and **13**.

## Experimental Part

**General:** Salicylaldehydes (Maybridge) and 1,2-diamino-2-methylpropane (Aldrich) were used as received without further purification. Manganese (Ega Chemie) was used as *ca.* 2 x 2 $cm^2$ plate. Elemental analyses were performed on a Carlo Erba 1108 CHNS−O elemental analyser. The IR spectra were recorded as KBr discs on a Nicolet PC5 FT-IR spectrophotometer. $^1H$ NMR spectra were recorded on a Bruker WH 300 MHz spectrometer using $CDCl_3$ as solvent. FAB mass spectra were recorded on a Kratos MS50 TC spectrometer connected to a DS90 data system, using m−nitrobenzyl alcohol as a matrix. Room-temperature magnetic susceptibilities were measured using a Digital Measurement system 1660 vibrating magnetometer operating at 5000 G. $HgCo(NCS)_4$ was employed as a susceptibility standard.

Cyclic and normal pulse voltammetry was performed with a Princeton Applied Research model 270 potentiostat and potential scanning unit with the operating program ECHEM. A Metrohm graphite disc (area 0.07 $cm^2$) coupled to a Metrohm model 628-10 rotating electrode device was used as a working electrode; a saturated calomel electrode was used as a reference and a Pt wire as an auxiliary electrode. Voltammograms were obtained from *ca.* 1 mM solutions of the complexes in DMF using 0.2 M $Bu_4NPF_6$ as a supporting electrolyte. All experiments were carried out under an atmosphere of dry $N_2$. Cyclic voltammetry measurements were performed with a static graphite electrode, whilst direct-current and pulse voltammograms were recorded with the graphite disc rotating at 2000 revolutions per minute.

Thermogravimetrical analyses were performed using a CAHN Instruments TG131 apparatus, the inert gas (nitrogen) flow being maintained at 50 $cm^3$ $min^{-1}$.

### *Synthesis of the Schiff bases*

The Schiff bases were prepared by a traditional method by the reaction of the appropriately substituted salicylaldehyde with the diamine, and is typified by the preparation of $H_2L^1$. To an ethanolic solution (100 mL) of 1,2-diamino-2-methylpropane (0.83 mL, 7.8 mmol) was added 3-OEt-salicylaldehyde (2.60 g, 15.60 mmol). The resultant yellow solution was refluxed for two hours over a Dean-Stark trap, then was concentrated. The solid which precipitated was collected by filtration, washed with diethylether and dried *in vacuo*. The purity of the prepared ligands was checked by elemental analysis, mass spectrometry, IR and $^1H$ NMR spectroscopy.

**$H_2L^1$**. Elemental analysis: $C_{22}H_{28}N_2O_4$ (M. W. = 384.47): C, 68.8 (68.7); N, 7.1 (7.3); H, 7.0 (7.3) %; m.p. 77 °C.

**$^1H$ NMR** (300 MHz, $CDCl_3$): $\delta$ = 1.43 (s, 6H), 1.52 (t, 6H), 3.71 (s, 2H), 4.05 (q, 4H), 6.6-6.9 (m, 6H), 8.26 (s, 2H), 13.70 (s, 2H) ppm.
**IR** (KBr): $\nu(CN_{imine})$ 1627 vs, $\nu(CO)$ 1272 s $cm^{-1}$.

**$H_2L^2$**. Elemental analysis: $C_{18}H_{18}N_4O_6$ (M. W. = 386.36): C, 55.4 (56.0); N, 14.3 (14.5); H, 4.6 (4.7) %; m.p. 233 °C.

**$^1H$ NMR** (300 MHz, $CDCl_3$): $\delta$ =1.43 (s, 6H), 3.91 (s, 2H), 6.9-8.0 (m, 6H), 8.45 (s, 1H), 8.54 (s, 1H) 13.65 (s, 1H), 14.22 (s, 1H) ppm.
**IR** (KBr): $\nu(CN_{imine})$ 1641 vs, $\nu(CO)$ 1330 s $cm^{-1}$.

**$H_2L^3$**. Elemental analysis: $C_{18}H_{16}Br_4N_2O_2$ (M. W. = 611.94): C, 35.5 (35.3); N, 4.2 (4.6); H, 2.6 (2.6) %; m.p. 137 °C.

**$^1H$ NMR** (300 MHz, $CDCl_3$): $\delta$ = 1.45 (s, 6H), 3.77 (s, 2H), 7.3-7.7 (m, 4H), 8.18 (s, 1H), 8.20 (s, 1H) 14.1 (s, 1H), 15.0 (s, 1H) ppm.
**IR** (KBr): $\nu(CN_{imine})$ 1625 vs, $\nu(CO)$ 1274 s $cm^{-1}$.

**$H_2L^4$**. Elemental analysis: $C_{18}H_{16}Cl_4N_2O_2$ (M. W. = 434.14): C, 49.6 (49.8); N, 6.4 (6.5); H, 3.6 (3.7) %; m.p. 150 °C.

**$^1H$ NMR** (300 MHz, $CDCl_3$): $\delta$ = 1.46 (s, 6H), 3.80 (s, 2H), 7.1-7.4 (m, 4H), 8.17 (s, 1H), 8.20 (s, 1H) 14.05 (s, 1H), 14.82 (s, 1H) ppm.
**IR** (KBr): $\nu(CN_{imine})$ 1627 vs, $\nu(CO)$ 1293 s $cm^{-1}$.

**$H_2L^5$**. Elemental analysis: $C_{18}H_{16}Br_2N_4O_6$ (M. W. = 544.14): C, 39.7 (39.7); N, 10.0 (10.3); H, 3.0 (3.0) %; m.p. 243 °C.

**$^1H$ NMR** (300 MHz, $CDCl_3$): $\delta$ = 1.60 (s, 6H), 3.90 (s, 2H), 8.2-8.4 (m, 4H), 8.51 (s, 1H), 8.52 (s, 1H) 15.0 (s, 1H), 15.7 (s, 1H) ppm.
**IR** (KBr): $\nu(CN_{imine})$ 1640 vs, $\nu(CO)$ 1328 s $cm^{-1}$.

**$H_2L^6$**. Elemental analysis: $C_{18}H_{16}Br_2Cl_2N_2O_2$ (M. W. = 523.03): C, 40.9 (41.3); N, 5.2 (5.4); H, 3.2 (3.1) %; m.p. 154 °C.

**$^1H$ NMR** (300 MHz, $CDCl_3$): $\delta$ = 1.37 (s, 6H), 3.61 (s, 2H), 7.0-7.4 (m, 4H), 8.03 (s, 1H), 8.09 (s, 1H) 13.9 (s, 1H), 14.7 (s, 1H) ppm.
**IR** (KBr): $\nu(CN_{imine})$ 1631 vs, $\nu(CO)$ 1290 s $cm^{-1}$.

**$H_2L^7$**. Elemental analysis: $C_{20}H_{22}Br_2N_2O_4$ (M. W. = 514.20): C, 46.5 (46.7); N, 5.6 (5.4); H, 4.5 (4.3) %. m.p. 133 °C.

**$^1H$ NMR** (300 MHz, $CDCl_3$): $\delta$ = 1.42 (s, 6H), 3.72 (s, 2H), 3.88 (s, 6H), 6.9-7.3 (m, 4H), 8.21 (s, 1H), 8.23 (s, 1H) 13.80 (s, 1H), 14.45 (s, 1H) ppm.
**IR** (KBr): $\nu(CN_{imine})$ 1632 vs, $\nu(CO)$ 1258 s $cm^{-1}$.

### *Electrochemical synthesis*

The complexes were obtained following an electrochemical procedure. The cell was a beaker (100 $cm^3$) fitted with a rubber bung, through which the electrochemical leads entered the cell [30]. A manganese metal platelet was suspended from a platinum wire and a platinum wire was used as a cathode. The Schiff base ligand (ca 0.4 g) was dissolved in acetonitrile (40 $cm^3$) and a small amount of tetramethylammonium perchlorate was added as a supporting electrolyte. During electrolysis nitrogen was bubbled through the solution to ensure the presence of an inert atmosphere, with the current being provided by a purpose built d. c. power supply. The cells can be summarized as follows: Pt(−)/MeCN + $H_2L^n$/Mn(+). During electrolysis hydrogen gas was evolved at the cathode. The solids were collected by filtration and washed successively with acetonitrile and diethyl ether before drying *in vacuo*.

### *Reactivity towards $SO_2$ in the solid state*

Exposure to $SO_2$ was carried out in a small Rotaflo tube by observing the increase in mass of a sample (0.20 g) of the complex. The vessel was initially evacuated and charged with the complex under an Ar atmosphere. The Ar was removed and the tube was filled with $SO_2$ at 1 atm pressure. Further $SO_2$ was added over several days until a constant mass was achieved. Full details of this procedure have been published previously [31].

### *Reactivity towards $SO_2$ in toluene slurries*

The metal complex (*ca.* 0.20 g) was placed in a predried round-bottomed flask fitted with a side arm and ground glass tap against a flow of Ar. Dry distilled toluene (100 $cm^3$) was added and the flask was then evacuated. The suspension was saturated with $SO_2$ and the flask was then sealed and the contents stirred for *ca.* 7

days, after which time the products were isolated by Schlenk techniques and dried in a stream of Ar.

## *Thermogravimetrical analysis*

Studies of the reversibility of the $SO_2$ absorption were performed with a thermogravimetrical balance TG-131 CAHN, by heating the adducts at 180 °C for 2 h under a $N_2$ stream. The mass-changes were monitored during the process. The resultant complexes were characterised by elemental analysis and IR spectroscopy.

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