Chloride as Supramolecular Glue: Anion-Directed Assembly of a 2D Network of Mn^{III} Complexes

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The Schiff base H_4L [where H_4L = *N*,*N*′-bis(3-hydroxysalicylidene)ethane-1,2-diamine], containing six potential donor atoms, is able to induce the formation of a novel [Mn^{III}(H_2L)(CH_3OH)$_2$]Cl (**1**) complex, which was characterized by elemental analysis, FAB mass spectrometry, IR, ^{1}H NMR and electronic spectroscopy, magnetic measurements, X-ray diffraction techniques and conductivity measurements. The study of its redox properties by cyclic and normal pulse voltammetry is also reported. The crystal structure of **1** is formed by monomeric cationic Mn^{III} complexes, where the manganese ion is in an octahedral environment and is coordinated in the equatorial plane to the N_2O_2 donor set of the inner Schiff-base compartment. The neutral condition of the complex is achieved with the presence of the chloride counterion, which behaves as a multiple acceptor of hydrogen bonds. The chloride is involved in four O–H···Cl bonds, connecting three neighbouring cationic complexes. To the best of our knowledge, this constitutes the first example of self-assembly of discrete units of Mn^{III} complexes in a 2D network in the solid state through hydrogen bonding, where the anion is acting as a supramolecular glue.

Introduction

Of the first-row transition metals, manganese has a particularly appealing coordination chemistry due to its rich redox behaviour, as demonstrated by the variety of structures and oxidation states in polynuclear manganese complexes.[1−3] In particular, manganese(III) derivatives from tetradentate Schiff-base ligands have a clear tendency to form infinite linear or helical chains, due to the predisposition of these ligands to occupy a planar configuration in an octahedral coordination geometry, leaving the axial positions free to develop polymerization through bidentate bridges.[4,5] Occasionally manganese−Schiff-base complexes can produce dimeric structures with μ-phenoxo[4b,4f,5] or μ-oxo bridges with the ligand in the equatorial plane around each metal centre[6] or, alternatively, μ-oxo bridges with the two ligands bridging both metal ions.[4b,4e,8] Moreover, some 2D polymerization processes via coordinative bonding have been reported.[9] In contrast, the aggregation of manganese(III) discrete complexes or infinite chains in multidimensional frameworks by metal-free supramolecular interactions (hydrogen bonding, π-π stacking, and so forth) are particularly rare.[10]

In the last years, part of our research program has been focused on reproducing the reactivity of some manganese redox enzymes, and we have reported an important number of active synthetic models of Mn^{III} systems derived from Schiff-base ligands. With the skill and the motivation acquired due to our recent successes in the construction of very appealing supramolecular architectures,[11] we are now interested in investigating the overlooked supramolecular chemistry of manganese(III). In particular, our new scheme consists in obtaining the aggregation of discrete manganese(III) complexes into multidimensional arrays through metal-free self-assembly.

In this paper we describe the results of this research work. We believed that the insertion of extra donor atoms out of the classical tetradentate compartment of a salen-type ligand would favour the aggregation of neighbouring complexes through hydrogen bonding. This represents a class of weaker, non-covalent interactions that not only induce supramolecular arrays through self-organization of molecules, but also plays a crucial role in fundamental biological processes, such as the expression and transfer of genetic information, and is essential for molecular recognition between receptors and substrates.[12] For this purpose, we designed the ligand H_4L that contains six potential donor atoms: two imine nitrogen and four phenolic oxygen atoms. The reaction of H_4L with manganese(II) chloride, in fact,

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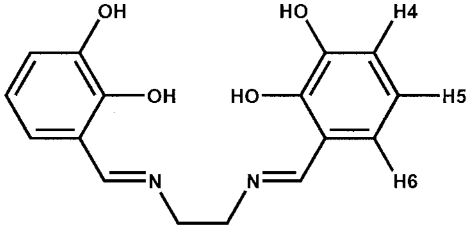
yields a supramolecular system, which we report herein and where the main intermolecular interactions come from the special role of the halide counterion as a kind of supramolecular glue. This type of networks, which have the ability to bind negatively charged ions, also constitute a hot subject of research in recent years due to their potential ability and selectivity to recognize anion receptors in solution.[13,14]

Results and Discussion

The hexadentate Schiff base, H_4L (see Scheme 1), reacts with the manganese(II) chloride salt to yield a black crystalline complex with the formula $[Mn(H_2L)(CH_3OH)_2]Cl$ (**1**), in accordance with the elemental analysis. The solid appears to be stable in the solid state and in solution; it melts at over 300 °C and is insoluble or sparingly soluble in water and also in common organic solvents, but quite soluble in MeOH, DMF and DMSO.



Scheme 1. Structure of the Schiff-base ligand H_4L

Spectroscopy techniques verified the coordination of the ligand to the manganese ion. Thus, the IR spectrum of **1** shows the shift of the $\nu(CN_{imine})$ band to lower frequency (-13 cm^{-1}) and a positive shift of the $\nu(CO_{phenol})$ mode ($+13$ cm^{-1}) with respect to the free ligand. These data suggest the coordination of the Schiff base in its dianionic form through the inner phenol oxygen and the imine nitrogen atoms.[14] The absence of $\nu(Mn-Cl)$ bands in the far IR spectrum indicates that the metal is not coordinated to the chloride, as confirmed by the crystal structure of this complex. The FAB mass spectrum shows a peak due to the fragment $[Mn(H_2L)]^+$, which thus further corroborates coordination of the ligand to the manganese ion.

The room temperature magnetic moment of **1** is 4.8 B.M., close to the spin-only value of 4.9 B.M., as expected for a high-spin magnetically diluted d^4 manganese(III) ion. The magnetic behaviour obeys the Curie−Weiss law in the range 40−300 K, showing little or no antiferromagnetic interaction between neighbouring metal centres. The electronic spectrum in methanol solution is also typical of a manganese(III) ion in an octahedral environment. On other hand, the conductivity measurements in DMF give a Λ_M value of 90 μS cm^{-1} for **1**, indicating behaviour that is attributable to 1:1 electrolytes.[16]

X-ray Diffraction Studies

Single crystals of $[Mn(H_2L)(CH_3OH)_2]Cl$ (**1**), suitable for X-ray diffraction studies were obtained as detailed in the Exp. Sect. An ORTEP view of **1**, together with the atomic numbering scheme, is shown in Figure 1. Experimental details are given in Table 1. Main bond lengths and angles are listed in Table 2. This structure reveals the existence of a cationic octahedral $[Mn(H_2L)(CH_3OH)_2]^+$ complex; the neutral condition is achieved by the presence of a chloride anion, which acts as a counterion despite the known tend-

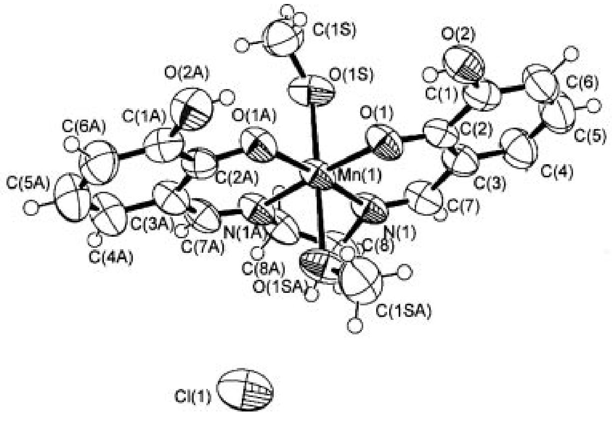


Figure 1. ORTEP plot of **1**; atoms showing the atomic numbering scheme are represented by their 50 % probability ellipsoids; symmetry operation to generate equivalent atoms: A $-x+2, y, -z+1/2$

Table 1. Crystal data and structure refinement for **1**

Empirical formula	$C_{18}H_{22}ClMnN_2O_6$
Molecular weight	452.77
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Pbcn*
a (Å)	7.6793(7)
b (Å)	14.8888(13)
c (Å)	17.7322(16)
Volume (Å^3)	2027.4(3)
Z	4
$D_{calcd.}$ (g cm^{-3})	1.483
Absorption coefficient (mm^{-1})	0.819
F(000)	936
Crystal size (mm)	0.40 × 0.30 × 0.30
Theta range for data collection	2.30 to 28.30°
Reflections collected	13540
Independent reflections	2527 (R_{int} = 0.0368)
Completeness to θ = 28.30°	99.9 %
Absorption correction	Empirical
Max. and min transmission	0.7911 and 0.7352
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2527/0/160
Goodness-of-fit on F^2	1.012
Final R_{int} [$I>2\sigma(I)$]	$R1 = 0.0366$, $wR2 = 0.0888$
R_{int} (all data)	$R1 = 0.0729$, $wR2 = 0.1017$
Largest diff. peak and hole	0.213 and −0.190 e·Å^{-3}

Table 2. Selected bond lengths (Å) and angles (°) for **1**

Mn(1)−O(1)	1.8755(14)	O(1)−Mn(1)−O1(A)	94.06(9)
Mn(1)−O(1A)	1.8755(14)	O(1)−Mn(1)−N(1A)	173.90(7)
Mn(1)−N(1)	1.9809(17)	O(1)−Mn(1)−N(1)	92.00(7)
Mn(1)−N(1A)	1.9809(17)	O(1A)−Mn(1)−N(1)	173.90(7)
Mn(1)−O(1S)	2.2675(19)	O(1A)−Mn(1)−N(1A)	92.00(7)
Mn(1)−O(1SA)	2.2675(19)	N(1)−Mn(1)−N(1A)	81.96(11)
Mn···Mn	7.67(9)	O(1)−Mn(1)−O(1S)	91.18(7)
		O(1A)−Mn(1)−O(1S)	91.21(7)
		N(1)−Mn(1)−O(1S)	89.37(7)
		N(1A)−Mn(1)−O(1S)	87.97(7)
		O(1S)−Mn(1)−O(1SA)	176.48(9)

H bonds D−H···A	d(D−H)	d(H···A)	d(D···A)	<(DHA)
O(1S)−H(1S)···Cl(1)#1[a]	0.73(3)	2.35(3)	3.081(2)	178(3)
O(2)−H(2A)···Cl(1)#2	0.77(3)	2.55(3)	3.218(2)	146(2)
O(2)−H(2A)···O(1)	0.77(3)	2.31(3)	2.668(2)	103.6(10)
C(7)−H(7)···O(2)#3	0.86(2)	2.51(7)	3.143(3)	130.6(2)

[a] Symmetry transformations used to generate equivalent atoms: #1 $x + 1/2, +y + 1/2, -z + 1/2$; #2 $x + 1, +y, +z$; #3 $x + 1/2, -y + 1/2 + 1, -z$.

ency to appear coordinated to the metal ion in similar Mn^{III} compounds.[4b,17]

The structure of discrete mononuclear $[Mn(H_2L)(CH_3OH)_2]^+$ cations comprises the planar Schiff-base ligand tightly bound to manganese(III) through the inner N_2O_2 compartment through the N_{imine} and O_{phenol} atoms ($Mn-N_{imine}$ bond lengths of 1.9809(17) Å and $Mn-O_{phenol}$ 1.8755(14) Å, typical of such complexes).[4,18] The coordination spheres of the slightly distorted octahedral manganese centres are then completed by capping *trans* methanol molecules [$Mn-O_{methanol}$ 2.2675(19) Å]. The elongation in the *trans* $Mn-O_{methanol}$ bonds is usually attributed to a Jahn−Teller distortion for a d^4 high-spin Mn^{III} system but in this case the poor donor strength of the methanol molecules may also contribute to this elongation. The MnN_2O_2 core forms two six-membered chelate rings, which are nearly planar [maximum deviation of any atom from its least-squares calculated plane is −0.1170(11) Å, with the manganese atom 0.1027(09) Å above this plane]. This indicates a slight distortion from the ideal geometry. The slight distortion of the octahedron is also shown by the angles between the manganese and adjacent donor atoms, which range from 81.96(11)° to 94.06(9)°. The angle between the metal atom and the *trans* donor atoms is 176.48(9)°. All distances and angles lie in the range expected for this type of Mn^{III} complexes;[4,17,18] the N(1)−C(7) bond length of 1.277(3) Å suggests a double bond, which is confirmed by the IR spectrum with a strong vibration band at 1620 cm^{-1}.

The $[Mn(H_2L)(CH_3OH)_2]^+$ cations are interconnected through the chloride anions by hydrogen bonds yielding a supramolecular structure. Each chloride anion is involved in four O−H···Cl hydrogen bonds with four different hydroxy groups from three neighbouring cationic complexes (see Figure 2).

Two of these interactions are in the range of strong hydrogen bonds with an almost linear angle O−H···Cl, and involve the hydroxy groups from the axial methanol ligands of two different complexes [H(1S)···Cl(1) 2.35(3), O(1S)···Cl(1) 3.081(2) Å and O(1S)−H(1S)···Cl(1) 178(3)°] (see Table 2).

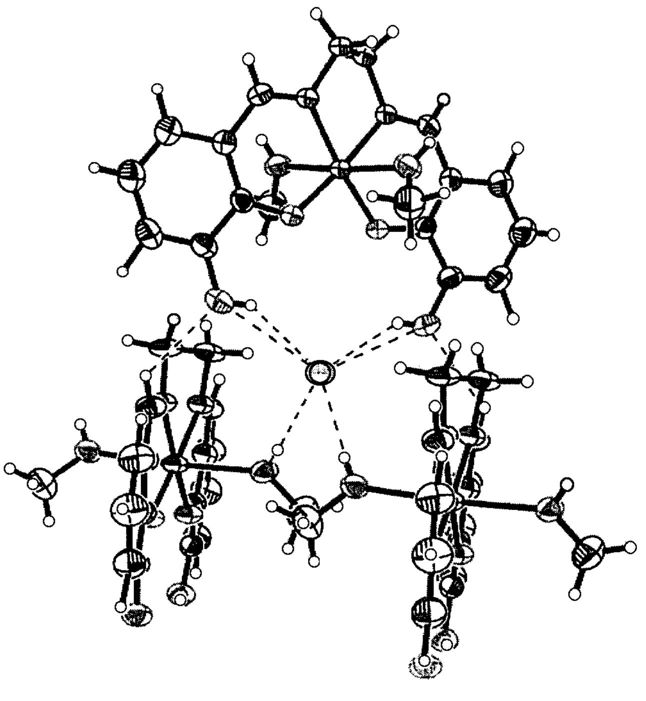


Figure 2. Part of the unit cell of **1**, exhibiting the net of interactions between three neighbouring cationic complexes; the chloride anion is tetra-coordinated to four hydroxy groups through hydrogen bonding

The other two intermolecular contacts imply the outer hydroxy groups of the third complex [H(2A)···Cl(1) 2.55(3), O(2)···Cl(1) 3.218(2) Å and O(2)−H(2A)···Cl(1) 146(2)°], and can be categorized as intermediate in strength,[19] probably because of the additional interaction of these outer hydroxy groups with the inner hydroxy groups through intramolecular hydrogen bonding [H(2A)···O(1) 2.31(3), O(2)···O(1) 2.668(2) Å and O(2)−H(2A)···O(1) 103.6(10)°].

This rich supramolecular structure is completed and further stabilized with intermolecular hydrogen bonds between carbon atoms from imine groups and oxygen atoms from the free phenolic sets of adjacent molecules. In this case the H(7)···O(2) distance is of 2.51(7) Å, the C(7)···O(2) distance is of 3.143(3) Å, and the C(7)−H(7)···O(2) angle is 130.6(2)°.

The packing of **1** determines the existence of a supramolecular structure in which the chloride counterions are acting as multiple acceptors, connecting three neighbouring complexes through very different hydrogen bonding. However, the Mn···Mn distances of 7.67(9) Å are too long to establish intermetallic interactions between neighbouring manganese ions, which is in accordance with the non-antiferromagnetic behaviour showed by the magnetic studies.

These multiple intermolecular interactions are extended into the solid to form an infinite array (see Figure 3) constituting, to the best of our knowledge, the first example of an anion-directed assembly of a 2D network of manganese(III) complexes.

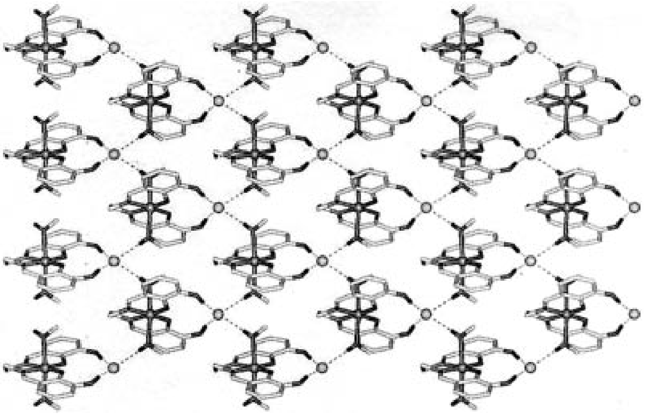


Figure 3. Perspective view of the 2D network formed, which shows the chloride's role as supramolecular glue in the assembly of the manganese(III) complexes

^{1}H NMR Studies

Paramagnetic ^{1}H NMR studies of **1** were undertaken using [D$_6$]DMSO as a solvent, and the data serve to substantiate the formation of the manganese(III) complex. The spectrum of **1** is essentially as would be expected, in accordance with the assignments proposed by Pecoraro[20] and also from our own results.[4d,18] The spectrum contains two upfield proton resonances at −16.3 and −28.1 ppm that lie outside the diamagnetic region (δ ca. 0−10) and must arise from the H5 and H4 protons of the aromatic rings, respectively.[4d]

Electrochemical Studies

The electrochemical behaviour of **1** in DMF solution was studied by cyclic and normal pulse voltammetry (see Figure 4). The oxidation state +III for the manganese ion in DMF solutions of **1** is determined by NPV, as it exhibited anodic and cathodic currents when an anodic potential scan was performed (Figure 4b), but when a cathodic potential scan was used, only cathodic current was observed (Figure 4c). This behaviour suggests that only the oxidized form of the implied redox system Mn^{II}−Mn^{III} is present in solution, as we have previously reported.[4b]

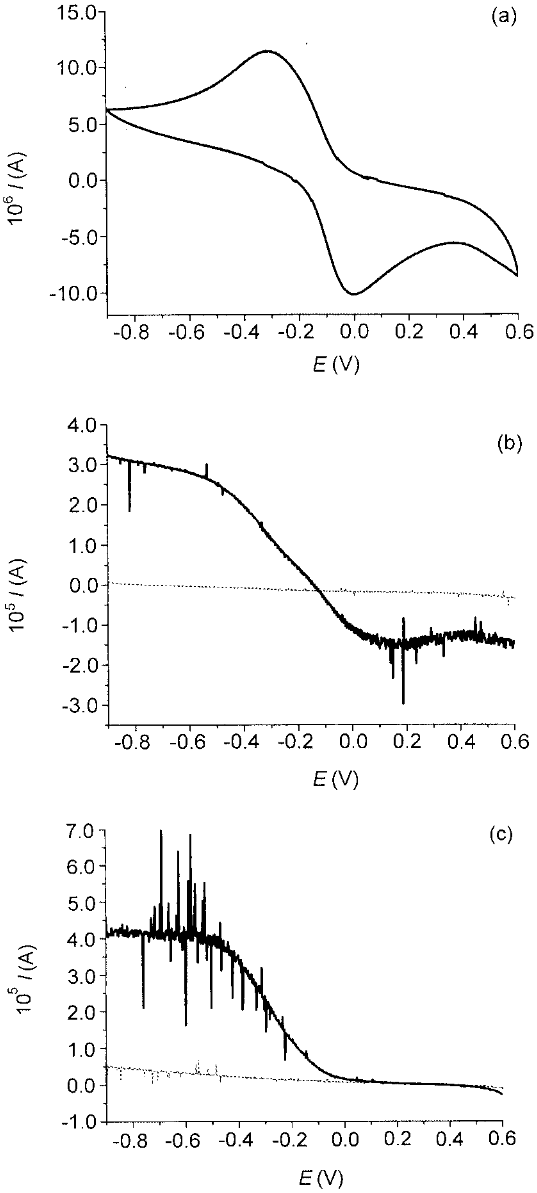


Figure 4. Cyclic voltammogram for **1** at a scan rate of 0.02 V s^{-1} (a); normal pulse voltammogram (NPV) with anodic scan of **1** (b); NPV with cathodic scan of **1** (c)

CV of **1** exhibits a quasi-reversible one-electron reduction−oxidation wave (Figure 4a) centred at $E_{1/2}$ = −0.159 V (versus saturated calomel electrode, SCE). Although this negative potential belongs to the range which would favour the potential catalytic activity, as we have previously reported for other manganese(III)−Schiff base systems,[4g] the peak-to-peak separation of 0.318 V (E_{ox} =

0.007 V; E_{red} = −0.311 V) becomes a significant handicap for the possible use of this complex in catalysis.

Conclusion

In the present work, we have shown how a ligand such as H_4L is able to induce, simultaneously, the formation of a manganese(III) complex and its aggregation into an infinite 2D array in the solid state through hydrogen bonding. The chloride anions, contrary to their typical behaviour, are not directly coordinated to the manganese atom at the first coordination sphere, but they act as multiple hydrogen-bonding-acceptor counterions as a kind of supramolecular glue, promoting the assembly of the Mn^{III} complexes. Finally, it must be noted that the development of molecular and supramolecular systems, such as this one, with the ability to bind negatively charged ions could play an important role in biology, medicine and the environment.

Experimental Section

General: Elemental analyses were performed on a Carlo Erba EA 1108 analyser. NMR spectra were recorded on a Bruker AC-300 spectrometer using $[D_6]$DMSO (296 K) as a solvent. Infrared spectra were registered as KBr pellets on a Bio-Rad FTS 135 spectrophotometer in the range 4000−200 cm^{-1}. Fast atom bombardment (FAB) mass spectra were obtained on a Kratos MS-50 mass spectrometer, employing Xe atoms at 70 KeV in *m*-nitrobenzyl alcohol as a matrix. Room-temperature magnetic susceptibilities were measured using a digital measurement system MSB-MKI, calibrated using tetrakis(isothiocyanato)cobaltate(II). Magnetic susceptibility measurements in the 40−300 K temperature range were obtained using a SQUID-QUANTUM model MPMS magnetometer operating at 5000 G. Electronic spectra were recorded on a Cary 230 spectrometer. Conductivities of 10^{-3} M solutions in DMF were measured on a Crison microCM 2200 conductivimeter.

Electrochemical Measurements: Measurements were performed using an EG&G PAR model, 273 potentiostat, controlled by an EG&G PAR model, 270 software. A Metrohm model, 6.1204.000 graphite disc, coupled to a Metrohm model, 628−10 rotating electrolyte device, was used as a working electrode. A saturated calomel electrode was used as a reference and a platinum wire as an auxiliary electrode.
Measurements were made with ca. 10^{-3} M solution of 1 in dimethylformamide using 0.1 M tetraethylammonium perchlorate as a supporting electrolyte. 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.

Syntheses: All solvents, 2,3-dihydroxybenzaldehyde (Maybridge), ethylenediamine (Aldrich), manganese(II) chloride tetrahydrate (Aldrich), and ABTS (Aldrich) were used as received without further purification.

Ligand Synthesis: Ethylenediamine (14.48 mol, 0.97 mL) was added to a methanolic solution (120 mL) of 2,3-dihydroxybenzaldehyde (28.96 mmol, 4 g).[21] This mixture was refluxed in a round bottomed flask fitted with a Dean−Stark trap to remove the water produced during the reaction. After refluxing for 3 h, the solution was concentrated to yield a yellow solid. The product was collected by filtration, washed with diethyl ether and dried in air. The yield was almost quantitative; M.p. 240 °C. $C_{16}H_{16}N_2O_4$ (300.2): calcd. C 63.9, H 5.4, N 9.3; found C 63.3, H 5.6, N 9.4. MS FAB (*m*/*z*): 301.1. IR (KBr): ν(O−H) 3258, 3389 (m), ν(C=N) 1633 (vs), ν(C−O) 1246 (s) cm^{-1}. ^1H NMR ($[D_6]$DMSO): δ = 3.93 (s, 4 H), 6.65 (t, 2 H), 6.82 (d, 2 H), 6.85 (d, 2 H), 8.54 (s, 2 H), 8.97 (br. s, 2 H), 13.46 (br. s, 2 H) ppm. ^{13}C NMR ($[D_6]$DMSO): δ = 58.0 (CH_2), 116−122 (C_{ar}), 145.8 ($C\text{-}OH_{inner}$), 151.0 ($C\text{-}OH_{outer}$), 167.2 (C=N) ppm.

Synthesis of the Complex $[Mn(H_2L)(CH_3OH)_2]Cl$ (1): H_4L (1.0 mmol, 0.30 g) was dissolved in methanol (40 mL) and $MnCl_2\cdot 4H_2O$ (1.0 mmol, 0.20 g), dissolved in methanol was added to the initial yellow solution, which changed to green. After stirring for 10 min, NaOH (2 mmol, 0.08 g), dissolved in a small quantity of water, was added and the mixture turned dark. The reaction mixture was refluxed for 2 hours, and then concentrated in vacuo to half its volume. The complex was obtained as black crystals, suitable for single X-ray-diffraction studies, after slow concentration of the solution. These crystals were isolated by filtration, washed with diethyl ether and dried in air, yield: 0.23 g, 50 %. $C_{18}H_{22}ClMnN_2O_6$ (452.77): calcd. C 47.7, H 4.9, N 6.2; found C 47.5, H 4.7, N 6.3. MS FAB (*m*/*z*): 353 $\{Mn(H_2L)\}$, 705 $\{Mn_2(H_2L)_2\}$. IR (KBr): ν(O−H) 3414 (br), ν(C=N) 1620 (vs), ν(C−O) 1259 (s) cm^{-1}. Magnetic moment μ_{eff}= 4.8 B.M. ^1H NMR (300 MHz, $[D_6]$DMSO): δ = −28.1, −16.3 ppm. Conductivity (in DMF) Λ_M= 90 μS cm^{-1}. E_{ox}= 0.007 V, E_{red}= −0.311 V, $E_{1/2}$= −0.159 V.

X-ray Crystallographic Studies: Crystals of **1**, suitable for X-ray diffraction studies, were obtained as described above. Data were collected with a Smart CCD-100 Bruker diffractometer employing graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation. The structure was solved by direct methods[22] and finally refined by full-matrix least-squares base on F^2. An empirical absorption correction was applied using SADABS.[23] All non-hydrogen atoms were anisotropically refined, and all hydrogen atoms were included in the model at geometrically calculated positions. Detailed data collection and refinement of the compound are summarized in Table 1.
CCDC-212667 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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