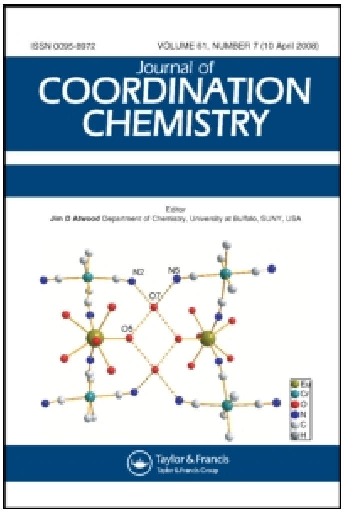

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Chattopadhyay, S. K. , Mitra, K. , Biswas, S. , Lucas, C. R. , Miller, D. O. and Adhikary, B.(2002) 'Studies on Mn(II) and Mn(IV) Complexes of an Unsymmetrical Bidentate Donor, *N*(4-Chlorophenyl)-Pyridine-2-Aldimine (ClL): Crystal Structure of [Mn(ClL)$_2$(NCS)$_2$]', Journal of Coordination Chemistry, 55: 12, 1409 — 1418
To link to this Article: DOI: 10.1080/0095897021000058808
URL: http://dx.doi.org/10.1080/0095897021000058808

J. Coord. Chem., 2002, Vol. 55, No. 12, pp. 1409–1418

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STUDIES ON Mn(II) AND Mn(IV) COMPLEXES OF AN UNSYMMETRICAL BIDENTATE DONOR, *N*(4-CHLOROPHENYL)-PYRIDINE-2-ALDIMINE (ClL): CRYSTAL STRUCTURE OF $[Mn(ClL)_2(NCS)_2]$

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(Received 21 September 2001; In final form 2 February 2002)

The synthesis, characterisation and X-ray structure of an Mn(II) compound, $[Mn(ClL)_2(NCS)_2]$, is described. Oxidation of the compound by H_2O_2 leads to a mononuclear Mn(IV) compound $[Mn(ClL)(ClL')(NCS)_2]ClO_4 \cdot 2H_2O$ where one of the ClL ligands is oxidised to the corresponding amide ClL′. Oxidation of $[Mn(ClL)_2(NCS)_2]$ by Ce(IV), however, leads to a binuclear Mn(IV) compound $[Mn_2O(ClL')_3(ClL)(H_2O)_2](NCS)_2ClO_4 \cdot 2MeCN$. Electron transfer behaviour of the compounds was investigated by cyclic voltammetry and differential pulse voltammetry.

Keywords: Mn(II) complexes; Mn(IV) complexes; μ-oxo Mn(IV) dimer; Crystal structure

INTRODUCTION

The last decade has witnessed publication of several studies [1–3] on complexes of manganese in various oxidation states. These were stimulated by the recognition of the role of manganese in various biological redox reactions [2–4] including Photosystem-II (PSII). However, the chemistry of mononuclear Mn(IV) complexes is still poorly explored. Though an Mn(IV) species of relatively high redox potential has been implicated in the S_4 state of PSII, which ultimately oxidises water to oxygen, the precursor enzymatic forms that may contain Mn(IV) (S_2 and S_3 state) must be of such redox potentials that they do not attack membrane components and proteins. Thus studies of the redox behaviour of Mn(IV) complexes in various ligand environments is essential to know how it is fine tuned by donor atoms and geometry. Again, though a large number of bis(μ-oxo) Mn(IV) dimers are well studied [1,4], examples of mono μ-oxo Mn(IV) dimers are relatively rare [5]. In this communication we report the synthesis, characterisation and X-ray structure of an Mn(II) complex,

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ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/0095897021000058808

$[Mn(ClL)_2(NCS)_2]$, derived from a bidentate *N*,*N* donor ligand *N*(4-chlorophenyl)-pyridine-2-aldimine (ClL). Isolation of a mononuclear and a μ-oxo binuclear Mn(IV) complex from the parent Mn(II) compound is also discussed. Redox behaviour of these complexes was explored by cyclic voltammetry and differential pulse voltammetry.

EXPERIMENTAL

All chemicals and solvents used for syntheses were commercially available reagents and used without further purification. ClL was prepared by a known procedure [6]. For electrochemical and spectroscopic measurements, HPLC grade solvents were used. TEAP was prepared as described in the literature [7].

Carbon, hydrogen and nitrogen were analysed on a Perkin-Elmer 2400 instrument. Electronic spectra were obtained using a JASCO 7850 spectrophotometer. IR spectra were recorded on a Perkin-Elmer 783 spectrometer. Electrochemical experiments were carried out using a PAR Versastat II potentiostat with a three electrode configuration consisting of a PAR glassy carbon working electrode, a Pt wire auxiliary electrode and Ag/AgCl as the reference electrode. Data were collected using 'Echem' software supplied by PAR.

$[Mn(ClL)_2(NCS)_2]$

Some 2 mmol (433 mg) of ClL was dissolved in 10 cm^3 of MeOH. To it 2 mmol (724 mg) of $Mn(ClO_4)_2 \cdot 6H_2O$ in 5 cm^3 of MeOH was added with stirring, causing the colour of the solution to turn orange. After 5 min, 8 mmol (608 mg) of NH_4SCN dissolved in 5 cm^3 of water was added dropwise to the reaction mixture, resulting in the formation of the yellowish orange precipitate. The mixture was stirred for two hours at room temperature and filtered. The residue was washed thoroughly with water and then with a small amount of MeOH before being recrystallised from CH_3CN. Yield: 395 mg (32.7%). Analysis: calculated for $[Mn(ClL)_2(NCS)_2]$ (%): C, 51.6; H, 2.9; N, 13.9. Found: C, 51.5; H, 2.8, N, 13.6. Conductance in MeCN (Λ_M): 32 S cm^2 mol^{-1}. Electronic spectrum in MeCN solution [λ nm ($\log \varepsilon$)]: 313 (4.34), 288 (4.47), 238 (4.47). μ_{eff} (300 K) = 6.10 BM.

$[Mn(ClL)(ClL')(NCS)_2]\ ClO_4 \cdot 2H_2O$

Some 1 mmol of $[Mn(ClL)_2(NCS)_2]$ (604 mg) was dissolved in 60 cm^3 of CH_3CN and 1.7 mmol (2 cm^3) of H_2O_2 (30%) was added dropwise. Within a few minutes the colour deepened from orange to deep red and finally to deep reddish brown. The solution was stirred at room temperature for 1 h and then filtered through celite. To the deep red filtrate about 5 cm^3 of a saturated sodium perchlorate solution in acetonitrile was added with stirring and the solution allowed to evaporate at room temperature. The crude compound that separated was removed by filtration and washed well with water. The residue after drying in a desiccator was dissolved in 1 : 1 chloroform : acetonitrile and chromatographed using a silica gel (60–120 mesh) column (32 cm × 1.5 cm). It was first eluted with 50 cm^3 of $CHCl_3$, followed by 100 cm^3 of 10% CH_3CN in $CHCl_3$, then 100 cm^3 of 20% CH_3CN in $CHCl_3$. The desired compound was obtained by eluting with 250 cm^3 of 30% CH_3CN in $CHCl_3$ (deep red solution), and evaporating the eluate. Yield: 170 mg (23%). Analysis: calculated for $[Mn(ClL)(ClL')(NCS)_2]\cdot 2H_2O$ (%): C, 41.5; H, 3.0; N, 11.1. Found: C, 41.2; H, 3.0; N, 10.9. Conductance in MeCN (Λ_M): 176 S cm^2 mol^{-1}. Electronic spectrum in MeCN solution [λ nm ($\log\varepsilon$)]: 500 (sh), 463 (4.03), 435 (sh), 375 (3.95), 325 (3.91), 250 (4.27), 238 (4.37), μ_{eff} (300 K) = 4.03 BM.

$[Mn_2O(ClL')_3(ClL)(H_2O)_2](NCS)_2ClO_4\cdot 2MeCN$

Some 1 mmol (604 mg) of $[Mn(ClL)_2(NCS)_2]$ was dissolved in 40 cm^3 of CH_3CN. To the solution 1 mmol (548 mg) of cerric ammonium nitrate in 12 cm^3 of CH_3CN was added dropwise at room temperature. The colour of the solution changed from red to dark red. It was stirred for 1 h at room temperature. Four cm^3 of a saturated sodium perchlorate solution in MeCN was added and the solution stirred for another 20 min, then filtered. The reddish brown filtrate was allowed to evaporate at room temperature. The residue was filtered after 96 h and washed well with water. The crude compound was dissolved in 1 : 1 $CHCl_3 : CH_3CN$ and chromatographed, as above. The desired compound was obtained by eluting with 250 cm^3 of 20% CH_3CN in $CHCl_3$ and evaporating the eluate. The solid was recrystallised from CH_2Cl_2/*n*-hexane. Analysis: calculated for $[Mn_2O(ClL')_3(ClL)(H_2O)_2](NCS)_2ClO_4\cdot 2MeCN$ (%): C, 47.3; H, 3.1; N, 12.2. Found: C, 47.5; H, 3.3; N, 12.4. Conductance in MeCN (Λ_M): 327 S cm^2 mol^{-1}. Electronic spectrum in MeCN solution [λ nm ($\log\varepsilon$)]: 820 (3.48), 637 (3.03), 500 (sh), 463 (4.42), 435 (sh), 375 (4.32), 325 (4.28), 250 (4.58), 238 (4.68). μ_{eff} (300 K) = 3.18 BM per Mn atom.

X-ray Analysis

An orange irregularly shaped crystal of $[Mn(ClL)_2(NCS)_2]$ of dimensions $0.30 \times 0.30 \times 0.45$ mm was chosen for X-ray crystallography. Data were collected on a Rigaku AFC6S diffractometer with graphite-monochromated Mo*Kα* radiation ($\lambda = 0.71073$ Å). Cell constants were obtained from 24 carefully centred reflection in the range $21.50 < 2\theta < 26.96°$. Crystal data are summarized in Table I and positional parameters and B(eq) values are provided in Table II. Data were collected at 26 ± 1°C using the ω–2θ scan technique, scan rate 4°min^{-1}, with a maximum 2θ value of 55.1°. Intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied. Of the 13 610 observed reflections 13 172 were unique. The structure was solved by direct methods [8] and expanded Fourier techniques, with a riding model for hydrogen atoms. For 5358 observed reflections ($I > 2\sigma(I)$), $R = 0.049$ and $R_w = 0.048$; Lorentz-polarization corrections were applied.

RESULTS AND DISCUSSION

Reaction of manganous perchlorate with *N*(4-chlorophenyl)-pyridine-2-aldimine (Fig. 1) in either 1 : 1 or 1 : 2 molar proportions in MeOH followed by addition of aqueous solution of ammonium thiocyanate yielded $[Mn(ClL)_2(NCS)_2]$.

TABLE I Crystal data and structure refinement details for $[\mathrm{Mn(ClL)_2(NCS)_2}]$

Empirical formula	$C_{26}H_{18}N_6Cl_2MnS_2$
Formula weight	604.43
Temperature (K)	299
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	16.656(4)
b (Å)	20.873(5)
c (Å)	16.925(6)
β (°)	109.56(2)
V (Å^3)	5545(3)
Z	8
$\rho_{\text{calc.}}$ (g cm^{-3})	1.448
μ (cm^{-1})	8.46
F(000)	2456
$R(F)$	0.049
$R_w(F)$	0.048
GOF	1.45

TABLE II Positional parameters and B(eq) values of non hydrogen atoms for $[\mathrm{Mn(ClL)_2(NCS)_2}]$

Atom	x/a	y/b	z/c	B (eq)
Mn(1)	0.63990(4)	0.15055(3)	0.74755(4)	3.70(2)
Mn(2)	1.11340(4)	0.14030(3)	0.71783(4)	4.16(2)
Cl(1)	0.8368(1)	−0.14208(7)	0.6388(1)	9.06(5)
Cl(2)	0.98945(8)	0.39694(7)	0.9055(1)	7.11(4)
Cl(3)	1.4651(1)	−0.09800(7)	0.9121(1)	9.03(5)
Cl(4)	1.39332(9)	0.38693(6)	0.64298(9)	6.54(4)
S(1)	0.38504(8)	0.02425(7)	0.6387(1)	6.36(4)
S(2)	0.49846(8)	0.25912(7)	0.91917(8)	5.39(3)
S(3)	0.99534(8)	0.02935(6)	0.90702(8)	5.18(3)
S(4)	0.85645(9)	0.25780(9)	0.57677(9)	7.60(5)
N(1)	0.6274(2)	0.2327(2)	0.6519(2)	3.80(9)
N(2)	0.6998(2)	0.1171(2)	0.6494(2)	3.72(9)
N(3)	0.6773(2)	0.0564(2)	0.8236(2)	4.4(1)
N(4)	0.7761(2)	0.1632(2)	0.8477(2)	3.93(9)
N(5)	0.5219(3)	0.1073(2)	0.6729(3)	5.5(1)
N(6)	0.5890(2)	0.2045(2)	0.8253(2)	4.9(1)
N(7)	1.1488(2)	0.2397(2)	0.7757(2)	3.99(9)
N(8)	1.2533(2)	0.1353(2)	0.8174(2)	3.92(9)
N(9)	1.1058(2)	0.0457(2)	0.6448(2)	4.18(9)
N(10)	1.1916(2)	0.1517(2)	0.6296(2)	3.69(9)
N(11)	1.0645(3)	0.0941(2)	0.8027(3)	6.4(1)
N(12)	0.9963(3)	0.1770(2)	0.6332(3)	6.0(1)
C(1)	0.5939(3)	0.2904(2)	0.6515(3)	4.9(1)
C(2)	0.5777(3)	0.3325(2)	0.5859(4)	6.1(2)
C(3)	0.5942(3)	0.3142(3)	0.5159(4)	6.4(2)
C(4)	0.6280(3)	0.2544(2)	0.5136(3)	5.2(1)
C(5)	0.6442(3)	0.2154(2)	0.5823(3)	4.1(1)
C(6)	0.6821(3)	0.1522(2)	0.5847(3)	4.3(1)
C(7)	0.7334(3)	0.0548(2)	0.6469(2)	3.8(1)
C(8)	0.8109(3)	0.0381(2)	0.7025(3)	5.7(1)
C(9)	0.8421(3)	−0.0235(3)	0.7007(3)	6.3(2)
C(10)	0.7954(4)	−0.0663(2)	0.6447(3)	5.5(1)
C(11)	0.7176(3)	−0.0511(2)	0.5891(3)	5.5(1)

(*continued*)

TABLE II Continued

Atom	*x/a*	*y/b*	*z/c*	*B* (eq)
C(12)	0.6863(3)	0.0102(2)	0.5905(3)	5.0(1)
C(13)	0.6328(3)	0.0019(3)	0.8109(3)	6.1(1)
C(14)	0.6576(4)	− 0.0512(3)	0.8622(4)	7.6(2)
C(15)	0.7310(4)	− 0.0484(3)	0.9290(4)	7.9(2)
C(16)	0.7788(3)	0.0069(3)	0.9426(3)	6.3(1)
C(17)	0.7499(3)	0.0580(2)	0.8882(3)	4.2(1)
C(18)	0.7999(3)	0.1170(2)	0.8988(3)	4.4(1)
C(19)	0.8277(3)	0.2192(2)	0.8642(3)	3.8(1)
C(20)	0.8606(3)	0.2470(2)	0.9434(3)	5.0(1)
C(21)	0.9103(3)	0.3005(2)	0.9558(3)	5.4(1)
C(22)	0.9264(3)	0.3280(2)	0.8894(3)	5.2(1)
C(23)	0.8939(3)	0.3026(3)	0.8109(3)	5.7(1)
C(24)	0.8435(3)	0.2490(2)	0.7980(3)	5.0(1)
C(25)	0.4645(3)	0.0728(2)	0.6575(3)	4.3(1)
C(26)	0.5503(3)	0.2273(2)	0.8642(3)	3.8(1)
C(27)	1.0993(3)	0.2915(2)	0.7578(3)	5.1(1)
C(28)	1.1265(3)	0.3513(2)	0.7903(3)	5.4(1)
C(29)	1.2074(3)	0.3587(2)	0.8425(3)	5.6(1)
C(30)	1.2596(3)	0.3061(2)	0.8622(3)	5.3(1)
C(31)	1.2280(3)	0.2473(2)	0.8284(3)	3.9(1)
C(32)	1.2806(3)	0.1898(2)	0.8506(3)	4.5(1)
C(33)	1.3079(3)	0.0815(2)	0.8394(3)	4.2(1)
C(34)	1.2690(3)	0.0217(2)	0.8303(3)	5.8(1)
C(35)	1.3178(4)	− 0.0332(3)	0.8512(4)	6.7(2)
C(36)	1.4044(4)	− 0.0290(3)	0.8813(3)	6.1(1)
C(37)	1.4435(3)	0.0294(3)	0.8876(3)	6.5(2)
C(38)	1.3956(3)	0.0845(2)	0.8668(3)	5.9(1)
C(39)	1.0624(3)	− 0.0075(2)	0.6499(3)	5.6(1)
C(40)	1.0542(3)	− 0.0598(2)	0.5987(4)	6.0(1)
C(41)	1.0930(3)	− 0.0584(2)	0.5394(3)	5.9(1)
C(42)	1.1404(3)	− 0.0052(2)	0.5334(3)	5.1(1)
C(43)	1.1449(3)	0.0459(2)	0.5871(3)	3.9(1)
C(44)	1.1931(3)	0.1042(2)	0.5840(2)	4.0(1)
C(45)	1.2416(3)	0.2068(2)	0.6278(2)	3.5(1)
C(46)	1.2027(3)	0.2619(2)	0.5887(3)	4.5(1)
C(47)	1.2499(3)	0.3161(2)	0.5912(3)	4.8(1)
C(48)	1.3354(3)	0.3160(2)	0.6372(3)	4.1(1)
C(49)	1.3751(3)	0.2626(3)	0.6767(3)	4.9(1)
C(50)	1.3280(3)	0.2068(2)	0.6711(3)	4.6(1)
C(51)	1.0354(3)	0.0668(2)	0.8460(3)	4.0(1)
C(52)	0.9379(3)	0.2107(2)	0.6088(3)	4.8(1)

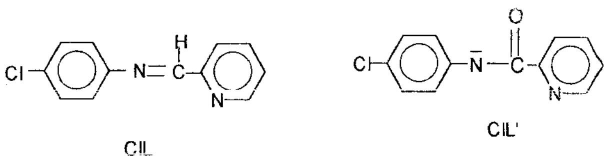


FIGURE 1 Structural formulae of ClL and ClL′.

The effective room temperature magnetic moment (6.01 BM) and electronic spectrum confirms the Mn(II) formulation. For complexes of the type [Mn(N–N′)$_2$X$_2$] (N = pyN, N = imine) five different isomers are possible. For X = NCS, the number of possible isomers is fifteen, as thiocyanate can be both *N*-bonded and *S*-bonded (plus optical antipodes).

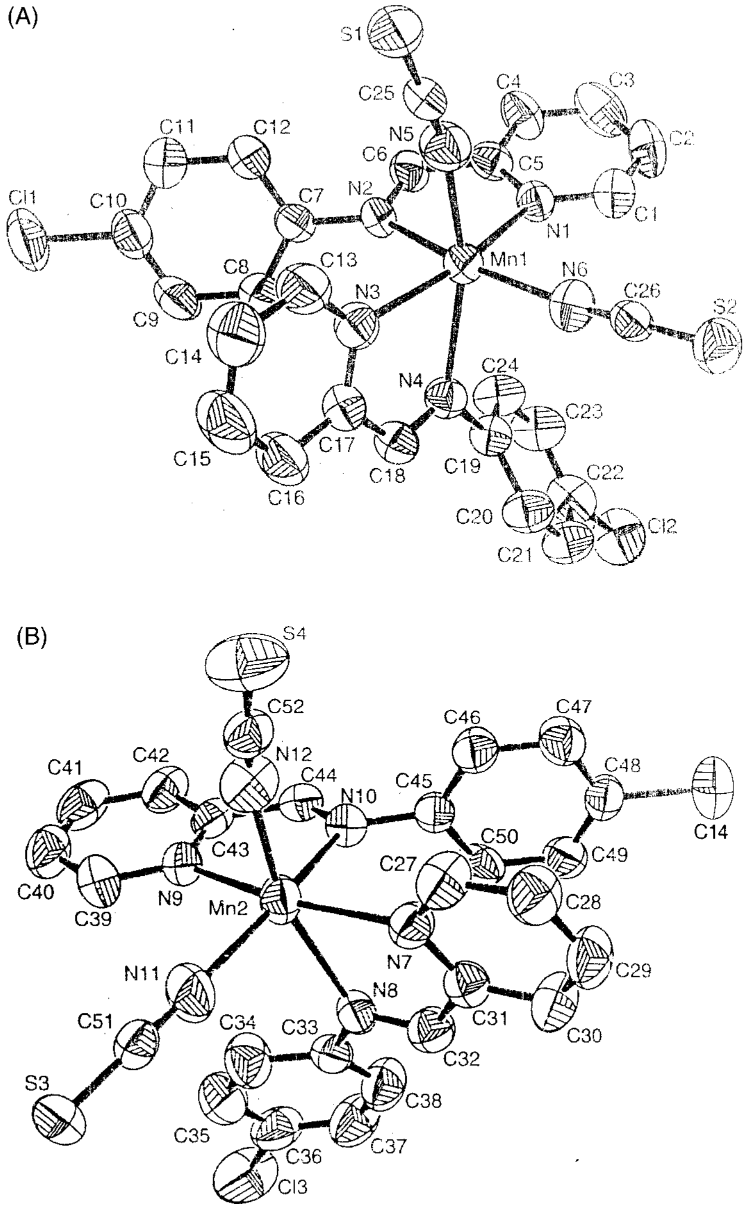


FIGURE 2 ORTEP diagram and atom numbering scheme for [Mn(ClL)$_2$(NCS)$_2$]. Both independent units are shown in A and B.

The X-ray structure determination of [Mn(ClL)$_2$(NCS)$_2$] uneqivocally establishes that both the thiocyanates are *N*-bonded and it is a *cis*-(thiocyanate)-*trans*-(PyN)-*cis*-(imino N′) or a *ctc* isomer.

An ORTEP diagram of the compound [Mn(L)$_2$(NCS)$_2$] is shown in Fig. 2. There are two crystallographically different manganese atoms in the unit cell, which are labelled Mn1 and Mn2. As Manganese(II) is present in an N6 coordination environment and the electronic structure of Mn(II) is spherically symmetrical not much deviation from octahedral geometry is expected. However, structural data reveal that Mn(II) lies in a highly distorted octahedral environment, with angles between *trans* ligands of less than 165°. The two thiocyanates coordinated to a particular Mn(II) atom are not identical even though both are *N*-bonded; in the Mn1 structure, both thiocyanates are bent, though by different amounts (Mn–N–C angles 169.2(4)° and 156.9(4)°). In the Mn2 structure one of the thiocyanates is linear (Mn–N–C angle 176.6(5)°) while the other is bent (Mn–N–C angle 157.6(5)°). All six Mn–N distances in a given structure are different. Though Mn–N distances with thiocyanate ligands are within the normal range [9] (average 2.130(5) Å for Mn(1) and 2.122(5) Å for Mn(2)), Mn–N distances of the ClL ligands are extremely large (average Mn–Npy 2.318(4) Å for Mn1 and 2.298(4) Å for Mn2, average Mn–N(imine) 2.331(4) Å and 2.338(4) Å for Mn1 and Mn2, respectively). In fact the Mn–N distance of 2.378(4) Å observed for Mn2–N8 is, to the best of our knowledge, the largest Mn–N distance observed for a Mn(II) octahedral complex, though it is still well short of the sum (2.82 Å) [10] of the van der Waals radii. Considering that the thermal parameters of the metal centres are larger than expected compared to the thermal parameters of some of the bonding atoms, the metal seems to be "rattling" within its coordination sphere. One explanation for this might be that lattice forces are holding the ligands apart slightly, thereby increasing bond distances.

The compound $[Mn(ClL)_2(NCS)_2]$ can be oxidised by hydrogen peroxide in MeCN and from the reaction mixture a compound $[Mn(ClL)(ClL')(NCS)_2]ClO_4 \cdot 2H_2O$ can be isolated in good yield. Transformation of coordinated *N*(Aryl) pyridine-2-aldimine to the corresponding amide by electrochemical or chemical (hydrogen peroxide or cerric(IV)) oxidation is well documented in the literature [11,12]. The following reaction scheme (Scheme I) may be proposed.

$$\left[Mn^{II}(ClL)_2(NCS)_2\right] + H_2O_2 \longrightarrow \left[Mn^{IV}(ClL)_2(NCS)_2\right]^{2+} + 2OH^- \qquad (1)$$

$$2\left[Mn^{IV}(ClL)_2(NCS)_2\right]^{2+} + H_2O \longrightarrow \left[Mn^{IV}(ClL)(ClL')(NCS)_2\right]^{+} + 3H^{+} + \left[Mn(ClL)_2(NCS)_2\right] \qquad (2)$$

SCHEME I

The IR spectrum of the compound $[Mn^{IV}(ClL)(ClL')(NCS)_2]ClO_4 \cdot 2H_2O$ exhibits a band at 1622 cm^{-1} due to the ν_{CO} vibration of the amide and a broad band at 1135–1091 cm^{-1} due to ν_{3ClO4}. Two ν_{CN} bands at 2062 and 2037 cm^{-1} indicate the thiocyanates are in *cis* positions. The compound behaves as a 1 : 1 electrolyte in MeCN. The room temperature effective magnetic moment of the sample is 4.03 BM in agreement with the Mn (IV) formulation. It is plausible that $[Mn(ClL)(ClL')(NCS)_2]ClO_4$ also possess a *cis*-*trans*-*cis* geometry. The visible region of the electronic spectrum of the complex in MeCN solution is dominated by strong ligand-to-metal charge transfer transitions characteristic of Mn(IV) complexes [13–15].

Oxidation of $[Mn(ClL)_2(NCS)_2]$ by Ce(IV) results in a μ-oxo Mn(IV) dimer of formula $[Mn_2O(ClL')_3(ClL)(H_2O)_2](NCS)_2ClO_4 \cdot 2MeCN$. A strong band at 1622 cm^{-1} in the IR spectrum of the complex is again assigned to ν_{CO}(amide), and a broad band around 1091 cm^{-1} is the $\nu_{3\mathrm{ClO4}}$ vibration. The ν_{CN} band of the thiocyanate is observed at 2052 cm^{-1}. The complex behaves as a 1 : 3 electrolyte in MeCN solution. The room temperature effective magnetic moment of 3.1 BM per manganese atom indicates moderate exchange coupling through the oxo bridge. The electronic spectrum of the complex in MeCN solution is nearly identical with that of $[\mathrm{Mn(ClL)(ClL)(NCS)_2}]\mathrm{ClO_4}$ except in the 600–850 nm region where the dimer exhibits a broad asymmetric band with a peak at 820 nm and another relatively weak absorption at ~638 nm. Extinction coefficients of these two bands are consistent with charge transfer transition and they may arise due to the oxo ligand Mn(IV) centre.

Electrochemical behaviour of the complexes was explored in MeCN solution using cyclic voltammetry and differential pulse voltammetry. $[\mathrm{Mn(ClL)_2(NCS)_2}]$ undergoes an irreversible oxidation at 1.0 V to form the Mn(III) complex $[\mathrm{Mn(ClL)_2(NCS)_2}]^+$; on scan reversal a new reversible peak is observed at ~0.11 V. This may be explained on the basis of following reactions (Scheme II).

$$[\mathrm{Mn^{II}(ClL)_2(NCS)_2}] \xrightarrow[1.0\mathrm{v}]{-\mathrm{e}} [\mathrm{Mn^{III}(ClL)_2(NCS)_2}]^+ \tag{3}$$

$$\begin{aligned}3[\mathrm{Mn^{III}(ClL)_2(NCS)_2}]^+ + \mathrm{H_2O} \longrightarrow {} & [\mathrm{Mn^{III}(ClL)(ClL')(NCS)_2}] + 3\mathrm{H}^+ \\ & + 2[\mathrm{Mn^{II}(ClL)_2(NCS)_2}]\end{aligned} \tag{4}$$

$$[\mathrm{Mn^{III}(ClL)(ClL')(NCS)_2}] \xrightarrow[0.11\mathrm{v}]{+\mathrm{e}} [\mathrm{Mn^{II}(ClL)(ClL')(NCS)_2}]^- \tag{5}$$

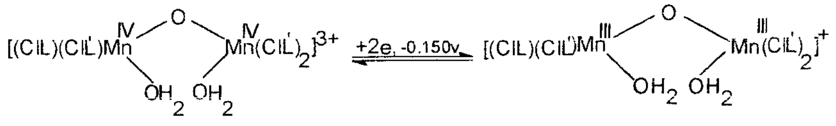
SCHEME II

On the reduction side a ligand based reduction at −1.2 V is observed for $[\mathrm{Mn(ClL)_2(NCS)_2}]$.

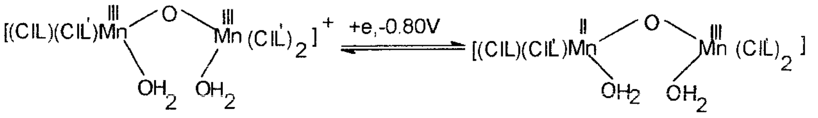
$[\mathrm{Mn(ClL)(ClL')(NCS)_2}]\mathrm{ClO_4}$ undergoes a two electron *quasi*-reversible reduction (reaction (6)) at −0.173 V (DPPV peak). In the cyclic voltammogram at a scan rate of 50 mv/s Epc = −0.250 V and Epa = +0.0496 with ΔEp increasing with scan rate.

$$[\mathrm{Mn^{IV}(ClL)(ClL')(NCS)_2}]^+ + 2\mathrm{e} \xrightleftharpoons{-0.173} [\mathrm{Mn^{II}(ClL)(ClL')(NCS)_2}]^- \tag{6}$$

$[\mathrm{Mn_2O(ClL)(ClL')_3(H_2O)_2}](\mathrm{NCS})_2\mathrm{ClO_4}$ undergoes a *quasi*-reversible, two electron reduction at E° = −0.150 V (DPPV peak), followed by a one electron reduction at −0.80 V.

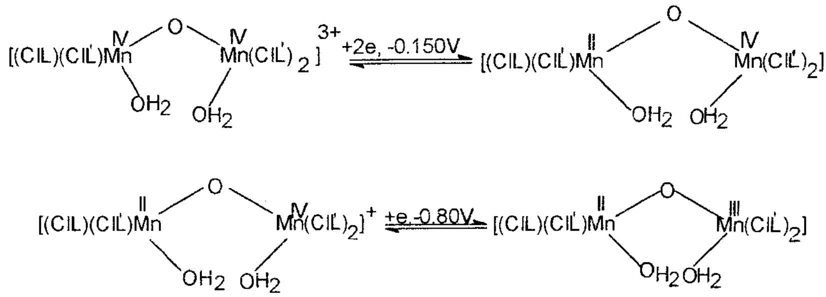


(7)



(8)

SCHEME III



(9)

(10)

SCHEME IV

Two reaction schemes, reactions (7) and (8) (Scheme III) or reactions (9) and (10) (Scheme IV) are plausible. However, comparison with reaction (6), along with the fact that Mn(IV) coordinated to two deprotonated amide ligands is likely to be more stable and unlikely to be reduced at the same potential as that of a Mn(IV) species coordinated to only one amide, makes Scheme IV more acceptable.

All similar mononuclear complexes reported so far in the literature are known to undergo reduction in two successive, one electron processes [13–15] leading to the corresponding Mn(II) species. However, ours is probably the first example where a Mn(IV) species undergoes a two electron reduction in a single step to the corresponding Mn(II) species. Such two electron transfer processes are biologically relevant as oxidation of water to oxygen or catalyzed disproportionation of hydrogen peroxide by enzymes like catalase involve two electron transfer processes. The negative Mn(IV)/Mn(II) potential clearly indicates the stabilisation of Mn(IV) by the chelating monoionic bidentate amide ClL′. The binuclear Mn(IV) complex, like the mononuclear analogues undergoes two electron reduction of one Mn(IV) centre in the first step, followed by a one electron reduction of the second Mn(IV) centre. Though binuclear Mn(IV) complexes reported in the literature are known to undergo two electron reductions, these are normally simultaneous one electron reductions of each of the Mn(IV) centres. Thus both the mononuclear and the binuclear Mn(IV) complexes reported in this article show novel electron transfer characteristics.

Acknowledgements

Financial assistance from UGC, CSIR and AICTE is gratefully acknowledged. KM thanks UGC for a Project Fellowship, SB thanks CSIR for award of a JRF. The authors also thank the AICTE-MODROBS programme for the purchase of the electrochemical unit.

References

[1] K. Wieghardt (1989). *Angew. Chem. Int. Ed. Engl.*, **28**, 1153.

[2] (a) V.K. Yachandra (1996). *Chem. Rev.*, **96**, 2927; (b) M. Yagi and M. Kaneko (2001). *Chem. Rev.*, **101**, 21.

[3] G.C. Dismukes (1996). *Chem. Rev.*, **96**, 2909.

[4] V.L. Pecoraro (Ed.) (1992). *Manganese Redox Enzymes*. VCH Publishers, New York.

[5] B.C. Schardt, F.J. Hollander and C.L. Hill (1982). *J. Am. Chem. Soc.*, **104**, 3964.

[6] E.V. Dose and L.J. William (1978). *Inorg. Chem.*, **17**, 2660.

[7] D.T. Sawyer, A. Sobkowiak and J.L. Roberts Jr., (1995). *Electrochemistry for Chemists*, 2nd Edn., p. 336. John Wiley and Sons, New York.

[8] A. Altomare, M. Cascarno, C. Giacovazzo and A. Guagliardi (1993). *J. Appl. Cryst.*, **26**, 343.

[9] M.G. Barandika, M.L.H. Pino, M.K. Urtiga, R. Cortes, L. Lezema, M.I. Arrirortua and T. Rojo (2000). *J. Chem. Soc. Dalton Trans.*, 1469.

[10] A. Deroche, I. Morgenstern-Badaram, M. Cesavio, J. Guilhem, B. Keita, L. Nadjo and C.H. Levin (1996). *J. Am. Chem. Soc.*, **118**, 4567.

[11] M. Menon, A. Pramanik, N. Bag and A. Chakravorty (1994). *Inorg. Chem.*, **33**, 403.

[12] B.K. Dirghangi, M. Menon, A. Pramanik and A. Chakravorty (1997). *Inorg. Chem.*, **36**, 1095.

[13] D. Kessissoglou, X. Li, W.M. Butler and V. Pecoraro (1987). *Inorg. Chem.*, **26**, 2487.

[14] S. Dutta, P. Basu and A. Chakravorty (1991). *Inorg. Chem.*, **30**, 4031.

[15] S.K. Chandra, P. Basu, D. Ray, S. Pal and A. Chakravorty (1990). *Inorg Chem.*, **29**, 2423.