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Spectroscopic and electrochemical investigation with coordination stabilities: Mononuclear manganese(II) complexes derived from different constituents macrocyclic ligands

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Abstract

Since the manganese(II) complexes are known as having a high degree of stability, some of them may be able to play a very important role in biosystems. We prepared manganese(II) complexes with different chromospheres containing macrocyclic ligands bearing N, S and O like functional donor atoms in order to obtain different models of compounds. So these new manganese(II) complexes were derived from macrocyclic ligands by chelating them with metal ions.

Thus, two macrocyclic ligands, L¹: 2,4-diphenyl-1,5-diaza-8,12-dioxo-6,7:13,14-dibenzocyclo tetradeca-1,4-diene[N₂O₂]ane; L²: 2,4,9,11-tetraphenyl-6,13-dimethyl-1,5,8,12-traazacyclotertr-adeca-1,4,8,11-tetraene[N₄]ane; and two more different form first one viz.—L³: 1,7-diaza-4-monothia-10,14-dioxo-8,9:15,16-cyclohexadecane[N₂O₂S]ane and L⁴: 4,13-diaoxa-1,7,10,16-hexazacyclooctadecane[N₄O₂]ane were prepared and their capacity to retain the manganese(II) ion in solid as well as aqueous solution was determined from various physiochemical techniques viz: characterized by elemental analyses, molar conductance measurements, magnetic susceptibility measurements, mass, IR, electronic, ESR spectral studies and cyclic voltammetric measurements.

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1. Introduction

We adopt a native point of view in our discussion in the spectroscopic characterization of our synthesized complexes with all the findings which are inventively clear. By spectroscopic studies we mean a whole characterization sets of such techniques which are sufficiently powerful to analysis our needs through this article and our intentions are clear to understand the capacity of our synthesized complexes for their vast applications in different fields and intricate importance for the development in this field. The synthesis of macrocyclic ligands with their manganese(II) metal complexes is a growing area of research in inorganic and bioinorganic chemistry, it is due to their importance in many biologically and chemical process. Coordination compounds containing macrocyclic ligands have been studied

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during the past decades due to their wide applications in biological and sensor fields [1,2]. Different neutral donors have been incorporated into the ligand backbone [3–6]. Macrocycles find wide applications in medicine, cancer diagnosis and in treatment of tumors, in metal ion techniques and treatment of kidney stone. Macrocyclic ligands have been used successfully for diverse processes such as separation of ions by transport through artificial and natural membrane, liquid–liquid or solid–solid phase transfer reaction, preparation of ion-selective electrodes, isotope separation and in the understanding of some natural processes through mimicry of metalloenzymes.

Very often the incorporation of a functional group into the ligand backbone is accompanied by changes in reactivity of the corresponding metal complex. Therefore, investigations of model compounds, which are closely related, electronically and structurally, to the supported catalysts need to be performed [7–13].

Our findings are quite interesting about the geometrical or geometrical classification with stereochemical of anions and centre on their coordination abilities which are further used for the investigation of model complexes. Needless to write,

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Fig. 1. Structures of macrocyclic ligands.

we follow the ligands reported earlier we report the synthesis and characterization as a combined way of manganese(II) complexes and our purpose in this article to develop some new manganese(III) complexes with macrocyclic ligands (Fig. 1) containing different donor atoms viz.—ligand L^1 : 2,4-diphenyl-1,5-diaza-8,12-dioxo-6,7:13,14-dibenzocyclotetradeca-1,4diene[N₂O₂]ane; ligand L^2 : 2,4,9,11-tetraphenyl-6,13-dimethyl-1,5,8,12-traazacyclotertr-adeca-1,4,8,11-tetraene[N₄]ane; ligand L³: 1,7-diaza-4-monothia-10,14-dioxo-8,9:15,16-cyclohexadecane[N₂O₂S]ane and ligand L⁴: 4,13-diaoxa-1,7,10,16hexazacyclooctadecane[N₄O₂]ane. Reported complexes are sufficiently powerful to develop required modeling for biosystems in the rest of this article.

2. Experimental

2.1. Materials and instrumentation

All the chemicals used in the present investigation were of AR grade, purchased from Sigma Chemical Co., USA. Ele-



Fig. 2. UV spectrum of MnL¹(NO³)₂ complexes.



Fig. 3. UV spectrum of MnL²(NCS)₂ complexes.

mental analyses (CHN) of all these complexes were carried out on a Carlo-Erba 1106 Elemental Analyzer. Molar conductance was measured on an ELICO conductivity bridge (Type CM82T). Magnetic susceptibility measurements were made on Gouy Balance at room temperature using CuSO₄·5H₂O as celebrant. Infrared spectra were recorded on a Perkin Elmer 137 instrument as KBr pellets. Electronic spectra were recorded in DMSO solution on a Shimadzu UV mini-1240 spectrophotometer. EPR spectra of the chromium(III) complexes were recorded as powder samples at room temperature on an E-4 EPR spectrometer using DPPH as the g-marker.

All solvents used were purified before use according to standard procedures.

All the ligands are prepared as reported earlier [12].



Fig. 4. UV spectrum of [Mn(L³)(NCS)](NCS) complexes.

Table 1
Analytical data of the manganese(II) complexes

Complexes/empirical formula	Yield (%)	Molar conductance $(\Omega^{-1} \operatorname{cm}^2 \operatorname{mol}^{-1})$	Color	Elemental analysis calcd. (found%)			
				Mn	С	Н	Ν
$\frac{[Mn(L^1)(NCS)_2]}{MnC_{36}H_{36}N_4}$	55	12.0	Light yellow	7.92 (7.90)	67.82 (97.23)	4.51 (4.59)	7.45 (7.79)
$[Mn(L^1)(NO_3)_2] \\ Mn C_{36}H_{36}N_4$	52	06.0	Light yellow	7.84 (7.80)	63.92 (63.25)	4.20 (4.26)	11.00 (11.11)
$[Mn(L^2)(NCS)_2] \\ Mn C_{30}H_{26}N_2O_2$	51	05.0	Yellow	8.39 (8.12)	64.97 (64.71)	4.28 (4.31)	11.10 (11.2)
$[Mn(L^2)(NO_3)_2] \\ Mn C_{30}H_{26}N_2O_2$	46	11.0	Yellow	7.88 (7.80)	64.25 (64.20)	3.90 (3.99)	7.85 (7.92)
[Mn(L3)NCS]NCSMnC40H28N6O2S2	68	85.0	Light yellow	7.39 (8.01)	64.59 (64.20)	3.50 (3.60)	10.65 (10.7)
[Mn(L ³)NO ₃]NO ₃ MnC ₃₈ H ₂₈ N ₆ O ₈	58	82.0	Light yellow	7.31 (7.25)	60.72 (60.42)	3.75 (3.65)	11.00 (11.17)
$[Mn(L^4)](NCS)_2 \\ MnC_{40}H_{28}N_6O_2S_2$	74	165.0	Yellow	7.39 (7.26)	64.59 (64.50)	3.69 (3.82)	7.46 (7.58)
$[Mn(L^4)](NO_3)_2 \\ MnC_{38}H_{28}N_6O_8 \\$	71	168.0	Light yellow	7.31 (7.28)	60.72 (59.00)	3.50 (3.56)	10.56 (10.61)

2.2. Preparation of manganese(II) complexes with macrocyclic ligands

A hot (~65 °C) ethanolic solution (20 ml) of the ligands (0.02 mol) and a hot (~55 °C) ethanolic solution (20 ml) of the manganese(II) metal salt (2 mmol) were mixed together with constant stirring. The mixture was refluxed for 5–6 h at 65–90 °C. On cooling the content to ~5 °C, the colored complexes were precipitated out. They were filtered, washed with cold EtOH and dried under vacuum over P_4O_{10} . The reactions (1), (2), (3) and (4) are quite facile and can be completed in 5–6 h of refluxing.

$$L^{1} + MnX_{2} \cdot nH_{2}O \rightarrow Mn(L^{1})X_{2} + nH_{2}O, \qquad (1)$$

 $L^{2} + MnX_{2} \cdot nH_{2}O \rightarrow Mn(L^{2})X_{2} + nH_{2}O, \qquad (2)$

 $L^{3} + MnX_{2} \cdot nH_{2}O \rightarrow Mn(L^{3})X_{2} + nH_{2}O, \qquad (3)$

$$L^{3} + MnX_{2} \cdot nH_{2}O \rightarrow Mn(L^{3})X_{2} + nH_{2}O, \qquad (4)$$

where
$$X = NO_3^-$$
 and NCS^- .

Table 2

3. Results and discussion

3.1. Manganese(II) complexes

On the basis of the elemental analyses, the complexes were assigned the compositions shown in Table 1. The molar conductance measurements of all the complexes in DMSO of L^1 and L^2 correspond to the non-electrolytic nature but complexes of ligands L^3 and L^4 are 1:1 and 1:2 electrolyte in nature. Thus, these complexes may be formulated as [Mn(L^1 or L^2)X₂], and [Mn(L^4)]X₂ [X = NCS⁻ and NO₃⁻].

The manganese(II) complexes show a magnetic moment at room temperature in the range of ($\mu_{eff} = 5.83-6.02$ B.M.) corresponding to five unpaired electrons.

3.2. Bands due to thiocyanate anions

We adopt a native point of view in our discussion on complexation behavior of the complexes as a result, all the important IR bands corresponding to various fragments of the ligands which are shifted to lower frequency as compared to the macrocyclic ligands. We assume that the coordination of ligand has occurred

Important I.R. absorption bands (cm ⁻¹)	of nitrato and thiocyanato manganese(II) complexes s of L^1 , L^2 , L^3 and L^4
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Complex	$\upsilon_{C=N}$	$v_{ m Ni-N}$	$v_{ m Ni-O}$	$v_{ m Ni-S}$	$v_{ m NO_3}$	$v_{ m NCS}$
$[Mn(L^1)(NO_3)_2]$	1588	620	_	_	_	_
$[Mn(L^1)(NCS)_2]$	1587	620	_	-	_	2080, 860, 410
$[Mn(L^2)(NO_3)_2]$	1582	620	-	310	_	-
$[Mn(L^2)(NCS)_2]$	1596	620	-	_	_	-
$[Mn(L^3)(NO_3)](NO_3)$	1581	620	509, 521	_	_	2050
[Mn(L ³)(NCS)](NCS)	1584	620	518, 522	-	1384	-
$[Mn(L^4)](NO_3)_2$				315		
$[Mn(L^4)](NCS)_2$				-		

Table 3 Magnetic moment and electronic spectra of the manganese(II) complexes

Complex	Meff. BM	$v_1 \ (\mathrm{cm}^{-1})$	$v_2 \text{ (cm}^{-1})$	$Y_3 ({\rm cm}^{-1})$	$v_4 \ (\mathrm{cm}^{-1})$
$\overline{[Mn(L^1)(NO_3)_2]}$	5.83	17,550	24,390	28,615	34,462
$[Mn(L^1)(NCS)_2]$	5.98	17,755	24,650	28,977	31,600
$[Mn(L^2)(NO_3)_2]$	5.93	17,865	22,222	29,001	32,258
$[Mn(L^2)(NCS)_2]$	5.89	17,621	23,145	28,554	-
$[Mn(L^3)(NO_3)](NO_3)$	5.89	18,023	24,910	28,633	32,894
$[Mn(L^3)(NCS)](NCS)$	6.02	17,421	24,449	28,944	31,550
$[Mn(L^4)](NO_3)_2$	6.01	18,911	23,555	27,895	_
[Mn(L ⁴)](NCS) ₂	6.00	17,868	23,690	28,012	31,007

through the donor atoms of the groups. It intensively cleared the coordination abilities of studied complexes.

3.3. IR spectra of the manganese(II) complexes

The IR spectra of nitrato complexes of L¹ and L² display three (N–O) stretching bands, at ~1418–1427 cm⁻¹ (ν_5), 1303–1311 cm⁻¹ (ν_1) and 1003–1012 cm⁻¹ (ν_2).

The position of bands in the IR spectra of the complexes indicates that both nitrate groups are coordinated to the central metal ion in a unidentate manner [14]. The reported nitrato complex of L^3 shows three IR spectral bands at 1420, 1310 and 1028 cm⁻¹. The separation of the two highest frequency bands is 110 cm⁻¹. The position of these bands indicates a monodentate coordination of this group as well as displays a sharp and shows a strong band at 1388 cm⁻¹ which suggests that the nitrate groups are uncoordinated. In the infrared spectra of Mn(L⁴)(NO₃)₂ complexes show sharp bands at 1383 cm⁻¹ corresponding to an uncoordinated nitrate group and this extends our previous results which are reported earlier [15] (Table 2).

3.4. Electronic spectra of manganese(II) complexes

The electronic spectra of the manganese(II) complexes exhibit four weak-intensity absorption bands in the ranges 17,421–18,911, 22,222–24,910, 27,895–29,001 and 31,007–34,462 cm⁻¹ which may be assigned to the transitions: ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}({}^{4}G)$, ${}^{6}A_{1g} \rightarrow {}^{4}E_{g}$, ${}^{4}A_{1g}({}^{4}G)$ (10B + 5C), ${}^{6}A_{1g} \rightarrow {}^{4}E_{g}({}^{4}D)$ (17B + 5C) and ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}({}^{4}P)$ (7B + 7C), respectively [16,17] (Figs. 2–4).

The parameters *B* and *C* were calculated and reported which have a good agreement with data reported earlier [18]. The calculated values of the ligand field parameters are given in Table 3.

Table 4 Ligand field parameters of the manganese(II) complex

These values are calculated from the second and third transitions because these transitions are free from the crystal field splitting and depend on *B* and *C* parameters.

Orgel [19] calculates the values of D_q with the help of curve, transition energies versus D_q , as given by the using the energy due to the transition ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}({}^{4}G)$. Parameters *B* and *C* are linear combinations of certain coulombs and exchange integral, which are generally, treated empirical parameters obtained from the spectra of the free ions. Slater Condon-shortly repulsion parameters F_2 and F_4 are related to Racah parameters *B* and *C* as: $B = F_2 - 5F_4$ and $C = 35F_4$, The electron–electron repulsion in the complexes is more than in the free ion, resulting in an increased distance between electrons, and thus, affects the size of the orbital. On increasing delocalization, the value of β decreases up to less than one in the complexes.

3.5. Ligand field parameters

The value of β can be calculated from the Nephelauxetic parameter for the ligand (hx) and the Nephelauxetic parameter for the metal ion (km) as $(1 - \beta) = hx \times km$. The value of the parameter hx for manganese(II) complexes have been calculated by using the co-valency contribution of manganese(II), while for the calculation of β , we used the numerical value of *B* for manganese(II) free ion which is 786 cm⁻¹. The observed values for parameter β and hx suggest that the complexes, reported here, have appreciable ionic character [19]. We have observed in this spectroscopic characterization that one of the basic concept of transitions and nephelouxetric parameters analysis is to study the bounded metal to donor atoms which are defined the geometries of our complexes to understand their stereochemistry. Related data are given in Tables 2 and 4 respectively.

Complex	$D_q (\mathrm{cm}^{-1})$	$B (\mathrm{cm}^{-1})$	$C (\mathrm{cm}^{-1})$	β	F_4	F_2	Hx
$[Mn(L^1)(NO_3)_2]$	1775	539	3800	0.68	108	979	4.5
$[Mn(L^1)(NCS)_2]$	1780	614	2702	0.78	77	999	3.1
$[Mn(L^2)(NO_3)_2]$	1730	760	2924	0.96	83	1175	_
$[Mn(L^2)(NCS)_2]$	1795	629	3371	0.80	96	1109	2.8
$[Mn(L^3)(NO_3)](NO_3)$	1795	680	3622	0.86	103	1195	2.0
$[Mn(L^3)(NCS)](NCS)$	1886	636	3617	0.80	103	1151	2.8
$[Mn(L^4)](NO_3)_2$	1830	620	3471	0.78	99	1115	3.1
$[Mn(L^4)](NCS)_2$	1760	644	3450	0.81	98	1134	2.7

3.6. EPR spectra of manganese(II)

Virtually, all the theory of this spectroscopy had its origin in characterization patterns. Our present interest, however, lies in the study of stability and oxidation state, not in exploring the many applications of this resonance technique to specific use of such complexes. This technique is therefore strongly oriented towards the stability and geometrical aspects of the synthesized complexes. ESR spectra were recorded at room temperature for a polycrystalline sample and in a solution of DMSO. And give ESR spectra containing the six lines arising due to the hyperfine interaction between the unpaired electron with the ⁵⁵Mn nucleus (1 = 5/2). The nuclear magnetic quantum number M_1 , corresponding to these lines, are -5/2, -3/2, -1/2, +1/2, +3/2and +5/2 from low to high field. ESR [19,20] parameters of the manganese(II) complex $(g_{\parallel}, g_{\perp}, A_0 \text{ and } g_{iso})$ are calculated and their values are found in the range 3.95-3.64, 1.99-1.87, 111-105 and 2.64-2.45.

3.7. Cyclic voltammetery

On comparing the cyclic voltammograms we observe that the variation in the oxidation and reduction potentials may be due to distortion in the geometry that arises due to different anions coordinated. Cyclic voltammetric data for complexes in (CH₂Cl₂) $E_{p,a1}$ (V), $E_{1/2}$ (mV), ΔE_{p1} (mV), $E_{p,a2}$ (V) and $E_{1/2}$ (mV) are calculated and found in the range 0.580–0.570, 495.0–490.0, 110.0–105.0, 0.8950–0.8940 and 800–798. The MnL complex shows two oxidation processes at $E_{p,a} = 0.58$ and 0.895 V. The first wave is nearly reversible with $\Delta E_p = 110$ mV. This process is consistent with a one-electron oxidation to form the mixed valence Mn(II, III) species. The second wave is irreversible at 0.895 V. The observed reaction voltages of the complexes of CuL and CoL are lower than that of the ligand, while the MnL one is higher [19].

We have prepared and fully characterized a family of four macrocyclic ligands which have several potential donor atoms, but due to different fragments of the constraints all the ligands can provide a approach to their coordination behavior through which they can effect the stability of the manganese(II) complexes and their importance in coordination chemistry as well as their biophysical systems. The maximum priority of taking such donor atoms which are characterized by such different spectroscopic techniques having different stereochemistry can be arranged to manage different structures with metal. On the



Fig. 5. Structures of manganese(II) complexes with L^1 .



Fig. 6. Structures of manganese(II) complexes with L^2 .



Fig. 7. Structures of manganese(II) complexes with L³.

basis of donor atoms of the ligands are coordinated to the metal, formed different models of complexes, it follows that the complexes would be four, five and six coordinate with respect to the all ligands. As these ligands are potentially teradentate, pentadentate and hexadentate. It is quite feasible that the metal ions are six coordinate with different anions, as shown in Figs. 5–8



Fig. 8. Structures of manganese(II) complexes with L⁴.

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around the metal were obtained, suggesting that an octahedral or distorted octahedral configuration around the metal is possible. The possibility of a square pyramidal configuration around the metal has been discarded from the conductivity measurements, which show corresponding different types of electrolytes. IR spectral studies are very helpful to explore the probability related to the geometrical findings.

4. Conclusion

A series of manganese(II) complexes with macrocyclic ligands have been prepared and fully characterized. It is some times said that coordination chemistry of manganese(II) is the study has its importance in biological functions and catalytic activities which are effected in the environment of macrocyclic cavities. By using spectroscopic techniques our observation provides a deeper look on the stability and characterization ability of manganese(II) with donor atoms in a cyclic environments. These observations will be used in the designing with approach towards their application in chemical, biological and industrial aspects. Naturally our simplifies matters; but it does come as close to the truth as an aphorism come. The studies of spectroscopy and their importance lead us to understand the molecular arrangements of the studied macrocyclic complexes. The coordinating behavior in the complexes of manganese(II) effected by the coordination stereochemistry of the macrocyclic ligands NCS and NO₃. Due to these coordinating sites of the ligands are affecting coordination behaviors of the NO3 and NCS ions. On the basis of above studies suggested structures of the complexes are given in Figs. 5-8.

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