

Synthesis and Characterization of Metal(II) Complexes with Macrocyclic Ligand, 1,4,5,7,8,11,12,14-octaaza-tetraoxo-6,13-dithio-1,4,5,7,8,11,12,14-octahydrocyclotetradecane

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Metal complexes of the type, $[ML(H_2O)_2]X_2$ [$M = Mn(II)$, $Fe(II)$ and $Zn(II)$, $X = Cl^-$, Br^- & NO_3^-] have been synthesized with macrocyclic ligand, 1,4,5,7,8,11,12,14-octaazatetraoxo-6,13-dithio-1,4,5,7,8,11,12,14-octahydrocyclotetradecane (OTDCT). The complexes are characterized by elemental analysis, conductivity measurements, electronic spectral data and magnetic susceptibility value. The ligand has been found to coordinate to metal ion through four imido nitrogen atoms. Further two coordination sites of metal ions are satisfied by the oxygen of water molecules. Thermal analysis of complexes show similar pattern of decomposition. Weight loss *ca.* 190 °C in one step with exothermal peak in DTA curve may be attributed to loss of two water coordinated molecules.

Key Words: Synthesis, Mn^{2+} , Fe^{2+} , Zn^{2+} complexes, Macrocyclic ligand.

INTRODUCTION

Macrocyclic complexes of both transition and non-transition elements have received considerable interest during the past two decades due to their wide diversity in chemical¹⁻⁸ and biological systems⁹⁻¹¹. Macrocyclic complexes having tetraaza¹²⁻¹⁶, dioxotetraaza^{17,18} and tetraoxo-tetraaza¹⁹ are well known. In the present communication, synthesis and characterization of metal(II) complexes with a macrocyclic ligand 1,4,5,7,8,11,12,14-octaaza-tetraoxo-6,13-dithio-1,4,5,7,8,11,12,14-octahydrocyclotetradecane (OTDCT) are reported.

EXPERIMENTAL

Hydrazine hydrate, diethyl oxalate, carbon disulphide, metal(II) salts are of analytical grade and used as supplied. The metal bromides were

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prepared by dissolving the metal carbonates in calculated quantity of hydrobromic acid followed by crystallization. It is also required to add a few drops of bromine during the preparation to get the product in pure state. The preparation of the metal complexes involves two steps. First the precursor complex, *bis*-(1,4-diamine-1,4-diaza-2,3-dioxobutane)metal(II) was synthesized by following literature method^{20,21}.

Preparation of [Fe (DDDB)₂(H₂O)₂]Cl₂: The ligand *bis*-(1,4-diamine-1,4-diaza-2,3-dioxobutane) (DDDB) was prepared by adding 80 % hydrazine hydrate (30.4 mL, 0.4 mol) drop wise with diethyl oxalate (27 mL, 0.2 mol). An exothermic reaction takes place and a precipitate was formed immediately. Then the precipitate was washed and crystallized from ethanol. To an ethanolic solution (25 mL) of DDDB (1.18 g, 0.01 mol) was added to appropriate Fe(II) salt (1.185 g, 0.005 mol) and the mixture was refluxed for about 3 h when a yellow coloured precipitate was settled down on cooling. It was washed with ethanol and dried in a desiccator for 24 h.

Preparation of [Fe(OTDCT)(H₂O)₂]Cl₂: The DDDB metal complex prepared in above of iron(II) was suspended (400 mg, 1 mmol) in dry ethanol. Through this carbon disulphide in excess (304 mg, 4 mmol) was added. It was kept at room temperature for 0.5 h; after that it was refluxed for another 2 h when a brown colour precipitate was obtained. It was filtered, washed several times with ethanol and finally dried *in vacuo* over fused CaCl₂.

The metal, halogen and sulphur contents of all complexes, have been estimated by standard methods. Nitrogen has been estimated by Kjeldahl's method. Carbon and hydrogen have been estimated with a MLW-CHN microanalyzer. The molecular weights of the complexes have been determined by Rast's method. The thermal analysis of the complexes were carried out, increasing the temperature at the rate of 10 °C per minute and in the range 200-700°C.

Infrared spectra of the complexes have been taken in KBr using Perkin-Elmer 389 spectrophotometer. The electronic spectra of the complexes are recorded in DMF medium using 2390 spectrophotometer.

RESULTS AND DISCUSSION

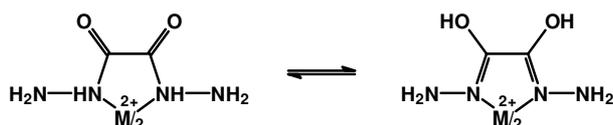
Metal(II) complexes of the ligand 1,4,5,7,8,11-octaaza-2,3,9,10-tetraoxo-6,13-dithio-1,4,5,7,8,11,12,14-octahydrocyclotetradecane (OTDCT) have been isolated with stoichiometry, [M(OTDCT)(H₂O)₂]X₂, where M = Fe(II), Mn(II) and Zn(II), X = Cl⁻, Br⁻ and NO₃⁻. The analytical data of the complexes recorded in Table-1. The complexes in dioxane/DMF have high molar conductance values suggested to be 1:2 electrolytes (Table-1).

TABLE-1
ANALYTICAL AND ELECTROCHEMICAL DATA OF OTDCT COMPLEXES

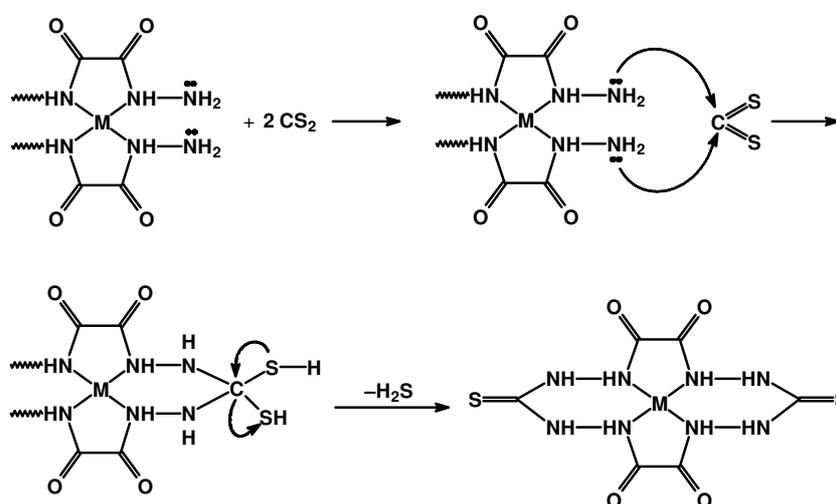
Complexes (Colour)	m.w. Found (Calcd.)	Elemental analysis (%): Found (Calcd.)						Λ_M (ohm ⁻¹ cm ⁻² mol ⁻¹)
		M#	C	H	N*	S	X**	
[Fe(OTDCT)(H ₂ O) ₂]Cl ₂ (Dark brown)	486 (494)	12.14 (12.72)	14.81 (15.18)	2.47 (2.21)	23.05 (24.08)	13.77 (13.59)	14.61 (15.39)	160
[Fe(OTDCT)(H ₂ O) ₂]Br ₂ (Middle buff)	575 (580)	10.09 (11.23)	12.52 (12.98)	1.39 (2.07)	19.48 (20.09)	11.13 (12.18)	27.83 (28.45)	140
[Fe(OTDCT)(H ₂ O) ₂](NO ₃) ₂ (Indian Red)	539 (544)	10.95 (11.57)	13.36 (14.01)	2.23 (1.94)	25.97 (26.76)	11.87 (12.33)	- -	138
[Mn(OTDCT)(H ₂ O) ₂]Cl ₂ (Saw Sienna)	486 (493)	12.17 (12.48)	14.81 (15.46)	2.47 (2.03)	23.05 (24.08)	13.17 (13.79)	14.61 (15.33)	156
[Mn(OTDCT)(H ₂ O) ₂]Br ₂ (Burnt Umbor)	575 (582)	10.09 (11.12)	12.52 (13.05)	1.39 (1.98)	19.48 (20.23)	11.13 (11.97)	27.83 (29.01)	148
[Mn(OTDCT)(H ₂ O) ₂](NO ₃) ₂ (Dark Brown)	539 (544)	10.95 (11.52)	13.36 (13.65)	2.23 (1.98)	25.97 (26.71)	11.87 (12.36)	- -	142
[Zn(OTDCT)(H ₂ O) ₂]Cl ₂ (Yellow)	491 (495)	13.03 (13.05)	14.66 (15.44)	2.44 (1.59)	22.81 (24.72)	13.08 (14.19)	14.46 (16.01)	170
[Zn(OTDCT)(H ₂ O) ₂]Br ₂ (Yellowish White)	580 (595)	10.94 (11.59)	12.41 (12.93)	1.38 (2.01)	19.31 (20.92)	11.03 (11.78)	27.58 (28.83)	152
[Zn(OTDCT)(H ₂ O) ₂](NO ₃) ₂ (Yellowish White)	546 (550)	11.76 (11.70)	13.24 (14.21)	2.21 (1.47)	25.74 (28.11)	11.76 (12.53)	- -	145

*Including nitrate nitrogen; **X = Cl⁻ and Br⁻; #M = Fe(II), Mn(II) and Zn(II).

The precursor complexes are expected to undergo amido-imidol tautomerization (**Scheme-I**). Their reaction with carbon disulphide may proceed in the way as depicted in **Scheme-II**.



Scheme-I



Scheme-II

In **Scheme-II**, the metal(II) ions envisages the formation of a six-membered metallocycle which will further stabilize the system due to chelate effect. The formation of macrocyclic complexes in **Scheme-II** is established on the basis of the results obtained from the molecular weight determination and analytical data (Table-1).

Infrared spectra

The ligand moiety in the complex is supposed to exist in different tautomeric forms consisting of amido-imidol, keto-enol tautomers including hydrogen bonding. The different tautomeric forms of the ligand moiety in the complexes expect bands due to hydrogen bonding, $\nu(\text{NH})$, $\nu(\text{C}=\text{N})$, $\nu(\text{C}=\text{O})$, $\nu(\text{C}-\text{O})$, $\nu(\text{C}=\text{S})$ and $\nu(\text{SH})$.

The IR spectra of these complexes are complicated and exhibit an identical pattern suggesting them to be structural. Attempts have been made to identify

some important bands which manifest the mode of bonding in the metal complexes with respect to the ligand.

Reaction of precursor complex of 1,4-diamine-1,4-diaza-2,3-dioxobutane (DDDB) with carbon disulphide bring about significant changes in the vibrational spectra of the products.

A broad band spreading over $3500\text{--}3400\text{ cm}^{-1}$ with its centre of gravity *ca.* 3450 cm^{-1} may be assigned to the combined mode of $\nu(\text{OH})$ and coordinated water molecules. The broadness of the band is probably due to strong inter-/intra-molecular hydrogen bonding as shown in Fig. 1.

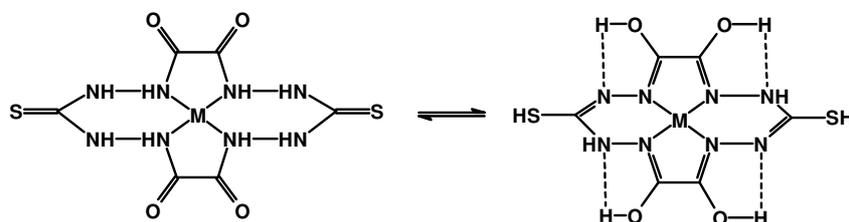


Fig. 1.

The most important feature of the spectra is the disappearance of asymmetric and symmetric stretching and deformation vibration of NH_2 groups in the region 3350 and 1665 cm^{-1} , respectively. But a group of three bands (multiplet) at 3250 , 3200 and 3100 cm^{-1} are obtained which may be due to secondary NH groups in different chemical environment²²⁻²⁴. This can be attributed to the condensation of CS_2 involving the *vic*-amino groups ($-\text{NH}_2$).

Another important aspect of the spectra of macrocyclic complexes is manifested by the appearance of some new bands at 1400 and 1080 cm^{-1} probably due to $\nu(\text{C}=\text{S})$ and wagging mode of vibration of NH groups, respectively^{25,26}. This indicates the reaction of CS_2 with the NH_2 groups of the precursor complexes.

The appearance of some new bands 2450 and 815 cm^{-1} are due to $\nu(\text{SH})$ and $\nu(\text{C}-\text{S})$ and bathochromic shift²⁷ of these bands suggest that the macrocyclic framework undergoes thio-keto enolization.

A doublet is observed at *ca.* 1600 and 1550 cm^{-1} due to stretching vibration of coordinated and free C-N group, respectively. An increase in the absorption frequency of coordinated C-N group compared to its precursor complex further confirms the coordination of metal ion through imido nitrogen, which is due to increase in the bond order of C-N bond²⁸⁻³¹. The appearance of the latter band suggests the formation of the macrocycle.

The bathochromic shift of the bands due to $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$ indicates the inter-/intra-molecular hydrogen bonding³² and keto enolization. In place of a single band due to $\nu(\text{C}-\text{N})$, as in precursor complex, a doublet has

been found to appear at *ca.* 1365 and 1325 cm^{-1} indicating that one of the C-N groups is coordinated while the other is free. A weak band *ca.* 2360 cm^{-1} due to $\nu(\text{N-C-O})$ arising out of the amido-imidol tautomerization³³ remains unaltered in the macrocycles.

Further, a sharp band of medium intensity³⁴ appears at *ca.* 1270 and 1240 cm^{-1} due to $\delta(\text{NH})$ the bathochromic shift of this band and appearance of $\nu(\text{M-N})$ band at 480 cm^{-1} , strongly support that the ligand is coordinated through imido nitrogen³⁵.

No bands in the region between *ca.* 1240 and 1020 cm^{-1} for the nitrate complex are observed, which suggest the non-coordination of nitrate groups³⁶. This is also supported by the high molar conductivity data of the complexes.

Thus from the foregoing observations, it is concluded that the free amino groups of the precursor complexes have undergone reaction with carbon disulphide resulting in the formation of a 14-membered macrocycle. The ligand framework in the complexes exists in keto-enol and amido-imidol tautomeric form and coordination occurs through amido NH groups. Based on the infrared spectral data, the structures of the complexes are elucidated as shown in (Fig. 2).

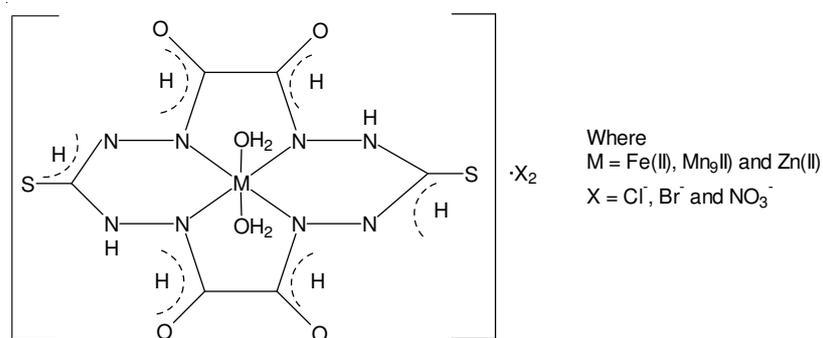


Fig. 2.

Thermal analysis: The thermograms of all the complexes follow the same pattern of thermal decomposition. The complexes remain almost unaffected upto 150 °C which indicates the absence of lattice water^{37,38}. After this, a slight depression up to 190 °C is observed with an endothermic peak at the same temperature. The weight loss at this temperature range corresponds to simultaneous elimination of two water molecules probably in the same chemical environment^{39,40}. The elimination of water molecules at a higher temperature and appearance of an endothermic peak clearly suggest the breaking of bond. Therefore, the weight loss can conclusively assigned to two molecules of coordinated water which is in conformity with present observations from IR spectral data. The dehydrated complexes

remain stable up to 340 °C and thereafter the complexes show rapid degradation, presumably due to the decomposition of organic constituents, as observed by the steep fall in the percentage of weight loss with a broad endothermic peak spread over the temperature range. The decomposition continues upto 450 °C beyond which there is no further weight loss. The weight of the final residues corresponds to the respective metal oxides.

Electronic spectra and magnetic properties

Iron(II) complexes: The iron(II) complexes are found to be diamagnetic in nature. The ground term of iron(II) in high spin state is 5D and in octahedral fields it splits into $^5T_{1g}$ and 5E_g , the former being in low energy state. Electronic spectra of high spin iron(II) complexes have been widely studied and well understood. However, electronic spectra of diamagnetic iron(II) compounds are yet to be thoroughly understood. In low spin iron(II) compounds 1A_1 is one of the split compounds of the term 1D and is the ground state in an octahedral field. Gutlick *et al.*⁴¹, have examined the cross over from $^5T_{2g}$ to 1A_1 (I) in *bis*(1,10-phenanthroline) complexes of iron(II) and have assigned bands arising from both states depending on the temperatures. The crystal spectra of low spin metal(II) complexes of 2,2'-bipyridyl have been examined⁴². They have concluded that the visible spectra are due to charge transfer transitions. The only evidence of *d-d* transition is a shoulder at 11,500 cm^{-1} which seems to arise from the spin forbidden $^1A_1 \rightarrow ^3T_1$ transitions. Electronic spectral bands (cm^{-1}) of the complexes are recorded in Table-2.

TABLE-2
ELECTRONIC SPECTRAL DATA (cm^{-1}) AND MAGNETIC MOMENT
VALUES OF IRON(II) COMPLEXES OF OTDCT

Complexes	μ_{eff} (BM at room temp)	Spin-forbidden $^1A_1 \rightarrow ^3T_1$ transition	CT Band
$[\text{Fe}(\text{OTDCT})(\text{H}_2\text{O})_2]\text{Cl}_2$	Diamagnetic	11500	23000
$[\text{Fe}(\text{OTDCT})(\text{H}_2\text{O})_2]\text{Br}_2$		11600	26000
$[\text{Fe}(\text{OTDCT})(\text{H}_2\text{O})_2](\text{NO}_3)_2$		11300	25400

Manganese(II) complexes: The magnetic moment of Mn(II) complexes are 5.92 BM. Its electronic spectrum shows a number of bands in the visible region, suggesting an octahedral geometry around the central metal ion in accordance with the previously reported values for Mn(II) ions^{42,43}. Bands observed around 27780, 2510, 21740 and 18870 cm^{-1} can be assigned to the transition $^6A_{1g}(\text{S}) \rightarrow ^4T_{2g}(\text{D}) \rightarrow ^4E_g \rightarrow ^4A_{1g}(\text{G}) \rightarrow ^4T_{2g}(\text{G}) \rightarrow$ and $^4T_{1g}(\text{G})$, respectively. The spectral bands are recorded in Table-3.

Zinc(II) complexes: All the Zn(II) complexes are diamagnetic and their electronic spectra show only charge transfer bands.

TABLE-3
ELECTRONIC SPECTRAL DATA (cm⁻¹) AND MAGNETIC MOMENT
VALUES OF IRON(II) COMPLEXES OF OTDCT

Complexes	μ_{eff} (BM)	Ligand field band positions (cm ⁻¹)			
		${}^6A_{1g}(S) \rightarrow$ ${}^4T_{2g}(D)$	${}^6A_{1g}(S) \rightarrow$ ${}^4E_g +$ ${}^4A_{1g}(G)$	${}^6A_{1g}(S) \rightarrow$ ${}^4T_{2g}(G)$	${}^6A_{1g}(S) \rightarrow$ ${}^4T_{1g}(G)$
[Mn(OTDCT)(H ₂ O) ₂]Cl ₂	5.02	27,780	25,000	21,740	18,870
[Mn(OTDCT)(H ₂ O) ₂]Br ₂	5.60	27,650	24,500	20,890	18,300
[Mn(OTDCT)(H ₂ O) ₂](NO ₃) ₂	5.81	27,830	25,100	20,820	18,590

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