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Spectroscopic approach in characterization of chromium(III), manganese(II), iron(III) and copper(II) complexes with a nitrogen donor tetradentate, 14-membered azamacrocyclic ligand

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Abstract

The complexes of Cr(III), Mn(II), Fe(III) and Cu(II) were synthesized with the macrocyclic ligand i.e. 2,3,9,10-tetraketo-1,4,8,11tetraazacyclotetradecane. The ligand was prepared by the [2 + 2] condensation reaction of diethyloxalate and 1,3-diamino propane. These complexes were found to have the general composition $M(L)X_3$ and $M'(L)X_2$ [where M = Mn(II) and Cu(II), M' = Cr(III) and Fe(III), L = ligand (N₄) and X = Cl⁻, NO₃⁻, 1/2SO₄²⁻ and [CH₃COO⁻]. The ligand and its transition metal complexes were characterized by the elemental analyses, molar conductance, magnetic susceptibility, mass, IR, electronic, and EPR spectral studies.

On the basis of IR, electronic and EPR spectral studies an octahedral geometry has been assigned for Cr(III), Mn(II) and Fe(III) and a tetragonal geometry for Cu(II) complexes.

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Keywords: Azamacrocyclic; Chromium(III); Manganese(II); Iron(III); Copper(II)

1. Introduction

The complexes of metal ions with macrocyclic ligands are significant because of there resemblance with many natural systems, such as porphyrins and cobalamines [1,2] The main interest in new macrocyclic bifunctional chelating agents arise due to their use in labeling monoclonal antibodies with radioactive metals [3–5] and for cancer diagnoses [6,7] as well as with permagnetic ions for magnetic resonance imaging [8].

The attachment of metal ions to proteins such as monoclonal antibodies can create new tools for use in biology and medicine [9]. This type of ligands has theoretical importance also because they are capable of furnishing an environment with controlled geometry and ligand field strength [10,11]. The reagents used for such attachments are called bifunctional chelating agents [12]. They have shown to be efficient catalyst for cleavage of the phosphate ester bond [13].

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In this paper, we report the synthesis and characterization of Cr(III), Fe(III), Mn(II) and Cu(II) complexes with 2,3,9,10-tetraketo-1,4,8,11-tetraazacyclotetradecane (Fig. 1). The possible geometry for complexes has been deduced by the elemental analyses, molar conductance, magnetic susceptibility, IR, electronic and EPR spectral studies.

2. Experimental

All the chemicals used were of AnalaR grade, and procured from Sigma-Aldrich, USA and E. Merck, Germany. Metal salts were purchased from E. Merck and Ranbaxy and were used as-received.

2.1. Synthesis of ligand

The hot ethanolic solution (20 mL), of diethyloxalate (2.9228 g, 0.02 mol), and a hot ethanolic solution (20 mL) of 1,3-diaminopropane (1.4826 g, 0.02 mol) were mixed slowly

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Fig. 1. Synthesis and structure of ligand (L).

with constant stirring. This mixture was refluxed at \sim 78 °C for 7 h in the presence of few drops of concentrated hydrochloric acid. On cooling a solid cream-colored precipitate formed, which was filtered, washed with cold EtOH, and dried under vacuum over P₄O₁₀. Yield \sim 78%, m.p. 240 °C. Elemental analyses found (%): C, 46.79; H, 6.31; N, 21.83. Calculated for C₁₀H₁₆N₄O₄ (atomic mass 256) was C, 46.88; H, 6.25 and N, 21.87%.

2.2. Synthesis of complexes

The hot ethanolic solution (20 mL), of ligand (0.5120 g, 0.002 mol) and hot ethanolic solution (20 mL), of corresponding metal salt (0.001 mol) were mixed together with constant stirring. The mixture was refluxed for 4–9 h at 78 °C. On cooling, colored complex precipitated out. It was filtered, washed with cold EtOH and dried under vacuum over P_4O_{10} and recrystallised.

2.3. Physical measurements

The C, H and N were analysed on a Carlo-Erba 1106 elemental analyzer. IR spectra (KBr) were recorded on an FTIR Spectrum BX-II spectrophotometer. The electronic spectra were recorded in DMSO on Shimadzu UV mini-1240 spectrophotometer. Molar conductance was measured on an ELICO (CM82T) conductivity bridge. Magnetic susceptibility was measured at room temperature on a Gouy balance using CuSO₄·5H₂O as a callibrant. Electron impact mass spectra were recorded on Jeol, JMS, DX-303 mass spectrometer. ¹H NMR spectra were recorded on Hitachi model R-600 FT-NMR spectrometer using CDCl₃ as solvent, chemical shifts are given in ppm relative to tetramethylsilane. EPR spectra of the complexes were recorded as polycrystalline sample at RT on E₄-EPR spectrometer using the DPPH as the *g*-marker.

3. Results and discussion

On the basis of elemental analyses, the complexes were assigned the composition shown in Table 1. The molar conductance measurements in DMSO correspond to 1:1 electrolytic nature for Cr(III) and Fe(III) complexes and non-electrolytes for the Mn(II) and Cu(II) complexes. Thus the complexes

Complex	MW ^a	Molar conductance	Color	M.P. (°C) ^c	Yield (%)	Elemental analys	es data found (calcul	ated, %)	
		$(\Omega^{-1} \operatorname{cm}^2 \operatorname{mol}^{-1})^{\mathrm{b}}$				Metal	C	Н	Z
Cr(L)Cl ₂]Cl CrC ₁₀ H ₁₆ N ₄ O ₄ Cl ₃	415	86	Dark green	256	73	12.49 (12.53)	28.84 (28.92)	3.91 (3.85)	13.42 (13.49)
Cr(L)(NO ₃) ₂]NO ₃ CrC ₁₀ H ₁₆ N ₇ O ₁₃	494	103	Green	273	84	10.36 (10.53)	24.09 (24.29)	3.19 (3.24)	19.57 (19.84)
$[Mn(L)Cl_2] MnC_{10}H_{16}N_4O_4Cl_2$	382	12	Light brown	269	78	14.33 (14.40)	31.47 (31.41)	4.13 (4.19)	14.61 (14.66)
$Mn(L)SO_4$] $MnC_{10}H_{16}N_4O_8S$	407	15	Brown	265	68	13.74 (13.51)	29.41 (29.48)	3.99 (3.93)	13.79 (13.76)
Fe(L)Cl ₂]Cl FeC ₁₀ H ₁₆ N ₄ O ₄ Cl ₃	418	107	Yellow	281	86	13.37 (13.40)	28.63 (28.71)	3.71 (3.83)	13.34 (13.40)
$Fe(L)(NO_3)_2]NO_3 FeC_{10}H_{16}N_7O_{13}$	498	96	Brown	278	73	11.26 (11.24)	24.03 (24.10)	3.27 (3.21)	19.63 (19.98)
$Cu(L)Cl_2$] $CuC_{10}H_{16}N_4O_4Cl_2$	391	11	Green	290	81	16.19 (16.37)	30.77 (30.69)	4.09(4.09)	14.21 (14.32)
$Cu(L)(NO_3)_2] CuC_{10}H_{16}N_6O_{10}$	444	6	Fast Green	283	79	14.27 (14.41)	27.09 (27.03)	3.67 (3.60)	18.98 (18.92)
Cu(L)SO ₄] CuC ₁₀ H ₁₆ N ₄ O ₈ S	416	16	Sky blue	295	68	15.37 (15.38)	28.63 (28.85)	3.91 (3.85)	13.42 (13.46)
Cu(L)(CH ₃ COO) ₂] CuC ₁₄ H ₂₂ N ₄ O ₈	438	12	Blue	288	74	14.46(14.61)	38.57 (38.36)	5.11 (5.02)	12.65 (12.79)

Decomposition temperature



Fig. 2. Electron impact mass spectrum of the ligand (L).

may be formulated as $[M(L)X_2]X$ and $[M'(L)X_2]$, respectively [where M = Mn(II) and Cu(II), M' = Cr(III) and Fe(III), L = ligand and X = Cl⁻, NO₃⁻, and CH₃COO⁻].

The mass spectra of ligand (L) (Fig. 2) confirm the proposed formula by showing a peak at 255 amu corresponding to the macrocyclic moiety $[(C_{10}H_{16}N_4O_4)^+$ calculated atomic mass = 256 amu]. It also shows a series of peaks at 42, 56, 72, 128, 184 and 200 amu corresponding to various fragments. Their intensity gives an idea of stability of fragments. The ¹H NMR spectrum of the metal-free ligand does not give any signal corresponding to primary diamine and ketonic group. It shows a signal at $\delta 3.7_{(q)}$ ppm, attributed to amide (-CH2-NH-C-) protons (4H). The signals appeared at $\delta 2.6_{(m)}$ ppm and $\delta 1.4_{(q)}$ ppm may be assigned to methylene protons [14]. IR spectrum of the ligand does not exhibit any band corresponding for the free primary diamine and ketonic group. Four new bands, Table 2, appear in the spectrum of ligand [15] in the regions 1651, 1518, 1226 and 762 cm⁻¹ are assignable to amide-I ν (C=O), amide-II [ν (C-N) + δ (N-H)], amide-III [δ (N–H)] and amide-IV [φ (C=O)] bands, respectively. This supports the macrocyclic nature of the ligand. A single sharp band observed at 3298 cm^{-1} , may be due to ν (N–H) of the secondary amino group [16]. On complexation the position of ν (N–H) bands shifted to lower frequency compared to the macrocyclic ligand and a new medium intensity band appears at 418–490 cm⁻¹ attribute to ν (M–N), it provide, strong evidence for the involvement of nitrogen in coordination. IR spectrum indicates that the ligand act as tetradentate coordinating through nitrogen [N₄].

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IR	spectral	data and	their	assignments	in cm-	1
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3.1. Chromium(III) complexes

Chromium(III) complexes show magnetic moment in the range 3.68–3.72 BM recorded at room temperature, corresponding to three unpaired electrons (Table 3). This value is close to the spin only value. IR spectrum (Fig. 3b) of Cr(III) nitrate complex shows three IR bands v_5 , v_1 and v_2 at 1437, 1318 and 1021 cm⁻¹, respectively. The difference of two highest frequency bands ($v_5 - v_1$) is 119 cm⁻¹, characteristics for unidentate behavior of nitrate ion. A sharp strong band at 1379 cm⁻¹ confirms the presence of a uncoordinated nitrate ion.

The electronic spectra (Fig. 3) of Cr(III) complexes recorded in DMSO solution at room temperature, display three bands in the range 18,586–18,605 ($\varepsilon = 41-42 \text{ L mol}^{-1}$ cm⁻¹) (ν_1), 22,290–22,386 ($\varepsilon = 56-58 \,\mathrm{L}\,\mathrm{mol}^{-1}\,\mathrm{cm}^{-1}$) (ν_2) and 24,920–24,948 ($\varepsilon = 65-67 \,\mathrm{L} \,\mathrm{mol}^{-1} \,\mathrm{cm}^{-1}$), characteristic to an octahedral geometry [17] (Fig. 4). These bands may be assigned to the transitions ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}$ (F) ν_2 and ${}^4A_{2g} \rightarrow {}^4T_{2g}$ (F) ν_1 , respectively, and third one is due to the charge transfer. Various ligand field parameters are calculated and given in Table 4. Dq values have been evaluated by using Orgel energy level diagram. The Nephelauxetic parameter β is obtained by using the relation: $\beta = B(\text{Complex})/B(\text{Free ion})$. The β values indicate that the complexes have appreciable covalent character. EPR spectra were recorded as a polycrystalline sample at room temperature. An isotropic EPR spectra of Cr(III) complexes recorded at room temperature as polycrystalline sample shows the g_{iso} values in the range 1.9965–2.0016 (Table 5).

3.2. Manganese(II) complexes

The room temperature magnetic moment of the manganese(II) complexes lies in the range 5.89–5.93 BM corresponding to five unpaired electrons.

IR spectrum of Mn(II) sulphate complex exhibits three bands at ~1123–1151, 970 and 617–609 cm⁻¹, assigned to v_3 , v_1 and v_4 , respectively. Both the bands v_3 and v_4 splits into two bands. It can be explained by assuming the lowering in symmetry from T_d to C_{3v} (unidentate manner of coordination of sulphate group), Fig. 5.

Complexes	ν(N-H)	Amide-I [v(C=O)]	Amide-II $[\nu(C-N) + \delta(N-H)]$	Amide-III [δ(N-H)]	Amide-IV $[\phi(C=O)]$	[v(M-N)]
Ligand (L)	3298	1651	1518	1226	762	_
[Cr(L)Cl ₂]Cl	3296	1653	1502	1209	759	487
$[Cr(L)(NO_3)_2]NO_3$	3299	1647	1505	1202	756	463
$[Mn(L)Cl_2]$	3295	1649	1495	1210	766	488
[Mn(L)SO ₄]	3298	1655	1499	1197	759	452
[Fe(L)Cl ₂]Cl	3293	1652	1506	1211	763	481
$[Fe(L)(NO_3)_2]NO_3$	3297	1647	1497	1205	762	467
$[Cu(L)Cl_2]$	3284	1650	1501	1201	755	438
$[Cu(L)(NO_3)_2]$	3289	1651	1490	1199	762	479
[Cu(L)SO ₄]	3296	1657	1503	1215	757	465
[Cu(L)(CH ₃ COO) ₂]	3298	1648	1492	1206	760	459

Table 3 Magnetic moment and electronic spectral data of the complexes

Complex	$\mu_{\mathrm{eff}}~(\mathrm{BM})^{\mathrm{a}}$	$\lambda_{\rm max}~({\rm cm}^{-1})$	Extinction coefficient, ε (L mol ⁻¹ cm ⁻¹)
[Cr(L)Cl ₂]Cl	3.68	18586, 22290, 24920	41, 58, 65
$[Cr(L)(NO_3)_2]NO_3$	3.72	18605, 22386, 24948	42, 56, 67
$[Mn(L)Cl_2]$	5.89	18349, 22883, 28329, 38462	46, 51, 59, 74
[Mn(L)SO ₄]	5.93	19685, 23474, 28011, 38610	47, 53, 58, 76
[Fe(L)Cl ₂]Cl	5.91	18939, 21008, 27027, 37037	73, 84, 97
$[Fe(L)(NO_3)_2]NO_3$	5.98	18627, 20593, 26762, 37842	71, 80, 96
$[Cu(L)Cl_2]$	1.92	15878, 20315, 31328	52, 68, 134
$[Cu(L)(NO_3)_2]$	2.01	16705, 20527, 31272	54, 69, 133
[Cu(L)SO ₄]	1.97	16764, 20109, 31478	54, 76, 135
[Cu(L)(CH ₃ COO) ₂]	1.90	16837, 20768, 31517	55, 70, 136

^a Error limit $\pm 4\%$.

Table 4

Ligand field parameters of the complexes

Complex	$Dq (cm^{-1})$	$B (\mathrm{cm}^{-1})$	$C (\mathrm{cm}^{-1})$	β	LFSE (kJ mol ⁻¹)
[Cr(L)Cl ₂]Cl	2229.00	329.15	1316.60	0.36	319.57
$[Cr(L)(NO_3)_2]NO_3$	2238.60	336.54	1314.16	0.37	320.95
$[Mn(L)Cl_2]$	1834.90	778.00	3020.60	0.89	00.00
[Mn(L)SO ₄]	1968.50	648.15	3398.50	0.83	00.00
[Fe(L)Cl ₂]Cl	1893.90	859.86	2481.88	_	00.00
$[Fe(L)(NO_3)_2]NO_3$	1862.70	881.29	2356.02	-	00.00

Electronic spectra of Mn(II) complexes exhibit four weak intensity absorption bands in the range 18,349–19,685 ($\varepsilon = 46-47 \,\mathrm{L} \,\mathrm{mol}^{-1} \,\mathrm{cm}^{-1}$), 22,883–23,474 ($\varepsilon = 51-53 \,\mathrm{L} \,\mathrm{mol}^{-1} \,\mathrm{cm}^{-1}$), 28,011–28,329 ($\varepsilon = 58-59 \,\mathrm{L} \,\mathrm{mol}^{-1} \,\mathrm{cm}^{-1}$), and 38,462–38,610 cm⁻¹ ($\varepsilon = 74-76 \,\mathrm{L} \,\mathrm{mol}^{-1} \,\mathrm{cm}^{-1}$). These bands may be assigned to the transitions: ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}({}^{4}G)$, ${}^{6}A_{1g} \rightarrow$



Fig. 3. Electronic spectra of the complexes.

 ${}^{4}\text{E}_{g}, {}^{4}\text{A}_{1g}({}^{4}\text{G})(10B + 5C) \text{ and } {}^{6}\text{A}_{1g} \rightarrow {}^{4}\text{E}_{g}({}^{4}\text{D})(17B + 5C), {}^{6}\text{A}_{1g} \rightarrow {}^{4}\text{T}_{1g}({}^{4}\text{P})(7B + 7C), \text{ respectively.}$

The value of B and C were calculated from the second and third transitions, because these transitions are free from the crystal field splitting and depend on B and C parameters [18,19]. The calculated values of the ligand field parameters are given in Table 4.

EPR spectra were recorded at room temperature as polycrystalline sample and in DMSO solution. The polycrystalline spectra were isotropic and exhibit the g_{iso} value in the range 1.9980–2.0018. The EPR spectra recorded in DMSO solution give well defined six line, arising due to the hyperfine interaction between the unpaired electron with the ⁵⁵Mn nuclear ($l = \frac{5}{2}$). The nuclear magnetic quantum number M₁, corresponding to these lines are $-\frac{5}{2}$, $-\frac{3}{2}$, $-\frac{1}{2}$, $+\frac{1}{2}$, $+\frac{3}{2}$ and $+\frac{5}{2}$ from low to the high field.



Fig. 4. Suggested structures of the complexes.

Table 5EPR spectral data of the complexes

Complexes	Data at ro	Data at room temperature				
	$\overline{g_{ }}$	g_{\perp}	$g_{\rm iso}/g$	G		
[Cr(L)Cl ₂]Cl	_	_	1.9965	_		
$[Cr(L)(NO_3)_2]NO_3$	-	-	2.0016	-		
[Fe(L)Cl ₂]Cl	_	-	2.0402	-		
[Fe(L)(NO ₃) ₂]NO ₃	_	_	2.0468	-		
$[Mn(L)Cl_2]$	_	_	1.9980	-		
[Mn(L)SO ₄]	_	-	2.0018	-		
$[Cu(L)Cl_2]$	2.0998	2.0499	2.0665	2.0000		
$[Cu(L)(NO_3)_2]$	2.2224	2.0531	2.1090	4.1890		
[Cu(L)SO ₄]	2.2107	2.0828	2.1254	2.5568		
[Cu(L)(CH ₃ COO) ₂]	2.0973	2.0236	2.0482	4.1229		

3.3. Iron(III) complexes

These complexes show magnetic moments corresponding to five unpaired electrons [20], which lie in the range 5.91–5.98 BM.

IR spectrum of iron nitrate complex (Fig. 5(b)) shows bands corresponds to bidentate nature. The presence of an uncoordinated nitrate group is also confirmed by the band (strong) present at 1386 cm^{-1} , in the IR spectra of the Fe(III) sulphate complex [21].

Electronic spectra of these complexes display three bands in the range 18,627–18,939 ($\varepsilon = 71-73 \text{ Lmol}^{-1} \text{ cm}^{-1}$), 20,593–21,008 ($\varepsilon = 80-84 \text{ Lmol}^{-1} \text{ cm}^{-1}$) and 26,762– 27,027 cm⁻¹ ($\varepsilon = 96-97 \text{ Lmol}^{-1} \text{ cm}^{-1}$). The assignments to these bands are difficult.



Fig. 5. IR spectral bands of the anions.

EPR spectra of iron(III) complexes were recorded as polycrystalline sample at room temperature. The isotropic spectra gives the g_{iso} values in the range 2.0402–2.0468.

3.4. Copper(II) complexes

The magnetic moment measurements of the Cu(II) complexes at room temperature lie in the range 1.90–2.01 BM corresponding to one unpaired electron. The complexes may be considered to possess a tetragonal geometry.

The IR spectra of Cu(II) nitrate complex displays three bands (ν_5 , ν_1 and ν_2) at 1429, 1325 and 1017 cm⁻¹. The position of these bands suggests the coordinated behavior of nitrate group as unidentate.

IR spectrum of sulphate complex exhibits four bands at 1098–1033, 986, 639–581 and 467 cm⁻¹. Assigned to ν_3 , ν_1 , ν_4 , and ν_2 , respectively. The ν_3 and ν_4 each splits into two bands. It suggests the unidentate behavior of the sulphate ion [21].

The IR spectrum of Cu(II) acetate complex shows the medium intensity bands at 1619 and 1332 cm^{-1} , assigned to $v_a(\text{C-O})$ and $v_s(\text{C-O})$, respectively. The difference between these two frequencies is ~287 cm⁻¹, which is greater than that for uncoordinated acetate ion by ~143 cm⁻¹ and for bidentate acetate ion by ~217 cm⁻¹. It strongly support that both the acetate ions are coordinated to the metal ion in the unidentate fashion [21].

Electronic spectra of copper complexes display bands in the range 15,878–16,764 ($\varepsilon = 52-55 \text{ Lmol}^{-1} \text{ cm}^{-1}$) (ν_1), 20,109–20,768 ($\varepsilon = 67-70 \text{ Lmol}^{-1} \text{ cm}^{-1}$) (ν_2) and 31,272–31,517 cm⁻¹ ($\varepsilon = 133-136 \text{ Lmol}^{-1} \text{ cm}^{-1}$) (ν_3), corresponding to the following transitions: ${}^2B_{1g} \rightarrow {}^2A_{1g} (d_{x^2-y^2} \rightarrow d_{z^2}) \nu_1$, ${}^2B_{1g} \rightarrow {}^2B_{2g} (d_{x^2-y^2} \rightarrow d_{zy}) \nu_2$ and ${}^2B_{1g} \rightarrow {}^2E_g$ ($d_{x^2-y^2} \rightarrow d_{zy}, d_{yz}$) ν_3 , respectively. These three spin allowed transitions may be expected in the visible region, suggesting D_{4h} or C_{4v} symmetry.

The complexes exhibit anisotropic EPR spectra characteristic of tetragonal copper. The observed g values are in the range 2.0482–2.1090.

 $G = (g_{||-2})/(g \perp -2)$, which measure the exchange interaction between the copper centers in a polycrystalline solid has been calculated. According to Hathaway and Billing [22] and Chandra [23] if G > 4, the exchange interaction is negligible but G < 4 indicates considerable exchange interaction in the solid complexes. The *G* value for chloride and sulphate complexes are <4, it indicates a considerable exchange interaction between two molecules of the complex while in the nitrate acetate complexes the value of *G* is >4 suggest the vice versa position.

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