Preparation and Characterization of Chromium (III) and Iron (III) Macrocyclic Complexes

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Abstract

Chromium (III) and iron (III) complexes of the general formula $[M(L_n)X_2]X$ {M = Cr (III) or Fe (III) ions ; L = macrocyclic ligand; n = 1 or 2, where L_1 = (8,9; 17, 18 - di (4-nitrobenzene) - 2,6 ; 11, 15 – tetraoxo -1,7 ; 10, 16-tetraazacyclooctadecane) or L_2 = (9,10 ; 19,20- di (4-nitrobenzene) -2 , 7; 12,17-tetraoxo-1,8;11,18-tetraazacyclo dodecane) ; X = Cl^- or NO_3^- }, containing 18 or 20 membered rings, have been synthesized by the template condensation of the aliphatic dicarboxylic acids HOOC-$(CH_2)_y$-COOH (y = 3 or 4) with 4 - nitro , 1 , 2-phenylenediamine in the presence of chromium(III) or iron(III) salts. The prepared complexes were characterized by metal content analyses, IR, electronic spectroscopy, magnetic susceptibility and conductivity measurements. I.R spectra confirm coordination of amide nitrogens to the central metal ion. An octahedral geometry has been suggested for all the complexes. The molar conductance values of the complexes show that they are 1:1 electrolytes.

Keywords : Macrocyclic complexes , chromium (III) and iron (III) ions, preparation

Introduction

The coordination chemistry of macrocyclic complexes is a fascinating area which has attracted the attention of inorganic chemists [1-5]. Macrocyclic complexes have been of great interest due to their importance as an essential metalloenzyme active site [6] and this will help us for firther understanding of biological systems [7]. Studies of macrocyclic complexes have shown that some of these complexes are involved in important biological processes [8], such as photosynthesis and dioxygen transport [9,10], in addition to their catalytic properties, which may lead to important industrial applications [10,11]. Their enhanced kinetic and thermodynamic stabilities led to a widespread study of the features which also influence their potential applications as metal extractant [12], radiotherapeutic [13], medical imaging agents [14] and as effective sequestering agents for toxic metals [15]. A tetraazamacrocycle has long been an extremely useful and versatile macrocyclic ligand in coordination, bioinorganic and biomimetic chemistry [16].

Metal template synthesis was found to be an effective method to synthesize macrocyclic complexes [17]. Here we report , the synthesis and characterization of tetraazamacrocyclic complexes $[M(L_n)X_2]X$ obtained from the template condensation reaction of 4-nitro, 1,2-phenylenediamine with glutaric and adipic acids, in the presence of chromium(III) or iron (III) salts.

Experimental

Materials :

All the chemicals used during these investigations including 4-nitro , 1 , 2-phenylenediamine (Merck), glutaric and adipic acids (Fluka) were used without further purification. The metal salts $CrCl_3.6H_2O$, $Cr(NO_3)_3.9H_2O$, $FeCl_3.6H_2O$ and $Fe(NO_3)_3.9H_2O$ used were of B.D.H. quality.

Analytical methods and physical measurements :

The metal contents were determined according to the standard procedure [18]. Melting points were determined by using Richerk Jung Heizbank melting point apparatus. Molar conductivities of the complexes have been measured in an electrolytic conductivity measuring set LF-42 using 0.001 M solution of the complexes in dimethylformamide (DMF) at room temperature. IR spectra were recorded on a Bruker tensor 27 spectrophotometer in the 400-4000 cm^{-1} range using KBr disc. Electronic spectra were recorded on a Shimadzu 160 spectrophotometer in DMF at 25^oc for 0.001 M solution of the complexes using a 1 cm quartz cell . Magnetic susceptibilities of the complexes have been measured using Bruker B.M.6.

Synthesis of the complexes :

1. synthesis of the $[M(L_1)X_2]X$ or $[M(L_2)X_2]X$ complexes :
These complexes were prepared using one pot template synthesis as following :
The reaction is carried out in 1:2:2 molar ratio. An ice cold solution of metal salt (0.005 mol) in ethanol was reacted with 4-nitro,1,2-phenylenediamine (1.53gm,0.01 mol) dissolved in ethanol. This is followed by the addition of an ethanolic solution of glutaric (1.32 gm, 0.01 mol) or adipic acid (1.46 gm , 0.01mol). The resulting mixture was stirred for 24 hr, then kept to stand for 6 hr at room temperature . The resulted fine compound was filtered off , washed with ethanol and then air dried .

Results and discussion

The prepared complexes are colored solids, stable in air at room temperature. The chemical analytical data of these synthesized chromium(III) and iron(III) complexes are listed in Table 1. The molar conductances of the complexes in DMF are in the range 68-90 $ohm^{-1}cm^2mol^{-1}$ (Table 1) indicating a 1:1 electrolytic nature [19].

Table (1) : Physical and analytical properties of the prepared complexes

Complexes	Colour	Yield %	m.p C⁰	% Metal		Molar Conductivity ohm^{-1} cm^2 mol^{-1}
				Found	Calculated	
[Cr(L$_1$)Cl$_2$]Cl	Dark Brown	82	193	8.32	7.91	88
[Cr(L$_1$)(NO$_3$)$_2$]NO$_3$	Brown	71	176	7.48	7.06	68
[Fe(L$_1$)Cl$_2$]Cl	Dark Brown	66	234	8.09	8.45	78
[Fe(L$_1$)(NO$_3$)$_2$]NO$_3$	Magenta	72	187	7.61	7.54	77
[Cr(L$_2$)Cl$_2$]Cl	Blackish Brown	59	180	7.24	7.59	90
[Cr(L$_2$)(NO$_3$)$_2$]NO$_3$	Brown	63	212	7.20	6.80	85
[Fe(L$_2$)Cl$_2$]Cl	Brownish Red	55	201	7.79	8.10	69
[Fe(L$_2$)(NO$_3$)$_2$]NO$_3$	Bright Brown	70	198	6.89	7.26	80

IR spectra :

The characteristic infrared frequencies of the complexes are summarized in Table 2. The spectra showed the absence of NH$_2$ stretching vibrations of diamine and the OH groups of the dicarboxylic acids implying their involvement in the formulation of tetraamidemacrocycles and provides evidence for this cyclization [20]. The appearance of four amide bands in the regions 1687-1632, 1597-1572, 1292-1247 and 671-630 cm^{-1} are due to the amide I [ν(C=O)], amide II [ν(C-N)+□(N-H)], amide III [□(N-H)] and amide IV [□(C=O)] bands, respectively [21, 22]. It provides a strong evidence for the presence of a closed cyclic product. The spectra of all the complexes showed a band in the region 3326-3287 cm^{-1}, which is associated with the N-H stretching mode of amide group [23].A new band in the region 524-509 cm^{-1} due to ν(M-N) vibrations [24,25] further confirms the involvement of nitrogen in coordination. Nitrate complexes of Cr(III) and Fe(III) showed absorption bands around 830, 1062 and 1223 cm^{-1}, which are consistent with the monodentate nature [26]. Also all the nitrate complexes showed absorption bands around 1370 cm^{-1}, which can be assigned to ionic nitrate [27]. Thus, in solution and the solid state, both the two nitrate groups behave as monodentate ligands as evidenced by the IR spectra whereas the third one is ionized. These observations are consistent with the given formula and conductivity measurements. The M-Cl bands do not appear due to instrument limitation whereas the third chloro group is ionized and the absorption associated with the chloride ion in all complexes was identified around 570 cm^{-1} and assigned for uncoordinated chloride ion [28].

Table (2) : Important IR spectral bands of the prepared complexes (cm^{-1})

Complexes	ν (C=O) amide I	ν (C-N)+□(N-H) amide II	□ (N-H) amide III	□ (C=O) amide IV	ν (N-H)	ν (M-N)
[Cr(L$_1$)Cl$_2$]Cl	1644	1572	1285	630	3326	509
[Cr(L$_1$)(NO$_3$)$_2$]NO$_3$	1632	1578	1272	642	3291	512
[Fe(L$_1$)Cl$_2$]Cl	1649	1579	1247	636	3315	524
[Fe(L$_1$)(NO$_3$)$_2$]NO$_3$	1652	1585	1267	637	3298	511
[Cr(L$_2$)Cl$_2$]Cl	1687	1582	1253	671	3287	509
[Cr(L$_2$)(NO$_3$)$_2$]NO$_3$	1682	1596	1255	652	3298	522
[Fe(L$_2$)Cl$_2$]Cl	1681	1597	1292	643	3289	522
[Fe(L$_2$)(NO$_3$)$_2$]NO$_3$	1672	1596	1288	666	3323	520

Electronic spectra and magnetic moments:

The electronic spectral bands of chromium(III) and iron(III) complexes with macrocyclic lignads are summarized in Table 3. The electronic spectra of chromium(III) complexes showed three absorption bands at 15649-16077, 23041-23923 and 27933-28653 cm^{-1} assigned to $^4A_{2g} \rightarrow {}^4T_{2g}$ (F)($ν_1$), $^4A_{2g} \rightarrow {}^4T_{1g}$ (F) ($ν_2$), and $^4A_{2g} \rightarrow {}^4T_{1g}$ (P) ($ν_3$) transitions, respectively, suggesting an octahedral geometry around the chromium ion [29]. The Cr(III) complexes under consideration have the magnetic moments values of 3.68-3.89 B.M. (Table 3), which matches the calculated value of 3.88 B.M. Thus, the magnetic moment values support an octahedral geometry around the metal ion in chromium complexes [30]. In the spectra of the Fe(III) complexes band at 16155-16694 cm^{-1} may be assigned to the $^6A_{1g} \rightarrow {}^4T_{1g}$ (E) transition. Another band appears at 20876-21834 cm$^-$

[1], which can be assigned to the $^6A_{1g} \rightarrow {}^4T_{2g}$ transition. The spectra suggest an octahedral geometry [31]. The magnetic moment for high spin octahedral Fe(III) ion ranges from 5.7 to 6.0 B.M. The observed magnetic moment values are well within the accepted range (Table 3) and hence an octahedral geometry [32] for the Fe(III) ion is proposed.

Table (3) : Magnetic moments and electronic spectral data of the complexes

Complexes	μ_{eff} B.M.	ν max (cm^{-1})
[Cr(L$_1$)Cl$_2$]Cl	3.77	16025 , 23041 , 27933
[Cr(L$_1$)(NO$_3$)$_2$]NO$_3$	3.75	15822 , 23255 , 28248
[Fe(L$_1$)Cl$_2$]Cl	5.97	16611 , 21413
[Fe(L$_1$)(NO$_3$)$_2$]NO$_3$	5.83	16155 , 21739
[Cr(L$_2$)Cl$_2$]Cl	3.68	15649 , 23419 , 28011
[Cr(L$_2$)(NO$_3$)$_2$]NO$_3$	3.89	16077 , 23923 , 28653
[Fe(L$_2$)Cl$_2$]Cl	5.82	16694 , 21834
[Fe(L$_2$)(NO$_3$)$_2$]NO$_3$	5.71	16339 , 20876

On the basis of the above discussions ; the structures of the prepared complexes can be proposed as shown in Fig.(1) :
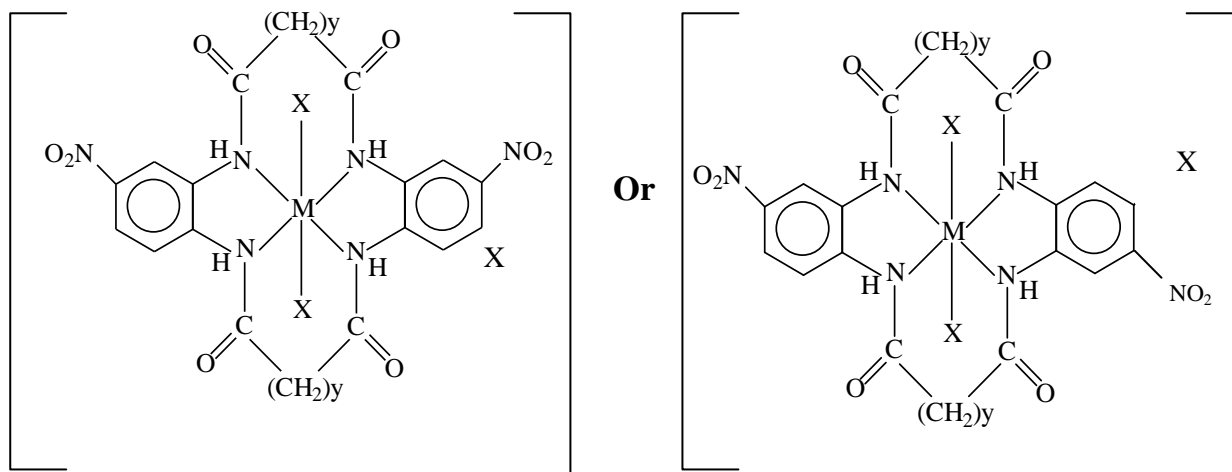
M = Cr (III) or Fe (III) ion
X = Cl$^-$ or NO$_3^-$ ion
y = 3 or 4

Figure 1. The proposed structures of the complexes

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تحضير وتشخيص بعض معقدات الكروم (III) والحديد (III) مع ليكاندات الحلقات الكبيرة

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الملخص

تم تحضير معقدات الكروم والحديد الثلاثية ذات الصيغة العامة $[M(L_n)X_2]X$ حيث كانت M = ايون Cr(III) او Fe(III) ؛ L = ليكاند حلقي كبير ؛ n = ١ او ٢ ، حيـث ان L_1 = (٨ ، ٩ ؛ ١٧ ، ١٨ – ثنائي (٤–نـايترو بنـزين)–٢ ، ٦ ؛ ١١ ، ١٥–رباعي اوكسـو– ١ ، ٧ ؛ ١٠ ،١٦–ربـاعي أزا اوكتاديكان الحلقي) ؛ او L_2 = (٩ ، ١٠ ؛ ١٩، ٢٠– ثنائي(٤– نايترو بنزين)–٢، ٧ ؛ ١٢ ،١٧–رباعي اوكسو–١ ، ٨ ؛ ١١ ،١٨–رباعي أزا دو ديكان الحلقي) ؛ X = Cl^- او NO_3^- .

حضرت المعقدات من التفاعل التكثيفي للحوامض الاليفاتيـة ثنائية الكاربوكسيل $COOH - (CH_2)_y - HOOC$ (y = ٣ او ٤) مـع ٤–نـايترو ، ١ ،٢– فنيلين ثنائي امين بوجود ايون الكروم او الحديد الثلاثي . شخصت هذه المعقدات من خلال التحليل الدقيق للفلز ، الاشعة تحت الحمراء ، الطيف الالكتروني ، القياسات المغناطيسية وقياسات التوصيلية المولارية . حيث اظهرت قياسات الاشعة تحت الحمراء ارتباط ايون الفلز مع الليكاندات مـن خـلال ذرات النتروجين أميد . اعتمادا على هذه القياسات يعتقد ان لهذه المعقدات شكل ثماني السطوح كما دلت قياسات التوصيلية الكهربائية لهذه المعقدات بانها موصلة بنسبة ١ : ١ .