

PREPARATION AND CHARACTERIZATION OF SOME NITROFURANTOIN METAL COMPLEXES

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Abstract

The synthesis and characterization of two types of complexes for nitrofurantoin of the formula $[M(NFD)Cl_2]Cl$ and $[M_2(NFD)_2Cl_2]Cl_4$ (Where $M=Ti(III)$, $Cr(III)$ and $Fe(III)$, $NFD =$ nitrofurantoin) were described.

They had been characterized by their elemental analysis, molar conductances, infrared and electronic spectra. The ligand exhibited tetradentate manner, in both types, to form with two chloride ions the most probable octahedral geometry around the trivalent ions.

Keywords: Nitrofurantoin, ligand, Titanium, Chromium, Iron.

Résumé

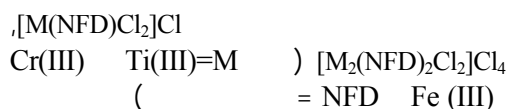
La synthèse et la caractérisation de deux types de complexes de nitrofurantoïne de formule $[M(NFD)Cl_2]Cl$ et $[M_2(NFD)_2Cl_2]Cl_4$ (où $M=Ti(III)$, $Cr(III)$ et $Fe(III)$, $NFD =$ nitrofurantoïne) sont décrites.

Elles ont été caractérisées par l'analyse élémentaire, les conductances molaires, les spectres infra-rouges et électroniques. Le ligand montre une complexation de type tétradentate, dans les deux cas, pour conduire, avec deux ions chlorures, à la structure octaédrique la plus probable, autour des ions trivalents.

Mots clés: Nitrofurantoïne, ligand, Titane, Chrome, Fer.

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derived

Nitrofurantoin is a synthetic antibiotic from nitrofurane. It is "1-[(5-nitrofurfurylidene) amino] imidazolidine-2, 4-dione" occurs as yellow crystalline, slightly soluble in water and ethanol and completely soluble in acetone and dimethyl formamide. It is recommended for the treatment of urinary tract infection [1]. Many workers applied the DC polarographic method for the determination of nitrofurantoin at different pH and concentrations [2,3]. Recently, Sulaiman and Hazim [4] applied the differential pulse polarographic study of nitrofurantoin in aqueous solution in human serum. Recent years witnessed the uses of β -lactum antibiotic as ligands in the preparation of complexes with transition and non-transitional elements, including ampicillin [5-7], amoxicillin [8-10] and cephalixin [11-13]. Nitrofurantoin possess many coordinational sites and considered as a relevant multidentate chelating ligand. As, continuation of our interest in preparation of medical complexes, we report, in the present paper, the preparation and characterization of two types of complexes for $Ti(III)$, $Cr(III)$ and $Fe(III)$ with nitrofurantoin as no report refer to such study in the literature so far.

EXPERIMENTAL

A. Chemicals

The nitrofurantoin (NFD) as a ligand was supplied from the general organization of drug and medical appliance, Samara-Iraq. All the other chemical were of Analar BDH and used without further purification.

B. Preparation of complexes

Two types of complexes were prepared:

Type I. They were prepared by reaction of aqueous solution of MCl_3 with ethanolic solution of the ligand nitrofurantoin ligand in 1:1 molar ratio.

The mixture, in each case, was refluxed for ~1 hr, evaporated to half its volume then cooled. The resulting products were filtered off, washed with ethanol and dry ether then dry.

Type II. The same procedures as in type I was used but, a double scale of both metal salts and the ligand (nitrofurantoin) were used, refluxed for ~6 hr and left overnight. The above steps were repeated to obtain the desired complexes.

C- Analytical and physical measurements

The contents of both types of complexes of carbon, hydrogen and nitrogen were estimated by Carlo – Erba Elemental Analyzer MOD 1106. The metal and the chloride amounts were found from the application of the standard procedure [14]. Molar conductivities of the complexes in $10^{-3}M$ DMF were taken on electrolytic conductivity measuring set model LF42.

IR Spectra recorded in KBr disc on Perkin – Elmer 557 spectrophotometer ($400-4000\text{ cm}^{-1}$). The electronic spectra were recorded on Shimadzu UV-106 spectrophotometer for $10^{-3}M$ solution of the complexes in DMF at 25°C using 1cm quartz cell.

RESULTS AND DISCUSSION

The synthesized complexes were prepared according to the following equations:

- $MCl_3 + NFD \rightarrow [M(NFD)Cl_2]Cl$
- $2MCl_3 + 2NFD \rightarrow [M_2(NFD)_2Cl_2]Cl_4$

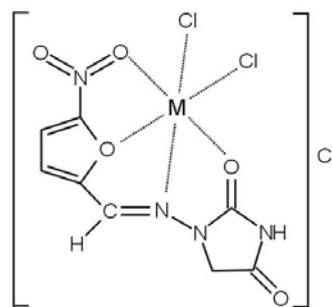
The resulting complexes were air stable both in solution and solid states. They were insoluble in water, methanol and ethanol but soluble in dimethyl formamide and dimethyl sulfoxide at room temperature. The conductance properties of both types of complexes were obtained on measuring their molar conductivities in dimethylformamide at $10^{-3}M$ (Table 1). Their molar conductivities were lied in two distinguishable ranges. These ranges were 72-86 and $312-322\ \Omega^{-1}\text{ mole}^{-1}\text{ cm}^2$

Table 1: Conductance properties of both types of complexes.

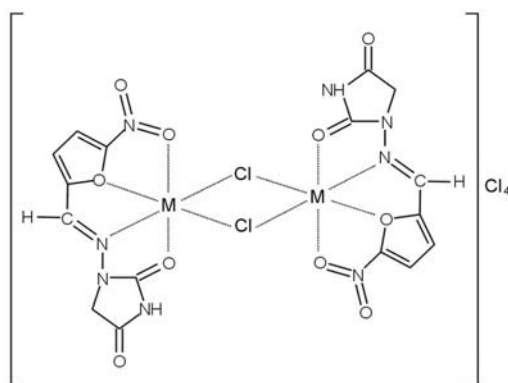
Complex (Color)	M.P. °C	Analysis % Calc. / (Found)						Λ_M (DMF)
		C%	H%	N%	a	B	M%	
[Ti(NFD)Cl ₂]Cl (Light blue)	192	24.53 (24.21)	1.27 (1.10)	14.31 (14.12)	18.12 (18.11)	9.06 (8.91)	12.23 (12.10)	72
[Cr(NFD)Cl ₂]Cl Light green	210	24.28 (24.10)	1.26 (1.22)	14.16 (14.08)	17.90 (17.66)	8.71 (8.25)	13.15 (12.94)	83
[Fe(NFD)Cl ₂]Cl (White)	230	24.04 (24.00)	1.25 (1.18)	14.02 (13.88)	17.76 (17.43)	8.88 (8.21)	13.98 (13.74)	86
[Ti ₂ (NFD) ₂ Cl ₂]Cl ₄ (Pale blue)	225	24.53 (24.31)	1.27 (1.11)	14.31 (14.13)	9.06 (8.81)	18.12 (18.00)	12.23 (12.00)	312
[Cr ₂ (NFD) ₂ Cl ₂]Cl ₄ Pale green	200	24.28 (24.12)	1.26 (1.21)	14.16 (14.00)	8.71 (8.42)	17.93 (17.62)	13.15 (12.99)	322
[Fe ₂ (NFD) ₂ Cl ₂]Cl ₄ (Grey)	240	24.04 (23.96)	1.25 (1.19)	14.02 (13.94)	8.88 (8.41)	17.76 (17.32)	13.98 (13.86)	316

indicating 1:1 and 1:4 ionic electrolytes for complexes of type I and II respectively [15].

The complexes of type I & II are depicted below :



Type I



Type II

The coordination sites in the ligand involved in the bonding with the metal ions had been determined by careful comparison of the i.r. spectra of the complexes of both types with that of the parent ligand. The ligand bands of diagnostic character of bonding with the metal ions were

Table 2: Ligand bands of diagnostic character of bonding with the metal ions.

Type of group	Assignment	ligand	Type I			Type II		
			1	2	3	1	2	3
Imidazole Group	ν C = O (at 2)	1715	1685	1680	1660	1675	1690	1665
	ν C = O (at 4)	1715	1715	1715	1715	1715	1715	1715
	ν C = N	1650	1620	1610	1615	1620	1600	1605
Furan ring	ν C – O – C	1085	1045	1025	1040	1020	1035	1030
Nitro group	ν N = O (asym)	1525	1490	1495	1480	1420	1470	1485
	ν N = O (sym)	1340	1330	1350	1355	1320	1360	1330
M-X	ν M-O		510	490	520	520	515	530
	ν M-N		460	455	470	480	465	475
	ν M-Cl*							

* The M-Cl spectra are out of the scale of our spectrophotometer.

Table 3: Electronic spectra of both types of complexes.

	Complex	Bands (cm ⁻¹)	Assignment	10 Dq (cm ⁻¹)	
Type I	[Ti(NFD)Cl ₂]Cl	ν 1	20,346	${}^2T_{2g} \rightarrow {}^2E_g$	20,346
	[Cr(NFD)Cl ₂]Cl	ν 1	17,150	${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$	17,150
		ν 2	24,340	${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$	
		ν 3	36,850	${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$	
	[Fe(NFD)Cl ₂]Cl	ν 1	18,440	${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$	14,080
		ν 2	22,860	${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$	
Type II	[Ti ₂ (NFD) ₂ Cl ₂]Cl ₄	ν 1	20,244	${}^2T_{2g} \rightarrow {}^2E_g$	20,244
	[Cr ₂ (NFD) ₂ Cl ₂]Cl ₄	ν 1	17,040	${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$	
		ν 2	24,210	${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$	
		ν 3	36,630	${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$	
	[Fe ₂ (NFD) ₂ Cl ₂]Cl ₄	ν 1	18,210	${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$	18,130
		ν 2	22,660	${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$	

taken into the consideration. These bands are tabulated in Table 2. There are two (C = O) of the imidazole ring at the positions 2,4, the C=N, the C-O-C of the furan ring and the N=O of the nitro group. The free ligand exhibited characteristic bands at 1715, 1650, 1085 cm^{-1} related to the first three categories, whilst, the NO₂ group showed two bands of symmetric and asymmetric NO stretching at 1340 and 1525 cm^{-1} respectively .

In the spectra of both types of complexes, the carbonyl groups of the imidazole were splitted into two bands. One almost unchanged while the other altered to lower values ($\Delta\nu=25-55\text{ cm}^{-1}$) This could interpreted as due to the coordination through one carbonyl group [17]. The C=N in both types of complexes were negatively shifted ($\Delta\nu =30-50\text{ cm}^{-1}$) as indication of the coordination of the nitrogen atom with metal ions [17]. The next diagnostic band in the parent ligand is that for the C-O-C(furan) which were negatively shifted ($\Delta\nu = 40-65\text{cm}^{-1}$) in the spectra of both types of complexes as due to the coordination of the oxygen atom with the metal ions [18-19]. The last characteristic bands are those for nitro group. It was concluded that if the difference between the two bands (asymmetric and symmetric) in their complexes equal to 260 cm^{-1} that means it coordinate in bidentate manner, and if the difference equal 190 cm^{-1} that means that the nitro group behave as monodentate ligand [20]. As the differences between the two bands in both types of complexes are less than 200, ($\Delta\nu = 100-160\text{ cm}^{-1}$), this is an indication of the monodentate behaviour of the nitro group [20]. On the other hand the spectra of both types of complexes showed new bands around 420-480 cm^{-1} and 490-530 cm^{-1} due to M-N and M-O respectively [21].

The electronic spectra of both types of complexes were tabulated in Table 3. For Ti (III) complexes in both types I and II one band was observed for each one and designed to ${}^2T_{2g} \rightarrow {}^2E_g$ transition in an octahedral environments [22]. For the Cr(III) complexes in I and II, three strong bands were observed in each case. These bands were attributed as due to transition from ${}^4A_{2g}$ (F) ground term to three excited quartet terms ${}^4T_{2g}$ (F), ${}^4T_{1g}$ (F) and ${}^4T_{1g}$ (P) in the octahedral environment [23]. In case of Fe (III) complexes the only sextet term of the d^5 configuration in the octahedral geometry is the ${}^6A_{1g}$ and does not split by ligand field. Consequently, all the excited states have different spin multiplicity from the ground term and the transition to them are spin forbidden. The first two bands of the spectrum of Fe(III) complexes are fitted to the transition from ${}^6A_{1g}$ to the lowest quartet terms the ${}^4T_{1g}$ (G) and ${}^4T_{2g}$ (G) respectively. The 10 Dq was determined from the relation Dq/B and ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (G)/B which estimated from the spectrum of the both types of the complexes [23].

CONCLUSION

In conclusion, the ligand has four coordination sites, the imidazole carbonyl group, the C=N, the oxygen furan ring and the oxygen of the nitro group for both types I & II. As well the presence of two terminal and bridged chloride ions in type I and type II complexes respectively gave the most probable octahedral geometry for both types of complexes.

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