

Preparation, Characterization and Antimicrobial Activity Study of Some Transition Metal Complexes of 4- Flourophenyl -4-Nitrobenzylidene

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Date of acceptance 9/2 / 2010

Abstract:

A new Schiff base of 4- flourophenyl-4- nitrobenzyliden (L), was prepared and used to prepare a number of metal complexes with Cr (III), Fe (III), Co(II), Ni (II) and Cu (II). These complexes were isolated and characterized by (FTIR), UV-Vis spectroscopy and flame atomic absorption techniques in addition to magnetic susceptibility, and conductivity measurements. The study of the nature of the complexes formed in ethanol was done following the molar ratio method gave results, agreed with those obtained from isolated solid state studies. The antibacterial activity for the ligand and its metal complexes were examined against two selected microorganisms, *Pseudomonas aeruginosa* and *Staphylococcus aureus*. The results indicated that the complexes show the enhanced activity in comparison to the free ligand; these were attributed to the synergetic effect between the metal ion and the ligand in addition to the difference in the structural varieties.

Key words: Synthesis; 4-Flourophnyl-4-nitrobenzylidene; Metal complexes.

Introduction:

Schiff base offer a versa file and flexible series of ligands capable to bind with various metal ions to give complexes with suitable properties for theoretical and practical applications (1). A large number of imine complexes have been structurally characterized and extensively investigated (1). Many transition elements have been extensively investigated with regard to their potential quality as anticancer agent (2), and they are found to be useful in catalysis, in medicine as antibiotics, anti-inflammatory agents and in industry as anticorrosion (3-7). However, several observations suggest that also other metals containing compounds might be suitable for the development of new

chemotherapeutics like La(III) salts have been reported to exert moderate antiproliferative effects in *vitro* (8) and in *vivo* (9). From this point we found it is interesting to isolate and study the biological activity of some new Cr(III), Fe(III), Co(II), Ni(II) and Cu(II) imines complexes.

Materials and methods:

All chemicals used were of the analytical grade (Analar) and of highest purity available. The metal analyses of the separated solid chelates for metal content were performed by using Shimadzu Atomic Absorption Spectrophotometer Flame (680-AA), Electronic spectra of the complexes were recorded on a Shimadzu UV – 160 Spectrophotometer. FTIR spectra

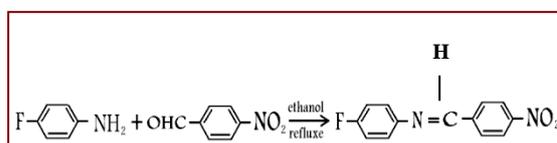
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of the samples were recorded on a Shimadzu IR Pesticide – 21 Spectrophotometer as CSI discs. Magnetic Susceptibility measurements of the complexes in the solid state were determined using Burker BM6 Instrumentation at room temperature. Molar conductance of the complexes were measured in DMF as solvent at room temperature using a (HANNA EC 214) conductivity type.

Preparation of 4-fluorophenyl -4-nitrobenzylidene (L):

An absolute ethanolic solution (30 ml) of 4-fluorophenyl -4-nitrobenzylidene (0.01mole) was refluxed with 4-para nitro benzaldehyde (0.01mole) for about 10 hrs. The formed solid produced cooled and was separated by filtration, purified by crystallization from ethanol, then washed with diethyl ether and dried in vacuum desiccator over anhydrous calcium chloride. The yellow product was collected and 92% Structural of the proposed ligand is shown below equation yield.



Preparation of complexes

Imine complexes under investigation were synthesized as follows; the ligand was dissolved in 20ml ethanol and added to metal salt in ethanolic solution. The reaction molar ratio was (1:2) metal: ligand for all prepared complexes except chromium complex (1:3). The mixture refluxed for 2 hrs. The products were filtered after cooling and washed several times with ethanol and dried over anhydrous CaCl_2 .

Study of complex formation in solution

Complexes of imine with metal ions were studied in solution using ethanol

as solvent, in order to determine the concentration of metal to ligand ratio in the complex following molar ratio method (10). A series of solutions were prepared having a constant concentration 10^{-4} M of each metal ion and the ligand. The [M: L] ratio was determined from the relationship between the absorption of the absorbed light and the mole ratio of the [M/L] at λ_{max} . The results of complexes formation in solution were listed in Table (1) and Figure (1).

Antimicrobial activity

Disc diffusion method was used for screening the ligand and its metal complexes. Nutrient agar plates were inoculated with 0.1ml of an appropriate dilution of the tested culture. Samples (1cm diameter) were suspended in (100) ml of sterile distilled water. About (20) ml of each suspension was added a filter paper disc (6mm diameter), which were placed on surface of previously inoculate plates. The plates were incubated at the appropriate temperature for 24hrs.

Results and Discussion:

A. Chemistry

Physical properties, metal analyses, magnetic susceptibility and conductivity data of the complexes are given in Table (1to3). The analytical data of the complexes correspond of the general formula can be deduced as $[\text{ML}_n\text{CL}_m] \cdot \text{H}_2\text{O}$, where ,M=Cr(III), Co(II) and n,m= 2,3 respectively and $\text{ML}_2(\text{NO}_3)_n(\text{H}_2\text{O})_m \cdot \text{XEtOH}$, where ,M=Fe (III), Ni(II) and Cu(II), n=1,0,2 and X=1,5,2,4 respectively .

The IR spectra of the complexes were compared with that of the free ligand to determine the changes that might have taken place during the complexation. The band at 1631 cm^{-1} is characteristic of the azomethine

nitrogen atom present in the free ligand. The lowering in this frequency region (1622-1600) cm^{-1} observed in all complexes indicates the involvement of the azomethine nitrogen atom in coordination [11, 12]. Moreover, new bands appeared in all compounds (459-535) cm^{-1} regions which assigned to ν (M-N) vibration (12). New bands appeared in chromium and cobalt complexes (266,220) cm^{-1} regions which assigned to ν (M-Cl) vibration indicating the formation of metal chloride coordinated bond (12, 13). Appearance of the nitrate band groups for the copper, iron, and nickel complexes, showing the linkage of this group through one oxygen atom (12). A broad band around (3425-3250) cm^{-1} indicating the presence of coordinated or lattice water or ethanol in all complexes.

The electronic spectrum of the chromium complex showed bands in the region (11.695, 22.222 and 27.700) cm^{-1} corresponding to the transition ${}^4A_{2g} \longrightarrow {}^4T_{2g}$, ${}^4T_{2g} \longrightarrow {}^4T_{1g(F)}$ and ${}^4A_{2g} \longrightarrow {}^4T_{1g(P)}$.

Respectively. The results are in good agreement with those reported for an octahedral geometry around Cr (III) ion (14, 15). The magnetic moment is (3.42BM) with three electrons in an octahedral configuration. Conductivity measurements in DMF showed that the chromium complex was to be non ionic.

The magnetic measurement showed that the iron ion in its brown complex to be high spin paramagnetic (5.23BM), of d^5 configuration. This suggestion was supported by the number of maxima observed in the electronic spectrum of this complex, which show three bands at (10,288,16,129 and 21,321) cm^{-1} , that may be assigned to the transition ${}^6A_{1g} \longrightarrow {}^4T_{1g(G)}$, ${}^6A_{1g} \longrightarrow {}^4T_{2g(G)}$ and ${}^6A_{1g} \longrightarrow {}^4A_{1g} + {}^4E_{(g)}$ respectively.

These data compare with those reported for an octahedral geometry around Fe (III) ion (14, 16). The conductivity measurements showed the complex to be non-electrolyte.

The Yellowish-green cobalt (II) complex with ligand showed a magnetic moment of (4.7BM), which indicates a high-spin type complex. Electronic spectrum in ethanol solution exhibited a split band in the range of (16.000-14.000) cm^{-1} , this split band is a typical tetrahedral spectra type and this band can be assigned as a ${}^4A_2 \longrightarrow {}^4T_{1(P)}$, in addition there is a band at 3430 cm^{-1} belong to be from infrared spectrum can be assigned to ${}^4A_2 \longrightarrow {}^4T_{2(F)}$ transition (17, 18). The molar conductance showed that the complex is non-electrolyte.

The Ni(II) complex shows two bands in the regions (20,833 and 18,181) cm^{-1} typical of 4-coordinate square planar geometry and can be assigned to ${}^1A_{1g} \longrightarrow {}^1B_{1g}$ and ${}^1A_{1g} \longrightarrow {}^1B_{2g}$ transitions (15,19,20). Also the absence of any band below 10.000 cm^{-1} eliminated the possibility of a tetrahedral environment in this complex. The conductivity behavior in DMF shows the complex to be non ionic. The magnetic measurement data is (0.98BM), which shows this complex to be diamagnetic.

The electronic spectrum of green copper (II) complex, showed one a broad band at 12.345 cm^{-1} which assigned to ${}^2E_g \longrightarrow {}^2T_{2g}$ transition, which conform the octahedral geometry. The value of magnetic moment at room temperature (1.8BM) is due to one unpaired of $3d^9$ electronic configuration in an octahedral complex of Cu (II) ion. The conductivity measurement of the copper complex showed it to be non ionic.

In solution study, the molar ratio method was carried out to determine the ratio of M: L. The results of the

complexes in ethanol can be shown in figure (2) suggests that the metal to ligand ratio was (1:3) for chromium complex and (1:2) for the other

complexes, which are monomeric nature for all compounds and then were comparable to these obtained from isolated solid state. Table (1)

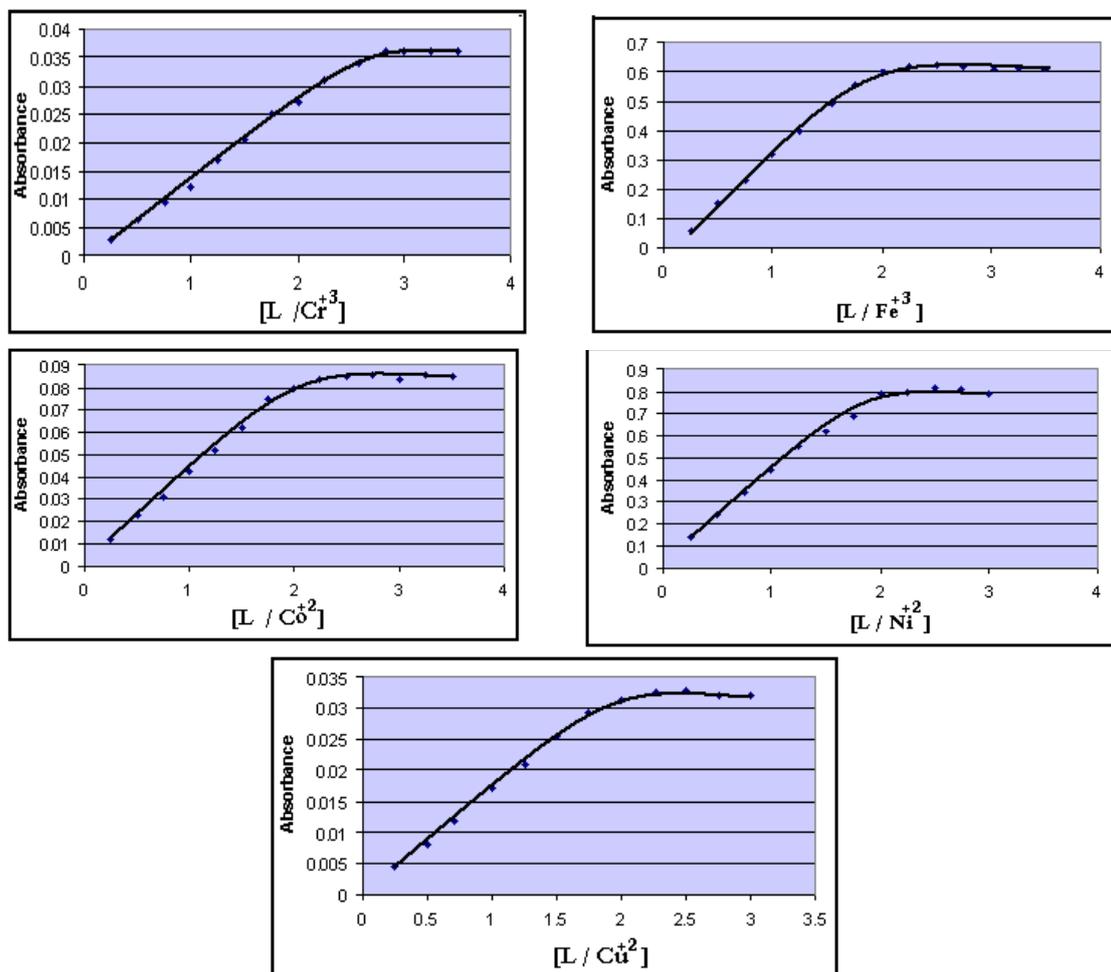
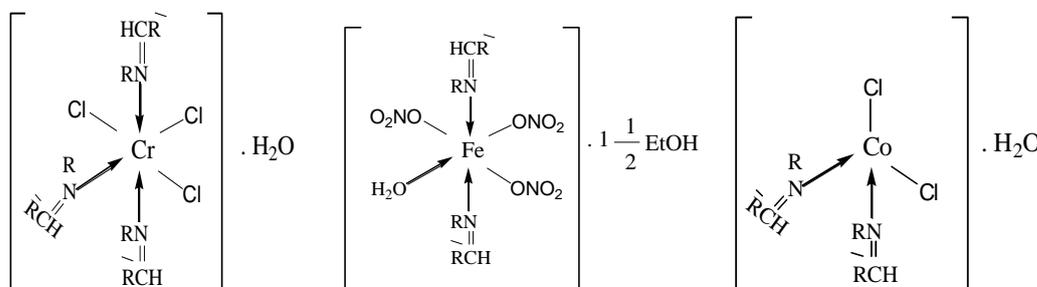
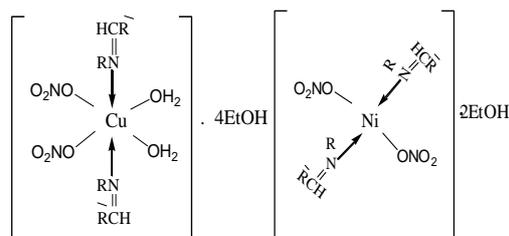


Fig (1): Molar ratio plot of all complexes prepared

The proposed coordination of the Schiff base complexes can be suggested as follows:





Where $R = C_6H_4F$
 $\bar{R} = C_6H_4NO_2$

Biological Activity

The results indicate that the complexes show more activity and the ligand do not have any activity against all organisms under identical experimental conditions in low concentration and slightly active at higher concentration. The antimicrobial activity could be

mainly due to the structure of these complexes and the oxidation state of the metal ions. These results would suggest that the chelation could facilitate the ability of the complex to cross the cell membrane (21). Coordination considerably reduces the polarity of the metal ion mainly because of partial sharing of its positive charge with the donor groups and possible electron delocalization over the whole coordination ligand. Such coordination could also enhance the lipophilic character of the central metal atom, which subsequently favors its permeation through the layer of the cell membranes (22).

Table (1): Physical properties of the ligand and it's metal complexes

Compound	Color	M.PC ^o	Yield %	Ratio M:L	Metal content Found (cal.)	Formula structure
L	Yellow	190-192	92	-	-	$C_{13}H_9 N_2 O_2 F$
CrL	darck green	110	62	1:3	6.44(5.91)	$[Cr L_3 Cl_3] \cdot H_2O$
FeL	Dark brown	298	75	1:2	7.51(6.90)	$[FeL_2(NO_3)_3(H_2O)] \cdot 1 \frac{1}{2} EtOH$
CoL	Yellowish-green	243	60	1:2	10.22(9.57)	$[CoL_2Cl_2] \cdot H_2O$
NiL	Orange	136	80	1:2	8.02(7.56)	$[NiL_2(NO_3)_2] \cdot 2EtOH$
CuL	green	275	76	1:2	7.82(7.25)	$[CuL_2(NO_3)_2(H_2O)_2] \cdot 4EtOH$

d:decomposed point .

Table (2): Most diagnostic Infrared bands (cm^{-1}) of the compounds under investigation

Compound.	$\nu-OH$	$\nu-C=N$	$\nu M-O$	$\nu M-N$	$\nu M-Cl$	$\nu-ONO_2$
L	-	1631	-	-	-	-
CrL	3284	1622	-	475	266	-
FeL	3425	1610	450	530	-	1000 1305 1410
CoL	3367	1621	-	462	220	-
NiL	3447	1621	-	535	-	1010 1315 1405
CuL	3484	1600	442	459	-	1000 1315 1410

Table (3): Electronic spectra, magnetic moment and conductivity measurements of the imine complexes under investigation

Compound	Bands λ (nm)	Bands $\nu(\text{cm})^{-1}$	assignment	μ off BM	μ scm ⁻¹	Geometry Suggested
CrL	855	11.695	$^4A_{2g} \rightarrow ^4T_{2g(F)}$	3.42	21	octahedral
	450	22.222	$^4A_{2g} \rightarrow ^4T_{1g(F)}$			
	367	27.700	$^4A_{2g} \rightarrow ^4T_{1g(P)}$			
FeL	972	10.288	$^6A_{1g} \rightarrow ^4T_{1g(G)}$	5.23	28	octahedral
	620	16.129	$^6A_{1g} \rightarrow ^4T_{2g(G)}$			
	469	21.32	$^6A_{1g} \rightarrow ^4A_{1g} + ^4E_{g(G)}$			
CoL	(674+652) av.	3430	$^4A_2 \rightarrow ^4T_2$	4.70	16	tetrahedral
		15.086	$^4A_2 \rightarrow ^4T_{1(P)}$			
NiL	550	18.181	$^1A_{1g} \rightarrow ^1B_{1g}$	0.98	20	square planer
	480	20.833	$^1A_{1g} \rightarrow ^1B_{2g}$			
CuL	810	12.345	$^2E_{2g} \rightarrow ^2T_{2g}$	1.8	19	octahedral

$\Delta\nu$ =average

Table (4): Effect of the Schiff base and it's metal complexes on the Bacterial growth.

compound	(-) <i>Pseudomonas aeruginosa</i>		(+) <i>Staphylococcus aureus</i>	
	5mM	10mM	5mM	10mM
L	-	+	-	+
CrL	++	+++	+	+
FeL	-	-	+	++
CoL	+	++	++	+++
NiL	++	+++	-	-
CuL	+	+	+++	++

(-) = (0-0.3) mm inhibition = inactive

(+) = (0.3 – 0.9) mm = slightly active

(+ +) = (0.9 – 1.2) mm = moderately active

(+ + +) = 1.2- 1.6) mm = active

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تحضير , تشخيص ودراسة الفعالية البايولوجية لبعض معقدات -4-فلورو فنيل -4- نايتروبنزلائين

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الخلاصة

تم تحضير قاعدة شف الجديدة 4-نايترو بنزلائين -4- فلوروانلين واستخدم هذا الليكاند مع أيونات عناصر ثلاثية التكافؤ (الكروم والحديد) وثنائية التكافؤ (الكوبلت والنيكل والنحاس) لتحضير سلسلة من المعقدات الجديدة. تم عزل المعقدات المحضرة واقترح شكلها الهندسي بعد تشخيصها باستخدام طيف الأشعة تحت الحمراء، الإشعة فوق البنفسجية – المرئية وقياسات الامتصاص الذري اللهي للعناصر فضلا عن قياسات الحساسية المغناطيسية والتوصيلية المولارية. تم كذلك دراسة طبيعة المعقد المتكون في الايثانول باتباع طريقة النسب المولية وقد اعطت هذه الدراسة نتائج متطابقة تقريبا مع تلك المعزولة في الحالة الصلبة.

تم تقييم الفعالية المضادة للبكتريا لليكاند و معقداته المحضرة , وأختير نوعان من البكتريا ذات الصبغة السالبة *Pseudomonas aeruginosa* وذات الصبغة الموجبة *Staphylococcus aureus* لهذا الغرض وبتركيزين مختلفين. اظهرت النتائج زيادة من الفعالية لبعض المعقدات المحضرة مقارنة بالليكاند وسبب الفعالية هو حصول التأثير التآزري بين الفلز والليكاند فضلا عن الاختلاف في تركيب المركبات .