Synthesis, Characterization of Some Metal Complexes With Mixed Ligands Derived from Sulfamethoxazole and 4, 4'-dimethyl-2, 2'-bipyridyl

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Abstract: ***Mixed ligand complexes of the 4-amino-N-(5-methylisoxazole-3-yl)-benzene-sulfonamide(L1) as a chelating ligand in presence of the co-ligand 4,4'-dimethyl-2,2'-bipyridyl(L2)were prepared by treated with V(IV), Cr(III), Co(II), Ni(II) and Cd(II) ions in alcoholic medium in order to prepare a series of new metal complexes. The complexes were characterized in solid state by using flame atomic absorption, elemental analysis C.H.N.S, FT-IR ,UV-Vis Spectroscopy, conductivity and magnetic susceptibility measurements. An octahedral geometry was suggested for CrL1L2 and NiL1L2 complexes and tetrahedral geometrywas suggested for CoL1L2, CdL1L2 complexes, while VL1L2 complex has a square pyramidal.Theligand L1, with the metal ions, clearly behaves as a bidentate through the O , N atoms of sulfonylamid group for all the prepared complexes except Ni(II),whichligand treatedas a tridentate chelate through the O , N atoms of sulfonylamid group and N atom of amine group,while L2 behaves as a bidentate ligand through two N atom. Conductivity measurements have shown that all the prepared complexes are ionic.Different bonding and structural behaviors were revealed throughout the study of coordination chemistry of the newly prepared metal complexes .The nature of bonding between the metal ion and the donor atoms of the ligands were demonstrated by calculating of the ligand field parameters which were calculated using suitable Tanaba-Sugano diagrams.***

Keywords: Sulfamethoxazole,4,4'-dimethyl-2,2'-bipyridyl, Chelating agent, Spectroscopy.

1. Introduction

Sulfamethoxazole, is a 4-amino-N-(5-methylisoxazol-3-yl)-benzenesulfonamide. The sulfamethoxazole belongs to the sulfonamides group of chemotherapeutics[1]. The molecular formula is $C_{10}H_{11}N_3O_3S$ (SMX) [1]. It is also known that the pharmacological activity of these derivatives has often been increased by coordination with metal ions [2]. The presence of donor atoms (N,S,O) at various positions in Sulfamethoxazole (SMX) molecules enable them to behave as multidentate ligands and thus form chelates of diverse structural types with a wide range of metal ions [3]. Studies on sulfanilamide metal chelates have much physiological and pharmacological relevance because the metal chelates of sulfadrugs have been found to be more bacteriostatic than the drugs themselves [4]. It is well known that through exchanges of different functional groups without modification of the structural$-S(O)_2N(H)-$ features, sulfonamide derivatives can exhibit a wide variety of pharmacological activities, such as antidiabetic, antibacterial and antitumor [5]. The chemistry of metal complexes with heterocyclic compounds containing nitrogen, sulfur, and /or oxygen as ligand atoms has attracted increasing attention which exhibit enhancedbactericidal, fungicidal, herbicidal, and insecticidal activities in addition to their application as potential drugs [6].The knowledge of metal complexes with drugs is essential to understand the complex physiological process and mode of action drugs and their effect on various body systems[6]. The stability constant of metal complexes with drugs is important to measure the metal ligand selectivity in terms of relative strength of metal ligand bonds [7].

2. Experimental

A-Instrumentation

Elemental C.H.N.S analysis were carried out on a EM-017.mth instrument, the FT-IR spectra in range (4000-400 cm^{-1}) and (400-200 cm^{-1}) were recorded by using KBrand CsI respectively discon IR-Prestige-21, Single beam path Laser, Shimadzu Fourier Transform infrared Spectrophotometer, UV-Visible spectra were measured using UV-1650PC Shimadzu, in the range (200-1100) nm. The magnatic susceptibility values of the prepared complexes were obtained at room temperature using Magnatic Suscceptibility Balance of Johanson mattey catalytic system division. Atomic absorption measurements of the prepared complexes were obtained using Shimadzu Atomic Absorption 680 Flame Spectrophotometer. The conductivity values of the prepared complexes were measured using 0.001M DMF as a solvent, (WTW) Conductometer. Melting point apparatus of Gallen Kamp M.F.B-60 was used to measure melting points for all prepared compounds.

B-Materials and Methods

Synthesis of Metal Complexes:

An ethanolic solution of thesulphamethoxazole as a primary (L1)1mmole0.2533 gmand 1 mmole 0.184 gm of 4,4'dimethyl-2,2`- bipyridyl (L2) as a co-ligand, were added slowly, into warm ethanolic solution of metal salts 1 mmole [[$VOSO_4.H_2O$ (0.1809 gm); $CrCl_3.6H_2O$ (0.2661 gm); $Co(NO_3)_2.6H_2O$ (0.2909 gm); $Ni(NO_3)_2.6H_2O$ (0.2906 gm) and $Cd(NO_3)_2.4H_2O$ (0.3084 gm)].The mixture solutions were heated and refluxed with stirring for about (2-3) hrs. The colored precipitates were filtered, washed several times with ethanol and finally ether, and dried using desiccator.

3. Results and Discussion

Stable complexes were isolated in all casesbasede on the metal analysis, spectroscopic data, molar conductance andmagnetic susceptibility studies. The general formula of the complexes can be depicted as: [VOL1L2]$SO_4.3H_2O$,[CrL1L2Cl_2]Cl.$H_2O$and [NiL1L2NO_3]$_2$(NO_3)$_2$.0.5H_2O, while[ML1L2](NO_3)$_{n.}$XH_20 , M=Co or Cd , n=2 , X=3 respectivly.

The analytical data together with some physical properties of the complexes are summarized in (Table 1).

Table 1: Some analytical and physical data of primary ligand (L1) with co-ligand (L2) and their metal complexes.

Compond / Color	M.P ^{O}C	Yield %	M.Wt g.mol^{-1}	Elemental analysis Found (Calc.)				Metal% Found (Calc.)
				C	*H*	N	S	
$C_{10}H_{11}N_30_3S$ (L1) White	167-169	—	253.3	—	—	—	—	—
$C_{12}H_{12}N_2$ (L2) White	174-175	—	184.24	—	—	—	—	—
[VOL1L2]SO_4.3H_2O Olive Green	282 d	90	654.4	40.25 (40.34)	4.39 (4.43)	10.22 (10.69)	9.52 (9.77)	8.01 (7.79)
[CrL1L2Cl_2]Cl.H_2O Dark green	133-135	76	613.8	43.23 (43.01)	4.73 (4.07)	11.68 (11.40)	5.21 (5.21)	8.95 (8.47)
[CoL1L2](NO_3)$_2$.3H_2O Greenish-blue	154-156	90	674.3	39.53 (39.15)	4.02 (4.30)	14.30 (14.53)	4.88 (4.74)	9.22 (8.74)
[NiL1L2NO_3]$_2$(NO_3)$_2$.0.5H_2O Green	195 d	92	1247.6	42.55 (42.32)	3.47 (3.76)	15.38 (15.71)	5.23 (5.12)	9.45 (9.29)
[CdL1L2](NO_3)$_2$.3H_2O Off-White	191-193	88	727.3	36.36 (36.29)	3.78 (3.98)	13.27 (13.47)	4.42 (4.39)	15.02 (15.39)

d = decomposition degree

FT-IR Spectra of the Complexes:

The tentative assignments of the peaks for the primary ligand (SMX) and the secondary ligand (4,4-dimethyl-2,2-bipyridyl) together with metals as a metal complexes are listed in (Table 2).(SMX) is a potentional ligand which may act as a bidentate or tridentate as illustred by its structure so it expected that IR mesurments are highly indicating with respect to the complexetion behivour with various metal ions. Infrared spectrum of the free ligand shows two strong bands at 3468 and 3375 cm^{-1} corresponding to the asymmetric and symmetric stretching vibrations, respectively of the aromatic amino group[8]. The medium and strong band which appeared at 3298 cm^{-1} is due to the presence of asymmetric sulfonamide –NH and a weak band at 3242 cm^{-1} as symmetric frequency. Another band observed at 1645 cm^{-1} is related to methoxazole ring stretching vibration. Others two bands appeared at 1365 and 1188 cm^{-1} are due to asymmetric and symmetric stretching frequencies of sulfonyl group [8]. The stretching frequencies of the C–N band of sulfonamide is exhibited in the 1311 cm^{-1} region. The spectrum also shows another medium band at (1597 cm^{-1}) which assigned to the stretching frequency of (C=C) band ,while the bands appeared at (829,and 686 cm^{-1}) may be assigned to the bending of (S-O) group [9].The bands related to aromatic amino group undergoes a slightly negative shift to lower frequencies from 2 to4 cm^{-1} in positions ofV(IV), Cr(III), Co(II) and Cd(II) complexes because of resonance contribution and also H-bonding [10],but in the case of Ni(II) the higher shift of ν NH_2 by (18) cm^{-1}indicating bonding of this ion to aniline N-atom [11]. The multiband and shifting of sulfonamide –NH in the spectra of the prepared complexes, indicating the involvement of this group in chelation with central metal ion by nitrogen of this group according to the data reported in literature [9]. The band related to methoxazole ring stretching vibrations suffered a very slight shift in range of ±5cm^{-1} in the spectra of the metal complexes indicating that the methoxazole moiety is not participation in coordination with metal ions [12]. The bands corresponding to asymmetric of sulfonyl group undergoes a shift toward higher frequencies which observed at (1373-1384) cm^{-1} in V(IV), Cr(III), Co(II) and Ni(II) complexes, but Cd(II) not undergo shiftting while a small bands of the symmetric stretching suffered of a shift toward lower frequencies about (23- 27) cm^{-1} in all complexes. According to these results , the coordination mode of this ligand with metal ions is clearlypredicted as a bidentate through the O , N atoms of sulfonylamid group for all complexes except Ni(II) ion throw O,N,N as a tridentate chelats, more evidence new bands which appeared in the range (439-501)cm^{-1} and (474-551) cm^{-1} due to the stretching frequency of (M-O) and (M-N) bonds respectively, and another new band in regions of 320 cm^{-1} in the spectrum of Cr(III) complexe which assigned to M–Cl stretching vibrations.The coordination of the secondary ligand is indicated by the positive shift of (C=C), (C=N) ring stretching frequencies. The position of this band has been completely changed in the spectra of all the complexes and confirming the coordination nature of co-ligand, the band at (424) cm^{-1} observed of pby (C-C out of plane bending) shifts to higher frequency and splits into two components in the complexes which again confirms the coordination of secondary ligand through two nitrogen[13],the new bands were recorded at (260-275) cm^{-1} in the spectra of all complexes are attributedto(M–N_{bpy})

bond indicating participation two nitrogen coordination with metal ion [14]. In all complexes a broad bandsappeared which refer to stretching of lattice water molecule or coordination in sphere[9].

Table 2: The most diagnostic FTIR bands of the mixed ligand SMX as primary ligand(L1) and bpy asco-ligand L2 and Their metal complexes in (cm $^{-1}$).

Compound	νNH_2 asy. sym.	ν NH asy. Sym.	ν Methax-azole Ring	C=C	ν S-0 Sulf0nyl asy.sym	ν C-N Sulfonyl	ν C=N + C=C	ν CH alph.+ arom.	δCH oop	δCH ip	ν M-N	ν M-O	ν M-N_{BPY}	Others
$C_{10}H_{11}N_30_3S$ (L1)	3468 3375	3298 3242	1645	1597	1365 1188	1311	…….	2931 3066 2870	925 887 829	1138	…..	….	….	……..
$C_{12}H_{12}N_2$ (L2)	………	…….	……..	……	………	……	1604,1519 1481,1450	2981 3078	821 848	1273,1168 1114,1080	…..	….	….	………..
[VOL1L2]SO_4 .3H_2O	3466 3379	3288 3213	1648	1597	1377 1161	1319	1616,1504 1465	3062 2978 2873	875 833 925	1273,1161 1116,1091	551	443	260	ν OH=3466 ν (SO_4)=1118, 1091 ν (V=O) = 975 $^{p}H_2O$=875
[CrL1L2Cl_2]Cl.H_2O	3464 3379	3287 3217	1647	1597	1373, 1384 1161	1315	1616, 1504 1473, 1438	3066,2985 2893,2827	883 833,925	1273,1161 1114,1091	509	439	275	ν OH=3700 ν Cr Cl=320
[CoL1L2]$(NO_3)_2$. 3H_2O	3465 3373	3285 3236	1640	1597	1373 1165	1323	1616,1519 1504,1477	3045 3070,2835 2860	833 898 945	1273,1165 1114,1091	547	501	271	νOH=3495 νNO_3= 1384,1165,945
[NiL1L2NO_3]$_2$ $(NO_3)_2$.0.5H_2O	3450 3360	3295 3250	1650	1593	1375 1165	1323	1616,1519 1556,1477	2985,2893 2831,3045	948 898 833	1273,1145 1091,1165	474	439	271	ν OH=3450 $^{p}H_2O$=898 νNO_3= 1435,1165,948 νONO_2 = 1365 s,1041 w
[CdL1L2]$(NO_3)_2$.3H_2O	3464 3371	3295 3251	1641	1597	1365 1161	1319	1616,1504 1558,1473 1438	3001,2893 ~3050,2843	821 891 941	1273,1161 1118,1091	482	439	260	νOH=3695 νNO_3= 1384,1161,941

oop=out of plane , ip=in plane, alph.=aliphatic , arom.=aromatic

Electronic spectral ,Conductance and Magnatic moment studies:

The electronic spectrum of the primary ligand (L1)exhibited two absorption bands in the ultraviolet region, the band at 212 nm assigned to the (π → π*) transition for the intera ligand aromatic system (C=C) and a strong absorption band at 270 nm which refer to (n → π*) transition for oxygen atom of S=O group or nitrogen atom of amine moiety and imine –N=C– group, respectively [15].The Electronic spectrum of L2 shows two main bands the first appeared at 243 nm due to inter a ligand (π-π*) transition located on (C=C) group. The second absorption appeared at 297 nm arises from (n-π*) transition may be located on nitrogen atom of imine –N=C-group[16], these data and the results data for the complexes are listed in (Table 3).

Electronic Spectrum of V(IV) Complex:

The spectrum of vanadium (IV) complexshows three bands, at 11764.70,17857.14,and at 22650.05 cm^{-1} which corresponds to $^2B_2g \rightarrow ^2Eg$,$^2B_2g \rightarrow ^2B_1g$ and $^2B_2g \rightarrow ^2A_1g$ transitions respectively. These are in accordance with the proposed square pyramidal geometry of Vanadium (IV)[17]**.**The magnetic moment of this complex is 2.02 B.M. This is in correlation with the spin only magnetic moment obtained for this complex with a single unpaired electron[18].The magnetic moment value is higher than the spin value of vanadium ion only. This result indicates a higher orbital contribution which is in accordance with the published data for square pyramid vanadium complexes[19]. Conductivity measurements showed the ionic behavior of this complex.

Electronic spectrum of Cr(III) Complex:

The electronic spectrum of dark green Cr(III) complex showed an absorption band in the regions 15586.03 and 21431.63 cm^{-1}which attributed to $^4A_2g \rightarrow ^4T_2g$, $^4A_2g \rightarrow ^4T_1g$ transitions. This has an indication with the published data for distorted octahedral geometry[18].The values of the 10Dq , Racah parameter B′, and ν_3 which came within the charge transfer.The nepelauxetic factor *β*and other ligand field parameters were estimated by using Tanaba-Sugano diagram for octahedral d^3 configuration.The magnetic behavior of octahedral Cr(III) is independent of the field strength of the ligand [20]. It is expected that the magnetic moment for this complex is 3.3 B.M. This value is in agreement with that reported for octahedral geometry [20]. The conductance measurements indicate the electrolyte behavior of this complex.

Electronic Spectrum of Co (II) Complex:

The electronic spectrum of the greenish blue Co(II) complex, showed three bands at 16103.05cm^{-1}, 16666.66, and19047.61 cm $^{-1}$ assigned to $^4A_2 \rightarrow {}^4T_{1p}$ ν_3 transition .This transition is known to be triplet in the divalent cobalt of the tetrahedral geometry[18,21]. This splitting is due to spin orbital coupling [20]; therefore, ν_3 has been calculated as the average of these three bands. While ν_1 $^4A_2 \rightarrow {}^4T_2$, and ν_2 $^4A_2 \rightarrow {}^4T_1$, they couldn't be seen since it is expected to appear in the range out of instrument scale, so the second transition ν_2 calculated by using Tanabe–Sugano diagram for d^7 system and found to be 4717.56 cm^{-1},The first transition ν_1 was calculated from the infrared spectrum and found to be 3495 cm^{-1}. Moreover, B' , Dq, and β were calculated by using $\boldsymbol{d^7}$ Tanabe-Sugano diagram **.**The magneticmeasurement 4.85 B.M indicates that the greenish blue Co (II) complex can be paramagnetic and it is a characteristic of the high spin geometry[22].The reported magnetic moment values for tetrahedral Co(II)complexes are greater than the spin only values 3.873B.M. because of the contribution of spin orbital Coupling[23] .The value of spin orbital coupling constant λ' has been calculated and compared with the value of free ion (130-160 cm^{-1}).This constant has been calculated using the following equation: $\boldsymbol{\mu_{obs} = \mu_{s.o} - 15.49\lambda'/10Dq}$
where:
μ_{obs} = the observed effective magnetic moment
$\mu_{s.o}$ =the electronic spin only magnetic moment

The observed value of λ' for the Co (II) complex was-212.53cm^{-1}. It is less than the value of a free ion and does not fit in the range of the regular geometry. The molar conductivitymeasurement shows that this complex is ionic and an tetrahedral geometry around Co(II) ion can suggested.

The electronic spectrum of nickel (II) complex, shows three bands , 11111.11,17391.30, and26136.95 cm^{-1} assigned to $^3A_2g \rightarrow {}^3T_2g$,$^3A_2g \rightarrow {}^3T_1g$, and$^3A_2g \rightarrow {}^3T_1g_{(p)}$ transitions respectively**.** The transitions observed at 14465.49 and 13411.11cm^{-1} correspond to spin forbidden $^3A_2g \rightarrow {}^1T_2g$and $^3A_2g \rightarrow {}^1Eg$[24].These bands indicate an octahedral geometry around Ni(II) ion[18,24]. Besides, the absence of the frequency at 20000cm^{-1} proves that the prepared complex is not a square planer [25]. A weak band is observed at 9803 cm^{-1} which suggests that the complex has an octahedral geometry[26] . The values of the nephelauxetic factor β and Racah parameter B' have been calculated by using Tanabe-Sugano diagram for octahedral d^8 system. By fitting the ratio of the frequencies (ν_2 / ν_1), which reach to 1.56, it indicates that the complex has a distorted octahedral geometry[26] while the value of a regular octahedral geometry equals to 1.6 [27]. Moreover, the degree of the distortion has been calculated using the following equation $\boldsymbol{\mu_{obs=} \mu_{s.o}\left(1 - \frac{4\lambda'}{10Dq}\right)}$and it has been found that λ'=-392.07 cm^{-1}.The magnetic value 2.83B.M for nickel(II) is observed and it is within the range of (2.8-3.5) B.M. This degree with octahedral geometry is around Ni (II) ion.[30] The increase in the magnetic moment is expected due to the presence of the contribution of spin orbital coupling[28].The limited solubility is done in the most organic solvent , i.e., a partial polymerization of this complex. The formula is further confirmed to be ionic by conductivity measurementsan octahedral geometry around Ni (II) ion can be proposed.

Electronic Spectrum of Cd (II) Complex:

According to the electronic spectrum of Cd(II) complex, no d-d transition is located as it belongs to $\boldsymbol{d^{10}}$[29]. The prepared complex is off white in color with the diamagnetic being expected. The ultraviolet-visible spectrum of this complex shows a relative change in the bands position compared to that of free ligands due to charge transfer between Cd (II) ion and ligands. The conductivity measurements for the prepared complex showed to be ionic.From spectroscopy and these information a Td geometry can be suggested.

Spectrum of Ni(II) Complex

Table 3: Electronic spectra,Conductance in DMF solventand magnetic moment(B.M)for the ligand L1, co-ligand L2 and thier metal complexes

Compound	L1	L2	VL1L2	CrL1L2	CoL1L2	NiL1L2	CdL1L2
Absorption Bands(cm^{-1})	37037 47169	42918 33670	11764.70 17857.14 22650.05	15586.03 21431.63 36435.535 (cal.)	3395 4263.13 (cal.) 17272.44	14465.49 13411.11 11111.11 17391.30 26136.95	32154 36101 40485 49019
Assignments	n →π* π →π*	n→π* π→π*	$^2B_2g \rightarrow {}^2Eg$ $^2B_2g \rightarrow {}^2B_1g$ $^2B_2g \rightarrow {}^2A_1g$	$^4A_2g \rightarrow {}^4T_2g$ $^4A_2g \rightarrow {}^4T_1g_{(F)}$ $^4A_2g \rightarrow {}^4T_1g_{(P)}$	$^4A_2g \rightarrow {}^4T_2g$ $^4A_2g \rightarrow {}^4T_1g_{(F)}$ $^4A_2g \rightarrow {}^4T_1g_{(P)}$	$^3A_2g \rightarrow {}^1Eg$ $^3A_2g \rightarrow {}^1T_2g$ $^3A_2g \rightarrow {}^3T_2g$ $^3A_2g \rightarrow {}^3T_1g_{(F)}$ $^3A_2g \rightarrow {}^3T_1g_{(P)}$	ILCT
B°	---	----	----	918.00	971.00	1035	----
B$^/$	---	----	---	740.60	767.00	736.28	----

ß	---	----	---	0.80	0.78	0.71	----
Dq/ $B^{/}$	---	----	---	2.10	0.45	1.42	----
10Dq	---	----	---	15552.70	3451.50	10455.24	----
LFSE	-----	----	----	224.85	49.90	151.16	-----
15$B^{/}$ Separation Term	---	----	---	11109.07	11505.00	11044.27	----
μ_{eff} B.M.	---	----	2.02 (1.73)	3.30 (3.87)	4.85 (3.87)	2.98 (2.82)	0.00 (0.00)
µscm^{-1}	---	----	67.80	95.50	102.00	133.40	124.20
Suggested Geometry	---	----	C_4V	O.h	T.d	O.h	T.d

ILCT: Internal ligand charge transfer

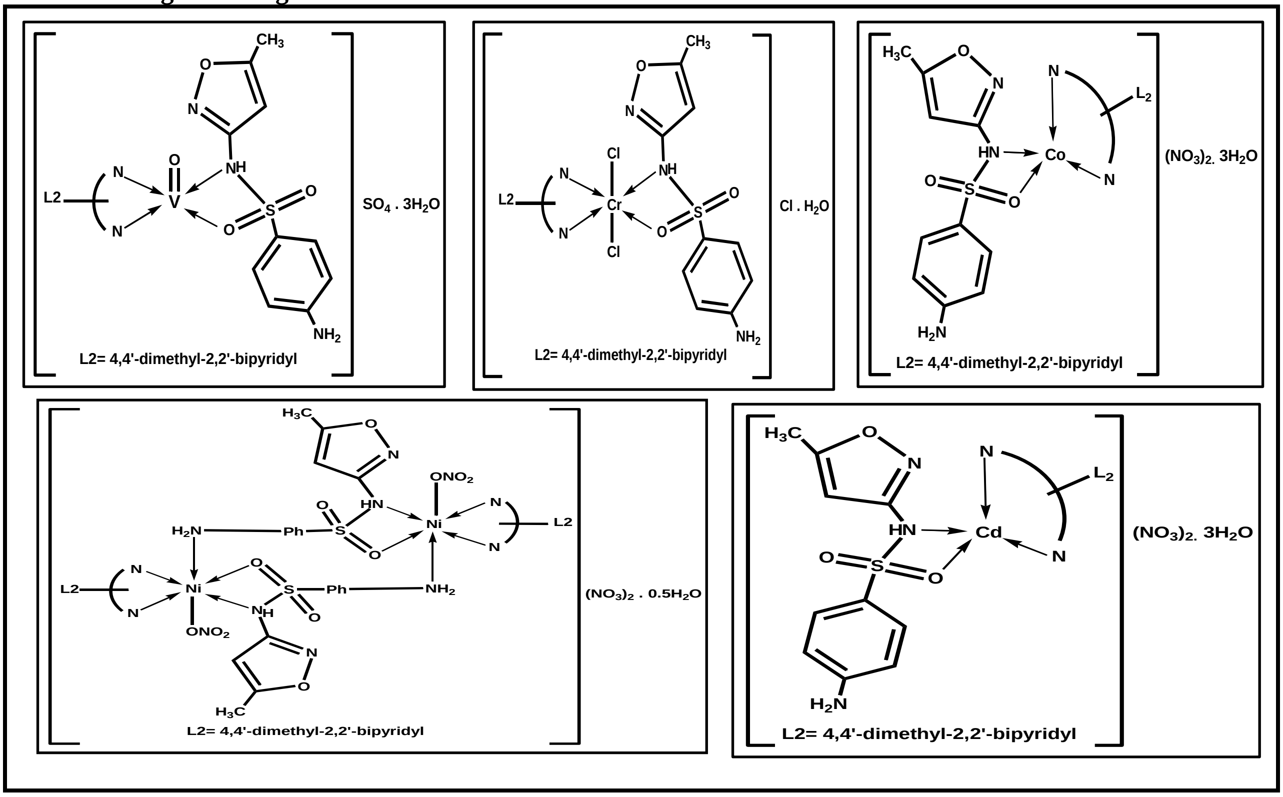

Figure 1: Suggested structure for the prepared complexes

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