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Synthesis and Characterization of Template Cr(III),Fe(III), Mn(II), Cd(II) and V(IV), Complexes Derived from 2,6-Diaminopyridine and 1,4-Dihydro-Quinoxalin-2,3-dione.

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Abstract: *A new series of tetradentate N2O2 acyclic complexes of type [M(L)X2]Xn where M = Mn(II), Cd, Cr(III) and Fe(III); L is tetradentate acyclic Schiff base formed via condensation reaction, and X = Cl-, n=1 for M(III), have been prepared on the basis of condensation of 2,6-diaminopyridine and 1,4-dihydro-quinoxalin-2, 3-dione by template method. The complexes are formulated as: [M(L)Cl]Cl where M=Cr, Fe(III),[MLCl2],MII=Mn, Cd(II) and [VOL]SO4 on the basis of elemental analyses,molar conductance and other spectral data. The organic moiety formed up on template condensation behaves as tetradentate N2O2 system through the two azomethine nitrogen atoms of –C=N- and the participation of O atoms of -C=O in 2-position of pyrazine ring. However, the pyridine nitrogen atom does not take part in coordination as confirmed by FTIR,UV-Visible and H NMR spectroscopy data. The newly template metal complexes have characterized with the help of various spectral techniques H NMR,13C NMR, F.T.I.R, elemental analyses, electronic spectra, molar conductivity measurements and magnetic susceptibilities. The octahedral geometry has been proposed for Cr(III),Fe(III), Mn (II) and Cd(II) while vanadyl complex was square pyramid configuration respectively.*

Keywords: *Template complex, Quinoxaline-3, 2-dione, Schiff bases.*

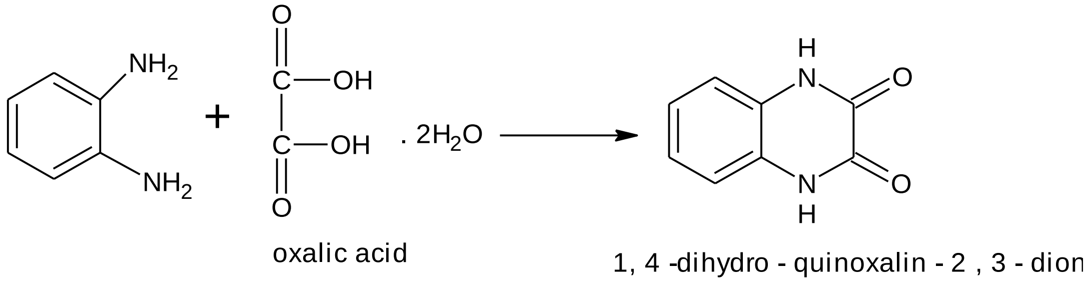
I. Introduction

The design and study of metal containing quinoxaline derivatives is an interesting field of chemistry(1). Over the last few years, very active research in macrocyclic chemistry has attracted the interest of inorganic chemists(2). The chemistry of tetraimino acyclic complexes is of considerable interest because of their applications for modeling bioinorganic systems, catalysis and analytical practice(3). Spontaneous self-assembly reactions have been considered as vehicles for reliable and economical preparation of macrocyclic complexes. Hence these reactions hold a fascination for chemists to mimic anabolic reaction without enzymes.Nature prefers macrocyclic derivatives for many fundamental biological functions such as photosynthesis and transport of oxygen in mammalian and other respiratory systems(4).The metal complexes of bivalent ions like Co,Ni and Cu(II)derived by direct complexation with quinoxalin-2-carbaldehydehave been showed high stability as compared to analogous open chain ligands(5).*In-situ* one pot template synthesis is the most widely adopted method for preparation of macrocyclic complexes(6).A number of nitrogen donor and oxygen macrocyclic and acyclic derivatives have been used for a long time in analytical, industrial and medical applications(7).The macrocyclic metal complexes are of great importance due to their resemblances with many natural systems such as porphyrins and cobalamines(8).Satish and co-workers have investigated the binuclear Co(II),Ni(II),Cu(II)and Zn(II)complexes with tetra dentate Shiff bases derived from 2,6-diformyl-4-methyl phenol with 2-hydroxy-3-hydrazino quinoxaline(9).In our recent papers involving template synthesis, the isolation of template Cr(III),Co(II),Ni(II),Cu(II)and Zn(II)with tetra dentate quinoxaline organic moiety of the N_2O_2 type have investigated on the GC-mass,H NMR and other analytical techniques(10).Some template metal(II) complexes involving quinoxalin-2-one have been found to exhibit potential antibacterial activities and rare electronic characterizations(11-12).Prompted by these, and the contiuous interesting with coordination chemistry of quinoxaline derivatives, in the present paper synthesis and characterization of chromium,iron(III),vanadyl(IV),manganese and cadimium(II) complexes derived from 2,6-diaminopyridine and 1,4-dihydro-quinoxalin-2,3-dione have been prepared and fully identified.

II. Experimental

Materials& Methods:

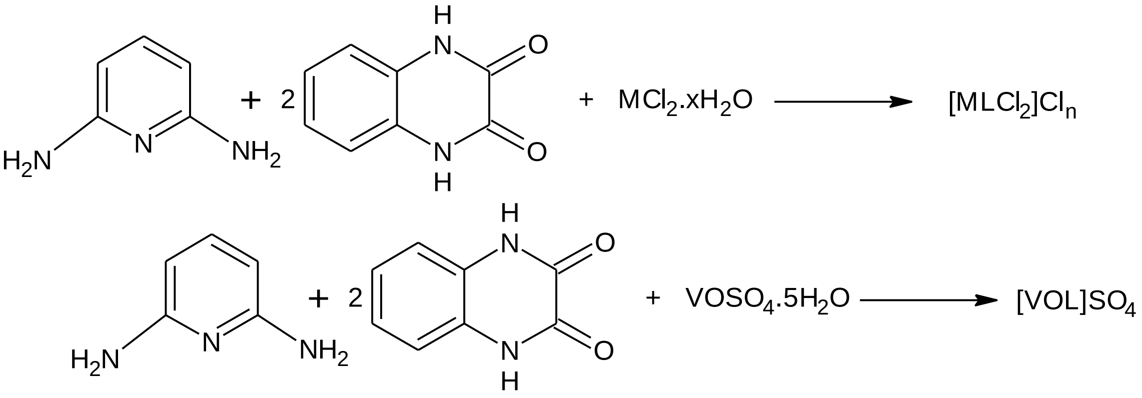
The anhydrous metal chlorides $CrCl_3$.,FeCl3,$MnCl_2$, $CdCl_2$ and $VOSO_4.5H_2O$ were purchased from Merck company and used without purification.The hydrated oxalic,2,6-diaminopyridine , 1,2-phenylenediamine and solvents,were supplied from Sigma Aldrich company in 99% purity.All other chemicals used were of AnalR grade. The 2,3-quinoxaline-dione has prepared according tothe method published in literature (13)scheme(**1**).



Scheme (1): Preparation of 1,4 - dihydro - quinoxalin - 2,3 -dione

Isolation of complexes:

Our several attempts to isolate the free macrocyclic or acyclic ligand were unsuccessful. Hence, all the complexes were obtained by template synthesis. To a stirring methanolic solution (~60cml.) of 2,6diaminopyridine(10 mmol) was added divalent, manganese,cadmium ,trivalent chromium or iron and vanadyl sulphate salts (5 mmol) dissolved in minimum quantity of methanol (20-15ml.). The resulting solution was refluxed for 16-18 hours. On overnight cooling dark coloured ,a precipitate was formed which then filtered, washed with methanol, acetone, diethyl ether and dried *in desicator*. (Yield 55-70%) The complexes were found soluble in DMF and DMSO,acetonitrile but were insoluble in common organic solvents and water.They were thermally stable up to ~368^{o}C and then decomposed. The template syntheses of the complexes may be represented by the following scheme **2**:



Scheme (2): Synthesis of template M= Mn,Cd(II) n=0,Cr,Fe(III) if n=1 and VO(IV) complexes,

Instrumens

C.H.N-elemental analyses of the new solid complexes were determined using Carlo-Erba 1106 Elemental analyzer .Electronic spectra were recorded for solutions of quinoxalin-2,3-dione and its metal template complexes using Shimdzu spectrometer in the range(200-800)nm in DMF solvent . Magnetic susceptibility measurements were carried out using Bruker14K-Magnetic balance at room temperature *via* Gouy method using $Hg[Co(SCN)_4]$ as calibrant.The H^1 and ^{13}C NMR spectra were carried at Al-bait -University on Bruker 300 MHZ spectrometer in DMDO-d6 solvent. Gas and Mass spectroscopy of Mn(II) and VO(IV) complex were recorded on Shimadzu GC MS- P2010 model spectrometer in assistance with specific column for metal in 0-700m/e range and vaporization in 100-450℃ range at Al-Yarmook (Jordan).

III. Results and Discussion

The analytical and physical data of template metal complexes are listed in table (1). The percents of C,H,N and M obtained from elemental and atomic absorption spectroscopy are in good agreement with the general molecular formula proposed for the complexes $[MLCl_2]$ where: M=Mn(II),Cd(II),$[MI^{III}LCl_2]Cl$,M=Cr and Fe(III) ions and $[VOL]SO_4$ respectively, whereas L=acyclic N_2O_2 organic segment formed by template route between substituted 2,6-diamino pyridine and 1,4-dihydro-quinoxalin-2,3-dione, as shown in structure (3).

Table (1)- Physical properties and elemental analysis of the prepared metal complexes.

compound	Colour	M.P℃	C% clac.(found)	H% Cal..(found)	N% calc..(found)	M% calc..(found)
[VOL]SO_4	Pale green	368	59.84 (58.77)	3.65 (3.00)	17.77 (16.99)	11.9 (11.01)
[MnLCl2]	Red	367d	47.99 (46.99)	2.55 (2.33)	17.99 (18.33)	12.12 (10.01)
[FeL Cl2]Cl	Brown	356d	50.00 (48.92)	4.11 (3.22)	17.11 (17.99)	10.37 (11.90)
[CdL Cl_2]	Pale yellow	364d	53.46 (52.88)	2.55 (2.08)	17.00 (18.33)	15.44 (14.82)
[CrL Cl_2]Cl	White off	360d	48.59 (46.00)	4.21 (3.70)	19.1 (19.99)	14.42 (14.97)

D=decomposed,calc.=calculated.

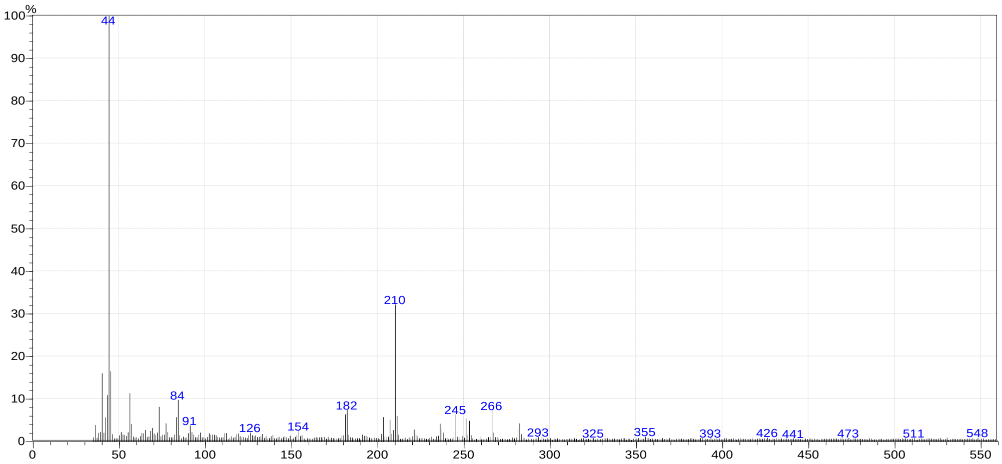
Mass spectra:

The gass chromatograghy mass spectra of all complexes showed ES-mass molecular ions for Cr(III),Fe(III), Mn(II),Cd(II) and VO(IV) complexes at 555,560,523,587 and 549 respectively. The most abundant fragments with relatives isotopic abundances at m/e=557 and 561of Cr and Fe(III)complexes respectively.The other fragments that close to base peak may be assigned to departure of SO_2 gas and hydroxyl ions for VO(IV) complexes which were displayed in table2(14) Figure(1).

Table(2)-GC-mass spectra of the template metal complexes.

complex	Peak data	Assignment peak
[CrLCl_2]Cl	555.5,520,449	*M^+,M-Cl,M-C_4H_6
[FeLCl_2]Cl	560,489,413	*M^+,M-Cl,M-2Cl
[MnLCl_2]	523,487.5,452	*M^+,M-Cl,M- C_4H_6
[CdLCl_2]	587,545.5,510,434	*M^+,M-Cl,M-2Cl
[VOL]SO_4	549,451	*M^+,M-SO_4

Where * refers to the molecular ion peak of the complex in gm./mole



Figure(1)-Mass spectrum of [VOL]SO_4complex.

IR spectra:

The preliminary identification of the acyclic metal template complexes has been obtained from its IR spectrum, which shows the absence of uncondensed functional groups –NH2 and C=O of 1,2-phenylenediamine and quinoxalin-2,3-dione(i.e., stretching modes of starting materials) and suggests the formation of the proposed acycle.The appearance of strong absorption band in the region 1600-1650 cm^{-1} corresponds to υ>C=N stretching frequency (where, υ = frequency).A single sharp band observed for the ligand at 3300 cm^{-1} corresponds to υN-H of secondary -CO-NH group, confirms the presence of lactam form corresponding to quinoxaline moiety.It was noted that a pair of bands are present in the spectrum of 2,6-diaminopyridine at 3200-3400 cm^{-1} corresponding to ν(NH_2) but are absent in the infrared spectra of all the complexes(15).Furthermore, no strong absorption band was observed near 1685-1670 cm^{-1} indicating the absence of >C=O of quinoxalin-2,3-dione at 2-position,this confirms the condensation of carbonyl group of quinoxaline and amino groups of 2,6-diaminopyridine(10),figure2.These results provide strong evidence for the formation of acyclic frame(14). A strong absorption band in the region ~1595-1633 cm^{-1} may be attributed to the C=N group(15).The lower values in the wave numbers of ν(C=N) may be explained on the basis of drift of lone pair density of azomethine nitrogen towards metal atom(1516).The bands present at ~33050-2966 cm^{-1} may be assigned due to ν(C-H) vibrations of quinoxaline and pyridine moietyies. The bands present in the range ~1330-1100 cm^{-1} are assigned due to ν(C-N) vibration. The IR spectra of the complexes do not show any change in the pyridine ring vibrations and interestingly enough, it appears that in these complexes pyridine nitrogen does not take part in coordination(17).Thus in the presence of metal salts, a quadridentate acyclic system is formed which coordinates through azomethine nitrogen and two oxygen atoms of –C=O positionized in 3position of lactam quinoxaline(17) of while pyridine nitrogen does not take part in coordination,figures3-5b. Moreover, the coordination through pyridine nitrogen does not take place, as it will result in the formation of unstable four membered rings. The far IR spectra show bands in the region ~550-490 and 444-422 cm^{-1} corresponding to ν(M-N) and M-O vibrations respectively(17).As well as the tautomer's of in position 2 of quinoxaline ring between C=O and C=N- supports the coordination of organic moiety with appearance of strong bands at 1700-1710 cm-1.thus the acyclic tetra dentate ligand behaves as N_2O_2system.Theoxovanadium(IV)complexes show a band at around 980-950 cm -1which is assigned to the ν(V=O) vibration(18).The presence of ionic sulfategroups in the complexes are confirmed by the appearance of three bands at ca. 1130-1135cm^{-1}(ν3), 955-960cm^{-1}(ν1) and60061 cm -1(ν4).The absence of a ν2 band and nonsplitting in the ν3 band indicate that the Td symmetry is retained (19),table3,Figures(3-6a and 5b).

Table (3)-FTIR absorptionsof the Quinoxalin-2,3-dione and its template metal complexes in υ $^{-1}$.

Complex	υ NH ,υ C= O	υ Ar – CH, (C – N)	υ M – N , υ M - O	Other bands
Quinoxalin-2,3-dione	3350 , 1685 (s) 1590 (s)	3050 , 2962(m) 1300 (s)		790-895
[VOL]SO_4	3150 (m), (1680-1651)(s) 1562	3100 (w) 1150 (s)	500 (m), 490(w) 1130-1135^b	980-950(V=O)^a 960-950
[MnLCl_2]	3180(m), 1705(s) 1560(s)	3080-2890(w) , 1220(s)	455 (w), 477 (m)	390-340(w)
[FeLCl_2]Cl	3338 , 1672 (s) 1562	3100(w) , 1125(s)	421(m), 469(w)	288-322(w)
[CdLCl_2]	3200 (br.) 1678, 1630	3050 (w) 1121(s)	440 ,550(m)	329,278(w)
[CrLCl_2]Cl	3177 (m.) 1670(s) ,1530(m)	3028-2966 (m) 1280(m)	498(w) 435(w)	366,278(w)

s=strong,m=medium,br.=broad,w=weak,a,b=vibrational modes of sulphate and vanadyl groups.

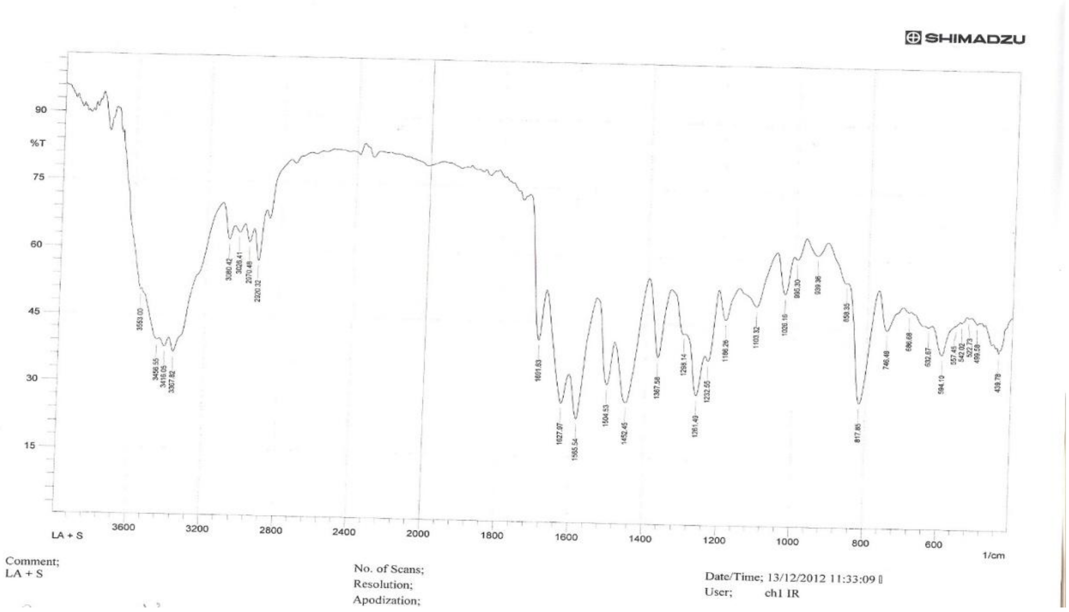
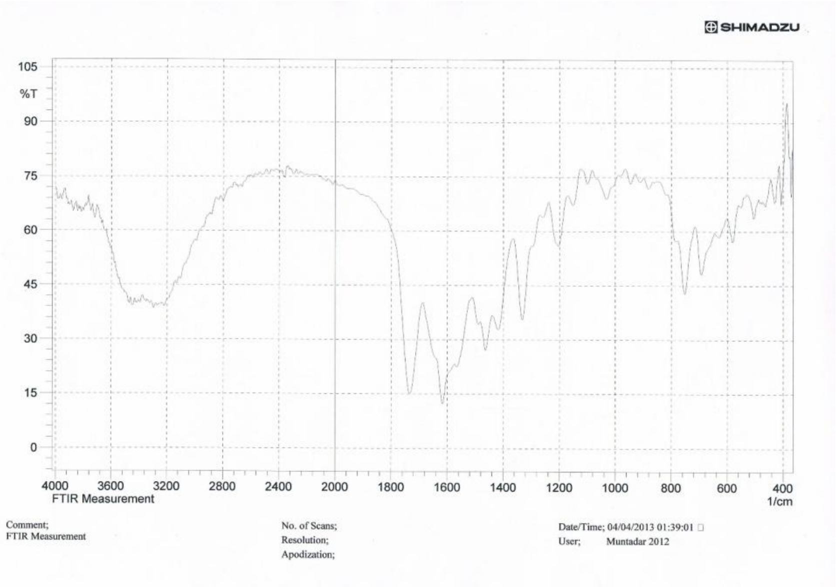


Figure (2)-FTIR of Quinoxaline-2,3-dione in KBr disc.



Figure(3)-FTIR of [$MnLCl_2$] complex in CsI – disc

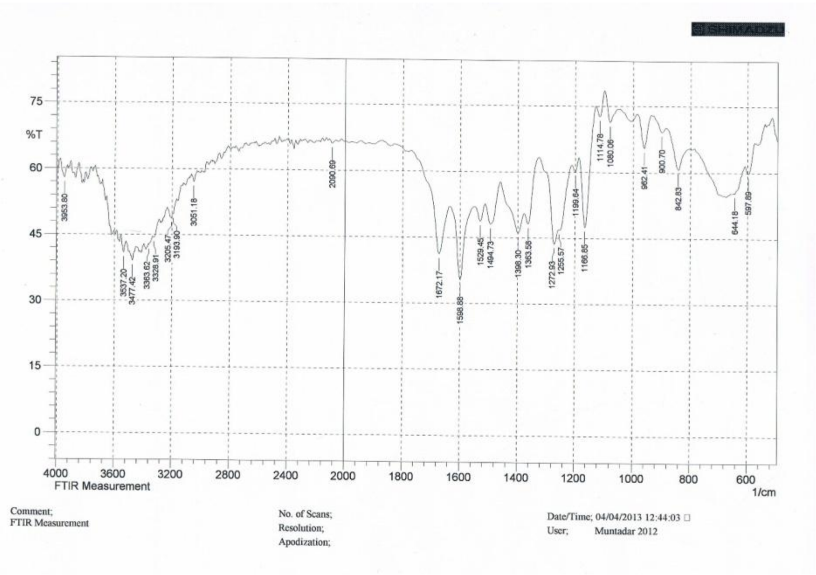
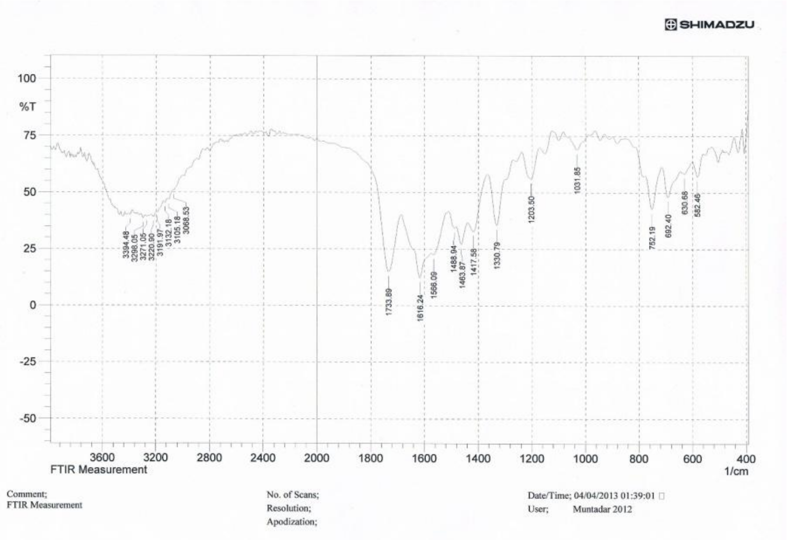
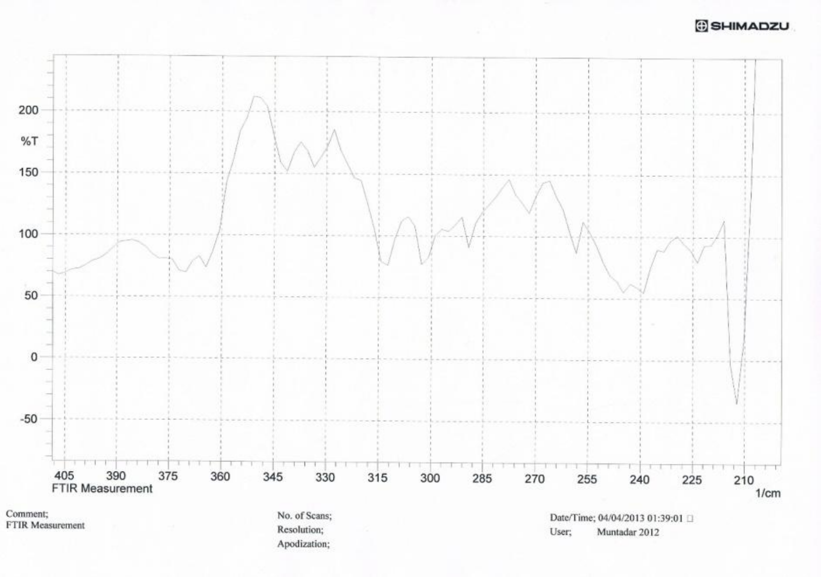


Figure (4)- FTIR of [VOL]SO4 complex in CsI disc.



Figure(5a)-FTIR spectrum of Fe(III) complex.



Comment;
FTIR Measurement

No. of Scans;
Resolution;
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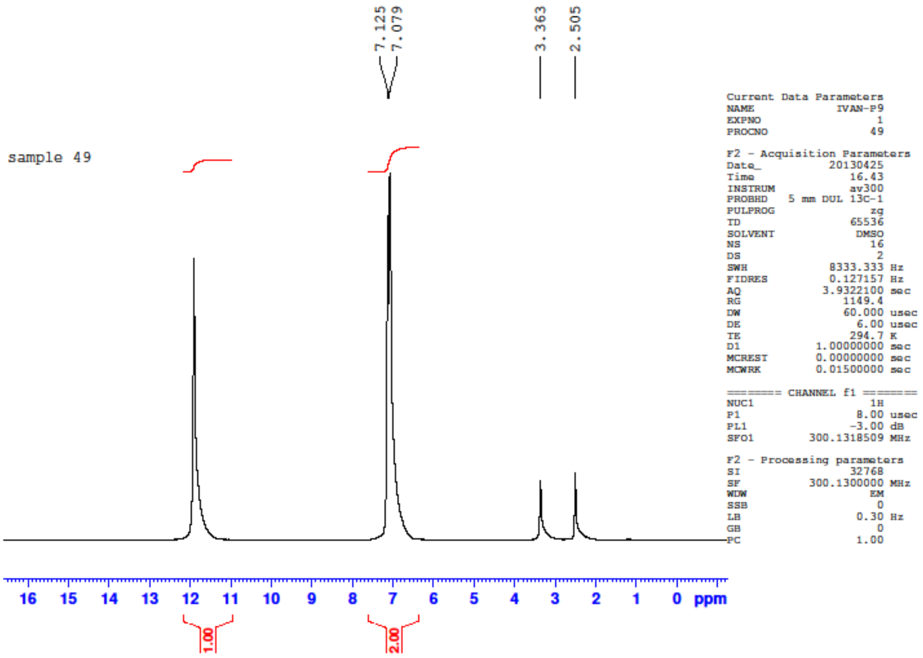
Figure(5b)-Far IR spectrum of Fe(III) complex in CsI disc

^{1}*H &C*^{13} *NMR spectra:*

The ^{1}HNMR spectrum of quinoxalin-2,3-dione in d6-DMSO solvent,figure(6) shows singlet absorption in the region δ411.10ppm (δ=chemical shift) and a multiple one at δ 6.7-8.00ppm corresponding to –NH and deshielded Ar-H protons respectively. As well as the figure 7 of 13 C NMR agree with the expected absorptions of C=O and C-N and C=C with equivalent C8 carbon atoms(20).The ^{1}H NMR spectrum of [CdL] complex,figure(8) shows a multiple signals observed at δ 6.5-7.33ppm that may be attributed to Ar-H and quinoxaline integrated with protons16,and 5.7-6.5ppm which may be assigned to Py-H.However,the deshielded chemical mshift in the region 8.62 ppm with area of 2NH- supporting the lactam form of benzopyrazine in the formed complexes.



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FIDRES          0.127157 Hz
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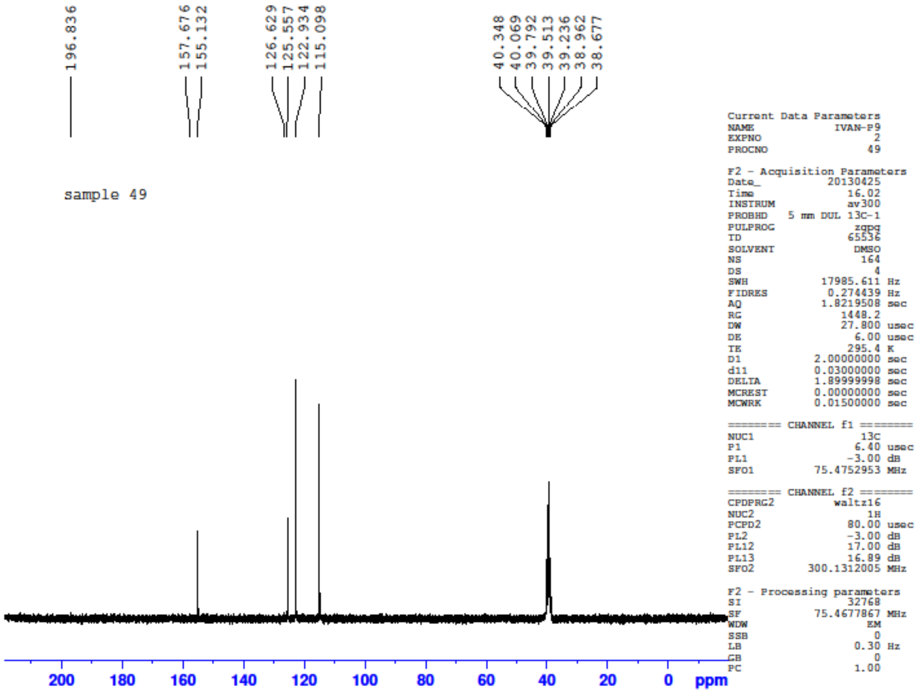
Figure (6)- ^{1}H NMR of 1,4-dihydro-quinoxalin-2,3-dione in DMSO-d6.



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d11           0.03000000 sec
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MCWRK         0.01500000 sec

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PL1                -3.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
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NUC2                  1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               17.00 dB
PL13               16.89 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
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Figure (7)-C¹³ NMR of 1,4-dihydro-quinoxalin-2,3-dione in DMSO-d6

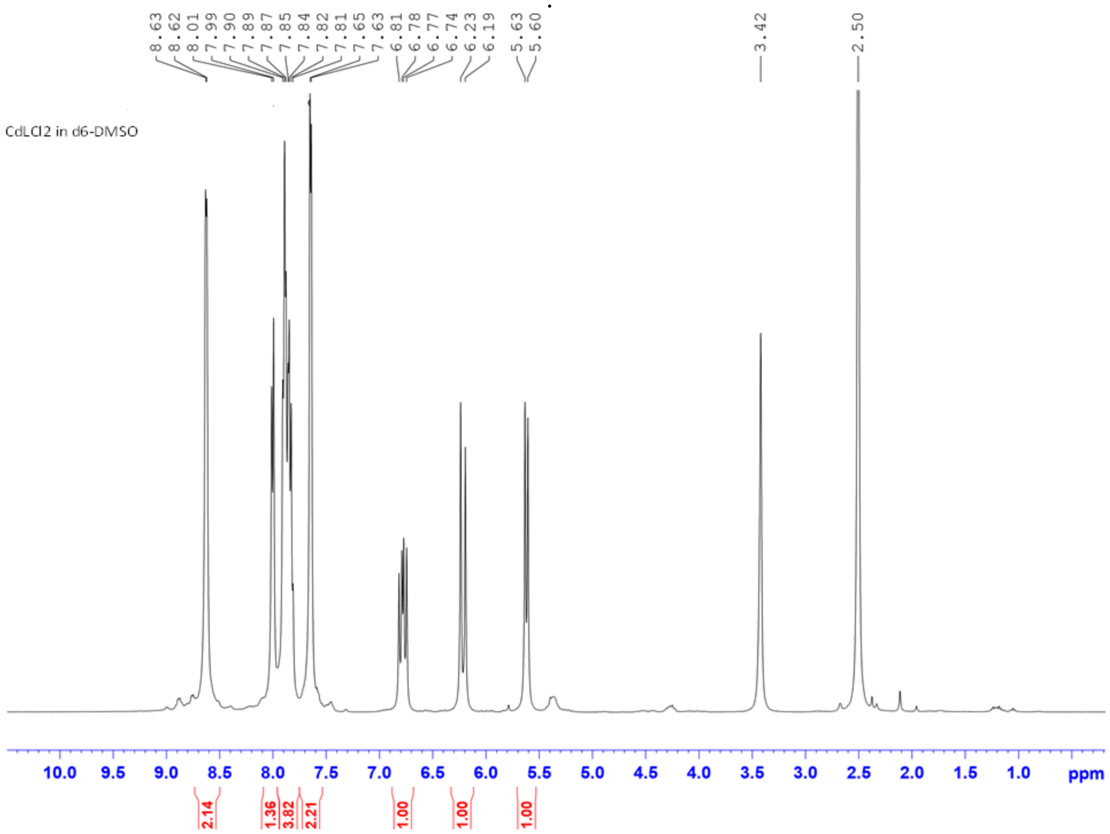


Figure (8)-H NMR of [CdLCl2] comlex in DMSO-d6.

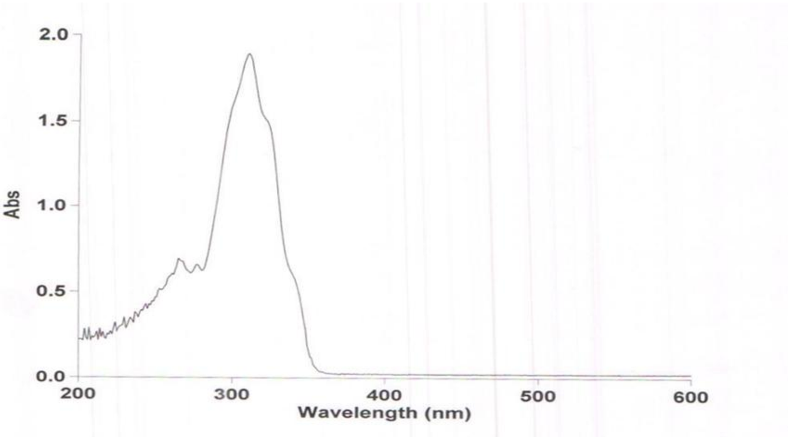
Magnetic Moment and UV.Visible Spectra:

The quinoxalin-2,3-dione solution in methanol exhibits two absorptions at 36101 and 31446.5cm^{-1} that are characteristic of ligand field (π→π*and n→π*)transitions respectively of C=N,C=O and C=C groupsfigure(9)$^{(10,12)}$.The electronic spectra and magnetic measurements were recorded in order to obtain information in table(4) about the geometry of the complexes .The nature of the ligand field around the metal ion has been deduced from the electronic spectra.The electronic spectrum of the [VO(L]SO4 complex was recorded in DMF. It exhibits bands at 17980,23550,and 36288 cm-¹, which are assignable to transitions $^2B2\rightarrow{}^2E$ (ν 1), $^2B_2\rightarrow{}^2B_1$(ν2), and $^2B_2\rightarrow{}^2A_1$(ν3), respectively$^{(21)}$.The geometry of the five coordinated mononuclear complex can be described in terms of a trigonal bipyramid distorted towards a tetragonal pyramid. The value of the magnetic moment for this complex is 1.720 B.M. It Indicates presence of one unpaired electron in VO(II) complex$^{(22)}$.The electronic The complexes also show the band in the region 40800cm^{-1} due to a charge transfer transition,figure10.The magnetic moment of Cr(II) complex was 3.34BM corresponds to an octahedral geometry of d^3 configuration, and its solution in DMF showed two spin- allowed transitions in the 22340(10Dq)and 26780cm^{-1} regions which may be assigned to $A_2g^4\rightarrow T_2g^4$ and $A_2g^4\rightarrow T_1g^4$ transitions respectively ,which agree well with peaks of octahedral geometry around Cr(III) ion.TheMn(II) complex exhibits forbidden-spin absorptions in the regions19669–19607 cm^{-1} and 21799–21734 cm^{-1} assigned to $^6A_1g_1$(F) →$T_2{}^4g$(F) (ν1) and $^6A_1g_1$(F) →T^4g(ν2) transitions, respectively, which suggests octahedral geometry around the Mn(II) ion$^{(22)}$.The UV-visible spectra of iron(III) complex in DMF solutions displays22669, 21913,33350 cm^{-1}assignable to metal to ligand charge transfer and $^6A_1g_1$(F)→E^4g (F) transitions respectively,figur11, which remarkably favors octahedral geometry around iron ions(III)$^{(22-23)}$.The magnetic moment values for iron complex 5.33 B.M$^{(23)}$.In contrast, the orange solution of Cd(II) complex in DMF shows high intensity peaks at 312250 and 27027 cm^{-1}, which are assignable to ligand field (π→π*,n→π*) and LMCT transitions$^{(22,24)}$.The molar conductance values of the synthesized template complexes with the mentioned metal ions under investigation were determined using 10^{-3}M DMF solvent, as shown in Table 3 are in the range of 60,77 and 84 ohm^{-1} cm^2 mol.$^{-1}$ for Cr,Fe(III) and VOL complexes indicating the electrolytic behavior in 1:1 ratio and confirming the expected formula$^{(25)}$. The molar conductance of MnL,CdL complexes in DMF lie in the range 18-23 ohm^{-1}.cm^2.mol^{-1} ,these values support the absence of chloride ions in the counter structure of the prepared complexes$^{(26-27)}$.

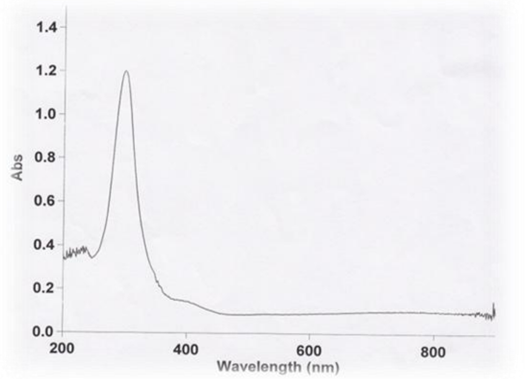
Table-(4)-Electronic spectra υ^{1-} (cm^{-1}),molar conductance and magnetic moments of the prepared complexes

complex	υ^{1-} (cm^{-1})	Λ_m	μ_{eff}(B.M)	**Geometry**
Quinoxaline-2,3-dione	36101, 31446.5			
CrL	18739(10Dq) ,27770	60	3.55	Oh.
FeL	22669, 21913,33350	77	5.33	Oh.
MnL	27900,30450	23	5.04	Oh.
VOL	17980,23550,36288,40000(C.T.)	84	1.70	Square pyramid
CdL	312250,27027	18	0	Oh.

sh=shoulder, a= charge transfer, m= molar conductance in ohm-¹ cm² mol^{-1}.inDMF.



Figure(9)-UV-Visible spectra of Quinoxalin-2,3-dione in DMF (10-³M).



Figure(10)-UV-Visible spectra of VOL complex in DMF.

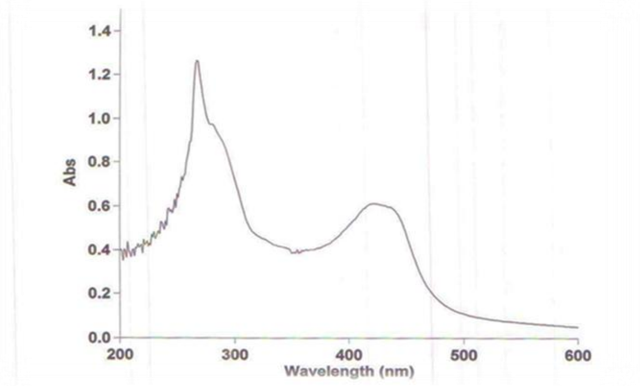
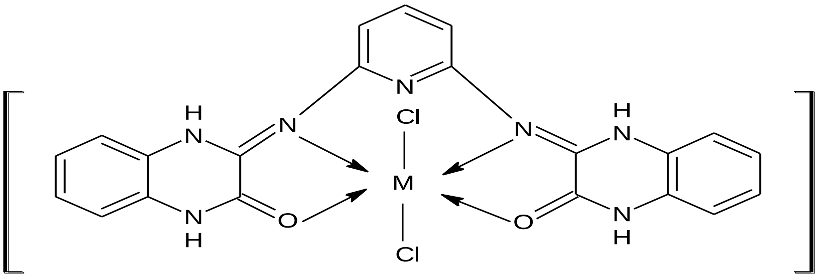


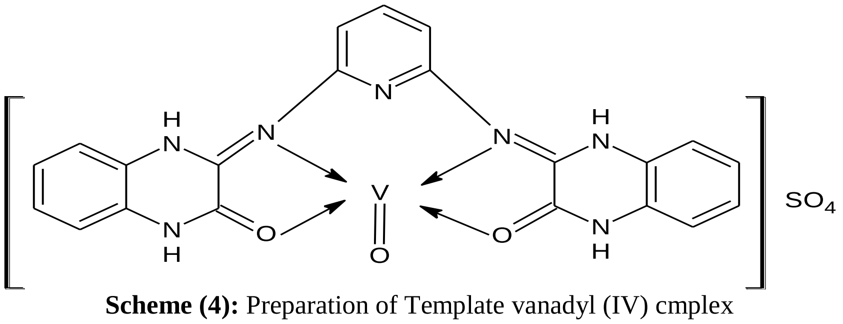
Figure (11)-UV-Visible spectrum of [$FeLCl_2$]Cl complex in DMF.

IV. Conclusion

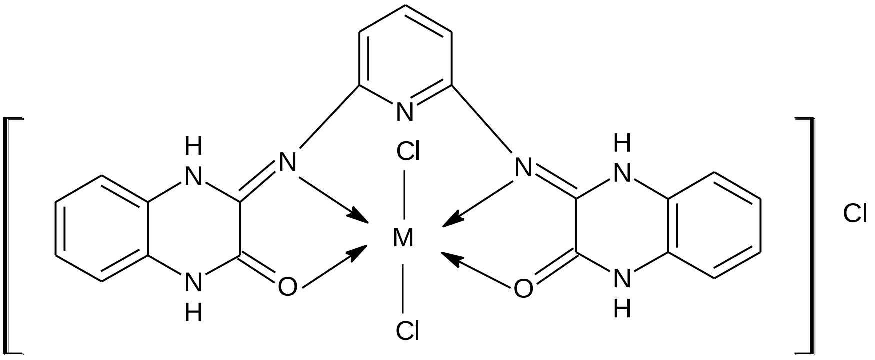
From the previous data [elemental analysis, molar conductance measurements infrared, electronic absorption ,NMR spectra, GC-mass spectra and magnetic susceptibilities, we can propose the following stereo chemical structures for the synthesized template metal complexes, as shown in schemes 3-5:



Scheme(3):structures of Mn(II) and Cd(II) complexes



Scheme (4): Preparation of Template vanadyl (IV) cmplex



Scheme (5):structures of Cr and Fe(III) complexes

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