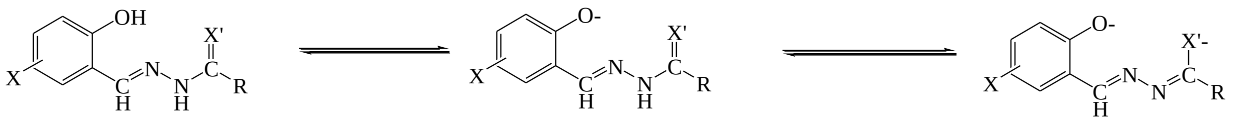
3. RESULT AND DISCUSSION

3.1 General Synthesis

A series of mononuclear, dinuclear and polynuclear oxomolybdenum(VI) complexes containing tridentate dianionic donating ligands and hexadentate tetraanionic donating ligands were prepared as shown in the overall reaction synthetic pathway, Scheme 2. In this work, the donating ligands are formed from the condensation reaction between a substituted hydrazone derivatives and a substituted salicylaldehydes.

An attractive feature of hydrazone Schiff base ligands is that they can exist in different coordination mode as implied in figure 8.



Neutral ligand

Ketonic coordination mode
in monoanionic mode

Enolic coordination mode
in dianionic mode

Figure 8: **Coordination mode of Ligands.** $X= OC_2H_5$ *or* Cl; $X'= S$ *or* O; $R= NH_2, NHC_2H_5, NHC_6H_5, C_6H_4OCH_3, C_4H_3O$

In the solid state, the ligands mainly exist in the neutral keto form whereas in the solution state, the enolate form predominates. Upon metal complexation, the ligands bind to the metal ions in keto form or enolate form depending on the reaction condition and nature of the ligands.

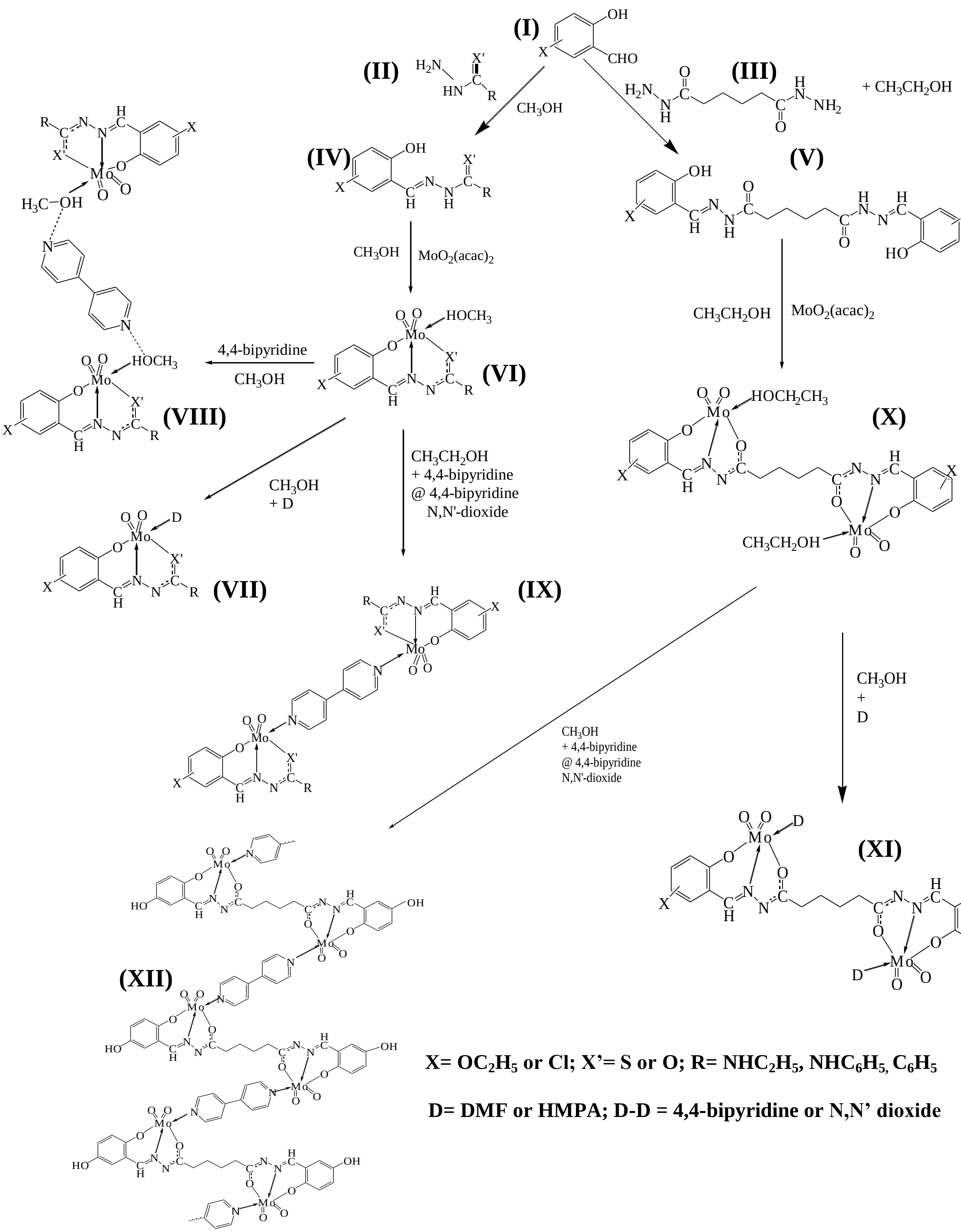
In the preparation of tridentate dianionic (ONO/ONS) ligands and hexadentate tetraanionic (ONO-ONO) ligands , diffferent substituted salicylaldehydes were reacted with monohydrazide and adipic acid dihydrazide compounds, respectively. The reaction of bis(acetylacetonato) dioxomolybdenum(VI) and the tridentate dianionic ligands by using methanol as refluxing medium afforded mononuclear oxomolybdenum(VI) complexes with ONO and ONS donor ligands system. These tridentate ligands were used for complexation as the complexes formed leave a labile coordination site that can be used for substrate binding. Several donating reagents such as DMSO, TMSO, HMPA, DMF and imidazole were used to complete the “open” coordination site (**D**) through ligand substitution reaction. In order to investigate the effect of different monodentate donor molecules at the sixth coordination site to the overall structure of the complexes formed, a series of mononuclear dioxomolybdenum(VI) complexes containing the *ONO* ligand system in the presence of various neutral monodentate ligands were prepared.

Subsequently, the synthetic work was extended to prepare dioxomolybdenum complexes with larger structural architecture, namely the binuclear arrays of molybdenum(VI) complexes. This can be done by replacing the neutral monodentate ligand of the mononuclear dioxomolybdenum(VI) complexes containing *ONS* ligands with bidentate ligands such as 4,4-bipyridine and 4,4 bipyridine *N,N’*dioxide, respectively. The resulting reactions gave rise to a series of dinuclear dioxomolybdenum(VI) complexes, in which two Mo atoms were bridged by the bidentate ligands. However, it was found that two types of bipyridyl bridging between the two adjacent dioxomolybdenum fragment are possible. In the first instance, the two mononuclear dioxomolybdenum(VI) complexes were bonded directly with bidentate 4,4-bipyridine or 4,4-bipyridydine N,N'-dioxide through N→Mo interaction (**compound IX, scheme 2**). The other possibility was discovered where the two adjacent dioxomolybdenum units were bridged by the 4,4-bipyridine indirectly due to the presence of water or ethanol molecule which was coordinated to the Mo atom and linked to the 4,4-bipyridine *via* H-bonding (**compound VIII, scheme 2**).

Different types of dinuclear dioxomolybdenum(VI) complexes were formed by the reaction of the hexadentate tetraanionic ligands with bis(acetylacetonato) dioxomolybdenum(VI) in the presence of ethanol. In this case, the two molybdenum atoms are not bridged directly by the bidentate ligand, but are coordinated at each end by the O,N,O donor atoms of the symmetrical hexadentate Schiff base ligand. The reactions were proceeded by displacing the ethanol molecules using monodentate ligands to yield other examples of dinuclear dioxomolybdenum(VI) complexes (**compounds X and XI, scheme 2**)

To complete the synthetic work, the preparation of tetranuclear oxomolybdenum(VI) complexes has been carried out by combining the dinuclear oxomolybdenum(VI) of the hexadentate tetraanionic ligand system with 4,4-bipyridine bidentate ligand. These reactions resulted in the formation of some 3-dimensional polymeric arrays of polynuclear dioxomolybdenum complexes (**compound XII, scheme 2**) containing the bidentate 4,4-bipyridine and the hexadentate tetraanionic ligand through strong donor-acceptor interaction as well as hydrogen bonding interaction.

Scheme 2: Reaction Synthetic Routes



X= OC$_2$H$_5$ or Cl; X'= S or O; R= NHC$_2$H$_5$, NHC$_6$H$_5$, C$_6$H$_5$

D= DMF or HMPA; D-D = 4,4-bipyridine or N,N' dioxide

3.1.1 Synthesis of Mononulcear Dioxomolybdenum(VI) Complexes with –ONO and ONS Ligands

The first part of this research project has been devoted to synthesize relatively simple dioxomolybdenum(VI) complexes with *–ONO* and *-ONS* tridentate ligands in the presence of different monodentate donors that are weakly bound to the dioxomolybdenum unit. These donor molecules coordinate to the Mo atom in a *trans* position with regard to the *oxo*-oxygen. The mononuclear dioxomolybdenum(VI) complexes were prepared by reacting a stoichiometric quantity of the synthesized ligands (**L1 – L9**) with bis(acetylacetonato) dioxomolybdenum(VI) in refluxing condition. Evaporation and recrystallization give rise to the formation of **C4** and **C5** compounds. However, the reaction mixture produced amorphous precipitate in poor yield. When DMSO, DMF, HMPA, TMSO or imidazole was added into the reaction mixture, fine crystalline complexes with the general formula **$MoO_2L(D)$**, (D = DMSO, HMPA, DMF, Imodazole) were obtained. This indicates that DMSO, DMF, HMPA, TMSO and imidazole are stronger donor solvents compared to methanol.

The complexes **C1- C15** are isostructures with respect to their coordination environment around the Mo atom. One of the significant differences between the structures is the bond length of the Mo-X heteroatom bond in **C9** which can be seen from the crystallographic description of the structure in the later section of this chapter. In the case of **C9**, DMF has been added during the preparation of the complex due to the low solubility of the complex in methanol. The preliminary crystal structure of **C9** revealed that HMPA is directly attached to the MoO_2^{2+} core instead of DMF. From the crystallographic data analysis, **C9** has a rather short Mo – O(6) bond distance than that of **C12**. This implicates that HMPA coordinates favorably to the MoO_2^{2+} core. The *oxo*-oxygen atom is responsible for the elongation and weakening of the bond in its *trans*-position and because of that, the corresponding ligands can be easily substituted by different substrates. In general, the six coordinate Mo(VI) complexes which are differing in the monodentate donor atom undergo facial displacement reaction readily at the sixth coordination site as shown in figure 9.

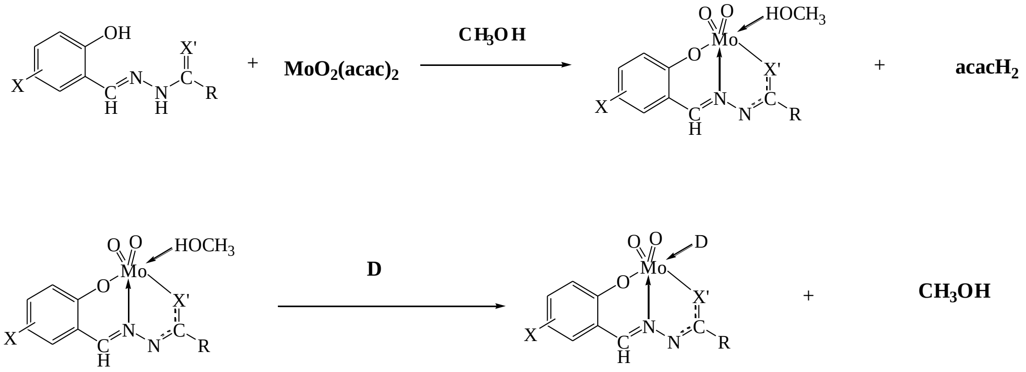


Figure 9: **Displacement reaction of dioxomolybdenum(VI) complexes**. *X=* OC_2H_5 *@ Cl; X'= O @ S; R=* NH_2*,* NHC_2H_5*,* NHC_6H_5*,* $C_6H_5OCH_3$*,* C_4H_3O *@* $C_6H_5(OH)_2$*/ D= DMSO, DMF, HMPA, TMSO @ imidazole*

Based on this type of reaction for the formation of [MoO_2(L)D], the strength of Mo-D bond is found to be in the order: EtOH<MeOH< TMSO<DMF<DMSO<HMPA.

3.1.2. Synthesis of Binulcear and Polynuclear Dioxomolybdenum(VI) Complexes

The reaction of bis(acetylacetonato)dioxomolybdenum with 5-dichlorosalicylaldehyde 4-ethylthiosemicarbazide **(L1 / L2)** in the presence of 4,4'-bipyridine (4,4'-bpy) or 4,4'-bipyridine *N,N'*-dioxide (4,4'-dpdo) gave binuclear *cis*-dioxomolybdenum complexes with the general formula, **$[(MoO_2)_2L_2(D\text{-}D)]$** in which the bidentate ligand, 4,4'-bipyridine or 4,4'-bipyridine *N,N'*-dioxide **(D-D)** formed a bridge between the two molybdenum atoms. The second type of binuclear dioxomolybdenum(VI) Schiff base complexes **$[(MoO_2)_2L'D_2]$** were formed by the reaction of bis(acetylacetonato)dioxomolybdenum with 1,4-bis(3-ethoxy-salicylaldehyde carbohydrazonato)butane **(L')** in the presence of ethanol or hexamethylphosphoramide **(D).** In this case, the two molybdenum atoms are not bridged directly by a bidentate ligand, but are coordinated at each end to the O,N,O donor atoms of the symmetrical hexadentate Schiff base ligand. The synthesis of polynuclear dioxomolybdenum(VI) **$[(MoO_2)L'(D\text{-}D)]_n$** complexes was achieved by the reaction of the second type of binuclear dixomolybdenum(VI) **$[(MoO_2)_2L'D_2]$** with the bidentate ligand, 4,4'-bipyridine **(D-D).** These types of polynuclear dioxomolybdenum complexes are found to adopt a 3-dimensional network structures which will be discussed in the later section. All the complexes were characterized by elemental analysis, electronic spectra, IR, ^1H and ^{13}C NMR spectroscopies, thermogravimetric analysis and cyclic voltammetry. The X-ray structures of most of these complexes were determined with good accuracy as can be seen in the later section.

3.2 Infra Red Spectra

Table 1: Characteristic IR bands of –*ONS* Donor Ligands and their Mononuclear Dioxomolybdenum(VI) Complexes

Compounds	**Wavenumbers, υ (cm^{-1})**					
	C=N	**C=S**	**N-H**	**O-H**	**Mo=O**	**Solvent Molecules**
L1	1613	1265	3406	3234	-	-
L2	1601	1269	3301	3128	-	-
L3	1606	1377	3365	3137	-	-
C1	1587	1262	3316	-	924,895	989 ($S{=}O_{DMSO}$)
C2	1588	1266	3303	-	939,905	825 ($S{=}O_{DMSO}$)
C3	1694	1272	-	-	929,889	861 ($S{=}O_{DMSO}$)

3.2.1 IR Spectral Studies of Mononuclear Dioxomolybdenum(VI) Complexes.

In order to study the binding mode of Schiff base ligand to the MoO_2^{2+} ion in the complexes, the IR spectra of the free ligands were compared with those of the corresponding complexes (table 1). The Schiff base ligands contain a few potential donor sites: (i) phenoxyl oxygen, (ii) acyclic azomethine nitrogen (iii) thioketone sulphur and (iv) amine nitrogen. Hence, changes in their stretching frequencies are expected when the ligands interact with the MoO_2^{2+} ions.

The Mo=O stretching frequency occur as a pair of sharp and strong bands at the region of 890 to 930 cm^{-1}, assigned to the anti-symmetry and symmetry stretching mode of dioxomolybenum(VI) moiety [47-48]. The IR spectra of the free ligands, **L1, L2** and **L3** show absorption bands at 3301-3406 cm^{-1} attributed to the υ(N-H) of secondary amide group, 3128-3327 cm^{-1} for υ(O-H), 1256-1377 cm^{-1} for υ(C=S) and 1601-1613 cm^{-1} for υ(C=N) [49-50]. The υ(O-H) are absent in the spectra of **C1, C2** and **C3** complexes as each ligand binds in binegative mode, losing proton from the two phenolic (O-H) group.

On the other hand , the υ(C=N) in **C1** and **C2** are found to have shifted to lower frequency while the υ(C=N) in **C3** is found to appear at *ca.* 90 cm^{-1} higher frequency compared to free ligands on complexation. The shift of azomethine bands to a frequency below 1600cm^{-1} upon metal binding is attributed to the conjugation of the p-orbital on the double bond with the d-orbital on the metal ion reducing the stretching force constant**.** However, a slight negative deviation was observed for the υ(C=S) in the spectra of the complexes. In addition, a sharp band observed at 989, 825 and 861cm^{-1} in **C1, C2** and **C3** are due to the stretching vibration of S=O, which in turn show the coordination by the oxygen atom of DMSO.

Table 2: Characteristic IR bands of –*ONO* Donor Ligands and Mononuclear Dioxomolybdenum(VI) Complexes

Compounds	**Wavenumbers, υ (cm^{-1})**					
	C=N	**C=O**	**N-H**	**O-H**	**Mo=O**	**Solvent Molecules**
L4	1590	1644	-	3429	-	-
L5	1601	1649	-	3134	-	-
L6	1608	-	-	3419, 3378, 3162	-	-
L7	1607	1652	-	3424	-	-
L8	1604	1637	-	3351	-	-
L9	1607	1654	-	3180	-	-
C4	1608	-	-	-	929,903	3430 (O-$H_{methanol}$)
C5	1567	1612	-	-	924,904	3382 (O-$H_{methanol}$)
C6	1549	1618	-	-	923,901	1033 (S=O_{DMSO})
C7	1521	1625	-	-	925,903	1004 (S=O_{DMSO})
C8	1546	1627	-	3127	928,907	825 (S=O_{DMSO})
C9	1540	1624	-	-	930,906	1156 (P=O_{HMPA})
C10	1564	1618	-	-	925,894	991 (S=O_{DMSO})
C11	1566	1618	-	-	929,903	1150 (P=O_{HMPA})
C12	1565	1616	-	-	931,906	1725 (C=O_{DMF})
C13	1561	1596	-	-	922,903	1518 (C=N_{Imz})
C14	1563	1617	-	-	922,896	998 (S=O_{TMSO})
C15	1533	1624	-	-	918,896	995 (S=O_{DMSO})

3.2.2 IR Spectra Studies of Mononuclear Complexes with –ONO Ligand System

Generally, for aroyl hydrazone ligands, the $\upsilon_{N\text{-}H}$ and $\upsilon_{C=O}$ modes of the lateral chain in the uncoordinated Schiff base appears at 3100-3400 cm^{-1} and 1600 – 1700 cm^{-1} , indicating that the ligands exist as keto form in the solid state (table 2). In solution, the ligands probably exist as tautomeric enol form. The absorption band at 3100 – 3400 cm^{-1} in the ligands was weakened due to the delocalization of electrons between the oxygen atom of the carbonyl group and the nitrogen atom of the imine group. The IR spectra of the complexes show a considerable negative shift of 15-20 cm^{-1} in $\upsilon_{C=O}$ absorption indicating the decrease in stretching force constant of C=O as a result of coordination through oxygen atom of the ligand. The Schiff base ligands show a sharp and strong band due to $\upsilon_{C=N}$ of the acyclic azomethine group at *ca.*1590-1615 cm^{-1}. The observed low energy shift of this band in the complexes at *ca.* 1550-1600 suggests the coordination of azomethine nitrogen to the molybdenum atom.

The precursor complex of $MoO_2(acac)_2$ has two sharp bands at 934 and 906 cm^{-1}, which are related to symmetrical and anti-symmetrical stretching of *cis*-MoO_2^{2+} , respectively. These bands in the complexes **C4** to **C15** appear between 894 – 939 cm^{-1}, indicating the symmetrical and anti-symmetrical stretching vibrations of MoO_2^{2+} are independent of the electron donating and accepting ability of the ligands. [51-52]

The IR spectra the **C4 - C15** showed a consistent reduction of υ(C=N) stretching frequency from *ca*.1608 cm^{-1} to *ca.* 1565 cm^{-1} indicating that nitrogen atom coordination existed in the complexes. The IR spectra of **L6** exhibit multiple bands for $υ_{(OH)}$ at 3102, 3378 and 3419 cm^{-1}. Upon coordinating to MoO_2^{2+}, these absorption bands vanished as were observed in their IR spectra. An absorption band at 3127cm^{-1} which was attributed to the -OH stretching of the 2,4 dihydroxy benzoic hydrazide was clearly observed. The Schiff base ligands exhibit a broad band at 3100-3400 cm^{-1}, indicating the involvement of the –OH group from the salicylaldehyde in intramolecular hydrogen bonding with the lone pair of azomethine nitrogen. It also suggests that the ligands exist in enol form in the solid state.

The dioxomolybdenum(VI) complexes exhibit IR absorption bands that is associated to the stretching frequencies of donor solvent molecules. Drago and Meek have assigned $υ_{S\text{-}O}$ at 1025-985 cm^{-1} when DMSO is coordinated to molybdenum center through oxygen atom [53]. Most of the DMSO containing dioxomolybdenum(VI) complexes shows S-O stretch at this region except for the case of **C8** in which the vibrational band gave a clear shifting to lower frequency at 825 cm^{-1}. In the case of **C9** and **C11,** the bands at 1156 and 1150 cm^{-1} are associated with the υ(P-O) stretching. The IR frequency of -C=O_{DMF} in **C12** displayed value at 725 cm^{-1} [54]

In free imidazole, absorption peaks were observed at *ca.* 1600-1675 cm^{-1} as reported by Otting [55]. In the spectrum of **C13,** the coordination of imidazole to molybdenum atom has shifted the peak to 1517 cm^{-1}.

Table 3: Characteristic IR bands Binuclear and Polynuclear Dioxomolybdenum (VI) Complexes

Compounds	**Wavenumbers, υ (cm^{-1})**					
	C=N	**C=S / C=O**	**N-H**	**O-H**	**Mo=O**	**Solvent Molecules**
L10	1607	1263	3438	3190	-	-
L11	1606	1663	-	3590	-	-
L12	1608	1680	-	3253	-	-
L13	1608	1681	-	3264	-	-
L14	1610	1680	-	3250	-	-
C16	1597	1628	-	-	923,912	1064, 1020, 975 ($C-N_{bipy}$).
C17	1596	1616	-	-	924,910	1056, 1011, 989 ($C-N_{bipy}$).
C18	1603	1283	-	-	927,898	1076, 1063, ($C-N_{bipy}$).
C19	1586	1212	-	-	922,892	823,834 ($N-O_{dpdo}$)
C20	1562	1614	-	-	942,911	1034 ($C-O_{ethanol}$)
C21	1539	1612	-	-	943,916	1036 ($C-O_{ethanol}$)
C22	1565	1621	-	-	927,900	1131,1192($P=O_{HMPA}$)
C23	1563	1618	-	-	930,899	737,763 ($C=O_{DMF}$)
C24	1547	1609	-	3255	926,883	1069, 1032, 984 ($C-N_{bipy}$)

3.2.3 IR Spectra Studies on Binuclear and Polynuclear Complexes

The IR spectra of the complexes, **C18-C24** were analyzed in comparison with that of the free ligand (table 3). The complexes **C18** to **C24** show two bands between 897 – 941 cm^{-1}, indicating the MoO_2^{2+} symmetrical and anti-symmetrical stretching vibrations. These data also indicate the presence of a *cis*-MoO_2 structure as a *trans*- MoO_2 would normally show one $\upsilon_{Mo=O}$ band due to the asymmetry stretch. From the IR spectra of **C18, C19** and **C24** it has been observed that the coordination of neutral bidentate N-N donor ligands (4,4-bipyridine/ 4,4-bipyridine *N,N'*-dioxide) has the effect of lowering the Mo =O stretching frequency [56]. In the IR spectra of free thiosemicarbazone and hydrazone ligands, the imine ($\upsilon_{C=N}$) stretching bands appeared between 1590-1610 cm^{-1}, but for the complexes, the characteristic imine bands were observed at higher stretching frequencies ranges 1610-1620 cm^{-1}, indicating the coordination of imine nitrogen atom to the metal center. The $\upsilon(C_{ar} – O)$ band in the range of 1530 -1550 cm^{-1} for the ligands was found to have shifted to higher frequency to 1560 ± 5 cm^{-1} suggesting the coordination of the deprotonated phenolic C – O group to the MoO_2 moiety. In the case of **C20-C24**, the absent of υ_{NH} signal, suggesting the possibility of second deprotonation of amide moiety that lead to the enolic coordination mode of the ligands in dianionic state to the Mo atom. On the other hand, the presence of a new band at 1250 ± 10 cm^{-1} in the complexes could be assignable to the υ (C_{enolic} -O). The coordination of 4,4-bipyridine is characterized by the ring breathing mode of pyridine, which occurs at 990 cm^{-1} in free pyridine [**57**]. The slight increase on chelation in the frequency of the pyridine breathing vibration (1003 cm^{-1}) for **C18** can be attributed to the coordination from the pyridine nitrogen to the metal ion. The IR spectrum of **C19** exhibits absorption bands at 823 and 834 cm^{-1} which is assigned as the N-O stretching. Free pyridine N-oxide exhibits a band at 1234 cm^{-1} [58]. The N-O stretching frequency which is lowered upon coordination is attributable to the weakening of the bond by reduction of the electron density in the N-O bond and the loss of double bond character of N-O bond when the oxygen atom coordinates to the d^0 metal ion [59-60]. In the case of **C22** and **C23**, the bands at 1131 cm^{-1} and 737 cm^{-1} are associated to the $\upsilon_{P=O}$ of HMPA and $\upsilon_{NC=O}$ of DMF solvent molecules, respectively.