Synthesis, Structural and Biological Evaluation of Dioxomolybdenum(VI) Complexes: Metal-Mediated C–C And M–M Bond Formation

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Introduction

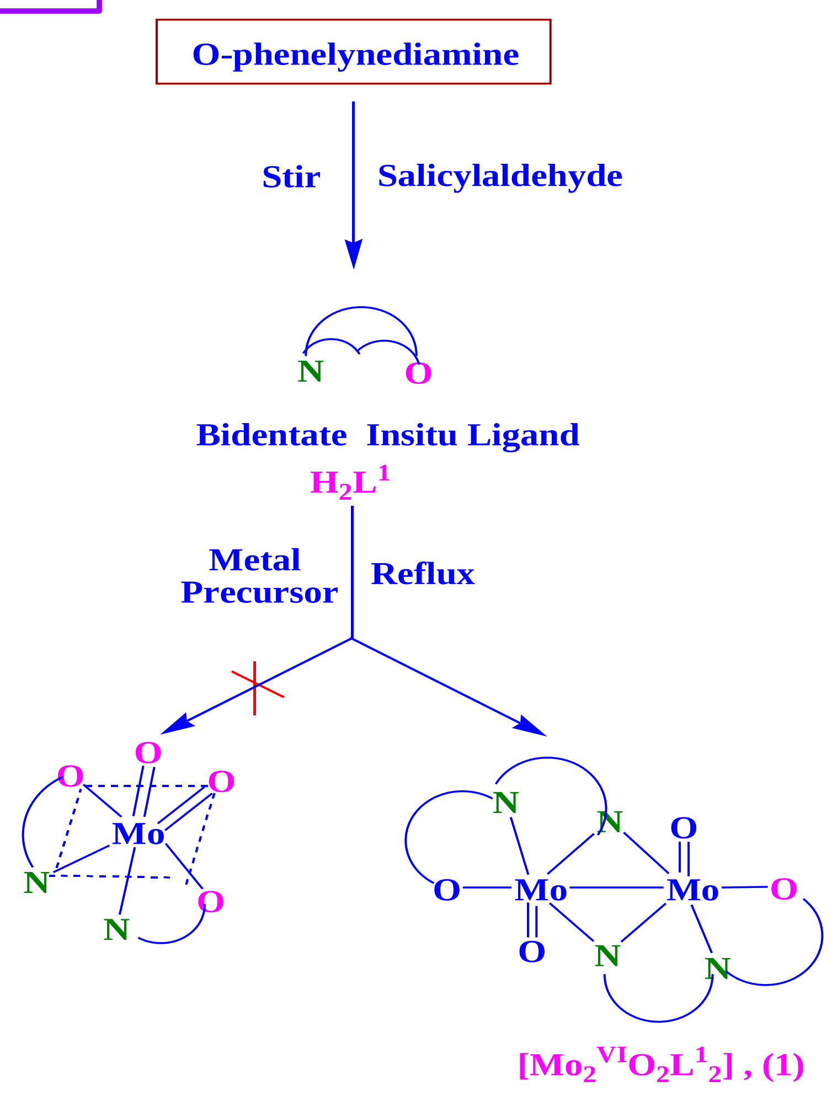
- The chemistry of Molybdenum is currently a subject of extensive research due to its biochemical role in metalloenzymes and complex chemistry.
- The presence of Mo=O bonds around the Mo(VI) centre has been explored a number of model complexes with terminal oxo molybdenum(VI) bonds that mimic the molybdoenzymes and function as effective catalysts and the presence of the terminal oxo donor is essential for the biochemical and catalytic activity of such complexes.
- Our sustained interest in the synthesis, structural, and spectroscopic study of dioxomolybdenum complexes promoted us to synthesize some dioxomolybdenum(VI) complexes and study their antibacterial activity.

Objectives

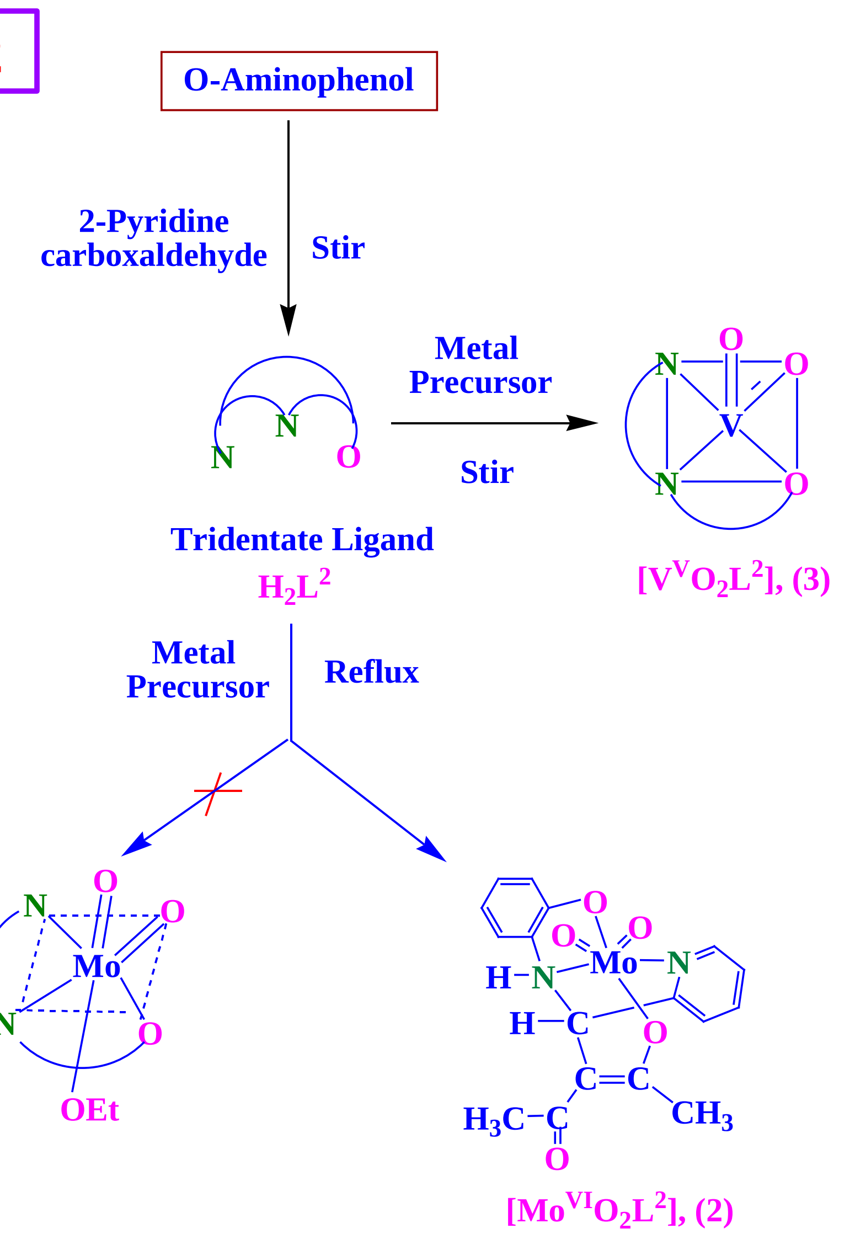
- ❖ Synthesis and characterization of Schiff's base ligands.
- ❖ Synthesis and spectral characterizations of novel dioxo-molybdenum(VI) complexes, $[Mo_2O_2L^1_2]$ and $[MoO_2L^2]$.
- ❖ X-Ray Structures of dioxo-molybdenum(VI) complexes, $[Mo_2O_2L^1_2]$ (1) and $[MoO_2L^2]$ (2) .
- ❖Synthesis and spectral characterizations of dioxo-vanadium(V) complex, $[VO_2L^2]$ (3) .
- ❖ To study the antibacterial activity of corresponding dioxomolybdenum(VI) and dioxovanadium(V) complexes.

Methodology and Work Plan

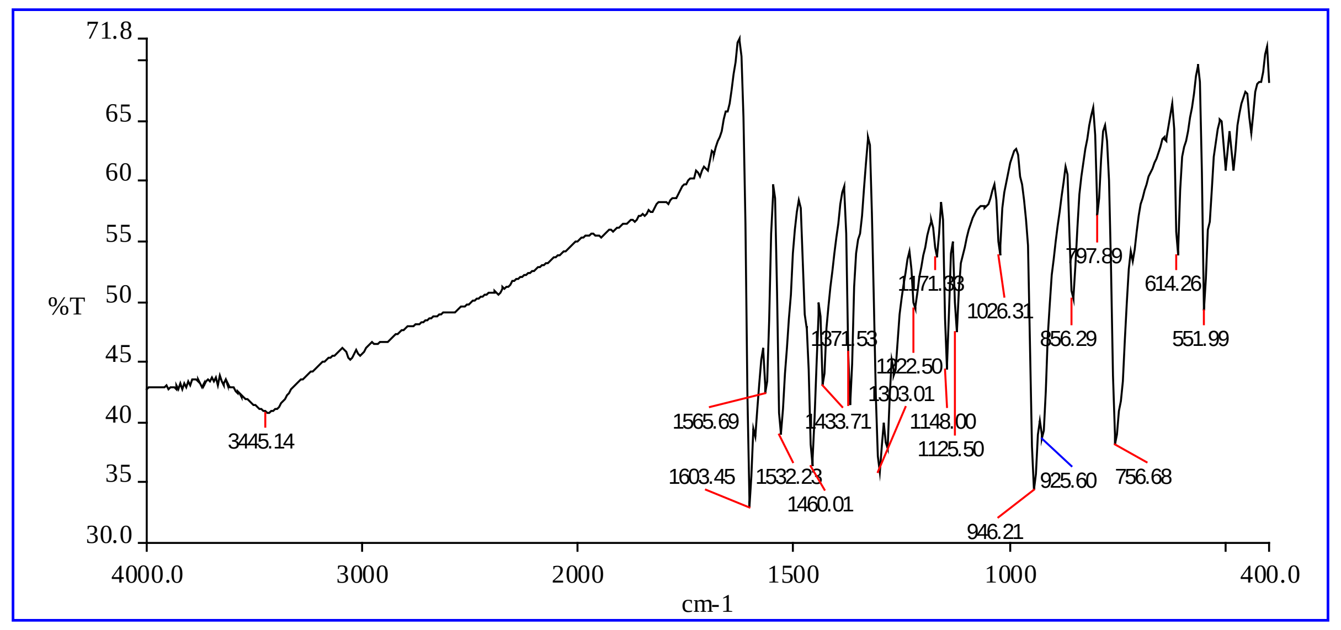
Scheme-1



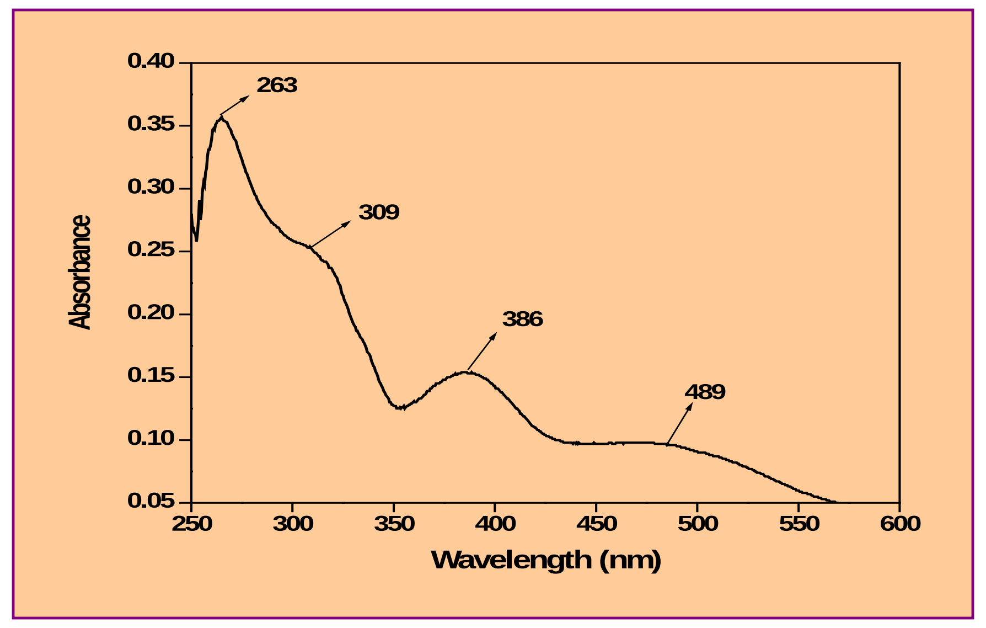
Scheme-2



Spectral Characterizations of $[Mo_2^{VI}O_2L^1_2]$, (1)



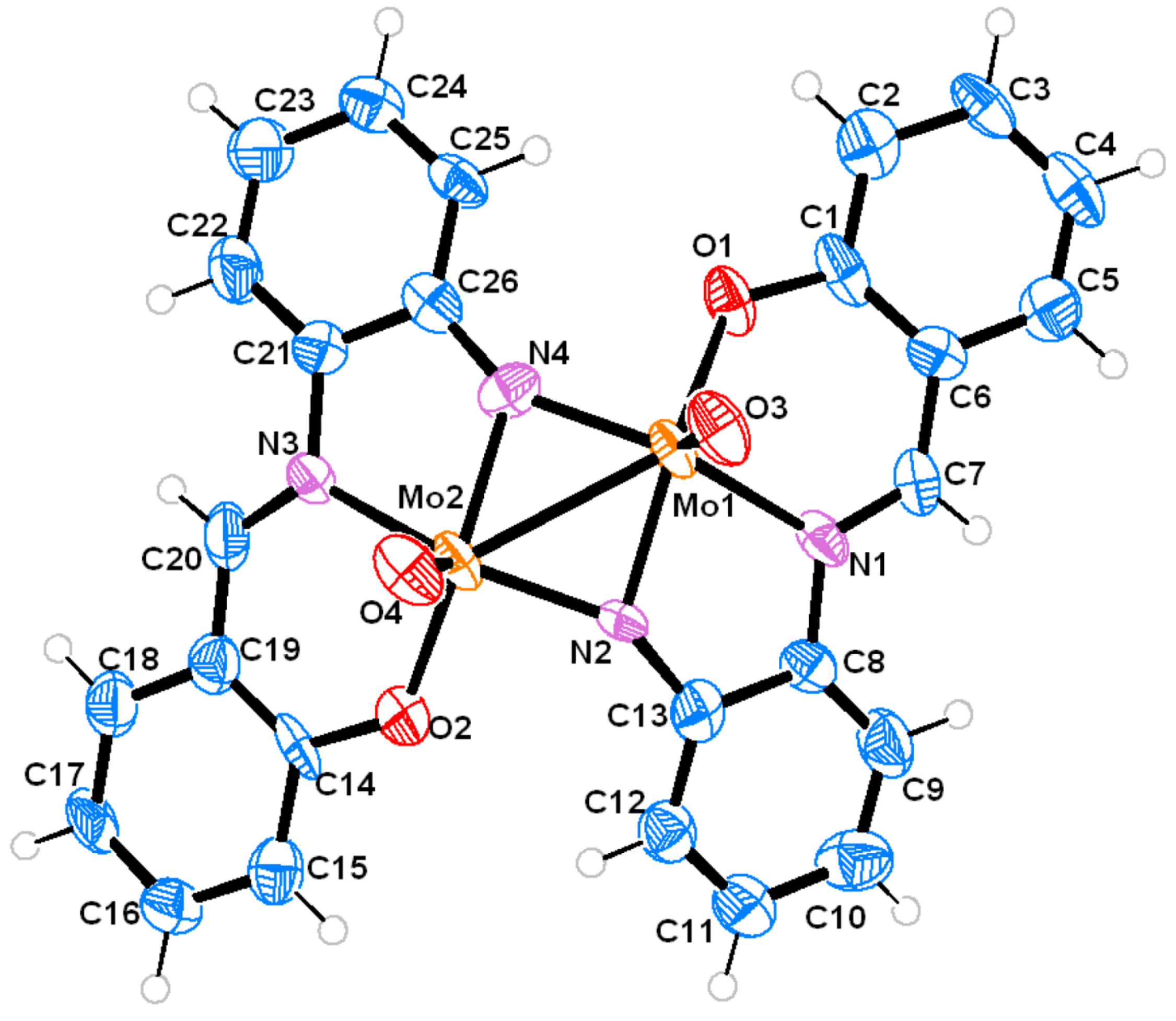
IR spectra of $Mo_2^{VI}O_2L^1_2]$, (1)



Electronic Spectra of $Mo_2^{VI}O_2L^1_2]$, (1)

^1H NMR spectra of $Mo_2^{VI}O_2L^1_2]$, (1)

X-Ray Structures of $[Mo_2^{VI}O_2L^1_2]$, (1)



X-Ray Structure of $[Mo_2^{VI}O_2L^1_2]$, (1)

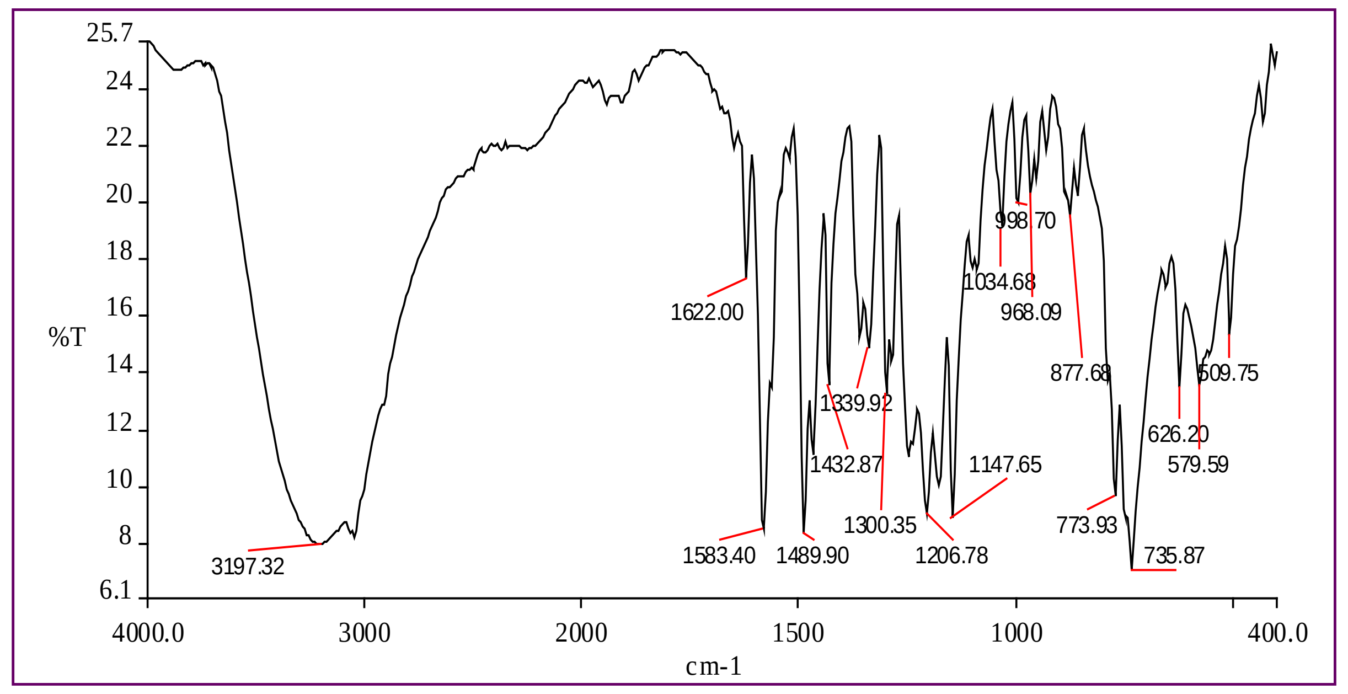
Bond Distances

Mo1-O1	2.028(5)	Mo2-O2	2.021(5)
Mo1-O3	1.683(4)	Mo2-O4	1.687(4)
Mo1-N1	2.170(6)	Mo2-N2	1.938(5)
Mo1-N2	1.947(5)	Mo2-N3	2.175(5)
Mo1-N4	1.935(5)	Mo2-N4	1.955(6)
Mo1-Mo2	2.650(9)		

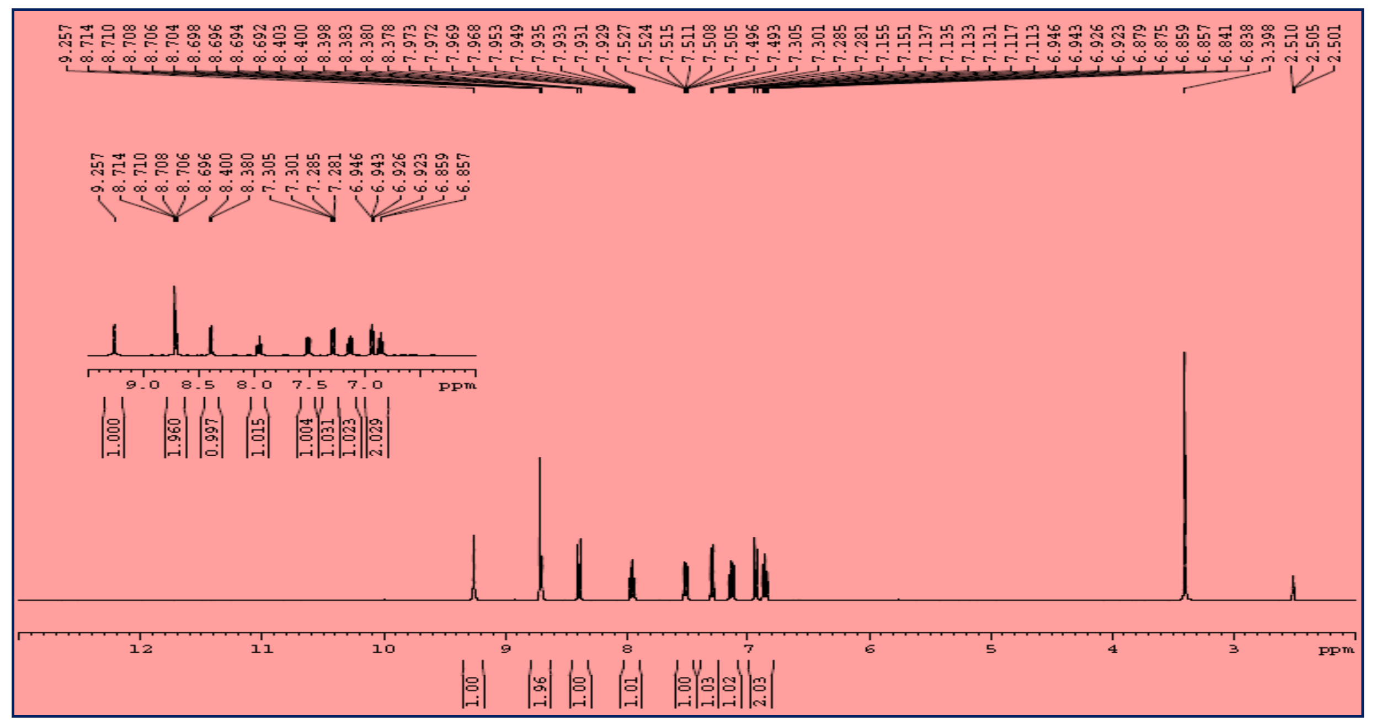
Bond Angles

O1-Mo1-O3	106.9(2)	O3-Mo1-N4	112.4(2)
O1-Mo1-N1	83.08(2)	N1-Mo1-N4	142.4(2)
O1-Mo1-N2	143.6(2)	N2-Mo1-N4	91.07(2)
O1-Mo1-N4	87.01(2)	Mo1-N2-Mo2	86.0(2)

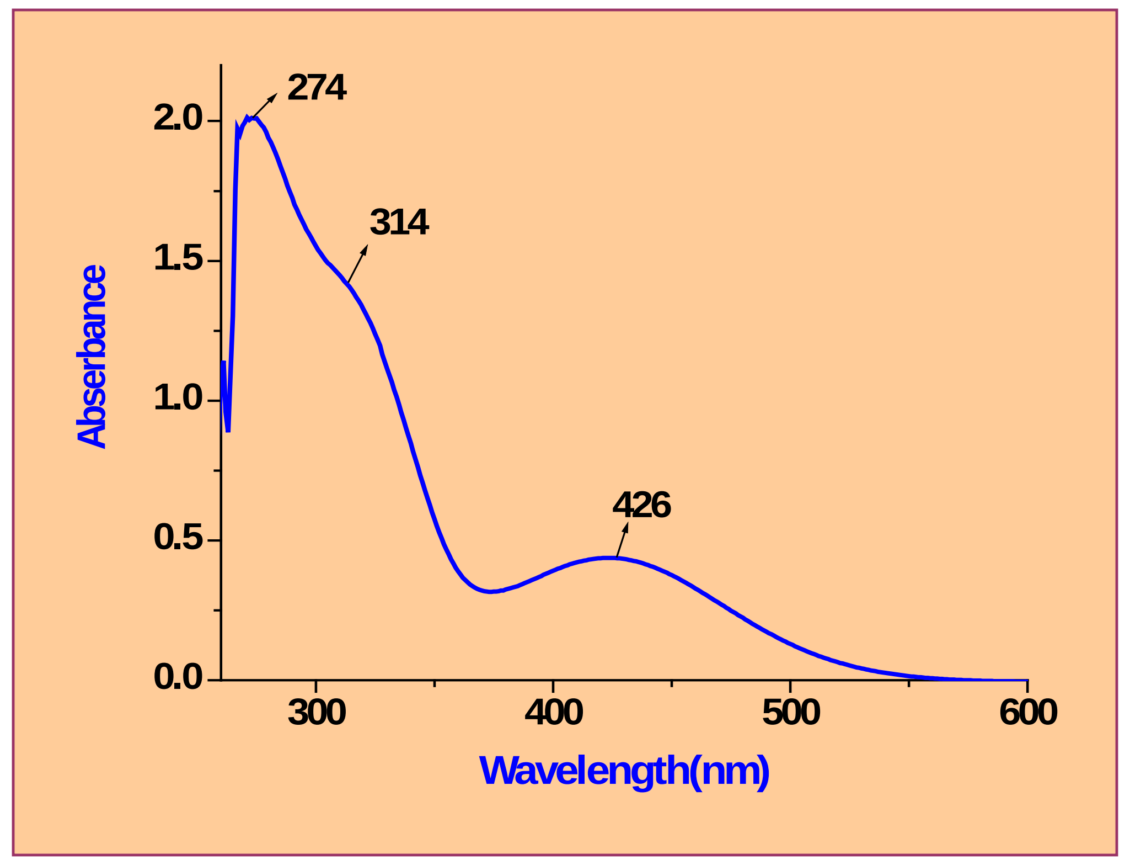
Characterizations and X-Ray Structure of $[Mo^{VI}O_2L^2]$, (2)



IR spectra of H_2L^2

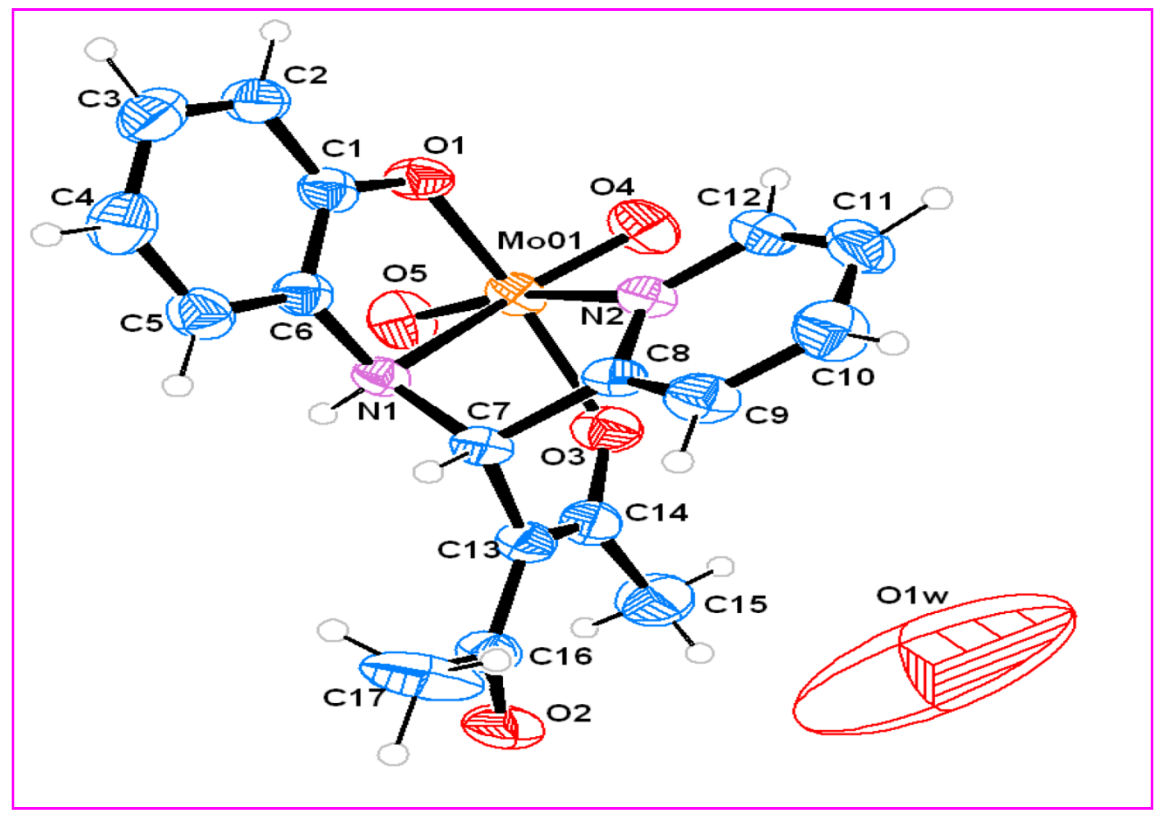


^1H NMR spectra of H_2L^2



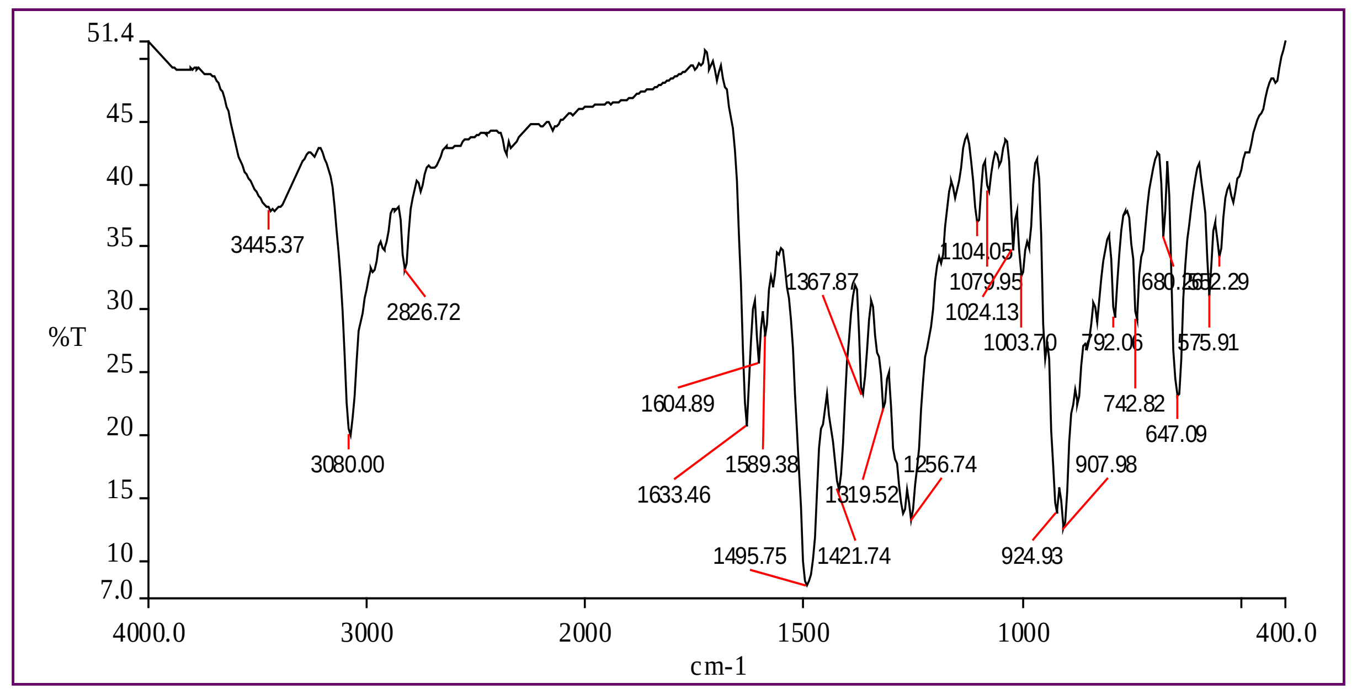
Electronic Spectra of $[Mo^{VI}O_2L^2]$, (2)

The complex exhibits two bands at 924 and 907 cm^{-1}, assigned to symmetric and antisymmetric vibrations respectively, of the *cis*-MoO_2 core. . In the NMR spectra of complex, the absence of signal due to aromatic–OH at 9.25 ppm indicates that the phenolic group is coordinated to the metal centre after proton replacement. The band near 426 nm is assigned to ligand to metal charge transfer transition, where as other higher energy bands are due to intraligand transitions.

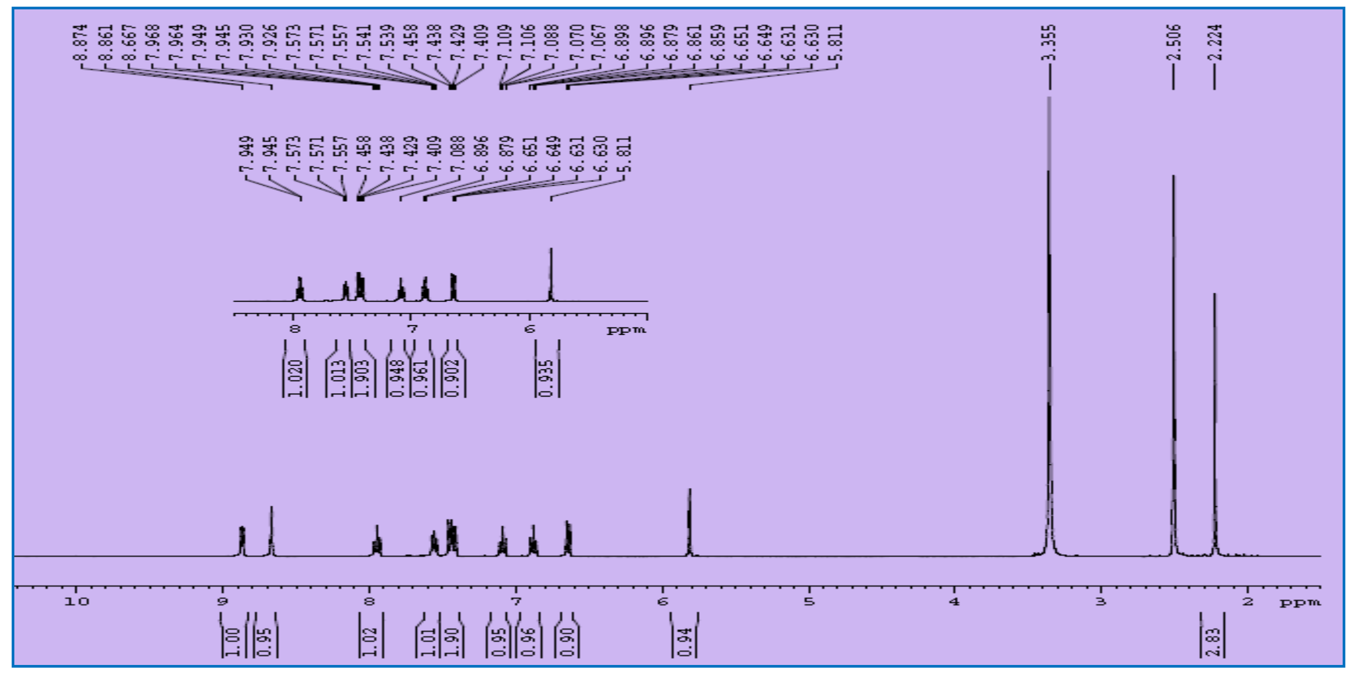


X-Ray Structure of $[Mo^{VI}O_2L^2]$, (2)

Bond Distances		Bond Angles	
Mo1-O1	1.946(3)	O1-Mo1-O3	152.95(9)
Mo1-O3	1.982(3)	O1-Mo1-O4	97.73(9)
Mo1-O4	1.698(3)	O1-Mo1-O5	99.94(9)
Mo1-O5	1.705(3)	O1-Mo1-N1	76.29(7)
Mo1-N1	2.326(3)	O3-Mo1-O4	98.41(9)
Mo1-N2	2.336(3)	O3-Mo1-O5	95.96(10)
C7-C8	1.517(4)	O3-Mo1-N1	88.88(8)
C16-O2	1.225(3)	O3-Mo1-N2	76.64(9)

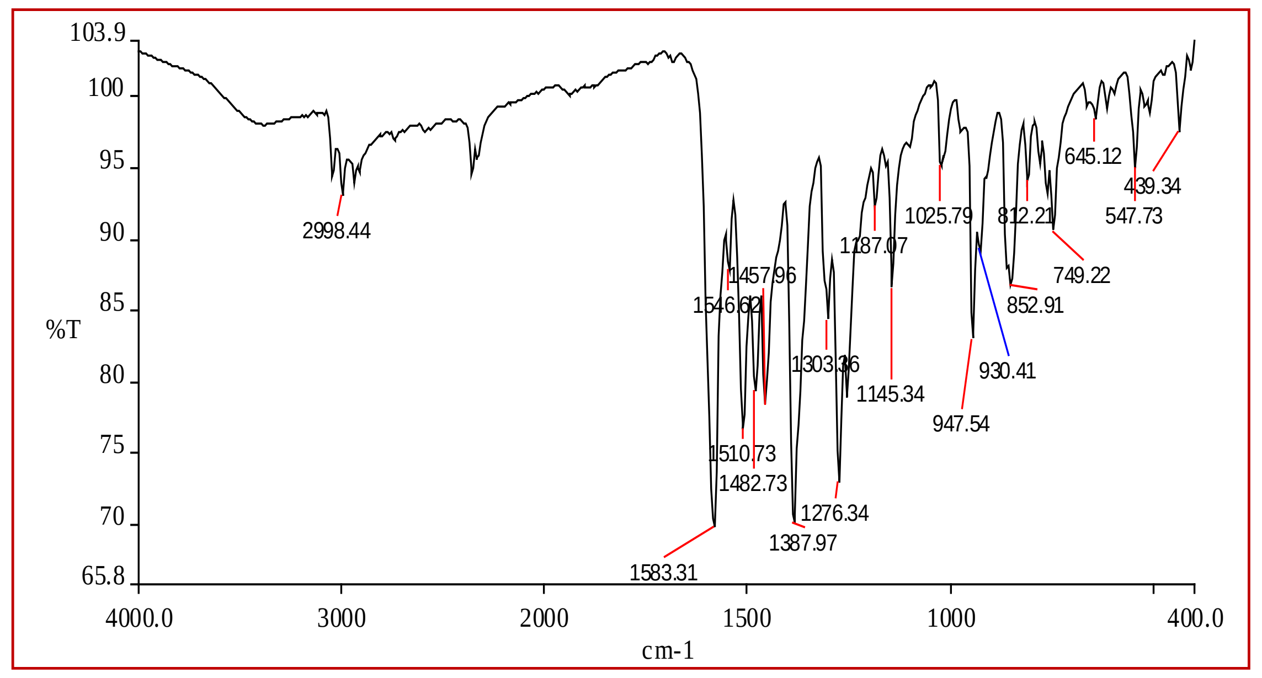


IR spectra of $[Mo^{VI}O_2L^2]$, (2)

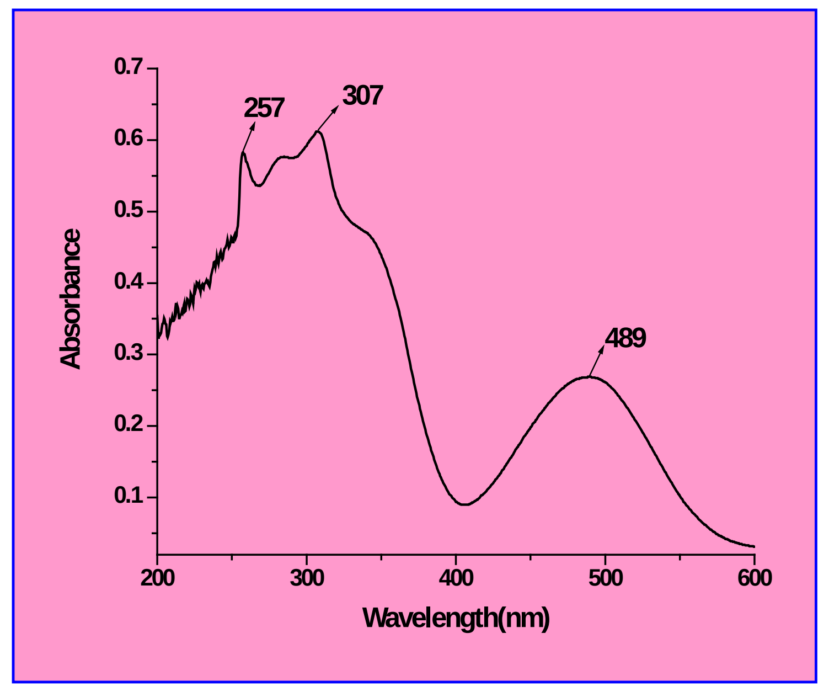


^1H NMR spectra of $[Mo^{VI}O_2L^2]$, (2)

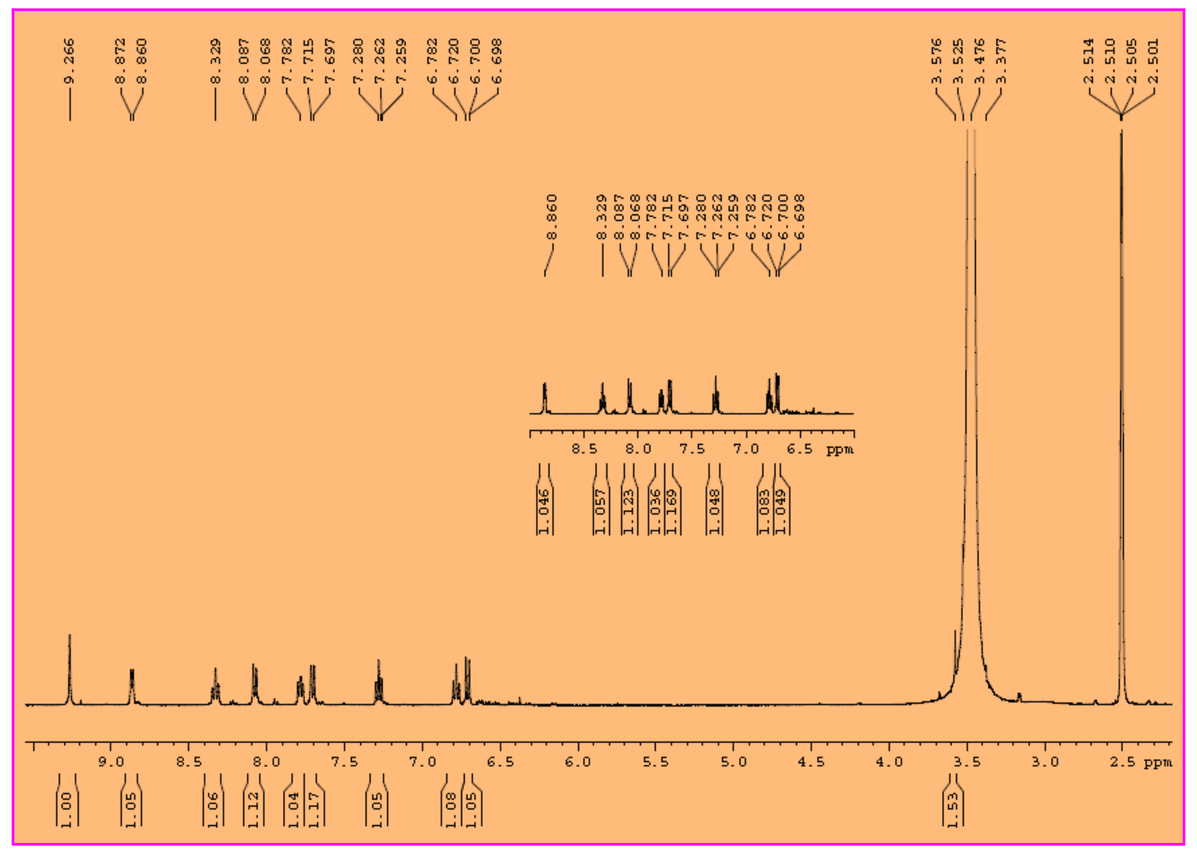
Spectral Characterizations of $[V^VO_2L^2]$, (3)



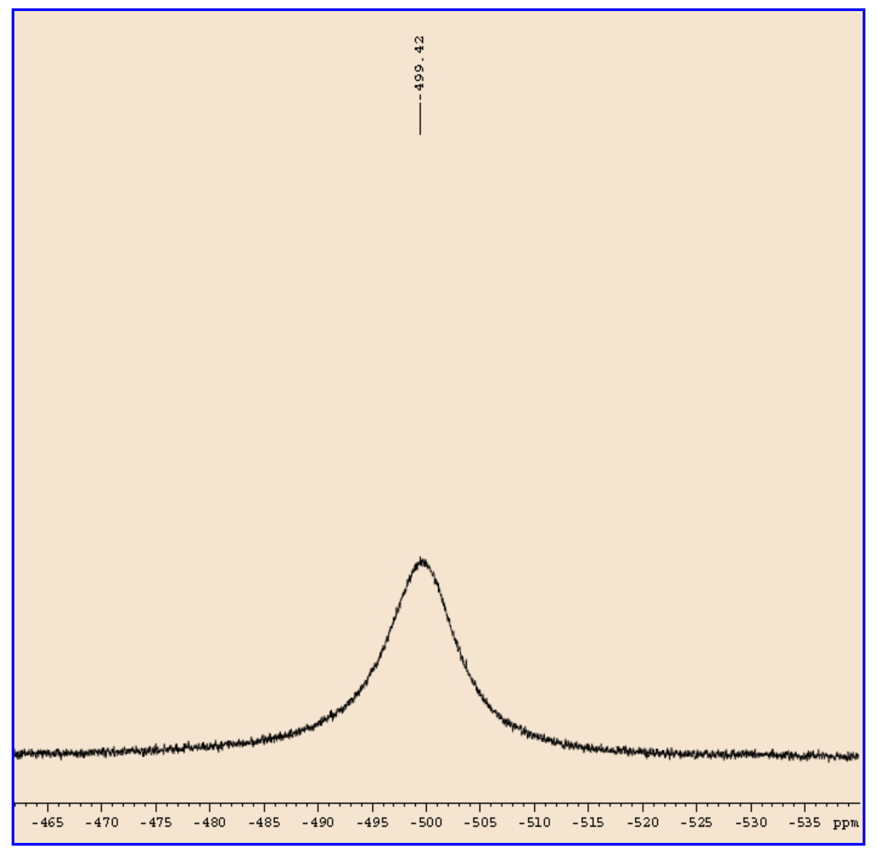
IR spectra of $[V^VO_2L^2]$, (3)



Electronic Spectra of $[V^VO_2L^2]$, (3)



^1H NMR spectra of $[V^VO_2L^2]$, (3)



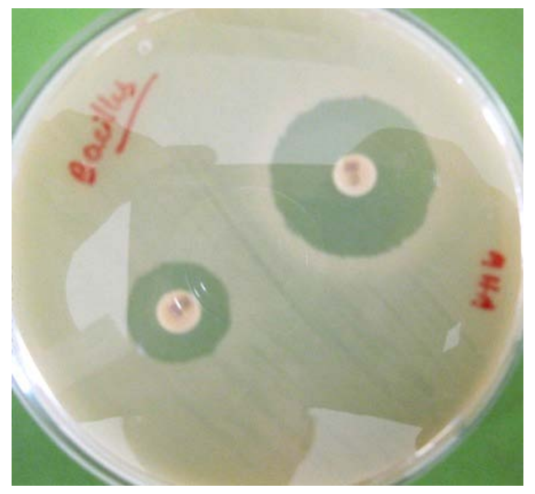
V^{51} NMR spectra of $[V^VO_2L^2]$, (3)

Study of Antibacterial Activity of Metal Complexes

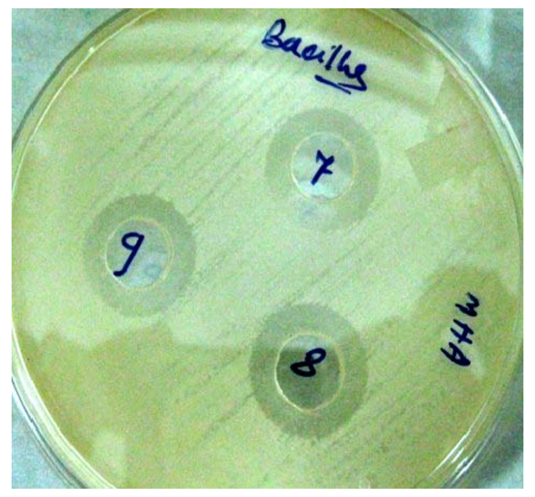
The ligands and their corresponding metal complexes have been screened for their antibacterial activity against *Escherichia coli, Bacillus and Proteus*. Minimum inhibitory concentration (MIC) of these complexes and antibacterial activity indicates the compound 1 & 2 as the potential lead molecule for drug designing.

	E.coli	Bacillus	Proteus
H_2L^2	--	--	--
$[Mo_2O_2L^1{}_2]$, 1	62.5	15.6	--
$[MoO_2L^2]$, 2	7.3	7.3	15.6
$[VO_2L^2]$, 3	62.5	125	--
Vancomycin	30	30	30
Chloramphenicol	--	40	--

Minimum Inhibitory Concentration (MIC) value in μg/mL of the Schiff base ligand (H_2L^{1-3}), oxomolybdenum(VI) complexes and standard drugs against pathogenic strains



Vancomycin and Chloramphenicol



$[MoO_2L^2]$, (2)

References

1. S. Pasayat, S. P. Dash, S. Bhakat, P. K. Majhi, Y. P. Patil, M. Nethaji, H. R. Dash, S. Das, R. Dinda, Polyhedron 2012, 38 , 198-204 .
2. S. P. Dash, S. Pasayat, Saswati, H. R. Dash, S. Das, R. J. Butcher, R. Dinda, Polyhedron 2012, 31, 524-529.
3. R. Dinda, P. K. Majhi, P. Sengupta, S. Pasayat, S. Ghosh, L. R. Falvello, T. C. W. Mak, Polyhedron 2010, 29 , 248-253.
4. R. Maurya, S. Khurana, C. Schulzke and D. Rehder, Eur. J. Inorg. Chem. 2001, 779.

Conclusion

- Schiff's base ligand was synthesized and characterized.
- All the dioxomolybdenum(VI) and dioxo-vanadium(V) complexes have been successfully synthesized and $[Mo_2{}^{VI}O_2L^1{}_2]$, (1) & $Mo^{VI}O_2L^2]$, (2) complexes structurally characterized.
- From X-ray structure it is found that in complex 1 & 2, the C 惘 C & M 惘 M bond is formed during metallation , but not in case of complex 3. Which suggest the process is Mo-mediated only.
- Antibacterial activity indicates the minimum inhibitory concentration of the complex 1 & 2 are more promising than the standard drugs.

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