

# Chemistry of Oxidometal (Mo and V) Complexes: Metal Assisted Organic Transformation and Novel Solution Behavior

Rupam Dinda

Department of Chemistry, National Institute of Technology, Rourkela 769008, Odisha, India

The chemistry of oxidomolybdenum and oxidovanadium complexes has gained substantial research importance in recent times due to their versatile reactivity and interesting coordination behaviour. Among them, metal-metal bonded molybdenum(V) complexes constitute an important class of compounds. Very few bis- $\mu$ -imido bridged metal-metal bonded oxidomolybdenum(V) complexes are reported in literature, although molybdenum(V) complexes with terminal imide groups have been long known. Further, metal assisted organic transformations of ligands have gained renewed interests in recent years. On another hand, in comparison to the well-known oxidovanadium(IV)/(V) complexes, relatively few non-oxido V<sup>IV</sup> complexes, have been isolated and structurally characterized. Interestingly, the solid state chemistry for a particular compound may be different from that in solution. Also mixed-valence metal complexes have received much attention.

Hence, we have been motivated to focus on our present work<sup>1-6</sup> which comprises of the chemistry of variable valence oxidometal (Mo and V) complexes. Mechanistic pathways of metal assisted ligand rearrangements have been predicted. Some bis- $\mu$ -imido bridged dimeric oxidomolybdenum(V) complexes synthesised from salophen has been reported. A novel  $\mu$ -oxidodivanadium compound, generated from the corresponding mononuclear complex, was characterized in solution and in the solid state. The mixed oxidation V(IV,V) species were detected through electro synthesis and characterized by EPR spectroscopy and DFT calculations.

## References

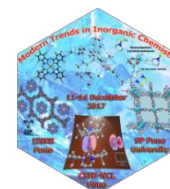
1. S. Majumder, R. Dinda et al. *Inorg. Chem.* **56** (2017) 11190–11210.
2. S. Roy, R. Dinda et al. *J. Inorg. Biochem.* **172** (2017) 110–121.
3. S. P. Dash, R. Dinda et al. *Inorg. Chem.* **55** (2016) 1165–1182.
4. S. P. Dash, R. Dinda et al. *Inorg. Chem.* **55** (2016) 8407–8421.
5. S. Pasayat, R. Dinda et al. *Eur. J. Inorg. Chem.* 2016, 1604–1618.
6. S. P. Dash, R. Dinda et al. *Dalton Trans.* **45** (2016) 18292–18307.
7. S. P. Dash, R. Dinda et al. *J. Inorg. Biochem.* **144** (2015) 1–12.
8. S. P. Dash, R. Dinda et al. *Dalton Trans.* **43** (2014) 10139–10156.
9. S. P. Dash, R. Dinda et al. *Inorg. Chem.* **52** (2013) 14096–14107.

# Chemistry of Oxidometal (Mo and V) Complexes: Metal Assisted Organic Transformation and Novel Solution Behavior

**Dr. Rupam Dinda**



**National Institute of Technology  
Rourkela-769008, Odisha, India**

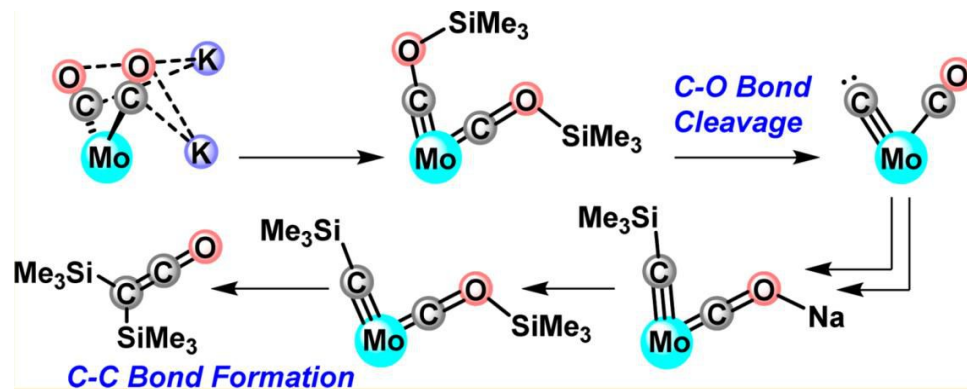


MTIC –XVII, Pune

# Introduction

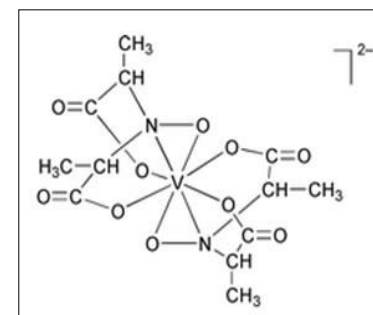
Transition metal mediated organic transformations have generated renewed interest in recent times. However, examples of such chemistry with oxidomolybdenum complexes are rare.

T. Agapie et al., *J. Am. Chem. Soc.* 2016, 138, 16466



Also, in comparison to the well-known oxido vanadium (IV or V) complexes relatively few non-oxido V(IV) complexes have been isolated and structurally characterized.

R. E. Berry et al., *Angew. Chem., Int. Ed.* 1999, 38, 795



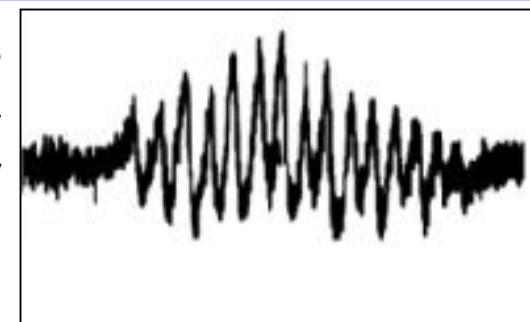
Amavadin

Again, for a particular system, the solid state chemistry may be different from that in solution. Also, In contrast to the well-known oxido vanadium(IV or V) complexes containing, relatively few mixed-oxidation (IV,V) complexes have been isolated and especially through electrosynthesis.

M. Moon et al., *Inorg. Chem.* 2001, 40, 554

A Chakravorty et al. *Inorg. Chem.* 1993, 32, 5343;

M. Chaudhury et al. *Inorg. Chem.* 1999, 38, 1982



Room Temperature EPR of  
Mixed valence V(IV,V) species

*Unprecedented Mo Assisted Organic  
Transformation*

*R. Dinda et al.*

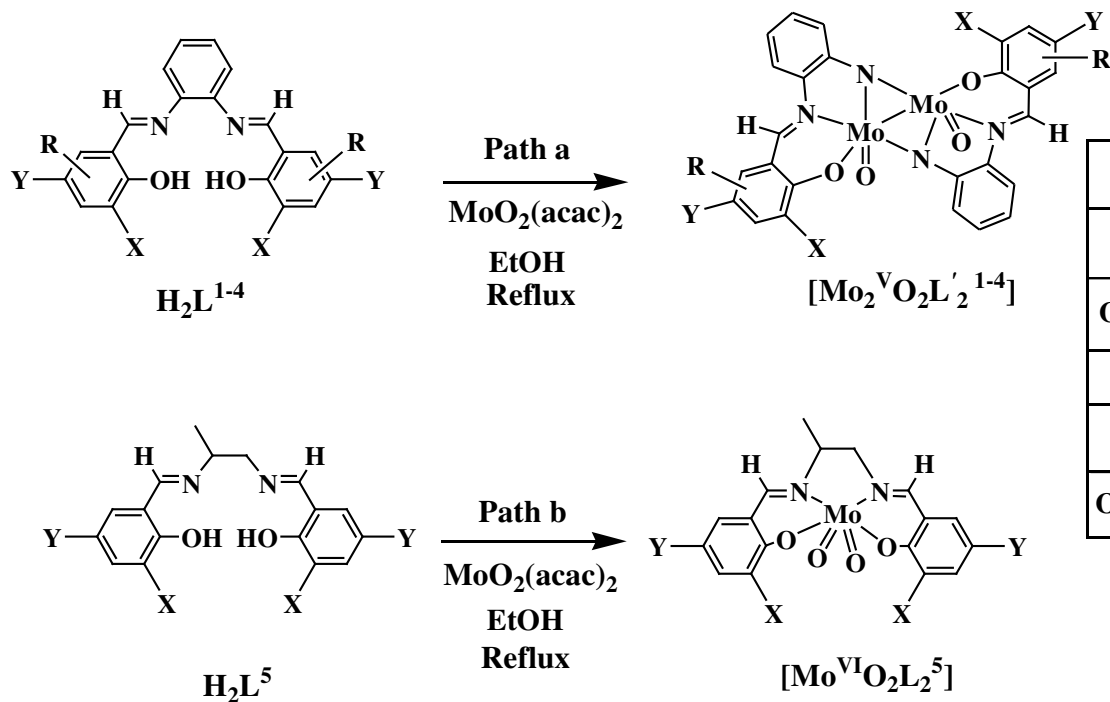
**Inorg. Chem. 2017, 56, 11190**

**J. Inorg. Biochem. 2017, 172, 110**

**Eur. J. Inorg. Chem., 2016, 1604**

**J. Inorg. Biochem. 2015, 144, 1**

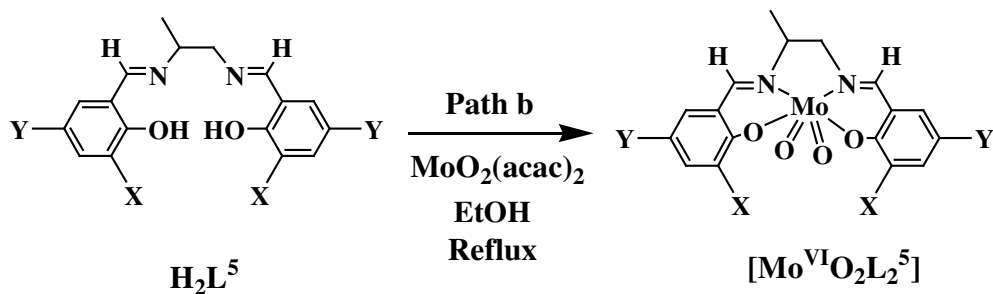
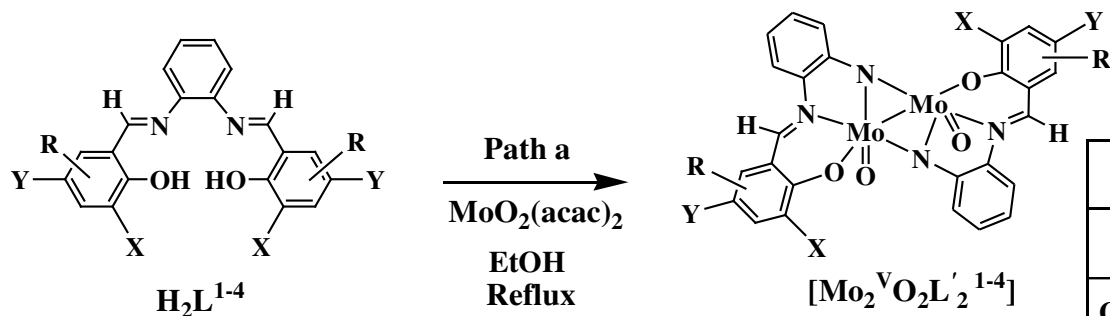
# Mono- and Dimeric Oxidomolybdenum(V and VI) Complexes, Cytotoxicity, DNA Interaction Studies: Unprecedented Mo Assisted C=N Bond Cleavage of Salophen Ligands



X	Y	R	Ligand	Rearranged Ligand	Complex
H	H	--	$H_2L^1$	$H_3L'^1$	$[Mo_2^V O_2 L_2'^1]$ (1)
OMe	H	--	$H_2L^2$	$H_3L'^2$	$[Mo_2^V O_2 L_2'^2]$ (2)
H	Br	--	$H_2L^3$	$H_3L'^3$	$[Mo_2^V O_2 L_2'^3]$ (3)
--	--	Ph	$H_2L^4$	$H_3L'^4$	$[Mo_2^V O_2 L_2'^4]$ (4)
OMe	H	--	$H_2L^5$	--	$[Mo^{VI} O_2 L_2^5]$ (5)

*R. Dinda et al., Inorg. Chem. 2017, 56, 11190*

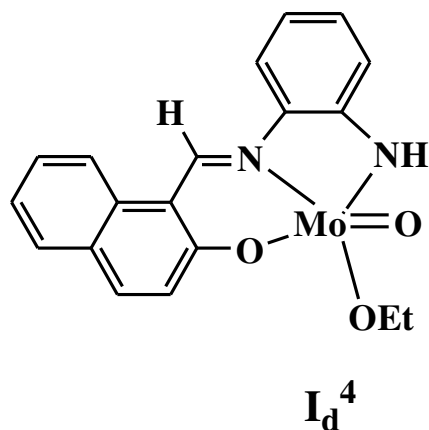
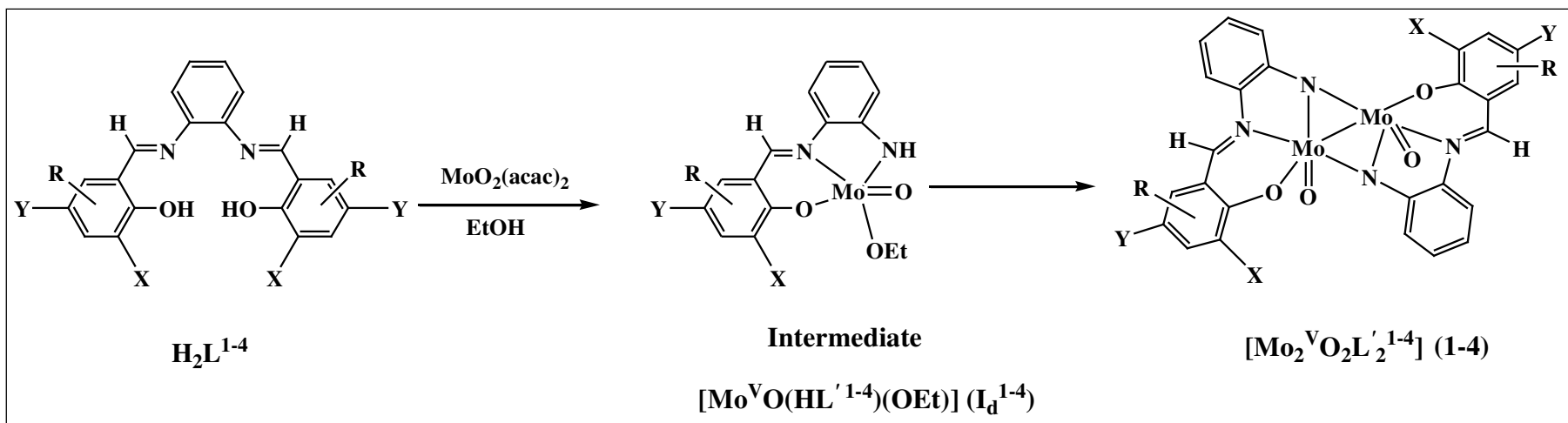
# Mono- and Dimeric Oxidomolybdenum(V and VI) Complexes, Cytotoxicity, DNA Interaction Studies: Unprecedented Mo Assisted C=N Bond Cleavage of Salophen Ligands



X	Y	R	Ligand	Rearranged Ligand	Complex
H	H	--	$\text{H}_2\text{L}^1$	$\text{H}_3\text{L}'^1$	$[\text{Mo}_2^{\text{V}}\text{O}_2\text{L}'_2{}^1]$ (1)
OMe	H	--	$\text{H}_2\text{L}^2$	$\text{H}_3\text{L}'^2$	$[\text{Mo}_2^{\text{V}}\text{O}_2\text{L}'_2{}^2]$ (2)
H	Br	--	$\text{H}_2\text{L}^3$	$\text{H}_3\text{L}'^3$	$[\text{Mo}_2^{\text{V}}\text{O}_2\text{L}'_2{}^3]$ (3)
--	--	Ph	$\text{H}_2\text{L}^4$	$\text{H}_3\text{L}'^4$	$[\text{Mo}_2^{\text{V}}\text{O}_2\text{L}'_2{}^4]$ (4)
OMe	H	--	$\text{H}_2\text{L}^5$	--	$[\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2{}^5]$ (5)

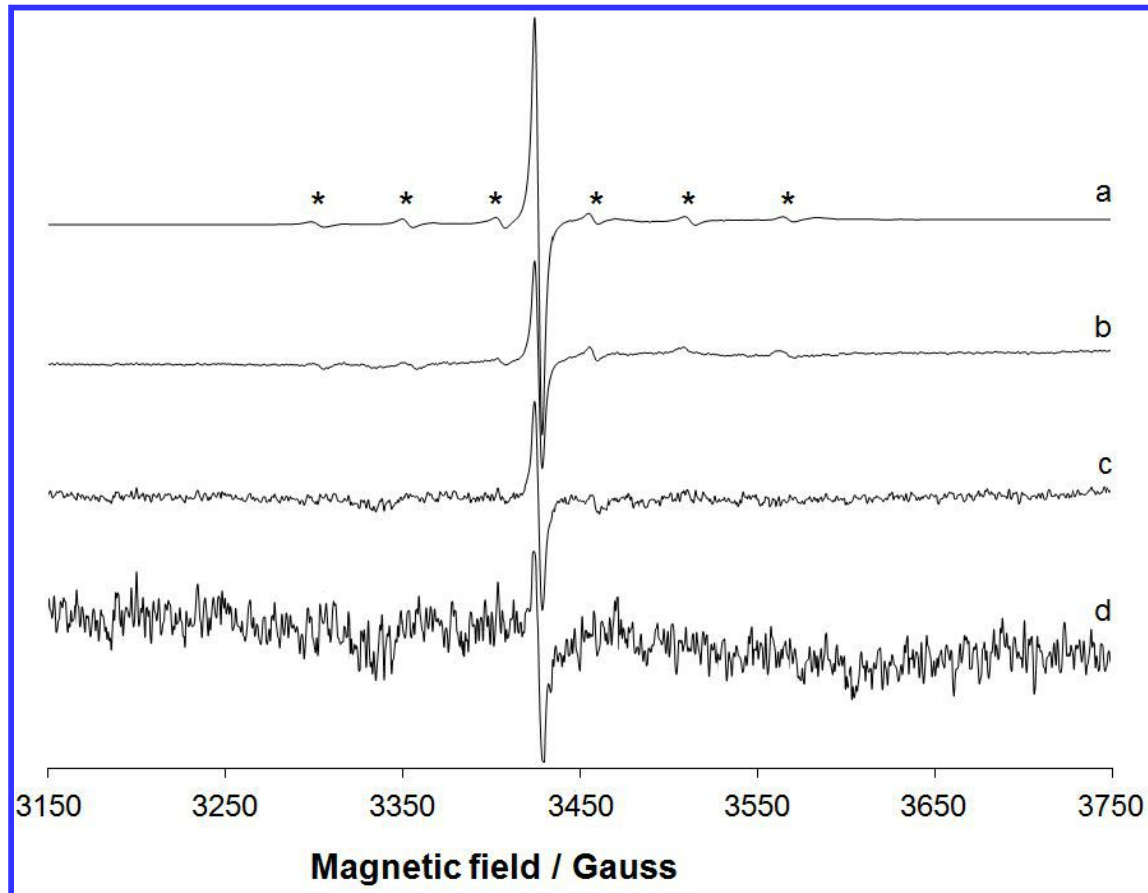
*R. Dinda et al., Inorg. Chem. 2017, 56, 11190*

# Mono- and Dimeric Oxidomolybdenum(V and VI) Complexes, Cytotoxicity, DNA Interaction Studies: Unprecedented Mo Assisted C=N Bond Cleavage of Salophen Ligands



*R. Dinda et al., Inorg. Chem. 2017, 56, 11190*

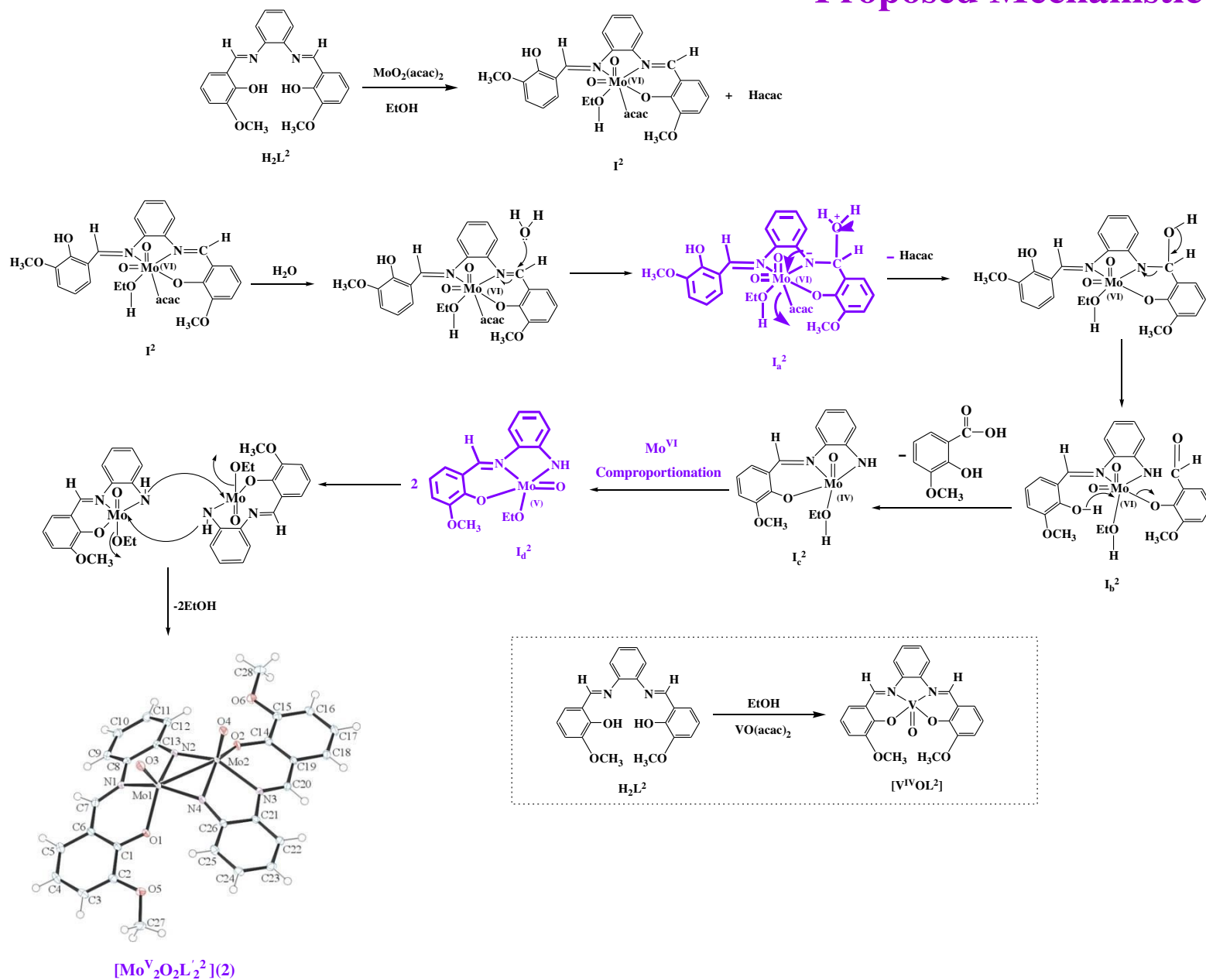
## EPR of $[\text{Mo}^{\text{V}}\text{O}(\text{HL}'^{1-4})(\text{OEt})] (\text{I}_d^4)$

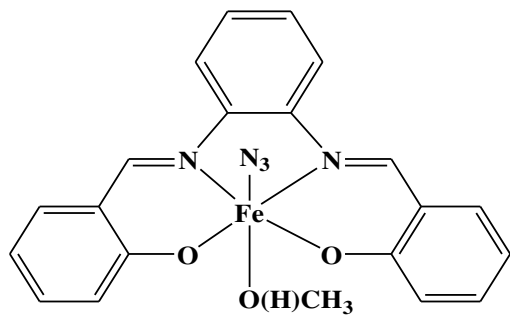


EPR spectra recorded at 298 K as function of the time on  $\text{I}_d^4$  dissolved in a degassed DMSO solution: (a)  $t = 7$  min; (b)  $t = 14$  min; (c)  $t = 20$  min; (d)  $t = 26$  min. With the asterisks the six hyperfine lines due to the coupling between the unpaired electron with  $^{95}\text{Mo}$  and  $^{97}\text{Mo}$  nuclei are indicated.

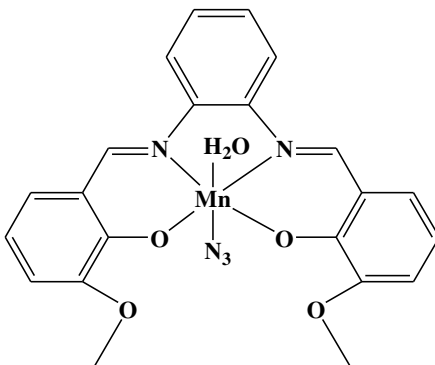


# Proposed Mechanistic pathway

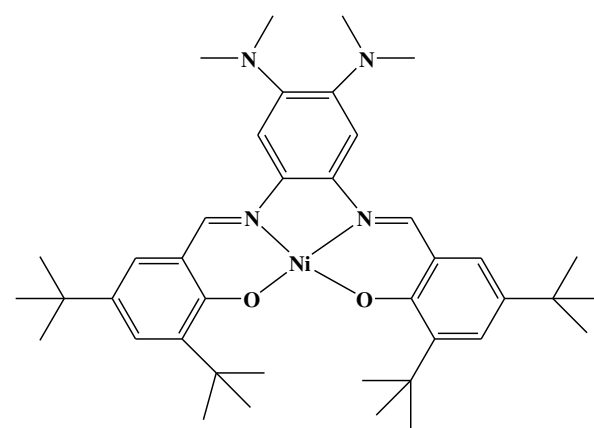




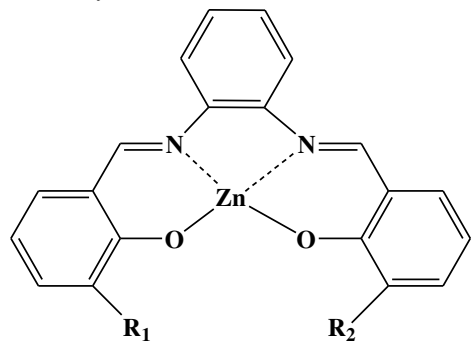
*Polyhedron* **2012**, *48*, 189



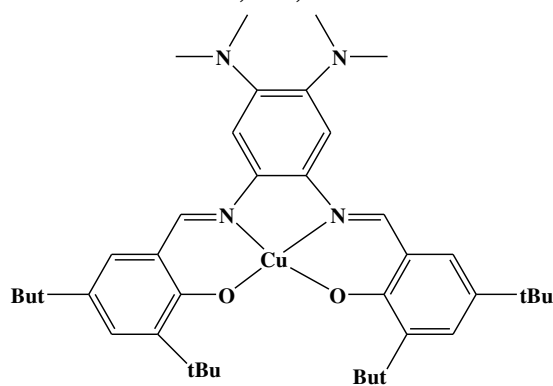
*Dalton Trans.* **2011**, *40*, 7916



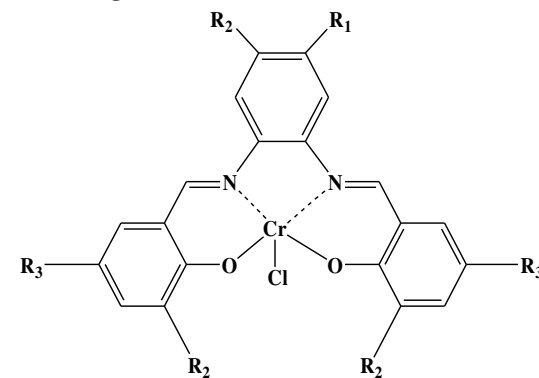
*Inorg. Chem.* **2012**, *51*, 12796



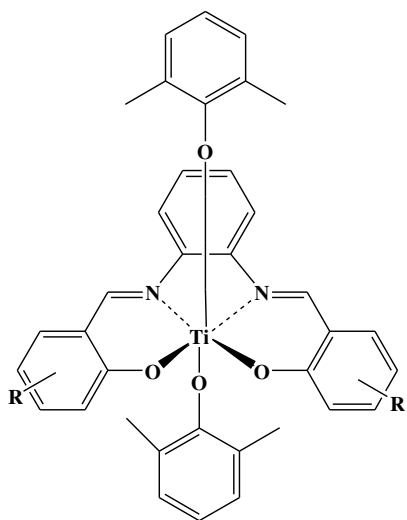
*Inorg. Chem.* **2007**, *46*, 7265



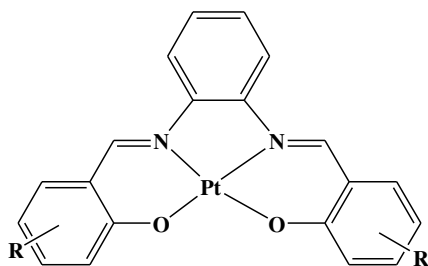
*Inorg. Chem.* **2015**, *54*, 9013



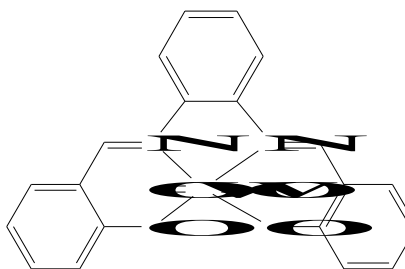
*ACS Catal.* **2016**, *6*, 5012



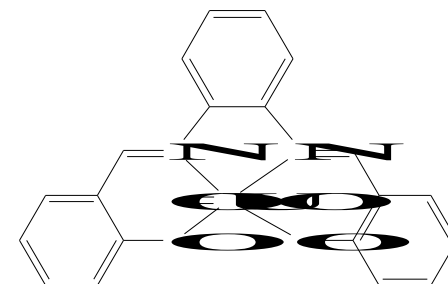
*Inorg. Chem.* **2011**, *50*, 7946



*ChemMedChem.* **2014**, *9*, 1176

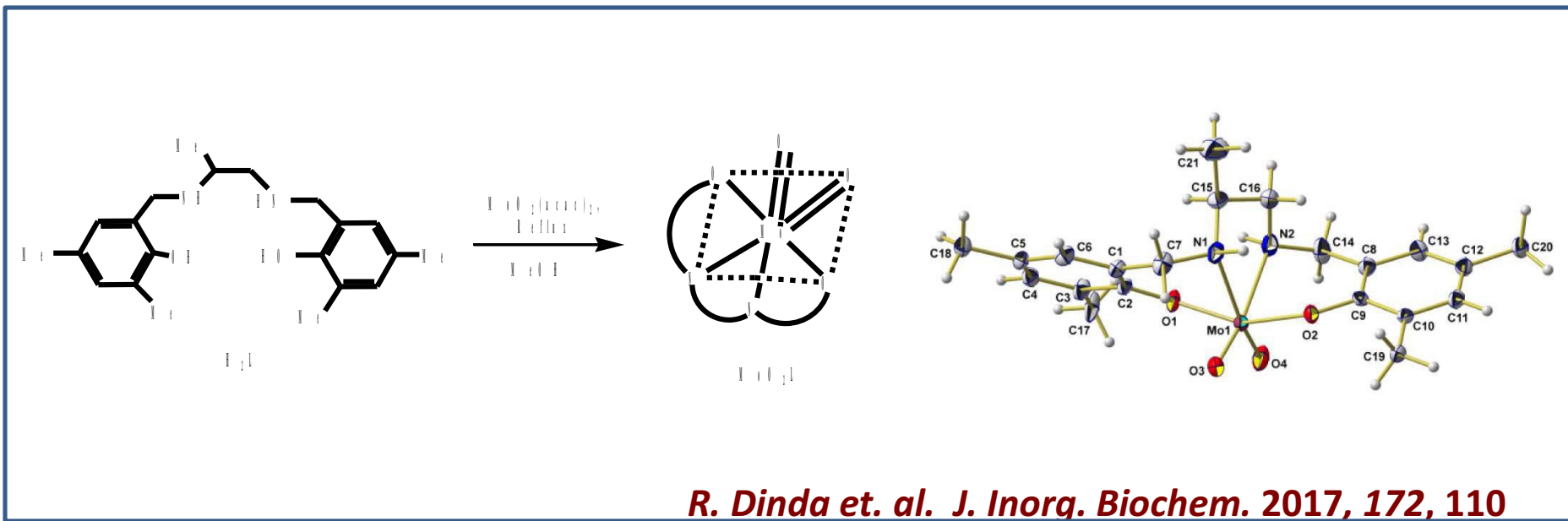
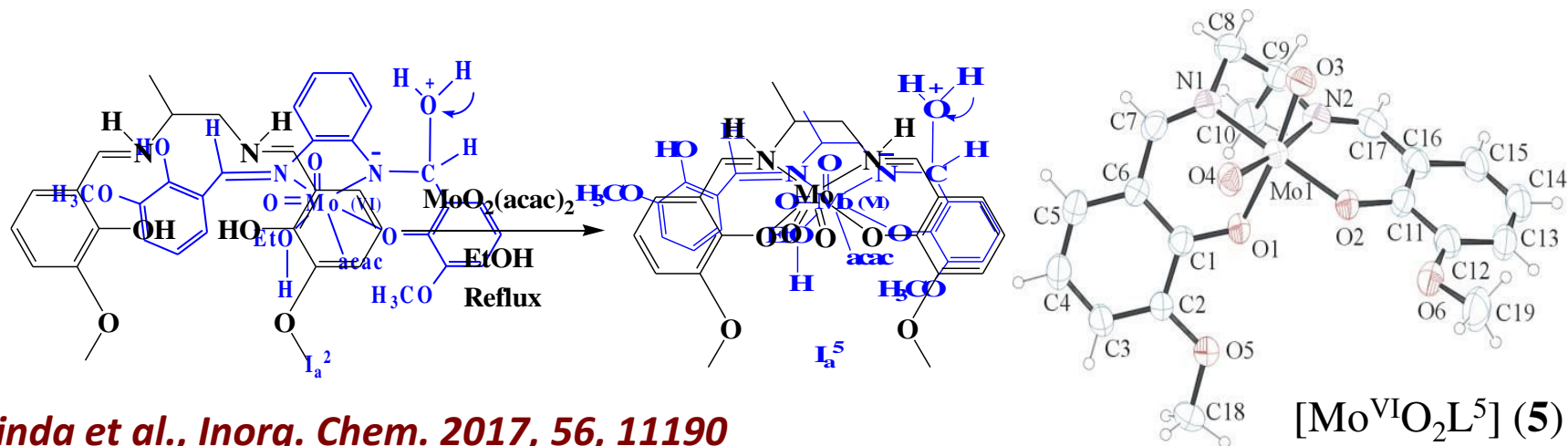


*Polyhedron*,  
**1991**, *8*, 819



*Polyhedron*, **1991**, *8*, 819

# Mono- and Dimeric Oxidomolybdenum(V and VI) Complexes, Cytotoxicity, DNA Interaction Studies: Unprecedented Mo Assisted C=N Bond Cleavage of Salophen Ligands



# Conclusions

- ❖ Some novel dioxidomolybdenum(V and VI) complexes containing salen type ligands have been synthesized and successfully characterized. The Molybdenum metal mediated C=N bond cleavage is highly specific and depends on the ligand structure. It has been validated that reactions using other transition metal complexes as a metal precursor do not initiate this type of ligand rearrangement.
- ❖ Non-oxido vanadium(IV) complexes reported here have been fully characterized by IR, UV-visible, ESI-MS, cyclic voltammetry and by single crystal X-Ray crystallography.
- ❖ The unique solution behavior of oxido alkoxidovanadium(V) complexes has been nicely explored.
- ❖ Electrogenerated oxidovanadium(IV) and mixed-valence divanadium(IV,V) complexes were successfully detected by chrono-coulometric, EPR and theoretical studies.