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# Molybdenum Schiff Base Complexes: Synthesis, Structural Analysis, and Catalytic Performance in Benzyl Alcohol Oxidation

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## INTRODUCTION & AIM

Molybdenum Schiff base complexes have emerged as highly efficient and versatile catalysts in modern inorganic and organometallic chemistry.[1] These complexes are formed through the coordination of molybdenum with Schiff bases-ligands derived from the condensation of primary amines and aldehydes or ketones.[2] The structural tunability, thermal stability, and redox properties of molybdenum centers make these complexes especially suitable for catalytic applications, particularly in oxidation reactions.

One of the key applications of molybdenum Schiff base complexes is in the selective oxidation of benzyl alcohol to benzaldehyde, a reaction of significant industrial importance.[3] Benzaldehyde is a valuable intermediate in the synthesis of dyes, perfumes, pharmaceuticals, and agrochemicals.[4] Traditionally, this transformation has relied on harsh oxidants like chromates or permanganates, or on benzyl halide derivatives such as benzyl chloride or benzyl bromide, which not only produce harmful byproducts but also pose environmental and safety concerns.[4]

In contrast, molybdenum Schiff base catalysts offer a greener and more sustainable alternative, often operating under milder conditions and using eco-friendly oxidants. These systems typically show high selectivity, minimizing over-oxidation to benzoic acid, and are often recyclable, aligning with the principles of green chemistry.[5]

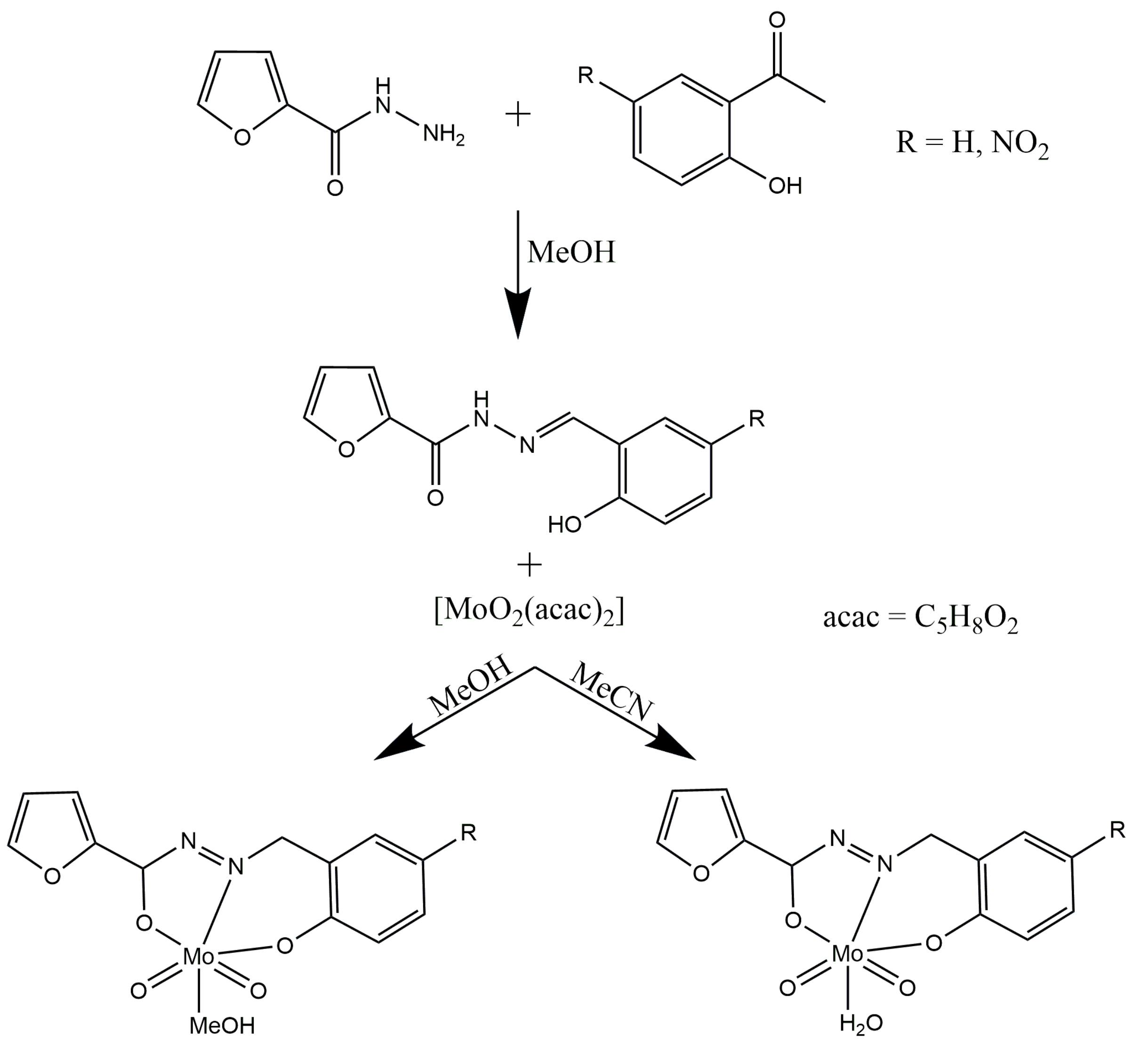
## METHOD

The ligand was synthesized via the reaction of 2-furoic hydrazide with either salicylaldehyde or 2-hydroxy-5-nitrobenzaldehyde. The resulting ligand ($H_2L^1$ or $H_2L^2$) coordinated with $[MoO_2(acac)_2]$ in methanol to form mononuclear complexes of the type $[MoO_2(L^1 \text{ or } L^2)(MeOH)]$. When the reaction was carried out in acetonitrile (MeCN), the corresponding mononuclear complexes $[Mo_2(L^1 \text{ or } L^2)(H_2O)]$ were obtained instead.

The synthesized complexes were characterized using thermogravimetric analysis (TGA), infrared attenuated total reflectance spectroscopy (IR-ATR), and single-crystal X-ray diffraction (SCXRD).

The catalytic activity of the complexes was investigated in the oxidation of benzyl alcohol using *tert*-butyl hydroperoxide (TBHP) as the oxidant in an aqueous medium. Different amounts of oxidant were tested to evaluate their effect on the conversion of benzyl alcohol and the selectivity towards benzaldehyde. The reaction was monitored over a period of five hours using an Agilent 8860 gas chromatograph (GC).

## RESULTS & DISCUSSION



**Scheme 1.** Synthetic route for the preparation of the ligands and their corresponding complexes.

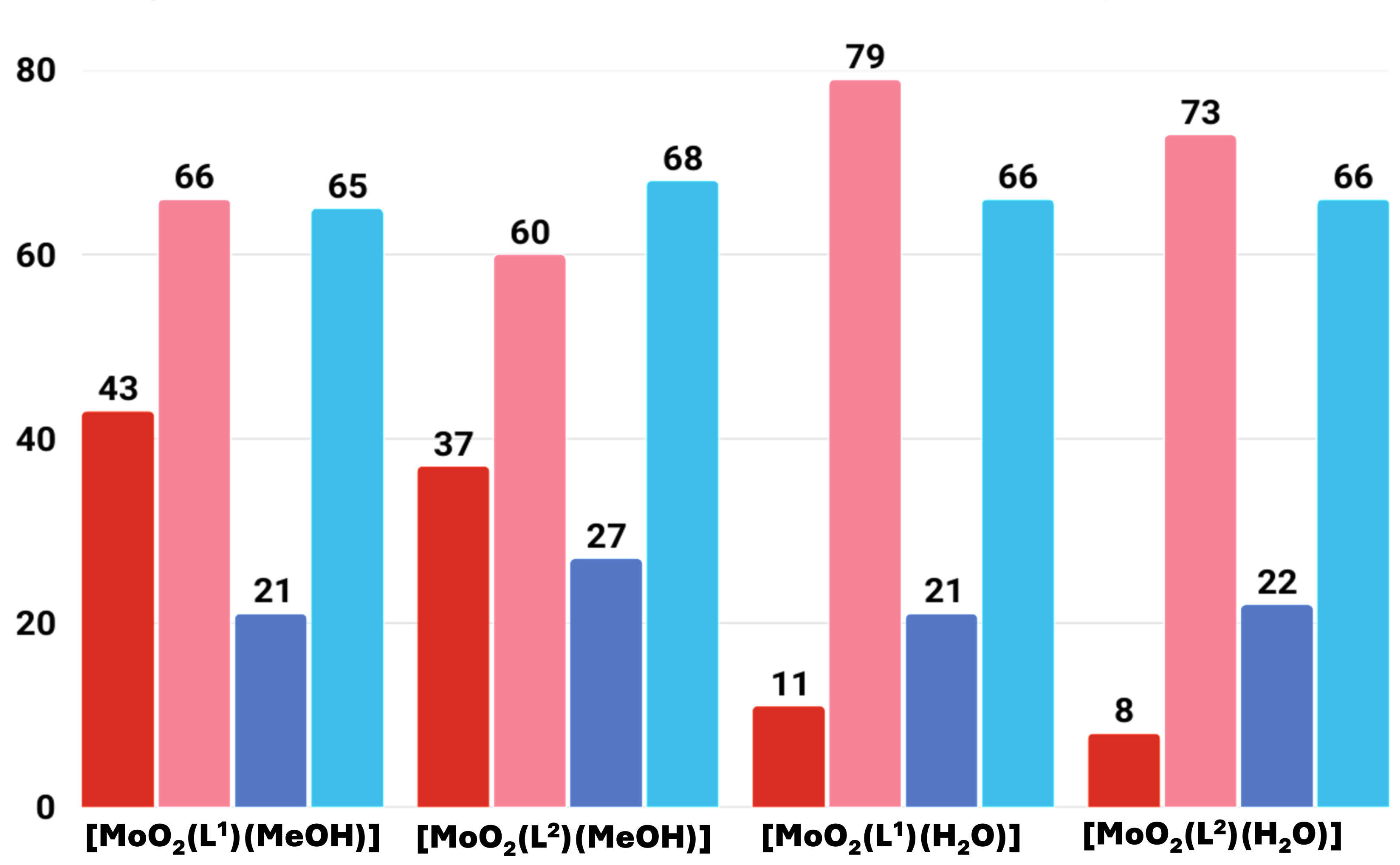


**Figure 1.** The catalytic activity of the synthesized molybdenum complexes was evaluated in the oxidation of benzyl alcohol using different molar equivalents of TBHP in an aqueous medium. **Reaction conditions:** Catalyst (0.1 mmol), aqueous TBHP (40 mmol), benzyl alcohol (20 mmol), 80 °C, 5 h.

## CONCLUSION

The synthesis of both ligands ($H_2L^1$ and $H_2L^2$) was successfully achieved, followed by coordination to a molybdenum center in MeOH, resulting in the formation of two mononuclear complexes of the type $[MoO_2(L^1 \text{ or } L^2)(MeOH)]$, where MeOH occupies the sixth coordination site. When the reaction was carried out in MeCN, analogous mononuclear complexes were obtained with water occupying the sixth coordination position, yielding $[Mo_2(L^1 \text{ or } L^2)(H_2O)]$.

Variation in the oxidant-to-substrate ratio significantly influenced the oxidation of benzyl alcohol and the selectivity toward benzaldehyde. For the MeOH-coordinated complexes, using a 2:1 oxidant-to-substrate ratio led to a 10-20% increase in conversion, while selectivity toward benzaldehyde remained largely unchanged. In contrast, the $H_2O$-coordinated complexes showed a ~10% increase in conversion with a 4:1 oxidant-to-substrate ratio, accompanied by a ~10% increase in selectivity towards.

## FUTURE WORK / REFERENCES

Future investigations will focus on evaluating the catalytic performance of molybdenum complexes using various oxidants, such as hydrogen peroxide. The influence of reaction temperature on the conversion of benzyl alcohol and the selectivity toward benzaldehyde will also be systematically studied.

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