

“Studies of Some Organic Oxidation Reactions in Homogeneous Phase Using Some Well Characterised Cobalt Complexes as Catalysts”

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Abstract :

Transition metal cobalt and its complexes with different ligands such as acetate, fumarate, isonicotinate, etc. have been used for different organic transformations which have great importance for the production of different value added products like oxidative cleavage of $>C=N-$ to corresponding carbonyls, conversion of amino group to nitro group, oxidation of benzyl halides to carbonyl, etc. Literature reveals that cobalt complexes with pyridine or substituted pyridine ligands have the excellent catalytic activity towards aerobic oxidation.

The pyridine or substituted pyridine complexes can be synthesized and the synthesized materials can be characterized by uv – vis, IR spectroscopy, XRD, TGA, etc. The aerobic oxidation of benzyl halides, conversion of amino acids, oxidative cleavage of $>C=N-$ can be done by the synthesized materials obeying green chemistry protocol.

Keywords : Cobalt complex, aerobic oxidation, oxidative cleavage, green chemistry.

1. Introduction

Transition metal cobalt has received considerable attention as a catalyst for numerous chemical and biochemical reactions. The presence of vacant d orbital in its valance shell makes cobalt a suitable candidate for thousands of organic transformations under both homogeneous and heterogeneous conditions. Not only elemental cobalt but also its complexes with a variety of ligands have traditionally been explored as catalysts for diverse organic transformations, oxidation of organic molecules are not exception. Most commonly used ligands include acetate, fumarate, isonicotinate and nitrogen containing heterocyclic ligands etc. Since, both the physical and chemical properties of cobalt complexes are largely determined by their structures, inorganic scientists always focus on synthesising complexes with different structures using a variety of ligands. In the recent times, tetrameric cobalt clusters possessing cubane and dimeric cubane geometries have been proven to be of paramount significance because of their structural motifs¹, unusual magnetic behaviour¹, and interesting catalytic properties.²³ The ability of the ligand system RCO_2^-/L ($L = N$ - and/or O-donor ligands) to assemble oligonuclear metal clusters makes it possible to form various tetrameric cobalt

clusters containing the cubane as well defect dicubane geometries. Literature suggests that cobalt(III) cubane-like complexes of the type $\text{Co}_4\text{O}_4(\text{O}_2\text{CR})_4\text{L}_4$, where **R** is either a methyl or an aryl group and **L** is either pyridine or a substituted pyridine are excellent catalytic properties in the oxidation of various organic substrates such as alkyl aromatics, alcohols and terpenoids under a greener protocols.⁴⁻⁶ The nature of R and L present in the complexes greatly influence catalytic activity and selectivity of these cobalt complexes which has been reflected in catalytic oxidation of benzyl alcohols using TBHP as an oxidant under homogeneous condition. The following organic transformations have been considered to be of great importance for the productions of different fine chemicals and value-added products.

- Oxidative cleavage of $>\text{C}=\text{N}-$ to corresponding carbonyls
- Conversion of amino group to nitro group
- Oxidation of benzyl halides to carbonyl

2. Literature review

Owing to their catalytic importance in diversified fields, numerous methods have been developed for the preparation of cobalt complexes using different ligands. Olive-green cobalt(III) complexes having the general formula $\text{Co}_4\text{O}_4(\text{O}_2\text{CMe})_4\text{L}_4$ where $\text{L} = \text{py}$, 4-Mepy, 4-Etpy, and 4-CNpy were prepared by the H_2O_2 oxidation of a mixture of Co^{2+} , MeCO_2^- , and pyridine or 4-substituted pyridines in a 1:2:1 molar ratio in methanol.¹ Among these the pyridine containing complex was found to be excellent catalytic for the aerobic oxidation of neat ethylbenzene and p-xylene. Paine *et al.* reported the oxidative C-N bond cleavage of (2-Pyridylmethyl)amine-based tetradentate supporting ligands in ternary cobalt(II)-carboxylate complexes.² In one instance, three new cobalt(II) complexes $[\text{Co}(\mu_2-\text{L})]_3(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$, $[\text{Co}(\text{L})(\text{NO}_3)]$, and $\{[\text{Co}(\mu_2-\text{L})(\text{MeOH})](\text{BPh}_4)(\text{MeOH})\}_n$, are prepared where L stands for 2-(bis(pyridin-2-ylmethyl)amino)acetate.³ In another instance, Das *et al.* reported the preparation, structure and properties of three cobalt(II) fumarates, viz. $[\text{Co}(\text{fum})(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$, $[\text{Co}(\text{fum})(\text{py})_2(\text{H}_2\text{O})_2]_2$, and $[\text{Co}(\text{fum})(4\text{-CNpy})_2(\text{H}_2\text{O})_2]$ (fum=fumarate, py=pyridine, 4-CNpy=4-cyanopyridine).⁴ Gupta *et al.* reported the synthesis of two mixed-valent μ_3 -oxo-bridged trinuclear cobalt complexes and one μ_4 -oxo-bridged tetranuclear cobalt complex.⁵ These complexes were found to be very effective in catalyzing benzyl alcohol. Recently, aerobic oxidation reactivity of well-defined cobalt(II) and cobalt(III) aminophenol complexes was reported by a group. They demonstrated that both these complexes are competent of catalyzing aerobic cyclisation.⁶

3. Problem statement/hypothesis

Regeneration of carbonyl compounds from oxime and semicarbazones requires drastic conditions, rare and toxic reagents and sometimes, long reaction times. Thus, there is still a need for improved methods for regeneration of the carbonyl compounds from the semicarbazones. A mild method of deprotection using cheap and readily available reagents would thus be highly attractive.

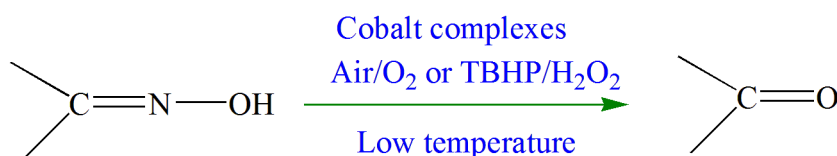
Thus, in our study, the some well characterized Co(III) complexes of the type $\text{Co}_4\text{O}_4(\text{O}_2\text{CMe})_4\text{L}_4$ where $\text{L} = \text{py}$, 4-Mepy, 4-Etpy, and 4-CNpy displaying an overall cubane-like geometry will be used as a catalysts for oxidation/deprotection of carbonyl group from corresponding oximes and semicarbazones. Other complexes of cobalt as well as selected complexes of copper will also be prepared for use as homogeneous catalysts/catalyst precursors. The work will also be extended for the oxidation of aromatic amines to corresponding nitro compounds. At the same time, other suitable complexes, *e.g.* those of cobalt and copper will also be included as part of the systematic studies to be undertaken during the course of these studies having importance from the points of view of organic as well as inorganic chemistry.

4. Objectives

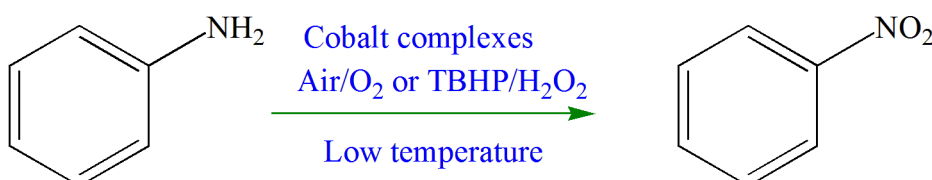
The main objectives of the present research proposal are as follows:

- ❖ Preparation of different cobalt complexes using some common ligands like pyridine, acetate, fumarate etc.
- ❖ Characterization of the complexes (to be prepared) with the help of different physical techniques such as single crystal XRD, UV–vis and IR spectroscopies.
- ❖ Study of thermal stability of the complexes by thermogravimetric analysis, magnetic behaviour by magnetic measurement instrument and electrical properties by cyclic voltammetry.
- ❖ Exploration of these complexes as catalysts in the following organic transformations under homogeneous conditions obeying the protocols of green chemistry:

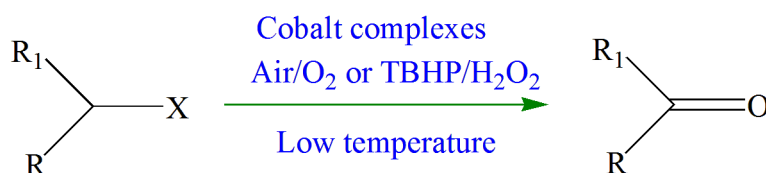
(i) Oxidative cleavage of $>\text{C}=\text{N}-$ to corresponding carbonyls



(ii) Conversion of amino group to nitro group



(iii) Oxidation of alcohols and benzyl halides to carbonyl compounds



where $\text{X} = \text{Cl, Br, OH}$
 $\text{R} = \text{alkyl, aryl}$
 $\text{R}_1 = \text{alkyl, aryl, H}$

5. Methodology

The present research work will be carried out in a step-wise manner and at each step proper methodology will be followed.

- Relevant literature survey using various search tools like Chemical Abstracts Services, Scopus, Web of Science, etc.
- Preparation of cobalt(III) and other transition metals complexes via reported procedures and self-developed procedures.
- Structural investigation of the complexes by single crystal XRD, spectroscopic and other analytical methods
- Oxidation of organic substrates using the metal complexes to be prepared as catalysts
- Exploration of various environmentally benign oxidants and mild reaction conditions
- Isolation and characterization of organic products using physical tools like NMR, GC-MS, GC
- Optimization of conditions

6. Probable outcome

If the proposed synthesis of metal complexes, as discussed in the objective section, can successfully be carried out, then there will likely be a number of new catalytic systems opened for many essentials organic transformations. These complexes (to be synthesized) will thoroughly be explored to obtain maximum conversion of the organic substrates and high selectivity for the desired products.

Most of the reactions mentioned in the objectives are usually carried out without the aid of catalysts. Using catalysts it is usually possible to (i) improve rates or reactions, (ii) improve product yields and selectivity and (iii) reduce energy requirement for the organic transformation under investigation. Thus there may be several Green Chemistry advantages to be accrued. Our work thus may be expected to several benefits to offer by way of developing new and improved methodologies for some important organic reactions. In addition, during the course of work new inorganic complexes are likely to be identified and depending on their properties it may become possible to expand the scope of the proposed study, e.g. by including new and important organic transformations for investigation under homogeneous / heterogeneous catalytic conditions.

7. References:

1. a) Winpenny , R. E. P. In *Comprehensive Coordination Chemistry*, McCleverty, J. A., Meyer, T. J. Eds; Pergamon Press; Oxford, U.K., **2004**, Vol. 7, Chapter 7.3, pp 125-175.
b) Winpenny , R. E. P., *Adv. Inorg. Chem.* **2001**, 52, 1-111.
c) Gatteschi, D., Scssoli, R., Corria, A. In *Comprehensive Coordination Chemistry*; McCleverty, Meyer, T.J. Eds; Pergamon Press Oxford, U.K., **2004**; Vol-7.13, pp 779-813.
2. a) Sumner, C.E , Jr., Morrell, K. A.; Howell, J.S. Little, J., *Inorg. Chem.* **2008**, 47, 2190-2195.
b) Lassahn, P.G; Timco G.A., Christian, P.; Janiac C., Winpenny, R. E. P, *J.Catal.* **2004**, 222, 260-267.
c) Carrel T. G.; Cohen S.; Dismukes , G. C. *J. Mol. Catal.A: Chem.* **2002**. 187, 3-15.
d) Chavan .S.A.; Srinivas . D., Ratnasamy, P. *J.Catal.* **2001**. 204, 409-419.
3. For reviews see
(a) Cady, C. W. ; Crabtree , R.H; Brudvig. G. W. *Coord. Chem. Rev.* **2008**, 252, 444-455.
b) Solomon, E.I; Sarrangi, R; Woertink, J. S., Augustine, A.J., Yoon, J., Ghosh, S. *Acc. Chem. Res.* **2007**, 40, 581.
c) Mukhopadhyay, S; Mandal, S. K. Bhaduri, S. Armstrong, W. H. *Chem. Rev.* **2004**, 104, 3981, 4026.
d) Lippard, S. J ;Tshuba, E. J. Y. *Chem. Rev.* **2004**, 104, 987, 1012.
e) Que, L., Jr. *J. Chem.Soc.,Dalton Trans.* **1997**, 3933-3940.
f) Holm, R. H., Kennepohl, P. Solomon, F. I. *Chem. Rev.*, **1996**, 96, 2239-2314.
g) Wallar, B. J., Lipscomb, J. D. *Chem. Rev.* **1996**, 96, 2625-2657.
4. Chakravarty, R.; Bora, S. J.; Das, B. K. *Inorg. Chem.* **2007**, 46, 9450-9462.

5. Sarmah, P.; Chakravarty, R.; Phukan, P.; Das, B. K. *J. Mol. Catal. A: Chem.* **2007**, 268, 36-44.
6. a) Chakravarty, R.; Das, L. K.; Clark, J. H. *Green Chem.* **2007**, 9, 845-848.
 b) Chakravarty, R.; Kalita, D.; Das, B. K. *Polyhedron* **2007**, 26, 1239-1244.
 c) Chakravarty, R.; Das, B. K. *J. Mol. Catal. A: Chem.*, **2004**, 223, 39-44.
7. Liu Jiaqi, C. Shanen, Lorraine, S. Brian, Dolinar, and M. Jessica, Hoover. *Inorg. Chem.*, 2022, 61,16, 6008-6016.
8. Kempe Rhett, DeibiNicklas. *J.Am. Chem. Soc.*, 2016, 138, 34, 10786-10789.
9. Ahmad Shaabani, Mostafa M. Amini, MehrdadShadi, FreshtehBarhi, MasoumehKarimiAlavijeh, Hassan Farhid, Journal of the Taiwan Institute of Chemical Engineers,2021, 211-222
10. Rajesh Chakrabarty, Sanchay J. Bora, and Birinchi K. Das, Inorganic Chemistry, Vol. 46, No. 22, 2007
11. BiswarupChakraborty,□ Ivy Ghosh,□ Rahul Dev Jana, and TapanKanti Paine, **Dalton Trans.**, 2020,**49**, 3463-3472
12. V P Daya, RajamonyJagan and Dillip Kumar Chand, *J. Chem. Sci.* (2022) 134:54
13. S. J. Borah, B. K. Das, Synthesis and properties of a few 1-*D* cobaltous fumarates, *J. Solid State Chem.* 192 (2012) 93-101.
14. Dr. Deepak Bansal, Samanta Yadav, Prof. Dr. Rajeev Gupta, 2022, <https://doi.org/10.1002/ejic.202200601>
15. Jiaqi Liu, Shannen C. Lorraine, Brian S. Dolinar, and Jessica M. Hoover, *Inorg. Chem.* 2022, 61, 16, 6008–6016

