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Substituted Macrocylces good Catalysts for Oxidations of Hydroquinones and 1, 2 Diphenylhydrazine

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ABSTRACT: Novel Co (II), Ni (II) and Cu (II) Complexes are synthesized with catalytic oxidation of Hydroquinones and 1, 2-Diphenylhydrazine. Macrocyclic ligands and their complexes were characterized by elemental analysis, molar conductivity measurements, UV/Vis, IR, NMR, and catalytic oxidation. On the basis of IR, and spectral studies, an octahedral geometry has been assigned for the Co (II), Ni (II) and Cu (II) Complexes. Further the complexes have been subjected to laundry application, chemical industry, and biological interest. The results suggest quasireversible behavior of most of the redox processes.

Keywords: Macrocyclic Complexes, Spectral Studies, Catalytic Oxidation

INTRODUCTION

A large amount of interest in the field of macrocyclic Chemistry of Cobalt, Copper and Nickel has arisen during past decades because of their multifarious role in Chemistry and Industry. The study of the macrocyclic complexes has also been received attention for synthetic catalysts which increased the oxidizing ability of H_2O_2. The use of H_2O_2 along with the synthetic macrocycles (termed as activators developed by Torrence Collins of carnegie Mellon University) are being used as catalyst [1-15]. The used of H_2O_2 synthetic macrocyclic activators has the potential to replace the chlorine containing complexes that are currently in use in paper delignification and bleaching processes. The H_2O_2 bleaching produces only environmentally benign byproduct such as H_2O and O_2, thus eliminating the chlorinated organic byproducts which are associated with chlorine delignification and bleaching processes. The macrocyclic activators have made the use of H_2O_2 as a bleaching agent more efficient as the macrocyclic complexes catalyse the reaction to promote the dissociation of H_2O_2 into hydroxyl radicals which are involved in the oxidation or bleaching of the remaining lignin, thus making H_2O_2 a more powerful oxidizing agent. The macrocyclic activators allows H_2O_2 to break down more lignin in a shorter amount of time of 1 hour in comparison to 6 hour as well as these retain high selectivity towards oxidizing lignin over Cellulose. Additionally in the presence of macrocyclic complexes for bleaching process by H_2O_2 lower reaction temperatures can be used as 50°C instead of 120°C [16-32].

In addition to catalyzing bleaching or delignification reaction macrocyclic activators can also be used in laundry application because they can keep dyes from transferring between fabrics and can activate the peroxides found in many bleaches. As the problem of dye transfer is in past flowing the adsorption of reduced-water washing machines, the use of macrocyclic activators in laundry applications could also result in reduced use of water supplies. Although the extensive investigations of oxygenation reactions have also been carried out in the presence of Cobaloxime because of biological interest [33-45].

EXPERIMENTAL

Materials

All the chemical and solvent used in this study were of Anal R grade. 1, 2-diphenylhydrazine, Catechol, Resorcinol and Triphenylphasphine procured from Sigma-Aldrich and Fluka. All Metal salts were purchased from E. Merck and used received. All solvent used were of standard/spectroscopic grade.

Isolation complexes

All the complexes were synthesized by template methods. The synthesis and catalytic oxidation of Hydroquinones and 1, 2-Diphenylhydrazine in the of synthesized macrocyclic complexes of Co (II), Ni (II) and Cu (II) have presence been carried out [46-51]. The axial legation constants and thermodynamic parameters for these types of macrocyclic complexes have already been reported [52-55]. Me_6 dibenzotetraazatetradecatetraene -N_4 Complexes of Co (II), Ni (II) and Cu (II) were used for catalytic oxidation of Hydroquinones and 1,2-Diphenylhydrazine. The oxidation was carried out in atmosphere of air in $CHC1_3$ solvent.

It has also been observed with substituted macrocyclic complex of Co (II) that substituent groups affect the rate of oxidation due to steric and/or electronic effects. Macrocyclic complexes Ni (II) and Cu (II) did not work as good catalyst for the oxidation of Hydroquinones. Accordingly, the results of an investigation of catalytic oxidation of some substrates using Co (II) macrocyclic complex (A) have been taken into account for these studies [56-60].

Proton NMR measurements were carried out in $CdCl_3$ at room temperature with (Brucker) model AC-300 spectrometer operating in the fourier transform mode. Chemical shifts were reported in ppm relative to TMS as an internal reference standard. Ultraviolet and visible spectra covering the 240-500 nm range were measured with a Shimadzu UV-VIS double beam spectrophotometer in $CHCl_3$ at room temperature.

Methyl substituted Me_6 Dibenzo [1, 4, 8, 11] tetraazacyclotetradecatetraene $-N_4$ Macrocyclic Complexes of Co (II) (A), Ni (II) (B) and Cu (II) (C) respectively were prepare according to literature method.

The autoxidation studies of hydroquinones and 1, 2-diphenylhydrazine in the presence macrocyclic complexes Co (II), Ni (II) and Cu (II) were carried out. The complex (0.25 mmol) was added to a solution of the hydroquinone (03 mmol) in chloroform (200 ml). Air was bubbled into the resulting mixture for 8 hrs with continuous stirring.

The crude reaction mixture was filtered and the filtrate was concentrated on rotavap and thus concentrate was applied on the top of a chromatographic silica gel (60-80 mesh) column and eluted with dichloromethane. The solid material, which was recovered by evaporating the eluate to dryness on rotavap and the recrystallized with petroleum ether to give the pure 1, 4-benzoquinone yellow needles. The data for all compounds are listed in Table 1.

Table 1: Oxidation products for a various of Hydroquinones in $CHCl_3$.

Substituent Group	**Yield (%) of 1,4,-benzoquinones**	**IR (cm^{-1}) ν(C=O)**	**1HNMR(ppm) aromatic**	**Melting point (°C) -CH_3**
H	46	1665	6.77(s)	114-116
2-CH_3	60	1656	6.62(q), 6.75(m), 2.11(d) (J=1.2Hz) (J=1.2Hz)	65-69
2-Cl	50	1660	6.85(d), 6.85(s), 7.00(d) (J=1.4Hz) (J=1.4Hz)	52-56
2-$C(CH_3)_3$	75	1655	6.62(d), 6.63(s), 6.66(d), 1.29(s) (J=1.0Hz) (J=1.0Hz)	55-58
2,3,5-$C(CH_3)_3$	70	1645	6.56(q), 2.02(s), 2.04(d) (J=1.8Hz) (J=1.8Hz) (J=1.8Hz)	32

The Autoxidation of Hydroquinone in the Presence of Cobalt (II) Macrocyclic Complex (A).

The oxidation reaction of Cobalt macrocyclic complex (A) (0.25mmol), hydroquinone (3.0 rnmol) and base (5.0 mmol), following the above procedure, gave the pure 1, 4-benzoquinone with the yield as shown in Table 2. It has been observed that the oxidation reaction of macrocyclic complex Co (II) (0.25 mmol) and substrates (catechol, resorcinol etc.) (2.0mmol) gave no product as shown in Table 4. Procedure for the autoxidation of 1, 2-diphenylhydrazine in the presence of Co (II) macrocyclic complex (A). The oxidation reaction of Macrocycle (A) (0.25 mmol) and 1, 2-diphenylhydrazine (2.70 mmol), gave pure azobenzene as reddish orange needles; yield (70%), and 452 nm. IR (KRr disk): 1585 Cm^{-1} (N = N str.). M.P. 65-69 °C UV 235 nm, 320 nm.

Table 2: Catalytic oxidation for hydroquinone in $CHCl_3$ in the presence of bases.

Catalyst (m. mol)	**Base (m. mol)**	**Yield % of 1,4-benzoquinone**
0.25	pyridine	36
0.25	pyridine	35
0.25	4-aminopyridine	10
0.25	No base	44

RESULTS AND DISCUSSION

In the presence of air, the cobalt (II) macrocyclic complex (A) catalyzes the oxidation of a variety of hydroquinones and 1, 2-diphenylhydrazine, added in a 10 fold over the catalyst. The oxidation reactions shown in scheme-1.

The yields of the oxidation products in equation (I) and (II) are in good agreement given in Tables 1 and 3. The catalytic effect of macrocycle (A) has been observed by the yields of the products, which has been compared with the blank experiments give in Table 4. 2, 3, 5-Trimethyl-hydroquinone was oxidized to 2, 3, 5-trimemyl-1, 4-benzoquinone. On the other hand, the yields of 1, 4-benzoquinone and 2-chloro-l, 4-benzoquinone were low ~40% and ~50% respectively. It seems that, with substituted Co (II) macrocyclic Complex (A), and substituent groups in the aromatic ring affect the rate of oxidation due to steric and/or electronic effects. Rest of the complexes Ni (II) (B) and Cu (II) (C) showed no catalytic effect for the oxidation of hydroquinone Table 4. The oxidation of hydroquinone catalyzed by Co (II) macrocyclic Complex (A) did not work in the presence under an atmosphere of nitrogen. However, this system could not catalyze the oxidation of catechol, resorcinol and triphenylphosphine under similar conditions Table 3. Me_6 Dibenzo [1, 4, 8, 11] tetraazacyclotetradecatetraene $-N_4$ Macrocyclic Complexes of Co (II) (A), Ni (II) (B) and Cu (II) (C) respectively. It has been observed that the catalytic activity of Co (II) macrocyclic complex (A) depends upon the properties of the added axial base. The yield of the oxidation product was low on addition of 4-aminopyridine as an axial base. It seems that 4-aminopyridine coordinates with cobalt atom at the axial site in Co (II) macrocyclic complex (A) and hinders the coordination of the substrates to the cobalt atom.

Scheme I

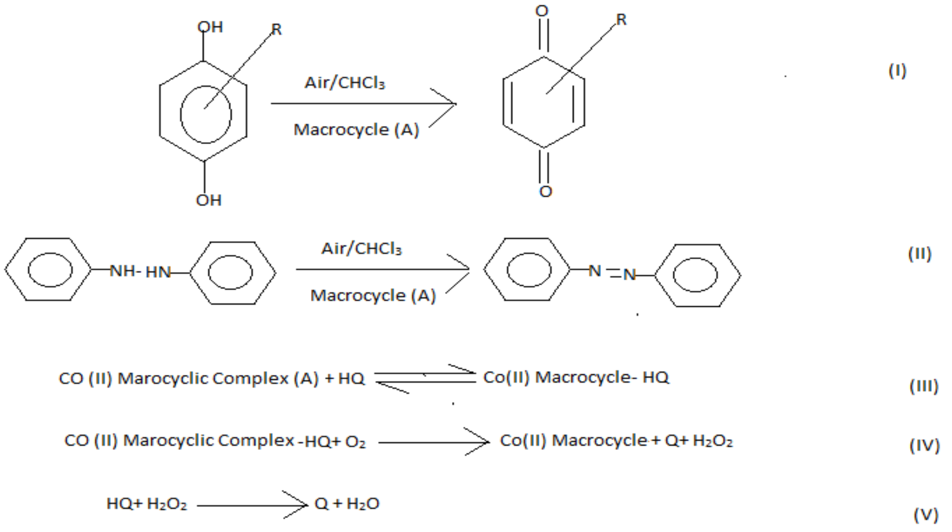


Table 3: Catalytic Oxidation for Various Substrates in $CHCl_3$.

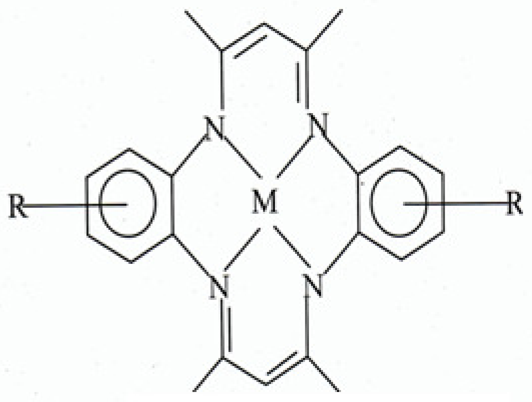
Substrate	Product	(Yield %)
1,2-Diphynylhydrazine	azobenzene	(75)
Catechol	1,2-benzoquinone	(0)
Resorcinol	………………..	(0)
Triphenylphosphine	Triphenylphosphine oxide	(0)

Table 4: Catalytic Oxidation for Various Substrates in $CHCl_3$.

Catalyst	Used gas	Yield (%) of 1,4-benzoquinone
Co (II) (A)	air	44
Ni (II) (B)	air	0
Cu (II) (C)	air	0
No catalyst added	air	0

It may be concluded that, the catalytic oxidations involve dehydrogenation for a variety of hydroquinones and 1, 2-diphenylhydrazine. However the dehydrogenation of hydroquinone (HQ) can be considered by stepwise H-atom transfer to O_2 and in the formation of 1,4-benzoquinon (Q) and hydrogen peroxide (H_2O_2) take place.

Similarly the oxidation mechanism of 1, 2-diphenylhydrazine in $CHCl_3$ can be shown. Thus the cobalt (II) macrocycle complex (A) function as more efficient catalyst for the oxidation of a variety of Hydroquinones and 1, 2-diphenylhydrazine. The substituent groups on the aromatic ring of hydroquinones may also influence the rate of oxidation due to steric and/ or electronic effects. Thus it has been observed that the substituted macrocycle complex (A) is also behaving like unsubstituted macrocycle more effectively [61-64].



Where= CO(II) (A), Ni (II) (B), Cu(II) (C)

R = CH_3

CONCLUSION

The present study revealed an octahedral geometry around the Co(II), Ni(II)and Cu(II) complexes, a square planar for Ni(II) and a tetragonal for Cu(II) complexes , in which the ligand acts as tetradentate manner coordination through the nitrogen atoms of ν(C=N) group. The catalytic oxidations involve dehydrogenation for a variety of hydroquinones and 1, 2-diphenylhydrazine. However the dehydrogenation of hydroquinone (HQ) can be considered by stepwise H-atom transfer to O_2 and in the formation of 1,4-benzoquinon (Q) and hydrogen peroxide (H_2O_2). It has also been proposed that concentration plays a vital role in increasing the degree of inhibition; as the concentration increase, the activity increases.

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