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OXIDATION OF PHENOLS WITH MOLECULAR OXYGEN CATALYSED BY [N,N'-BIS(2'-PYRIDINECARBOXAMIDO)-1,2-BENZENE]COBALT(II),CHELATE*

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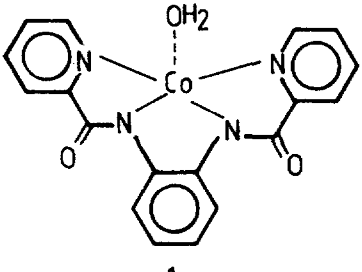
Abstract: A cobalt(II) bis-amide chelate, aqua[N,N'-bis(2'-pyridinecarboxamido)-1,2-benzene]cobalt(II), [Co(bpb)H_2O] selectively catalysed oxidation of substituted phenols with molecular oxygen to give corresponding 1,4-benzoquinones. Effect of the solvent on the reaction is studied.

A number of transition metal complexes are known to activate molecular oxygen by reversibly binding it to the metal centre[1,2]. Such oxygen carrier metal complexes are of interest as catalysts for oxidation of organic compounds, and as models for oxygenase enzymes[3,4]. Oxidation of hindered phenols using an oxygen carrier chelate and molecular oxygen gives corresponding quinones, coupled products, or polymer depending on the solvent and the reagents. Several workers have made investigations to increase the catalytic efficiency and selectivity of oxygen carrier complexes, towards the oxygenation of phenols, by modification of the ligand structure[5-7]. The majority of the reported oxygen carriers are complexes of cobalt(II) with Schiff base ligands[2]. This communication presents the first report on the catalytic activity of a bis-amide cobalt(II) chelate, aqua[N,N'-bis(2'-pyridinecarboxamido)-1,2-benzene]cobalt(II), [Co(bpb)H_2O][8] (1) as a catalyst for selective oxidation of phenols with molecular oxygen.



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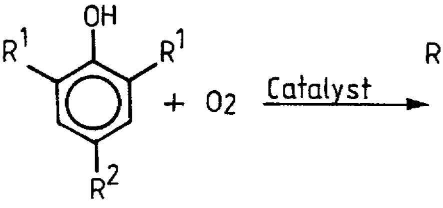
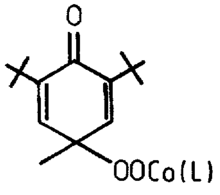
The chelate **1**, 0.15 mmol and a phenol (**2**), 3.0 mmol (substrate-catalyst mole ratio 20:1) in a solvent (10 ml) were stirred magnetically at room temperature under an atmosphere of molecular oxygen for 1 to 5 h. The progress of the reaction was monitored by TLC, and the products were isolated by column chromatography over silica gel. The results are shown in the Table 1.

Oxygenation of 2,6-di-tert-butylphenol (**2a**) and 2,6-dimethylphenol (**2b**) using **1** in CH_3CN gave corresponding 1,4-benzoquinones selectively in nearly quantitative yields in 2h. The absence of diphenoquinone, a radical coupling product, in the reaction shows the high selectivity of **1** as compared to many cobalt salen type complexes[1]. The formation of diphenoquinone in the oxygenation of phenols reflects the poor oxygen carrier ability of the metal chelate catalyst[7,9]. Similarly, oxygenation of 1,4-hydroquinone (**2c**) gave 1,4-benzoquinone. The formation of quinhydrone was not observed in this reaction. Oxygenation of 2,6-di-tert-butyl-4-methylphenol (**2d**) in CH_3CN using **1** gave a pale yellow precipitate of peroxy-p-quinalato-cobalt complex **4**[10] as the only product. Isolation of such a complex supports the intermediacy of $Co(L)\text{-}OO^{\bullet}$ in the reaction[11].



2 **3**



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a R^1 = t-Bu; R^2 = H
b R^1 = CH_3; R^2 = H
c R^1 = H; R^2 = OH
d R^1 = t-Bu; R^2 = CH_3

The catalytic activity of **1** was compared with that of a known oxygen carrier cobalt(II) chelate, CoSMDPT (5)[9,12] using **2a** as the substrate in CH_3CN (substrate-catalyst mole ratio 100:1). It was observed that, under identical conditions, **1** gave a higher turnover number (100) as compared to CoSMDPT (71), indicating the superiority of **1** over CoSMDPT (run 9 and 10).

Table 1. Oxygenation of 2 Catalysed by [Co(bpb)H_2O]

Run	Substrate (3.0 mmol)	Catalyst (0.15 mmol)	Solvent (10 ml)	Time (h)	Product(yield %)[a]
1	**2a**	**1**	CH_3CN	2	**3a** (96)
2	**2b**	**1**	CH_3CN	2	**3b**(94)
3	**2c**	**1**	CH_3CN	5	**3c**(63)
4	**2d**	**1**	CH_3CN	4	**4** (47)[b]
5	**2a**	**1**	DMF	1	**3a** (100)
6	**2a**	**1**	DMSO	1	**3a** (100)
7	**2a**	**1**	CH_2Cl_2[c]	4	No reaction
8	**2a**	1	CH_2Cl_2,Py[d]	6	**3a** (44)
9	**2a**[e]	1	CH_3CN	6	**3a** (100)
10	**2a**[e]	5	CH_3CN	6	**3a** (71)

[a] Isolated yield based on phenol; [b] Yield based on catalyst charged;
[c] Catalyst was partially soluble; [d] Pyridine (10 equiv.) added;
[e] Substrate, 15 mmol was taken.

The catalytic activity of oxygen carrier chelates is influenced by the nature of the solvent. Polar solvents are known to facilitate the formation of Co(L)-OȮ adduct[13]. The catalytic activity of **1** was also observed to be solvent sensitive. DMF and DMSO were found to be better solvents than CH_3CN for oxygenation reaction. Oxygenation of **2a** in DMF and DMSO were complete in 1 h giving quantitative yield of **3a** (run 5 and 6). In CH_2Cl_2, where the catalyst was sparingly soluble, no reaction occurred (run 7). However, addition of pyridine (10 mole equiv.) solubilized the catalyst giving 44% yield of **3a** (run 8).

[Co(bpb)H_2O] (**1**) presents an example of a bis-amide cobalt(II) chelate as an efficient catalyst for oxygenation of phenols with molecular oxygen. High selectivity and ability to work under milder condition (stirring at room temperature under an atmosphere of molecular oxygen) makes it an attractive catalyst for oxygenation of phenolic compounds.

References and Notes

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