

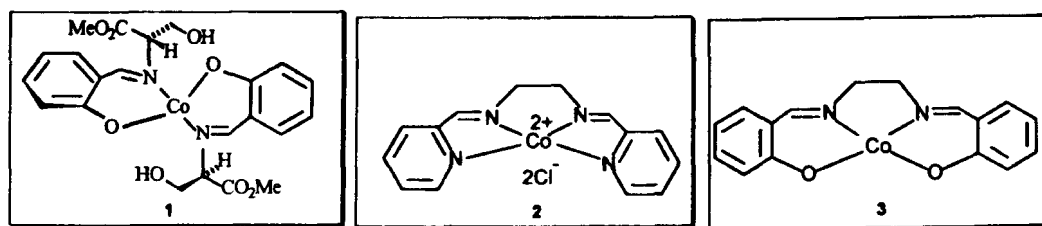
Cobalt(II) Schiff base catalyzed biomimetic oxidation of organic substrates with dioxygen

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Abstract: Cobalt(II) Schiff base complexes **1**, **2** and **3** catalyze the oxidation of a wide range of organic substrates in the presence of carbonyl compounds and dioxygen. EPR studies on **1** indicate that these reactions are proceeding via a cobalt(III)-superoxo complex formed under the aegis of carbonyl compounds and dioxygen. Catalysts **1-3** exhibit diverse reactivity profile and this has been attributed to the nature of ligand around cobalt which causes the formation of different active species from dioxygen.

Cobalt(II) Schiff base complexes are known to bind dioxygen in the presence of an axial nitrogen donor ligand (**1**). Earlier studies have indicated that four coordinated cobalt(II) complexes are very poor dioxygen binders whereas the corresponding five coordinated complexes readily bind it at ambient pressure. In view of the fascinating chemistry associated with cobalt(III)-dioxygen complexes we have undertaken a study on the formation and reactivity of these species. This presentation reveals that aliphatic aldehydes and cyclic β -ketoesters (**2**) also act as good ligands to cobalt(II) Schiff base complex **1** (**2**) in promoting the formation of monomeric cobalt(III)-dioxygen species. *These carbonyl compounds not only help in the formation of cobalt(III)-dioxygen species but also act as the reducing agent during oxygen atom transfer to organic substrates.*



The formation of cobalt(III)-superoxo complex in the presence of carbonyl compounds is demonstrated by EPR studies. Thus, mixing an equal amount of catalyst **1** and aldehydes or ketones in acetonitrile under ambient oxygen pressure gives initially the signal at 2666 G (g_{iso} 2.5021) due to cobalt(II) high spin complex but as the reaction progresses a new sharp signal appears at \sim 3332 G which may be attributed to the formation of oxygen centered radical of type Co-O-O \cdot . The EPR spectra of cobalt(III)-dioxygen adduct in the presence of some carbonyl compounds and **1** are shown in Figure 1.

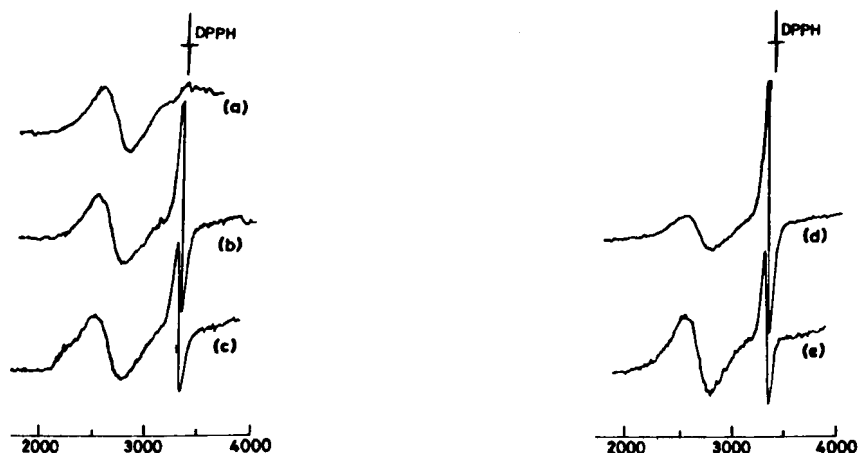


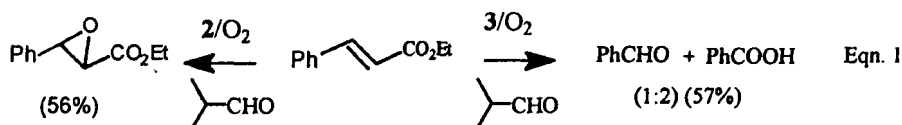
Figure 1. EPR spectra at ambient temperature in acetonitrile and dioxygen atmosphere: a) catalyst 1 ($g_{iso}=2.5201$). b) Catalyst 1 and 2-methylpropanal ($g_{iso}=2.0149$). c) Catalyst 1 and propanal ($g_{iso}=2.0112$). d) Catalyst 1 and ethyl 2-oxocyclopentanecarboxylate ($g_{iso}=2.0187$). e) Catalyst 1 and methyl 2-oxocyclohexanecarboxylate ($g_{iso}=2.0189$). (Catalyst 2 and 3 do not exhibit any sharp signal at 3300 G.)

The reactivity of some cyclic alkenes in the presence of catalyst 1 or 2 and 2-methylpropanal is presented in table 1. It is clearly evident from these results that catalyst 1 promotes allylic and alcohol oxidation of α -pinene, 3-carene and cholesterol respectively whereas 2 mainly encourages their epoxidation (entries 1-3, table 1). It is also interesting to note that catalyst 2 does not affect oxidation of the hydroxy group in cholesterol (table 1, entry 3) and it differs in the reactivity from 1 during the oxidation of ethylcinnamate. Thus epoxidation of ethylcinnamate can be performed in the presence of catalyst 2 in good yields whereas 1 shows very little tendency for this transformation. Interestingly,

TABLE 1. Catalyst 1 or 2 catalysed oxidation of cyclic alkenes with dioxygen

entry	alkene	product(s) (yield %) ^{a,c,d}	
		catalyst 1	catalyst 2
1		 (47) ^b	 (70)
2		 (35) ^e	 (48)
3		 (69)	 (49)

a) Isolated yield. b) An equal mixture of allylic alcohols are obtained. c) The epoxides were obtained as mixture of diastereomers. d) Alkene (5mmol), Isobutanol (10 mmol) and catalyst 1 or 2 (~5 mol%) were stirred in acetonitrile (30 mL) under dioxygen balloon at ambient temperature for 15-17 h. e) 3-carene epoxide is also obtained as a minor product.



catalyst **3** also differs in its reactivity from **1** and **2** as it promotes the cleavage of double bond of ethylcinnamate to give a mixture of benzaldehyde and benzoic acid (Eqn 1). The diverse reactivity profile exhibited by catalysts **1**, **2** and **3** (3) may be due to the formation of different active oxygen species under these conditions (1). These observations also indicate that the nature of ligand around cobalt metal plays a profound role towards the formation of the active species from dioxygen. This is also reflected in the EPR of catalysts **2** and **3** as neither of these show a sharp signal at 3332 G analogous to that of **1** (4).

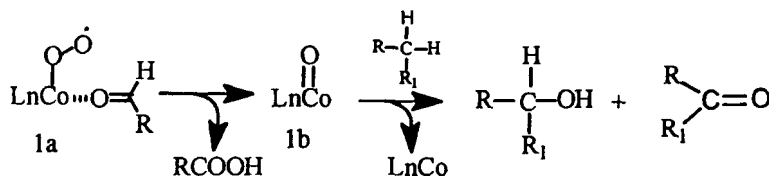
Cobalt complex **1** is also efficient in oxidizing a wide range of organic substrates in the presence of carbonyl compounds and dioxygen. Thus, oxidation of *cis*-2-octene and tetralin can be performed in the presence of β -ketoester, catalyst **1** and dioxygen to give the corresponding ketones (table 2, entry 1 and 2). Similarly, longifolene can be oxidized to carboxylic acid by using 2-methylpropanal as reducing agent (table 2, entry 3). Interestingly, cyclohexane can be oxidized to a mixture of cyclohexanol and cyclohexanone in moderate yields (table 2, entry 4) whereas anthracene can be oxidized to anthraquinone in good yields (table 2, entry 5). In view of the versatile nature of this

TABLE 2. Cobalt complex **1** catalysed oxidation of various organic substrates in the presence of carbonyl compounds and dioxygen

entry	substrate	carbonyl compound	product(s)	yield % ^{a,b}
1				51
2				61
3				55
4				(1:1) (20) ^c
5				(57) ^{c,e}

a) Isolated yield. *b*) Oxidised products 2-methylpropanoic acid and ethyl 1-hydroxy2-oxocyclopentanecarboxylate were obtained as by products from 2-methylpropanal and ethyl 2-oxocyclopentanecarboxylate respectively. *c*) These reactions were carried out under 1 atm oxygen pressure. *e*) Yield determined by HPLC.

oxidation, the formation of a highly reactive species from cobalt(III)-superoxo complexes is envisaged as the former may be a cobalt(IV)-oxo intermediate 1b resulting due to an oxygen atom transfer to the carbonyl compound in cobalt(III)-superoxo complex 1a derived from 1 (Scheme 1). The highly reactive cobalt(IV)-oxo species 1b, which is analogous to the iron(V)-oxo species proposed earlier for cytochrome P-450 model (5), is likely to exhibit versatility and that is why a wide range of organic substrates are oxidized under these conditions (table 2).



Scheme 1

In conclusion, we have demonstrated that certain ketoester and aldehyde act as good ligands in initiating the formation of cobalt(III)-superoxo species from cobalt(II) Schiff base complex and dioxygen. It is also evident that these carbonyl compounds subsequently act as reducing agents during the process of oxidation of organic substrates by cobalt(III)-superoxo complex. These studies also establish that different active oxygen species are formed by changing the ligand around cobalt.

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