A Cobalt(II) Complex of a New Salen Analogue as an Oxygenation Catalyst of Higher Activity

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A cobalt(II) complex of 6,6'-bis(benzoylamino)-2,2'-bipyridine {[Co(babp)]} has been found to take up and activate oxygen and act as a catalyst of higher activity and selectivity than the structurally similar N,N'-di(salicylidene)ethylenediamine complexes in the oxygenation of 2,6-di-t-butyl phenol to 2,6-di-t-butyl-p-benzoquinone.

The cobalt(II) complexes of salen [N,N'-di(salicylidene)ethylenediamine] and its derivatives are known to be catalysts forthe oxygenation of phenols to the corresponding*p*-benzoquinones,¹ but their durability is low,*i.e.*, in most cases,the turnover numbers did not exceed 200 owing to the oxidative degradation of the Schiff base ligands or some other process.^{2—4} Many efforts have been made to improve the catalytic activity and stability of these complexes, mostly by modification of the amine and/or salicylaldehyde units of the Schiff base ligands.^{3,5,6} We adopted a different strategy to





solve this problem, *i.e.*, the N₂O₂ co-ordination sites of salen were reconstructed using entirely different building blocks, bipyridine and an amide structure. Here we report that the cobalt(11) complex of this salen analogue, 6,6'-bis(benzoyl-amino)-2,2'-bipyridine (babpH₂),⁷ shows high catalytic activity and stability in the selective oxygenation of 2,6-di-t-butylphenol (DTBP) to 2,6-di-t-butyl-*p*-benzoquinone (DTBQ).

The complex [Co(babp)],[†] the deprotonated form of the cobalt(II) complex of babpH₂ {[Co(babpH₂)]²⁺}, has been shown to have the same N₂O₂-type square-planar structure as that of salen,^{7.8} and, in addition, is thermally stable up to its melting point under aerobic atmosphere.⁸ E.s.r. spectroscopy of [Co(babp)] in pyridine or dimethyl sulphoxide under aerobic conditions at room temperature shows a signal characteristic of a cobalt(III)-superoxide type complex (Figure 1),⁹ which disappears under reduced pressure (<2 Torr) and is restored on the introduction of oxygen. The result indicates that the oxygen adduct of [Co(babp)] is formed reversibly at room temperature.

Oxygenation of DTBP was performed in a 50 cm³ flask with oxygen bubbling through (1 atm, *ca.* 5 cm³ min⁻¹, room temp.). The reaction was complete after 24 h in the presence of >1% (v/v) of pyridine (Table 1), and the product was almost exclusively DTBQ. Less than 1% of diphenoquinone derivatives was detected as a byproduct by t.l.c. No reaction took place in the absence of any one of [Co(babp)], pyridine, or oxygen. The catalytic activity and selectivity of [Co(babp)] are similar to or higher than those of [Co(salen)] and its derivatives.^{1,3,5,6}

The catalytic activity of [Co(babp)] remained after completion of the first reaction, and subsequent feeding of the same amount of DTBP into the reaction mixture resulted in the conversion of more than 80% of DTBP into DTBQ after another 24 h (Table 1). The initial reaction rate of the second run, however, was slower than that of the first run. This deactivation of the catalyst was found to be suppressed to some extent by increasing the amount of pyridine added or by adding anhydrous sodium carbonate.⁵ Thus the [Co(babp)] is



Figure 1. E.s.r. spectra of [Co(babp)] in dimethyl sulphoxide during an oxygenation-deaeration cycle at room temperature: (a) oxygen bubbling, (b) deaeration.

Table 1. Oxygenation of DTB	catalysed by	[Co(babp)].
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	19 % Pyridine ^b (2nd Reaction ^c	
Entry		1st Reaction % DTBQ (turnover)	% DTBQ (turnover) ^d	Relative rate ^e
1	0	0(0)	_	_
2	0.1	71(142)		
3	1	100(200)	82(364)	0.24
			100(400)s	0.70
4	100	100(200)	96(392)	0.53
5f	100	100(200)	100(400)	0.76

^a Initial [DTBP] 5×10^{-1} mol dm⁻³, in 20 cm³ of toluene-pyridine, molar ratio [DTBP]/[[Co(babp)]] 200, reaction time 24 h. The amounts of DTBP and DTBQ were determined by gas chromatography employing naphthalene as internal standard. ^b % Pyridine (v/v) in the solvent. ^c See text. ^d Total turnover of first and second reactions. ^e Initial rate relative to that of the first reaction. ^f In the presence of anhydrous sodium carbonate. ^g Reuse of [Co(babp)] after recovery from the first reaction, see text.

much more stable than [Co(salen)]. Furthermore, [Co(babp)] could easily be recovered from the reaction mixture, after removing DTBQ and solvent, by heating up to 200 °C under reduced pressure and recycled as a catalyst in another batch (Table 1, entry 3). It was found that the recovered [Co(babp)] retained 70% of its initial catalytic activity. The third use of the same catalyst after recovery showed 52% of its initial catalytic activity, demonstrating that the catalyst is reusable.

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⁺ The complex [Co(babp)] was obtained by complexation of babpH₂ with cobalt(\mathfrak{ll}) acetate tetrahydrate followed by deprotonation with potassium hydroxide under nitrogen.^{7,8} M.p. 330 °C (slow decomp. above this temperature).