Catalytic Oxidations of Hydroquinones and 1,2-Diphenylhydrazine in the Presence of (Dibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)cobalt(II)

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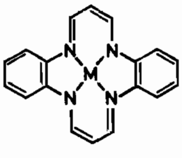
Although there have been extensive investigations of oxygenation reactions in the presence of salcomine [1] and cobaloxime [2] because of biochemical interest, little attention has been devoted to the utilization of unsaturated N_4-macrocyclic cobalt(II) complexes as catalysts.

We reported the synthesis and spectroscopic properties of oxovanadium(IV), isothiocyanatomanganese(III), nickel(II), copper(II) and palladium(II) complexes with one of the unsaturated N_4-macrocycles; 5,14-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine [3, 4] and also reported the axial-ligation constants and thermodynamic parameters for the axial reaction of (dibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)cobalt(II) (**1-Co**) with some pyridines and alicyclic amines [5]. Greenaway *et al.* studied the ESR spectra of **1-Co** with the effect of axial pyridine ligation [6]. Accordingly, we now report the results of an investigation of catalytic oxidation of some substrates using **1-Co**.



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M = Co(II), Ni(II), Cu(II)

Experimental

Physical Measurements

Infrared spectra in the region of 400–4000 cm^{-1} were taken on a Hitachi 260-10 spectrophotometer at room temperature by a KBr disk method. Proton NMR measurements were carried out with a JEOL JNM-FX 60 spectrometer operating in the Fourier transform mode. The NMR spectra were measured in chloroform-d at room temperature and chemical shifts were presented in ppm relative to tetramethylsilane as an internal reference standard. Ultraviolet and visible spectra covering the 240–500 nm range were measured with a Shimadzu UV-200S double beam spectrophotometer for dichloromethane at room temperature. Mass spectrum was recorded on a JEOL JMS-DX 300 gas chromatograph–mass spectrometer at 70 eV.

Preparation of Macrocyclic Complexes

(Dibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)cobalt(II) (1-Co), (dibenzo[b,i]-[1,4,8,11]tetraazacyclotetradecinato)nickel(II) (1-Ni) and (dibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)copper(II) (1-Cu)

Preparation of the complexes has been reported previously [3, 5].

Catalytic Oxidation of Various Substrates

General procedure for the autoxidation of a variety of hydroquinones in the presence of 1-Co, 1-Ni and/or 1-Cu

The complex (0.26 mmol) is added to a solution of the hydroquinone (2.72 mmol) in chloroform (200 ml). Air (3.5–4.5 dm^3 min^{-1}) was introduced into the resulting mixture at 20 ± 1 °C for 6 h with continuous stirring. The crude reaction mixture was filtered and the filtrate was dried over anhydrous calcium chloride overnight. The dried filtrate was concentrated *in vacuo* and the concentrate was applied to the top of a chromatographic column of silica gel (60–80 mesh, Kanto Chemical Co., Inc.) and eluted with dichloromethane. The solid material, which was recovered by evaporating the eluate to dryness *in vacuo*, was recrystallized from petroleum ether to give the pure 1,4-benzoquinone as yellow needles. Melting points and spectroscopic data for all compounds are listed in Table I with those of the literature.

General procedure for the autoxidation of hydroquinone in the presence of 1-Co and the added base

The oxidation reaction of **1-Co** (90 mg, 0.26 mmol), hydroquinone (300 mg, 2.72 mmol) and base (0.62–6.21 mmol), following the above procedure, gave the pure 1,4-benzoquinone with the yield as shown in Table II.

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TABLE I. Oxidation Products for a Variety of Hydroquinones in Chloroform kept at 20 ± 1 °C

Substituent group (R)	Yield (%) of 1,4-benzoquinones	IR (cm^{-1})[a] ν(C=O)	^{1}H NMR (ppm)[b]		Melting point (°C)		Reference
			aromatic	$-CH_3$	this study	literature	
H	45	1660	6.78(s)		114–116	111–113	7
2-CH_3	59	1655	6.61(q), 6.74(m) (J = 1.2 Hz)	2.07(d) (J = 1.2 Hz)	66–68	68–69	8
2-Cl	53	1655	6.86(d), 6.88(s), 7.01(d) (J = 1.4 Hz) (J = 1.4 Hz)		53–55	54–55	9
2-$C(CH_3)_3$	78	1650	6.61(d), 6.67(s), 6.68(d) (J = 1.0 Hz) (J = 1.0 Hz)	1.29(s)	54–56	56–57	10
2,3,5-$(CH_3)_3$	72	1640	6.55(q) (J = 1.8 Hz)	2.02(s), 2.04(d) (J = 1.8 Hz)	30	30–31	8

[a] Measured by the KBr disk method at room temperature. [b] Measured in chloroform-d at room temperature with TMS as an internal reference. Multiplicity of a proton signal is given in parentheses after δ value: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

TABLE II. Catalytic Oxidation for Hydroquinone in Chloroform on Addition of Bases kept at 20 ± 1 °C

Catalyst of 1-Co (mmol)	Added base (mmol)	Yield (%) of 1,4-benzoquinone
0.26	no base added	45
0.26	pyridine (0.62)	36
0.26	pyridine (6.21)	30
0.26	4-aminopyridine (2.66)	6

General procedure for the autoxidation of catechol, resorcinol and/or triphenylphosphine in the presence of 1-Co

The oxidation reaction of **1-Co** (90 mg, 0.26 mmol) and substrates (2.72 mmol), following the above procedure, gave no product as shown in Table III.

TABLE III. Catalytic Oxidation for Various Substrates in Chloroform kept at 20 ± 1 °C

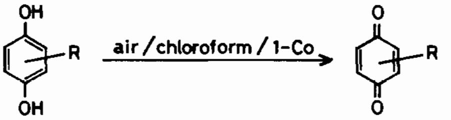
Substrate	Product (yield (%))
Catechol	1,2-benzoquinone (0)
Resorcinol	(0)
1,2-Diphenylhydrazine	azobenzene (77)
Triphenylphosphine	triphenylphosphine oxide (0)

Procedure for the autoxidation of 1,2-diphenylhydrazine in the presence of 1-Co

The oxidation reaction of **1-Co** (90 mg, 0.26 mmol) and 1,2-diphenylhydrazine (500 mg, 2.71 mmol), following the above procedure, gave pure azobenzene as reddish orange needles; yield 380 mg (77%), melting point 66.2–69.5 °C. UV (isooctane): 231, 319 and 450 nm. IR (KBr disk): 1580 cm^{-1} (N=N str.). The mass spectrum showed M$^+$ at *m/e* 182.

Results and Discussion

In an atmosphere of air, under gentle conditions, the cobalt(II) complex (**1-Co**) catalyzes the oxidation of a variety of hydroquinones and 1,2-diphenylhydrazine, added in a 10.5-fold over the catalyst. These oxidation reactions are revealed by the following equations:



(1)

(2)

In chloroform solvent, the yields of the oxidation products in eqns. (1) and (2) are good or excellent as given in Tables I and III. The catalytic effect of **1-Co** is apparently proved by the yields of the products, compared with those of the blank experiments summarized in Table IV. 2,3,5-Trimethylhydroquinone was smoothly oxidized to 2,3,5-trimethyl-1,4-benzoquinone in 72% yield and 2-tert-butylhydroquinone was also oxidized to 2-tert-butyl-1,4-benzoquinone in 79% yield. On the other hand, the yields of 1,4-benzoquinone and 2-chloro-1,4-benzoquinone were 45% and 53%, respectively. It therefore appears that, as with **1-Co**, substituent groups in the aromatic ring can exert a marked influence on the rate of oxidation due to

TABLE IV. Catalytic Oxidation for Hydroquinone in Chloroform kept at 20 ± 1 °C

Catalyst[a]	Used gas	Yield (%) of 1,4-benzoquinone
1-Co	air	45
1-Ni	air	0
1-Cu	air	0
1-Co	nitrogen	0
No catalyst added	air	0

[a] **1-Co**, (dibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)-cobalt(II); **1-Ni**, (dibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)nickel(II); **1-Cu**, (dibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)copper(II).

steric and/or electronic effects. The other complexes (**1-Ni** and **1-Cu**) do not function as efficient catalysts for the air oxidation of hydroquinone as shown in Table IV. The oxidation of hydroquinone catalyzed by **1-Co** resulted in no product under an atmosphere of nitrogen. Moreover, **1-Co** employed in the present work does not catalyze the oxidation of catechol, resorcinol and triphenylphosphine under gentle conditions (Table III). The compound remained unreactive.

According to the data given in Table II, the catalytic activity of **1-Co** depends on the character of the added axial base. The yield of the oxidation product is poor by the addition of 4-aminopyridine as an axial base. It is thought that 4-aminopyridine coordinates the cobalt atom at the axial site in **1-Co** [5] and disturbs the coordination of the substrates to the cobalt atom.

Consequently, the catalytic oxidations reported in the present paper seems to involve dehydrogenation for a variety of hydroquinones and 1,2-diphenylhydrazine, though no definitive evidence can be provided for the reaction pathway at this stage. The dehydrogenation of hydroquinone (HQ) can be visualized by assuming stepwise H-atom transfer to O_2, resulting in the formation of 1,4-benzoquinone (Q) and hydrogen peroxide (H_2O_2):

$$1\text{-Co} + \mathrm{HQ} \rightleftarrows 1\text{-Co-QH} \tag{3}$$

$$1\text{-Co-QH} + \mathrm{O_2} \longrightarrow 1\text{-Co} + \mathrm{Q} + \mathrm{H_2O_2} \tag{4}$$

followed by

$$\mathrm{H_2O_2} + \mathrm{HQ} \longrightarrow \mathrm{Q} + \mathrm{H_2O} \tag{5}$$

Similar steps can be written for the oxidation mechanism of 1,2-diphenylhydrazine in chloroform.

In conclusion, the cobalt(II) complex (**1-Co**) functions as an efficient catalyst for the oxidation of a variety of hydroquinones and 1,2-diphenylhydrazine. The substituent groups in the aromatic ring of hydroquinones exert the unambiguous influence on the rate of oxidation due to steric and/or electronic effects. The oxidation mechanism assumes eqns. (3)–(5).

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