Non-symmetric Schiff Base Co(II) Complexes. Synthesis and Catalytic Activity in the Oxidation of 2,6-Di-tert-butylphenol by Molecular Oxygen

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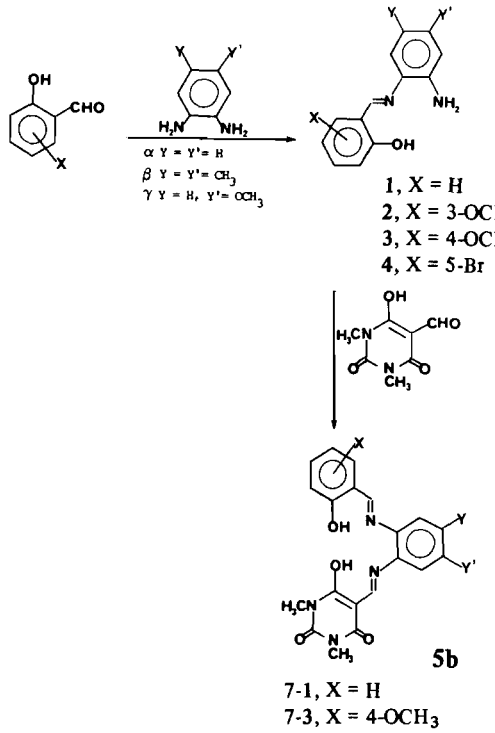
Abstract

We report the synthesis of a series of unsymmetrical tetradentate Schiff base ligands. In the reaction of *o*-phenylenediamines with aromatic aldehydes, use of chloroform as a solvent allows a kinetic control of the formation of mono-Schiff base. Further condensation of the half-unit with 5-formyl 1,3-dimethyl barbituric acid leads to the non-symmetric Schiff base. Cobalt(II) complexes of these ligands have been prepared and the influence of the structure of the ligands on half-wave Co(II)/Co(III) potential values and the catalytic activation of O_2 has been investigated.

Introduction

Symmetric Schiff bases derived from aromatic *o*-hydroxy aldehyde (e.g. salicylaldehyde) or ketones and α, ω-diamino-alkanes have been known for a long time and often used in coordination chemistry due to their good complexing properties towards a variety of transition metal cations. Non-symmetric Schiff bases have been previously prepared by reaction of two distinct aldehydes or ketones with aliphatic diamines [1–4] and studied as synthetic analogues of the metal binding sites of zinc and copper proteins. To our knowledge, only two examples of non-symmetric ligands derived from *o*-phenylene diamine have been described [5, 6].

In this paper, we report the synthesis of mono-Schiff bases (half-units) by condensation of various aromatic *o*-hydroxy aldehydes with symmetric and non-symmetric *o*-phenylene-diamines (Scheme 1). Non-symmetric Schiff bases were then obtained by reacting the half-units with 5-formyl 1,3-dimethyl barbituric acid in 95% ethanol at room temperature. The corresponding cobalt(II) complexes were synthesized and studied for their capacity to catalyse the oxidation of 2,6-di-tert-butylphenol by molecular oxygen.



Scheme 1.

Experimental

Materials

Tetraalkylammonium perchlorate (TEAP) was purchased from Fluka, dried overnight at 40 °C under vacuum and used without further purification. Merck Uvasol DMSO was dried for 48 h over 4 Å molecular sieves before use.

The various substituted salicylaldehydes were commercially available and were used without further purification. Methyl-substituted *o*-phenylene diamines were recrystallized before use. The 4-methoxy *o*-phenylene diamine was obtained by reduction of the 4-methoxy *2*-nitro aniline with Sn/HCl and purified by distillation under reduced pressure. 5-formyl 1,3-dimethyl barbituric acid was prepared as previously reported [7].

Physical Measurements

^{1}H NMR spectra were recorded on a Perkin-Elmer R 32 using $CDCl_3$ solutions and TMS as reference.

Cyclic voltammetric measurements were carried out on a three-electrode system with an EGG Model

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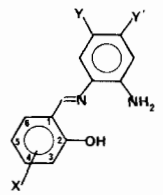
TABLE I. Temperature Reaction, Time and Yields of the Reaction of Monocondensation of Substituted Salicylaldehydes with Aromatic Diamines:



	X	Y Y′	H α: H	CH_3 β: CH_3	H γ: OCH_3
1	H		R, 24 h, 70%	R, 24 h, 73%	R, 14 h, 75%
2	3-OCH_3[a]		R, 36 h, 72%	R, 36 h, 76%	R, 12 h, 97%
3	4-OCH_3[a]		R, 24 h, 74%	R, 24 h, 86%	R, 16 h, 81%
4	5-Br		20 °C, 5 h, 73%	20 °C, 12 h, 46%	20 °C, 18 h, 85%

R = reflux. [a]Chloroform can be replaced by 95% ethanol.

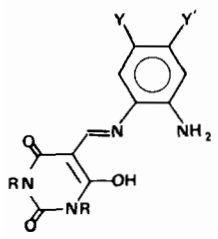
362 Scanning potentiostat. The working electrode was a platinum button and a platinum wire served as a counter-electrode. A saturated calomel electrode (SCE) was used as the reference electrode and was separated from the bulk of the solution by a fritted-glass bridge. The solutions of the different complexes were 0.06 mM in DMSO.

Synthesis

Half-units (1–4, 6)

In a typical experiment, a solution of the aldehyde (1 mmol) and the diamine (1 mmol) in $CHCl_3$ (25 ml) was stirred at room temperature or above (see Table I) until completion of the reaction (checked by TLC-silica gel- CH_2Cl_2: CH_3OH 98:2). The solvent was evaporated to dryness and the crude products **1**, **2**, **3** and **4** recrystallized in hexane. Yields and melting points are given in Table I.

Slightly different conditions were used to prepare the mono-Schiff bases **6a** and **6b** (Scheme 2) respectively from 5-formyl barbituric acid (**5a**) and 5-formyl 1,3-dimethyl barbituric acid (**5b**): condensation with the diamine was achieved in water solution in the presence of one equivalent of NEt_3 [7].



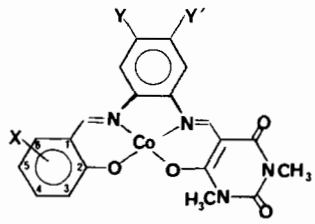
Scheme 2. **6a**, R = H; **6b**, R = CH_3.

Non-symmetric Schiff bases (7)

To a solution of 1 mmol of the half-unit in 95% ethanol was added 1 mmol of 5-formyl 1,3-dimethyl barbituric acid. The mixture was stirred at room temperature for one night. The ligand was filtered off, washed with 95% ethanol and dried under vacuum.

Co(II) complexes (8) (Scheme 3)

The syntheses were carried out under argon atmosphere. To a suspension of 0.5 mmol of the ligand in 25 ml of MeOH were added two equivalents of NaOH (pellets). The suspension was stirred at room temperature for 30 min during which time the colour of the solution changed from pale yellow to intense yellow. An excess of $Co(OAc)_2 \cdot 2H_2O$ (0.55 mmol) was added to this suspension which was then heated for 3 h. After cooling, the brown precipitate was filtered off, washed a few times with degassed methanol and dried under argon.



Scheme 3. **8-1α**, X = H, Y = Y′ = H; **8-1γ**, X = H, Y = H, Y′ = OCH_3; **8-1γ′**, X = H, Y = OCH_3, Y′ = H; **8-3α**, X = 4-OCH_3, Y = Y′ = H.

Oxidation of 2,6-Di-tert-butylphenol

To a solution of the starting phenol (0.1 M) in acetonitrile (5 cc) was added the catalyst (0.01 M) in DMSO (0.5 cc). The solution was stirred in a two-necked flask connected to a gas-burette filled with oxygen (pressure: 1 atm.). After 1, 4 or 28 h, an aliquot was taken off and the products were extracted with hexane, the solvent evaporated off and the products characterized by NMR spectroscopy [8].

The microanalysis of all the compounds and the NMR spectra of the ligands are available as 'Supplementary Material'.

Results and Discussion

Ligands

The selective obtention of mono-Schiff bases in the reaction of *o*-phenylene diamines with substituted salicylaldehydes relies on a careful choice of the solvent which, in turn, depends on the reactivity of the aldehyde: chloroform is a suitable solvent for reactive aldehydes whereas with less reactive ones, 95% ethanol can also be used. Thus salicylaldehydes substituted by an electron-donating group, e.g. OCH_3, give rise to the corresponding 'half-units' both in chloroform and in 95% ethanol. On the other hand, with 5-bromo salicylaldehyde, which contains a more electrophilic carbonyl group than the unsubstituted salicylaldehyde, the half-unit can be obtained only in chloroform. This phenomenon can be best explained by assuming variations of the rates of condensation reactions with the solvent: the condensation reactions are much faster in ethanol than in chloroform, so that the mono-adduct can be isolated only with the latter solvent, the bis-adduct being the unique reaction product in the case of ethanol (Scheme 1).

The various products were isolated in good yields (Table I). One remark in the case of 4-methoxy *o*-phenylene diamine: only one of the possible isomers was obtained as shown by the NMR spectra which exhibited one set of signals: we assume that it results from the condensation of the more nucleophilic NH_2 group (in *para* position with respect to the OCH_3 group).

The half-units proved to be not very stable: for example, attempts to purify them by chromatography resulted in the formation of the starting aldehyde. Furthermore, various experiments to obtain non-symmetric ligands with two differently substituted salicylaldehydes were unsuccessful and led to a mixture of the three possible condensation products as observed previously by Chiswell *et al.* [9]. This is best explained by assuming that under the conditions used, the formation of the imines is reversible and leads to redistribution of the aldehyde moieties.

$$RCHO + H_2NR' \rightleftharpoons RCH = NR' + H_2O$$

In fact, non-symmetric ligands can be obtained only by condensation of the half-units with 5-formyl 1,3-dimethyl barbituric acid because the reaction products precipitate as soon as they are formed, which displaces the above equilibrium to the right.

The various products **7** obtained in this condensation were characterized by microanalysis (see 'Supplementary Material') and infra-red spectra*.

As we were interested in studying the influence of the position of the methoxy group on the values of $E_{1/2}$ (Co(II)/Co(III)), we have limited the synthesis to the ligands containing a methoxy group on the salicylaldehyde or on the *o*-phenylene diamine moieties.

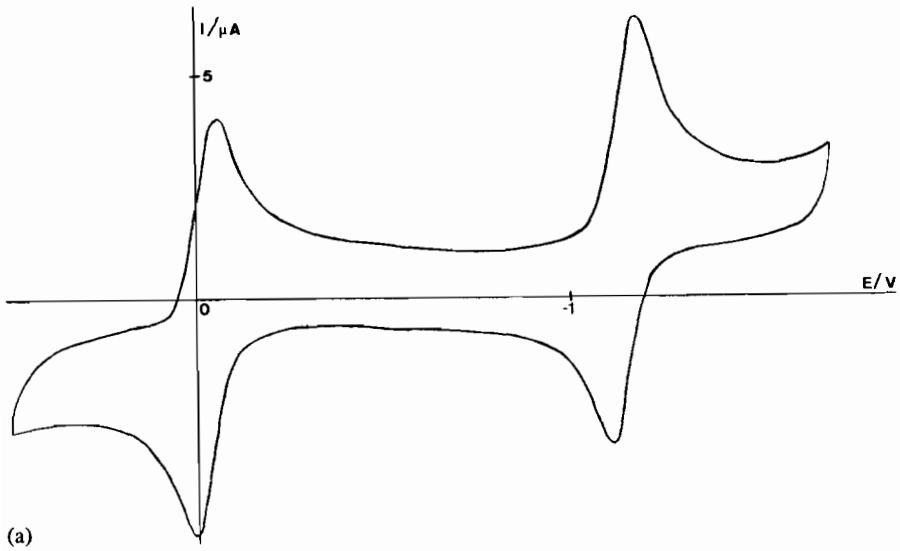
Effect of Varying the Position of the Methoxy Group on $E_{1/2}$ (Co(II)/Co(III))

We have measured the values of the half-wave potentials of the Co(II) complexes (**8**) and compared them to those of the corresponding symmetric complexes: Co Salophen (**9**) and Co DiMeBarphen (**11**) (Scheme 4) which show quite different values of $E_{1/2}$, respectively −0.04 and +0.28 V. As expected, the values of $E_{1/2}$ Co(III)/Co(II) for non-symmetric complexes lie between these values (Table II). It appears

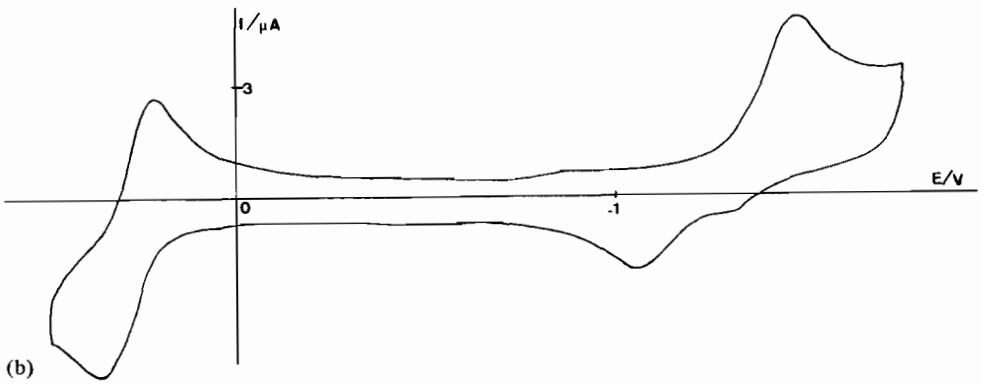
*By comparing the spectra of the symmetric ligands with those of non-symmetric ones, characteristic vibrational bands could be observed: for compounds with at least one barbiturate ring, a weak band at 1710 cm^{-1} for the non-symmetric ligands or a strong one for the symmetric ones is always observed; bands at 1555, 1270 and 900 cm^{-1} are always present for compounds derived from salicylaldehydes.

TABLE II. Half-wave Potentials of Co(II) Complexes and Yields in the Oxidation of 2-6-Di-tert-butylphenol

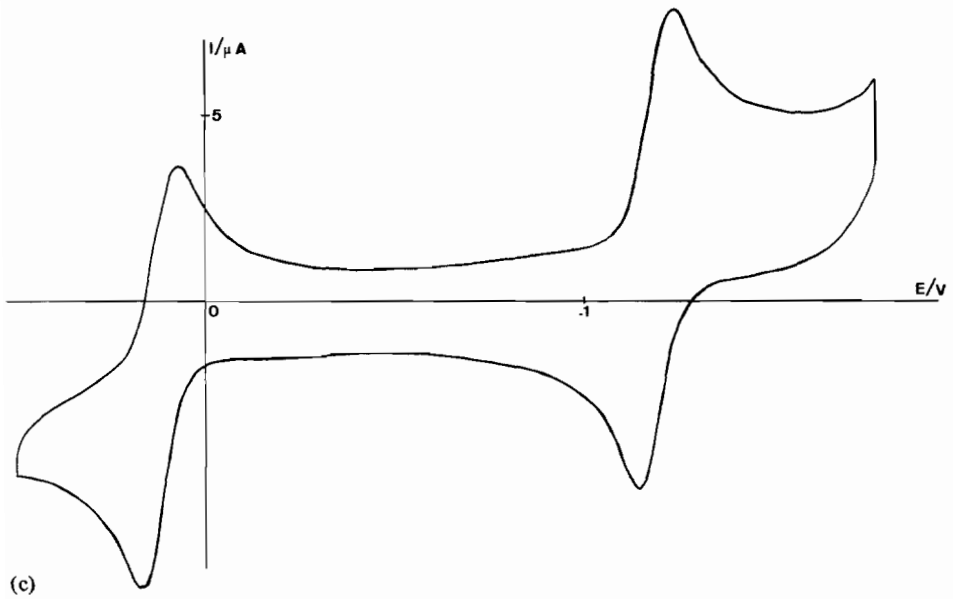
Compound	$E_{1/2}$ Co(III)/Co(II) (V)	Yield in oxidation product		
		1 h	4 h	28 h
9 Co Salophen	−0.04	72	80	100
10 Co SalOMephen	−0.04		100	
11 Co DiMeBarphen	+0.28	33	57	73
12 Co DiMeBarOMephen	+0.27		60	86
8-1α	+0.11	35	83	100
8-3α	+0.12		78	100
8-1γ	+0.11		83	100
8-1γ'	+0.11		81	91



(a)



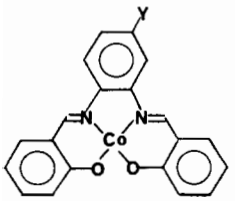
(b)

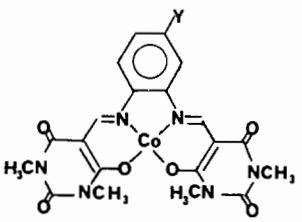


(c)

Fig. 1. Voltammograms of Co(II) complexes. (a) Co Salophen 9, (b) Co DiMeBarphen 11, (c) 8-1α.

that the methoxy group has no significant influence on the values of the half-wave potentials, whatever its position.





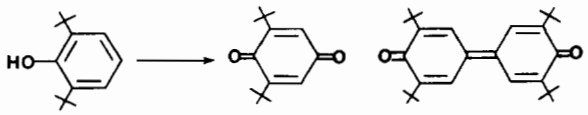
9 Co Salophen (Y = H)
10 Co SalOMephen (Y = OCH_3)

11 Co DiMeBarphen (Y = H)
12 Co DiMeBarOMephen (Y = OCH_3)

Scheme 4.

Cyclic voltammetric scans reveal two reversible redox processes (Fig. 1c). The reduction which occurs at $E_{1/2} = +0.12$ V is assigned to the Co(III)/Co(II) equilibrium whereas the one at $E_{1/2} = -1.2$ V is assigned to the Co(II)/Co(I) couple. For the cobalt complexes of symmetric ligands derived from 1,3-dimethyl barbituric acid, the first reduction process is reversible whereas the second one is showing an cathodic peak at −1.5 V associated to two anodic peaks at −1.65 and −1.1 V (Fig. 1b). Therefore, the incorporation of one phenoxy group in the ligand leads to Co(II) complexes for which the two redox process are reversible and occur each in one step.

Catalysis of the Oxidation of 2,6-di-tert-butylphenol by Molecular Oxygen [8]



a **b**

In the oxidation of 2,6-di-tert-butylphenol, all complexes exhibited a high selectivity, the only product which was obtained being the benzoquinone (**a**), the other possible product, the diphenoquinone (**b**), being absent.

We have compared the efficiency of the non-symmetric complexes with those of the symmetric ones (Table II). There does not seem to be a simple relationship between the values of $E_{1/2}$ (Co(II)/Co(III)) and the efficiency of the catalyst.

The highest reaction rates and yields are observed with the complexes having the lowest $E_{1/2}$ values e.g. complexes **9** and **10** with which more than 80% of the starting phenol was oxidized after 4 h. Slower reactions and lower yields characterize complexes **11** and **12** which have more positive $E_{1/2}$ values. The non-symmetric complexes **8-1**α, **8-3**α, **8-1**γ and γ' which show intermediate $E_{1/2}$ values are slightly less efficient than complexes **9** and **10** though nearly quantitative yields of the quinone were also obtained after 28 h.

However, one should be careful in trying to infer the catalytic efficiency of a cobalt complex from its $E_{1/2}$ value: the latter can give useful information only on its ability to bind molecular oxygen [10] but not on the rates of the subsequent steps of the oxidation reaction which involve several other intermediates [8].

Supplementary Material

Microanalysis of all the compounds and NMR spectra of the ligands are available from the authors on request.

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