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Spectroscopy and electrochemistry of cobalt(III) salophen complexes

Ali Hossein Sarvestani* and Sajjad Mohebbi

Department of Chemistry, Kurdistan University, Sanandaj, Iran

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Novel Co(III) complexes with general formula, $[Co(chel)(PBu_3)]ClO_4.H_2O$, where chel = 5-Brsalophen, 5-NO_2salophen, 5-MeOsalophen and 4-MeOsalophen, were synthesised and characterised. The spectroscopic and electrochemical properties of these complexes and $[Co(salophen)(PR_3)]ClO_4.H_2O$ (R = PBu_3 and PPh_3) complexes were investigated.

Keywords: Cobalt, schiff base, spectroscopic, electrochemistry

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Cobalt complexes with ligands derived from salicylaldehyde have been well studied.[1] They are regarded as models for the Cobalamine (B_{12}) coenzymes,[2-4] classified as an oxygen carrier[5] and used as a catalyst for the preparative oxygenation of phenols,[6] indols[7] and amines.[8] The catalytically active species contains cobalt in the Co(III) oxidation state.[9] The catalytic activity of Co(III) with salen[10-15] and BAE[16] complexes has been investigated. In continuation of our studies on spectroscopy and electrochemical behaviour of cobalt(III) complexes containing Schiff base ligands,[17] the Co(III) salophen (salophen = bis(salicylaldehyde) phenylenediimine) complexes, were selected and the effect of the extention of π-system on these properties was investigated. We report the novel complex $[Co(chel)(PBu_3)]ClO_4.H_2O$, where chel = 5-Brsalophen, 5-NO_2salophen 5-MeOsalophen and 4-MeOsalophen. We have also studied correlation of electronic spectra and the electrochemical behavior of a series of Co(III) salophen complexes with the goal of evaluating the effect of equatorial substitutions on d orbitals distortions (Fig. 1).

Experimental

Materials and physical measurements

All materials were used as received from Merck, Aldrich and Fluka. The spectral datas, elemental analysis and voltammograms were carried out like earlier work.[17]

Synthesis of the complexes

Schiff base ligands used in this research were prepared according to the literature by condensation of 1,2-ethylenediamine with the appropriate amount of aldehyde (1:2 mole ratio) in methanol or ethanol.[18-20] $[Co(salophen)(PR_3)]ClO_4.H_2O$ (PR_3 = PBu_3, and PPh_3) were prepared by the methods described previously.[21,22] The new complexes $[Co(5\text{-}MeOsalophen)(PBu_3)]ClO_4.H_2O$ and $[Co(4\text{-}MeOsalophen)(PBu_3)]ClO_4.H_2O$, were made according to the known method,[23] than recrystalised in methanol. The 5-Brsalophen, 5-NO_2salophen, cobalt(II) complexes are precipitated in methanol, therefore the reaction was done in DMF. After formation of final complex, it was precipitated by adding H_2O and washed with water and ethanol and dried.

Elemental analysis calculated(found) as percent for $[Co(5\text{-}Brsalophen)(PBu_3)]ClO_4.H_2O$, $C_{32}H_{41}Br_2CoClN_2O_7P$ (M.Wt = 850.850), yield: 85%: C 45.2(45.3), H 4.9(4.9), N 3.3(3.3).

$[Co(5\text{-}MeOsalophen)(PBu_3)]ClO_4.H_2O$, $C_{34}H_{47}CoClN_2O_9P$ (M.Wt = 752.92), yield: 65%: C 54.2(54.4), H 6.3(6.3), N 3.7(3.8).

$[Co(4\text{-}MeOsalophen)(PBu_3)]ClO_4.H_2O$, $C_{34}H_{47}CoClN_2O_9P$ (M.Wt = 752.92), yield: 70%: C 54.2(54.5), H 6.3(6.3), N 3.7(3.8).

$[Co(5\text{-}NO_2salophen)(PBu_3)]ClO_4.H_2O$, $C_{32}H_{41}CoClN_4O_{11}P$ (M.Wt = 782.9), yield: 65%: C 49.1(49.7), H 5.3(3.3), N 3.6(3.6).

Results and discussion

*IR spectra***:** In the IR spectrum, H_2salophen shows a broad band characteristic of the OH group at 3300–3500 cm^{-1}. The disappearance of this band in the IR spectra of complexes is indicative of the fact that the equatorial ligand is coordinated. The $\upsilon(C = N)$ band of H_2salophen at 1615 cm^{-1} also shifted (υ = 10 cm^{-1}) due to the loss of hydrogen bonding and the formation of a new chelate ring between the imine nitrogens and cobalt.[24-26] The absence of the coordinated water in the complexes studied was confirmed by the absence of the absorption band 3100 cm^{-1}.[22]

Electronic spectra: The UV-vis(> 280 nm) spectrum of H_2salophen in methanol consists of a relatively intense band centred at 337 nm ($\varepsilon \approx 14{,}500$), assigned to $\pi \rightarrow \pi^*$ transition and a second band at 362nm ($\varepsilon \approx 12{,}100$), corresponding to $n \rightarrow \pi^*$ excitation.[27] After complexation with Co(III), several transition appear below 400nm still involving principally interligand $\pi \rightarrow \pi^*$ excitation. Moreover two bands appeared in the visible region. The transition with the lowest energy (550–700 nm) is attributable to $d \rightarrow d$ transition. In the same way that we discussed in the last work,[17] electron-withdrawing groups decrease the energy of d orbitals via π-interactions and increase the energy of the $d \rightarrow d$ excitations, while electron donating groups operate it in the reverse trend. The axial ligand also affects this transition through σ-intraction with the dz^2 orbital (Table 1). In the complexes studied here, the $d \rightarrow d$ excitation for $[Co(5\text{-}MeOsalophen)(PBu_3)]^+$ and $[Co(salophen)(PPh_3)]^+$ appeared as a peak, for $[Co(4\text{-}MeOsalophen)(PBu_3)]^+$ and $[Co(salophen)(PBu_3)]^+$ as shoulder and for [Co(5-

Table 1 Electronic absorption data for $[Co(X\text{-}salophen)(PR_3)]ClO_4.H_2O$, complexes.

No.	X	PR_3	$\lambda_{nm}(\varepsilon M^{-1}.\ cm^{-1})$			
1	H	PPh_3	686(1000) 740(450)[a]	489(8300)	378(20000)	313(26000)
2	H	PBu_3	600(880) 633(1150)[a]	485(7700)	379(18000)	315(16000)
3	5-MeO	PBu_3	650(900) 667(1050)[a]	530(9400)	387(20000)	300(18000)
4	4-MeO	PBu_3	600(1300) 635(940)[a]	464(14000)	383(26000)	324(22000)
5	5-Br	PBu_3	– 629(1000)[a]	491(10000)	381(22000)	316(21000)
6	5-NO_2	PBu_3	– 589(1500)[a]	465 (14000)	363(47000)	307(42000)

[a]See ref. 17.

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* Correspondent. E-mail: asarvestani@uok.ac.ir

Brsalophen)(PBu$_3$)]$^+$ and [Co(5-NO$_2$salophen)(PBu$_3$)]$^+$ shifted to higher energy and mixed with d → π* charge transfer. The π-system is more extended in salophen Schiff base as a ligand relative to the salen ligand because of its unsaturated amine bridge. Therefore the π- interaction between the Co(III) salophen orbital system and the metal d orbitals is more than in the salen complexes. *Via* this property, in the Co(III) salophen complexes the d → d transition has a blue shift relative to Co(III)salen complexes (see ref. 17 and Table 1).

The complexes studied here show an intense transition that appears in the 450–550nm region. Theoretical calculations and experimental evidence lead to assignment of this transition as a d → π* charge transfer transition.[24,27,28] Note that there is a major contribution of d → d transitions in the low-energy region (Table 1). For example the d → d transitions for 5-nitrosalophen and 5-Brsalophen is completely mixed with d → π* charge transfer and were seen as shoulders. So we believe that for determination of energy level and the excitation bands, more experimental evidence and theoritical calculations are needed.

The axial ligand has no effect on this transition (Table 1) in the five-coordinated complexes but, in the presence of the axial ligand, in contrast to the d → d transition, the d → π* charge transfer has a red shift. This is due to formation of a hexacoordinated complex thus increasing the charge on the metal centre.

For studying the electronic effect of equatorial Schiff base ligands on the d → π* charge transfer, some of the salophen derivatives were investigated. The excitation energy for the above transition is increased in the order of 4-MeOsalophen ≈ 5-nitrosalophen>salophen ≈ 5-Brsalophen>5-MeOsalophen (Table 1). This trend is similar to the d → d transition and is due to π-interactions between the salophen Schiff base ligand and the metal d orbitals. By decreasing the energy level of a metal d orbital via π-interaction with a Schiff base, the excitation energy of the d → π* charge transfer is increased. A methoxy group in the *para* position to the azomethane group in the [Co(4-MeOsalophen)(PBu$_3$)]$^+$ complex gives interesting results. For example it has no effect on the d → d transition. It seems there is no π-interaction between the Schiff base ligand and the metal d-orbitals. Electrochemical studies show that 4-MeOsalophen has the least π-acceptor property and the highest reduction potential for Co(II/I). In contrast to these properties it has the highest d → π* excitation energy. MeO as an electrodonating group can increase the energy level of the π* orbitals on the Schiff base ligands. By increasing the π* energy level, the d– π* interaction is reduced and this reduces the π-acceptor property of 4-MeOsalophen. So, *via* increasing the π* energy level the excitation energy of d → π* charge transfer increases, while this change has no effect on the d → d transition.

Electrochemical study

A typical cyclic voltammogram of [Co(salphen)(PBu$_3$)]$^+$ complex in the potential range from +0.2 to –1.5 V (vs Ag/AgCl) in DMF solution is shown in Fig. 2a. A first reduction peak is observed at about *ca* –0.400V which is due to the one electron transfer process [Co^{III}(salophen)(PBu$_3$)]$^+$ + e$^-$ → [Co^{II}(salophen)] + PBu$_3$. The electron is added to the anti-bonding dz^2 orbital and the product of the Co(III) complex loses its axial ligand in weakly coordinating solvents.[16] The second quasi-reversible prosess at *ca* –1.100V is observed with about unit ratio of anodic to cathodic peak currents (i$_{pa}$/i$_{pc}$), corresponding to the simple one electron process [Co^{II}(salophen)] + e$^-$ → [Co^{I}(salophen)]. Upon reversal of the scan direction, the Co(II) complex is oxidised to Co(III) at higher potentials (about Ca. 100mV). Then, in a rapid consecutive reaction, the five-coordinate species [Co^{III}(salophen)(PR$_3$)]$^+$ is formed again (*i.e.*, the electron transfer is followed by a chemical reaction).[16] Multiple scans resulted in nearly superposable cyclic voltammograms, thereby showing the marked stability of the three oxidation states of cobalt involved in the electrochemical study. The reduction potentials for the different complexes are set out in Table 2.

The formal potentials for the reversible Co(II/I) redox couple were calculated as the average of the cathodic(E_{pc}) and anodic(E_{pa}) peak potentials of this process. In this study the effect of phosphine as axial ligand and equatorial Schiff base ligand on the electrochemical behaviour of Co(III) Schiff base complexes were investigated.

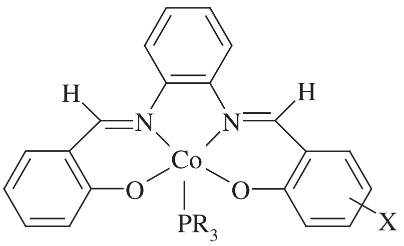

Fig. 1 The structure of [Co(Chel)(PR$_3$)]ClO$_4$.H$_2$O, complexes. X = H (R = Bu and Ph), 5-NO$_2$, 5-Br, 5-OMe and 4-OMe (R = Bu).

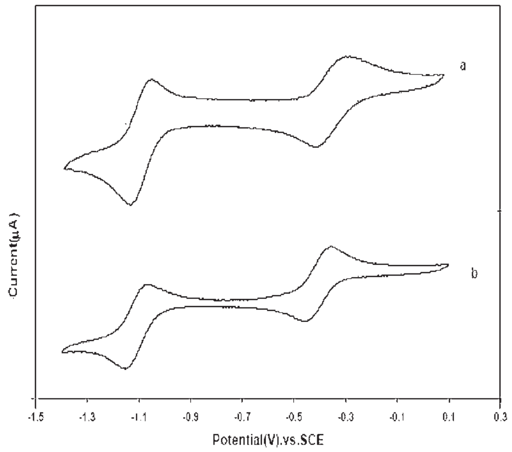

Fig. 2 Cyclic voltamogram of (a) [Co(salophen)(PBu $_3$)]ClO$_4$.H$_2$O, (b) in presens of 0.001M, PBu$_3$ in DMF at room temprature. Scan rate: 100mV/s.

Table 2 Reduction potentials(in V) for [Co(X-salophen)(PR$_3$)]ClO$_4$.H$_2$O, in DMF

No.	X	PR$_3$	E$_{pa}$(II→III)	E$_{pc}$(III→II)	E$_{1/2}$(II↔I)	E$_{1/2}$(II↔I)(salen)
1	H	PPh$_3$	+0.120	–0.0800	–1.100	(–1.218)^a
2	H	PBu$_3$	–0.290	–0.400	–1.100	(–1.218)^a
3	5-MeO	PBu$_3$	–0.282	–0.420	–1.113	(–1.263)^a
4	4-MeO	PBu$_3$	–0.282	–0.410	–1.165	(–1.316)^a
5	5-Br	PBu$_3$	–0.219	–0.327	–0.968	(–1.085)^a
6	5-NO$_2$	PBu$_3$	–0.053	–0.195	–0.825	(–0.928)^a

^{a}See ref. 17.

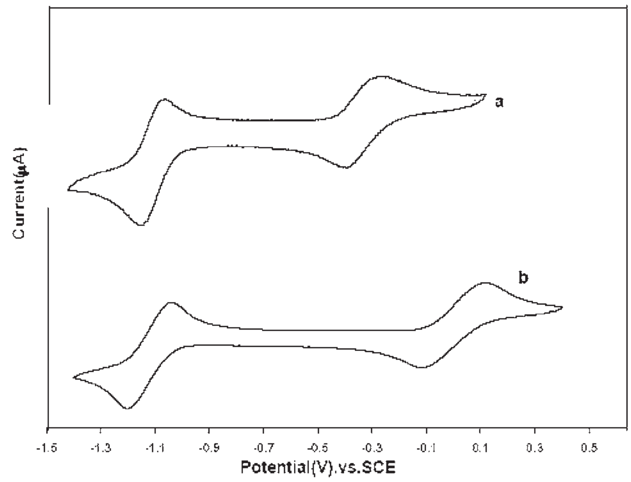

Fig. 3 Cyclic voltamogram of [Co(salophen)(PR$_3$)]ClO$_4$.H$_2$O, a (R = Ph), b (R = Bu) in DMF at room temprature. Scan rate: 100mV/s.

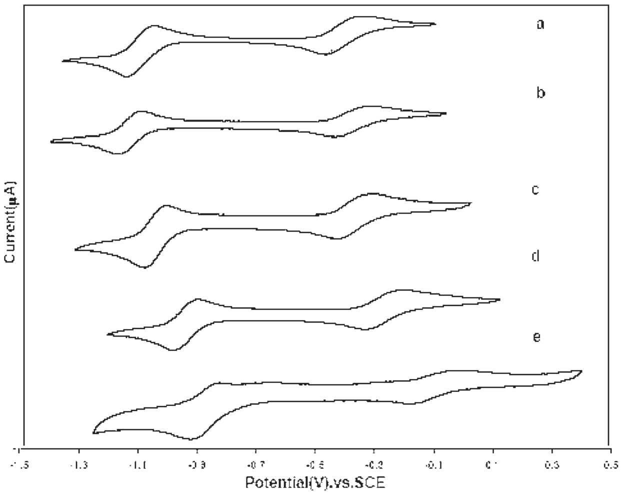

Fig. 4 Cyclic voltamogram of [Co(5-X-salophen)(PBu$_3$)]ClO$_4$. H$_2$O, a (X = 5-MeO), b (X = 4-MeO), c (X = H), d (X = 5-Br), e (X = NO$_2$) in DMF at room temprature. Scan rate: 100mV/s.

Figure 2b shows the effect of PR$_3$ concentration on the electrochemical behaviour of [Co^{III}(salophen)(PR$_3$)]$^+$: upon addition of phosphine (0.001M), oxidation occurs at lower potential whereas the reduction wave is shifted in the negative direction (hexa-coordinated complex is formed). The changes are due to increasing the antibonding character of dz^2 orbital via addition of PR$_3$. In contrast, the Co(II/I) couple is not affected by the concentration of phosphine (Table 2).

The observed cathodic peak potentials E_{pc} for the reduction process Co(III) + e$^-$ → Co(II) strongly depend on the nature of the axial ligand PR$_3$ and the σ-donor strength of the phosphine axial ligand.[16] The σ-donor strength of the different axial ligands is also reflected in the spectra of the complexes. The energy of the transition between 550–700nm decreases in the order of PBu$_3$>PPh$_3$. Similar trends are observed for the reduction of Co(III) to Co(II) and oxidation of Co(II) to Co(III). The complexes involved PBu$_3$ as axial ligands is reduced at about –0.400V, whereas the reduction wave for the PPh$_3$ complexes anodically shifted and reduced at –0.0800V. This trend is observed for the oxidation of Co(II) → Co(III) + e$^-$ (Table 2 and Fig. 3)

Equatorial ligand substitutions generally affect reduction potentials less than the axial ligands, a finding that is consistent with electron transfer to dz^2 by formation of Co(II). The functional groups like NO$_2$ and Br on the Schiff base lead to an anodic shift of peak potentials (E_{pc}) for complexes with the same axial ligand, thus making the salophen substituted complexes easier to reduce (Table 2 and Fig. 4). This is because the electron-withdrawing character of the substitutions, which decreases the electron density on the metal centre.[16] The effect of equatorial salophen Schiff base ligands on the reduction potentials is more than the salen complexes. While the maximum range of Co(III/II) potentials in Co(III)salen complexes is only 130mV[17](for same axial ligand), the range of the corresponding Co(III/II) couples of salophen complexes is about 225mV (Table 2). This is because of the greater π-acceptor property of salophen Schiff base complexes.

The Co(II/I)(salophen) couples are not influenced by potential axial ligands, which indicates that only four-coordinate species are involved in the electrode reactions. Equatorial substituents affect these potentials in the same way as for Co(III/II) couples. However, while the maximum range of Co(III/II) potentials is 225mV(for constant axial ligand), the range of the corresponding Co(II/I) couples are about 394 mV. The greater dependence of the Co(II/I) couple on the nature of the equatorial ligand is due to the lower oxidation states that are better electron donors to the π* orbitals of the Schiff base.[16] Thus, from the Co(II/I) couple, the π-acceptor property of the studied salophen Schiff base derivatives is changed in the following trend:

5-nitrosalophen>5-Brsalophen>salophen>
5-MeOsalo-phen>4-MeOsalophen.

Because of the extension of π orbitals in salophen Schiff bases, in contrast to the corresponding salen[17], π-interaction between the Co(III) salophen and metal d orbitals is high and the salophen complexes are better π-acceptors. So the Co(II) salophen complexes are reduced at lower potentials relative to Co(II)salen complexes (Table 2). This property is also reflected in d → d transitions.

Conclusions

From the spectroscopy and electrochemical results, we conclude that d-orbital energy levels are affected by the axial and equatorial ligands, explaining the changes in d → d and MLCT bands and the reduction potentials of the studied complexes. The decrease/increase in the wavelength absorbance of the d → d transition depending on the phosphane axial ligand and equatorial Schiff base ligand suggests that the d → d band arises from field d-orbitals to dz^2. The equatorial Schiff base ligands affect d → d band via π-interaction with field d-orbitals and the axial ligand affects it through σ-intraction with the dz^2 orbital. The MLCT also changes according to the π-acceptor property of the Schiff base ligand and by increasing the π-acceptor property of the Schiff base ligand, the MLCT is shifted to high energy.

The reduction potential of Co(III/II) is strongly dependent on the phosphane axial ligand, while the Co(II/I) couples are not influenced by axial ligand. The π-acceptor property of Schiff base ligands were reflected in the Co(II/I) couples. The NO$_2$ and Br electron-withdrawing groups make the Schiff base a good π-acceptor, while the MeO electron donating group makes it poor one. The salophen complexes are better π-acceptors than corresponding salen complexes.

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