Synthesis, spectroscopy and electrochemistry of cobalt(III) Schiff base complexes

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Three Co(III) complexes of the type [Co(chel)(PBu_3)]$ClO_4.H_2O$, (chel = 5-BrSalen, 5-MeOSalen and 4-MeOSalen), were synthesised and characterised by elemental analysis, IR, UV-Vis and ^1H NMR spectroscopy. In their electronic spectra, the absorptions between 550 and 750 nm of these complexes are attributable to the lowest d–d transition. The axial ligands affect this transition through a σ-intraction with the dz^2 orbital and the equatorial ligands affect it by π-interaction with populated d-orbitals. On the basis of an electronic structural model, in which the dz^2 orbital is populated in forming cobalt(II), it is suggested that equatorial ligand substitution affects the reduction potentials less than axial ligand substitution.

Keywords: cobalt, Schiff base, spectroscopy, electrochemistry

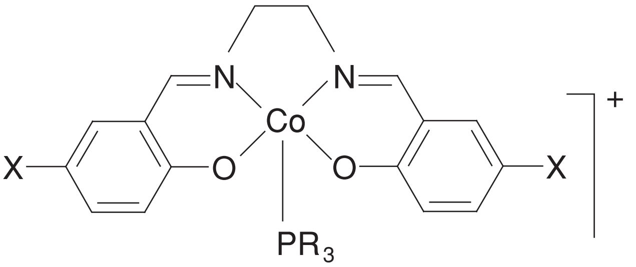

Fig. 1 The structure of [Co(Chel)(PR_3)]$ClO_4.H_2O$, complexes. X = H, NO_2, Br, MeO, and 4-MeO, R = Bu, Ph and Me_2Ph.

Table 1 Electronic absorption data for [Co(X-Salen)(PR_3)]$ClO_4.H_2O$, complexes

No.	X	PR_3	$\lambda_{nm}(\varepsilon M^{-1}cm^{-1})$	
1	H	PPh_3	740(450)	402(5200)
2	H	PMe_2Ph	632(900)	402(6500)
3	H	PBu_3	633(1150)	402(7700)
4	5-MeO	PBu_3	667(1050)	418(7300)
5	4-MeO	PBu_3	635(940)	388(9700)
6	5-Br	PBu_3	629(1000)	409(5700)
7	5-NO_2	PBu_3	589(500)	362(4600)

The cobalt complexes of tetradentate Schiff base ligands have been used extensively to mimic cobalamin(B_{12}) coenzymes, dioxygen carriers, oxygen activators, and enantioselective reductions.[1-8] For finding the catalytic power of these type of complexes, the electrochemical properties of Co(III) salen [salen = bis(salicylaldehyde)ethylenediimine] and similar Schiff bases have been investigated extensively.[9-15] Electrochemical behaviour of [Co(chel)(PR_3)]$ClO_4.H_2O$, as a molecular model of vitamin B_{12} was investigated.[16] In continuation of our studies on the cobalt(III) complexes containing Schiff base ligands,[17-19] we report the novel complex [Co(chel)(PBu_3)]$ClO_4.H_2O$, (chel = 5-BrSalen, 5-MeOSalen or 4-MeOSalen). We have also studied the electronic spectra and the electrochemical behavior of a series of Co(III) salen complexes with the goal of evaluating the effects of substitution of the axial and equatorial ligands (Fig. 1).

Experimental

Ethylenediamine, salicylaldehyde, 5-nitrosalicylaldehyde, 5-methoxysalicylaldehyde, 4-methoxysalicylaldehyde, 5-bromosalicylaldehyde, cobalt(II)acetatetetrahydrate, tributylphosphine, dimethylphenylphosphine, triphenylphosphine, methanol, ethanol, DMF and sodium perchlorate monohydrate were purchased from Merck, Aldrich and Fluka.

Infrared spectra were recorded by a Perkin Elmer 781 IR spectophotometer. Electronic absorption spectra were recorded on a Jasco V-530 spectrometer. NMR spectra were obtained on a Bruker Avance DPX 250 MHe NMR spectrometer. Elemental analysis were performed using a Heraeus CHN-O-RAPID elemental analyser.

Cyclic voltammograms were performed using an autolab modular electrochemical system (ECO Chemie, Ultrecht, The Netherlands) equipped with a PSTA 20 module and driven by GPES (ECO Chemie) in conjunction with a three-electrode system and a personal computer for data storage and processing. An Ag/AgCl(saturated KCl)/3M KCl reference electrode, a Pt wire as counter electrode and a glassy carbon electrode as working electrode were employed for the electrochemical studies. Voltametric measurements were performed at room temperature under argon in DMF solution with 0.1M [NEt_4]ClO_4 as the supporting electrolyte.

Synthesis of the complexes

H_2Salen and other Schiff bases were prepared acoording to the literature by condensation of 1,2-ethylenediamine with an aldehyde (1:2 mole stochiometric ratio) in methanol or ethanol.[20] The complexes [Co(Salen)(PR_3)]$ClO_4.H_2O$ (PR_3 = PBu_3, PPh_3 or PMe_2Ph) and [Co(5-nitroSalen)(PBu_3)]$ClO_4.H_2O$ were prepared by the methods described previously.[17,21,22] The new complexes were made according to the known method.[19]

Analysis calculated(found) for [Co(5-BrSalen)(PBu_3)]$ClO_4.H_2O$, $C_{28}H_{41}Br_2CoClN_2O_7P$ (M.Wt = 800.5), yield: 85%: C 42.0 (42.2), H 5.2(5.2), N 3.5(3.6). [Co(5-MeOSalen)(PBu_3)]$ClO_4.H_2O$, $C_{30}H_{47}CoClN_2O_9P$ (M.W = 702.5), yield: 65%: C 51.3(51.7), H 6.7(6.7), N 4.0(4.1). [Co(4-MeOSalen)(PBu_3)]$ClO_4.H_2O$, $C_{30}H_{47}CoClN_2O_9P$ (M.W = 702.5), yield: 70%: C 51.3(51.7), H 6.7(6.7), N 4.0(4.1).

Results and discussion

Spectral characterisation

IR spectra: The absence of coordinated water in the complexes studied was confirmed by the absence of a absorption band[22] at around 3100 cm^{-1}. The absorption band around 1600 cm^{-1} is related to the azomethine group.[24,25]

Electronic spectra: The electronic spectral data of the complexes in ethanol are listed in Table 1. The absorption spectrum of the H_2Salen ligand exhibits three bands in the region of 405nm ($\varepsilon \approx 700M^{-1}cm^{-1}$), 317nm ($\varepsilon \approx 8500M^{-}1\ cm^{-1}$) and 257nm ($\varepsilon \approx 17000M^{-1}\ cm^{-1}$), that are assigned to $n_N \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and $n_O \rightarrow \pi^*$ respectively. The first transition disappeared upon coordination of Salen to the cobalt ion.[25,26] In the Co(III) Schiff-base complexes the $\pi \rightarrow \pi^*$ and $n_O \rightarrow \pi^*$ bands are observed at similar energy to the free ligand. Some transitions are observed in Co(III) Schiff-base complexes in addition to these bands.

[Co(Chel)(PR_3)]$^+$ complexes are green and exhibit a low-energy transition in the visible region of the spectrum.[17,21,22] This transition has been interpreted as being characteristic of five-coordinated, square pyramidal geometry[22] and is assigned

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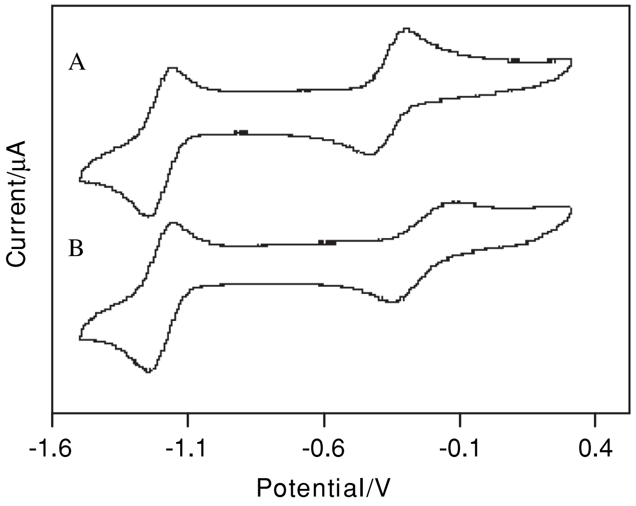

Fig. 2 Cyclic voltamogram of [Co(Salen)(PBu_3)]$ClO_4.H_2O$, A(0.001M, PBu_3) in DMF at room temprature. Scan rate: 100 mV/s.

to a d–d transition.[23,28] In presence of axial ligands,[17-19,21,22] the green solutions of [Co(chel)(PR_3)]$^+$ changes to deep red, and the low-energy transition is replaced by more intensive absorptions in the range of 16–22 kK. This is due to formation of hexa-coordinated complexes in the presence of the axial ligands. The transition energy of this band decreases in the trend, $PMe_2Ph \approx PBu_3 > PMePh_2 > PPh_3$. Calculations for an empirical crystal field model show that the ligand field strengths for the phosphines as axial ligand in this type of complex decrease in the order, $PMe_2Ph \geq PBu_3 > PMePh_2 > PPh_3$.[22] By increasing the ligand field strength of the axial ligand in five-coordinated complexes of [Co(Chel)(PR_3)]$^+$ and the hexacoordinated form of [Co(Chel)$(PR_3)_2$]$^+$ complexes, the antibonding character of the dz^2 orbital is increased. These results show that dz^2 is the LUMO in this transition.

The electronic effect of equatorial Schiff-base ligands on the electronic spectra of Co(III) complexes was investigated. It can be seen that the exitation energy for the above transition increases in the order, 5-nitroSalen > 5-BrSalen ≈ Salen ≈ 4-MeOSalen > 5-MeOSalen (Table 1). The ligand field parameter D_q^{yx} for Salen complexes was shown to be about 2560cm^{-1} from the two lowest energy bands of the spectra in ethanol (95%).[22,27] Correlation of ligand field transition (d–d transition) and ligand field strength in the Co(III) Schiff-base complexes show that the ligand field strength increases in the trend, 5-nitroSalen > Salen > 5-MeOSalen. As a result of their functional groups, the σ-donation power of these ligands increases in the reverse trend, thus we assume π-interactions between d orbitals and π* orbitals on the Schiff-base ligands. The filled d orbitals(d_{xz}, d_{yz} and d_{xy}) can interact with π* orbitals on the equatorial Schiff-base *via* π-backbonding. In this interaction, the energy level of the d orbitals decreases while the energy level of the π* orbitals increases.[28] This change is strongly related to the interaction between the two set of orbitals. The cobalt π-donation to the Schiff-base equatorial ligand is increased by electron-withdrawing groups on the Schiff-base ligand, and decreased by electron-donating groups. Thus the π-backbonding interactions decrease in the order 5-nitroSalen > Salen > 5-MeOSalen and the filled d orbital s energy level has a reverse trend in related complexes. Similarly, the field energy of the d orbitals (HOMO orbitals) increases in the trend 5-nitroSalen < Salen < 5-MeOSalen and the excitation energy changes in the reverse order.

Table 2 Reduction potentials(in V) for [Co(X-Salen)(PR_3)]$ClO_4.H_2O$, in DMF

No.	X	PR_3	E_{pa}(II → III)	E_{pc}(III → II)	$E_{1/2}$(II ↔ I)
1	H	PPh_3	+0.109	+0.056	–1.218
2	H	PMe_2Ph	–0.220	–0.412	–1.218
3	H	PBu_3	–0.218	–0.415	–1.218
4	5-MeO	PBu_3	–0.211	–0.401	–1.262
5	4-MeO	PBu_3	–0.218	–0.415	–1.316
6	5-Br	PBu_3	–0.150	–0.367	–1.085
7	5-NO_2	PBu_3	–0.137	–0.284	–0.928

The second important transition is seen about 400nm. The excitation energy of this transition does not change for a typical Schiff base with the different phosphine axial ligands. On the other hand, for different equatorial Schiff-base ligands, excitation energy increases in the order 5-nitroSalen > 4-MeOSalen > Salen > 5-BrSalen > 5-MeOSalen (Table 1). It seems that this is an inter-ligand π → π* transition and its energy level is changed by the type of functional group on the Schiff-base ligands.[26] Theoretical calculations are necessary to allow extension of this discussion.

Electrochemical investigation

A typical cyclic voltammogram of a [Co(Salen)(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. The first reduction peak is observed at about –0.415V which is due to the process

$$[Co^{III}(Salen)(PBu_3)]^+ + e^- \rightarrow [Co^{II}(Salen)] + PBu_3$$

The electron is added to the antibonding dz^2 orbital of the Co(III) complex and the product losses its axial ligand in weakly coordinating solvents.[15] The second quasi-reversible prosess at *ca* –1.276V is observed with about unit ratio of anodic to cathodic peak currents (i_{pa}/i_{pc}), corresponding to the simple one electron process

$$[Co^{II}(Salen)] + e^- \rightarrow [Co^{I}(Salen)]$$

Upon reversal of the scan direction, the Co(II) complex is oxidised to Co(III) at higher potentials (about 100 mV). Then, in a rapid consecutive reaction, the five-coordinate species [Co^{III}(Salen)(PR_3)]$^+$ is formed again(*i.e.*, the electron transfer is followed by a chemical reaction).[15] 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.

Figure 2B shows the effect of PR_3 concentration on the electrochemical behaviour of [Co^{III}(Salen)(PR_3)]$^+$: upon addition of phosphine (0.001M); oxidation occures at lower potential whereas the rduction wave is shifted in the negative direction (hexa-coordinated complex is formed). The changes are due to increasing the antibonding character of the 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 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.

The observed chatodic 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

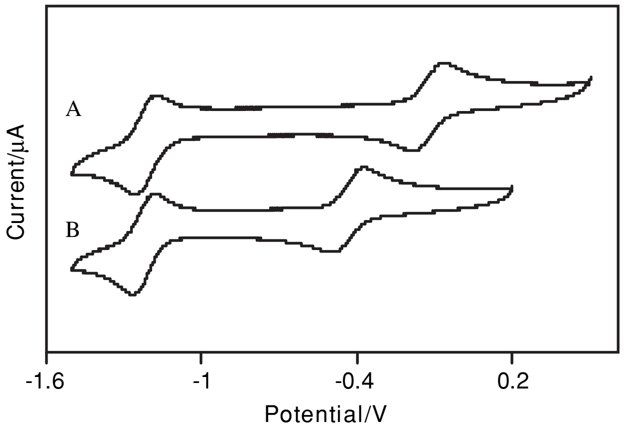

Fig. 3 Cyclic voltamogram of [Co(Salen)(PR$_3$)]ClO$_4$.H$_2$O, A(R = Ph), B(R = Bu). in DMF at room temprature. Scan rate: 100 mV/s.

axial ligand.[15,22] 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 and 750nm decreases in the order PBu$_3$ ≈ PMe$_2$Ph > 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$_3$ and PMe$_2$Ph as axial ligands are reduced at about –0.415V, whereas the eduction wave for the PPh$_3$ complex is anodically shifted and it reduces at +0.056V. This trend is observed for the oxidation Co(II) + e$^-$ → Co(III) (Table 2 and Fig. 3)

Equatorial ligand substitutions genrally 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 Salen substituted complexes easier to reduce (Table 2 and Fig. 4). The reason for this is the electron-withdrawing character of the substituents, which decreases the electron density on the metal centre.[15]

The Co$^{(II/I)}$(Salen) couples are not influenced by potential axial ligands,[29] 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 only 130mV (for constant axial ligand), the range of the corresponding Co(II/I) couples is about 388 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.[15] Thus for the Co(II/I) couple, the π-acceptor property of the studied Salen Schiff base derivatives is changed in the following trend:

5-nitroSalen > 5-BrSalen > Salen >
5-MeOSalen > 4-MeOSalen

Conclusions

By considering the Vis-spectroscopy and electrochemical behaviour of penta-coordinate Co(III) Schiff base complexes, the following conclusions have been drawn:

(a) The ligand field strength of a pentacoordinate Co(III) Schiff base complex like [Co(chel)(PR$_3$)]ClO$_4$.H$_2$O is changed according to the following trend for phosphine axial ligands: PMe$_2$Ph ≈ PBu$_3$ > PPh$_3$

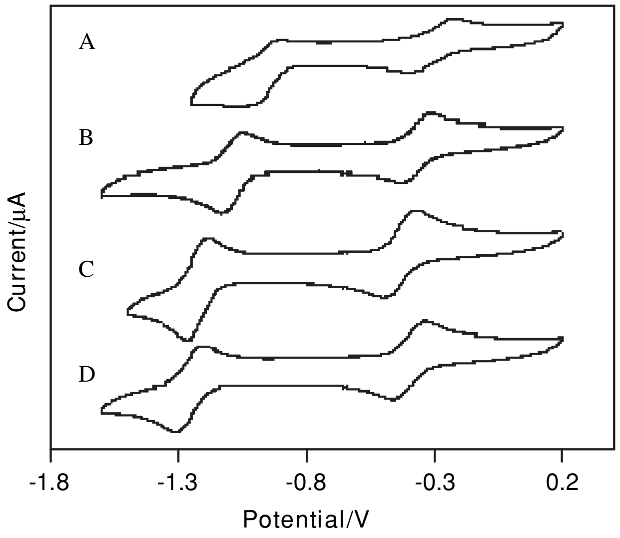

Fig. 4 Cyclic voltamogram of [Co(5-X-Salen)(PBu$_3$)]ClO$_4$.H$_2$O, A(X = NO$_2$), B(X = Br), C(X = H), D(X=MeO), in DMF at room temprature. Scan rate: 100 mV/s.

(b) From the electronic spectra, the π-acceptor property of pentacoordinate Co(III) Schiff base complexes like [Co(chel)(PR$_3$)]ClO$_4$.H$_2$O is changed according to the following trend for the Schiff-base ligands: 5-nitroSalen > Salen > 5-MeOSalen.

(c) The cathodic peak potentials E$_{pc}$ for the reduction process Co(III) + e$^-$ → Co(II) depend on the nature of the axial ligand PR$_3$ and change according to the following trend for phosphine axial ligands: PMe$_2$Ph ≈ PBu$_3$ > PPh$_3$

(d) The Co$^{(II/I)}$(Salen) couples are not influenced by potential axial ligands.[29]

(e) From the reduction potentials the π-acceptor property of the studied Salen derivatives is changed in the following trend

5-nitroSalen > 5-BrSalen > Salen >
5-MeOSalen > 4-MeOSalen

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29 for 5-nitroSalen the $Co^{(II/I)}$(Salen) couple is changed about 40mv in the presence of additional phosphine and it seems that Co^{II}(nitroSalen) is in equilibrium with PBu_3 in high concentration of phosphine.