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Spectrophotometric Study of Adduct Formation Between [Co(Salen)PPh₃]ClO₄.H₂O and [Co(7,7'-Dimethylsalen)PPh₃]ClO₄.H₂O with Amines Donors in Acetonitrile

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Abstract: The equilibrium quotient of the adduct formation of [Co(Salen)PPh₃]ClO₄.H₂O and [Co(7,7'-dimethylSalen)PPh₃]ClO₄.H₂O, as acceptor with amines donors are studied by spectrophotometer. Thermodynamics of these pentacoordinate cobalt(III) Schiff-base complexes have been examined with *n*-butylamine, *sec*-butylamine, *tert*-butylamine, benzylamine and diethylamine in constant ionic strength of 0.1 M sodium perchlorate and acetonitrile solvent at room temperature. We aimed to investigate the effects of different electronic and steric situations of donor and acceptor by comparing their equilibrium quotient for any adduct.

Keywords: Thermodynamic, Cobalt Schiff-base, Adduct, Equilibrium quotient.

Introduction

The Schiff base prepared from condensation reactions between carbonyl group and amine with lost water. Whether the carbonyl compound is an aldehyde or a ketone, the Schiff bases may be an aldimine or a ketimine, respectively. Both aldimine and ketimine containing a C=N bond and so these procedures are a general method for development of nitrogen heteroatom in organic, organometallic and bioorganic compounds. Schiff base ligands are able to coordinate many different metals and to stabilize them in various oxidation states, enabling the use of Schiff base metal complexes for a large variety of useful catalytic transformations¹. Schiff base improved conservative reactions such as allylic alkylation,

hydrosilation of acetophenones, decomposition of hydrogen peroxide, michael addition, annulation, carbonylation, Heck reaction, benzylation of alanine, amidation and aziridination of hydrocarbons, isomerization of norbornadiene to quadricyclane, addition of cyanides to imine, cyclopropanation, silylcyanation of aldehydes, desymmetrization of *meso* compounds, Diels–Alder reaction, aldol condensation reaction².

Condensation two equivalents of salicylaldehydes or salicylaldehyde derivatives with 1,2-diamines leads to the formation of one extremely important class of ligands, generally known as ‘‘Salens’’ (Figure 1)^{3,4}. The so-called Salen ligands, with four coordinating sites and two axial sites open to ancillary ligands, are very much like porphyrins, but more easily prepared. Although the term Salen was used originally only to describe the tetradentate Schiff bases derived from ethylenediamine, the more general term Salen-type is used in the literature to describe the class of [O, N, N, O] tetradentate bis-Schiff base ligands (Figure 1). The term Schiff base is used for most propose in situation to the tetradentate bis-Schiff base ligand, regularly⁴.

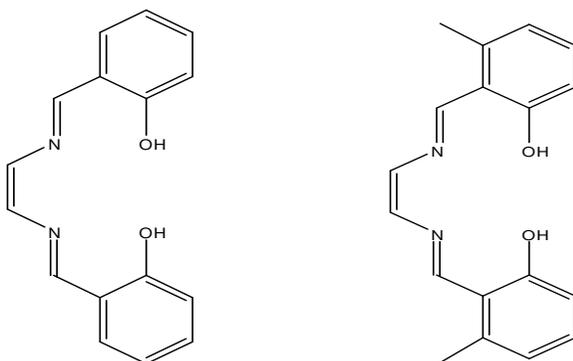


Figure 1. Tetradentate bis-Schiff base Salen and 7,7'- dimethylsalen ligands

Schiff base ligands are coordinate to different metals and a range of coordination numbers in various oxidation states. The most important coordination numbers for Schiff base ligands are four, five and six. The coordination of Schiff base ligands with cobalt is attractive with three major reason, because of biological roles, stability of examination and suitability in times of changes⁴.

Co(III) Schiff base complexes with bonded carbon and phosphines as axial ligands were proposed as model molecules for comparing the activities with biological Co(III) complexes^{5,6}, like vitamin B₁₂. Recently in the article review, the role of Schiff base in various biological systems, polymers and dyes are investigated⁷. (Also see corresponding references cited in the article) pentacoordinated Schiff base can be found in a large number of compounds which display biological activity. The biological activity of the compounds is mainly dependent on their molecular structures. It is also known that the spectral behavior of a molecule is strongly related to its structure. Based on these knowledges, a considerable work has been reported on the spectroscopic behavior of Schiff bases⁴.

In this study, we aimed to investigate the effects of different electronic and steric situations of pentacoordinate Schiff base complexes like [Co(Salen)(PPh₃)]ClO₄·H₂O and [Co(7,7'-dimethylSalen)(PPh₃)]ClO₄·H₂O with amine donors in acetonitrile solvent.

Experimental

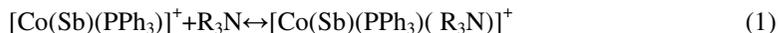
[Co(Salen)(PPh₃)]ClO₄·H₂O and [Co(7,7'-dimethylSalen)(PPh₃)]ClO₄·H₂O used as prepared and characterized according to corresponding reference^{8,9}. The other materials used are as follows with mass fraction purity as stated: *n*-butylamine (Merk, > 99%), *sec*-butylamine (Merk, 99%), *tert*-butylamine (Merk, 99%), benzylamine (Merk, 99%), diethylamine (Merk, 99%), acetonitrile (Merk, 99%) and sodium perchlorate monohydrate (Merk, 99%).

Instrumentation

All of the scanning UV-Vis spectra were recorded by Lambda 25 Perkin Elmer spectrophotometer.

Thermodynamic studies

The adduct complexes were obtained from the reaction of the acceptors with the donors, according to the following equations:



Where Sb = Schiff-base (Salen and 7,7'-dimethylSalen); R₃N = *n*-butyl amine, *sec*-butyl amine, *tert*-butyl amine, benzyl amine and diethyl amine.

A solution from each complex with concentration at about 5.0×10⁻⁵ M and constant ionic strength (I=0.1 M) by sodium perchlorate was prepared. A total of 3.0×10⁻³ dm³ was transferred into the cell compartment of the UV-Vis instrument, which was titrated by amine. Adding aliquots of amine with a Hamilton microlitre syringe carried out the titration at 25 °C. The donor concentrations were varied one to ten fold in excess.

When amine as a donor (D) reacts with [Co(Sb)(PPh₃)]⁺ ions as acceptors (A) to form a 1:1 adduct complex (AD), Q for equation (1) are:

$$Q = \frac{[\text{Co}(\text{Sb})(\text{PPh}_3)(\text{amine})^+]}{[\text{Co}(\text{Sb})(\text{PPh}_3)^+] \times [\text{amine}]} \quad (2)$$

The absorption measurements were carried out in the range of 200-800 nm. The electronic spectra of [Co(Salen)(PPh₃)]ClO₄·H₂O and [Co(7,7'-dimethylSalen)(PPh₃)]ClO₄·H₂O show an absorption at 600 to 700 nm region in non-coordinating solvent. In attendance of an amines donor a six-coordinated species formed that absorb at 365 to 410 nm region¹⁰ with respect to kind of amine and complex (Figure 2).

Results and Discussion

The absorption measurements were carried out at various wavelengths in the 200 to 800 nm region during the equilibrium was matched. All measurements for the thermodynamic studies were carried out in this range. As an example, the variation of the electronic spectra for [Co(Salen)(PPh₃)]⁺ titrated with *t*-butyl amine in CH₃CN at 25 °C, is shown in Figure 2 in the 280 to 580 nm region. The isosbestic points at 287, 369, 420 and 489 nm for this system indicating that only one amine is added to the substrate and that this is a 1:1 system. The similar isosbestic points are observed for other systems that revealed only one reaction in equilibrium.

In Figure 2, we simplified the vertical axis by selecting the smaller number of titration for variation of electronic spectrum of [Co(Salen)(PPh₃)]⁺ with *t*-butyl amine in CH₃CN at 25 °C.

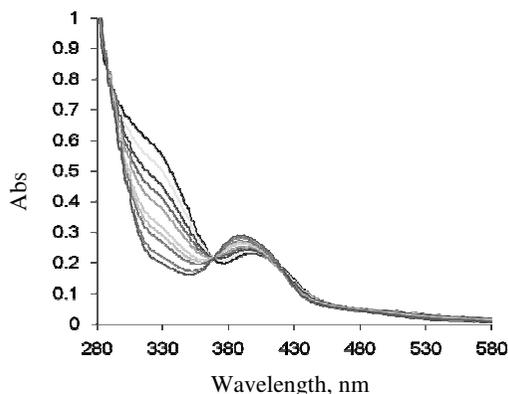


Figure 2. Variation of electronic spectra of $[\text{Co}(\text{Salen})(\text{PPh}_3)]^+$ with *tert*-butylamine in CH_3CN at 25°C in 280 to 580 nm region for number of titration correspondent to 10 series

The absorption measurements were carried out for a series of spectral wavelengths where the difference in absorption between the substrate and the product were the large after the equilibrium were assessed. The equilibrium quotients for any adduct formation were determined by squad program. In this program, the non-negative linear squares algorithm should be used and the sum of squares of calculated and observed molar absorptivities minimized by refinement the equilibrium quotients. For run the program, the number of wavelength under study, number of titration, initial acceptor concentration in cell, initial donor concentration and volume of titrant (*i.e.* amine donor) that in each titration has been added to titrate (*i.e.* complex acceptor) should be written separately for every adduct between $[\text{Co}(\text{Sb})(\text{PPh}_3)]^+$ as acceptor with amines donors. The equilibrium quotients of the studied cobalt (III) Schiff base complexes are shown in Table 1.

Table 1. The logarithmic equilibrium quotients for $[\text{Co}(\text{Sb})(\text{PPh}_3)]\text{ClO}_4\cdot\text{H}_2\text{O}$ with various amine donors in acetonitrile solvent

Sb→	Salen	7,7'-Dimethyl Salen
amine donors↓	log Q	log Q
<i>n</i> -butylamine	5.01 ± 0.23	4.53 ± 0.03
<i>sec</i> -butylamine	4.50 ± 0.06	5.75 ± 0.01
<i>ter</i> -butylamine	4.36 ± 0.01	3.46 ± 0.01
benzylamine	4.59 ± 0.05	5.48 ± 0.12
diethylamine	5.94 ± 0.03	5.62 ± 0.09

The $[\text{Co}(\text{Salen})(\text{PPh}_3)]^+$ and $[\text{Co}(7,7'\text{-dimethylSalen})(\text{PPh}_3)]^+$ are stable in solution and they are in equilibrium with sixth ligand. As a result, we are measured the equilibrium quotients for 1:1 adduct formation of these complexes as acceptors with *n*-butyl, *sec*-butyl, *ter*-butyl, benzyl and diethylamine as donors. The measurements were carried out spectrophotometrically in acetonitrile solvent and in constant ionic strength ($I=0.1\text{ M}$) at 25°C . The equilibrium quotient for complex formation of pentacoordinate cobalt(III) Schiff base complexes with amines as donors was determined by making use of numerically squad program. The trend of the reactivity of the amine donors toward $[\text{Co}(\text{Salen})(\text{PPh}_3)]\text{ClO}_4\cdot\text{H}_2\text{O}$ is in operation: diethylamine > *n*-butylamine > benzylamine > *sec*-butylamine > *ter*-butylamine and also, the trend of the reactivity of the amine donors toward $[\text{Co}(7,7'\text{-dimethylsalen})(\text{PPh}_3)]\text{ClO}_4\cdot\text{H}_2\text{O}$ is in operation: *sec*-butylamine > diethylamine > benzylamine > *n*-butylamine > *ter*-butylamine.

For [Co(Salen)(PPh₃)]ClO₄·H₂O we have a lower steric effect and so, the diethylamine with two electron donating group in the nitrogen, has maximum of equilibrium quotient. But the orders of lability of diethylamine cannot be maximum value for the [Co(7,7'-dimethylSalen)(PPh₃)]ClO₄·H₂O, that may possibly be reflect the increasing of steric effect from two methyl group in dimethylsalen with two ethyl group of diethylamine and so lowering the equilibrium quotient for complex formation to the second order. The orders of lability of *sec*-butylamine has a maximum value for the [Co(7,7'-dimethylSalen)(PPh₃)]ClO₄·H₂O, that may be reflect the competition both steric and electronic effects.

There are apparent that toward both complexes *tert*-butylamine has a minimum of equilibrium quotient that returned to the steric effect between donor and acceptor as determining effect. This trend shows that the steric factor is more important than the electronic factor for each donor toward a given acceptor.

Conclusion

From the present investigation, the following conclusion can be acquired:

- The trend of the reactivity of the amine donors toward [Co(Salen)(PPh₃)]ClO₄·H₂O is in order: diethylamine > *n*-butylamine > benzylamine > *sec*-butylamine > *tert*-butylamine
- The trend of the reactivity of the amine donors toward [Co(7,7'-dimethylsalen)(PPh₃)]ClO₄·H₂O is in order : *sec*-butylamine > diethylamine > benzylamine > *n*-butylamine > *tert*-butylamine.
- The steric factor is more important than the electronic factor for each amine donor toward given cobalt Schiff base acceptor.

Acknowledgment

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