

Reactivity Study of Ion -Paired Associated Cobalt (III) Complexes with Schiff Bases

Dr. Sanjib Kumar Bhar

Department of Chemistry, Khalisani Mahavidyalaya, Chandannagar, Hooghly, India

Received: Revised: , Accepted:.

Published online:

Abstract: Double complexes / Ion – paired associated complexes of cobalt (III) are always under investigation due to poor solubilities and hence it becomes difficult to bring them into effective reaction with other ligands. The present work involves to reactivity study of double complex $[\text{Co}(\text{en})_3][\text{Co}(\text{NO}_2)_6].3\text{H}_2\text{O}$ with bidentate and tetradentate Schiff bases and characterization by IR, UV, TG -DTG and FAB -MS

Keywords: Schiff base, Cobalt, Mixed ligand complex, SALEN, SALOP

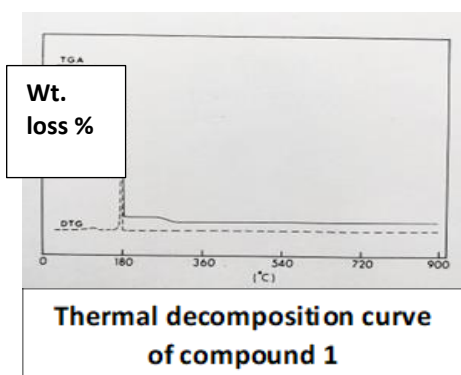
1. Introduction

A large variety of organic molecules can usually be attached to transition metals. Among the different molecules, the Schiff bases have been found to play a very significant role as chelating agents for a large variety of metal ions^(1,2,3). In these transition metal complexes, NH_3 , pyridine (Py), Cl^- , SCN^- etc. or organic moieties like $-\text{CH}_3$, $-\text{C}_6\text{H}_5$ and **acac** (acetylacetonate), **sal** (Salicylaldehyde) etc. and for chelates, the dibasic tetradentate Schiff base takes a vital role for the biological system. Experimental data regarding state properties and thermodynamic, kinetic aspects of reactivity, show a varying influence of axial and equatorial ligands. Thus, different interactions may be due to different bonding situations around the central metal ion. All these studies lead to clarify the exact role of metal ions in the overall catalytic functions of vitamin B₁₂ compounds. Although few ion-paired associated complexes or the so-called double complexes of cobalt(III) i.e. $[\text{Co}(\text{X})\text{m}][\text{Co}(\text{Y})\text{n}]$ are known^(4,5,6,7) and moreover further studies regarding synthesis, characterization and possible reactivity have been reported also^(8,9). But no systematic approach has been made towards the optimization of their formations, reactions and spectral as well as their thermal properties. To go ahead with this approach, investigations on the reactivity of Schiff bases and related ligands on cobalt (III) complexes, a couple of ion – pair associated complexes have been prepared which in turn subjected to reactions with both bi- and tetradentate Schiff base ligands whereby reactivity may take place either in one ionic part or in both the ionic parts. The present work involves reactivity studies of double complexes, $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$ and $[\text{Co}(\text{en})_3][\text{Co}(\text{NO}_2)_6].3\text{H}_2\text{O}$ etc. towards bidentate and tetradentate Schiff bases.

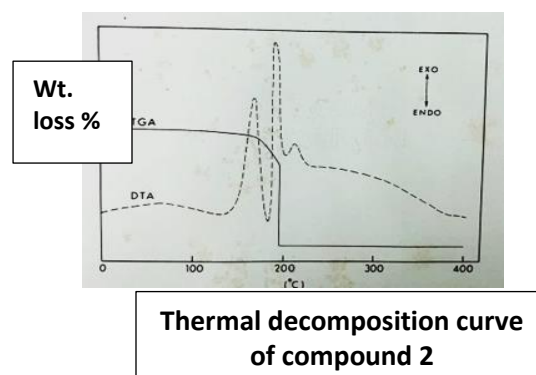
2. Preparation of double complexes

Equimolar quantities of $[\text{Co}(\text{en})_3]\text{Cl}_3$ and $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ were dissolved separately in two beakers in minimum volume of water. Slow addition of orange colour solution of $[\text{Co}(\text{en})_3]\text{Cl}_3$ into reddish-orange colour solution of $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ led to immediate formation of orange -yellow colour heavy precipitate of $[\text{Co}(\text{en})_3][\text{Co}(\text{NO}_2)_6].3\text{H}_2\text{O}$ (**1**) and the reaction mixture was allowed to kept at room temperature for half an hour for the completion of reaction. It was filtered, washed thoroughly with water and finally with ethanol and then kept for drying in air oven for 12 hrs. **Yield ~ 82 %**, **m.p. 185 °C (dec)**. Another double complex, $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$ was prepared in the same way from the equimolar mixing of solutions of starting materials $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$. **Yield ~ 81 %**, **m.p. 165 °C (dec)**. Both $[\text{Co}(\text{en})_3][\text{Co}(\text{NO}_2)_6].3\text{H}_2\text{O}$ and $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$ (**2**) are sparingly soluble in water, alcohol and common organic solvents but found to soluble in polar solvents like DMF, DMSO and pyridine.

*Corresponding author e-mail: skbhar2020@gmail.com



(Fig. 1)



(Fig. 2)

Thermal decomposition studies of the complexes $[\text{Co}(\text{en})_3][\text{Co}(\text{NO}_2)_6] \cdot 3\text{H}_2\text{O}$ (**1**) and $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$ (**2**) were carried out in the temperature range 30 – 900 °C and corresponding data are presented in **Table-1**

Table 1: Thermal decomposition data of double complexes (**1**) & (**2**)

Compound	Temperature in °C	Weight loss %		Species formed	DTA / DTG (°C)
		Obs.	Calcd.		
$[\text{Co}(\text{en})_3][\text{Co}(\text{NO}_2)_6] \cdot 3\text{H}_2\text{O}$ (1)	90 -130	8.59	8.42	$[\text{Co}(\text{en})_3][\text{Co}(\text{NO}_2)_6]$ Co_3O_4	114.6 (DTG) 181.4 (DTG)
	130 -350.6	74.13	74.41		
$[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$ (2)	65 -70	20.46	20.57	2 $\text{Co}(\text{NO}_3)_3$ Co_3O_4	Exo Exo (162, 187,209)
	70 -230	66.78	67.50		

The TGA curve of the compound (**1**) [Fig.1] suggests that it loses lattice water at around 115 °C, resulting to the formation of anhydrous compound, $[\text{Co}(\text{en})_3][\text{Co}(\text{NO}_2)_6]$ and then begins to lose mass rapidly up to 182 °C and remains constant after 192 °C due to formation of cobalt oxide as residue, Co_3O_4 . The TGA curve of the compound (**2**) [Fig.2] shows that it is thermally stable up to 110 °C, began to lose mass slowly up to 150 °C and reasonably fast at 190 °C and remained constant after 195°C due to formation of as Co_3O_4 residue. The electronic spectra of ion -paired complexes (**1**) & (**2**) are reported in **Table 2**.

Table 2: Electronic spectral data of complexes (**1**) & (**2**)

Compound	λ max (cm^{-1})
(1)	35700, 23255, 19607
(2)	35710, 23200, 19601

All of them show bands in the near UV, visible and near IR region. The bands near 3500 cm^{-1} may be due to $d\pi \rightarrow \pi$ transition of the NO_2^- ligands. The bands at higher frequencies 24000 – 23500 cm^{-1} may be attributed to the first $d-d$ transition of the anionic moiety whereas

the latter ones in the lower frequency region 20000 – 19000 cm^{-1} may be assigned to first $d-d$ transition of the cationic moiety. The bands near 24000 – 23500 cm^{-1} and 24000 – 23500 cm^{-1} corresponds to ${}^1\text{A}_1 \rightarrow {}^1\text{A}_2$ and ${}^1\text{A}_1 \rightarrow {}^1\text{E}$ transitions respectively ⁽⁷⁾ whereas bands near I.R. region 11764 – 11440 cm^{-1} may be considered as due to low energy ion -pair charge transfer transitions ⁽¹⁰⁾. The I.R. spectral data shows a medium but sharp band at 3500 -3400 cm^{-1} region and regarded as $\nu(\text{OH})$ of the lattice water molecules of compound (**1**). The band pair in the region 3300 -3100 cm^{-1} corresponds to symmetric and anti-symmetric stretching of $\nu(\text{NH}_2)$. Again, appearance absorptions of around 1650 – 1560 cm^{-1} due to mix up of bindings of $\delta(\text{NH}_2)$ and $\delta(\text{HOH})$. The bands at ~ 1350 and 1320 cm^{-1} and at 830 cm^{-1} are assigned asymmetric $\delta(\text{NO}_2)$ and symmetric $\nu(\text{NO}_2)$ and $\delta(\text{NO}_2)$ vibrations. The bands near 500 and 416 cm^{-1} are probably due to $\nu(\text{Co-N})$ absorptions arising out of the $\text{Co-N}(\text{NH}_2)$ and $\text{Co-N}(\text{NO}_2)$ co-ordinations (**Table -3**).

Table 3: I.R. spectral data of ion -paired Complexes (1) & (2)

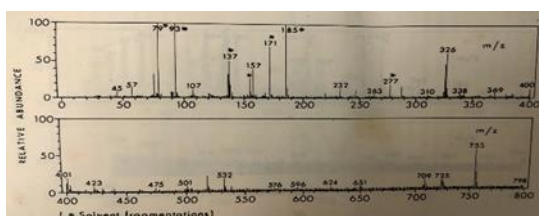
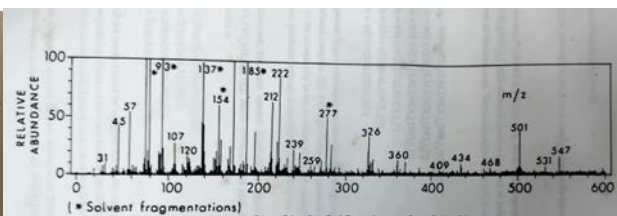
Compound	Bands (cm ⁻¹)
(1)	3516 (s), 3445 (m), 3267 (sh), 3210 (s), 3149 (sh), 3099 (sh, sharp), 2985 (sh), 2906 (sh), 1653 (sh), 1613 (m), 1582 (s), 1557 (s), 1462 (s), 1398 (vs), 1329 (vs), 1298 ((sh), 1248 (sh), 1155 (m), 1120 (m), 1054 (s), 1016 (w), 893 (w), 829 (w), 772 (m), 627 (m), 578 (m), 518-439 (w, sh), 416 (m)
(2)	3180-3030 (m, br), 2740 (w), 2640 (w), 1660-1590 (s, br), 1420(sh), 1385 (m), 1355-1320 (m, br), 1170 (w), 870 (sh, sharp), 840 (vs), 732 (w). 630 (sh), 600 (m)

3. Results & Discussion

The present work involves the reaction of double complex, [Co(en)₃][Co(NO₂)₆].3H₂O (**1**) with tetradentate Schiff bases like SALENH₂ and 5-Br SALENH₂ and bidentate Schiff bases e.g. SALOPH and SALENOLH.

Reaction of, [Co(en)₃][Co(NO₂)₆].3H₂O (**1**) with Schiff bases (both bidentate & tetradentate) were found to be very difficult to take place. Ethanolic suspension of the double complex (**1**) when brought into reactions with Schiff bases, no reaction took place even after vigorous refluxing. But, on addition of few ml water, it was found that reaction became occurring indicated by the deepening of the colour of the reaction mixture. However, the reaction was allowed to reflux for 2 hrs. Thus, on reaction with both tetradentate and bidentate Schiff bases, brown to deep brown colour mixed ligand complexes, [Co(SALEN)(en)][Co(SALEN)(NO₂)₂] (**3**), [Co(5-BrSALEN)(en)][Co(5-BrSALEN)(NO₂)₂] (**4**), [Co(SALOP)₂(en)][Co(SALOP)₂(NO₂)₂] (**5**), [Co(SALENOL)₂(en)][Co(SALEOL)₂(NO₂)₂] (**6**), were obtained as residue. After filtration, the volume of the filtrate was reduced to half and subsequent cooling, solid crystals of [Co(SALEN)(NO₂)(H₂O)](**7**), [Co(5-BrSALEN)(NO₂)(H₂O)] (**8**), [Co(SALOP)₂(NO₂)(H₂O)] (**9**), [Co(SALENOL)₂(NO₂)(H₂O)] (**10**) were obtained and latter recrystallized.

All double complexes (**3**) – (**6**) are found to be insoluble in ethanol, water, and other organic solvents but highly soluble in DMF, DMSO. On the other hand, the neutral complexes (**7**) – (**10**) are reasonably soluble in ethanol on warming and subsequent cooling. The mass spectra (FAB-MS) in glycerol of the complex (**3**) showed molecular ion peak at m/z = **755** [Fig. 3] i.e. M⁺ - NO₂ where M is the molecular weight of the Compound (3). The molecular ion peak identified as m /z = 709 (= [Co(SALEN)(en)]⁺); 651 (= [Co₂(SALEN)₂]⁺); 532 (= [(SALEN)₂]⁺); 325 (= [Co(SALEN)]⁺)


(Fig. 3)

(Fig. 4)

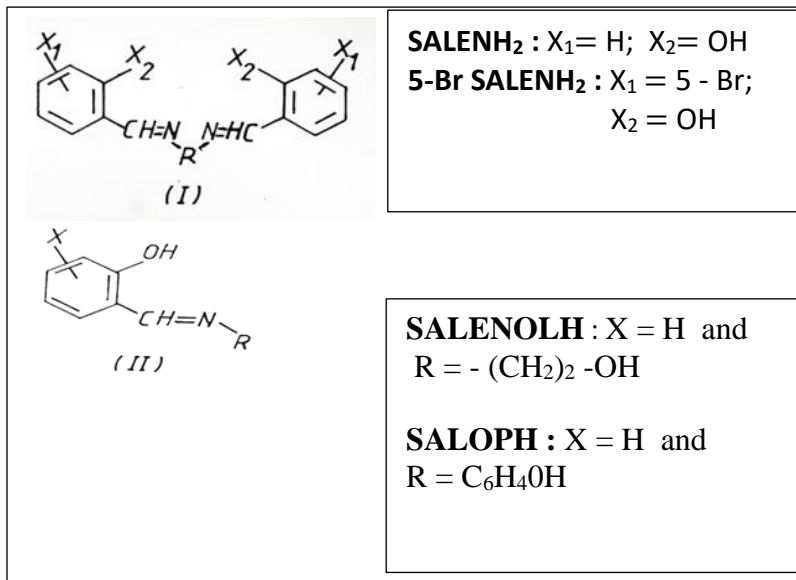
On the other hand, mass spectra (FAB-MS) [Fig. 4] in glycerol of the compound [Co(SALOP)₂(NO₂)(H₂O)] (**9**) shows molecular ion peak at m/z = 501 (= [Co(SALOP)₂(H₂O)]⁺); = 271 (= [Co(SALOP)]⁺); = 259 (= [(SALOP)(NO₂)]⁺); = 212 (= [(SALOP)]⁺).

The electronic spectra of all the complexes show bands at about 47000-40000 cm⁻¹ and 29000-24000 cm⁻¹ and 21200-19607 cm⁻¹ region which may be considered as typical pseudo-octahedral geometry around cobalt (III) ⁽⁹⁾. The bands near 21200-19607 cm⁻¹ may be due to ¹A_{1g} → ¹T_{2g} transitions together with the metal to ligand (t_{2g} → π) transitions ⁽¹¹⁾. The bands near 41000 cm⁻¹ are due to d π → π* transition of the Schiff bases and the other intensive band near 35000 cm⁻¹ (log ε = 4.88) may be due to d π → π transition of the NO₂ ligand.

The I.R. spectrum of the compounds show medium broad band in the region 3420-3200cm⁻¹ which may be considered as due to the mixing of ν(OH) of the bidentate Schiff bases along with ν(NH₂) of the coordinated ethylenediamine ^(9, 11). The medium sharp band at 2950 cm⁻¹ assigned as ν(C-H) vibrations ⁽¹²⁾. The bands appeared in the region 1650-1600 cm⁻¹ are possibly due to the presence of the coordinated ν(C = N) groups of Schiff bases ⁽¹¹⁾. The presence of ν(C = C) and δ(OH) vibrations make the assignment of ν(C = N) bands somewhat complicated. Absorptions appeared in 1620-1550 cm⁻¹ are possibly due to δ(NH₂). Bands near 1445 and 1365 cm⁻¹ are due to δ(C-H) of the -CH₂ groups. Whereas bands near 1350 and 1320cm⁻¹ are considered to be asymmetric and symmetric stretching modes of -NO₂ groups bonded through nitrogen and the band at ~ 829 cm⁻¹ due to bending vibrations ^[1]. The bands at appeared in the region 845 – 840 cm⁻¹ may

be regarded as $\delta(\text{HOH})$ ⁽¹⁴⁾. The bands at ~ 536 , ~ 500 and $\sim 460 \text{ cm}^{-1}$ are possibly due to $\delta(\text{Co-N})$ absorptions of coordinated $>\text{C}=\text{N}$, $-\text{NH}_2$ and $-\text{NO}_2$ groups respectively whereas bands near $\sim 470 \text{ cm}^{-1}$ clearly assigned as $\nu(\text{Co-O})$ ⁽¹⁴⁾.

3.1 Abbreviations / Symbols used:



4. Conclusions

Although mixed ligand displacement in simple complex system can easily be studied but in the case of ion-paired / double complex system, such prediction is too complicated. So, rigorous and specific analysis such as FAB-MS, single crystal X-ray diffraction study is much needed. In most of the cases, it is the tedious job to get the isolated compound in the single crystal form. The most fabulous aspect of these mixed ligand chelates involving Schiff bases, is the similarity in their physicochemical behavior with vitamin B₁₂ complexes, tremendous biological importance and considered as models for B₁₂ complex.

Acknowledgement

The author is indebted to the faculty members of the Department of Mathematics of Khalisani Mahavidyalaya for their constant encouragement during the preparation of this article.

References

1. M.D. Hobday and T.D. Smith, *Coord. Chem. Rev.*, **9**, 311 (1973)
2. L.F. Linday, *Quart Rev.*, **25**, 379 (1971)
3. R.H. Holm, G. W. Evertt and A. Chakraborty, *Prog. Inorg. Chem.*, **7**, 83 (1966)
4. J.H. Bigelow, *Inorg. Synth.*, **2**, 225 (1966)
5. B.P. Block, *J. Inorg. Nucl. Chem.*, **14**, 294 (1960)ei
6. M. Mozzei, M. Lederer, *Journal of Chromatography A*, **31**, 196-201 (1967)
7. Beata Nowicka, Georg Schmauch, Teiji Chihara, Frank W. Heinemann, Masaguki Hagiwara, Yasu Wakaksuki, Horst Kish, *Bulletin of the Chemical Society of Japan*, **75**, 2169 – 2175 (2002)
8. J. Casabo, T. Flor, F. Teixidor and J. Ribas, *Inorg. Chem.*, **25**, 3166 (1986)
9. T. Flor and J. Casabo, *Polyhedron*, **6**, 1563 (1987)
10. A. Vogler and H. Kumkely, *J. Inorg. Nucl. Chem.*, **14**, 294 (1961)
11. D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221(1961); **22**, 183 (1962)
12. K. Nakamoto "Infrared Spectra of Inorganic and Coordination Compound", Willey, New York, 1978
13. J.E. Covacic, *Spectrochim Acta*, Part A, **23**, 183 (1967).
14. K.L. Legg and D.W. Cooke, *Inorg. Chem. Nucl. Chem.*, **4**, 1576 (1965); **5**, 594 (1966)