



RESEARCH ARTICLE

Studies on mixed ligand cobalt(III) complexes**Sindhu Yesodharan***Department of Chemistry, All Saints College, Thiruvananthapuram-695007, Kerala, India*

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Abstract

A series of cationic mixed ligand cobalt(III) complexes have been synthesized with some selected monobasic tridentate and dibasic tridentate Schiff bases. The mixed ligand complexes have been characterized on the basis of their elemental analysis, molar conductance measurements, magnetic susceptibility data, infrared and electronic spectral studies. Magnetic moment values indicate that all the complexes are diamagnetic in nature. On the basis of the diamagnetic nature and observed electronic spectral features, a distorted octahedral structure has been proposed for the complexes.

Introduction

Interest in mixed ligand complexes has increased steadily in recent years, mainly because of their involvement in many biological processes. Most of these studies have been conducted in solutions relating to genetics and molecular biology. Mixed ligand complexes containing pyrimidine, uracil and substituted uracil with several bivalent metals have been reported. Interaction of uracil with divalent metal ions can be achieved under various conditions. However studies on mixed ligand complexes with cobalt(III) are very rare. Studies of mixed ligand transition metal complexes which bind specific site along a DNA strand as reactive models for protein-nucleic acid interaction provide drug design as well as means to develop sensitive chemical probes for DNA. However, studies on mixed ligand complexes in solid state form are comparatively less. Apart from this, mixed ligands should be

able to cater to the special needs of metal ions better.

Experimental

It was observed that synthesis of complexes of the type $[\text{Co}(\text{tridentate})_2\text{NO}_3]$ and $[\text{Co}(\text{tridentate})(\text{tridentate})\text{NO}_3]$ could be prepared using the same precursor. Hence attempt were made to prepare cobalt(III) complexes of the above type with some selected monobasic tridentate and dibasic tridentate Schiff bases. The Schiff bases used are, potassium *N*-(2-hydroxy-1-naphthylidene)glycinate (KHNA¹), 2-[*N*-(*o*-hydroxyacetophenone)amino]-3-carboxyethyl-4,5-dimethylthiophene (HAAT), 2-[*N*-(2-hydroxy-1-naphthylidene)amino]-3-carboxyethyl-4, 5-dimethyl thiophene (HNAT) and 2-[*N*-(2-thiophenylmethylene)amino]benzoic acid (HNTB).

Synthesis of the ligands

The Schiff bases of various aminoacids were prepared by the following general procedure. The α - amino acids (glycine, α -alanine, phenylalanine, leucine, histidine, or tryptophane) (0.01 m) was added to

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an ethanolic solution (50 mL) of KOH (0.01 mol) and the mixture was stirred magnetically at room temperature. When the mixture became homogeneous, a solution of 2-hydroxy-1-naphthaldehyde (0.01 mol) in ethanol (20 mL) was added and the mixture was refluxed for 3 h. The product separated on cooling the solution, was filtered, washed, dried and recrystallized from ethanol.

HAAT

2-Amino-3-carboxyethyl-4,5-dimethylthiophene prepared using Gewald synthesis [1] was used as the starting material for the synthesis of the Schiff base. 2-Amino-3-carboxyethyl-4,5-dimethylthiophene (0.01 mol) was dissolved in ethanol (30 mL) and to this solution, o-hydroxyacetophenone (0.01 mol) in ethanol (20 mL) was added slowly with constant stirring. The reaction mixture was then refluxed on a water-bath for 4 h. The product formed was filtered, washed and dried in vacuum over P_4O_{10} .

HNAT

This ligand was prepared by the condensation of 2-amino-3-carboxyethyl-4,5-dimethylthiophene with 2-hydroxy-1-naphthaldehyde. 2-Amino-3-carboxyethyl-4,5-dimethyl thiophene (0.01 mol) dissolved in ethanol was added slowly to a solution of 2-hydroxy-1-naphthaldehyde (0.01 mol) in ethanol. The reaction mixture was then refluxed for about 3 h and the crystalline product formed was separated and dried.

HNTB

The ligand 2-[N-(2-thiophenylmethylene)amino]benzoic acid was prepared by refluxing equimolar mixtures of 2-aminobenzoic acid (0.01 mol) and thiophene-2-aldehyde (0.01 mol) in ethanol (30 mL) for about 4 h. The volume of the reaction mixtures was reduced to one-third of its initial volume, cooled and allowed to crystallize. The Schiff base formed was filtered, washed with ether and dried in vacuum over P_4O_{10} .

Synthesis of the metal complexes

a) Preparation of $[\text{Co}(\text{NAA}^1)(\text{NH}_3)_3]\text{X}$; ($\text{X} = \text{NO}_3, \text{Cl}, \text{Br}, \text{I}$ or ClO_4)

The complexes containing different anions were prepared by a general procedure. Saturated aqueous solution (20 mL) of the appropriate salt (potassium chloride, potassium bromide, potassium iodide and potassium perchlorate) as the case may be, was added to a 0.001 mol solution of $[\text{Co}(\text{NAA}^1)(\text{NH}_3)_3]\text{NO}_3$ in ethanol (20 mL) and refluxed for about 3 h and concentrated to about 25 mL. The resulting solution was cooled to room

temperature and allowed to stand preferably overnight. During this time the product was precipitated. The precipitated complex was filtered, washed successively with water, ethanol and ether and finally dried in vacuum.

b) Preparation of $[\text{Co}(\text{NH}_3)_3(\text{AAT})](\text{NO}_3)_2$

To the carbonato complex (0.001 mol) in refluxing ethanol (30 mL), ethanolic solution (30 mL) of the ligand (HAAT) (0.001 mol) was added in small portions. The resulting mixture was refluxed on a water-bath for 30 min. and then added KNO_3 (0.001 mol) dissolved in aqueous ethanol (30 mL). After adjusting the pH of the solution to ~ 5.0 , the refluxing was continued for 5 h. The solution was concentrated on a water-bath to about 30 mL. The complex formed was filtered, washed successively with alcohol, ether and finally dried in vacuum over P_4O_{10} .

c) Preparation of $[\text{Co}(\text{NH}_3)_3(\text{NAT})](\text{NO}_3)_2$

To an ethanolic solution (20 mL) of pentammine-carbonatocobalt(III) nitrate, (0.001 mol), added an ethanolic solution (20 mL) of the mono basic tridentate ligand (HNAT) (0.001 mol) in small portions. After complete addition of the ligand the reaction mixture was refluxed for 30 min. KNO_3 (0.001 mol) dissolved in aqueous ethanol (30 mL) was then added and the pH was adjusted to ~ 5.0 . The refluxing was continued for 5 h. The solution was allowed to cool and the crystalline product separated was filtered, washed, dried and recrystallized from ethanol.

d) Preparation of $[\text{Co}(\text{NH}_3)_3(\text{NTB})](\text{NO}_3)_2$

The carbonato complex (0.001 mol) in ethanol (50 mL) was heated on a water bath and to the refluxing solution, added an ethanolic solution (30 mL) of the ligand (HNTB) (0.001 mol). After 30 min., KNO_3 (0.001 mol) dissolved in aqueous ethanol (30 mL) was added and the pH of the solution was adjusted to ~ 5.0 . The mixture was further refluxed on a water bath for 5 h. The solution was then allowed to cool, product formed was filtered, washed with ethanol and recrystallized.

e) Preparation of $[\text{Co}(\text{tridentate})(\text{tridentate}')]\text{NO}_3$

The monobasic tridentate ligand (HAAT) (0.005 mol) dissolved in ethanol (20 mL) was added gradually to an ethanolic solution of pentamminecarbonato cobalt(III) nitrate (0.01 mol). After complete addition of the ligand the pH of the mixture was adjusted to ~ 5.0 and the reaction mixture was refluxed in a water bath. To this refluxing solution an ethanolic solution

(20 mL) of another monobasic tridentate ligand (HNAT) (0.005 mol) was then added gradually. The refluxing was continued further for 5 h. The contents were filtered and the filtrate was concentrated on a water-bath to half of its initial volume. The solution was allowed to cool and the product formed was filtered, washed, dried and recrystallized from ethanol.

f) Preparation of $[\text{Co}(\text{tridentate})(\text{tridentate})](\text{NO}_3)$

The monobasic tridentate ligand (HAAT)(0.005 mol) dissolved in ethanol was added gradually to a ethanolic solution of pentamminecarbonato cobalt(III) nitrate (0.01 mol). It was stirred well and the pH was adjusted to 5.0. The resulting mixture was refluxed and to this an ethanolic solution of the second monobasic tridentate ligand (HNTB) (0.005 mol) was added in small portions. The solution was refluxed further for 5 h and allowed to cool. The complex thus obtained was separated and dried over P_4O_{10} .

g) Preparation of $[\text{Co}(\text{tridentate})(\text{tridentate})](\text{NO}_3)$

To a suspension of the carbonato complex, $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{NO}_3 \cdot 1/2\text{H}_2\text{O}$ (0.01 mol) in refluxing ethanol (30 mL) was added gradually an ethanolic solution (30 mL) of a monobasic tridentate ligand (HNAT) (0.005 mol). After complete addition of the first ligand the pH was adjusted to ~5.0 and the reaction mixture was refluxed further. To the refluxing solution an ethanolic solution (30 mL) of another monobasic tridentate ligand (HNTB) (0.005 mol) was then added gradually and the solution was again refluxed for about 5 h. The contents were concentrated on a water-bath to half of its initial volume and the crystalline product formed was filtered, washed, dried and recrystallized from ethanol.

Results and discussion

The reactions of metal carbonato and carbon dioxide complexes including their kinetic and mechanistic details of formation and aquation reactions have been exhaustively reviewed by Palmer and Van Eldik [2,3]. Some reactions of metal complexes that appear to involve substitution may actually occur without breaking M-O bond present in the carbonato complex. The ^{18}O labeling studies revealed that the metal-oxygen bond remained intact [4]. This seems to be a general characteristic of monodentate carbonato complexes [3]. For chelated carbonato complexes, initial ring opening proceeds with metal-oxygen bond breaking followed by CO_2 elimination [5]. Formulation of the mixed ligand complexes has been made on the basis of their elemental analytical data, molar conductance measurements,

infrared and electronic spectral data. The purity of the complexes was tested by TLC (silica gel). These complexes could be recrystallized repeatedly from ethanol without change in composition. Molar conductance values adequately confirm the electrolytic nature of the complexes. All the complexes are diamagnetic and uncoordinated nature of the anions could be inferred from their infrared spectral data.

Structure of $[\text{Co}(\text{NH}_3)_3(\text{NAA}^1)]\text{X}$

Molar conductance values adequately support the electrolytic nature of the complexes [6]. The complexes showed characteristic bands due to the coordination of ligand, potassium N -(2-hydroxy-1-naphthylidene)-glycinate (KHNA 1), as dibasic tridentate. In addition, to this the band due to coordinated NH_3 has been observed at 3345 and 3405 cm^{-1} . Apart from this, the cobalt(III) complex exhibited characteristic bands at 1390, 835 and 715 cm^{-1} for ionic nitrate [7]. The ligand acted as dibasic tridentate coordinating through quinone oxygen, deprotonated amino nitrogen and a carboxylate oxygen [8]. Ionic nature of the perchlorate group was also revealed from the infrared spectrum. A strong band appearing at 1110 cm^{-1} and another band at 630 cm^{-1} support the fact that perchlorate group present in the complex is not coordinated and has Td symmetry, showing its ionic nature [9].

Infrared spectra of the complexes $[\text{Co}(\text{NH}_3)_3(\text{NAA}^1)]\text{X}$ are indicative of weak hydrogen bonded interaction of coordinated ammonia with the nitrate ion. This interesting aspect was examined by replacing the nitrate from $[\text{Co}(\text{NH}_3)_3(\text{NAA}^1)]\text{NO}_3$ by other anions like chloride, bromide, iodide and perchlorate. Position and appearance of the $\nu(\text{N-H})$ bands of the complexes $[\text{Co}(\text{NH}_3)_3(\text{NAA}^1)]\text{X}$ have been found dependent on the anions (NO_3^- , Cl^- , Br^- , I^- , or ClO_4^-) or changing from broad band at lower frequency in the chloride complex, to sharper and better resolved bands at higher frequencies, with increasing size of the anion. This shows that the strength of the $\text{N-H}\cdots\text{X}$ hydrogen bond decreases in the order $\text{Cl}^- > \text{Br}^- > \text{I}^- > \text{NO}_3^- > \text{ClO}_4^-$. Since charge density increases with decreasing size of the anion, the above trend is expected. This type of weak interactions are of great importance in the building up of supra molecular array.

Structure of $[\text{Co}(\text{NH}_3)_3(\text{NTB})](\text{NO}_3)_2$

Molar conductance value of the complex revealed the electrolytic nature of the complex. The infrared spectrum of the ligand 2-[N -(2-thiophenylmethylene) amino]benzoic acid exhibits a medium intensity band at 1600 cm^{-1} due to $\nu(\text{C}=\text{N})$ of azomethine linkage.

The $\nu(\text{C=O})$ and $\nu(\text{OH})$ vibrations have been observed at 1700 and 3500 cm^{-1} . Bands due to $\nu_{\text{sym}}(\text{COO})$ and $\nu_{\text{asym}}(\text{COO})$ have been found at 1590 and 1425 cm^{-1} respectively. An intense band at 843 cm^{-1} can be attributed to $\nu(\text{C-S-C})$ of the thiophene moiety. Vibrations observed at 1522, 1425 and 1355 cm^{-1} are characteristics of substituted thiophene nucleus [10].

The IR data of the mixed ligand complex has been compared with those of the free ligand in order to determine the bonding sites involved in coordination. In the spectrum of mixed ligand complex the characteristic vibration due (C=N) of the ligand has been found depressed by 20 cm^{-1} indicating the azomethine nitrogen coordination. The strong band at 843 cm^{-1} assigned to thiophene $\nu(\text{C-S-C})$ has been shifted upwards by 25 cm^{-1} in the spectrum of complex. This indicates the bonding of thiophene ring sulphur to the metal ion [10].

The coordination by the ring sulphur of thiophene moiety has been also confirmed by the perturbation of the thiophene ring vibrations [10]. The participation of the carboxylate oxygen atom during chelation was evidenced by the shift of $\nu_{\text{sy}}(\text{COO})$ and $\nu_{\text{asy}}(\text{COO})$ vibrations [9]. The broad band due to (OH) disappeared from the region 3500 cm^{-1} indicating the deprotonation and formation of metal-oxygen bond. Bands due to ionic nature of the NO_3^- group were also revealed by IR spectral bands at 1392, 825 and 710 cm^{-1} . Non ligand bands found in the far IR spectrum \sim 510, 456 and 428 cm^{-1} can be assigned to $\nu(\text{M-O})$, $\nu(\text{M-N})$ and $\nu(\text{M-S})$ vibrations respectively [10]. Therefore, from the IR spectrum it can be concluded that the ligand is coordinated to the metal atom through its deprotonated carboxylate oxygen, azomethine nitrogen and thiophene ring sulphur atom. As expected the infrared spectra of the mixed ligand complexes containing two strikingly similar tridentate ligands revealed too many broad bands in the relevant regions. Hence assignments of peaks are rendered difficult.

The electronic spectral features of all the above complexes are strikingly similar. The visible spectra of all the above complexes exhibited a strong band centered \sim 17,200 cm^{-1} with a shoulder \sim 19,800 cm^{-1} assigned to $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ and $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$ transitions respectively. Similar bands have been reported by earlier investigators for some low-spin octahedral cobalt(III) complexes [11,12]. On the basis of the diamagnetic nature and observed electronic spectral features, a distorted octahedral structure has been proposed for the complexes [11].

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