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Second sphere coordination in anion binding: Synthesis, spectroscopic characterization and single crystal X-ray structure determination of hexaamminecobalt(III) dichloride tetrafluoroborate

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Abstract

The reaction of hexaamminecobalt(III) chloride with sodium tetrafluoroborate in hot aqueous medium (1:1 molar ratio) leads to formation of hexaamminecobalt(III) dichloride tetrafluoroborate, $[Co(NH_3)_6]Cl_2{\cdot}BF_4$. This cobalt(III) complex has been characterized by elemental analyses and spectroscopic techniques (e.g. UV–vis and IR). X-ray structure determination of this complex salt revealed the presence of discrete ions i.e., cation $[Co(NH_3)_6]^{3+}$ and two different anions, two Cl^- and one BF_4^- in the solid state. Crystal lattice is stabilized by electrostatic forces of attractions and hydrogen bonding interactions i.e. $N–H\cdots F^-$ and $N–H\cdots Cl^-$. The formation of definite salt of composition with tetrafluoroborate ion suggest that $[Co(NH_3)_6]^{3+}$ may be used as purely inorganic anion binding agent for weakly complexing fluoroanion, BF_4^-. This is the first X-ray structure determination of hexaamminecobalt(III) salt with tetrafluoroborate ion.

Keywords: Anion binding agent; Cobalt(III); Infrared spectroscopy; Second sphere coordination; Tetrafluoroborate ion; X-ray crystallography

1. Introduction

Anions play important roles in chemical, biological and environmental processes and therefore the molecular recognition of anions or anion binding is an area of current interest [1–7]. Due to their varied shapes and sizes [8], anions pose a greater challenge as compared to isoelectronic cations, which are usually spherical in shape. One important class of charged fluoroanions is the commercially significant tetrafluoroborate ion [9]. The fluoboric acid, HBF_4 is used for esterification of cellulose to clean metal electrolyte for plating metals (Fe, Cu, Zn, etc.) and as a catalyst for preparing acetals [9]. The commercially available sodium/potassium salts of fluoboric acid are used as fluorinating agents [10,11] and also have a number of applications in industry such as flux for soldering and brazing, filtrate in resin bonded grinding wheels and as corrosion-resistant paint for galvanization of Fe or Zn surfaces [12]. Moreover, fluoroanion, BF_4^- and cation, 1-ethyl-3-methylimidazolium were applied to electrolyte materials for double-layer capacitors at low temperature [13]. Therefore, the development of selective anion receptor (binding agent), which may find potential applications [14] and especially in polar solvents such as water is of particular interest [15,16].

Although cationic organic anion receptors have been extensively investigated [17] but cationic metal complexes have not received much attention [18]. One such cationic metal complex is hexaamminecobalt(III) cation which possesses all the characteristic features [19] to act as a potential anion receptor: (a) hydrogen bond donor groups, (b) a positively charged component for effective electrostatic interactions and (c) a suitable framework onto which these structural components can be assembled. This cation is tripositively charged, possesses eighteen N–H hydrogen bond donor groups and a stable structural framework onto which anionic components can be assembled. Perhaps it is the first purely

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inorganic anion receptor. We envisaged that, if cations and anions are properly functionalized to incorporate hydrogen bonds, novel network architectures may ensue and stabilize the lattice. Although the synthesis and single crystal X-ray structure determinations of a variety of hexaamminecobalt(III) complex salts have been reported in the literature [20], including metal chloroanions, $[MCl_5]^{2-}$ and $[MCl_6]^{3-}$ [20f] but only one with complex fluoroanion, SiF_6^{2-} which was recently reported by our group [21]. The present work reports synthesis, spectroscopic studies and single crystal X-ray structure determination of $[Co(NH_3)_6]Cl_2{\cdot}BF_4$ in continuation of our interest [22] in hexaamminecobalt(III) complex salts. The title complex salt is stabilized by extensive hydrogen bonding besides electrostatic forces of attractions. We have already reported the potential use of cationic hexaamminecobalt(III) as anion receptor for inorganic oxo-anions [22a–d], organic oxo-anions [22e–g] and fluoroanions [21].

2. Results and discussion

2.1. Synthesis

Hexaamminecobalt(III) salts can react with sodium tetera-fluoroborate in number of ways depending upon the stoichiometric ratios of reactants as shown below:

$$[Co(NH_3)_6]Cl_3 + 3NaBF_4 \overset{H_2O}{\longrightarrow} [Co(NH_3)_6](BF_4)_3 + 3NaCl \qquad \text{(i)}$$

$$[Co(NH_3)_6]Cl_3 + 2NaBF_4 \overset{H_2O}{\longrightarrow} [Co(NH_3)_6]Cl \cdot (BF_4)_2 + 2NaCl \qquad \text{(ii)}$$

$$[Co(NH_3)_6]Cl_3 + NaBF_4 \overset{H_2O}{\longrightarrow} [Co(NH_3)_6]Cl_2 \cdot BF_4 + NaCl \qquad \text{(iii)}$$

The single crystals of new hexaamminecobalt(III) complex salt (shown in Eq. (iii)) have been prepared by reacting $[Co(NH_3)_6]Cl_3$ with $NaBF_4$ in 1:1 molar ratio in hot aqueous medium according to expectation. We have also attempted the reactions to get complex salts of composition $[Co(NH_3)_6](BF_4)_3$ and $[Co(NH_3)_6]Cl(BF_4)_2$ as given in Eqs. (i) and (ii), respectively, but the efforts were unsuccessful. The complex salt $[Co(NH_3)_6]Cl_2{\cdot}BF_4$ was formed even when the stoichiometric ratios were 1:2 and 1:3. The chemical composition of newly synthesized complex salt was initially confirmed by elemental analyses. This complex salt is soluble in water and DMSO but insoluble in any other commonly used organic solvents (chloroform, ethanol, acetone).

2.2. Measurement of solubility products

Solubility of ionic salts in water differs to a great extent and on the basis of solubility criterion, the salts are classified into three categories (a) solubility >0.1 M (soluble), (b) solubility between 0.01 and 0.1 M (slightly soluble) and (c) solubility <0.01 M (springly soluble). The solubility measurement at room temperature (Table 1) shows that $[Co(NH_3)_6]Cl_2{\cdot}BF_4$ and $[Co(NH_3)_6]Cl_2{\cdot}IO_3{\cdot}H_2O$ are slightly soluble in water whereas $[Co(NH_3)_6]Cl_2{\cdot}ClO_3$ and $[Co(NH_3)_6]Cl_3$ are soluble. It is observed that the binding (association) of tetrafluoroborate and iodate ions with $[Co(NH_3)_6]^{3+}$ is much more as compared to chlorate and chloride ions i.e., the binding affinities are in the order $IO_3^- > BF_4^- \gg ClO_3^- > Cl^-$. As reported in the Section 3, when the appropriate amounts of the reactants were mixed in minimum amount of water the crystals appeared after two days resulting in the formation of title complex salt. This is because ionic products are greater than solubility products, K_{sp} at the crystallization point (Table 1). The binding of ClO_3^- ion is more in complex salt $[Co(NH_3)_6]Br_2{\cdot}ClO_3$ as compared to $[Co(NH_3)_6]Cl_2{\cdot}ClO_3$ which shows the affect of co-anion also.

Table 1
Solubility products (K_{sp}) of hexaamminecobalt(III) salts

Complex salts	Solubility (M)	K_{sp}
$[Co(NH_3)_6]Cl_3$	0.26052	0.12
$[Co(NH_3)_6]Cl_2{\cdot}ClO_3$	0.31695	0.04
$[Co(NH_3)_6]Br_2{\cdot}ClO_3$	0.06923	9.19×10^{-5}
$[Co(NH_3)_6]Cl_2{\cdot}IO_3{\cdot}H_2O$	0.04706	1.96×10^{-5}
$[Co(NH_3)_6]Cl_2{\cdot}BF_4$	0.09449	3.19×10^{-4}

2.3. Infrared spectroscopy

2.3.1. Hexaamminecobalt(III) cation

The infrared spectrum of the title complex salt has been measured in the range 4000–500 cm^{-1}. In the title complex salt (Fig. 1), N–H stretching vibrations of the coordinated NH_3 molecule are lower (by 40–200 cm^{-1}) than those of the free NH_3 molecules for two reasons, one is the effect of coordination and the other is the effect of the counter ions i.e. Cl^- and BF_4^-. This is attributed to the weakening of the N–H bond due to the formation of $N\text{–}H{\cdots}Cl^-$ and $N\text{–}H{\cdots}F^-$ type of hydrogen bonds. Some of the aspects of the presented assignments can be described as follows:

- It is seen that antisymmetric and symmetric vibrations of coordinated NH_3 molecules appears in the region 3300–3100 cm^{-1}. In title complex salt antisymmetric, ν_{as} is clearly outlined at 3266 cm^{-1} with small shoulder for symmetric stretch, ν_s.

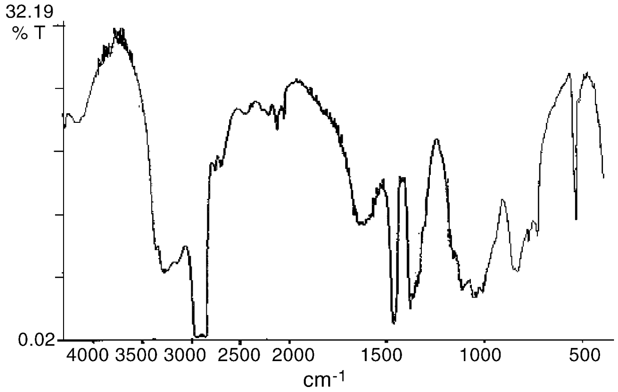

Fig. 1. FT-IR spectrum of $[Co(NH_3)_6]Cl_2{\cdot}BF_4$.