Journal of Molecular Structure 920 (2009) 119–127

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Second sphere coordination in binding of fluoroanions: Synthesis, spectroscopic characterization and single crystal X-ray structure determination of $[Co(phen)_3](BF_4)_3{\cdot}H_2O$ and $[Co(phen)_3](PF_6)_3{\cdot}CH_3COCH_3$

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ARTICLE INFO

Article history:
Received 22 September 2008
Received in revised form 19 October 2008
Accepted 22 October 2008
Available online 5 November 2008

Keywords:
Second sphere coordination
Tetrafluoroborate
Hexafluorophosphate
Anion receptor
X-ray crystallography

ABSTRACT

In an effort to capture fluoroanions by cationic cobalt(III) complex, two new cobalt(III) complex salts of composition $[Co(phen)_3](BF_4)_3{\cdot}H_2O$ (**1**) and $[Co(phen)_3](PF_6)_3{\cdot}CH_3COCH_3$ (**2**) have been synthesized by the reaction of tris(1,10-phenanthroline)cobalt(III)chloride with sodium salts of tetrafluorborate and hexafluorophosphate (1:3 molar ratio) in aqueous medium. Single crystals of **1** were obtained directly from the reaction mixture when the solution was allowed to evaporate slowly at room temperature and single crystals of **2** were obtained by recrystallizing the precipitated product from acetone and water solution by slow evaporation. The newly synthesized complex salts were characterized by elemental analyses, TGA spectroscopic studies (IR, UV/Visible, ^1H, ^{13}C, ^{19}F and ^{11}B NMR), solubility product and conductance measurements. X-ray structure determination revealed ionic structures consisting of one $[Co(phen)_3]^{3+}$, three $[BF_4]^-$ ions and one lattice water molecule in complex salt **1**, one $[Co(phen)_3]^{3+}$, three $[PF_6]^-$ anions and one acetone molecule as solvent of crystallization in complex salt **2**. The three 1,10-phenanthroline ligands (each bidentate) coordinated to cobalt(III) showed distorted octahedral geometry around the central metal ion. Supramolecular hydrogen bonding networks between ionic groups [Co-phenCH$^{\delta+}\cdots F^{\delta-}_{anion}$] by second sphere coordination have been observed that stabilize crystal lattice besides electrostatic forces of attraction. The structural studies suggest that $[Co(phen)_3]^{3+}$ is a promising anion receptor for the fluoroanions $(BF_4)^-$ and $(PF_6)^-$in aqueous medium.

1. Introduction

The design and synthesis of efficient anion receptors (complextants) for binding of biologically and environmentally important anionic species is a field of great interest with enormous applications [1–4]. The design and synthesis of anion receptors revolves basically around the functionalities incorporated on the organic frameworks/ligands that can take part in hydrogen bonding with the anionic species. In this practice, all the attention is focused on ligands incorporating the N—H groups. In some cases metal coordination is also employed to orient these groups. The use of C—H donor groups is very limited in the literature because these groups are not strong hydrogen bond donors as compared to N—H groups, but in conjunction with other interactions like O—H···O, C—H···π, cation···π and π···π stacking interactions, they can form strong hydrogen bonding networks. It is evident from our previous studies that unison of these strong and weak interactions plays a very important role in stabilization of crystal lattice. These C—H donor groups generally form a second sphere coordination spread around the cation through hydrogen bond acceptor groups of anions. Although, several examples of second-sphere complexes with aquo [5] and ammine [6] coordination compounds have appeared in the literature but the second sphere coordination, as a strategy has not been much exploited for capturing anionic species.

Although cationic organic based anion receptors have been extensively investigated, cationic metal complexes have not received much attention [7–9]. A few salts containing the cation, $[Co(phen)_3]^{3+}$ are reported in the literature [10] but its potential as anion receptor has not been explored. The complex cation $[Co(phen)_3]^{3+}$ seems to be a good candidate for this purpose as it possesses all the properties of a good anion receptor: a positively charged component for effective electrostatic interactions, hydrogen bond donor groups (twenty-four C—H groups per cationic species) and a stable framework onto which the anionic structural components can be assembled. As compared to other synthetic anion receptors, Co(III) complex based cationic anion receptors are easier to synthesize in high yields, stable for longer period of time and effective in the aqueous medium.

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doi:10.1016/j.molstruc.2008.10.036

Inorganic fluoroanions are biologically and industrially important class of anions [11]. Tetrafluoroborate (BF_4^-) in the form of fluoroboric 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. Sodium/potassium salts of fluoroboric acid are used as fluorinating agents [12,13] and also used in industry (e.g. flux for soldering and brazing, filtrate in resin bonded grinding wheels and as corrosion-resistant paint for galvanization of Fe or Zn surfaces [14]). Moreover, fluoroanion, BF_4^- and the cation, 1-ethyl-3-methylimidazolium were applied to electrolyte materials for double-layer capacitors at low temperature [15a]. Similarly, salts of PF_6^- are major component of capacitors and battery electrolyte. Air stable imidazolium salts with BF_4^- and PF_6^- anions are tolerant to a variety of polar functional groups which enable their use in a wide range of chemical and electrochemical applications [15b]. Therefore, the development of selective anion receptor (binding agent) which may find potential applications [16] especially in polar solvents such as water, is of particular interest [17].

In the present work, we envisaged that the presence of twenty four C—H hydrogen bond donor groups on positively charged cation $[Co(phen)_3]^{3+}$ would facilitate the interaction with properly oriented negatively charged fluorine atoms of the fluoroanions, $[BF_4]^-$ and $[PF_6]^-$. This may result in the formation of a donor-acceptor complex (crystal engineering) involving second sphere coordination because hydrogen bond interactions are directional in nature. Understanding of such complexes of judicially chosen cations and anions would be rewarding as it can provide means of constructing intricate and novel molecular entities based on second-sphere coordination. Thus in continuation of our research programme to explore cationic cobalt(III) complexes as anion receptor[18], we report herein the utility of $[Co(phen)_3]^{3+}$ as anion receptor for fluoroanions: synthesis, characterization and single crystal X-ray structure determination of $[Co(phen)_3](BF_4)_3 \cdot H_2O$ and $[Co(phen)_3](PF_6)_3 \cdot CH_3COCH_3$.

2. Experimental

2.1. Materials

Analytical grade reagents were used without any further purification. $[Co(phen)_3]Cl_3$ has been prepared by reacting $[Co(NH_3)_5Cl]Cl_2$ and 1,10-phenanthroline monohydrate according to the method described in the literature [10a].

2.2. Instruments and measurements

C, H, N were estimated micro analytically by automatic PERKIN ELMER 2400CHN elemental analyzer. Cobalt was determined by standard volumetric method of estimation [19]. UV/Visible spectra were recorded using HITACHI 330 spectrometer in water as solvent in **1** and acetone in **2**. Infrared spectra of the title complex salts were recorded using PERKIN ELMER spectrum RX FT-IR system using KBr pellet. ^1H, ^{13}C, ^{59}Co, ^{11}B and $^{19}F^*$ NMR spectra of title complex salts were run in the solvent D_2O (in complex salt **1**) and DMSO-d_6 (in complex salt **2**) at 25° C by using BRUKER AC 400 F (400 MHz) spectrophotometer. The chemical shift values are expressed as δ value (ppm) down field from tetramethylsilane as an internal standard. The chemical shift values in ^{11}B NMR are expressed as δ value (ppm) up field from H_3BO_3 as an internal standard. In case of ^{19}F NMR the chemical shift values are expressed as δ value (ppm) upfield from $CFCl_3$ as an internal standard. Conductance measurements were performed on Pico Conductivity Meter (Model CNO4091201, Lab India) in aqueous medium at 25 °C by using double distilled water. Thermogravimetric (TGA) curves were measured with a Mettler TG50 Thermobalance. The samples were heated in air at a rate of 10 °C/min.

2.3. Synthesis of $[Co(phen)_3](BF_4)_3 \cdot H_2O$ (**1**)

Tris(1,10-phenanthroline)cobalt(III)chloride (0.5 g, 0.7 mmol) was dissolved in 5 ml of water and in another beaker 0.501 g (2.1 mmol) of sodium tetrafluoroborate was dissolved in 5 ml of water. Upon mixing the two solutions, the colour of the resulting solution changed from yellow to orange. When it was allowed to evaporate slowly at room temperature, orange coloured single crystals started appearing after three days, which were allowed to grow. The crystals were then separated and dried in air. The yield was 70%. The complex salt starts decomposing after 245 °C. The composition was established by elemental analyses. $[Co(phen)_3](BF_3)_3 \cdot H_2O$. Found: (%) C, 48.90; H, 2.46; N, 9.01; Co, 5.98. Calculated; (%) C, 49.20; H, 2.96; N, 9.56; Co, 6.71.

2.4. Synthesis of $[Co(phen)_3](PF_6)_3 \cdot CH_3COCH_3$ (**2**)

To a 10 ml solution of $[Co(phen)_3]Cl_3$ (0.5 g, 0.7 mmol) in water, 5 ml solution of $NaPF_6$ (0.316 g, 2.1 mmol) was added. On mixing, immediate precipitation took place and yellow coloured precipitated product was obtained in 65% yield. It decomposed at 240 °C. Yellow coloured single crystals suitable for X-ray structure determination were obtained by recrystallizing this precipitated product from acetone–water mixture which were separated and dried in air. Its composition was established by elemental analyses. $[Co(phen)_3](PF_6) \cdot CH_3COCH_3$. Found: (%)C, 46.53; H, 2.06; N, 7.40; Co, 5.05. Calculated; (%) C, 46.85; H, 2.70; N, 7.69; Co, 5.40.

2.5. X-ray structure determination

The single crystal X-ray data for complex salts **1** and **2** were collected on a CCD Bruker APEX II at 150(2) K using graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). The crystals of both compounds were positioned at 35 mm from the CCD and the spots were measured using a counting time of 40 s for 1 and 80 s for **2**. Data reduction and empirical absorption were carried out using the SAINT-NT from Bruker XS. The structures were solved using SHELXS-97 [20] and refined using full-matrix least squares in SHELXL-97 [21]. The C—H hydrogen atoms were included at calculated positions whereas the hydrogen atoms bonded to water molecules were located from final difference Fourier maps except those of disordered water molecule of **1**. These hydrogen atoms were not included in the structure refinement. Anisotropic thermal parameters were used for all non-hydrogen atoms while the hydrogen atoms were refined with isotropic parameters equivalent 1.2 times those of the atom to which they are attached. Final *R*-values together with selected refinement details are given in Table 1.

3. Results and discussion

In the literature, there are limited reports of complex salts containing $[Co(phen)_3]^{3+}$ and crystal structure of some of them have been reported [10]. The complex salts of $[Co(phen)_3]^{3+}$ with fluoroanions are very few, only one complex salt, tris(1,10-phenanthroline)cobalt(III) tetrafluoroborate has been reported so far [10e] but its crystal structure was not determined and even its method of preparation is quite different from the one used in this paper. Thomas et al. have prepared this complex salt by oxidation of Co(II) salt by bromine water followed by addition of HBF_4. The fluorine atoms of BF_4^- and PF_6^- groups can involve in the C—H...F interactions with phenanthroline groups attached to the cobalt(III) center and may also form C—H...O hydrogen bonds with lattice water molecules or other solvent molecules. Recent theoretical and