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Second sphere interaction in fluoroanion binding: Synthesis, spectroscopic and X-ray structural study of *trans*-dichlorobis (ethylenediamine) cobalt(III) terafluoroborate

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Abstract

Trans-dichlorobis(ethylenediamine) cobalt(III) terafluoroborate was synthesised and detailed packing analysis was undertaken to delineate the topological complimentarity of [*trans*-Co(en)$_2$Cl$_2$]$^+$ and BF$_4^-$ ions by second sphere coordination. The complex was completely characterised by elemental analyses, solubility product measurement and spectroscopic studies (IR, UV–Vis, multinuclear NMR). In the crystal lattice, discrete ions [*trans*-Co(en)$_2$Cl$_2$]$^+$ and BF$_4^-$ are arranged in A–B–A–B pattern (in both *a* and *c* directions of the lattice) forming columns of anions and cations. Crystal lattice is stabilized by electrostatic forces of attraction and hydrogen bonding interactions, i.e. N–H···F$^-$ and N–H···Cl involving second sphere coordination. It appears that the topological features of [*trans*-Co(en)$_2$Cl$_2$]$^+$ are conducive for generating second sphere interactions. This strategy may be used as a viable method for the capture of other fluoroanions.

Keywords: Cobalt(III); Coordination chemistry; Tetrafluoroborate; X-ray crystallography; Spectroscopy and layered solids

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1. Introduction

Anionic species play very important roles in chemistry, medicine, catalysis, molecular assembly and in biology, yet their binding characteristics have not received much recognition. Inorganic fluoroanions are biologically important class of anions. One of them is tetrafluoroborate. The 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. The commercially available sodium/potassium salt of fluoroboric acid is used as fluorinating agent [1,2] and also has a number of applications in industry (for example, flux for soldering and brazing, filtrate in resin bonded grinding wheels and as corrosion-resistant paint for galvanization of Fe or Zn surfaces [3]). Moreover, fluoroanion, BF$_4^-$ and cation, 1-ethyl-3-methylimidazolium were applied to electrolyte materials for double-layer capacitors at low temperature [4]. Therefore, the development of selective anion receptor (binding agent), which may find applications [5] and especially in polar solvents such as water is of particular interest [6]. This may result in the formation of materials that may find application in anion recovery.

The coordination chemistry of anions may be expected to yield a great variety of novel structures and properties of both chemical and biological significance. In this regard, second sphere coordination of cationic and anionic groups is an active area of research in metallosupramolecular chemistry [7]. Cationic organic anion receptors have been extensively investigated [8], but cationic metal complexes have received much less attention [9]. We have undertaken an extensive research programme to exploit cationic cobaltammines, e.g. [*trans*-Co(en)$_2$Cl$_2$]$^+$, [*trans*-Co(en)$_2$(NO$_2$)$_2$]$^+$ and [*cis*-Co(en)$_2$(N$_3$)$_2$]$^+$, etc. as anion receptors [10] because cationic cobaltammines are easy to synthesize in high yields from readily available materials and could be stored for months without any noticeable decomposition. The cationic cobaltammine [*trans*-Co(en)$_2$Cl$_2$]$^+$ present in [*trans*-Co(en)$_2$Cl$_2$]Cl fulfills the criterion [7a] of an anion receptor, i.e. unit positive

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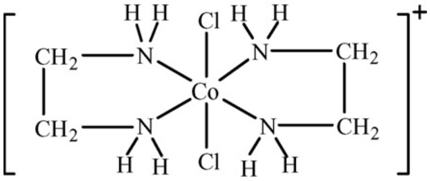
charge for electrostatic interaction, eight N–H hydrogen bond donor groups and a relatively stable framework. In the present work, we envisaged that the presence of eight N–H hydrogen bond donor groups on each positively charged cation [*trans*-$Co(en)_2Cl_2]^+$ would facilitate the interaction with properly oriented negatively charged fluorine atoms of the fluoroanion $[BF_4]^-$, resulting in the formation of a donor-acceptor complex involving second sphere coordination.



In the solid state, in all probability, these two ions should form an intricate network of hydrogen bonds stabilizing the entire lattice. Understanding such a network of interactions of judicially chosen cations and anions would be rewarding as it can provide a means of constructing intricate and novel molecular entities based on second-sphere coordination. We report here the potential of the [*trans*-$Co(en)_2Cl_2]^+$ cation present in [*trans*-$Co(en)_2Cl_2]Cl$ by isolating and characterizing the solid formed on mixing the appropriate salts.

2. Results and discussion

2.1. Synthesis

Trans-dichlorobis(ethylenediamine)cobalt(III)chloride can react with sodium tetrafluoroborate in number of ways depending upon the stoichiometric ratios of reactants.

$$[\textit{trans}\text{-Co(en)}_2\text{Cl}_2]\text{Cl} + \text{NaBF}_4 \rightarrow [\textit{trans}\text{-Co(en)}_2\text{Cl}_2]\text{BF}_4 + \text{NaCl} \qquad \text{(i)}$$

$$[\textit{trans}\text{-Co(en)}_2\text{Cl}_2]\text{Cl} + 2\text{NaBF}_4 + \text{H}_2\text{O} \rightarrow [\text{cis/trans-Co(en)}_2(\text{H}_2\text{O})\text{Cl}](\text{BF}_4)_2 + 2\text{NaCl} \qquad \text{(ii)}$$

$$[\textit{trans}\text{-Co(en)}_2(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2 + \text{H}_2\text{O} + 3\text{NaBF}_4 \rightarrow [\textit{trans}\text{-Co(en)}_2(\text{H}_2\text{O})_2](\text{BF}_4)_3 + 3\text{NaCl} \qquad \text{(iii)}$$

$$[\textit{trans} - \text{Co(en)}_2(\text{H}_2\text{O})_2]\text{Cl}_3 + 3\text{NaBF}_4 \xrightarrow{\Delta} [\textit{trans} - \text{Co(en)}_2(\text{BF}_4)_2]\text{BF}_4 + 3\text{NaCl} + 2\text{H}_2\text{O} \qquad \text{(iv)}$$

In the present case, reaction of [*trans*-$Co(en)_2Cl_2]Cl$ with sodium tetrafluoroborate in 1:1 stoichiometric ratio (Eq. (i)) in aqueous medium afforded [*trans*-$Co(en)_2Cl_2]BF_4$. The chemical composition of newly synthesized complex salt was initially indicated by elemental analyses. This is freely soluble in water and DMSO but insoluble in ethanol. It decomposed at 205 °C.

2.2. Measurement of solubility product

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 are (sparingly soluble). The solubility measurements at room temperature show that the complex salt [*trans*-$Co(en)_2Cl_2]BF_4$ is slightly soluble in water, as is [*trans*-$Co(en)_2(Cl)_2]Cl$ which is readily soluble. The solubility product of [*trans*-$Co(en)_2Cl_2]BF_4$ is 1.37×10^{-3} which indicated that the affinity or binding of cationic cobaltammine [*trans*-$Co(en)_2Cl_2]^+$ is greater for tetrafluoroborate ion than chloride ion. As reported in the experimental section, when the appropriate amounts of the reactants were mixed in a minimum amount of water, the crystals appeared with in few hours, resulting in the formation of title complex salt. This is because the ionic product is greater than solubility product, K_{sp} at the crystallization point. A comparison of the solubility products of various [*trans*-$Co(en)_2Cl_2]^+$ salts is given in Table 1. It is evident from this table that the affinity of [*trans*-$Co(en)_2Cl_2]^+$ is same for ClO_3^-, BrO_3^- and BF_4^- ions but more for $[CdX_4]^{2-}$, X = Br or I and even more for N_3^-.

2.3. Infrared spectroscopy

Infrared spectrum of the newly synthesized complex salt has been recorded in the region 4000–400 cm^{-1} and tentative assignments have been made on the basis of earlier reports in the literature [11]. The absorption band at 887 cm^{-1} is assigned to CH_2 rocking region and a band at 1592 cm^{-1} is assigned to NH_2 asymmetric deformation [12]. There are four normal modes of vibration in a tetrahedral BF_4^- ion. All the four vibrations are Raman active, whereas only ν_3, degenerate stretching mode (ν_d) and ν_4, degenerate deformation mode (δ_d) are IR active [11]. Assignments of the IR bands in 1050 cm^{-1} region are complicated as discussed previously [13]. As reported in the literature there are characteristic regions for degenerate stretching mode (1000–1150 cm^{-1}) and degenerate deformation mode (530 cm^{-1}) arising from BF_4^- ion [14]. In the spectrum of the title complex salt (Fig. 1) there is strong peak at 1051 cm^{-1} with small shoulders at 1114 and 1003 cm^{-1} which were assigned to the degenerate stretching mode, ν_d for BF_4^- ion, while the very strong band at 522 cm^{-1} corresponded to the degenerate deformation mode (δ_d, BF_4^-). These values are also in agreement with those tetra-butylammonium tetrafluoroborate, $Bu_4N.BF_4$ [15]. The cation belongs to near D_2H symmetry due to which the IR band at 473 cm^{-1} is assigned to asymmetric stretching of Co–N while symmetric Co–N stretch is IR inactive.

Table 1
Solubility products (K_{sp}) of dichlorobis(ethylenediamine) cobalt(III) salts

Complex salts	Solubility (g/l)	K_{sp}
[*trans*-$Co(en)_2(Cl)_2]ClO_3$	11.0	1×10^{-3}
[*trans*-$Co(en)_2(Cl)_2]BrO_3$	20.0	2×10^{-3}
[*trans*-$Co(en)_2Cl_2]_2CdBr_4$	10.0	1×10^{-4}
[*trans*-$Co(en)_2Cl_2]_2CdI_4$	4.0	1×10^{-5}
[*trans*-$Co(en)_2Cl_2]N_3$	10.0	9×10^{-6}
[*trans*-$Co(en)_2Cl_2]BF_4$	12.5	1×10^{-3}

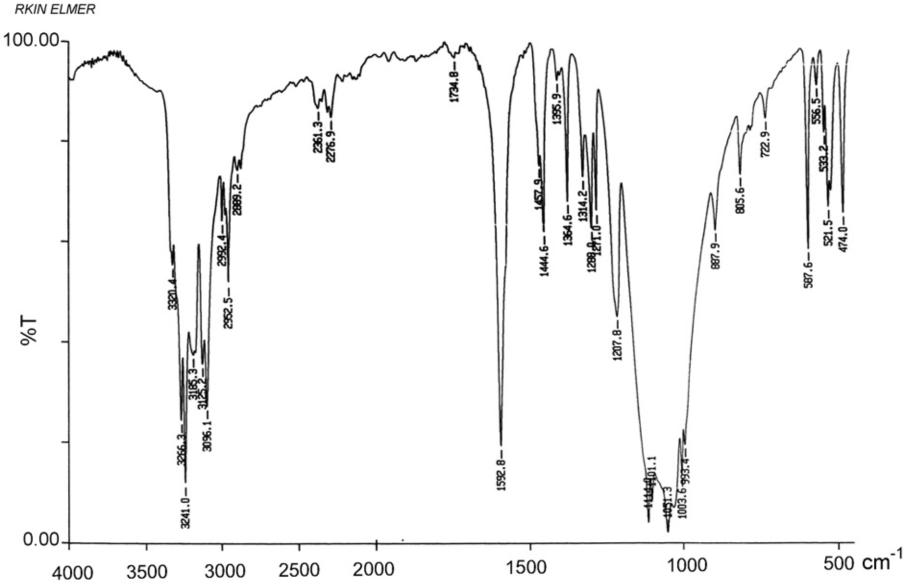


Fig. 1. FT-IR spectrum of [*trans*-Co(en)$_2$Cl$_2$]BF$_4$.

2.4. UV–vis spectroscopy

The electronic spectrum of the newly synthesized complex salt has been recorded in H_2O. The solution state UV–Vis absorption spectrum of the title complex show strong absorptions at 616, 344 and 247 nm. These absorptions correspond to d–d transitions typical for octahedral low spin cobalt(III) complexes [16]. These transitions are from $^1A_{1g}$ ground state of cobalt(III) to singlet state $^1T_{1g}$ (low energy) and from $^1A_{1g}$ ground state to $^1T_{2g}$ (higher energy). In the complexes of the type CoA_4B_2 (*cis* or *trans*) the $^1T_{1g}$ state split, the splitting in *trans* isomer being more [17], thus justifying the three absorption peaks in the title complex salt.

2.5. NMR spectroscopy

NMR spectra of the complex salt were recorded in D_2O and DMSO-d_6. The chemical shift values are expressed as δ value (ppm) downfield from tetramethylsilane as an internal standard. When ^1H NMR is recorded in DMSO (Fig. 2c), the singlet at 5.25 ppm is observed due to NH_2 protons and singlet at 2.81 ppm is observed due to CH_2 protons. The peak area observed is 8:8 for both types of protons as indicated by the chemical formula of the complex salt and no coupling was observed. But when ^1H NMR is recorded in D_2O, the singlet at 5.26 ppm is observed due to NH_2 protons and singlet at 2.93 ppm is observed due to CH_2 protons [18]. The peak area observed is again 1:1 for both type of protons and coupling was also observed between protons of –CH_2-group and –NH_2-group of the ligand ethylenediammine, which may be due to the exchange of some of the hydrogens by deuterium. The value of the coupling constant calculated is $J = 3$ Hz. The ^{13}C NMR spectrum showed the characteristic signal [19] at 45 ppm for carbon atoms of ethylenediamine group.

^{11}B NMR spectrum the complex salt was also recorded in D_2O. The chemical shift values are expressed as δ value (ppm) up field from H_3BO_3 as an internal standard. The spectrum (Fig. 2a) shows the characteristic single peak at -2.3 due to BF_4^-, which is in agreement with the ^{11}B NMR reported for ionic BF_4^-, i.e. -2.2 ppm [20].

^{19}F NMR spectrum of the title complex salt was recorded in D_2O. The chemical shift values are expressed as δ value (ppm) up field from $CFCl_3$ as an internal standard. The spectrum (Fig. 2b) shows the characteristic single peak at -150.0 ppm due to BF_4^- ion. This is in agreement with the chemical shift value reported for ionic BF_4^-, i.e. -151.1 ppm [20]. These signals are observed at -155.13 and -155.24 ppm in (phen)($Bu_4N.BF_4$) and Pb(phen)($Bu_4N.BF_4$)$_3$(NO_3)$_2$, respectively [14]. This clearly confirmed the presence of fluoroanion, in the complex salt.

2.6. X-ray crystallography

X-ray crystal structure of [*trans*-Co(en)$_2$Cl$_2$]BF$_4$ has been unambiguously determined by single crystal X-ray crystallography and the ORTEP diagram is shown in Fig. 3. All other relevant information about the data collection is presented in Table 2.The asymmetric unit of the newly formed complex salt consists of *trans*-dichlorobis(ethylenediamine)cobalt(III) cations split over two sites of symmetry and a disordered tetrafluoroborate ion (major occupancy 56%). The disorder in BF_4^- is more a rule than an exception as can be seen in many BF_4^- compounds [21,22]. A view of the crystal structure is shown in Fig. 4. The unit cell of the complex has layers of [*trans*-Co(en)$_2$Cl$_2$]$^+$ spanning to both *b* and *c* directions (view of the packing down the *a* axis is shown in Fig. 4) and tetrahedral BF_4^- is located in between these layers. Probably, this layered nature of [*trans*-Co(en)$_2$Cl$_2$]$^+$ provides sufficient volume for alternate orientation of small tetrahedral BF_4^- ions in the lattice (without much expenditure of lattice energy) paving way for their disorder. Nevertheless, these ions are held to their position by unison of weak N–H$\cdots$F interactions Table 3 as depicted in

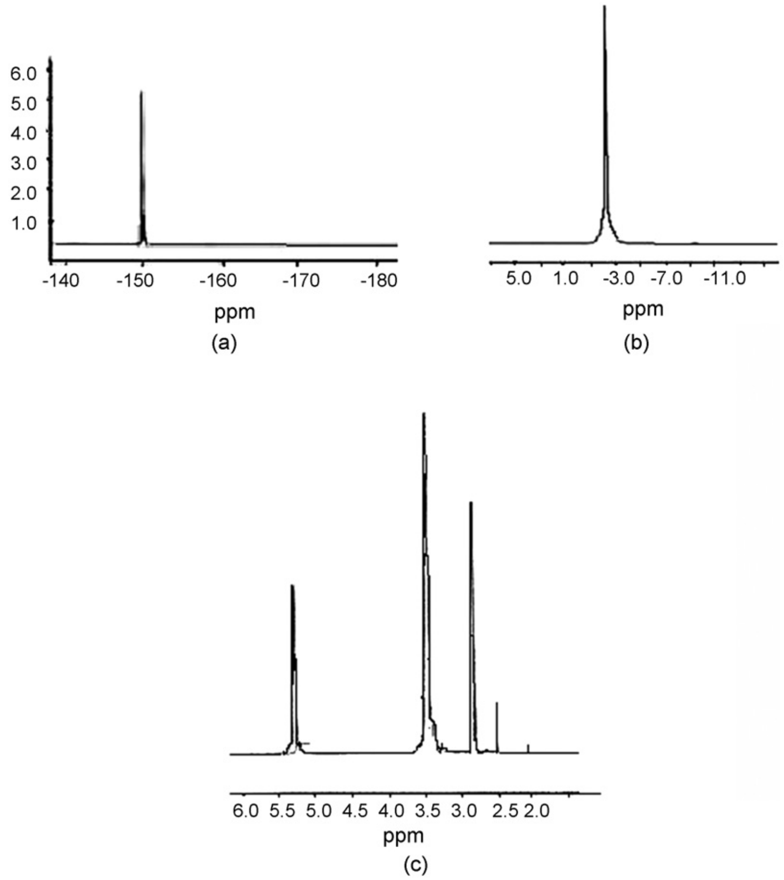


Fig. 2. Multinuclear NMR spectra of [*trans*-Co(en)$_2$Cl$_2$]BF$_4$. (a) ^{11}B NMR spectrum for [*trans*-Co(en)$_2$Cl$_2$]BF$_4$ (solvent: D$_2$O), (b) ^{19}F NMR spectrum for [*trans*-Co(en)$_2$Cl$_2$]BF$_4$ (solvent: D$_2$O), and (c) ^{1}H NMR spectrum for [*trans*-Co(en)$_2$Cl$_2$]BF$_4$ (solvent: DMSO-d_6).

Fig. 5. Thus, alternate layers of cations and anions are arranged in repeated –A–B–A–B– pattern along the *c* direction of the lattice. What is noteworthy here is that, this packing is reminiscent of the packing of [*trans*-Co(en)$_2$Cl$_2$]ClO$_3$, which also forms the layered –A–B–A–B– packing with the aid of weak interactions [23] as

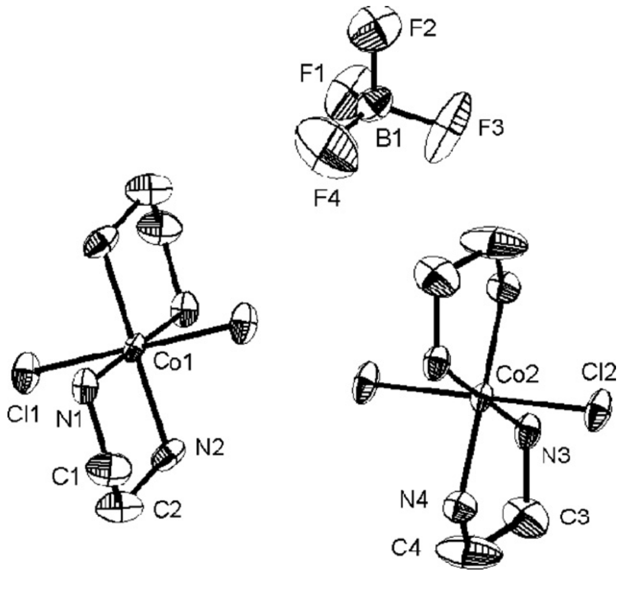


Fig. 3. An ORTEP (50% probability) view of [*trans*-Co(en)$_2$Cl$_2$]BF$_4$ showing just the major component for BF$_4$$^-$.

Table 2
Crystal data and structure refinement parameters of [*trans*-Co(en)$_2$Cl$_2$]BF$_4$

Empirical formula	$C_4H_{16}BCl_2CoF_4N_4$
Formula weight	336.85 g/mol
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 6.4127(7) Å α = 78.067(8)° b = 8.3210(10) Å β = 78.673(8)° c = 12.2407(13) Å γ = 75.170(8)°
Volume	610.61(12) Å^3
Z	2
Calculated density	1.832 g/cm^3
Absorption coefficient	15.386 mm^{-1}
F(0 0 0)	340
Crystal size	0.18 mm × 0.18 mm × 0.18 mm
Theta range for data collection	3.73–70.29°
Limiting indices	$-7 \le h \le 7$, $-10 \le k \le 9$, $-14 \le l \le 14$
Reflections collected	3840
Independent reflections	2025 [R(int) = 0.0560]
Completeness to θ = 70.29°	86.6%
Max. and min. transmission	0.1682 and 0.6810
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2025/138/177
Goodness-of-fit on F^2	1.041
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0621, w$R2$ = 0.1625
R indices (all data)	$R1$ = 0.0669, w$R2$ = 0.1676
Largest diff. peak and hole	0.973 and −0.671 e Å^{-3}

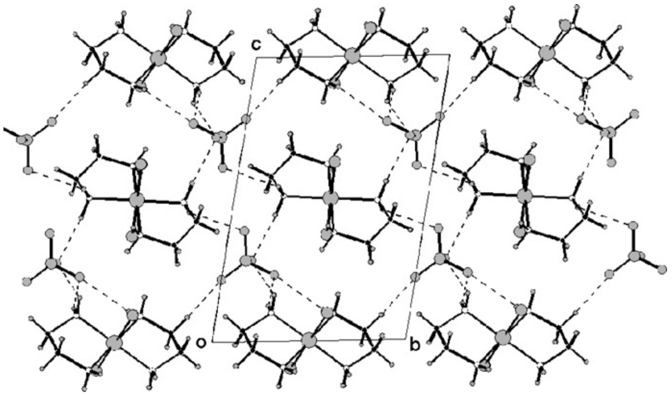


Fig. 4. A view of the crystal structure down the *a*-axis showing intermolecular N–H···F contacts as dashed lines. Also can be seen the alternate cation–anion layers forming A–B–A–B– pattern throughout the lattice.

Table 3
Hydrogen bonding parameters (Å, °) of [*trans*-Co(en)$_2$Cl$_2$]BF$_4$

D–H···A	D–H	D···A	H···A	$\angle$D–H···A
N1–H1C···Cl2	0.900	3.392	2.585	149.55
N1–H1D···F2^{i}	0.900	3.276	2.558	137.20
N1–H1D···Cl1^{i}	0.900	3.447	2.701	141.04
N2–H2C···F1^{ii}	0.900	3.052	2.262	146.35
N2–H2D···F2A^{iii}	0.900	2.911	2.043	161.61
N2–H2D···F2^{iii}	0.900	2.973	2.130	155.68
N3–H3C···Cl2^{iv}	0.900	3.476	2.679	148.13
N3–H3D···Cl1^{v}	0.900	3.436	2.704	139.23
N4–H4C···F4A^{vi}	0.900	3.022	2.197	151.97
N4–H4C···F3^{vi}	0.900	3.222	2.568	130.15
N4–H4D···F1	0.900	3.112	2.242	162.43

Symmetry transformations used to generate equivalent atoms: (i) $x + 1, y, z$; (ii) $-x, -y + 1, -z + 2$; (iii) $-x - 1, -y + 1, -z + 2$; (iv) $-x + 1, -y + 1, -z + 1$; (v) $-x, -y + 1, -z + 1$; (vi) $-x - 1, -y + 2, -z + 1$.

Table 4
Selected bond distances (Å) and angles (°) of [*trans*-Co(en)$_2$Cl$_2$]BF$_4$

N(1)–Co(1)	1.956 (4)	N(4)–Co(2)	1.954 (5)
N(2)–Co(1)	1.940 (4)	Cl(1)–Co(1)	2.2466 (12)
N(3)–Co(2)	1.951 (4)	Cl(2)–Co(2)	2.2473 (12)
N(2)#1–Co(1)–N(2)	180.0	N(3)–Co(2)–N(3)#2	180.0
N(2)#1–Co(1)–N(1)	93.7 (2)	N(3)–Co(2)–N(4)	85.9 (2)
N(2)–Co(1)–N(1)	86.3 (2)	N(3)#2–Co(2)–N(4)	94.1 (2)
N(1)–Co(1)–N(1)#1	180.0	N(4)–Co(2)–N(4)#2	180.0 (3)
N(2)–Co(1)–Cl(1)#1	90.56 (15)	N(3)–Co(2)–Cl(2)	90.07 (13)
N(1)–Co(1)–Cl(1)#1	89.53 (13)	N(3)#2–Co(2)–Cl(2)	89.93 (13)
N(2)–Co(1)–Cl(1)	89.44 (15)	N(4)–Co(2)–Cl(2)	90.03 (16)
N(1)–Co(1)–Cl(1)	90.47 (13)	N(4)#2–Co(2)–Cl(2)	89.97 (16)
Cl(1)#1–Co(1)–Cl(1)	180.0	Cl(2)–Co(2)–Cl(2)#2	180.0

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y + 1, -z + 2$ #2 $-x, -y + 1, -z + 1$.

shown in Fig. 6. The small size, unit negative charge and shape complementarity of these anions (ClO_3^-, BF_4^-, both tetrahedral) may play the similar role, thus getting sandwiched between the layers of [*trans*-Co(en)$_2$Cl$_2$]$^+$ ions in their respective crystal structures.

The N–H···F bond length is in the range 2.33–2.57 Å in [*cis*-Co(tren)(NO$_2$)$_2$]BF$_4$ [24] and 2.07–2.56 Å in [Co(NH$_3$)$_6$]Cl$_2$·BF$_4$ [25] which is comparable with the N–H···F bond length in the title complex salt (2.04–2.56 Å). Cation coordination is in the form of slightly distorted octahedral (Table 4), with Co–N bonds in the range 1.940(4)–1.956(4) Å, Co–Cl bond distances of 2.2473(12) and 2.2466(12) Å and N–Co–N angles in the range 85.9(2)–94.1(2)°.

2.7. Conclusions

The potential of cationic cobaltammine [*trans*-Co(en)$_2$Cl$_2$]$^+$ has been explored by isolating and characterizing the solid obtained by mixing the aqueous solutions of [*trans*-Co(en)$_2$Cl$_2$]Cl and NaBF$_4$. Single crystal X-ray structure determination revealed the presence of discrete ions and the crystal lattice is stabilized by and hydrogen bonding interactions involving N–H···F and N–H···Cl besides electrostatic forces of attraction. The present study shows that cationic cobaltammine [*trans*-Co(en)$_2$Cl$_2$]$^+$ is a promising anion receptor for the [BF$_4$]$^-$ anion in aqueous medium in contrast to other synthetic receptors which are effective in non-aqueous solvents.

3. Experimental

Analytical grade reagents were used without any further purification. [*trans*-Co(en$_2$)Cl$_2$]Cl has been prepared according to literature method [26].

3.1. Synthesis of [trans-Co(en)$_2$Cl$_2$]BF$_4$

One gram (0.003 mol) of [*trans*-Co(en)$_2$Cl$_2$]Cl was dissolved in 25 ml water and filtered. 0.38 g (0.003 mol) of sodium tetrafluoroborate dissolved in minimum amount of water was added to this solution. Green coloured single crystals suitable for X-ray structure determination were obtained within half an hour. The crystals were collected by drawing off the mother liquor and air-dried (yield, 80%). The elemental analysis is consistent with the composition [*trans*-Co(en)$_2$Cl$_2$]BF$_4$. Found: C, 14.4; H, 4.6; N, 16.8; Co, 17.5 for the complex salt, the calculated values C, 14.3; H, 4.7; N, 16.7; Co, 17.6. Solubility: 1.25 g/100 ml at 25 °C, $K_{sp} = 1.3 \times 10^{-3}$.

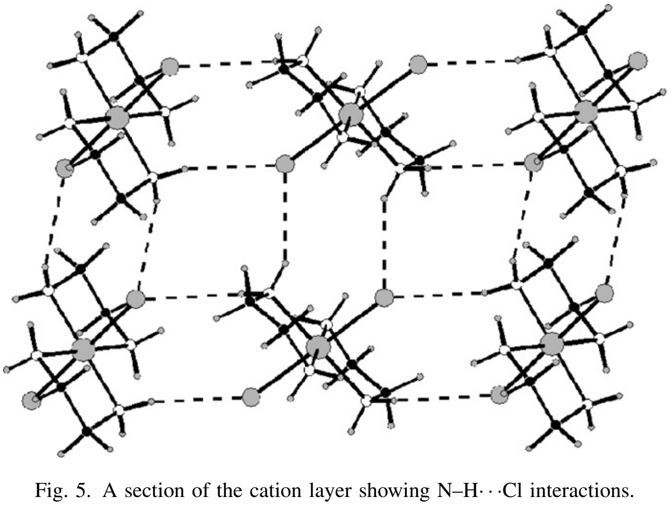


Fig. 5. A section of the cation layer showing N–H···Cl interactions.

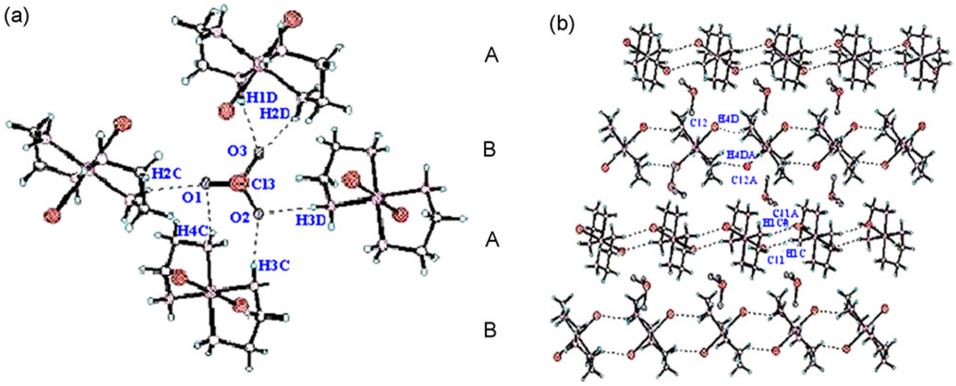


Fig. 6. (a) Multiple sandwich' packing of $[Co(en)_2Cl_2]ClO_3$ viewed down *b*-axis showing the formation of molecular tapes through N–H· · ·Cl hydrogen bonding. Four such tapes are shown. Slice B has tapes formed through Co_2 anions whereas slice A has the same with Co1. Note the occupation of chlorate anions in between the layers. (b) The bifurcated N–H· · ·O hydrogen bonding pattern of the chlorate anion in the crystal lattice. The oxygen atoms are saturated in terms of their proton accepting capability.

3.2. Instrumentation

Cobalt was determined by standard method [27] and C, H, N were estimated micro-analytically by automatic PerkinElmer 2400 CHN elemental analyser. IR spectrum was recorded as KBr pellets on a PerkinElmer Spectrum RXFT-IR system. ^{1}H, ^{13}C NMR, ^{11}B and ^{19}F spectra were recorded in D_2O respectively on JEOL AL 300MHz FT NMR spectrophotometer. UV–vis spectrum was recorded in water using Hitachi 330 spectrometer.

3.3. Crystal structure determination

X-ray data recorded at room temperature on a Bruker Smart 6000 diffractometer equipped with a CCD detector and a copper tube source. A single crystal was mounted on a glass fibre using epoxy resin and structure solution as well as refinement were performed using SHELXL [28]. Hydrogen atoms were located in the difference Fourier map and refined using a riding model.

Crystallographic data for the structural analysis of the title compound has been deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK, and are available free of charge from the Director on request quoting the deposition number CCDC 609220 (Fax: +44 1223 336033, email: deposit@ccdc.cam.ac.uk).

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