



Binding of fluorine containing anions by new cationic Co(III) complex: Competitive interaction of chloride and hexafluorophosphate with $[\text{Co}(\text{phen})(\text{H}_2\text{biim})_2]^{3+}$

Raj Pal Sharma^{a,*}, Ajnesh Singh^a, Paloth Venugopalan^a, Valeria Ferretti^{b,**}

^a Department of Chemistry, Panjab University, Chandigarh 160014, India

^b Centro di Strutturistica Diffattometrica and Dipartimento di Chimica, University of Ferrara via L. Borsari 46, I-44100 Ferrara, Italy

ARTICLE INFO

Article history:

Received 2 February 2011

Received in revised form 20 April 2011

Accepted 27 April 2011

Available online 6 May 2011

Keywords:

Cobalt(III)

Anion receptor

Hexafluorophosphate

X-ray crystallography

ABSTRACT

A new mixed ligand cobalt(III) complex salt $[\text{Co}(\text{phen})(\text{H}_2\text{biim})_2]\text{Cl}_3$ (**1**) (where phen = 1,10-phenanthroline, H_2biim = 2,2'-biimidazole) has been synthesized for the first time. In an effort to explore this new cationic complex $[\text{Co}(\text{phen})(\text{H}_2\text{biim})_2]^{3+}$ as binding agent for fluoroanions, complex salt $[\text{Co}(\text{phen})(\text{H}_2\text{biim})_2](\text{PF}_6)_2\text{Cl}\cdot 2\text{H}_2\text{O}$ (**2**) has been synthesized and characterized. Single crystal X-ray structure determination has revealed that complex salt **2** crystallizes in monoclinic crystal system with space group $P2_1/c$ and consist of one complex cation, one chloride, two hexafluorophosphate anions and two water molecules of crystallization. The packing analyses revealed that the complex cations are arranged in such a way that N–H groups of biimidazole moiety are involved in N–H \cdots Cl interaction with chloride ion while C–H groups of phen/ H_2biim are involved in C–H \cdots F interaction with hexafluorophosphate to keep these groups in close proximity. A strong network of hydrogen bond interactions C–H \cdots F, N–H \cdots O, N–H \cdots Cl, C–H \cdots O (water) and O–H \cdots O (water) are responsible for the stabilization of 3D supramolecular architecture. To the best of our knowledge, this is the first crystal structure of any salt containing the cation $[\text{Co}(\text{phen})(\text{H}_2\text{biim})_2]^{3+}$.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Anion binding is an area that has been receiving a lot of attention in the past two decades due to the applications of anionic species in biological processes, catalysis, ion transport studies, etc. [1–6]. Most of the biomolecules like peptides, proteins, nucleotides (DNA, RNA) and carbohydrates are anionic or at least have anionic substrates and majority of enzyme substrates and co-factors are also anionic. Irrespective of the challenges [7–11] (larger size of anions, large free energies of solvation, wide range of geometries and pH sensitivity) in synthesis of anion receptors, recent years have seen an immense interest in anion recognition chemistry and a variety of novel anion-binding strategies have emerged. In most of the cases N–H groups of amide, thioamides, urea, ammonium, pyrroles, guanidinium, imidazolium, etc. have been utilized for the interaction with the anionic species [12,13]. Literature survey revealed that organic and organometallic based anion receptors have been extensively studied as compared to metal based anion

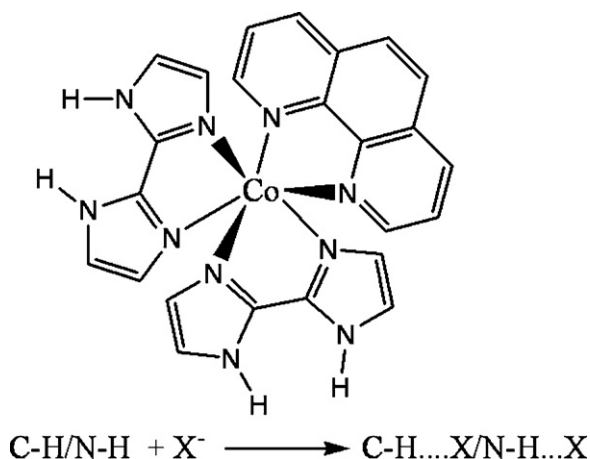
receptors [14–24]. Thus, in continuation of our research program to exploit cobalt(III) complexes as anion receptors (complexants) [25–30], we have synthesized a new mixed ligand cationic complex $[\text{Co}(\text{phen})(\text{H}_2\text{biim})_2]^{3+}$ as its chloride salt. The complex cation possesses all the characteristic features [31] of good binding agent: (i) three unit positive charge for effective electrostatic interactions, (ii) hydrogen bond donor groups (C–H and N–H) and (iii) a stable framework onto which these structural components can be assembled. It was envisaged that presence of C–H groups of phen ligand in addition to four N–H groups of the 2,2'-biimidazole ligands will facilitate the binding of anion (Scheme 1). It is also interesting to know that how these C–H and N–H groups will behave in a competitive way.

It is worth mentioning that these complexes are the first representative of this series of 2,2'-biimidazole and 1,10-phenanthroline containing cobalt(III) complexes in which 2,2'-biimidazole is acting as a neutral ligand. Thus, present work represents the first successful synthesis of cationic complex $[\text{Co}(\text{phen})(\text{H}_2\text{biim})_2]^{3+}$ and its utility to bind fluoroanion and also presents an example of the competitive interaction of Cl^- and PF_6^- anions with $[\text{Co}(\text{phen})(\text{H}_2\text{biim})_2]^{3+}$. The fluoro-containing anion is selected because fluorinated compounds have been known for their fascinating properties as fluorine can impart significant effect on their properties such as increased chemical/metabolic stability,

* Corresponding author. Tel.: +91 0172 2534433; fax: +91 0172 2545074.

** Corresponding author. Tel.: +39 0532 455144; fax: +39 0532 240709.

E-mail addresses: rpsharmapu@yahoo.co.in (R.P. Sharma), frt@unife.it (V. Ferretti).



Scheme 1. Second sphere interactions between the coordinated phen/H₂biim in the complex cation and anion.

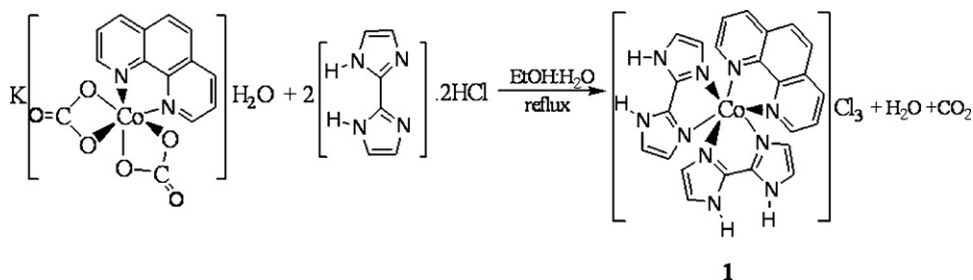
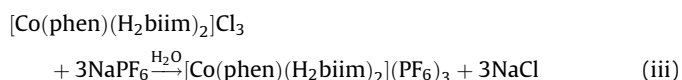
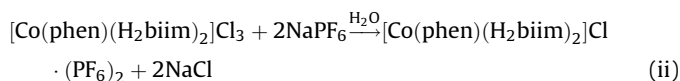
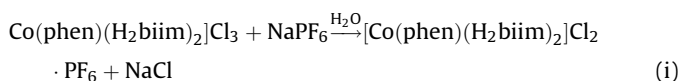
lipophilicity, solubility, dipole–dipole and hydrogen bonding interactions. One of such fluoro-anion is PF₆[−] which is a major component of capacitors and battery electrolyte. Air stable imidazolium salts with PF₆[−] anion are tolerant to a variety of polar functional groups, which enables their use in a wide range of chemical and electrochemical applications [32].

2. Results and discussion

2.1. Synthesis

The ligand 2,2'-biimidazole (H₂biim) was prepared by reaction of ammonium acetate and glyoxal by the method of Xiao et al. [33] and its salt H₂biim·2HCl was prepared by reported method [34]. The new mixed ligand cobalt(III) complex, [Co(phen)(H₂biim)₂]Cl₃ (**1**) has been synthesized by the reaction of K[Co(phen)(CO₃)₂]H₂O [35] and H₂biim·2HCl in ethanol–water (4:1) mixture as shown in Scheme 2.

For anion exchange reactions, complex salt **1** and sodium hexafluorophosphate were reacted in number of ways (in aqueous medium) depending upon the stoichiometric ratio of reactants as follows:



Scheme 2. Schematic presentation of synthetic procedure.

Microscopic examination of the nature, texture and morphology of the crystals obtained from different reactions ((i)–(iii)) showed that the products obtained were same and their elemental analyses were consistent with the formula [Co(phen)(H₂biim)₂](PF₆)₂·Cl·H₂O (**2**) as shown in Eq. (ii). This was further confirmed by the single crystal structure determination. There are examples of reactions of [Co(NH₃)₆]Cl₃ in which partial replacement of chloride ions was achieved even though the reaction stoichiometry was conducive for total replacement (methanesulphonate, mesitylenesulphonate, BF₄[−] and p-nitrobenzoate) [36–39].

2.2. Solubility product measurement

Solubility of the ionic salts in the water differs to greater extent. On the basis of solubility the ionic salts are classified as soluble, slightly soluble and sparingly soluble and the measurement of the solubility product provides an idea about the affinity of cation and anion towards each other. Solubility measurements at room temperature show that complex salt **1** is highly soluble as compared to **2** which is sparingly soluble. The K_{sp} values of **1** and **2** are 1.24, 4.1 × 10^{−7}, respectively, indicating that the [Co(phen)(H₂biim)]³⁺ cation has more affinity for hexafluorophosphate as compared to Cl[−] which might be the driving force behind the reaction.

2.3. Molar conductance measurement

Conductance measurement was carried out at 25 °C in water and graph was plotted between Δ (molar conductance) and square root of concentration. When the concentration was extrapolated to zero, it gave Δ₀ = 428 and 450 S cm² mol^{−1} for complex salts **1** and **2** which indicated the 1:3 electrolytic behaviour [40].

2.4. Spectroscopic characterization

Vibrational spectra of newly synthesized complex salts have been recorded in the region 400–4000 cm^{−1}. In FT-IR spectra of complex salts, peaks in the region 3600–3400, 1636–1612, 848–841, 460 cm^{−1} were assigned to ν(O–H), ν(C=C), δ(=C–H) and ν(Co–N), respectively. The δ(C–H), δ(N–H) and ring vibrations have been observed in the region 1185–1188, 1139–1140, 1037–1016 cm^{−1}. The IR spectra of complex salts show a broad band at 3500–3050 cm^{−1} which was assigned to ν(N–H) vibrations. The shift of these bands to higher energies compared to position in free ligand (2,2'-biimidazole) is indicative of their coordination as bidentate chelating ligand [41]. In complex salt **2**, the presence of counter anion, PF₆[−] was confirmed by the characteristic bands at 842 and 557 cm^{−1} in the infrared spectrum and these were assigned to ν(P–F) and δ(F–P–F), respectively. The band observed at 842 cm^{−1} was slightly broadened due to the overlapping of IR band due to δ(=C–H) at 847 cm^{−1}. In the case of Cu(II) complex containing ionic PF₆[−] ion, the two IR active band were observed at 845 and 560 cm^{−1} [42] while in case of [Co(phen)₃](PF₆)₃·CH₃·

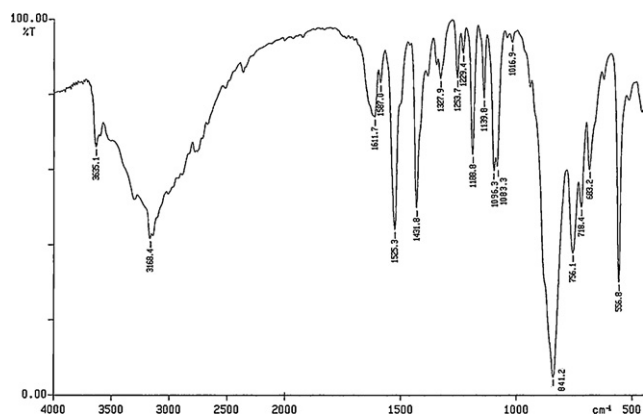


Fig. 1. FT IR spectrum of complex salt **2**.

CH_3COCH_3 , these bands were observed at 845 and 560 cm^{-1} [25]. The peak assignments have been made in consultation with literature values [43]. The FT-IR spectrum of complex salt **2** is shown in Fig. 1.

NMR spectra of the newly synthesized complex salt were recorded in DMSO-d_6 . In complex salts **1** and **2**, ^1H and ^{13}C NMR chemical shift values are in good agreement with the literature values reported for related complexes [44–46]. Doublets in region 9.17–9.13, 7.98–7.93, 7.75–7.72, 7.57–7.53, 6.53–6.49, 6.38–6.37, singlet at 8.52–8.50 and triplet at 8.17–8.14 were assigned to protons $\text{H}_{\text{phen}} 2/9$, $\text{H}_{\text{phen}} 4/7$, $\text{H}_{\text{biim}} 5'$, $\text{H}_{\text{biim}} 5$, $\text{H}_{\text{biim}} 4'$, $\text{H}_{\text{biim}} 4$, $\text{H}_{\text{phen}} 5/6$, and $\text{H}_{\text{phen}} 3/8$, respectively. The presence of PF_6^- anion has also been confirmed by ^{19}F NMR in which typical doublet at 5.98 ppm (using CF_3COOH as reference) with $J = 754.5 \text{ Hz}$ [25] has been observed. ^1H NMR spectrum of complex salt **2** is shown in Fig. 2.

The electronic spectra of complex salts **1** and **2** were recorded in water. For Co(III) complexes two type of transitions, i.e. $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ and $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$ are expected. In complex salts **1** and **2** these transitions were observed around 450 and 340 nm as reported in the literature [47–49]. In complex salts **1** and **2** these values are observed around 477 and 349 nm, respectively. Other transitions due to phenanthroline and biimidazole groups attached to the complex cation were also observed around 296 and 273 nm [47–49].

2.5. Structure description

2.5.1. Coordination geometry and bonding

The newly synthesized cobalt(III) complex salt **2** has been structurally characterized by X-ray crystallography [43]. The ORTEP III [50] diagram and atomic labeling scheme for complex

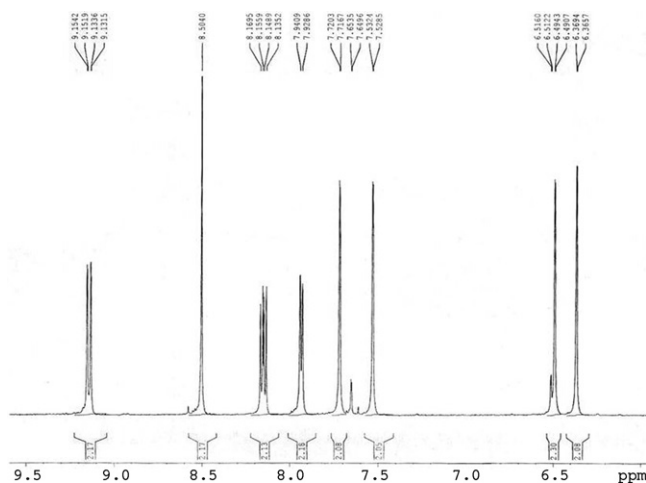


Fig. 2. ^1H NMR spectrum of complex salt **2**.

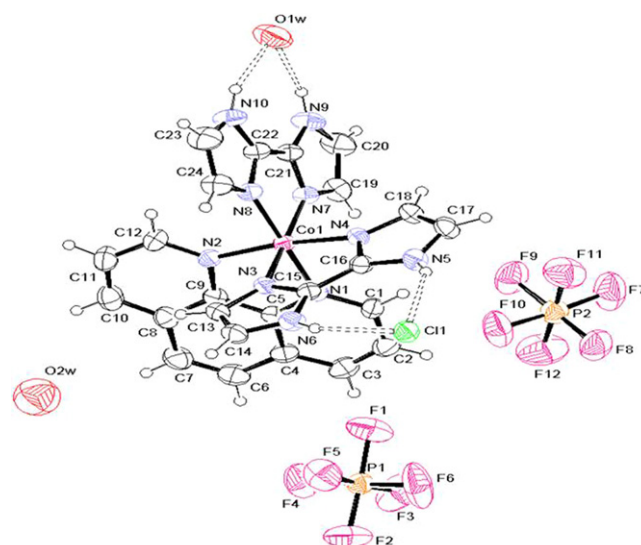


Fig. 3. ORTEP diagram of complex salt **2**, selected structural parameters: Co1–N1 = 1.951(3) Å, Co1–N2 = 1.945(3) Å, Co1–N3 = 1.925(2) Å, Co1–N4 = 1.935(3) Å, Co1–N7 = 1.928(2) Å, Co1–N8 = 1.920(3) Å, and Co–N = 1.920(3)–1.951(3) Å and bond angles N–Co–N range 82.5(1)–94.6(1)°.

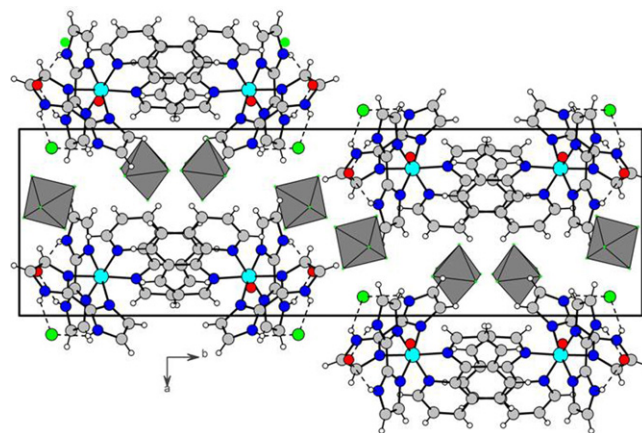
salt **2** is shown in Fig. 3. The asymmetric unit is constituted by one molecule of $[\text{Co}(\text{phen})(\text{H}_2\text{biim})_2]^{3+}$ complex, two PF_6^- and one Cl^- anions and two water molecules. The cobalt(III) metal ion is coordinated to one phenanthroline and two biimidazole ligands through N atoms, in a slightly distorted octahedral geometry. The average Co–N(phen) bond length is 1.948(3) Å while average Co–N(H_2biim) bond length is 1.927(3) Å which is slightly shorter than Co–N(phen) bond lengths. The Co–N bond lengths are in agreement with those found in other similar complexes; in particular, Cu–N(H_2biim) lengths agree well with the mean value of 1.94[1] Å calculated on 7 similar Co complexes retrieved from the Cambridge Crystallographic Database (38 observations). The PF_6^- anions possess nearly equal P–F distances ranging from 1.553(4) to 1.593(4) Å, and the geometry around each P atom is almost perfectly octahedral. The Co–N(phen), Co–N(H_2biim), P–F bond lengths and N–Co–N, F–P–P bond angles are in good agreement with those reported in literature [25,28–30,51,52]. Selected bond lengths and angles are reported in Table 1. To the best of our knowledge, this is the first crystal structure of a salt containing the cation $[\text{Co}(\text{phen})(\text{H}_2\text{biim})_2]^{3+}$.

2.5.2. Crystal packing

The crystal lattice is stabilized by a three-dimensional network of intermolecular N–H...Cl/O, C–H...F, O–H...O, C–H...O hydrogen bonds besides electrostatic forces of attraction. The hydrogen bonding parameters are given in Table 2. The complex cation moieties are arranged in the lattice in such a way that both the N–H hydrogen atoms of the H_2biim ligands are involved in N–H...Cl, N–H...O hydrogen bond interactions with O1w and Cl atoms (i.e. one H_2biim moiety is forming two N–H...O bonds with O1w atom while second H_2biim moiety is forming two N–H...Cl hydrogen bonds with chlorine Cl1 atom) (Fig. 3). This arrangement gives rise to two R_2^1 (7) rings motifs for each Co(III) complex. In turn, Cl and O1w are linked through close contacts of 3.237(6) Å. The overall packing pattern is shown in Fig. 4. The hexafluorophosphate anions are located in zig-zag channels running along the c direction and are connected to the metallorganic part of the structure via weak C–H...F interactions (Table 2). It is noteworthy to mention that most of the fluorine atoms are involved in the C–H...F second sphere interactions as shown in Fig. 5. In case of first PF_6^- molecules (P1) five significant C–H...F interactions of magnitude

Table 1
Selected bond lengths (Å) and angles (°) for complex salt **2**.

Co1–N1	1.951(3)	P1–F4	1.570(4)
Co1–N2	1.945(3)	P1–F5	1.588(3)
Co1–N3	1.925(2)	P1–F6	1.553(4)
Co1–N4	1.935(3)	P2–F7	1.564(4)
Co1–N7	1.928(2)	P2–F8	1.591(4)
Co1–N8	1.920(3)	P2–F9	1.596(3)
P1–F1	1.585(4)	P1–F10	1.593(3)
P1–F2	1.564(4)	P1–F11	1.577(4)
P1–F3	1.559(4)	P1–F12	1.572(5)
N1–Co1–N2	83.8(1)	F2–P1–F5	86.5(2)
N1–Co1–N3	92.1(1)	F2–P1–F6	91.8(2)
N1–Co1–N4	92.3(1)	F3–P1–F4	90.8(2)
N1–Co1–N7	93.8(1)	F3–P1–F6	90.5(3)
N2–Co1–N3	90.3(1)	F4–P1–F5	90.3(2)
N2–Co1–N7	94.6(1)	F5–P1–F6	88.4(2)
N2–Co1–N8	93.5(1)	F7–P2–F8	92.0(2)
N3–Co1–N4	82.7(1)	F7–P2–F9	89.7(2)
N3–Co1–N8	91.8(1)	F7–P2–F11	87.6(2)
N4–Co1–N7	92.8(1)	F7–P2–F12	93.6(2)
N4–Co1–N8	90.9(1)	F8–P2–F10	89.5(2)
N7–Co1–N8	82.5(1)	F8–P2–F11	88.5(2)
F1–P1–F3	88.8(2)	F8–P2–F12	93.3(2)
F1–P1–F4	89.5(2)	F9–P2–F10	88.7(2)
F1–P1–F5	91.3(2)	F9–P2–F11	90.1(2)
F1–P1–F6	89.6(2)	F9–P2–F12	88.0(2)
F2–P1–F3	93.4(2)	F10–P2–F11	88.7(2)
F2–P1–F4	89.0(2)	F10–P2–F12	89.9(2)

**Fig. 4.** Packing diagram of complex salt **2** viewed along *c* direction. PF₆[−] anions are drawn as grey octahedra.

2.54–2.64 Å are observed while in other (P2) five C–H...F (2.50–2.65 Å) and one N–H...F (N9–H19–F8 = 2.39(4) Å) interaction have been observed (Table 2). Other anionic species, chlorine atom is singly involved in interaction with N–H groups of the H₂biim moieties, i.e. chlorine atoms are posing great challenge to PF₆[−] groups to get involved in N–H...F interactions. The only one N–H...F contact is on that side of H₂biim moiety where N–H groups are having N–H...O interactions with water molecule of crystallization. In other words chlorine atoms arrange all the constituents in such a way that PF₆[−] groups selectively involved in C–H...F interaction while itself is involved only in N–H...Cl interactions. No π – π interaction arises between the phenanthroline aromatic rings, the centroids of adjacent moieties being some 4.16 Å far apart.

2.6. Conclusions

In the present work synthesis of a new mixed ligand cobalt(III) complex [Co(phen)(H₂biim)₂]³⁺ has been described. This cationic

complex salt has been utilized in the binding of fluoroanion by isolating and characterizing new complex salt [Co(phen)(H₂biim)₂]Cl.(PF₆)₂·2H₂O. The isolation of complex salt **2** coupled with solubility product measurements have shown that [Co(phen)(H₂biim)₂]³⁺ has more affinity for hexafluorophosphate than chloride ion. Single crystal X-ray structure determination has revealed that the crystal lattice is stabilized by C–H...X(F/Cl) and C–H...O through second sphere interactions besides electrostatic forces of attraction. One interesting feature is that PF₆[−] groups are selectively interacting with complex cations by C–H...F interactions and chloride ions by N–H...Cl interactions.

3. Experimental

3.1. Materials

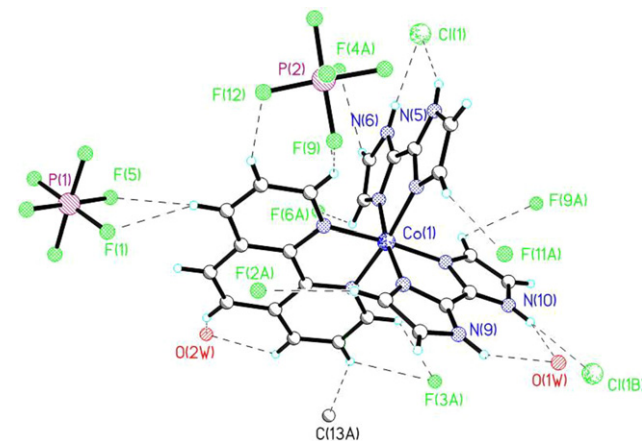
Analytical grade reagents were used without any further purification. H₂biim, H₂biim·2HCl and K[Co(phen)(CO₃)₂]H₂O were prepared by the reported methods[33–35].

3.2. Instruments and measurements

C, H and N were determined using a Perkin Elmer 2400 CHN elemental analyzer. The cobalt content was established by a volumetric method [53]. The aqueous UV/vis spectra were recorded using a Hitachi 330 spectrometer and the IR spectra

Table 2
Hydrogen bonding parameters of [Co(phen)(H₂biim)₂](PF₆)₂·Cl·2H₂O.

D–H...A	D...A (Å)	H...A (Å)	D–H...A (°)
N5–H17...Cl1	3.207(3)	2.47(2)	147(2)
N6–H18...Cl1	3.151(3)	2.36(4)	155(3)
N9–H19...O1W	2.923(7)	2.22(6)	138(4)
N10–H20...O1W	2.914(5)	2.14(4)	150(3)
N9–H19...F8 ^{x+y,z−1}	3.001(4)	2.39(4)	128(3)
C10–H6...O2w	3.36(1)	2.65	133
C1–H1...F9	3.252(5)	2.61	127
C1–H1...F10	3.148(6)	2.50	127
C2–H2...F12	3.486(7)	2.61	156
C3–H3...F1	3.435(6)	2.59	151
C3–H3...F5	3.403(6)	2.60	145
C11–H7...F3 ^{x+1,−y+1/2,z−1/2}	3.221(7)	2.64	121
C12–H8...F3 ^{x+1,−y+1/2,z−1/2}	3.178(7)	2.54	126
C18–H12...F11 ^{−x+1,−y,−z}	3.521(5)	2.65	157
C19–H13...F2 ^{x,−y+1/2,z−1/2}	3.504(6)	2.60	163
C24–H16...F12 ^{x+1,y,z}	3.360(5)	2.57	143
Short contact			
Cl1...O1W ^{2−x,−y,−z}	3.237(6)		

**Fig. 5.** Second sphere interactions between complex cation, PF₆[−], Cl[−] anions and water molecules.

(KBr pellet) were recorded using a Perkin Elmer RX FT-IR system. ^1H and ^{13}C NMR spectra were recorded in DMSO- d_6 by using a Bruker AC 400 F (400 MHz) spectrophotometer. The chemical shift values are expressed as δ values (ppm) downfield from tetramethylsilane 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 a Pico Conductivity Meter (Model CNO4091201, Lab India) at 25 °C by using double distilled water.

3.2.1. Synthesis of $[\text{Co}(\text{phen})(\text{H}_2\text{biim})_2]\text{Cl}_3$ (1)

The complex salt $\text{K}[\text{Co}(\text{phen})(\text{CO}_3)_2]\cdot\text{H}_2\text{O}$ (2.4 mmol, 1 g) and $\text{H}_2\text{biim}\cdot 2\text{HCl}$ (4.8 mmol, 0.995 mg) were refluxed in a ethanol:water mixture (4:1, v/v) for 3 h. The reaction mixture was filtered and concentrated approximately to 5 mL. To the concentrated solution, 0.5 mL of 1 M HCl was added and orange coloured product was precipitated with the help of acetone. The precipitated product was dried over P_2O_5 under vacuum. Overall yield: 70%. Anal. Calcd. For $\text{C}_{24}\text{H}_{20}\text{N}_{10}\text{Cl}_3\text{Co}$ (1): C, 49.94; H, 3.26; N, 22.82; Co, 9.62; Cl, 17.36%. Found: C, 49.60; H, 3.10; N, 22.50; Co, 9.60; Cl, 17.20. IR/ cm^{-1} (KBr): 3395(b), 3114(w), 2765(w), 1636(bs), 1519(s), 1428(s), 1323(m), 1185(s), 1098(s), 932(m), 849(s), 763(sb), 715(s), 682(m), 460(w). ^1H NMR (DMSO- d_6): cation, $[\text{Co}(\text{phen})(\text{H}_2\text{biim})_2]^{3+}$, δ = 9.16(d, H9/2), 8.51(s, H5/6), 8.15(t, H3/8), 7.97(d, H4/7), 7.75(s, H5'), 7.56(s, H5), 6.53(s, H4'), 6.38(s, H4). ^{13}C NMR (DMSO- d_6): δ = 153.09, 146.07, 141.17, 139.29, 130.75, 128.45, 128.18, 127.07, 125.76, 124.42, 123.52 ppm. Solubility in water (25 °C) = 30 g/100 mL. UV/vis (H_2O): 463, 297, 273 nm.

3.2.2. Synthesis of $[\text{Co}(\text{phen})(\text{H}_2\text{biim})_2](\text{PF}_6)_2\cdot\text{Cl}\cdot 2\text{H}_2\text{O}$ (2)

To a 10 mL solution of $[\text{Co}(\text{phen})(\text{H}_2\text{biim})_2]\text{Cl}_3$ (0.25 g, 0.41 mmol) in water (containing 3–4 drops of 1 M HCl), 10 mL solution of NaPF_6 (0.069 g, 1.23 mmol) was added. Orange coloured precipitated product was isolated which was re-crystallized from acetone water mixture (water was slightly acidified with dil. HCl before use). The orange coloured long rectangular crystals appeared after two days on slow evaporation at room temperature. Yield 65%. The complex salt decomposed at 230 °C. Anal. calcd. for $\text{C}_{24}\text{H}_{20}\text{CoN}_{10}\cdot 2(\text{F}_6\text{P})\cdot 2(\text{H}_2\text{O})\cdot\text{Cl}$ (%): C, 33.15; H, 2.76; N, 16.11; Cl, 4.08; Co, 6.79. Found: C, 33.08; H, 2.65; N, 15.98; Cl, 3.98, Co, 6.70. IR/ cm^{-1} (KBr): 3635(w), 3168(b), 1612(bm), 1525(s), 1431(s), 1327(w), 1253(w), 1189(m), 1096(m), 1083(m), 841(bs), 756(m), 718(w), 556(s). ^1H NMR (DMSO- d_6): cation, $[\text{Co}(\text{phen})(\text{H}_2\text{biim})_2]^{3+}$, δ = 9.14(d, H9/2), 8.50(s, H5/6), 8.15(t, H3/8), 7.93(d, H4/7), 7.72(s, H5'), 7.53(s, H5), 6.50(s, H4'), 6.37(s, H4). ^{13}C NMR (DMSO- d_6): δ = 153.47, 146.58, 141.60, 139.96, 131.22, 128.86, 128.66, 127.51, 126.21, 125.16, 124.26 ppm. Solubility in water (25 °C) = 1.54 g/100 mL. UV/vis (H_2O): 477, 349, 296, 273 nm.

3.3. X-ray crystallography

The X-ray diffraction data for the complex salt **2** were collected at room temperature using a Nonius Kappa CCD diffractometer with graphite-monochromated Mo $\text{K}\alpha$ radiation (λ = 0.7107 Å). Data sets were integrated using the DENZO-SMN package and corrected for Lorentz, polarization and absorption [54] effects. The structure was solved by direct methods [55] and refined on F^2 by full-matrix least-squares methods using the SHELX97 program [56]. All non-H atoms were refined anisotropically, apart from the O2w atom, disordered over two equivalent positions and refined isotropically. N–H atoms of the H_2biim ligands were found in the Difference Fourier map and refined isotropically; H atoms belonging to the solvent molecules were not included in the refinement; all other hydrogens were given calculated positions.

Table 3

Selected crystal data and refinement details of complex salt **2**.

Chemical formula	$\text{C}_{24}\text{H}_{20}\text{CoN}_{10}\cdot 2(\text{F}_6\text{P})\cdot 2(\text{H}_2\text{O})\cdot\text{Cl}$
M_r	868.85
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	295
a, b, c (Å)	10.2459 (2), 31.4844 (4), 11.1372 (2)
β (°)	112.8671 (6)
V (Å ³)	3310.35 (8)
Z	4
μ (mm ^{−1})	0.81
Crystal size (mm)	$0.52 \times 0.14 \times 0.12$
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	33882, 7990, 5531
R_{int}	0.083
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.059, 0.194, 1.13
No. of reflections	7990
No. of parameters	484
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ^{−3})	0.84, −1.24

All calculations were accomplished using WINGX [57]. The selected crystal data and refinement details are given in Table 3.

Supplementary data

Crystallographic data of the title complex salt have been deposited with the Cambridge Crystallographic Data Center allocated with the deposit number CCDC-762998. A copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

The authors gratefully acknowledges the financial support of CSIR vide grant no. 09/135/0594/2010/EMR-I.

References

- [1] J.L. Sessler, P.A. Gale, W.-S. Cho, Anion Receptor Chemistry, The Royal Society of Chemistry, Cambridge, UK, 2006.
- [2] P.D. Beer, P.A. Gale, Angew. Chem. Int. Ed. 40 (2001) 486–516.
- [3] Al Kraytsberg, Y. Ein-Eli, J. Power Sources 196 (2011) 886–893.
- [4] A. Aldrey, C. Núñez, V. García, R. Bastida, C. Lodeiro, A. Macías, Tetrahedron 66 (2010) 9223–9230.
- [5] X. He, F. Herranz, E.C.-C. Cheng, R. Vilar, V.W.-W. Yam, Chem. Eur. J. 16 (2010) 9123–9131.
- [6] K.R. Dey, T. Horne, F.R. Fronczek, Md.A. Hossain, Inorg. Chem. Commun. 13 (2010) 1515–1518.
- [7] S.R. Gadre, C. Kolmel, I.H. Shrivastava, Inorg. Chem. 31 (1992) 2279–2281.
- [8] F.P. Schmidtchen, M. Berger, Chem. Rev. 97 (1997) 1609–1646.
- [9] B. Valeur, I. Leray, Coord. Chem. Rev. 205 (2000) 3–40.
- [10] P.A. Gale, Coord. Chem. Rev. 213 (2001) 79–128.
- [11] A.P. Davis, R.S. Wareham, Angew. Chem. Int. Ed. 38 (1999) 2978–2996.
- [12] P.A. Gale, S.E. Garcia, J. Garric, Chem. Soc. Rev. 37 (2008) 151–190.
- [13] B.A. Moyer, L.H. Delmau, C.J. Fowler, A. Ruas, D.A. Bostick, J.L. Sessler, E. Katayev, G.D. Pantos, J.M. Llinares, M.A. Hossain, S.O. Kang, K.B. James, in: R. Eldik, K.B. James (Eds.), Advanced Inorganic Chemistry, vol. 59, Academic Press, 2006, pp. 175–204.
- [14] Md.A. Hossain, J.M. Llinares, D. Powell, K.B. James, Inorg. Chem. 40 (2001) 2936–2937.
- [15] B.P. Hay, T.K. Firman, B.A. Moyer, J. Am. Chem. Soc. 127 (2005) 1810–1819.
- [16] S. Nieto, J. Perez, V. Riera, D. Miguel, C. Alvarez, Chem. Commun. (2005) 546–548.
- [17] S. Goswami, S. Jana, H.-K. Fun, CrystEng. Commun. 10 (2008) 507–517.
- [18] D.R. Turner, M.J. Paterson, J.W. Steed, Chem. Commun. (2008) 1395–1397.
- [19] C.A. Llioudis, D.A. Tocher, J.W. Steed, J. Am. Chem. Soc. 126 (2004) 12395–12402.
- [20] P.D. Beer, Chem. Commun. (1996) 689–696.
- [21] P.D. Beer, M.G.B. Drew, D. Heseck, R. Jagessar, Chem. Commun. (1995) 1187–1187.
- [22] A.W. Czarnik, Acc. Chem. Res. 27 (1994) 302–308.
- [23] H. Miyaji, P. Anzenbacher Jr., J.L. Sessler, E.R. Bleasdale, P.A. Gale, Chem. Commun. (1999) 1723–1724.
- [24] M.S. Fonari, E.V. Ganin, V.O. Gelmboldt, S.S. Basok, B.S. Luisi, B. Moulton, Inorg. Chem. Commun. 11 (2008) 497–501.
- [25] R.P. Sharma, A. Singh, P. Brandão, V. Félix, P. Venugopalan, J. Mol. Struct. 920 (2008) 119–127.

- [26] R.P. Sharma, R. Bala, R. Sharma, B.M. Kariuki, *Inorg. Chem. Commun.* 9 (2006) 852–855.
- [27] R.P. Sharma, A. Singh, T. Aree, P. Venugopalan, *J. Mol. Struct.* 928 (2009) 18–24.
- [28] R.P. Sharma, A. Saini, S. Singh, P. Venugopalan, W.T.A. Harrison, *J. Fluorine Chem.* 131 (2010) 456–460.
- [29] A. Singh, R.P. Sharma, T. Aree, P. Venugopalan, *J. Fluorine Chem.* 130 (2009) 650–655.
- [30] R. Sharma, R.P. Sharma, B.M. Kariuki, *J. Fluorine Chem.* 29 (2008) 325–331.
- [31] C.R. Bondy, P.A. Gale, S.J. Loeb, *J. Am. Chem. Soc.* 126 (2004) 5030–5031.
- [32] C.F. Poole, *J. Chromatogr. A* 1037 (2004) 49–82.
- [33] J.-C. Xiao, J.M. Shreeve, *J. Org. Chem.* 70 (2005) 3072–3078.
- [34] S. Belonger, A.L. beauchamp, *Acta Crystallogr. C* 52 (1996) 2588–2590.
- [35] Y. Ida, K. Imai, M. Shibata, *Bull. Chem. Soc. Jpn.* 51 (1978) 2742–2744.
- [36] R.P. Sharma, R. Bala, R. Sharma, P. Venugopalan, *J. Mol. Struct.* 694 (2004) 229.
- [37] R.P. Sharma, R. Bala, R. Sharma, K.N. Singh, V. Ferretti, *J. Mol. Struct.* 784 (2006) 117.
- [38] R.P. Sharma, R. Bala, R. Sharma, P. Venugopalan, J.M. Salas, M. Quiros, *J. Fluorine Chem.* 126 (2005) 1543.
- [39] R.P. Sharma, R. Bala, R. Sharma, J. Perez, D. Miguel, *J. Mol. Struct.* 797 (2006) 49.
- [40] W.J. Geary, *Coord. Chem. Rev.* 7 (1971) 81–122.
- [41] L.M. Gruia, F.D. Rochon, A.L. Beauchamp, *Inorg. Chim. Acta* 360 (2007) 1825–1840.
- [42] S. Youngme, N. Chaichit, *Polyhedron* 21 (2002) 247–253.
- [43] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., John Wiley & Sons, New York, 1997.
- [44] Y. Cui, H.-J. Mo, J.-C. Chen, Y.-L. Niu, Y.-R. Zhong, K.-C. Zheng, B.-H. Ye, *Inorg. Chem.* 46 (2007) 6427–6434.
- [45] E.C. Niederhoffer, A.E. Martell, P. Rudolf, A. Clearfield, *Inorg. Chem.* 21 (1982) 3734–3741.
- [46] H.O. Kalinowski, S. Berger, S. Braun, *Carbon-13 NMR Spectroscopy*, John Wiley & Sons, New York, 1986.
- [47] B.J. Clark, T. Frost, M.A. Russell, U.V. Spectroscopy Techniques, Instrumentation, Data Handling, vol. 4, Chapman and Hall, London, 1993.
- [48] C. Thomos, K. Pringle, G.B. Dsacon, *J. Chem. Educ.* 68 (1989) 516–517.
- [49] R. Indumathy, T. Weyhermuller, B.U. Nair, *Dalton Trans.* 39 (2010) 2087–2097.
- [50] M.N. Burnett, C.K. Johnson, ORTEP III. Report ORNL-6895, Oak Ridge National Laboratory, Oak Ridge, TN, USA, 1996.
- [51] S. Busi, M. Lahtinen, J. Valkonen, K. Rissanen, *J. Mol. Struct.* 875 (2008) 549–559.
- [52] E. D'Oria, J.J. Novoa, *CrystEngCommun.* 10 (2008) 423–436.
- [53] G.G. Schlessinger, *Inorg. Synth.* 9 (1967) 160–165.
- [54] R.H. Blessing, *Acta Crystallogr. A* 51 (1995) 33–38.
- [55] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* 32 (1999) 115–119.
- [56] G.M. Sheldrick, *SHELX97*, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
- [57] L.J. Farrugia, *J. Appl. Crystallogr.* 32 (1999) 837–838.