

## Weak C–H...F–C interactions in carboxylate anion binding: Synthesis, spectroscopic and X-ray structural studies of $[\text{Co}(\text{phen})_2\text{CO}_3]_2(\text{C}_7\text{H}_3\text{O}_2\text{FCl})\text{Cl}\cdot 11\text{H}_2\text{O}$ and $[\text{Co}(\text{phen})_2\text{CO}_3](\text{C}_7\text{H}_3\text{NO}_4\text{Cl})\cdot 6\text{H}_2\text{O}$

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**Abstract.** Two new complex salts containing 2,5-substituted benzoate ions,  $[\text{Co}(\text{phen})_2\text{CO}_3]_2(\text{C}_7\text{H}_3\text{O}_2\text{FCl})\text{Cl}\cdot 11\text{H}_2\text{O}$  (**1**) and  $[\text{Co}(\text{phen})_2\text{CO}_3](\text{C}_7\text{H}_3\text{NO}_4\text{Cl})\cdot 6\text{H}_2\text{O}$  (**2**) (where phen = 1,10-phenanthroline,  $\text{C}_7\text{H}_3\text{O}_2\text{FCl}$  = 2-chloro-5-fluorobenzoate (**cfbz**) and  $\text{C}_7\text{H}_3\text{NO}_4\text{Cl}$  = 2-chloro-5-nitrobenzoate (**cnbz**)) were synthesized by reacting carbonatobis(1,10-phenanthroline)cobalt(III) chloride with appropriate salts in aqueous medium. A detailed packing analysis has been undertaken to delineate the role of second sphere C–H...F and C–H...O interactions amid other heteroatom interactions. The complex salts have been characterized by elemental analyses, spectroscopic studies (IR, UV/Visible, multinuclear NMR), conductance and solubility product measurements. Single crystal X-ray structure determination revealed ionic structures of both the complex salts having discrete ions along with lattice water molecules. Crystal lattice is stabilized by a variety of hydrogen bonding interactions, i.e. O–H...O, C–H...O and C–H...F involving second sphere coordination besides  $\pi$ – $\pi$  interaction. Furthermore, packing analyses reveal that C–H...F interactions can manifest even in the presence of a large number of heteroatom interactions.

**Keywords.** Cobalt(III); second sphere coordination chemistry; 1,10-phenanthroline; 2-chloro-5-fluorobenzoate; C–H...F interactions.

### 1. Introduction

Fluorinated organic compounds have been known for their fascinating properties as fluorine can impart significant effect on their properties such as increased chemical/metabolic stability, lipophilicity, solubility, dipole–dipole and hydrogen bonding interactions. As a result, they have number of applications: (i) about 20–25% of drugs in pharmaceuticals contain at least one fluorine atom in their molecules, (ii) fluorine substitution is commonly used in medicinal chemistry to improve the metabolic stability, bioavailability and protein–ligand interactions<sup>1</sup> and (iii) fluorine labelling is employed as an approach for the analysis of secondary structure of RNA.<sup>2</sup> More recently, the use of fluorinated compounds in ‘self disproportion of enantiomers’ of increased magnitude has been reported and it is believed that fluorine containing substances may hold great potential in facilitating the study and further practical applications in self disproportion of

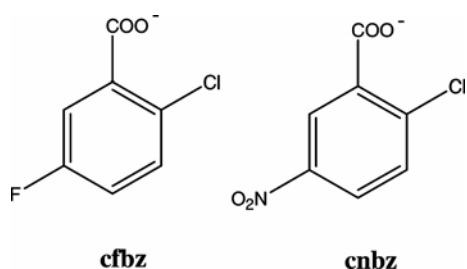
enantiomers.<sup>3,4</sup> In all this, the other interesting aspect is that how the fluorinated molecules are self assembled in the solid state leading to minimum energy (or at least low energy) ensembles in the shallow regions of lattice energy surfaces. The role of non-covalent C–H...F and F...F interactions immediately warrants consideration, but their role in lattice stabilization has elicited immense importance and debate.<sup>5–8</sup> Earlier view about organic fluorine is that it hardly involves in the hydrogen bonding and does not contribute to the crystal packing.<sup>9,10</sup> But Shimoni and Glusker, however, pointed out that although C–H...F–C interactions are weak as compared to the C–H...O–H interactions, their contribution in determining the modes of molecular packing in fluorinated complexes and in crystals cannot be overlooked.<sup>11</sup> Recent investigations have also augmented this point of view.<sup>12–16</sup> It was observed that when two fragments involved in the interactions are neutral, C–H...F interactions behave as weak hydrogen bonds with interaction energy around  $-0.4 \text{ kcal mol}^{-1}$ .<sup>17</sup>

In this backdrop it is worth mentioning that we have undertaken an extensive research programme to

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exploit cationic cobalt(III) complex,  $[\text{Co}(\text{phen})_2\text{CO}_3]^+$  as anion receptors.<sup>18–22</sup> and the detailed packing analyses of the complexes formed by this cation show that the role of the oxygen atoms of the carbonate group (hydrogen bond acceptor) and the hydrogen atom of the 1,10-phenanthroline moiety (C–H donor) is complementary towards lattice stabilization. Considering such a cohesive behaviour, our recent investigation on  $[\text{Co}(\text{phen})_2\text{CO}_3]$  (pentafluorobenzoate)·6H<sub>2</sub>O<sup>22</sup> clearly demonstrated that other than the individual strength of C–H...F interactions, their cooperative contribution is substantial in lattice stabilization. The use of pentafluorobenzoate as a counter anion with a relative high F/C ratio could furnish evidence regarding the role of C–H...F interactions especially in the absence of other strong intermolecular forces (O–H...O/N hydrogen bonding). This led us to an open question: will C–H...F interaction be operative and also play a dominant role when there is other halogen (especially chlorine) present? By now it is well conceived that hydrogen bonding involving heavier halogens (Cl, Br, I) is significant in pre-organizing molecules and C–H...X and X...X (X = Cl, Br, I) is a well established paradigm for supramolecular synthons in crystal engineering.<sup>23–31</sup>

At this stage, a careful choice of the counter anion becomes essential as we are trying to evaluate molecular events that differ at an energy level less than or equal to 1–2 kcal/mol. The choice of a cation was readily met with  $[\text{Co}(\text{phen})_2\text{CO}_3]^+$  from our previous experience<sup>18–22</sup> and consideration of the topological features and charge distribution led to the carboxylate anions; 2-chloro-5-fluorobenzoate (**cfbz**) and 2-chloro-5-nitrobenzoate (**cnbz**).



Our choice for these anions were based on the following considerations; (i) Chlorine and fluorine atoms must be as far as away as possible to minimize their interaction interferences in lattice stabilization, (ii) the plane of the carboxylate moiety should deviate to the maximum extent from the molecular plane to minimize the resonance effect with

aromatic ring current (larger chloro group rather than fluoro group at ortho position would satisfy this condition), (iii) bromine or iodine is less preferable as the difference in their atomic radii with fluorine is much more pronounced; **cfbz** readily satisfies these conditions. The selection of **cnbz** also has a purpose: –NO<sub>2</sub> is a strong hydrogen bond acceptor group (as it can involve in C–H...O hydrogen bonds) than fluorine and hence replacing fluoro by nitro group may ensue an entirely different interaction pattern in the crystal lattice. Moreover, chlorine is at *ortho* position in both these compounds; therefore its role through C–H...Cl interaction and its subtle variation can be investigated by detailed packing analyses through X-ray crystallography. This will be an added bonus to the study. Thus, this paper reports the role of weak C–H...F interactions in carboxylate anion binding in the presence of another halogen atom (Cl) and a detailed packing analysis of  $[\text{Co}(\text{phen})_2\text{CO}_3]_2(\text{C}_7\text{H}_3\text{O}_2\text{FCl})\text{Cl}\cdot 11\text{H}_2\text{O}$  (**1**) and  $[\text{Co}(\text{phen})_2\text{CO}_3](\text{C}_7\text{H}_3\text{NO}_4\text{Cl})\cdot 6\text{H}_2\text{O}$  (**2**). To the best of our knowledge this is the first crystal structure report of any salt containing 2-chloro-5-fluorobenzoate anion.

## 2. Experimental

### 2.1 Materials and measurements

Analytical grade reagents were used without any further purification  $[\text{Co}(\text{phen})_2\text{CO}_3]\text{Cl}\cdot 5\text{H}_2\text{O}$  has been prepared by the reaction between  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ , 1,10-phenanthroline and sodium bicarbonate.<sup>32</sup> C, H and N were estimated micro analytically by automatic PERKIN ELMER 2400 CHN elemental analyser. Cobalt was estimated by volumetric method.<sup>33</sup> UV/Visible spectra were recorded using HITACHI 330 spectrophotometer in water. Infrared spectra of the title complex salts were recorded using PERKIN ELMER spectrum RX FT-IR system using KBr pellet. <sup>1</sup>H, <sup>19</sup>F NMR spectra of title complex salts were run in the solvent D<sub>2</sub>O by using BRUKER AC 400 F (400 MHz) spectrometer. The chemical shift values are expressed as  $\delta$  value (ppm) down field from tetramethylsilane as an internal standard. In <sup>19</sup>F NMR, chemical shift values are expressed as  $\delta$  value (ppm) with respect to CCl<sub>3</sub>F.

### 2.2 Synthesis of $[\text{Co}(\text{phen})_2\text{CO}_3]_2(2\text{-chloro-5-fluorobenzoate})\cdot 11\text{H}_2\text{O}$ (**1**)

To a 10 mL solution of  $[\text{Co}(\text{phen})_2\text{CO}_3]\text{Cl}\cdot 5\text{H}_2\text{O}$  (0.5 g, 0.8 mmol) in water, 10 mL solution of

sodium salt of 2-chloro-5-fluorobenzoic acid (prepared by the reaction of 0.144 g, (0.8 mmol) of 2-chloro-5-fluorobenzoic acid and 0.033 g, (0.8 mmol) sodium hydroxide in 10 mL of water) was added. Light pink coloured crystals were obtained after ten days when the reaction mixture was allowed to evaporate slowly at room temperature (Yield: 65%). The composition was established by elemental analyses;  $[\text{Co}(\text{phen})_2\text{CO}_3]_2(2\text{-chloro-5-fluorobenzoate})\text{Cl}\cdot 11\text{H}_2\text{O}$ , Found (%): C, 50.01; H, 4.11; N, 8.18; Co, 8.50. Calculated (%): C, 50.10; H, 4.17; N, 8.20; Co, 8.64.

### 2.3 Synthesis of $[\text{Co}(\text{phen})_2\text{CO}_3](2\text{-chloro-5-nitrobenzoate})\cdot 6\text{H}_2\text{O}$ (**2**)

To a 10 mL solution of  $[\text{Co}(\text{phen})_2\text{CO}_3]\text{Cl}\cdot 5\text{H}_2\text{O}$  (0.5 g, 0.8 mmol) in water, 10 mL solution of sodium salt of 2-chloro-5-nitrobenzoic acid (prepared by the reaction of 0.166 g, (0.8 mmol) of 2-chloro-5-nitrobenzoic acid and 0.033 g, (0.8 mmol) sodium hydroxide in 10 mL of water) was added. Light pink coloured crystals started appearing after few hours from the reaction mixture (yield: 80%). The composition was established by elemental analyses;  $[\text{Co}(\text{phen})_2\text{CO}_3](2\text{-chloro-5-nitrobenzoate})\cdot 6\text{H}_2\text{O}$ , Found (%): C, 48.60; H, 3.85; N, 8.76; Co, 7.65. Calculated (%): C, 48.73; H, 3.93; N, 8.88; Co, 7.84.

### 2.4 X-ray data collection

The X-ray diffraction data were collected on a Bruker X8 APEX II KAPPA CCD diffractometer (at the Scientific and Technological Research Equipment Centre of Chulalongkorn University) at 298 K using graphite monochromatized Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The crystal was positioned at 37.5 mm from the CCD and the diffraction spots were measured using a counting time of 10 s. Data reduction and multi-scan absorption correction was carried out using the APEX II program suite.<sup>34</sup> The structures were solved using SHELXS-97<sup>35</sup> and refined using full-matrix least squares with SHELXL-97.<sup>35</sup> Anisotropic thermal parameters were used for all non-H atoms. The hydrogen atoms of C–H groups were riding with isotropic thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Most of the hydrogen atoms of water molecules were located from difference Fourier map and were included in the refinement as riding hydrogen atoms. The residual

electronic density was within the expected values. Final R-values together with selected refinement details are given in table 1.

## 3. Results and discussion

### 3.1 Synthesis

The complex salts **1** and **2** were synthesized by reaction of  $[\text{Co}(\text{phen})_2(\text{CO}_3)\text{Cl}\cdot 5\text{H}_2\text{O}$  and sodium salt of respective acids, i.e. 2-chloro-5-fluorobenzoic acid and 2-chloro-5-nitrobenzoic acid, in 1 : 1 molar ratio in the aqueous medium (scheme 1). The newly formed complex salts are soluble in water, methanol, ethanol, DMSO and insoluble in acetone. Both the complex salts were not decomposed till 250°C. The complex salts have been characterized by elemental analyses, spectroscopic studies (IR, UV/Visible, <sup>1</sup>H and <sup>19</sup>F NMR), solubility product and conductance measurements. The crystal structure has been unambiguously established by single-crystal X-ray crystallography.

### 3.2 Measurements of solubility products

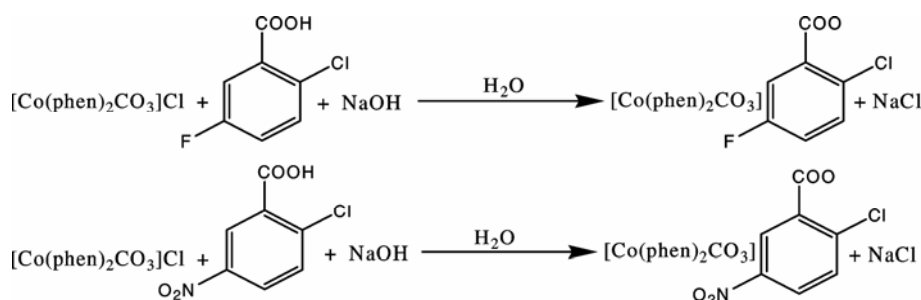
The solubility product (K<sub>sp</sub>) for complex salts **1** and **2** were determined as  $9.15 \times 10^{-6}$  and  $7.39 \times 10^{-5}$  (compared to  $9.80 \times 10^{-3}$  of  $[\text{Co}(\text{phen})_2\text{CO}_3]\text{Cl}\cdot 5\text{H}_2\text{O}$ ) which indicated that the affinity for binding of cationic complex  $[\text{Co}(\text{phen})_2\text{CO}_3]^+$  for 2,5-substituted carboxylates is in the order **cfbz** > **cnbz** > **Cl**. Although nearly thousand-fold and hundred-fold decrease in the solubility products of **1** and **2** points towards greater affinity, it is to be mentioned that hydration influences the solubility product, especially in the case of different sizes of concerned ions.

### 3.3 Molar conductance measurements

Molar conductance of complex salts **1** and **2** were measured in aqueous medium in the concentration range  $(0-100) \times 10^{-4} \text{ M}$  at 25°C. The limiting molar conductance at infinite dilution ( $\Lambda_0$ ) was obtained by plotting the square root of concentration versus molar conductance and extrapolating concentration to zero. The  $\Lambda_0$  obtained for salts **1** and **2** are 273 and  $119 \text{ Sm}^2 \text{ mol}^{-1}$  which indicates double salt (i.e.  $[\text{Co}(\text{phen})_2\text{CO}_3]^+$ , **cfbz** and  $[\text{Co}(\text{phen})_2\text{CO}_3]^+$ , **Cl**) and single salt (i.e.  $[\text{Co}(\text{phen})_2\text{CO}_3]^+$ , **cnbz**) nature

**Table 1.** Crystal data and refinement parameters of [Co(phen)<sub>2</sub>CO<sub>3</sub>]<sub>2</sub>(2-chloro-5-fluorobenzoate).Cl.11H<sub>2</sub>O (**1**) and [Co(phen)<sub>2</sub>CO<sub>3</sub>](2-chloro-5-nitrobenzoate).6H<sub>2</sub>O (**2**).

|   | <b>1</b>  | <b>2</b>   |
|---|---|--|
| Empirical formula   | C <sub>57</sub> H <sub>57</sub> Cl <sub>2</sub> Co <sub>2</sub> FN <sub>8</sub> O <sub>19</sub> | C <sub>32</sub> H <sub>31</sub> ClCoN <sub>5</sub> O <sub>13</sub> |
| <i>M<sub>w</sub></i>  | 1365.87   | 788.00   |
| Crystal system  | Triclinic   | Triclinic  |
| Space group   | P $\bar{1}$   | P $\bar{1}$  |
| <i>a</i> /[Å]   | 7.2801(15)  | 10.383(2)  |
| <i>b</i> /[Å]   | 19.585(4)   | 12.805(3)  |
| <i>c</i> /[Å]   | 21.295(4)   | 13.094(3)  |
| <i>α</i> /[°]   | 83.07(3)  | 82.24(3)   |
| <i>β</i> /[°]   | 86.82(3)  | 84.31(3)   |
| <i>γ</i> /[°]   | 81.24(3)  | 77.26(3)   |
| <i>V</i> [Å <sup>3</sup> ]  | 2976.9(10)  | 1678.2(6)  |
| <i>Z</i>  | 2   | 2  |
| <i>D<sub>c</sub></i> [mg m <sup>-3</sup> ]                                | 1.524   | 1.551  |
| <i>μ</i> [mm <sup>-1</sup> ]  | 0.732   | 0.667  |
| Reflections collected   | 20400   | 21982  |
| Unique reflections, [ <i>R<sub>int</sub></i> ]                            | 8373 [0.0503]   | 6517 [0.0329]  |
| Final <i>R</i> indices  |   |  |
| <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ <i>I</i> ] | <i>R</i> <sub>1</sub> = 0.0606, <i>wR</i> <sub>2</sub> = 0.1622                                 | <i>R</i> <sub>1</sub> = 0.0520, <i>wR</i> <sub>2</sub> = 0.1476    |
| <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)                 | <i>R</i> <sub>1</sub> = 0.1063, <i>wR</i> <sub>2</sub> = 0.1840                                 | <i>R</i> <sub>1</sub> = 0.0679, <i>wR</i> <sub>2</sub> = 0.1581    |

**Scheme 1.** Schematic representation of chemical reaction.

of **1** and **2** respectively. Thus conductance measurements revealed 1:1 electrolytic behaviour<sup>36</sup> of the complex salts in aqueous media.

### 3.4 Spectroscopic characterization

FT-IR spectra of newly synthesized complex salts have been recorded in the region of 400–4000 cm<sup>-1</sup>. The IR spectral bands in the range 3363–3371, 3042–3088, 1665–1673, 1634–1602 and 478–481 cm<sup>-1</sup> were assigned to  $\nu(\text{O-H})$  of H<sub>2</sub>O,  $\nu(\text{C-H})$ ,  $\nu(\text{C=O})$ ,  $\nu(\text{C=C})/\nu(\text{C=N})$  and  $\nu(\text{Co-N})$ , respectively in complex salts **1** and **2**. These peaks are characteristic for the carbonato and 1,10-phenanthroline ligands attached to the cobalt(III) center.

In case of complex salt **1**, the bands at 1491, 1344, 850, 857 and 747 cm<sup>-1</sup> were assigned to

$\nu_{\text{as}}(\text{COO})$ ,  $\nu_{\text{s}}(\text{COO})$ ,  $\nu(\text{C-F})$ ,  $\delta(\text{C=C})$  and  $\nu(\text{C-Cl})$ , respectively. These bands indicate the presence of ionic **cfbz**. Similar bands at 1650, 1490, 1320, 940 and 1638, 1495, 1284, 746 cm<sup>-1</sup> were observed in Er(Pfbz)<sub>3</sub><sup>37</sup> and [Zn(phen)<sub>2</sub>(Pfbz)(H<sub>2</sub>O)](Pfbz)(H<sub>2</sub>O)<sub>2</sub>,<sup>38</sup> respectively which were assigned to  $\nu(\text{CO})$ ,  $\nu_{\text{as}}(\text{COO})$ ,  $\nu_{\text{s}}(\text{COO})$  and  $\nu(\text{C-F})$  vibrations. In case of complex salt **2**, the bands at 1602, 1426, 1515, 1341 and 744 cm<sup>-1</sup> were assigned to  $\nu_{\text{as}}(\text{COO})$ ,  $\nu_{\text{s}}(\text{COO})$ ,  $\nu_{\text{as}}(\text{NO}_2)$ ,  $\nu_{\text{s}}(\text{NO}_2)$  and  $\nu(\text{C-Cl})$ , respectively. These bands are in accordance with ionic **cnbz**. Similar bands have been reported for sodium salt and lanthanides(III) of 2-chloro-5-nitrobenzoate<sup>39</sup> at 1570–1610, 1380–1395, 1540, 1355–1350, 744–750 cm<sup>-1</sup> and they were assigned to  $\nu_{\text{as}}(\text{COO})$ ,  $\nu_{\text{s}}(\text{COO})$ ,  $\nu_{\text{as}}(\text{NO}_2)$ ,  $\nu_{\text{s}}(\text{NO}_2)$  and  $\nu(\text{C-Cl})$ , respectively. The peak assignments have been made in consultation with literature values.<sup>40,41</sup>

The  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra of the title complex salts were recorded in  $\text{D}_2\text{O}$ . In  $^1\text{H}$  NMR spectrum of complex salt **1**, doublets at 9.21, 8.93, 8.50, 8.08 and 7.97 ppm were assigned to protons H9, H7, H2, H5, H6 and multiplets at 8.30, 7.43 ppm were assigned to protons H8, H3,4 of the ligand 1,10-phenanthroline coordinated to Co(III). Other signals, two doublets and one singlet at 7.11, 6.91 and 6.79 ppm were assigned to H3, H6 and H4 protons of anion **cfbz**. Also in  $^{19}\text{F}$  NMR spectrum of complex salt, signal is observed at  $-115.8$  ppm due to fluorine atom attached to C5 carbon atom of the anion **cfbz**. Similar peak at  $-113$  ppm has been reported for compound methyl *p*-fluorobenzoate.<sup>42</sup>

In  $^1\text{H}$  NMR spectrum of complex salt **2**, doublets at 9.22, 8.99, 8.54, 8.16 and 8.08 ppm were assigned to protons H9, H7, H2, H5, H6 and multiplets at 8.33, 7.47 ppm were assigned to protons H8 and H3,4 of the ligand 1,10-phenanthroline. Other signals at 7.93, 7.71 and 7.47 ppm were assigned to H3, H6 and H4 protons of anion **cnbz**. The signals observed in the NMR spectra are in good agreement with reported values in the literature.<sup>42,43</sup>

The electronic spectra of complex salts were recorded in water. For Co(III) complexes, two types of electronic transitions, i.e.  $^1\text{A}_{1g} \rightarrow \text{T}_{1g}$  and  $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$  are expected. In the  $[\text{Co}(\text{phen})_2\text{CO}_3]^+$  complexes, these transitions were observed around 500 and 360 nm as reported in the literature.<sup>44</sup> In the title complex salts, these transitions were observed around 509 and 334 nm. Characteristic peaks due to 1,10-phenanthroline groups coordinated to the Co(III) were observed at 269, 220 and 271, 220 nm, respectively for **1** and **2** as in other related complex salts reported in the literature.<sup>45</sup>

### 3.5 X-ray crystallography

**3.5a Coordination geometry and bonding:** The complex salt  $[\text{Co}(\text{phen})_2\text{CO}_3]_2(2\text{-chloro-5-fluorobenzoate})\text{Cl}\cdot 11\text{H}_2\text{O}$  (**1**) crystallizes in triclinic crystal system (space group  $\text{P}\bar{1}$ ). The asymmetric unit consists of two complex cations,  $[\text{Co}(\text{phen})_2\text{CO}_3]^+$ , one 2-chloro-5-fluorobenzoate, one chloride anion and eleven lattice water molecules. The ORTEP diagram of complex salt is shown in figure 1.

In complex salt **1**, the coordination around Co(1) is distorted octahedral in which the bite angle of carbonato group is deviated to the extent of  $19.50^\circ$  (ideal value =  $90^\circ$ ). The two 1,10 phenanthroline ligands coordinated to metal ion are almost orthog-

onal to the extent of  $85.48^\circ$  (angle between the best least square planes). The pyridyl rings of each of the phenanthroline moieties attached to Co(1) are having average N–N bite of  $2.599 \text{ \AA}$ , whereas the O–O bite distance of carbonato group is much lower to  $2.167 \text{ \AA}$ . As a consequence of the distorted octahedral coordination geometry, the phenanthroline moieties are not perfectly planar as evidenced from the torsional angles of  $3.02^\circ$  (N1–C6–C7–N2) and  $2.00^\circ$  (N3–C18–C19–N4). Another noteworthy feature is that the coordinated carbonato group is highly strained as angle O(2)–C(1)–O(3) is  $110.27^\circ$  whereas the other two angles subtended around C1 are  $123.04^\circ$  and  $126.68^\circ$  respectively.

The coordination around other cation (Co(2)) is hexacoordinated with a distorted octahedral environment in which the bite angle of carbonato group is deviated to the extent of  $20.04^\circ$  (ideal value =  $90^\circ$ ) slightly higher than that of Co(1). On the other hand, the two 1,10 phenanthroline ligands coordinated to metal ion are deviated more from the orthogonality as they are making angle of  $78.54^\circ$  with each other. In other related cobalt(III) phenanthroline complexes investigated, these aromatic rings are found almost orthogonal to each other.<sup>18–22</sup> Probably, the structural constraints of the lattice necessitate such larger deviation. The pyridyl rings of each of the phenanthroline moieties are almost coplanar having torsional angles  $-0.30^\circ$  (N5–C31–C32–N6) and  $0.55^\circ$  (N7–C43–C44–N8). As desired, the carboxylate group of the **cfbz** anion is almost perpendicular to the aromatic moiety (C56–C51–C57–O8 torsion angle =  $83.76^\circ$ ), which would minimize the resonance effect with the aromatic moiety.

The complex salt  $[\text{Co}(\text{phen})_2\text{CO}_3](2\text{-chloro-5-nitrobenzoate})\cdot 6\text{H}_2\text{O}$  (**2**) also crystallizes in triclinic crystal system (space group  $\text{P}\bar{1}$ ). The asymmetric unit consists of one complex cation,  $[\text{Co}(\text{phen})_2\text{CO}_3]^+$ , one 2-chloro-5-nitrobenzoate anion and six lattice water molecules (figure 2) out of which two water molecules are found disordered over two positions (due to this disorder any interaction involving these oxygen atoms (O8 and O12) are not discussed further). The coordination around the metal centre as well as other features described for complex **1** is also true for **2**. Here the distorted octahedral coordination deviates by angle of  $20.38^\circ$  (from the ideal value of  $90^\circ$ ) as revealed from the geometrical parameters. The observed N–N and O–O bite distances are  $2.61$  and  $2.15 \text{ \AA}$  and the orthogonality between two phenanthroline moieties is  $79.97^\circ$ .

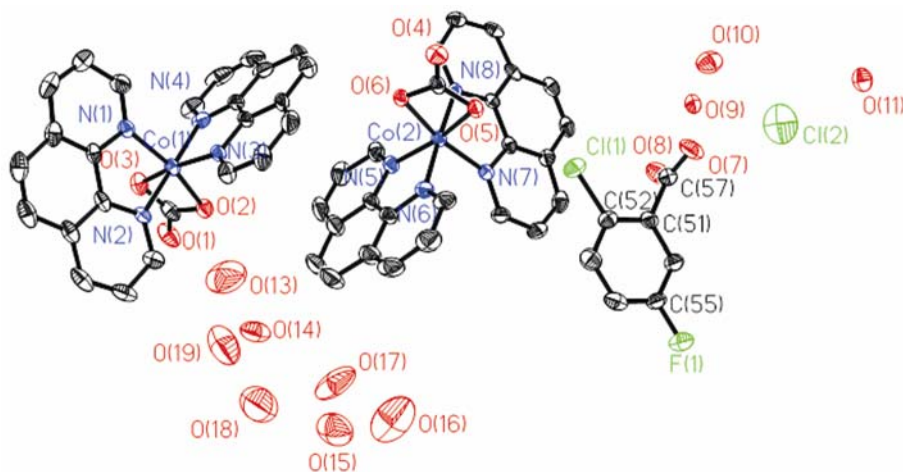


Figure 1. ORTEP diagram of complex salt 1.

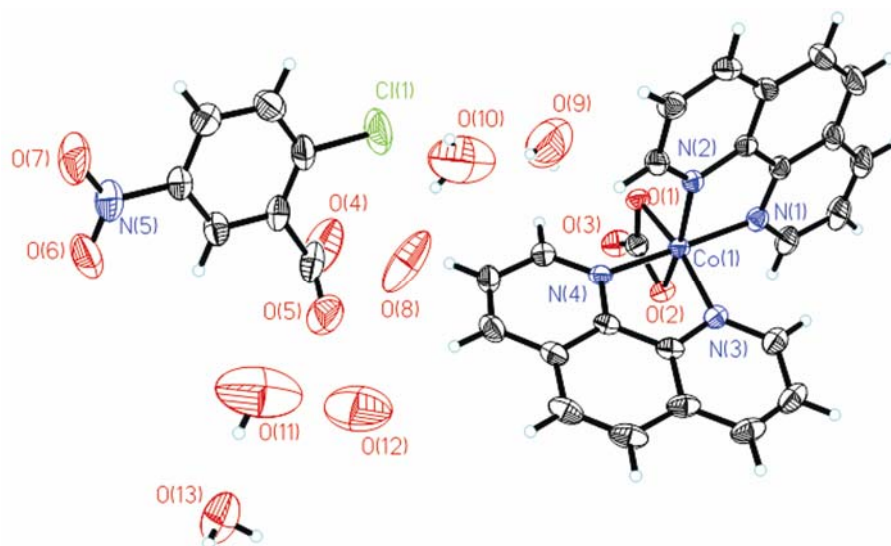


Figure 2. ORTEP diagram of complex salt 2.

The carboxylate group of the anion **cnbz** is also oriented out of plane from the aromatic ring (C27–C26–C32–O4 torsion angle of  $-60.88^\circ$ ). But, it is much less than in **cfbz** ( $83.76^\circ$ ) of complex salt 1. Probably, the steric crowding coupled with second sphere interactions (*vide intra*) control the out of plane twist of respective carboxylate groups in 1 and 2. The  $-\text{NO}_2$  group is almost in the plane of the benzene ring (C29–C30–N5–O7 torsion angle is  $-0.51^\circ$ ).

In both complex salts 1 and 2, the average Co–N, Co–O bond lengths and bond angles O–Co–O, *cis*-N–Co–N and *trans*-N–Co–N are quite similar to those reported in related complexes.<sup>18–22</sup> As expected, the bond lengths and bond angles for anion, i.e. **cnbz** in complex salts 2 are similar to those ionic

complexes of **cnbz** reported in the literature.<sup>46–49</sup> It is to be noted that no complex salt containing **cfbz** is reported till now. Selected bond lengths and bond angles of the complex salt 1 and 2 are given in tables 2 and 3.

**3.5b Packing:** The packing analysis of complex salt 1 reveals that crystal lattice is stabilized by a combination of strong and weak hydrogen bonding interactions of type the O–H...O (water), O–H...O (carbonato), O–H...O (benzoate), C–H...O (water), C–H...O (carbonato), C–H...Cl (free), C–H...Cl (benzoate) and C–H...F along with  $\pi$ – $\pi$  stacking interactions. The hydrogen bonding parameters are given in table 4. It is clear from these hydrogen bonding interactions that hydrogen bonding

**Table 2.** Selected bond lengths and bond angles (Å, °) for complex salt [Co(phen)<sub>2</sub>CO<sub>3</sub>]<sub>2</sub> (2-chloro-5-fluorobenzoate).Cl.11H<sub>2</sub>O (1).

|                  |            |                  |            |
|------------------|------------|------------------|------------|
| <b>Cation 1</b>  |            |                  |            |
| Co(1)–N(1)       | 1.958(4)   | Co(1)–O(2)       | 1.890(4)   |
| Co(1)–N(2)       | 1.940(4)   | Co(1)–O(3)       | 1.884(4)   |
| Co(1)–N(3)       | 1.953(4)   | Co(1)–N(4)       | 1.947(4)   |
| O(3)–Co(1)–O(2)  | 70.10(18)  | O(3)–Co(1)–N(3)  | 169.00(18) |
| N(1)–Co(1)–N(2)  | 83.63(19)  | O(2)–Co(1)–N(3)  | 99.66(17)  |
| N(1)–Co(1)–N(3)  | 92.04(17)  | N(2)–Co(1)–N(3)  | 96.18(17)  |
| N(1)–Co(1)–N(4)  | 95.86(18)  | N(4)–Co(1)–N(3)  | 83.6(2)    |
| N(1)–Co(1)–O(2)  | 167.61(17) | O(3)–Co(1)–N(4)  | 92.08(19)  |
| N(1)–Co(1)–O(3)  | 98.47(19)  | O(2)–Co(1)–N(4)  | 89.50(17)  |
| O(2)–Co(1)–N(2)  | 91.05(17)  | N(2)–Co(1)–N(4)  | 179.44(19) |
| O(3)–Co(1)–N(2)  | 88.22(16)  |                  |            |
| <b>Cation 2</b>  |            |                  |            |
| Co(2)–N(5)       | 1.946(4)   | Co(2)–O(5)       | 1.886(3)   |
| Co(2)–N(6)       | 1.946(4)   | Co(2)–O(6)       | 1.897(3)   |
| Co(2)–N(7)       | 1.950(4)   | Co(2)–N(8)       | 1.948(4)   |
| O(5)–Co(2)–O(6)  | 69.57(15)  | N(6)–Co(2)–N(7)  | 93.92(17)  |
| O(5)–Co(2)–N(5)  | 166.44(16) | O(5)–Co(2)–N(7)  | 99.54(16)  |
| O(6)–Co(2)–N(5)  | 97.61(16)  | N(8)–Co(2)–N(7)  | 84.06(17)  |
| O(5)–Co(2)–N(6)  | 90.95(17)  | N(6)–Co(2)–N(8)  | 177.72(18) |
| O(6)–Co(2)–N(6)  | 89.84(16)  | O(5)–Co(2)–N(8)  | 88.36(15)  |
| N(5)–Co(2)–N(6)  | 84.42(19)  | O(6)–Co(2)–N(8)  | 91.96(15)  |
| O(6)–Co(2)–N(7)  | 168.56(15) | N(5)–Co(2)–N(8)  | 96.73(17)  |
| N(5)–Co(2)–N(7)  | 93.51(17)  |                  |            |
| <b>Anion</b>     |            |                  |            |
| C(51)–C(57)      | 1.537(7)   | O(7)–C(57)       | 1.240(6)   |
| Cl(1)–C(52)      | 1.762(5)   | O(8)–C(57)       | 1.239(6)   |
| F(1)–C(55)       | 1.366(6)   |                  |            |
| O(7)–C(57)–O(8)  | 126.2(6)   | O(7)–C(57)–C(51) | 116.8(5)   |
| O(8)–C(57)–C(51) | 117.0(5)   |                  |            |

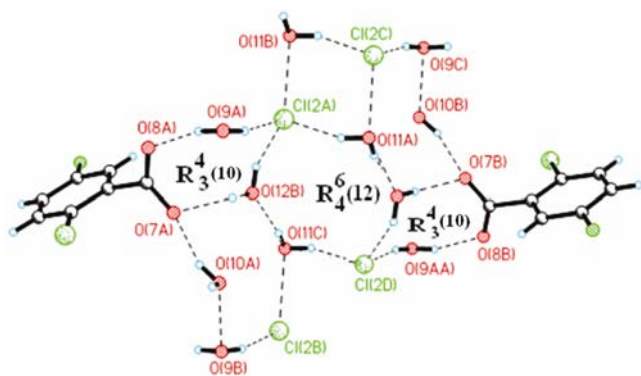
**Table 3.** Selected bond lengths and bond angles (Å, °) for complex salt [Co(phen)<sub>2</sub>CO<sub>3</sub>] (2-chloro-5-nitrobenzoate)·6H<sub>2</sub>O (2).

|                 |           |                  |           |
|-----------------|-----------|------------------|-----------|
| <b>Cation</b>   |           |                  |           |
| Co(1)–O(1)      | 1.890(2)  | Co(1)–N(4)       | 1.934(2)  |
| Co(1)–O(2)      | 1.895(2)  | O(1)–C(25)       | 1.312(3)  |
| Co(1)–N(1)      | 1.937(2)  | O(2)–C(25)       | 1.322(3)  |
| Co(1)–N(3)      | 1.964(2)  | O(3)–C(25)       | 1.219(4)  |
| Co(1)–N(2)      | 1.964(2)  |                  |           |
| O(2)–Co(1)–O(1) | 69.23(9)  | N(4)–Co(1)–N(3)  | 83.97(10) |
| O(1)–Co(1)–N(4) | 91.69(9)  | N(1)–Co(1)–N(3)  | 95.11(10) |
| O(2)–Co(1)–N(4) | 91.05(9)  | O(1)–Co(1)–N(2)  | 97.60(9)  |
| O(1)–Co(1)–N(1) | 89.97(9)  | O(2)–Co(1)–N(2)  | 166.34(9) |
| O(2)–Co(1)–N(1) | 92.38(10) | N(4)–Co(1)–N(2)  | 93.04(9)  |
| N(4)–Co(1)–N(1) | 176.53(9) | N(1)–Co(1)–N(2)  | 83.73(10) |
| O(1)–Co(1)–N(3) | 165.92(9) | N(3)–Co(1)–N(2)  | 69.00(10) |
| O(2)–Co(1)–N(3) | 97.39(9)  |                  |           |
| <b>Anion</b>    |           |                  |           |
| N(5)–O(7)       | 1.204(5)  | O(7)–N(5)–O(6)   | 122.9(4)  |
| N(5)–O(6)       | 1.220(5)  | O(7)–N(5)–C(30)  | 118.9(4)  |
| N(5)–C(30)      | 1.462(4)  | O(6)–N(5)–C(30)  | 118.2(4)  |
| O(4)–C(32)      | 1.201(6)  | O(4)–C(32)–O(5)  | 126.8(5)  |
| O(5)–C(32)      | 1.251(6)  | O(4)–C(32)–C(26) | 117.5(5)  |
| C(26)–C(32)     | 1.518(6)  | O(5)–C(32)–C(26) | 115.7(4)  |

**Table 4.** Hydrogen bonding parameters (Å, °) for complex salt [Co(phen)<sub>2</sub>CO<sub>3</sub>]<sub>2</sub> (2-chloro-5-Fluorobenzoate).Cl.11H<sub>2</sub>O (1).

| D–H...A                       | D...A     | H...A     | Angle D–H–A |
|-------------------------------|-----------|-----------|-------------|
| O9–H9B...Cl2                  | 2.723(5)  | 1.889(4)  | 166.1(3)    |
| O9–H9C...O8                   | 2.747(6)  | 1.889(4)  | 164.9(3)    |
| O10–H10B...O7                 | 2.778(6)  | 1.991(4)  | 158.2(3)    |
| O10–H10C...O4 <sup>i</sup>    | 2.873(6)  | 2.083(4)  | 152.3(3)    |
| O11–H11B...O12                | 2.801(5)  | 1.934(4)  | 164.1(3)    |
| O11–H11C...Cl2                | 2.785(6)  | 1.942(4)  | 160.0(3)    |
| O12–H12B...Cl2 <sup>ii</sup>  | 2.894(6)  | 2.197(4)  | 139.5(3)    |
| O12–H12C...O7 <sup>ii</sup>   | 2.839(7)  | 2.013(5)  | 161.8(3)    |
| O13–H13B...O1 <sup>iii</sup>  | 2.731(10) | 1.952(5)  | 154.5(6)    |
| O13–H13C...O19                | 2.759(12) | 1.910(8)  | 179.2(6)    |
| O14–H14C...O19                | 3.073(10) | 2.266(8)  | 174.7(4)    |
| O15–H15B...O17                | 3.011(12) | 2.223(10) | 152.5(6)    |
| O16–H16B...O15                | 2.709(12) | 1.915(8)  | 154.8(7)    |
| O16–H16C...O17 <sup>v</sup>   | 3.136(13) | 2.564(8)  | 123.5(7)    |
| O17–H17B...O14                | 2.863(9)  | 2.115(6)  | 152.2(6)    |
| O18–H18C...O19                | 2.510(11) | 1.654(8)  | 173.6(7)    |
| C2–H2A...O12 <sup>vi</sup>    | 3.388(8)  | 2.603(4)  | 142.5(4)    |
| C2–H2A...O11 <sup>vi</sup>    | 3.302(8)  | 2.648(4)  | 128.0(4)    |
| C4–H4A...O8 <sup>vii</sup>    | 3.328(8)  | 2.586(4)  | 137.1(4)    |
| C11–H11A...O1 <sup>viii</sup> | 3.462(9)  | 2.539(5)  | 171.9(4)    |
| C12–H12A...F1 <sup>v</sup>    | 3.326(7)  | 2.423(3)  | 163.7(4)    |
| C14–H14A...O1 <sup>iii</sup>  | 3.102(8)  | 2.343(5)  | 138.5(4)    |
| C16–H16A...O6                 | 3.274(8)  | 2.487(3)  | 142.5(4)    |
| C22–H22A...O9 <sup>vi</sup>   | 3.332(9)  | 2.602(4)  | 135.7(5)    |
| C24–H24A...O11 <sup>ix</sup>  | 3.475(9)  | 2.550(4)  | 172.9(6)    |
| C27–H27A...O4 <sup>iv</sup>   | 3.216(7)  | 2.349(4)  | 155.0(4)    |
| C35–H35A...O14                | 3.508(10) | 2.630(5)  | 157.6(5)    |
| C37–H37A...O16 <sup>x</sup>   | 3.376(12) | 2.647(10) | 135.8(5)    |
| C39–H39A...O15 <sup>v</sup>   | 3.369(9)  | 2.544(7)  | 148.1(4)    |
| C40–H40A...O18 <sup>v</sup>   | 3.402(10) | 2.505(8)  | 162.2(4)    |
| C46–H46A...O4 <sup>vi</sup>   | 3.466(7)  | 2.548(4)  | 169.2(4)    |
| C48–H48A...O5 <sup>vi</sup>   | 3.479(7)  | 2.709(4)  | 140.7(3)    |
| C48–H48A...C11 <sup>vi</sup>  | 3.648(5)  | 2.907(2)  | 137.7(3)    |
| C50–H50A...O9 <sup>vi</sup>   | 3.297(6)  | 2.534(4)  | 139.5(3)    |
| C54–H54A...O14 <sup>v</sup>   | 3.735(8)  | 2.810(5)  | 172.7(4)    |

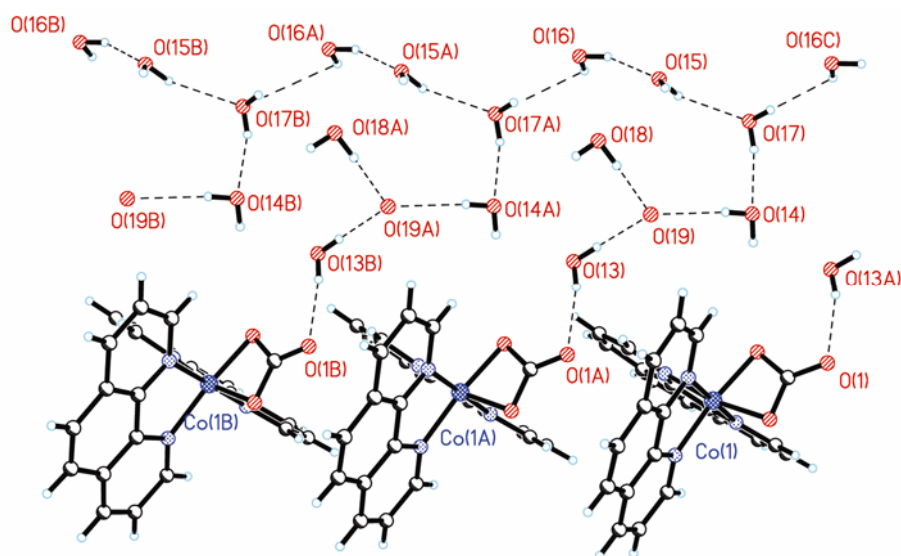
*D* = donor, *A* = acceptor. Equivalent positions: (i)  $-x + 1, -y + 1, -z + 1$ , (ii)  $-x + 1, -y, -z + 1$ , (iii)  $x + 1, +y, +z$ , (iv)  $x - 1, +y, +z$ , (v)  $-x, -y + 1, -z + 2$ , (vi)  $-x, -y + 1, -z + 1$ , (vii)  $x, +y + 1, +z$ , (viii)  $-x - 1, -y + 2, -z + 2$ , (ix)  $-x - 1, -y + 1, -z + 1$ , (x)  $-x + 1, -y + 1, -z + 2$

**Figure 3.** First set of clustered water molecules with their graph set patterns. Dotted lines represent hydrogen bonds.

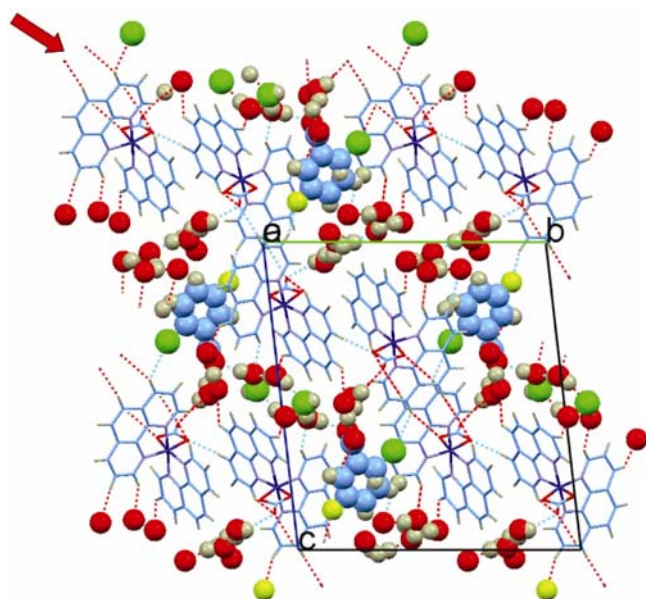
capabilities of all groups that can act as hydrogen bond acceptor are utilized fully towards lattice stabilization. The two carboxylate oxygen atoms O7 and O8 are involved in bifurcated hydrogen bonds of type O–H...O and C–H...O (O10–H10B...O7 = 1.991, O12–H12C...O7 = 2.013, O9–H9C...O8 = 1.889 and C4–H4A...O8 = 2.586 Å). The oxygen atoms of the carbonato groups are also involved in hydrogen bonding as they are forming one O–H...O and two C–H...O hydrogen bonds (table 4).

It is noteworthy that the lattice water molecules are clustered into two sets. In the first set, water molecules O9, O10, O11, O12 and two oxygen atoms of **cfbz** (O7 and O8) and the free chloride





**Figure 4.** Second set of clustered water molecules. First (figure 3) and second set of cluster are not directly linked, but through charged species in the lattice.



**Figure 5.** Packing of **1** viewed down 'a' axis. Note the orientation of  $[\text{Co}(\text{phen})_2\text{CO}_3]^+$  cation along the diagonal of the  $bc$  plane of the unit cell (marked as an arrow). Hydrogen bonds are marked as dotted lines.

ions are involved. This organization resulted in the formation of two graph set hydrogen bonding patterns.<sup>50–52</sup> of type  $R^4_3$  (10) and  $R^6_4$  (12) (figure 3). In  $R^4_3$  (10), hydrogen atoms of O9 and O12 are acting as donor atoms and Cl(2), O7 and O8 are acting as acceptors while in  $R^6_4$  (12), O11, O12 and Cl(2) are involved. In the second cluster, seven lattice water

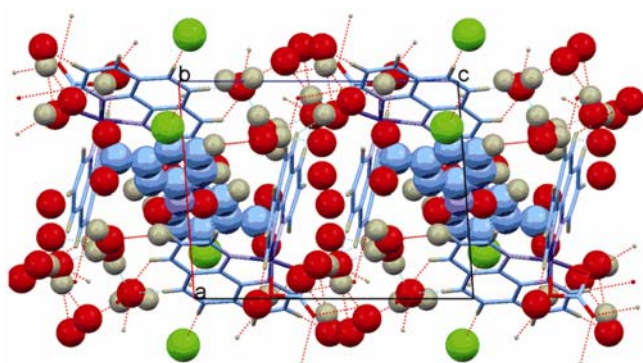
molecules (O13, O14, O15, O16, O17, O18 and O19) are involved in hydrogen bonding interactions which are further joined to oxygen atom of the carboxylate groups (figure 4). Interestingly, these two clustered set of water molecules are themselves not linked though any O–H...O type hydrogen bonds. That is, they are located separately in two different pockets of the lattice and are only linked to the ionic species in the lattice. The complex cations are arranged in zig-zag layers (shown as stick model in figure 5). Both the phenanthroline moieties attached to cobalt(III) are involved in the  $\pi$ – $\pi$  stacking interactions from both sides, the nearest approach being 3.564 Å (one side) and 3.461 Å (from the other side). In between the layers, anions **cfbz**,  $\text{Cl}^-$  and lattice water molecules reside (shown as space-filling model in figure 5). Overall, the unison of large number of non-covalent interactions of type O–H...O (water), C–H...O (benzoate), C–H...O (water), C–H...O (carbonato), C–H...F, C–H...Cl, is stabilizing the crystal lattice and provide the driving force for the formation of complex of the composition  $[\text{Co}(\text{phen})_2\text{CO}_3]_2(2\text{-chloro-5-fluorobenzoate})\text{Cl}\cdot 11\text{H}_2\text{O}$  in addition to the electrostatic forces of attraction.

The crystal lattice of the complex salt **2** is also stabilized by the interplay of large number of non-covalent interactions like O–H...O, C–H...O (water), C–H...O (nitro), C–H...O (carbonato), C–H...Cl type hydrogen bonding interactions (table 5)

**Table 5.** Hydrogen bonding parameters(Å, °) for complex salt [Co(phen)<sub>2</sub>CO<sub>3</sub>] (2-chloro-5-nitrobenzoate)·6H<sub>2</sub>O (**2**).

| D–H...A                       | D...A     | H...A    | Angle D–H–A |
|-------------------------------|-----------|----------|-------------|
| O9–H9B...O10                  | 2.955(10) | 2.122(9) | 160.2(6)    |
| O11–H11B...O5                 | 2.855(9)  | 2.314(5) | 119.7(5)    |
| O11–H11C...O13                | 2.757(8)  | 1.894(4) | 159.5(5)    |
| O10–H10C...C11                | 3.701(9)  | 2.968(2) | 149.2(6)    |
| C2–H2A...O13 <sup>i</sup>     | 3.514(7)  | 2.631(5) | 158.6(3)    |
| C9–H9A...C11                  | 3.766(9)  | 2.837(2) | 178.5(3)    |
| C11–H11A...O6 <sup>ii</sup>   | 3.473(6)  | 2.657(5) | 146.9(2)    |
| C12–H12A...O7 <sup>ii</sup>   | 3.240(6)  | 2.421(5) | 147.0(2)    |
| C13–H13A...O4 <sup>iii</sup>  | 3.531(6)  | 2.741(5) | 143.4(2)    |
| C15–H15A...O13 <sup>iii</sup> | 3.455(5)  | 2.659(4) | 144.0(2)    |
| C20–H20A...O3 <sup>iv</sup>   | 3.347(5)  | 2.496(2) | 152.3(2)    |
| C22–H22A...O9 <sup>iv</sup>   | 3.561(9)  | 2.761(8) | 144.7(3)    |
| C23–H23A...O4                 | 3.726(6)  | 2.820(5) | 165.1(2)    |
| C24–H24A...O10                | 3.349(8)  | 2.560(7) | 142.8(3)    |
| C28–H28A...O11 <sup>ii</sup>  | 3.499(8)  | 2.609(7) | 160.4(3)    |

D = donor, A = acceptor. Equivalent positions: (i)  $x + 1, +y + 1, +z$ , (ii)  $-x + 1, -y + 2, -z$ , (iii)  $x, +y + 1, +z$ , (iv)  $x - 1, +y, +z$



**Figure 6.** Packing of **2** showing the box-like voids of phenanthroline moiety generated through  $\bar{1}$ . The anions and lattice water molecules reside in these voids and extensively hydrogen bonded (dotted line).

and  $\pi$ - $\pi$  stacking interactions. A detailed perusal of table 5 shows that all the hydrogen bond acceptor groups ( $-\text{NO}_2$ ,  $-\text{COO}$ ,  $-\text{Cl}$  and  $>\text{C}=\text{O}$ ) are oriented in such a way that their hydrogen bonding capabilities are fully utilized. The two oxygen atoms of nitro group are involved in hydrogen bonding with C–H groups of 1,10-phenanthroline moiety (C11–H11A...O6 = 2.657 Å, C12–H12A...O7 = 2.421 Å). The phenanthroline moieties coordinated to the cobalt(III) center are wide apart in spatial disposition (angle between the least square planes = 79.97°) and this arrangement, when placed centrosymmetrically, box-like voids are created (figure 6). Due to  $\bar{1}$  symmetry, anions are arranged in such a way that the  $-\text{COO}^-$  and  $-\text{NO}_2$  moieties of neighbouring

molecules are placed just opposite to each other and are extensively hydrogen bonded. The box-like arrangement of the cations infinitely repeats with a number of C–H...O hydrogen bonds to complete the packing in third dimension. The anionic moieties placed in the box-like arrangement are also involved in  $\pi$ - $\pi$  interactions (3.720 Å, distance between the centeroids of two anionic moieties).

If packing of both the salts is compared, it is apparent that C–H...F interactions are playing an important role in the lattice stabilization and fluorine atom is involved in C–H...F–C (C12–H12A...F1 = 2.423 Å) hydrogen bonds of comparable strength as C–H...O (C11–H11A...O6 = 2.657, C12–H12A...O7 = 2.421 Å) hydrogen bonds formed by oxygen atoms (strong hydrogen bond acceptor) of the  $-\text{NO}_2$  group in **2**. The strength of C–H...Cl hydrogen bonds in both complexes **1** (C48–H48A...C11 = 2.907 Å) and **2** (C9–H9A...C11 = 2.837 Å) are almost the same.

#### 4. Conclusions

The potential of weak second sphere interactions (C–H...F and C–H...O) in the binding of 2,5-substituted carboxylates by cationic cobalt(III) complex  $[\text{Co}(\text{phen})_2\text{CO}_3]^+$  has been explored by isolating and characterizing the two new Co(III) complex salts,  $[\text{Co}(\text{phen})_2\text{CO}_3]_2(2\text{-chloro-5-fluorobenzoate})\cdot 11\text{H}_2\text{O}$  (**1**) and  $[\text{Co}(\text{phen})_2\text{CO}_3](2\text{-chloro-5-nitrobenzoate})\cdot 6\text{H}_2\text{O}$  (**2**). As laid down as an objective at

the outset to evaluate C–H...F interactions amid the presence of chloro group has shown that C–H...F interactions can indeed manifest in complex **1**. In addition, replacement of a fluoro group with a nitro group has profound effect in the packing arrangement as seen in the complex salt **2**, still the complex has C–H...Cl interactions along with large number of C–H...O interactions. Comparison of the packing features of **1** and **2** shows that C–H...X (X = halogen) interaction can manifest even in ionic compounds having a large number of hetero atom interactions like O–H...O, C–H...O and  $\pi$ – $\pi$  stacking interactions. Thus, it is important to consider the cooperative interplay of weak second sphere interaction of the kind C–H...F and C–H...Cl even in ionic solids in which molecules are endowed with halogen (F and Cl) substitution. Such consideration may facilitate the crystal engineering of this kind of ionic solids in which weak second sphere coordination has a marked influence even in the presence strong ionic interactions.

### Supplementary data

Crystallographic data of the title complex salts have been deposited with the Cambridge Crystallographic Data Center allocated with the deposit number CCDC 748423 and 748424. 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.

### Acknowledgements

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### References

- Purser S, Morre P R, Swallow S and Gouverneur V 2008 *Chem. Soc. Rev.* **37** 320
- Graber D, Moroder H and Micura R 2008 *J. Am. Chem. Soc.* **130** 17230
- Curran D P, Mikami K and Soloshonok V A 2006 *J. Fluorine Chem.* **127** 454
- Dolbier Jr W R and Prakash G K S 2008 *J. Fluorine Chem.* **129** 896
- Taylor R and Kennard O 1982 *J. Am. Chem. Soc.* **104** 5063
- Desiraju G R and Parthasarathy R 1989 *J. Am. Chem. Soc.* **111** 8725
- Shimoni L, Carrell H L, Glusker J P and Coombs M M 1994 *J. Am. Chem. Soc.* **116** 8162
- Weis H-C, Blaser D, Boese R, Nangia A and Desiraju G R 1998 *J. Am. Chem. Soc.* **120** 8702
- Howard J A K, Hoy V J, O'Hagan D and Smith G T 1996 *Tetrahedron* **52** 12613
- Dunitz J D and Taylor R 1997 *Chem. Eur. J.* **3** 89
- Shimoni L and Glusker J P 1994 *Struct. Chem.* **3** 383
- Prasanna M D and Guru Row T N 2000 *Cryst. Eng. Comm.* **2** 134
- Choudhury A R, Urs. U K, Smith P S, Goddard R, Howard J A K and Guru Row T N 2002 *J. Mol. Struct.* **641** 225
- Weis H-C, Blaser D, Boese R, Nangia A and Desiraju G R 1999 *Acta Cryst.* **B55** 1005
- Vangala V R, Nangia A and Lynch V M 2002 *Chem. Commun.* 1304
- Choudhury A R, Bhat R G, Guru Row T N and Chandrasekaran S 2007 *Cryst. Growth Des.* **7** 844
- D'Oria E and Novoa J J 2008 *Cryst. Eng. Comm.* **10** 423
- Sharma R P, Singh A, Brandão P, Félix V and Venugopalan P 2008 *J. Mol. Struct.* **892** 452
- Sharma R P, Singh A, Brandão P, Félix V and Venugopalan P 2009 *J. Mol. Struct.* **921** 227
- Singh A, Sharma R P, Ferretti V, Rossetti S and Venugopalan P 2009 *J. Mol. Struct.* **927** 111
- Sharma R P, Singh A, Aree T and Venugopalan P 2009 *J. Mol. Struct.* **928** 18
- Singh A, Sharma R P, Aree T and Venugopalan P 2009 *J. Fluorine Chem.* **130** 650
- Forni A, Metrangolo P, Pilati P and Resnati G 2004 *Cryst. Growth Des.* **4** 291
- Lommerse J P M, Stone A J, Taylor R and Allen F H 1996 *J. Am. Chem. Soc.* **118** 3108
- Fontana F, Forni A, Metrangolo P, Panzeri W, Pilati T and Resnati G 2002 *Supramol. Chem.* **14** 47
- Metrangolo P and Resnati G 2001 *Chem. Eur. J.* **7** 2511
- Walsh R B, Padgett C W, Metrangolo P, Resnati G, Hanks T W and Pennington W T 2001 *Cryst. Growth Des.* **1** 165
- Lagon A C 1999 *Angew. Chem. Int. Ed.* **38** 2686
- Jay J I, Padgett C W, Walsh R D B, Hanks T W and Pennington W T 2001 *Cryst. Growth Des.* **1** 501
- Thaimattam R, Sharma C V K, Clearfield A and Desiraju G R 2001 *Cryst. Growth Des.* **1** 103
- Garden S J, Fontes S P, Wardell J L, Skakle J M S, Low J N and Glidewell C 2002 *Acta Cryst.* **B58** 701
- Fu X-C, Wang X-Y, Li M-T, Wang C-G and Deng X-T 2006 *Acta Cryst.* **E62** m1263
- Schlessinger G G 1967 *Inorg. Synth.* **9** 160
- Bruker-Nonius 2006 APEX2, Version 2.0-2; Bruker AXS: Madison, WI, USA
- Sheldrick G M 2008 *Acta Cryst.* **A64** 112

36. Geary W J 1971 *Coord. Chem. Rev.* **7** 81
37. Roh S-G, Oh J B, Nah M-K, Baek N S, Lee Y and Kim H K 2004 *Bull. Korean Chem. Soc.* **25** 1503
38. Zehang X-D, Ge C-H, Zhang X-Y, Guo Y-N and Liu Q-T 2008 *Russ. J. Coord. Chem.* **34** 729
39. Ferenc W, Bocian B and Walków-Dziewulska A 2004 *J. Therm. Anal. Cal.* **76** 179
40. Nakamoto K 1997 *Infrared and Raman spectra of inorganic and coordination compounds* (New York: Wiley) 3rd edn
41. Nyquist R A and Kagel R O 1971 *Infrared spectra of inorganic compounds* (New York and London: Academic Press)
42. Silverstein R M and Webster F X 2006 *Spectrometric identification of organic compounds* (India: John Wiley and Sons) 6th edn, p. 288
43. Francis D J and Jordan R B 1972 *Inorg. Chem.* **11** 461
44. Niederhoffer E C, Martell A E, Rudolf P and Clearfield A 1982 *Inorg. Chem.* **21** 3734
45. Thomas N C, Pringle K and Deacon G B 1989 *J. Chem. Edu.* **68** 516
46. Sugiyama T, Meng J-B and Matsuura T 2002 *Acta Cryst.* **C58** o242
47. Tan T 2007 *J. Mol. Struct.* **840** 6
48. Ishida H, Rahman B and Kashino S 2001 *Acta Cryst.* **C57** 1450
49. Bernstein J, Davis R E, Shimon L and Chang N L 1995 *Angew. Chem. Int. Ed. Engl.* **34** 1555
50. Etter M C 1990 *Acc. Chem. Res.* **23** 120
51. Etter M C 1991 *J. Phys. Chem.* **95** 4601
52. Etter M C, MacDonald J C and Bernstein J 1990 *Acta Cryst.* **B46** 25