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# Binding of arylsulphonates by cationic cobalt(III) complex: Syntheses, characterization and single crystal structure determination of $[Co(phen)_2CO_3](arylsulphonate) \cdot nH_2O$

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#### HIGHLIGHTS

- ▶ Two cobalt(III) complexes containing arylsulphonate anions have been synthesized.
- ► Complexes have been characterized by TGA, spectroscopy and X-ray crystallography.
- ▶ Non-covalent interactions are playing crucial role in lattice stabilization.
- ▶ Bi-layered and zig-zag layered packing arrangements have been observed.

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#### ABSTRACT

In an effort to study the binding of substituted arylsulphonates by cationic cobalt(III) complex  $[Co(phen)_2-CO_3]^+$ , two complex salts  $[Co(phen)_2CO_3](4$ -chlorobenzenesulphonate)· $H_2O$ , **1** and  $[Co(phen)_2CO_3](2,4$ -dinitrobenzenesulphonate)· $H_2O$ , **2** have been synthesized. These complex salts were characterized by elemental analysis, solubility product, conductivity measurements, thermal and spectroscopic studies. The crystal structures of **1** and **2** have been determined by single-crystal X-ray structure determination. Both complex salts, crystallize in triclinic system (space group  $P\bar{1}$ ) with cell dimensions a = 10.215(5) Å, b = 12.013(5) Å, c = 12.822(5) Å,  $\alpha = 69.497(5)$ ,  $\beta = 88.855(5)$ ,  $\gamma = 78.430(5)^\circ$ , Z = 2, V = 1441.6(11) Å<sup>3</sup> for **1** and a = 7.730(5) Å, b = 13.958(5) Å, c = 14.020(5) Å,  $\alpha = 73.763(5)$ ,  $\beta = 88.352(5)$ ,  $\gamma = 81.035(5)^\circ$ , Z = 2, V = 1434.5(11) Å<sup>3</sup> for **2**. The hydrogen bonding (C-H···O and O-H···O) and  $\pi - \pi$  stacking interactions result in the formation of bi-layered and zig–zag structures in **1** and **2** respectively. The facile formation of complex salts with small  $K_{sp}$  values and detailed packing analysis suggests that the  $[Co(phen)_2CO_3]^+$  complex in may be effective as a binding agent for substituted arylsulphonates in an aqueous medium.

#### 1. Introduction

The recognition and binding of anionic species is an area of current interest in supramolecular chemistry [1]. The continuing interest in the development of new binding agents (anion receptors) and detailed study of their interactions with anionic species originates from their potential applications in analytical chemistry, biology, catalysis, etc. [2]. On the other hand, anions play crucial role in biological processes, medicine, catalysis and molecular assembly. Additionally, various pollutant anions are believed to have deleterious effects on the environment [3,4]. A number of methodologies have been devised to achieve the goal to synthesize new, cheap and effective binding agents. The directional nature of  $O-H\cdots O$ ,  $O-H\cdots N$  and  $N-H\cdots O$  hydrogen bonds has been extensively utilized to generate well-defined host-guest association patterns [5]. One strategy to achieve the effective binding is to use metal complexes as cationic hosts because they can provide Lewis-acidic binding sites, carry positive charge and also potentially increase the strength of the non-covalent interactions by optimal orientation of the hydrogen-bond donor groups. The presence of a metal centre confers useful optical, electrochemical and catalytic properties to the receptor molecules, which are helpful in detection of anions and in determining the degree of receptor molecule-anion association.

Our previous investigations have demonstrated that secondsphere interactions along with other non-covalent interactions impart significant binding opportunities to different organic and inorganic anions [6]. In continuation of our studies on anion recognition properties, the binding of substituted arylsulphonates by



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Scheme 1. The arylsulphonate anions used.

cationic Co(III) complex [Co(phen)<sub>2</sub>CO<sub>3</sub>]<sup>+</sup> has been investigated. The interesting characteristic features of [Co(phen)<sub>2</sub>CO<sub>3</sub>]<sup>+</sup> as a binding agent include its high water solubility as its chloride salt, its positive charge for electrostatic interactions with the anions and no fewer than 16 C-H groups of its two coordinated phenanthroline ligands that might act as weak hydrogen bond donor groups in C-H··X interactions. The arylsulphonates were chosen for study because they have number of industrial applications as surfactants, dyes, lubricants, detergents and non-linear optical materials [7], besides these, they are used in pharmaceutical preparations [8]. These interesting applications of arylsulphonates prompted us to investigate the binding of substituted arylsulphonates such as 4-chlorobenzenesulphonate and 2,4-dinitrobenzenesulphonate (Scheme 1) by using cationic cobalt(III) complex [Co(phen)<sub>2</sub>CO<sub>3</sub>]<sup>+</sup>. Although, these substituted arylsulphonates have been used as catalysts for nitration, sporadic reports are available in the literature related to their structural characterization [9,10]. We now describe the syntheses, spectroscopic studies and single crystal X-ray structure determinations of [Co(phen)<sub>2</sub>CO<sub>3</sub>](4-chlorobenzenesulphonate).  $3H_2O$ , **1** and  $[Co(phen)_2CO_3](2,4-dinitrobenzenesulphonate) H_2O,$ **2**.

#### 2. Experimental

Table 1

#### 2.1. Materials and physical measurements

All reagents and solvents were commercially available and used directly without any further purification. The starting material, [Co(phen)<sub>2</sub>CO<sub>3</sub>]Cl·5H<sub>2</sub>O was prepared by the reaction of CoCl<sub>2</sub>-

Crystal data, data collection ad refinement details of complex salts 1 and 2.

Complex celt	1	2
complex salt	I	2
Chemical formula	C31 H26 N4O9SCICo	C <sub>31</sub> H <sub>21</sub> N <sub>6</sub> O <sub>11</sub> SCo
CCDC	879592	879593
M (g mol <sup>-1)</sup>	725.00	744.53
T (K)	100	100
λ (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	ΡĪ	ΡĪ
a (Å)	10.215(5)	7.730(5)
b (Å)	12.013(5)	13.958(5)
<i>c</i> (Å)	12.822(5)	14.020(5)
α (°)	69.497(5)	73.763(5)
β (°)	88.855(5)	88.352(5)
γ (°)	78.430(5)	81.035(5)
V (Å <sup>3</sup> )	1441.6(11)	1434.5(11)
Ζ	2	2
$ ho~({ m g~cm^{-3}})$	1.670	1.724
$\mu$ (mm <sup>-1</sup> )	0.827	0.751
Unique reflections	14302	14182
R(int)	0.033	0.032
GOF on F <sup>2</sup>	1.094	1.099
R1 $[I > 2\sigma(I)]$	0.045	0.038
wR2 $[I > 2\sigma(I)]$	0.118	0.099
$R1 [I > 2\sigma(I)]$ wR2 [I > 2\sigma(I)]	0.045 0.118	0.038 0.099

6H<sub>2</sub>O, 1,10-phenanthroline and sodium bicarbonate according to the modified literature method [11]. C, H and N were estimated micro-analytically by automatic PERKIN ELMER 2400CHN elemental analyzer. Cobalt was determined by standard volumetric method of estimation [12]. UV/Visible spectra were recorded using HITACHI 330 spectrometer in water as solvent. Infrared spectra of the title complex salts were recorded using PERKIN ELMER spectrum RX-1 FT-IR system using KBr pallet. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of title complex salts were recorded in the solvent DMSO-d<sub>6</sub> at 25 °C by using BRUKER AC 400 F (400 MHz) spectrophotometer. The chemical shift values are expressed as  $\delta$  value (ppm) down field from tetramethylsilane as an internal standard. Conductance measurements were performed on Pico Conductivity Meter (Model CNO4091201, Lab India) in aqueous medium at 25 °C by using double distilled water.

#### 2.2. General synthesis

## 2.2.1. Synthesis of $[Co(phen)_2CO_3](4-chlorobenzenesulphonate) \cdot 3H_2O$ (1)

[Co(phen)<sub>2</sub>CO<sub>3</sub>]Cl·5H<sub>2</sub>O (0.2 g, 0.33 mmol) was dissolved in 5 mL of water and to this, 5 mL aqueous solution of 0.063 g (0.33 mmol) 4-chlorobenzenesulphonic acid and 0.013 g (0.33 mmol) sodium hydroxide was added. When the resultant solution was allowed to evaporate slowly at room temperature, reddish-pink coloured crystals started appearing next day, which were collected and dried in air (yield 75%). The complex salt decomposed at 210 °C. Anal. Calcd. for C<sub>31</sub>H<sub>26</sub>CoClN<sub>4</sub>O<sub>9</sub>S: C, 51.31; H, 3.59; N, 7.72; Co, 8.14. Found (%): C, 51.03; H, 3.40; N, 7.50; Co, 7.96. IR/  $cm^{-1}$  (KBr pellet, b = broad, s = strong, m = medium, w = weak): 3440(b), 3057(w), 1657(s), 1633(s), 1517(m), 1427(s), 1341(w), 1223(m), 1190(s), 1120(w), 1004(s), 856(s), 752(s), 719(s), 647(s), 562(w), 482(m). <sup>1</sup>H NMR/ppm (DMSO-d<sub>6</sub>): cation, [Co(phen)<sub>2</sub>CO<sub>3</sub>]<sup>+</sup>,  $\delta = 9.25(d, H9), 9.20(d, H7), 8.91(d, H2), 8.89-8.40(m, H8/6/5),$ 7.83–7.75(m, H3/4); anion  $[C_6H_4SO_3Cl]^- \delta = 7.57(d, H2/6), 7.35(d, H2/6)$ H3/5). <sup>13</sup>C NMR/ppm (DMSO-d<sub>6</sub>):  $\delta$  = 163.14, 154.11, 151.66, 147.31, 147.04, 146.82, 140.83, 139.82, 139.73, 132.88, 130.31, 130.16, 128.12, 127.99, 127.79, 127.66, 127.49, 127.45, 126.85. Solubility (H<sub>2</sub>O, 25 °C) = 0.205 g/100 mL,  $K_{sp} = 8.0 \times 10^{-6}$ . UV/Vis (λ<sub>max</sub>, H<sub>2</sub>O): 509, 351, 272 and 224 nm.

2.2.2. Synthesis of  $[Co(phen)_2CO_3](2,4-dinitrobenzesulphonate) \cdot H_2O$  (2)

 $[Co(phen)_2CO_3]Cl \cdot 5H_2O$  (0.3 g, 0.5 mmol) was dissolved in 10 mL of water in a beaker and to this, 10 mL aqueous solution of 0.134 g (0.5 mmol) sodium 2,4-dinitrobenzenesulphonate, separately dissolved in another beaker, was added. When the resultant solution was allowed to evaporate slowly at room temperature, reddish-pink coloured crystals started appearing next day, which were collected and dried in air (yield 78%). The complex salt decomposed at 205 °C. Anal. Calcd. (%) for C<sub>31</sub>H<sub>21</sub>CoN<sub>6</sub>O<sub>11</sub>S: C, 49.96; H, 2.82; N, 11.28; Co, 7.92. Found (%): C, 49.50; H, 2.70; N, 11.35; Co, 7.52. IR/cm<sup>-1</sup>(KBr): 3479(b), 3068(w), 1671(s), 1636(m), 1603(w), 1522(s), 1430(m), 1347(m), 1246(m), 1115(s), 1026(w), 850(s), 748(m), 718(s), 637(w), 555(w), 481(w). <sup>1</sup>H NMR/ppm (DMSO-d<sub>6</sub>): cation,  $[Co(phen)_2CO_3]^+$ ,  $\delta = 9.26 - 9.20(m, m)_2CO_3$ H9/7), 8.90(d, H2), 8.53-8.36(m, H8/5/6), 7.83-7.75(m, H3/4); Anion,  $[C_6H_3N_2O_7S]^-$ ,  $\delta = 8.53 - 8.36(m, H3/5)$ , 8.07(d, H6). <sup>13</sup>C NMR/ ppm (DMSO-d<sub>6</sub>):  $\delta$  = 163.14, 154.08, 151.62, 147.39, 147.03, 146.81, 144.69, 140.81, 139.76, 130.75, 130.29, 130.14, 127.98, 127.77, 126.82, 125.65, 118.35, Solubility (H<sub>2</sub>O, 25 °C) = 0.034 g/ 100 mL,  $K_{\rm sp}$  = 2.07 × 10<sup>-7</sup>. UV/Vis ( $\lambda_{\rm max}$ , H<sub>2</sub>O): 509, 349, 271, 224 and 206 nm.



Scheme 2. Schematic representation of synthetic procedure.

#### Table 2

Selected bond lengths and bond angles around Co(III) metal centre in complex salt 1.

Bond distances (Å)			
Co1-02C	1.898(2)	Co1—N1B	1.932(3)
Co1-01C	1.905(2)	Co1—N8B	1.943(3)
Co1–N1A	1.924(3)	Co1–N8A	1.962(3)
Bond angles (°)			
O1C-Co1-N1A	91.36(10)	02C-Co1-01C	69.30(9)
O2C-Co1-N1B	92.65(10)	02C-Co1-N1A	89.11(10)
O1C-Co1-N1B	91.11(9)	N1A-Co1-N1B	177.35(10)
02C-Co1-N8B	165.13(9)	O1C-Co1-N8B	96.17(9)
N1A-Co1-N8B	94.52(10)	N1B-Co1-N8B	84.27(11)
02C-Co1-N8A	94.50(9)	01C-Co1-N8A	163.33(9)
N1A-Co1-N8A	84.25(10)	N1B-Co1-N8A	93.64(10)
N8B-Co1-N8A	100.20(10)		

#### Table 3

Selected bond lengths and bond angles around Co(III) metal centre in complex salt 2.

Bond lengths (Å)			
Co1-01C	1.8879(17)	Co1—N1B	1.933(2)
Co1-02C	1.8928(18)	Co1–N8B	1.947(2)
Co1–N1A	1.921(2)	Co1–N8A	1.955(2)
Bond angles (°) 01C-Co1-O2C 02C-Co1-N1A 02C-Co1-N1B 01C-Co1-N8B N1A-Co1-N8B 01C-Co1-N8A	69.91(8) 88.93(8) 90.67(8) 99.75(8) 96.11(9) 169.92(7)	01C-Co1N1A 01C-Co1N1B N1ACo1N1B 02C-Co1N8B N1BCo1N8B 02CCo1N8A	91.89(8) 87.97(8) 179.60(8) 168.71(8) 84.28(9) 100.66(8)
N1A-Co1-N8A	84.21(8)	N1B-Co1-N8A	95.86(8)
N8B-Co1-N8A	89.92(8)		

#### 2.2.3. Single-crystal structure determination

Suitable single crystals of **1–2** were mounted on glass fibre and used for X-ray data collection. Data were collected with a Bruker AXS APEX CCD area detector equipped with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) by applying the  $\omega$ -scan method. The data were processed with APEX2 [13] and corrected for absorption using SADABS [14]. The structures were solved by direct methods using SIR97 [15], revealing positions of all nonhydrogen atoms. These atoms were refined on  $F^2$  by a full matrix least-squares procedure using anisotropic displacement parame-

#### Table 4

A comparison of structural parameters of complex salts 1,2 and related complex salts.



**Fig. 1.** ORTEP diagram of complex salt **1**. The displacement ellipsoids are drawn at 40% probability and hydrogen atoms are removed for clarity.

ters [16]. All hydrogen atoms were located in difference Fourier maps and included as fixed contributions riding on attached atoms with isotropic thermal displacement parameters 1.2 times those of the respective atoms. In general, the structures have disorder problems with the solvent molecules. For this reason, in complexes **1** and **2** some hydrogen atoms have been omitted. Crystal data, data collection and final refinement parameters are reported in Table 1.

#### 3. Results and discussion

#### 3.1. Syntheses

The complex salts **1** and **2** were synthesized by the reaction of  $[Co(phen)_2CO_3]Cl\cdot5H_2O$  with sodium salts of respective sulphonic acids in the aqueous medium in 1:1 M ratio (Scheme 2). The newly formed complex salts are soluble in methanol, dimethylformamide, dimethylsulphoxide and sparingly soluble in water. The complex salts **1** and **2** decomposed in the range 200–210 °C. These new complexes have been characterized on the basis of elemental analyses, spectroscopic studies (IR, UV/Visible, <sup>1</sup>H and <sup>13</sup>C NMR) and conductance measurements. The crystal structures of both these complex salts have been unambiguously established by single crystal X-ray structure determination.

#### 3.2. Thermal studies

The thermal behaviour of complex salts **1** and **2** were examined by TGA under nitrogen atmosphere. In complex salts **1**, the weight

t comparison of structural parameters of complex sures 1,2 and related complex sures.							
S. no.	Complex salt	Bond lengths		Bond angles		References	
		S—0	S—C	S—Cl	0—S—0		
Comple	x salt <b>1</b>						
1	2,4-dichloroanilinium 4-chlorobenzenesulphonate	1.441(2)	1.753(3)	1.733(4)	112.32(17)		[26a]
2	2,5-dichloroanilinium 4-chlorobenzenesulphonate	1.436(2)	1.766(2)	1.744(3)	112.75(10)		[26b]
3	1-Methyl-4-[(E)-2-(2-thienyl)ethenyl] pyridinium 4-chlorobenzenesulphonate	1.455(1)	1.781(2)	1.711(2)	113.09(7)		[26c]
4	[Co(phen) <sub>2</sub> CO <sub>3</sub> ](4-chlorobenzenesulphonate)·3H <sub>2</sub> O	1.453(2)	1.785(3)	1.740(3)	113.10(15)		Present work
Complex salt <b>2</b>							
		S—0	S—C	N-0	0—N—O	0—S—0	
1	1H-1,2,4-Triazol-4-ium 4-nitro-benzene-sulphonate H <sub>2</sub> O	1.446(2)	1.779(2)	1.223(3)	123.5 (2)	112.9(1)	[27a]
2	Triethyl-ammonium 4-nitrobenzene-sulphonate	1.456(1)	1.787(1)	1.225(2)	123.5(1)	113.3(1)	[27b]
3	$[Co(phen)_2CO_3](2,4-dinitrobenzenesulphonate) H_2O$	1.447(2)	1.799(2)	1.226(3)	124.5(2)	113.6(1)	Present work

#### Table 5

Hydrogen bonding parameters	of [Co(phen) <sub>2</sub> CO <sub>3</sub> ](4-chlorobenzenesulphonate) 3H <sub>2</sub> C
1	

D—H···A	$D{\cdots}A~({\mathring{A}})$	H···A (Å)	D–H···A (°)
01W-H11W043D	2.854	2.094	161.38
02W-H21W041D	2.822	2.076	166.51
O2W−H22W···O3C <sup>i</sup>	2.891	2.130	162.03
C3B—H3B····O1W <sup>iii</sup>	3.363	2.521	150.73
C4A—H4A· · · O41D <sup>iv</sup>	3.246	2.368	157.39
C4B—H4B····O1W <sup>v</sup>	3.464	2.567	162.55
C10A—H10A· · · O42D <sup>iii</sup>	3.160	2.410	137.65
C6D—H6D· · · O41D <sup>vi</sup>	3.615	2.782	149.65
C9B—H9B····O2W <sup>vi</sup>	3.057	2.353	132.26
C13A—H13A· · ·O3W <sup>vii</sup>	3.169	2.546	124.69
C13A—H13A····O2C <sup>vii</sup>	3.182	2.381	144.27
C13B–H13B···O1C <sup>viii</sup>	3.382	2.624	139.13
C14A—H14A· · · O43D <sup>iv</sup>	3.468	2.596	156.48
C14B—H14B…O3C i <sup>x</sup>	3.353	2.458	161.61

Equivalent positions: (i) x - 1, +y + 1, +z, (ii) -x + 2, -y + 1, -z, (iii) -x + 1, -y + 1, -z + 1, (iv) x + 1, +y, +z, (v) x, +y - 1, +z, (vi) -x + 1, -y + 2, -z, (vii) -x + 2, -y + 1, -z + 1, (viii) -x + 1, -y + 1, -z, (ix) x - 1, +y, +z.

loss of 7.21% in the temperature range of 30-100 °C, corresponds to the loss of three water molecules of crystallization (calc 7.44%). Further heating to 1000 °C led to continuous weight loss and no clear steps were observed.

In case of complex salt 2, the first weight loss of 2.9% (calc 2.42%) corresponds to the loss of one water molecule of crystallization. After the loss of water molecule, the complex has shown similar thermal behaviour as to that of complex 1.

#### 3.3. Solubility products measurement

Solubility of ionic salts in the water differ to greater extend. The measurement of the solubility product provides an idea about the magnitude of interactions between cations and anions. The values



**Fig. 3.** ORTEP diagram of complex salt **2**. The displacement ellipsoids are drawn at 40% probability and hydrogen atoms are removed for clarity.

of solubility product ( $K_{sp}$ ) determined at 25 °C for complex salts **1** and **2** were  $8.0 \times 10^{-6}$  and  $2.07 \times 10^{-7}$  respectively. These values showed that complex cation  $[Co(phen)_2CO_3]^+$  has more affinity for 2,4-dinitrobenzenesulphonate than 4-chlorobenzenesulphonate. This affinity may be due to the increased interactions between cations and anions.

#### 3.4. Molar conductivity measurements

Molar conductivities of complex salts **1** and **2** were measured at 25 °C in aqueous medium. The limiting molar conductivity at



Fig. 2. Packing diagram of complex salt 1 showing bi-layered structure. The benzene sulphonate anions are shown in space-filling model while on right side bottom only complex cations are shown in space filling model for clarity.

Table 6

Hydrogen bonding parameters of  $[Co(phen)_2CO_3](2,4-dinitrobenzene sulphonate)$  H<sub>2</sub>O, **2**.

D—H···A	D· · ·A (Å)	H⊷A (Å)	$D - H \cdot \cdot \cdot A$ (°)
01W-H12W···01C <sup>i</sup>	3.122	2.496	131.5
01W−H12W···O3C <sup>i</sup>	3.073	2.331	146.4
01W-H11W021D	2.898	2.158	152.3
C2A−H2A····O12D <sup>i</sup>	3.310	2.547	139.6
C4A—H4A····O3C <sup>i</sup>	3.127	2.358	139.8
C4B—H4B· · ·O21D <sup>ii</sup>	3.352	2.492	153.9
C6D—H6D···O2C	3.465	2.672	143.6
C9A—H9A· · · O51D <sup>iii</sup>	3.349	2.555	143.6
C9B—H9B···O3C <sup>iv</sup>	3.310	2.596	134.0
C10B—H10B· · ·O1W <sup>v</sup>	3.240	2.609	125.5
C11A—H11A···O52D <sup>iv</sup>	3.303	2.705	122.8
C11A—H11A…O23D <sup>vi</sup>	3.288	2.541	137.6
C11B—H11B· · ·O1C <sup>vii</sup>	3.302	2.562	136.9
C13A—H13A…O23D <sup>vi</sup>	3.196	2.399	143.7
C14A—H14A···O11D <sup>iv</sup>	3.177	2.509	129.0
C11B—H11B· · ·O1W <sup>viii</sup>	3.474	2.669	145.4

Equivalent positions: (i) -x, -y + 1, -z + 1, (ii) x + 1, +y - 1, +z, (iii) -x, -y, -z + 2, (iv) x - 1, +y, +z, (v) -x - 1, -y + 1, -z + 1, (vi) -x - 1, -y + 1, -z + 2, (vii) -x, -y, -z + 1, (viii) x, +y - 1, +z.

infinite dilution ( $\Lambda_0$ ) was calculated by plotting molar conductivity versus square root of concentration. The  $\Lambda_0$  values obtained for salts **1** and **2** (116 and 61 S cm<sup>2</sup> mol<sup>-1</sup>) were closer to the range of 1:1 electrolytes [17]. The lower value observed in the case of complex salt **2** may be ascribed to ion-pair formation.

#### 3.5. Spectroscopic characterization

For low spin Co(III) complexes, two types of transitions i.e.  ${}^{1}A_{1g} \rightarrow T_{1g}$  and  ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$  are expected. In  $[Co(phen)_2CO_3]^+$  complex salts, these transitions were observed around 500 and 350 nm as reported in the literature [18]. For the complex salts **1** and **2**, these values were observed around 510 and 350 nm, respectively. Other transitions due to *phen* (1,10-phenantholine) groups coordinated to the cobalt(III) were also observed. Peaks observed around 272 and 224 nm in complex salts **1** and **2** were assigned to  $\pi$ - $\pi$ \* transition in coordinated *phen* groups [19]. The detailed peak assignments are given in experimental section.

Vibrational spectra of newly synthesized complex salts have been recorded in the range 400–4000 cm<sup>-1</sup>. In the FT IR spectra of complex salts **1** and **2**, bands in the regions 3479–3440, 3069–3057, 1671–1657, 1630–1620, 856–850 and 482–481 cm<sup>-1</sup> were assigned

to v(O-H) of H<sub>2</sub>O, v(=C-H), v(C=O) and  $v(C=C/N) \delta(H-C=)$  and v(CO-N) vibrations, respectively. These spectral assignments have been made in consultation with literature values [20].

In case of complex salt **1**, the bands at 1233, 1189, 562 and 671 cm<sup>-1</sup> were assigned to  $v_{as}(SO_3)$ ,  $v_s(SO_3)$ ,  $\delta_{as}(SO_3)$  and v(C-S) respectively, while in case of complex salt **2**, the bands at 1246, 1226, 554, 509 and 637 cm<sup>-1</sup> were assigned to  $v_{as}(SO_3)$ ,  $v_s(SO_3)$ ,  $\delta_{as}(SO_3)$ ,  $\delta_s(SO_3)$  and v(C-S) respectively. These bands are characteristic for the presence of anion, i.e. sulphonates. The presence of similar bands were also reported in complex salts  $[Co(en)_2(N_3)_2]$   $[(CH_3)_3 \cdot C_6H_2 \cdot SO_3] \cdot 0.5H_2O$  [21a] and  $[Co(NH_3)_6](CH_3SO_3)_3$  [21b]. The IR bands due to  $v_{as}(NO_2)$  and  $v_s(NO_2)$  vibrations were observed at 1522 and 1347 cm<sup>-1</sup>, respectively in case of complex salt **2**. IR bands at 1573, 1322 cm<sup>-1</sup> and 1586, 1337 cm<sup>-1</sup> due to  $v_s(NO_2)$  and  $v_{as}(NO_2)$  vibrations have been reported in the complex salts containing nitrophenolate anions;  $[Co(NH)_6](4-np)_3 \cdot 4H_2O$  [22] and  $[PPh_3)_3Cu(4-np)]_2$  [23], respectively.

In complex salts **1** and **2**, <sup>1</sup>H and <sup>13</sup>C NMR chemical shift values are in good agreement with literature values reported for complex cation  $[Co(phen)_2CO_3]^+$  and different arylsulphonates [19b,24]. The detailed NMR peak assignments for complexes **1** and **2** are given in experimental section.

#### 3.6. Structure descriptions

#### 3.6.1. Coordination geometry and bonding

The geometry around Co(III) metal centre is distorted octahedral and the extent of distortion is 20.7 and 20.09° in **1** (Fig. 1) and **2** (Fig. 3) respectively from the ideal value of 90° for *cis* N—Co—N bond angles (as revealed from the geometrical parameters reported in Tables 2 and 3). The coordination around Co(III) is completed by two bidantate 1,10-phenanthroline and one carbonato ligands. In complex salts **1** and **2**, the average Co—N, Co—O bond lengths and bond angles O(1)—Co—O(2), N(1)—Co—N(2) and N(3)—Co—N(4)are quite similar to those of reported related complexes [11,18,19b,c,25]. The density values of the two structures are in the range 1.501–1.769 g/cm<sup>3</sup> reported for similar complexes in the literatures. Therefore, complex salts **1** and **2** can be classified as ionic salts.

The aromatic rings of the *phen* moieties attached to the cobalt(III) centre are almost planar in both complex salts. The angles between the least square planes of *phen* rings in complex salts **1** and **2** are 114.38° and 87.36°, respectively. The significant deviation from orthogonality in **1** can be explained on the basis of arrangement of anions in the 'V' shaped arrangement of *phen* rings



Fig. 4. Packing diagram of complex salt 2 showing the zig-zag arrangement of complex cations and anions are shown by space filling model. For clarity the arrangement of only complex cations is shown in ball-stick model.

coordinated to Co(III) centre. In the complex salt **2**, the nitro group at the *ortho* position in 2,4-dinitrobenzesulphonate anion is out of plane from the aromatic ring (C2D—C1D—N11D—O12D torsion angle of  $-61.73^{\circ}$ ) while nitro group presents at *para* position is almost planar to the benzene ring (C4D—C5D—N51D—O51D = 4.59^{\circ}). Probably, the presence of sulphonate group and nitro groups at adjacent positions (steric crowding) necessitates this out of plane twist of NO<sub>2</sub> group. As expected, the bond lengths and bond angles for anions (i.e. arylsulphonates) are similar to those ionic complexes of arylsulphonates reported in the literature [19b,10,26– 28]. A comparison of structural parameters is given in Table 4 shows that there is no significant effect of change of counter cations on structural parameters of arylsulphonates.

#### 3.6.2. Packing

3.6.2.1. Complex salt 1. The complex salt 1 crystallizes in triclinic crystal system with space group  $P\bar{1}$ . The asymmetric unit of **1** contains one 4-chlorobenzenesulphonate anion, one [Co(phen)<sub>2</sub>CO<sub>3</sub>]<sup>+</sup> cation and three water molecules of crystallization (Fig. 1). The hydrogen bonding parameters are given in Table 5. The crystal lattice is stabilized by the non-covalent interactions like O-H···O(water/sulphonate), C—H···O(water/sulphonate), anion··· $\pi$  and  $\pi$ - $\pi$  stacking. In the crystal lattice, the water molecules of crystallization are involved in the O-H...O interaction with oxygen O3C of complex cation and oxygen atoms O41D and O43D of anion i.e. they act as a linker between the cationic and anionic moieties. These O-H--O interactions results  $R_3^4(9)$  graph set pattern [29] (Fig. 2). When packing of the complex salt is viewed down a axis, a bilayered structure can be visualized as shown in Fig. 2. One layer is constituted by complex cations which are arranged in such a way that both the phen moieties of the complex cation are involved in the  $\pi$ - $\pi$  stacking interactions with the *phen* moieties originated from the other two complex cations on the respective sides. These *phen* moieties have  $\pi$ - $\pi$  stacking of 3.637 and 3.585 Å (distance between the centroids of respective rings). The other layer is formed by anions and water molecules of crystallization. These cationic and anionic layers are anchored in the crystal lattice by hydrogen bond interaction as described in the graph set pattern. Each of the anionic moieties are placed in the 'V' shaped arrangement of two *phen* moieties that are coordinated to cobalt(III) centre. The anionic moiety has short contacts both the phen moieties as C2D···C13A = 3.228 Å and to  $C5D \cdot C9B = 3.387$  Å. This may be the reason for the strong deviation of the *phen* moieties from the orthogonality. The anionic species are also involved in the anion  $\dots \pi$  interactions of magnitude S41D—O42D—Cg = 3.162 Å (where Cg = centroid of ring defined by atoms C7B N8B, C9B-C12B). It is also noteworthy that there are interactions between  $H_2O$ ...anion,  $H_2O$ ...cation, cation...cation but there is no interaction between anion. ...anion. This may be due to the presence of anionic moieties in the 'V' shaped arrangement which restricts any contact between anionic moieties. In addition to other interactions, oxygen atom O3C and Cl1 is having a short contact of 3.141 Å.

3.6.2.2. Complex salt **2**. The complex salt **2** crystallizes in triclinic crystal system with space group  $P\overline{1}$ . The asymmetric unit of **2** contains 2,4-dinitrobenzenesulphonate anion, one  $[Co(phen)_2CO_3]^+$  cation and one water molecule of crystallization as shown in Fig. 3. The hydrogen bonding parameters are given in Table 6. In the crystal lattice, the constituent units are held together by a network of hydrogen bonds (O—H···O and C—H···O) and  $\pi$ – $\pi$  stacking interactions. In this case, the oxygen atoms of the sulphonate group and nitro groups of the 2,4-dinitrobenzenesulphonate anions are strongly interacting with C—H groups of the cation that result in the zig–zag layered arrangement of the complex cations (Fig. 4). The anions and water molecule of crystallization are residing in the voids created by the two layers. Anions are held in the voids by C—H···O hydrogen bonds and  $\pi$ – $\pi$  stacking interactions between anion and *phen* ring (centroid–centroid distance between

aromatic ring of anion and central *phen*-ring is 3.756 Å). In the cationic layers, the carbonato oxygen atom O3C plays a crucial role by connecting different cationic units. It is involved in two C–H···O and one O–H···O hydrogen bonding interactions. Additionally, O3C is also involved in O··· $\pi$  interaction with *phen* moiety with oxygen to centroid of aromatic ring distance of 3.081 Å. These interactions are complemented by  $\pi$ - $\pi$  stacking interaction between *phen* rings of the complex cations (centeroid to centeroid distance between *phen* rings is 3.659 Å).

#### 4. Conclusions

In an effort to investigate the binding of substituted arylsulphonates by cationic cobalt(III) complex, two salts [Co(phen)<sub>2</sub>CO<sub>3</sub>](4chlorobenzenesulphonate) 3H<sub>2</sub>O, 1 and [Co(phen)<sub>2</sub>CO<sub>3</sub>] (2,4-dinitrobenzenesulphonate) H<sub>2</sub>O, 2 have been synthesized and characterized by elemental analyses, solubility product, conductivity measurement, thermal, spectroscopy (FT IR, NMR and UV/Vis) studies and single crystal X-ray crystallography. Single crystal Xray structure determination revealed the presence of ionic structures with  $[Co(phen)_2CO_3]^+$  complex cation, respective arylsulphonate anions and water molecules of crystallization. The crystal packing of complex salts is stabilized by interplay of non-covalent interactions like O–H···O, C–H···O,  $\pi$ ··· $\pi$  and O··· $\pi$  besides electrostatic forces of attraction. Thus, non-covalent interactions play crucial role in binding of substituted arylsulphonates. On the basis of solubility product measurements and packing analyses, it has been shown that cationic metal complex is a promising binding agent for substituted arylsulphonates in aqueous medium.

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