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Second sphere coordination in binding large size anions: Synthesis, characterisation and X-ray structure determination of [*trans*-$Co(en)_2Cl_2$] $C_6NO_2SO_3H_3Cl$ and [*trans*-$Co(en)_2Cl_2]_2S_4O_6$

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Abstract

In an effort to explore [*trans*-$Co(en)_2Cl_2]^+$ as anion receptor for large size anions, 2-chloro,5-nitrobenzenesulphonate and tetrathionate ion, green coloured single crystals of [*trans*-$Co(en)_2Cl_2]C_6NO_2SO_3H_3Cl$ **I** and [*trans*-$Co(en)_2Cl_2]_2S_4O_6$ **II** have been obtained by slowly mixing the separately dissolved *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride with metal salts of 2-chloro,5-nitrobenzenesulphnic acid and tetrathionic acid in aqueous medium in 1:1 and 2:1 molar ratio, respectively. The newly synthesized complex salts were characterized on the basis of elemental analyses and spectroscopic techniques (IR, UV/visible, ^{1}H and ^{13}C NMR). Single crystal X-ray structure determinations revealed that **I** crystallizes in the monoclinic space group $P2_1/c$ and **II** crystallizes in the triclinic space group $P\bar{1}$. Supramolecular hydrogen bonding networks between ionic groups: oxygen atoms of 2-chloro,5-nitrobenzenesulphonate or tetrathionate and NH groups of coordinated ethylenediamine molecules, i.e. $N–H\cdots O^-$ interactions by second sphere coordination besides electrostatic forces of attraction have been observed. This suggests that [*trans*-$Co(en)_2Cl_2]^+$ is a promising anion receptor for the weakly coordinating sulphonate and tetrathionate ions. The solubility product measurements indicate that the affinity of cationic cobaltammine [*trans*-$Co(en)_2Cl_2]^+$ is greater for 2-chloro,5-nitrobenzenesulphonate than tetrathionate ion.

Keywords: Cobalt(III); Second sphere coordination; Tetrathionate; Chloronitrobenzenesulphonate; Hydrogen bonding; X-ray crystallography

1. Introduction

The coordination of anionic guest species by hydrogen bond donating receptors is an area of supramolecular chemistry that continues to attract attention [1] because of the crucial role anions play in biological processes, medicine, catalysis and molecular assembly. Additionally, various pollutant anions are believed to have deleterious effects on the environment.

A high proportion of the anion receptors reported so far are organic based such as the cationic polyamines [2] but sporadic reports are available with cationic transition metal complexes based anion receptors, i.e. alkoxide-bridged dinuclear Zn(II) complex [3], urea based Pt(II) receptor [4], bipyridine Ru(II) complexes [5], Pd(II) receptor [6] and Cu(II) based receptor [7]. Recently Fe(II) complexes have been utilized as receptors for chloride ion binding [8]. However, the preparation of such type of receptors can often be synthetically challenging, a fact that prompted us to look for alternative means of arranging hydrogen bond donating groups in space. It occurred to us that some easy to prepare metal ligand complexes could be exploited [9]. As compared to the relatively simple design principles for cation receptors (electronic interaction and sizes), there are more factors that can influence the effectiveness of the artificial anion receptors. Due to the fact that anions are larger than isoelectronic cations and thus have a smaller charge to radius ratio, electrostatic interactions are less effective for anions than their corresponding isoelectronic cations. Solvation effects are also more prominent for anions than their isoelectronic cations. To achieve the desired sensitivity and selectivity, the combination of electrostatic interaction, hydrogen bonding and stacking effects all need to be taken into consideration when designing an artificial anionic host or sensor. Two fundamental points in the design [10] of any architecture, are the physical features of the units to be assembled and the means by which these items are to

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be held together. A reliable synthon to act as anion receptor (binding agent) for molecular recognition in supramolecular chemistry refers to molecular couples, typically functional groups or faces of molecules, which have a high degree of complimentarity with respect to intermolecular interactions.

Given the inherent intermolecular nature of these interactions, their implementation as a means of assembling metal complexes is a logical extension of chemistry of discrete species. We chose to study cationic cobaltammines due to their ease of synthesis and possibility of the NH hydrogen involving itself in potential NH⋯O (anion) hydrogen bonding. We have undertaken an extensive research programme to explore cationic cobaltammines $[Co(en)_2X_2]^+$ ($X=NO_2$ or N_3) [11] as anion receptors in continuation of our interest in cobalt(III) complex salts [12]. This is because these cationic metal complexes could be easily synthesized in excellent yields from readily available materials and stored for months without any noticeable decomposition. This paper reports the utility of [*trans*-$Co(en)_2Cl_2]^+$ present in [*trans*-$Co(en)_2Cl_2]Cl$ as anion receptor for large size anions: weakly coordinating anions, i.e. $C_6NO_2SO_3H_3Cl$ and $S_4O_6^{2-}$. Recovery of these anions is biologically and commercially important [13]. 2-Chloro,5-nitrobenzene sulphonate belongs to the class of commercially important organosulphonates, which have longstanding industrial applications as surfactants, dyes, fuel and lubricant, detergents or antioxidants [14]. They have been studied as potential liquid crystalline [15] and non-linear optical materials [16,17] besides pharmaceutical salt preparation [18]. Sulphonate anions are a relatively unexplored class of ligands for the construction of coordination framework because of the misconception that sulphonate group is a poor ligand, incapable of forming stable coordinate bond with the metal ions [19]. Thionates and tetrathionates have traditionally been very useful for precipitating coordination cations and useful also for structural work. Tetrathionate salts are used as pesticides. Therefore, the search for new and efficient anion receptors for sulphonate and tetrathionate ion. We have recently reported the utility of [*trans*-$Co(en)_2Cl_2]^+$ as an anion receptor for small anion, i.e. synthesis, spectroscopic characterisation and crystal structure of [*trans*-$Co(en)_2Cl_2]N_3$ [20]. This is the first crystal structure of a salt containing 2-chloro,5-nitrobenzenesulphonate ion.

2. Experimental

2.1. Materials

Analytical grade reagents were used without any further purification. [*trans*-$Co(en_2)Cl_2]Cl$ has been prepared according to literature method [21].

2.2. Instruments

Cobalt was determined by standard method [22]. C, H, N were estimated microanalytically by automatic Perkin–Elmer 2400 CHN elemental analyzer. Infrared spectrum was recorded using Perkin–Elmer spectrum RX FT-IR system by using Nujol mulls in KBr plates. ^1H and ^{13}C NMR were recorded in DMSO-d_6 using JEOL AL 300 MHz FT NMR spectrometer with TMS as internal reference. UV/visible spectra were recorded using Hitachi 330 spectrometer in H_2O as solvent.

2.3. Synthesis of [trans-$Co(en)_2Cl_2]C_6NO_2SO_3H_3Cl$ (**I**)

An aqueous solution of 1 g (0.003 mol) of [*trans*-$Co(en)_2Cl_2]Cl$ in 25 ml water was taken and filtered. This was added to an equimolar quantity of (0.96 g) potassium 2-chloro,5-nitrobenzene sulphonate dissolved in minimum amount of water. The green crystals of [*trans*-$Co(en)_2Cl_2]C_6NO_2SO_3H_3Cl$ appeared within half an hour of mixing the two reactants, which were collected by drawing off the mother liquor and air-dried (yield 80%). The complex is soluble in water and DMSO but insoluble in ethanol and acetone. The newly formed complex salt **I** decomposes at 212 °C. The elemental analysis is consistent with the composition [*trans*-$Co(en)_2Cl_2]C_6NO_2SO_3H_3Cl$. Found: C, 24.8; H, 3.7; N, 14.2; Co, 12.0 (%). Calculated C, 24.6; H, 3.9; N, 14.3; Co, 12.1. Solubility: 0.6 g/100 ml at 25 °C, $K_{sp}=1\times10^{-4}$.

2.4. Synthesis of [trans-$Co(en)_2Cl_2]_2(S_4O_6)$ (**II**)

One gram (0.003 mol) of [*trans*-$Co(en)_2Cl_2]Cl$ was dissolved in 25 ml water. In another beaker 0.47 g (0.001 mol) of $Na_2S_4O_6$ was dissolved in 10 ml of water at room temperature. Both the solutions were mixed. The green crystals of [*trans*-$Co(en)_2Cl_2]_2(S_4O_6)$ appeared within half an hour of mixing the two reactants, which were collected by drawing off the mother liquor and air-dried (yield 70%). The complex is soluble in water as well as DMSO and stable in air but insoluble in acetone and ethanol. The newly formed complex salt **II** decomposes at 180 °C. The elemental analysis is consistent with the composition [*trans*-$Co(en)_2Cl_2]_2(S_4O_6)$. Found: (%) C, 13.3; H, 4.3; N, 15.5; Co, 8.0. Calculated C, 13.2; H, 4.4; N, 15.4; Co, 8.1. Solubility: 1.2 g/100 ml at 25 °C, $K_{sp}=2\times10^{-4}$.

2.5. X-ray crystallography

Prismatic green coloured single crystals of [*trans*-$Co(en)_2Cl_2]C_6NO_2SO_3H_3Cl$ (**I**) and [*trans*-$Co(en)_2Cl_2]_2(S_4O_6)$ (**II**) suitable for X-ray diffraction studies were grown from water by slow evaporation method. A single crystal with dimension $0.30\times0.24\times0.12$ mm^3 in **I** and $0.29\times0.22\times0.14$ mm^3 in **II** were mounted along the largest dimension and used for data collection. The data for structures **I** and **II** were collected on a Nonius Kappa CCD diffractometer at room temperature using graphite-monochromated Mo Kα radiation ($\lambda=0.71073$ Å) with a φ scan followed by ω scan to fill the sphere. All intensities were corrected for Lorentz, polarization and absorption [23] effects. The structures were solved by direct methods with the SIR97 program [24] and refined on F^2 by full-matrix least-squares methods with anisotropic non-H atoms. All H atoms of structures **I** were found in the difference Fourier map and refined isotropically, while in compound **II** to

Table 1
Crystal data and structure refinement parameters for **I** and **II**

	I	**II**
Chemical formula	$[Co(en)_2C_{l2}]C_6NO_2SO_3H_3Cl$	$[Co(en)_2Cl_2]_2S_4O_6$
Formula weight	486.64	724.32
Cell setting, space group	Monoclinic, $P2_1/c$	Triclinic, $P-1$
Unit cell dimensions	$a=13.4874(3)$ Å	$a=9.1570(2)$ Å, $\alpha=79.895(1)°$
	$b=7.4501(2)$ Å, $\beta=80.56\ (1)°$	$b=12.0630(2)$ Å, $\beta=87.048(1)°$
	$c=12.0231(3)$ Å	$c=12.7150(2)$ Å, $\gamma=71.2990(9)°$
Volume (Å^3)	1146.59(5)	1309.71(4)
Z	4	2
D_x (Mg m^{-3})	1.802	1.837
M (Mo Kα) (mm^{-1})	1.553	2.035
Crystal form, colour and size (mm^3)	Prismatic, green $0.30\times0.24\times0.12$	Prismatic, green $0.29\times0.22\times0.14$
Absorption correction	Empirical (SORTAV)	Empirical (SORTAV)
θ Range (°)	3.0–29.0	2.63–28.0
No. of measured, independent and observed reflections	14252, 4652, 3559	17539, 6260, 5257
Criterion for observed reflections	$I>2\sigma(I)$	$I>2\sigma(I)$
R_{int}	0.034	0.035
Refinement on	F^2	F^2
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, Goodness of fit	0.034, 0.080, 1.036	0.035, 0.089, 1.055
No. of observed reflections/no. of parameters	4652/302	6260/410
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0509P)^2+1.5086P]$, where $P=(F_o^2+2F_c^2)/3$	$w=1/[\sigma^2(F_o^2)+(0.0974P)^2+0.5528P]$, where $P=(F_o^2+2F_c^2)/3$

those belonging to the C atoms of ethylendiamine ligands or the disordered part were given calculated positions. All other calculations were accomplished using SHELX97 [25], WINGX [26] and PARST [27]. Crystal data are given in Table 1 and a selection of bond distances and angles is reported in Table 2. ORTEPIII [28] views of the structures **I** and **II** are shown in Figs. 1 and 2, respectively. A total of three inorganic structures containing tetrathionate anion [29] have been retrieved from the Inorganic Crystal Structure Database (Version 2005-01, FIZ Karlsruhe, Germany and The National Institute of Standards and Technology, USA) and a total of ten metallorganic structures containing tetrathionate anion [30] have been retrieved from the Cambridge Crystallographic Database (November 2004 version) [31].

3. Results and discussion

3.1. Synthesis

trans-dichlorobis(ethylenediamine)cobalt(III)chloride has been known for a long time in the history and has played a pivotal role in the development of coordination chemistry. The preparation of normal *trans*-dichlorobis(ethylenediamine)cobalt(III) salts are often difficult because of hydrolysis.

In the present work, [*trans*-Co(en)$_2$Cl$_2$]Cl and potassium 2-chloro,5-nitrobenzenesulphonate or sodium tetrathionate were reacted in appropriate molar ratio in water with the following expectation.

The chemical composition of the complex salts, **I** and **II** were initially indicated by elemental analysis. On the basis of chloride ion test, the chloride ion was found to be absent and so based on these studies, we proposed that the abovesaid ionic structures may be present. These are green coloured solids and are stable in air and light.

3.2. Measurement of solubility product

Solubility of ionic salts in water differs to a great extent and on the basis of solubility criterion, the salts are classified into three categories (a) solubility > 0.1 M (soluble), (b) solubility between 0.01 and 0.1 M (slightly soluble) and (c) solubility < 0.01 M are (sparingly soluble). The solubility measurements at room temperature show that both the salts [*trans*-Co(en)$_2$(Cl)$_2$]C$_6$NO$_2$SO$_3$H$_3$Cl and [*trans*-Co(en)$_2$(Cl)$_2$]$_2$S$_4$O$_6$ are slightly soluble in water but it is more for the former. [*trans*-Co(en)$_2$(Cl)$_2$]Cl is readily soluble in water. The solubility products of [*trans*-Co(en)$_2$(Cl)$_2$]C$_6$NO$_2$SO$_3$H$_3$Cl and [*trans*-Co(en)$_2$(Cl)$_2$]$_2$S$_4$O$_6$ are 1.0×10^{-4} and 2.0×10^{-4}, which indicates that the affinity or binding of cationic cobaltammine [*trans*-Co(en)$_2$Cl$_2$]$^+$ is greater for 2-chloro,5-nitrobenzenesulphonate ion than tetrathionate ion, which is obviously more as compared to that of chloride, i.e. in the order $C_6NO_2SO_3H_3Cl > S_4O_6 > Cl$. As reported in Section 2, when the appropriate amounts of the reactants were mixed in minimum amount of water the crystals

$$\underset{\text{(Green)}}{[\textit{trans}\text{-Co(en)}_2\text{Cl}_2]\text{Cl}} + \text{KC}_6\text{NO}_2\text{SO}_3\text{H}_3\text{Cl} \xrightarrow{\text{H}_2\text{O}} \underset{\text{(Green)}}{[\textit{trans}\text{-Co(en)}_2\text{Cl}_2]\text{C}_6\text{NO}_2\text{SO}_3\text{H}_3\text{Cl}} + \text{KCl} \qquad (1)$$

$$2\underset{\text{(Green)}}{[\textit{trans}\text{-Co(en)}_2\text{Cl}_2]\text{Cl}} + \text{Na}_2\text{S}_4\text{O}_6 \xrightarrow{\text{H}_2\text{O}} \underset{\text{(Green)}}{[\textit{trans}\text{-Co(en)}_2\text{Cl}_2]_2(\text{S}_4\text{O}_6)} + 2\text{NaCl} \qquad (2)$$

Table 2
Selected bond distances (Å) and angles (°) for **I** and **II**

I		**II**	
Co1–N1	1.945(2)	Co1–Cl6	2.256(1)
Co1–N2	1.966(2)	Co1–N14	1.945(2)
Co1–N3	1.957(2)	Co1–N18	1.960(2)
Co1–N4	1.965(2)	Co2–Cl5	2.248(1)
Co1–Cl1	2.259(1)	Co2–N15	1.957(3)
Co1–Cl2	2.234(1)	Co2–N17	1.955(2)
C5–C6	1.393(3)	Co3–Cl8	2.256(1)
C6–C7	1.384(3)	Co3–N13	1.948(3)
C7–C8	1.375(4)	Co3–N16	1.946(2)
C8–C9	1.372(3)	Co4–Cl11	2.236(1)
C9–C10	1.379(3)	Co4–N23	1.959(3)
C5–C10	1.381(3)	Co4–N24	1.964(2)
C5–S1	1.794(2)	S7–S12	2.121(1)
S1–O3	1.447(2)	S7–O19	1.442(2)
S1–O4	1.455(2)	S7–O20	1.443(3)
S1–O5	1.450(2)	S7–O25	1.447(2)
Cl3–C6	1.729(2)	S9–S10	2.126(1)
N5–C9	1.468(3)	S9–O22	1.434(2)
O1–N5	1.235(3)	S9–O34	1.432(2)
O2–N5	1.219(3)	S9–O27	1.444(2)
Cl1–Co1–Cl2	179.2(1)	S10–S12	2.019(1)
Cl1–Co1–N1	89.5(1)	Cl6–Co1–N14	89.3(1)
Cl1–Co1–N2	90.4(1)	Cl6–Co1–N18	89.3(1)
Cl1–Co1–N3	90.0(1)	N14–Co1–N18	86.2(1)
Cl1–Co1–N4	90.5(1)	Cl5–Co2–N15	89.2(1)
Cl2–Co1–N1	90.6(1)	Cl5–Co2–N17	90.2(1)
Cl2–Co1–N2	88.8(1)	N15–Co2–N17	86.2(1)
Cl2–Co1–N3	89.9(1)	Cl8–Co3–N13	91.0(1)
Cl2–Co1–N4	90.3(1)	Cl8–Co3–N16	89.1(1)
N1–Co1–N2	85.8(2)	N13–Co3–N16	86.7(1)
N1–Co1–N3	178.7(1)	Cl11–Co4–N23	90.5(1)
N1–Co1–N4	93.0(1)	Cl11–Co4–N24	90.5(1)
N2–Co1–N3	95.4(1)	N23–Co4–N24	84.8(1)
N2–Co1–N4	178.5(1)	S12–S7–O19	107.3(1)
N3–Co1–N4	85.8(1)	S12–S7–O20	107.3(1)
O3–S1–O4	113.3(1)	S12–S7–O25	98.0(1)
O3–S1–O5	113.2(1)	O19–S7–O20	112.6(1)
O3–S1–C5	105.4(1)	O19–S7–O25	114.6(1)
O4–S1–O5	112.9(1)	O20–S7–O25	115.5(1)
O4–S1–C5	105.4(1)	S10–S9–O22	106.8(1)
O5–S1–C5	105.7(1)	S10–S9–O34	98.9(1)
		S10–S9–O27	107.5(1)
		O22–S9–O34	115.3(2)
		O22–S9–O27	111.8(2)
		O34–S9–O27	115.1(2)
		S9–S10–S12	105.5(1)
		S7–S12–S10	105.8(1)

appeared almost immediately resulting in the formation of title complex salts. This is because ionic products are greater than solubility products, K_{sp}.

3.3. Spectroscopy

Infrared spectra of the newly synthesized complex salts have been recorded in the region 4000–400 cm^{-1} and tentative assignments have been made on the basis of earlier reports in literature [32]. The IR band at 887 cm^{-1} is assigned to CH_2 rocking region and a band at 1595 cm^{-1} to δNH_2 [33] in **I**. The corresponding bands appear at 886 and 1591 in **II**. The IR band at 1513 cm^{-1} is assigned to ν_{as} (aromatic NO_2) and a band at 1343 cm^{-1} is assigned to ν_s (NO_2). The peak at 2953 cm^{-1} is due to the ring ν (C–H) vibrations. The strong absorption bands at 1219, 1116, 618 cm^{-1} and a weak band at 686 cm^{-1} are assigned to ν_{as} ($-SO_3^-$), ν_s ($-SO_3^-$), δ_{as} ($-SO_3^-$) and ν (C–S), respectively. These bands appear at 1202, 1112, 602 and 666 cm^{-1} in Tl(m-$NO_2C_6H_4SO_3$) [34]. Tetrathionate is an analogue of or is structurally similar to thiosulfate. The strong absorption bands at 1113, 1003 and 641 cm^{-1} are assigned to

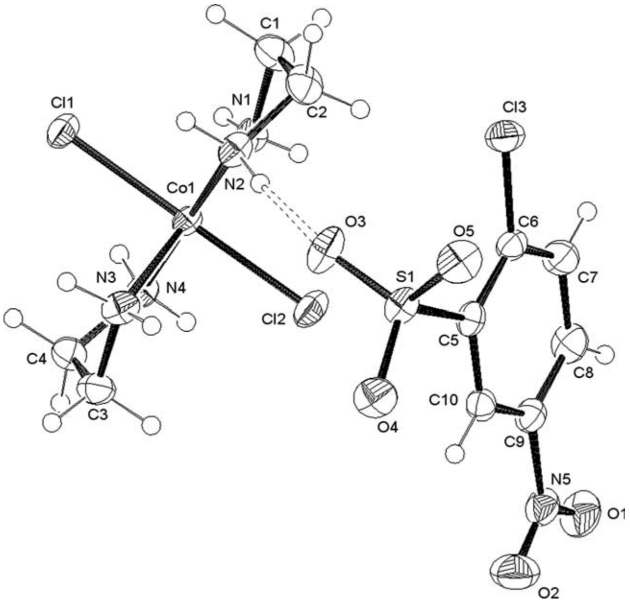


Fig. 1. ORTEP III view and atom numbering scheme for compound **I**. The displacement ellipsoids are drawn at 40% probability.

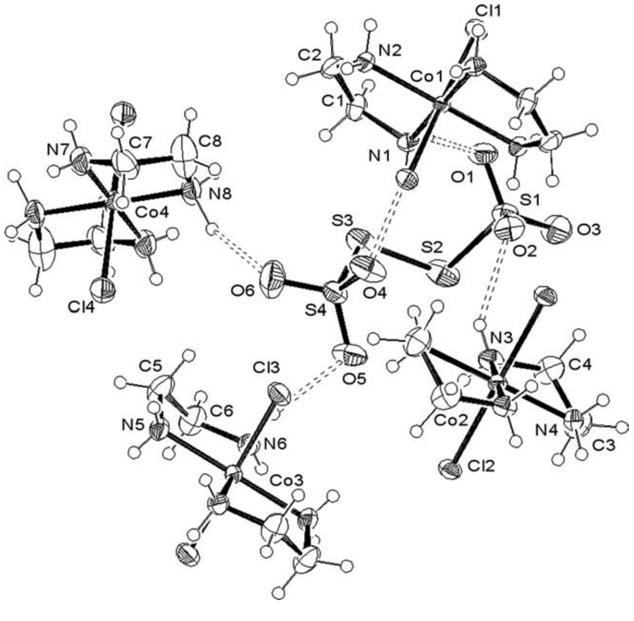
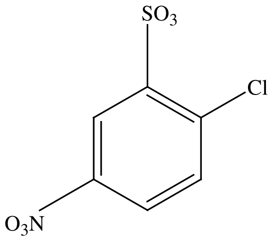


Fig. 2. ORTEP III view and atom numbering scheme for compound **II**. The displacement ellipsoids are drawn at 40% probability. For the sake of clarity, only two cations are shown.

ν_a (SO_3) ν_s ($–SO_3^-$) and $^1\nu_1$ (S–S), respectively, which are close to these frequencies in the sodium salt of the free $S_2O_3^{-2}$ ion (1120, 999 and 667) [35,36]. The lowering in stretching frequency of S–O bond in complex salt **II** may be due to N–H···O type of hydrogen bonding, which weakens S–O bond.

The electronic spectra of the newly synthesized complex salts have been recorded in H_2O. The solution state UV/visible absorption spectra of the title complex salts show absorption at 614, 454 and 247 nm in **I** and at 616, 454, 246 in **II**. These absorptions correspond to d–d transitions typical for octahedral low spin cobalt(III) [37]. These values are comparable with those of [*trans*-Co(en)$_2$Cl$_2$]SCN and [*trans*-Co(en)$_2$Cl$_2$]N$_3$ [20], which are 618, 302, 247 nm and 612, 302, 246, respectively. These transitions are from $^1A_{1g}$ ground state of cobalt(III) to singlet state $^1T_{1g}$ (low energy) and from $^1A_{1g}$ ground state to $^1T_{2g}$ (higher energy). In the complexes of the type CoA_4B_2 (cis or trans) the $^1T_{1g}$ state is split, the splitting [38] in trans isomer being more, thus justifying the three absorption peaks in the title complex salts.

NMR spectra of the newly synthesized complex salts are recorded in DMSO-d_6. The chemical shift values are expressed as δ value (ppm) downfield from tetramethylsilane as an internal standard. In ^{1} NMR, the signal at 5.30 ppm is attributed to nitrogen protons of ethylenediamine while CH_2 protons of ethylenediamine [39] group are observed at 2.86 ppm in **I**. The signals at 7.7, 8.2 and 8.6 in **I** are attributed to proton bonded to C-5, C-6 and C-2, respectively. The ^{13}C NMR spectrum shows the characteristic signal at 44.8 ppm for carbons [40] of ethylenediamine group in **I**. In the chloronitrobenzene sulphonate group signals at 123.0 ppm are ascribed for C-2, 124.0 for C-5, 132.1 ppm for C-4, 137.8 for C-6, 145.5 for C-1 and 146.3 for C-3 as shown in Scheme 1. In **II**, the signal at 5.22 ppm is attributed to nitrogen protons of ethylenediamine while CH_2 protons of ethylenediamine group are observed at



Scheme 1. Molecular structure of chloro,nitrobenzenesulphonate.

Table 3
Hydrogen bonding parameters (Å, °) for **I** and **II**

D–H···A	D–H	D···A	H···A	<D–H···A
I				
N2–H2A···O3	0.85(3)	3.016(2)	2.17(3)	172(3)
N1–H1A···O5^{i}	0.86(3)	2.869(2)	2.03(3)	167(2)
N4–H4A···O4^{i}	0.97(3)	3.053(2)	2.09(3)	171(2)
N4–H4B···O1^{ii}	0.85(3)	3.186(2)	2.57(3)	130(2)
N2–H2B···Cl1^{iii}	0.94(3)	3.387(2)	2.63(3)	138(2)
N3–H3A···Cl1^{iv}	0.85(3)	3.372(2)	2.75(3)	131(3)
II				
N13–H13A···O27	0.87(3)	3.060(3)	2.22(4)	162(3)
N24–H24A···O34	0.98(5)	3.165(4)	2.34(5)	141(4)
N16–H16A···Cl5^{v}	0.75(3)	3.384(2)	2.71(3)	150(3)
N14–H14A···O22^{vi}	0.82(4)	2.986(3)	2.20(3)	160(3)
N14–H14B···O19^{vi}	0.79(4)	3.058(4)	2.29(3)	163(3)
N13–H13B···O25^{vii}	0.82(3)	2.995(3)	2.20(3)	161(3)
N15–H15A···O20^{vii}	0.83(4)	3.057(3)	2.35(4)	144(3)
N23–H23A···Cl6^{viii}	0.72(5)	3.264(3)	2.55(5)	173(5)
N17–H17A···O22^{ix}	0.88(4)	2.968(4)	2.21(4)	144(3)
N17–H17B···Cl8^{xi}	0.83(3)	3.385(2)	2.63(3)	151(3)

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

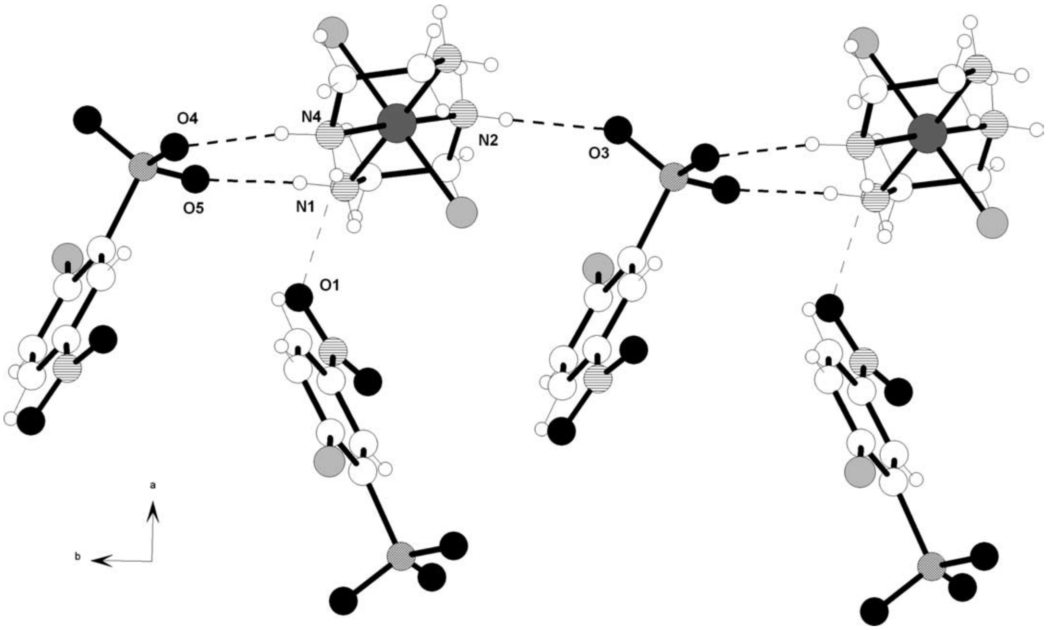
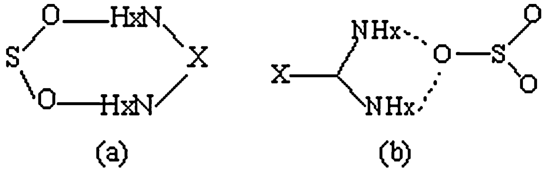


Fig. 3. Packing diagram of [*trans*-Co(en)$_2$Cl$_2$]C$_6$NO$_2$SO$_3$H$_3$Cl.



Scheme 2. Different bonding modes of sulphonate ion.

2.80 ppm. The ^{13}C NMR spectrum shows the characteristic signal at 44.8 ppm for carbons of ethylenediamine group in **I**.

3.4. Crystal structure

3.4.1. Coordination geometry and bonding

The X-ray crystal structures of the title complex salts have been unambiguously determined by single crystal X-ray crystallography. The complex salt **I** crystallizes in monoclinic space group $P2_1/c$ and **II** crystallizes in triclinic space group $P\bar{1}$. ORTEPIII views of title complex salt and numbering scheme employed are shown in Figs. 1 and 2.

The cobalt(III) cations in both structures are coordinated to two chloride and two ethylenediamine molecules in trans position. The geometry of the complexes is slightly distorted octahedral because of the bite of the chelating ethylenediamine ligands, for which N–Co–N angles are less than 90°. The counterion of the cobalt complex in **I** is 2-chloro,5-nitrobenzenesulfonate in 1:1 ratio, while the asymmetric unit of **II** is quite complicated, being formed by four Co complexes positioned on an inversion centre and one tetrathionate counterion in general position. The (C28–C33) moiety belonging to one ethylenediamine linked to Co1 is disordered over two almost equivalent positions (refined occupancies: 0.48 and 0.52). Co–N and Co–Cl distances of both compounds are in the range 1.945(2)–1.966(2) and 2.234(1)–2.259(1) Å, respectively, in agreement with the reported mean values [41] for this kind of bonds. The selected bond lengths and angles are given in Table 2. The tetrathionate anion in **II** has an 'elicoidal' conformation with a S–S–S–S torsion angle of −97.0(1)°. This conformation is conserved in all the structures retrieved from CSD and ICSD, where the same torsion angle ranges from 91 to 107°. We also examined the Crystal Structure Database, which does not list a single entry of X-ray structure of 2-chloro,5-nitrobenzenesulfonate salt and therefore this is the first X-ray structural report of a salt with this anion.

3.4.2. Packing

In both structures the different units interact with each other through intermolecular N–H···O and N–H···Cl hydrogen bonds (Table 3). The packing pattern of **I** is easy to describe by using the graph set approach [42], taking into account only the strongest hydrogen bonds. Anions and cations are linked by two N–H···O hydrogen bonds to form R_2^2 (8) rings, which, in turn, are connected in C_2^2 (8) chains running along the *b* direction by the N2–H···O3 hydrogen bond, as shown in Fig. 3. These chains are connected along *a* by N4–H···O1 longer contacts (see Table 3). The packing pattern of **II** is conversely quite complicated. Each tetrathionate anion links four Co complexes by not very strong N–H···O hydrogen bonds; these supramolecular moieties are connected by the N13 atom, which uses its hydrogens to form H-bonds with O25 and O27 belonging to different asymmetric units. The result is a complicated 3D H-bonding network. This packing pattern can be compared with the structure of a similar compound retrieved from CSD, i.e. bis(ethylenediamine)-ammonio-bromo-cobalt tetrathionate [30a]. Even in this case, the tetrathionate is linked to four Co-complexes cations by N–H···O hydrogen bond whose N···O distances are strictly comparable with those of Table 3, ranging from 2.95 to 3.04 Å. Out of the various types of structural motifs found by CSD survey [43], two types of structural motifs are observed in the title complex salt **I**. One of the simplest and most commonly

Table 4
A comparison of bond lengths and bond angles for cation and anion in **I** and **II**

Formula of the salt	Bond lengths				Bond angles			Ref.
	Co–N	Co–Cl	C–N	C–C	N–Co–N	Co–N–C	N–Co–Cl	
Cation								
[*trans*-Co(en)$_2$Cl$_2$]Cl	1.99	2.22	1.47	1.54	90	105	90	[47a]
[*trans*-Co(en)$_2$Cl$_2$]NO$_3$	1.99	2.26	1.46	1.59	85.6	109	–	[47c]
[*trans*-Co(en)$_2$Cl$_2$]ClO$_4$	1.95(3)	2.24(1)	1.48(6)	1.49(7)	86.2(2)	109.6(3)	89.9(1)	[47d]
[*trans*-Co(en)$_2$Cl$_2$]CoCl$_4$	1.92(2)	2.24(5)	–	–	90(7)	–	90	[47b]
[*trans*-Co(en$_2$)Cl$_2$][*trans*-Co(en)$_2$ (S$_2$O$_3$)$_2$]	1.95(17)	2.33(5)	1.48(3)	1.50(3)	85.7(7)	109.2(13)	89.9(5)	[11e]
[*trans*-Co(en)$_2$Cl$_2$]C6NO$_2$SO$_3$H$_3$Cl	1.94(2)	2.23(1)	1.48(3)	1.50(3)	85.8(1)	–	89.2(5)	This work
[*trans*-Co(en)$_2$Cl$_2$] $_2$S$_4$O$_6$	1.94(2)	2.21(1)	1.48(1)	1.51(4)	85.7(1)	–	90.5(7)	This work

Formula of the salt	S$_4$O$_6$					Ref.
	S–S	S–O	S–S–S	O–S–S	O–S–O	
Anion						
K[Co(tren)(NH$_3$)(SO$_4$)]S$_4$O$_6$	2.06(2)	1.43(4)	103.8(8)	106.7(2)	–	[30c]
[cis-Co(NH$_3$)Br]S$_4$O$_6$	2.06(2)	1.43(4)	103.4(4)	106.2(2)	114.0(3)	[30a]
Cu(C$_{20}$H$_1$6N$_4$)S$_4$O$_6$	2.12 (2)	1.45(5)	–	107.1(3)	114.0(3)	[30b]
Na$_2$ S$_4$O$_6$	2.11(1)	–	103.9(1)	–	–	[46]
[*trans*-Co(en)$_2$Cl$_2$]C$_6$NO$_2$SO$_3$H$_3$Cl	2.12(1)	1.44(3)	105.5(1)	107.3(1)	113.8(1)	Present work

occurring motifs formed between sulphonate oxygen atoms and N–H donor (ethylenediamine) is a bidentate motif (Scheme 2a) resulting in an eight membered hydrogen bonded ring R_2^2 (8). The other motif formed between sulphonate oxygen atoms and N–H donor (ethylenediamine) is monodentate resulting in a six membered hydrogen bonded ring R_2^1 (6) as shown in Scheme 2b.

The bond length values for the anion in **I** are S–O 1.46(7), N–O 1.22(7) Å. The corresponding values for 2-chlrorophenyl 3-nitrobenzenesulphonate [44] are 1.42(1) and 1.232(17). The S–O bond length in $[Sc(OH_2)(O_2NC_6H_4SO_3)_4(H_2O)_2]$ [45] is 1.40(8). Any pair of the neighbouring metal atoms along the *b*-axis are bridged by two sulfonato ions forming an infinite chain structure in this. The bonding parameters are comparable in this anion. A comparison of bond lengths and bond angles for the tetrathionate ion in the title complex salts with the previously reported salts of this anion in literature can be seen in Table 4 [46]. The bonding parameters of the cation present in the two title complex salts are comparable with those in the complex salts reported in literature having the same cation, which indicates that the presence of different anions affects the Co–N bond length in the cation considerably while all other bond length values remain unaffected as shown in Table 4 [47].

4. Conclusions

In conclusion, two new salts of composition [*trans*-$Co(en)_2Cl_2]C_6NO_2SO_3H_3Cl$ **I** and [*trans*-$Co(en)_2Cl_2]_2S_4O_6$ **II** have been synthesized and characterized. X-ray crystal structure determination of **I** and **II** has revealed the presence of discrete ions. The structure is stabilized by electrostatic forces of attraction and H-bonding interactions involving second sphere coordination. The present study shows that cationic cobaltammine [*trans*-$Co(en)_2Cl_2]^+$ present in [*trans*-$Co(en)_2Cl_2]Cl$ is a promising anion receptor for these anions in aqueous medium in contrast to other synthetic receptors, which are effective in non-aqueous solvents as it forms complex salts of definite composition. The solubility product of **II** is greater than **I** thereby indicating that the affinity of cation [*trans*-$Co(en)_2Cl_2]^+$ is more for 2-chloro,5-nitrobenzenesulfonate as compared to tetrathionate ion.

5. Supplementary data

Crystallographic data for the structural analysis of the title compound has been deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK, and are available free of charge from the Director on request quoting the deposition number CCDC 285721 for **I** and 285722 for **II**. (Fax: +44 1223 336033, email: deposit@ccdc.cam.ac.uk).

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