Second sphere coordination in anion binding: Synthesis, characterization and X-ray structure of *cis*-diazidobis(ethylenediamine)cobalt(III) mesitylenesulphonate hemihydrate

Raj Pal Sharma [a,*], Rajni Sharma [a], Ritu Bala [a], Kamal Nain Singh [a],
Loretta Pretto [b], Valeria Ferretti [b,**]

[a] *Department of Chemistry, Panjab University, Chandigarh-160014, India*
[b] *Centro di Strutturistica Diffrattometrica and Dipartimento di Chimica, University of Ferrara via L. Borsari 46, I-44100, Ferrara, Italy*

Abstract

cis-diazidobis(ethylenediamine)cobalt(III) mesitylenesulphonate hemihydrate, [*cis*-Co(en)$_2$(N$_3$)$_2$]C$_9$H$_{11}$SO$_3 \cdot$0.5H$_2$O was crystallized from a solution of *cis*-diazidobis(ethylenediamine) cobalt(III) nitrate and sodium mesitylenesulphonate in aqueous medium in 1:1 molar ratio. Elemental analysis, spectroscopic studies (IR, UV/visible, ^{1}H and ^{13}C NMR) and conductance studies were undertaken for characterizing the complex salt. The compound crystallizes in the triclinic space group $P-1$ with $a=7.15220(10)$, $b=14.5218(3)$, $c=20.6925(5)$, $V=2058.48(7)$, $Z=4$. X-ray structure determination revealed an ionic structure consisting of [*cis*-Co(en)$_2$(N$_3$)$_2$]$^+$ cation, mesitylenesulphonate anion and half water molecule. In the complex cation [*cis*-Co(en)$_2$(N$_3$)$_2$]$^+$, the cobalt(III) is bonded to six nitrogen atoms, originating from two ethylenediamines, and two azide groups showing an octahedral geometry around cobalt. The crystal lattice is stabilized by electrostatic forces of attraction and hydrogen bonding interactions predominantly N–H…O$^-$, suggesting that [*cis*-Co(en)$_2$(N$_3$)$_2$]$^+$ is a promising anion receptor for the mesitylenesulphonate ion. This is the first report of a sulphonate salt containing the present cationic cobaltammine.

1. Introduction

Anion coordination chemistry, the binding of anions by receptor molecules, has been recognized and developed as a new area of chemistry [1,2]. This is due to the crucial roles anions play in biological processes, medicine, catalysis and molecular assembly. The design and synthesis of smart molecules that are able to function as sensors of charged species is of immense interest [3–5]. Although cation receptors have been studied extensively, the design of anion receptors (binding agents) has only recently been investigated [6,7]. Because of their varied shapes and sizes [8], anions pose a greater challenge than cations. The capture of oxoanions in particular, is difficult because of their large ionic radii, high energy of solvation and lower Lewis basicities [9]. Such receptors could be valuable if they are capable of complexing or sensing the presence of these anions. Traditional design has relied on the use of hydrogen donors and cationic Lewis acid site-attracting anions. Although, several examples of second-sphere complexes with aquo [10] and ammine [11] coordination compounds have appeared in the literature, the second sphere interaction as a synthetic strategy has not been much exploited for the construction of extended or layered solid structures. Generation of extended solids by exploiting both primary and secondary sphere interactions in metal sulphonate complexes has been extensively studied by Shimizu and coworkers [12,13]. As these interactions, (i.e. second sphere interactions) are essentially inter-molecular in nature, we reasoned that if cations and anions are properly functionalised to incorporate hydrogen bonds, novel network

* Corresponding authors. Tel.: +91 172 2544433; fax: +91 172 2545074.
** Tel.: +39 0532 291132; fax: +39 0532 240709.
E-mail addresses: rpsharma@yahoo.co.in (R.P. Sharma), frt@unife.it (V. Ferretti).

architecture may ensue and stabilize the lattice. The question regarding the proper selection of cations and anions for this assembly must take into consideration the availability of properly oriented hydrogen bond donors and acceptors, i.e. complementarity. This approach was utilized by us for design and synthesis of bilayered structure of hexaamminecobalt(III) chloride dimethanesulphonate that is stabilized by NH…O$^-$ and NH…Cl$^-$ interactions. Single crystal X-ray structure determination revealed the formation of a planar 2-dimensional 'rosette or honeycomb structure' through a network of hydrogen bonds involving second sphere coordination [14].

Organosulphonates have longstanding industrial applications as surfactants, dyes, fuel and lubricant, detergents or antioxidants [15]. They have been studied as potential liquid crystalline [16] and non-linear optical materials [17,18] besides pharmaceutical salt preparation, [19] and therefore, the search for new and efficient anion receptors for sulphonate ion. Sulphonate anions are a relatively unexplored class of ligands because of the misconception that sulphonate group is a poor ligand, incapable of forming stable coordinate bond with the metal ions [20]. We have recently reported the synthesis, characterization and X-ray structure determination of thallium *meta*-nitrobenzenesulphonate [21] and two copper(II) naphthalene-2-sulphonates [22].

Although, cationic organic anion receptors have been extensively investigated [23] but cationic metal complexes have not received much attention [24]. The cationic cobaltammine, [*cis*-Co(en)$_2$(N$_3$)$_2$]$^+$ fulfills the criterion [24a] of an anion receptor, i.e. unit positive charge for electrostatic interaction, eight N–H hydrogen bond donor groups and a stable framework. We envisaged that the presence of eight N–H hydrogen bond donor groups on each positively charged cation [*cis*-Co(en)$_2$(N$_3$)$_2$]$^+$ will facilitate the interaction with properly oriented negatively charged oxygen of oxoanion and this may result in the formation of a donor acceptor complex involving second sphere coordination. In the solid state, with all probabilities, these two ions should form an intricate network of hydrogen bonds stabilizing the entire lattice. Understanding of such network interactions of judicially chosen cations and anions would be rewarding as it can provide means of constructing intricate and novel molecular entities based on second-sphere coordination. We report here the potential use of [*cis*-Co(en)$_2$(N$_3$)$_2$]$^+$ cation present in diazidobis(ethylenediamine)cobalt(III) nitrate as anion receptor for mesitylenesuphonate anion, i.e., synthesis, characterization and X-ray structure determination of *cis*-diazidobis (ethylenediamine)cobalt(III) mesitylenesulphonate, [*cis*-Co(en)$_2$-(N$_3$)$_2$]C$_9$H$_{11}$SO$_3$·0.5H$_2$O (racemic mixture) in continuation of our interest in cobalt(III) complexes [25]. Incidentally, this is the first crystal structure of a salt containing [*cis*-Co(en)$_2$(N$_3$)$_2$]$^+$ cation and a sulphonate anion. We have already reported the utility of this cation as anion receptor for fluoroanions [26] and picrate ion [27].

2. Experimental

Caution: Azide salts as well as their complexes should be handled with care due to their explosive nature.

2.1. Materials

Technical grade reagents were used throughout this work without any further purification. [*cis*-Co(en)$_2$(N$_3$)$_2$]NO$_3$ has been prepared according to literature method [28,29].

2.2. Instruments

Cobalt was determined by standard method [30] and C, H, N were estimated micro-analytically by automatic Perkin Elmer 2400 CHN elemental analyzer. IR spectrum was recorded as KBr pellets on PERKIN ELMER SPECTRUM RXFT-IR system. ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 by using BRUCKER AC 300 F (300 MHz) spectrophotometer with TMS as internal reference. UV/visible spectrum was recorded in H$_2$O using HITACHI 330 SPECTROMETER.

2.3. Synthesis of [cis-Co(en)$_2$(N$_3$)$_2$]C$_9$H$_{11}$SO$_3$

An aqueous solution of 1 g (0.003 mol.) [*cis*-Co(en)$_2$(N$_3$)$_2$] NO$_3$ in 100 ml water was taken and filtered. This was added to

Table 1
Crystal data and structure refinement parameters for [*cis*-Co(en)$_2$(N$_3$)$_2$] C$_9$H$_{11}$SO$_3$·0.5H$_2$O

Chemical formula	[Co(en)$_2$(N$_3$)$_2$]C$_9$H$_{11}$SO$_3$·0.5H$_2$O
M_r	471.44
Cell setting	Triclinic
Space group	P-1
a (Å)	7.15200(10)
b (Å)	14.5218(3)
c (Å)	20.6925(5)
α (°)	74.2130(7)
β (°)	84.7130(8)
γ (°)	87.0010(9)
V (°^{3})	2058.43(7)
Z	4
D_x(Mg m^{-3})	1.521
μ (Mo Kα) (mm^{-1})	0.975
Crystal form, colour and size (mm^3)	Prism, dark red 0.50×0.28×0.10
Absorption correction	Empirical (SORTAV)
θ range (°)	3.0–28.0
No. of measured, independent and observed reflections	21693, 9677,7352
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.052
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$, wR(F^2), Goodness of fit	0.044, 0.126, 1.000
No. of observed reflections/ No. of parameters	7352/677
Weighting scheme	$w = 1/(\sigma^2 (Fo^2) + (0.0791P)^2 + 0.0380P$, where $P = (Fo^2 + 2Fc^2)/3$