

Second sphere coordination in anion binding: Synthesis and spectroscopic characterisation of [*trans*-Co(en)₂Cl₂]X (X = SCN or N₃). Single crystal X-ray structure determination and packing of [*trans*-Co(en)₂Cl₂]N₃

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Abstract

In an effort to explore [*trans*-Co(en)₂Cl₂]⁺ as anion receptor for linear thiocyanate and azide ions, green coloured microcrystalline [*trans*-Co(en)₂Cl₂]SCN **I** and single crystals of [*trans*-Co(en)₂Cl₂]N₃ **II** have been obtained by slowly mixing the separately dissolved *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride with ammonium thiocyanate and sodium azide respectively in aqueous medium in 1:1 molar ratio. The newly synthesised complex salts were characterised on the basis of elemental analysis and spectroscopic techniques (IR, UV/vis, ¹H and ¹³C NMR). Single crystal X-ray structure determination of **II** revealed that it crystallizes in the triclinic space group *P* $\bar{1}$ with *a* = 6.293(1) Å, *b* = 6.696(1) Å, *c* = 7.116(1) Å, α = 94.02(1)°, β = 111.42(1)°, γ = 99.86(1)°, *V* = 272.13(7) Å³, *Z* = 1, *R* = 0.0183. Supramolecular hydrogen bonding networks between ionic groups: nitrogen atoms of azide group and NH groups of coordinated ethylenediamine molecules, i.e. N–H...N[−] interactions by second sphere coordination besides electrostatic forces of attraction have been observed which probably exist in case of thiocyanate also. This suggests that [*trans*-Co(en)₂Cl₂]⁺ is a promising anion receptor for the linear ions SCN[−] and N₃[−]. The solubility product measurements indicate that the affinity of cationic cobaltamine [*trans*-Co(en)₂Cl₂]⁺ is greater for azide ion than thiocyanate ion.

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1. Introduction

The coordination chemistry of anions [1] continues to attract increasing interest from the supramolecular chemistry community. This is due to 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. Due to their varied shapes and sizes [2] e.g. Cl[−], Br[−], I[−] (spherical), CO₃^{2−}, NO₃[−] (trigonal planar), PO₄^{3−}, SO₄^{2−} (tetrahedral), [FeCN₆]^{4−}, [CoCN₆]^{3−} (octahedral), DNA (double helix), N₃[−], SCN[−] (linear), anions pose a greater challenge than cations. One important class of monoanions is linear anions. The design and synthesis of receptors for linear mono-anions has not attracted much interest. Thiocyanate and

azide ions are two such linear mono-anions with a number of applications [3]. An important aspect of modern supramolecular chemistry [4] is the utilization of ‘hydrogen bonding’ in the development of receptors for the recognition of anions. Compared to the relatively simple design principles for cation receptors (electronic interaction and sizes), there are more factors that 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 [5] of any architecture, are the physical features of the units to be assembled and the means by which these items are to 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

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a high degree of complementarity with respect to intermolecular interactions.

Although, several examples of second-sphere complexes with aquo [6] and ammine [7] coordination compounds have appeared in the literature, the second sphere interaction as a synthetic strategy has not been exploited much for the construction of extended or layered solid structures. 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 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 $\text{NH}\cdots\text{O}^-$ and $\text{NH}\cdots\text{Cl}^-$ interactions. Single crystal X-ray structure determination revealed the formation of a planar two-dimensional 'rosette or honeycomb structure' through a network of hydrogen bonds involving second sphere coordination [8]. Although cationic organic anion receptors have been extensively investigated but cationic metal complexes have not received much attention [9,10] The cationic cobaltamine, $[\text{trans-Co}(\text{en})_2\text{Cl}_2]^+$ fulfills the criterion [10a] 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 $[\text{trans-Co}(\text{en})_2\text{Cl}_2]^+$ will facilitate the interaction with properly oriented negatively charged nitrogen of azide ion 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 judiciously chosen cations and anions would be rewarding as it can provide means of constructing intricate and novel molecular entities based on second-sphere coordination. In continuation of our interest in cobalt(III) complex salts [11], we have undertaken an extensive research programme to explore cationic cobaltamines $[\text{Co}(\text{en})_2\text{X}_2]^+$ ($\text{X} = \text{Cl}, \text{NO}_2$ or N_3) as anion receptors [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 potential use of $[\text{trans-Co}(\text{en})_2\text{Cl}_2]^+$ cation present in dichlorobis(ethylenediamine)cobalt(III) chloride as anion receptor for linear anions SCN^- and N_3^- . Recovery of these linear anions (thiocyanate and azide) is biologically and commercially important due to the fact that the metal salts of the former is used in primer mix for small arms cartridges, safety matches and dyeing. The azide and its salts are used in preparation of hydrozoic acid, lead azide etc. and also used as preservatives for laboratory agents, agriculture nematocides, herbicide and propellant for inflating automotive safety bags [3] although these are highly toxic may cause hypotension, hypothermia,

convulsions and severe headache. Therefore, the development of selective anion receptor (binding agent), which may find potential applications [13] and especially in polar solvents such as water is of particular interest. This may result in the formation of new and interesting salts. Although a few salts containing the cation $[\text{trans-Co}(\text{en})_2\text{Cl}_2]^+$ have been known for a long time, this is first such study regarding the exploitation of $[\text{trans-Co}(\text{en})_2\text{Cl}_2]^+$ as anion receptor. We have recently reported the synthesis, spectroscopic characterisation and crystal structure of $[\text{trans-Co}(\text{en})_2\text{Cl}_2]$ $[\text{trans-Co}(\text{en})_2\text{S}_2\text{O}_3]$ [12].

2. Experimental

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

2.1. Materials

Analytical grade reagents were used without any further purification. $[\text{trans-Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ has been prepared according to literature method [14].

2.2. Instruments

Cobalt was determined by standard method [15]. 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 D_2O 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 $[\text{trans-Co}(\text{en})_2\text{Cl}_2]\text{SCN}$ (I)

One gram (0.003 mol) of $[\text{trans-Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ was dissolved in 25 ml water. In another beaker 0.26 g (0.003 mol) of NH_4SCN was dissolved in 10 ml of water at room temperature. Both the solutions were mixed. The green microcrystalline $[\text{trans-Co}(\text{en})_2\text{Cl}_2]\text{SCN}$ appeared within half hour of mixing the two reactants, which was filtered and air-dried. (yield 80%). 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 **I** decomposes at 190 °C. The elemental analysis is consistent with the composition $[\text{trans-Co}(\text{en})_2\text{Cl}_2]\text{SCN}$. Found: (%) C, 19.7; H, 5.0; N, 22.9; Co, 19.1. Calculated C, 19.5; H, 5.2; N, 22.8; Co, 19.2. Solubility: 0.5 g/100 ml at 25 °C, $K_{\text{sp}} = 2 \times 10^{-4}$.

2.4. Synthesis of $[\text{trans-Co}(\text{en})_2\text{Cl}_2]\text{N}_3$ (II)

An aqueous solution of one gram (0.003 mol) of $[\text{cis-Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ in 25 ml water was taken and filtered. This was added to an equimolar quantity of (0.2289 g) of sodium azide dissolved in minimum amount of water. The green crystals of $[\text{trans-Co}(\text{en})_2\text{Cl}_2]\text{N}_3$ appeared within half hour of mixing

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