

Second sphere coordination complexes via hydrogen bonding: Synthesis, spectroscopic characterisation of $[trans-Co(en)_2Cl_2]CdX_4$ ($X = Br$ or I) and single crystal X-ray structure determination of $[trans-Co(en)_2Cl_2]CdBr_4$

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Abstract

In an effort to explore $[trans-Co(en)_2Cl_2]^+$ as anion receptor for tetrabromocadmiate and tetraiodocadmiate ion, green coloured single crystals of $[trans-Co(en)_2Cl_2]CdBr_4$ **I** and $[trans-Co(en)_2Cl_2]CdI_4$ **II** have been obtained by slowly mixing the separately dissolved *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride with potassium tetrabromocadmiate and tetraiodocadmiate in aqueous medium in 2:1 molar ratio. The newly synthesized complex salt was characterized on the basis of elemental analysis and spectroscopic techniques (IR, UV/visible, ¹H and ¹³C NMR). Single crystal X-ray structure determination of $[trans-Co(en)_2Cl_2]_2CdBr_4$ revealed that it crystallizes in the orthorhombic space group *Pbca* with $a = 18.6201(10)$, $b = 12.0872(6)$, $c = 24.0877(12)$ Å, $V = 5421.3(5)$ Å³, $Z = 8$, $R = 0.0727$. Supramolecular hydrogen bonding networks between ionic groups: bromide ions of tetrabromocadmiate group and NH groups of coordinated ethylenediamine molecules, i.e. N–H···Br[−] 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 tetrabromocadmiate.

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1. Introduction

Halocadmates(II) have received a great deal of attention from both theoretical and experimental point of view for their peculiar properties (related to their polymorphic behaviour), impurity, electronic configurations and lattice locations, which are the key problems in semiconductor physics [1–3]. Besides supramolecular [4] and bioinorganic studies [5] cadmium complexes also play an important role in luminescence research [6]. Complex cadmium(II) halide salts are known with cadmium to halide proportions of 1:3, 1:4, 1:5 and 1:6 [7]. It became apparent from literature that the structure of the cations and the number of hydrogen bonds are important factors to determine the shape of cadmium(II) halide complex

anions. The shapes of the complex anions are quite variable: isolated tetrahedral [8,9], complex chain structures [10–12] and two-dimensional layered structures [13]. The size, shape and charge of the cation plays a determinant role in stabilizing the anion, for example, $CuCl_4^{2-}$ (distorted tetrahedral) is precipitated by R_4N^+ , $CuCl_4^{2-}$ (square planar) is precipitated by $[Pt(NH_3)_4]^{2+}$, $CuCl_5^{3-}$ (trigonal bipyramidal) is precipitated by $[Cr(NH_3)_6]^{3+}$ (octahedral), $CuCl_6^{4-}$ (octahedral) is precipitated by biguanidinium(2+) ion.

Therefore, 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. 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 complementarity with respect to intermolecular interactions. As these interactions, (i.e. second sphere interactions) are essentially inter-molecular in nature, we reasoned that if cations and anions are properly

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functionalised to incorporate hydrogen bonds, novel network architecture may ensue and stabilize the lattice. 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 [14]. Although cationic organic anion receptors have been extensively investigated but cationic metal complexes have not received much attention [15]. A number of salts containing the cation, $[\text{trans-Co}(\text{en})_2\text{Cl}_2]^+$ have been known for a long time but its potential as anion receptor has not been explored much. Synthetic receptor for anion should have following characteristic features: (i) a positively charged component for effective electrostatic interactions, (ii) hydrogen bond donor groups and (iii) a suitable framework onto which these structural components can be assembled. The cationic cobaltamine, $[\text{trans-Co}(\text{en})_2\text{Cl}_2]^+$ fulfills the criterion [16] of an anion receptor, i.e. unit positive charge for electrostatic interaction, eight N–H hydrogen bond donor groups and a fairly 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. 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 [17] in continuation of our interest in cobalt(III) complex salts [18]. 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 tetrabromocadmate and tetraiodocadmate ions. We have recently reported the synthesis, spectroscopic characterisation of $[\text{trans-Co}(\text{en})_2\text{Cl}_2]\text{X}$ ($\text{X}=\text{SCN}$ or N_3) and single crystal X-ray structure determination of $[\text{trans-Co}(\text{en})_2\text{Cl}_2]\text{N}_3$ [19].

2. Experimental

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 [20].

2.2. Instruments

Cobalt was determined by standard method [21]. 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 $[\text{trans-Co}(\text{en})_2\text{Cl}_2]_2\text{CdBr}_4$ (I)

One gram (0.003 mol) of $[\text{trans-Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ was dissolved in 30 ml water. In another beaker 0.89 g (0.0017 mol) of potassium tetrabromocadmate(II) was dissolved in 20 ml of water at room temperature. Both the solutions were mixed. The green crystals of $[\text{trans-Co}(\text{en})_2\text{Cl}_2]_2\text{CdBr}_4$ appeared within 30 min 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 as well as DMSO and stable in air and light but insoluble in acetone. The newly formed complex salt **I** decomposes at 210°C . The elemental analysis is consistent with the composition $[\text{trans-Co}(\text{en})_2\text{Cl}_2]_2\text{CdBr}_4$. Found: (%) C, 10.3; H, 3.4; N, 12.0; Co, 12.6. Calculated C, 10.4; H, 3.3; N, 12.1; Co, 18.9. Solubility: 1 g/100 ml at 25°C , $K_{\text{sp}}=1\times 10^{-4}$.

2.4. Synthesis of $[\text{trans-Co}(\text{en})_2\text{Cl}_2]_2\text{CdI}_4$ (II)

An aqueous solution of 1 g (0.003 mol) of $[\text{trans-Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ in 30 ml water was taken and filtered. This was added to 1.23 g (0.0017 mol) of potassium tetraiodocadmate dissolved in minimum amount of water. The green crystals of $[\text{trans-Co}(\text{en})_2\text{Cl}_2]_2\text{CdI}_4$ appeared within 30 min 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 **II** decomposes at 180°C . The elemental analysis is consistent with the composition $[\text{trans-Co}(\text{en})_2(\text{Cl})_2]_2\text{CdBr}_4$. Found: (%) C, 8.5; H, 2.8; N, 10.0; Co, 10.5. Calculated C, 8.7; H, 2.8; N, 9.8; Co, 10.3. Solubility: 0.4 g/100 ml at 25°C , $K_{\text{sp}}=1\times 10^{-5}$.

2.5. X-ray crystallography

Intensity data for a crystal with dimensions $0.42\times 0.33\times 0.18\text{ mm}^3$ were measured at room temperature on a Bruker Smart Apex CCD diffractometer fitted with graphite monochromatized $\text{Mo K}\alpha$, $\lambda=0.71073\text{ \AA}$. The structure was solved using the SHELX-97 system of program [22] and refined by a full-matrix least squares procedure based on F^2 . Crystallographic data is given in Table 1. Selected interatomic parameters are given in Table 2 and the numbering scheme employed is shown in Fig. 1 drawn using Xtal_GX [23].

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