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Journal Name

ARTICLE

Racemic and Conglomerate 1-(4-Haloaryl)ethylammonium Tetrachlorocobaltate Salts: Formation of Helical Structures

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Racemic ligand rac-1-(4-fluorophenyl)ethylamine (*rac*-fpea) reacts with cobalt(II) chloride in the presence of hydrochloric acid forming an A_2CoCl_4 type salt, [*rac*-fpeaH]$_2$[CoCl$_4$] (**1**). The salt crystallizes in the centro-symmetric $P\bar{1}$ space group. In contrast, under identical conditions the chloro derivative *rac*-1-(4-chlorophenyl)ethylamine (*rac*-cpea) yields a conglomerate of A_3CoCl_4Cl type salts, namely, [(*R*)-cpeaH]$_3$[CoCl$_4$]Cl (**2R**) and [(*S*)-cpeaH]$_3$[CoCl$_4$]Cl (**2S**), which crystallize in the chiral space group $P2_1$. Single crystal X-ray diffraction data for the crystals reveal nearly identical unit cells but different chirality. The two enantiomers crystallize out together and do not form separate colonies and exhibit similar morphology and color. In order to ascertain the assignment of chiral structures to the conglomerate crystals, the two salts are also independently synthesized from enantiomerically pure R-(4-chlorophenyl)ethylamine. We propose that the weak Cl···N interaction found in the structures may be involved in the conglomerate formation from *rac*-cpea. In addition, the analogous salt from *R*-1-(phenyl)ethylamine, [(*R*)-peaH]$_3$[CoCl$_4$]Cl (**3R**), is also synthesized and characterized. The packing of the chiral cations and [CoCl$_4$]$^{2-}$ anions in the crystals of **1**, **2R**, **2S** and **3R** are characterized by helices formed through inter-ionic H-bonding interactions. Thermogravimetric data measured in the range of 25 – 650 °C under a nitrogen atmosphere reveal that the compounds are stable up to T < 170 °C.

Introduction

The chirality of α-amino acids which act as the basic building blocks of polypeptides, DNA and proteins imparthelicity to the structures of the biological systems.[1] The naturally occurring helical structures have served as inspiration toward the synthesis of useful materials in diverse areas such as molecular recognition,[2,3] nonlinear optical materials research,[4] chiral catalysis[5-8] and magneto-chiral induction.[9,11] Recently, a great number of metal-organic compounds with helical networks have been synthesized.[1,12] As could be expected the use of chiral building blocks invariably leads to chiral helices.[13-15] Surprisingly, some syntheses using racemic building blocks also lead to the formation conglomerate crystals containing either of the right and left handed helices.[16] Of course, most of the syntheses with racemic ligands form the expected meso products which contain both the right- and left-handed helices in the asymmetric units of their crystals which are often related by a crystallographic inversion center.[17-21]

As part of our investigation of magneto-chiral materials that contain tetrahalotransitionmetallate anions ([MCl$_4$]$^{2-}$), we are interested in the polymeric networks produced from the interaction of chiral and racemic alkylamines with transition metal chlorides under acidic conditions.[22-24] In this work, we report such reactions of racemic 1-(4-fluorophenyl)- and racemic and enantiopure 1-(4-chlorophenyl)ethylamines with cobalt(II) chloride in the presence of stoichiometric excess of hydrochloric acid. The products form extended one-dimensional helical networks through H-bonding interaction between the ions as will be described below.

Results and discussion

The tetrachlorocobaltate(II) salt of rac-1-(4-fluorophenyl)ethylamine (*rac*-fpea) and its chloro-analogue (*rac*-cpea) were synthesized as described in Experimental and as shown in eq 1. In a typical synthesis, the chiral amines and $CoCl_2$ are taken in acidified ethanol and refluxed for 3 h. Subsequently, the solvent is removed and the products are isolated as dark blue residues. Recrystallization of the residues from ethanol by slow evaporation in the fridge results in the formation of dark blue crystals. The product from the reaction with *rac*-fpea is characterized as [(*rac*-fpeaH))]$_2$[CoCl$_4$] (**1**) on the basis of elemental analysis and single crystal X-ray diffraction data (ESI Fig. S2). The dark blue crystals are uniformly plate-like and belong to the centrosymmetric triclinic space group $P\bar{1}$. The asymmetric unit of **1** consists of two 1-(4-fluorophenyl)ethylammonium cations and one $CoCl_4^{2-}$ anion revealing that the product is an A_2CoCl_4 type salt. The

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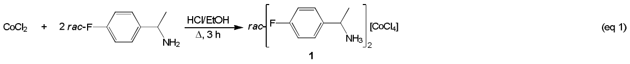
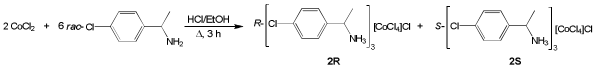
Electronic Supplementary Information (ESI) available: [Characterization data, Figure of hydrogen bonding N-H…X interactions. Crystallographic data table and cif files of **1**,**2*R***, **2*S*** and **3*R***. Crystal parameters, ORTEP diagrams of **1**,**2*R***, **2*S*** and **3*R***, H-bonding data]. See DOI: 10.1039/x0xx00000x geometry of the cobalt(II) center in the anion is pseudo tetrahedral and the anion is unexceptional with typical Co-Cl bond distances and Cl-Co-Cl bond angles.[25] The important feature of the structure is the presence of both left- and right-handed helices formed through weak H-bonding interaction between the cobaltate anions and the ethylammonium cations. The M and P helices are present successively in the crystals as required by the centrosymmetric space group. The presence of the two type of helices reveal the retention of the racemic nature of the *rac*-1-(4-fluorophenyl)ethylamine used in the synthesis.

The synthesis of the analogous tetrachlorocobaltate salts with the closely related *rac*-1-(4-chlorophenyl)ethylamine under identical conditions results in the formation of conglomerate crystals (eq 2). Two types of crystals could not be distinguished from their color or crystal habit. Therefore, we are unable to separate the two enantiomers. However, single crystal X-ray diffraction data (ESI Fig. S3-S4) measured for four different crystals unambiguously demonstrate that the two products are the *R* and *S* optical isomers of $[(\text{cpeaH}))]_3[\text{CoCl}_4]\text{Cl}$. Both enantiomers, namely, $[(R\text{-cpeaH}))]_3[\text{CoCl}_4]\text{Cl}$ and $[(S\text{-cpeaH}))]_3[\text{CoCl}_4]\text{Cl}$ are dark blue plate-like rectangular prisms. The asymmetric units of both crystals contain three 1-(4-chlorophenyl)ethylammonium cations, one $[\text{CoCl}_4]^{2-}$ anion one Cl^- anion on general positions suggesting $\text{A}_3\text{CoCl}_4\text{Cl}$ formulation for the salts.



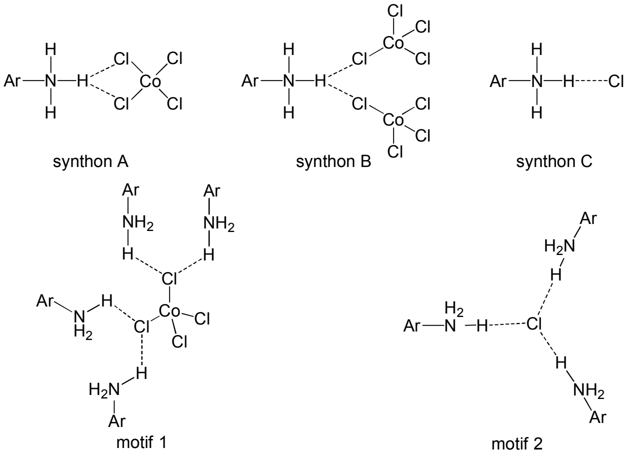
(eq 1)



(eq 2)

The cations and anions in these crystals are also weakly H-bonded forming helices as seen in **1**. Significantly, in contrast to **1**, both crystals belong to the same chiral monoclinic space group *P2₁* with either left- or right-handed helices. The two crystals exhibit similar structural features and differ only in the handedness of the helices. The absolute configuration of the ethylammonium cations are assigned *R* and *S* by the refinement of the Flack parameter,[25] 0.011(7) and 0.004(14) for **2R** and **2S**, respectively. In order to ascertain the chirality of **2R** and **2S**, we have also synthesized both of these compounds using enantiopure *R*-cpea and *S*-cpea, respectively. The products were recrystallized and their structural data, IR spectra and thermal decomposition data measured. The crystal structures are identical to those measured for conglomerate crystals isolated from the synthesis using *rac*-cpea. The IR and TG-DTA data are also identical (see later) demonstrating the conglomerate formation during the reaction of *rac*-cpea with cobalt(II) chloride under acidic conditions.

The conglomerate formation observed during the reaction with *rac*-cpea and racemate retention with *rac*-fpea under identical reaction conditions illustrate the involvement of some poorly understood fine forces in the synthetic and crystallization steps. Although there is no explanation for the spontaneous chiral resolution of some compounds during their synthesis or recrystallization, clearly salts appear to be more prone to chiral resolution than neutral organic molecules.[26] In addition, crystals of coordination complexes which feature a variety of interionic strong and weak interactions and those that form helical chains exhibit even more frequent chiral resolution. As Han and Hong pointed out,[27] the synthesis of homochiral helical polymers such as the coordination polymers obtained from the complexation of ZnCl_2 and HgBr_2 with the achiral 2,5-diphenyl-3,4-di(3-pyridyl)cyclopenta-2,4-dien-1-one,[28] are rare. However, a number of such spontaneous chiral resolution are reported in the literature recently.[29,30] These syntheses also make use of achiral starting materials but produce mechanically isolable colonies of enantiomers. In some cases, achiral ligands undergo chiral resolution upon complexation forming a conglomerate of enantiomers similar to the current synthesis of **2R** and **2S** from *rac*-cpea.[31] Interestingly, most of these polymers exhibit the two associated and ubiquitous natural phenomena of helicity and chirality. Although H-bonding and other interionic and intra-strand interactions are speculate to cause the chiral resolution,[28-31] no satisfactory explanation is available for the preference of the chiral helical structure in nature. In this context, the conglomerate formation of the constituent *R*- and *S*-cpea amines in *rac*-cpea as $[(R\text{-cpeaH}))]_3[\text{CoCl}_4]\text{Cl}$ (**2R**) and $[(S\text{-cpeaH}))]_3[\text{CoCl}_4]\text{Cl}$ (**2S**) crystals deserves particular attention. A comparison of the structure of **1** with those of **2R** and **2S**, suggests the presence of 3 synthons as shown in scheme 1.[32]



Scheme1. Synthons and connectivity motifs present in **1**, **2R** and **2S**.

The helices in compound **1** are constituted through synthon A (ESI Fig. S6). The strong H-bonding interaction between two of the chloride ligands of the CoCl_4^{2-} anion and one of the benzylammonium $-\text{NH}_3$ hydrogen atoms (synthon A) results in a 1-D linear helical chain arrangement of the cations and anions as shown in Fig. 1.

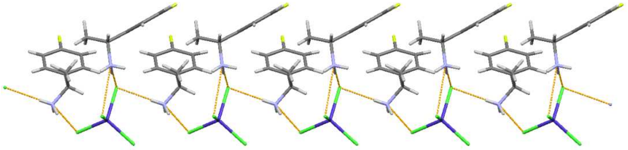


Fig. 1. Strong H-bonding interaction between tetrachlorocobaltate anions and 1-(-4-fluorophenyl)ethylammonium cations **1**.

The structures of **2R** and **2S** feature H-bonding interactions in the form of synthons B and C (Scheme 1). The free chloride anion present in these crystals is involved in classical H-bonds with all of the three 1-(4-chlorophenyl)ethylammonium cations present in the asymmetric unit. The H-bonding interactions through synthons B and C employ two motifs (scheme 1) to form sheets of the ions as shown in Fig. 2. The $[CoCl_4]^{2-}$ and Cl^- anions form a 2-D layer structure with two independent circuits A and B with the 4-chloro-α-phenylethylammonium cations as shown in Fig. 2 and Fig. S6. The H-bonding interactions by the protonated chiral amines lead to helicity, as shown in Fig. 3. In general, crystals with structural helicity are found to be racemic or in low enantiomeric excess when achiral or racemic building blocks are used, since both the left- and right-handed helical structures are produced with equal probability as in the structure of **1**. The *anti*-parallel and *racemic* left- and right-handed helices contain both enantiomers on the opposite side of the crystallographic screw axis cancelling out the overall polarity. In the case of the synthesis with *rac*-cpea, additional H-bonding interactions involving Cl^- anions appear to effect resolution of the protonated amines.

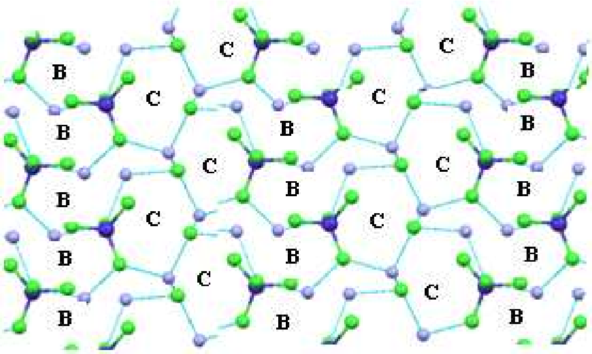


Fig. 2. 2D sheet arrangement adopted by **2R** and **2S** with two independent circuits B and C and propagated by N–H¨Cl–Co and N–H¨Cl hydrogen bonds.

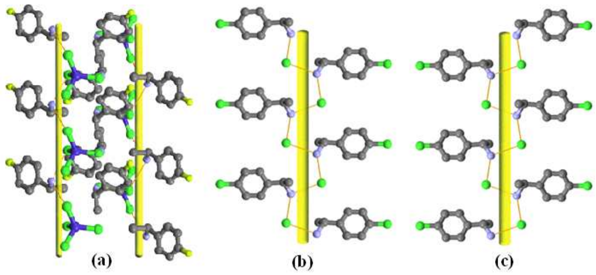


Fig. 3. Helical chains present in **1** (a), **2R** (b) and **2S** (c). Hydrogen atoms and $CoCl_4^{2-}$ are omitted for clarity.

The H-bonded chains are extended along the *b*-axis with a helical pitch of 7.554 Å for **2R** and 7.598 Å for **2S**, while chains are present along the *a*-axis with a helical pitch of 7.178 Å in the structure of **1**. In the helices of **2R** and **2S**, two 1-(4-chlorophenyl)ethylammonium cations and two Cl^- anions constitute one turn. The groove of the helical chain is intercalated by one $CoCl_4^{2-}$ and one 1-(4-chlorophenyl)ethylammonium cation units belonging to two adjacent helices generated by a 2-fold screw symmetry operation along the *b*-axis (Fig. 4). This mode of packing stabilizes the helical structure and is possible only in the presence of a free chloride ion, which results in the formation of conglomerates.

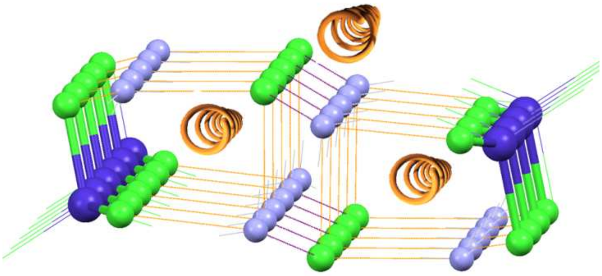


Fig. 4 Adjacent helices present along the *b*-axis in **2R** and **3R**.

To examine the generality of the formation of helical structures, we subjected enantiopure *R*-1-(phenyl)ethylamine (*R*-pea) to the self-assembly process with $CoCl_2$, and obtained the analogous A_3CoCl_4Cl salt $[R\text{-peaH}]_3[CoCl_4]Cl$ (**3R**). Single crystal X-ray diffraction data confirms the presence of helical chains as in the structures of **2R** and **2S** (ESI, Fig. S5). The H-bonded helical chains in **3R** are also oriented along the *b*-axis with a helical pitch of 7.503 Å**.**

The robustness of the structural features in all of the products is examined by TG-DTA data. The TG-DTA plots are similar and reveal a two-step decomposition process. The first mass loss occurs at T > 170 °C revealing the strength of the helical chains. The mass losses correspond to the loss of the amines and HCl in the first step and that of HClin the second step leaving $CoCl_2$ at the completion of the thermal decomposition process (eqs 3-6).

$$\underset{\mathbf{1}}{[rac\text{-fpeaH}]_2[\mathrm{CoCl_4}]} \xrightarrow[\substack{\text{- 2fpea - HCl} \\ \text{- 65.6\% (calc)}}]{\substack{\text{443 - 551 K} \\ \text{- 65.6\% (obsd)}}} \mathrm{HCoCl_3} \xrightarrow[\substack{\text{- HCl} \\ \text{- 7.5\% (calc)}}]{\substack{\text{552 - 590 K} \\ \text{- 7.6\% (obsd)}}} \mathrm{CoCl_2} \qquad \text{(eq 3)}$$

$$\underset{\mathbf{2R}}{[R\text{-cpeaH}]_3[\mathrm{CoCl_4}]\mathrm{Cl}} \xrightarrow[\substack{\text{- 3cpea - 2HCl} \\ \text{- 71.5\% (calc)}}]{\substack{\text{441 - 540 K} \\ \text{- 71.5\% (obsd)}}} \mathrm{HCoCl_3} \xrightarrow[\substack{\text{- HCl} \\ \text{- 5.1\% (calc)}}]{\substack{\text{541 - 590 K} \\ \text{- 5.1\% (obsd)}}} \mathrm{CoCl_2} \qquad \text{(eq 4)}$$

$$\underset{\mathbf{2S}}{[S\text{-cpeaH}]_3[\mathrm{CoCl_4}]\mathrm{Cl}} \xrightarrow[\substack{\text{- 3cpea - 2HCl} \\ \text{- 71.5\% (calc)}}]{\substack{\text{441 - 540 K} \\ \text{- 71.5\% (obsd)}}} \mathrm{HCoCl_3} \xrightarrow[\substack{\text{- HCl} \\ \text{- 5.1\% (calc)}}]{\substack{\text{541 - 590 K} \\ \text{- 5.1\% (obsd)}}} \mathrm{CoCl_2} \qquad \text{(eq 5)}$$

$$\underset{\mathbf{3R}}{[R\text{-peaH}]_3[\mathrm{CoCl_4}]\mathrm{Cl}} \xrightarrow[\substack{\text{- 3pea - 2HCl} \\ \text{- 72.5\% (calc)}}]{\substack{\text{443 - 555 K} \\ \text{- 69.9\% (obsd)}}} \mathrm{HCoCl_3} \xrightarrow[\substack{\text{- HCl} \\ \text{- 6.1\% (calc)}}]{\substack{\text{556 - 589 K} \\ \text{- 6.9\% (obsd)}}} \mathrm{CoCl_2} \qquad \text{(eq 6)}$$

Conclusions

The tetrachlorocobaltate salts of two related racemic amines exhibit very different chiral resolution behaviour. Whereas *rac*-1-(4-fluorophenyl)ethylamine retains its racemic nature yielding an A_2CoCl_4 salt, *rac*-1-(4-chlorophenyl)ethylamine forms a conglomerate of A_3CoCl_4Cl salts. Though the two enantiomers can be distinguished by single crystal X-ray diffraction data, their separation could not be achieved either chemically or mechanically. The two enantiomers possess identical crystal morphology, color and solubility. The chiral resolution is confirmed by a comparison of crystallographic, IR and thermal decomposition data measured for the two independently synthesized salts of the enantiopure *R*- and *S*-1-(4-chlorophenyl)ethylamine. The differential behaviour of the two *rac* amines illustrates the complexity associated with the spontaneous resolution or conglomerate formation of chiral products. The crystallographic and packing properties of the isolated tetrachlorocobaltates reveal the presence of three types of synthons. An extra pair of 1-(4-chlorophenyl)ethylammonium cation and chloride anion is present in the resolved cobaltate synthesis. Although, serendipitous in present case, the usefulness of the chloride-centered synthons in the self-assembly-driven resolution of racemic compounds may be worth exploring.

Experimental

Materials and methods

Elemental analyses were performed using a Perkin Elmer Series II 2400 elemental analyzer. The IR spectra were recorded in the 4000-400 cm^{-1} region using KBr pellets and a Perkin Elmer RX1 Spectrophotometer. Thermogravimetric analyses (TG-DTA) were performed for single crystal samples using an SII TG/DTA 6300 EXSTAR Analyser under N_2 atmosphere at the heating rate of 10°C/min.

$CoCl_2$, *rac*-1-(4-fluorophenyl)ethylamine, *rac*-1-(4-chlorophenyl)ethylamine, *R*-1-(4-chlorophenyl)ethylamine, *S*-1-(4-chlorophenyl)ethylamine and *R*-1-(phenyl)ethylamine are obtained from commercial sources.

[(*rac*-fpeaH))]$_2$[$CoCl_4$] (**1**).

Conc. HCl (2 mL) was added to abs. ethanol (10 mL) with stirring. To the acidified ethanolic solution (10 mL) were added 1-(*rac*-4-fluorophenyl)ethylamine (0.028 g, 0.2 mmol) and $CoCl_2$ (0.013 g, 0.1 mmol). The mixture was heated to reflux for 3 h. The resulting dark-blue coloured solution was rotary-evaporated to dryness and the residue washed with ether and dried. The residue was re-dissolved in 2 mL of abs. ethanol, filtered and the clear dark blue solution was allowed to evaporate at low temperature in the fridge. Dark blue plate-like crystals of **1** formed were filtered and dried. Yield: 0.026 g (54)%.

[(*R*-cpeaH))]$_3$[$CoCl_4$]Cl (**2R**) and [(*S*-cpeaH))]$_3$[$CoCl_4$]Cl (**2S**).

Conc. HCl (2 mL) was added to abs. ethanol (10 mL) with stirring. To the acidified ethanolic solution (10 mL) were added 1-(*rac*-4-chorophenyl)ethylamine (0.031 g, 0.2mmol) and $CoCl_2$ (0.013 g, 0.1 mmol). The mixture was heated to reflux for 3 h. The resulting dark-blue coloured solution was rotary-evaporated to dryness and the residue washed with ether and dried. The residue was re-dissolved in 2 mL of abs. ethanol, filtered and the clear dark blue solution was allowed to evaporate at low temperature in the fridge. A conglomerate of dark blue plate-like crystals of **2R** and **2S** formed were filtered and dried. Yield: 0.025 g (53%).

[(*R*-cpeaH))]$_3$[$CoCl_4$]Cl (**2R**) from enantiopure *R*-1-(4-chorophenyl)ethylamine. The procedure described above with 1-(*rac*-4-chorophenyl)ethylamine was followed.

[(*S*-cpeaH))]$_3$[$CoCl_4$]Cl (**2S**) from enantiopure 1-(*S*-4-chorophenyl)ethylamine. The procedure described above with 1-(*rac*-4-chorophenyl)ethylamine was followed.

[(*R*-peaH))]$_2$[$CoCl_4$] (**3R**) from enantiopure 1-(*R*-phenyl)ethylamine. The procedure described above with 1-(*rac*-4-chorophenyl)ethylamine was followed. The dark blue crystals formed were uniformly plate-like. Yield: 0.026 g (55%).

Crystallography

Single-crystal data of compounds were collected on a Bruker Smart 1000 CCD Diffractometer, with Mo Kα radiation. All empirical absorption corrections were applied by using the SADABS program.[33] The structures were solved using direct methods, which yielded the positions of all non-H atoms. These were refined first isotropically and then anisotropically. All of the H atoms of the ligands were placed in calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL software program.[34] The crystallographic data for **1**, **2R**, **2S** and **3R** structure refinement parameters are listed in Table S1. CCDC No.916616, 916614, 916613 and 916615 contains the crystallographic data for the compounds **2R**, **2S**, **1**and **3R** respectively. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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