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Is the unexpected behaviour of the resolved $K_3[Cr^{III}(C_2O_4)_3]$ in aqueous solution responsible for the formation of pure chiral solid phase of a two-dimensional (2D) $[Mn^{II}Cr^{III}(C_2O_4)_3\ NEt(n\text{-}Pr)(n\text{-}Bu)(n\text{-}C_5H_{11})]$ network?

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Racemic and resolved $[Cr^{III}(C_2O_4)_3]K_3$ dissolved in water were investigated by IR spectroscopy. Compared to the racemic compound, the spectrum of the resolved one exhibits additional peaks, which have a complex temporal evolution. These peaks are attributed to water molecules coordinated to the metal ion and tentatively related to the formation of a pure chiral solid phase of two-dimensional (2D) oxalate-based Mn–Cr networks starting from partially resolved $[Cr^{III}(C_2O_4)_3]^{3-}$.

The chemistry of two-dimensional (2D) bimetallic oxalate-based networks is very well documented.[1] We studied the synthesis, structure and physical properties of 2D bimetallic networks obtained in their optically active forms.[2] We have prepared various $[M^{II}M^{III}(C_2O_4)_3cat]$ networks (M^{II} and M^{III} are transition metal ions and cat is a mono-cation) in the optically active forms using resolved (Δ) or (Λ) $[M^{III}(C_2O_4)_3]^{3-}$ (M^{III} = Co, Cr) anionic bricks as chiral inductors.

These networks are composed of honeycomb anionic layers with cations in the inter-lamelar spaces. In a given anionic layer, configurations of the adjacent chiral centres alternate $[\Delta^*M^{II}\Lambda^*M^{III}(ox)_3]^-$. In an achiral structure,[1(*n*)] two adjacent layers present opposite configurations. In contrast, in a chiral structure, all the anionic layers have the same configuration.[3,4] As exemplified for $[MnFe(C_2O_4)_3N(n\text{-}C_5H_{11})_4]$,[4] chiral structures can be obtained starting from racemic reagents. They result from a spontaneous resolution occurring during the self-assembly process. Nevertheless, a rational design of optically active 2D networks deserves the use of a chiral inductor, *e.g.*, resolved $[M^{III}(C_2O_4)_3]^{3-}$ (M^{III} = Co, Cr).[2]

Recently, using a racemic mixture of $[NEt(n\text{-}Pr)(n\text{-}Bu)(n\text{-}C_5H_{11})]^+$ chiral ammoniun in the presence of Mn^{2+} we have shown[3] that starting from the racemic *rac*-$[Cr^{III}(C_2O_4)_3]^{3-}$ in a water/methanol solution leads to an achiral 2D network. The crystal structure obtained belongs to the achiral $R3c$ space group. This means that the self-assembly process does not occur with a spontaneous resolution. Starting from the resolved Δ- or Λ-$[Cr^{III}(C_2O_4)_3]^{3-}$, we have obtained optically active crystalline powders having a chiral $P6_3$ space group. Such results confirm those obtained previously with the achiral $[N(n\text{-}Bu)_4]^+$ template cation.[5]

Surprisingly, in both cases, the purity of the $P6_3$ crystalline phase obtained from the resolved Δ- or Λ-$[Cr^{III}(C_2O_4)_3]^{3-}$ anionic bricks is independent of the enantiomeric purity of the starting anionic material. According to the fact that the racemic anionic bricks lead to a pure $R3c$ achiral 2D solid phase, we expected a mixture of the $R3c$ and $P6_3$ phases for the 2D networks from partially resolved anionic bricks.

We do exclude the achiral Mn^{2+} cation, as well as the achiral or chiral racemic ammonium (cat) template, as the origin of this phenomenon. Consequently, the anionic $[Cr^{III}(C_2O_4)_3]^{3-}$ brick seems to be responsible for this intriguing feature. At this stage, the following question is addressed: ‘Is a structural difference between the racemic and the partially resolved $[Cr^{III}(C_2O_4)_3]K_3$ in aqueous solution able to drive the self-assembly process *via* a unique chiral arrangement?’

rac-$[Cr^{III}(C_2O_4)_3]K_3$ crystallises in the achiral $P2_1/c$ space group as a true racemate.[6] The IR[†] and Raman spectra of this compound show spectral changes between the racemate and the resolved species due to different organisations and, consequently, to different symmetries in the solid state.[7] The synthesis of our 2D networks was performed in a mixed water/methanol solution, $[Cr^{III}(C_2O_4)_3]K_3$ being soluble in water. The partially resolved Λ-$[Cr^{III}(C_2O_4)_3]K_3$ {$[\alpha]_D^{20}$ = 1200° (c = 0.02, H_2O)} was obtained by the usual resolution procedure by means of $[Ni(phen)_3]^{2+}$ as the resolving reagent.[8]

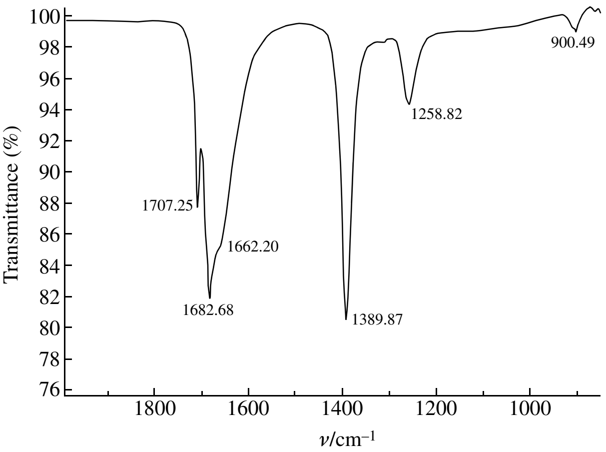

Figure 1 IR spectrum (transmittance) in the region 680–2000 cm⁻¹ for *rac*-$[Cr^{III}(C_2O_4)_3]K_3$ in water (0.12 mol dm⁻³).

Then, we examined the IR spectra of *rac*-$[Cr^{III}(C_2O_4)_3]K_3$ and Λ-$[Cr^{III}(C_2O_4)_3]K_3$ in water at a concentration of 0.12 mol dm⁻³ (60 mg cm⁻³), which was also used in the synthesis of the 2D networks.

In the region 850–1800 cm⁻¹, the spectrum of the *rac*-$[Cr^{III}(C_2O_4)_3]K_3$ in water is very close to that obtained for the solid phase (KBr pellet) (*): ν(C=O) at 1707, 1683 with a shoulder at 1662 cm⁻¹ (*vs* 1714, 1687, 1665, 1644 cm⁻¹); ν(C–O) at 1390 and 1259 cm⁻¹ (*vs* 1392 and 1260 cm⁻¹) and ν(C=C) at 900 cm⁻¹ (*vs* 898 cm⁻¹) (see Figure 1).

For the Λ-$[Cr^{III}(C_2O_4)_3]K_3$ enantiomer, the same picture is observed immediately after the preparation of the IR sample. Then, three additional intense peaks appear at 1099, 1049 and 986 cm⁻¹ and grow following a complex kinetic process

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[†] The FTIR spectra were recorded on a Magna-IR 860 FT-IR spectrometer (Nicolet Instrument Corp. Madison,WI) equipped with a standard DTGS detector and a germanium on cesium iodide (Ge/CsI) beam splitter at room temperature. Each spectrum was obtained by collecting 100 Fourier-transformed double-side interferograms, at a spectral resolution of 4 cm⁻¹. The spectra in H_2O were obtained by means of the Attenuated Total Reflectance technique using a 45° zinc selenide (ZnSe) trough-shaped plate filled with 2.5 ml of each solution under study. The OMNIC internal routines software was used to correct the baseline and to determine peak positions.

HPLC grade water as an IR solvent was purchased from ACROS and used as received.

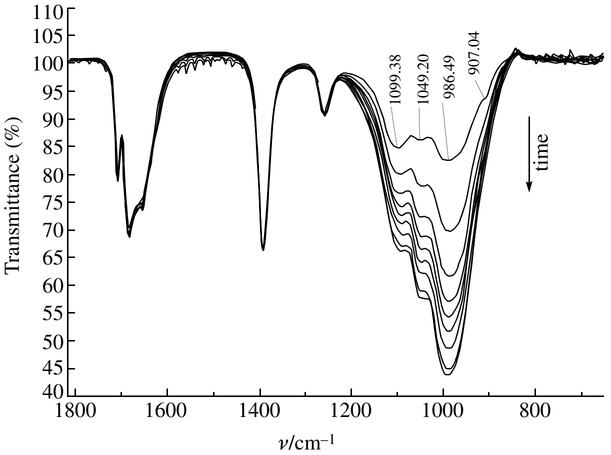

Figure 2 IR spectrum (transmittance) in the region 680–1350 cm^{-1} for Λ-[Cr^{III}(C$_2$O$_4$)$_3$]K$_3$ in water (0.12 mol dm^{-3}).

(Figure 2). Intensity of these peaks reaches a maximum after 15 min and decreases very slowly. After several days, only the peak at 1099 cm^{-1} remained with a lowered intensity.

According to their wavenumber, broadness and intensity, these extra peaks could be attributed to co-ordinated H_2O molecules. Indeed, a specific aquation happens when the resolved Λ-[Cr^{III}(C$_2$O$_4$)$_3$]K$_3$ is sampled but not with the racemic mixture. We note, as it was demonstrated by different techniques,[9] that the racemisation process of optically active tris(oxalato)chromate in water occurs *via* an aquation process beginning by the dissociation and the solvation of the charged species. The half-life time of such a racemisation process depends on the used solvent, as well as the counter-cation or on the presence of other salts, in the solution. It was determined to 56 min at 35 °C for [Cr^{III}(C$_2$O$_4$)$_3$]$^{3-}$ in a water/ethanol (70:30) mixture.[10]

Taking into consideration that the racemisation is an equilibrium between the (Δ) and (Λ) enantiomeric forms of [Cr^{III}(C$_2$O$_4$)$_3$]K$_3$, one can *a priori* expect the same behaviour of the racemic and resolved species. Our results do not support this proposal.

The key point of the problem seems to be the resolution procedure of the tris(oxalato)chromate itself for which the separation of each isomer is achieved by selective precipitation of the homochiral K[Δ-Ni(phen)$_3$][Δ-Cr(ox)$_3$] or K[Λ-Ni(phen)$_3$]-[Λ-Cr(ox)$_3$]. This partial resolution is concomitant to the precipitation of the other diastereomers K[Δ-Ni(phen)$_3$][Λ-Cr(ox)$_3$] or K[Λ-Ni(phen)$_3$][Δ-Cr(ox)$_3$]. The replacement of [Ni(phen)$_3$]$^{2+}$ by 2K$^+$ leads to an enriched mixture of one enantiomer over the other, without the presence of a true racemate regardless of the enantio-purity of the major isomer obtained by the resolution process. Thus, the kinetic process highlighted by means of the IR technique for the resolved compound is a specific aquation preliminary to the racemization process itself.

Since the formation of the 2D networks is faster than the aquation process, it is obvious that these networks are formed from a mixture of enriched enantiomeric [Cr^{III}(C$_2$O$_4$)$_3$]$^{3-}$ bricks reacting independently and leading to a mixture of chiral *P*6$_3$ solid phases enriched in one enantiomer according to the reactions

$$\Lambda\text{-}[\mathrm{Cr^{III}(C_2O_4)_3}]^{3-} + \mathrm{Mn^{2+}} + \mathrm{cat^+} = [\Delta\text{-}\mathrm{Mn^{II}}\Lambda\text{-}\mathrm{Cr^{III}(C_2O_4)_3cat}]\ \text{major};$$

$$\Delta\text{-}[\mathrm{Cr^{III}(C_2O_4)_3}]^{3-} + \mathrm{Mn^{2+}} + \mathrm{cat^+} = [\Lambda\text{-}\mathrm{Mn^{II}}\Delta\text{-}\mathrm{Cr^{III}(C_2O_4)_3cat}]\ \text{minor}.$$

We are aware that the results and interpretations discussed in this paper require additional experiments to validate our hypothesis. Nevertheless, we would like to present these preliminary results as a contribution to the discussion concerning the enantioselective self-assembly process leading from elemental bricks to supramolecular chiral materials.

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