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# Preferential Precipitation of $\Delta$-$[Co(en)_3]_2(d\text{-}C_4H_4O_6)_3$ by Alcohol Addition to the $[Co(en)_3]^{3+}$-$d$-$C_4H_4O_6^{2-}$ Aqueous Systems

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**Synopsis.** Alcohol addition to the aqueous $[Co(en)_3]^{3+}$—$d$-tart systems causes the preferential precipitation of $\Delta$-$[Co(en)_3]_2(d\text{-tart})_3$. The yield lies in between 54—55% under experimental conditions employed.

Tris(ethylenediamine)cobalt(III) ($[Co(en)_3]^{3+}$) ion is the prototype of many tris-chelated cobalt complexes. The optical activity and the interaction with $d$-$C_4H_4O_6^{2-}$ ($d$-tart) ions of $[Co(en)_3]^{3+}$ have attracted much interest of many workers.[1-6] The fact that the $\Lambda$-form of $[Co(en)_3]^{3+}$ can easily be precipitated by $d$-tart ions while the $\Delta$-form can not has long been used as the method of resolution[7] of $[Co(en)_3]^{3+}$ by way of $\Lambda$-$[Co(en)_3]X\cdot(d\text{-tart})$ ($X=Cl^-$, $Br^-$). Thus, the specific interaction, as found[8,9] for the system $\Lambda$-$[Co(en)_3]^{3+}$—$PO_4^{3-}$, between $\Lambda$-$[Co(en)_3]^{3+}$ and $d$-tart ions may be supposed operative in such resolution processes.

It is reported here that the alcohol addition to the aqueous $[Co(en)_3]^{3+}$—$d$-tart systems causes the precipitation of $[Co(en)_3]_2$ ($d$-tart)$_3$ and that the dominant diastereoisomer is $\Delta$-$[Co(en)_3]_2(d\text{-tart})_3$. This result is somewhat contrary to the expectation from the above-mentioned method of resolution.

## Experimental

Complexes used in this work are prepared after the literature methods.[10,11] Sixty-eight grams of $[Co(en)_3]Cl_3.3H_2O$ and 172 g of $KNa(d\text{-}C_4H_4O_6)$ are dissolved in water to a volume of 1500 ml. To every 100 ml of the solution is added the varying amount of alcohol. The identity of the precipitated complex has been confirmed by chemical analysis. Found: C, 25.69; H, 6.91; N, 15.01%. Calcd for $[Co(C_2H_8N_2)_3]_2(d\text{-}C_4H_4O_6)_3\cdot 11(12)H_2O$: C, 25.72(25.31) H, 7.37(7.43); N, 15.00(14.76)%. The precipitate redissolved in water is passed through an anion exchanger (Dowex-1 X8) to convert the tartrate to the chloride. The optical rotation has been measured on a Yanaco OR-50D automatic digital polarimeter and the concentration of the complex is determined spectrophotometrically. The CD spectra are recorded on a JASCO Model ORD/UV-5 spectrometer with a CD attachment. Similar procedure has been applied to tris(ethylenediamine)cobalt(III) bromide and acetate.

## Results

The results are summarized in Fig. 1, which shows the variation of the amount of $\Delta$-$(-)_{589}$-$[Co(en)_3]_2$ ($d$-tart)$_3$ precipitated against the volume of added alcohol. It is clear that more precipitation of $\Delta$-diastereoisomer than the $\Lambda$-isomer is induced by the alcohol addition to the aqueous $[Co(en)_3]^{3+}$—$d$-tart systems(see, Fig. 2). Tris(ethylenediamine)cobalt(III) acetate behaves in a similar manner to the corresponding chloride and bromide and the result for the acetate has been deleted. The best attainable yield of the $\Delta$-form is low and lies in between 54—55%. The above results contrast, in two points, well with the case of the usual method for resolution of $[Co(en)_3]^{3+}$;[7] first, $[Co(en)_3]_2(d\text{-tart})_3$ is precipitated while in the latter case $[Co(en)_3]X\cdot d$-tart precipitates; second, $\Delta$-$[Co(en)_3]_2(d\text{-tart})_3$ predominates, though slightly, while in the latter $\Lambda$-$[Co(en_3]X\cdot d$-tart is dominant.

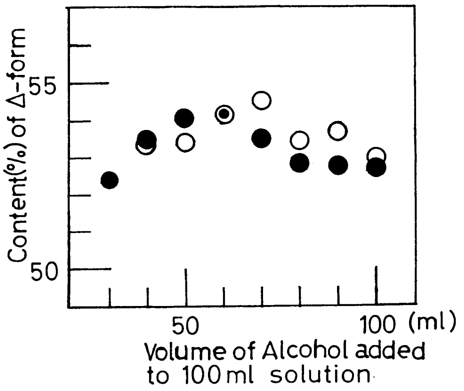

Fig. 1. The variation of the fraction of $\Delta$-$(-)_{589}$-$[Co(en)_3]_2(d\text{-tart})_3$ precipitated against the volume of added alcohol. Open and closed circles refer to chloride and bromide starting materials, respectively.

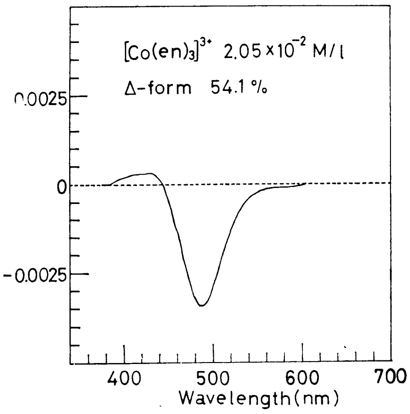

Fig. 2. The CD spectrum obtained when 60 ml alcohol is added to the 100 ml chloride solution.

Concentration by evaporation of the solution containing $[Co(en)_3]X_3$($X=Cl^-$, $Br^-$) and $d$-tart ions yields $\Lambda$-$(+)_{589}$-$[Co(en)_3]X\cdot d$-tart, which is consistent with the conventional procedure for resolution. Of the two diastereoisomers $\Delta$-$(-)_{589}$-$[Co(en)_3]_2(d\text{-tart})_3$ was observed to be the first to precipitate also in aqueous solution, because the reaction of $[Co(en)_3]X_3$($X=Cl^-$, $Br^-$) with $Ag_2(d\text{-tart})$ precipitates first the $\Delta$-diastereoisomer when evaporated. Alcohol is responsible, therefore, for the formation of $[Co(en)_3]_2(d\text{-tart})_3$ and the preferential precipitation of the $\Delta$-diastereoisomer occurs both in pure and alcoholic water.

The problem remains to be settled why alcohol addition causes the precipitation of the form $[Co(en)_3]_2(d\text{-tart})_3$ rather than $[Co(en)_3]X\cdot d\text{-tart}$. More interesting is why *d*-tart ions prefer $\Delta$-$[Co(en)_3]^{3+}$ in the case of $[Co(en)_3]_2(d\text{-tart})_3$ while $\Lambda$-$[Co(en)_3]^{3+}$ in $[Co(en)_3]X\cdot d\text{-tart}$. The association constant between $\Delta$- and $\Lambda$-$[Co(en)_3]^{3+}$ and *d*-tart ions may shed some light on these problems. The work along this direction is in progress.

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