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OPTICAL RESOLUTION OF COBALT(III) COMPLEXES *via* CYCLODEXTRIN INCLUSION COMPOUNDS

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Tris(chelate)cobalt(III) complexes with a long alkyl or bromoalkyl chain, $[Co(en)_2(NH_2CH_2CH_2SR)]^{3+}$ (R=$(CH_2)_nBr$ and $(CH_2)_nCH_3$), were partially resolved by stereoselective inclusion of the free side-chain into α- or β-cyclodextrin(CDX). α- and β-CDX preferentially include the Δ- and Λ-complexes, respectively.

Optical resolution of chiral compounds *via* diastereomeric inclusion complexes of cyclodextrin(CDX) was first explored by Cramer and Dietsche.1) The procedure has successfully been applied to the resolution of organic compounds such as alkyl alkylphosfinates,2) sulfoxides,3) and O-alkyl alkylsulfinates.4) However, no example has been known for metal complexes. Here we report the first application to optical resolution of cobalt(III) complexes.

Racemic cobalt(III) complexes $[Co(en)_2(NH_2CH_2CH_2SR)]X_3$ (R=$(CH_2)_nBr$ and $(CH_2)_nCH_3$; X=Cl and/or Br) were obtained by the reaction of *rac*-$[Co(en)_2(NH_2CH_2CH_2S)](ClO_4)_2$ and appropriate bromoalkanes.5) Optically active complexes were prepared by starting from Δ- or Λ-$[Co(en)_2(NH_2CH_2CH_2S)](ClO_4)_2$ ($\Delta\varepsilon_{522}=\pm1.32$). Since all the cobalt(III) complexes are soluble in water, our procedure for selective inclusion is quite different from the standard Benschop's procedure,2) in which 5-6 molar excess racemic compound was mixed with CDX in the presence of a small amount of water.

An equimolar mixture of cobalt(III) complex and CDX was dissolved in as small amount of water as possible. The solution was kept at room temperature for several days until the inclusion compound appeared, which was filtered off, dried, and analysed. Trituration of the compounds containing β-CDX with methylene chloride-water(1/1, v/v) released the partially resolved cobalt(III) complexes into the liquid phase. The inclusion compounds of α-CDX were decomposed by the column chromatography.

Optical purities and absolute configurations of the resolved cobalt(III)

Table 1. Stereoselective inclusion of $[Co(en)_2(NH_2CH_2CH_2SR)]X_3$ in CDX

complex			α-CDX			β-CDX		
	R	X	optical purity (%)	absolute configuration[a)]	molar ratio of complex and CDX[b)]	optical purity (%)	absolute configuration[a)]	molar ratio of complex and CDX[b)]
a	$(CH_2)_{12}Br$	Cl	0	—	1:2			
b	$(CH_2)_{10}Br$	Cl	61	Δ	1:2	2.0	Λ	1:1
c	$(CH_2)_8Br$	Cl	9.2	Δ	1:1.3	0.3	Λ	1:0.12
d	$(CH_2)_{10}Br$	Br	30	Δ	1:1.5	1.5	Λ	c)
e	$(CH_2)_8Br$	Br	12	Δ	1:0.88	3.3	Λ	d)
f	$(CH_2)_{10}CO_2H$	Br[e)]	12	Δ	1:2			
g	$(CH_2)_{11}CH_3$	Br	20	Δ	1:2	0.8	Λ	1:1.33
h	$(CH_2)_9CH_3$	Br	6.4	Δ	1:0.7	2.9	Λ	1:1
i	$(CH_2)_7CH_3$	Br	53	Δ	1:2			

a) From reference 5. b) Based on elemental analyses. c) The precipitate contains no β-CDX. d) Coprecipitated with an excess of β-CDX. e) The composition of this complex agrees with $[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_{10}CO_2H\}]Br_3 \cdot [Co(en)_2\{NH_2(CH_2)_2S(CH_2)_{10}CO_2\}]Br_2$.

complexes are collected in Table 1. The data are for those after the first inclusion procedure. Optical purities increased by repeating the inclusion process or by fractional crystallization of the solid. Inclusion of the cobalt(III) complexes except a into α-CDX is stereoselective. The complexes with Δ-configuration are preferentially included into α-CDX. The best resolution was achieved in the case of $R=(CH_2)_{10}Br$ and X=Cl (b), corresponding to 61% of optical purity. The molar ratios of complexes a, b, or c and α-CDX in the isolated inclusion compounds are very similar to those for fatty acids;[6)] the same plateau of ratio 2 was indicated for C_{10}-, C_{11}-, and C_{12}-acids. However, this ratio deviates depending on the kinds of substituent groups and counter ions.

On the other hand, inclusion into β-CDX is less stereoselective. The best value of optical purity is only 3.3%. This fact means that α-CDX which has the narrower cavity than β-CDX is more effective for the stereoselective inclusion of the present cobalt(III) complexes. Interestingly, β-CDX included the cobalt(III) complexes with opposite chirality and the inclusion compounds showed the different compositions as compared with the corresponding α-CDX compounds.

References

1) F. Cramer and W. Dietsche, Chem. Ber., 92, 378 (1959). 2) H. P. Benschop and G. R. Van den Berg, Chem. Commun., 1970, 1431. 3) M. Mikołajczyk, J. Drabowicz, and F. Cramer, Chem. Commun., 1971, 317. 4) M. Mikołajczyk and J. Drabowicz, Tetrahedron Lett., 1972, 2379. 5) K. Yamanari and Y. Shimura, Bull. Chem. Soc. Jpn., 53, 3605 (1980). 6) H. Schlenk and D. M. Sand, J. Am. Chem. Soc., 83, 2312 (1961).

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