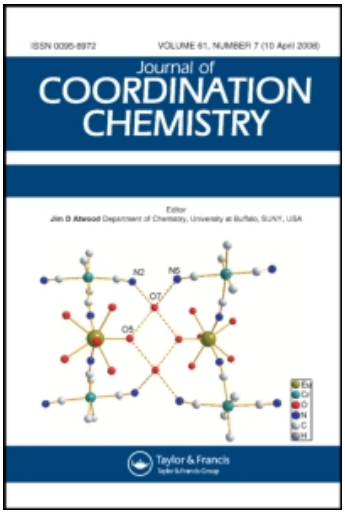

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COMPLETE CHROMATOGRAPHIC RESOLUTION OF AXIALLY CHIRAL β-DIKETONATE COMPLEXES ON CELLULOFINE C-200 [1]

Yoshiharu Nakano[a]; Takeshi Kawaguchi[a]; Yuzo Yoshikawa[b]
[a] Faculty of Science, Ibaraki University, Bunkyo, Mito, Japan [b] Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama, Japan

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COMPLETE CHROMATOGRAPHIC RESOLUTION OF AXIALLY CHIRAL β-DIKETONATE COMPLEXES ON CELLULOFINE C-200 [1]

YOSHIHARU NAKANO[a*], TAKESHI KAWAGUCHI[a] and YUZO YOSHIKAWA[b]

[a]*Faculty of Science, Ibaraki University, Bunkyo 2-1-1, Mito, 310 Japan;* b*Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama, 700 Japan.*

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New chromatography on Cellulofine C-200 (modified polysaccharide ion exchanger) completely resolved the atropisomers reported previously [2]. The present technique needs no optically active eluting agents, differing from conventional chromatography on SP-Sephadex. The chromatographed atropisomers, axially chiral β-diketonate cobalt(III)-tren complexes, are listed in the table in the text.

Keywords: axial chirality, cellulofine C-200, β-diketonate cobalt(III)-tren complexes

INTRODUCTION

Various methods have been developed to separate a racemic mixture into a pair of enantiomers. Although diastereomeric fractional crystallizations are popular, every substrate needs a proper and particular resolving agent for each racemate. Since various convenient approaches of liquid chromatographic system and optically active packing materials have been developed, liquid chromatographic methods were popular in the 1970's for various racemates. Optical resolution by means of liquid chromatography can now be accomplished with various conditions (packing materials and eluents, *etc.*) [3].

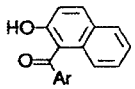
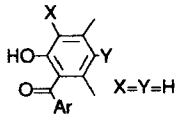
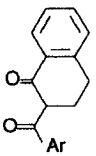
Yoshikawa and Yamasaki developed this method for a wide range of cobalt(III) complexes using optically active tartrate solutions as eluting agents

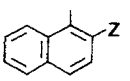
*Author for correspondence.

and Sephadex ion exchangers as packing materials [4a]. They also established a recycling chromatographic system which might be the most efficient of the open column systems [4b].

Utilizing an open column of SP-Sephadex, we also succeeded in resolving the optical isomers of a series of cobalt(III)-tren complexes whose chirality arises from restricted rotation of the substituent and whose syntheses have been reported previously [2].

In the present manuscript, we report that the modified polysaccharide (Cellulofine C-200) is very useful to resolve [1-(2-methylnaphth-1-yl)-nphthoato][tris(2-aminoethyl)amine]cobalt(III) complexes, $[Co(bidentate)(tren)]^{2+}$ even without optically active eluents. The other cobalt(III)-tren complexes of analogous β-diketone type ligands (listed in the Table) were also resolved in this manner.

complex		f-A	f-B	s-A	s-B
1a		(+)	(-)	(-)	(+)
1b		(-)	(+)	(-)	(+)
2a	 X=Y=H	(+)	(-)	(-)	(+)
2b		(-)	(+)	(-)	(+)
2'a	X=Br,Y=H	(-)	(+)	(-)	(+)
2"a	X=Y=Br	(+)	(-)	(-)	(+)
2"'a	$X=NO_2$ Y=H	(+)	(-)	(-)	(+)
3a				(-)	(+)
3b		(-)	(+)	(-)	(+)

Ar = 

a Z=methyl

b Z=methoxy

EXPERIMENTAL

Cellulofine C-200(Seikagaku Kogyo Co. Ltd.) and SP-Sephadex C-25(Pharmacia) were used as packing materials and 0.3-0.5 M NaCl as eluents. Open columns of three sizes were used according to the desired extent of separation of cobalt complexes (diameter × length in cm; 5.5 × 95 cm (A column), 3 × 150 cm (B column), and 2 × 210 cm (C column)). The pair of possible geometrical isomers was separated first with A or B column of SP-Sephadex C-25 using 0.3-0.5 M NaCl as eluents except for 3a in which case only one geometrical isomer was isolated. The two isomers eluted fast and slow were named as f- and s-isomers respectively. We determined the structure of the f-isomer of 2a by X-ray diffraction and found that the 2-methylnaphthoyl group was *cis* to the tertiary nitrogen atom of tren [5]. The optical absorbances of the two bands were measured and used to determine the yield of the isomeric complexes. The f-

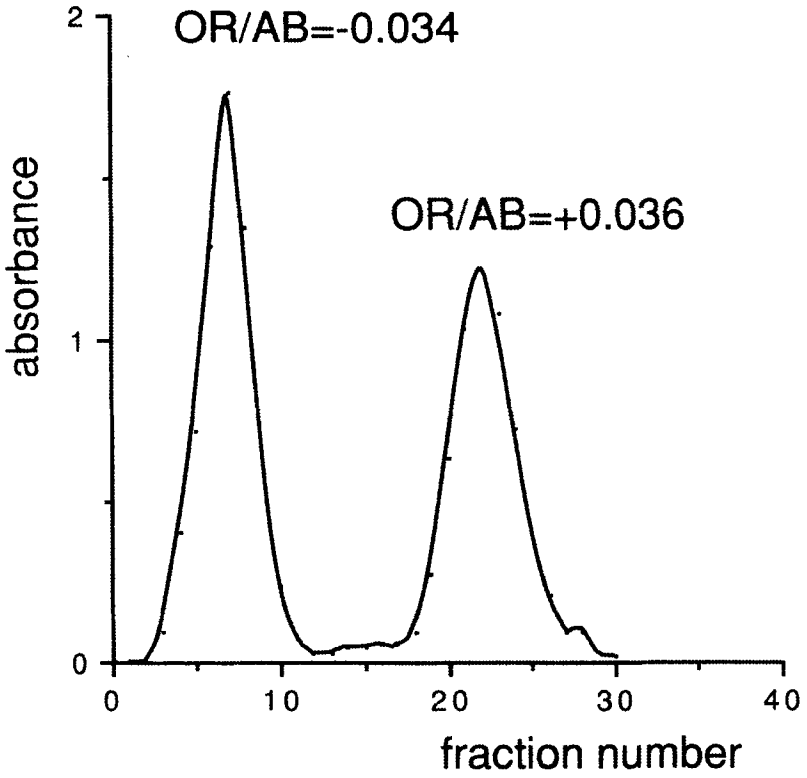


FIGURE 1 Elution curve of **1a**-s using an open column (1.2 × 150 cm) of Cellulofine C-200.

isomer or s-isomer were again charged on the B or C column of Cellulofine C-200.

RESULTS AND DISCUSSION

Cellulofine has better permeability than Sephadex resin. Elution of the cobalt(III) complexes (listed in the Table) through a column of Cellulofine C-200 required less than one third of the time required for SP-Sephadex C-25. Results of the chromatographic resolution are also summarized in the Table. All the s-isomers were resolved completely into two bands with the B column. For all of the s-isomers, (−)-enantiomers were eluted fast and (+)-enantiomers slowly. As an example, Figure 1 exhibits the elution curve of **1a**-s. The agreement of the absolute values, (optical rotation)/absorbance (OR/AB), at the top of two eluted

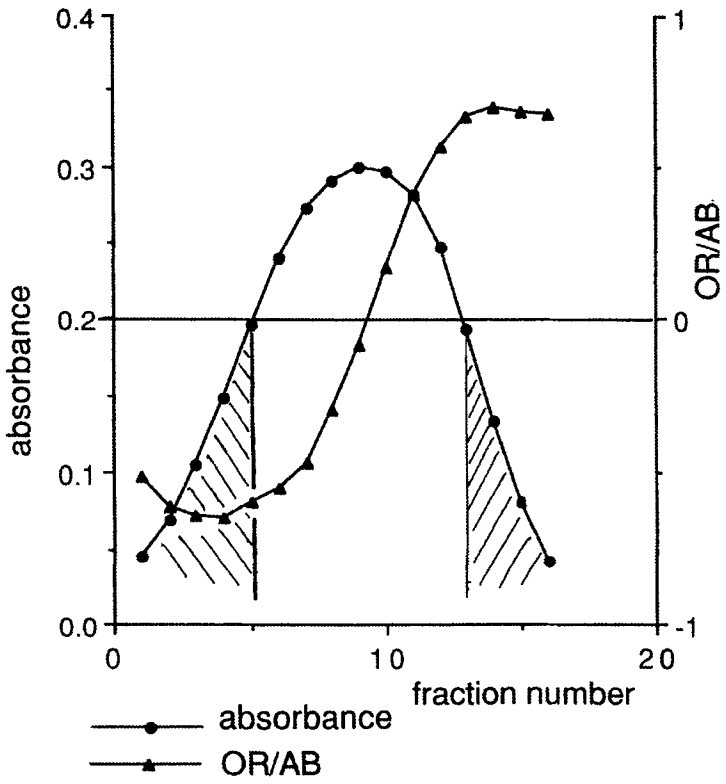


FIGURE 2 Elution curve of **3b**-f in which • and ▲ indicate absorbance and optical rotation/absorbance (OR/AB) of each fraction respectively. Shaded parts seem to be optically pure enantiomers.

bands confirmed that the two eluted bands were enantiomeric to each other and optically pure.

On the other hand, all the f-isomers were only partially resolved. Thus head and tail fractions of all elution bands showed optical rotations with an opposite sign to each other. The elution curve shown in Figure 2 provides an example. The figure shows plots of absorbance and OR/AB *vs.* fraction number of the **3b**-f racemate. We assumed that the flat part (shaded parts) in head fractions and tail fractions of the OR/AB were enantiomerically pure.

We also examined the applicability of using Cellulofine C-200 for other complexes. A similar experiment for $[Ni(o\text{-}phen)_3]^{2+}$ showed some tendency toward resolution. Thus the head fractions and tail fractions of an eluted band showed (+) and (−) optical rotations, respectively. Thus $[Ni(o\text{-}phen)_3]^{2+}$ was partially resolved. Non-aryl complexes such as $[Co(en)_3]^{3+}$ and $[\{Co(tren)\}_2(tae)]^{4+}$ [3b], were not resolved. At present, optical resolution with Cellulofine C-200 is applicable to complexes of structurally special types whose chiralities arise from the combination of more than two aromatic rings.

References

[1] Following abbreviations were used through this manuscript; tren for tris(2-aminoethyl)amine; o-phen for 1,10-phenanthroline; en for ethylenediamine; tae for 3,4-diacetyl-2,5-hexanedione(tetraacetylethane).

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[5] Crystal structure of **2a**-f will be reported in detail later.