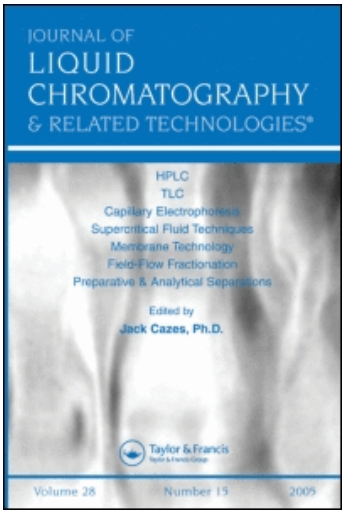

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X. -Y. Zhu[a]; Y. -C. Cai[a]; Y. -H. Zhang[a]; L. -R. Chen[a]; Y. -M. Li[a]
[a] Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, P.R. China

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HPLC Enantioseparation of Novel Chiral Tetrahedral Heterometal Clusters on a Cellulose *tris*-(3,5-Dimethylphenylcarbamate) CSP

X.-Y. Zhu, Y.-C. Cai, Y.-H. Zhang, L.-R. Chen, and Y.-M. Li*

Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, P.R. China

ABSTRACT

A series of novel tetrahedral heterometal cluster enantiomers have been separated on cellulose *tris*-(3,5-dimethylphenylcarbamate) stationary phase by high performance liquid chromatography, using hexane as the mobile phase with various alcohols as modifiers. The chromatographic parameters, retention factors (k), separation factors (α), and resolution factors (Rs) of all solutes were presented. The influence of the mobile phase composition on the enantioselectivity has been discussed, and the effect of structural variation of the solutes on their enantioseparation was also investigated and compared.

*Correspondence: Dr. Yongmin Li, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Tianshui Road 342, Lanzhou 730000, P.R. China; Email: zxylz@yahoo.com.

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Key Words: CSP; Tetrahedral heterometal clusters; Enantioseparation.

INTRODUCTION

Optically active clusters with chiral frameworks can provide the proof that a cluster as a whole, not one of its fragments, can act as a catalyst, by inducing an asymmetric reaction with the subsequent isolation of chiral products.[1] Using a framework chirality cluster as the asymmetric reaction catalyst would not only bring a basic conceptual breakthrough in the asymmetric catalysis, in which the most asymmetric induction originates from the central or planar chirality of P or N ligand, but also extend the methodology in the designs of new chiral catalysts. Although a number of chiral tetrahedral transition metal clusters have been synthesized,[2–11] there remains another major problem of enantiomeric separation; an asymmetric reaction should be induced by the optical isomers. Vahrenkamp reported that optically active phosphine ligands can replace the carbonyl bound to transition metal to form cluster diastereoisomers, but in some cases the auxiliary phosphine cannot be removed without destruction of the cluster or loss of the optical activity after separation of diastereoisomers.[12,13] On the other hand, high-performance liquid chromatography, which has been applied extensively to separation of numerous organic and biochemically active compounds, was characterized by high speed and efficiency and requires mild separation conditions, and can be coupled to sensitive detectors.[14] Moreover, if the tetrahedral cluster enantiomers are separated directly without derivatization by HPLC on a chiral stationary phase, the destruction of the chiral cluster, or loss of the optical purity, can also be avoided. There are various types of chiral stationary phases (CSPs) available, among them, cellulose-based CSPs has been proven to be quite versatile. A wide variety of enantiomeric compounds, including chiral aromatic alcohols,[15] enantiomeric amides,[16] pyriproxyfen,[17] amino alcohols,[18] diol,[19] β-blockers,[20] racemic carboxylic acid,[21] and other miscellaneous compounds[22] have been separated on these CSPs. It was noted that the cellulose *tris*-(3,5-dimethylphenylcarbamate) (CDMPC) stationary phase was particularly effective.

In this paper, the retention factors (k'), separation factors (α), and the resolution factors (*Rs*) of five pairs of chiral heterometal tetrahedral clusters, were studied on the CDMPC-CSP. The results obtained under various mobile phase compositions were compared and the effect of structural variation of the solutes on their enantioseparations was also investigated. No paper on the direct optical resolution of these novel tetrahedral clusters on CDMPC–CSP has been reported previously.

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EXPERIMENTAL

Materials

Microcrystalline cellulose was purchased from The Fourth Reagent Factory of Shanghai (China). 3,5-Dimethylphenylisocyanate from ACROS (New Jersey, USA). 3-Aminopropyltriethoxy-silane was a product of Liaoning Chemical Plant (China). The spherical silica gel (with a mean particle size of 5 μm, a mean pore diameter of 12 nm and a specific surface area of $110\,m^2\,g^{-1}$) was made in our laboratory. All other reagents used were analytical grade from Tianjin Second Chemical Reagent Plant (China).

Five pairs of tetrahedral cluster enantiomers were synthesized by the Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. The structures of the five pairs of structurally related enantiomers were shown in Fig. 1. These samples injected were dissolved in mobile phase. All solvents were filtered and degassed in an ultra-sonic bath before use.

Apparatus

The HPLC system consisted of a Waters 515 HPLC pump (Waters, USA), a Waters 2487 double absorbance detector (Waters, USA), and the chromatograms were acquired and processed by a Millennium^{32} chromatography manager software.

Chromatographic Conditions

Cellulose *tris*-(3,5-dimethylphenylcarbamate) was prepared as described in Ref.[23] and coated on aminopropylated silica gel with a coating amount of 15% (w/w). The CSP prepared was packed into a stainless steel column (25 cm × 4.6 mm) by the conventional high pressure slurry-packing procedure.

The mobile phase compositions were various alcohols with different percentages in *n*-hexane. The flow-rate was 1.0 or $1.5\,mL\,min^{-1}$. The column temperature was 25°C. UV detection was performed at 254 nm. The retention factor (k') was determined as $k' = (t_R - t_0)/t_0$. The dead time (t_0) was determined using *n*-hexane as reference. The separation factor (α) was calculated as $\alpha = k'_2/k'_1$, where k'_1 and k'_2 were retention factors for the first and second eluting enantiomer, respectively. The resolution factor (Rs) was calculated by the following formula: $Rs = 2(t_2 - t_1)/(w_1 + w_2)$, where w_1 and w_2 are the respective baseline peak widths.

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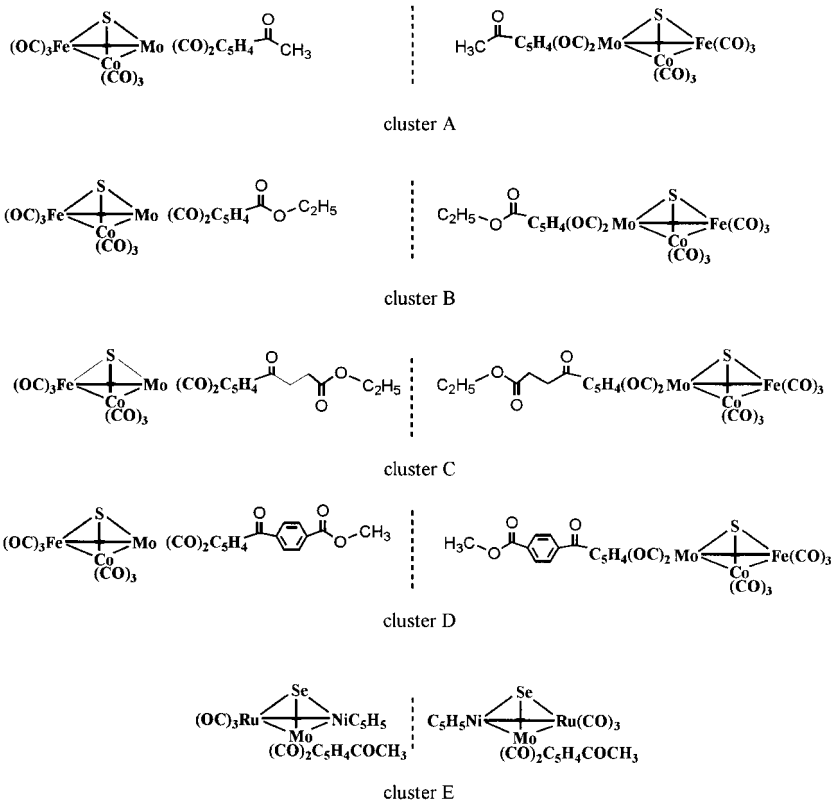

Figure 1. Structures of the five pairs of tetrahedral metal cluster enantiomers.

RESULTS AND DISCUSSION

Chiral Separation of the Tetrahedral Metal Cluster Enantiomers on Cellulose *tris*-(3,5-Dimethylphenylcarbamate) Chiral Stationary Phase

It has been assumed that the separation of enantiomers on the cellulose-based CSPs was due to the formation of solute-CSP complexes by the solute entering the chiral cavities in the higher order structures of the CSPs.[24,25] In the CSPs with carbamate derivatives, such as the CDMPC-CSP used in our study, the binding of the solutes to the CSPs was achieved through interactions between the solutes and the polar carbamate groups on the CSPs.[24–26] The carbamate groups on the CSP can interact with solutes through

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hydrogen bonding using the C═O and NH groups and through dipole–dipole interactions using the C═O moiety. In addition to these polar interactions, π–π interactions between phenyl groups of the CSPs and aromatic groups of a solute may play a role in the recognition of chirality.[15] Chiral discrimination between the enantiomers was due to the differences in their steric fit in the chiral cavities of the CSP which caused different stability of solute-CSP complexes.[24–26]

In our study, it was found that not only the structure and concentration of alcohol in mobile phase, but also the structural variation of the solute, had a large effect on their enantioseparation. All the affecting factors were investigated in detail and the optimum separation for different clusters were obtained by this investigation.

The Influence of the Structure and Concentration of Mobile Phase Modifier on Retention and Enantioselectivity

The effect of the structure of mobile phase modifier (MPM) on the retention factor k', separation factor α, and resolution factors *Rs* was investigated using a series of alcohols as MPM, the results of this study were presented in Table 1. It could be seen that the chiral clusters showed different retention and enantioselectivity using different alcohols as MPM, for example, cluster A could be resolved using ethanol, 1-propanol, and 2-propanol as MPM, and the most effective MPM was 2-propanol. Cluster B could be separated by 1-propanol and 2-butanol as MPM and the optimum MPM was 2-butanol. Cluster C could be resolved using ethanol, 1-propanol and 2-propanol as MPM and the most effective MPM appeared to be ethanol. Cluster E could be resolved using most of the alcohols in our study and 1-butanol was the most effective MPM, however, cluster D could not be resolved under any of the chromatographic conditions in our study. A possible explanation was that there was a competition between the alcohol and the solute to bind with the CSP and the competition was different between different alcohols and the solute, which caused different retention of the chiral clusters using different alcohols as MPM. On the other hand, the alcohol not only competes for binding sites with the solute but also can alter the steric environment of the chiral cavities on the CSP by binding to achiral sites at or near the chiral cavities, thus the enantioselectivity would also be affected by the structure of the alcohol modifier.

From the data shown in Table 2, it was evident that consecutive increases in the concentration of various alcohols resulted in corresponding decreases in retention factors k' as would be normally expected. However, the increase in alcohol concentration had little effect on the separation factor α, it meant that

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Table 1. Effect of structure of alcohol modifiers on the chiral separation of clusters A and B.

Solute	Ethanol	1-Propanol	2-Propanol	1-Butanol	2-Butanol	tert-Butyl alcohol	2-Pentanol
A							
k'_1	3.13	4.50	4.77	6.91	4.17	5.92	4.29
α	1.11	1.11	1.14	1.00	1.00	1.00	1.00
Rs	0.56	0.63	0.78	0.00	0.00	0.00	0.00
B							
k'_1	3.79	1.40	2.06	3.90	1.70	1.60	1.36
α	1.00	1.14	1.00	1.00	1.17	1.00	1.00
Rs	0.00	0.60	0.00	0.00	0.67	0.00	0.00
C							
k'_1	5.57	3.63	9.00	7.26	9.39	10.65	8.18
α	1.12	1.09	1.08	1.00	1.00	1.00	1.00
Rs	0.54	0.43	0.26	0.00	0.00	0.00	0.00
D							
k'_1	4.93	6.20	8.33	5.95	7.43	6.82	5.25
α	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Rs	0.00	0.00	0.00	0.00	0.00	0.00	0.00
E							
k'_1	3.30	4.16	4.86	3.38	4.08	7.14	2.60
α	1.16	1.20	1.09	1.30	1.11	1.00	1.00
Rs	0.93	1.11	0.34	1.27	0.52	0.00	0.00

Note: Mobile phase: *n*-hexane/alcohol = 95/5, v/v, flow rate: 1.5 mL min^{-1}, column temperature: 25°C, $\lambda = 254$ nm.

Table 2. Effect of alcohol modifiers concentration (%, v/v) on the chiral separation of chiral cluster E.

Modifier	Concentration (%)	k_1'	α	*Rs*
Ethanol	2	5.40	1.17	0.92
	5	3.30	1.16	0.91
	10	1.88	1.16	0.81
	20	1.22	1.16	0.59
1-Propanol	2	5.91	1.21	1.14
	5	4.16	1.20	1.11
	10	3.20	1.20	1.05
	20	2.17	1.16	0.90
2-Propanol	2	8.00	1.09	0.44
	5	4.86	1.09	0.34
	10	3.37	1.09	0.32
	20	2.00	1.09	0.21
1-Butanol	2	5.29	1.28	1.61
	5	3.38	1.30	1.27
	10	2.23	1.29	1.24
	20	1.45	1.30	1.09
2-Butanol	2	6.84	1.14	0.71
	5	4.08	1.11	0.52
	10	3.09	1.13	0.53
	20	1.84	1.13	0.60

Note: Mobile phase: *n*-hexane/alcohol, v/v, flow rate: 1.5 mL min^{-1}, column temperature: 25°C, $\lambda = 254$ nm.

the enantioselectivity was mainly affected by the structure but not the concentration of the alcohol modifier. For the resolution factors *Rs*, there were remarkable increases as the concentration of alcohol decreased, whereas, too low concentration of alcohol may result in band broadening in some cases.

It could be concluded that both the concentration and the structure of the alcohol influenced the retention and the enantioselectivity. The influence of alcohol modifiers was investigated and the optimum enantiomeric separation of clusters A, B, C, E was obtained and shown in Fig. 2.

The Influence of the Structures of the Tetrahedral Clusters on Their Enantioseparation

From the structures of the tetrahedral metal cluster enantiomers (shown in Fig. 1), it could be found that the chirality of the tetrahedral heterometal

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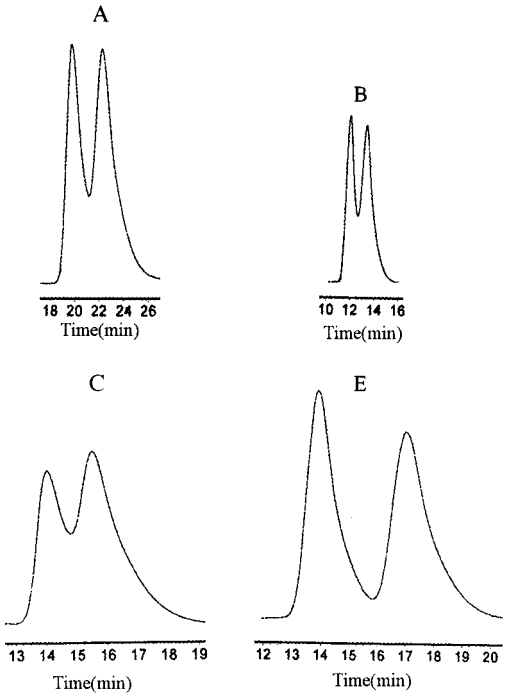

Figure 2. Optimum chromatograms of chiral clusters A, B, C, and E. (A) Chromatographic conditions: OD column (250 mm × 4.6 mm) with hexane : 2-propanol (95 : 5, v/v) as the mobile phase; flow-rate: 1.0 mL min^{-1}; column temperature: 25°C; UV detector: 254 nm. (B) Chromatographic conditions: OD column (250 mm × 4.6 mm) with hexane : 2-butanol (98 : 2, v/v) as the mobile phase; flow-rate: 1.0 mL min^{-1}; column temperature: 25°C; UV detector: 254 nm. (C) Chromatographic conditions: OD column (250 mm × 4.6 mm) with hexane : ethanol (98 : 2, v/v) as the mobile phase; flow-rate: 1.5 mL min^{-1}; column temperature: 25°C; UV detector: 254 nm. (E) Chromatographic conditions: OD column (250 mm × 4.6 mm) with hexane : 1-butanol (98 : 2, v/v) as the mobile phase; flow-rate: 1.5 mL min^{-1}; column temperature: 25°; UV detector: 254 nm.

clusters is different from the classical chiral organic molecules. There is no distinct monatomic chiral centers like chiral organic molecules, the chirality is due to the general asymmetry of the tetrahedral framework.

The structures of clusters A–D are similar (seen from Fig. 1); the four pairs of clusters all contain a SCoFeMo framework and the substitute group in the S, Co, Fe cores are same, the subtle difference is the substitute group in the Mo core. Just for this difference, their enantioseparation were also different.

The optimum modifier was different for them and their retention factors k', separation factors α, and resolution factors *Rs* were also different under the same chromatographic conditions (as shown in Table 1), especially for cluster D, which has the most bulky substitute group, it could not be resolved under any chromatographic conditions in our study. It has been assumed that the binding of the solutes to the CSPs was achieved through interactions between the solutes and the polar carbamate groups on the CSPs. The carbamate groups on the CSP can interact with solutes through hydrogen bonding using the C═O and NH groups and through dipole–dipole interactions using the C═O moiety. In addition to these polar interactions, π–π interactions between phenyl groups of the CSP and aromatic groups of a solute may play a role in the recognition of chirality. Therefore, the cluster of different substitute groups had different interaction with the CSP and there would be differences in their retention. On the other hand, chiral discrimination between the enantiomers was due to the differences in their steric fit in the chiral cavities of the CSP, which caused different stability of solute-CSP complexes. It was difficult for bulky substitute groups to enter the chiral cavities of the CSP, therefore, there were few differences in their steric fit in the chiral cavities of the CSP between the enantiomers, and the separation factors α and resolution factors *Rs* decreased, even as the cluster D, which could not be resolved under any of the separation conditions in our study.

Cluster E has a very different structure from the other four pairs of chiral clusters, not only the substitute group, but also the framework was different from clusters A–D. From the data given in Table 1 and the optimum separation shown in Fig. 2, it could be seen that the separation of cluster E was much better than that of the other four clusters. Cluster E could be resolved satisfactorily under most of the chromatographic conditions in our study. The results showed that not only the metal core of the tetrahedral framework, but also the substitute group of the clusters, have a large effect on the chiral separation.

CONCLUSION

The separation of chiral tetrahedral heterometal clusters was successfully achieved on CDMPC–CSP by HPLC. The structure and the concentration of the alcohol modifiers had a large effect on the chiral separation. Increases in the percentage of alcohol in the mobile phase resulted in decreases in retention factors k' and resolution factors *Rs*, but had little effect on the separation factors α. The structure of alcohol also had a large effect on the chiral separation; the optimum MPMs were different for different clusters. The results showed that the most effective MPM appeared to be 2-propanol for

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cluster A, 2-butanol for cluster B, ethanol for cluster C, and 1-butanol for cluster E. However, cluster D could not be resolved under any of the chromatographic conditions in our study.

Furthermore, the chiral separation of the tetrahedral metal clusters was affected by not only the element in the metal core of the tetrahedral framework, but also the substitute group of the clusters, therefore, the separation conditions were different for various chiral clusters and should be examined specifically for every cluster.

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REFERENCES

1. Pittman, C.U.; Richmond, G.M.; Absi-Halabi, M.; Beurich, H.; Richter, F.; Vahrenkamp, H. Photoinitiated hydrosilations in presence of tetrahedral heterometallic clusters: catalysis intact clusters. Angew. Chem., Int. Ed. Engl. **1982**, *21*, 786–787.
2. Yin, Y.Q.; Sun, H.S.; Jin, D.S. Synthesis and characterization of tri-metal cluster compounds: x-ray structure determination of [$Co_2Mo(\mu_3$-$CC_6H_5)Br(CO)_8$(bipy)]. J. Organomet. Chem. **1992**, *439*, 45–51.
3. Wu, H.P.; Yin, Y.Q.; Huang, X.Y.; Yu, K.B. Synthesis and x-ray crystal structure of the chiral trimetal carbonyl clusters (μ_3-CPh)FeCoMo(-$CO)_8$(RCOCp)H (R = H, CH_3 or C_2H_5O) derived from the clusters (μ_3-CPh)$Co_2Mo(CO)_8$(RCOCp). J. Organomet. Chem. **1995**, *498*, 119–125.
4. Wu, H.P.; Zhao, Zh.Y.; Yin, Y.Q.; Jin, D.S.; Huang, X.Y. Synthesis, characterization and crystal structure of heterometal clusters $RCCo_2Mo(CO)_8(CH_3Cp)$ and $RCCoM_2(CO)_7(CH_3Cp)_2$. Polyhedron. **1995**, *14*, 1543–1546.
5. Ding, E.R.; Liu, Sh.M.; Yin, Y.Q.; Sun, J. Synthesis and characterization of chiral $SFeCoM(CO)_8$(RCp) [M = Mo, W; R = $C_6H_5C(O)$,$CH_3OC(O)C_6H_4C(O)$] clusters and the crystal structure of $SFeCoMo(CO)_8$[CH_3O-$C(O)C_6H_4C(O)Cp$] and $SFeCoW(CO)_8$[$CH_3OC(O)C_6H_4C(O)Cp$]. Polyhedron **1997**, *16*, 3273–3278.
6. Ding, E.R.; Yin, Y.Q.; Sun, J. Synthesis, characterization and reaction of the cluster complexes containing tetrahedral core MRuCoSe. The single crystal x-ray structures of the clusters $RuCoMo(CO)_8(\mu_3$-Se)$C_5H_4C(O)R$ [R = CH_3, $C_6H_4C(O)OCH_3$]. J. Organomet. Chem. **1998**, *559*, 157–164.

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7. Wu, Sh.L.; Ding E.R.; Yin, Y.Q.; Sun, J. Synthesis and expansion reaction of ferrocenylacetylene dimetal carbonyl compounds. The molecular structures of μ-FeCCHCoMo(CO)$_5$Cp and μ_3-FeCHCFeCo$_2$(CO)$_9$. J. Organomet. Chem. **1998**, *570*, 71–78.
8. Chen, X.N.; Zhang J.; Yin, Y.Q.; Huang, X.Y. Reaction of 1,8-nonadiyne with $Co_2(CO)_8$ and $Mo_2(C_5H_4R)_2(CO)_4$ and crystal structures of $[M_2L_2(CO)_4][m\text{-}HC_2(CH_2)_5C_2H\text{-}m][Me_2(C_5H_4R)(CO)_4]$ (M = Co, L = CO; M = Mo, L = C_5H_4R, R = H, $COCH_3$, $COOC_2H_5$). Organometallics **1999**, *18*, 3164–3169.
9. Wu, Sh.L.; Ding, E.R.; Li, Q.Sh.; Chen, X.N.; Yin, Y.Q.; Sun, J. Preparation and characterization of cluster complexes derived from ferrocenylacetylene. J. Coord. Chem. **1999**, *47*, 341–347.
10. Zhang, Y.H.; Yuan, J.C.; Lao, W.J.; Yin, Y.Q.; Huang, Z.X.; Wu, J.J. Synthesis, characterization and reactions of cluster complexes containing SeRuCoM (M = Mo or W) core and a functionally substituted cyclopentadienyl ligand. J. Organomet. Chem. **2001**, *628*, 123–130.
11. Zhang, Y.H.; Yuan, J.C.; Yin, Y.Q.; Zhou, Zh.Y.; Chan, Albert S.C. Preparation and reactions of tetrahedrane-type clusters containing SCoFeM (M = Mo or W) core. The single crystal x-ray structure of the cluster (μ_3-S)CoFeMo(CO)$_8$ [η^5-$C_5H_4C(O)CH_2CH_2CO_2Me$]. Polynedron **2001**, *20*, 1859–1865.
12. Roland, E.; Vahrenkamp, H. Darstellung und chemie des clusters SruCo$_2$(CO)$_9$. Chem. Ber. **1984**, *117*, 1039–1051.
13. Blumhofer, R.; Vahrenkamp, H. Chirale μ_3-alkylidin-trimetall-cluster darstellung und untersuchungen zur optischen aktivitat. Chem. Ber. **1986**, *119*, 683–698.
14. Antonella, C.; Alessandro, M.; Giovanni, P. Applications of high-performance liquid chromatography to metal carbonyl and cluster chemistry. Chem. Rev. **1989**, *89*, 407–418.
15. Wainer, I.W.; Stiffin, R.M.; Shibata, T. Resolution of enantiomeric aromatic alcohols on a cellulose tribenzoate high-performance liquid chromatography chiral stationary phase. J. Chromatogr. **1987**, *411*, 139–151.
16. Wainer, I.W.; Alembik, M.C. Resolution of enantiomeric amides on a cellulose-based chiral stationary phase. J. Chromatogr. **1986**, *358*, 85–93.
17. Okamato, M.; Nakazawa, H. Reversal of elution order during direct enantiomeric separation of pyriproxyfen on a cellulose-based chiral stationary phase. J. Chromatogr. **1991**, *588*, 177–180.
18. Balmer, K.; Lagerstrom, P.-O.; Persson, B.-A.; Schill, G. Reversed retention order and other stereoselective effects in the separation of amino alcohols on chiralcel OD. J. Chromatogr. **1992**, *592*, 331–337.
19. O'Brien, T.; Crocker, L.; Thompson, R. Mechamistic aspects of chiral discrimination on modified cellulose. Anal. Chem. **1997**, *69*, 1999–2007.

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20. Krstulovic, A.M.; Fouchet, M.H.; Burke, J.T. Direct enantiomeric separation of betaxolol with applications to analysis of bulk drug and biological samples. J. Chromatogr. **1988**, *452*, 477–483.
21. Okamoto, Y.; Aburatani, R.; Kaida,Y.; Hatada, K. Direct optical resolution of carboxylic acids by chiral HPLC on Tris(3,5-dimethylphenylcarbamate)s of cellulose and amylose. Chem. Lett. **1988**, 1125–1128.
22. Okamoto, Y.; Kaida, Y.; Hayashida, H.; Hatada, K. Tris(1-phenylethylcarbamate)s of cellulose and amylose as useful chiral stationary phases for chromatographic optical resolution. Chem. Lett. **1990**, 909–912.
23. Okamoto, Y.; Kawashima, M.; Hatada, K. Chromatographic resolution. Controlled chiral recognition of cellulose triphenylcarbamate derivatives supported on silica gel. J. Chromatogr. **1986**, *363*, 173–186.
24. Okamoto, Y.; Yashima, E. Polysaccharide derivatives for chromatographic separation of enantiomers. Angew. Chem., Int. Ed. Engl. **1998**, *37*, 1020–1043.
25. Okamoto, Y.; Kaida, Y. Resolution by high-performance liquid chromatography using polysaccharide carbamates and benzoates as chiral stationary phases. J. Chromatogr. A **1994**, *666*, 403–419.
26. Yashima, E.; Okamoto, Y. Chiral discrimination on polysaccharides derivatives. Bull. Chem. Soc. Jpn. **1995**, *68*, 3289–3307.

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