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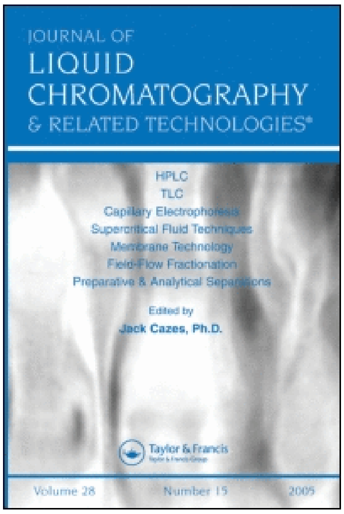

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

The Separation of the New Chiral Metal Cluster (μ_3-Se)RuCoW (CO)$_8$-C$_5$H$_4$C(O)CH$_3$ on an Amylopectin Tris-(Phenylcarbamate) Chiral Column by HPLC

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To cite this Article Zhou, Z. Q. , Ding, E. R. , Hou, J. G. , Chen, L. R. and Yin, Y. Q.(1998) 'The Separation of the New Chiral Metal Cluster (μ_3-Se)RuCoW (CO)$_8$-C$_5$H$_4$C(O)CH$_3$ on an Amylopectin Tris-(Phenylcarbamate) Chiral Column by HPLC', Journal of Liquid Chromatography & Related Technologies, 21: 19, 3021 — 3030

To link to this Article: DOI: 10.1080/10826079808006883

URL: http://dx.doi.org/10.1080/10826079808006883

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J. LIQ. CHROM. & REL. TECHNOL., 21(19), 3021–3030 (1998)

THE SEPARATION OF THE NEW CHIRAL METAL CLUSTER (μ_3-Se)RuCoW $(CO)_8$-$C_5H_4C(O)CH_3$ ON AN AMYLOPECTIN TRIS-(PHENYLCARBAMATE) CHIRAL COLUMN BY HPLC

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ABSTRACT

The preparation of amylopection tris(phenylcarbamate) (ATP) chiral stationary phases(CSPs) coated on a small-particle (5μm, 120Å) spherical silica support, according to a process that is reported, is presented. A new chiral tetrahedral cluster (μ_3-Se)$RuCoW(CO)_8C_5H_4C(O)CH_3$ **2** which was synthesized by the thermal reaction of the precursor (μ_3-Se)$RuCo_2(CO)_9$ **1** with the functionally substituted cyclopentadienyl tricarbonyl metal complex anions $[W(CO)_3C_5H_4C(O)CH_3]^-$ is resolved on the amylopectin tris (phenylcarbamate) chiral stationary phases.

INTRODUCTION

Resolution of enantiomer by liquid chromatography on (CSPs) has become a practical and useful method for obtaining optical isomers and determining their purities.[1,2] Several different types of chiral stationary phases have been developed and a wide range of applications has been published during the last decade.[3] Polysaccharide based phases have been identified as versatile and useful chiral sorbents for the separation of enantiomers.[4] A variety of cellulose

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and amylose derivatives, as polymer coatings on large pore silica gel, have been introduced for the same purpose by Okamoto and co-workers.[3,4] Most of these coated silica materials are commercially available and they show different selectivity depending on the type of polysaccharide and on the derivatizing groups on the polysaccharide. More recently, Felix introduced a new type of polysaccharide called amylopectin substituted by phenycarbamate moieties, which is capable of remarkable chiral recognition.[5] We report here synthesis and characterization of a new chiral metal cluster $(\mu_3\text{-Se})RuCoW(CO)_8C_5H_4C(O)CH_3$ which was able to induce an asymmetric reaction,[6] and the results of the study using 5 μm aminopropylated sperical silica (APS) as the support of ATP. The optical purity of the cluster is determined on the ATP coated chiral stationary phase.

EXPERIMENTAL

Apparatus

Separations were carried out at room temperature on an HPLC system with a Model M6000 pump (Waters, Milford, MA, USA), a K501 injector (10 μL, Scientific Instrument Plant of Shanghai, China), a Model SPD-1 spectrophotometer detector (Shimadzu, Kyoto, Japan), and a recorder (Analytical Instrument Plant of Shanghai, China).

IR spectra were recorded on a Nicolet FT-IR 10D spectrophotometer, ^1H NMR spectra were recorded on Brucker Am-300MHz spectrometer, Elemental analysis and FAB MS were performed on a Carbo Erba 1106-type analyzer and Finnigan Mat 8430 respectively.

Reagents

Spherical silica was made by ourselves and had the following properties: particle size, 5 μm, pore size, 120 Å; surface area, 110m^2/g. Amylopectin and phenylisocyanate were purchased from Sigma Co. $(\mu_3\text{-Se})RuCo_2(CO)_9$ and $NaC_5H_4C(O)CH_3$ were prepared according to the literature.[7,8] All the reagents used were analytical grade.

Chromatographic Conditions

Chromatography was performed using the different phase composition (hexane/2-propanol) at a flow rate of 0.5mL/min at room temperature. The dead

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time of columns was determined by injection of 1,3, 5-tri-tert-butylbenzene used as non-retained compound. The separation factor (α) was calculated as $\alpha = k_2/k_1$, and capacity factor (k) as $k_1 = (t_1-t_0)/t_0$ and $(t_2-t_0)/t_0$, where t_1 and t_2 refer to the retention times for the first and second eluting enantiomers, respectively.

Preparation of Stationary Phase

Spherical silica (5µm, 120Å) was treated with 3-aminoproryltriethoxsilane in toluene at 110° for 24h, the product was filtered off and washed with toluene and THF, the dried at 80° under vacuum.

A 1.0 g amount of amylopectic dissolved in freshly distilled pyridine (40mL), an excess amount of phenylisocyanate was added and the mixture was refluxed for 48h. After 30mL of cooling methanol was added, and the precipitate was filtered and washed twice with methanol. Yield: ~100%. We did not found the absorption of hydroxyl groups (~3470) in it's IR spectra, and its elemental analyses were satisfactory.

A 2.45g amount of APS silicagel was added to 0.45g of ATP dissolved in THF (30mL). The mixture was stirred for 15 min, and then the solvent was removed under vacuum.

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Preparation of the Enantiomer

A 100mL three-necked flask was fitted with a magnetic stir-bar, a nitrogen inlet tube and a reflux condenser was charged with $W(CO)_6$ (264mg, 1.0mmol), sodium formylcyclopentadienide (116mg, 1.0mmol) and THF (20mL). The mixture was heated to reflux for 16h. Then 550mg(1.0mmol) of cluster $(\mu_3\text{-}Se)RuCo_2(CO)_9$ was added and the mixture was stirred at 60° for 2h. The solvent was removed under vacuum, the residue was extracted by minimum amount of CH_2Cl_2 and the product chromatographed on a 2.5×20 cm silica gel column using CH_2Cl_2/hexane as eluent. The main product of 2 (340mg, 52%) was obtained as black solid. Anal. Calcd for $C_{14}H_5O_9RuCoWSe$: C, 23.89; H, 0.94. Found: C, 23.79; H, 0.81. IR(KBr disk) 2077vs, 2044vs, 2036vs, 2012vs, 1984vs, 1974vs, 1892vs, 1857s, 1687vs cm^{-1}. ^1H NMR ($CDCl_3$) δ5.55-5.90 (q, 4H, C_5H_4); δ2.41(m, 3H, CH_3).

RESULTS AND DISCUSSION

The reaction of the cluster $RuCoMo(\mu_3\text{-}Se)(CO)_9$ 1 with $[W(CO)_3(\eta^5\text{-}C_5H_4)C(O)CH_3]^-$ in refluxing THF afforded a moderate yield of clusters

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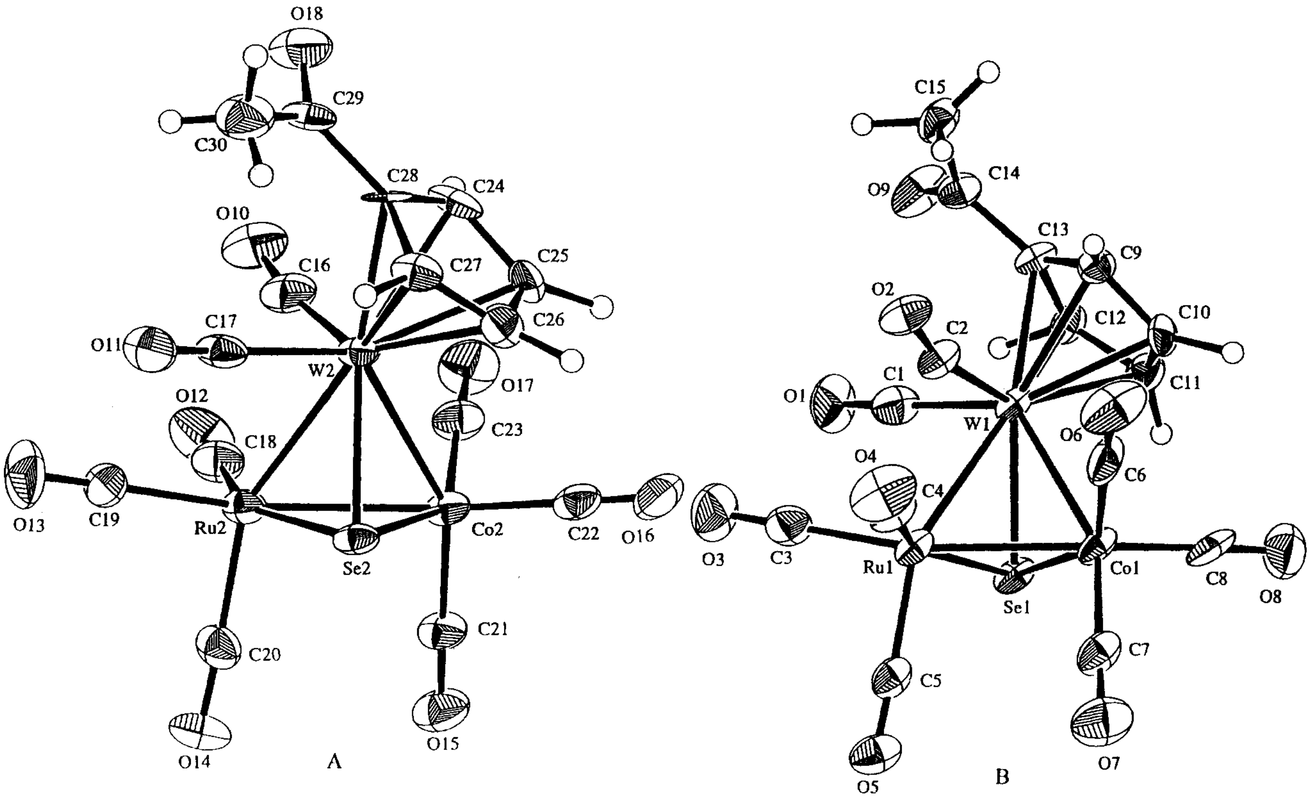
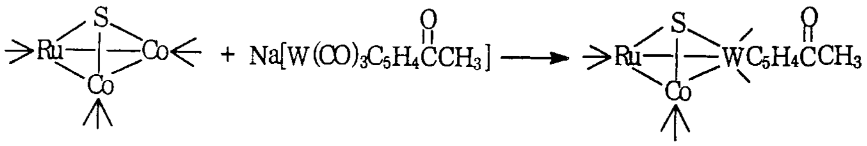


Figure 1. The crystal structure of the cluster (μ_3-Se)RuCoW(CO)$_8$C$_5$H$_4$C(O)CH$_3$.



Scheme 1

Table 1

Crystal and Refinement Data for the Clusters 2

Formula	$C_{30}H_{14}O_{18}Ru_2Co_2W_2Se_2$
Mr	1508.06
System	Orthorhombic
Space group	Pbca
F(000)	5568.00
a(Å)	26.326(4)
b(Å)	18.231(4)
c(Å)	15.956(3)
V(Å^3)	7658(4)
Z	8
Dcalc(g/cm^3)	2.616
μ(MoKα)cm^{-1}	95.83
Crystal dimensions	0.20 0.20 0.30 mm
Temperature(°C)	20.0
Scan type	ω-2θ
2θmax (deg)	45
No. Refluctions Measured	Total 4890
No. Observations [I>3.00(s)]	3492
No. Variables	505
Refelection/Parameter Ratio	6.91
R	0.029
Rw	0.036

RuCoW(μ_3-Se)(CO)$_8$C$_5$H$_4$C(O)CH$_3$ 2 as shown in Scheme 1. This air-stable cluster is black in solid and red-purple in solution. Data of C/H analysis, IR, ^{1}H NMR, ^{13}C NMR, and MS of it were consistent with the expected structure presented in Fig 1. The results showed that one of the Co(CO)$_3$ units in cluster **1** could be exchanged by an isoelectronic W(CO)$_2$C$_5$H$_4$C(O)CH$_3$ unit to give the

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Table 2

Selected Bond Lengths (Å) and Angles (deg) for the Cluster 2

Molecular A

W(1)-Ru(1)	2.881(1)	W(1)-Se(1)	2.503(1)
W(1)-Co(1)	2.764(1)	W(1)-C(1)	2.01(1)
W(1)-C(2)	1.98(1)	W(1)-C(Cp,ave)	2.34
Ru(1)-Se(1)	2.453(2)	Ru(1)-Co(1)	2.647(2)
Ru(1)-C(3)	1.92(1)	Ru(1)-C(4)	1.93(1)
Ru(1)-C(5)	1.91(1)	Se(1)-Co(1)	2.320(2)
Co(1)-C(6)	1.76(1)	Co(1)-C(7)	1.77(1)
Co(1)-C(8)	1.81(2)	C-O(t-co,ave)	1.13
O(9)-C(14)	1.21(1)	C(13)-C(14)	1.49(1)
C(14)-C(15)	1.50(1)		

Molecular B

W(2)-Ru(2)	2.889(1)	W(2)-Se(2)	2.496(1)
W(2)-co(2)	2.772(1)	W(2)-C(16)	1.95(1)
W(2)-C(17)	2.02(1)	W(2)-C(Cp,ave)	2.32
Ru(2)-Se(2)	2.443(2)	Ru(2)-Co(2)	2.646(2)
Ru(2)-C(18)	1.90(1)	Ru(2)-C(19)	1.91(1)
Ru(2)-C(20)	1.90(1)	Co(2)-C(21)	1.79(1)
Co(2)-C(22)	1.79(2)	Co(2)-C(23)	1.78(1)
C-O(t-co,ave)	1.13	O(18)-C(29)	1.21(1)
C(28)-C(29)	1.48(2)	C(29)-C(30)	1.49(2)

new chiral skeleton cluster **2**. Cluster **2** showed a large number of terminal carbonyl absorption bands in the range of 2086 - 1866 cm^{-1} in its IR spectra. The IR spectrum of **2** also showed corresponding C=O absorption at 1653 cm^{-1}. For ^{1}H NMR assignment of **2**, proton chemical shifts of substituted cyclopentadienyl group appeared further downfield than the unsubstituted cyclopentadienyl,[9] since acetyl is a well known electron-withdrawing group.

It is interesting that the ^{1}H NMR spectra of cyclopentadienyl in the cluster showed A_2BB' pattern at 5.55 - 5.90 ppm instead of two group triplets (A_2B_2) or two group broad signals assigned to protons of cyclopentadienyl. We believe that was caused by the chirality of the tetrahedral cluster core RuCoWSe. The FAB MS spectra of **2** exhibit loss of carbonyls from the molecular ion, but they do not contain molecular ion.

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Table 3

Selected Bond Angles (°) of the Cluster SeRuCoW$(CO)_8C_5H_4C(O)CH_3$

Molecular A

Ru(1)-W(1)-Se(1)	53.64(3)	Ru(1)-W(1)-Co(1)	55.89(5)
Ru(1)-W(1)-C(1)	81.4(4)	Ru(1)-W(1)-C(2)	65.0(3)
Se(1)-W(1)-co(1)	51.99(4)	Se(1)-W(1)-C(1)	83.4(3)
Se(1)-W(1)-c(2)	118.7(3)	Co(1)-W(1)-C(1)	130.2(3)
Co(1)-W(1)-C(2)	94.3(3)	W(1)-Ru(1)-Se(1)	55.27(3)
W(1)-Ru(1)-Co(1)	59.81(4)	W(1)-Ru(1)-C(3)	101.7(4)
W(1)-Ru(1)-C(4)	111.4(4)	W(1)-Ru(1)-C(5)	148.2(4)
Se(1)-Ru(1)-Co(1)	53.97(4)	Se(1)-Ru(1)-C(3)	110.5(4)
Se(1)-Ru(1)-C(4)	153.3(4)	Se(1)-Ru(1)-C(5)	93.2(4)
Co(1)-Ru(1)-C(3)	160.0(4)	Co(1)-Ru(1)-C(4)	94.3(5)
Co(1)-Ru(1)-C(5)	100.2(3)	W(1)-Se(1)-Ru(1)	71.09(4)
W(1)-Se(1)-Co(1)	69.80(5)	Ru(1)-Se(1)-Co(1)	67.30(5)
W(1)-Co(1)-Ru(1)	64.30(4)	W(1)-Co(1)-Se(1)	58.21(4)
W(1)-Co(1)-C(6)	83.5(4)	W(1)-Co(1)-C(7)	154.1(4)
W(1)-Co(1)-C(8)	101.7(4)	Ru(1)-Co(1)-Se(1)	58.74(5)
Ru(1)-Co(1)-C(6)	94.04(4)	Ru(1)-Co(1)-C(7)	90.3(4)
Ru(1)-Co(1)-C(8)	156.1(4)	Se(1)-Co(1)-C(6)	139.2(4)
Se(1)-Co(1)-C(7)	105.1(4)	Se(1)-Co(1)-C(8)	97.6(4)
W(1)-C-)(ave)	169.5	Ru-C-O(ave)	177
Co-C-O(ave)	176.7	C(13)-C(14)-C(15)	117.6(10)

Molecular B

Ru(2)-W(2)-Se(2)	53.36(3)	Ru(2)-W(2)-Co(2)	55.68(4)
Ru(2)-W(2)-C(16)	69.3(4)	Ru(2)-W(2)-C(17)	78.1(3)
Se(2)-W(2)-Co(2)	51.94(4)	Se(2)-W(2)-C(16)	122.6(4)
Se(2)-W(2)-C(17)	84.3(3)	Co(2)-W(2)-c(16)	94.3(3)
Co(2)-W(2)-C(17)	128.8(3)	W(2)-Ru(2)-Se(2)	55.05(3)
W(2)-Ru(2)-Co(2)	59.91(4)	W(2)-Ru(2)-C(18)	109.5(4)
W(2)-Ru(2)-C(19)	103.7(3)	W(2)-Ru(2)-C(20)	149.5(4)
Se(2)-Ru(2)-Co(2)	54.06(5)	Se(2)-Ru(2)-C(18)	152.9(4)
Se(2)-Ru(2)-C(19)	110.7(4)	Se(2)-Ru(2)-C(20)	95.1(4)
Co(2)-Ru(2)-C(18)	99.5(4)	co(2)-ru(2)-C(19)	161.6(4)
Co(2)-Ru(2)-C(20)	98.9(4)	W(2)-Se(2)-Ru(2)	71.59(4)
W(2)-Se(2)-Co(2)	70.17(5)	Ru(2)-Se(2)-Co(2)	67.43(5)
W(2)-co(2)-Se(2)	57.90(4)	W(2)-co(2)-Ru(2)	64.41(4)
W(2)-co(2)-C(21)	152.1(4)	W(2)-Co(2)-C(22)	99.3(4)

(continued)

Table 3 (continued)

Selected Bond Angles (°) of the Cluster SeRuCoW(CO)$_8$C$_5$H$_4$C(O)CH$_3$

W(2)-Co(2)-C(23)	87.3(4)	Ru(2)-Co(2)-Se(2)	58.52(5)
Ru(2)-Co(2)-C(21)	88.9(4)	Ru(2)-co(2)-C(22)	157.8(4)
Ru(2)-Co(2)-C(23)	94.7(4)	Se(2)-Co(2)-C(21)	102.1(4)
Se(2)-Co(2)-C(22)	100.5(4)	Se(2)-co(2)-C(23)	142.0(4)
W-C-O(ave)	172.5	Ru-C-O(ave)	177.7
Co-C-O(ave)	177.7	C(28)-C(29)-C(30)	188
O(18)-C(23)-C(28)	119	O(18)-C(29)-C(30)	121
C(24)-C(28)-C(29)	123	C(24)-C(28)-C(27)	107.7(10)

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Cluster **2** was determined by X-ray structure analysis. Crystal data was collected in Table 1. Table 2 and 3 give the selected bond length and angles of **2**. The structure of **2** is unexpectedly revealed in the presence of two isomeric molecules in a unit cell, which are shown respectively in Fig.1 (A&B); the tetrahedral core of each molecule in **2** is composed of four elements that are Ru, Co, W, and Se. The acute angles in tetrahedral geometry of **2** about the basal atoms range from 53.07 to 64.62°, and those about the selenium atom average 69.98°, which deviates a bit from a perfect tetrahedral geometry. The electron count for **2** is conventional. Chiral cluster **2** is structurally related to known clusters SFeCoMo(CO)$_8$C$_5$H$_4$C(O)R [R = H, CH$_3$, C$_2$H$_3$O, C$_6$H$_4$CO$_2$CH$_3$].[10] It is isostructural and isoelectronic with both of these.

In our attempts to obtain the enantiomers we found that a general separation procedure cannot be given, however, the enantiomer separation via the chromatography over an optically active adsorbent was more successful .

The chiral ability of the CSP depends on the thickness of the coating. Usually, the greater the amount of chiral agent, the better is the chiral discrimination. For the coated cellulose CSP, Okamoto and co-workers[11] chose a rate of coating of about 20-25% by mass. However, we found that these had very low optical resolution ability on the 25%(w/w) ATP-coated phase. A coating of 15% by mass appears to be the best average. This indicates it is important to reduce non-chiralinteractions with Si-OH or -NH$_2$ groups by a well-distributed and ordered coating. However, overloading may destroy this characteristic. Fig.2 showed the chromatograms of cluster (μ_3-Se)RuCoW(CO)$_8$C$_5$H$_4$C(O)CH$_3$ on a 15%(w/w) coated phase.

Three hydrocarbons, pentane, hexane and heptane were selected for evaluation, the effect of the aliphatic component in the mobile phase has received little attention.

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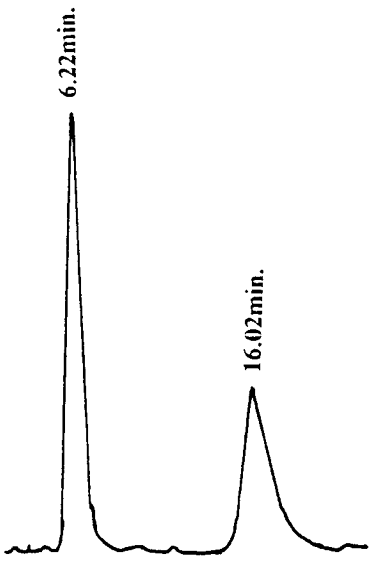

Figure 2. The chromatograms of resolution of the cluster **2** on a 15% ATP-coated column. Mobile phase: hexane/2-propanol = 95:5 (v/v); Flow rate: 0.5 mL/min.; 0, 02 AUF.

Table 4

The Effects of 2-Propanol Concentration on the Resolution

Hexane: 2-Propanol	k_1	k_2	α
100:0	60 min. no eluting		
95:5	1.22	4.72	3.87
90:10	1.12	3.99	3.56
85:15	0.85	2.87	3.38
70:30	0.64	0.64	1.00

The effects of 2-propanol concentration on the retention and resolution had been investigated. The concentration of 2-propanol was increased, retention was reduced and resolution was decreased. We attempted to use hexane only but failed. Table 4 gives the results of resolution of the cluster on different amounts of 2-propanol. We found the best separation of the (μ_3-Se) RuCoW-$(CO)_8C_5H_4C(O)CH_3$ was 15% ATP-coated with hexane and 2-propanol (95:5) based mobile phase.

ACKNOWLEDGMENT

This work was supported by the Chinese Academy of Sciences.

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Received November 1, 1997
Accepted March 17, 1998
Manuscript 4662

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