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METAL CHELATE POLYMERS AS SELECTIVE SORBENTS FOR GAS CHROMATOGRAPHY

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SUMMARY

Metal complexes of bis-β-diketonate ligands form polymers that are useful as selective sorbents for gas chromatography. The sorbents are capable of selectively retaining many oxygen- and nitrogen-containing compounds. The retained compounds can be desorbed for subsequent analysis by heating the metal polymer. The sorbent properties of the complexes depend on both the metal and the ligand. Temperature also has an effect on the retention properties of the sorbents. It is possible to employ series of sorbents with different metal polymers. Application of such a series permits the conversion of a sample with a complex chromatogram into a set of samples with simpler chromatograms.

INTRODUCTION

Gas chromatography is a powerful method for the separation of complex mixtures of volatile organic compounds. Even with state-of-the-art capillary columns, however, most environmental and biological samples remain too complex to achieve complete resolution of all volatile components. Several workers have derived theoretical expressions that describe the number of components of mixtures that can be resolved by gas chromatography[1–3]. Other workers have developed computer programs for deconvoluting overlapping peaks[4–6]. An alternative method for the conversion of complex samples into simpler mixtures is through the use of selective sorbents. With the development of air-actuated flow-switching valves and thermostatically controlled traps, the use of sorbents in gas chromatography has become routine.

Class specific sorbents for olefins[7–15], aromatics[12,13,15,16], alcohols[17–21], aldehydes[18,19,22–24], ketones[18–20,23–26], carboxylic acids[18,27] and amines[21,28–30] have been developed and reported in the literature. With most of these sorbents the organic compounds either react chemically with the sorbent or are irreversibly adsorbed. In either case it is impossible to retrieve the organic compound for subsequent analysis. This represents a serious detriment to the widespread utility of these sorbents. In one study it was possible to recover amines by washing the sorbent with a

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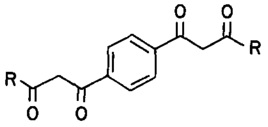
solution of potassium hydroxide[30]. Such a procedure is cumbersome, however, and not in context with the automated valve switching systems in use today. The sorbents we will describe exhibit reversible adsorption of organic compounds. The compounds can be recovered by heating the sorbent under a flow of nitrogen gas.

The sorbents are based on a series of metal chelate complexes with ligands of structure I. An Eu^{3+} complex with I has been employed as a selective sorbent for gas chromatography[31,32]. We have found that the sorbent properties of metal complexes with I depend on both the metal and the substituent group of the ligand. Temperature also influences the retention properties of these sorbents. These variables have enabled us to select sorbents with significantly different retention properties. Application of these sorbents in series permits the conversion of a sample with one complex chromatogram into a set of simpler chromatograms. The sorbents we describe are useful for many oxygen- and nitrogen-containing compounds. Coupling of these traps to an olefin specific trap recently described in the literature[33] should provide for further fractionation of complex samples.



I

EXPERIMENTAL

Reagents

Acetophenone, dimethoxyethane, dimethylterephthalate, ethyl acetate, ethyl trifluoroacetate, ethyl heptafluorobutyrate, *p*-diacetylbenzene, sodium hydride and sodium methoxide were purchased from Aldrich (Milwaukee, WI, U.S.A.).

Preparation of p-di(1,1,1-trifluoro-1,3-butanedionyl)benzene, $H_2(ptb)$

The ligand was synthesized by a modification of a literature preparation[31]. A 2-l, three neck, round-bottomed flask was fitted with a reflux condenser, dropping funnel and magnetic stirrer. The reaction was maintained under an atmosphere of prepurified nitrogen gas. To the flask was added 100 ml of anhydrous ether, 8.9 g (0.063 mol) of ethyl trifluoroacetate and 7.0 g (0.130 mol) of sodium methoxide. The flask was placed in an ice bath and 5.0 g (0.031 mol) of *p*-diacetylbenzene was added over the next 45 min. The mixture was stirred for an additional 90 min. The ice bath was replenished and 50 ml of 6 *M* hydrochloric acid was slowly added. This was followed by the addition of 100 ml of distilled water and 100 ml of diethyl ether. Crude product that remained insoluble in the diethyl ether layer was collected by suction filtration. The diethyl ether layer was removed and reduction of the volume by rotary evaporation yielded more crude product. The two portions of product were combined and recrystallized from methanol. The desired ligand was obtained as a light yellow solid (m.p. 147–150°C); NMR(C^2HCl_3) δ 8.06 (s, 4, aryl H), 6.61 (s, 2, CH). Anal. calc. for $C_{14}H_8O_4F_6$: C, 47.47; H, 2.28. Found: C, 47.66; H, 2.34.

Preparation of p-di(4,4,5,5,6,6,6-heptafluoro-1,3-hexanedionyl)benzene, H_2(dihed)

This ligand was prepared from ethyl heptafluorobutyrate and *p*-diacetylbenzene using the same procedure described for H_2(ptb). The product was identical in all respects to a previous literature characterization[31].

Preparation of p-di(3-phenyl-1,3-propanedionyl)benzene, H_2(ppb)

This ligand was prepared by a modification of a literature method[34]. The same apparatus described for the synthesis of H_2(ptb) was employed. To the flask was added 300 ml of anhydrous ether, 10.0 g (0.051 mol) of dimethyl terephthalate and 12.0 g (0.222 mol) of sodium methoxide. A solution of 14 ml (14.42 g, 0.12 mol) of acetophenone in 15 ml of anhydrous diethyl ether was added dropwise over a period of 5 min. The mixture was then allowed to stir overnight under an atmosphere of nitrogen. Additional anhydrous diethyl ether was added when necessary to keep the mixture from becoming too thick. After neutralization with hydrochloric acid, the two layers were filtered, the diethyl ether layer was isolated and the volume was reduced by rotary evaporation. The crude product was recrystallized four times from methanol. The ligand was obtained as a light yellow solid and was identical in all respects to a previous literature characterization[34].

Preparation of p-di(1,3-butanedionyl)benzene, H_2(pbb)

Considerable difficulty was encountered in attempting to synthesize and isolate this ligand using standard literature methods[34]. The following procedure, which is a modification of a literature method used for synthesizing β-diketones, was employed[35]. Ethyl acetate (5.5 g, 0.062 mol), a 60% dispersion of sodium hydride in mineral oil (6.2 g), and 100 ml of freshly distilled dimethoxyethane was added to a round-bottomed flask equipped as previously described. The mixture was heated to reflux and a solution of 5.0 g (0.031 mol) of *p*-diacetylbenzene in 100 ml of freshly distilled dimethoxyethane was added dropwise over the next 100 min. The mixture was heated under reflux for an additional 2 h, after which it was allowed to cool to room temperature and then placed in an ice bath. Neutralization was carried out by the slow addition of 50 ml of 6 *M* hydrochloric acid. A layer of mineral oil was removed and discarded, and the remaining liquid was filtered. Addition of 1 l of water to the filtrate resulted in the formation of a brown, oily solid. Attempts to recrystallize the crude product from methanol were unsuccessful. The NMR spectrum of the crude product confirmed the presence of the desired ligand; NMR(C^2HCl_3) δ 7.97 (s, 4, aryl H), 6.24 (s, 2, CH), 2.27 (s, 6, CH_3), enol H not observed. The crude product was used directly in the preparation of metal complexes.

Syntheses of the La(III) complex with dihed

A procedure similar to one described for the synthesis of lanthanide tris-β-diketonates was employed[36]. A solution of 1.5 g (0.0027 mol) of H_2(dihed) in hot methanol was neutralized with 1.35 ml of 4 M sodium hydroxide. The neutralized solution of the ligand was added dropwise over 30 min to a stirred solution of 0.83 g (0.0019 mol) of lanthanum nitrate hexahydrate in 50 ml of methanol. The resulting mixture was added dropwise over 1 h to 500 ml of vigorously stirred distilled water. The solid product was collected by suction filtration and dried *in vacuo* over P_4O_{10} overnight. Heating the complex to 300°C resulted in a slight discoloration with no melting. Anal. calc. for $[La_2(C_{18}H_6O_4F_{14})_3 \cdot 4H_2O]_n$: C, 32.32; H, 1.31. Found: C, 32.08; H, 1.20.

Synthesis of the La(III) complex with ptb

By the procedure described, a solid with a decomposition point of approximately 230°C was obtained. Anal. calc. for $[La_2(C_{14}H_6O_4F_6)_3 \cdot 6H_2O]_n$: C, 36.33; H, 2.18; Found: C, 36.24; H, 2.11.

Synthesis of the La(III) complex with ppb

By the procedure described, a solid that did not change in appearance at temperatures up to 300°C was obtained. Anal. calc. for $[La_2(C_{24}H_{16}O_4)_2(OH)_2 \cdot 4H_2O]_n$: C, 51.44; H, 3.78. Found: C, 51.13; H, 3.59. The formation of mixed β-diketonate-hydroxo complexes of the lanthanide ions is not unusual[37] and was used by Picker and Sievers[31] to explain the elemental analysis of their Eu(III) complex with dihed.

Synthesis of the La(III) complex with pbb

By the procedure described, a solid that did not melt or appear to decompose at temperatures up to 300°C was obtained. Anal. calc. for $[La_2(C_{14}H_{12}O_4)_3 \cdot 5H_2O]_n$: C, 45.83; H, 4.21. Found: C, 46.12; H, 5.39.

Synthesis of the Cu(II) complex with dihed

The copper complexes were prepared by a modification of a standard literature method for Cu(II) bis-β-diketonates[38]. The ligand (1.5 g, 0.0027 mol) was dissolved with heating in 225 ml of methanol. It was immediately added to a hot solution of 0.75 g (0.0037 mol) of cupric acetate monohydrate in 60 ml of distilled water. After cooling to room temperature, the dark green product was collected by suction filtration. No melting or noticeable decomposition occurred at temperatures up to 400°C. Anal. calc. for $[Cu(C_{18}H_6O_4F_{14})]_n$: C, 35.11; H, 0.98. Found: C, 35.30; H, 1.24.

Synthesis of the Cu(II) complex with ptb

A green solid that did not melt and discolored at 350°C was obtained. Anal. calc. for $[Cu(C_{14}H_6O_4F_6)]_n$: C, 40.45; H, 1.45. Found: C, 39.66; H, 1.35.

Synthesis of the Cu (II) complex with ppb

A dark green solid with a melting point of 247–258°C was obtained. Anal. calc. for $Cu_2(C_{24}H_{16}O_4)(OH)_2 \cdot H_2O$: C, 52.65; H, 3.68. Found: C, 53.19; H, 4.07. This empirical formula, which was found to be most consistent with the analysis data, does not represent a polymeric material.

Synthesis of the Cu(II) complex with pbb

A green solid was collected from the reaction. Anal. calc. for $Cu(C_{14}H_{12}O_4)_2$: C, 60.92; H, 4.38. Found: C, 62.13, H, 7.21. This empirical formula, which was found to be most consistent with the analysis data, does not represent a polymeric material.

Synthesis of the Ni(II) complex with dihed

The complexes of Ni(II) with the bis-β-diketonate ligands were prepared by a modification of a literature method[39]. To 200 ml of hot methanol was added 1.5 g

(0.0027 mol) of H_2(dihed) and 0.8 g (0.0034 mol) of $NiCl_2 \cdot 6H_2O$. After the ligand and metal were dissolved. 1 ml of concentrated aqueous ammonia was added with stirring. The solution became cloudy upon addition of the ammonia. The volume was reduced in half by heating, and the remaining mixture was added dropwise to 500 ml of vigorously stirred distilled water. The green solid was collected by suction filtration. It discolored at 240°C. Anal. calc. for $[Ni(C_{18}H_6O_4F_{14}) \cdot 2H_2O]_n$: C, 33.42; H, 1.56. Found: C, 33.52; H, 1.58.

Synthesis of the Ni(II) complex with ptb

A green solid that discolored at 230°C was obtained. Anal. calc. for $[Ni(C_{14}H_6O_4F_6) \cdot 2H_2O]_n$: C, 37.62; H, 2.25. Found: C, 36.85; H, 2.19.

Synthesis of the Ni(II) complex with ppb

A green solid that did not change in appearance at 300°C was obtained. Anal. calc. for $Ni_2(C_{24}H_{16}O_4)(OH)_2 \cdot 5H_2O$: C, 47.26; H, 4.62. Found: C, 46.74; H, 4.88. This empirical formula was most consistent with the analysis data, but does not represent a polymer.

Synthesis of the Ni(II) complex with pbb

The complex was isolated as a green solid. Anal. calc. for $[Ni(C_{14}H_{12}O_4)]_n$: C, 55.50; H, 3.99. Found: C, 54.70; H, 6.92.

Synthesis of the Zn(II) complex with dihed

Using Zn(II) chloride, the desired complex was synthesized by a procedure identical to that for Ni(dihed). The product was isolated as a white solid that decomposed over the range of 290–293°C. Anal. calc. for $[Zn(C_{18}H_6O_4F_{14}) \cdot 3H_2O]_n$: C, 32.18; H, 1.80. Found: C, 31.99; H, 1.54.

Synthesis of the Zn(II) complex with ptb

A white solid that discolored from 253–275°C was obtained. Anal. calc. for $[Zn(C_{14}H_6O_4F_6) \cdot 2H_2O]_n$: C, 37.07; H, 2.22. Found: C, 37.07; H, 1.99.

Synthesis of the Zn(II) complex with ppb

A white solid that decomposed from 195–230°C was obtained. Anal. found: C, 35.22; H, 4.20. There was no empirical formula consistent with these values.

Synthesis of the Zn(II) complex with pbb

A white solid was isolated from the reaction. Anal. calc. for $Zn_2(C_{14}H_{12}O_4)(OH)_2$: C, 41.11; H, 3.45. Found: C, 41.20; H, 4.63. This empirical formula is most consistent with the elemental analysis, but does not represent a polymer.

Apparatus

The apparatus employed in our study consisted of four valves and sorbent traps (Fig. 1). The valves, heated traps with insulating covers, and temperature controllers for the traps were purchased from Valco (Houston, TX, U.S.A.). Sample introduction was from the Tenax trap preceding valve 1. The traps on valves 1, 2

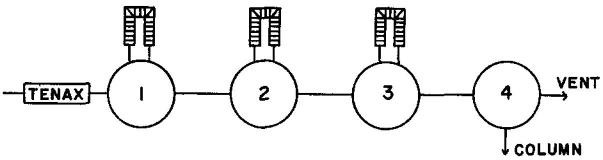


Fig. 1. Schematic of the valve system employed with the sorbents.

and 3 contained the metal polymers. Each trap had its own temperature controlling device. Switching of the air-actuated values was controlled by the microprocessor of the gas chromatograph. Valve 4 provides the option of sending the flow stream to either the column or vent. The positions of valves 1, 2 and 3 allow for flow through, or bypass of, the traps. Up to three metal polymer sorbents can be used in series.

The valve system was attached to a Hewlett-Packard 5880A gas chromatograph. This instrument was equipped with subambient (carbon dioxide) thermal focussing. Chromatograms were run on a 25-m cross-linked 5% phenyl methyl silicone fused-silica capillary column (Hewlett-Packard) at a flow-rate of 1 ml/min using nitrogen as the carrier gas.

Preparation of pre-column containing the metal polymers

The metal polymers were too fine a powder to be packed directly into short pre-columns. Gas Chrom Z 80/100 (Applied Science) was used as the solid support for coating of the metal polymers. The Gas Chrom Z was first coated with a layer of 3% SE-30 to deactivate the surface. The deactivated Gas Chrom Z was then coated with a 3% layer of the metal polymers of ppb, pbb, and ptb. A 5% coating of the dihed complexes was used to account for the higher molecular weight of the ligand. The polymers were dissolved in methanol for this coating step. The metal polymers were not coated directly only the support because of the possibility of uneven coating leaving active sites exposed. The coated support was then packed into 10 × 1/8 in. I.D. heated pre-columns (Valco). The sorbents were conditioned overnight at 150–180°C under a flow of nitrogen gas.

Use of the sorbents

The pre-columns containing the metal polymers were usually maintained at 100°C when employed as sorbents. The sample was introduced into the sorbent series by desorption from the Tenax trap preceding valve 1 (Fig. 1). The desorption of the Tenax was carried out for 5 min. During this desorption step, the effluent from valve 4 was passed onto the analytical column and thermally focussed at a temperature of -50°C. At the end of the desorption, all the sorbents were cooled to room temperature. A chromatogram of the thermally focussed sample, which corresponds to compounds unretained by the metal polymers, was then performed.

The contents of each sorbent were subsequently analyzed. The retained compounds were desorbed over a 5-min period and thermally focussed at the head of the analytical column. The desorption of the metal polymer sorbent was carried out at temperature ranging from 150 to 180°C.

RESULTS AND DISCUSSION

The orientation of the two β-diketone units of I is such that they cannot both coordinate to the same metal ion. In addition, two of these ligands cannot be oriented in such a way as to completely satisfy the requirements of two metal atoms in the 2+ oxidation state. As a result polymeric materials of low volatility and high thermal stability appear to have been obtained for most of the metal chelates[40–43]. The proposed structure of the polymer for Ni(II) is shown in Fig. 2. The elemental analyses for the complexes of Ni(II), Cu(II) and Zn(II) with dihed and ptb, and the Ni(II) complex with pbb are consistent with the structure illustrated in Fig. 2. Empirical formulas most consistent with the analyses of the Cu(II) and Ni(II) complex with ppb, and Zn(II) and Cu(II) complex with pbb indicate monomeric species. Only in the case of Zn(II) and ppb was it impossible to determine an empirical formula consistent with the elemental analysis. The analysis for this compound indicated some type of zinc complex with ppb.

The elemental analyses for the La(III) complexes with dihed, ptb and pbb were consistent with a ratio of two lanthanide ions to three ligands. In the case of La(III) with ppb, a mixed ligand–hydroxo polymeric compound of the formula $La_2(ppb)_2(OH)_2 \cdot 4H_2O$ was most consistent with the analysis data. Picker and Sievers[31] proposed a similar compound to explain analysis data for the Eu(III) complex with dihed.

The metal ions in the β-diketonate polymers are coordinatively unsaturated and will bond to suitable electron pair donors. The equilibrium constant for adduct formation (eq. 1) between a metal β-diketonate complex

$$M(\beta\text{-dik})_x + D \leftrightarrows M(\beta\text{-dik})_x D \qquad (1)$$

and a donor depends on the nature of the chelate ligand[37,44–47], the metal ion of the complex[44,48–51] and steric and electronic effects of the donor. In sorbent applications, which involve the interaction of a gas phase donor with a solid metal chelate, the

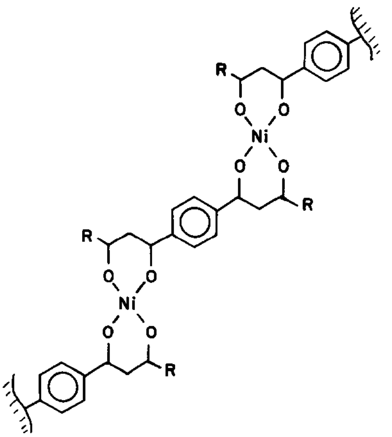


Fig. 2. Proposed structure for the complex of Ni(II) with I.

TABLE I

INFLUENCE OF THE LIGAND ON SORBENT PROPERTIES

Organic	*La(dihed) (%)*	*La(ptb) (%)*	*La(pbb) (%)*	*La(ppb) (%)*
Ketones				
C_5	100*	88	20	8
C_6	100	90	92	29
C_7	100	98	100	29
C_8	100	100	100	78
Methyl esters				
C_1	100	100	16	0
C_2	100	100	<5	7
C_3	100	100	15	15
C_4	100	100	56	58
C_7	100	–**	–	–
C_8	100	–	–	100
Alcohols				
C_4	100	83	100	–
C_5	100	89	100	21
C_6	100	94	100	20
C_7	100	97	100	39
C_8	100	–	–	58
Pyridine	100	–	>95	–
4-Picoline	100	–	–	–
Tetrahydrofuran	100	100	26	–

* Percentage of the compound that was retained by the sorbent at 100°C. See Experimental section for identity of the ligands and preparation of the sorbent traps.

** Compound not analyzed on this sorbent.

magnitude of the association constant is highly dependent on temperature. The influence of metal and ligand on sorbent properties was studied through the use of selected ketones, esters, alcohols, ethers and amines.

Metal chelate polymers of four ligands (R = $-CH_3$, $-CF_3$, $-C_3F_7$ and $-C_6H_5$) were studied as sorbents. Table I lists the percentage of sample injected that was retained by the La(III) complexes with these ligands. These results are representative of the general influence of the ligand on sorbent properties. The ligand influenced the sorbent properties through a combination of electronic and steric effects. It has been demonstrated[46] from studies with NMR shift reagents that the presence of fluorine atoms in the ligand increases the Lewis acidity of the metal. A harder Lewis acid would be expected to associate more strongly with hard Lewis bases. The data in Table I is generally consistent with this conclusion.

The La(III) complex with dihed (R = $-C_3F_7$), the most electron withdrawing ligand of those studied, exhibited the greatest retention of ketones, esters, alcohols, ethers and amines. The complex with ppb (R = phenyl), the most electron donating ligand of those studied, exhibited the least retention. The results with La(ptb) and La(pbb) cannot be explained by electronic effects alone. The retention of ketones, esters and tetrahydrofuran (THF) with these sorbents was consistent with electronic

TABLE II

INFLUENCE OF THE METAL ON SORBENT PROPERTIES

Organic	*La(pbb) (%)*	*Ni(pbb) (%)*	*Cu(pbb) (%)*	*Zn(pbb) (%)*
Ketones				
C_5	20*	30	0	<5
C_6	92	83	<5	4
C_7	100	100	15	36
C_8	100	100	73	93
Methyl esters				
C_1	16	<5	0	0
C_2	<5	8	0	0
C_3	15	17	0	2
C_4	56	74	18	6
Alcohols				
C_4	100	80	3	3
C_5	100	100	31	40
C_6	100	100	66	96
C_7	100	100	100	100
Pyridine	>95	100	82	100
4-Picoline	–**	–	100	100
Tetrahydrofuran	26	23	0	<5

* Percentage of compound that was retained by the sorbent at 100°C. See experimental section for identity of the ligand and preparation of the sorbent traps.

** Compound not analyzed on this sorbent.

effects, whereas the retention of alcohols was not. Alcohols were retained completely by La(pbb) and partially by La(ptb). Increased steric effects of the $-CF_3$ group compared to the methyl group may explain this observation.

Partial retention of members of a homologous series has been noted previously with Eu(dihed)[31]. The association constants between a gas phase donor and solid polymer are lower for more volatile members of a homologous series. The progression from completely unretained to retained compounds typically occurred over three to four carbon atoms.

The influence of metal on sorbent properties is demonstrated by the retention data in Table II. The data in Table II for complexes with the pbb ligand is representative of the results obtained with all four ligands. The sorbent properties of the La(III) and Ni(II) complexes are quite similar, as are the sorbent properties of the Cu(II) and Zn(II) complexes. The enhanced retention of donor compounds by La(III) and Ni(II) compared to Zn(II) and Cu(II) is in agreement with association constants previously reported[44,48–51].

The influence of electronic effects on the retention of a donor can also be noted from the data in Tables I and II. From studies with lanthanide NMR shift reagents, it has been shown that, steric effects being equal, the association constants vary in the following order[52].

amine > alcohol > ketone > ether > ester

TABLE III

INFLUENCE OF TEMPERATURE ON THE SORBENT PROPERTIES OF La(ptb)

Organic	*100°C*	*120°C*	*140°C*
Ethyl acetate	100%*	100%	0%
1-Butanol	100%	67%	0%
Tetrahydrofuran	100%	58%	0%
Butyraldehyde	100%	40%	0%

* Percentage of the compound that was retained by the sorbent. See Experimental section for the preparation of the sorbent trap.

The association of donor compounds with nickel complexes exhibits the following order[53].

amines > alcohols > aldehydes > ketones > esters > ethers > hydrocarbons

The retention data in Tables I and II are consistent with these general rankings. Amines and alcohols were retained more strongly than esters and ketones. The cyclic ether THF exhibited less retention than the C_4 ester and C_4 alcohol in most instances. Aliphatic ethers such as diethylether, because of greater steric hindrance than THF, are not expected to be retained by any of these sorbents[31,37,54,55]. Normal alkanes, benzene and chloroform were not retained by any of the sorbents.

The influence of temperature on sorbent properties is illustrated by the results in Table III. The sorbent employed in this study was the La(III) complex with ptb. Ethyl acetate, 1-butanol, THF, and butyraldehyde were used as donor compounds. At 140°C none of the four compounds were retained by the sorbent. At 120°C ethylacetate was completely retained by the sorbent and the other compounds exhibited partial retention. At 100°C all four compounds were completely retained by the sorbent.

A possible problem with sorbents such as these is that the metal ion may catalyze chemical reactions. It was found by Picker and Sievers[31] that the compound linalyl acetate decomposed to acetic acid and 3-methylene-7-methyl-1,6-octadiene when passed through the Eu(dihed) sorbent. We encountered problems of this nature when employing Ni(dihed) with esters. In this case the esters adsorbed onto the polymer, but attempts at desorbing the esters for subsequent analysis proved unsuccessful. The chromatograms obtained after the desorption step exhibited a large peak with a retention time the same as that of methanol. One possibility is that the Ni(dihed) catalyzes the hydrolysis of esters to alcohols and carboxylic acids. The carboxylic acids, which were not observed in the chromatograms, may have been irreversibly bonded to the sorbent. Therefore, Ni(dihed) was judged unacceptable for general usage as a sorbent.

After proper conditioning, the blank chromatograms of most of the sorbents exhibited only a few small peaks and were judged acceptable for use. The only notable exceptions were the complexes with the ptb ligand. With these sorbents, several large peaks were routinely observed in the chromatograms. The number and size of these peaks increased in the chromatogram of the retained compounds. This is consistent with decomposition of the ligand of the polymer. The proposed structure in Fig. 2 does not explain all the structural features of these complexes. Chain ending free *β*-diketone groups or sodium *β*-diketonate groups must exist to some extent in the polymer. Complexes with the ptb ligand appear to be the most thermally unstable of those studied. Metal complexes with the ptb ligand were therefore judged unacceptable for use as selective sorbents.

The practical utility of these selective sorbents is illustrated by the analyses presented in Figs. 3 and 4. Fig. 3 shows the chromatograms obtained from the analysis of a mixture of selected compounds. A series of two sorbents containing Cu(dihed) and La(dihed), each maintained at 100°C, was employed. Fig. 3a is the chromatogram of compounds unretained by the two sorbents. Only the straight chain alkanes were observed. The chromatogram of those compounds retained by Cu(dihed) is shown in Fig. 3b. Fig. 3c is the chromatogram of those compounds that were unretained by the Cu(dihed) but retained by the La(dihed). Pyridine, the C_7 ester, and the C_8 alcohol were completely retained by the Cu(II) sorbent. The C_2, C_3 and C_4 esters and C_5, C_6 and C_7 ketones were unretained by the Cu(II) sorbent and completely retained

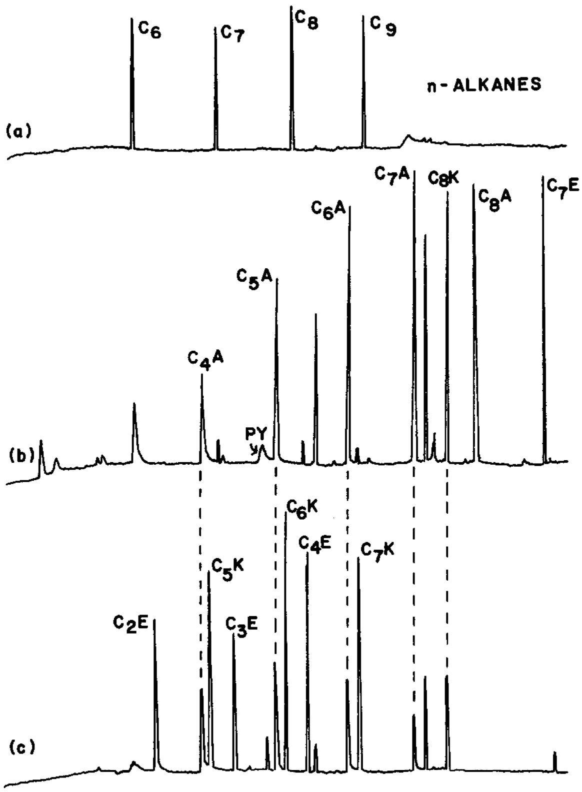


Fig. 3. Chromatograms for a test mixture of compounds: (a) unretained, (b) retained by Cu(dihed) at 100°C and (c) unretained by Cu(dihed) and retained by La(dihed) at 100°C. A = alcohols, K = ketones, E = esters, PY = pyridine. Thermally focussed at −50°C for 5 min and then 3°C/min to 150°C. See Experimental section for column and sorbent description.

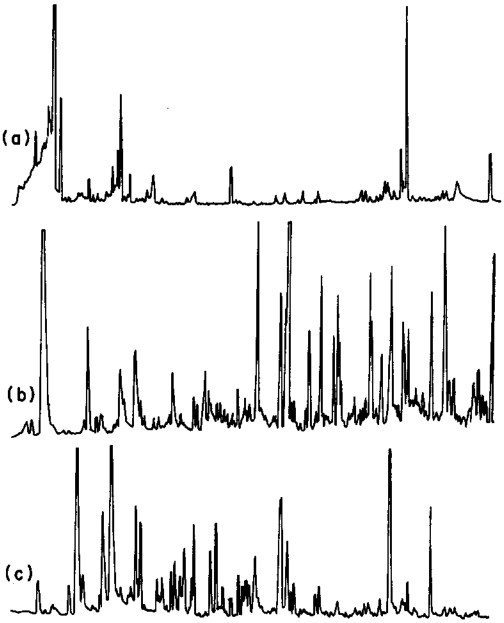


Fig. 4. Chromatograms for cigarette smoke. (a) Unretained, (b) retained by Cu(dihed) at 100°C and (c) unretained by Cu(dihed) and retained by La(dihed) at 100°C. Thermally focussed at $-50°C$ for 5 min and then 2°C/min to 150°C. See Experimental section for column and sorbent description.

by the La(III) sorbent. The Cu(II) complex partially retained the C_8 ketone, and the C_4, C_5, C_6 and C_7 alcohols. The enhanced retention of longer chain alcohols by the Cu(II) sorbent is apparent by inspection of the peak heights in Fig. 3b.

The application of the same series of sorbents to cigarette smoke is shown in Fig. 4. The sample was obtained by drawing smoke from the end of a cigarette through a trap containing Tenax-GC. Fig. 4a, b and c show the chromatograms for those compounds that were unretained, retained by Cu(dihed), and retained by La(dihed), respectively. Significant differences are observed between the chromatograms for compounds retained by the copper and lanthanum sorbents. The larger peaks in the chromatogram of those compounds retained by the copper sorbent (Fig. 4b) are in the latter half, and are therefore the less volatile Lewis bases in the sample. The copper sorbent does retain some volatile compounds, as inferred by the early eluting peaks. Many of these peaks exhibit tailing, which is indicative of highly polar compounds such as alcohols and amines. The chromatogram of those compounds retained by the lanthanum sorbent (Fig. 4c) exhibits larger peaks in the first half. These peaks probably correspond to the more volatile Lewis bases in the sample. The chromatograms of the unretained compounds (Fig. 4a) contains a considerable number of small peaks. Adjusting the attenuation of the instrument, or increasing the initial sample size, would facilitate the analysis of the unretained compounds.

Based on our preliminary findings, which include an assessment of the blanks, catalytic activity, and sorbent properties, the series Zn(ppb), Cu(dihed), La(pbb), and La(dihed) offers the widest degree of selectivity for the retention of oxygen- and nitrogen-containing compounds. When used in the order listed above, this series provides the opportunity to convert a sample with one complex chromatogram into a set of five simpler chromatograms. If particular compounds are of interest, only the sorbents on which they were retained could be analyzed. The influence of temperature allows for a certain degree of "fine tuning" of a sorbent to insure complete retention of a particular compound.

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