Journal of Chromatography, 349 (1985) 469–479
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROMSYMP. 667

GAS CHROMATOGRAPHIC AND LIQUID CHROMATOGRAPHIC SEPARATIONS OF GEOMETRICAL ISOMERS OF TRIS(2,2,7-TRIMETHYLOCTANE-3,5-DIONATO)CHROMIUM(III) AND COBALT(III) CHELATES AND OTHER Cr-β-DIKETONATES

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SUMMARY

A number of metal chelates with the anion of the recently synthesized ligand, 2,2,7-trimethyloctane-3,5-dione (Htod) have been investigated for their use in gas and liquid chromatographic separations of transition metals. $Cr(tod)_3$ shows extraordinary stability in gas chromatographic columns at temperatures high enough to produce reasonably rapid elution. $Cr(tod)_3$ and $Co(tod)_3$ form geometrical isomers, which can be separated on a 5-μm particle size, reversed-phase (RP), surface-bonded silica analytical high-performance liquid chromatographic (HPLC) column with acetonitrile and water as eluents, on a normal-phase column, and by thin-layer chromatography (TLC) and HPTLC with hexane and methylene chloride. The metal chelates and the isomers of the more stereochemically rigid complexes have been characterized by thermogravimetric analysis, mass spectrometry, and, in the case of the diamagnetic $Co(tod)_3$ by nuclear magnetic resonance spectrometry. Additionally, the separation of all of the geometrical isomers in a mixture of $Cr(tfa)_3$, $Cr(fod)_3$ and $Cr(tod)_3$ was accomplished in a single RPLC experiment. (Abbreviations: Htfa = 1,1,1-trifluoro-2,4-heptanedione; Hfod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione.)

INTRODUCTION

Gas and liquid chromatographic methods for trace analysis of metals generally include a chelation step to yield uncharged complexes. β-Diketones have been used for chelation, and Lederer[1] suggested in 1955 that they could be used for gas chromatography (GC). Books by Moshier and Sievers[2] and Guiochon and Pommier[3] and reviews by Uden and Henderson[4] and Sievers and Sadlowski[5], provide comprehensive coverage of this subject up to 1978. The search for more volatile, more uni-

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0021-9673/85/$03.30

versally applicable complexing agents has been intriguing and continues to be a challenge. The introduction of fluorinated moieties, such as CF_3-, C_2F_5- and C_3F_7-, or of bulky butyl and benzoyl groups, results in metal chelates with greater volatility and other interesting properties. Among the many metal chelates which can be separated and detected by GC, the Cr-β-diketonates are especially interesting[6–12]. Improved separations have been accomplished with capillary columns 5–10 m in length[13–16].

β-Diketonates were employed for high-performance liquid chromatographic (HPLC) separations of metals by Huber *et al.*[17] in 1972. Since that time, a number of papers on HPLC have appeared, but so far GC applications have been more common[18–30]. The separation of geometrical isomers by normal-phase LC has been reported by Uden *et al.*[20] and by Tollinche and Risby[27] and the reversed-phase (RP) LC of Cr(benzoylacetone)$_3$ by Gurira and Carr[31].

In 1981, Sievers and Wenzel[32] reported the synthesis of the ligand, 2,2,7-trimethyloctane-3,5-dione(Htod), and of several rare-earth chelates of this ligand. Studies of this ligand, chelated with some other metal ions, have been conducted[33,34]. In the present case, we have studied the thermal stability and gas–liquid chromatographic behavior of metal–tod chelates. Additionally, we have examined LC separation of the Cr(tod)$_3$ and of some other Cr-β-diketonates on reversed-phase C_{18}-bonded silica columns.

EXPERIMENTAL

Preparation of Htod

Htod was prepared according to the Claisen condensation procedure reported earlier[32,33].

Instruments

Thermogravimetric analyses (TGA) were performed by means of a Perkin-Elmer TGS-2 thermogravimetric analyzer system. The sample was kept under a flow of helium (60 ml/min) while being heated at 10°C/min. The ultraviolet and visible spectrum of Htod was obtained with a Cary 219 UV–VIS spectrophotometer (Varian Assoc.). HPLC was performed with a Hewlett-Packard 1084B liquid chromatograph equipped with a 79850B terminal. The detector with a 10-mm path length flow-cell, having a volume of 12 μl, was operated at 275 nm. RP-HPLC columns contained silica to which *n*-octyl or *n*-octadecyl groups were bonded [RP-8, 10 μm, 200 × 4.6 mm I.D. (Hewlett Packard 79918B) with a Whatman Pellicular C_{18} Pre-column; Alltech RP-18, 5 μm, 250 × 4.6 mm I.D.; Rainin Microsorb C_{18}, 5 μm, 250 × 4.6 mm I.D. or Alltech Si 60, 5 μm, 250 × 4.6 mm I.D. were employed]. A Hewlett-Packard 79825A fraction collector was used. Two gas chromatographs were used: (a) a Hewlett-Packard 5830A with a Grob-type injection port and flame ionization detector and (b) a Hewlett-Packard 5880A, equipped for on-column injection and with a flame ionization detector.

GC–mass spectrometry (MS) experiments were performed with a Hewlett-Packard 5982A gas chromatograph–mass spectrometer–data system that was equipped with a Grob-type injection port and modified so that a fused-silica capillary column (DB5, 0.31 mm I.D., 1-μm film thickness) (J & W Scientific, Rancho Cordova, CA, U.S.A.) was coupled directly to the ion source of the mass spectrometer. The column head pressure was 10 p.s.i.g. Mass spectra of pure solid compounds were obtained with a Varian MAT CH5 mass spectrometer. NMR spectra were obtained with a Varian EM 390 spectrometer.

RESULTS AND DISCUSSION

HPLC

For the RPLC separations, the detector wavelength was 275 nm. Because Htod and its chelate derivatives have a maximum absorbance in the range of 200–450 nm, the eluents selected were HPLC-grade methanol, acetonitrile, water, hexane and methylene chloride. The water was deionized, distilled, and filtered through a 0.45-μm Millipore filter. In one experiment, 0.1% triethylamine (Eastman Kodak) was added to methanol as an auxiliary complexing agent, but this did not reduce tailing. The metal complexes, dissolved in either methanol or acetonitrile, were kept in standard injection vials, which were sealed with a rubber/aluminium cap. Injection volumes of 2–10 μl were used, but a constant volume was used for comparable experiments.

Syntheses of the complexes of tod are reported elsewhere[32]. The tod complexes of chromium(III) and cobalt(III) exhibit peaks with longer retention times (t_R) than the peaks from the other metal complexes. We have demonstrated by MS of collected fractions (*vide infra*) that $Cr(tod)_3$ and $Co(tod)_3$ are eluted intact. The use of greater proportions of water in the eluent increased the peak tailing of all complexes, except for $Cr(tod)_3$ and $Co(tod)_3$. It is possible to separate $Cr(tod)_3$ and $Co(tod)_3$ from the other tod complexes by starting with acetonitrile, and, after the elution of the chromium(III) and cobalt(III) compounds, changing the eluent to methanol. A broad band of peaks from the other compounds [*e.g.*, $Ni(tod)_2$] then appears after those from $Co(tod)_3$ and $Cr(tod)_3$. The tod chelates of chromium(III) and cobalt(III) have relatively long retention times, even with very small amounts of water in acetonitrile. $Cr(tod)_3$ and $Co(tod)_3$ each give rise to two peaks when this eluent is used (Fig. 1).

UV–VIS spectra were obtained for each of the two geometrical isomers of $Cr(tod)_3$ and of $Co(tod)_3$. These stopped-flow spectra were measured at maximum peak height from 190 to 540 nm when background absorbance is subtracted auto-

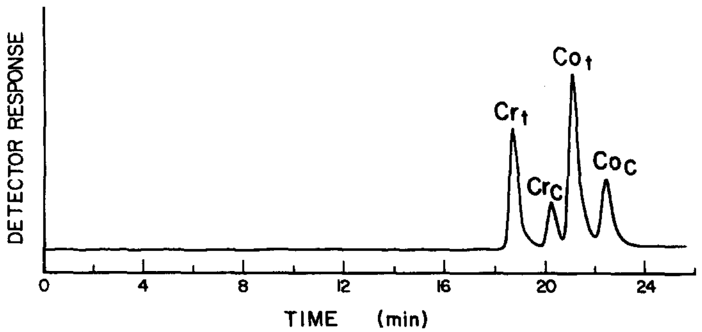


Fig. 1. HPLC separation of $Cr(tod)_3$ and $Co(tod)_3$. t = *trans*; c = *cis*. Conditions: RP-18 (5 μm) analytical column; detector, 275 nm; eluent, acetonitrile–water (98.7:1.3); flow-rate, 1 ml/min.

TABLE I

ABSORPTION BANDS OF $Cr(tod)_3$ AND $Co(tod)_3$

		λ_{max} (nm)
$Cr(tod)_3$	*trans*	260, 278, 340
	cis	260, 278, 340
$Co(tod)_3$	*trans*	238, 268, 325 (shoulder)
	cis	238, 268, 325 (shoulder)

matically. Each metal chelate shows three absorption bands, but without significant differences between the two isomers formed from each metal (see Table I). Htod is an unsymmetrical β-diketone, which can form geometrical isomers with *trans*(*mer*) and *cis*(*fac*) configurations about an octahedral coordination sphere (Fay–Piper) (Fig. 2). Characterization of these isomers was accomplished by using appropriate fractions from the HPLC separations. Sufficient material for crystallization and MS characterization or NMR studies [in the case of the diamagnetic cobalt(III) complex] was obtained by repeating the separation twenty times. Evaporation of the solvent mixture of acetonitrile and water at room temperature under a stream of nitrogen yielded a solid, from which mass spectra were obtained. These data are reported in Table II. The spectra show in all cases the characteristic metal isotope peaks for $M(tod)^+$; $M(tod)_2^+$ and $M(tod)_3^+$. For comparison with the spectra obtained by the magnetic sector instrument, additional quadrupole mass spectra of $Cr(tod)_3$ were obtained after GC separation. The GC–MS (quadrupole) results are shown in Table III.

The separation of geometrical isomers can also be accomplished by using polar normal-phase LC material[20,27].

TLC experiments with $Cr(tod)_3$ and $Co(tod)_3$ are easily performed. Mixtures of methylene chloride and hexane are appropriate[20,27]. The TLC plates can be used without further equilibration. An optimized TLC separation can easily be applied in HPLC. Mobile phase mixtures containing less than 50% methylene chloride yielded low R_F values and gave poor separation. A mobile phase of methylene chloride containing up to 10% hexane separates the isomers of $Cr(tod)_3$ and $Co(tod)_3$, but the *mer* isomer of $Co(tod)_3$ is not well separated from the *fac* isomer of $Cr(tod)_3$. A solution of 20% hexane in methylene chloride was used for the separation and then applied in column chromatography (Fig. 3).

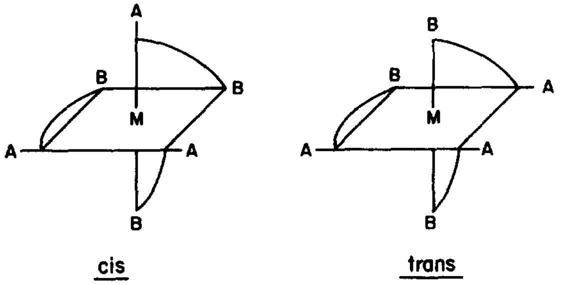


Fig. 2. Geometrical isomers of octahedrally coordinated metals with non-symmetrical bidentate ligands.

TABLE II

MAGNETIC SECTOR MASS SPECTRAL DATA (RELATIVE ABUNDANCE > 10%)

		m/z	*Rel. abundance*	*Assignments*
Cr(tod)$_3$	*trans*	57	11	Butyl
		235	33	^{52}Crtod$^+$
		418	100	^{52}Cr(tod)$_2^+$
		419	62	
		420	17	
		601	90	^{52}Cr(tod)$_3^+$
		602	44	
		603	12	
Cr(tod)$_3$	*cis*	235	27	^{52}Crtod$^+$
		361	11	Cr(tod)$_2^+$-butyl
		416	12	
		418	100	^{52}Cr(tod)$_2^+$
		419	58	
		420	18	
		601	84	^{52}Cr(tod)$_3^+$
		602	42	
		603	16	
Co(tod)$_3$	*trans*	57	32	Butyl
		127	30	Htod-butyl
		242	27	Co(tod)$^+$
		368	100	Co(tod)$_2^+$-butyl
		369	22	
		422	30	
		423	10	
		425	70	Co(tod)$_2^+$
		426	20	
		608	32	Co(tod)$^+$
		609	12	
Co(tod)$_3$	*cis*	43	43	
		57	33	Butyl
		127	37	tod-butyl
		242	27	Co(tod)$^+$
		341	14	
		368	100	Co(tod)$_2^+$-butyl
		369	22	
		382	11	
		422	29	
		423	11	
		425	73	Co(tod)$_2^+$
		426	20	
		608	29	Co(tod)$_3^+$
		609	12	

On reversed-phase columns, the isomers of Co- and Cr(tod)$_3$ are eluted in this sequence, while on normal-phase columns the *mer* isomers are eluted before the *fac* isomers. The mean difference in retention times for the isomers of each chelate is higher in normal-phase than in reversed-phase chromatography (Table IV).

TABLE III

GC–QUADRUPOLE MASS SPECTRAL DATA OF Cr(tod)$_3$ ISOMERS

		m/z	*Rel. abundance* (≥*10%*)	*Assignments*
Cr(tod)$_3$	*trans*	57	11	$C_4H_9^+$
		235	56	$^{52}Cr(tod)^+$
		236	13	
		361	15	$^{52}Cr(tod)_2^+$-butyl
		418	100	$^{52}Cr(tod)_2^+$
		419	83	
		420	26	
		601	16	$^{52}Cr(tod)_3^+$
Cr(tod)$_3$	*cis*	57	10	$C_6H_9^+$
		235	49	$^{52}Cr(tod)^+$
		236	11	
		361	11	$^{52}Cr(tod)_2^+$-butyl
		418	100	$^{52}Cr(tod)_2^+$
		419	80	
		420	26	
		601	20	$^{52}Cr(tod)_3^+$
		602	10	

RPLC-separation of the isomers of some Cr.β-diketonates

In addition to obtaining data on the separation of complexes of different metals, we have separated several different β-diketonate complexes of chromium(III) in a single chromatographic experiment. β-Diketone chelates of chromium(III) were

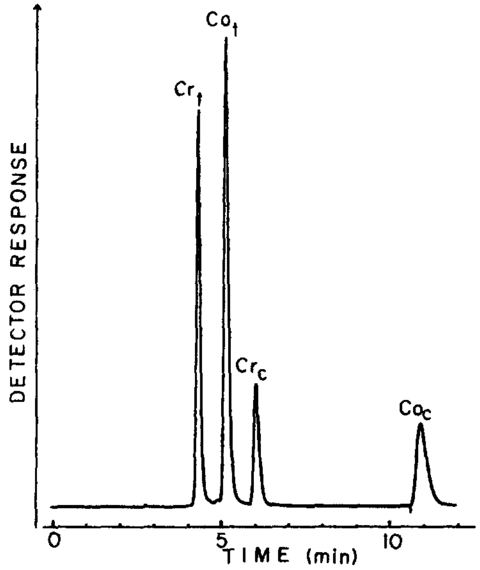


Fig. 3. HPLC separation of Cr(tod)$_3$ and Co(tod)$_3$. t = *trans*; c = *cis*. Conditions: NP Si 60 (5 μm) analytical column; detector, 275 nm; eluent, methylene chloride–hexane (80:20); flow-rate, 1 ml/min.

TABLE IV

k' VALUES OF *mer* AND *fac* $Cr(tod)_3$ AND $Co(tod)_3$

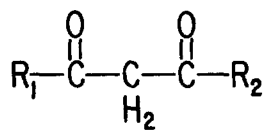
For conditions see Figs. 1 and 3

		Normal phase	*Reversed phase*
$Cr(tod)_3$	*trans*	1.30	5.57
$Cr(tod)_3$	*cis*	1.82	6.05
$Co(tod)_3$	*trans*	1.55	6.28
$Co(tod)_3$	*cis*	3.28	6.72

prepared with each of the following ligands: 1,1,1,5,5,6,6,6,7,7,7-decafluoro-2,4-heptanedione (Hdfhd); 1,1,1-trifluoro-2,4-heptanedione (Htfa); and 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione(Hfod) (Fig. 4).

Good resolution of the chromium(III) complexes of dfhd, tfa, fod and tod was obtained with the RP-8 column and a pre-column, but the geometrical isomers of each were not separated. The chromatogram is shown in Fig. 5. Using a C_{18} (5 μm) column with acetonitrile (a less polar eluent) and a different gradient, the isomers of the $Cr(tfa)_3$, $Cr(fod)_3$ and $Cr(tod)_3$ were also separated (Fig. 6). The isomers of $Cr(dfhd)_3$ were not separated under these conditions. The elution order was *cis*-$Cr(tfa)_3$, *trans*-$Cr(tfa)_3$, *cis*-$Cr(fod)_3$, *trans*-$Cr(fod)_3$, *trans*-$Cr(tod)_3$, *cis*-$Cr(tod)_3$. These assignments were made by comparison with the retention times of the pure compounds. The results obtained are in reasonably close agreement with the statistically expected (3:1) ratio of *trans*:*cis* isomers.

The elution order of the isomers with fluorinated ligands is expected because, with tfa and fod, the *cis* isomers are much more polar than the trans isomers, as all



$R_1-C(=O)-CH_2-C(=O)-R_2$

—t-butyl	—isobutyl	:	H(tod)
—t-butyl	$-C_3F_7$	:	H(fod)
$-CF_3$	$-C_3F_7$	:	H(dfhd)
$-CF_3$	$-CH_3$	:	H(tfa)

Fig. 4. β-Diketones studied (in *keto* form; the *enol* form is usually predominant).

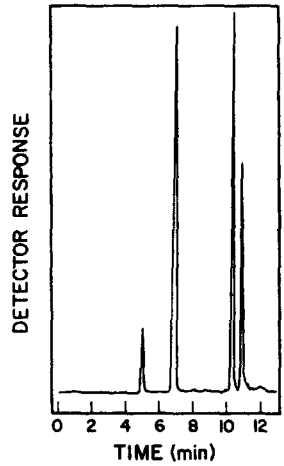


Fig. 5. HPLC separation of $Cr(dfhd)_3$, $Cr(tfa)_3$, $Cr(fod)_3$ and $Cr(tod)_3$ (listed in order of elution). Conditions: RP-8 (10 μm) 20 cm × 4.6 mm I.D. with a 3-cm pre-column; detector, 275 nm; eluents:- 0–8 min gradient methanol–water (50:50 to 95:5), after 8 min, isocratic with methanol–water (95:5); flow-rate, 1 ml/min.

the fluorinated end groups lie above the three edges of one area of the octahedron, while in the *trans* isomer the fluorinated groups are more evenly distributed on all sides, making this isomer less polar and less readily eluted in the reversed-phase mode.

The alteration in the elution order from *cis* then *trans* with the fluorinated compounds to *trans* then *cis* with the non-fluorinated tod should be noted. In the case of Cr(tod)$_3$, differences in permanent dipoles, generated by differing locations of the *tert.*-butyl groups *vs.* iso-butyl groups, are much smaller than those observed for methyl *vs.* trifluoromethyl in Cr(tfa)$_3$. Consequently, an induced dipole effect may predominate. The *cis* isomer of tod, with the longer alkyl-chains on one side of the octahedron, may interact more strongly with surface-bonded octadecyl groups. As only a part of the complex can interact with the bonded stationary phase, the more symmetrical *cis*-tod-isomer is retained longer than the non-symmetrical *trans*-isomer.

Thermogravimetric analysis

To establish sufficient volatility and stability of compounds, TGA studies were performed. If a compound is readily and totally volatilized, it can be used for GC separations. For the TGA studies, 2–6 mg of the metal complex were placed in a small platinum pan and heated at 10°C/min from 25 to 450°C under a stream of flowing helium.

The results of studies on the volatility and thermal stability of metal–tod chelates are given in Table V as the temperature at which 50% of the weight has been

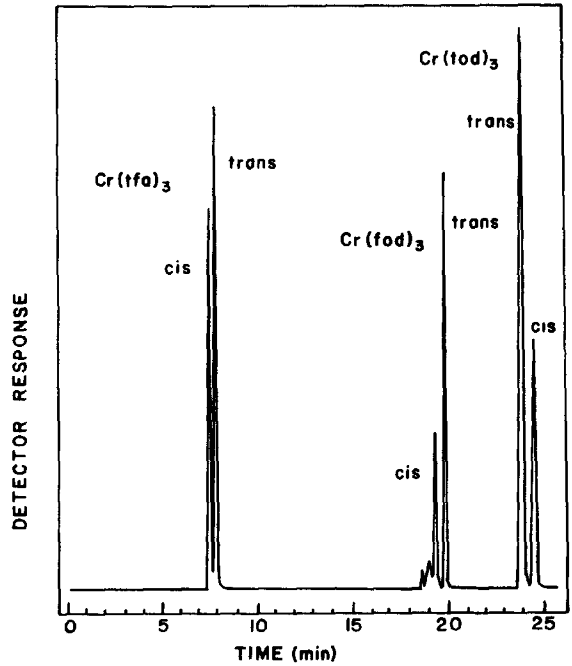


Fig. 6. Separation of geometrical isomers of Cr(tfa)$_3$, Cr(fod)$_3$ and Cr(tod)$_3$ by HPLC. Conditions: RP-18 (5 μm) analytical column; detector, 275 nm; eluent: 0–9 min, isocratic acetonitrile–water (75:25); 9–12 min, gradient acetonitrile 75–100% then 100% acetonitrile; flow-rate, 1 ml/min.

TABLE V

TGA STUDIES OF METAL–tod COMPLEXES

Metal	*$T_{1/2}$ (°C)*	*Residue at 450°C (%)*
$Cr(tod)_3$	209	1
$Co(tod)_3$	207	2.5
$Cu(tod)_2$	206	2
$Pd(tod)_2$	210	1.5

lost, ($T_{1/2}$), and as the mass of residue after heating to 450°C, expressed as a percentage of the initial sample. Weight loss from $Cr(tod)_3$, $Co(tod)_3$, and $Pd(tod)_2$ chelates occurred over narrow temperature ranges, and less than 2% residue remained.

$Cr(tod)_3$ appears to exhibit excellent thermal stability. It is easily volatilized, but at higher temperatures than the chromium(III) complexes of several fluorinated β-diketones studied earlier. It may be worth noting that Htod is synthesized from methyl isobutyl ketone and pivalic acid, which are much less expensive starting materials than those from which the fluorinated ligands are derived.

Gas chromatography of metal–tod complexes

The data from the TGA experiments show that only four of the tod complexes studied are not readily decomposed when heated under helium: $Cu(tod)_2$, $Cr(tod)_3$, $Co(tod)_3$ and $Pd(tod)_2$. These compounds were selected for further study by GC. Optimum resolution and separation conditions were obtained with fused-silica capillary columns (10 m × 0.31 mm I.D.), coated either with SE-54 or its crossed-linked analogue (Ultra No. 2, Hewlett-Packard). On-column injection is preferable to eva-

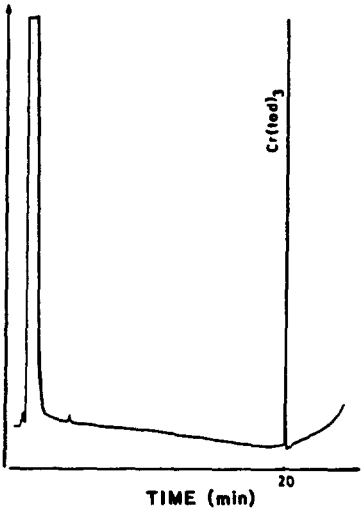


Fig. 7. Flame ionization detection chromatogram of $Cr(tod)_3$ dissolved in hexane. Conditions: injection port, 200°C; starting temperature, 100°C; heating rate, 4°C/min. Fused-silica capillary column; stationary phase, SE-54 polymethyl phenylvinylsiloxane, 25 m × 0.31 mm I.D.

porizing injection methods, which cause decomposition of the complexes, with the exception of $Cr(tod)_3$, which appears to be stable in both methods. Generally, improved performance was obtained at linear velocities of carrier gas that were two to five times greater than those normally used.

In all cases, a flame ionization detector was used, except for the determination of the $Cr(tod)_3$ isomers, in which case GC–MS data were obtained with a capillary column (J&W Scientific, DB5, 30 m × 0.31 mm I.D., 1-μm cross-linked polysiloxane film thickness). When helium was used as a carrier gas, slightly longer retention times were observed than with hydrogen.

$Cu(tod)_2$ complexes were partly decomposed under the gas chromatographic conditions described (see Fig. 7). $Pd(tod)_2$ also decomposes under these conditions. In both cases, decomposition occurs on the column, and there was always only a very small peak with a retention time corresponding with that of Htod. Mixtures of $Cu(tod)_2$ or $Pd(tod)_2$ with $Co(tod)_3$ and $Cr(tod)_3$ could not be resolved without reactions occurring in the chromatograph, which yielded irreproducible results for all of the complexes except $Cr(tod)_3$. $Cr(tod)_3$ was stable under all conditions studied, even in the presence of the other metal tod chelates. (Fig. 7)

CONCLUSIONS

The ligand Htod reacts to form metal chelates with many bivalent and trivalent metal ions. It was the aim of these studies to determine whether complexes of this ligand would be suitable for chromatographic separations either by LC or by GC. $Cr(tod)_3$ is volatile and thermally very stable. It appears to have the broadest possibilities for chromatographic separations or other applications in which vapor phase transport is required. The TGA shows a sharp end point; the complex is completely volatilized and has a sufficient vapor pressure for analysis by GC. It is eluted without any apparent decomposition and it is stable enough to survive volatilization from an injection port maintained at 250°C. The resulting GC peaks are symmetrical. $Co(tod)_3$ is less stable and is eluted from a GC column only under specific conditions, such as high carrier-gas flow-rate at 165°C. For $Co(tod)_3$ elution, the column should not be longer than 10 m. The necessity of using short columns for somewhat less stable compounds has been noted earlier[16]. A gas chromatographic separation of $Co(tod)_3$ from $Cr(tod)_3$ is possible, but, in the presence of other metal–tod compounds, $Co(tod)_3$ decomposes slowly.

$Cr(tod)_3$ and $Co(tod)_3$ differ widely in their LC behavior and are easy to separate from all other metal–tod compounds studied, especially when a less polar eluent is used in the reversed-phase mode. With acetonitrile and a small amount of water, each of three different chromium(III) chelates with non-symmetrical ligands is resolved into two peaks, which have been identified as arising from the respective geometrical isomers. Complexes of tod with metals such as V(IV), Mn(III), Ni(II), Cu(II), Pd(II), Hg(II), Ce(IV) and Pr(III) were not separated under the HPLC conditions studied.

Additionally, a separation by HPLC of four different β-diketonates of Cr(III) on a reversed-phase column was obtained. It was also shown that during a single HPLC experiment, the isomers of $Cr(tfa)_3$, $Cr(fod)_3$ and $Cr(tod)_3$ can be separated.

ACKNOWLEDGEMENTS

The assistance of K. C. Brooks, R. S. Hutte and J. N. Gillis with some of the experiments is gratefully acknowledged. B.W. thanks the Department of Chemistry and Biochemistry, and the Cooperative Institute for Research in Environmental Sciences for staff support during his studies there.

This work was supported by the Air Force Office of Scientific Research under Grant No. AFOSR-84-0093.

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