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Comparison of the liquid and gas chromatography of five classes of metal complexes

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Abstract

The chromatographic behaviour (GC and/or LC) of metal complexes of five ligand types (various salicylaldimines and Schiff bases, a fluorinated β-diketone and β-dithione and a hexadentate macrocycle) is reported. Metal ions included the lanthanides, transition metals, platinum, palladium, and zinc. Dissociation and thermal instabilities were seen as the main limitations in the chromatography of such derivatives. These effects were minimised by the use of selected multidentate or macrocyclic ligands. If the latter have suitable chromophore properties, they may be useful precolumn derivatizing reagents for trace metal analysis by LC. Diastereoisomers of oxovanadium(IV) complexes of tetradentate Schiff bases were resolved by both GC and LC.

Keywords: Complexation; Metal complexes

1. Introduction

Complexation chromatography can be considered as a generic term encompassing all chromatographic separations dependent on complexation (Lewis acid–base interactions) including the use of metal ions or metal complexes in the stationary phase [1]. The versatility of complexation chromatography is due, in part, to its suitability in all areas of chromatography including gas chromatography (GC), thin-layer chromatography (TLC), high-performance liquid chromatography (HPLC) and supercritical fluid chromatography [2,3]. Other reasons are the vast range of Lewis acids, bases and complexes available, the different ways that they can be incorporated in the chromatographic column and the fact that in many cases conventional chromatographic columns or packings (e.g. silica adsorption, reversed phase and ion exchange) may be utilized.

One aspect of complexation chromatography has been exploited in both GC [4] and LC [2] for the ultra-trace determination of metal ions. The range of ligands examined for this purpose is extensive [2–7]. In some instances, this application has involved the separation of naturally occurring complexes such as the photosynthetic pigments [8] but, in the more usual case, it involves a pre-column derivatisation of the metal ions with a suitable complexing agent. While the number of successful applications in GC is limited, the LC of complexed metal ions is a valuable analytical technique [2,3,9] which combines the advantages of versatility, specificity and sensitivity with the capacity for simultaneous determi-

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nation. These advantages have justified the on-going search for suitable derivatising reagents.

This paper presents data on five groups of metal complexes relevant to the determination of metal species as complex derivatives by GC or LC. The success of pre-column derivatization depends on a number of factors: ligand selectivity, and thermodynamic and kinetic stabilities of the complexes and components of the chromatographic system (i.e. mobile phase, stationary phase and metal components) [2,6,9–13].

2. Experimental

2.1. Reagents

Water was obtained from a Millipore Milli-Q system. HPLC-grade solvents were used without further purification other than filtration through Millipore filters. Other reagents were used as purchased.

2.2. Syntheses

The various ligands (Fig. 1) and complexes were prepared as follows.

(1) Salicylaldimine complexes of divalent copper, nickel, palladium, platinum, cobalt, zinc, cadmium and beryllium plus iron(III), oxovanadium(IV) and dioxouranium(VI): salicylideneaminomethane (I) was available from commercial sources. The ligands *N,N′*-disalicylideneethylenediamine (H_2enSal$_2$) (II) and 1,1,1-tris(salicylideneaminomethyl)ethane (H_3tren(sal)$_3$) (III) were prepared by reacting salicylaldehyde in 2 or 3 molar ratios with ethylenediamine or 1,1,1-triaminomethylethane, respectively, in boiling ethanol. The crude products were recrystallised from aqueous ethanol. Complexes of I and II were prepared by reacting ammoniacal solutions of the appropriate metal ion (as above) with the purified ligands. The precipitated complexes were recovered by filtration, washed with water and recrystallised from aqueous methanol. The copper(II) and iron(III) complexes of III were prepared by the addition of small amounts of solid ligand to a methanolic solution of the metal acetate. The mixture was heated for 10 min and cooled. Following addition of water, the complex was extracted with dichloromethane and purified by column chromatography on silica gel. The electron impact ionization (EI) mass spectra of the copper(II) and iron(III) complexes of III exhibited molecular ion peaks, peaks at m/z 349 corresponding with the loss of (metal ion+C_6H_5) from the molecular ion and peaks at m/z 176.

(2) Complexes of 4-thiolopent-3-ene-2-thione (IV) with divalent nickel, palladium, platinum and zinc and trivalent iron, rhodium and chromium were prepared according to published procedures [14].

(3) The ligand 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione (Hfod, V) and corresponding lanthanide chelates were prepared as previously described [15].

(4) Oxovanadium(IV) complexes of the Schiff bases, VI: synthesis of 2,3-propylenebis(4-aminopent-3-ene-2-one) [H_2aapd; VIa], 2,3-propylenebis(4-amino-1,1,1-trifluoropent-3-ene-2-one) [H_2fapd; VIb], 2,3-propylenebis(5-amino-2,2-dimethylhex-4-ene-3-one) [H_2papd; VIc], 2,3-propylenebis(3-amino-1-phenylbut-2-ene-1-one) [H_2bapd; VId] and 2,3-propylenebis(4-amino-1,1,1-trifluoro-6-methylhept-3-ene-2-one) [H_2tbmpd; VIe] was obtained by the 2:1 condensation of pentane-2,4-dione, 1,1,1-trifluoropentane-2,4-dione, 2,2-dimethylhexane-2,4-dione, phenylbutane-1,3-dione or 1,1,1-trifluoro-6-methylheptane-2,4-dione, respectively, with racemic 1,2-propylenediamine in ethanol. The reaction mixture was heated on a steam bath for 1 h to affect condensation following which water was added and a white crystalline precipitate was obtained on cooling in each case. The compounds were collected by filtration, washed with cold water and recrystallised from aqueous ethanol.

The resolution of racemic 1,2-propylenediamine was obtained by fractional crystallisation of the tartrate salts from water (at 35°C) by the procedure of Dwyer et al. [16] and steam distilled from solid NaOH. H_2fapd(−) and H_2fapd(+) were prepared and purified as described above.

The oxovanadium(IV) complexes were prepared by reacting vanadyl acetate with ligand in methanol, the former being prepared by reacting vanadyl sulfate with a stoichiometric amount of ammonium acetate in methanol and filtering to remove the precipitated ammonium sulfate. The mixture was

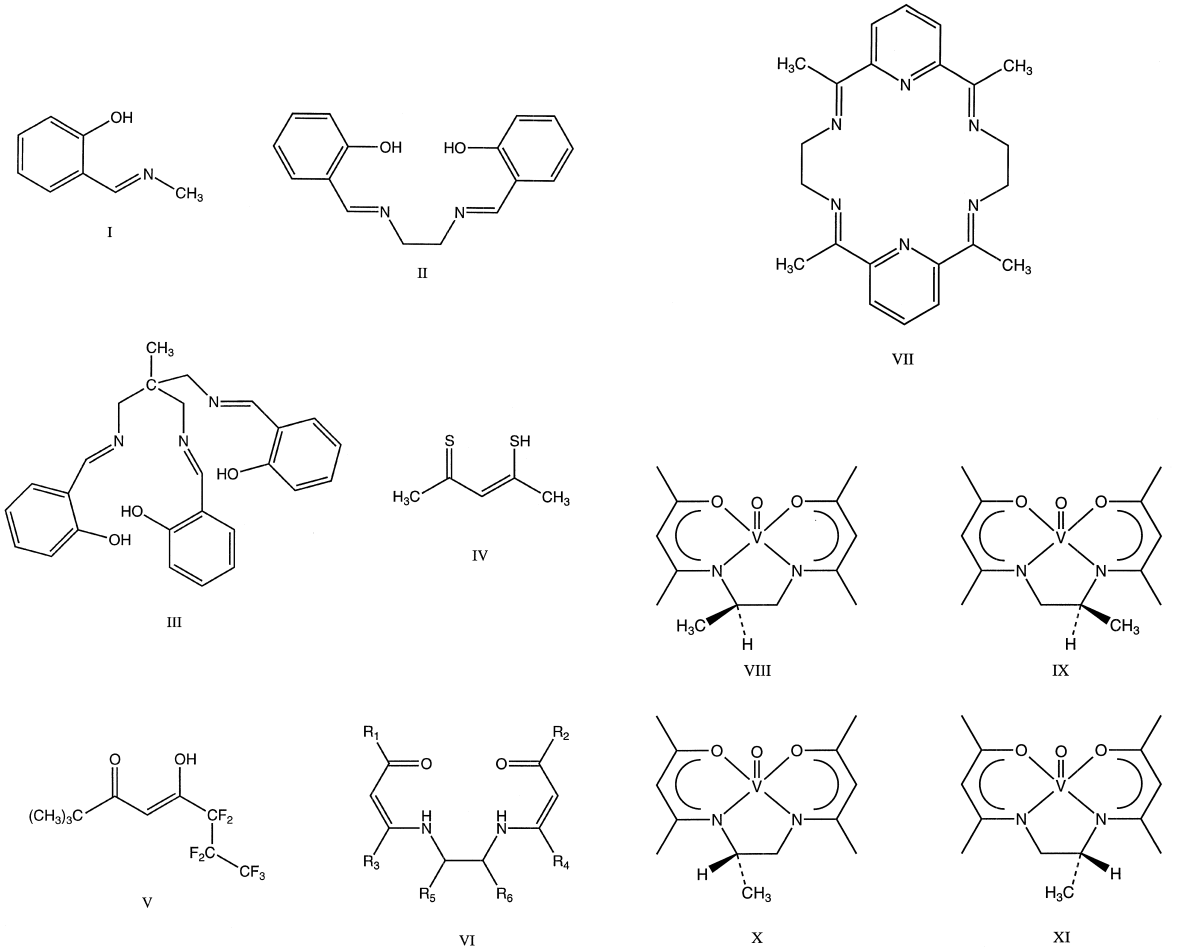

Fig. 1. Chemical structures of the various ligands and stereoisomers of the oxovanadium(IV) complexes of ligand VIa.

Substituents in Structure VI

Compound	R_1	R_2	R_3	R_4	R_5	R_6
VIa	CH_3	CH_3	CH_3	CH_3	CH_3	H
VIb	CF_3	CF_3	CH_3	CH_3	CH_3	H
VIc	$C(CH_3)_3$	$C(CH_3)_3$	CH_3	CH_3	CH_3	H
VId	Ph	Ph	CH_3	CH_3	CH_3	H
VIe	CF_3	CF_3	$CH_2CH(CH_3)_2$	$CH_2CH(CH_3)_2$	CH_3	H

heated on a steam bath for 1 h, following which most of the methanol was allowed to evaporate. On cooling, water was added. In the case of VO(fapd) this caused precipitation of the violet-pink complex which was collected by filtration and recrystallised from aqueous acetone. The remaining complexes were recovered by extraction with chloroform and purified by column chromatography on silica gel eluting with ethyl acetate–methanol (5:1). Colours of the purified complexes were greyish-blue (VOaapd), violet-blue (VOtbmpd), dark green (VOpapd) and green (VObapd). Solutions of the complexes were prepared in either dichloromethane, chloroform or methanol for chromatographic studies.

(5) Lanthanide complexes of VII were prepared according to published procedures [17].

In all cases, satisfactory microanalyses were obtained for C, H and N.

2.3. Methods

2.3.1. Thermal analyses

Thermal data were collected as previously described [18] on an instrument (Rigaku, Thermoflex) combining both thermogravimetry and differential thermal analysis (TG-DTA).

2.3.2. Gas chromatography

GC was performed on a Perkin-Elmer GC system incorporating flame ionisation detection and splitless injection. Bonded-phase fused-silica columns of various lengths and film thicknesses were used; typical columns being BP1, 2 m×0.2 mm, 0.25 μm film and BP1, 12 m×0.53 mm, 3 μm film. Nitrogen (46 cm s^{-1}) or hydrogen (80 cm s^{-1}) was used as carrier gas.

2.3.3. Thin-layer chromatography

TLC was performed on pre-coated Kieselgel 60 or RP_{18} plates without any further activation or pretreatment. Separated chelates were detected by their intrinsic colours or with the aid of a UV lamp.

2.3.4. HPLC

A Perkin-Elmer Series 10 LC was used equipped with a PE LC-235 Diode array Detector. A variety of columns and elution conditions were investigated.

2.3.5. Spectra

Ultraviolet absorbance and circular dichroism spectra of complexes at approximately 6×10^{-5} *M* in chloroform were recorded on a PU8800 UV–Visible spectrophotometer or Jasco J-500C spectropolarimeter using matched quartz cells.

3. Results and discussion

3.1. Thermal properties and gas chromatography

The complexes of I–VI exhibited limited volatility and/or thermal stability suggesting that GC was unlikely to be a viable approach for these compounds. These complexes were relatively involatile and typically sublimed above 230°C with extensive decomposition. The only exceptions were the nickel and beryllium chelates that sublimed with minimal decomposition. Consistent with this behaviour, the complexes of I eluted at 230°C from a non-polar BP1 column (25 m) with retention times varying between 7 and 21 min but with poor peak shape, elevated baselines and poor reproducibility. Calibration curves were non-linear with non-zero intercepts. In extreme cases, complete retention of the complexes occurred within the column. This adverse behaviour has been attributed [2,6], not unreasonably, to low kinetic stability of certain complexes and the resultant likelihood of dissociation and/or ligand-exchange reactions within the column. Retention of the dissociated species can be partial or complete and reversible or irreversible. The sites of irreversible adsorption of such neutral complexes in silica-based columns have been identified as residual (uncapped) silanol groups and Lewis acid sites associated with metal impurities. Consistent with this interpretation was the elution of further metal species (as confirmed by fraction collection and analysis of the eluate) following subsequent injection of solutions of free ligand onto the column. Complexes of IV exhibited similar thermal properties (sublimation above 240°C but with significant decomposition except for the nickel complex) decomposing probably by a free radical initiated reaction analogous to that previously proposed for complexes of β-diketones [6][1].

Lanthanide complexes of V were obtained as hydrated species (confirmed by microanalysis and infrared spectrometry) which were readily dehydrated by storage over phosphorus pentoxide at reduced pressure for 3 days. TG-DTA confirmed the thermal stability and volatility of the anhydrous compounds. Volatility decreased in the series from Lu to La, that is, complexes derived from the metal ion of higher ionic mass and smaller ionic radii were the more volatile. Mass loss exceeded 98% for each complex and occurred between 130 and 260°C. GC

[1] TG-DTA data for the nickel complexes of fluorinated dithio-β-diketones revealed these to be even more volatile and stable than those of IV.

of the hydrated complexes proved unsuccessful on non-polar columns. Although peaks were observed, these tailed badly. Reproducibility was poor with a non-linear response to changes in concentration of metal complex. Such behaviour is typical of on-column decomposition reactions and probably involves thermal pyrolysis of the hydrated derivative to a hydroxocomplex as shown:

$$Ln(fod)_3 \cdot H_2O \rightarrow Ln(fod)_2 \cdot OH + Hfod$$

Column activity was monitored using a standard test mix to ascertain the effects of the lanthanide complexes on the column. The results shown in Table 1 demonstrate a significant increase in column activity following the introduction of chelate, with octan-1-ol being most affected. This suggests an increase within the column in the number of Lewis acid sites as would occur, for example, if Ln^{3+} or complex was being retained. The retention was irreversible as demonstrated by the change in peak area and height ratios [19]. The change in column activity was permanent and unaffected by either column temperature conditioning or flushing the column with free ligand. Moreover, the activity was not reduced by removing a 26-cm segment from the injection end of the column. However, enhanced column activity remained following the injection of dehydrated complexes onto a new column.

TG-DTA data demonstrated the thermal stability and volatility of the oxovanadium(IV) complexes of VI which was substantiated by their successful elution from a range of GC columns as discussed below.

3.2. Liquid chromatography

TLC was used to assess the likely behaviour of the complexes in HPLC. Moreover, TLC as an open bed technique provides a visual display of the elution characteristics. In the case of complexes of I, the results (Table 2) demonstrated the unsuitability of both adsorption and reversed-phase systems for the separation of metal ion mixtures. A range of mobile phases with silica and octadecyl phases failed to achieve the selectivity necessary for the separation of all eight complexes of I due, in part, to the extensive tailing observed for most complexes which precluded the assignment of accurate R_F values. In fact, the best separation achieved was the partial resolution of two complexes. This behaviour was paralleled in HPLC where the individual complexes eluted from reversed-phase systems (C_{18} column eluted with various mixtures of water, methanol, acetonitrile) as symmetrical peaks with distinct retention times, whilst there were no identifiable peaks when all complexes were injected in admixture. A second small peak was observed for the palladium(II) complex corresponding to the *cis* isomer [20]. The peak height and area for the palladium(II), cobalt(III) and zinc(II) complexes was unaltered under stopped flow conditions (20 min) indicating the on-column stability of these species. In contrast, using the same conditions, the iron(III) and copper(II) complexes showed significant on-column decomposition. These complexes also gave very broad chromatographic peaks. The performance of the remaining complexes varied between these extremes.

Table 1
Effect of injection of lanthanide complexes of V on the activity of a BP1 column (12 m×0.53 mm) as expressed by the peak area and height ratios of standard solutes injected before and after injection of the complexes and following specified column treatments[a]

Solute	Before use		After injection of complex		Following removal of 26 cm column from injector end		Following column flushing with free ligand	
	Area ratio	Height ratio	Area ratio	Height ratio	Area ratio	Height ratio	Area ratio	Height ratio
Octan-2-one	0.40	1.50	0.42	1.41	0.41	1.29	0.40	1.33
Octan-1-ol	0.49	1.10	0.34	0.48	0.34	0.44	0.34	0.56
2,4-Dimethylphenol	0.63	1.29	0.55	0.71	0.58	0.84	0.62	1.07
2,4-Dimethylamine	0.83	1.26	0.78	1.16	0.80	1.13	0.79	1.11
Naphthalene	1.08	1.46	1.02	1.36	1.05	1.35	1.05	1.35
n-Dodecane	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
n-Tridecane	1.36	0.76	1.34	0.76	1.34	0.76	1.13	0.72

[a] Conditions: column temperature, 105°C with nitrogen (46 cm s^{-1}) carrier gas; injector and detector temperatures, 170°C.

Table 2
TLC data for complexes of I on silica gel 60 (A) and RP_{18} layers (B)

Solvent	R_F							
	Cu	Ni	Pd	Pt	Co	Fe	Zn	Be
A								
Hexane–dichloromethane (80:20)	0.33	0.32	0.00	0.00	0.32	0.33	0.35	0.37
Dichloromethane	0.40	0.27	0.64	0.85	0.09	0.23	0.23	0.46
Methanol–acetonitrile (65:15)	0.8	0.8	0.0	0.8	0.85	0.75	0.6	0.6
Methanol	0.55	0.57	0.0	0.0	0.65	0.57	0.57	0.62
B								
Methanol–acetonitrile (65:15)	0.7	0.1	0.0	0.7	0.8	0.6	0.0	0.7
Methanol–water (50:50)	0.00	0.00	0.00	0.00	0.80	0.05	0.00	0.18

Of the tetradentate complexes, II, the copper(II) (R_F 0.50), nickel(II) (0.70), palladium(II) (0.78) and oxovanadium(IV) (0.89) complexes were readily resolved by TLC using silica gel and acetonitrile. This group was also successfully resolved by HPLC. Sharp symmetrical peaks were obtained for nickel, palladium and oxovanadium complexes only although the behaviour of the copper(II) complex was improved by gradient elution (Fig. 2a). Under these conditions and with detection at 240 nm, detection limits (expressed as ng of metal) were 60, 70, 2 and 30 ng for the nickel, palladium, oxovanadium and copper complexes, respectively. Chromatograms of the other complexes of II exhibited broad peaks (Fig. 2b) characteristic of on-column decomposition. Elution behaviour was marginally inferior on a reversed-phase system.

The copper(II) and iron(III) complex of III eluted as sharp symmetrical peaks from both silica and reversed-phase columns with a range of mobile phases. This is in marked contrast to the behaviour of the iron(III) complex of the related bidentate ligand, I, and indeed most other ligands. The improved behaviour can be attributed to enhanced kinetic stability conferred by the hexadentate ligand as previously proposed [2]. This ligand warrants closer examination as a potential reagent for the ultratrace analysis of mixtures by HPLC.

The lanthanide complexes of V migrated reproducibly on silica gel layers generally as sharp spots with R_F values of 0.8 using 10% aqueous methanol solvent. Early results on reversed-phase columns were not reproducible. Following sequential washing of the column with distilled water, aqueous EDTA, distilled water and methanol, significant retention of the chelates was still observed. After thorough washing of the column with free ligand, the complexes eluted more reproducibly albeit with significant tailing and concentration-dependent retention times. Incorporation of free ligand in the mobile phase produced sharp symmetrical peaks with typical detection limits of 5–10 ng. These results suggest that, in spite of the relatively high formation constants, lanthanide complexes of V undergo on-column dissociation. Gurira and Carr [21] reached a similar conclusion about the behaviour of a number of complexes. The improved behaviour with free ligand can be attributed to an equilibrium shift in favour of the undissociated complexed metal ion. Surprisingly, the complexes eluted from silica with methanol as sharp symmetrical peaks with detection limits typically in the low nanogram range. Nevertheless, separation of the lanthanide complexes could not be effected on either adsorbents or reversed-phase systems. For example, using a Partisil 5 column and methanol the resolution factor of adjacent lanthanides (e.g., Eu and Gd complexes; retention time, 14.5 min) was of the order of 10^{-3}.

The latter system may warrant closer examination for the separation of lanthanides, although ion-interaction chromatography (IIC) may be a more viable alternative [22]. Lanthanide complexes of VII were ionic, water-soluble species which readily formed ion pairs with, for example, citrate that were extractable into nonpolar solvents. Moreover, they are kinetically stable and exhibit strong absorption at 300 nm with molar absorptivities exceeding $10^4\ M^{-1}\ cm^{-1}$ which facilitates detection in both TLC and

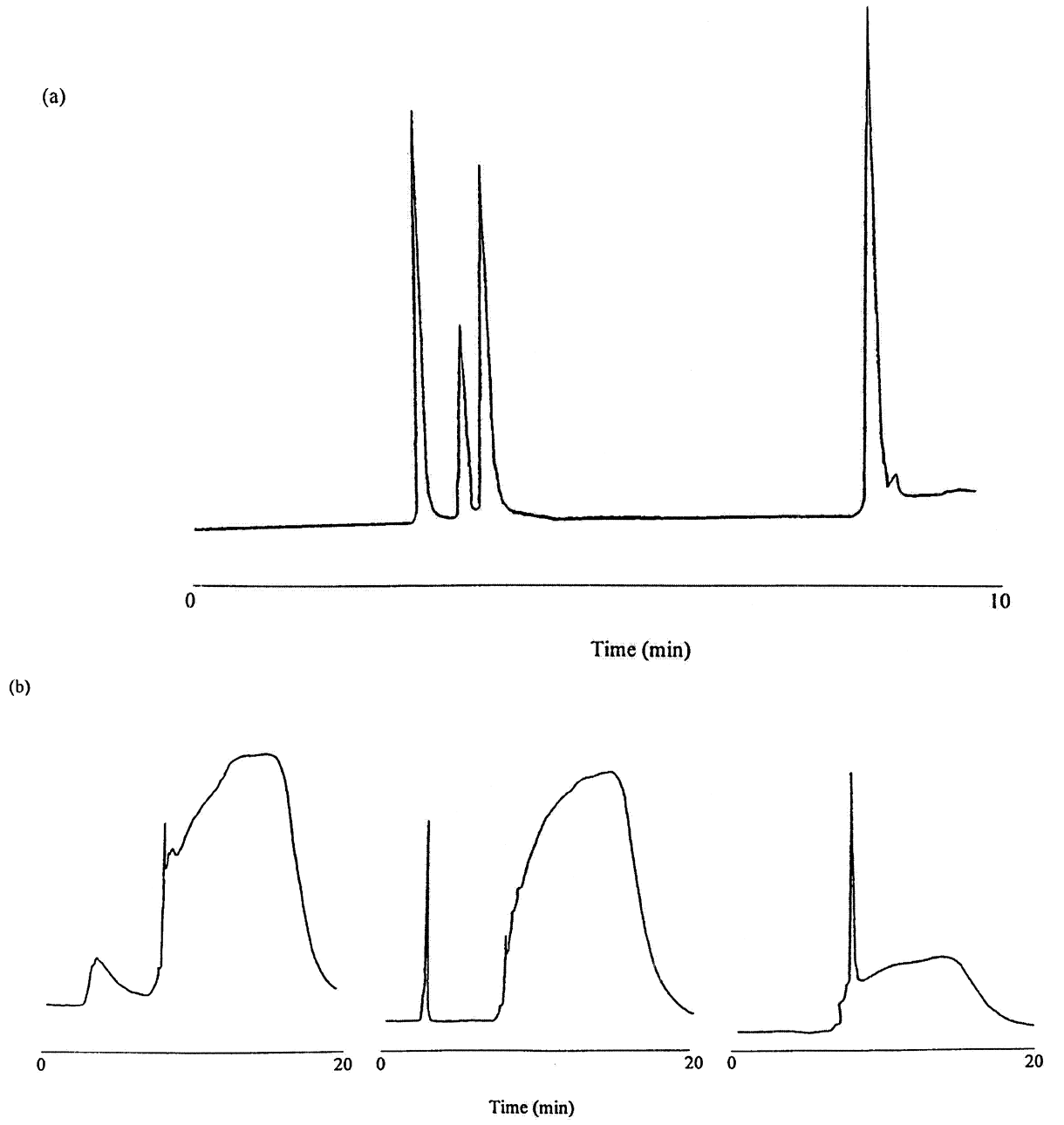

Fig. 2. Chromatograms showing the gradient elution of complexes of II on a silica column (Brownlee Labs, 22 cm×0.5 mm, 5 μm). (a) Complexes of oxovanadium(IV) (retention time, 2.8 min), palladium(II) (3.3 min), nickel(II) (3.6 min) and copper(II) (8.2 min) and (b) Complexes of cadmium(II), platinum(II) and dioxouranium(VI). Mobile phase: 2% methanol in acetonitrile, 3.6 min then programmed to 100% methanol at 4.6 min followed by a further isocratic period with flow rate of 1 ml min^{-1}; detection, 240 nm.

HPLC. Alternatively, measurement of fluorescence at 342 nm following excitation at 246 nm provided a sensitive means of detection. Data for the TLC of these complexes as presented in Table 3 can be explained in terms of an ion-pairing model. The IIC of the complexes on silica-based reversed phases was unsuccessful in that total retention of the complexes occurred presumably as a result of a strong interaction with residual silanol groups on the phase. Polystyrene-based phases may prove suitable for the ultratrace separation and determination of the lanthanides using reagent VII.

The elution of the oxovanadium(IV) complexes of VI by both GC and HPLC was exceptional in that the number of peaks was dependent on the ligand, column and, in the case of GC, also on column temperature. The separation of non-labile isomers of these complexes appeared a likely explanation for these observations.

Evidence of isomerism in the oxovanadium(IV) chelates was first encountered in gas chromatographic studies of these complexes [23] on packed columns. In complexes of VI with $R_5 = H$, only single chromatographic peaks attributable to chelate were observed. However, with $R_5 =$ methyl in structure VI, i.e., in VO(aapd), VO(papd), VO(fapd), VO(bapd) and VO(tbmpd), broadened or partially resolved peaks were obtained on packed columns. Oxovanadium complexes of this type occur as two pairs of optical isomers VIII–XI. Thus, in principle, if the complexes do not isomerise rapidly, it should be possible to separate all four on suitable optically active GC or HPLC columns. Hence, the broadened GC peaks are attributed to partial separation of the diastereomeric pairs VIII and IX from X and XI. The possibility that the observed peaks were due to nonideal column behaviour, decomposition products or impurities has to be considered. In excluding on-column decomposition and abnormal column behaviour, it is cited that complexes with $R_5 = H$ and those with $R_5 =$ methyl both have similar stabilities and volatilities [23], and it is therefore unlikely that the latter would behave substantially differently to the first group which elute as single peaks. Further evidence is provided by the separations obtained on bonded-phase fused-silica columns (Fig. 3) which are more complete with linear detector response and no ridge between the chromatographic peaks. However, the number of peaks was dependent on column temperature reflecting the occurrence of on-column isomerisation.

Table 3
TLC data for lanthanide complexes of VII on RP_{18} layers (a–c) and Kieselgel 60 (d, e)[a]

Metal	R_F				
	a	b	c	d	e
La	0.0	0.53	0.31	0.0	0.3
Ce	0.0	0.25	0.10	0.0	0.3
Nd	0.0	0.27	0.10	0.0	0.3
Sm	0.0	0.22	0.08	0.0	0.3
Eu	0.0	0.40	0.17	0.0	0.3
Gd	0.0	0.21	0.06	0.0	0.3
Dy	0.0	0.37	0.26	0.0	0.3

[a] Mobile phases were (a) aqueous methanol (various ratios), (b) 1% sodium hexanoate in methanol–water (80:20), (c) 1% sodium hexanesulfonate in methanol–water (90:10), (d) aqueous methanol or methanol–dichloromethane (90:10), (e) 1% ammonium citrate in methanol–water (60:40). Spots were visualised under UV lamp.

Diastereomer separations of oxovanadium(IV) complexes were more conveniently obtained by HPLC using both reversed phases and adsorbents (Fig. 4). Diode array spectra of the separated species were indistinguishable as shown in Fig. 4 supporting the assignment of the peaks as isomeric compounds. Elution of the intact complexes was also confirmed by fraction collection and mass spectrometry. The two isomers of VO(fapd) separated by preparative scale HPLC were obtained as a mauve-pink solid (Band 1 in HPLC) and a pink solid (Band 2). The latter had the shorter retention time in GC and is assigned the structure IX in which the bridge-methyl group is in the axial position [24]. A more detailed study involving the preparative-scale separation and characterization of isomeric complexes on chiral HPLC columns is published separately.

4. Conclusions

These data indicate that pre-column derivatization and GC is unlikely to provide a viable method for the ultratrace determination of metal ions except in rare circumstances [6]. On the other hand, liquid chromatography of complexed metal ions is a valuable technique that combines the advantages of

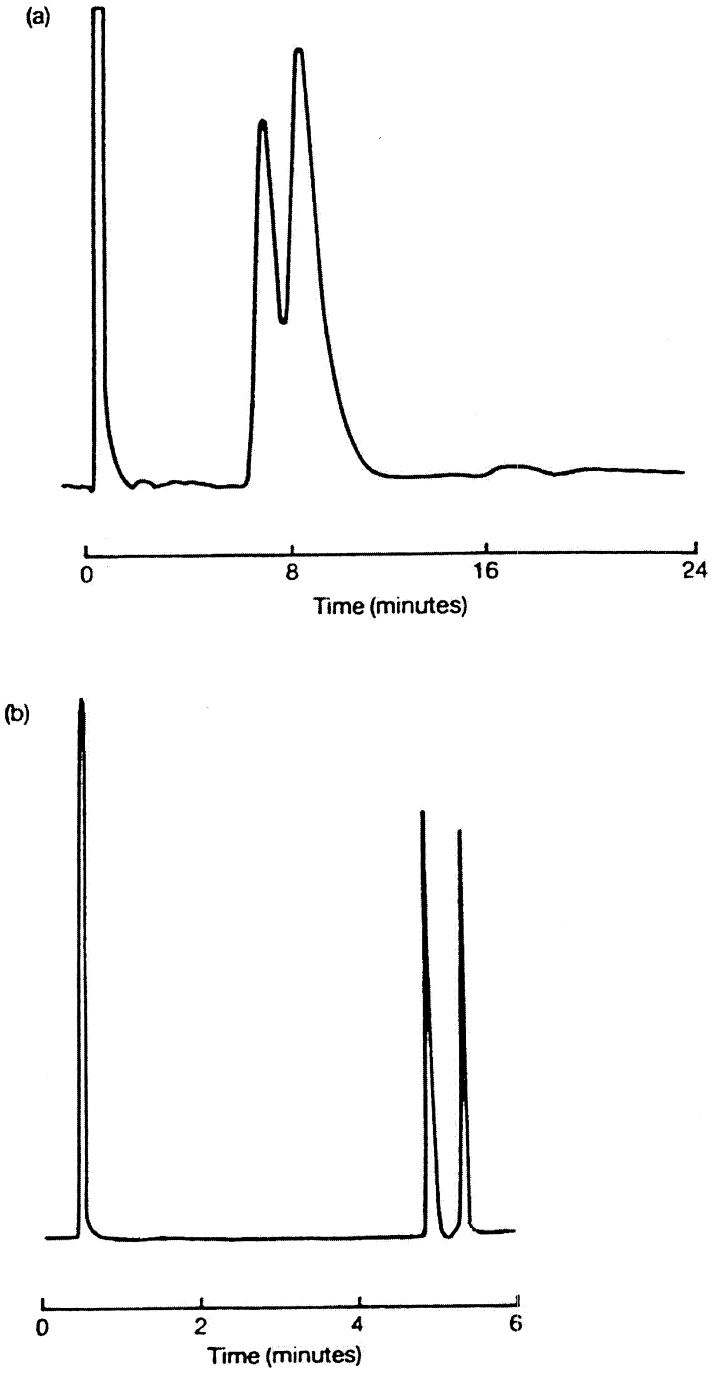

Fig. 3. Chromatograms showing the elution of VO(aapd) on (a) packed SE-30 column and (b) BP1 at 195°C with hydrogen carrier gas and flame ionisation detection.

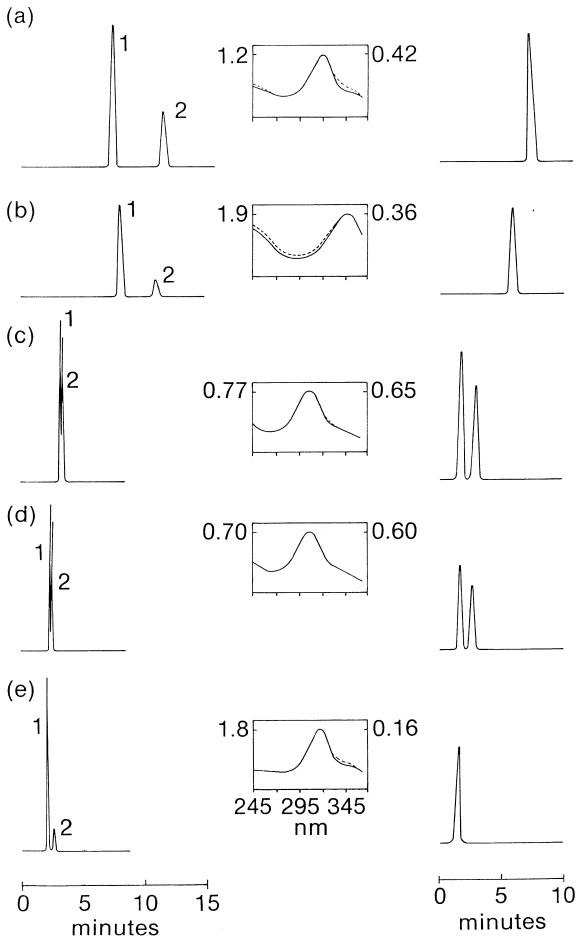

Fig. 4. Chromatograms showing the separation of the oxovanadium(IV) complexes of (a) H_2papd (1.0 mg ml^{-1}), (b) H_2bapd (1.0 mg ml^{-1}), (c) H_2fapd (0.4 mg ml^{-1}), (d) H_2tbmpd (0.4 mg ml^{-1}), and (e) H_2aapd (0.2 mg ml^{-1}) on Techsil 10 Silica (250×4.6 mm, 10 μm) (left hand series) or Pecosphere 3×3 CR C_{18} column (3 μm) (right hand). Mobile phase: Techsil 10 column dichloromethane (2.00 ml min^{-1}) with the exception of (e) ethyl acetate–hexane (78:22); Pecosphere C_{18} column: methanol–water (60:40) in (a), (b) and (d) or (40:60) in (c) and (e). Detection: UV at 305 nm. Diode array spectra for the separated isomers are solid curve with left absorbance scale (isomer 1) and dotted curve with right absorbance scale (isomer 2).

versatility, specificity and sensitivity with the capacity for simultaneous determination and speciation.

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