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GAS CHROMATOGRAPHY OF SOME OXOVANADIUM(IV) TETRADENTATE β -KETOAMINE CHELATES

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SUMMARY

The gas chromatographic elution behaviour is reported, for the first time, for the oxovanadium(IV) chelates of seven tetradentate β -ketoamines on a non-polar column. Interaction with Chromosorb W as support is shown to be appreciably greater than with Chromosorb 750. Detection limits using the Chromosorb 750 support and flame ionization detection are less than nanogram amounts of elemental vanadium. The separation of copper and nickel from vanadium complexes is demonstrated.

INTRODUCTION

Although Schiff base chelating agents have been extensively used and studied as analytical reagents it was not until recently that their potential for forming volatile and thermally stable metal chelates in gas-liquid chromatography (GLC) was demonstrated. Thus Moshier and Sievers¹ in 1965 made no reference to the gas chromatography (GC) of Schiff base chelates and Jungreis and Thabet², who reviewed the analytical applications of Schiff bases in 1968, did not refer to GC either.

Miyazaki *et al.*³ first showed that bidentate β -ketoamines such as 4-aminopentan-3-en-2-one could be used successfully for the GC of Ni(II), thereby demonstrating the dramatic effect of changing one donor atom in a β -diketone. In the search for alternative chelating agents for metal ions which did not form volatile β -diketonates, or were otherwise unsuitable for GLC because of polymer formation or hydration (*e.g.*, Cu(II), Ni(II)), it was shown⁴⁻⁶ that fluorinated and non-fluorinated tetradentate β -ketoamines (and bi-dentate ligands, also), derived from the condensation of a diamine and a β -diketone, were excellent reagents for forming volatile chelates with metals such as Cu(II), Ni(II), Pd(II), and Pt(II) having square-planar coordination requirements. This group of chelates had a lower volatility than the corresponding β -diketonates but a higher thermal stability and, importantly, did not polymerize or form adducts with neutral donors (including water).

Subsequent work by Uden and co-workers⁷⁻⁹ demonstrated the excellent GC properties of the copper and nickel chelates. The fluorinated types were successfully

eluted and detected at sub-nanogram to picogram levels whilst even the non-fluorinated chelates were eluted and detected at near-nanogram levels.

Interestingly, Richardson and Sievers¹⁰ and Cummings and Sievers¹¹ were rather unfortunate in not successfully preparing suitably volatile Schiff base chelates. In the first of two studies¹⁰, the tetradentate Schiff base formed from hexafluoroacetylacetone and ethylenediamine was difficult to obtain because of the tendency of this condensation reaction to give side products. Although volatile copper compounds were reported, no well characterised Schiff base chelate was obtained and no GC studies were pursued. In the second study¹¹, the preparation of dibasic, hexadentate Schiff bases formed between trifluoroacetylacetone or hexafluoroacetylacetone and triethylenetetramine did not give volatile complexes with Ni(II) and Cd(II). The reason for this is not clear since, for Ni(II) at least, the chelates are analogous to those just discussed but include, in addition, two amino groups to coordinatively saturate the metal ion. It may be that the steric conditions do not allow the amino groups to closely coordinate at the unsaturated sites, or the amino groups do not form particularly strong donors at these sites and serve no purpose but to take part in intermolecular hydrogen bonding.

Our studies of vanadium β -diketonates^{12,13} have shown that oxovanadium(IV) chelates do not have high thermal stability and do not elute well on non-polar columns in GC. In fact, these compounds decompose near 200°, show strong interaction with supports and undergo on-column reactions. Vanadium(III) β -diketonates were superior to those of the IV-oxidation state in elution behaviour and limits of detection but the former suffered slow oxidation in solution by molecular oxygen and, therefore, could be unsuitable for analytical applications.

This communication presents the GC behaviour of seven oxovanadium(IV) chelates derived from a group of related tetradentate Schiff bases. Several of the ligands and vanadium chelates have not been reported previously, as is also the case of a number of the nickel(II) and copper(II) chelates used for comparison in separations with a non-polar stationary phase (SE-30). Selection of an inert support is shown to be important for the successful chromatography of the oxovanadium(IV) complexes.

EXPERIMENTAL

The preparation and characterization of the ligands and chelates were based on procedures previously described in the literature for oxovanadium(IV) compounds^{14,15} and for nickel and copper complexes^{6,16}. Details will be published in a later communication.

The ligands and vanadium chelates described in this paper are listed and identified in Table I.

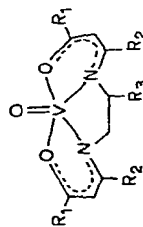
Instrumentation and chromatographic columns

A Hewlett-Packard Model 5750 gas chromatograph with flame ionization detection (FID) was used for all the experimental work. Commercial nitrogen of high purity was employed, without further purification, as carrier gas (35 ml/min). The temperatures of the injection block, column, and detector were 210, 200, and 210°, respectively.

TABLE I
STRUCTURES AND ABBREVIATIONS FOR β -KETOAMINES AND THE CORRESPONDING OXOVANADIUM(IV) COMPOUNDS

Ligands*		Chelates		Name	Abbreviation	Abbreviation
Substituents		R ₂	R ₃			
CH ₃		CH ₃	H	N,N'-Ethylenebis(acetylacetonimine)oxovanadium(IV)	AAED	VO(AAED)
CH ₃		CH ₃	CH ₃	N,N'-1,2-Propylenebis(acetylacetonimine)oxovanadium(IV)	AAPD	VO(AAPD)
<i>tert</i> -Butyl		CH ₃	H	N,N'-Ethylenebis(pivaloylacetonimine)oxovanadium(IV)	PAED	VO(PAED)
<i>tert</i> -Butyl		CH ₃	CH ₃	N,N'-1,2-Propylenebis(pivaloylacetonimine)oxovanadium(IV)	PAPD	VO(PAPD)
Isopropyl		CH ₃	H	N,N'-Ethylenebis(isobutyrylacetonimine)oxovanadium(IV)	IBAED	VO(IBAED)
CF ₃		CH ₃	H	N,N'-Ethylenebis(trifluoroacetylacetonimine)oxovanadium(IV)	TFAED	VO(TFAED)
CF ₃		CH ₃	CH ₃	N,N'-1,2-Propylenebis(trifluoroacetylacetonimine)oxovanadium(IV)	TFAPD	VO(TFAPD)

* General structures are given by:



Columns were borosilicate glass coils (3 ft. \times 1/4 in. O.D.) packed with Chromosorb W or Chromosorb 750 (both 80–100 mesh, AW, DMCS treated) which had been coated with SE-30 (3% w/w). The columns were conditioned for two days at 220° then, following silylation with both HMDS and BSTFA at 180° (200 μ l each), the columns were re-conditioned at 220° for one day before use. The chelate solutions were injected directly onto the column.

Chelate solutions

Each chelate (10 mg) was prepared in dichloromethane (10 ml) as a 0.1% solution (w/v). Due to poor solubility in less polar solvents, the oxovanadium(IV) chelates containing fluorine were dissolved in acetonitrile. Further dilution with dichloromethane provided solutions containing 1.0, 0.1, 0.01, and 0.001 μ g chelate for each injection (1 μ l). Detection limits were determined by making serial injections beginning with the most concentrated of the above solutions.

RESULTS AND DISCUSSION

Effects of support and ligand structure on elution behaviour

The importance of both the column support and the ligand emerge as vital factors in the elution behaviour of the oxovanadium(IV) chelates studied. Fig. 1

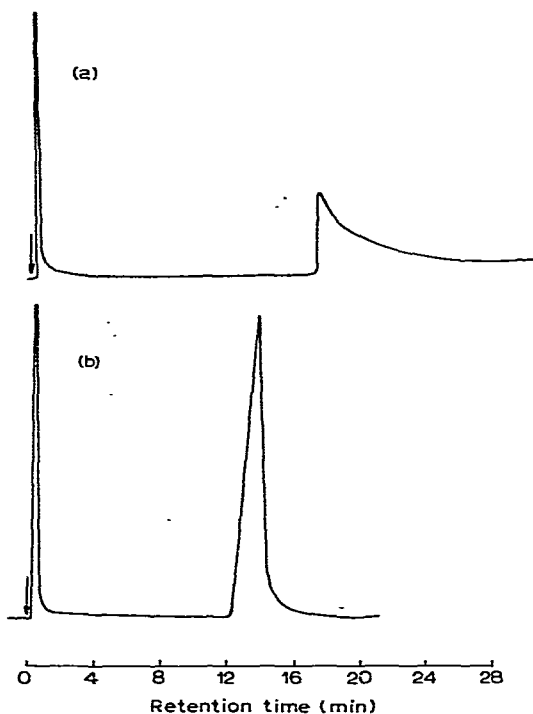


Fig. 1. Chromatograms showing the elution behaviour for 10 μ g of VO(AAED) with (a) Chromosorb W and (b) Chromosorb 750 supports, under identical experimental conditions.

shows the elution observed for 10 μg of the chelate VO(AAED) on the supports Chromosorb W and Chromosorb 750 with the same experimental conditions. The improvement with Chromosorb 750 is of such a magnitude that the practical use of the oxovanadium(IV) chelate becomes a distinct possibility only because of the marked superiority of such a support material. Indeed, the GC behaviour of the oxovanadium(IV) chelates is such that we advocate their use for the purpose of grading the inertness of supports. Improved chromatographic behaviour on this support has been reported⁹ for the corresponding nickel and copper chelates, however, comparative data were not supplied.

The elution behaviour of all seven vanadium chelates on Chromosorb 750 and Chromosorb W is summarized in Table II in the form of tailing indices. The tailing index (T) has been defined¹³ for specific experimental conditions as the ratio of front to back widths of a chromatographic peak, measured from the perpendicular drawn through its maximum point for specified fractions of the peak height. Although this index does not unambiguously define the original peak, we have found it useful for numerically describing the degree of tailing exhibited by the various compounds. For example, a symmetrical peak has $T = 1.0$, whereas peaks of increasingly severe tailing show correspondingly increasing values of T . Values of the index, as may be expected, tend to be larger for small fractions of the height of the tailing peak.

The results in Table II are given for 50, 10, 5, and 2% of the peak height. It is seen that all chelates demonstrate a considerably greater degree of tailing on the Chromosorb W than on the Chromosorb 750 support. Amongst the various chelates, however, the lack of branched substituents or the presence of a trifluoromethyl group on the β -diketone moiety of the ligand tends to increase the degree of tailing exhibited by the corresponding vanadium chelate, while branching at the bridging ethylene group of the ligand has no significant effect.

The degree of interaction with the solid support is perhaps not too surprising in view of the coordinative unsaturation of the complexes, the presence of the π -electron systems of the chelate rings, the unshared pair of electrons on the nitrogen

TABLE II

COMPARATIVE TAILING INDICES FOR OXOVANADIUM(IV) CHELATES ON CHROMOSORB 750 AND CHROMOSORB W

The tailing index is represented by T_y^x , where x is the amount of chelate (μg) injected onto the column and y is a fraction (50, 10, 5, or 2%) of the peak height.

Ligand	Tailing indices of oxovanadium(IV) chelates							
	Chromosorb 750 support				Chromosorb W support			
	$T_{0.5}^{10}$	$T_{0.1}^{10}$	$T_{0.05}^{10}$	$T_{0.02}^{10}$	$T_{0.1}^{10}$	$T_{0.2}^{10}$	$T_{0.05}^{10}$	$T_{0.02}^{10}$
AAED	0.9	1.7	2.1	3.1	7.7	34	large*	large*
PAED	0.6	0.4	0.5	0.6	1.6	3.3	5	7.8
IBAED	0.5	0.3	0.5	0.9	1.5	4.6	8.5	16.5
TFAED	0.6	4.2	5.3	5.7	8.7	22	large*	large*
AAPD	0.6	0.6	0.8	1.5	7.5	>10	>10	>10
PAPD	0.6	0.7	0.7	1.1	2.2	4.	7.7	11.1
TFAPD	2.5	4.0	5.3	6.1	7.0	22	large*	large*

* The measured widths of the elution curve were too small for accurate determination of T .

and oxygen atoms, and the polar oxovanadium ($V = O$) group, the presence of which allows such chelate molecules to act both as Lewis acids and Lewis bases with any potential groups both on the support surface and also in the stationary phase.

In Table III are shown the tailing indices for each chelate on Chromosorb 750 at levels of 1.0, 0.1, and 0.01 μg injected chelate. All chelates show higher values of T at the 0.01 μg (10 ng) level, as may be anticipated, but this is not severe when compared with the T values at the 10 μg level on Chromosorb W. The complexes VO(PAED), VO(IBAED), and VO(PAPD) exhibit fronting at 10 μg but not at 1, 0.1, or 0.01 μg , as is evident from the less-than-unity T values.

TABLE III

TAILING INDICES FOR OXOVANADIUM(IV) CHELATES ON CHROMOSORB 750 SUPPORT

See Table II for representation of tailing index, T .

Ligand	Tailing indices of oxovanadium(IV) chelates											
	$T_{0.5}^1$	$T_{0.1}^1$	$T_{0.05}^1$	$T_{0.02}$	$T_{0.5}^{0.1}$	$T_{0.1}^{0.1}$	$T_{0.05}^{0.1}$	$T_{0.02}^{0.1}$	$T_{0.5}^{0.01}$	$T_{0.1}^{0.01}$	$T_{0.05}^{0.01}$	$T_{0.02}^{0.01}$
AAED	1.4	1.7	2.6	5.0	2.1	4.8	7.2	11.2	5.0	8.5	12	12
PAED	0.9	1.2	1.3	1.6	1.0	1.7	2.3	3.7	1.3	2.4	2.9	3.9
IBAED	0.7	1.0	1.3	1.8	1.0	1.8	2.0	3.0	2.0	3.5	4.4	5.2
AAPD	1.3	1.5	1.8	2.5	0.7	2.4	2.6	3.0	2.0	4.3	5.7	5.7
TFAED	1.0	1.5	1.9	2.8	1.3	2.2	2.8	3.0	2.0	1.6	2.0	3.0
TFAPD	1.0	1.5	1.7	2.5	1.3	2.3	2.8	3.1	2.0	1.5	2.0	2.8
PAPD	0.9	1.0	1.0	1.2	1.0	1.6	1.8	2.5	1.0	1.8	2.7	3.2

The retention of peak symmetry at the nanogram levels is a tribute to the superior chromatographic properties of the Schiff base chelates. In contrast, the fluorinated oxovanadium(IV) β -diketonates which we have studied exhibit severe tailing on both Chromosorb W and Chromosorb 750 and cannot be eluted at the nanogram level¹³.

In Table IV the detection limits (expressed as nanograms of chelate and elemental vanadium) are shown for the Chromosorb 750 column with the FID. No

TABLE IV

DETECTION LIMITS (FID) FOR OXOVANADIUM(IV) CHELATES OF TETRADENTATE β -KETOAMINES

Detection limits were based on a twice-noise level criterion using Chromosorb 750 as the support material.

Ligand	Detection limit (ng)	
	Chelate	Vanadium
AAED	20	3
PAED	0.8	0.1
IBAED	1	0.1
TFAED	1	0.1
TFAPD	2	0.2
PAPD	0.8	0.1
AAPD	5	0.8

particular optimisation of the experimental conditions was made to obtain these values. Furthermore, none of the chelates displayed a detection limit controlled by adsorption.

Retention data

The retention times of all chelates are given in Table V together with relative retention times compared to VO(AAED). Fig. 2 shows a composite chromatogram.

TABLE V

RETENTION DATA FOR OXOVANADIUM(IV) CHELATES OF TETRADENTATE β -KETOAMINES

The data are determined using Chromosorb 750 as the support material.

Ligand	Chelates	Retention time (min)	Relative retention time
AAED		13.6	1.00
PAED		21.8	1.60
IBAED		17.2	1.26
TFAED		7.6	0.56
TFAPD		6.0	0.44
PAPD		15.6	1.15
AAPD		11.0	0.81

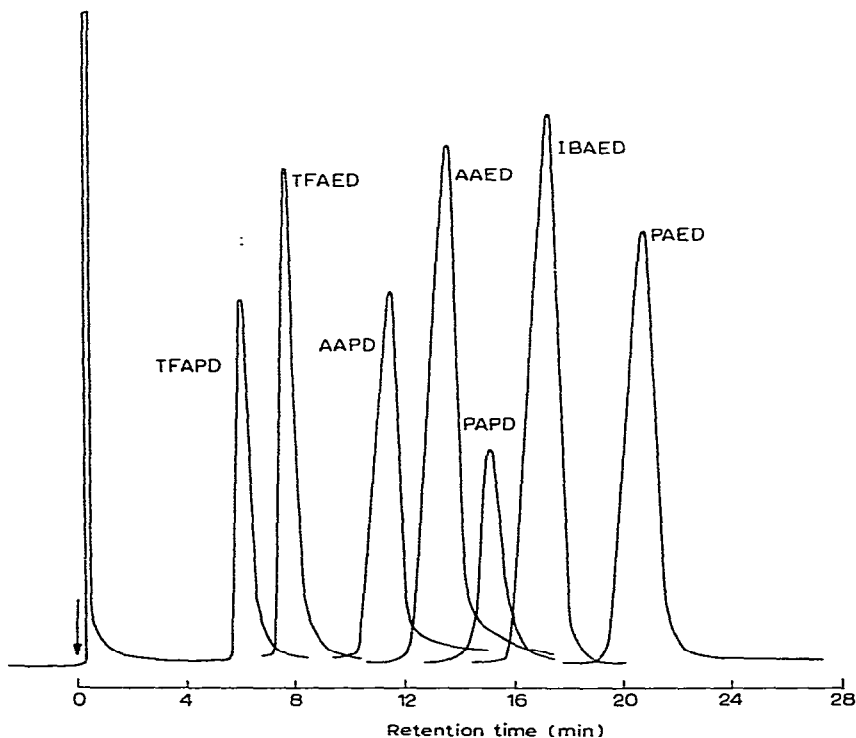


Fig. 2. Chromatograms of oxovanadium(IV) chelates (approx. 1 μ g) for the seven ketoamines studied. Experimental conditions are identical, except for amplifier gain.

of all the chelates investigated on Chromosorb 750. Because the amounts of chelates injected were only nominal ($1 \mu\text{g}$), the relative peak heights are not significant.

It has been found¹⁷ in thermogravimetric studies that the relative volatility of the oxovanadium(IV) chelates is:



whereas the order of increasing elution time for the chelates (see Table V and Fig. 2) is:



Comparison of these trends leads to the conclusion that increasing branching of substituents (R_1 or R_2) increases the retention even though the resulting chelates have higher volatility (*e.g.*, compare the chelates of PAED and AAED). This indicates more favourable partitioning into the non-polar stationary phase for chelates with increasing branching. Furthermore, branching at the bridging ethylene of the ligand results in higher volatility and a decrease in the elution time. This trend has been

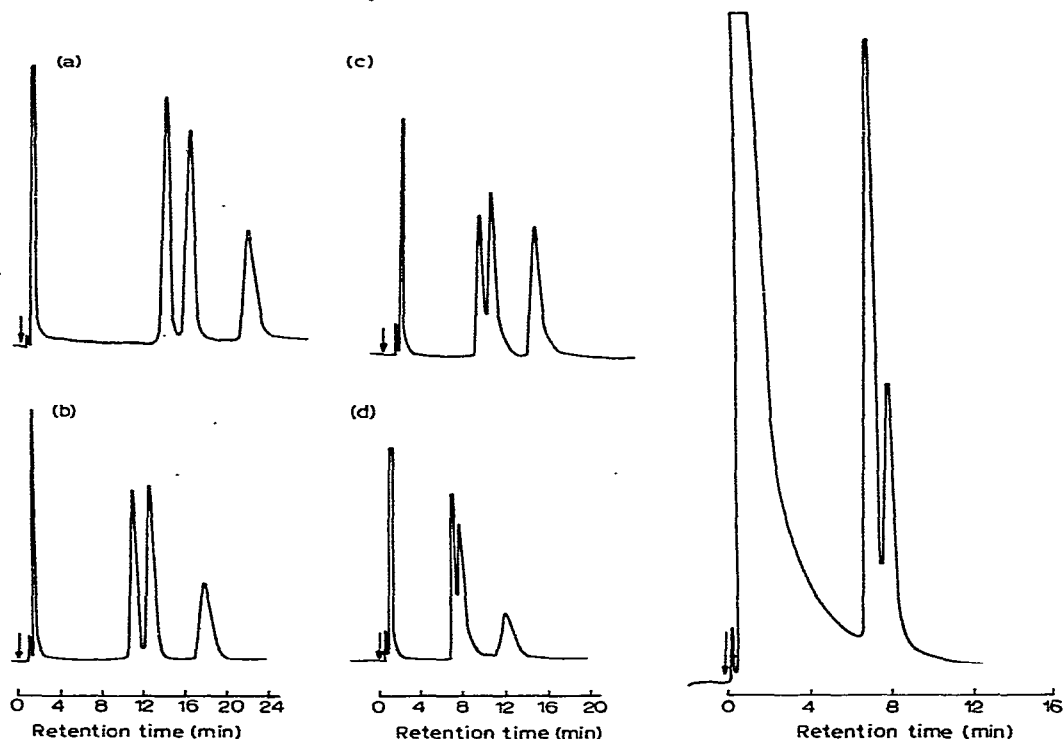


Fig. 3. Chromatogram showing the separation of Cu(II), Ni(II), and oxovanadium(IV) chelates of (a) PAED, (b) IBAED, (c) AAPD, and (d) AAED on Chromosorb 750. The elution of elements is as listed.

Fig. 4. Chromatograms showing the incomplete separation of the TFAED chelates of Cu(II) and Ni(II) from the oxovanadium(IV) species on Chromosorb 750. The elution of elements is as listed.

noted⁶ previously for some chelates of Cu(II), Ni(II), and Pd(II). Finally, the presence of trifluoromethyl groups in the ligand results in a shorter elution time despite the lower volatility of these chelates, indicating poor partitioning into the non-polar stationary phase. Again, these trends have been observed⁶ previously for Cu(II), Ni(II), and Pd(II).

Separation of Cu(II), Ni(II), and oxovanadium(IV) chelates

Figs. 3 and 4 show the separation achieved for Cu(II), Ni(II), and oxovanadium(IV) chelates of five of the ligands. The copper and nickel chelates, in this order, tend to elute close together and before the vanadium chelate. In all cases vanadium was clearly separated from the other two elements, except for the TFAED chelate. For the copper and nickel chelates, too, the presence of branched substituents tends to result in a greater separation, probably due to a more favourable interaction between the chelates and the stationary phase, as noted above. This observation was noted by Barratt¹⁸ in a reference to unpublished work.

Separation of copper and nickel chelates of TFAED was not attained under the conditions employed (see Fig. 4). However, the use of the polar stationary phase QF-1 has been shown to effect⁶ a separation between these two chelates.

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