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## VOLATILITY STUDIES OF METAL CHELATES

### VII\*. GAS CHROMATOGRAPHIC BEHAVIOUR OF CHELATES DERIVED FROM THE AROMATIC $\beta$ -DIKETONES 1-PHENYLBUTANE-1,3-DIONE AND 4,4,4-TRIFLUORO-1-(PENTAFLUOROPHENYL)BUTANE-1,3-DIONE

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#### SUMMARY

Gas chromatographic behaviour of chelates derived from the aromatic  $\beta$ -diketones 1-phenylbutane-1,3-dione and 4,4,4-trifluoro-1-(pentafluorophenyl)butane-1,3-dione are reported. Although the chelates of the non-fluorinated ligand fail to elute from a wide range of liquid phases and supports, several of the fluorinated chelates can be successfully chromatographed, consistent with their thermoanalytical behaviour. Included here are the chromium(III), aluminium(III), iron(III), vanadium(III), copper(II) and oxovanadium(IV) derivatives. In contrast, the zinc, cobalt(II), cobalt(III), manganese(II), nickel(II) and dioxouranium(VI) chelates are totally retained on diverse supports despite, in some cases, adequate volatility and stability. Even for those chelates which elute satisfactorily, abnormalities are apparent. Several chelates of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione were used to elucidate these factors by coupled gas chromatography-mass spectrometry.

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#### INTRODUCTION

In previous papers<sup>1-3</sup> on the thermal and chromatographic behaviour of aryl  $\beta$ -diketonates the role of the coordinating ligand has been emphasized. Whilst the importance of establishing the effect of ligand structure on these properties is obvious, the need to investigate the effect of the central metal ion is equally apparent, especially when the ultimate purpose of such studies is the separation and quantification of metal ions by gas chromatography (GC).

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\* Part VI, see ref. 3.

Bearing in mind these considerations, the thermal and chromatographic data for derivatives of 1-phenylbutane-1,3-dione (Hba) and 4,4,4-trifluoro-1-(pentafluorophenyl)butane-1,3-dione (HF<sub>5</sub>bta) with copper (II), chromium(III), aluminium(III), iron(III), vanadium(III), oxovanadium(IV), cobalt(III), cobalt(II), nickel(II), zinc(II), manganese(II) and dioxouranium(VI) are presented in this paper. These ligands were chosen because they represent the extremes of thermal behaviour in that the derivatives of Hba [with the exception of chromium(III)] are non-volatile whereas many of the HF<sub>5</sub>bta chelates are thermally stable at typical gas chromatographic column temperatures. Although thermal and chromatographic data have been presented<sup>4-7</sup> for the alkyl and fluoro-alkyl  $\beta$ -diketone derivatives of various metal ions, this is the first systematic study highlighting the role of the central metal ion in the aryl  $\beta$ -diketonates. Finally, a number of chelates of the ligand 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione (Hhpm) are utilized, because of their greater volatility, to demonstrate with the aid of combined gas chromatography-mass spectrometry (GC-MS) a number of adverse on-column effects.

## EXPERIMENTAL

### Thermal analysis

The thermal data were obtained as previously reported<sup>1</sup> using simultaneous thermogravimetry-differential thermal analysis (TG-DTA). The DTA data are presented as temperatures measured at peak maxima for the various transitions which are indicated as fusion (F), decomposition (D) and dehydration (H).

### Gas chromatography

Although the details are as reported elsewhere<sup>3</sup>, it is relevant to point out that on-column silylation was employed as a routine procedure. Nitrogen (60 ml/min) was used as carrier gas. Columns were borosilicate glass of 0.5 m length for all data other than that given in Fig. 7 (1 m) and Table I (0.7 m).

### Gas chromatography-mass spectrometry

GC-MS was performed on a Shimadzu 6A-MPF gas chromatograph coupled by an all-glass heated line with an AEI MS12 mass spectrometer. A 1-m glass column at 140°C (3% w/w SE 30 on Chromosorb 750) was employed together with on-column silylation and helium carrier gas (40 ml min<sup>-1</sup>).

### Syntheses

The ligands and several of the chelates have been described previously<sup>2,3</sup>. Details for the five additional chelates, not previously described, are as follows.

*Tris(1-phenylbutane-1,3-dionato)cobalt(III)*. The cobalt(III) chelate of Hba was prepared by the cautious addition of hydrogen peroxide (30%, 30 ml), with heating, to the corresponding cobalt(II) chelate (0.02 mol). After cooling the product was recovered by filtration, and dried under vacuum to yield a dark green solid which was purified on silica gel with benzene, m.p. 196°C (lit.<sup>4</sup> *cis* 158°C, *trans* 200°C). (Found: C, 66.7; H, 5.0. Calc. for C<sub>30</sub>H<sub>27</sub>CoO<sub>6</sub>: C, 66.4; H, 5.0%). DTA: F, 198°C; D, 254°C.

*Tris[4,4,4-trifluoro-1-(pentafluorophenyl)butane-1,3-dionato]cobalt(III)*. The above method was unsuitable for preparing the corresponding chelate of HF<sub>3</sub>bta, since prolonged exposure to excess hydrogen peroxide (30 times) failed to produce any significant oxidation. The chelate was prepared by the slow addition of the anhydrous trivalent metal fluoride (0.09 mol) to HF<sub>3</sub>bta (0.04 mol) while heating at 70°C. After 4 h benzene was added, the warm solution filtered and processed on a silica gel column to give a dark green tacky solid. Repeated processing failed to achieve solidification which did occur, however, on prolonged standing. (Found: C, 36.4; H, 0.1. C<sub>30</sub>H<sub>3</sub>CoF<sub>24</sub>O<sub>6</sub> requires C, 37.0; H, 0.3%). DTA: D, 263°C.

*Bis[4,4,4-trifluoro-1-(pentafluorophenyl)butane-1,3-dionato]bisdimethylformamidecobalt(II)*. Prepared from the corresponding hydrate by slow crystallization from dimethylformamide solution. The crystalline product was washed with hexane and dried under vacuum. m.p. 172–177°C (darkens) (Found: C, 38.3; H, 1.9; N, 3.4. C<sub>26</sub>H<sub>16</sub>CoF<sub>16</sub>N<sub>2</sub>O<sub>6</sub> requires C, 38.3; H, 2.0; N, 3.4%). DTA: 117°C (loss of dimethylformamide); F, 173°C; D, 273°C.

*Bis[4,4,4-trifluoro-1-(pentafluorophenyl)butane-1,3-dionato]aquomanganese(II)*. This compound was prepared<sup>3</sup>, by reaction of the ligand with manganese(II) acetate, as a yellow solid recrystallized from aqueous ethanol. m.p. 128–131°C

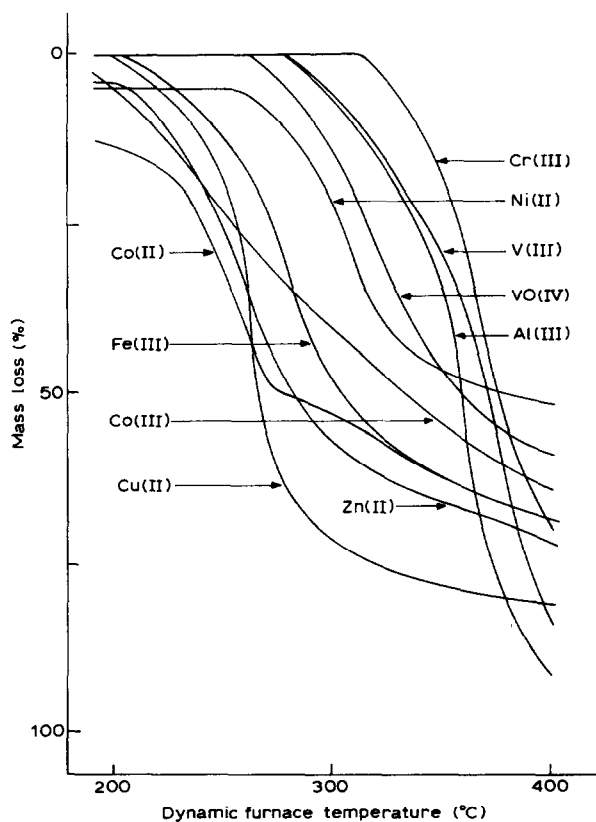


Fig. 1. TG curves for the chelates of 1-phenylbutane-1,3-dione.

(Found: C, 34.7; H, 0.6.  $C_{20}H_4F_{16}MnO_5$  requires C, 35.1; H, 0.6%). DTA: H, 109°C; D, 273°C.

*Bis[4,4,4-trifluoro-1-(pentafluorophenyl)butane-1,3-dionato]aquodioxouranium(VI)*. Prepared, as described for the manganese(II) derivative, as a yellow solid recrystallized from aqueous ethanol. m.p. 150–153°C (darkens) (Found: C, 26.3; H, 0.4.  $C_{20}H_4F_{16}O_7U$  requires C, 26.7; H, 0.4%). DTA: D, 302°C.

## RESULTS AND DISCUSSION

### Thermal analysis

It is appropriate to distinguish the chelates of Hba from those derived from  $HF_5bta$  insofar as thermal decomposition is the dominant process observed for the majority of chelates of Hba whereas several of the  $HF_5bta$  chelates vaporize quantitatively. Thermogravimetric curves for the chelates of Hba are presented in Fig. 1 and, based on the temperature corresponding to 30% weight loss, the trend in thermal

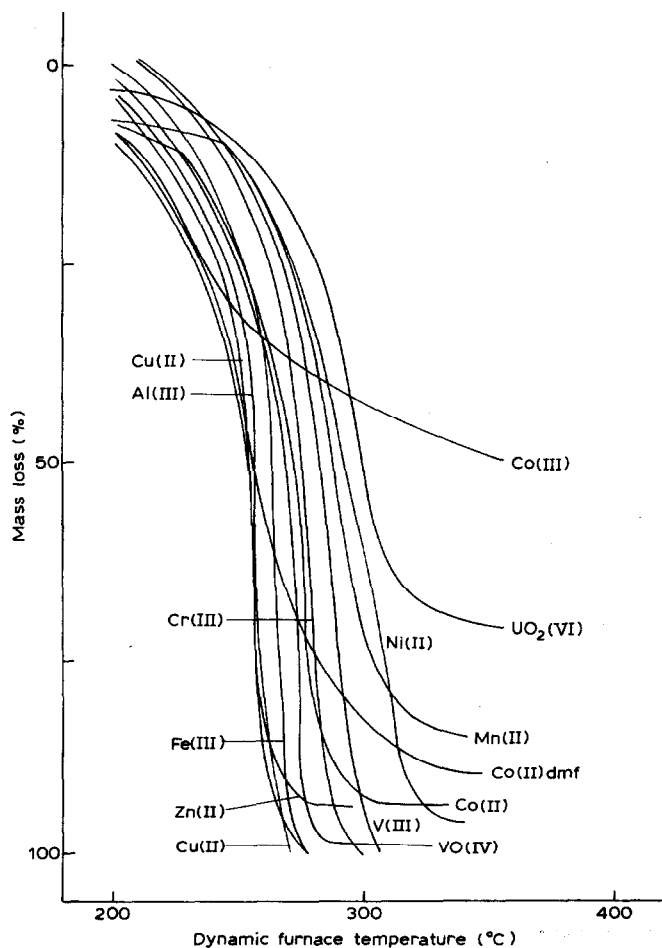


Fig. 2. TG curves for the chelates of 4,4,4-trifluoro-1-(pentafluorophenyl)butane-1,3-dione.

TABLE I

ELUTION BEHAVIOUR OF THE COPPER(II), ALUMINIUM(III), CHROMIUM(III) AND IRON(III) CHELATES OF 4,4,4-TRIFLUORO-1-(PENTAFLUOROPHENYL)BUTANE-1,3-DIONE

Data are reported as the retention times (min) and tailing indices<sup>3</sup> at 20% peak height for the injection of 10 µg chelate. Nominal 3% phase loading. For systems\* baseline elevation is too severe to measure the tailing index whereas for systems ≠, a reproducible peak was not obtained.

Column	Column temperature (°C)	Chelates of HF <sub>5</sub> bta							
		Cu(II)		Al(III)		Cr(III)		Fe(III)	
		t <sub>R</sub>	T <sub>0.2</sub> <sup>0</sup>	t <sub>R</sub>	T <sub>0.2</sub> <sup>0</sup>	t <sub>R</sub>	T <sub>0.2</sub> <sup>0</sup>	t <sub>R</sub>	T <sub>0.2</sub> <sup>0</sup>
SE-30; Chromosorb 750	180	6.86	*	7.00	0.35	9.60	0.96	11.40	*
Kel F Wax; Chromosorb 750	150	1.95	*	2.00	*	2.03	0.96	5.28	*
QF-1; Chromosorb 750	170	8.88	0.95	15.60	0.98	21.60	0.98	27.12	0.91
OV-3; Chromosorb 750	185	7.44	*	7.50	1.00	12.24	0.98	14.40	*
QF-1; Chromosorb W-HP	170	9.89	0.80	18.75	0.92	25.68	0.97	30.07	0.70
Apiezon L; Chromosorb 750	160	≠		14.40	0.85	27.36	0.87	≠	
OV-17; Chromosorb 750	170	11.51	*	9.87	0.93	16.32	1.00	18.72	*
DEGS; Chromosorb 750	110	3.00	0.27	3.50	0.94	3.90	*	≠	
QF-1; Carbon	220	≠		≠		62.00	0.66	≠	
QF-1; Porapak Q	200	≠		≠		≠		≠	

stability is: Co(II) < Co(III) ≈ Zn(II) < Cu(II) < Fe(III) < Ni(II) < VO(IV) < Al(III) ≈ V(III) < Cr(III), which shows some variation from earlier reported trends<sup>8</sup> probably due to the criterion used to assess stability.

The thermal behaviour (see Fig. 2) of the derivatives of HF<sub>5</sub>bta divides them into three groups: (i) the chelates of Cu(II), Al(III), Cr(III), Fe(III) and V(III) which volatilise quantitatively and yield copious quantities of condensate in the cold, furnace exit-tube, (ii) the compounds [Zn(II), VO(IV), Co(II), Ni(II)] which yield significant quantities of condensate but with traces of residue, and (iii) the non-volatile derivatives of Co(III), Co(II) adduct, Mn(II), and UO<sub>2</sub>(VI) which exhibit extensive decomposition with little or no volatilization. If a comparison of the volatility trend for the HF<sub>5</sub>bta chelates\* with that for the derivatives of other fluorinated aryl β-diketones<sup>3</sup> is now made, the following summary is obtained: 4,4,4-trifluoro-1-(pentafluorophenyl)butane-1,3-dione chelates: Zn(II) > Cu(II) > Al(III) > VO(IV) ≈ Fe(III) ≈ Co(II) > Cr(III) > V(III) > Ni(II); 4,4,4-trifluoro-1-phenylbutane-1,3-dione chelates: Cu(II) > Al(III) > Fe(III) > V(III) > Cr(III); 4,4,4-trifluoro-1-(4'-fluorophenyl)butane-1,3-dione chelates: Cu(II) > Al(III) > Fe(III) > V(III) >

\* For H<sub>5</sub>bta, the order can only be assigned approximately because of the simultaneous decomposition and volatilization of the group (ii) chelates.

Cr(III); 4,4,4-trifluoro-1-(2'-trifluoromethylphenyl)butane-1,3-dione chelates: Cu(II) > Al(III) > Fe(III)  $\approx$  V(III)  $\approx$  Cr(III); 4,4,4-trifluoro-1-(3'-trifluoromethylphenyl)butane-1,3-dione chelates: Cu(II) > V(III) > Fe(III)  $\approx$  Cr(III). From the differences in volatility of the individual chelates, the metal ion is seen to play an important role in the volatility of aryl  $\beta$ -diketonates but in a manner that inextricably involves the ligand itself.

### Gas chromatography

The thermal data suggest the suitability of the group (i) and group (ii) chelates of HF<sub>5</sub>bta for gas chromatographic analysis. However, the zinc(II), cobalt(II), and nickel(II) chelates do not elute from a wide range of supports and stationary phases,

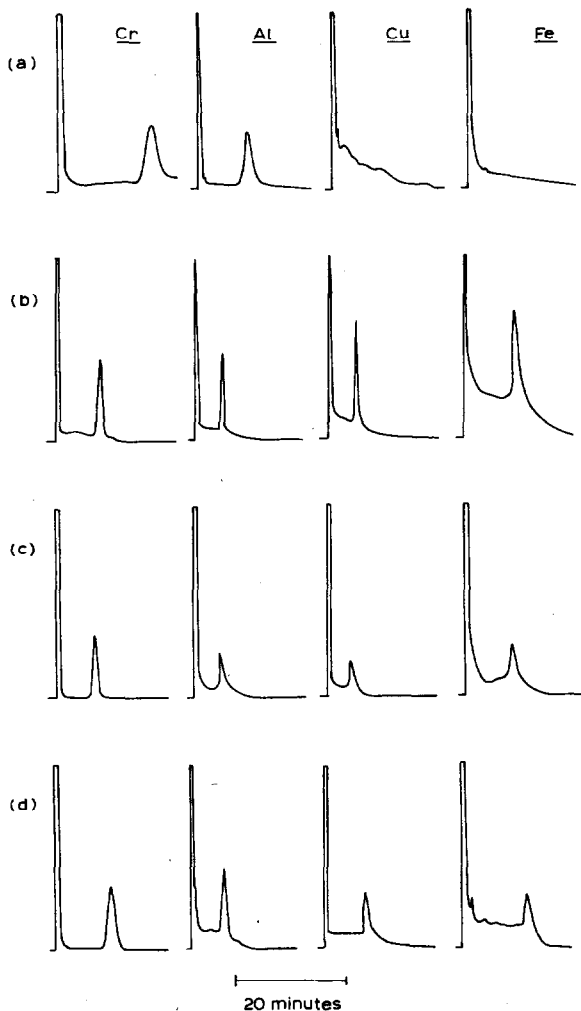


Fig. 3. Chromatograms showing the elution of Cr(F<sub>5</sub>bta)<sub>3</sub> (6  $\mu$ g), Al(F<sub>5</sub>bta)<sub>3</sub> (8  $\mu$ g), Cu(F<sub>5</sub>bta)<sub>2</sub> (8  $\mu$ g) and Fe(F<sub>5</sub>bta)<sub>3</sub> (30  $\mu$ g) on coated (3% nominal loading) Chromosorb 750. Phases are identified as (a) Apiezon L, (b) OV-3, (c) SE-30 and (d) OV-17. Column temperatures are 165°C, 175°C, 175°C and 170°C, respectively.

whereas the oxovanadium(IV) chelates undergo on-column transformation. Thus, the data of Table I are restricted to the copper(II), aluminium(III), chromium(III) and iron(III) derivatives and, with the exception of OV-17, the same elution sequence is observed for all columns. The importance of heteromolecular interactions<sup>5</sup> occurring in the GC column is emphasized since the iron(III) chelate is more volatile than the chromium derivative.

Whereas  $\text{Cr}(\text{F}_5\text{bta})_3$  generally elutes as a sharp, symmetric peak at the 10- $\mu\text{g}$  level, the copper(II), aluminium(III) and iron(III) chelates exhibit varying degrees of peak asymmetry and elevation of the baseline preceding the main chelate peak. The latter implies some form of on-column decomposition. As anticipated, the four chelates interact extensively with Porapak Q and with uncoated, diatomite supports such

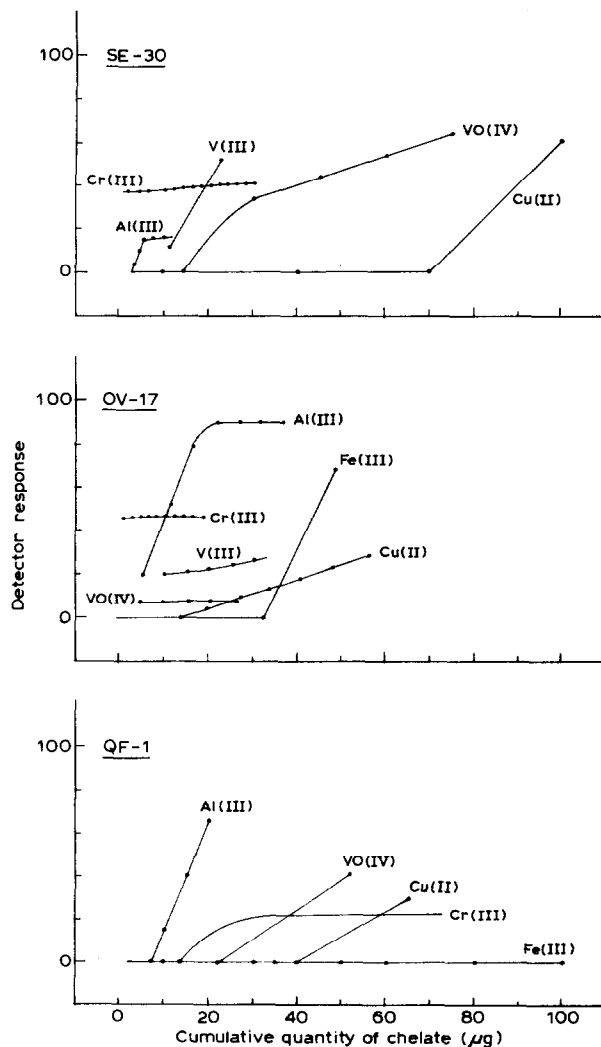


Fig. 4. Column loading curves for the chelates of  $\text{HF}_5\text{bta}$  on coated Chromosorb 750 (3% nominal loading of stationary phases).

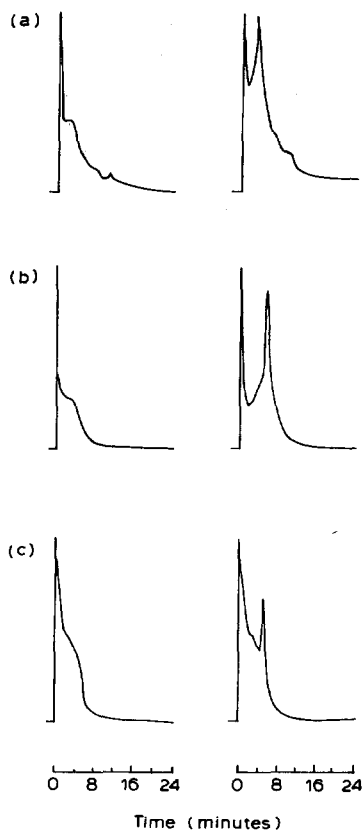


Fig. 5. Chromatograms illustrating elution of chelates on Chromosorb 750. (a)  $\text{Al}(\text{F}_5\text{bta})_3$ , 1  $\mu\text{g}$  on Kel F Wax; (b)  $\text{Cu}(\text{F}_5\text{bta})_2$ , 14  $\mu\text{g}$  on SE-30 and (c)  $\text{VO}(\text{F}_5\text{bta})_2$ , 15  $\mu\text{g}$  on SE-30. In each case, chromatograms are shown for an unused column (left) and on a column following priming (right).

as Chromosorb W HP and Chromosorb 750. Of the supports, Chromosorb 750 is superior and its use became more critical as the performance of the chelate deteriorated in the order chromium, aluminium, copper and iron(III).

Considering the liquid phases, exceptionally short retention times are observed on Kel F Wax. Although this phase exhibits a low retention of the chelates, the extent of unfavourable interactions, as gauged by the tailing index, is enhanced. Of the stationary phases examined, QF-1 exhibits the most satisfactory overall performance although there are disadvantages<sup>3</sup> associated with its use. Of more importance is the interaction of the stationary phase and the metal ion in determining elution behaviour, as is illustrated in Fig. 3. Thus, the copper(II) and iron(III) derivatives are totally retained on Apiezon L in contrast to the behaviour of the aluminium and chromium chelates and yet, even here, elution abnormalities are apparent. The chelates of all four ions are eluted on the remaining phases (OV-3, SE-30 and OV-17) with, once again, considerable variation in the performance of the individual chelates. The elevated baselines observed with many of the chelates are consistent with a dissociative ion-exchange mechanism<sup>5</sup> of chelate retention.

Influence of the metal ion on column retention, illustrated in Fig. 4 for the



chelates of  $\text{HF}_3\text{bta}$  on OV-17, QF-1 and SE-30 on Chromosorb 750, is seen to decrease in the order  $\text{Fe(III)} > \text{Cu(II)} > \text{VO(IV)} > \text{V(III)} > \text{Al(III)} > \text{Cr(III)}$  which also reflects the change in detection limit in the series. In the particular case of SE-30 and Chromosorb 750, detection limits ranged from 10 ng for the chromium(III) chelate to 5  $\mu\text{g}$  for the iron(III) chelate. Overall, it is evident from these data that wide variations exist in the behaviour of the different metal ion derivatives. In addition to quantitative changes (such as detector response) effected by column loading, qualitative changes in the peak shape, for example, also occur as illustrated in Fig. 5 for selected chelates. Furthermore, on unused columns, chelate decomposition is a common occurrence and can produce spurious peaks as shown in Fig. 5 for the aluminium, copper(II) and oxovanadium(IV) chelates.

A further factor which may be critical in determining the column performance of a chelate is the actual injection technique. This is illustrated in Fig. 6 where rapid withdrawal ( $< 15$  sec) of the syringe from the injection port can result in visible aerosol formation in the vicinity of the septum whilst prolonged exposure of the needle to the heated injection port also has adverse effects due to the appearance of several additional peaks in the region of the solvent and the reduced height of the chelate peak.

We conclude with evidence (see Fig. 7) to show that the adverse behaviour of the derivatives of the two aryl  $\beta$ -diketones is not a unique feature of this group of compounds containing aromatic substituents. Here, employing the aluminium(III), iron(III), chromium(III), cobalt(III), manganese(III), vanadium(III), and copper(II) chelates of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione, whose thermal stability and volatility are well established<sup>5,9</sup>, GC-MS confirmed several important aspects of the behaviour. Notable among these are the elution of free ligand as a decomposition product of several of the chelates, the failure of the intact manganese(III) chelate to elute, the presence of copper(II) chelate in the region prior to

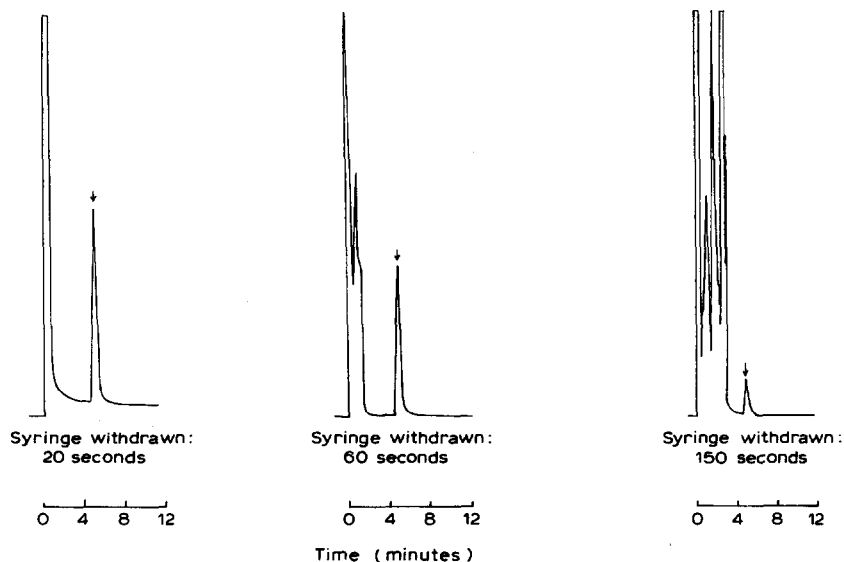


Fig. 6. Chromatograms showing the syringe-induced decomposition of  $\text{Cr}(\text{F}_3\text{bta})_3$  (shown as  $\downarrow$ ) on OV-3 and Chromosorb W HP at a column temperature of 195°C and an injection port temperature of 215°C.

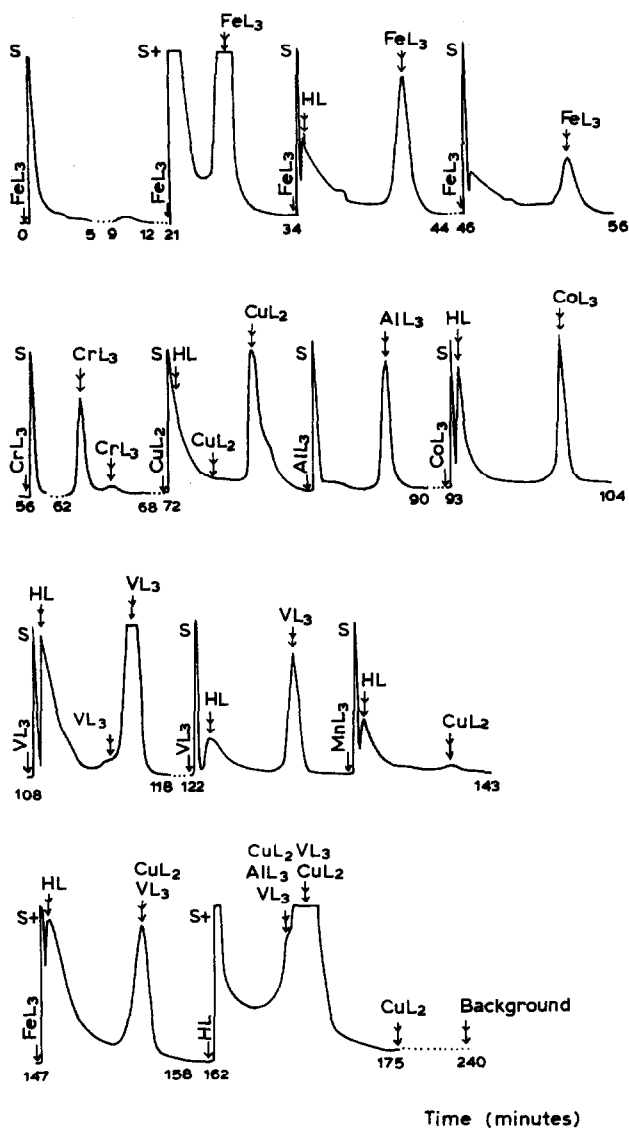


Fig. 7. Continuous record of chromatograms of the chelates of Hhpm (HL). Arrows indicate the points of injection ( $\downarrow$ ) of the chelates (or ligand) and identity ( $\uparrow$ ) of the eluate based on mass spectrometry. Solvent is denoted by either S or S+ (where other components are present), as appropriate.

emergence of the main chelate peak, the elution of several of the chelates upon injection of free ligand and various displacement effects. Indeed, although not conclusive, the identification of free ligand in the column eluate provides direct support for the proposed<sup>5</sup> ion-exchange mechanism of chelate retention.

It remains for us to show in a later paper that a capillary system can reduce or eliminate unwanted effects, otherwise a judicious choice of support, stationary phase and ligand is necessary for a particular application. As in the previous paper<sup>3</sup>

in this series, these results emphasize the diversity of on-column reactions, and the need to better understand and control them, if a wider application of the  $\beta$ -diketones is to be achieved.

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