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VOLATILITY STUDIES OF METAL CHELATES

VI*. GAS CHROMATOGRAPHIC BEHAVIOUR OF ARYL β -DIKETONES AND THEIR METAL CHELATES

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SUMMARY

Gas chromatographic data are reported for a series of aryl β -diketonates. Although thermoanalytical data show that the chelates are thermally stable and volatile at typical column temperatures, several adverse phenomena, including peak asymmetry, baseline elevation, displacement and priming effects, are observed during the elution of the chelates. Column components and the extent of fluorination in the chelate are established as contributing factors to the adverse behaviour which is interpreted in terms of the physical and diverse chemical interactions occurring within the column.

INTRODUCTION

In an earlier paper¹, the thermal behaviour of a series of copper(II) aryl β -diketonates, as established by simultaneous thermogravimetry-differential thermal analysis (TG-DTA), was rationalized. Despite the extensive variation in the ligand structure, the metal ion was not varied. Since volatility and thermal stability are determined^{2,3} by a complex interplay of metal ion and ligand parameters, the earlier work has been extended to a study of the thermal and gas chromatographic behaviour of other metal ion derivatives.

Although many chelates exhibit the volatility and thermal stability necessary for gas chromatography (GC)¹⁻⁶, analytical applications using metal chelate GC are somewhat restricted due to adverse on-column behaviour, manifestations of which can be seen⁷, and demonstrated⁸, in early publications. Yet rarely has this been

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considered⁹⁻¹¹ in later work. More recently, the adverse behaviour^{12,13}, which is accentuated¹⁴ at trace levels with obvious implications for analytical work, has been attributed to physical and chemical effects occurring within the column in addition to the desirable partitioning process. Thus, whereas the mainly physical effects include true adsorption, which ultimately sets the chromatographic limits of detection, and since weak forces are generally involved, this process is reversible and leads to such phenomena, as tailing, seen also in the early literature¹⁵ of the GC of polar organic solutes. However, when highly reactive solutes such as metal chelates are considered, additional retention mechanisms become important. These effects are often chemical in nature and arise from diverse irreversible chemical reactions in the column. Retention mechanisms included in this category are reactions of the chelates with the column packing and include any impurities in the column (residual catalyst from the synthesis of the stationary phase, for example), impurities introduced with the chelates (for example, oxygen and water) and reaction on any hot metal surfaces. Specific effects which may arise are the thermally induced redox reactions as observed in the case of vanadium(III)-oxovanadium(IV) chelates³, acid-base phenomena, and catalytic phenomena. Indeed, it is only recently that catalytic activity has been considered¹⁶ in relation to organic solutes.

Within this context, this paper presents the gas chromatographic properties of chelates derived from a series of aryl β -diketones with metal ions, including chromium(III), iron(III), vanadium(III), aluminium(III), copper(II), zinc(II), nickel(II), cobalt(II) and oxovanadium(IV). Ligand systems include 4,4,4-trifluoro-1-phenylbutane-1,3-dione (Hbta); 4,4,4-trifluoro-1-(pentafluorophenyl)butane-1,3-dione (HF₃bta) and 4,4,4-trifluoro-1-(2'-trifluoromethylphenyl)butane-1,3-dione (HoCF₃bta). These ligands were chosen to represent various degrees of fluorination in the substituents in these molecules. Moreover, gas chromatographic data have not previously been reported for derivatives of these extensively fluorinated aryl β -diketones. Many of the chelates are reported for the first time.

EXPERIMENTAL

Thermal analysis

The thermal data were obtained on a combined TG-DTA instrument as previously reported¹. DTA data are presented as temperatures measured at peak maxima for the various transitions, identified as fusion (F), volatilization (V), decomposition (D) and dehydration (H), as appropriate.

Gas chromatography

An instrument equipped with flame ionisation detectors was used for this work. Direct on-column injection minimised contact of the chelate vapours and hot metal surfaces. Carrier gas was filtered, high-purity, dry nitrogen at a flow-rate of 50 ml/min.

Borosilicate glass columns (0.5 m \times 4 mm I.D.) containing a 3% nominal loading of stationary phase are identified as follows: (1) uncoated Chromosorb 750; (2) OV-17 on Chromosorb W AW; (3) OV-17 on Chromosorb 750; (4) QF-1 on Chromosorb W HP; (5) QF-1 on Chromosorb 750; (6) OV-3 on Chromosorb W HP; (7) Kel F Wax on Chromosorb 750; (8) SE-30 on Chromosorb 750; (9) Apiezon L

on Chromosorb 750; (10) OV-17 on Porasil F; (11) OV-17 on Porasil E; (12) OV-17 on Porasil C; (13) OV-210 on Chromosorb 750. Silanized glass wool was used to plug the ends of the column. Prior to use, columns were conditioned for 12 h following on-column silylation with N,O-bis(trimethylsilyl)trifluoroacetamide ($5 \times 40 \mu\text{l}$ injections) then hexamethyldisilazane ($5 \times 40 \mu\text{l}$). Injection port and detector temperatures were maintained at 20°C above that of the column.

Data for loading curves were obtained by plotting detector response against the cumulative amount of chelate injected onto the column. A new column was used to collect the data for each chelate. Since the use of an internal standard was precluded by the abnormal elution of the chelates the results must be considered as semi-quantitative. However, the reproducibility of the injection technique ($\pm 1\%$ peak height) was established with methyl esters of fatty acids and tris[4,4,4-trifluoro-1-(pentafluorophenyl)butane-1,3-dionato]chromium(III). Comparisons must also allow for the variation in injection quantity.

Relative retention data (t'_R) in the numerical listing of compounds in the *Synthesis of chelates* section were collected, using a $1\text{-}\mu\text{l}$ injection ($10 \mu\text{g}$ chelate), on a borosilicate glass column (1.5 m long) packed with Chromosorb 750 coated with SE-30 (3% w/w). Column temperature was maintained at 220°C and the nitrogen carrier gas flow at 60 ml/min.

Synthesis of ligands

The β -diketones were prepared¹⁷ by a Claisen condensation of the appropriate ethyl ester and ketone with sodium hydride or sodium *tert.*-butoxide as condensing agent. Abbreviations used to identify the ligands are derived from trivial names. Thus, Hbta refers to benzoyltrifluoroacetone whereas all other abbreviations refer to ring-substituted derivatives of this ligand.

Synthesis of chelates

Zinc(II), cobalt(II) and nickel(II) chelates. These chelates were prepared as described previously¹ for the copper(II) chelates with modification to allow for the greater Lewis acidity of these ions. This variation entailed use of the appropriate metal acetate and noting that pH control was essential. All chelates were heated under vacuum for 5 h (0.2 mmHg; $60\text{--}80^\circ\text{C}$) to remove excess ligand, prior to recrystallization. Zinc chelates were recrystallized from a variety of solvents to yield white solids whereas the cobalt and nickel chelates were recrystallized from aqueous ethanol to yield yellow and green solids, respectively. Infrared spectra indicated that all purified chelates were hydrated.

(1) Bis[4,4,4-trifluoro-1-(pentafluorophenyl)butane-1,3-dionato]aquozinc(II). Recrystallized from hexane, m.p. $148\text{--}150^\circ\text{C}$ (Found: C, 34.2; H, 0.5. $\text{C}_{20}\text{H}_4\text{F}_{16}\text{O}_5\text{Zn}$ requires C, 34.6; H, 0.6%). DTA: H, 88°C ; V, D, 208°C .

(2) Bis[4,4,4-trifluoro-1-(4'-fluorophenyl)butane-1,3-dionato]zinc(II). Recrystallized from aqueous ethanol, m.p. $139\text{--}142^\circ\text{C}$ (Found: C, 45.2; H, 2.0. $\text{C}_{20}\text{H}_{10}\text{F}_8\text{O}_4\text{Zn}$ requires C, 45.2; H, 1.9%). DTA: F, 143°C ; V, D, 292°C .

(3) Bis[4,4,4-trifluoro-1-phenylbutane-1,3-dionato]diaquozinc(II). Recrystallized from aqueous ethanol, m.p. $139\text{--}144^\circ\text{C}$ (Found: C, 45.2; H, 3.0. Calc. for $\text{C}_{20}\text{H}_{16}\text{F}_6\text{O}_6\text{Zn}$: C, 45.2; H, 3.0%). DTA: H, 103°C ; F, 183°C ; V, D, 298°C .

(4) Bis[4,4,4-trifluoro-1-(4'-chlorophenyl)butane-1,3-dionato]zinc(II). Recrys-

tallized from aqueous ethanol, m.p. 174–176°C (Found: C, 42.2; H, 1.8. $C_{20}H_{10}Cl_2F_6O_4Zn$ requires C, 42.5; H, 1.8%) DTA: F, 175°C; V, D, 303°C.

(5) Bis[4,4,4-trifluoro-1-(4'-bromophenyl)butane-1,3-dionato]aquozinc(II). Recrystallized from aqueous ethanol, m.p. 185–186°C (Found: C, 35.9; H, 1.6. $C_{20}H_{12}Br_2F_6O_5Zn$ requires C, 35.7; H, 1.8%). DTA: ?, 169°C; F, 189°C; D, 318°C.

(6) Bis[4,4,4-trifluoro-1-(4'-*tert.*-butylphenyl)butane-1,3-dionato]aquozinc(II). Recrystallized from aqueous ethanol, m.p. 195–197°C (Found: C, 54.1; H, 4.9. $G_{28}H_{30}F_6O_5Zn$ requires C, 53.7; H, 4.8%). DTA: H, 153°C; F, 196°C; D, 319°C.

(7) Bis[4,4,4-trifluoro-1-(pentafluorophenyl)butane-1,3-dionato]aquocobalt(II). m.p. 160–171°C darkens (Found: C, 34.7; H, 0.6. $C_{20}H_4CoF_{16}O_5$ requires C, 34.9; H, 0.6%). DTA: ?, 128°C; V, D, 289°C.

(8) Bis[4,4,4-trifluoro-1-(4'-fluorophenyl)butane-1,3-dionato]diaquocobalt(II). m.p. 151°C darkens, 158–166°C fuses (Found: C, 42.5; H, 2.4. $C_{20}H_{14}CoF_8O_6$ requires C, 42.8; H, 2.5%). DTA: H, 81°C; ?, 105°C; ?, 155°C; D, 298°C.

(9) Bis[4,4,4-trifluoro-1-phenylbutane-1,3-dionato]diaquocobalt(II). m.p. 155°C darkens, 163–169°C fuses (Found: C, 45.6; H, 3.2. Calc. for $C_{20}H_{16}CoF_6O_6$: C, 45.7; H, 3.0%). DTA: H, 120°C; V, 162°C; D, 308°C.

(10) Bis[4,4,4-trifluoro-1-(4'-chlorophenyl)butane-1,3-dionato]diaquocobalt(II)*. m.p. 158°C darkens, 164–171°C fuses (Found: C, 40.7; H, 2.4. $C_{20}H_{14}Cl_2CoF_6O_6$ requires C, 40.4; H, 2.4%). DTA: H, 75°C; H, 109°C; ?, 151°C; D, 318°C.

(11) Bis[4,4,4-trifluoro-1-(4'-bromophenyl)butane-1,3-dionato]diaquocobalt(II). m.p. 165–174°C darkens (Found: C, 34.9; H, 2.0. $C_{20}H_{14}Br_2CoF_6O_6$ requires C, 35.1; H, 2.1%). DTA: H, 103°C; D, 321°C.

(12) Bis[4,4,4-trifluoro-1-(4'-*tert.*-butylphenyl)butane-1,3-dionato]aquocobalt(II). m.p. 98–134°C darkens (Found: C, 54.0; H, 4.7. $C_{28}H_{30}CoF_6O_5$ requires C, 54.3; H, 4.8%). DTA: D, 324°C.

(13) Bis[4,4,4-trifluoro-1-(pentafluorophenyl)butane-1,3-dionato]diaquonickel(II). m.p. 167°C alters, 180–182°C fuses (Found: C, 33.7; H, 0.9. $C_{20}H_6F_{16}NiO_6$ requires C, 34.0; H, 0.9%). DTA: H, 81°C; V, D, 304°C.

(14) Bis[4,4,4-trifluoro-1-(4'-chlorophenyl)butane-1,3-dionato]diaquonickel(II). m.p. 179–183°C (Found: C, 40.4; H, 2.1. $C_{20}H_{14}Cl_2F_6NiO_6$ requires C, 40.4; H, 2.4%). DTA: D, 331°C.

(15) Bis[4,4,4-trifluoro-1-(4'-fluorophenyl)butane-1,3-dionato]diaquonickel(II). m.p. 168–172°C (Found: C, 43.0; H, 2.8. $C_{20}H_{14}F_8NiO_6$ requires C, 42.8; H, 2.5%). DTA: H, 113°C; V, D, 328°C.

(16) Bis[4,4,4-trifluoro-1-phenylbutane-1,3-dionato]diaquonickel(II). m.p. 176–183°C (Found: C, 45.3; H, 3.0. Calc. for $C_{20}H_{16}F_6NiO_6$: C, 45.7; H, 3.0%). DTA: H, 134°C; D, 238°C; D, 328°C.

(17) Bis[4,4,4-trifluoro-1-(4'-*tert.*-butylphenyl)butane-1,3-dionato]aquonickel(II). m.p. 174–180°C (Found: C, 54.2; H, 4.7. $C_{28}H_{30}F_6NiO_5$ requires C, 54.3; H, 4.9%). DTA: D, 348°C.

(18) Bis[4,4,4-trifluoro-1-(4'-bromophenyl)butane-1,3-dionato]aquonickel-

* This compound exists in two easily interconverted forms. For example, heating the yellow form under vacuum (40°C; 10 mmHg) produces a green solid, which gradually reverts to the yellow solid on exposure to air.

(II). m.p. 169–177°C (Found: C, 36.1; H, 2.0. $C_{20}H_{12}Br_2F_6NiO_5$ requires C, 36.1; H, 1.8%). DTA: H, 132°C; D, 316°C.

Oxovanadium(IV) chelates. Preparation involved¹⁸ reaction of oxovanadium(IV) sulphate with the appropriate ligand in sodium acetate buffered solution. The crude products were purified by recrystallization following removal of excess ligand under vacuum to yield anhydrous solids.

(19) Bis[4,4,4-trifluoro-1-(pentafluorophenyl)butane-1,3-dionato]oxovanadium(IV). Recrystallized from chloroform–hexane as a light yellow-buff solid. m.p. 219–221°C (Found: C, 35.7; H, 0.1. $C_{20}H_2F_{16}O_5V$ requires C, 35.5; H, 0.3%). DTA: F, 220°C; V, D, 285°C.

(20) Bis[4,4,4-trifluoro-1-(2'-trifluoromethylphenyl)butane-1,3-dionato]oxovanadium(IV). Recrystallized from hexane–benzene as a light green solid. m.p. 221°C (Found: C, 41.7; H, 1.4. $C_{22}H_{10}F_{12}O_5V$ requires C, 41.7; H, 1.6%). DTA: F, 221°C; D, 280°C; D, 298°C.

(21) Bis[4,4,4-trifluoro-1-(4'-fluorophenyl)butane-1,3-dionato]oxovanadium(IV). Recrystallized from aqueous ethanol as orange-yellow crystals. m.p. 238–239°C (lit.³ 238–239°C) (Found: C, 44.8; H, 1.9. Calc. for $C_{20}H_{10}F_8O_5V$: C, 45.0; H, 1.9%). DTA: F, 236°C; V, D, 310°C.

(22) Bis[4,4,4-trifluoro-1-phenylbutane-1,3-dionato]oxovanadium(IV). Recrystallized from aqueous ethanol as orange-yellow crystals. m.p. 280°C (lit.³ 281–282°C) (Found: C, 48.2; H, 2.6. Calc. for $C_{20}H_{12}F_6O_5V$: C, 48.3; H, 2.4%). DTA: F, 283°C; V, D, 319°C.

(23) Bis[1-phenylbutane-1,3-dionato]oxovanadium(IV). Recrystallized from chloroform–hexane as a green amorphous solid. m.p. 218°C (lit.³ 217–218°C) (Found: C, 61.7; H, 4.7. Calc. for $C_{20}H_{18}O_5V$: C, 61.7; H, 4.6%). DTA: F, 218°C; D, 321°C.

Vanadium(III) chelates. The vanadium(III) chelates were prepared by a dithionite reduction¹⁸ of oxovanadium(IV), prior to reaction with the β -diketone. Purified chelates were anhydrous brown solids.

(24) Tris[4,4,4-trifluoro-1-(pentafluorophenyl)butane-1,3-dionato]vanadium(III). m.p. 189–193°C (Found: C, 37.2; H, 0.2. $C_{30}H_3F_{24}O_6V$ requires C, 37.3; H, 0.3%). DTA: F, 193°C; V, 288°C.

(25) Tris[4,4,4-trifluoro-1-(3'-trifluoromethylphenyl)butane-1,3-dionato]vanadium(III). m.p. 133–138°C (Found: C, 44.3; H, 1.6. $C_{33}H_{15}F_{18}O_6V$ requires C, 44.0; H, 1.7%). DTA: F, 138°C; V, 296°C.

(26) Tris[4,4,4-trifluoro-1-(2'-trifluoromethylphenyl)butane-1,3-dionato]vanadium(III). m.p. 71–72°C (Found: C, 44.2; H, 1.6. $C_{33}H_{15}F_{18}O_6V$ requires C, 44.0; H, 1.7%). DTA: F, 72°C; V, 309°C.

(27) Tris[4,4,4-trifluoro-1-(4'-fluorophenyl)butane-1,3-dionato]vanadium(III). m.p. 185–190°C (lit.³ 181–190°C) (Found: C, 48.2; H, 2.1. Calc. for $C_{30}H_{15}F_{12}O_6V$: C, 48.0; H, 2.0%). DTA: F, 190°C; V, 324°C.

(28) Tris[4,4,4-trifluoro-1-phenylbutane-1,3-dionato]vanadium(III). m.p. 151–152°C (lit.³ 151–153°C) (Found: C, 52.4; H, 2.6. Calc. for $C_{30}H_{18}F_9O_6V$: C, 51.7; H, 2.6%). DTA: F, 152°C; V, D, 325°C.

(29) Tris[1-phenylbutane-1,3-dionato]vanadium(III). m.p. 230–232°C (lit.³ 228–230°C) (Found: C, 67.5; H, 5.2. Calc. for $C_{30}H_{27}O_6V$: C, 67.4; H, 5.1%). DTA: F, 233°C; D, 381°C.

Aluminium chelates. These compounds were prepared by reacting the ligand

with aluminium chloride in hot aqueous ethanol, buffered to pH 6.5 with sodium acetate. Purification involved elution with benzene from a bed of alumina, prior to recrystallization to yield white solids.

(30) Tris[4,4,4-trifluoro-1-(pentafluorophenyl)butane-1,3-dionato]aluminium(III). m.p. 119°C (Found: C, 37.9; H, 0.6. $C_{30}H_3AlF_{24}O_6$ requires C, 38.2; H, 0.3%). DTA: F, 118°C; V, 265°C.

(31) Tris[4,4,4-trifluoro-1-(2'-trifluoromethylphenyl)butane-1,3-dionato]aluminium(III). m.p. 153°C (Found: C, 45.1; H, 1.9. $C_{33}H_{15}AlF_{18}O_6$ requires C, 45.2; H, 1.7%). DTA: F, 153°C; V, 293°C.

(32) Tris[4,4,4-trifluoro-1-(4'-fluorophenyl)butane-1,3-dionato]aluminium(III). m.p. 118°C (lit.³ 120°C) (Found: C, 49.8; H, 1.9. Calc. for $C_{30}H_{15}AlF_{12}O_6$: C, 49.6; H, 2.1%). DTA: F, 118°C; V, D, 301°C.

(33) Tris [4,4,4-trifluoro-1-phenylbutane-1,3-dionato]aluminium(III). m.p. 194°C (lit.³ 192°C) (Found: C, 53.6; H, 2.5. Calc. for $C_{30}H_{18}AlF_9O_6$: C, 53.6; H, 2.7%). DTA: F, 194°C; V, D, 314°C.

(34) Tris[1-phenylbutane-1,3-dionato]aluminium(III). m.p. 219–220°C (lit.³ 223°C) (Found: C, 70.4; H, 5.4. Calc. for $C_{30}H_{27}AlO_6$: C, 70.6; H, 5.3%). DTA: F, 222°C; D, 363°C.

Iron(III) chelates. These chelates were prepared by the addition of a hot aqueous solution of iron(III) chloride hexahydrate (0.25 M: 20 ml) to a hot ethanolic solution (40 ml) containing a 10% excess of the ligand. Where precipitation of the chelate did not occur, this was induced with water and the crude product recovered by filtration, washed and dried. The product was recrystallized following removal of excess ligand, as above to give red solids.

(35) Tris[1-phenylbutane-1,3-dionato]iron(III). m.p. 218°C (lit.¹⁹ 218°C; lit.²⁰ 211°C) (Found: C, 66.7; H, 5.1. Calc. for $C_{30}H_{27}FeO_6$: C, 66.8; H, 5.0%). DTA: F, 220°C; D, V, 272°C.

(36) Tris[4,4,4-trifluoro-1-(pentafluorophenyl)butane-1,3-dionato]iron(III). m.p. 78–79°C (Found: C, 37.3; H, 0.2. $C_{30}H_3F_{24}FeO_6$ requires C, 37.1; H, 0.3%). DTA: F, 79°C; V, 271°C.

(37) Tris[4,4,5,5,6,6,6-heptafluoro-1-(4'-fluorophenyl)hexane-1,3-dionato]iron(III). m.p. 44–46°C (Found: C, 41.2; H, 1.3. $C_{36}H_{15}F_{24}FeO_6$ requires C, 40.9; H, 1.4%). DTA: V, 298°C.

(38) Tris[4,4,5,5,5-pentafluoro-1-(4'-fluorophenyl)pentane-1,3-dionato]iron(III). m.p. 127°C (Found: C, 43.8; H, 1.7. $C_{33}H_{15}F_{18}FeO_6$ requires C, 43.8; H, 1.6%). DTA: F, 127°C; V, 300°C.

(39) Tris[4,4,4-trifluoro-1-(3'-trifluoromethylphenyl)butane-1,3-dionato]iron(III). m.p. 128°C (Found: C, 44.0; H, 1.7. $C_{33}H_{15}F_{18}FeO_6$ requires C, 43.8; H, 1.6%). DTA: F, 126°C; V, 304°C.

(40) Tris[4,4,4-trifluoro-1-(2',4'-difluorophenyl)butane-1,3-dionato]iron(III). m.p. 142°C (Found: C, 44.5; H, 1.4. $C_{30}H_{12}F_{15}FeO_6$ requires C, 44.5; H, 1.5%). DTA: F, 143°C; V, 303°C.

(41) Tris[4,4,4-trifluoro-1-(2'-trifluoromethylphenyl)butane-1,3-dionato]iron(III). m.p. 163°C (Found: C, 44.1; H, 1.6. $C_{33}H_{15}F_{18}FeO_6$ requires C, 43.8; H, 1.6%). DTA: F, 163°C; V, 308°C.

(42) Tris[4,4,5,5,5-pentafluoro-1-(4'-chlorophenyl)pentane-1,3-dionato]iron(III). m.p. 47–48°C (Found: C, 42.3; H, 1.8. $C_{33}H_{15}Cl_3F_{15}FeO_6$ requires C, 41.5; H, 1.6%). DTA: V, 320°C.

(43) Tris[4,4,4-trifluoro-1-(4'-fluorophenyl)butane-1,3-dionato]iron(III). m.p. 154°C (lit.³ 156°C) (Found: C, 47.5; H, 2.0. Calc. for $C_{30}H_{15}F_{12}FeO_6$: C, 47.7; H, 2.0%). DTA: F, 153°C; V, 314°C.

(44) Tris[4,4,4-trifluoro-1-phenylbutane-1,3-dionato]iron(III). m.p. 129°C (lit.³ 128–129°C) (Found: C, 51.6; H, 2.6. Calc. for $C_{30}H_{18}F_9FeO_6$: C, 51.4; H, 2.6%). DTA: F, 128°C; V, 331°C.

(45) Tris[4,4,5,5,6,6,6-heptafluoro-1-(4'-chlorophenyl)hexane-1,3-dionato]iron(III). m.p. 40–41°C (Found: C, 39.7; H, 1.5. $C_{36}H_{15}Cl_3F_{21}FeO_6$ requires C, 39.1; H, 1.4%). DTA: V, 330°C.

(46) Tris[4,4,4-trifluoro-1-(2',5'-dimethylphenyl)butane-1,3-dionato]iron(III). m.p. 63–66°C (Found: C, 54.8; H, 3.6. $C_{36}H_{30}F_9FeO_6$ requires C, 55.0; H, 3.8%). DTA: V, 338°C.

(47) Tris[4,4,4-trifluoro-1-(3'-chlorophenyl)butane-1,3-dionato]iron(III). m.p. 201°C (Found: C, 44.5; H, 2.0. $C_{30}H_{15}Cl_3F_9FeO_6$ requires C, 44.8; H, 1.9%). DTA: F, 201°C; V, 341°C.

(48) Tris[4,4,4-trifluoro-1-(2',4'-dimethylphenyl)butane-1,3-dionato]iron(III). m.p. 64–68°C (Found: C, 55.0; H, 3.9. $C_{36}H_{30}F_9FeO_6$ requires C, 55.0; H, 3.8%). DTA: V, 343°C.

(49) Tris[4,4,4-trifluoro-1-(2'-chlorophenyl)butane-1,3-dionato]iron(III). m.p. 66–70°C (Found: C, 45.1; H, 2.0. $C_{30}H_{15}Cl_3F_9FeO_6$ requires C, 44.8; H, 1.9%). DTA: V, 345°C.

(50) Tris[4,4,4-trifluoro-1-(4'-methylphenyl)butane-1,3-dionato]iron(III). m.p. 87–88°C (Found: C, 53.0; H, 3.1. $C_{33}H_{24}F_9FeO_6$ requires C, 53.3; H, 3.2%). DTA: V, 343°C.

(51) Tris[4,4,4-trifluoro-(4'-chlorophenyl)butane-1,3-dionato]iron(III). m.p. 167–168°C (Found: C, 45.0; H, 2.2. $C_{30}H_{15}Cl_3F_9FeO_6$ requires C, 44.8; H, 1.9%). DTA: F, 168°C; V, 355°C.

(52) Tris[4,4,4-trifluoro-(3',4'-dimethylphenyl)butane-1,3-dionato]iron(III). m.p. 102–104°C (Found: C, 54.7; H, 3.9. $C_{36}H_{30}F_9FeO_6$ requires C, 55.0; H, 3.8%). DTA: V, 358°C.

(53) Tris[4,4,4-trifluoro-1-(4'-tert.-butylphenyl)butane-1,3-dionato]iron(III). m.p. 111°C (Found: C, 58.1; H, 5.2. $C_{42}H_{42}F_9FeO_6$ requires C, 58.0; H, 4.8%). DTA: F, 113°C; V, 364°C.

Chromium(III) chelates. Chromium(III) acetate (0.005 mol) and the required ligand (0.016 mol) were heated in ethanol (85 ml, 50°C) for 7 h, when solvent was allowed to evaporate. The green, tacky residue was heated under vacuum for five hours (0.2 mm, 60–80°C) to remove any excess ligand, then purified on alumina with benzene: hexane (proportions varied for each compound). In all instances, more polar compounds were retained on the column.

(54) Tris[1-phenylbutane-1,3-dionato]chromium(III). m.p. 223°C (lit.²¹ *cis* 200°C; *trans* 235°C) (Found: C, 67.1; H, 5.3. Calc. for $C_{30}H_{27}CrO_6$: C, 67.3; H, 5.0%). DTA: F, 222°C; D, V, 378°C.

(55) Tris[4,4,4-trifluoro-1-(pentafluorophenyl)butane-1,3-dionato]chromium(III). m.p. 54–55°C (Found: C, 36.9; H, 0.3. $C_{30}H_3CrF_{24}O_6$ requires C, 37.2; H, 0.3%). DTA: V, 275°C. $t_R = 0.15$.

(56) Tris[4,4,5,5,5-pentafluoro-1-(pentafluorophenyl)pentane-1,3-dionato]chromium(III). Tacky gum (Found: C, 35.6; H, 0.4. $C_{33}H_3CrF_{30}O_6$ requires C, 35.5; H, 0.3%). DTA: V, 275°C. $t_R = 0.15$.

(57) Tris[4,4,4-trifluoro-1-(3'-trifluoromethylphenyl)butane-1,3-dionato]chromium(III). m.p. 148–151°C (Found: C, 43.6; H, 1.6. $C_{33}H_{15}CrF_{18}O_6$ requires C, 44.0; H, 1.7%). DTA: F, 152°C; V, 303°C. $t'_R = 0.33$.

(58) Tris[4,4,5,5,6,6,6-heptafluoro-1-(4'-fluorophenyl)hexane-1,3-dionato]chromium(III). m.p. 73–76°C (Found: C, 40.9; H, 1.6. $C_{36}H_{15}CrF_{24}O_6$ requires C, 41.1; H, 1.4%). DTA: F, 76°C; V, 305°C. $t'_R = 0.49$.

(59) Tris[4,4,5,5,5-pentafluoro-1-(4'-fluorophenyl)pentane-1,3-dionato]chromium(III). m.p. 74–77°C (Found: C, 44.1; H, 2.0. $C_{33}H_{15}CrF_{18}O_6$ requires C, 43.9; H, 1.7%). DTA: F, 76°C; V, 304°C. $t'_R = 0.52$.

(60) Tris[4,4,4-trifluoro-1-(2',4'-difluorophenyl)butane-1,3-dionato]chromium(III). m.p. 67–69°C (Found: C, 44.5; H, 1.4. $C_{30}H_{12}CrF_{15}O_6$ requires C, 44.7; H, 1.5%). DTA: V, 304°C. $t'_R = 0.54$.

(61) Tris[1-(pentafluorophenyl)butane-1,3-dionato]chromium(III). m.p. 65–71°C (Found: C, 44.9; H, 1.5. $C_{30}H_{12}CrF_{15}O_6$ requires C, 44.7; H, 1.5%). DTA: V, 308°C.

(62) Tris[4,4,4-trifluoro-1-(2'-trifluoromethylphenyl)butane-1,3-dionato]chromium(III). m.p. 70–72°C (Found: C, 44.1; H, 1.8. $C_{33}H_{15}CrF_{18}O_6$ requires C, 44.0; H, 1.7%). DTA: F, 72°C; V, 313°C. $t'_R = 0.59$.

(63) Tris[4,4,4-trifluoro-1-(4'-fluorophenyl)butane-1,3-dionato]chromium(III). m.p. 119–122°C (lit.³ 96–108°C; lit.²² 114–115°C) (Found: C, 47.6; H, 2.4. Calc. for $C_{30}H_{15}CrF_{12}O_6$: C, 47.9; H, 2.0%). DTA: F, 118°C; V, 320°C. $t'_R = 0.72$.

(64) Tris[4,4,4-trifluoro-1-phenylbutane-1,3-dionato]chromium(III). m.p. 154°C (lit.³ 169°C; lit.²³ 150°C; lit.²⁴ 170°C) (Found: C, 51.6; H, 2.6. Calc. for $C_{30}H_{18}CrF_9O_6$: C, 51.6; H, 2.6%). DTA: F, 154°C; V, 321°C. $t'_R = 1.00$.

(65) Tris[4,4,5,5,6,6,6-heptafluoro-1-(4'-chlorophenyl)hexane-1,3-dionato]chromium(III). Tacky solid (Found: C, 39.4; H, 1.5. $C_{36}H_{15}Cl_3CrF_{21}O_6$ requires C, 39.1; H, 1.4%). DTA: V, 331°C. $t'_R = 3.14$.

(66) Tris[4,4,5,5,5-pentafluoro-1-(4'-chlorophenyl)pentane-1,3-dionato]chromium(III). Tacky solid (Found: C, 41.9; H, 1.6. $C_{33}H_{15}Cl_3CrF_{15}O_6$ requires C, 41.7; H, 1.6%). DTA: V, 328°C.

(67) Tris[4,4,4-trifluoro-1-(2',5'-dimethylphenyl)butane-1,3-dionato]chromium(III). m.p. 68–70°C (Found: C, 55.6; H, 3.6. $C_{36}H_{30}CrF_9O_6$ requires C, 55.3; H, 3.8%). DTA: V, 331°C. $t'_R = 2.28$.

(68) Tris[4,4,4-trifluoro-1-(2',4',6'-trimethylphenyl)butane-1,3-dionato]chromium(III). m.p. 74–76°C (Found: C, 57.2; H, 4.5. $C_{39}H_{36}CrF_9O_6$ requires C, 56.9; H, 4.4%). DTA: V, 336°C. $t'_R = 3.37$.

(69) Tris[4,4-dimethyl-1-(4'-fluorophenyl)pentane-1,3-dionato]chromium(III). m.p. 230–232°C (Found: C, 65.2; H, 6.1. $C_{39}H_{42}CrF_3O_6$ requires C, 65.4; H, 5.9%). DTA: F, 235°C; V, 339°C.

(70) Tris[4,4,4-trifluoro-1-(2'-chlorophenyl)butane-1,3-dionato]chromium(III). m.p. 72–76°C (Found: C, 44.7; H, 2.0. $C_{30}H_{15}Cl_3CrF_9O_6$ requires C, 45.0; H, 1.9%). DTA: F, 76°C; V, 338°C. $t'_R = 2.36$.

(71) Tris[4,4,4-trifluoro-1-(3'-chlorophenyl)butane-1,3-dionato]chromium(III). m.p. 122–124°C (Found: C, 45.2; H, 2.1. $C_{30}H_{15}Cl_3CrF_9O_6$ requires C, 45.0; H, 1.9%). DTA: F, 125°C; V, 339°C. $t'_R = 2.79$.

(72) Tris[4,4,4-trifluoro-1-(2',4'-dimethylphenyl)butane-1,3-dionato]chromium(III). m.p. 181–182°C (Found: C, 55.0; H, 3.8. $C_{36}H_{30}CrF_9O_6$ requires C, 55.3; H, 3.8%). DTA: F, 181°C; V, 342°C.

(73) Tris[4,4,4-trifluoro-1-(4'-chlorophenyl)butane-1,3-dionato]chromium(III). m.p. 104–107°C (Found: C, 45.2; H, 2.0. $C_{30}H_{15}Cl_3CrF_9O_6$ requires C, 45.0; H, 1.9%). DTA: F, 106°C; V, 347°C.

(74) Tris[4,4,4-trifluoro-1-(4'-methylphenyl)butane-1,3-dionato]chromium(III). m.p. 114–118°C (Found: C, 53.5; H, 3.4. $C_{33}H_{24}CrF_9O_6$ requires C, 53.6; H, 3.2%). DTA: V, 345°C. $t'_R = 2.86$.

(75) Tris[4,4,4-trifluoro-1-(3'-bromophenyl)butane-1,3-dionato]chromium(III). m.p. 79–82°C (Found: C, 38.8; H, 1.8. $C_{30}H_{15}Br_3CrF_9O_6$ requires C, 38.5; H, 1.6%). DTA: V, 358°C.

(76) Tris[4,4,4-trifluoro-1-(2',5'-dichlorophenyl)butane-1,3-dionato]chromium(III). m.p. 79–81°C (Found: C, 40.0; H, 1.3. $C_{30}H_{12}Cl_6CrF_9O_6$ requires C, 39.8; H, 1.3%). DTA: F, 84°C; V, 360°C. $t'_R = 5.54$.

(77) Tris[4,4,4-trifluoro-1-(2',4'-dichlorophenyl)butane-1,3-dionato]chromium(III). m.p. 79–82°C (Found: C, 40.2; H, 1.6. $C_{30}H_{12}Cl_6CrF_9O_6$ requires C, 39.8; H, 1.3%). DTA: F, 81°C; V, 345°C.

(78) Tris[4,4,4-trifluoro-1-(3',4'-dimethylphenyl)butane-1,3-dionato]chromium(III). m.p. 96–99°C (Found: C, 55.0; H, 4.0. $C_{36}H_{30}CrF_9O_6$ requires C, 55.3; H, 3.8%). DTA: V, 358°C. $t'_R = 6.49$.

(79) Tris[4,4-dimethyl-1-phenylpentane-1,3-dionato]chromium(III). m.p. 199–201°C (Found: C, 71.0; H, 6.7. Calc. for $C_{39}H_{45}CrO_6$: C, 70.8; H, 6.8%). DTA: F, 201°C; V, 366°C. $t'_R = 6.33$.

(80) Tris[4,4,4-trifluoro-1-(3',4'-dichlorophenyl)butane-1,3-dionato]chromium(III). m.p. 80–83°C (Found: C, 39.9; H, 1.6. $C_{30}H_{12}Cl_6CrF_9O_6$ requires C, 39.8; H, 1.3%). DTA: V, 364°C.

(81) Tris[4,4,4-trifluoro-1-(4'-bromophenyl)butane-1,3-dionato]chromium(III). m.p. 187–190°C (Found: C, 38.5; H, 1.6. $C_{30}H_{15}Br_3CrF_9O_6$ requires C, 38.5; H, 1.6%). DTA: F, 188°C; V, 363°C.

(82) Tris[4,4,4-trifluoro-1-(4'-*tert.*-butylphenyl)butane-1,3-dionato]chromium(III). m.p. 110–112°C (Found: C, 58.5; H, 5.0. $C_{42}H_{42}CrF_9O_6$ requires C, 58.3; H, 4.9%). DTA: F, 110°C; V, 384°C. $t'_R = 12.61$.

(83) Tris[4,4-dimethyl-1-(4'-*tert.*-butylphenyl)pentane-1,3-dionato]chromium(III). m.p. 141–143°C (Found: C, 73.8; H, 8.4. $C_{51}H_{69}CrO_6$ requires C, 73.8; H, 8.3%). DTA: F, 143°C; V, 380°C. $t'_R = 15.58$.

RESULTS AND DISCUSSION

Thermal analyses

Although not presented here, the thermal behaviour of the chelates reveals an interesting distinction insofar as several of the copper(II)¹, oxovanadium(IV), vanadium(III), aluminium(III), iron(III) and chromium(III) chelates volatilized quantitatively, or nearly so, whereas the chelates derived from zinc, cobalt, and nickel, exhibited some degree of thermal decomposition, irrespective of the ligand structure. The lack of volatility of the zinc(II), cobalt(II) and nickel(II) chelates, which inevitably results in thermal decomposition, is a direct consequence of the high Lewis acidity^{2,5} of all three metal ions. In contrast, the behaviour of the oxovanadium(IV) chelates varied from that of the highly fluorinated compounds 19, 21 and 22 for which copious quantities of condensed vapour were recovered with very little residue,

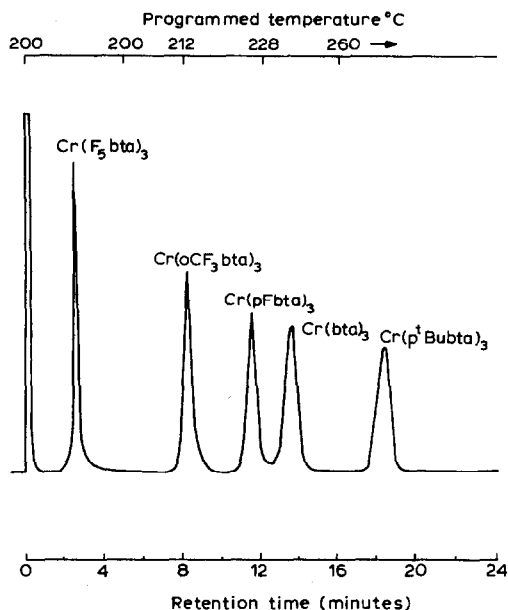


Fig. 1. Chromatogram showing the elution of chromium(III) chelates ($2 \mu\text{g}$ in benzene).

to compound 23 which decomposed extensively during heating, with little or no volatilization. Compound 20 was unusual in that extensive decomposition occurred to yield significant quantities of a brown solid, later identified from appearance, melting point and mass spectrum as the corresponding vanadium(III) chelate. It has been proposed that the vanadium(III) chelate results³ from reaction of undecomposed chelate with some inorganic decomposition product, and possibly V_2O_3 or, alternatively, reaction of V_2O_3 with free ligand formed from the pyrolysis of the oxovanadium chelate. Whichever applies, the result suggests destabilization of the chelates of the higher relative to the lower oxidation state.

The relative volatility of the oxovanadium(IV) chelates [that is, $19 > 21 > 22 (> 23)$] may be rationalised by considering the influence of the β -diketone substituents on intermolecular interactions, an interpretation invoked previously to account for volatility trends in copper(II) aryl β -diketonates¹. However, in the case of oxovanadium(IV) chelates, additional specific interactions can be envisaged^{26,27} and all are susceptible to electronic and steric effects.

Among the trivalent species, extensive thermal decomposition occurred in four compounds (compounds 29, 34, 35 and 54) whereas the remaining chelates volatilized quantitatively, or nearly so, as the unaltered β -diketonate. Volatility trends for these chelates follow the numerical sequences in the Experimental Section. The same group of ligands which enhanced volatility in the copper(II) chelates is again responsible for improving volatility.

Gas chromatography

Elution behaviour. Retention data for the chromium(III) chelates were obtained on a non-polar SE-30 stationary phase. The value of thermogravimetry as an indi-

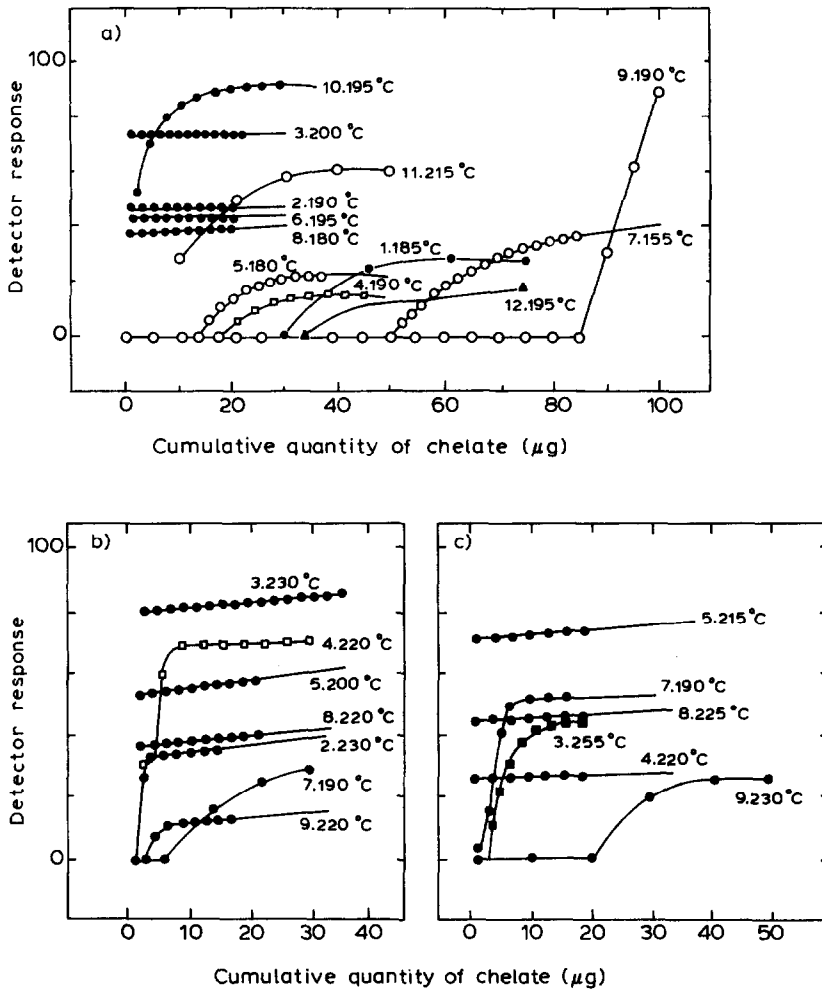


Fig. 2. Column loading curves for (a) $\text{Cr}(\text{F}_3\text{bta})_3$, (b) $\text{Cr}(\text{oCF}_3\text{bta})_3$ and (c) $\text{Cr}(\text{bta})_3$. Curves identify column number and temperature.

cator of chromatographic behaviour is apparent in the failure of the cobalt, nickel, zinc and non-volatile derivatives of chromium(III), vanadium(III), oxovanadium(IV), aluminium(III), iron(III) and copper(II) to elute from the SE-30 column. Of greater significance, however is the correlation established for the chromium(III) chelates between relative retention time on a non-polar stationary phase (see numerical listing in Experimental section for t'_R data) and the volatility trends predicted from TG. Fig. 1 shows a typical chromatogram for a mixture of chromium chelates on OV-17. Elution data for several copper(II) and chromium(III) chelates on coated diatomite support are presented in Table I. Two features of the data are noteworthy. The marked influence of the stationary phase in determining elution behaviour is clearly established. Furthermore, since the tailing index¹³ is a representation of peak asymmetry, the data of Table I signify poor elution as a common feature in the GC

TABLE I
ELUTION BEHAVIOUR OF CHROMIUM(III) AND COPPER(II) ARYL β -DIKETONATES

Data are presented as retention times (t_R , min) and tailing indices [$T_{0.5}^0$] where x is the amount of chelate (μg) injected onto the column and y is a fraction of the peak height for the various compounds. Borosilicate glass columns (0.7 m \times 4.5 mm I.D.) containing Chromosorb 750 coated with 3% stationary phase were used. An asterisk identifies chelates where the baseline elevation precludes use of the Tailing Index. Hbpb = 4,4,5,5,5-pentafluoro-1-phenylpentane-1,3-dione; Hbbp = 4,4,5,5,6,6,6-heptafluoro-1-phenylhexane-1,3-dione.

Chelate	Retention times and tailing indices of chelates									
	SE-30		Kef F Wax		QF-1		OV-3		OV-17	
	t_R	$T_{0.5}^0$	t_R	$T_{0.5}^0$	t_R	$T_{0.5}^0$	t_R	$T_{0.5}^0$	t_R	$T_{0.5}^0$
Cr(F ₃ bpb) ₃	3.44	0.98	1.80	0.97	7.44	0.98	5.28	1.00	1.68	1.00
Cr(F ₃ bta) ₃	4.33	0.98	2.00	0.96	8.54	0.98	6.72	1.00	2.30	1.00
Cr(2,4F ₂ bta) ₃	14.62	0.96	5.52	0.81	10.08	0.97	26.54	1.06	7.68	0.96
Cr(mCF ₃ bta) ₃	10.32	0.98	7.20	0.92	17.28	0.94	16.64	1.00	16.80	0.98
Cr(oCF ₃ bta) ₃	17.52	0.95	13.20	*	14.64	1.28	33.12	1.93	22.08	1.00
Cr(pFbpb) ₃	19.20	0.86	7.20	0.73	12.96	1.13	31.68	1.48	15.36	0.94
Cr(pFbhp) ₃	19.98	0.65	8.88	*	12.98	1.14	30.48	1.00	11.04	0.94
Cr(bta) ₃	35.29	0.89	*	*	19.68	4.32	71.84	1.64	73.90	1.29
Cu(F ₃ bpb) ₂	10.08	*	1.87	*	4.81	0.90	3.13	*	1.92	*
Cu(F ₃ bta) ₂	11.40	*	1.98	*	6.00	0.88	3.82	*	4.56	*
Cu(2,4F ₂ bta) ₂	32.81	1.03	2.88	*	8.40	2.31	12.48	*	17.28	*
Cu(mCF ₃ bta) ₂	39.12	1.11	7.20	*	14.41	2.96	13.20	*	13.20	0.90
Cu(oCF ₃ bta) ₂	22.08	0.91	2.40	*	6.52	0.93	8.40	*	11.51	0.89
Cu(pFbpb) ₂	38.40	0.95	4.56	0.09	8.88	0.98	12.71	*	14.40	0.90
Cu(pFbhp) ₂	41.79	0.90	6.00	0.20	10.32	4.03	13.00	*	11.97	0.93
Cu(bta) ₂	57.60	0.71	3.60	0.05	11.28	2.54	22.56	*	39.60	1.12

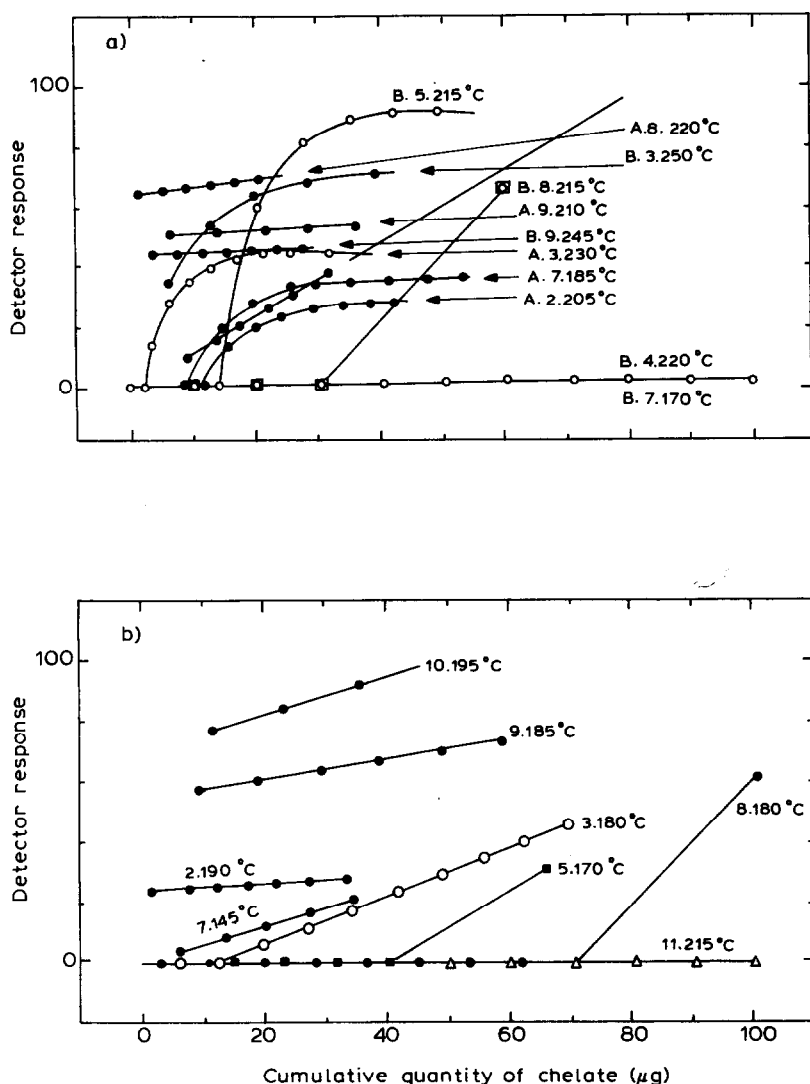


Fig. 3. Column loading curves for (a) $\text{Cu}(\text{oCF}_3\text{bta})_2$ (A) and $\text{Cu}(\text{bta})_2$ (B) and (b) $\text{Cu}(\text{F}_5\text{bta})_2$. Curves are identified as in Fig. 2.

of the copper aryl β -diketonates. The data also indicate an unfavourable interaction of the chelates with the stationary phase and/or the support material, behaviour which is not surprising in the case of $\text{Cu}(\text{II})$ chelates in view of their coordinative unsaturation.

The generally poorer elution behaviour of the aryl chelates relative to chelates containing non-aromatic groupings may be attributed to the reduced volatility of the aryl chelates, thus requiring higher column temperatures and, in turn, enhancing thermal decomposition and chemical reactivity within the column. Such an explanation is not totally acceptable, however, since column temperatures were signifi-

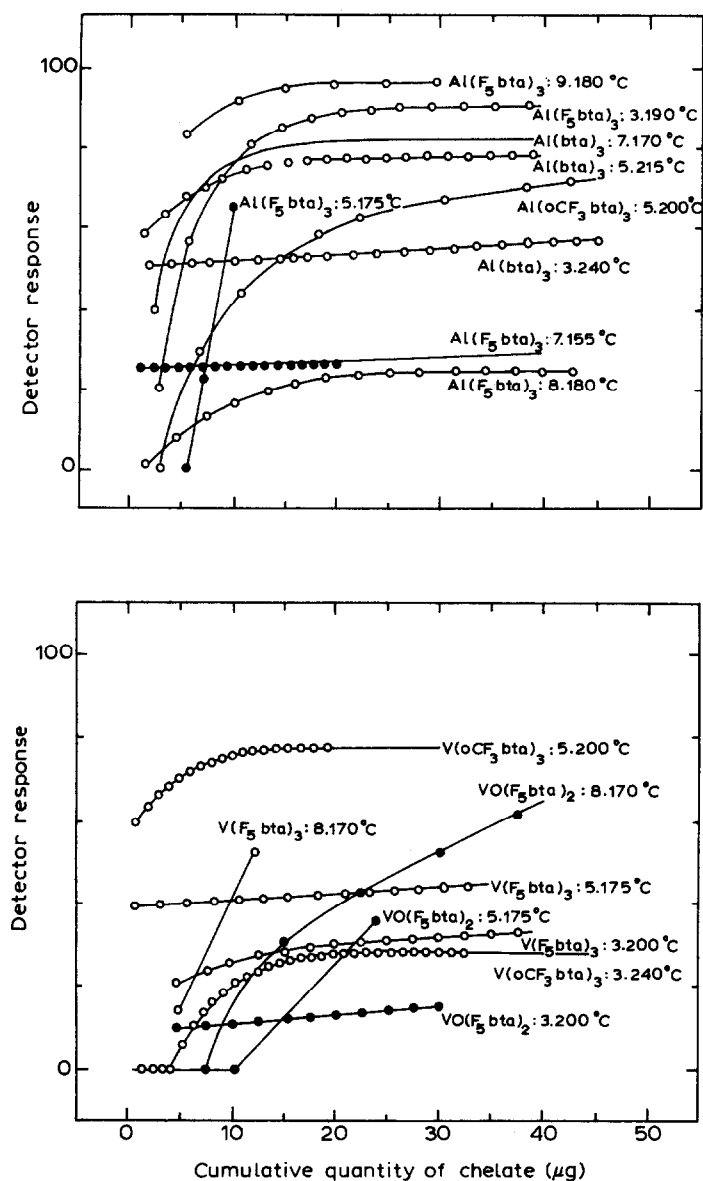


Fig. 4. Column loading curves for (a) aluminium(III) chelates and (b) vanadium(III) and oxovanadium(IV) chelates. Curves are identified as in Fig. 2.

cantly lower than TG volatilization temperatures. A more plausible explanation of the behaviour involves a greater dissociation of the aromatic chelates in the liquid phase together with an enhanced interaction of the chelates and the chromatographic system under the influence of the polarizable aromatic ring.

Column effects on retention. Column loading curves, which are presented in Figs. 2, 3 and 4 for selected chelates, imply that the saturation of active sites in the

column involves the solid support, stationary phase, or glass wool plugs. Indeed, the current data implicate all three sites in chelate retention.

Diatomite supports and, in particular, uncoated Chromosorb 750 and Chromosorb W HP were investigated because of their demonstrated³ efficiency and suitability for the separation of metal chelates. For $\text{Cr}(\text{F}_5\text{bta})_3$, injection of 30 μg chelate onto the uncoated, on-column silylated Chromosorb 750 column was necessary to produce a detector response. Following this, peak height and shape steadily improved with subsequent injections, becoming reproducible after the injection of a total of 60 μg . With a column primed in this way, the peak remained unsymmetrical and displayed an elevated baseline ahead of the main chelate peak. The baseline elevation, together with an unusually large solvent peak, suggests significant chelate decomposition. Mass spectral and spectrographic analysis of the column packing and glass wool plugs revealed a nearly uniform concentration of chromium in the support with a maximum in the glass wool plug of the injection port end, thereby establishing these areas as active sites for chelate retention. On the other hand, our failure to detect any chelate by mass spectrometry was consistent with the observed on-column decomposition.

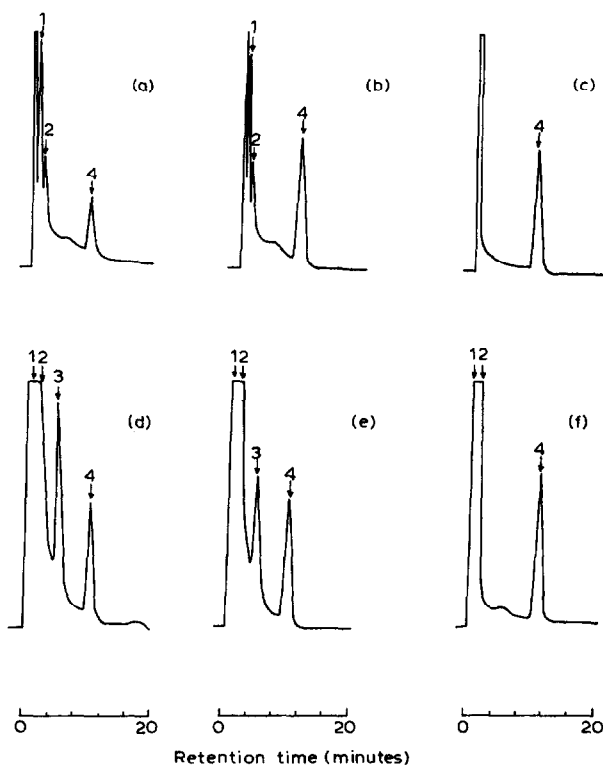
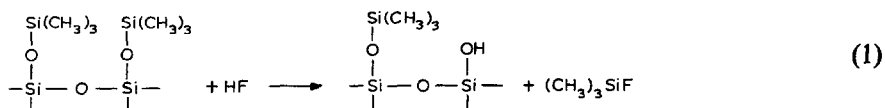


Fig. 5. Chromatograms showing the decomposition of $\text{Cr}(\text{F}_5\text{bta})_3$ on QF-1 at 180°C (Column 4). Elution of 700 ng chelate (a) and 10 μg chelate (b) on an unprimed column is compared to the behaviour of 700 ng of chelate following priming (c) and injection of free ligand (d). Subsequent injections of chelate are shown in (e) (700 ng) and (f) (10 μg). Attenuation is constant for the series. Numbered arrows locate decomposition products (1, 2 and 3) and chelate (4).

In an attempt to clarify further the role of the support, several columns containing coated Porasils were examined. As anticipated, column loading increased with the surface area of the support and ranged for $\text{Cr}(\text{F}_5\text{bta})_3$ from 20 μg on Porasil F (specific surface 2–6 $\text{m}^2 \text{g}^{-1}$) to 40 μg on Porasil E (10–20 $\text{m}^2 \text{g}^{-1}$) and 60 μg for Porasil C (50–100 $\text{m}^2 \text{g}^{-1}$). Other adverse behaviour was also enhanced.

Contribution by the stationary phase to column loading was established by its variation for the same chelates on different phases. For example, with $\text{Cr}(\text{F}_5\text{bta})_3$, the column loading was greater on QF-1 and Apiezon L than on either OV-17 or SE-30 (see Fig. 2a) suggesting that the phase is capable of satisfying some of the sites in the uncoated support. This is most clearly seen by comparing the results for columns 1 (uncoated Chromosorb 750) and 3 (OV-17 on Chromosorb 750). Similarly, the phases may introduce an additional (and variable) type of site for interaction. Indeed, in the case of Kel F Wax (column 7) and Apiezon L (column 9) the column loading was greater than for the uncoated support. Referring to Fig. 2, $\text{Cr}(\text{F}_5\text{bta})_3$ elutes from columns 2, 3, 6 and 8 without evidence of column loading from the 2 μg level and, with approximate detection limits ranging from 10 to 40 ng. For $\text{Cr}(\text{F}_5\text{bta})_3$ on columns 2, 3, 6 and 8 calibration curves (detector response *versus* quantity of chelate injected) were linear over the range of 0.5 to 10 μg .

Introduction of a trifluoropropyl group into the stationary phase (columns 4 and 5), which adversely effected the retention (see Fig. 2), may be related to the relative instability of QF-1*. Moreover, for $\text{Cr}(\text{F}_5\text{bta})_3$ chromatographed on QF-1 at 180°C, the observation of two volatile decomposition products, not evident at lower temperatures, suggests that decomposition is temperature dependent. Although inconclusive, retention times indicate that the earlier eluting decomposition product is either HF_5bta or the corresponding chromone³¹, or both. In addition, Fig. 5 shows the on-column interaction of $\text{Cr}(\text{F}_5\text{bta})_3$ and QF-1. Following priming of the column there is no evidence of chelate decomposition (Fig. 5c) although subsequent injection of free ligand and chelate, once again results in decomposition (Fig. 5d, e and f). It is significant that in the absence of on-column silylation, decomposition was not observed. This is the only instance in this work where on-column silylation exerts an adverse influence on chelate performance probably because in the case of fluorinated β -diketonates, HF is a potential on-column degradation product. For chelates derived from HF_5bta where the liberation of free ligand in the column can lead to HF formation by an intramolecular ring-closure³¹, subsequent reaction with the column packing (see eqn. 1) may lead to the formation of volatile decomposition products such as trimethylfluorosilane³².



Considering the chromium(III) chelates of Hbta and HoCF_3bta , the stationary phases Kel F Wax and Apiezon L again exhibited the greatest propensity towards column loading and the most striking difference was noted for QF-1. Whereas on

* QF-1 is known to thermally decompose²⁸ in the presence of acetone, potentially a thermal degradation product of β -diketonates²⁹, glass surfaces and residual catalyst used in its manufacture³⁰.

QF-1 the curves for $\text{Cr}(\text{bta})_3$ and $\text{Cr}(\text{oCF}_3\text{bta})_3$ were linear, $\text{Cr}(\text{F}_5\text{bta})_3$ exhibited a column loading of $30 \mu\text{g}$ attributed to its decomposition on QF-1. The results also reveal an interesting distinction in the behaviour of the three chelates on Kel F Wax. In summary, it may be stated that increased fluorination in these three compounds is associated with an enhanced column loading and appears to exert two influences. Firstly, by reducing the interactions involved in the partitioning process, retention times are reduced. Secondly, fluorination increases the interactions leading to unfavourable column interactions and, more specifically, to a higher column loading.

Figs. 3 and 4 present column loading curves for copper(II), aluminium(III), vanadium(III) and oxovanadium(IV) chelates. The results are complicated by decomposition of the chelates and, in the case of vanadium, by on-column redox transformation of the oxovanadium(IV) chelates. The extent of the latter varied considerably with the stationary phase and the β -diketone. In particular, on columns 3, 5, 7 and 8, the injection of the oxovanadium(IV) chelates of HF_5bta , HoCF_3bta and Hbta showed initial total retention (or decomposition) of the vanadyl chelate and elution of the vanadium(III) chelate generated in the column. With several further injections, elution of both vanadyl and vanadium(III) species suggests that the vanadium(III) chelates were formed rapidly at the injection port. In the case of $\text{VO}(\text{F}_5\text{bta})_2$, thermal instability was confirmed by vacuum pyrolysis*. Further support for the mechanism was provided by the elution of both vanadium chelates on subsequent injection of free ligand, the retention times depending on the β -diketone injected and not on the vanadyl chelate previously introduced. This suggests that ligand was reacting with a deposit of mixed composition to give VOL_2 and VL_3 chelates. Decomposition of $\text{VO}(\text{oCF}_3\text{bta})_2$ was predictable from thermogravimetric data.

In contrast to the oxovanadium(IV) chelates, the vanadium(III) derivatives showed an improved chromatographic behaviour. Of these, $\text{V}(\text{oCF}_3\text{bta})_3$ was the most suitable derivative with some potential for use in analysis because of its elution as a symmetrical peak at the $0.5\text{-}\mu\text{g}$ level. Elution of vanadium(III) and oxovanadium(IV) chelates is compared in Fig. 6.

The high column loading of $\text{Cr}(\text{F}_5\text{bta})_3$ on Kel F Wax contrasts with the linear loading curves for the aluminium(III) chelate. Considerable reduction in the retention of this chelate [relative to $\text{Cr}(\text{F}_5\text{bta})_3$] was also observed on Apiezon L but the situation was reversed on SE-30 and OV-17.

On-column silylation. On-column silylation was established as an important factor effecting chelate performance. With the single exception of the instance noted above, chelate performance was either unaltered or improved by on-column silylation. Chromatograms presented in Fig. 7 emphasize the qualitative changes effected by on-column silylation.

These observations are consistent with previously proposed mechanisms¹⁴ for the retention of the β -diketonates, involving partial dissociation of the chelate followed by its exchange at free silanol groups. In the event of such a mechanism being operative, the variation in retention on different phases is a reflection of the influence of phase polarity on the extent of chelate dissociation and, hence retention. The

* After reaction at 190°C for 20 min, mass spectrometry confirmed the presence of both vanadium(III) and oxovanadium(IV) chelate in the residue.

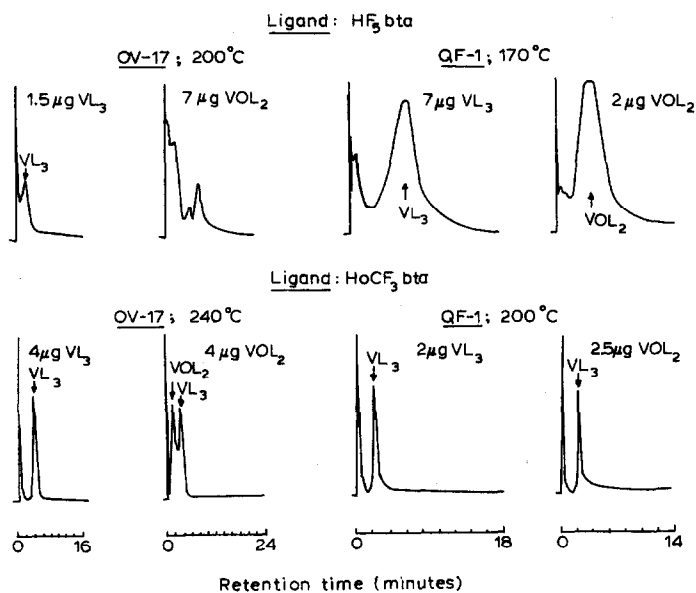


Fig. 6. Chromatograms showing the elution of the vanadium(III) and oxovanadium(IV) chelates of HF_5bta and HoCF_3bta on coated Chromosorb 750. Labelled arrows identify the chelate where L is the ligand anion.

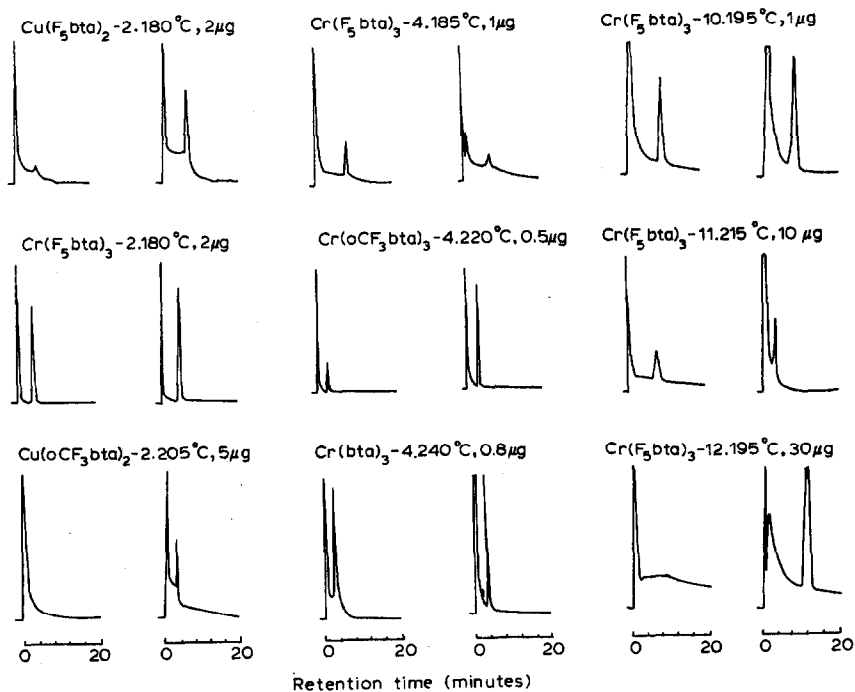


Fig. 7. Chromatograms showing the effect of on-column silylation on the elution behaviour of aryl β -diketonates. Column details are presented as in Fig. 2. In each case the second chromatogram was obtained with the silylated column.

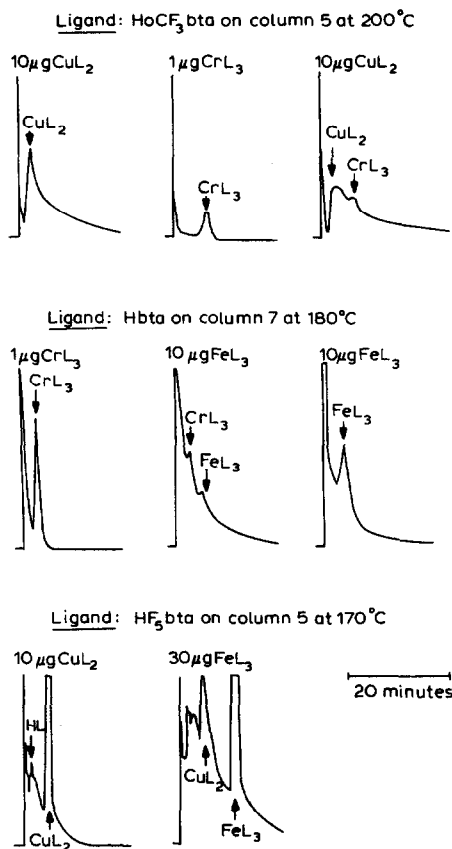


Fig. 8. Chromatograms illustrating the displacement of a previously retained chelate. Labelled arrows identify the chelate where L is the ligand anion.

observation of scrambling reactions in mixtures of β -diketonates suggests that such ionic equilibria do, indeed, occur. Moreover, the degree of interchange or lability of a chelate, provides a reliable guide to the extent of such ionisation. For example, when five chromium(III) β -diketonates were mixed in benzene solution, at ambient temperature, and the solution examined after 30 min³³, no scrambling had occurred whereas similar experiments with the HF_3bta , HoCF_3bta and Hbta derivatives of other metal ions produced complex mixtures suggesting a difference between the behaviour of chromium(III) β -diketonates (or other highly inert complexes) and labile chelates. The implication is that retention of chromium(III) chelates by an ion-exchange mechanism is relatively unimportant. Consistent with the proposed dissociative mechanisms for labile chelates is the observation³⁴ that free ligand in the carrier gas stream improves chelate elution considerably, probably by maintaining the equilibrium in favour of the undissociated chelate.

Displacement phenomena. Displacement of chelates previously injected onto a column was observed in all the chromatographic systems studied. However, an important distinction in the behaviour of chromium(III) chelates when injected onto

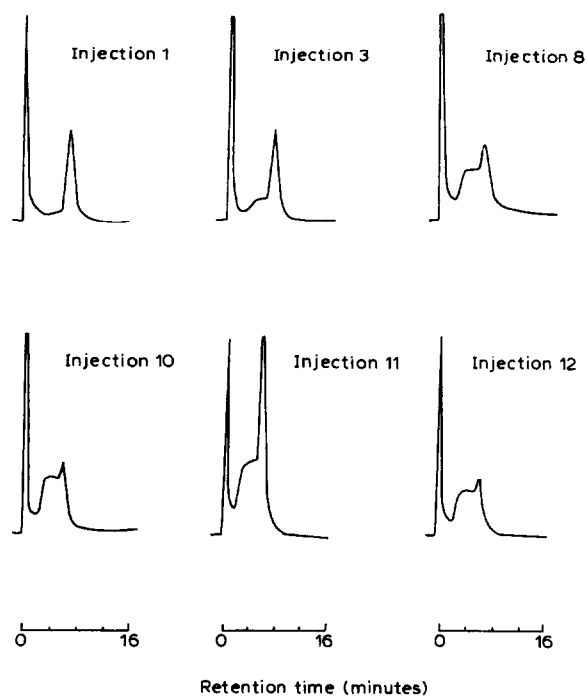


Fig. 9. Chromatograms showing the serial injection of $\text{Al}(\text{bta})_3$ [$3 \mu\text{g}$ except for injection 11 ($6 \mu\text{g}$)] on Chromosorb 750 coated with OV-17 (Column 3), at 240°C .

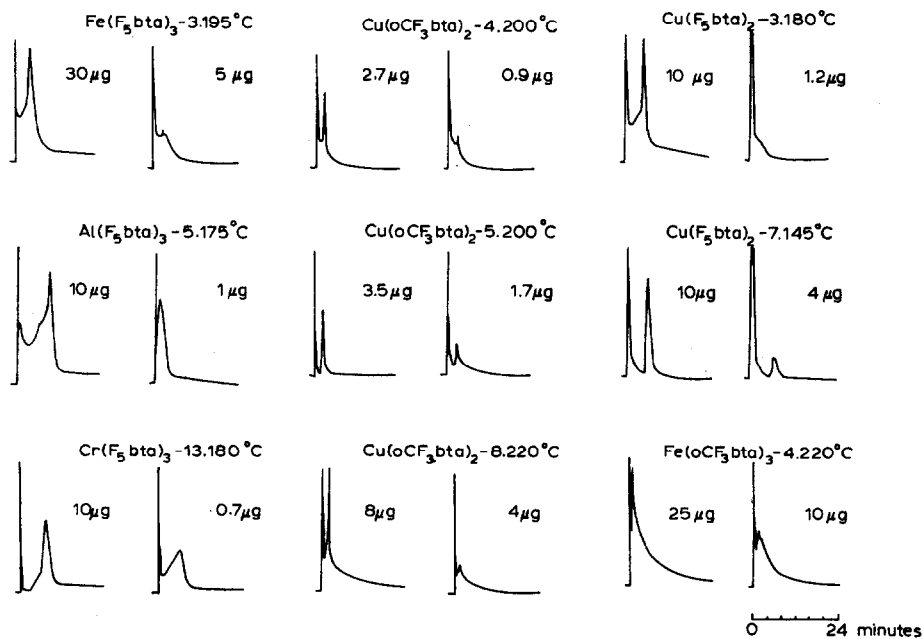


Fig. 10. Chromatograms showing the elution behaviour of several chelates. Column details follow the presentation in Fig. 2.

columns previously used for other metal ion derivatives was their inability to cause displacement (see Fig. 8a), whereas the reverse did apply. The displaced chelates, appearing as sharp bands with retention times indicating that displacement occurred from the vicinity of the injection port, were identified by mass spectrometry. This may be interpreted as an example of exchange or competitive chemisorption³⁵.

Mass spectral examination of the eluate showed that, in addition to the above displacement, a smaller portion of chelate was continuously desorbed as confirmed for $\text{Cu}(\text{F}_5\text{bta})_2$ over 20 h. This desorption is understandable if a mainly adsorptive process is involved. A further distinction may be made in that following overnight conditioning columns remained primed for chromium(III) chelates, but not for derivatives of other metal ions.

The behaviour of $\text{Al}(\text{bta})_3$ on OV-17 and Chromosorb 750 was unusual in that only the first injection onto a new column eluted as a symmetrical peak. Thereafter, a peak of increasing size preceded the main chelate peak until the 10th injection, when it became constant. Results for $\text{Al}(\text{bta})_3$ on a new column, and reproduced in Fig. 9, show that the size of the earlier peak was relatively independent of the quantity injected.

Finally, it may be noted that calibration curves (in the range 1–25 μg) for the aryl β -diketonates other than chromium(III) were seldom linear. Equally important are the qualitative changes observed at different concentrations of chelate, shown in the representative chromatograms of Fig. 10.

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