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Chromatographic Analysis of Electrophilic Substitution Reactions of Cobalt(III) and Chromium(III) 2,4-Pentanedionates

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Bromination of cobalt(III) and chromium(III) 2,4-pentanedionates has been thoroughly investigated by GC and HPLC. GC was found to be unsuitable for analysis of the cobalt complexes and HPLC was recommended for monitoring electrophilic substitutions of metal β-diketonates, especially chelates which are labile or thermally unstable. Thermogravimetric and Differential Thermal Analyses of the partially and fully brominated chelates have been used to explain their GC behaviour. Reaction components giving rise to the various chromatographic peaks were identified by mass spectrometry and ^{13}C NMR.

Introduction

Much of the intensive research on the electrophilic substitution reactions of metal β-diketonates was performed in the early sixties and has been reviewed by Collman [1] and Mehrotra *et al.* [2]. In general, it was observed that reaction with a variety of electrophilic reagents led to substitution on the central (or γ) carbon of the chelate ring. However, if the γ-carbon position was blocked by the presence of another substituent, then reaction would occur elsewhere [3,4].

Collman and co-workers concentrated mainly on reactions of metal 2,4-pentanedionates, in particular the trivalent metal complexes, and mixed-ligand species arising from electrophilic reactions were isolated by classical chromatographic techniques such as TLC and florisil column chromatography [1, 5]. The full potential of modern highly efficient chromatographic techniques in monitoring the electrophilic substitutions of metal β-diketonates has not been investigated.

Some of the first metal chelates to be successfully eluted by gas chromatography were metal acetylacetonates, however, due to their lack of volatility and thermal stability, analysis was limited to the chelates of chromium, aluminium and beryllium [6]. Use of fluorinated derivatives extended the range of metals capable of gas chromatographic elution [6, 7] and we have recently applied GC to the separation of the products of bromination of tris(1,1,1-trifluoro-2,4-pentanediono)chromium(III) [8].

High Performance Liquid Chromatography (HPLC) has also been used successfully for separation of metal acetylacetonates [9] and it may be more appropriate to use this technique rather than GC for analysis of electrophilic substitution reactions of thermally labile and/or involatile metal β-diketonates.

In this paper, we wish to report the results of our investigations on the application of GC and HPLC to the separation of the products of bromination of both tris(2,4-pentanediono)chromium(III) and cobalt(III).

Experimental

The metal acetylacetonates were prepared by documented procedures [10, 11] and purified by recrystallisation from benzene/petroleum spirits.

Brominations of the metal acetylacetonates were carried out by mixing appropriate amounts of the metal chelate and N-bromosuccinimide in carbon tetrachloride, stirring the mixture at ambient temperatures for 4 hr., filtering and removal of the solvent under a stream of nitrogen. The resulting solid was washed with aqueous sodium bisulphite and water and finally air dried. Other previously reported procedures for bromination were also performed [12–15].

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Gas chromatography was carried out using a Perkin Elmer F11 chromatograph fitted with a flame ionization detector. Peak areas were computed by a Laboratory Data Control LDC-308 electronic integrator. After packing, all columns were silanized with silyl-8 before use. Internal standards used to obtain quantitative data were either n-docosane or n-tetracosane.

Liquid chromatographic data were obtained using a microprocessor controlled Altex 420 liquid chromatograph at a wavelength of 254 nm. The column used throughout this work was a 5 μm Partisil silica column, dimensions 250 mm × 4.6 mm i.d. and the eluents used are described elsewhere in the text.

A Waters PrepLC-system 500 liquid chromatograph was used for preparative scale chromatography. The column consisted of a PrepPAK-500 silica radial compression cartridge and the detector was a refractive index detector.

Mass spectra of the solid chelates were recorded on a JEOL D-100 Mass Spectrometer using a direct insertion probe. Varying temperatures were required depending on the volatility of the metal chelate and an electron impact voltage of 70 eV was used throughout.

Thermogravimetric and Differential Thermal Analysis data were obtained using a Rigaku-Denki Thermal Analysis System Type-Thermoflex 8085. Samples of mass 8–10 mg were placed in open platinum crucibles and measurements were made in an atmosphere of nitrogen at a flow rate of 100 cm^3 min^{-1}. Thermograms were run at a programmed heating rate of 10 °C min^{-1} and alumina was used as reference throughout.

The ^{13}C Nuclear Magnetic Resonance spectra were recorded on a JEOL JNM-FX200 Fourier transform NMR spectrometer coupled to a JEOL JEL-980B computer. Saturated solutions of all samples were made up in deuterobenzene and tetramethylsilane was used as internal standard.

Results and Discussion

Gas Chromatography

Chromium(III) β-diketonates have previously proved amenable to gas chromatographic elution from packed columns with the greater success being achieved on silicone type liquid phases [6, 7]. In the present study, efforts were directed towards achieving rapid elution of fully and partially brominated acetylacetonates in admixture and it seemed obvious that similar silicone based columns might give ideal chromatography.

In general, investigation of various liquid phases on Chromosorb 750, packed in glass or stainless steel columns, led to successful elution of tris(3-bromo-2,4-pentanediono)chromium(III), $Cr(Bracac)_3$, from OV101, QF1 and PS-300 columns. In order to minimize decomposition of the fully brominated chelate, it was found necessary to use on-column injection, glass rather than stainless steel columns and column temperatures less than 170 °C. At higher temperatures, decomposition of the brominated chelate is characterized by an increase in detector background response between the solvent peak and the chelate peak followed by normal background response after the latter. In order to achieve rapid elution and baseline resolution of all components in a bromination mixture, an OV101 column with 2.5% loading was preferred for the remainder of this work.

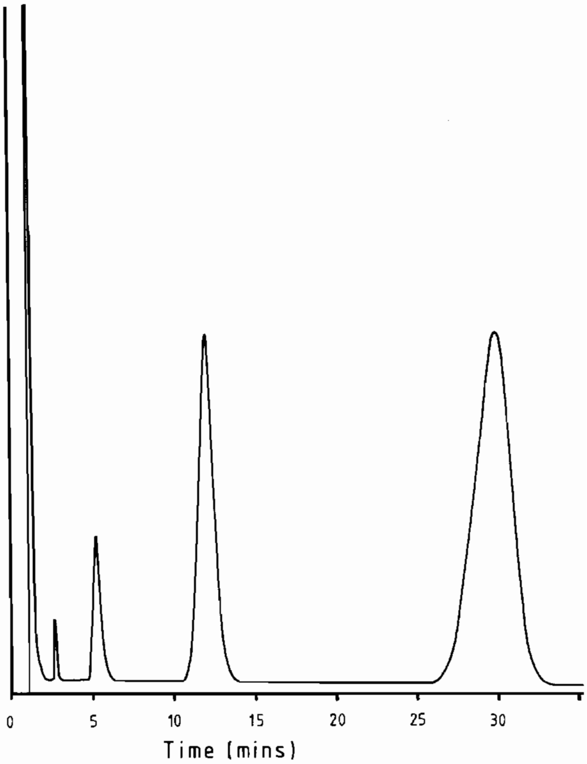

Fig. 1. Gas Chromatogram of the brominated products of chromium acetylacetonate. Column: glass (1 m × 5 mm i.d.) packed with 2.5% OV101 on Chromosorb W. Conditions: oven, 160°; injector and detector, 200 °C; N_2 flow-rate, 45 cm^3 min^{-1}.

GC analysis of a bromination reaction in an acetic acid medium [12] yielded four peaks in the chromatogram as shown in Fig. 1. Under the conditions employed, the retention times of the first (1.6 min) and last (28.8 min) peaks correspond to those of unreacted $Cr(acac)_3$ and the fully brominated chelate $Cr(Bracac)_3$, respectively. The two remaining peaks at 4.2 and 11.0 mins were identified by mass spectrometry (see later) to be the mono-substituted complex (3-bromo-2,4-pentanediono)bis(2,4-pentane-

TABLE I. Distribution of Complexes in the Bromination of Chromium Acetylacetonate as Determined by Gas Chromatography. Conditions as in Fig. 1 Abbrevs: A = $acac^-$; B = $Bracac^-$.

Mole Ratio of Initial Reactants	CrA_3 (%)	CrA_2B (%)	$CrAB_2$ (%)	CrB_3 (%)
1:1	7.7	77.9	14.4	0
2:1	0	8.8	83.6	8.2
3:1	0	0	5.2	94.8
4:1	0	0	0	100.0

diono)chromium(III), $Cr(Bracac)(acac)_2$, and the bi-substituted complex bis(3-bromo-2,4-pentanedionoX2,4-pentanediono)chromium(III), $Cr(Bracac)_2(acac)$, respectively. The chelates in the reaction mixture are eluted, therefore, in order of their degree of bromination.

Collman *et al.* [1, 5] reported that the partially substituted species rather than the fully substituted species could be generated by using limited amounts of the electrophilic reagent. Although classicial chromatographic procedures were used to isolate fractions of the individual substituted products [1], accurate determinations of the composition of reaction brews were not reported. On the basis of the work described above, gas chromatography can now be used to generate these analytical data. Integrated peak areas at various mole ratios of brominating reagent (NBS) to metal chelate ($Cr(acac)_3$) yielded the data presented in Table I. It is interesting to note that a mole ratio of 3:1 does not generate sufficient bromine to completely substitute the available parent metal acetylacetonate, yet this ratio has often been quoted as the requirement for synthesis of the fully brominated complex [12, 14, 15]. The G.C. data in Table I clearly suggest that a mole ratio of closer to 4:1 is required to ensure complete substitution of the original metal chelate.

It has also been found that for any column at a fixed oven temperature the logarithm of the retention time, log t_R, for each complex in a series of brominated complexes is linearly related to the number of bromine atoms substituted on that complex. This relationship is analogous to that between carbon number and log t_R in an homologous series of organic compounds or the recently reported relationship between log t_R and the carbon number of an alkyl substituent on the central carbon of metal β-diketonates [16].

With on-column injection, it was found possible to elute $Co(acac)_3$ from an OV101 column at oven temperatures in the range 120–140 °C, but even under these mild operating conditions there was some decomposition of the metal complex as several miscellaneous peaks were observed at retention times shorter than that of the main peak. Attempts to achieve elution of the brominated cobalt acetylacetonates under a wide variety of gas chromatographic conditions proved unsuccessful.

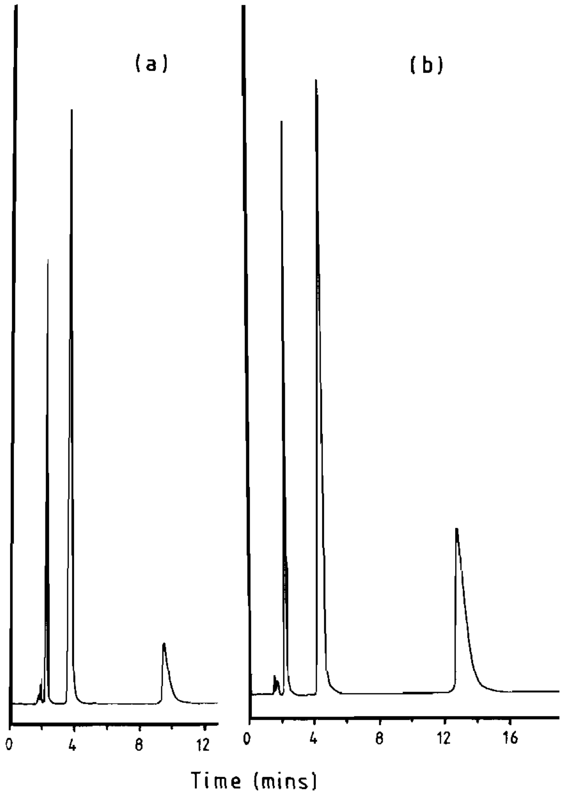

Fig. 2. Liquid chromatograms for bromination of (a) chromium and (b) cobalt(III) acetylacetonates. Eluent: 5% CH_3CN in dichloromethane at 2 cm^3 min^{-1}. Column: 5 μm Partisil silica, 250 mm × 4.6 mm i.d. Detector wavelength, 254 nm.

High Performance Liquid Chromatography

As thermally labile metal complexes have occasionally proved to be suitable for separation by liquid chromatography [17, 18] attempts were made here to elute the brominated acetylacetonates by normal-phase HPLC.

Using 5% acetonitrile in dichloromethane as eluent, it was found possible to achieve complete resolution of all the components in the bromination reactions of both cobalt(III) and chromium(III) acetylacetonates. The order of elution was established to be the reverse of that obtained for GC elution of the chromium chelates, *i.e.* the fully brominated complex, $M(Bracac)_3$, elutes with the smallest retention volume and the parent acetylacetonate has the largest retention volume (Fig. 2). The identity of the component in each chromatographic peak was

TABLE II. Liquid Chromatographic Retention Data for Cobalt(III) and Chromium Acetylacetonates and Brominated Acetylacetonates. Conditions as in Fig. 2. Abbrevs. as in Table I.

Metal Complex	Retention Volume (cm^3)		k′ values	
	Cr	Co	Cr	Co
MB_3	3.0	3.0	0.1	0.1
MAB_2	4.2	4.6	0.5	0.6
MA_2B	7.9	8.8	1.8	2.1
MA_3	18.6	25.6	5.6	8.1

TABLE III. Percent Distribution of Complexes in the Bromination of Cobalt(III) and Chromium Acetylacetonates as Determined by HPLC.

Metal	Mole ratio NBS/MA_3	Percent Distribution			
		MA_3	MA_2B	MAB_2	MB_3
Cr	1:1	7.8	76.8	15.4	
	2:1		9.1	81.0	9.9
	3:1			5.5	94.5
	4:1				100
Co	1:1	8.6	76.7	14.8	
	2:1		13.6	78.5	7.9
	3:1			3.8	96.2
	4:1				100

confirmed by sample collection accompanied by mass spectrometry. The measured retention volumes and k′ values for all of the cobalt and chromium complexes are listed in Table II and it is interesting to note that the cobalt complexes are more strongly retained than their chromium analogues. HPLC has the advantage of being able to resolve the thermally labile cobalt complexes and it provides a more rapid procedure for analysis of the decomposition of bromination reaction mixtures.

Using limited amounts of N-bromosuccinimide, the products of bromination reactions of cobalt(III) and chromium acetylacetonates were separated by normal-phase HPLC and the results for reactions that had reached steady state are presented in Table III. It is clear from these data that there is good agreement between the GC and HPLC results for the chromium system. Furthermore, there are no significant differences in the steady state distribution of products for either the chromium or the cobalt system under a given ratio of initial reactants.

In order to identify and characterize each component in an electrophilic substitution reaction mixture it is necessary to isolate sufficient quantities of the pure partially substituted metal complexes. Fractional recrystallization from a variety of solvents and solvent mixtures proved unsuccessful in the isolation of the partially brominated chelates of chromium and cobalt. Satisfactory separations were achieved using classical liquid chromatography on florisil, silica gel or alumina [1, 5] but this technique was somewhat tedious and time consuming for the isolation of sample sizes larger than a few milligrams. The analytical liquid chromatography described above suggests that rapid isolation and purification of the brominated chelates could be achieved by preparative liquid chromatography (prepLC). Gram quantities of each mixed-ligand complex were isolated using prepLC and a PrepPAK-500 Silica radial compression cartridge; a mobile phase consisting of 5% ethyl acetate in dichloromethane at a flowrate of 100 cm^3 min^{-1} led to complete separation of all components in the bromination reaction mixtures in about 45 min. The purity of the isolated products was determined by analytical HPLC and in each case, it was found to be greater than 99%.

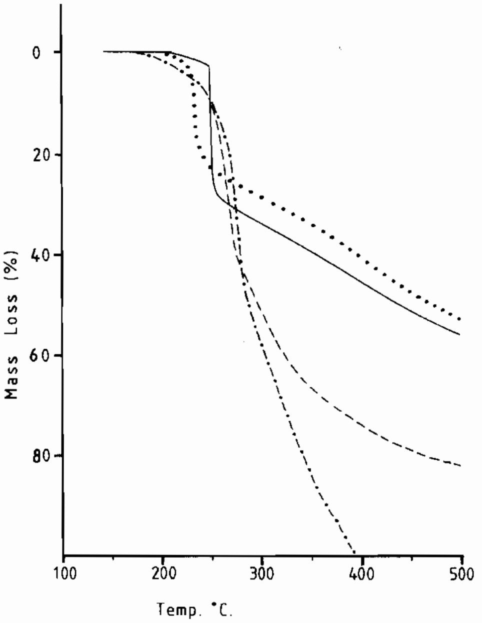

Fig. 3. Thermograms for chromium acetylacetonate and its brominated derivatives in a nitrogen atmosphere. Conditions as in the text. $Cr(acac)_3$, (–·–·–); $Cr(Bracac)(acac)_2$, (------); $Cr(Bracac)_2(acac)$, (······); $Cr(Bracac)_3$, (———).

Thermal Analysis

Thermogravimetric (TG) analysis has frequently been used to compare the relative thermal stabilities

TABLE IV. DTA and Melting-Point Data for Chromium and Cobalt(III) Acetylacetonates and their Brominated Derivatives. Abbrevs: A = acac$^-$; B = Bracac$^-$; dec = apparent decomposition; N.D. = not detected.

Complex	DTA data (°C)			Recorded[a] Mpt (°C)	Lit. Mpt (°C)
	M. pt (endo-)	Vaporization (endo-)	Decomposition (exo-)		
CrA_3	215	270	N.D.	215	216 [10]
CrA_2B	170–8 (split peak)	252[b]	252[b]	168–9	
$CrAB_2$	182	N.D.	232	181–2	
CrB_3	230	N.D.	255	227–8	227–9 [12, 13]
CoA_3	216	235	N.D.	211–2	212 [11, 20]
CoA_2B	176	186[b]	190[b]	dec.	
$CoAB_2$	180	N.D.	186	173	
CoB_3	184[c]	N.D.	184[c]	182–3	182–3 [13] 232–3 [12]

[a] Recorded in melting-point apparatus. [b] Overlap of vaporisation and decomposition peaks. [c] Overlap of melting point and decomposition peaks.

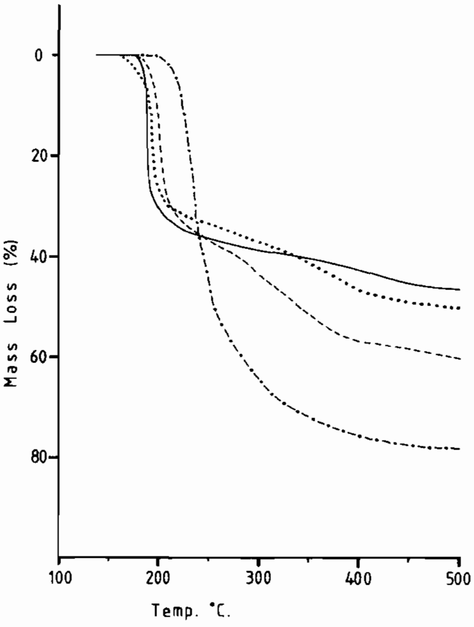

Fig. 4. Thermograms for cobalt(III) acetylacetonate and its derivatives under conditions described in the text. Curve designation as for the corresponding Cr complexes in Fig. 3.

and volatilities of metal complexes prior to their attempted elution by gas chromatography. In the present study, Differential Thermal Analysis (DTA) and TG analysis of the brominated Cr and Co complexes were carried out simultaneously in order to provide more reliable information on the thermal processes observed for these metal chelates.

The TG curves for the Cr and Co chelates are presented in Figs. 3 and 4, respectively. It is clear that only $Cr(acac)_3$ is completely volatile but there is some degree of volatilization for the mono-brominated chromium chelate, $Cr(Bracac)(acac)_2$, and $Co(acac)_3$. In general, it is observed for both metals that the unsubstituted parent acetylacetonate is more thermally stable than any of the brominated members of the group and the thermal stability decreases with the extent of bromine substitution of the chelate. In addition, it is apparent that the chromium complexes are more thermally stable and more volatile (where applicable) than the corresponding cobalt compounds.

In contrast to the TG data, sublimation studies under vacuum (0.5 mm Hg) show that all three brominated Cr chelates are volatile without decomposition around 120 °C whereas the corresponding Co chelates are involatile under similar conditions. At temperatures below the TG decomposition temperatures, the brominated Cr complexes obviously have the desired vapour pressures to permit their elution in gas chromatography but the Co complexes do not.

On the basis of data derived from the DTA curves (Table IV), the thermal behaviour of the two series of metal chelates can be summarized in three categories. The first group shows a well-defined fusion endotherm and a broad volatilization endotherm; Figure 5A reproduces the curve for $Cr(acac)_3$ and there is no evidence for decomposition taking place, consistent with the TG curve. Figure 5A is identical to that reported by Yoshida *et al.*, [19] who suggest that the

TABLE V. Relative Intensities in the Mass Spectra of some Substituted Acetylacetonates of Cobalt and Chromium. Ligand anion abbreviations: B ≡ Bracac$^-$; A = acac$^-$.

Ion (M = Co or Cr)	CoB_3	CoB_2A	$CoBA_2$	CrB_2A	$CrBA_2$
MB_3^+	14				
$(MB_3-Br-CH_3CO)^+$	4				
MB_2A^+		12		28	
MBA_2^+			8		22
MB_2^+	100	8		2	
$(MB_2-CH_3)^+$	12	1			
$(MB_2-Br)^+$	11				
$(MBBr)^+$	14				
$(MB_2-Br-CO)^+$	12				
$(MBBr-CH_3)^+$	8				
MBA^+		100	8	100	8
$(MBA-CH_3)^+$		20	4		<1
MA_2^+		28	100	8	100
$(MA_2-CH_3)^+$		25	42	1	4
MB^+	14	8	1	10	3
$(MB-Br)^+$	8				
MA^+		75	65	44	50
$(MA-CH_3)^+$			9		

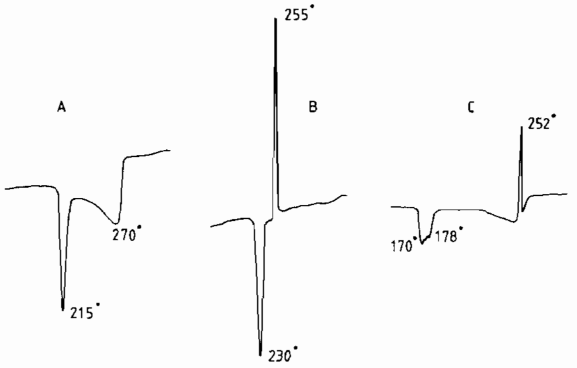

Fig. 5. DTA curves selected to represent the different thermal behaviour of chromium and cobalt acetylacetonates and their brominated derivatives. Curve A, $Cr(acac)_3$; Curve B, $Cr(Bracac)_3$; Curve C, $Cr(Bracac)(acac)_2$.

endotherm at higher temperatures is due to decomposition rather than volatilization, an observation consistent with measurements made in a hermetic-sealed sample holder whereas the present study was carried out with an open sample holder. The corresponding cobalt compound may also be included in this group but the classification is uncertain because the second endotherm overlaps a sharp endotherm which would appear to be characteristic of melting. Yoshida *et al.* [19] claim that $Co(acac)_3$ decomposes without showing a fusion peak yet there are reports of melting points having been observed [11, 20] and our data confirms this (see Table IV). It is likely that the chelate undergoes decomposition (reduction) or decomposition plus volatilization during the melting process; note that the TG curve does not indicate 100% mass loss for $Co(acac)_3$ and this supports the suggestion that decomposition and volatilization are taking place simultaneously.

The second group includes the bi- and tri-brominated chelates of both metals and the DTA curves display a sharp melting endotherm followed by a sharp exotherm characteristic of decomposition of the chelate (Fig. 5B); for $Co(Bracac)_3$, both DTA peaks overlap at about 184 °C. In this group of chelates, only the TG curve of $Cr(Bracac)_3$ has been reported previously [11] and the results presented here are in good agreement with the observed decomposition.

The third group consists of the mono-substituted chelates, which appear to show behaviour common to both the preceding groups. In general, a sharp melting endotherm is followed by a rather complex trace composed of a sharp exotherm superimposed on a broad endotherm (Fig. 5C). It is proposed that vaporisation and decomposition are occurring almost simultaneously and the mass losses in the corresponding thermograms seem to support this hypothesis.

TABLE VI. ^{13}C Chemical Shifts of Cobalt(III) Acetylacetonate and its Brominated Derivatives in C_6D_6; δ in ppm with TMS as Internal Standard.

Complex	$\delta(^{13}CH_3)$	$\delta(^{13}CBr)$	$\delta(^{13}CH)$	$\delta(^{13}CO)$
CoA_3	25.8		97.1	189.2
CoA_2B	25.7	95.0	97.1	189.6
	25.8			189.3
	29.4			188.1
$CoAB_2$	25.7	94.9	97.2	189.7
	29.4			188.4
	29.5			188.1
CoB_3	29.9	95.0		188.3

Sample Identification

As indicated earlier, the identity of the metal complex giving rise to each chromatographic peak was established by mass spectrometry. The mass spectra of several acetylacetonates of trivalent metals have been discussed in detail by MacDonald and Shannon [22] and some tri-substituted acetylacetonates of chromium by Bancroft *et al.* [23]. The spectra of $Cr(acac)_3$, $Co(acac)_3$ and $Cr(Bracac)_3$ are in excellent agreement with these previous reports and therefore the data need not be presented here. Although the mass spectra of the mixed-ligand complexes and $Co(Bracac)_3$ have not been reported previously, it seems inappropriate to discuss them in detail in this paper. In general, mass spectral identification of the complexes is simplified if bromine is present as its isotopic abundance gives rise to characteristic splitting patterns which are dependent on the number of bromines in the ionic species. The tri-brominated chelates show parent ions of intensity ratio 1:2:2:1, the bi-brominated species have ratios of 1:2:1 and the mono-brominated species ratios of 1:1.

The relative intensities of all except very minor peaks and ligand or ligand fragment peaks in the mass spectra of the mixed-ligand complexes and $Co(Bracac)_3$ are given in Table V. Although molecular ion peaks were observed for all the chelates studied, the most intense peak in all spectra corresponds to the ion generated after loss of one ligand, an observation consistent with the data reported for the unsubstituted acetylacetonates of Co(III) and Cr [22, 23]. On the basis of the fragmentation patterns observed for the mixed-ligand chelates and the relative intensities of the fragment ions, it is concluded that processes which involve loss of a brominated ligand are preferred to those which involve loss of unsubstituted ligand. The most important peaks in the mass spectra of the tri- and bi-brominated chelates are adequately accounted for by mechanisms proposed by Bancroft *et al.* [23], whereas the mono-brominated chelates initially behave like other brominated chelates but after the loss of the brominated ligand, the features of the spectra are characteristic of unsubstituted metal acetylacetonates [22].

Although mass spectrometry is useful in the identification of chromatogrpahic peaks, it does not provide conclusive evidence of the location of the bromine substitutent on the ligand. This was achieved in the present study by using ^{13}C NMR spectroscopy of samples of the cobalt chelates collected by preparative liquid chromatography.

The data for the chemical shifts of the three brominated complexes and $Co(acac)_3$ in deuterobenzene are given in Table VI. Previous data for $Co(acac)_3$ obtained in deuterochloroform are in good agreement with our data [24, 25]. For the brominated complexes, only the ^{13}C-carbonyl shift in the fully brominated complex has been reported previously [26]. On bromine substitution, there is virtually no change (about 1 ppm upfield) in the carbonyl chemical shift whereas the methyl carbon's chemical shift is more deshielded. In the mixed-ligand complexes, the bromine-substituted carbon is readily distinguished from the methine carbon resonance as the latter gives the characteristic doublet in the coupled spectrum whereas the former remains as a singlet, slightly upfield from the methine carbon shift.

The interesting feature of the decoupled spectra of the mixed-ligand complexes is the splitting of the carbonyl and methyl resonances into groups of three peaks (see Table VI). In the coupled spectra, each methyl shift shows the expected quartet splitting pattern and each carbonyl shift appears as a singlet. These observations cannot be explained as being due to the presence of impurities since analytical HPLC and mass spectrometry confirm the purity of the samples. The presence of the bromine substituent on one or two of the three available coordinated ligands would appear to lead to three non-equivalent pairs of methyl and carbonyl carbons. Similar observations were made for the methyl groups in the ^{1}H-NMR of mono- and bi-substituted acetylacetonates of Co(III) and Rh(III) and the splitting was explained as being due to long-range intramolecular anisotropic shielding by the cyclic system of π-electrons in adjacent chelate rings [27]. It is hoped to obtain further evidence to support this explanation by applying I.N.E.P.T. pulse sequence techniques [28] to these and other mixed-ligand metal complexes and this work will be reported at a later date. In the present study, it is concluded from the ^{13}C NMR spectra that bromine is also substituted in the 3-position in each of the mixed-ligand complexes isolated by chromatography.

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