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## HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY OF THE METAL CHELATES OF DIALKYLDITHIOPHOSPHORIC ACIDS

### I. FORMATION OF MIXED-LIGAND CHELATES OF CHROMIUM(III) AND COBALT(III)

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#### SUMMARY

Mixtures of any two dialkyldithiophosphate chelates of cobalt(III) readily undergo ligand exchange in solution and four peaks were resolved by adsorption high-performance liquid chromatography. Under vigorous conditions, the inert chromium(III) chelates can also be forced to react. The identities of the mixed-ligand chelates have been established by mass spectrometry. Mixtures of three chelates gave rise to ten species, one of which has been attributed to a mixed-ligand chelate with three different ligands. Ligand generation with two alcohols rather than one led to very complex mixtures of mixed-ligand chelates and good resolution of all the species has been achieved.

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#### INTRODUCTION

High-performance liquid chromatography (HPLC) has been used by several research groups to separate mixed-ligand metal chelates generated by interaction of two or more chelates, mainly in solution. To date, mixed-ligand metal chelates have been observed by HPLC in systems involving either  $\beta$ -diketone or N,N-dialkyldithiocarbamic acid ligands.

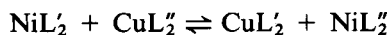
Uden *et al.*<sup>1</sup> reported that the mixed-ligand chromium(III) complexes of trifluoro- and hexafluoroacetylacetone could be resolved using isocratic and gradient elution adsorption HPLC with methylene chloride-hexane eluents. Almost complete separation of this series of complexes and their geometrical isomers was achieved with gradient elution.

Liska *et al.*<sup>2</sup> initially reported that injection of a mixture of two nickel(II) dialkyldithiocarbamates gave rise to three peaks in the chromatogram, the additional

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peak being due to the mixed-ligand chelate. Further studies<sup>3</sup> indicated that these exchange reactions occurred for zinc and lead but not for cobalt(II) and copper(II) chelates. In addition, it was possible to obtain exchange between bis(dithiocarbamate) complexes which contain different ligands and metals, thus



Contrary to the above findings, Moriyasu and Hashimoto<sup>4</sup> found that the Cu(II) dithiocarbamates are more labile than those of Ni and the mixed-ligand chelate disproportionates in the column. Slow exchange for Co(III) chelates was claimed to give rise to four peaks in the chromatogram, but no further details were given.

Continuing our studies on the chromatography of metal dialkyldithiophosphates<sup>5,6</sup>, we wish to report here our investigations on the HPLC separation of tris(dithiophosphato) chelates of chromium(III) and cobalt(III), the formation of several different mixed-ligand chromium(III) dialkyldithiophosphates and their resolution by HPLC.

## EXPERIMENTAL

The Cr(III) chelates were prepared by methods described previously<sup>5</sup>. Co(III) chelates were prepared by adding  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  to an alcoholic ligand solution followed by aerial oxidation<sup>7</sup>. Purification of the complexes was achieved by alumina column chromatography using chloroform–heptane (1:1) as eluent and recrystallization from the appropriate alcohol.

Electronic spectra were run on a Shimadzu UV-240 recording spectrophotometer. Mass spectra were obtained on a V.G. Micromass 7070F spectrometer operating at 70 eV.

Liquid chromatography was carried out on a chromatograph consisting of an Altex Model 110A single-piston pump, a Rheodyne 7125 injector fitted with a 20- $\mu\text{l}$  sample loop and a Hitachi Model 100-10 variable-wavelength spectrophotometric detector with 20- $\mu\text{l}$  Altex Model 155 flow cell. The analytical column used throughout this study was a Phase Separations 250  $\times$  4.6 mm 5- $\mu\text{m}$  Spherisorb silica (S5W) column. Semi-preparative liquid chromatography was carried out by injecting 200  $\mu\text{l}$  of a saturated chelate solution on to a 300  $\times$  7.5 mm column which was dry packed with 30  $\mu\text{m}$  LiChrosorb SI 60.

## RESULTS AND DISCUSSION

A wealth of information exists in the chemical literature on metal dialkyldithiophosphates with short alkyl chains and the present study includes some of the derivatives of trivalent metals. Chelates of general formula,  $\text{M}[\text{S}_2\text{P}(\text{OR})_2]_3$ , have been prepared; R = ethyl, isopropyl and isobutyl for M = Co(III) or Cr(III) and R = *n*-propyl, *n*-butyl and *sec.*-butyl for M = Cr(III). The dimethyl-derivatives were not included in this study because of their poor solubility in the non-polar solvents found to be suitable for elution of these chelates by liquid chromatography.

Electronic spectra of all the above chelates were run to determine the most suitable wavelengths for spectrophotometric detection of eluates in liquid chromato-

graphy. Heptane solutions ( $10^{-4}$  M) displayed bands at 210, 280 and 310 (sh) nm for the chromium complexes and at 210, 335 and 405 (sh) nm for the cobalt complexes, in agreement with previously reported data<sup>8,9</sup>. The intense bands at 280 and 335 nm led to a choice of these wavelengths for the detection of the chromium and cobalt chelates, respectively, and 310 nm was used for solutions which contained both metal chelates.

The high solubility of these chelates in non-polar and moderately polar solvents suggested they might be amenable to elution by normal-phase HPLC. Non-polar solvents such as the light hydrocarbons or petroleum spirits do not lead to elution of the metal dialkyldithiophosphates within a reasonable time period unless the polarity of the mobile phase is modified by addition of an alcohol. In general, the optimum composition of the eluent is dependent on a number of factors but ideal chromatography is achieved using 0.01–0.1% of a lower alcohol in HPLC (or Nano-grade) quality hexane or pentane. Fig. 1 shows a typical elution profile for a series of chromium(III) dialkyldithiophosphates using 0.06% isobutanol in hexane as the eluent: The order of elution is unchanged for the cobalt complexes and under identical conditions the latter are retained longer than the corresponding chromium complexes. It is important to note that the column is slow to equilibrate and in order to achieve reproducible chromatograms it is essential to condition the column with the eluent at a flow-rate of about  $3 \text{ cm}^3 \text{ min}^{-1}$  for at least 30 min. The retention data are summarized in Table I and because of the excellent liquid chromatographic efficiencies ( $N > 40,000/\text{m}$ ) displayed by these chelates, the dialkyldithiophosphoric acids could prove to be suitable derivatizing agents for trace metal analysis by HPLC.

One interesting feature in the chromatograms of mixtures of two or more cobalt chelates was the appearance of minor peaks, intermediate in retention volumes

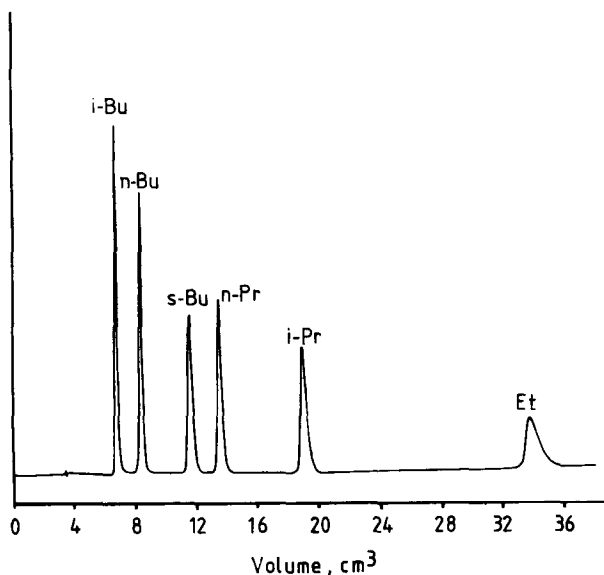


Fig. 1. Elution of six different Cr(III) dialkyldithiophosphates with 0.06% isobutanol in hexane as eluent. Solution concentration:  $10^{-4}$  M in each complex. Flow-rate:  $1.0 \text{ cm}^3 \text{ min}^{-1}$ . Detector: 280 nm.

TABLE I

CAPACITY FACTORS ( $k'$  VALUES) FOR SOME COBALT(III) AND CHROMIUM(III) DI-ALKYLDITHIOPHOSPHATES

LC conditions as in Fig. 1.

	<i>i</i> -Bu	<i>n</i> -Bu	<i>sec</i> -Bu	<i>n</i> -Pr	<i>i</i> -Pr	Et
Cr	1.0	1.5	2.4	3.0	4.5 <sub>s</sub>	8.9
Co	1.1 <sub>s</sub>	—	—	—	5.3 <sub>s</sub>	10.1 <sub>s</sub>

relative to the major components. As the solutions aged, the minor peaks grew in intensity whereas the major peaks diminished, therefore suggesting that mixed-ligand metal complexes were being generated as a result of ligand exchange processes taking place in solution. In contrast, mixtures of chromium chelates in solution do not undergo any discernible reaction at room temperature but reaction proceeds rapidly under more vigorous conditions. The lability of the cobalt complexes leads to dis-

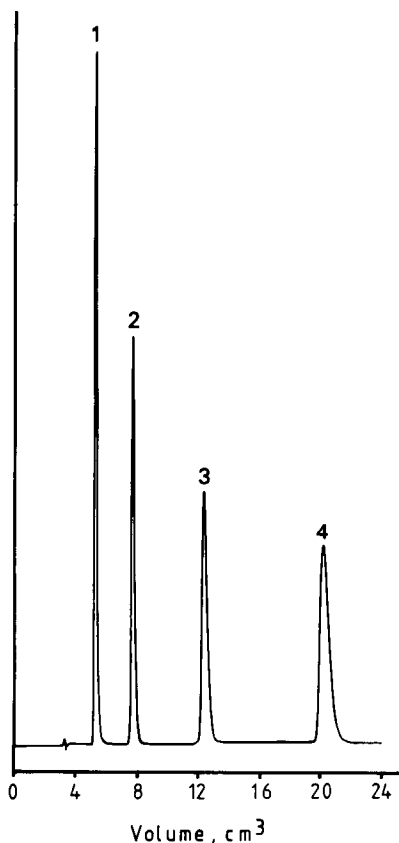
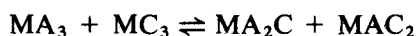


Fig. 2. Chromatogram for the reaction mixture of tris(diethylthiophosphato)chromium(III) and tris(di-isobutylthiophosphato)chromium(III). Eluent: 0.08% isobutanol in pentane at  $1.0 \text{ cm}^3 \text{ min}^{-1}$ . Detector: 280 nm. Peaks: 1 =  $\text{CrA}_3$ ; 2 =  $\text{CrA}_2\text{C}$ ; 3 =  $\text{CrAC}_2$ ; 4 =  $\text{CrC}_3$  [A =  $(\text{iso-C}_4\text{H}_9\text{O})_2\text{PS}_2^-$ ; C =  $(\text{C}_2\text{H}_5\text{O})_2\text{PS}_2^-$ ].

proportionation of their mixed-ligand species making it impossible to isolate them pure<sup>10</sup> and this led to a choice of the stable chromium complexes in further studies of the ligand exchange reactions. Fig. 2 is an example of the separation of the constituents of the reaction of equimolar amounts of the diethyl- and diisobutyldithiophosphates of chromium(III) after refluxing in xylene; this chromatogram represents a reaction which has not established equilibrium, but this may be achieved after about 4 h at these temperatures. Two mixed-ligand species are expected according to the equilibrium expression



where A and C symbolise the bidentate diisobutyl- and diethyldithiophosphate anions, respectively. As the diisobutyl derivative elutes before the diethyl derivative, it is concluded by analogy with similar redistribution reactions<sup>1</sup> that the order of elution is  $MA_3 < MA_2C < MAC_2 < MC_3$ . Collection of fractions of the second peak in Fig. 2 by preparative liquid chromatography and analysis of the samples by mass spectrometry confirm the expected order of elution.

Similar chromatograms showing other possible mixed-ligand species can be obtained by sampling other binary combinations of chromium complexes. If a mixture initially composed of three pure trivalent metal dialkyldithiophosphates undergoes ligand-exchange reactions, it is predicted that the resulting chromatograms should display ten peaks and one of these peaks should correspond to a complex with a unique formula containing three different dialkyldithiophosphate ligands. The

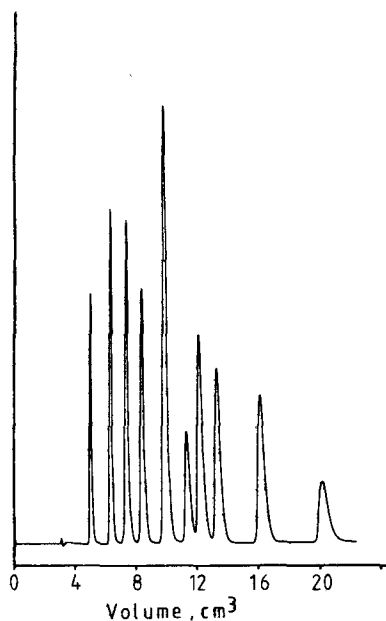


Fig. 3. Chromatogram for the reaction mixture of tris(diethyldithiophosphato)chromium(III), tris(diisopropyldithiophosphato)chromium(III) and tris(diisobutyldithiophosphato)chromium(III). LC conditions as in Fig. 2. For peak identification; see Table II.

TABLE II

## RETENTION DATA FOR COMPONENTS IN REACTION MIXTURES OF DIFFERENT CHROMIUM(III) DIALKYLDITHIOPHOSPHATES

LC conditions as in Figs. 2 and 3. Abbreviations: A = (i-C<sub>4</sub>H<sub>9</sub>O)<sub>2</sub>PS<sub>2</sub><sup>-</sup>; B = (i-C<sub>3</sub>H<sub>7</sub>O)<sub>2</sub>PS<sub>2</sub><sup>-</sup>; C = (C<sub>2</sub>H<sub>5</sub>O)<sub>2</sub>PS<sub>2</sub><sup>-</sup>.

Initial reactants	<i>k'</i> values for reaction components									
	MA <sub>3</sub>	MA <sub>2</sub> B	MA <sub>2</sub> C	MAB <sub>2</sub>	MABC	MB <sub>3</sub>	MAC <sub>2</sub>	MB <sub>2</sub> C	MBC <sub>2</sub>	MC <sub>3</sub>
MA <sub>3</sub> /MB <sub>3</sub>	0.7	1.1	—	1.7	—	2.6	—	—	—	—
MA <sub>3</sub> /MC <sub>3</sub>	0.7	—	1.4	—	—	—	2.9	—	—	5.3
MB <sub>3</sub> /MC <sub>3</sub>	—	—	—	—	—	2.6	—	3.2	4.1	5.3
MA <sub>3</sub> /MB <sub>3</sub> /MC <sub>3</sub>	0.6	1.0	1.3	1.6	2.1	2.6	2.8	3.2	4.1	5.3

example chosen which highlights the scrambling of ligands in a ternary mixture is one initially containing the diethyl-, diisopropyl- and diisobutyldithiophosphates, complexes which individually are extremely well resolved under the conditions used (see Fig. 3). The retention data derived from the appropriate ternary reaction mixtures are used to identify all except one of the components arising from the ternary reaction mixture and it is concluded that the peak with a retention volume of 9.85 cm<sup>3</sup> (*k'* = 2.1) corresponds to the metal complex with three different dithiophosphate ligands (see Table II).

HPLC can also be used to demonstrate another interesting aspect of these mixed-ligand metal complexes which may have important consequences in the development of LC procedures for metal analysis using dialkyldithiophosphoric acids. Due to the instability of these acids, it is customary to prepare the ligand solutions afresh by reaction of the appropriate alcohol with phosphorus pentasulfide. If two alcohols in admixture are used in the ligand generation step, the resulting solution will contain three dialkyldithiophosphoric acid ligands according to the reactions



It is predicted that reaction of this mixture of bidentate ligands with a trivalent metal ion should yield ten different metal complexes, some of which would not have been encountered in reactions described earlier in this paper.

As tris(diethyldithiophosphato)chromium(III) and the corresponding diisobutyl derivative are well resolved by liquid chromatography, ethanol and isobutanol were chosen as the two alcohols in the synthetic generation of the above mixture of metal chelates. Equal volumes of the two alcohols were used to prepare the solution of ligands and after addition of the chromium(III) salt, the mixture was analysed by HPLC (Fig. 4). The chromatogram contains at least sixteen peaks rather than the predicted ten, but the additional peaks may be explained by taking into consideration the geometrical isomerism possible for some of the complexes in the reaction mixture. Using the abbreviations adopted earlier in this paper for ligand anions and defining the new ligand anion containing two different alkyl groups as D = (i-C<sub>4</sub>H<sub>9</sub>O)

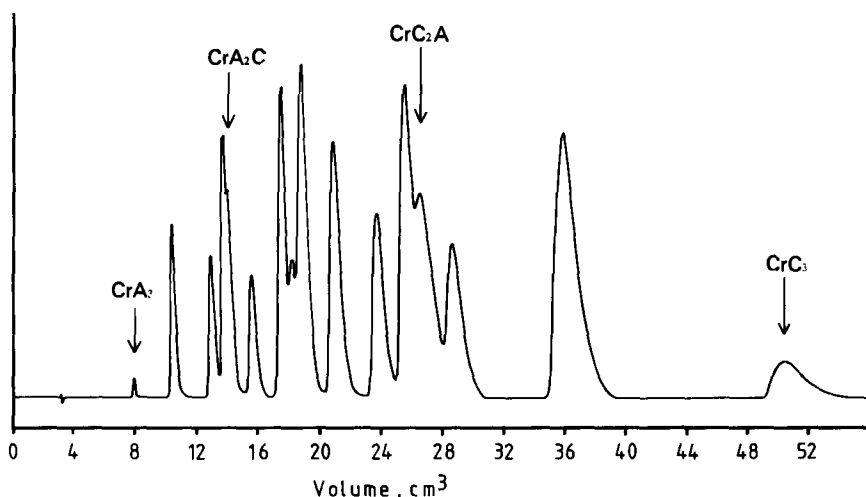


Fig. 4. Separation of the components of the reaction mixture obtained by using ethanol and isobutanol in the generation of the ligand solution before chelate formation with chromium(III). Eluent: 0.02% isobutanol in pentane at  $1.0 \text{ cm}^3 \text{ min}^{-1}$ . Detector: 280 nm.

$(\text{C}_2\text{H}_5\text{O})\text{PS}_2^-$ , then the ten major metal complexes of different formulae ought to be  $\text{CrA}_3$ ,  $\text{CrD}_3$ ,  $\text{CrC}_3$ ,  $\text{CrACD}$ ,  $\text{CrA}_2\text{D}$ ,  $\text{CrD}_2\text{A}$ ,  $\text{CrC}_2\text{A}$ ,  $\text{CrC}_2\text{D}$ ,  $\text{CrA}_2\text{C}$  and  $\text{CrD}_2\text{C}$ . The effect of the presence of the unsymmetrical ligand D is to give rise to the likelihood of geometrical isomerism in some of these complexes. For example,  $\text{CrD}_3$  and  $\text{CrACD}$  may each have two isomers whereas  $\text{CrD}_2\text{A}$  and  $\text{CrD}_2\text{C}$  may each have three and if all of these isomers exist in the above reaction mixture, this would account for the sixteen peaks observed in the chromatogram. At this stage of our investigations, only the arrowed peaks have been identified by spiking as being identical to the four complexes separated in Fig. 2 and the remaining peaks must await their identification after isolation of individual components by semi-preparative liquid chromatography. The order of elution of the identified components and the grouping of the remaining peaks strongly suggest that (i) the three peaks appearing near  $\text{CrA}_2\text{C}$  ( $V_R = 14.2 \text{ cm}^3$ ) arise from the isomers of  $\text{CrD}_2\text{A}$ , (ii) the three peaks near  $\text{CrC}_2\text{A}$  ( $V_R = 26.8 \text{ cm}^3$ ) correspond to the isomers of  $\text{CrD}_2\text{C}$  and (iii) the four peaks with retention volumes of  $17.7\text{--}21.0 \text{ cm}^3$  are due to the isomers of  $\text{CrD}_3$  and  $\text{CrACD}$ .

## CONCLUSIONS

Labile metal dialkyldithiophosphates such as those of Co(III) readily generate mixed-ligand species in solution. The formation of these mixed-ligand complexes may prove to be a disadvantage in the development of LC procedures for trace metal analysis using dialkyldithiophosphoric acids.

Further complications may arise if more than one alcohol is used in the synthesis of the ligand solution. The extent of this interference will depend on a number of factors including the nature and concentration of the trace alcohol, the relative reactivities of different alcohols with phosphorus pentasulfide in ligand generation

and the relative reactivities of the mixture of ligands towards the metal ion in the formation of the chelates. However, the high purity of common analytical-grade alcohols implies that the concentration of mixed-ligand complexes from this source is likely to be low and the interference negligible.

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