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## HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY OF THE METAL CHELATES OF DIALKYL DITHIOPHOSPHORIC ACIDS

### II\*. LABILITY OF COBALT(III) CHELATES

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(Received October 2nd, 1985)

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#### SUMMARY

Mixtures of cobalt(III) dialkyldithiophosphates undergo rapid ligand exchange in solution at 40°C and the components may be resolved by adsorption high-performance liquid chromatography. Under optimum conditions, additional components are observed and these have been identified as disulfide dimers arising from oxidation of the ligand during syntheses of the metal complexes. Exchange reactions in the metal chelates are accompanied by exchange in the organic disulfides.

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#### INTRODUCTION

In a previous paper<sup>1</sup>, we have demonstrated the applicability of high-performance liquid chromatography (HPLC) to the resolution of mixed-ligand dialkyldithiophosphates of chromium(III) and cobalt(III). The chromium(III) chelates were found to be highly inert and mixed-ligand species could only be produced after refluxing the initial reactants in xylene for several hours.

Moriyasu and Hashimoto<sup>2</sup> claimed that exchange between cobalt(III) dithiocarbamates was slow and four peaks were observed in the chromatogram as expected. In contrast, we have found that exchange between cobalt(III) dithiophosphates is reasonably fast<sup>1</sup> and in this paper, we wish to report our recent findings on these labile metal complexes.

#### EXPERIMENTAL

Cobalt(III) diethyl- and diisopropyldithiophosphates were prepared by the method of Cavell *et al.*<sup>3</sup>. The dialkyldithiophosphoric acid was freshly prepared by addition of an excess (50 cm<sup>3</sup>) of the appropriate alcohol to phosphorus pentasulfide (0.025 mol) in a nitrogen atmosphere. The mixture was heated for 20 min on a steam bath until the solution was clear and hydrogen sulfide had been expelled. A slurry

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\* For Part I, see ref. 1.

of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.02 mol) in the appropriate alcohol was added and the mixture allowed to stand in air to produce the Co(III) complex. The solid was filtered, washed with the appropriate alcohol and dissolved in chloroform to remove unreacted metal salts. After evaporation of chloroform, the brown solid was recrystallised from 50:50 (v/v) dichloromethane and the alcohol. The identities of the chelates were confirmed by mass spectrometry.

HPLC was carried out using a LDC Constametric IIG pump and Model 1203 Monitor III at 254 nm. Sample solutions in hexane were injected with a Rheodyne 7125 valve fitted with a 20- $\mu\text{l}$  loop and the column (150  $\times$  4.6 mm I.D.) was slurry-packed with 7- $\mu\text{m}$  Zorbax silica.

Mass spectra of all samples were recorded on a V.G. Micromass 7070F spectrometer operating at 70 eV.

## RESULTS AND DISCUSSION

In a previous paper<sup>1</sup>, we have reported that excellent resolution of tris(di-alkyldithiophosphato)chromium(III) chelates and their mixed-ligand derivatives can be achieved on a silica column using eluents containing 0.1% or less alcohol in a hydrocarbon<sup>1</sup>.

After equilibration of the column with ethanol-hexane (0.08:99.92), the chromatogram of a mixture of diethyl- and diisopropyldithiophosphates of cobalt(III) showed four peaks as expected (Fig. 1),

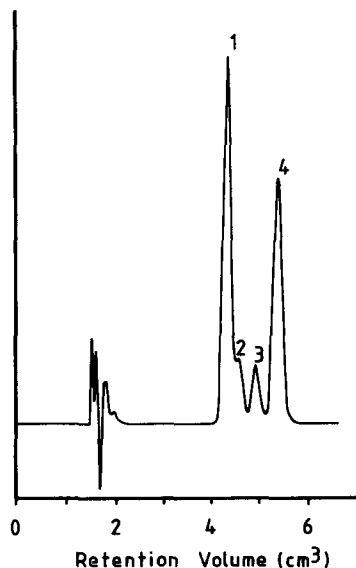
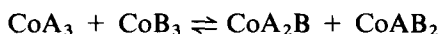


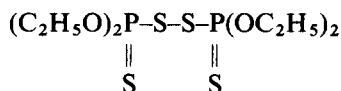
Fig. 1. Liquid chromatogram of a mixture of diethyl- and diisopropyldithiophosphates of cobalt(III) sampled shortly after mixing. Eluent: ethanol-hexane (0.08:99.92) at 1.0  $\text{cm}^3 \text{min}^{-1}$ . Column: 150  $\times$  4.6 mm I.D. packed with 7- $\mu\text{m}$  Zorbax silica. Wavelength: 254 nm. Peak identities: 1 =  $\text{CoA}_3$ ; 2 =  $\text{CoA}_2\text{B}$ ; 3 =  $\text{CoAB}_2$ ; 4 =  $\text{CoB}_3$ , where A =  $(i\text{-C}_3\text{H}_7\text{O})_2\text{PS}_2^-$  and B =  $(\text{C}_2\text{H}_5\text{O})_2\text{PS}_2^-$ ; abbreviations as in the text.

where  $A = (i\text{-C}_3\text{H}_7\text{O})_2\text{PS}_2^-$  and  $B = (\text{C}_2\text{H}_5\text{O})_2\text{PS}_2^-$  (these abbreviations will be used throughout this paper). The peaks with retention volumes of 4.4 and 5.4  $\text{cm}^3$  were identified as  $\text{CoA}_3$  and  $\text{CoB}_3$ , respectively, by injections of solutions of the individual complexes. Assuming that the additional peaks are due to the formation of the mixed-ligand species according to the redistribution reaction above, the order of elution is  $\text{CoA}_3 < \text{CoA}_2\text{B} < \text{CoAB}_2 < \text{CoB}_3$  by analogy with the chromium(III) chelates reported previously<sup>1</sup>. The appearance of the mixed-ligand peaks shortly after mixing  $\text{CoA}_3$  and  $\text{CoB}_3$  at room temperature indicates that these complexes are much more reactive than the corresponding chromium(III) complexes, the latter requiring elevated temperatures for the reaction to proceed. Hence, reactions involving cobalt(III) complexes may be more suitable for generation of kinetic and equilibrium data for the redistribution of metal dialkyldithiophosphates.

Attempts were made to optimize the resolution of the four components involved in the redistribution reaction of cobalt(III) complexes by varying the alcohol content of the eluent or by changing the alcohol. During the optimization process, it is essential that sufficient time be allowed for conditioning of the column with the new mobile phase otherwise retention data will vary from one injection to the next. In general, a decrease in the alcohol content or an increase in alcohol chain lengths leads to increases in retention volumes.

A decrease in the ethanol content of the eluent to 0.06% or less produced a surprising result with more than four peaks being observed in the chromatogram of a mixture of cobalt(III) diethyl- and diisopropyldithiophosphates which had been maintained at 40°C for about 2 h. The use of alcohols other than ethanol in the eluent had the same effect although the number of peaks observed depended on the composition of the eluent. The most striking examples of the chromatography of these reaction mixtures are shown in Fig. 2 using isobutanol-hexane (0.05:99.95) as the eluent. Seven peaks were resolved for the redistribution reaction of equimolar amounts of cobalt(III) diethyl- and diisopropyldithiophosphates which had reached equilibrium (Fig. 2a). For identification of the individual components in the mixture, chromatograms of the initial reactants,  $\text{CoA}_3$  and  $\text{CoB}_3$ , were obtained (Figs. 2b and c). It is concluded that peaks 1 and 3 are impurities in the synthesised samples of  $\text{CoA}_3$  and  $\text{CoB}_3$ , the latter eluting as peaks 4 and 7, respectively, in Fig. 2a.

A sample of the impurity peak from an injection of Co(III) diethyldithiophosphate was collected and analysed by mass spectrometry. The relative intensities and probable assignments for the fragment ions are listed in Table I. The parent ion at  $m/e = 370$  and the fragmentation pattern provided good evidence for the identity of the impurity as the disulfide, bis(diethoxyphosphinothioyl)disulfide:



The additional peak in the chromatogram of cobalt(III) diisopropyldithiophosphate was identified as the corresponding isopropyl derivative.

These disulfide impurities are not observed in the chromatography of chromium(III) dialkyldithiophosphates<sup>1</sup> and it is most likely that the contaminants are produced during the final stages of syntheses of the cobalt(III) complexes. After

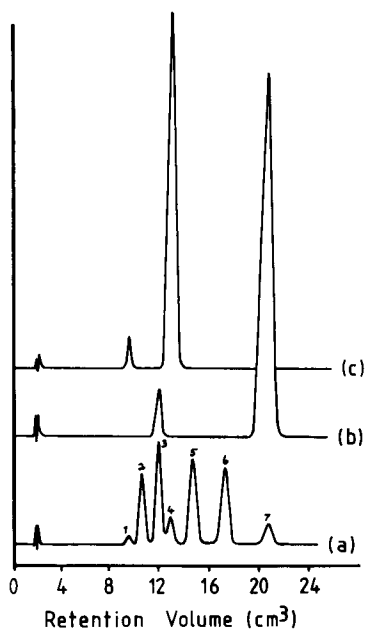


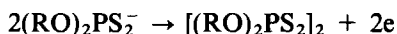
Fig. 2. (a) Liquid chromatogram of an equilibrated exchange reaction mixture of  $\text{CoA}_3$  and  $\text{CoB}_3$  containing traces of disulfide impurities. Eluent: isobutanol-hexane (0.05:99.95) at  $1.0 \text{ cm}^3 \text{ min}^{-1}$ . Other conditions, as in Fig. 1. Peak identities: 1 =  $[(i\text{-C}_3\text{H}_7\text{O})_2\text{PS}_2]_2$ ; 2 =  $(i\text{-C}_3\text{H}_7\text{O})_2\text{PS}_2\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2$ ; 3 =  $[(\text{C}_2\text{H}_5\text{O})_2\text{PS}_2]_2$ ; 4 =  $\text{CoA}_3$ ; 5 =  $\text{CoA}_2\text{B}$ ; 6 =  $\text{CoAB}_2$ ; 7 =  $\text{CoB}_3$ ; abbreviations as in the text. (b) Chromatogram of  $\text{CoB}_3$  containing the disulfide impurity,  $[(\text{C}_2\text{H}_5\text{O})_2\text{PS}_2]_2$ . (c) Chromatogram of  $\text{CoA}_3$  containing the disulfide impurity,  $[(i\text{-C}_3\text{H}_7\text{O})_2\text{PS}_2]_2$ .

TABLE I

MASS SPECTRAL DATA FOR THE IMPURITY IN THE SAMPLE OF COBALT(III) DIETHYL-DITHIOPHOSPHATE

<i>m/e</i>	Relative intensity (%)	Fragment ion assignment
370	33.5	$\text{M}^+$
325	10.1	$[\text{M} - \text{C}_2\text{H}_5\text{O}]^+$
306	16.7	$[\text{M} - 2\text{S}]^+$
185	26.4	$\frac{1}{2}\text{M}^+$
157	13.7	$[\frac{1}{2}\text{M} - \text{C}_2\text{H}_4]^+$
153	50.0	$[\frac{1}{2}\text{M} - \text{S}]^+$
129	34.0	$[(\frac{1}{2}\text{M} - \text{C}_2\text{H}_4) - \text{C}_2\text{H}_4]^+$
125	80.0	$[(\frac{1}{2}\text{M} - \text{S}) - \text{C}_2\text{H}_4]^+$
121	71.4	$[(\frac{1}{2}\text{M} - \text{S}) - \text{S}]^+$
97	100.0	$[\text{SP}(\text{OH})_2]^+$
93	43.4	$[\text{P}(\text{OH})(\text{OC}_2\text{H}_5)]^+$

addition of a cobalt(II) salt to the ligand solution, the mixture is allowed to oxidize in air to form the cobalt(III) complex and it is feasible that aerial oxidation of the ligand anion proceeds according to the following reaction



It is not uncommon for mild oxidizing agents to convert dialkyldithiophosphoric acids or their simple salts to bis(dialkoxyphosphinothiyl)disulfides<sup>4,5</sup>.

Organic disulfides are known to undergo exchange reactions under various conditions<sup>6</sup> and mixed disulfides derived from dialkyldithiophosphates are well-known<sup>7</sup>. It is clear that the first three peaks in Fig. 2a arise from exchange in the tetraethyl (BB) and tetraisopropyl (AA) disulfides to produce a mixed disulfide (AB) *i.e.*,  $\text{AA} + \text{BB} \rightleftharpoons 2\text{AB}$ . Under the HPLC conditions used, the order of elution was found to be  $\text{AA} < \text{AB} < \text{BB}$ . Bishop *et al.*<sup>8</sup> obtained similar results for the separation of disulfides derived from dithiocarbamates using normal-phase chromatography and dichloromethane as eluent, with the mixed disulfide intermediate in retention volume.

Attempts were made to isolate pure samples of the mixed-ligand cobalt(III) complexes by fraction collection from the analytical column. Fractions were collected in chilled sample vials and analysed immediately to determine their purity. Fig. 3 shows a typical chromatogram for a sample of  $\text{CoAB}_2$  and a similar result is obtained for the other mixed-ligand complex,  $\text{CoA}_2\text{B}$ . It is interesting to note that highly pure samples of the corresponding chromium(III) mixed-ligand complexes are readily obtained by the above collection procedure<sup>1</sup>. It is concluded that the mixed-ligand cobalt(III) complexes are very labile and they disproportionate during the collection

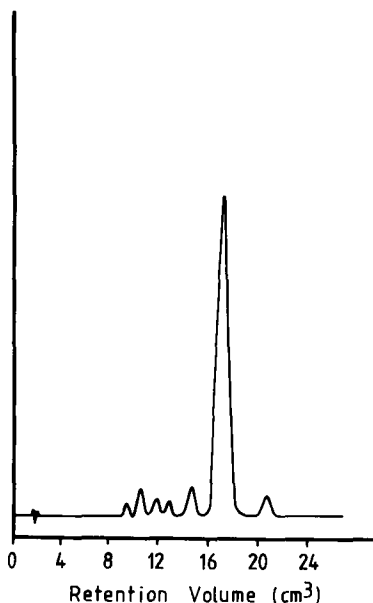


Fig. 3. Liquid chromatogram of a sample of  $\text{CoAB}_2$  run immediately after fraction collection. Eluent as in Fig. 2, other conditions as in Figs. 1 and 2.

process. The presence of the disulfide peaks in Fig. 3 suggests that dissociation of the metal complex may also be taking place followed by oxidation of the free ligands. If the sample giving rise to the chromatogram in Fig. 3 is analysed about 48 h after collection and storage at room temperature (20°C), disproportionation and exchange of the metallic species and organic disulfides are almost complete and the resulting chromatogram is similar to that presented in Fig. 2a.

## CONCLUSIONS

Cobalt(III) dialkyldithiophosphates are extremely labile in solution and the complexes undergo exchange processes leading to formation of mixed-ligand species. Organic disulfides are formed during synthesis of the metal complexes. The presence of these disulfide impurities and the lability of the cobalt(III) complexes may prove to be serious disadvantages in the analysis of mixtures of metal dialkyldithiophosphates by HPLC.

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