

osmium are increased in contradiction to Pauling's principle. This indicates unequivocally the importance of the  $\pi$ -character of Ir-Cl and Os-Cl bonds.

Although the present discussion is open to criticism as to the adequacy of the assumed extent of s character of sp hybridized orbitals, the extent of  $\pi$ -character of

Os-Cl bonds in a hexachloroösmate(IV) ion, etc., the present authors believe that at least an interpretation is presented which is consistent with the experimental data obtained and assumptions made and can throw light upon some phases of the problem of the nature of metal-halogen bonds in complexes.

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## Gas Phase Chromatography of Metal Chelates of Acetylacetone, Trifluoroacetylacetone, and Hexafluoroacetylacetone<sup>1</sup>

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Received December 17, 1962

The gas phase chromatography of metal chelates of acetylacetone, trifluoroacetylacetone, and hexafluoroacetylacetone was investigated. Chelates of the fluorine-containing  $\beta$ -diketones are more volatile and can be eluted at much lower column temperatures than corresponding complexes of acetylacetone. Trifluoroacetylacetonato complexes of beryllium(II), aluminum(III), indium(III), chromium(III), iron(III), copper(II), rhodium(III), zirconium(IV), and hafnium(IV) were successfully eluted in the gas phase. Separations of multi-component mixtures of chelates were rapid and efficient. Geometrical isomers of chromium(III) trifluoroacetylacetonate were separated by gas-liquid chromatography. The separation of optical isomers by gas-liquid and gas-solid chromatography is discussed.

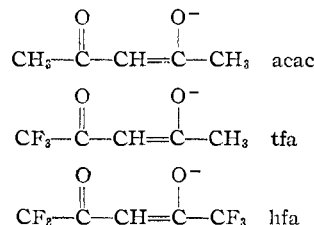
### Introduction

Gas chromatography has enjoyed remarkable success in the separation and analysis of countless organic compounds. Extraordinary speed, power of resolution, and sensitivity are characteristics which render the technique attractive for separative and analytical purposes.

Several investigations have been concerned with the separation of anhydrous metal halides<sup>4-7</sup> by gas chromatography. With a few exceptions, high column temperatures are required to elute the halides and reactivity of the compounds presents a problem in sample handling and in choice of materials with which to pack the column.<sup>5</sup> A more serious problem arises from the polymeric, non-volatile characteristics of many metal halides. Recent studies<sup>8,9</sup> have indicated that beryllium(II), aluminum(III), and chromium(III) acetylacetonates are sufficiently volatile and thermally stable to be subjected to gas chromatography. Brandt and Heveran<sup>9</sup> have recently reported that gas chromatography can be used for trace analysis of chromium.

This study was initiated to explore the applicability

of gas phase chromatography to the separation of volatile metal chelates. Gas phase chromatographic separations of mixtures of metal chelates, of *cis* and *trans* isomers, and of optical isomers were studied. Metal chelates containing anions of the following  $\beta$ -diketones were investigated: 2,4-pentanedione (acac), 1,1,1-trifluoro-2,4-pentanedione (tfa), and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfa).



### Experimental

**Reagents.**—2,4-Pentanedione was purchased from Matheson, Coleman and Bell and was used without further purification. 1,1,1-Trifluoro-2,4-pentanedione and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione were purchased from Columbia Organic Chemical Co. and redistilled prior to use.

**Synthesis of Chelates.**—The acetylacetonates were prepared by conventional methods and purified by recrystallization and, in some cases, by sublimation at reduced pressure.

The trifluoroacetylacetonates were prepared by methods similar to previously reported procedures.<sup>10,11</sup> In most instances this involved the addition of an aqueous solution of trifluoroacetylacetone, neutralized with ammonium hydroxide, to an aqueous solution of the metal ion. The product was separated by filtration or extraction and purified by recrystallization and, in some instances, by sublimation at reduced pressure. The zirconium(IV) and hafnium(IV) complexes of trifluoroacetylacetone were

(1) Presented in part by R. E. Sievers, R. W. Moshier, and B. W. Ponder, 141st National Meeting, American Chemical Society, Washington, D. C., March, 1962.

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conveniently synthesized by a method substantially different from previous syntheses.<sup>12</sup> In the present synthesis, trifluoroacetylacetone was added directly to anhydrous zirconium(IV) or hafnium(IV) chloride suspended in carbon tetrachloride, and the mixture was briefly refluxed. Hydrogen chloride was rapidly evolved, so the addition of a base was unnecessary. Small amounts of insoluble impurities were removed from the hot reaction mixture by filtration, and the product was crystallized by evaporation of the solvent. The product was further purified by sublimation at 110° under 0.05 mm. pressure.

A mixture of the *cis* and *trans* isomers of *tris*-(1,1,1-trifluoro-2,4-pentanedionato)-chromium(III) was separated by fractional crystallization from carbon tetrachloride. The less soluble and more abundant fraction is the *trans* isomer. Fay and Piper<sup>13</sup> have independently separated the isomers by conventional liquid-solid chromatography and have unequivocally established the configurations of the isomers by a combination of nuclear magnetic resonance spectroscopy and X-ray powder patterns. Melting points of the *cis* (112–114°) and *trans* (154.5–155°) isomers differ sufficiently to easily distinguish the two compounds.

The chromium(III) and rhodium(III) complexes of hexafluoroacetylacetone were synthesized and purified by previously reported methods.<sup>14,15</sup>

**Preparation of Gas Chromatography Columns.**—There are several factors which must be taken into consideration if gas phase chromatography of metal chelates is to be successful. The chelate must have a large enough vapor pressure to be eluted in a reasonable length of time at column temperatures low enough that thermal degradation does not occur. Therefore, it is desirable to select columns from which the chelates can be eluted at the lowest possible column temperature. "Lightly loaded columns," *i.e.*, columns in which the solid support material is only thinly coated with the stationary liquid phase, are best suited for this purpose.<sup>16–18</sup> General purpose columns ordinarily contain solid supports coated with *ca.* 20% of liquid phase. In a lightly loaded column the liquid phase percentage is usually less than 1%. By use of such columns it was possible to elute at lower column temperatures than are required for conventional columns. Although there are some drawbacks to the use of lightly loaded columns, the Clausius-Clapeyron advantage may compensate for these in some instances.<sup>18</sup>

Another factor to consider in the gas chromatography of metal chelates is the reactivity of the column materials. The chelates must not undergo reaction with the liquid phase, with the solid which supports this phase, or with the walls of the column. Therefore, non-reactive liquid phases and solid support materials were selected, and glass columns were used in preference to the conventional ones made of metal.<sup>19</sup> Some of the chelates, *e.g.*, the chromium(III) complexes, were found to be sufficiently volatile and stable to allow metal columns containing large percentages of liquid phases to be used without difficulty.

Numerous columns containing a variety of liquid partitioning agents and solid supports have been used during the course of this investigation. Some of the columns which proved most satisfactory are described below.

(12) E. M. Larsen, G. Terry, and J. Leddy, *J. Am. Chem. Soc.*, **75**, 5107 (1953).

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(19) Considerable difficulty was encountered in early experiments in which stainless steel was used. Apparently the walls of the column either catalyzed decomposition or reacted directly with some of the less stable chelates. When trifluoroacetylacetone was injected into a freshly prepared stainless steel column at 135°, a red compound having the same ultraviolet spectrum as  $\text{Fe}(\text{tfa})_3$  was collected from the effluent stream. In flow systems constructed of Pyrex or Teflon, as are commercially available or readily constructed, this difficulty is avoided.

The solid support was coated with the liquid partitioning agent by dissolving a weighed quantity of the liquid phase in enough chloroform to cover the solid support material and then removing the chloroform under reduced pressure by heating with constant agitation and mixing. Subsequently, the coated solid support material was slowly introduced into the column. A mechanical vibrator was used to facilitate uniformity in packing. A small plug of glass wool was inserted in both ends of the column to hold the column packing in place. Before use, each column was conditioned for several hours under a stream of helium at a temperature slightly in excess of that anticipated during actual operation.

Column A was constructed of Pyrex glass tubing, with an inner diameter of  $\frac{1}{8}$  in. and a length of 4 ft., which was packed with Haloport F (powdered Teflon) coated with 0.5% Tergitol NPX (Union Carbide Co.). Tergitol NPX is a non-ionic detergent, derived from nonylphenol, having the approximate formula  $p\text{-}(n\text{-C}_9\text{H}_{19})\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{10.5}\text{H}$ .

Column B had the same dimensions as column A, but was packed with glass microbeads<sup>20</sup> (60–80 mesh) coated with 0.5% Dow Corning high-vacuum silicone grease.

Column C was constructed of 0.25 in. o.d. copper tubing, 10 ft. long, and contained Chromosorb W (30–60 mesh), coated with 5% Dow Corning high-vacuum silicone grease.

Column D was fabricated from Pyrex tubing, 8 ft. long with an inner diameter of 0.25 in. It was packed with glass microbeads (60–80 mesh) coated with 1% dibutyl-*d*-tartrate (Matheson, Coleman and Bell).

**Equipment.**—Three types of gas chromatography equipment were used during the investigation. The majority of the work was done on a Burrell Model K-7 gas chromatography apparatus, equipped with a thermionic emission ionization detector, fraction collector, flash vaporizer unit, and a temperature programmer. The carrier gas used throughout the study was helium.

A simpler apparatus, the Burrell Model K-2, was used in some of the screening tests and in the attempt to separate optical isomers of chromium(III) hexafluoroacetylacetonate. This unit utilizes a thermal conductivity detector.

The study of the separation of the *cis* and *trans* isomers of chromium(III) trifluoroacetylacetonate was performed on an Aerograph A-90-P gas chromatography apparatus, equipped with a thermal conductivity detector.

**Operating Procedures and Conditions.**—The chelates were dissolved in carbon tetrachloride, benzene, or chloroform prior to introduction into the flash vaporizer chamber. Saturated or nearly saturated solutions were introduced into the gas stream through a silicone rubber septum by means of a microsyringe. Sample sizes ranged from 0.2 to 20  $\mu\text{l}$ .

Column temperatures varied from 30 to 250°, depending on the column being used and the metal chelates being chromatographed. Above 200° thermal degradation becomes a problem for all but the most stable chelates.

The temperatures of the flash vaporizer chamber and detector cell bath were maintained 20–30° above the column temperature for each experiment in order to ensure proper vaporization of the sample and to prevent condensation in the detector cell.<sup>21</sup> High flash vaporizer temperatures should be avoided so that the less stable complexes do not undergo thermal decomposition. The chelate molecules in the sample already are somewhat dispersed by reason of being in solution, and they are further dispersed and diluted by the helium stream when the solvent is volatilized. Consequently, much lower flash vaporizer temperatures are required to ensure instantaneous volatilization under these conditions than would be the case if the complexes were introduced as crystalline solids.

Flow rates of the carrier gas, helium, ranged from 80 to 140 ml./min.

**Collection and Identification of Eluted Compounds.**—It is

(20) Obtained from Microbeads, Inc., Jackson, Miss.

(21) One exception was the separation of  $\text{Cr}(\text{hfa})_3$  and  $\text{Rh}(\text{hfa})_3$ , in which case the flash vaporizer temperature was 100°, while the column temperature was only 30°.

imperative that samples of the eluate fractions be collected and identified if gas chromatography data are to be interpreted unambiguously. If a chelate decomposes very rapidly to yield a product which is volatile, the product may appear as a well defined peak in the chromatogram. In most cases volatile decomposition products are eluted much more rapidly than the chelates, but one case illustrates the necessity for confirming the identity of the eluate. In an attempt to chromatograph  $\text{Co}(\text{acac})_3$  a sharp, well defined peak, distinct from the solvent peak, appeared in the chromatogram. The peak appeared at roughly the same retention time as had been observed for other complexes which had been shown to be eluted without decomposition. However, collection and examination of the eluate revealed that the peak originally thought to have arisen from  $\text{Co}(\text{acac})_3$  was caused instead by a decomposition product.

Fraction collectors were fabricated from Pyrex tubing and were affixed to the exit port of the apparatus. The U-shaped fraction collectors were immersed in a Dry Ice-acetone bath. Standard taper joints were used so the receivers could be changed rapidly to collect each compound as it emerged from the column. The Model K-7 apparatus was equipped with an effluent stream splitting device so that only a very small percentage of the effluent stream entered the detector chamber, and the majority of the stream passed directly to the fraction collector.

For each peak attributed to a metal chelate, a sample was collected and the compound was identified by ultraviolet spectroscopy. For all chelates successfully eluted the spectra were identical with those of original samples. In some instances melting points and infrared spectra were also obtained to corroborate the identity of the fraction.

### Results and Discussion

A study was conducted to determine which of the metal complexes of acetylacetonate, trifluoroacetylacetonate, and hexafluoroacetylacetonate are sufficiently volatile and stable to be subjected to gas chromatography. A column (column B) containing glass microbeads coated with silicone grease was selected for the survey. The screening experiments showed that many of the chelates were eluted from the column at temperatures far below their boiling points and, in most cases, near or below their melting points. Acetylacetonates of beryllium(II), aluminum(III), copper(II), vanadium(IV) (as vanadyl acetylacetonate), and chromium(III) were eluted at column temperatures between 150 and 200°. Attempts to chromatograph acetylacetonate complexes of zirconium(IV), hafnium(IV), cobalt(III), and thorium(IV) at column temperatures between 150 and 230° were unsuccessful.

It was found that trifluoroacetylacetonate complexes of beryllium(II), aluminum(III), indium(III), copper(II), iron(III), rhodium(III), zirconium(IV), and hafnium(IV) were eluted at column temperatures between 100 and 150°. Chromium(III) and rhodium(III) complexes of hexafluoroacetylacetonate were eluted at 30°.

In going from the acetylacetonates to the fluorine-containing complexes a striking trend in volatility<sup>22</sup> was observed. The latter complexes are considerably more volatile and can be eluted at much lower column

(22) Some confusion arises from the use of the word, "volatility." Two compounds may exhibit the same vapor pressure at one temperature and substantially different vapor pressures at another temperature. For this discussion, prime concern is placed on the vapor pressure range (estimated to be on the order of 1-10 mm.) which permits moderately rapid elution of the type of columns employed in this study.

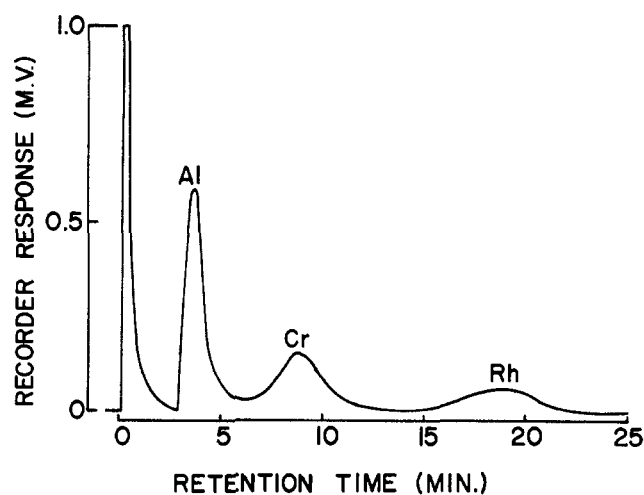


Fig. 1.—Separation of  $\text{Al}(\text{tfa})_3$ ,  $\text{Cr}(\text{tfa})_3$ , and  $\text{Rh}(\text{tfa})_3$  by gas chromatography. Column A, packed with 0.5% Tergitol NPX on powdered Teflon; column temp., 150°; He flow rate, 150 ml./min.; sample, 10  $\mu\text{l}$ . of a mixture of the chelates in  $\text{CCl}_4$ .

temperatures than the acetylacetonates. A case in point is chromium(III) hexafluoroacetylacetonate, which was eluted rapidly at as low a column temperature as 30°. For chromium(III) acetylacetonate to be eluted in the same time period the column temperature must be more than 100° higher.

Chromium(III) hexafluoroacetylacetonate melts at 84° and sublimates rapidly at room temperature and 0.05 mm. pressure.<sup>14</sup> Increased volatility in the fluorine-containing chelates appears to be a general phenomenon.<sup>23-25</sup> It has been suggested<sup>26</sup> that replacing methyl groups with trifluoromethyl groups increases the covalency of the metal-oxygen bond, thereby making the complex more volatile. However, in view of the electron-withdrawing effect of the trifluoromethyl group, it would appear that this explanation is questionable.<sup>27</sup>

The increase in volatility may be accounted for in part by a reduction in van der Waals forces and possibly by a decrease in intermolecular hydrogen bonding in the fluorine-containing complexes. In octahedral complexes of hexafluoroacetylacetonate there are 18 fluorine atoms. These electronegative atoms occupy a large portion of the outer periphery of the molecule and the intermolecular attractive forces are consequently weaker than in analogous unfluorinated complexes. Because of the spatial disposition which the ligands assume upon coordination, the metal ion is encased in what approximates a fluorocarbon shell.

**Separation of Mixtures of Metal Chelates.**—Multi-component mixtures of metal chelates were separated rapidly and efficiently by gas chromatography. Figure 1 is a chromatogram showing the separation of a mixture

(23) A. L. Henne, M. S. Newman, L. L. Quill, and R. A. Staniforth, *J. Am. Chem. Soc.*, **69**, 1819 (1947).

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(27) See ref. 12 for a discussion of the effect of the trifluoromethyl group on the metal-oxygen bond character.

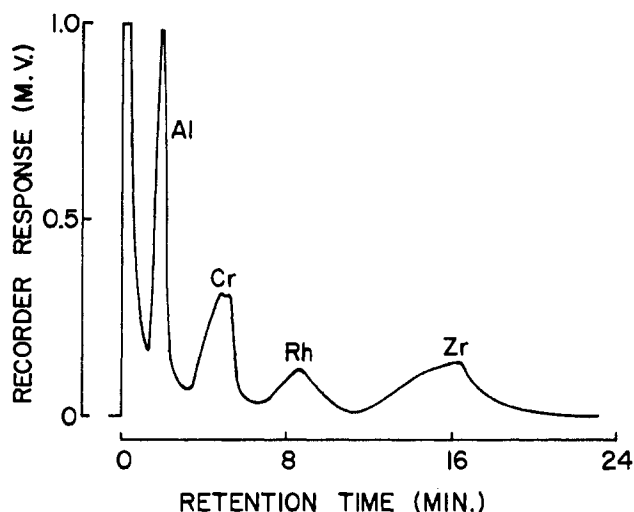


Fig. 2.—Separation of  $\text{Al}(\text{tfa})_3$ ,  $\text{Cr}(\text{tfa})_3$ ,  $\text{Rh}(\text{tfa})_3$ , and  $\text{Zr}(\text{tfa})_4$  by gas chromatography. Column B, packed with 0.5% silicone grease on glass microbeads; column temp.,  $135^\circ$ ; He flow rate, 130 ml./min; sample, 15  $\mu\text{l}$ . of a mixture of the chelates in benzene.

of aluminum(III), chromium(III), and rhodium(III) trifluoroacetylacetonates. The first peak, which is off-scale, arises from the solvent, carbon tetrachloride. Three minutes after injection of the sample, the aluminum chelate begins to be eluted. The third peak arises from the chromium(III) complex and the last peak from the rhodium(III) complex.

When the beryllium(II) complex was added to the above mixture and the experiment repeated under the same conditions, it was found that the beryllium and aluminum complexes were eluted together, with beryllium having only a slightly shorter retention time than the aluminum complex. By reducing the column temperature, consequently increasing the residence time in the column, it was possible to improve the separation of beryllium and aluminum, but this also caused the retention time of the rhodium complex to become excessively long. This difficulty was partially resolved by use of "temperature programming."

The effectiveness of temperature programming was demonstrated in the separation of a mixture of the four complexes. The column temperature was  $100^\circ$  when the sample was injected. The temperature was raised  $10^\circ/\text{min}$ . until it reached  $150^\circ$  and was held constant thereafter. Under these conditions the retention times are 6.5, 9, 14, and 22 min. for the beryllium(II), aluminum(III), chromium(III), and rhodium(III) che-

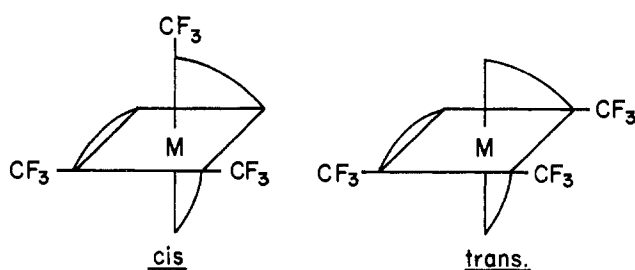


Fig. 3.—Geometrical isomers of octahedral metal trifluoroacetylacetonates.

lates, respectively. The result was a better separation of beryllium and aluminum with only a small increase in the retention time of the rhodium complex.

The separation of a mixture of aluminum(III), chromium(III), rhodium(III), and zirconium(IV) trifluoroacetylacetonates is shown in Fig. 2. This chromatogram was obtained on a column in which the liquid phase was silicone grease. It should be noted that, in spite of the lower column temperature and carrier gas flow rate, the chelates are eluted considerably more rapidly than in the chromatogram in Fig. 1. This observation is significant in that it indicates that the use of non-polar stationary phases will permit rapid elution of metal chelates at low column temperatures, with the result that thermal degradation becomes a less important problem.

The off-scale peak in Fig. 2, as in all of the chromatograms, is caused by the solvent. The choice of the solvent is important with this particular mixture of chelates. Benzene proved to be quite satisfactory as a solvent, but when carbon tetrachloride was used, no peak could be obtained for the zirconium complex. The same behavior was observed for the hafnium(IV) complex when carbon tetrachloride was used as the solvent. Under the conditions in the gas chromatography column, zirconium(IV) and hafnium(IV) trifluoroacetylacetonates apparently undergo some sort of reaction with carbon tetrachloride.

Attempts were made to separate a mixture of zirconium and hafnium trifluoroacetylacetonates dissolved in benzene. Column B was used for the test and the column temperature was  $150^\circ$ . The sample size in each instance was 4  $\mu\text{l}$ . and saturated solutions were used. The carrier gas flow rate was 120 ml./min. Solutions of each of the chelates were injected into the column to determine the respective retention times. The retention times were similar; that of the hafnium complex was *ca.* 9 min., and that of the zirconium complex was *ca.* 10 min. Under the same conditions, a mixture of the chelates gave a broader peak than either of the pure compounds, but there was no significant separation. Attempts to obtain a better separation of the mixture by using lower column temperatures and flow rates were unsuccessful. The use of more selective stationary phases should enhance the possibility of separating this mixture.

The hexafluoroacetylacetonato complexes of chromium(III) and rhodium(III) were separated under rather surprising conditions. The chelates were eluted rapidly from column B at a column temperature of  $30^\circ$ . This is indicative of the extraordinary volatility of the complexes. With the carrier gas flow rate set at 80 ml./min., the retention time of the chromium complex was 8 min., and of the rhodium complex, 16 min.

**Separation of Geometrical Isomers.**—Octahedral complexes of unsymmetrical bidentate ligands may exist in two geometrically isomeric structures. Figure 3 shows the two geometrical isomers of octahedral metal trifluoroacetylacetonates. The structures are simplified so as to show only the symmetry factors

which give rise to the two isomers. In the *cis* isomer, all three trifluoromethyl groups are adjacent and lie above the upper front face of the octahedron. In the *trans* isomer, one of the ligands is reversed so that its trifluoromethyl group is still *cis* to one of the  $\text{CF}_3$  groups but is *trans* to the other. Since the *cis* isomer has all three of the  $\text{CF}_3$  groups on one side of the molecule, it should be more polar than the *trans* isomer.

It was of interest to determine whether geometrical isomers of this type can be separated by gas chromatography. Because of the greater polarity of the *cis* isomer one would expect it to be less volatile than the *trans* isomer. Therefore the *trans* isomer should be more readily eluted. These expectations were realized in the separation of the *cis* and *trans* isomers of chromium(III) trifluoroacetylacetonate. Figure 4 shows that the *trans* isomer was eluted prior to the *cis*.

There was some question as to whether isomerization might occur at the high column temperature, but chromatograms of the pure *trans* isomer under the same conditions showed a single sharp peak and no evidence of isomerization. The diagnostic value of gas chromatography is apparent in the rapid separation of the geometrical isomers. The isomers were separated and their relative amounts determined in approximately 20 min.

**Separation of Optical Isomers.**—Previous methods of resolving optical isomers of inner complexes have been based on preferential adsorption on an optically active solid<sup>28-32</sup> or on differences in solubility in an optically active liquid.<sup>33, 34</sup> One method involves passing a solution of the racemic mixture through a column containing an optically active solid. This technique is moderately successful, but it is likely that only partial separation of isomers has been accomplished.<sup>32</sup>

For volatile compounds, gas phase chromatography may be inherently better suited for the resolution of optical isomers than conventional liquid-solid chromatography. In liquid-solid chromatography a polar eluent frequently is not capable of discriminating between two compounds of similar polarities, and therefore both compounds are eluted with equal facility. When this occurs a less polar eluent is selected, with the result that the two compounds are generally eluted with differing ease.

The same principles can be extended from liquid phase chromatography to gas phase chromatography. Helium approaches the limit of non-polarity and therefore should be an ideal eluent for mixtures possessing extremely subtle differences in retentive tendencies. Optical isomer pairs are good examples of such mixtures. Since optical isomers have identical polarities, differ-

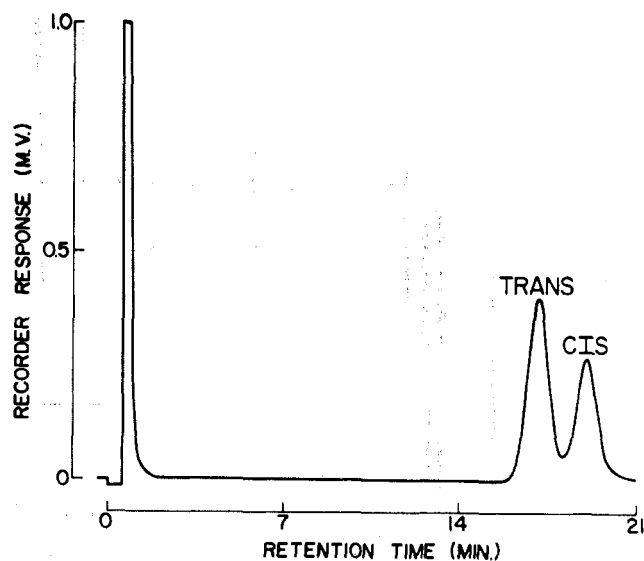


Fig. 4.—Separation of *cis* and *trans* isomers of  $\text{Cr}(\text{tfa})_3$  by gas chromatography. Column C, packed with 5% silicone grease on Chromosorb W; column temp., 115°; He flow rate, 140 ml./min.; sample, 0.5  $\mu\text{l}$ . of a 10% solution of a mixture of the isomers dissolved in benzene.

ences in retentive properties must arise only from spatial considerations.

In gas-solid chromatography, separation of optical isomers is based on differences in adsorptive properties on the surface of an optically active solid. On an asymmetric surface the adsorption of one isomer may be thermodynamically or kinetically favored over that of the other isomer. In an earlier communication<sup>14</sup> we reported the partial resolution of *dl*-chromium(III) hexafluoroacetylacetonate by gas-solid chromatography on a *dextro* quartz column. It was noted, however, that the compound was eluted slowly and that tailing was very extensive. Tailing is often a serious problem in gas-solid chromatography, but it is not encountered as frequently or as extensively in gas-liquid chromatography. Therefore attempts were made to resolve the same complex by gas-liquid chromatography.

In gas-liquid chromatography, when the stationary phase is an optically active liquid, one isomer may be slightly more soluble than its mirror image, owing to stereospecificity in solvation.<sup>35</sup> The existence of stereospecific solvation effects was demonstrated by Patterson and Buchanan,<sup>36</sup> who showed that, while the molecular volumes of a pair of enantiomers were identical when measured in a symmetrical solvent, they differed when measured in an asymmetric solvent.

In the present experiments a column containing glass beads coated with 1% dibutyl-*d*-tartrate (column D) was used. The first test was conducted with the temperature of the column at 55° and with a helium flow rate of 80 ml./min., the same conditions used previously in the partial resolution of *dl*-chromium(III) hexafluoroacetylacetonate by gas-liquid chroma-

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(33) F. P. Dwyer and E. C. Gyarfas, *Nature*, **168**, 29 (1951).

(34) V. F. Doron and S. Kirschner, *Inorg. Chem.*, **1**, 539 (1962).

(35) See G. Goldby and W. A. Ross, *Chem. Ind. (London)*, 657 (1962), and references cited therein for a discussion of attempts to separate optical isomers of organic compounds by gas-liquid chromatography.

(36) T. S. Patterson and C. Buchanan, *J. Chem. Soc.*, 290 (1940)

tography. Under these conditions, however, the chelate was not eluted and the test was discontinued after several hours. Another attempt with the column temperature at 80° was similarly unsuccessful. Apparently the complex is strongly solvated by dibutyl-*d*-tartrate, inasmuch as it was readily eluted from the silicone grease column at 30°. A final attempt was made at 110°, but at this temperature dibutyl-*d*-tartrate bled rapidly from the column, so the experiments were discontinued.

It was concluded that it will be necessary to use

an optically active liquid that is less volatile and/or polar than dibutyl-*d*-tartrate if gas-liquid chromatography is to be successful in separating optical isomers of inner complexes.

**Acknowledgment.**—The authors wish to thank Drs. J. C. Bailar, Jr., J. P. Collman, D. W. Meek, T. S. Piper, and R. C. Fay for samples of some of the compounds used in this study. We also are indebted to Mr. W. D. Ross for valuable discussions regarding techniques and equipment.

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## Studies on Phosphato and Methyl Phosphato Complexes of the Pentaamminecobalt(III) Class

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Received December 15, 1962

A method of preparing the compound  $\text{Co}(\text{NH}_3)_5\text{PO}_4 \cdot 2\text{H}_2\text{O}$  is described. The compound dissolves to form solutions in which  $\text{PO}_4^{-3}$  is directly bound to  $\text{Co}(\text{NH}_3)_5^{+3}$ . Dissociation of  $\text{PO}_4^{-3}$  is slow in acidic solution so that the affinity of the bound  $\text{PO}_4^{-3}$  for  $\text{H}^+$  in each of the three stages of association can be measured. These measurements have been made and, in addition, the equilibrium quotient governing the replacement of bound  $\text{H}_2\text{PO}_4^-$  by  $\text{H}_2\text{O}$  has been determined. Evidence is presented for substantial outer-sphere affinity of  $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{+3}$  for  $\text{H}_2\text{PO}_4^-$ . Methods of preparing  $\text{Co}(\text{NH}_3)_5\text{PO}_4(\text{CH}_3)_3^{+3}$  and  $\text{Co}(\text{NH}_3)_5\text{PO}_4(\text{CH}_3)_2^{+2}$  in solution are described. The former ion aquates and hydrolyzes rapidly with bond-breaking at both Co-O and P-O positions, but without ester hydrolysis.  $\text{Co}(\text{NH}_3)_5\text{PO}_4(\text{CH}_3)_2^{+2}$  aquates and hydrolyzes much less rapidly, and again without ester hydrolysis. In the reaction of  $\text{Co}(\text{NH}_3)_5\text{PO}_4\text{H}_2^{+2}$  or of  $\text{Co}(\text{NH}_3)_5\text{PO}_4(\text{CH}_3)_2^{+2}$  with  $\text{Cr}^{+2}$ , the phosphate group is transferred, but when  $\text{Co}(\text{NH}_3)_5\text{PO}_4(\text{CH}_3)_3^{+3}$  reacts no transfer takes place, and in this system the reaction with  $\text{Cr}^{+2}$  waits on the formation of  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$ .

Methods<sup>1,2</sup> for the preparation of phosphato complexes of the pentaamminecobalt(III) class have been described, but later workers<sup>3,4</sup> have expressed doubt that the preparations were successful. Daniel and Salmon<sup>4</sup> state that they were unable to prepare a solid phase containing the species  $\text{Co}(\text{NH}_3)_5\text{PO}_4$ . In this paper we report a method for the preparation of  $\text{Co}(\text{NH}_3)_5\text{PO}_4 \cdot 2\text{H}_2\text{O}$ ; our investigations of acidified solutions of this compound show that  $\text{PO}_4^{-3}$  is indeed bound to the residue  $\text{Co}(\text{NH}_3)_5^{+3}$ . Our experience leads us also to doubt that Duff and Duval and Duval actually had the phosphatopentaammine cobalt(III) complex in hand, and we think it likely that phosphate salts containing  $\text{Co}(\text{NH}_3)_5\text{OH}^{+2}$  or  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$  as cations actually were prepared by them. It seems necessary at the outset to correct the erroneous statement made by one of us<sup>5</sup> that the phosphato complex is very labile, a statement which was based on the assumption that Duff's procedure actually leads to the inner-sphere complex.

In addition to describing the conditions which we found optimum for the preparation of the phosphato complex, we describe methods for the prep-

aration of  $\text{Co}(\text{NH}_3)_5\text{PO}_4(\text{CH}_3)_3^{+3}$  in trimethylphosphate and of  $\text{Co}(\text{NH}_3)_5\text{PO}_4(\text{CH}_3)_2^{+2}$  in water. Compounds of both ions appear to be remarkably soluble and our efforts to prepare pure solids were unsuccessful. The equilibria involving the association of  $\text{H}^+$  with  $\text{Co}(\text{NH}_3)_5\text{PO}_4$  in each of the three stages were studied, and the equilibrium quotient for the replacement of  $\text{H}_2\text{O}$  from  $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{+3}$  by  $\text{H}_2\text{PO}_4^-$  has been measured. The aquation and hydrolysis of the phosphate complexes have been investigated as well as the reaction of each of the complexes with  $\text{Cr}^{+2}$ . Of particular interest to us was the possibility that electron transfer through phosphate or through the dimethyl complex leads to activation effects analogous to those observed in the reaction of  $\text{Cr}^{+2}$  with complexes of organic half-esters.<sup>6</sup> Such activation effects have been eliminated as possibilities in some of the systems, but they remain as possibilities in others which have not been studied directly.

### Experimental

**Materials.**— $\text{Co}(\text{NH}_3)_5\text{H}_2(\text{ClO}_4)_3^7$  and  $\text{Co}(\text{NH}_3)_5\text{Br}_3^8$  were prepared by standard methods. A solution containing  $\text{Cr}^{+2}$  was produced by electrolytic reduction of  $\text{Cr}^{+3}$  in acid perchlorate

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