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Volatile Metal Complexes

Certain chelates are useful as fuel additives, as metal vapor sources, and in trace metal analysis.

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Since 1960 there has been growing interest in metal chelates that are volatile. This interest is due to a combination of physical and chemical properties that make certain volatile complexes useful as fuel additives, catalysts, metal vapor sources, and gas transport reagents. In particular, fundamental studies of volatile metal complexes have led to new methods of ultratrace metal analysis based on gas chromatography.

Summary. Fundamental investigations of the chemical and physical properties of metal β-diketonate complexes have revealed unusual volatility, as well as solvolytic and thermal stability and solubility in organic solvents. Certain general rules describing the volatility of metal β-diketonates on the basis of ligand shell character and metal ion size have arisen from extensive gas chromatographic and vapor pressure studies. Several practical applications of volatile β-diketonates take advantage of their special properties. In ultratrace metal analysis by gas chromatography, use of these chelates has allowed the detection of smaller amounts of certain metals than can be detected by any other analytic method. Certain rare earth β-diketonates have been found useful as antiknock additives in gasoline and as catalysts for the removal of carbonaceous deposits from the combustion chambers of internal combustion engines.

Although most metal compounds are nonvolatile because of large ionic contributions to bonding, several classes of compounds have been chromatographed in the gas phase: metal halides, hydrides, alkyls, alkoxides, metal carbonyls, π-bonded metal complexes, and metal chelates. Most of these have properties that render them unsuitable for gas chromatographic analysis. For example, metal hydrides, halides, and some alkyls are extremely sensitive to atmospheric moisture. Certain metal carbonyls are highly toxic. For gas chromatographic analysis, a large number of metals must undergo reaction with a single reagent, forming quantitative yields of volatile, thermally stable metal derivatives that require no special handling procedures.

Only a few classes of derivatives to which metals may be converted meet these requirements. Uncharged metal chelates, particularly certain β-diketonates, are readily obtained quantitatively and are stable in the ambient atmosphere. A wide variety of metals in many matrices can be converted into volatile, thermally stable metal β-diketonate complexes for gas chromatographic separation and analysis.

The volatile metal β-diketonates have been used in a wide range of applications, including trace metal analysis by gas chromatography; studies of the stereochemistry and isomerization of metal complexes, ligand exchange, and interaction of complexes with weak nucleophiles; gasoline antiknock additives; and catalysts for the removal of carbon deposits from internal combustion engines. This article describes the properties and reviews the recent fundamental studies and applications of these volatile metal chelates.

Trends in the Volatility

The β-diketonates are unusually volatile metal complexes. What contributes to making a compound volatile is hard to define; one can only enumerate factors that tend to decrease vapor pressure, and eliminate or reduce them. Charged or highly polar species in which intermolecular forces are high are generally nonvolatile. Adduct formation, polymerization, and hydrogen bonding also tend to reduce volatility. The β-diketone ligands (Fig. 1) shield the metal ion from the intermolecular forces that render it nonvolatile by surrounding it with a hydrocarbon or fluorocarbon shell. For maximum volatility, the ligands must be designed so that both steric and inductive effects will minimize the tendency to form adducts or polymers.

Substituting fluorine atoms for hydrogen atoms in the ligand shell greatly increases the volatility of the β-diketonate complexes. This effect may be explained in part by envisioning the electronegative fluorine atoms as dominating the outer periphery of the complex. The fluorocarbon shell may reduce the van der Waals forces and intermolecular hydrogen bonding between fluorine-substituted β-diketonates (*1*). The increase in volatility of fluorine-containing β-diketonates corresponds directly to the extent of fluorine substitution.

Clausius-Clapeyron plots of vapor pressure as a function of temperature (Fig. 2) depict the effect of fluorine content on the volatility of the metal complex. Wolf *et al.* (*2*) measured the vapor pressures of several metal β-diketonates

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and showed that complexes containing highly fluorinated ligands are more volatile than complexes with fewer fluorines substituted for hydrogens, in the order hfa >> tfa > fod >> acac. Sievers and Eisentraut (*3*) applied thermogravimetric analysis to determine the relative volatilities of various metal β-diketonates and confirmed the dependence of volatility on the extent of fluorination.

A second interesting trend in the volatility of β-diketonate complexes is illustrated in Fig. 3 (*4*). Complexes of the rare earth metals with smaller ionic radii are much more volatile than those with larger ionic radii. This relationship between the ionic radius of the metal and the volatility of β-diketonate complex was later shown to be a general phenomenon. The trend also appears in the Al(III), Ga(III), In(III) family (*5*), the alkali metals (*5*), the alkaline earths (*6*), and other rare earth complexes (*7, 8*).

Possible explanations for the size-related trend in volatility have been advanced (*4*). The size of the complex decreases with the radius of the metal ion, and the local dipole present can either decrease in size or become more effectively shielded from the attractive forces of neighboring molecules. The smaller complex may also have a reduced tendency to form oligomers. All of these factors enhance the volatility of the β-diketonate with a smaller metal ionic radius. Appreciable mass effects were ruled out on the basis of evidence (*3, 9*) that $Y(thd)_3$ behaves the same as complexes with similar ionic radii but much greater masses [$Ho(thd)_3$ and $Er(thd)_3$].

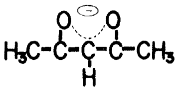
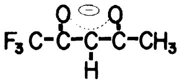
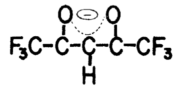
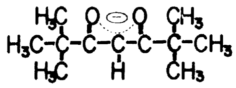
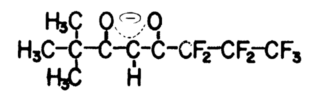
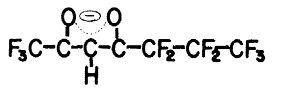
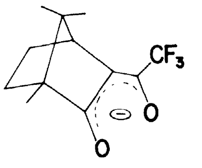
Ligand	Structure of Anion	Abbreviation
acetylacetone	 $H_3C-\overset{O}{C}-\underset{H}{C}-\overset{O}{C}-CH_3$	acac
trifluoroacetylacetone	 $F_3C-\overset{O}{C}-\underset{H}{C}-\overset{O}{C}-CH_3$	tfa
hexafluoroacetylacetone	 $F_3C-\overset{O}{C}-\underset{H}{C}-\overset{O}{C}-CF_3$	hfa
2,2,6,6-tetramethyl-3,5-heptanedione		thd
6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione		fod
1,1,1,5,5,6,6,7,7,7-decafluoro-2,4-heptanedione	 $F_3C-\overset{O}{C}-\underset{H}{C}-\overset{O}{C}-CF_2-CF_2-CF_3$	dfhd
trifluoroacetyl-d-camphor		facam

Fig. 1. Structures of β-diketone ligands.

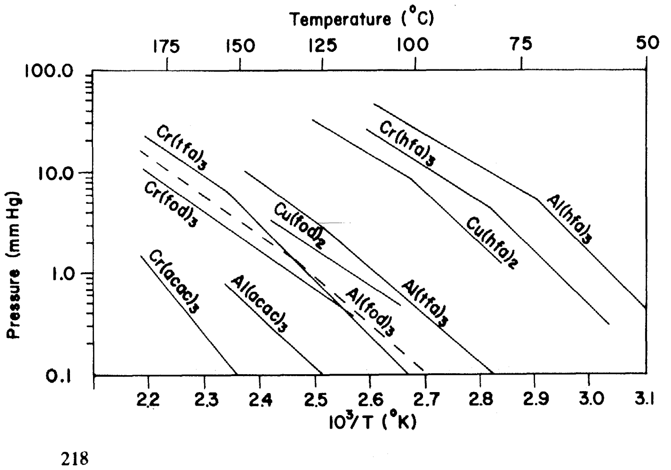


Fig. 2. Clausius-Clapeyron plots for various metal β-diketonate complexes. If one compares the vapor pressures of the acetylacetonates (acac) with those of analogous fluorinated complexes, it can be seen that the volatility increases with the extent of fluorine substitution in the ligand; for example, $Cr(acac)_3 < Cr(tfa)_3 < Cr(hfa)_3$ and $Al(acac)_3 < Al(tfa)_3 < Al(hfa)$.

Sicre *et al.* (*4*) studied the vapor pressures of the lanthanide thd complexes as a function of temperature. The effect of the lanthanide contraction (ionic radius decreasing across the series with increasing atomic number) on the volatility of the complexes is apparent in the Clausius-Clapeyron plot in Fig. 3. Remarkably, more than half of the lanthanide thd complexes exhibit higher vapor pressures than the saturated hydrocarbon *n*-tetracosane. For example, *n*-tetracosane has a vapor pressure of 1 millimeter at 184°C, and the thd complex of lutetium displays the same vapor pressure at 170°C. This is surprising when the empirical formula for *n*-tetracosane, $C_{24}H_{50}$, is compared with that of the lutetium complex, $Lu(C_{33}H_{57}O_6)$. Even considering the shape differences between the two compounds and the partial shielding of the metal-oxygen bonds, the vapor pressures of certain lanthanide β-diketonates are unexpectedly high. It is this high volatility, coupled with excellent solubility in nonpolar solvents, that facilitates the introduction of these compounds into the combustion chambers of automobile engines (discussed below).

Gas Chromatography of Metal Chelates

Gas chromatography has been extensively used for separating and analyzing mixtures of volatile compounds since its introduction by James and Martin in 1952 (*10*). The components of a mixture are distributed between a gaseous mobile phase and a liquid stationary phase, and the component that is less soluble in the stationary phase and more volatile is eluted before the component that is more soluble in the stationary phase and less volatile. Thus, separation of mixtures of volatile metal compounds requires differences in solubility or vapor pressure, or both. Elution is possible only if the compounds are sufficiently volatile and thermally stable at operating temperatures.

Many separations of volatile metal β-diketonates have been achieved by the application of gas chromatography (*11*). Lengthy and difficult separations found impractical by other means may be relatively simple by this method. The quantitative formation of metal chelates and the use of extremely sensitive detection devices allow the gas chromatographic determination of ultratrace quantities of metals.

If gas chromatography is to be successfully applied to trace metal analysis, the derivative to which the metal is converted must be sufficiently volatile to be chromatographed in the gas phase. For most purposes, the metal compound must exhibit a vapor pressure on the order of 0.1 to 1 mm to move through the column at a reasonable rate. Certain metal β-diketonates, particularly the fluorine-substituted complexes, have a sufficiently high vapor pressure to be eluted from the gas chromatographic column rapidly at relatively low column temperatures.

Volatile metal complexes must also be thermally stable to be eluted without decomposition. This requirement becomes less crucial for the fluorinated β-diketonates, since the lower column temperature needed for elution reduces the problem of thermal decomposition. Furthermore, the metal compound must be solvolytically stable to the liquid phase in the gas chromatographic column. Solvolysis will occur if the liquid phase strongly coordinates the metal ion. Another stability consideration is that toward the air. Most of the β-diketonates show no extreme reactivity toward atmospheric moisture or oxygen, which greatly facilitates sample preparation and handling.

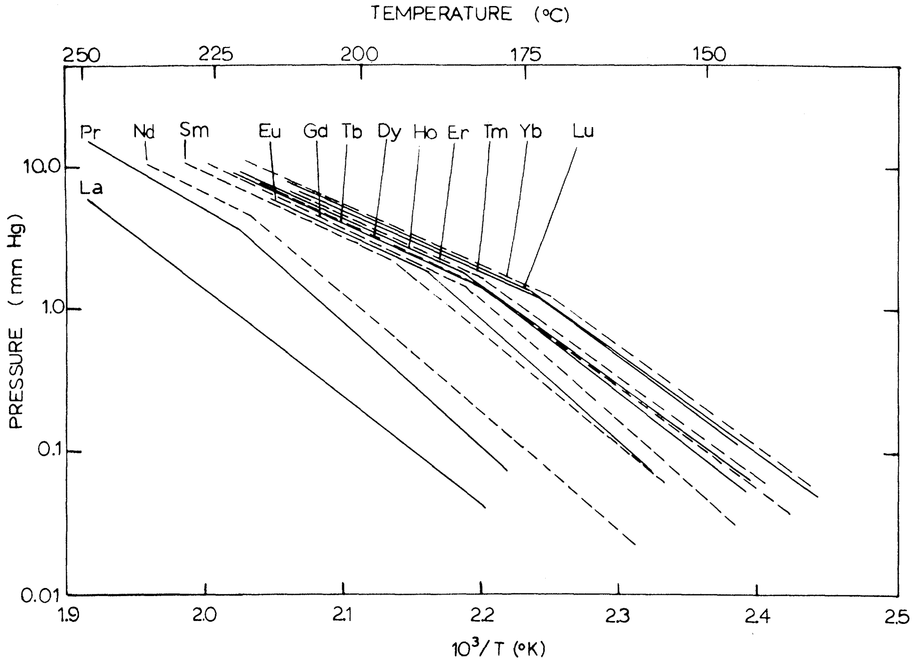


Fig. 3. Clausius-Clapeyron plots for lanthanide thd complexes. Complexes of lanthanides with higher atomic numbers are more volatile than those of larger, lighter members of the lanthanide series. For clarity, plots for lanthanides with even atomic numbers are given in dashed lines. Breaks occur at experimentally observed melting points, and arise from relatively large heats of fusion. [From Sicre *et al.* (*4*)]

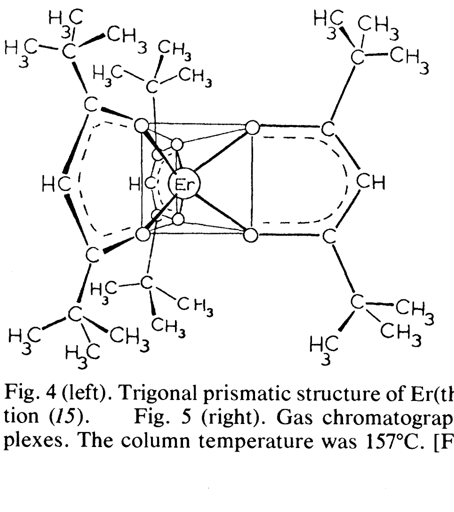
A metal compound must be obtainable in a high and reproducible yield to be useful for gas chromatographic metal analysis. The β-diketones are useful reagents for converting metals in various matrices into volatile complexes, reacting quantitatively, or nearly so, with most metals and metal salts. The bidentate β-diketone ligands readily convert aquated metal ions to metal chelates and remove and concentrate them in organic solvents by simple solvent extraction.

Early work with volatile metal β-diketonates was directed toward the development of ligands that could react with a wide variety of metals to form complexes suitable for elution from the gas chromatographic column. Morgan and Moss (*12*) indicated that certain acac complexes were volatile and could be sublimed. Later, Floutz (*13*) obtained chromatographic peaks from beryllium, chromium, and aluminum acetylacetonates. However, most acac complexes lack sufficient thermal stability to be eluted from chromatographic columns. These β-diketonates tend to occur as hydrates that polymerize or hydrolyze at the high column temperatures needed for vaporization. For example, the lanthanide acac complexes have coordination numbers exceeding 6 and form hydrates that undergo self-hydrolysis at elevated temperatures (*14*).

Workers have searched for many years for stable, volatile rare earth metal complexes. Eisentraut and Sievers (*9*) have succeeded in synthesizing volatile complexes of the rare earths. The thd ligand used contains bulky *tert*-butyl groups (Fig. 4) (*15*) that decrease the tendency of water to become bonded to the metal ion. Mixtures of these volatile, anhydrous complexes were separated by gas chromatography without decomposition (Fig. 5). Researchers have also synthesized and studied volatile thd complexes of the alkaline earths (*6*), alkali metals (*16*), and actinides (*17*), but attempts to separate complex mixtures of these chelates by gas chromatography have not been as successful as was hoped.

As shown by the vapor pressure data in Fig. 2, the fluorinated β-diketonates are much more volatile than complexes without fluorine. Metal hfa complexes are eluted more readily than tfa or acac complexes at column temperatures only slightly above room temperature (*1*). The less severe instrument conditions required to elute the fluorinated complexes reduce the problem of thermal decomposition. Because of their desirable properties, tfa and hfa complexes have been extensively used in gas chromatographic studies.

An effort to combine the shielding effect of the bulky *tert*-butyl group with the enhanced volatility of fluorinated moieties in one ligand led to the design and synthesis of the fod ligand. Sievers and co-workers (*8*, *18*) synthesized 15 rare earth fod complexes and demon-



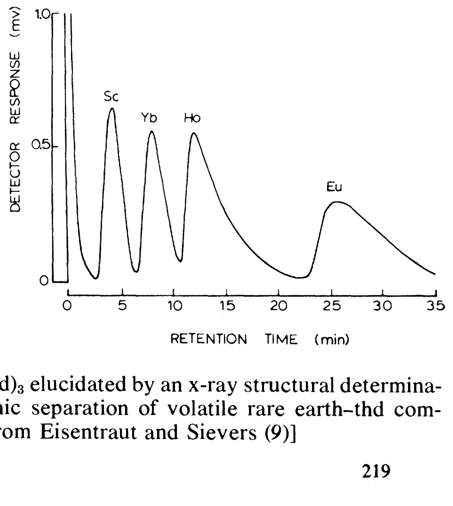


Fig. 4 (left). Trigonal prismatic structure of Er(thd)$_3$ elucidated by an x-ray structural determination (*15*). Fig. 5 (right). Gas chromatographic separation of volatile rare earth–thd complexes. The column temperature was 157°C. [From Eisentraut and Sievers (*9*)] strated that the fod chelates are even more volatile than the thd complexes. The fod complexes are isolated as hydrates but can be dehydrated at elevated temperatures or reduced pressures with no appreciable hydrolysis. This allows even the hydrated chelates to be eluted from the gas chromatographic column without decomposition. Springer and coworkers (*19*) studied the states of hydration of the lanthanide fod complexes and the tendency of these coordinatively unsaturated complexes to self-associate and form adducts with solvent molecules. The most important use of the fod complexes is as lanthanide nuclear magnetic resonance shift reagents (*20*). Other β-diketonates used for gas chromatographic metal analysis include 1,1,1,5,5,6,6,7,7,7-decafluoro-2,4-heptanedione and 1,1,1,5,5,6,6,6-octafluoro-2,4-hexanedione (*21*).

There has been some interest in the monothio-β-diketonates. The chelates of the many divalent transition metals [Ni(II), Cu(II), Zn(II), Fe(II), Pb(II), Pt(II), and Cd(II)] with monothiotrifluoroacetylacetone are volatile enough to be studied in the gas phase (*22*). Developments in the use of monothio-β-diketonates and β-ketoamines for metal analysis by gas chromatography have been reviewed (*23*).

Fujinaga *et al.* (*24*) found that the chromatograms of certain metal chelates are improved by using the ligand vapor as a carrier-gas additive. The addition of a constant amount of ligand vapor to the carrier gas suppresses the dissociation of the metal chelates in the gas chromatographic column and also scavenges the metal chelates that are adsorbed on the solid support. The method allows quantitative elution and therefore broader analytic applications of metal β-diketonates that show anomalous peaks by the conventional gas chromatographic method. Recently, Fujinaga *et al.* (*25*) employed ligand vapor gas chromatography to separate mixtures of neighboring rare earth tfa complexes.

Trace Metal Analysis by Gas Chromatography

Formation of volatile chelates coupled with gas chromatographic separation is an attractive technique for trace metal analysis because of its speed, simplicity, and sensitivity. Chelation is achieved by extraction of the metal from an aqueous medium with the ligand in a suitable immiscible organic solvent, or by direct reaction of the ligand with the metal sample (no solvent). Workers have focused on developing new chelating agents and techniques and on improving the sensitivity of detection. Although early efforts in metal analysis involved the separation of relatively large quantities of metals in mixtures, recent emphasis has been on determining trace metals in biological substances and determining microquantities of one metal in the presence of macroquantities of others.

Lederer (*26*) first put forth the idea of analyzing metals as volatile metal chelates, but did no experiments to confirm the concept. Biermann and Gesser (*27*) succeeded in chromatographing mixtures of aluminum, chromium, and beryllium acac complexes. However, acac complexes were generally unsuitable for gas phase analysis, and the fluorinated tfa and fod complexes were introduced and proved to be more useful. The volatile, stable metal complexes of tfa and fod can be sensitively measured by electron capture detection because they contain electronegative fluorinated moieties.

Several types of detectors have been used in the gas chromatographic analysis of trace metals. Early workers utilized the conventional flame ionization and thermal conductivity detectors. Later, Ross (*28*) found that the electron capture detector responded to extremely small concentrations of fluorine-containing β-diketonates, with detection limits on the order of 10^{-14} gram of the metal. Recently, workers have employed the microwave emission detector, which is comparable in sensitivity to the electron capture detector and has the added advantage of great selectivity. The detector is highly selective because a monochromator is set to monitor a single emission line characteristic of the element being detected. The electron capture and microwave emission detectors, because of their high sensitivities, have been shown to be the most suitable for metal analysis at the trace level.

Kawaguchi *et al.* (*29*) and Dagnall *et al.* (*30*) first applied microwave emission detection to the determination of volatile metal β-diketonates separated by gas chromatography. Sakamoto *et al.* (*31*) applied gas chromatography coupled with microwave emission detection to the analysis of trace impurities in metal samples. Traces of copper and aluminum were extracted from zinc metal into a trifluoroacetylacetone solution, and were measured at the level of parts per million (ppm), using selective microwave emission detection of the individual metals. Sakamoto *et al.* (*32*) developed a sensitive and rapid method for determining parts-per-million levels of beryllium in aluminum metal and aluminum-magnesium alloy samples by gas chromatography with microwave emission detection. Black and Sievers (*33*) were able to measure chromium in human blood serum at the level of 1 part per billion by a similar method. They utilized the microwave emission detector to monitor a single emission line of chromium, after converting the chromium in the matrix to $Cr(tfa)_3$ and separating it from other compounds by gas chromatography. This extraordinary selectivity allowed detection of the chelate peak without detectable interference from other compounds. Although a fluorinated complex was used in the study, the method is not limited to chelates with high electron affinities, as is electron capture detection.

Highly efficient solvent extraction techniques and gas chromatographic instrument conditions have been developed for quantitative metal analysis. The solubility of metal β-diketonates in organic solvents and their insolubility in water facilitate the chelation and extraction of metal ions from various media. Morie and Sweet (*34*) applied quantitative methods to the extraction and gas chromatographic separation of an aluminum and iron mixture. Moshier and Schwarberg (*35*) outlined a general procedure for alloy analysis, using quantitative chelation and extraction. This early work demonstrated feasibility, and in recent years researchers have succeeded in analyzing trace amounts of important elements in metal mixtures and organic matrices.

The widespread use and severe toxicity of beryllium-containing compounds and alloys necessitated the development of sensitive analytical techniques for the detection of this metal in biological fluids (*36–38*) and environmental samples (*39–42*). As little as 4×10^{-14} g of beryllium in the form of the tfa complex has been detected by electron capture gas chromatography. A general scheme for analysis (*43*) involves extracting beryllium from the medium with trifluoroacetylacetone in benzene, washing the organic phase with aqueous sodium hydroxide, and injecting the organic layer into the gas chromatograph. The excess ligand used for the extraction is eliminated by washing with NaOH solution to avoid poisoning the detector with large quantities of unreacted ligand. Extension of this basic scheme allowed Sievers *et al.* (*36*) to detect a few parts per billion of beryllium in blood, urine, and tissue samples. Eisentraut *et al.* (*42*) determined beryllium at a concentration of less than 1 ppm in lunar material from the Apollo 11 and 12 missions and in me-

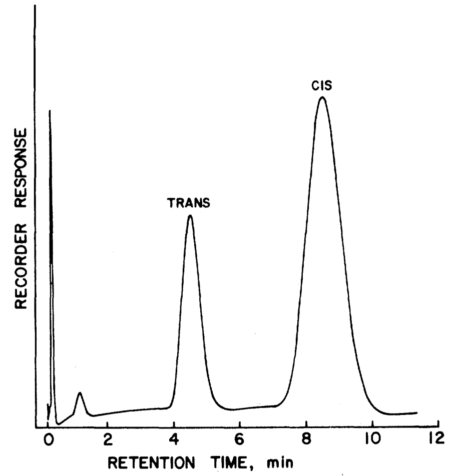


Fig. 6. Separation of geometric isomers of Cr(tfa)$_3$ by gas chromatography. The column temperature was 85°C. [From Sievers and Kutal (*53*)]

teorites. Pyle *et al.* (*41*) employed chelation, extraction, and gas chromatography to determine beryllium concentrations in ambient air particulates.

Chelation and gas chromatography have been applied to several other metals in various matrices. Savory *et al.* (*44*) measured 3×10^{-14} g of chromium from human blood serum as the tfa complex. Trace quantities of chromium were measured in air and soil (*40*), in liver tissue (*45*), and in lunar samples, where a mass spectrometer was used as a detection device (*46*). Gas chromatographic analysis was successfully applied to inorganic systems by Genty *et al.* (*47*), who detected 0.1 ppm of aluminum in uranium.

A more simplified application of metal chelation and gas chromatography employs direct reaction of the chelating agent in the metal alloy or compound (*48*). The ligand can act as both oxidizing agent and solvent; however, inorganic acids or hydrogen peroxide are sometimes added, and the samples are usually heated to accelerate the reaction. A quantitative scheme for the determination of chromium in ferrous alloys by direct reaction with trifluoroacetylacetone has been developed (*49*), using catalytic amounts of nitric acid and applying heat to accelerate the reaction by which the chromium complex is formed.

Direct reaction, using a sealed capillary as a microreactor, was the method chosen for the determination of iron in Mesabi ore with 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione (*50*). The ore was heated with the ligand in a sealed glass capillary. The microreactor was crushed in the injection port of the gas chromatograph, introducing the iron complex into the column. In this method, the less sensitive thermal conductivity detector was employed, and relatively large samples were required. The use of direct reaction techniques and electron capture detection allowed Ross *et al.* (*51*) to measure 10^{-11} g of cobalt from vitamin B_{12} (cyanocobalamin).

Stereochemical Studies

The stereochemistry of volatile metal β-diketonates can be studied by gas chromatography. This is illustrated in Fig. 6 by the gas chromatographic separation of the geometric isomers of Cr(tfa)$_3$. The synthesis of complexes from tfa, an unsymmetrical bidentate ligand, yields two geometric isomers that are separable by differences in polarity (Fig. 7). *Cis* (facial) and *trans* (meridional) isomers of Rh(tfa)$_3$ have also been separated by gas chromatography (*52*), and in this and the chromium case the less polar *trans* isomer was eluted before the *cis* isomer.

Mixed ligand complexes can also be separated and studied by gas chromatography. For example, from the combination of ligands that are symmetrical and unsymmetrical, there are seven chromium(III) complexes with the formula Cr(tfa)$_{3-x}$ (*11*). All seven compounds are separable by gas chromatography. The first peak eluted is caused by Cr(hfa)$_3$, the second peak by Cr(hfa)$_2$(tfa), the third through fifth by *trans-cis*, *cis-cis*, and *cis-trans* isomers of Cr(hfa)(tfa)$_2$, and the sixth and seventh by *cis* and *trans* Cr(tfa)$_3$.

Gas chromatographic data for β-diketonate complexes provide insight into the kinetics and equilibrium of isomerization (*53, 54*). It is possible to monitor the formation and disappearance of the facial and meridional isomers of octahedral complexes. For example, Sievers and Kutal (*53*) studied the mechanism of *cis-trans* isomerization of Cr(tfa)$_3$ by gas chromatography. The absence of solute-solvent interactions in the gas phase allowed the examination of intrinsic thermodynamic and kinetic properties. It was concluded that the stereochemical rearrangement proceeds through a bond twist process, rather than through a bond rupture mechanism.

Resolution of optical isomers of metal β-diketonate complexes in the gas phase has been achieved by gas chromatography. Since optical isomers have identical polarities and volatilities, separation is achieved only by providing an asymmetric environment in the column. Differences in the solution or adsorption of the optical isomers by the column are the basis for the separation. Sievers *et al.* (*55*) achieved partial separation of *d*- and *l*-Cr(hfa)$_3$, shown in Fig. 8, by gas-solid chromatography, using a column packed with powdered *d*-quartz. The work of Feibush and Gil-Av (*56*) in separating optical isomers of amino acid derivatives by gas-liquid chromatography has extended this concept to a wide range of practical problems in organic chemistry and biochemistry.

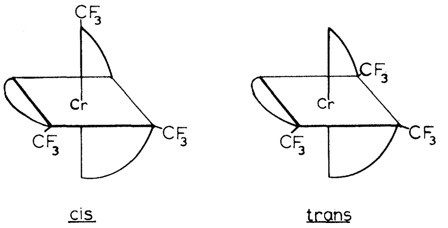


Fig. 7. Geometric isomers of octahedral Cr(tfa)$_3$.

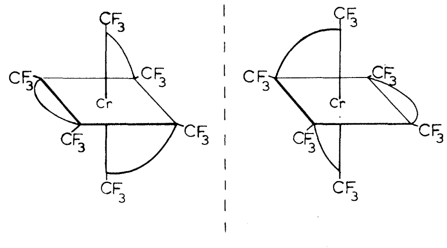


Fig. 8. Optical isomers of Cr(hfa)$_3$.

Metal Vapor Applications

In addition to gas chromatography, a variety of applications requiring the use of volatile compounds have been found for metal β-diketonate complexes. Metals and metal compounds can be deposited from the gas phase by vaporization and reaction of β-diketonates (*57, 58*). These compounds can also be used as sources of metal chelate vapor in x-ray photoelectron spectroscopy studies (*59*). Differences in the volatility of metal β-diketonate complexes has allowed the separation of metals by fractional distillation and sublimation (*60*).

Certain volatile β-diketonates are useful as metal vapor sources for metal deposition from the gas phase (*57*). Thin films of metals such as copper, nickel, lead, and cobalt can be deposited by the vaporization and reduction of metal hfa and tfa complexes. These metal chelates are readily reduced at atmospheric pressure and temperatures as low as 250°C, permitting the plating of metals on a broad range of target materials. The vapor plating process yields a conducting metal deposit of high purity and allows good control over the thickness and uniformity of the film. The metal can be deposited in intricate patterns and on complicated surfaces.

In the vapor plating process, the metal chelate is vaporized in a heated chamber and transported to the target to be plated by a flow of hydrogen, the carrier and reducing gas. The gaseous chelate is reduced to a metal deposit at the heated surface of the target. The hydrogen carrier gas transports the unreacted metal chelate and regenerated ligand out of the vapor plating assembly and these are trapped. The regenerated chelating agent can be reused in a cyclic process.

Other workers (*58*) utilized the vapor phase reaction between $Cd(hfa)_2 \cdot NH_3 \cdot H_2O$ and hydrogen sulfide to deposit cadmium sulfide, a semiconductor coating. The cadmium complex is vaporized and transported into a heated reaction zone by a flow of nitrogen, where it comes in contact with the hydrogen sulfide gas, leaving a thin film of cadmium sulfide on the target. These experiments demonstrated that metal compounds as well as pure metals can be deposited from gas phase reactions of volatile metal β-diketonates.

Recently, volatile metal β-diketonates were used as a source of metal chelate vapor for x-ray photoelectron spectroscopy (*59*). X-ray photoelectron spectroscopy is useful for determining atomic charge distributions within molecules in the gas phase, and was used in this case to study the valence electron distribution and bonding in a series of *tris* β-diketonates. Specifically, the core electron binding energies of aluminum in β-diketonate complexes and ligand atoms in hfa complexes were measured. The data for metal hfa complexes show that the metal *d* orbitals are not appreciably involved in the bonding and suggest that there is no strong ligand→metal donor bonding.

Because of the remarkable volatility and thermal stability of certain metal β-diketonates, it is possible to separate mixtures by fractional distillation and sublimation. Harris *et al.* (*60*) separated mixtures of rare earth metals by converting them to thd complexes, and distilling them under reduced pressure with a codistilling agent. The enriched fractions were acidified, regenerating the rare earth salts and chelating agent. Sakanoue and Amano (*61*) described the separation of thd complexes of americium and californium by sublimation. The volatility of the actinide β-diketonates decreases with the increasing size of the metal ion. This behavior is entirely consistent with that observed for the lanthanides (Fig. 3). The fractional sublimation of ^{86}Zr and ^{87m}Y as fluorinated β-diketonate complexes is an example of the separation of radioisotopes with short lifetimes (*62*).

Antiknock Additives and Combustion Catalysts

Lead alkyls, particularly tetraethyllead (TEL), have been widely used as antiknock gasoline additives since the early 1920's. As the Environmental Protection Agency has determined that the use of lead alkyls as antiknock agents in fuel contributes significantly to environmental pollution, steps are being taken to reduce the lead content of gasoline. Unless replacements for lead additives are developed, the octane rating of fuel will have to be improved by increasing the content of aromatic hydrocarbons. Large amounts of aromatics in gasoline create undesirable exhaust emissions, and increased exposure to benzene, which has been linked to leukemia, and other aromatics also poses an occupational safety problem for service station and garage employees. In addition to the environmental penalty, an energy problem arises if suitable substitute antiknock additives cannot be found. It has been estimated (*63*) that removal of lead alkyls from gasoline will reduce the amount of gasoline recoverable from each barrel of crude oil by about 6 percent. The development of acceptable substitutes could effectively restore this loss to our dwindling reserves.

It is therefore imperative that a lead-free antiknock agent be found to improve the octane rating of fuel without adversely affecting the environment and decreasing fuel reserves. The use of catalytic exhaust converters also necessitates the development of alternative antiknocks, because lead compounds poison the noble metal catalysts now installed on new automobiles. Another antiknock additive recently used in lead-free gasoline, methylcyclopentadienylmanganese tricarbonyl (MMT), reportedly also causes the catalysts in exhaust converters to malfunction; the addition of MMT to gasoline intended for use in automobiles equipped with exhaust catalysts has been forbidden in California.

Recent work of Sievers and co-workers (*64, 65*) and of Hartle (*66*) indicated that certain rare earth β-diketonate complexes possess significant antiknock activity. The possibility of substituting rare earth β-diketonates for alkyl lead antiknocks merits further exploration, because rare earth compounds are far less toxic than the lead salts produced by combustion of TEL. Unlike TEL and MMT, the rare earth chelates are unlikely to poison noble metal catalysts.

The thd complexes of the rare earths exhibited the greatest activity of the lanthanide compounds studied. Although the thd complex of cerium was superior to that of any other single rare earth, a mixture of rare earth thd complexes performed essentially as well as $Ce(thd)_4$. This observation is important because the mixture of rare earth thd complexes can be prepared from an unpurified rare earth ore that contains primarily cerium, lanthanum, praseodymium, and neodymium. It is not necessary to separate the rare earths, so costs are reduced. The raw materials from which the new gasoline additives are synthesized are neopentanoic acid, acetone, and rare earth ore. Rare earth ore is not rare (*67*)—U.S. reserves are more than adequate to treat gasoline derived from all the world's known petroleum reserves.

The rare earth mixture has performed effectively as an antiknock additive in the standard single-cylinder engine ASTM (American Society for Testing and Materials) tests (*64, 66*). Road tests are currently being done with various rare earth mixtures. An increase of about 1.5 in the road octane number of a clear base fuel was obtained when the Sun Oil Co. tested $Ce(thd)_4$ in standard automobile engines in the Uniontown test (*67*). The lanthanide thd complexes are stable, volatile, and highly soluble in hydrocarbon fuel. In addition to exhibiting antiknock properties, the rare earth fuel additives may catalytically eliminate combustion products of fuels. Rare earth oxides, which are formed during combustion of the thd complexes, have been found to catalyze the low-temperature oxidation of organic compounds (*68*) and the decomposition of nitrogen oxides (*69*). Thus the lanthanide oxides may act as high-surface-area catalysts dispersed in the combustion and exhaust system. Clearly, the rare earth thd complexes show promise as gasoline additives and as possible catalysts for reducing exhaust pollutants.

As an automobile engine ages, carbonaceous material builds up inside the cylinders; this leads to a combination of undesirable effects. The engine exhibits what is termed octane requirement increase (ORI). As time passes and deposits build up, the engine requires higher-octane fuel, if knocking and other undesirable performance characteristics are to be avoided. Preignition is catalyzed by hot carbon surfaces, and the engine may exhibit "dieseling" or run-on after the electrical ignition key is turned off. Octane requirement increase is caused in part by the insulating effect of the deposits, which raises the temperature of the fuel-air mixture in the combustion chamber. Furthermore, deposits occupy space in the combustion chamber, increasing the compression ratio, which in turn raises the octane requirement. The deposits consist partly of carbon particles bound together in a resinous matrix.

Data are already available that prove that various rare earth chelate additives catalyze the elimination of carbonaceous deposits from the combustion chambers of internal combustion engines (*69*). When the lanthanide chelate additives are combusted they appear to form oxides, which catalyze the oxidation of the deposits, reducing the mass of the resinous binder and increasing thermal conductivity. In tests conducted by Amoco, the percentage of the benzene-soluble binder in deposits was reduced from 11.8 to 3.3 when a mixture of rare earth thd chelates was added to gasoline (*70*). The cleaning of deposits from spark plugs is apparent even on visual inspection, and the expected effect is a cleaner engine, with elimination of preignition and dieseling, better fuel economy, and a reduction in the ORI.

These effects may turn out to be more important than the antiknock properties. Furthermore, they can be brought about by intermittent addition of rare earth chelates to the individual user's car at the service station, which simplifies storage and distribution problems. The effect of these and other new fuel additives on exhaust emission requires further examination, but they appear to have great promise.

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