

simply mean that spin-free Co(II) is produced directly when I^- reacts with $Co(NH_3)_5I^{++}$.

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Coördination Compounds of Trivalent Metals with Unsymmetrical Bidentate Ligands. II. Trifluoroacetylacetonates¹

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The preparation and characterization of trifluoroacetylacetonates of a variety of trivalent metals is reported. *cis* and *trans* geometrical isomers of the inert complexes ($M = Cr, Co, Rh$) were separated by chromatography on alumina. Only the *trans* isomer was isolated in the solid state in the case of the labile complexes ($M = Al, Ga, In, Mn, Fe$). Vibration and electronic spectra of the isomers are nearly identical. The geometrical configuration of the isomers was established by proton and fluorine n.m.r. spectra and X-ray powder patterns. The n.m.r. chemical shifts are discussed in terms of electronic structure. Equilibrium constants for isomerization of the cobalt, aluminum, and gallium compounds in chloroform solution were evaluated at several temperatures by fluorine n.m.r. spectra. The free energy for *trans* to *cis* isomerization is slightly less than 1 kcal./mole, to which the heat and entropy terms contribute about equally.

Introduction

Coördination of three unsymmetrical bidentate ligands to a trivalent metal ion offers the possibility of two geometric isomers. Recently, by means of n.m.r. spectroscopy a number of trivalent metal benzoylacetonates have been shown to exhibit *cis-trans* isomerism.³ The present work reports the preparation, separation, and determination of configuration of isomeric complexes of a variety of trivalent metals with 1,1,1-trifluoro-2,4-pentanedione [hereafter often referred to as $M(tfac)_3$ and called metal trifluoroacetylacetonates]. The trifluoroacetylacetonates were of particular interest because fluorine resonance could be observed. In addition to establishing the configuration of the isomers, the n.m.r. studies provide useful information about electronic structure and equilibria in solution.

Experimental

With the exception of the aluminum and iron^{4,5} compounds, methods for the preparation of trifluoroacetylacetonates of trivalent metals have not been previously reported. The methods of preparation reported here are similar to those which have been employed for the simple metal acetylacetonates.⁶⁻⁹ 1,1,1-Trifluoro-2,4-pentanedione was used as obtained from Columbia Organic Chemicals Co., Inc.

Tris-(1,1,1-trifluoro-2,4-pentanediono)-chromium(III).—A mixture of chromium chloride hexahydrate (2.66 g., 0.0100 mole), 1,1,1-trifluoro-2,4-pentanedione (5.17 g., 0.0345 mole), and urea (20 g.) in 100 ml. of water was heated on the steam bath for 7 hr. with stirring. The olive-drab product was collected, washed with water, and air dried. After purification by chromatography on alumina, the yield was 2.23 g. (44%).

Tris-(1,1,1-trifluoro-2,4-pentanediono)-cobalt(III).—1,1,1-Trifluoro-2,4-pentanedione (4.63 g., 0.030 mole) was dissolved in 50 ml. of aqueous alcohol (40% ethanol). $Na_3[Co(CO_3)_3] \cdot 3H_2O^{10}$ (3.62 g., 0.010 mole) and 5 ml. of 6 *N* HNO_3 were added,

and the mixture was allowed to reflux for 0.5 hr. The resulting green precipitate was then collected, washed with water, air dried, and purified by chromatography on alumina. The yield was 1.45 g. (28%).

Tris-(1,1,1-trifluoro-2,4-pentanediono)-rhodium(III).—A solution of rhodium nitrate (0.0114 mole), prepared as described previously,³ was treated with solid sodium bicarbonate until pH 4 was attained. 1,1,1-Trifluoro-2,4-pentanedione (5.28 g., 0.0342 mole) was added, and the mixture was allowed to reflux for 0.5 hr. After readjusting the pH to 4.5-5 with more sodium bicarbonate, refluxing was continued for 15 min. longer. Finally an additional 1.00 g. of 1,1,1-trifluoro-2,4-pentanedione was added, and the mixture was refluxed for 0.5 hr. longer. The orange-yellow product was collected and purified by chromatography. The yield of purified product was 3.21 g. (50%).

Tris-(1,1,1-trifluoro-2,4-pentanediono)-aluminum(III).—1,1,1-Trifluoro-2,4-pentanedione (9.45 g., 0.0614 mole) was added to a solution of aluminum isopropoxide (4.16 g., 0.0204 mole) in 40 ml. of benzene. The resulting solution was allowed to stand for 2 hr. The benzene and 2-propanol which were produced were removed by vacuum distillation at room temperature. The yield of the white crystalline product was 8.9 g. (91%).

Tris-(1,1,1-trifluoro-2,4-pentanediono)-gallium(III).—Gallium metal (0.78 g., 0.0112 mole) was dissolved in aqua regia and the solution evaporated nearly to dryness. After solution of the residue in 25 ml. of water, 25 ml. of an aqueous solution containing 1,1,1-trifluoro-2,4-pentanedione (5.18 g., 0.0336 mole) and 7 ml. of conc. NH_4OH was added. The white precipitate which formed immediately was collected, washed with water, and air dried. Extraction of the solid with benzene and subsequent vacuum distillation of the solvent yielded 0.48 g. (8%) of $Ga(tfac)_3$.

Tris-(1,1,1-trifluoro-2,4-pentanediono)-indium(III).—Indium trifluoride 9-hydrate (2.25 g., 0.00675 mole) was converted to the water soluble chloride by evaporation with 6 *N* HCl . The chloride was taken up in 25 ml. of water, and 25 ml. of an aqueous solution containing 1,1,1-trifluoro-2,4-pentanedione (3.12 g., 0.0202 mole) and conc. NH_4OH (3 ml.) was added. The product was purified in the same manner as the gallium compound. The yield of the ivory-colored $In(tfac)_3$ was 1.2 g. (31%).

Tris-(1,1,1-trifluoro-2,4-pentanediono)-manganese(III).—A solution of potassium permanganate (0.32 g., 0.0020 mole) in 25 ml. of water was added to a solution of manganese(II) sulfate monohydrate (1.35 g., 0.0080 mole) in 25 ml. of water. Immediately 1,1,1-trifluoro-2,4-pentanedione (9.5 g., 0.062 mole) was added, and the mixture was heated on the steam bath. During the first 5 min. of heating, 10 ml. of 6 *N* NH_4OH was added slowly. After digesting for 10 min. longer, the mixture was cooled, and the dark brown precipitate was collected and air dried. The yield of crude product, after separation from unreacted manganese(III) hydroxide by extraction with acetone, was 3.25 g. (63%). Since the product was still contaminated with manganese(II) trifluoroacetylacetonate, the $Mn(tfac)_3$ was concentrated by extraction with 20 ml. of benzene. Recrystallization from hot benzene-pentane yielded large clumps of badly twinned $Mn(tfac)_3$ and a few fine yellow crystals of the manganese(II) complex. The latter could be readily removed by washing with ethanol. The yield of purified product was 0.8 g.

Tris-(1,1,1-trifluoro-2,4-pentanediono)-iron(III).⁵—An aqueous solution (100 ml.) containing iron(III) chloride hexahydrate

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(2) (a) National Science Foundation Fellow, 1960-1962; (b) Alfred P. Sloan Foundation Fellow.

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(7) Rhodium—F. P. Dwyer and A. M. Sargeson, *J. Am. Chem. Soc.*, **75**, 984 (1953).

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(9) Manganese—G. H. Cartledge, U. S. Patent 2,556,316, June 12, 1951; *Chem. Abstr.*, **46**, 1585b (1952).

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TABLE I
 ISOMERIC METAL TRIFLUOROACETYLACETONATES

Compound	Color	Dichroism ^a	M.p., °C.	Carbon, %		Hydrogen, %		Metal, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
<i>cis</i> -Cr(tfac) ₃	Dk. viol.	Red, viol.	112-114	35.24	34.98	2.37	2.34	10.17	10.41
<i>trans</i> -Cr(tfac) ₃	Dk. viol.	Viol., red	154.5-155	35.24	35.34	2.37	2.40	10.17	9.99
<i>cis</i> -Co(tfac) ₃	Green	Gn., olive drab	129-129.5	34.77	34.88	2.34	2.52	11.37	11.38
<i>trans</i> -Co(tfac) ₃	Green	Gn., olive drab	158-158.5	34.77	34.84	2.34	2.43	11.37	11.27
<i>cis</i> -Rh(tfac) ₃	Yel.		148.5-149	32.05	32.23	2.15	2.21	18.31	18.22
<i>trans</i> -Rh(tfac) ₃	Yel.	Gn. yel., or yel.	189.5-190	32.05	31.93	2.15	2.14	18.31	18.07
<i>trans</i> -Al(tfac) ₃	White		121-122 ^b	37.05	36.90 ^c	2.49	2.47 ^c	5.55	5.66
<i>trans</i> -Ga(tfac) ₃	White		128.5-129.5	34.06	34.16	2.29	2.45	13.18	13.29
<i>trans</i> -In(tfac) ₃	Ivory		118-120	31.39	31.42	2.11	2.31	19.99	20.28
<i>trans</i> -Mn(tfac) ₃	Dk. g.-bn.	Gn., red-bn.	113-114	35.04	35.20	2.35	2.39	10.68	10.75
<i>trans</i> -Fe(tfac) ₃	Red		114 ^d	34.98	34.86	2.35	2.17	10.84	11.10

^a The first color listed is observed when the electric vector is parallel to the length of the tablet or needle. ^b Reported, 117°. ^c Upon contact with air, % carbon decreased and % hydrogen increased indicating that Al(tfac)₃ is somewhat unstable with respect to hydrolysis. This compound was stored over P₂O₅. ^d Reported, 115°.

(2.7 g., 0.010 mole) and sodium acetate (5 g.) was shaken with 1,1,1-trifluoro-2,4-pentanedione (7.4 g., 0.048 mole) in 20 ml. of ethanol. After ca. 10 min. the red crystalline solid which had precipitated was collected, washed with water, and air dried. The yield was 2.8 g. (54%).

Separation of Geometric Isomers.—The inert metal trifluoroacetylacetonates (M = Cr, Co, Rh) were separated into *cis* and *trans* isomers by column chromatography on acid washed alumina using benzene-hexane mixtures as the eluting solvent. Since the *cis* isomers are more soluble in solvents than the *trans* isomers, the *cis* isomers may be first concentrated by extraction with benzene-hexane or ethanol. [Solubility data for *cis*-Co(tfac)₃ at 24°, g./100 ml.: benzene, 38; ethanol, 3.14; cyclohexane, 0.28. Data for *trans*-Co(tfac)₃ at 24°, g./100 ml.: benzene, 14.5; ethanol, 0.85; cyclohexane, 0.11; chlorobenzene, 5.14.] The details of the procedure are similar to those already reported for separation of the *cis*- and *trans*-metal benzoylacetonates.³ It should be noted, however, that the trifluoroacetylacetonates adhere to alumina less tightly, and consequently a solvent mixture of lower polarity must be employed. Benzene-hexane mixtures containing up to 30% benzene were found to be satisfactory. The *cis* isomers were eluted in the later fractions and the *trans* isomers in the early fractions, in accord with the expected dipole moments of the two compounds. The relative yield of the two isomers was 17, 20, and 19% *cis* for the chromium, cobalt, and rhodium compounds, respectively.

The yield of the *cis* isomer may be increased by isomerization of the *trans* isomer at elevated temperatures. For Co(tfac)₃, equilibrium (ca. 20% *cis*) was achieved by refluxing in benzene for 6-10 hr. After removing the benzene by vacuum distillation, the *cis* isomer was concentrated by extracting the most soluble 25-30% of the solid with ethanol or benzene-hexane. The residue was then redissolved in benzene, and the isomerization and extraction process was repeated. After repeating the process four times, ca. 50% of the original material is converted to the *cis* isomer. The extracts may then be combined and the *cis* isomer purified by chromatography.

The *trans* isomers of the labile metal trifluoroacetylacetonates (M = Al, Ga, In, Mn, Fe) were obtained by crystallization from benzene-cyclohexane or benzene-pentane. Since these compounds decompose on alumina, a search for the more soluble *cis* isomer was made by extracting the most soluble 10-20% of the reaction products with cyclohexane. The crystals obtained upon evaporation of the cyclohexane had X-ray powder patterns which were identical with those of the less soluble *trans* isomers, with the exception of the Al(tfac)₃ patterns. Here some additional lines were found in the more soluble fraction. These reflections are probably due to aluminum complexes containing both trifluoroacetylacetonate and isopropoxide since complexes of this type have already been reported.⁸

Characterization of *cis*- and *trans*-Tris-(1,1,1-trifluoro-2,4-pentanedione)-metal(III) Complexes.—The compounds isolated in the solid state from benzene-pentane or benzene-cyclohexane solution are listed in Table I together with optical properties, melting points, and analyses. Microscopic examination and X-ray powder patterns indicate that the less soluble isomers of the inert complexes (*trans*) and the labile complexes form isomorphous crystals. These crystals are pseudohexagonal plates which have two mirror planes and which give parallel extinction. Preferential growth of another set of faces frequently occurs, giving the crystals the external shape of a long tablet or a rectangular plate. These crystals are clearly orthorhombic, and the observed *d* spacings correspond to those calculated from the unit cell dimensions which Jarrett has reported for the trifluoroacetylacetonates of aluminum, chromium, and iron.¹¹

(11) H. S. Jarrett, *J. Chem. Phys.*, **27**, 1298 (1957).

 TABLE II
 VISIBLE AND ULTRAVIOLET SPECTRA OF ISOMERIC METAL TRIFLUOROACETYLACETONATES^a

<i>cis</i> -Cr(tfac) ₃		<i>trans</i> -Cr(tfac) ₃	
λ _{max} , mμ	ε	λ _{max} , mμ	ε
563	69.0	564	69.1
386	348	386	391
338	12,000	340	12,000
277	9,440	278	9,750
264	9,800	264	9,800
<i>cis</i> -Co(tfac) ₃		<i>trans</i> -Co(tfac) ₃	
597	131	597	130
332	6,240 ^b	332	6,500 ^b
253	35,400 ^b	252	37,700 ^b
235	35,000 ^b	236	36,000 ^b

^a In absolute ethanol unless otherwise indicated. ^b In cyclohexane.

The *cis*-chromium, cobalt, and rhodium compounds are not isomorphous. The chromium compound forms needles which are probably monoclinic, since some give parallel extinction and others give oblique extinction. A prismatic crystal which exhibits oblique extinction is the most common crystalline form for *cis*-Co(tfac)₃. The *cis*-rhodium compound forms tiny needles which show symmetric extinction.

X-Ray Powder Patterns.—X-Ray powder patterns were obtained with iron-filtered Co Kα radiation using 0.5 mm. capillary tubes and a Debye-Scherrer camera of 14.01 cm. diameter. The *d* spacings and visually estimated intensities of the stronger lines are listed.

cis-Cr(tfac)₃: 9.12(4), 7.36(7), 6.75(3), 5.57(2), 5.28(2), 5.02(1), 4.77(1), 4.61(2), 3.93(10), 3.38(2), 3.20(1), 3.04(1), 2.564(1), 2.399(1).

cis-Co(tfac)₃: 9.19(7), 7.13(9), 6.51(8), 5.50(5), 4.78(5), 3.85(10), 3.54(1), 3.37(2), 2.890(1), 2.578(1), 2.183(1), 2.097(1), 1.924(1).

cis-Rh(tfac)₃: 8.15(4), 7.43(10), 6.30(2), 5.50(3), 5.08(2), 4.81(1), 4.24(3), 3.77(4), 3.46(2), 2.816(1), 2.511(1), 2.384(1), 2.306(1), 1.975(1).

trans-Cr(tfac)₃: 10.15(4), 6.51(9), 5.54(1), 4.93(3), 4.49(3), 4.26(2), 4.05(10), 3.87(2), 3.64(2), 3.37(3), 2.534(1), 2.262(1), 2.017(1), 1.936(1).

trans-Co(tfac)₃: 9.95(5), 6.49(10), 5.49(1), 4.92(2), 4.73(1), 4.48(2), 4.26(1), 4.02(10), 3.86(2), 3.63(2), 3.31(2), 2.534(1), 2.255(2), 2.149(1), 2.012(1), 1.935(1).

trans-Rh(tfac)₃: 9.95(6), 6.48(10), 5.50(3), 4.94(1), 4.74(3), 4.49(1), 4.26(1), 4.03(8), 3.86(2), 3.64(2), 2.536(2), 2.257(2), 2.153(2), 2.013(1), 1.940(1).

trans-Al(tfac)₃: 9.95(4), 7.11(2), 6.48(9), 4.91(4), 4.47(4), 4.03(10), 3.63(2), 3.33(2), 2.264(2), 2.022(1), 1.944(1).

trans-Ga(tfac)₃: 10.11(5), 6.54(10), 5.51(1), 4.90(3), 4.49(3), 4.06(9), 3.87(1), 3.65(2), 3.37(1), 2.539(2), 2.269(2), 2.025(1), 1.946(1).

trans-In(tfac)₃: 10.07(8), 6.88(8), 6.58(4), 5.68(7), 5.00(1), 4.50(2), 4.28(2), 4.06(10), 3.68(3), 2.561(2), 2.482(1), 2.365(1), 2.109(1), 2.038(1), 1.942(1).

trans-Mn(tfac)₃: 10.19(4), 7.15(1), 6.53(9), 4.90(3), 4.48(3), 4.07(10), 3.64(1), 2.534(1), 2.267(1).

trans-Fe(tfac)₃: 10.24(5), 6.92(4), 6.51(3), 5.73(2), 5.49(1), 4.92(2), 4.46(2), 4.25(2), 4.07(10), 3.92(1), 3.66(2), 3.43(2), 3.27(1), 2.89(1), 2.367(1), 2.267(1).

Vibration and Electronic Spectra.—Infrared spectra in potassium bromide disks were obtained with a Perkin-Elmer Model

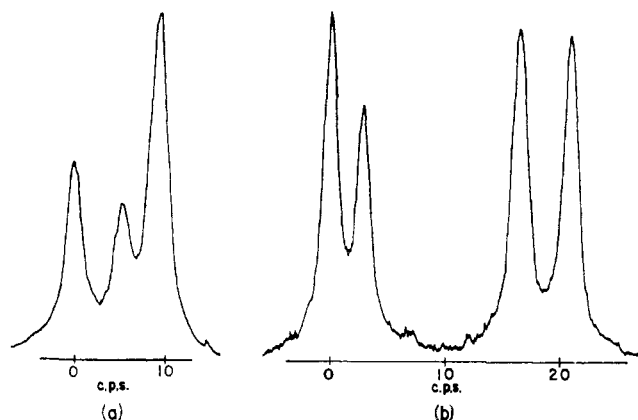


Fig. 1.—Fluorine resonance spectrum of a mixture of *cis*- and *trans*-Co(tfac)₃ (ca. 18% *cis*) at (a) 25.5° and (b) -40°.

21 recording infrared spectrometer. Visible and ultraviolet spectra were taken at 26° in ethanol or cyclohexane solutions in 1 cm. quartz cells with a Cary Model 14 recording spectrophotometer. Solutions were ca. $5 \times 10^{-3} M$ (visible) and $5 \times 10^{-3} M$ (ultraviolet). The extinction coefficients reported (Table II) are believed to be accurate to $\pm 1\%$.

N.m.r. Spectra, Equilibria in Solution.—Proton magnetic resonance spectra were run at 25° on Varian Associates model V-4300-2 and model A-60 high resolution spectrometers at 60 Mc. Fluorine resonance spectra were obtained on the model V-4300-2 at 56.4 Mc. The reported proton chemical shifts were obtained on the model A-60 and are believed to be accurate to ± 0.3 c.p.s. (Table III). They were measured relative to tetramethylsilane which was present as an internal standard (1% by volume). Fluorine chemical shifts were measured relative to the single sharp trifluoromethyl resonance of *cis*-Rh(tfac)₃ which was present in chloroform solution (11.3 g./100 ml.) in a sealed 1.5 mm. o.d. capillary tube. A 250 ± 1 c.p.s. audio-frequency sideband was used for scale calibration. The chemical shift of *cis*-Rh(tfac)₃ relative to CFCl₃ in a solution containing 11.3 g. of *cis*-Rh(tfac)₃ and 25 g. of CFCl₃ per 100 ml. of chloroform was found to be +72.1 p.p.m. Unless otherwise noted, solutions contained 11.3 ± 0.3 g. of M(tfac)₃ per 100 ml. of deuteriochloroform or chloroform, which had been passed through alumina to remove the ethanol, and 1% by volume tetramethylsilane. In some cases, spectra were also obtained in chlorobenzene (11 g./100 ml.).

The spectra of the *trans* isomers consist of groups of three closely spaced resonances. These were examined at slow sweep rate (0.2 c.p.s./sec. and 0.4 c.p.s./sec.) in order to achieve maximum resolution and measure more accurately the difference in chemical shift between the three non-equivalent methyl, CH, and trifluoromethyl groups (Table IV). With but a few noted exceptions, the proton shifts were obtained on the model A-60 and are accurate to ± 0.06 c.p.s. The chemical shift differences between the non-equivalent trifluoromethyl groups were obtained with the aid of a 20 c.p.s. audio-frequency sideband and are believed to be accurate to ± 0.3 c.p.s.

***cis-trans* Equilibria in the case of M(tfac)₃ (M = Al, Ga)** were studied in the temperature range -25.5° to +29.5°. Low temperature fluorine resonance spectra were obtained using Varian Variable Temperature NMR Probe Accessory, model V-4340 and Dewar Probe Insert model V-4331-THR. The sample was cooled with nitrogen or helium gas which had been passed through a copper coil immersed in liquid nitrogen. Temperature was maintained constant to $\pm 1.5^\circ$ by keeping the flow rate of the cooling gas constant with the aid of a flow meter. Temperature measurements were made periodically with a copper-constantan thermocouple immersed in the sample tube. Temperature equilibrium was achieved rapidly (<5 min.). The samples were allowed to remain in the probe for about 10 min. before recording spectra in order to assure the attainment of *cis-trans* equilibrium.

In the case of Co(tfac)₃, equilibrium was investigated at 79.1, 99.2, and 115° by suspending a sealed 5 mm. o.d. tube containing the sample solution in the vapors of boiling benzene, water, and pyridine. After an appropriate length of time, the equilibrium was quenched by plunging the sample into Dry Ice-acetone. The fluorine resonance spectrum was then recorded at -40°. Integrated intensities were obtained by measuring the area under the absorption curves with a planimeter. At 79.1 and 99.2° the equilibrium position was approached from both sides in order to make certain that equilibrium had been attained.

It was found that Co(tfac)₃ undergoes limited decomposition at elevated temperatures with the production of a Co(II) containing species as one of the products. The presence of this paramagnetic impurity broadened the n.m.r. resonances and

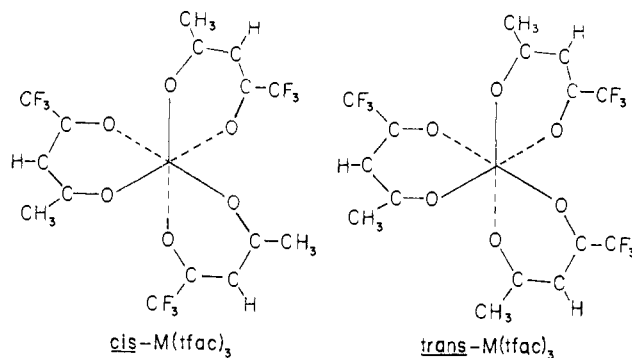


Fig. 2.—Configuration of *cis* and *trans* isomers of M(tfac)₃.

resulted in unfavorable overlap of the peaks due to the *cis* and *trans* isomers. Thermal decomposition was minimized by degassing and sealing *in vacuo* before heating. All equilibrium measurements were made in chloroform or deuteriochloroform; the concentration of M(tfac)₃ was 11.3 ± 0.3 g./100 ml. of solvent.

Equilibrium constants for the aluminum and gallium compounds were obtained by comparing the relative peak heights of the resonance due to the *cis* isomer and the lowest field resonance of the *trans* isomer. These resonance lines are sharp (line width ca. 0.9 c.p.s.) and exhibit no appreciable overlap with each other nor with the doublet due to the *trans* isomer at higher field, with one exception. In the case of Ga(tfac)₃ at 29.5°, there is a small amount of overlap which could result in an equilibrium constant which may be ca. 2% high. Data obtained at this temperature are not included in calculations of the heat of isomerization. Peak heights were used for the aluminum and gallium compounds rather than areas because of the sharpness of the lines and because of greater ease in measurement. Equilibrium constants obtained from areas were very similar, but the reproducibility was not as good due to random variations in sweep rate which are only partially averaged when sweeping through a narrow resonance line. The radio-frequency power level was kept a factor of ten below that where saturation was noticeable even though the equilibrium constants appeared to be rather insensitive to effects of saturation. The temperature region of observation was limited at the high temperature end by overlap of the *cis* and *trans* resonances and at the low temperature end by the quenching of the equilibrium.

In the case of Co(tfac)₃, the *cis* and *trans* resonances overlap very badly at room temperature (see Fig. 1). At -40°, however, the chemical shifts are larger, and the spectrum is separated into a low-field doublet and a high-field doublet with only a small region of overlap. The low-field doublet consists of one of the *trans* resonances and the *cis* resonance. The equilibrium constant may be determined by subtracting one-half the area of the high-field doublet from the area of the low-field doublet and then dividing by three-halves the area of the high-field doublet.

Results and Discussion

Vibration and Electronic Spectra.—Infrared, visible, and ultraviolet spectra are of no aid in the assignment of isomeric configuration. The infrared spectra are similar to the spectrum of copper trifluoroacetylacetonate reported by Belford.¹² The *cis* and *trans* isomers give nearly identical spectra in the region 2.5–15 μ except for slight shifts in the energy (<5 cm.⁻¹) of some of the bands and minor intensity differences. The visible and ultraviolet bands of the two isomers have nearly identical shape and energy (Table II). With the exception of the band at 386 m μ for the chromium isomers, the intensities are also nearly the same.

Geometrical Configuration of M(tfac)₃ Isomers.—The *cis*- and *trans*-metal trifluoroacetylacetonates may be distinguished by means of proton and fluorine magnetic resonance spectra and X-ray powder patterns. In the *cis* isomer all three methyl groups, all three CH protons, and all three trifluoromethyl groups are equivalent by a threefold rotation axis; in the *trans* isomer, which has no symmetry, the three methyl groups, CH protons, and trifluoromethyl groups are all non-equivalent (see Fig. 2). Therefore, in absence of exchange, we may assign the *cis* configuration to compounds which

(12) R. L. Belford, A. E. Martell and M. Calvin, *J. Inorg. & Nuclear Chem.*, **2**, 11 (1956).

exhibit a single resonance line and the *trans* structure to compounds which give three resonances.

The n.m.r. spectra are presented in Fig. 3. In the case of the inert complexes ($M = \text{Co}, \text{Rh}$), the more soluble, less easily eluted isomers give single resonance lines and, therefore, have the *cis* configuration; the less soluble, more easily eluted isomers exhibit three resonances, and hence may be assigned the *trans* structure. The coincidence of two of the trifluoromethyl resonances in chloroform solution must be attributed to solvent effects since the unresolved doublet is clearly resolved in chlorobenzene solution and also in chloroform at other temperatures (see Fig. 1). The configuration of the $\text{Cr}(\text{tfac})_3$ isomers may be assigned because of crystal isomorphism between the less soluble, more easily eluted isomer and the *trans* cobalt and rhodium compounds.

The labile complexes ($M = \text{Al}, \text{Ga}, \text{In}, \text{Mn}, \text{Fe}$) may be assigned the *trans* structure in the solid state, again because of crystal isomorphism. In solution the situation is considerably more interesting. The proton resonance of the aluminum and gallium compounds suggests that the predominant species in solution is the *trans* isomer. The possible presence of the *cis* isomer in small concentrations, however, cannot be eliminated because of the greater intensity of the center peaks and the fact that proton resonances of *cis* and *trans* trifluoroacetylacetonates have very similar chemical shifts. The n.m.r. spectra of the trifluoromethyl groups show that the *cis* isomer is indeed present in solution and that about 18% of the total concentration is due to the *cis* isomer. At room temperature the resonance due to *cis*- $\text{Al}(\text{tfac})_3$ coincides with the second *trans* resonance; the two resonances are clearly separated, however, at lower temperatures. The indium complex exhibits only a single methyl, CH, and trifluoromethyl resonance. One should not infer, however, that the solution contains only the *cis* isomer, since the equilibrium concentrations of the *cis* and *trans* isomers are not expected to differ greatly from those found for the aluminum and gallium compounds. Rather, the single resonance line is to be interpreted in terms of a rate process which rapidly exchanges the nuclei between the four possible environments of the *cis* and *trans* molecules. We have observed coalescence of n.m.r. signals into a single line due to exchange for the aluminum and gallium compounds at elevated temperatures; the mechanism of exchange will be discussed in a future publication.

Chemical Shifts.—The proton and fluorine chemical shifts are presented in Table III; the values reported for the *trans* isomers are the mean chemical shift of three resonances. The data are for 11.3% (wt./vol.) solutions. However, the proton chemical shifts of *cis*- $\text{Co}(\text{tfac})_3$ were investigated in the concentration range 0.8–11.3%, and the variation in chemical shift was found to be only ± 0.3 c.p.s. Similarly, the concentration dependence of the fluorine chemical shifts was found to be small. In Table IV the differences in chemical shift between the various non-equivalent methyl groups, CH protons, and trifluoromethyl groups in the *trans* isomers are tabulated.

The variation in the proton chemical shifts as a function of the metal ion is not large, as has already been pointed out in the case of the CH resonances of metal acetylacetonates.¹³ It is clear from Table III, however, that the resonances of the cobalt and rhodium compounds occur at lower magnetic field than the resonances of the corresponding group III compounds. The fluorine shifts are larger and are probably more reliable as a measure of the electron withdrawing ability of the metal ion. The electron withdrawing ability is seen to decrease in the order $\text{Rh} > \text{Co} > \text{In} > \text{Ga} >$

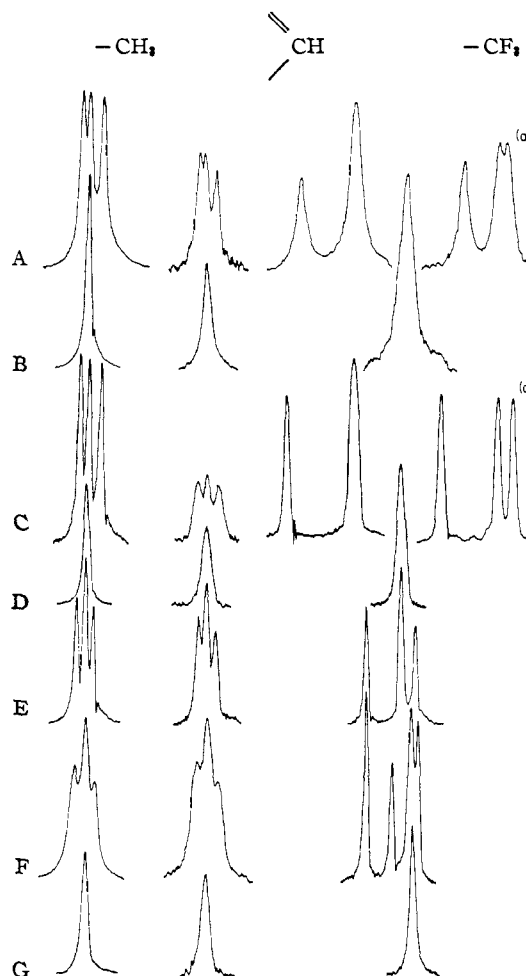


Fig. 3.—Proton and fluorine resonance spectra of metal trifluoroacetylacetonates at room temperature: A, *trans*- $\text{Co}(\text{tfac})_3$; B, *cis*- $\text{Co}(\text{tfac})_3$; C, *trans*- $\text{Rh}(\text{tfac})_3$; D, *cis*- $\text{Rh}(\text{tfac})_3$; E, *cis*- and *trans*- $\text{Al}(\text{tfac})_3$; F, *cis*- and *trans*- $\text{Ga}(\text{tfac})_3$; G, $\text{In}(\text{tfac})_3$, time averaged spectrum. Sweep rate and amplitude are not the same for all spectra. Solvent is chloroform except it is chlorobenzene for A.

Al. The same order is obtained from the methyl resonances, excepting the inversion of cobalt and rhodium. The greater electron withdrawal of cobalt(III) and rhodium(III) relative to the group III ions may be

TABLE III
PROTON AND FLUORINE CHEMICAL SHIFTS IN METAL TRIFLUOROACETYLACETONATES^a

Compound	—CH ₃	=CH—	—CF ₃
<i>cis</i> - $\text{Co}(\text{tfac})_3$	-144.0	-362.7	40.9
<i>trans</i> - $\text{Co}(\text{tfac})_3$	-145.1	-362.9	40.7, 49.3 ^b
<i>cis</i> - $\text{Rh}(\text{tfac})_3$	-141.8	-359.3	± 0.0
<i>trans</i> - $\text{Rh}(\text{tfac})_3$	-142.4	-360.3	4.5, 14.0 ^b
<i>cis</i> - $\text{Al}(\text{tfac})_3$			182.8
<i>trans</i> - $\text{Al}(\text{tfac})_3$	-133.9	-359.0	181.5
<i>cis</i> - $\text{Ga}(\text{tfac})_3$			168.9
<i>trans</i> - $\text{Ga}(\text{tfac})_3$	-134.8	-355.2	170.0
$\text{In}(\text{tfac})_3^c$	-135.3	-353.4	162.9

^a Proton shifts are in c.p.s. relative to TMS. Fluorine shifts are in c.p.s. relative to *cis*- $\text{Rh}(\text{tfac})_3$. Concentration is 11.3 g./100 ml. of chloroform or deuteriochloroform unless otherwise noted. Temperature is 25°. In the case of the *trans* isomers, the mean chemical shift is reported. ^b 11 g./100 ml. of chlorobenzene. ^c Time averaged chemical shifts.

readily understood in terms of electronic structure. In an octahedral field the six d electrons of cobalt(III) and rhodium(III) occupy the t_{2g} orbitals which point in directions between the ligands. The effective nuclear

TABLE IV

PROTON AND FLUORINE CHEMICAL SHIFTS IN *trans*-METAL TRIFLUOROACETYLACETONATES^a

Compound	—CH ₃ —		=CH—		—CF ₃ —	
	m.f.	h.f.	m.f.	h.f.	m.f.	h.f.
Co(tfac) ₃	0.81 ^b	2.66 ^b	1.01 ^b	3.2 ^b	9.8	7.4 ^c 9.4 ^c
Rh(tfac) ₃	1.15	2.76	1.30	2.96	12.4	10.3 ^c 13.2 ^c
Al(tfac) ₃	1.42	2.91	1.01	2.48	7.1	10.4
Ga(tfac) ₃	1.36	2.76	1.17 ^b	2.46 ^b	8.8	10.1

^a Chemical shifts of the resonances which occur at mid-field (m.f.) and highest field (h.f.) are reported in c.p.s. relative to the resonance which occurs at lowest field. All spectra were obtained in chloroform solution unless otherwise indicated. Temperature is 25°. ^b Two or all three of the *trans* resonances were unresolved in A-60 spectra. Resolution was obtained with model V-4300-2, but chemical shifts are accurate only to ±0.1 c.p.s. ^c In chlorobenzene solution.

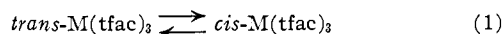
charge in the directions of the ligands, therefore, is considerably greater than that in the case of the spherically symmetrical group III ions. Greater electron withdrawal for cobalt(III) and rhodium(III) has also been indicated by the methyl resonances of the metal benzoylacetates³ and acetylacetates.¹⁴

Turning to the group III metals, a variety of methods for evaluating electronegativity have indicated that gallium is more electronegative than either aluminum or indium, but that aluminum and indium have rather similar electronegativities.¹⁵⁻¹⁷ Although the order of electron withdrawing ability Ga > Al seems reasonable, the position of indium as the most electron withdrawing of the three metals is unexpected.

The proton chemical shift differences between the non-equivalent methyl groups and CH protons of a given *trans* isomer (Table IV) are somewhat larger than in the corresponding metal benzoylacetates,³ which is expected since the trifluoromethyl group is more electron withdrawing than the phenyl group.

The line widths of the proton and fluorine resonances of the cobalt compounds were considerably broader than the resonances of the other metal complexes. The shorter relaxation times may perhaps be associated with the well-known temperature independent paramagnetism of trivalent cobalt.¹⁸

Equilibria in Solution.—Equilibrium constants for the



reaction where M = Al, Ga, and Co are presented in Tables V and VI. The values reported are, in general, the mean of five to ten n.m.r. spectral determinations. The errors are estimated at the 95% confidence level.

It will be noted that the equilibrium constants for Co(tfac)₃ are very nearly 0.25 in excellent agreement with the nearly 20% yield of *cis* isomer which has been obtained consistently in preparations of the inert complexes. In every case the equilibrium constants are

(14) R. C. Fay and T. S. Piper, unpublished data.

(15) H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955).

(16) A. L. Allred and E. G. Rochow, *J. Inorg. & Nucl. Chem.*, **5**, 264 (1958).

(17) S. Brownstein, B. C. Smith, G. Ehrlich and A. W. Laubengayer, *J. Am. Chem. Soc.*, **81**, 3826 (1959).

(18) J. S. Griffith and L. E. Orgel, *Trans. Faraday Soc.*, **53**, 601 (1957).

TABLE V

EQUILIBRIUM CONSTANTS FOR Al(tfac)₃ AND Ga(tfac)₃ IN CHLOROFORM SOLUTION

Temp., °C.	K, Al(tfac) ₃	K, Ga(tfac) ₃
-25.5	0.201 ± 0.006	0.177 ± 0.002
-12	.209 ± .006	.186 ± .006
0	.213 ± .007	.194 ± .008
+3	.210 ± .002	.196 ± .010
+29.5		.214 ± .003

TABLE VI

EQUILIBRIUM CONSTANTS FOR Co(tfac)₃ IN CHLOROFORM SOLUTION

Temp., °C.	Starting material	Heating time, hr.	K
79.1	<i>trans</i>	13.75	0.244 ± 0.018
79.1	<i>cis</i>	13.9	.247 ± .018
99.2	<i>trans</i>	3.5	.254 ± .019
99.2	<i>cis</i>	1.0	.253 ± .019
115	<i>trans</i>	3.5	.256 ± .018

considerably less than the statistical value of 0.333. In the case of Co(tfac)₃ equilibrium is established very slowly at room temperature, but with the group III compounds equilibrium is achieved rapidly. Failure to isolate the *cis* isomers of the group III metal compounds in the solid state at room temperature may now be assigned to the rapid shift of the equilibrium in the direction of the *trans* isomer as the less soluble *trans* isomer crystallizes out.

Heats of isomerization were obtained from log *K* versus 1/*T* plots. The data were treated by a least squares analysis including all data points (five to ten at each temperature). From the least squares straight lines, free energies and entropies of isomerization at 25° were calculated. These data are collected in Table VII for reaction 1 as written. The errors cited are estimated at the 95% confidence level.

TABLE VII

THERMODYNAMIC DATA FOR *cis-trans* EQUILIBRIA IN CHLOROFORM SOLUTION AT 25°

Compound	Δ <i>H</i> , kcal./mole	Δ <i>F</i> , kcal./mole	-Δ <i>S</i> , e.u.
Al(tfac) ₃	0.24 ± 0.19	0.897 ± 0.016	2.2 ± 0.6
Ga(tfac) ₃	.47 ± .22	.930 ± .016	1.5 ± 0.7
Co(tfac) ₃	.34 ± .71	.887 ± .046	1.8 ± 2.4

The heat and entropy terms make approximately equal contributions to the small free energy difference between the two geometric isomers. The *trans* isomer is seen to be more stable as is expected because of its lower dipole moment; the heat of isomerization is to be associated primarily with the partial destruction of the *cis* dipole upon isomerization. The greater entropy of the *trans* isomer may be attributed to a first approximation to the difference in symmetry number. If symmetry were the only contributing factor, the entropy of isomerization would be $-R \ln 3$ or -2.18 e.u.

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