off the internuclear axis and toward lithium. If the deviations from orthogonality observed by Juan and Gutowsky[18] are assumed to be operative in the present case, the angle is more like 8 to 10°.

The above argument indicates the possibility of some small degree of covalent bonding involving lithium. It is quite clear from the sharp C_1–Li–C_3 angle of 93.6°, however, that lithium does not employ all of its valence shell orbitals in such covalent bonding as may exist. As a tentative scheme, we suggest that lithium sp-hybrid orbitals directed along the chain axis may overlap to some extent with the aluminum and carbon atomic orbitals.

Lithium aluminum tetraethyl is soluble to some extent in benzene; the solubility increases rapidly with temperature. It was not possible to obtain useful n.m.r. spectra of the compound in benzene, but both proton and ^{7}Li resonances were observed for ether solutions. The proton spectrum is typical of an A_2X_3 system, with the CH_3 triplet largely obscured by solvent absorption. The chemical shift of the CH_2 quartet lies at 7.71 p.p.m. upfield from benzene as internal standard; $J_{AX} = 8.0$ c.p.s. The corresponding values for ethyllithium in ether are 8.12 p.p.m. and 8.4 c.p.s.[6] The quartet lines are quite broad; the line widths are not appreciably affected by concentration change nor by lowering of the temperature to $-48°$. Since ^{27}Al possesses a sizable quadrupole moment, it is possible that the broadening arises from a spin–spin interaction between aluminum and the protons. This in turn would require that the rate of exchange of alkyl groups between metal atoms be slow in relation to the *Al*-C-*H* coupling constant. A slow exchange of alkyl groups in a system of this type in ether would be novel, and the matter is under further study.

The ^{7}Li resonance line is quite sharp (half-width about 1.5 c.p.s. in the temperature range 30 to $-48°$ and appears at a chemical shift of 1.47 p.p.m. upfield from 70% aqueous lithium bromide. This is to be compared with a chemical shift of -1.00 p.p.m. from the same standard for ethyllithium in the same solvent.

The structure of lithium aluminum tetraethyl in a coordinating solvent such as ether is a matter of considerable interest. Among the more likely possibilities are (a) extensive dissociation into ethyllithium and triethylaluminum, which are individually solvated, (b) formation of solvated Li^+ and $Al(C_2H_5)_4^-$ ion pairs, and (c) partial retention of the structure of the solid, with short chains terminated by coordinated solvent. The ^{7}Li n.m.r. result rules out (a), but no further conclusions regarding the ether solutions are justified at this time.

Acknowledgment.—This research was sponsored by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, and by the National Science Foundation. Computer services were furnished by the University of Illinois Digital Computer Laboratory.

CONTRIBUTION FROM THE W. A. NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS,
AND BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, NEW YORK

Stereochemistry of Metal β-Diketonates. Complexes with Two Different Ligands

BY RICHARD A. PALMER,[1a] ROBERT C. FAY,[1b] AND T. S. PIPER[1a,c]

Received February 4, 1964

For cobalt and chromium β-diketonates of the series $M(CF_3COCHCOCH_3)_n(CH_3COCHCOCH_3)_{3-n}$ where n is 1 or 2, the isomers have been separated and characterized. The dipole moments and both fluorine and proton n.m.r. spectra of the cobalt compounds with $n = 1, 2,$ and 3 are reported and interpreted. Coalescence of fluorine n.m.r. lines as a function of temperature for the corresponding aluminum compounds in the presence of excess of the β-diketones indicates that exchange of CF_3 groups between different chemical environments for a given value of n occurs by an intramolecular mechanism.

Introduction

In a recent study of the tristrifluoroacetylacetonates of trivalent metals, Fay and Piper have shown the utility of n.m.r. spectroscopy in the assignment of configuration to the two geometrical isomers[2] as well as in studies of the kinetics and mechanisms of their interconversion.[3] This work suggested a study of the complete series of compounds $M(CF_3COCHCOCH_3)_n(CH_3COCHCOCH_3)_{3-n}$ where n is 0, 1, 2, or 3. We will abbreviate these compounds hereafter as M-$(tfac)_n(acac)_{3-n}$ where $(tfac)^-$ indicates the anion of 1,1,1-trifluoro-2,4-pentanedione and $(acac)^-$ indicates the anion of 2,4-pentanedione. These compounds afford another interesting set of geometrical isomers when n is 2. Furthermore, one may study the equilibrium distribution of products and the mechanisms of reactions such as isomerization, racemization, and ligand exchange with free β-diketone in solution.

In this paper we report the synthesis, separation, and characterization of the three isomeric $M(tfac)_2(acac)$ complexes and of $M(tfac)(acac)_2$ for both cobalt(III) and chromium(III). The assignment of configuration

---

(1) (a) University of Illinois; (b) Cornell University; (c) Alfred P. Sloan Foundation Fellow.

(2) R. C. Fay and T. S. Piper, *J. Am. Chem. Soc.*, **85**, 500 (1963).

(3) R. C. Fay and T. S. Piper, *Inorg. Chem.*, **3**, 348 (1964).

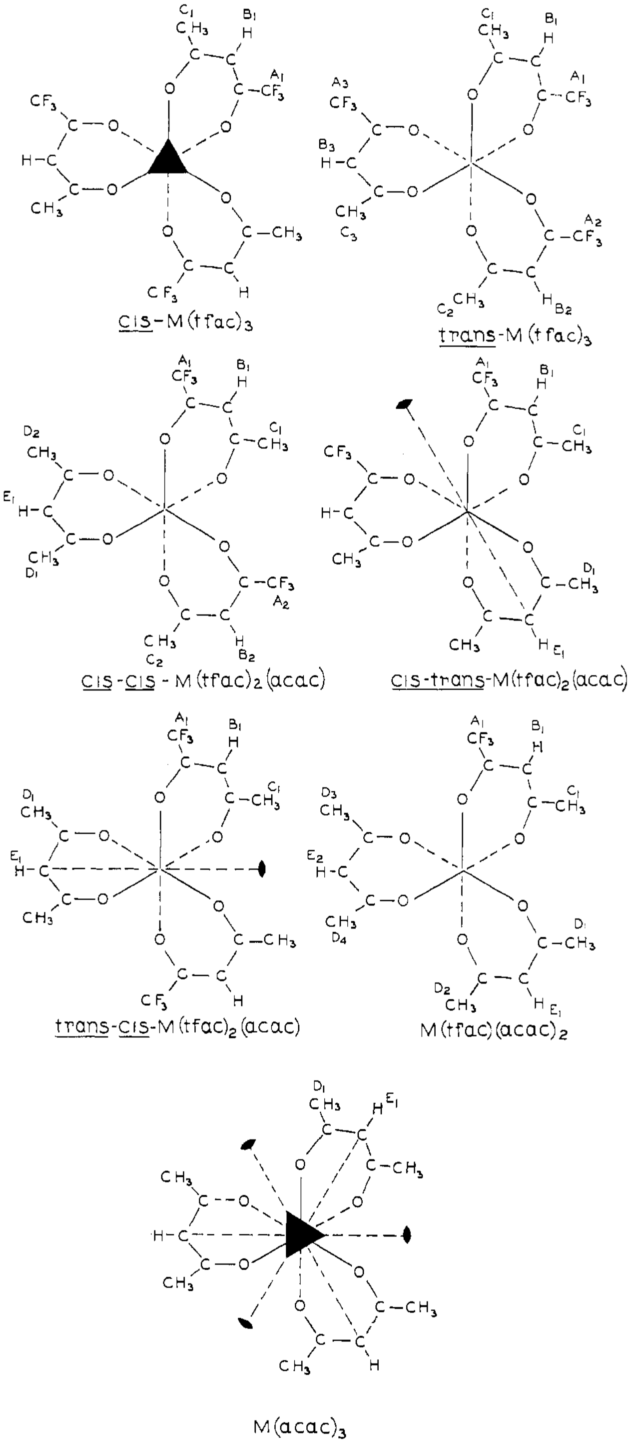


Fig. 1.—Geometrical isomers of the series of compounds M(tfac)$_n$(acac)$_{3-n}$. The symmetry elements are indicated with the standard crystallographic symbols. The parent molecule M(acac)$_3$ belongs to the point group D_3. The remaining molecules if they possess any symmetry belong to the subgroups C_3 or C_2 as indicated.

to the isomeric complexes is based on molecular dipole moment determination as well as analysis of proton and fluorine n.m.r. spectra. The assignment of the proton and fluorine resonances to the various configurations of the inert diamagnetic cobalt(III) complexes has been extended to the labile aluminum complexes in a study of coalescence of fluorine resonance lines as a function of temperature.

Before describing the results of these studies, let us consider the stereochemistry and nomenclature of these compounds. The geometrical isomers are illustrated in Fig. 1. The isomers of M(tfac)$_2$(acac) present a novel problem in descriptive nomenclature. A natural extension of the common system to these isomers is proposed and illustrated in the figure. In this notation, considering for example the *trans-cis* isomer, the first prefix, *trans*, refers to the relative orientation of the trifluoroacetyl groups and the second, *cis*, to the relative orientation of the acetyl groups of the trifluoroacetylacetonato chelate rings. We believe that this nomenclature is consistent, brief, and at the same time descriptive. In the figure the distinct proton and fluorine containing groups (*i.e.*, not related by a symmetry operation) are lettered for later reference in the n.m.r. spectral assignments.

Discussion

The complexes M(tfac)$_n$(acac)$_{3-n}$ are obtained by employing a mixture of the two β-diketones in the usual preparations of M(acac)$_3$. Invariably the product consists of a mixture of all members of the series. An additional synthetic technique is to equilibrate any member(s) of the series with excess of the appropriate β-diketone. For instance this procedure can be used to convert Co(tfac)(acac)$_2$ to a mixture containing a high percentage of the stereochemically more interesting isomers of M(tfac)$_2$(acac).

Separation and Identification.—Using chromatographic procedures similar to those employed by Fay and Piper[2] the product mixtures may be analyzed to obtain all but two of the seven possible geometrical configurations of M(tfac)$_n$(acac)$_{3-n}$ in pure form. We have been unable to separate *cis-cis-* and *cis-trans*-M(tfac)$_2$(acac) isomers completely by this technique. In all cases the order of elution is: band 1, *trans*-M(tfac)$_3$ followed by *cis*-M(tfac)$_3$; band 2, *trans-cis*-M(tfac)$_2$(acac); band 3, *cis-trans-* and *cis-cis*-M(tfac)$_2$(acac); band 4, M(tfac)(acac)$_2$; and band 5, M(acac)$_3$. Except for the pair in band 3 all of these complexes are readily distinguishable by analysis, melting points, microscopic examination of the crystals, and X-ray powder patterns. The order of elution depends upon the number of trifluoromethyl groups in the molecule and upon the molecular dipole moment (see below). The former effect is clearly the more important as is evident from the fact that *trans*-M(tfac)$_3$ ($\mu \approx 3.8$ D.) is eluted not only before *cis*-M(tfac)$_3$ ($\mu \approx 6.5$ D.) but also before *trans-cis*-M(tfac)$_2$(acac) ($\mu \approx 0.9$ D.). For geometrical isomers, however, the order of elution is accurately predicted by the dipole moments. The *cis* and *trans* isomers of M(tfac)$_3$ with a dipole moment difference of 2.68 D. can be quantitatively separated by three successive chromatograms. An appreciably smaller dipole difference would make separation very difficult; however, for isomers with fewer trifluoromethyl groups separability is improved for a given dipole difference. The virtual inseparability of the *cis-cis* and *cis-trans* isomers is consistent with their similar dipole moments, estimated below to be 4.55 and 4.00 D., respectively.

The identification of the three isomers of M(tfac)$_2$(acac) rests on the cumulative evidence of dipole moments and n.m.r. spectra presented in detail below. An especially difficult problem was encountered for the *cis-cis* and *cis-trans* pair which are not only eluted in the same chromatographic band but which are virtually indistinguishable in other of their properties, for example crystal morphology, X-ray powder patterns, and solubility. They appear to form mixed crystals and show only minor intensity differences in some powder pattern lines. This behavior may be due to the structural similarity of the pair in that the polar trifluoromethyl groups are *cis* to one another in both. As predicted by dipole moment estimates and proved by n.m.r., however, the *cis-trans* isomer can be concentrated in the leading part and the *cis-cis* in the tail of a very careful chromatogram of the mixture.

Dipole Moments.—The expected molecular dipole moments of the six polar molecules of the series M(tfac)$_n$(acac)$_{3-n}$ were calculated using the C–CH$_3$ and C–CF$_3$ group moments obtained for gaseous monosubstituted benzenes,[4] which are 0.37 and 2.56 D., respectively. These group moments were added vectorially as indicated in Fig. 2. We assume that the C–C bonds of both groups make an angle of 12.5° with the Cartesian coordinates defined by the metal–oxygen framework as has been found in the crystal structure[5] of Fe(acac)$_3$.

The calculated dipole moments are given in Table I together with the experimental values for the four polar isomers of the cobalt(III) series which could be separated and purified. The consistent agreement of calculated and experimental moments supports the assumptions made in the calculation and furthermore confirms the assignment of configuration of the *trans-cis* isomer previously based on the elution order. It may be noted at this point that this isomer is indistinguishable from the *cis-trans* isomer on the basis of the n.m.r. spectra since both have the symmetry C$_2$.

TABLE I

DIPOLE MOMENT DATA

Compound	P_∞,[a] cm.^{3}	μ_{calcd}, D.	μ_{exptl}, D.
trans-Co(tfac)$_3$	425.50	3.50	3.80
cis-Co(tfac)$_3$	989.62	6.08	6.48
trans-cis-Co(tfac)$_2$(acac)	146.50	0.90	0.89
cis-trans-Co(tfac)$_2$(acac)	. . .	4.00	. . .
cis-cis-Co(tfac)$_2$(acac)	. . .	4.55	. . .
Co(tfac)(acac)$_2$	332.04	2.92	3.14

[a] Total measured polarization at infinite dilution in benzene solution at 25.00°.

Equilibria in Solution.—The equilibrium between the *cis* and *trans* isomers of M(tfac)$_3$ complexes has been reported previously.[2] The equilibria involving the three isomers of Co(tfac)$_2$(acac) have been investigated in this study. In Table II are recorded the relative concentrations of the three isomers present at equilibrium as determined from integrated fluorine n.m.r. resonance intensities. The distribution is very close to that predicted on statistical grounds, namely, 1:1:2 where the *cis-cis* isomer has the weight 2. Obviously the temperature dependence is much smaller than the scatter of the data. The ΔH values for the three isomerizations are therefore zero within experimental error. A value less than the 0.25 to 0.5 kcal./mole observed for the M(tfac)$_3$ isomers could well be expected in view of the fact that there is one less polar trifluoromethyl group.

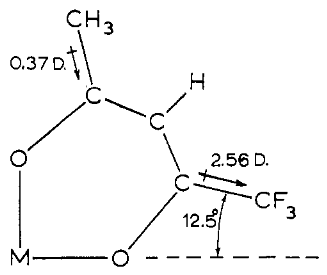


Fig. 2.—The orientation of the group moments in the chelate ring.[5]

TABLE II

EQUILIBRIUM RELATIVE CONCENTRATIONS OF THE ISOMERS OF Co(tfac)$_2$(acac)

Temp., °C.	Relative concentration *trans-cis*	*cis-trans*	*cis-cis*
66.4	1	0.94	1.81
79.2	1	0.97	2.07
90.2	1	0.95	1.75
99.5	1	0.96	1.95
115.0	1	0.84	2.13

Assignment of the N.m.r. Resonances.—The proton and fluorine n.m.r. spectra of the inert and labile M(tfac)$_3$ isomers have been described previously.[2,3] We begin our discussion of the remaining members of the M(tfac)$_n$(acac)$_{3-n}$ series with the inert diamagnetic cobalt(III) complexes. Once the assignments have been firmly established we can extend the study to the labile aluminum(III) complexes.

The data for the cobalt complexes are recorded in Table III. By comparison with the spectra of *cis*- and *trans*-Co(tfac)$_3$ and of Co(acac)$_3$, the proton resonances in the region -330 to -360 c.p.s. at 60 Mc. relative to tetramethylsilane may be divided into those due to the trifluoroacetylacetonate ring protons at lower field from -358 to -364 c.p.s. and those due to the acetylacetonate ring protons at higher field from -331 to -339 c.p.s. The ratios of intensities of these two clusters, low-field to high-field, are 2:1 for the Co(tfac)$_2$(acac) isomers and 1:2 for Co(tfac)(acac)$_2$, confirming the assignment. By a similar comparison the CH$_3$ resonances may be divided into a cluster at lower field from -139 to -146 c.p.s. and another at higher field from -130 to -137 c.p.s. which we

---

[4] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p. 314.

[5] R. B. Roof, Jr., *Acta Cryst.*, **9**, 781 (1956).

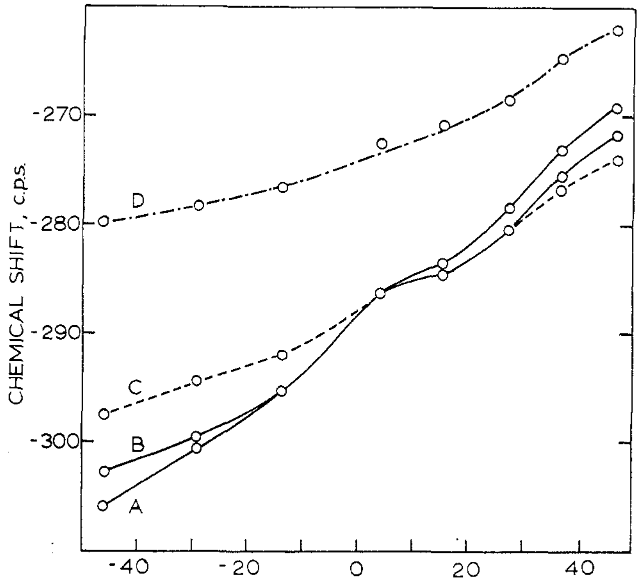


Fig. 3.—Fluorine n.m.r. spectra of Co(tfac)$_2$(acac) as a function of temperature. The lines are assigned to the isomers as follows: A and B, *cis-cis;* C, *trans-cis;* and D, *cis-trans.* The reference is trifluoroacetylacetone in a capillary.

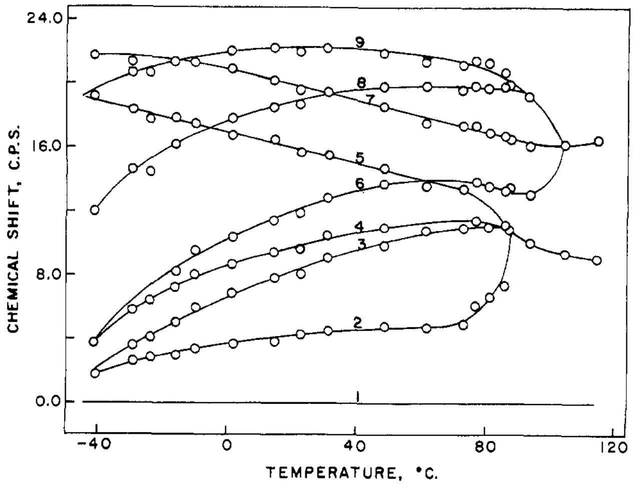


Fig. 4.—Temperature dependence of fluorine n.m.r. lines of Al(tfac)$_n$(acac)$_{3-n}$ in chloroform solution containing excess of the β-diketones. The chemical shifts are expressed relative to that of Al(tfac)(acac)$_2$, line 1. Lines 2 through 5 are assigned to Al(tfac)$_2$(acac), lines 6 through 9 to Al(tfac)$_3$.

assign tentatively to the trifluoroacetylacetonate methyl and the acetylacetonate methyl proton resonances, respectively. However, in this instance the intensities are consistent with either this assignment or the reverse, since, for example, in the case of the isomers of M-(tfac)$_2$(acac) there are two CH$_3$ groups of each kind. Furthermore, the separation between the clusters is considerably smaller. The assignments for the incompletely separated *cis-trans* and *cis-cis* isomers are consistent with the relative intensities of peaks in both fluorine and proton n.m.r. spectra of chromatographic fractions in which one or the other of the isomers is concentrated (~80%). For example, the fluorine n.m.r. spectrum of a fraction taken from the tail of a careful chromatogram of a mixture of the two isomers shows a doublet and a less intense singlet. We assign the doublet to the *cis-cis* isomer and the singlet to the *cis-trans* isomer in accord with their symmetries. In a fraction from the leading edge of the band, on the other hand, the singlet resonance is more intense. By a similar comparison the proton resonances of the two isomers may be distinguished.

Table III

Proton Chemical Shifts

	Chemical shift[a]			
	CH$_3$(acac)	CH$_3$(tfac)	CH(acac)	CH(tfac)
trans-Co(tfac)$_3$	...	−143.5	...	−361.0
	...	−145.5	...	−363.2
	...	−146.2	...	−364.0
cis-Co(tfac)$_3$	...	−144.0	...	−362.7
trans-cis-Co(tfac)$_2$-(acac)[b]	−133.4	−144.3	−334.2	−359
cis-trans-Co(tfac)$_2$-(acac)[b]	−136.4	−139.4	−338.5	−358
cis-cis-Co(tfac)$_2$-	−133.9	−139.4	−336.2	−358
(acac)	−135.3	−144.0	...	−358
Co(tfac)(acac)$_2$	−132.0	−140.0	−335	−358.0
	−132.3	...	−338	...
	−134.2	...	...	...
	−137.0	...	...	...
Co(acac)$_3$	−129.6	...	−331.1	...

[a] In c.p.s. at 60 Mc. relative to TMS; temperature 25.0°; concentration, 110 mg./ml. (unless otherwise noted) in deuteriochloroform. [b] 55 mg./ml.

The peaks in the fluorine n.m.r. spectra of the cobalt complexes are readily assigned to the various isomers without ambiguity. The peaks are incompletely resolved at room temperature but quite well separated below −40° and above +40°. The temperature dependence of the chemical shifts of the isomers of Co-(tfac)$_2$(acac) is given in Fig. 3 (the proton resonances show little or no dependence of chemical shift on temperature). Co(tfac)(acac)$_2$ shows a single resonance at −273.3 c.p.s. at 27.5° on the same scale.

The N.m.r. Spectra of the Al(tfac)$_n$(acac)$_{3-n}$ Complexes.—Upon addition of H(acac) to Al(tfac)$_3$ in chloroform solution, the four fluorine resonances characteristic of the isomers of Al(tfac)$_3$[3] decrease in intensity and six additional lines appear. The line at highest field is due to trifluoroacetylacetone and those mainly at lower field are due to the mixed-ligand compounds. The temperature dependence of the spectrum is presented in Fig. 4. Since a nearly statistical distribution of Al(tfac)$_2$(acac) isomers is expected, the four lines of approximately equal intensity (lines 2 through 5) are assigned to these isomers while line 1, of considerably different intensity, is attributed to Al-(tfac)(acac)$_2$. The assignment of lines 2 through 5 may be made by comparison to those of the corresponding cobalt complexes. We assign the higher field line 5 to the *cis-trans* isomer. The closely spaced doublet, lines 3 and 4, is probably due to the lower symmetry *cis-cis* isomer; the remaining line 2 is assigned to the *trans-cis* isomer.

The resonance lines assigned to the Al(tfac)$_2$(acac) isomers begin to merge at temperatures above 73°. A single broad line is obtained at 87 ± 2° which subsequently sharpens as the temperature is raised. The four resonance lines of *cis*- and *trans*-$Al(tfac)_3$ merge at slightly less than 104.5°. Coalescence at 103 ± 2° was reported previously and attributed to a rapid intramolecular process or processes which exchange CF_3 groups among all four stereochemical positions of these isomers.[3] For the corresponding exchange of CF_3 groups in the $M(tfac)_2(acac)$ isomers we use the approximations previously described[3] and calculate a mean rate constant of 43 $sec.^{-1}$ at the coalescence temperature (87°) as well as a free energy of activation ΔF^* of 18.5 ± 1.6 kcal./mole. (the estimated error assumes an order of magnitude error in the rate constant). These values may be compared with a rate constant of 34 $sec.^{-1}$ (103°) and ΔF^* of 19.6 ± 1.7 kcal./mole for the corresponding $Al(tfac)_3$ exchange.

We have cited evidence which favors bond rupture and a five-coordinate intermediate for exchange of CF_3 groups in the tristrifluoroacetylacetonates.[3] It is likely that the same mechanism operates for the present complexes although conclusive evidence on this point is not yet available. The coalescence behavior, however, does allow two important conclusions. First, the exchange does not proceed by an intermolecular mechanism, since such a mechanism would predict further coalescence of resonance lines. In fact, above 105° and up to 135° there are four separate resonance lines due to the three aluminum compounds $Al(tfac)_n(acac)_{3-n}$ (n = 1, 2, or 3) and excess trifluoroacetylacetone (37.1 c.p.s. relative to $Al(tfac)_2(acac)$ at 135°). From these data the lower limit of ΔF^* for exchange with free diketone is estimated to be about 20 kcal./mole. Second, we conclude from the n.m.r. spectra that the intramolecular exchange of $Al(tfac)_2(acac)$ does not proceed *via* the trigonal twist mechanism.[3,6-8] In Fig. 5 we illustrate how this mechanism provides a path for exchange of the nonequivalent CF_3 groups in the *cis-cis* isomer. It also makes possible interchange of CF_3 groups in the *trans-cis* and *cis-trans* isomers. However, the trigonal twist mechanism cannot account for the observed merging of all four $Al(tfac)_2(acac)$ resonances.

Experimental

Source of Reagents.—Commercial grade 2,4-pentanedione was distilled; the fraction boiling between 136 and 138° was used. The 1,1,1-trifluoro-2,4-pentanedione was used as received from Columbia Organic Chemicals Co., Inc. All other reagents were standard reagent grade chemicals and were used without further purification. It is to be emphasized that no great pains were taken to achieve maximum yields.

Preparation of $Co(tfac)_n(acac)_{3-n}$. A.—To 2.4 g. of $CoCO_3$ (0.02 mole) was added 4.6 g. of 2,4-pentanedione (0.046 mole) and 6.9 g. of 1,1,1-trifluoro-2,4-pentanedione (0.045 mole). To this slurry 10.2 ml. of 10% H_2O_2 was added dropwise with rapid stirring over a period of 5 min. The mixture was stirred for 0.5 hr. and the crude product of green crystals filtered off, washed with alcohol, and air dried (4.0 g.). After separation as described below the yield was $Co(acac)_3$, 0.11 g.; $Co(tfac)(acac)_2$, 2.27 g.; $Co(tfac)_2(acac)$, 0.75 g.; and $Co(tfac)_3$, 0.41 g., or 3.8, 67.1, 19.6, and 9.7 mole %, respectively; total 3.54 g. or 61% based on cobalt carbonate.

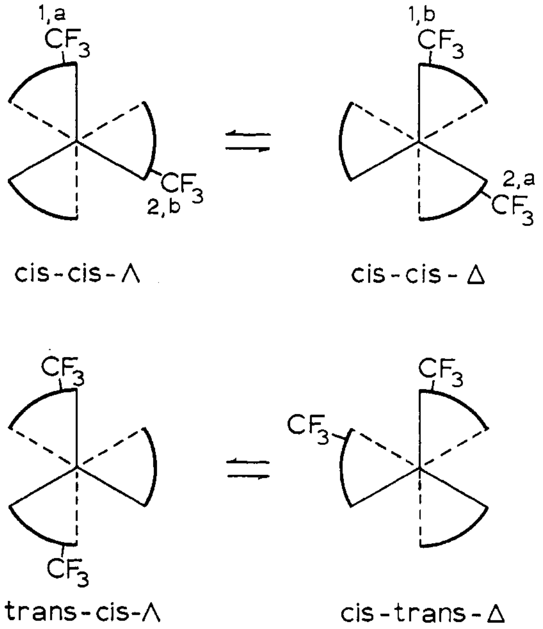


Fig. 5.—Exchange of CF_3 groups in $Al(tfac)_2(acac)$ complexes by the trigonal twist mechanism. Numbers label CF_3 groups and letters indicate environments.

B.—$Co(tfac)_3$ (3.82 g., 0.00738 mole) and 2,4-pentanedione (2.22 g., 0.0222 mole) dissolved in 40 ml. of $CHCl_3$ were heated in a sealed, degassed flask at 100° for 7 hr. Separation of the product mixture gave the following distribution of products: $Co(acac)_3$, 0.06 g.; $Co(tfac)(acac)_2$, 0.53 g.; $Co(tfac)_2(acac)$, 0.79 g.; and $Co(tfac)_3$, 1.91 g., or 2.5, 18.8, 24.8, and 53.8 mole %, respectively; total conversion, 42%; loss to decomposition, 9%.

Preparation of $Cr(tfac)_n(acac)_{3-n}$.—Anhydrous $CrCl_3$ (10 g., 0.063 mole) was converted to $Cr(acetone)_3Cl_3$.[9] To a slurry of the crude intermediate in acetone was added 1,1,1-trifluoro-2,4-pentanedione (26.3 g., 0.171 mole) and 2,4-pentanedione (8.5 g., 0.085 mole), both dissolved in 100 ml. of benzene. Vigorous reaction began immediately and the mixture turned deep green. The mixture was then heated under reflux for 1 hr., after which the condenser was removed and the acetone removed by distillation. During this process 200 ml. of benzene was added and the boiling continued until the solution temperature was constant at 78°. At this point the solution was deep maroon. Analysis of the product mixture as outlined below gave the following results: $Cr(acac)_3$, 0.80 g.; $Cr(tfac)(acac)_2$, 3.00 g.; $Cr(tfac)_2(acac)$, 14.66 g.; and $Cr(tfac)_3$, 1.52 g., or 5.1, 16.6, 71.6, and 6.7 mole %, respectively, a total of 18.98 g. or 70% based on $CrCl_3$.

Chromatography.—Procedures analogous to those described previously[2] were used. A specific example is offered as illustrative. The crude product $Co(tfac)_n(acac)_{3-n}$ (15.7 g.) was rapidly chromatographed on 0.75 lb. of acid-washed Al_2O_3 in pure benzene, then taken up in 100 ml. of benzene, and the solution was diluted with cyclohexane to 1500 ml. or 6.7% (by volume) benzene. This dilute solution was then placed on a 6.5 × 63 cm. Al_2O_3 column (1500 g. of Al_2O_3) and developed with 7% benzene in cyclohexane for 48 hr. at about a 14 ml./min. flow rate. After this development the separation of the five bands (see above) was quite distinct. The polarity of the solvent was then increased in 5% steps (500 ml./step) to 30% benzene as *trans*-$Co(tfac)_3$ began to come off. This polarity was maintained while the *trans*-$Co(tfac)_3$ was eluted. The *cis*-$Co(tfac)_3$ was

---

(6) W. G. Gehman, Ph.D. Thesis, Pennsylvania State University, University Park, Pa., 1954.

(7) L. Seiden, Ph.D. Thesis, Northwestern University, Evanston, Ill., 1957.

(8) J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **8**, 165 (1958).

(9) K. Taylor and C. E. Milstead, U. S. Patent 3,076,833; *Chem. Abstr.*, **59**, 3579e (1963).

Table IV

Analytical Data and Melting Points

Compound	Calcd., % C	Calcd., % H	Calcd., % M	Found, % C	Found, % H	Found, % M	M.p., °C.
trans-cis-Co(tfac)$_2$(acac)	38.80	3.23	12.70	39.00	3.78	12.88	141–143
cis-trans-Co(tfac)$_2$(acac)	38.80	3.23	12.70	38.55	3.20	12.37	140–142[a]
cis-cis-Co(tfac)$_2$(acac)	38.80	3.23	12.70				137–138[a]
Co(tfac)(acac)$_2$	43.90	4.39	14.40	43.67	4.36	14.11	158–160
trans-cis-Cr(tfac)$_2$(acac)	39.39	3.28	11.38	39.71	3.49	11.40	156–158
cis-trans-Cr(tfac)$_2$(acac)	39.39	3.28	11.38	39.34	3.39	11.28	131.2[a]
cis-cis-Cr(tfac)$_2$(acac)	39.39	3.28	11.38				121.3[a]
Cr(tfac)(acac)$_2$	44.66	4.47	12.90	44.51	4.47	13.19	151.5–153

[a] For substantially pure *cis-trans* or *cis-cis* isomer contaminated with some of the other isomer.

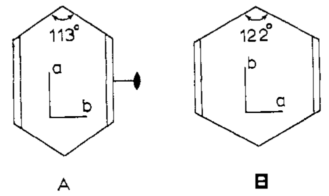


Fig. 6.—Crystals of M(tfac)$_2$(acac): A, *trans-cis* isomer; B, *cis-trans* and *cis-cis* isomers; with the electric vector parallel to *a* the color is purple (Cr) or green (Co), and with it parallel to *b*, red (Cr) or olive (Co).

eluted with 35% benzene, the *trans-cis*-Co(tfac)$_2$(acac) with 40%, and the *cis-trans*-and *cis-cis*-Co(tfac)$_2$(acac) with 50%. As the last of the *cis-cis* band was coming off the polarity was again increased in 10%/500 ml. increments to pure benzene. The Co(tfac)(acac)$_2$ was then eluted rapidly as the per cent of ether in benzene was increased by increments to 15%. The Co(acac)$_3$ was then stripped off with pure ether. The column operating time for this amount of sample is approximately 100 hr.

Some decomposition on the column invariably occurred in the chromium complex separations, especially for more lengthy chromatograms. Decomposition apparently was obviated in the separations of the cobalt complexes by protecting the column from light.

Crystal Morphology.—The crystals of the cobalt(III) and chromium(III) complexes were studied using a polarizing microscope with a Bertrand lens. The corresponding complexes of the two series for $n = 1$ and 2 are isomorphous as confirmed by X-ray powder patterns. The crystal morphology of the isomers of M(tfac)$_3$ has been reported previously.[2]

The M(tfac)(acac)$_2$ complexes crystallize as rhomboidal prisms which show symmetric extinction and biaxial interference figures. The dichroism is red (Cr) or olive (Co) with the electric vector parallel to the long prism axis and purple (Cr) or green (Co) with the electric vector perpendicular to this axis.

The crystals of the M(tfac)$_2$(acac) isomers are depicted in Fig. 6. The crystal of the *trans-cis* isomer, though superficially similar to that of the other two, is easily distinguished by its opposite dichroism and by the difference in interfacial angles. Microscopically the (apparently mixed) *cis-cis,cis-trans* crystal is indistinguishable from that of the *trans*-M(tfac)$_3$ complex.[2] Like the *trans*-M(tfac)$_3$ crystal, the mixed *cis-cis,cis-trans* crystal appears orthorhombic, whereas the *trans-cis*-M(tfac)$_2$(acac) and M(tfac)(acac)$_2$ crystals are apparently monoclinic.

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–Sherrer camera. The *d*-spacings and visually estimated intensities of the stronger lines of M(tfac)(acac)$_2$ and the isomers of M(tfac)$_2$(acac) for Co(III) and Cr(III) have been submitted to A.S.T.M.

Melting Points.—Melting points were obtained using a 6406-H Thomas–Hoover melting point apparatus and standard technique. Melting points and analytical data are given in Table IV.

N.m.r. Spectra and Equilibria in Solution.—The equipment and techniques used to obtain n.m.r. spectra and to study equilibria in solution have been described previously[2] with the following exception: in measuring the temperature dependence of the fluorine resonance chemical shifts as a function of temperature, pure 1,1,1-trifluoro-2,4-pentanedione contained in a capillary was used as an external standard. Previously we used *cis*-Rh(tfac)$_3$ as a standard. The rhodium compound has its resonance at −316.9 c.p.s. relative to trifluoroacetylacetone at 27.5°. Other commonly used pure liquid standards such as CFCl$_3$[10] have resonances several thousand cycles per second removed from those under investigation here.

Dipole Moments.—Dipole moments were evaluated from dielectric constant measurements on dilute benzene solutions. The solvent was purified by recrystallizing Merck reagent grade benzene twice, distilling the recrystallized material from P$_2$O$_5$ through a 3-ft. packed column, and storing the distillate sealed over fresh sodium wire for 1 month. The carefully rechromatographed samples, checked for purity by fluorine n.m.r., were recrystallized twice very slowly from reagent cyclohexane–absolute ether solution and dried *in vacuo*. The absence of isomerization was confirmed by n.m.r.

The dielectric constants were measured using a Wissenshaftlich-Technische Werkstatten Dipolemeter Type DMO 1 with Type DFL-2 cell (volume 4 ml.) (Kahl Scientific Instrument Corp., San Diego, California). The equipment was calibrated with nitrogen and benzene. The dielectric constant of nitrogen at 25° is 1.0005.[11] The dielectric constant of benzene at 20° $\epsilon_{20} = 2.2826 \pm 0.00002$ with $\Delta\epsilon/\Delta T = -0.00196$, and thus $\epsilon_{25} = 2.2728$.[12] The linearity of the scale was determined by measurement of the dielectric constant of pure, dry cyclohexane. The densities of the solutions and pure solvent were determined using a direct weighing pycnometer.[13]

The dielectric constant data were evaluated using the Halverstadt–Kumler equation.[14] The value of the electronic polarization of Co(acac)$_3$,[15] 99.4 cm.^{3}, was assumed to be modified in each case only by the constitutive corrections for replacement of the appropriate number of C–H groups by C–F groups. For example, using 1.70 and 1.83 cm.^{3}, respectively, for these bond polarizations,[16] we find P_E of Co(tfac)$_2$(acac) to be 100.2 cm.^{3}. It was also assumed that the atomic polarizations of all the members of the series would be practically the same, and the value of $P_A = 30.1$ cm.^{3} for Co(acac)$_3$[16] was used throughout.

Acknowledgments.—We are deeply grateful for the grant support of this research by the National Science Foundation. R. A. P. expresses gratitude for a fellowship from the Socony-Mobil Corporation. We thank

---

[10] G. Filipovitch and G. V. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

[11] A. A. Maryott and E. R. Smith, Table of Dielectric Constants of Pure Liquids, National Bureau of Standards Circular 514, Aug. 10, 1951.

[12] R. Mecke and K. Rosswog, *Z. Elektrochem.*, **60**, 47 (1956).

[13] M. R. Lipkin, J. A. Davidson, W. T. Harvey, and S. S. Kurtz, Jr., *Ind. Eng. Chem., Anal. Ed.*, **16**, 55 (1944).

[14] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

[15] A. E. Finn, G. C. Hampson, and L. E. Sutton, *J. Chem. Soc.*, 1255 (1938).

[16] Reference 4, p. 409.

Mr. O. W. Norton for assistance in taking the n.m.r. spectra; we thank Mr. J. Nemeth and the staff of our microanalytical laboratory for the microanalyses. We are indebted to Mr. James Ellern for the initial preparation and partial separation of the cobalt compounds described here.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF CLARK UNIVERSITY, WORCESTER, MASSACHUSETTS, AND ILLINOIS INSTITUTE OF TECHNOLOGY, CHICAGO 16, ILLINOIS

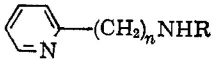
New Multidentate Ligands. I. Coordinating Tendencies of Polyamines Containing α-Pyridyl Groups with Divalent Metal Ions[1,2]

BY R. G. LACOSTE AND A. E. MARTELL[3]

Received February 10, 1964

The synthesis of several polyamines containing α-pyridyl groups is described. The compounds prepared are 2-aminomethylpyridine (AMP), N-hydroxyethyl(2-aminomethyl)pyridine (HEAMP), ethylenebis-α,α'-(2-aminomethyl)pyridine (EDAMP), 2-(2-aminoethyl)pyridine (AEP), and N-aminoethyl-2-(2-aminoethyl)pyridine (EAEP). The acid dissociation constants and the stability constants of the Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) chelates are reported. The results are compared with the chelating tendencies of analogous aliphatic polyamines.

The synthesis of polyamines containing pyridyl groups was undertaken as part of a general program of investigation of the relationship between chelating tendencies and the structure of the ligand. Although the stabilities of metal chelates of dipyridyl, ethylenediamine, and analogous aliphatic polyamines have been known for some time, the properties of chelating agents containing a combination of basic aliphatic and heterocyclic nitrogen atoms had not been reported at the time of completion of this work,[1] and very few compounds containing these groups correctly arranged for the formation of metal chelate rings have been synthesized. Since pyridine-2-aldehyde, which has recently become available, offers a convenient route for the synthesis of compounds of type I, it was decided to undertake a study of polyamines containing 2-aminoalkylpyridine groups. Of the possible compounds containing favorable arrangements of nitrogen atoms, 2-aminoethylpyridine[4,5] and 2-β-aminoethylpyridine[6] had been described in the literature. Subsequent to the completion of this work, Goldberg and Fernelius[7] reported the equilibrium constants and heats of reaction of metal ions with two of the ligands (AMP and AEP) described below.



I

Experimental

Ethylenebis-α,α'-(2-aminomethyl)pyridine (EDAMP).—An alcoholic solution containing 36 g. (0.15 mole) of bis(2-pyridinal)-ethylenediimine, prepared as described by Busch and Bailar,[8] and 1 g. of 10% Pd–C catalyst was reduced for 3 hr. in a Parr hydrogenation apparatus at 50 p.s.i. pressure and at room temperature. The catalyst was filtered off and the solvent was removed under vacuum at water-bath temperature. The viscous liquid which remained was distilled under 24 mm. of pressure in the range 130–135°. The yield of distilled product, a pale yellow oil, was 25 g., or 72% of the theoretical amount. It forms a crystalline tetrahydrochloride which melts at 208–208.5°.

Anal. Calcd. for $C_{14}H_{18}N_4\cdot 4HCl$: C, 43.52; H, 5.69; N, 14.50; mol. wt., 388. Found: C, 42.36; H, 6.05; N, 14.8; equiv. wt., 402.

2-Aminomethylpyridine (2-Picolylamine) (AMP).—Although now an article of commerce, 2-aminomethylpyridine was prepared by reduction of the corresponding Schiff's base as described for EDAMP. The product was isolated as the dihydrochloride.

Anal. Calcd. for $C_6H_8N_2\cdot 2HCl$: C, 40.00; H, 5.6; N, 15.6; mol. wt., 180. Found: C, 39.99; H, 6.8; N, 15.8; equiv. wt., 187.

N-Hydroxyethyl(2-aminomethyl)pyridine (HEAMP).—A mixture of 0.30 mole (18.3 g.) of monoethanolamine, dissolved in 150 ml. of absolute ethanol, and 32.1 g. (0.30 mole) of 2-pyridinecarboxaldehyde was heated on a steam bath for 15 min. To the cooled reaction mixture was added 1.0 g. of 10% Pd–C catalyst, and it was then reduced at room temperature and an initial pressure of 50 p.s.i. After 3 hr. the reduction was complete, and the catalyst and solvent were removed in the usual way. The residue, a viscous oil, was distilled under 18 mm. of pressure and the material which distilled over at 164–165° (with partial decomposition) was collected as the desired product. The yield of N-hydroxyethyl(2-aminomethyl)pyridine was 32 g., which represents 72% of the theoretical amount. The product is a viscous, pale yellow oil which forms a crystalline dihydrochloride having a melting point of 123–124°.

Anal. Calcd. for $C_8H_{12}ON_2\cdot 2HCl$: C, 42.86; H, 6.25; N, 12.50; mol. wt., 225. Found: C, 42.84; H, 6.72; N, 12.70; equiv. wt., 240.

N-Aminoethyl-2-(2-aminoethyl)pyridine (EAEP).—The addi-

---

(1) Abstracted from a dissertation submitted by R. G. Lacoste to the faculty of Clark University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1957.

(2) The authors express their appreciation to the Dow Chemical Company for a research grant in support of this work.

(3) Department of Chemistry, Illinois Institute of Technology, Chicago 16, Ill.

(4) R. Graf, *J. Prakt. Chem.*, **140**, 39 (1934).

(5) L. Craig and R. Hixon, *J. Am. Chem. Soc.*, **53**, 4367 (1931).

(6) F. K. Kirchner, J. R. McCormick, C. J. Cavallito, and L. C. Miller, *J. Org. Chem.*, **14**, 388 (1949).

(7) D. E. Goldberg and W. C. Fernelius, *J. Phys. Chem.*, **63**, 1246 (1959).

(8) D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **78**, 1137 (1956).