Stereochemical Rearrangements of Metal Tris-β-diketonates. I. Partial Resolution and Racemization of Some Tris(acetylacetonates)[1a]

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Abstract: Partial resolution of the tris(acetylacetonates) of Cr(III), Co(III), Ru(III), and Rh(III), and also the cis and trans isomers of cobalt(III) benzoylacetonate has been effected by column chromatography on D-(+)-lactose. An approximately tenfold increase in the degree of resolution was achieved by crystallization of racemate from benzene–hexane solutions of the partially resolved complexes. Rates of racemization of $Cr(acac)_3$ and $Co(acac)_3$ were studied polarimetrically in chlorobenzene solution in the temperature ranges 96–135° and 79–109°, respectively. Activation energies, frequency factors, and activation entropies are 34.9 ± 0.9 kcal/mol, $10^{14.74\pm0.51}$, and 7 ± 2 eu for $Cr(acac)_3$ and 34.8 ± 0.6 kcal/mol, $10^{16.38\pm0.36}$, and 14 ± 2 eu for $Co(acac)_3$. $Ru(acac)_3$ and $Rh(acac)_3$ are optically stable in chlorobenzene solution for 8 hr at 135° and 10 hr at 165°, respectively; more rigorous conditions resulted in thermal decomposition.

Although hundreds of papers have been published on the chemistry of metal tris-β-diketonates,[2] surprisingly little is known about the kinetics of racemization of these enantiomeric complexes. Several qualitative observations have been recorded. Moeller and Gulyas[3] have reported that racemization of chromium(III) acetylacetonate, $Cr(acac)_3$,[4] in 1:1 *n*-hexane–benzene is 50% complete at ~25° in ~8 days. $Co(acac)_3$ is reported to be optically stable at room temperature for at least 2 days in 1:1 petroleum ether–benzene[3] and for more than 5 weeks in chloroform solution in the absence of sunlight,[5,6] but this complex loses ~30% of its optical activity upon sublimination at 110°.[5,6] One can infer that the acetylacetonates of Fe(III), Ga(III), and In(III) racemize rapidly since attempts to partially resolve these complexes by an established method have been unsuccessful.[3] Only for *cis*-$Cr(bzac)_3$ have quantitative data been published; rate constants for inversion in 1,1,2,2-tetrachloroethane are 0.0023 min^{-1} at 95.5° and 0.009 min^{-1} at 105.0°.[7]

The paucity of kinetic data for racemization of tris-β-diketonates is doubtless due to the difficulty and tedium involved in resolving electrically neutral, inner complexes. Nevertheless, such complexes can be partially resolved by a variety of techniques,[3,5–13] and recently Collman and Sun[14] have achieved complete resolution of $Co(acac)_3$ by a combination of repeated chromatography on *d*-lactose and repeated crystallization. We also have found that the crystallization of racemate from solutions of partially resolved complexes can be employed to markedly improve the degree of resolution. The present paper describes the application of this technique in the partial resolution of several tris-β-diketonates including $Ru(acac)_3$ and *cis*- and *trans*-$Co(bzac)_3$, which have been resolved for the first time, and presents quantitative kinetic data for racemization of $Cr(acac)_3$ and $Co(acac)_3$. Subsequent papers in this series will deal with the kinetics of (1) inversion, cis–trans isomerization, and ligand-exchange reactions of $Co(bzac)_3$ and (2) racemization, linkage isomerization, and ligand-exchange reactions of deuterioacetyl-substituted cobalt(III) acetylacetonates.

Experimental Section

Preparation of Complexes. The tris(acetylacetonates) of Cr(III), Mn(III), Co(III), Mo(III), and Rh(III) were prepared by standard methods.[15–19] $Ru(acac)_3$ was synthesized as described by Wilkinson,[20] mp 237–238°. $Co(bzac)_3$ was prepared by reaction of benzoylacetone with $Na_3[Co(CO_3)_3]\cdot 3H_2O$[17] and was separated into the cis and trans isomers[21] by column chromatography on Florisil.[22] The same method was employed for synthesis and separation of *cis*- and *trans*-$Co(tmb)_3$. *Anal.* Calcd for $Co(C_{11}H_8F_3O_3)_3$: C, 49.89; H, 3.04; Co, 7.42. Found for the cis isomer (last eluted): C, 50.04; H, 3.36; Co, 7.32; mp, 182–184°. Found for trans isomer (first eluted): C, 50.13; H, 3.16; Co, 7.15; mp, 141–143°. The purity of the isomers was verified by ^{19}F nmr spectroscopy.

The ligand 1,1,1-trifluoro-4-*p*-methoxyphenyl-2,4-butanedione, Htmb, was prepared by Claisen condensation of ethyl trifluoroacetate with *p*-methoxyacetophenone using a procedure similar to that described by Reid and Calvin.[23] Recrystallization from 95% ethanol afforded large, colorless crystals: yield, 81% of the theoretical; mp, 57.5–58° (lit.[24] 57–58°). *Anal.* Calcd for $C_{11}H_9$-

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[1] (a) Abstracted in part from the Ph.D. thesis of Amal Y. Girgis, Cornell University, Jan 1970; (b) American Association of University Women Predoctoral Fellow, 1968–1969.

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[4] The following abbreviations will be used in this paper for β-diketonate anions: acac, acetylacetonate; bzac, benzoylacetonate; tmb, 1,1,1-trifluoro-4-*p*-methoxyphenyl-2,4-butanedionate.

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Table I. Chromatographic Data for Partial Resolution of Some Metal Diketonates on a D-(+)-Lactose Column[a]

Complex	Quantity, g	Breakthrough, hr	Elution time, hr
Cr(acac)$_3$	0.10	26.5	33.0
Mn(acac)$_3$	0.10	27.9	36.0
Ru(acac)$_3$	0.05, 0.10	27.0	35.9
Rh(acac)$_3$	0.10	26.3	33.8
cis-Co(bzac)$_3$	0.11	26.9	35.7
trans-Co(bzac)$_3$	0.10	26.7	36.6
cis-Co(tmb)$_3$	0.05	26.0	35.7

		First-eluted fraction before crystallization			Second-eluted fraction before crystallization		
Complex	λ, mμ	Concn × 10^3, mol/l.	Obsd rotation, deg	Molecular rotation[b]	Concn × 10^3, mol/l.	Obsd rotation, deg	Molecular rotation[b]
Cr(acac)$_3$	578	5.12	+0.064	+630 (+230)[c] (+89)[d]	5.23	−0.041	−390 (−120)[c]
Mn(acac)$_3$	436, 546, 578		0.000	0		0.000	0
Ru(acac)$_3$	589	1.02	−0.005	−250	3.82	+0.044	+580
Rh(acac)$_3$	436	2.48	−0.033	−670 (−83)[e]	3.86	+0.075	+970 (+99)[d] (+67)[e]
cis-Co(bzac)$_3$	546	2.91	−0.035	−600	2.72	+0.050	+900
trans-Co(bzac)$_3$	546	2.66	−0.018	−340	2.45	+0.021	+430
cis-Co(tmb)$_3$	546		0.000	0		0.000	0

		First-eluted fraction after one crystallization			Second-eluted fraction after one crystallization		
Complex	λ, mμ	Concn × 10^3, mol/l.	Obsd rotation, deg	Molecular rotation	Concn × 10^3, mol/l.	Obsd rotation, deg	Molecular rotation
Cr(acac)$_3$	578	6.74	+0.485	+3,600	6.26	−0.656	−5,240
Ru(acac)$_3$	589	0.659	−0.025	−1,900	1.03	+0.043	+2,090
Rh(acac)$_3$	436	1.69	−0.250	−7,370	3.11	+0.563	+9,050
cis-Co(bzac)$_3$	546	3.42	−0.373	−5,450	3.42	+1.057	+15,500
trans-Co(bzac)$_3$	546	3.44	−0.216	−3,140	3.33	+0.410	+6,160

[a] Rotations were measured at room temperature with a 2-cm polarimeter cell. [b] Specific rotation times molecular weight divided by 100; literature values are listed in parentheses. [c] Reference 3. [d] Reference 13. [e] Reference 6.

F$_3$O$_3$: C, 53.68; H, 3.68; F, 23.14. Found: C, 53.49; H, 3.75; F, 22.89.

Partial Resolution of Optical Isomers. D-(+)-Lactose (Baker Analyzed reagent) was dried for 48 hr at 110° and then sieved to 100 mesh. A 230 × 3.9 cm o.d. chromatographic column which narrowed to 3.0 cm at the midpoint was packed by a modification of the procedure of Collman, *et al.*[6] The lactose (~4 lb) was added in ~50 g quantities as a slurry in hexane, and periodic vibration, from an electric vibrator attached to the top of the column (rather than pressure), was employed to achieve very tight packing. When the column was filled, the vibrator was allowed to run for an additional 12–15 hr. The free volume of the column was ~550 ml.

The complex to be resolved (generally 0.10 g), dissolved in 5 ml of benzene, was placed on the column and eluted with 1:1 (v/v) benzene–hexane at a flow rate of 0.3–0.4 ml/min. The optical rotation of the eluent was monitored by polarimetric observation of portions of the solution, and the positive- and negative-rotating fractions were collected separately. Typical results are set out in the upper part of Table I. After the solvent was removed by blowing air over the solution, further concentration of the enantiomer in excess was effected by dissolving the residue in a minimum of warm benzene (~50°), adding one to four times the volume of hexane, and allowing the solution to stand in the refrigerator. This resulted in crystallization of roughly 90% of the complex as racemic crystals and gave an approximately tenfold enhancement in the molecular rotation of the material left in solution. This enhancement is shown in the lower part of Table I. In order to obtain an adequate supply of optically active material for racemization studies, it is convenient to combine fractions having the same sign of rotation from several separate chromatograms before applying the crystallization technique. Finally, the optically active solution is evaporated to dryness by blowing air over it, and the partially resolved complex is stored as a solid.

For Cr(acac)$_3$, Co(acac)$_3$, and *cis*- and *trans*-Co(bzac)$_3$ the first-eluted fractions show a dominant positive Cotton effect in the region of the lowest energy, spin-allowed d–d transition. The first-eluted fractions for Ru(acac)$_3$ and Rh(acac)$_3$ appear to exhibit a negative Cotton effect at long wavelength; however, in these cases it is doubtful that the dominant features of the ORD curves arise from d–d transitions. ORD curves for *partially* resolved samples of Cr(acac)$_3$, Ru(acac)$_3$, and Rh(acac)$_3$ are presented in Figures 1–3.

Preparation of Solutions for Kinetic Runs. Rates of racemization were measured in freshly distilled, degassed chlorobenzene (Matheson Coleman and Bell, reagent grade) which had been dried by refluxing for at least 12 hr over calcium hydride. Because many metal diketonates undergo oxidative decomposition at elevated temperatures,[25] solutions were prepared in an all-glass vacuum system (5 × 10^{-4} Torr) in order to exclude air. We find that solutions of Co(III) diketonates which have been heated in the presence of air exhibit broadened nmr lines, owing presumably to decomposition to Co(II)-containing species.

The optically active complex (~20 mg) was dissolved in chloroform, placed on a 10 × 0.7 cm o.d. column of Florisil to remove any impurities, and eluted with chloroform. The solution was then distributed among four to eight polarimeter cells (2 or 5 cm long, 1-cm o.d., Opticell) which were equipped with a side arm having a $^{14}/_{35}$ standard-taper joint. The cells were in turn attached to the vacuum system, the chloroform was removed under reduced pressure, and degassed chlorobenzene was distilled in. The cells were then sealed under vacuum and the concentration of the solutions was determined spectrophotometrically.

Rates of Racemization. The rates of racemization of Cr(acac)$_3$ and Co(acac)$_3$ were determined in the temperature range 96–135° and 79–109°, respectively, using a Perkin-Elmer 141 polarimeter. Two methods were employed for thermostating the solutions. (1) For the Cr(acac)$_3$ runs and the lower temperature Co(acac)$_3$ runs, the polarimeter cell was totally immersed in a constant-temperature bath (±0.1° up to 116°, ±0.2° at 126°, ±0.3° at 135°) and was removed periodically for rotation measurements; the reaction was quenched by plunging the cell into cold water. Optical activity due to strain in the cell windows was avoided by allowing the cells to stand at room temperature for ~1 hr before rotations were recorded. Time intervals were corrected for an experimentally determined warm-up time of 0.55 min.[26] In the

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(26) The warm-up time is defined as the time which must be subtracted from experimental heating times in order to correct for the fact that

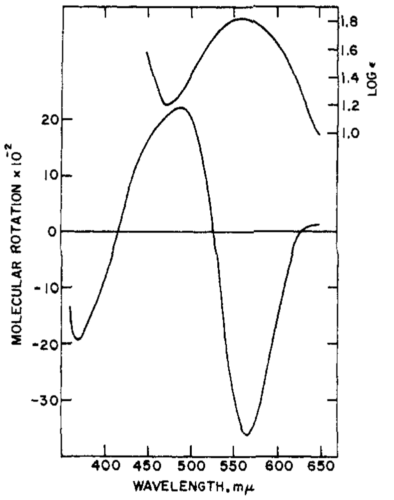

Figure 1. Absorption spectrum and optical rotatory dispersion curve for $Cr(acac)_3$ in chloroform solution, last-eluted fraction from lactose.

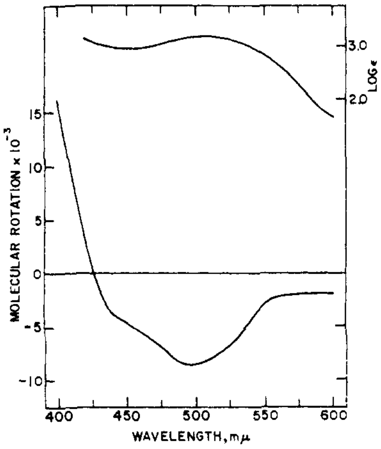

Figure 2. Absorption spectrum and optical rotatory dispersion curve for $Ru(acac)_3$ in chloroform solution, first-eluted fraction from lactose.

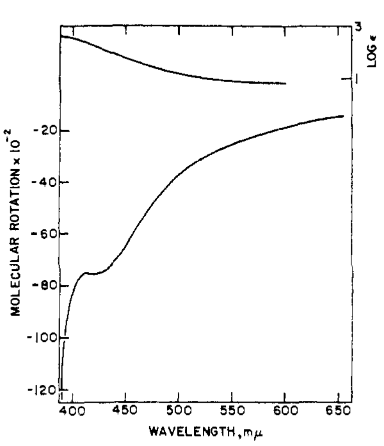

Figure 3. Absorption spectrum and optical rotatory dispersion curve for $Rh(acac)_3$ in chloroform solution, first-eluted fraction from lactose.

higher temperature $Cr(acac)_3$ runs, several cells were used to minimize the error due to experimental uncertainty in the warm-up time; the minimum heating time per cell between kinetic points was 15 min. (2) For the higher temperature $Co(acac)_3$ runs, the cell was surrounded by a brass holder through which was circulated water or oil from a constant-temperature bath. The brass holder was housed directly in the sample compartment of the polarimeter, which eliminated the need for a warm-up correction. After each run the cell was opened and the temperature was measured by inserting a thermocouple into the solution. Exposure of the solution to the light beam was varied from continuous exposure to exposure only during readings (~20 sec); the exposure time had no effect on the racemization rates. Kinetic runs were continued for at least 2.5 half-lives. Rotations were measured to $\pm 0.003°$ at 578 and 546 mμ for $Cr(acac)_3$ and at 546 mμ for $Co(acac)_3$. Initial rotations were generally ~0.2 to 0.5°. The visible spectrum of solutions was recorded before and after kinetic runs in order to verify that no appreciable decomposition had occurred; ordinarily absorbance changes were less than 2%.

Essentially the same procedure was used to investigate the optical stability of $Ru(acac)_3$ and $Rh(acac)_3$ in chlorobenzene. Rotations were measured at 589 and 436 mμ, respectively.

Results and Discussion

Partial Resolution of Optical Isomers. Partial resolution of the tris(acetylacetonates) of Cr(III), Co(III), Ru(III), and Rh(III) and the *cis* and *trans* isomers of cobalt(III) benzoylacetonate has been effected by column chromatography on D-(+)-lactose. Typical results are presented in Table I. After chromatography, an approximately tenfold increase in the degree of resolution was achieved by crystallization of the less soluble racemate from a benzene–hexane solution of the partially resolved complex (*cf.* Table I). This approach is based on the observations of Collman, *et al.*,[5,6] who found that slow, stepwise crystallization of partially resolved $Co(acac)_3$ from benzene–hexane resulted in a series of increases in the molecular rotation of the filtrates. In fact, Collman and Sun[14] have recently employed repeated crystallization and repeated chromatography to effect complete resolution of $Co(acac)_3$; molecular rotations at 546 mμ for the dextro and levo enantiomers were +29,070 and −28,920. The molecular rotations obtained in the present work after one crystallization are much larger than previously published values for $Cr(acac)_3$ and $Rh(acac)_3$[3,6,13] but still smaller than the molecular rotation of completely resolved $Co(acac)_3$.[14] The largest molecular rotation, +15,500 for *cis*-$Co(bzac)_3$ (Table I), corresponds to ~50% resolution if one assumes that $Co(acac)_3$ and *cis*-$Co(bzac)_3$ have comparable molecular rotations at 546 mμ. Repeated crystallization of partially resolved *cis*-$Co(bzac)_3$ gave molecular rotations as large as −23,400 and +19,300 (after the third crystallization). In no case, however, was complete resolution achieved.

Attempts to resolve $Mn(acac)_3$ and the fluorine-containing chelate, *cis*-$Co(tmb)_3$ (**1**), on the same lactose column were unsuccessful. Failure to resolve $Mn(acac)_3$ is almost certainly due to rapid racemization at room temperature. Lack of resolution for the kinetically inert *cis*-$Co(tmb)_3$ seems to be associated with

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thermal equilibrium is not attained immediately upon immersing the cell in the bath. The following procedure was used to estimate the warm-up time. Uncorrected rate constants k_u were first determined assuming that the solution reaches thermal equilibrium immediately. In a separate series of experiments the actual solution temperature was followed as a function of time until thermal equilibrium was attained. Temperature was measured continuously with a thermocouple which was immersed in the solution and connected to a millivolt recorder. An average value of the rate constant for the warm-up period was calculated from the equation $\bar{k} = \Sigma_i \Delta t_i k_{iu}/t$, where $\bar{k}$ is the average rate constant over the time t needed to reach thermal equilibrium, Δt_i is a small time interval during which the average temperature is T_i, and k_{iu} is the uncorrected rate constant at temperature T_i (k_{iu} being determined from a plot of log k_u *vs.* $1/T$). The warm-up time was then calculated from the expression $t(k_u - \bar{k}_u)$. The warm-up times (~0.55 min) were nearly independent of the temperature of the kinetic run.

Table II. Rate Constants for Inversion of Cr(acac)$_3$ and Co(acac)$_3$ in Chlorobenzene Solution

Cr(acac)$_3$			Co(acac)$_3$		
Temp, °C	Concn × 10^3, mol/l.	k × 10^5,[a] sec^{-1}	Temp, °C	Concn × 10^3, mole/l.	k × 10^5, sec^{-1}
96.1	1.20	0.134 ± 0.002[b]	78.8	1.2	0.650 ± 0.009[b]
	2.68	0.127 ± 0.005		3.3	0.641 ± 0.009
116.0	1.14	1.48 ± 0.04	85.0	5.5	1.44 ± 0.04
	3.03	1.42 ± 0.04	88.5	3.8	2.32 ± 0.04
126.1	1.07, 3.30[c]	4.44 ± 0.31		3.9	2.43 ± 0.07
	1.62, 9.90[c]	4.29 ± 0.32	88.8	2.0	2.65 ± 0.04
135.0	1.07, 1.25, 2.89[c]	12.2 ± 0.5		5.4	2.53 ± 0.05
	1.66, 1.69, 4.47[c]	13.0 ± 1.1	98.2	1.1	8.06 ± 0.05
			99.8	2.5	10.3 ± 0.5
				6.4	10.6 ± 0.3
			103.9	3.1	16.6 ± 0.4
			108.9	2.1	33.3 ± 0.7
				9.8	33.2 ± 0.4

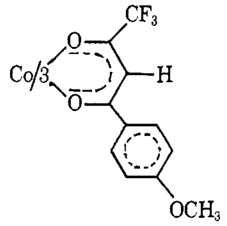
[a] These data were obtained from rotations measured at 578 mμ. Rate constants determined at 546 mμ were in satisfactory agreement with those measured at 578 mμ, but experimental errors were larger because of the smaller molecular rotation at 546 mμ. [b] All errors are estimated at the 95% confidence level. [c] More than one solution was used in these runs in order to keep the heating intervals for a given solution ≥15–20 min.

Table III. Kinetic Data for Inversion of M(acac)$_3$ in Chlorobenzene Solution

Compound	Temp, °C	k × 10^5, sec^{-1}	E_a, kcal/mol	Log A	ΔS^*, eu
Cr(acac)$_3$	98.2	0.17[a]	34.9 ± 0.9	14.74 ± 0.51	7 ± 2
Co(acac)$_3$	98.2	8.06[b]	34.8 ± 0.6	16.38 ± 0.34	14 ± 2
Ru(acac)$_3$	135.0	<0.30	>39.2		
Rh(acac)$_3$	165.0	<0.24	>42.3		

[a] Calculated from $\ln k = \ln A - E_a/RT$. [b] Experimental value.

the presence of CF$_3$ groups, since previous attempts to resolve cobalt(III) trifluoroacetylacetonate were similarly unsuccessful.[7] This is unfortunate because tris chelates containing unsymmetrical, fluorinated ligands are prime candidates for mechanistic studies of racemization and geometrical isomerization; rather precise kinetic data for isomerization can be obtained from the fluorine nmr spectra.[7]



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An attempt to resolve Mo(acac)$_3$ failed because of oxidation on the column. This complex is expected to be kinetically inert, and its resolution should be possible if precautions are taken to exclude air.

Rates of Racemization. Rate constants, k, for inversion[27] of Cr(acac)$_3$ and Co(acac)$_3$ in chlorobenzene solution are presented in Table II. Rate constants were obtained from the slopes of least-squares plots of log α *vs.* time. First-order kinetics is indicated by the linearity of these plots and also by the concentration independence of the rate constants. The Arrhenius activation energy, E_a, and frequency factor, A, were evaluated from the log k *vs.* $1/T$ plots presented in Figure 4, and the activation entropy, ΔS^*, extrapolated to 25°, was calculated from the relation

$$\Delta S^* = R[\ln A - \ln (RT/Nh)] - R$$

The activation parameters are given in Table III along with rate constants at a common temperature. All errors in Tables II and III are estimated at the 95% confidence level, which corresponds to 2.1–2.4 standard deviations, depending on the number of data points.

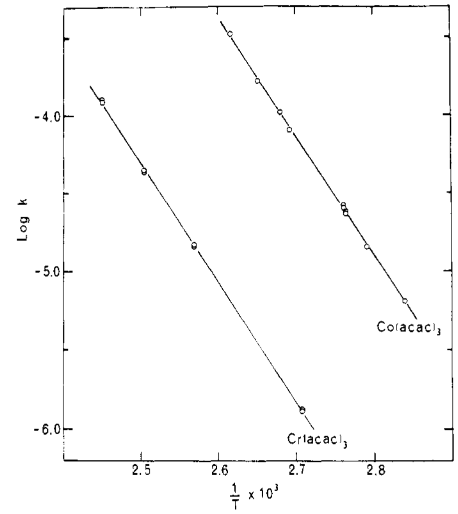

Figure 4. Arrhenius plots for inversion of Cr(acac)$_3$ and Co(acac)$_3$.

The activation parameters in Table III indicate that Cr(acac)$_3$ and Co(acac)$_3$ are considerably more inert with respect to racemization than might have been anticipated on the basis of earlier qualitative observations.[3] The extrapolated rate constants for inversion at 25° are 1.6 × 10^{-11} and 8.1 × 10^{-10} sec^{-1}, respectively, which correspond to half-lives for loss of optical activity of 700 and 14 years, respectively. It is note-

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(27) The rate of inversion is the rate at which the enantiomers are interconverted and one-half times the rate of loss of optical activity.

worthy that the cobalt complex is the more labile, owing to a more favorable activation entropy; the activation energies are identical within experimental uncertainty. These results are not expected on the basis of the simple crystal-field theory,[28] which predicts a higher activation energy for the cobalt complex, and they are in contrast with the generally observed lability order, Cr(III) > Co(III).[28] For the tris(oxalates), for example, the rate of racemization at 18° in aqueous solution is 20 times faster, and the activation energy 10 kcal lower, for the chromium complex.[29]

As expected, the complexes of the elements of the second transition series proved to be even more inert. A chlorobenzene solution of $Ru(acac)_3$ which had a rotation of 0.200° at 589 mμ showed no loss of optical activity after heating for 8 hr at each of the following temperatures: 96.1, 116.0, 126.0, and 135.0°. Slow loss of activity was observed at 165°; however, rate constants measured at this temperature were not reproducible, and absorption spectra and column chromatography indicated thermal decomposition. A chlorobenzene solution of $Rh(acac)_3$ (0.325° at 436 mμ) was optically stable for 10 hr at 165°. After 15 hr at 165° a decrease in rotation was observed, but again, this resulted from thermal decomposition rather than racemization. From the above qualitative observations and an assumed log A of 15.56, the average of the values found for $Cr(acac)_3$ and $Co(acac)_3$, one can estimate maximum rate constants and minimum activation energies for $Ru(acac)_3$ and $Rh(acac)_3$. These estimates are collected in Table III.

Acknowledgments. The support of this research by National Science Foundation Grant No. GP-16280 is gratefully acknowledged. A. G. wishes to thank the American Association of University Women for a fellowship. We also thank Professor J. P. Collman for a copy of part of the thesis cited in ref 14.

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