Stereochemical Rearrangements of Metal Tris-β-diketonates. II. Kinetics and Mechanism of Geometrical Isomerization, Optical Inversion, and Ligand-Exchange Reactions of Cobalt(III) Benzoylacetonate[1a]

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Abstract: The cis and trans isomers of cobalt(III) benzoylacetonate, $Co(bzac)_3$, have been separated by column chromatography on Florisil and have been partially resolved by chromatography on D-(+)-lactose. The degree of resolution was substantially increased by crystallization of racemate from benzene–hexane solutions of the partially resolved complexes, but complete resolution was not achieved. Rate constants and equilibrium constants for geometrical isomerization in chlorobenzene (56.0–104.6°) and in benzene, chloroform, acetone, and acetonitrile at 95.8° were determined from the methyl region of the proton nmr spectrum. Rates of optical inversion of the cis and trans isomers in chlorobenzene (56.0–96.1°) were measured by polarimetry. All reactions were found to be first order. The rates of isomerization and inversion of the cis isomer are nearly equal, and isomerization occurs predominantly with inversion of configuration. Inversion rates for the cis and trans isomers are equal within experimental uncertainty. Activation energies (kcal/mol) and activation entropies (eu), respectively, are 32.7 ± 0.5 and 11.0 ± 1.3 for cis-to-trans isomerization, 32.7 ± 0.6 and 8.8 ± 1.8 for trans-to-cis isomerization, 32.9 ± 0.7 and 11.9 ± 2.0 for inversion of the cis isomer, and 32.3 ± 0.9 and 10.0 ± 2.6 for inversion of the trans isomer. Equilibrium constants for trans-to-cis isomerization in chlorobenzene are ~0.37 and are temperature independent; the isomerization enthalpy and entropy are −0.17 ± 0.33 kcal/mol and −2.5 ± 0.9 eu, respectively. The variation in isomerization rates on changing the solvent is only a factor of 2, and the variation is not related to the dielectric constant of the solvent. Rates of ligand exchange between $Co(bzac)_3$ and $Co(bzac\text{-}d_4)_3$ in chlorobenzene (96.1–126.1°) were measured by mass spectrometry and were found to be ~300 times slower than rates of isomerization and inversion; the activation energy and entropy for ligand exchange are 48 ± 4 kcal/mol and 40 ± 10 eu, respectively. The isomerization and inversion reactions have been characterized by six microscopic rate constants, and the relative values of these rate constants have been examined in relation to the more probable rearrangement mechanisms. The following conclusions have been made. (1) Isomerization and inversion occur primarily by a common, intramolecular mechanism. (2) The trigonal-twist mechanism and bond rupture to give (a) an equatorial trigonal-bipyramidal intermediate (dangling ligand equatorial) or (b) a square-pyramidal intermediate having a cis arrangement of bzac ligands can be ruled out as the primary rearrangement path. (3) The most probable paths are (a) a twist mechanism involving ~80% rhombic twist and ~20% trigonal twist or (b) bond rupture to give ~80% axial trigonal-bipyramidal intermediates (dangling ligand axial) and ~20% square-pyramidal intermediates. The bond-rupture mechanism is favored by the activation parameters.

The mechanism of stereochemical rearrangements of metal chelates is a subject of considerable interest and importance. Both intermolecular and intramolecular mechanisms have been suggested for rearrangements of complexes containing three bidentate ligands. The proposed mechanisms include (1) the complete dissociation of one ligand to give a four-coordinate intermediate (intermolecular),[2] (2) rupture of one metal–ligand bond to give a five-coordinate intermediate (intramolecular),[3] and (3) intramolecular twisting processes,[4–10] which effect rearrangement without cleavage of any metal–ligand bonds. The proposed twisting mechanisms generate trigonal (near-D_{3h}) or rhombic (near-C_{2v}) transition states; these mechanisms are referred to herein as the trigonal and rhombic twists, respectively.

Within the past few years, a number of nmr studies of stereochemical rearrangements of octahedral metal β-diketonates have been reported.[6,8,11–17] Rearrangements of group III,[6,8,11–17] titanium(IV),[12,14,16] and tin(IV)[13] complexes appear to proceed by an intramolecular mechanism. For cobalt(III) diketonates, however, intermolecular mechanisms have not yet been excluded. Pertinent are the results of Collman and Sun,[18] who found that linkage isomerization of formyl-substituted cobalt acetylacetonates is accompanied by extensive ligand exchange.

The limited evidence presently available tends to favor a one-bond rupture mechanism for intramolecular rearrangements of metal diketonates. The trigonal-

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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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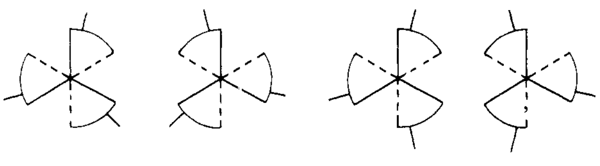
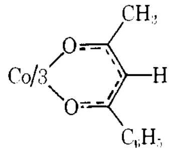
twist mechanism has been definitely eliminated as the sole reaction path for geometrical isomerization of $Cr(bzac)_3$, $Al(tfac)_3$, and $Ga(tfac)_3$,[19] and the solvent dependence of the nmr coalescence temperature suggests charge separation in the transition state, and hence a bond-rupture process, for isomerization of $Al(tfac)_3$.[6] It has also been possible to rule out certain twisting mechanisms for rearrangements of the dihalo bis(chelate) complexes, $Ti(bzac)_2X_2$.[15] On the other hand, Bradley and Holloway[12] have cited evidence in support of a twisting process for rearrangements of the related dialkoxy compounds, $Ti(acac)_2(OR)_2$.

A promising approach[6,20] to the mechanism problem for rearrangements of tris chelates involves comparison of rates of optical inversion and geometrical isomerization for complexes which contain three unsymmetrical bidentate ligands. Complexes of this type can exist as dissymmetric cis and trans isomers[21-24]



cis-Δ[25] cis-Λ trans-Δ trans-Λ

and the relative rates of optical inversion and cis–trans isomerization of these isomers depend on the mechanism of the rearrangement.[6] For example, if one begins with a partially resolved cis isomer, the trigonal-twist mechanism gives inversion without geometrical isomerization, the rhombic twist effects simultaneous inversion and isomerization, and a one-bond rupture mechanism involving a trigonal-bipyramidal intermediate predicts simultaneous inversion and isomerization if the dangling ligand occupies an axial position, but isomerization without inversion if the dangling ligand occupies an equatorial position. Thus, one should be able to at least eliminate certain of the possible reaction paths by kinetic study of a suitable tris-chelate system. For this purpose, we have chosen the "inert," diamagnetic complex $Co(bzac)_3$ (**1**), which gives well-resolved methyl



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proton resonances for the cis and trans isomers in chlorobenzene solution. The relative intensities of the methyl resonances have been employed to determine rates and activation parameters for geometrical isomerization; analogous data for optical inversion have been obtained by polarimetry. In order to assess the importance of an intermolecular mechanism, the kinetics of ligand exchange between $Co(bzac)_3$ and $Co(bzac\text{-}d_4)_3$ have been studied by mass spectrometry.

Experimental Section

Preparation of $Co(bzac)_3$ and $Co(bzac\text{-}d_4)_3$. Benzoylacetone was deuterated by refluxing a solution of 8 g of the diketone (Eastman Organic Chemicals) and 0.5 g of potassium carbonate in 50 ml of 1:1 (v/v) dioxane–D_2O.[26] During reflux, the system was protected from atmospheric water vapor with an oil bubbler. After a reflux time of ~48 hr, the diketone was extracted with six 40-ml portions of anhydrous ether. The ether was vacuum distilled, and the diketone was recycled using fresh D_2O. This procedure was repeated eight times. The resulting dark brown oil was extracted with hexane, the hexane was pumped off, and the benzoylacetone-d_5 (1.0 g, 12%) was purified by sublimation; mp 55–57°. *Anal.* Calcd for $C_{10}H_5D_5O_2$: C, 71.85; H and D, 8.98. Found: C, 71.90; H and D, 8.82. Nmr analysis after each exchange cycle indicated rapid exchange at the γ-carbon atom but slow exchange at the methyl carbon; a total heating time of ~385 hr was required to achieve 97% deuteration. The nmr spectrum of the final product showed 2% hydrogen on the γ carbon and 3% hydrogen on the methyl carbon.

$Co(bzac)_3$ was prepared as described by Bauer and Drinkard.[27] Using an analogous procedure, $Co(bzac\text{-}d_4)_3$ was synthesized by reaction of benzoylacetone-d_5 and D_3PO_4 with freshly prepared $Na_3[Co(CO_3)_3]\cdot 3H_2O$ in 1:1 (v/v) acetone–D_2O. The complex was isolated by extraction with ether and was purified by column chromatography on deuterated alumina (7% by weight D_2O) followed by recrystallization from benzene–hexane; mp 193–194°. The nmr spectrum (CCl_4 solution) indicated that the complex contained 12% hydrogen on the γ-carbon atom and 3% hydrogen on the methyl carbon.

Separation of Geometrical Isomers. Complete separation of *cis*- and *trans*-$Co(bzac)_3$ was effected by chromatography on Florisil. A 125 × 2.8 cm o.d. Pyrex column, equipped with an electric vibrator, was packed to a height of 84 cm with ~180 g of Florisil (200 mesh, Florodin Co.). The Florisil was added in portions as a thick slurry in hexane. After each addition, the column was allowed to drain with continuous vibration in order to achieve even settling and tight packing. The complex (0.50 g) was applied to the column in a minimum of 1:1 (v/v) benzene–hexane and was eluted with 19:1 (v/v) benzene–ether at a flow rate of 2 ml/min. Separation of the cis and trans bands was generally observed when the front of the first band (trans) was less than halfway down the column; the separation of the bands increased during the course of the chromatogram to a maximum of ~5 cm between the tail of the trans band and front of the cis band. After the first band was eluted, the flow rate was increased to 8 ml/min. In order to obtain an adequate supply of material for isomerization studies, fractions of the same isomer from several separate chromatograms were combined, passed through the column once again, and finally recrystallized from benzene–hexane. The purity of the isomers was verified by their melting points (Table I) and by their proton nmr spectra (Table II).

The above procedure is superior to an earlier method[21] using alumina, which gave only partial separation, and it is of considerable generality. It has been applied to achieve complete separation of the cis and trans isomers of $M(bzac)_3$, $M(tmb)_3$, and $M(tfac)_3$ (M = Co and Cr); optimum conditions and chromatographic data are presented in Table I. Experiments at eluent flow rates of 2 and 5–6 ml/min indicated that the more reproducible and sharper separations were obtained at 2 ml/min; faster flow rates gave more diffuse bands. The optimum eluent polarity is independent of the metal but depends on the ligand, since adsorption on Florisil increases in the order $M(tfac)_3 < M(tmb)_3 < M(bzac)_3$. In every case the elution order is trans > cis, the same as that observed previously for chromatography on alumina.[21,22] If the complexes are first purified by passing them through a short Florisil column, the 84 × 2.8 cm column can be reused repeatedly. In order to achieve a narrow, sharp band at the start of the next chromatogram, 50 ml of hexane was passed through the column before the next sample was applied.

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(19) The following abbreviations will be used in this paper for β-diketonate anions: acac acetylacetonate; bzac, benzoylacetonate; tfac, trifluoroacetylacetonate; tmb, 1,1,1-trifluoro-4-*p*-methoxyphenyl-2,4-butanedionate; triac, triacetylmethanate.

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Table I. Optimum Conditions and Chromatographic Data for Separation of Geometrical Isomers[a]

Compound	Quantity taken, g	Eluent	Maximum separation between bands, cm	Break-through, hr	Total elution, hr	% re-covered	% cis	Mp, °C[b] Cis	Mp, °C[b] Trans
$Co(bzac)_3$	0.50[c]	19:1 benzene–ether	5	5.5	8.5		27	158.5–159.5 (158–159)	200.5–201.5 (199.5–200)
$Cr(bzac)_3$	0.51[c]	19:1 benzene–ether	5	4.5	6.8	100	17	197.5–198.5 (196–196.5)	234–235 (235)
$Co(tmb)_3$	1.10	3:1 benzene–hexane	9	5.8	9.0	100	19	182–184	141–143
$Cr(tmb)_3$	1.05	3:1 benzene–hexane	4	4.3	7.8	91	24	203–204	173.5–175
$Co(tfac)_3$	1.03	1:1 benzene–hexane	9	3.7	6.5	94	16	127.5–128 (129–129.5)	158–159 (158–158.5)
$Cr(tfac)_3$	1.06	1:1 benzene–hexane	8	2.8	6.0	96		125–126 (112–114)	155–156 (154.5–155)

[a] All separations were carried out on the same 84 × 2.8 cm o.d. Florisil column at a flow rate of 2 ml/min; the flow rate was increased to 8 ml/min after the trans band was eluted. [b] Literature values[21,22] are listed in parentheses. [c] The column is overloaded and poor separations result if more than 0.5 g is used.

Table II. Chemical Shifts for *cis*- and *trans*-$Co(bzac)_3$[a]

Isomer	Chlorobenzene -CH=	Chlorobenzene $-CH_3$	Benzene -CH=	Benzene $-CH_3$
Cis	−6.13	−2.07	−6.17	−2.03
Trans	−6.13	−2.12	−6.17	−2.06
		−2.13		−2.08
		−2.17		−2.10

[a] Ppm (±0.01) relative to an internal reference of tetramethylsilane (1% by volume). Concentrations are 3.4–4.9 g/100 ml.

Partial Resolution of Optical Isomers. *cis*- and *trans*-$Co(bzac)_3$ were partially resolved by chromatography on D-(+)-lactose, and the enantiomer in excess was concentrated by crystallization of the less soluble racemate from a benzene–hexane solution of the partially resolved complex. The procedure used is described in detail in the preceding paper.[28]

Table III. Optical Rotation of Partially Resolved *cis*- and *trans*-$Co(bzac)_3$ at 546 mμ after Crystallization of Racemate

	First-eluted fraction Concn × 10^3, mol/l.	First-eluted fraction Obsd rotation, deg[a]	First-eluted fraction Molecular rotation[b]	Second-eluted fraction Concn × 10^3, mol/l.	Second-eluted fraction Obsd rotation, deg[a]	Second-eluted fraction Molecular rotation[b]
Cis isomer						
First crystallization	2.60	−0.171	−3,290	4.02	0.213	2,650
Second crystallization	3.20	−0.966	−15,100	2.68	0.780	14,600
Third crystallization	3.23	−1.509	−23,400	2.50	0.963	19,300
Trans isomer						
First crystallization	2.66	−0.276	−5,190	3.15	0.270	4,290
Chromatography	3.25	−0.420	−6,460			
Second crystallization	2.03	−0.459	−11,300	2.70	0.674	12,500
Third crystallization	2.60	−0.602	−11,600	2.08	0.654	15,700
Fourth crystallization	1.59	0.425	−13,400			

[a] Rotations were measured at room temperature with a 2-cm polarimeter cell. [b] Specific rotation times molecular weight divided by 100.

Because knowledge of the molecular rotations of the completely resolved cis and trans isomers would facilitate analysis of the inversion kinetics, attempts were made to effect complete resolution. Fractions having the same sign of rotation from five separate chromatograms were combined, and crystallization was repeated until the small amount of material remaining in solution rendered further crystallization unfeasible. A series of increases in the molecular rotation of the filtrates was observed (Table III), as has been reported previously for $Co(acac)_3$ by Collman and coworkers.[29,30] In the case of the first-eluted *trans* isomer repeated chromatography was also tried (*cf.* Table III), but this proved to be less effective than crystallization. The data in Table III indicate that complete resolution was not achieved although quite large molecular rotations were obtained. If one assumes that the molecular rotations of completely resolved *cis*- and *trans*-$Co(bzac)_3$ are comparable to the value of ±29,000 found for completely resolved $Co(acac)_3$,[30] then the maximum rotations in Table III correspond to ~80% and ~55% resolution for the cis and trans isomers, respectively. ORD curves for some partially resolved samples and electronic spectra are presented in Figures 1–3; these were recorded, respectively, with a Cary Model 60 spectropolarimeter and a Cary Model 14 spectrophotometer.

Solvents and Preparation of Solutions. Rates of geometrical isomerization, optical inversion, and ligand exchange and equilibrium constants for isomerization were measured in chlorobenzene (Matheson Coleman and Bell, reagent grade) which had been dried by refluxing for at least 12 hr over calcium hydride. In order to investigate solvent effects, rates of isomerization and equilibrium constants were also determined at one temperature in benzene, chloroform, acetone, and acetonitrile. Benzene and chloroform (Mallinckrodt, reagent grade) and acetonitrile (Matheson Coleman and Bell, spectroquality reagent grade) were dried by refluxing over calcium hydride; acetone (Mallinckrodt, reagent grade) was dried by refluxing over calcium sulfate. The freshly distilled solvents were degassed and stored under vacuum.

Solutions were prepared or were degassed in an all-glass vacuum system (5 × 10^{-4} Torr) in order to exclude air which produces decomposition and broadens the nmr lines.

A. Geometrical Isomerization. Chlorobenzene solutions were prepared by distilling *in vacuo* 0.5 ml of degassed solvent into a 5-mm o.d. nmr tube which contained a weighed amount of sample (~20 mg). The tube was then sealed under vacuum, and the concentration was determined by measuring the height of the solution. In the case of benzene, chloroform, acetone, and acetonitrile solutions, a stock solution containing a weighed amount of sample in 10 ml of solvent was prepared, and this was evenly distributed

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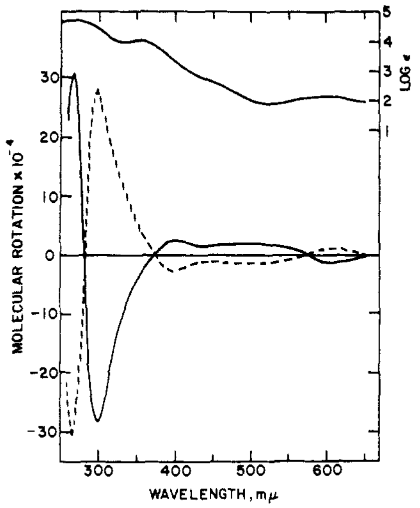

Figure 1. Absorption spectrum and optical rotatory dispersion curves for partially resolved *cis*-Co(bzac)$_3$ in chloroform solution: (---) first-eluted fraction, (—) last-eluted fraction from lactose.

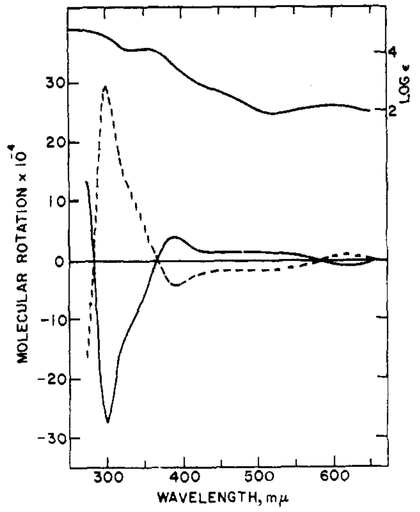

Figure 2. Absorption spectrum and optical rotatory dispersion curves for partially resolved *trans*-Co(bzac)$_3$ in chloroform solution: (---) first-eluted fraction, (—) last-eluted fraction from lactose.

among seven nmr tubes. The solutions were then degassed and the tubes sealed under vacuum.

B. **Optical Inversion.** Solutions for measurement of rates of optical inversion were prepared as described in the preceding paper.[28]

C. **Ligand Exchange.** Co(bzac)$_3$ (0.073 mmol) and Co(bzac-d_4)$_3$ (0.073 mmol) were dissolved in 10 ml of chlorobenzene, and the resulting equimolar solution was distributed among 25 Pyrex tubes. The solutions were then degassed and the tubes sealed under vacuum.

Rates of Isomerization and Equilibrium Constants. Rates and equilibrium constants for cis–trans isomerization were determined in chlorobenzene solution in the temperature range 56.0–104.6° and also in benzene, chloroform, acetone, and acetonitrile at 95.8°. The sample solutions, sealed in nmr tubes, were placed in a constant-temperature bath (±0.1°) for an appropriate length of time, and the isomerization reaction was then quenched by plunging the sample tube into cold water. Relative concentrations of the cis and trans isomers were determined by integration of the methyl region of proton nmr spectra of chlorobenzene solutions. The methyl region was recorded in quadruplicate at ambient temperature with a Varian A-60A spectrometer at a sweep width of 50 cps, and integrations were performed to within ±2% accuracy with a planimeter. Representative spectra are presented in Figure 4. Figure 4 and Table II show that, in chlorobenzene solution, the three lines due to the trans isomer are well separated from the higher field resonance due to the cis isomer. The excellent resolution of the spectrum apparently derives in part from stereospecific solvation by, and the diamagnetic anisotropy of, the aromatic solvent molecules, since spectra of chlorobenzene and benzene solutions (*cf.* Table II) are much better resolved than previously reported spectra in chloroform.[21] Care was taken to record spectra at values of the rf field well below saturation. In kinetic runs, time intervals were corrected for an experimentally determined warm-up time of 24 sec.[31] Several sample tubes were used in the higher temperature runs in order to keep the heating intervals for a given tube ≥20 min. The number of relative concentration measurements per kinetic run were 11–15 for the chlorobenzene solutions and 7 for the benzene, chloroform, acetone, and acetonitrile solutions. In the latter cases seven sample tubes were used, one for each concentration measurement. At the end of a run these were opened, the solvent was pumped off, and the resulting solid was dissolved in chlorobenzene. The methyl region of the nmr spectrum was then recorded in quadruplicate. In general, kinetic runs were followed for ~3.5 half-lives; solutions used for the determination of equilibrium constants were heated for at least eight half-lives.

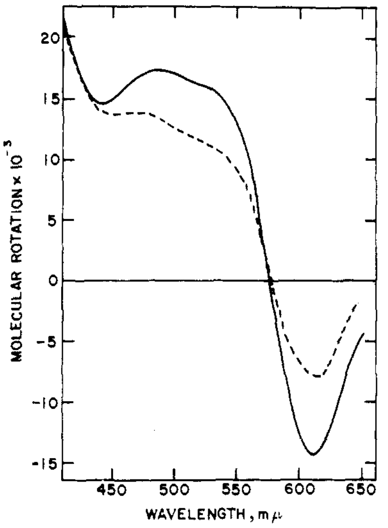

Figure 3. Optical rotatory dispersion curves (visible region) for partially resolved *cis*-Co(bzac)$_3$ (—) and *trans*-Co(bzac)$_3$ (---) in chloroform solution, last-eluted fractions from lactose.

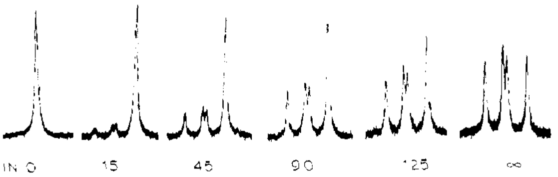

Figure 4. Methyl region of the proton nmr spectra at a sweep width of 50 cps for Co(bzac)$_3$ in chlorobenzene after heating a 0.072 *M* solution of the cis isomer for various numbers of minutes at 96.1°. The spectrum at infinite time was recorded after heating for 7 hr.

Rates of Optical Inversion. Rates of optical inversion of *cis*- and *trans*-Co(bzac)$_3$ were measured in chlorobenzene solution in the temperature range 56.0–96.1°. The experimental procedure was the same as that described in detail in the preceding paper; solutions were thermostated and warm-up corrections applied as described for the Cr(acac)$_3$ runs.[28] Rotations, measured to ±0.003°, were followed for two to four half-lives at 546 mμ. Initial rotations ranged from 0.15 to 1.5° but generally were 0.2–0.5°.

Rates of Ligand Exchange. Rates of ligand exchange between Co(bzac)$_3$ and Co(bzac-d_4)$_3$ were measured in chlorobenzene solution in the temperature range 96.1–126.1°. Sample tubes, generally five or six per kinetic run, were immersed in a constant-tempera-

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(31) The method used to estimate the warm-up time for solutions in nmr tubes was the same as that described for polarimeter cells in ref 26 of the preceding paper.

ture bath (±0.1°) for an appropriate period of time, and the reaction was then quenched. Solutions were passed through a 6 × 0.7 cm o.d. Florisil column using chloroform as eluent in order to remove any decomposition product. The solvent was then pumped off and relative concentrations of the parent and mixed-ligand complexes were determined from the molecular ion region of the mass spectrum of the residues. Mass spectra were recorded with an Associated Electrical Industries MS 902 mass spectrometer at an electron energy of 70 eV. Samples were introduced directly into the ion source; the temperature of the ion source was ~170°. The molecular ion was usually detected within 1-2 min. After the spectrum was strong enough for quantitative measurement, eight or more copies of the molecular ion region were recorded at 15-sec intervals.

The nmr spectrum of the Co(bzac-d_4)$_3$ used in these experiments indicated that the complex contained 12% hydrogen on the γ carbon and 3% hydrogen on the methyl carbon; *i.e.*, the deuterated complex, which we shall represent hereafter as Co(bzac*)$_3$, was a mixture of Co(bzac-d_4)$_3$, Co(bzac-d_4)$_2$(bzac-d_3), Co(bzac-d_4)(bzac-d_3)$_2$, etc. Using standard probability considerations and taking into account the isotopic abundances of ^{13}C and ^{18}O, the molecular-ion region of the mass spectrum of Co(bzac*)$_3$ was found to agree with that calculated for hydrogen contents of (a) 17% H on the γ carbon, assuming the nmr value of 3% H on the methyl carbon, and (b) 5% H on the methyl carbon, assuming the nmr value of 12% H on the γ carbon. Both of these compositions are in satisfactory agreement with the nmr spectrum, and the final relations between concentrations and mass spectral peak intensities are quite insensitive to which composition is used. Using the former, the isotopic composition of the deuterated ligand, bzac*, was calculated to be 75.7% bzac-d_4, 22.5% bzac-d_3, 1.7% bzac-d_2, and 0.05% bzac-d_1. The isotopic compositions and mass spectra of the mixed-ligand complexes, Co(bzac)$_2$(bzac*) and Co(bzac)(bzac*)$_2$, were next calculated, and the calculated spectra, along with observed spectra for Co(bzac)$_3$ and Co(bzac*)$_3$, were used to derive eq 1–4, which

$$[\text{Co(bzac)}_3] \propto 1.406 I_{542} \tag{1}$$

$$[\text{Co(bzac)}_2(\text{bzac*})] \propto 1.672 I_{546} - 0.001 I_{550} \tag{2}$$

$$[\text{Co(bzac)(bzac*)}_2] \propto 2.008 I_{550} - 0.041 I_{554} \tag{3}$$

$$[\text{Co(bzac*)}_3] \propto 2.544 I_{554} \tag{4}$$

relate relative concentrations of the parent and mixed-ligand complexes to the intensities I of major peaks in the mass spectra of mixtures. The intensities were taken to be proportional to peak heights. In general, the spectra of mixtures showed 15 molecular ion peaks at *m/e* 542–556; the prominent peaks at 542, 546, 550, and 554 correspond to Co(bzac)$_3^+$, Co(bzac)$_2$(bzac-d$_4$)$^+$, Co(bzac)(bzac-d_4)$_2^+$, and Co(bzac-d_4)$_3^+$, respectively.

The measurement of ligand-exchange rates in solution was complicated by ligand exchange in the ion source of the mass spectrometer. Figure 5 shows a plot of the intensity ratio I_{546}/I_{542} *vs.* time after sample insertion for an equimolar mixture of Co(bzac)$_3$ and Co(bzac*)$_3$. This sample was prepared in the same way as those used for kinetic runs; however, the chlorobenzene solution was not heated. Therefore, in the absence of exchange in the mass spectrometer, I_{546}/I_{542} should be 0. Figure 5 indicates a small, relatively constant amount of exchange in the spectrometer during the first 4 min after sample insertion but a rapid increase in the amount of exchange after 4–5 min. Plots of I_{546}/I_{542} *vs.* time for the kinetic samples exhibited a similar, relatively flat region followed by a rapid rise after ~4 min. The spectra used for concentration measurements were those for which the I_{546}/I_{542} ratio fell in the flat region of the plots; in general, it was possible to record eight to nine copies of the spectrum before exchange in the spectrometer became serious. The averaged intensities from these copies were substituted into eq 1–4 to obtain the relative concentrations. Ordinarily, two or three separate portions of each sample were introduced successively into the ion source, which gave two or three independent spectral determinations of the relative concentrations.

It was found that ligand exchange in the ion source was catalyzed by a thermal decomposition product of Co(bzac)$_3$, probably a Co(II) species. The decomposition product was detected in the higher temperature runs (116.1 and 126.1°) by chromatography on Florisil. In order to eliminate this complication, the chlorobenzene solutions were passed through a short Florisil column before mass spectra were recorded; the decomposition product adhered to the top of the column. In a separate experiment, it was shown that this chromatographic procedure did not affect the isotopic composition of deuterated Co(bzac)$_3$. It was also found that the amount of ligand exchange in the mass spectrometer depended on the history of the ion source. Consequently, the ion source was cleaned at the beginning of this work, and the spectrum of a previously unheated, equimolar mixture of Co(bzac)$_3$ and Co-bzac*)$_3$ was run at the beginning and end of each day to verify that the amount of ligand exchange in the ion source was small and relatively constant.

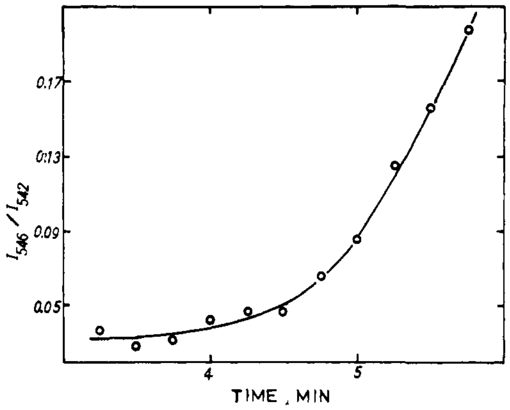

Figure 5. Intensity ratio, I_{546}/I_{542}, *vs.* time after insertion into the mass spectrometer for an equimolar mixture of Co(bzac)$_3$ and Co-(bzac*)$_3$. The original chlorobenzene solution, 7.3 × 10^{-3} *M* in each parent complex, had not been heated.

Results and Discussion

Kinetic Rate Laws. A. Geometrical Isomerization and Optical Inversion. The possible interconversions among the four isomers of a tris chelate having three unsymmetrical bidentate ligands are set out in eq 5.

$$\begin{tikzcd}
\text{cis-}\Delta \arrow[r, shift left, "k_1"] \arrow[d, shift right, "k_3"'] \arrow[dr, shift left, "k_2"] & \text{cis-}\Lambda \arrow[l, shift left, "k_1"] \arrow[d, shift left, "k_3"] \arrow[dl, shift left, "k_2"'] \\
\text{trans-}\Delta \arrow[u, shift right, "k_{-3}"'] \arrow[r, shift left, "k_4"] \arrow[ur, shift left, "k_{-2}"] & \text{trans-}\Lambda \arrow[l, shift left, "k_4"] \arrow[u, shift left, "k_{-3}"] \arrow[ul, shift left, "k_{-2}"']
\end{tikzcd} \tag{5}$$

The kinetics of these interconversions is characterized by six microscopic rate constants: k_1, k_2, k_{-2}, k_3, k_{-3}, and k_4. Only five of these are independent since $k_2/k_{-2} = k_3/k_{-3}$.

It is evident from (5) that the rate law for geometrical isomerization is given by

$$-\frac{\text{d[cis]}}{\text{d}t} = (k_2 + k_3)[\text{cis}] - (k_{-2} + k_{-3})[\text{trans}] \tag{6}$$

where [cis] = [cis-Δ] + [cis-Λ] and [trans] = [trans-Δ] + [trans-Λ] are the total concentrations of the geometrical isomers, $k_2 + k_3$ is the rate constant for cis-to-trans isomerization, and $k_{-2} + k_{-3}$ is the rate constant for trans-to-cis isomerization. For isomerization of pure cis isomer, the integrated form of the rate law can be written as

$$\log[x - K^{-1}(1 - x)] = \frac{-(k_2 + k_3)(1 + K^{-1})t}{2.303} \tag{7}$$

where x and $(1 - x)$, respectively, are the mole fractions of the cis and trans isomers at time t, and

$$K^{-1} = (k_{-2} + k_{-3})/(k_2 + k_3) = k_{-2}/k_2 = k_{-3}/k_3 \tag{8}$$

is the equilibrium constant for trans-to-cis isomerization. The rate constant, $k_2 + k_3$, can be evaluated

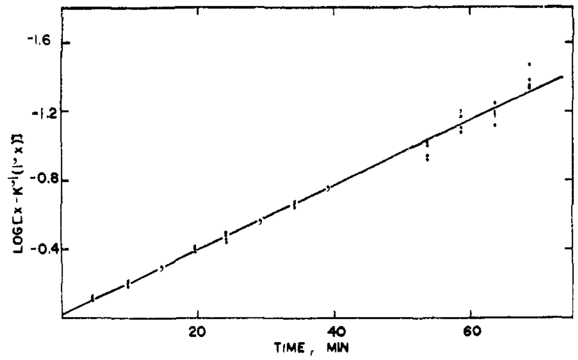

Figure 6. First-order rate plot for isomerization of *cis*-Co(bzac)$_3$ in chlorobenzene solution at 104.6°. Each data point represents an independent spectral determination of x.

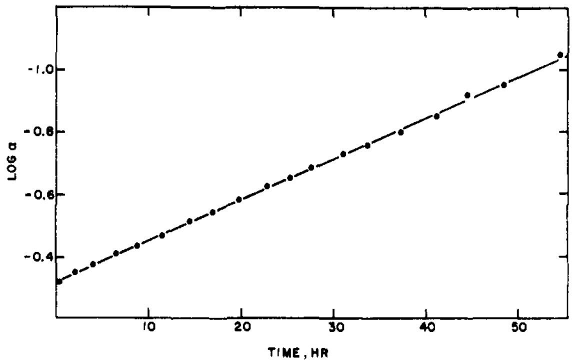

Figure 7. First-order rate plot for optical inversion of *cis*-Co(bzac)$_3$ in chlorobenzene solution (2.34×10^{-3} M) at 66.2°.

from the slope of a linear plot of log $[x - K^{-1}(1 - x)]$ *vs.* time, and the reverse rate constant, $k_{-2} + k_{-3}$, can be calculated from $k_2 + k_3$ and the equilibrium constant. A typical log $[x - K^{-1}(1 - x)]$ *vs.* time plot is presented in Figure 6.

The term, optical inversion, or simply inversion, is used in this paper to denote a change in the helicity of the chelate rings, *i.e.*, the reaction

$$\Delta \rightleftharpoons \Lambda \qquad (9)$$

without regard to the cis or trans nature of the reactants and products. It follows from (5) that

$$-\frac{d}{dt}([\text{cis-}\Delta] - [\text{cis-}\Lambda]) = (2k_1 + k_2 + k_3)([\text{cis-}\Delta] - [\text{cis-}\Lambda]) + (k_{-2} - k_{-3})([\text{trans-}\Delta] - [\text{trans-}\Lambda]) \qquad (10)$$

and

$$-\frac{d}{dt}([\text{trans-}\Delta] - [\text{trans-}\Lambda]) = (k_2 - k_3)([\text{cis-}\Delta] - [\text{cis-}\Lambda]) + (k_{-2} + k_{-3} + 2k_4)([\text{trans-}\Delta] - [\text{trans-}\Lambda]) \qquad (11)$$

Therefore, the total rate of optical inversion is given by

$$-\frac{d[\Delta]}{dt} = \frac{d[\Lambda]}{dt} = (k_1 + k_2)([\text{cis-}\Delta] - [\text{cis-}\Lambda]) + (k_{-2} + k_4)([\text{trans-}\Delta] - [\text{trans-}\Lambda]) \qquad (12)$$

where $[\Delta] = [\text{cis-}\Delta] + [\text{trans-}\Delta]$ and $[\Lambda] = [\text{cis-}\Lambda] + [\text{trans-}\Lambda]$ are the concentrations of the Δ and Λ enantiomers, $k_1 + k_2$ is the rate constant for inversion of the cis isomer, *i.e.*

$$\text{cis-}\Delta(\Lambda) \xrightarrow{k_1 + k_2} \text{cis-}\Lambda(\Delta) + \text{trans-}\Lambda(\Delta) \qquad (13)$$

and $k_{-2} + k_4$ is the rate constant for inversion of the trans isomer, *i.e.*

$$\text{trans-}\Delta(\Lambda) \xrightarrow{k_{-2} + k_4} \text{cis-}\Lambda(\Delta) + \text{trans-}\Lambda(\Delta) \qquad (14)$$

The corresponding rate law for loss of optical activity can be written as

$$-(d/dt)(\alpha_C/[M_C^0] + \alpha_T/[M_T^0]) = 2(k_1 + k_2)\alpha_C/[M_C^0] + 2(k_{-2} + k_4)\alpha_T/[M_T^0] \qquad (15)$$

where α_C and α_T represent the optical rotations of the cis and trans isomers, and $[M_C^0]$ and $[M_T^0]$ are the corresponding molecular rotations of the completely resolved isomers. The observed rotation, $\alpha = \alpha_C + \alpha_T$, is a simple exponential function of time only if

$$[M_C^0] = [M_T^0] \qquad (16)$$

and

$$k_1 + k_2 = k_{-2} + k_4 \qquad (17)$$

If eq 16 holds, eq 15 reduces to

$$-\frac{d\alpha}{dt} = 2(k_1 + k_2)\alpha_C + 2(k_{-2} + k_4)\alpha_T \qquad (18)$$

and if eq 17 holds as well, eq 18 can be integrated.

In the kinetic studies, optical rotations were recorded at 546 mμ. The approximate validity of eq 16 at 546 mμ is indicated by an experimental value for $[M_C^0]_{546}/[M_T^0]_{546}$ of 1.18 ± 0.31 (*vide infra*) and by the fact that the isomers show similar electronic spectra and ORD curves (*cf.* Figures 1–3). The isomers are expected to have nearly equal molecular rotations at 546 mμ because the optical activity in the region of the d–d transitions should depend primarily on the helicity of the chelate rings and much less on the orientation of the more distant methyl and phenyl substituents. The approximate validity of eq 17 for Co(bzac)$_3$ is indicated by the following experimental results: (1) the equilibrium constants for trans-to-cis isomerization in chlorobenzene solution are very close to the statistical value of $^1/_3$ and the enthalpy of isomerization is 0 within experimental uncertainty; (2) the activation parameters for inversion of the cis and trans isomers are identical within experimental uncertainty; and (3) the rate constants for inversion of the cis and trans isomers, evaluated by the procedure described below, are in fact found to be nearly equal. Thus, the energy of the cis and trans isomers, the energy of the transition states for inversion, and the rates of inversion are relatively insensitive to the orientation of the methyl and phenyl ring substituents.

In order to evaluate the inversion rate constants, we need not require that eq 17 hold exactly. We assume only that $k_1 + k_2$ and $k_{-2} + k_4$ are comparable, *i.e.*, that $(k_{-2} + k_4) - (k_1 + k_2) = \delta$, where $|\delta|$ is small compared with $k_1 + k_2$ and $k_{-2} + k_4$. Then eq 18 can be written in the forms

$$-\frac{d\alpha}{dt} = 2(k_1 + k_2)\alpha + 2\delta\alpha_T \qquad (19a)$$

Table IV. Rate Constants and Equilibrium Constants for Geometrical Isomerization of Co(bzac)$_3$ in Chlorobenzene Solution[a]

Temp, °C	Concn × 10^2, mol/l.	$(k_2 + k_3) \times 10^5$, sec^{-1}	$(k_{-2} + k_{-3}) \times 10^5$, sec^{-1}	K^{-1} [b]
56.0	8.1	0.0808 ± 0.0029	0.0306 ± 0.0014	0.379 ± 0.010
	10.2	0.0806 ± 0.0032	0.0305 ± 0.0015	
66.1	8.1	0.334 ± 0.010	0.119 ± 0.005	0.357 ± 0.007
	8.3	0.329 ± 0.015	0.117 ± 0.006	
	9.0	0.349 ± 0.009	0.125 ± 0.004	
75.5	8.3	1.38 ± 0.07	0.52 ± 0.03	0.377 ± 0.009[c]
	8.5	1.26 ± 0.06	0.48 ± 0.02	
86.1	8.5	5.12 ± 0.22	1.85 ± 0.10	0.362 ± 0.011
	8.9	5.00 ± 0.17	1.81 ± 0.08	
	9.2	4.95 ± 0.21	1.79 ± 0.09	
96.1	5.9, 6.3[d]	19.8 ± 0.9	7.4 ± 0.4	0.377 ± 0.008
	7.2	17.5 ± 0.5	6.5 ± 0.2	0.366 ± 0.009
	8.1	17.7 ± 0.5	6.6 ± 0.2	
	6.5, 6.6[d]	18.8 ± 0.9[e]	6.8 ± 0.4[e]	0.364 ± 0.010[e]
104.6	8.1, 8.7, 9.2[d]	53.3 ± 1.6	19.1 ± 0.9	0.359 ± 0.013

[a] All errors are estimated at the 95% confidence level. Concentrations are quoted at ~25°. [b] Equilibrium constants are the average of at least eight spectral measurements; all of the solutions in column two were used and the results averaged. The starting material was the cis isomer. [c] Using the trans isomer as the starting material a value of 0.368 ± 0.023 was obtained. [d] More than one sample was used in these runs in order to keep the heating intervals for a given solution ≥20 min. [e] Solvent is chlorobenzene saturated with water.

and

$$-\frac{d\alpha}{dt} = 2(k_{-2} + k_4)\alpha - 2\delta\alpha_C \tag{19b}$$

If we begin with pure cis isomer, the concentration of the trans isomer will be small in the early stages of the reaction, and the term $2\delta\alpha_T$ in eq 19a can be neglected. Hence the integrated rate law for the initial stages of the reaction is

$$\log \alpha = \log \alpha_0 - \frac{2(k_1 + k_2)t}{2.303} \tag{20}$$

where α_0 is the initial rotation; $k_1 + k_2$ can be evaluated from the *initial* slope of a plot of log α *vs.* time. Similarly, if we begin with the trans isomer, eq 19b leads to

$$\log \alpha = \log \alpha_0 - \frac{2(k_{-2} + k_4)t}{2.303} \tag{21}$$

and the *initial* slope of a log α *vs.* t plot affords a value for $k_{-2} + k_4$. The log α *vs.* t plots are not expected to be linear over a wide time interval unless the molecular rotations (eq 16) and inversion rates (eq 17) are equal for the cis and trans isomers. Kinetic plots for *cis*- and *trans*-Co(bzac)$_3$ exhibit no deviations from linearity over two to four half-lives, other than random scatter (*cf.* Figure 7), and this, together with the fact that the slopes give nearly equal values for $k_1 + k_2$ and $k_{-2} + k_4$, strongly suggests that eq 16 and 17 hold to a good degree of approximation.

B. Ligand Exchange. If rearrangements of Co(bzac)$_3$ occur by complete dissociation of bzac ligands, isomerization and inversion will be accompanied by the first-order ligand exchange reaction

$$\mathrm{Co(bzac)_3 + Co(bzac^*)_3} \underset{k_{ex}/3}{\overset{k_{ex}}{\rightleftarrows}} \mathrm{Co(bzac)_2(bzac^*) + Co(bzac)(bzac^*)_2} \tag{22}$$

and the kinetics of ligand exchange can be analyzed in terms of the dissociative processes

$$\mathrm{CoL_3} \underset{k_a}{\overset{k_d}{\rightleftarrows}} \mathrm{CoL_2^+ + L^-} \tag{23}$$

$$\mathrm{CoL_3^*} \underset{k_a}{\overset{k_d}{\rightleftarrows}} \mathrm{CoL_2^* + L^{*-}} \tag{24}$$

$$\mathrm{CoL_2L^*} \underset{k_a}{\overset{k_d/3}{\rightleftarrows}} \mathrm{CoL_2^+ + L^{*-}} \tag{25}$$

$$\mathrm{CoL_2L^*} \underset{k_a}{\overset{2k_d/3}{\rightleftarrows}} \mathrm{CoLL^{*+} + L^-} \tag{26}$$

$$\mathrm{CoLL^*_2} \underset{k_a}{\overset{k_d/3}{\rightleftarrows}} \mathrm{CoL_2^{*+} + L^-} \tag{27}$$

$$\mathrm{CoLL_2^*} \underset{k_a}{\overset{2k_d/3}{\rightleftarrows}} \mathrm{CoLL^{*+} + L^{*-}} \tag{28}$$

In these equations L and L* are abbreviations for bzac and bzac*, respectively, k_d is the first-order rate constant for complete dissociation of any one of the three ligands, k_a is the rate constant for recombination, and k_{ex} (eq 22) is the first-order rate constant for ligand exchange. Because we use equal concentrations of CoL$_3$ and CoL$_3$*, it follows that $k_{ex} = k_d/2$. Applying the steady-state approximation to the ionic species in eq 23–28, the integrated rate law for ligand exchange is found to be

$$\log\left(1 - \frac{4y}{3c_0}\right) = -\frac{4}{3}\left(\frac{k_{ex}t}{2.303}\right) \tag{29}$$

where y is the concentration of the mixed ligand complexes at time t and c_0 is the initial concentration of the parent complexes. Values of y/c_0 can be obtained from the mass spectral peak intensities *via* eq 1–4, and k_{ex} evaluated from the slope of a plot of log $(1 - 4y/3c_0)$ *vs.* time.

Kinetic Results. This section presents experimental results for isomerization, inversion, and ligand-exchange reactions of Co(bzac)$_3$. All errors are estimated at the 95% confidence level, which generally corresponds to 2.0–2.3 standard deviations, depending on the number of data points.

Rate constants and equilibrium constants for geometrical isomerization in chlorobenzene solution are set out in Table IV. Rate constants for cis-to-trans isomerization, $k_2 + k_3$, were obtained from least-squares plots of log $[x - K^{-1}(1 - x)]$ *vs.* t, and values of $k_{-2} + k_{-3}$ were calculated from $k_2 + k_3$ and the equilibrium constant. The estimated errors in the rate constants (±3–6%) take into account the errors in K^{-1}. First-order kinetics is indicated by the linearity of the log $[x - K^{-1}(1 - x)]$ *vs.* t plots (*cf.* Figure

Table V. Rate Constants and Equilibrium Constants for Geometrical Isomerization of Co(bzac)$_3$ in Various Solvents at 95.8° [a]

Solvent	Dielectric constant[b]	Starting material	Concn × 10^2, mol/l.	$(k_2 + k_3) \times 10^5$, sec^{-1}	$(k_{-2} + k_{-3}) \times 10^5$, sec^{-1}	K^{-1} [c]
Benzene	2.14	Cis	5.4	13.0 ± 0.6	5.4 ± 0.4	0.425 ± 0.030
		Trans	2.6			0.405 ± 0.023
Chloroform	3.90	Cis	2.8	21.5 ± 1.4	9.9 ± 0.8	0.477 ± 0.035
		Trans	2.4			0.441 ± 0.036
Chlorobenzene	4.77	Cis	5.9–10.2	17.3 ± 1.8[d]	6.3 ± 0.8[d]	
Acetone	13.6	Cis	3.3	26.4 ± 1.3	9.9 ± 0.6	0.397 ± 0.029
		Trans	1.2			0.354 ± 0.012
Acetonitrile	23.4	Cis	1.3	18.9 ± 0.9	6.0 ± 0.4	0.322 ± 0.014
		Trans	1.4			0.313 ± 0.021

[a] All errors are estimated at the 95% confidence level. [b] Extrapolated from data in the "International Critical Tables," Vol. 6, McGraw-Hill, New York, N. Y., 1963, pp 82–89. [c] Equilibrium constants are the average of four or five spectral measurements. [d] These are calculated values obtained from least-squares log $(k_2 + k_3)$ *vs.* $1/T$ and log $(k_{-2} + k_{-3})$ *vs.* $1/T$ plots of the data in Table IV.

Table VI. Rate Constants for Optical Inversion of *cis*- and *trans*-Co(bzac)$_3$ in Chlorobenzene Solution[a]

	Cis		Trans	
Temp, °C	Concn × 10^3, mol/l.	$(k_1 + k_2) \times 10^5$, sec^{-1}	Concn × 10^3, mol/l.	$(k_{-2} + k_4) \times 10^5$, sec^{-1}
56.0	0.66	0.0971 ± 0.0029	0.76	0.0878 ± 0.0028
	1.42	0.0951 ± 0.0053	0.87	0.0865 ± 0.0031
66.2	1.15	0.423 ± 0.004	1.96	0.469 ± 0.021
	2.34	0.420 ± 0.006	3.29	0.423 ± 0.015
76.2	2.19	1.94 ± 0.06	1.94	1.68 ± 0.29
	2.53	1.99 ± 0.11	5.84	1.76 ± 0.07
85.0	1.20, 3.52[b]	5.45 ± 0.09	1.26. 2.72[c]	5.00 ± 0.21
	1.72, 3.22[b]	5.56 ± 0.11	1.78, 2.47[c]	4.59 ± 0.36
			6.19	4.69 ± 0.10
96.1	1.20, 3.13, 2.23[b]	22.1 ± 1.1	1.59	19.9 ± 1.2
	1.69, 1.04, 2.93[b]	22.9 ± 1.3	3.38	19.2 ± 1.6

[a] All errors are estimated at the 95% confidence level. Concentrations were determined spectrophotometrically at ~25° and are based on $\epsilon_{600\ \mathrm{m}\mu}$ = 158 (cis) and 160 (trans). [b] More than one sample was used in these runs in order to keep the heating interval for a given solution >15 min. [c] More than one sample was used to keep the heating interval ≥40 min.

Table VII. Rate Constants for Ligand Exchange between Co(bzac)$_3$ and Co(bzac*)$_3$ in Chlorobenzene Solution[a]

Temp, °C	$k_{ex} \times 10^6$, sec^{-1}
96.1	0.72 ± 0.17[b]
106.0	3.73 ± 0.33
116.1	22.0 ± 7.5
126.1	91.3 ± 8.9

[a] Equimolar solution of Co(bzac)$_3$ (7.3 × 10^{-3} *M*) and Co(bzac*)$_3$ (7.3 × 10^{-3} *M*). [b] All errors are estimated at 95% confidence level.

6) and by the concentration independence of the rate constants. The data at 96.1° show that the presence of water has no measurable effect on the rates. The equilibrium constants K^{-1} are independent of temperature and very close to the statistical value of $^1/_3$. A least-squares plot of log K^{-1} *vs.* $1/T$ gives $\Delta H° = -0.17 \pm 0.33$ kcal/mol and $\Delta S° = -2.5 \pm 0.9$ eu for trans-to-cis isomerization; within experimental uncertainty these values are identical with the statistical values of $\Delta H° = 0$ and $\Delta S° = -R \ln 3 = -2.18$ eu.

Kinetic and equilibrium data for isomerization of Co(bzac)$_3$ in benzene, chloroform, acetone, and acetonitrile at 95.8° are presented in Table V. The rate constants increase as the solvent varies in the order benzene < chlorobenzene ~ acetonitrile < chloroform $\lesssim$ acetone. However, the variation in rates is only a factor of 2 and does not appear to be related to the dielectric constant of the solvent.

cis-Co(bzac)$_3$ was found to be stable with respect to isomerization in the solid state. No trans isomer was detected by nmr after heating for 11 hr at 96.1° (~14 half-lives for a chlorobenzene solution).

Rate constants for inversion of *cis*- and *trans*-Co(bzac)$_3$ in chlorobenzene were obtained from least-squares plots of log α *vs.* t, in accord with eq 20 and 21. Results are collected in Table VI. First-order kinetics is indicated by the linearity of the log α *vs.* t plots and by the concentration independence of the rate constants. The average estimated error in the individual rate constants is *ca.* ±5%.

Rate constants for ligand exchange between Co(bzac)$_3$ and Co(bzac*)$_3$ in chlorobenzene solution are presented in Table VII. These were obtained from least-squares plots of eq 29. The kinetic plots were fairly good straight lines; however, owing to ligand exchange in the mass spectrometer, there was considerably more scatter in the data than for the isomerization and inversion measurements, and the estimated errors are correspondingly larger (±9–34% in k_{ex}).

Arrhenius activation energies, E_a, and frequency factors, A, for isomerization, inversion, and ligand exchange were determined from log k *vs.* $1/T$ least-squares plots of the data in Tables IV, VI, and VII. Activation enthalpies, ΔH^*, and activation entropies, ΔS^*, extrapolated to 25°, were calculated from the relations

$$\Delta H^* = E_a - RT \qquad (30)$$

and

$$\Delta S^* = R[\ln A - \ln (RT/Nh)] - R \qquad (31)$$

Arrhenius plots are presented in Figure 8, and activation parameters are collected in Table VIII along with rate constants at a common temperature. The rate constants in Table VIII are average experimental values, and the estimated errors in the rate constants are de-

Table VIII. Rate Constants and Activation Parameters for Geometrical Isomerization, Optical Inversion, and Ligand-Exchange Reactions of $Co(bzac)_3$ in Chlorobenzene Solution[a]

	Isomerization		Inversion		Ligand exchange
	cis-$Co(bzac)_3$	*trans*-$Co(bzac)_3$	*cis*-$Co(bzac)_3$	*trans*-$Co(bzac)_3$	$Co(bzac)_3$–$Co(bzac^*)_3$
$k \times 10^4$, sec^{-1} at 96.1°	1.83 ± 0.12	0.68 ± 0.05	2.25 ± 0.23	1.96 ± 0.24	0.0072 ± 0.0027
E_a, kcal/mol	32.7 ± 0.5	32.7 ± 0.6	32.9 ± 0.7	32.3 ± 0.9	48 ± 4
Log A[b]	15.63 ± 0.29	15.15 ± 0.39	15.84 ± 0.44	15.41 ± 0.57	22.0 ± 2.2
ΔH^*, kcal/mol	32.0 ± 0.5	32.0 ± 0.6	32.2 ± 0.7	31.6 ± 0.9	47 ± 4
ΔS^*, eu	11.0 ± 1.3	8.8 ± 1.8	11.9 ± 2.0	10.0 ± 2.6	40 ± 10

[a] All errors are estimated at the 95% confidence level. This corresponds to 2.2–2.3 standard deviations for the isomerization and inversion data, and 4.3 standard deviations for the ligand exchange data. [b] A is expressed in sec^{-1}.

Table IX. Polarimetric Data for Isomerization and Inversion of $(-)_{546}$-*cis*-$Co(bzac)_3$

	Starting material $(-)_{546}$-Cis isomer	Products after heating for 11 min: Cis isomer	Products after heating for 11 min: Trans isomer
Concn × 10^3, M[a]	1.23 ± 0.02	1.04 ± 0.02	0.138 ± 0.002
Obsd rotation, deg[b]	−0.987 ± 0.003	−0.789 ± 0.003	+0.092 ± 0.003
Molecular rotation	−16,100 ± 300	−15,200 ± 300	+13,300 ± 500

[a] Determined spectrophotometrically at ~25°. Absorption spectra measured before and after heating indicated that no decomposition occurred during the 11-min heating time. [b] At ~25°, 5-cm cell. The observed rotation of the 1.23×10^{-3} M solution after heating but before separation of the cis and trans isomers was −0.737°; calcd from $k_1 + k_2$, −0.734°.

rived from least-squares analysis of the Arrhenius plots; *i.e.*, these errors reflect the scatter of the data over a temperature range. The more important results contained in Table VIII and Tables IV, VI, and VII are the following. (1) The inversion rates for the cis and trans isomers differ on average by ~10%; however, this difference is within the estimates of experimental error. (2) For the cis isomer, the rates of inversion are slightly (~20%) higher than the rates of isomerization. (3) The rate of ligand exchange at 96.1° is ~300 times slower than the rates of isomerization and inversion. (4) The activation parameters for the four isomerization and inversion processes are identical within experimental uncertainty; the activation energies agree within 0.6 kcal/mol.[32] (5) The activation energy for ligand exchange is ~15 kcal higher than for isomerization and inversion, and the activation entropy is more positive by ~30 eu.

The following relationships between the microscopic rate constants of (5) are indicated by the kinetic data

$$k_1 + k_2 \approx k_{-2} + k_4 \qquad (32)$$

and

$$k_1 + k_2 \approx 1.2(k_2 + k_3) \qquad (33)$$

The difference between $k_1 + k_2$ and $k_2 + k_3$ is probably outside of random experimental error; at 96.1°, $(k_1 + k_2)/(k_2 + k_3) = 1.23 \pm 0.15$. A minor source of systematic error which may contribute to this difference is decomposition. Absorption spectra revealed up to 3% decomposition in some of the inversion runs. Since the decomposition product is probably an optically inactive Co(II) species, decomposition will contribute to the observed values of $k_1 + k_2$. In the isomerization runs, where more concentrated solutions were used, decomposition was not detected. Moreover, if the cis and trans isomers decompose at equal rates, decomposition will not contribute to the observed values of $k_2 + k_3$, since the measured quantity in the isomerization runs is the cis/trans ratio.

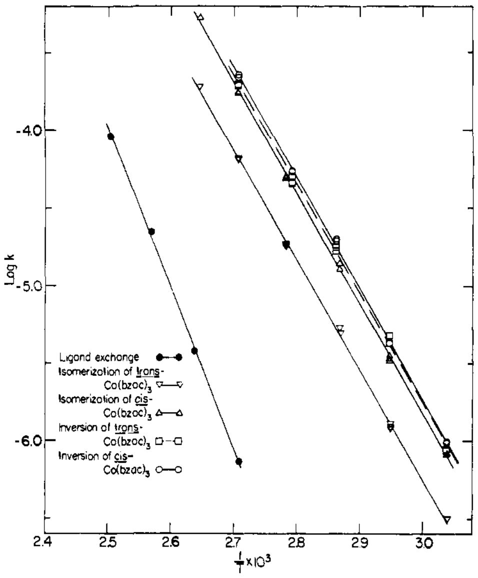

Figure 8. Arrhenius plots for optical inversion of *cis*- and *trans*-$Co(bzac)_3$, isomerization of *cis*- and *trans*-$Co(bzac)_3$, and ligand exchange between $Co(bzac)_3$ and $Co(bzac^*)_3$ in chlorobenzene solution.

The individual microscopic rate constants and the ratio of the molecular rotations of the completely resolved cis and trans isomers may be estimated by investigating the optical activity of the products produced in the initial stages of isomerization of a partially resolved sample of the cis isomer. A sample of $(-)_{546}$-*cis*-$Co(bzac)_3$ was heated in chlorobenzene solution at 96.1° for 11 min (0.24 isomerization half-life). The geometric isomers were then separated by column chromatography on a 45 × 1.3 cm o.d. Florisil column, and the optical rotations of the cis and trans fractions were measured. Results are presented in Table IX.

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(32) There is, of course, a real difference between the activation entropies for isomerization of the cis and trans isomers. This difference is more precisely evaluated from equilibrium data which give $\Delta S° = \Delta S^*_{trans} - \Delta S^*_{cis} = -2.5 \pm 0.9$ eu. Owing to this symmetry-determined entropy difference, isomerization of the trans isomer is about three times slower than isomerization of the cis isomer.

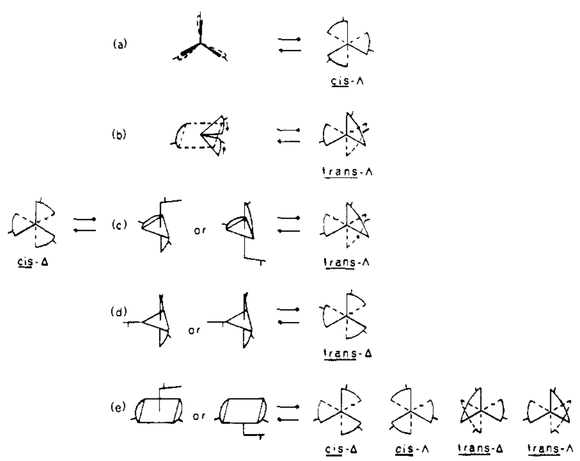

Figure 9. Intramolecular rearrangements of the cis-Δ isomer *via* (a) the trigonal-twist mechanism, (b) the rhombic-twist mechanism, (c) an axial trigonal-bipyramidal intermediate, (d) an equatorial trigonal-bipyramidal intermediate, and (e) a square-pyramidal intermediate.

In the initial stages of isomerization, the back-reactions of the trans isomer can be neglected and eq 10 and 11 reduce to

$$-\frac{d}{dt}([\text{cis-}\Delta] - [\text{cis-}\Lambda]) \approx (2k_1 + k_2 + k_3)([\text{cis-}\Delta] - [\text{cis-}\Lambda]) \quad (34)$$

$$-\frac{d}{dt}([\text{trans-}\Delta] - [\text{trans-}\Lambda]) \approx (k_2 - k_3)([\text{cis-}\Delta] - [\text{cis-}\Lambda]) \quad (35)$$

Under these conditions

$$[\text{cis-}\Delta] - [\text{cis-}\Lambda] = [\text{cis}][M_C]/[M_C^0] \approx [\text{cis}]_0(\exp[-(k_2 + k_3)t])[M_C]/[M_C^0] \quad (36)$$

and

$$[\text{trans-}\Delta] - [\text{trans-}\Lambda] = [\text{trans}][M_T]/[M_T^0] \approx [\text{cis}]_0(1 - \exp[-(k_2 + k_3)t])[M_T]/[M_T^0] \quad (37)$$

where $[\text{cis}]_0$ is the initial concentration of the cis isomer, $[M]$ is the molecular rotation at time t, and $[M^0]$ is the molecular rotation of a completely resolved isomer. Integrating eq 34 and taking account of eq 36 yields

$$k_1 \approx \frac{1}{2t} \ln \frac{[M_C]_0}{[M_C]} \quad (38)$$

where $[M_C]_0$ is the initial molecular rotation of the cis isomer. Similarly, it can be shown[33] that integration of eq 35 under conditions appropriate to the initial stages of the reaction affords the following expression for the ratio of the molecular rotations of the completely resolved isomers

$$\frac{[M_C^0]}{[M_T^0]} \approx \frac{(k_3 - k_2)}{(k_2 + k_3)} \frac{[M_C]_0}{[M_T]} \quad (39)$$

Equation 38 was used together with the relation $k_{-2}/k_2 = k_{-3}/k_3 = K^{-1}$ (eq 8), the rate constants in Table VIII, and the molecular rotations in Table IX to determine the following values of the microscopic rate constants (sec^{-1}) at 96.1°

$k_1 = (0.44 \pm 0.21) \times 10^{-4}$ $k_3 = (0.02 \pm 0.33) \times 10^{-4}$
$k_2 = (1.81 \pm 0.31) \times 10^{-4}$ $k_{-3} = (0.01 \pm 0.12) \times 10^{-4}$
$k_{-2} = (0.67 \pm 0.12) \times 10^{-4}$ $k_4 = (1.29 \pm 0.27) \times 10^{-4}$

Finally, eq 39 was employed to calculate

$$[M_C^0]_{546}/[M_T^0]_{546} = 1.18 \pm 0.31$$

It is apparent from these results that the principal reaction of the cis isomer is isomerization with inversion of configuration; in terms of the rate constants, k_1 and k_3 are small compared with k_2.

Mechanism of Rearrangements. Stereochemical rearrangements of $Co(bzac)_3$ may occur by (1) complete dissociation of one bidentate ligand, (2) rupture of one metal–ligand bond to give a five-coordinate intermediate, or (3) twisting mechanisms, which effect rearrangement without metal–ligand bond rupture.

The comparable rates and nearly identical activation parameters which have been obtained for geometrical isomerization and optical inversion of *cis*- and *trans*-$Co(bzac)_3$ (Table VIII) strongly suggest that isomerization and inversion occur primarily by the same mechanism. Comparison of the isomerization and inversion rates with rates of ligand exchange between $Co(bzac)_3$ and $Co(bzac^*)_3$ indicates that the primary path for isomerization and inversion does not involve dissociation of bzac ligands. The dissociation mechanism predicts equal rates of inversion and ligand exchange and rates of cis-to-trans isomerization 1.0 to 1.5 times the rates of ligand exchange, depending on the relative amounts of the cis and trans four-coordinate intermediates; the observed ligand-exchange rate at 96.1° is ~300 times slower than the rates of inversion and isomerization. Thus, the contribution of an intermolecular mechanism in the inversion and isomerization processes is only ~0.3% at 96.1°, and even less at the lower temperatures because of the higher activation energy for ligand exchange. The activation parameters for ligand exchange, especially the large positive activation entropy (40 eu), are consistent with a dissociative mechanism for the exchange process.

The more likely intramolecular mechanisms for rearrangement of $Co(bzac)_3$ are set out in Figure 9. For each mechanism we shall examine the products derived from one of the cis enantiomers, since the relative amounts of the products are related to the relative values of the microscopic rate constants, k_1, k_2, and k_3. The trigonal-twist mechanism[5] (Figure 9a) and the rigid ring analog proposed by Springer and Sievers[7] effect inversion without isomerization; *i.e.*, $k_1 \neq 0$ but $k_2 = k_3 = 0$ (also $k_4 \neq 0$, $k_{-2} = k_{-3} = 0$). The rhombic twist mechanism (Figure 9b[34]) predicts isomerization of the cis isomer with inversion of configuration; *i.e.*, $k_1 = k_3 = 0$, $k_2 \neq 0$. A one-bond rupture mechanism *via* a trigonal-bipyramidal intermediate gives the same result if the dangling ligand is in an axial position (Figure 9c), but gives isomerization without inversion; *i.e.*, $k_1 = k_2 = 0$, $k_3 \neq 0$ (and also $k_{-2} = k_4 = 0$, $k_{-3} \neq 0$) if the dangling ligand is in an equatorial position

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(33) J. G. Gordon, II, and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 5319 (1970).

(34) The rhombic (pseudo-C_{2v}) transition state in Figure 9b may be considered to be generated by the motion originally proposed by Ray and Dutt[4] or by an octahedral face rotation about an imaginary C_3 axis.[7] These are equivalent descriptions of essentially the same twisting motion,[10] and the stereochemistry of the reaction products does not, of course, depend on which description is adopted. Our nomenclature is simply to name the twisting mechanisms after the symmetry of the transition states.

(Figure 9d). These intermediates are referred to in the subsequent discussion as axial and equatorial trigonal-bipyramidal intermediates. Rearrangement of the cis isomer *via* a square-pyramidal intermediate is considered most likely to involve intermediates which have a cis orientation of the chelate rings at the base of the pyramid (Figure 9e) since these are the intermediates which can form with a minimum of rearrangement after bond rupture. Assuming that ring closure at the four basal positions is equally probable, this mechanism predicts equal rates of inversion and isomerization ($k_1 = k_2 = k_3$); $k_2 = k_3$ is required by symmetry independent of assumptions about ring closure. The relative rates of inversion and isomerization, $(k_1 + k_2)/(k_2 + k_3)$, and the rate constant ratios, k_1/k_2 and k_3/k_2, predicted by mechanisms a–e of Figure 9, are summarized in Table X along with the experimental values.

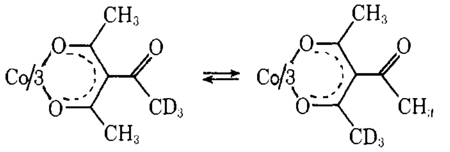
Table X

Mechanism	$(k_1 + k_2)/(k_2 + k_3)$	k_1/k_2	k_3/k_2
a	∞	∞	
b	1	0	0
c	1	0	0
d	0		∞
e	1	1	1
Exptl	1.2 ± 0.2	0.24 ± 0.12	0.01 ± 0.18

Comparison of the predicted and observed rate constant ratios indicates that none of the mechanisms in Figure 9 can be the *sole* reaction path for rearrangements of Co(bzac)$_3$ and mechanisms a, d, and e can be ruled out as the *primary* path. The trigonal twist, mechanism a, and bond rupture *via* an equatorial trigonal-bipyramidal intermediate, mechanism d, can be excluded as the primary path because isomerization and inversion of the cis and trans isomers occur simultaneously and the rates of isomerization and inversion of the cis isomer are nearly equal. The maximum possible contribution of the trigonal twist in the inversion of *cis*-Co(bzac)$_3$ can be estimated from $k_1/(k_1 + k_2)$ to be 19 ± 9%. The observed values of $k_3/(k_2 + k_3) = k_{-3}/(k_{-2} + k_{-3}) \approx 0$ agree best with no isomerization *via* equatorial trigonal-bipyramidal intermediates and exclude more than 19% isomerization by this path. Rearrangement *via* square-pyramidal intermediates (e) can also be ruled out as the primary path because $k_3 \ll k_2$.

The following combinations of mechanisms are in accord with the observed rate constant data: (1) a twisting mechanism which involves ~80% rhombic transition states and ~20% trigonal transition states; (2) a bond-rupture mechanism which produces ~80% axial trigonal-bipyramidal intermediates and ~20% square-pyramidal intermediates. Major participation of rhombic twist or axial trigonal-bipyramidal transition states is required to account for the observed inversion of configuration upon isomerization; minor participation of trigonal-twist or square-pyramidal transition states is invoked to account for the nonzero value of k_1. The involvment of more than one transition state is not unreasonable, since the axial trigonal-bipyramidal and square-pyramidal transition states should not differ greatly in energy, and the same can be said for the two twist transition states.

An unequivocal choice between a twisting and a bond-rupture mechanism cannot be made on the basis of the kinetic data. The small solvent effects on the isomerization rates (Table V) provide no convincing support for bond rupture. Neither, however, do they exclude bond rupture. The only type of mechanism which would appear to be ruled out by the solvent effects is one in which the solvent is intimately involved in the transition state, *e.g.*, a square-pyramidal transition state which has a solvent molecule bound to the metal at the sixth coordination position. A bond-rupture mechanism does appear to be favored by the activation parameters (Table VIII). It has been proposed[4] that twisting mechanisms will have low Arrhenius frequency factors, and hence negative activation entropies, because a relatively long time interval is required to get the activation energy into the appropriate vibrational modes for a twisting motion, with a consequent increase in the chance of deactivation. This notion is lent some support by recent results for racemization of the tris(oxalate) complex, $Co(C_2O_4)_3{}^{3-}$. In aqueous solution, where a one-ended dissociation of oxalate ligands is known to occur,[35] the activation energy and frequency factor for racemization are 26.0 kcal/mol and $10^{14.5}$ sec^{-1}, respectively;[36] for racemization in the solid state, where a twisting mechanism has been implicated, the corresponding values are 1.9 kcal/mol and $10^{-4.8}$ sec^{-1}.[37] Comparison of these values with the activation energies of 32.3–32.9 kcal/mol and frequency factors of $10^{15.2}$–$10^{15.8}$ sec^{-1} for isomerization and inversion of Co(bzac)$_3$ indicates that the Co(bzac)$_3$ rearrangements probably occur by a bond-rupture mechanism. The same conclusion is indicated by a comparison of the frequency factors for rearrangement of Co(bzac)$_3$ with the frequency factor of $10^{15.5}$ for inversion of cobalt(III) triacetylmethanate, Co(triac)$_3$.[38] Inversion of Co(triac)$_3$ is believed to occur, at least in part, by Co–O bond rupture because inversion is accompanied by linkage isomerization



(40)

Linkage isomerization cannot occur by a twisting mechanism. Finally, it is relevant that only 48 kcal/mol is required for complete dissociation of a bzac ligand (*cf.* Table VIII); hence, 33 kcal/mol should suffice to break one Co–O bond and would appear to be a reasonable activation energy for a one-bond rupture mechanism.

Recently we have learned of a closely related study by Gordon and Holm[33] of the isomerization and racemization of tris(5-methylhexane-2,4-dionato)cobalt(III), Co(mhd)$_3$. Gordon and Holm present a detailed and complete description of the possible transition states for the various intramolecular mechanisms, including transition states derived from the trans as

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(35) C. A. Bunton, J. H. Carter, D. R. Llewellyn, C. O'Connor, A. L. Odell, and S. Y. Yih, *J. Chem. Soc.*, 4615 (1964); A. J. McCaffery and S. F. Mason, *Proc. Chem. Soc. London*, 388 (1962).

(36) E. Bushra and C. H. Johnson, *J. Chem. Soc.*, 1937(1939).

(37) C. D. Schmulbach, J. Brady, and F. Dachille, *Inorg. Chem.*, **7**, 287 (1968).

(38) U. Klabunde and R. C. Fay, unpublished results.

well as the cis isomer. They also consider square-pyramidal transition states which are accessible by somewhat more extensive rearrangement than that permitted in Figure 9e. For the most part, kinetic results for Co(mhd)$_3$ and Co(bzac)$_3$ are similar, and both studies point to a bond-rupture mechanism involving a high percentage of axial trigonal-bipyramidal transition states.

Acknowledgments. The support of this research by National Science Foundation Grant No. GP-16280 is gratefully acknowledged. A. G. thanks the American Association of University Women for a fellowship. We also thank Professor R. H. Holm for a preprint of ref 33 and Professor J. W. Faller for some helpful comments on the evaluation of the microscopic rate constants.

Iron(II), Cobalt(II), Nickel(II), and Zinc(II) Complexes of a Series of New Macrocyclic Sexadentate Ligands

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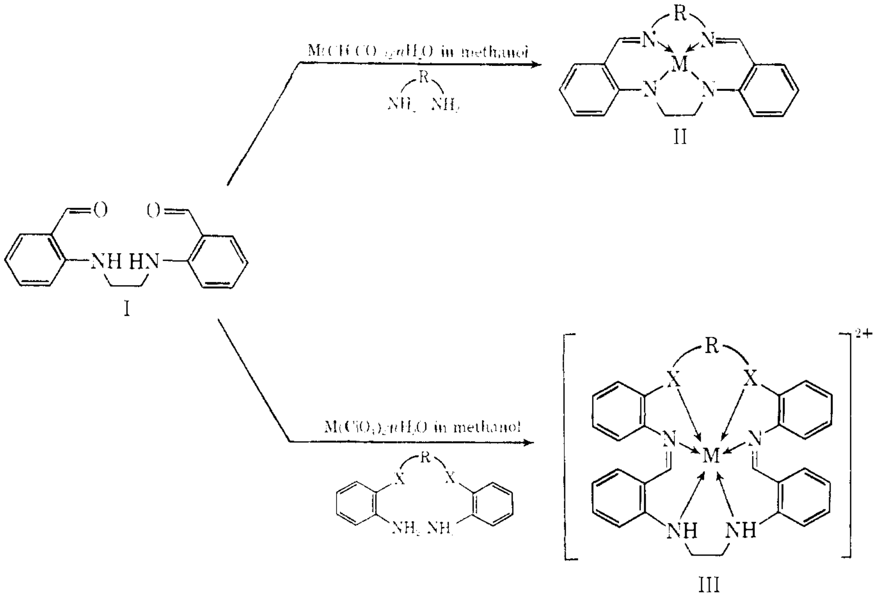
Abstract: The reaction *in situ* of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione, the appropriate metal(II) perchlorate, and the appropriate diamine containing two additional donor sites (*e.g.*, 1,2-bis(2-aminophenylthio)ethane) in methanol gives metal complexes of the type [M(L)](ClO$_4$)$_2$·CH$_3$OH, where L represents a macrocyclic sexadentate ligand (*e.g.*, 15,18-dithia-1,5,8,12-tetraaza-3,4:9,10:13,14:19,20-tetrabenzocycloeicosane-1,11-diene (N$_4$S$_2$)). The physical properties of the complexes are consistent with a formulation with all six donor sites in the macrocycle bonded to a single metal ion. This arrangement was confirmed for the [Fe(N$_4$S$_2$)]$^{2+}$ cation by a single-crystal X-ray structure determination, which also established which of the three possible geometric isomers is present.

When 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (I) is condensed with various diamines in the presence of methanolic solutions of metal(II) acetates, the quadridentate macrocyclic planar complexes (II) are obtained (reaction 1, R = –(CH$_2$)$_2$–, –(CH$_2$)$_3$–, –(CH$_2$)$_4$–, and *o*-C$_6$H$_4$).[1] We wish to report here the use of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (I) to synthesize the sexadentate macrocyclic ligand complexes (III) according to the scheme outlined in reaction 2. In these complexes (III), the ligands are uncharged and closely resemble the macrocycle (IV) reported recently by Busch and Lindoy.[2] Transition metal complexes of four other cyclic sexadentate ligands have been reported recently. The ligands V,[3] VI,[4]



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(1) M. Green and P. A. Tasker, *Chem. Commun.*, 518 (1968); M. Green and P. A. Tasker, in preparation.

(2) L. F. Lindoy and D. H. Busch, *J. Amer. Chem. Soc.*, **91**, 4690 (1969).

(3) D. St. C. Black and I. A. McLean, *Chem. Commun.*, 1004 (1968).

(4) J. D. Curry and D. H. Busch, *J. Amer. Chem. Soc.*, **86**, 592 (1964).