

magnetic moment which would seem to preclude the possibility of tetrahedral Cu(II). The spectrum (Table II) is in accord with those of known planar Cu(II) complexes, though a highly distorted tetragonal complex involving bidentate nitrate groups cannot be positively rejected. The compound gives a spectrum similar to that of $\text{Cu}(\text{NO}_3)_2 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$ for which square planar geometry has been assumed.¹⁶ The ϵ values are greater by a factor of ten than those¹⁷ for $\text{Cu}(\text{NO}_3)_4^{-2}$, implying a square planar or highly distorted tetragonal structure for $\text{Cu}(\text{HMPA})_2(\text{NO}_3)_2$.

The compound $\text{Co}(\text{NO}_3)_2 \cdot 2\text{HMPA}$ gives a spectrum which exhibits a single visible band of intermediate intensity ($\epsilon \sim 175$), somewhat lower than intensities normally associated with tetrahedral Co(II). However, the magnetic moment of the compound given in the Experimental section would seem to preclude possible octahedral coordination although a highly distorted tetragonal structure involving chelate or bridging nitrate cannot be eliminated. Similar effects have been noted for other Co(II) complexes in which NO_3^- is a ligand. It was concluded that these complexes were tetrahedral.¹⁶⁻¹⁸ The compound $\text{Ni}(\text{NO}_3)_2 \cdot 2\text{HMPA}$, a yellow solid, exhibits an absorption spectrum very much different from those normally associated with tetrahedral Ni(II). The spectrum shows several bands

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of low intensity suggestive of centrosymmetric Ni(II). Two possibilities exist here. The complex could be tetragonal due to bidentate nitrate groups¹⁷ or could be a radically distorted tetrahedral (*i.e.*, D_{2d}) structure. The spectrum of the compound is very similar to that reported for $\text{Ni}(\text{NO}_3)_2 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$ ¹⁶ for which a D_{2d} structure has been suggested. The spectra of both of these compounds agree qualitatively with predictions of the appearance of the spectrum for Ni(II) in a ligand field of D_{2d} symmetry.^{19,20} Once again, the possibility of tetragonal coordination cannot be completely dismissed.

On the basis of evidence presented in earlier sections, it is concluded that the compounds: $\text{CoX}_2 \cdot 2\text{HMPA}$ ($X = \text{Cl}, \text{Br}, \text{I}, \text{NCS}, \text{NO}_3$) contain Co(II) in pseudo-tetrahedral (C_{2v}) environments and the compounds $\text{NiX}_2 \cdot 2\text{HMPA}$ ($X = \text{Cl}, \text{Br}, \text{I}$) contain Ni(II) in the same geometrical arrangement. $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{HMPA}$ is thought to be a planar complex while Ni(II) in $\text{Ni}(\text{NO}_3)_2 \cdot 2\text{HMPA}$ probably experiences a pseudo- D_{2d} ligand field.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, NORTH CAROLINA

The Chemistry of Metal Chelate Rings. IV. Electrophilic Substitution of Optically Active Tris-acetylacetonates¹⁻³

By JAMES P. COLLMAN, ROBERT P. BLAIR, ROGER L. MARSHALL, AND LAIRD SLADE

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The tris-acetylacetonates of chromium(III), cobalt(III), and rhodium(III) were resolved by chromatography on a 16-ft. column of *D*-lactose hydrate. The optically active chelates were subjected to a variety of electrophilic substitution reactions including chlorination, bromination, thiocyanogenation, nitration, and acetylation. In each instance, the substituted chelates were found to be optically active, suggesting that the chelate rings are not ruptured during electrophilic substitution. The optical stabilities of the cobalt and rhodium chelates were examined. Several of the cobalt chelates were found to racemize during crystallization whereas the rhodium chelates exhibited remarkable optical stability.

Introduction

During the past three years, experiments in these and other laboratories have demonstrated that several metal acetylacetonates and related chelate systems undergo a variety of electrophilic substitutions of the central carbon of the chelate rings in the manner of an aromatic

system.⁴⁻¹² By such processes, the inert tris-acetyl-

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acetonates of chromium(III), cobalt(III), and rhodium(III) have been substituted with chloro,⁵ bromo,⁵ iodo,⁵ thiocyno,^{6,13} nitro,⁸ dimethylaminomethyl,¹³ chloromethyl,¹³ acetyl,⁴ butyryl,¹³ benzoyl,¹³ and formyl groups.³ A wide variety of chelates in which the three rings have been substituted with different groups have been prepared.^{11,13} The proton magnetic resonance spectra of the diamagnetic mixed ring acetylacetonates have provided evidence for aromatic "ring currents" in these chelates.¹¹

From the inception of our studies, it seemed that the mechanisms describing these substitutions could be divided into three limiting possibilities²: (a) complete dissociation of one acetylacetonate anion followed by reaction of this free ligand with the electrophile and subsequent recombination to form the substituted chelate ring; (b) formation of a five-coördinate intermediate species by cleavage of one metal-oxygen bond prior to or after electrophilic attack on that chelate ring undergoing rupture and then loss of a proton and formation of a substituted chelate ring; (c) reaction in the manner of an aromatic system with the chelate ring remaining intact during a two-step process. Intuitively mechanisms (b) and (c) seemed much more likely.

Since these chelates are potentially resolvable racemates, the present study was undertaken in order to make use of the asymmetry of these substrates in determining the mechanism of the ring substitution reactions. It was obvious that mechanism (a) would be attended by racemization of the optically active substrate and that mechanism (c) would not lead to loss of optical integrity. The stereochemical course of mechanism (b) was not so clearly defined. Since the completion of the experimental work outlined herein, Piper has presented convincing evidence for a symmetrical five-coördinate intermediate during the racemization of acetylacetonates and interconversion of *cis-trans* and coördination isomers of other β -dicarbonyl chelates. The significance of these elegant experiments to the present problem will be discussed later.

The separation of sufficient amounts of chromium, cobalt, and rhodium acetylacetonates of significant optical activity to study these electrophilic substitutions was a serious experimental difficulty. Since these chelates are molecular substances and do not contain acidic or basic groups which would allow stoichiometric combination with optically active resolving agents, unconventional methods must be applied to these resolutions. Three physical methods had been reported previously to effect apparently meager, partial resolution of these acetylacetonates.¹⁴⁻¹⁶

Moeller¹⁴ partially resolved chromium and cobalt acetylacetonates by chromatographic adsorption on *d*-lactose hydrate columns, using benzene-petroleum ether as an eluent. In this manner Moeller obtained samples of cobalt(III) acetylacetonate with molar rotations¹⁷ as high as -570° using a 90-cm. column.

Dwyer and Gyarfas¹⁵ effected partial resolution of cobalt and chromium acetylacetonates by adding *d* or *l*-tris-(ethylenediamine)cobalt(III) iodide to solutions of the metal acetylacetonates in ethanol and then salting out the acetylacetonates with ammonium chloride at 4°. These results were explained by the concept that the activities of the enantiomorphic forms of the asymmetric chelates are unequal in solutions containing optically active ions.

A recent, ingenious method of resolution devised by Kirschner confirms the unequal activities of these enantiomorphic chelates in an asymmetric solution.¹⁶ Kirschner effected a partial resolution of cobalt(III) acetylacetonate by carrying out a zone-melting operation on a frozen solution of the chelate and sodium (*d*)-dibenzoyltartarate in dioxane-water.

After some experimentation with these methods, the chromatographic technique of Moeller was chosen as the most convenient route to relatively large quantities of partially resolved chromium, cobalt, and rhodium acetylacetonates. Two modifications of Moeller's method make this a powerful technique of general applicability. It was found that none of the chelate was retained on the column after the chromatography and thus the column could be used over and over again without loss of effectiveness. Furthermore, longer columns gave a higher degree of resolution.

Experimental

Resolution by Chromatography.—A chromatographic column 16 ft. long and 1.5 in. in i.d. was constructed from heavy wall Pyrex tubing and equipped with a porous fitted glass disk plate, a Teflon stopcock, and a drip tip at the bottom end. The lower end of the column was connected to a Rinco automatic fraction collector fitted with a siphon to collect 25-ml. samples and a wheel to accept 236 fractions. During the chromatography operation, the eluent was automatically fed to the column from a 3-l. bottle, constructed from an erlenmeyer flask with the open end drawn into a 12-mm. tube which extended just below the surface of the eluent in the column.

The column was packed with 100 mesh Mallinckrodt *d*-lactose hydrate U.S.P. grade. The column was filled to two-thirds of its height with 1:1 benzene-heptane (by volume) and lactose then was added in the form of a slurry consisting of 1 part lactose by volume and 3 parts 1:1 benzene-heptane. The column was allowed to drain, adding solvent periodically to keep the solvent level well above the adsorbant bed. The drainage was continued after each addition until the level of the lactose would settle no further. At this time the rate of solvent flow was increased by applying 10-15 lb. of pressure at the top of the column from a nitrogen tank. This caused more rapid flow of the eluent and a visible decrease in the height of the packing material. During this pressure treatment, the eluent level always was maintained well above the lactose level by periodically recycling the solvent. Further packing was effected by tapping the column with a rubber covered dowel until no further settling of the lactose was observed. The pressure then was removed and another addition of the lactose slurry was made. This entire process was repeated with every addition of lactose until the whole column was packed. It was found that the above procedure was necessary to prepare an efficient column.

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The lactose is completely insoluble in 1:1 benzene-heptane. Solvent blanks taken on the polarimeter were unchanged after passing the solvent through the column. The solvent flow rate was 250 to 300 ml./hr. under normal operating conditions. During a typical run 1.0 g. of the acetylacetonate in 50 ml. of benzene was introduced into the top of the packed column and allowed to penetrate. Any residues were washed carefully into the adsorbant with small amounts of benzene. Elution then was begun with 1:1 benzene-heptane. Approximately 40 hr. elapsed between application of the racemic chelate solution and collection of the first sample of solution containing the partially resolved chelate. The chelate was completely recovered by the elution in 20-25 portions of 25 ml. each. The concentrations of the samples were measured spectrophotometrically after adjustment of the sample volume to 25 ml. in a volumetric flask.

Polarimetry.—The optical activity of the various samples was determined with a Rudolph Model 80 high-precision polarimeter fitted with a Rudolph photoelectric attachment and standard sodium and mercury sources. The reported sensitivity of this instrument is $\pm 0.003^\circ$. Throughout these studies, a precision of 0.003° or better (total deviation per set of measurements) was obtained. The tubes used were 4 dm. long and had a capacity of 26 ml. Solvent blanks and *d,l* chelate blanks were read periodically to check for the proper functioning of the instrument. Periodically readings were rechecked after rotating the polarimeter tube 90° to check for distortion caused by strained glass end plates. Each time a reading on an optically active product was obtained, a *d,l* product blank also was read.

The high absorbance of the chromium and cobalt chelates made necessary the use of very low concentrations of samples (5 to 12 mg.) in the polarimeter tubes in order to obtain sufficient light transmission. Larger concentrations of the rhodium chelates (up to 150 mg.) were possible because of the decreased absorbance. However, the measured rotations of the rhodium chelates are correspondingly less because their rotatory dispersion curves are flat in the visible region.

The method of symmetrical angles was used for all readings. For each individual sample, at least four sets of readings were obtained that agreed within 0.003° and then these sets were averaged. The extinction point average then was corrected for the racemic blank. The molecular rotation, $M[\alpha]$, is defined as specific rotation \times molecular weight \div 100.¹⁷

Typical column profiles are illustrated in Tables I and II. The authenticity of optically active cobalt acetylacetonate was confirmed by the recombination of the calculated amounts of partially resolved *d* and *l* isomers to form racemic material.

Optical Stability.—The optical stability of chromium acetylacetonate has been studied by Moeller,¹⁴ who found its half-life to be 8 days in 1:1 benzene-hexane at 25°. The same workers reported that cobalt acetylacetonate did not racemize under these conditions in 2 days. Rhodium acetylacetonate had not been resolved previously.

A solution of optically active cobalt acetylacetonate in chloroform exhibited no loss in optical activity after 5 weeks at room temperature. Other solutions of this chelate in chloroform decomposed to form pink solids after a few days. The nature of these decompositions is not clear, but impurities in the chloroform, oxygen, and sunlight may be involved. Measurements on the

TABLE I
RESULTS OF A TYPICAL CHROMATOGRAPHIC RESOLUTION OF
COBALT(III) ACETYLACETONATE

| Fraction no. | Wt. of solute in fraction, mg. | Wt. of sample used for reading, mg. | Obsd. rotation, deg. | Molecular rotation |
|--------------|--------------------------------|-------------------------------------|----------------------|--------------------|
| 1 | 6.68 | 6.68 | -1.285 | -4450 |
| 2 | 102.28 | 10.23 | -0.430 | -970 |
| 3 | 134.92 | 6.91 | -0.075 | -250 |
| 4 | 187.96 | 12.08 | +0.059 | +110 |
| 5 | 141.39 | 13.58 | +0.400 | +680 |
| 6 | 58.47 | 11.92 | +0.253 | +490 |
| 7 | 78.42 | 10.03 | +0.136 | +310 |

TABLE II
RESULTS OF A TYPICAL CHROMATOGRAPHIC RESOLUTION OF
RHODIUM(III) ACETYLACETONATE

| Fraction no. | Wt. of solute in fraction, mg. | Obsd. rotation, deg. | Molecular ¹⁷ rotation |
|--------------|--------------------------------|----------------------|----------------------------------|
| 1 | 3 | -0.009 | -83 |
| 2 | 9 | -0.026 | -72 |
| 3 | 27 | -0.049 | -45 |
| 4 | 62 | -0.065 | -26 |
| 5 | 106 | -0.054 | -13 |
| 6 | 138 | -0.025 | -4 |
| 7 | 132 | +0.017 | +3 |
| 8 | 122 | +0.022 | +4 |
| 9 | 98 | +0.035 | +9 |
| 10 | 74 | +0.040 | +13 |
| 11 | 51 | +0.040 | +20 |
| 12 | 35 | +0.031 | +22 |
| 13 | 22 | +0.028 | +32 |
| 14 | 12 | +0.021 | +45 |
| 15 | 7 | +0.016 | +59 |
| 16 | 4 | +0.012 | +67 |

cobalt chelate in glacial acetic acid showed a 60% loss of optical activity during 5 weeks, but visual evidence of decomposition may account for the loss of optical activity.

Sublimation of the cobalt acetylacetonate at 110° and 0.5 mm. pressure resulted in the loss of 30% of its optical activity. The optical activity of this chelate was not affected by chromatography on active alumina or exposure of a chloroform solution to activated charcoal for 12 hr.

It was found that slow crystallization of cobalt acetylacetonate resulted in total loss of optical activity in the crystalline material.¹⁸ The optically active nitro and bromo cobalt chelates exhibited a similar loss of activity upon crystallization. There was little or no loss of optical activities when solutions of the cobalt chelates were evaporated in a current of air to yield a fine powder. The optically active powder exhibited no obvious crystallinity when examined under a polarizing microscope, whereas the *d,l* chelates were all obviously crystalline.

Stepwise slow crystallization of the optically active cobalt chelate from a benzene-hexane solution gave rise to a series of increases in the molecular rotation of the filtrates, whereas the crystalline precipitates were all inactive. When crystallization was complete, all optical activity had been lost. These results are summarized in Table III. The same result was found by crystallization from ethanol. Because of this strange racemization phenomenon, the reactions on optically active cobalt acetylacetonate were carried out in such a manner that the substituted chelates were kept in solution until the optical activity of the product was measured and then the solutions were evaporated in a slow stream of air and the powdered chelates were weighed and identified by comparison of their infrared spectra with the spectra of the authentic *d,l* samples. This procedure was used for all of the substitution reactions of optically active cobalt and chromium chelates.

TABLE III
RECRYSTALLIZATION OF OPTICALLY ACTIVE COBALT(III)
ACETYLACETONATE^a

| Mother liquor after crystal crop removed | Molecular rot. of soln. at Hg line | Time, hr. |
|--|------------------------------------|-----------|
| Starting solution | -490 | 0 |
| First crystallization | -720 | 18 |
| Second | -730 | 24 |
| Third | -950 | 48 |
| Fourth | -1500 | 72 |
| Fifth | No sample left | 120 |

^a All crystal crops showed no optical activity.

The optical stabilities of the partially resolved chromium chelates were not studied. Optically active rhodium acetylacetonate was not racemized after repeated recrystallizations, chromatography on active alumina, or treatment with aluminum chloride.

Reactions of Partially Resolved Metal Acetylacetonates.—Most of the racemic products have been described elsewhere, the others are included herein.

Bromination of Racemic Tris-(2,4-pentanediono)-rhodium(III).—A solution of 200 mg. (0.5 mmole) of rhodium acetylacetonate¹⁹ and 356 mg. (2.0 mmoles) of N-bromosuccinimide in 25 ml. of chloroform was heated at reflux for 10 min. The solution was cooled to room temperature and an additional 25 ml. of chloroform was added to keep the product in solution. The organic solution was extracted three times with water to remove the succinimide. The organic phase was dried with CaCl₂, filtered, and then evaporated at room temperature. The residue was suspended in a boiling 1:1 chloroform-ethanol mixture and benzene was added dropwise until the solid dissolved. This solution was allowed to cool slowly and the yellow crystals then were collected and air dried. The tribromo chelate chloroform solvate exhibited the following properties: weight 290 mg.; m.p. 245–248° dec.; infrared peaks (KBr pellet) 1540, 1410, 1325, 1270, 1212, 1020, 975, 685, and 660 cm.⁻¹; ultraviolet peaks (CHCl₃) 268 m μ (7280), 343 m μ (9630); n.m.r. (CCl₄) 7.49, 2.70 τ .

The tribromorhodium chelate was freed from chloroform by heating the solvate at 65° under vacuum for 5 hr. The product was an amorphous powder, m.p. 230–260° dec.; infrared peaks (KBr) 1540, 1410, 1326, 1270, 975, 920, 683, and 660 cm.⁻¹; n.m.r. 7.49 τ .

Anal. Calcd. for C₁₅H₁₈O₆Br₃Rh: C, 28.28; H, 2.85. Found: C, 28.63; H, 3.02.

Chlorination of Racemic Tris-(2,4-pentanediono)-rhodium(III).—A solution of 200 mg. (0.5 mmole) of rhodium acetylacetonate and 333 mg. (2.5 mmoles) of N-chlorosuccinimide in 50 ml. of chloroform was heated at reflux for 15 min., then cooled rapidly to room temperature. This solution was extracted several times with water to remove the succinimide. The organic layer was dried with calcium chloride, filtered, and slowly evaporated at room temperature. Recrystallization of the residue from hot benzene-heptane yielded 150 mg. (60%) of yellow crystals, m.p. 252–253°; infrared spectrum (KBr pellet) 1550, 1445, 1415, 1335, 1275, 1035, 920 cm.⁻¹; ultraviolet spectrum (CHCl₃) 270 m μ (7270), 342 m μ (10,400); proton magnetic resonance spectrum (CCl₄) 7.57 τ . A second crop of less pure crystals was obtained by evaporation of the mother liquor.

Anal. Calcd. for C₁₅H₁₈O₆Cl₃Rh: C, 35.77; H, 3.60; Cl, 21.12. Found: C, 35.48; H, 3.38; Cl, 21.71.

Repeated Crystallization of Optically Active Rhodium Acetylacetonate.—A 197 mg. sample of *l*-rhodium acetylacetonate, $M[\alpha]_{5461} -24$, was recrystallized three times from hot benzene-hexane. The crystalline yellow chelate exhibited the same activity after three recrystallizations.

Attempted Acetylation of *d*-Rhodium Acetylacetonate.—Treatment of 175 mg. of *d*-rhodium acetylacetonate, $M[\alpha]_{5461} 18$, with 350 mg. of anhydrous aluminum chloride and 207 ml. of acetyl chloride in 25 ml. of 1,2-dichloroethane at –20 to –15° for 30 min. followed by the usual work-up afforded a crude product. Chromatography of this product on alumina yielded only *d*-rhodium acetylacetonate, $M[\alpha]_{5461} 18$. No trace of the acetylated chelate was detected. Two additional attempted acetylations afforded only starting material with no loss of optical activity. No chelate decomposition was evident in the work-up of these reactions. The presence of HCl may account for the failure of these attempts.

Acetylation of *d*-Rhodium Acetylacetonate.—A 192-mg. sample of *d*-rhodium acetylacetonate, $M[\alpha]_{5461} 22$, was treated with acetyl chloride which had been purified by refluxing for 2 hr. and distilling through a packed column (a center cut was taken for

TABLE IV
ASYMMETRIC CHELATES FROM DIRECT SUBSTITUTION REACTIONS

| Reaction prod. | Molecular rot. of starting matl. | Molecular rot. of prod. | Obsd. rot. of prod., deg. |
|---|----------------------------------|-------------------------|---------------------------|
| [BrCAc ₂] ₃ Cr | +363 | +297 | +0.092 |
| [BrCAc ₂] ₃ Co | –765 | –752 | –0.150 |
| | +514 | +488 | +0.080 |
| [BrCAc ₂] ₃ Rh | +20 | +18 | +0.038 |
| [O ₂ NCAc ₂] ₃ Cr | +390 | +500 | +0.016 |
| [O ₂ NCAc ₂] ₃ Co | –765 | –388 | –0.125 |
| [O ₂ NCAc ₂] ₃ Rh | –12 | –26 | –0.031 |
| [NCSAc ₂] ₃ Co | –765 | –858 | –0.151 |
| [ICAc ₂] ₃ Cr | +363 | +362 | +0.083 |
| [AC ₃ C][HCAc ₂] ₃ Rh | +22 | +56 | +0.033 |
| [ClCAc ₂] ₃ Rh | +20 | +18 | +0.050 |

this experiment) and with aluminum chloride in the manner described above. The infrared spectrum of the crude product indicated the presence of some acetylated chelate. Chromatographic separation on alumina in benzene yielded two compounds which were identified by their infrared spectra: 167 mg. of *d*-rhodium acetylacetonate, $M[\alpha]_{5461} 22$, and 25.7 mg. (12%) of *d*-(3-acetyl-2,4-pentanediono)-bis-(2,4-pentanediono)-rhodium(III),¹³ $M[\alpha]_{5461} 56$.

Discussion

The data in Table IV clearly show that total racemization does not accompany electrophilic substitution of the three chelate rings. This rules out mechanism (a) involving total ligand exchange. Since complete resolution of the substituted or unsubstituted acetylacetonates has never been achieved, it is impossible at this time to determine the optical purity of the products or the starting materials in these reactions. Therefore, the possibility of small losses of optical purity during such reactions cannot be ascertained. However, since the molar rotations of the substitution products over a wide range of different reactions and metals are of the same order of magnitude as the starting materials, it seems likely that significant racemization does not take place. Comparison of certain data in Table IV further supports this. Bromination of chromium acetylacetonate produces a bromo chelate of lower molar rotation than the starting material.

However, in the nitration reaction the cobalt product is less active and the chromium product more active than their respective starting materials. It seems likely that these data reflect changes in molar rotations instead of optical purity.

The reliability of the molar rotation data in each experiment is best reflected by the magnitude of the observed rotations since that figure has an inherent error of about 0.003°. Comparison of the bromination of both *d*- and *l*-cobalt acetylacetonate shows the reproducibility of this type of experiment.

The significance of these data in defining the mechanism of electrophilic substitution of metal acetylacetonates can be reduced to one question: does the racemization of tris-acetylacetonates proceed through bond rupture and a five-coördinate intermediate? Such a process would demand a symmetrical five-coördinate intermediate. There are four feasible five-coördinate intermediates, a symmetrical and an asymmetric tetragonal pyramid and a symmetrical and an asymmetric tri-

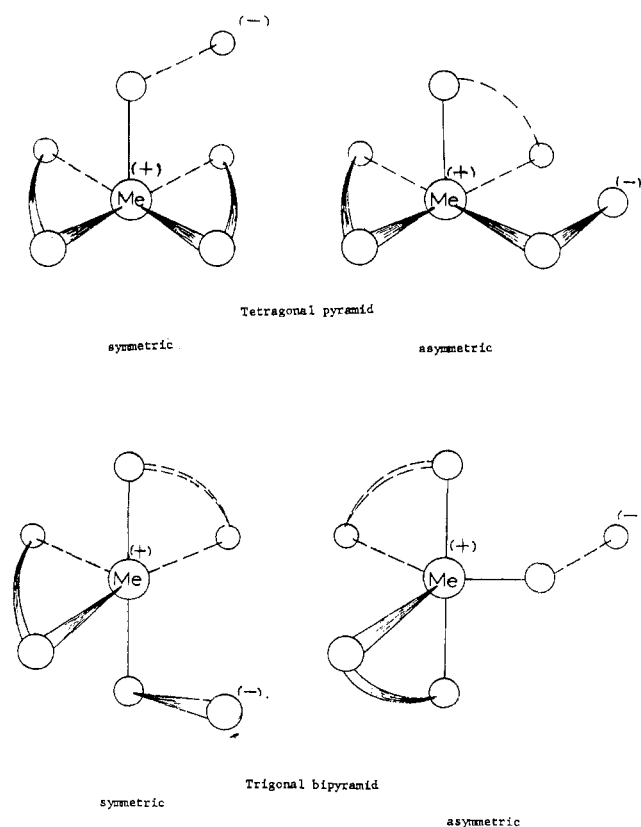
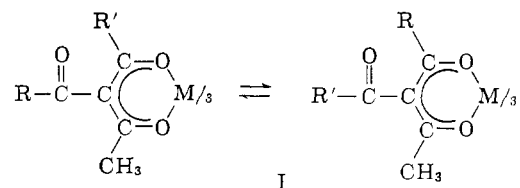


Fig. 1.—Five-coördinate intermediates.

gonal bipyramid (Fig. 1). In the poor donor solvents used in these experiments, it seems likely that the trigonal bipyramid structures would be favored. Furthermore, the energy barrier between the symmetrical and unsymmetrical trigonal bipyramids would seem low—only a vibrational motion being required. However, it is not possible to predict without experimental evidence the nature of such a five-coördinate intermediate. In addition it has been suggested that a trigonal antiprism six-coördinate transition state could be involved in the racemization of tris-acetylacetonates, the "Bailar twist" mechanism.^{20,21} Another intramolecular rearrangement without bond rupture has been postulated by Ray and Dutt.²²

In a series of elegant experiments, Piper^{21,23} has provided strong evidence for a symmetrical five-coördinate intermediate in isomerism reactions of tris-1,3-dicarbonyl chelates. Piper has demonstrated that the twist mechanism cannot be used to explain the *cis-trans* isomerism of a number of metal chelates of trifluoroacetylacetonate by measuring the merging of the fluorine magnetic resonance signals as a function of temperature. Further, he has demonstrated charge separation in the transition state of these isomerizations by examining the solvent dependence of the rate data.²³ The racemization of cobalt acetylacetyl-

acetone was found to be first order and it seems probable if the *cis-trans* isomerism goes by way of a five-coördinate intermediate that the racemization of the acetylacetonates also involves bond breaking. Another experiment devised by Piper gives proof of such bond rupture during a racemization. We had earlier predicted the "coördination isomerism" of acylated complexes such as I.⁸ Piper²³ has shown that in the case $R' = CD_3$, $R = CH_3$ such isomerism takes place at the same rate as the racemization of the complex $R = CH_3 = R'$. The geometry of this system demands bond rupture during isomerization.



It therefore seems certain that mechanism (b) would proceed through a symmetrical five-coördinate intermediate and would lead to total racemization. Thus mechanism (c), substitution as a quasi-aromatic system without ring cleavage, best describes these reactions.

One final aspect of these experiments deserves comment. The strange racemization of optically active cobalt acetylacetonate during crystallization is probably a surface reaction whereby the racemic crystal preferentially forms, enriching the solution in the excess enantiomorph. When the supply of the deficient enantiomorph becomes exhausted at the surface of the crystal, racemization of the other enantiomorph probably takes place. The mechanism of this racemization may involve the formation of a defective crystal surface as the wrong enantiomorph is imbedded in the growing lattice (one side of each of the two enantiomorphous molecules has the same shape). The "defective" enantiomorph is then labilized through electron transfer from a cobalt(II) species embedded in the lattice. Preferential formation of the racemic crystal may be either kinetic or thermodynamically controlled. This hypothesis is only speculative and may not withstand further experimentation.

It would be most interesting to see if chromium(III) acetylacetonate undergoes such a surface racemization since the chromium(II) state is relatively a much higher energy species than the cobalt case. It is interesting to note that rhodium(III) acetylacetonate does not racemize under these conditions and that a lower oxidation number is not known for this type of rhodium complex.

Another problem which remains undone is to effect the complete resolution of the tris-metal acetylacetonates and their substitution products and to study the kinetics of racemization of these chelates. Such a resolution probably would best be accomplished by chemical means (*i.e.*, reversibly substituting a basic group on the chelate ring). Experiments are in progress to test these ideas.

(20) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958, p. 273.

(21) T. S. Piper, Seventh International Conference on Coördination Chemistry, Stockholm, Sweden, June, 1962. Note that supplemental mimeographed data presented at this meeting supersedes material in the Abstracts.

(22) P. Ray and N. K. Dutt, *J. Indian Chem. Soc.*, **18**, 289 (1941); **20**, 81 (1943).

(23) T. S. Piper, private communication.