Coordination Chemistry Reviews
Elsevier Publishing Company, Amsterdam – Printed in The Netherlands

OPTICAL AND GEOMETRICAL ISOMERIZATION OF β-DIKETONATE COMPLEXES

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(Received August 21st, 1970)

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Coord. Chem. Rev., 6 (1971) 331–375

A INTRODUCTION

Several reviews have been written recently on metal β-diketonate complexes. There has been one general review[1] along with specific reviews on the stereochemistry[2] and ligand exchange reactions[3] of such compounds The usefulness of nuclear magnetic resonance in the study of very rapid rates and mechanisms of optical inversion and geometrical isomerization of complexes was first shown by Fay and Piper[4] The great importance of NMR in the structural studies of octahedral complexes of β-diketones had already been established[5-8].

The work on isomerization covered herein will be limited to that dealing with geometrical and optical isomerization The primary purpose of this paper is to show what has been done and future possibilities in the application of NMR to the study of geometrical and optical isomerization. Although a review of the resolution of β-diketonate complexes is not intended, some examples are mentioned to illustrate slower interconversion processes and also to indicate some methods to separate isomers of the more stereochemically inert complexes

B. MECHANISMS

Before attempting to place in perspective the experimental data thus far determined it will be useful to examine the proposed mechanisms which might be involved in isomerization of octahedral complexes with bidentate ligands This will allow briefer reference to them in later sections Some systems of other geometries will be considered in a later section.

(i) Intramolecular processes

(a) Bond rupture mechanisms

The first intramolecular mechanism for the isomerization of bidentate chelate complexes was proposed by Werner[9] in 1912 The trigonal-bipyramidal transition state is pictured in Fig. 1 for the tris-(chelate) complexes and in Fig 2 for complexes with two monodentate ligands Another transition state could be pictured as a tetragonal pyramid. These are depicted in Figs 3 and 4 With a polar solvent it is possible that the transition state is solvated The efficacy of these mechanisms in causing optical inversion and/or geometrical isomerization will be discussed in the section on experimental studies The possibilities vary greatly with the various combinations of symmetric and unsymmetric ligands. It should be noted that in addition to the obvious translation and reattachment of the dissociated group, in every case substantial rearrangements of the rings that do not become dissociated are required

(b) Twisting mechanisms (non-bond rupture)

Isomerization without bond breaking can supply a low-energy path for optical and/ or geometrical interconversions at least for some classes of compounds[10]. These processes have come to be known as twist mechanisms and the structure of their transition states

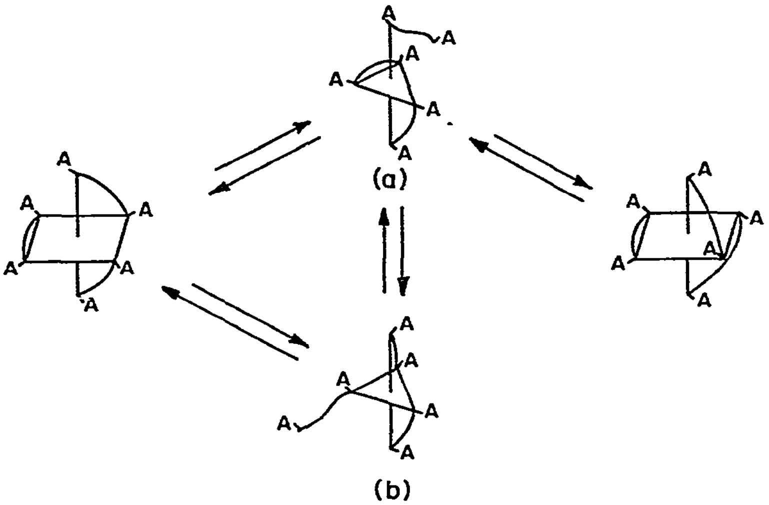


Fig 1 Optical inversion of a tris bidentate chelate complex by an intramolecular bond-rupture mechanism involving a trigonal-bipyramidal transition state (a) Axial mode; (b) equatorial mode Note that the two transition states are pictured with idealized geometry and should be considered together statistically, as the true transition state in such a mechanism might well be of some intermediate form

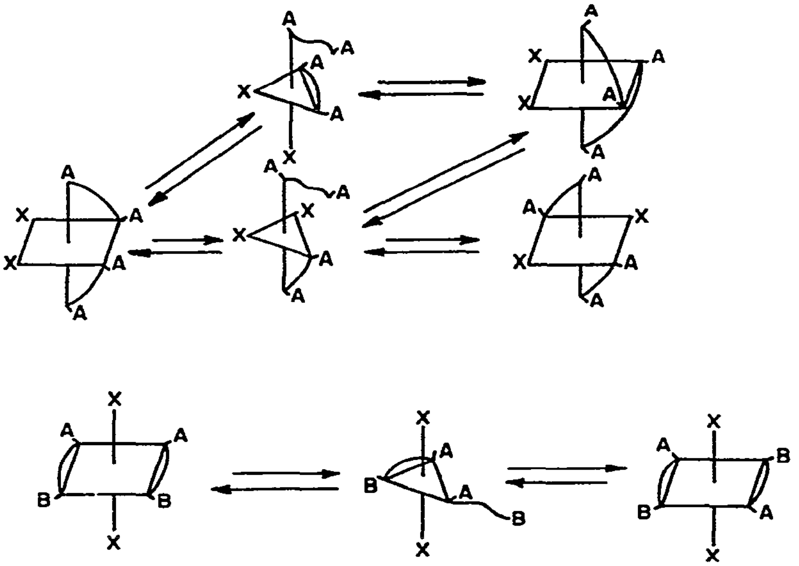


Fig 2 Intramolecular bond-rupture isomerization mechanism involving trigonal bipyramidal transition states for complexes of two bidentate ligands and two monodentate ligands The upper portion depicts the axial modes which can cause both optical and geometrical isomerization The lower portion depicts the equatorial mode which can cause isomerization only if the chelate ligand is unsymmetrical.

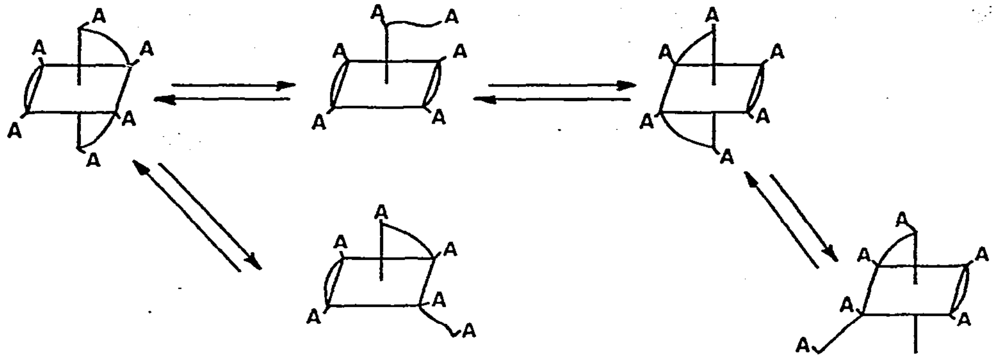


Fig. 3. An intramolecular bond-rupture mechanism for optical inversion of a complex with three symmetric bidentate ligands through a square-based-pyramidal transition state. Note that the geometry of the transition states is idealized and a slight amount of distortion of the base of the pyramids would result in a trigonal bipyramid.

can be pictured as trigonal prisms. Additional credibility has been lent to such mechanisms by the discovery of trigonal-prismatic complexes of some other bidentate ligands in the crystalline state. The volume of activation for the solid state racemization of crystalline potassium tris(oxalato)cobalt(III) has been used to argue[11,12] for such a process. However, both of these observations are only inferential.

The first mechanism for stereochemical rearrangement of octahedral chelate complexes that does not involve any bond breaking was proposed by Rây and Dutt[13] in 1943. They pictured the mechanism as the simultaneous translation of two of the chelate rings in their respective planes, one moving up with respect to the plane of the third chelate ring and the other moving down. This motion is shown in Fig. 5. It should be noted that three different pairs of rings could be subject to this motion and depending on the relative symmetry of the rings this could result in transitions between different geometrical and/or

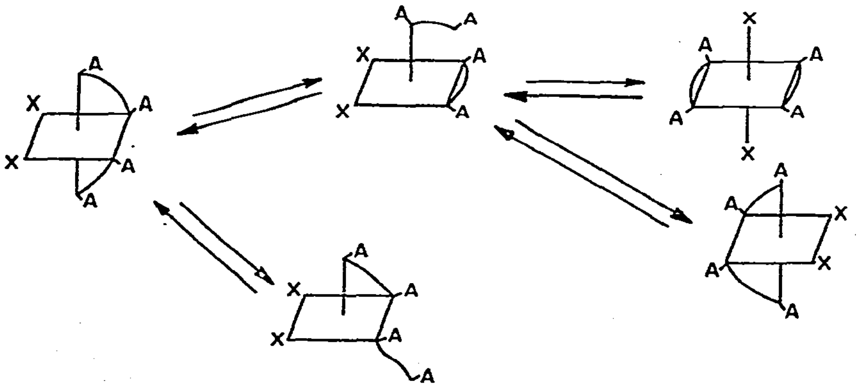


Fig. 4. Intramolecular bond rupture isomerization mechanisms involving square-based-pyramidal transition states for complexes of two bidentate ligands and two monodentate ligands.

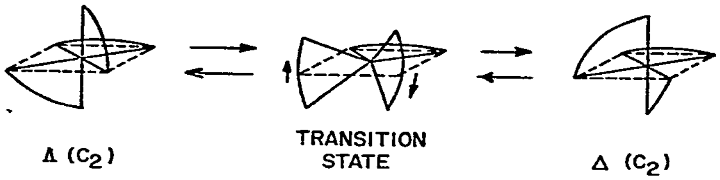


Fig 5. The Rây and Dutt twist mechanism for intramolecular isomerization of complexes of three bidentate ligands without bond breaking Note that the transition state is of C_{2v} symmetry if all of the ligands are the same and symmetric This transition state may sometimes be called a rhombic intermediate.

optical forms. While during the motions as pictured the 90° angle for the donor–metal–donor (DMD) intra-ring angles would be maintained, the DMD angles between any two rings are reduced in the transition state. The transition state is seen in Fig. 5 to be a trigonal prism in which the plane of one ligand is perpendicular to the planes of the other two. This transition state is sometimes referred to as the rhombic intermediate.

Bailar[14] and others[15] pictured a non-bond-rupture mechanism with slightly different

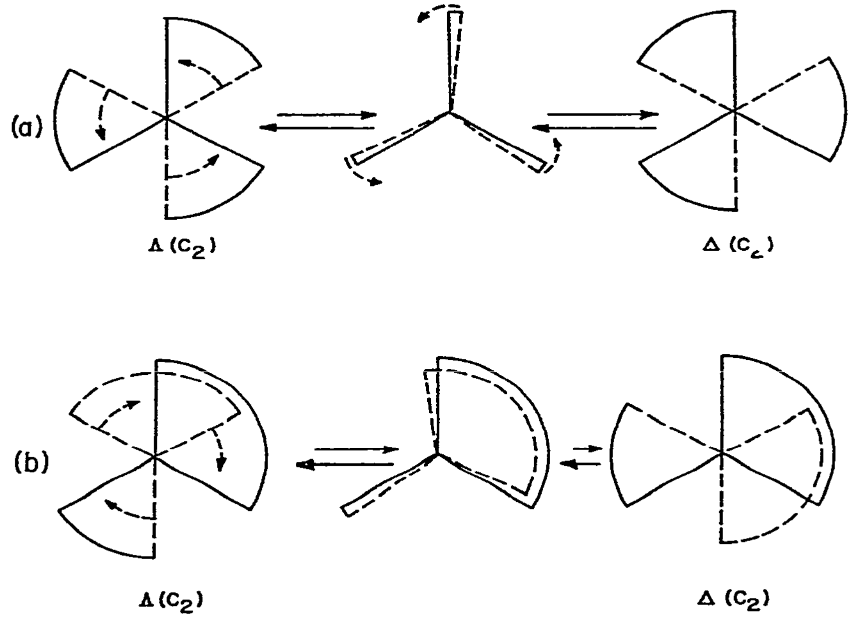


Fig 6. The Bailar twist mechanism for intramolecular isomerization of complexes of three bidentate ligands without bond breaking The dashed lines extend below the plane of the paper while the solid lines extend above the plane In (a) is depicted a twist about a real or pseudo C_3 axis, depending on the symmetry and sameness of the ligands A twist about one of the imaginary C_3 axes is depicted in (b). Note that if three identical symmetrical ligands are used the transition state in (a) has D_{3v} symmetry and the transition state in (b) has C_{2v} symmetry. These transition states are sometimes called the trigonal prismatic and the rhombic transition states, respectively

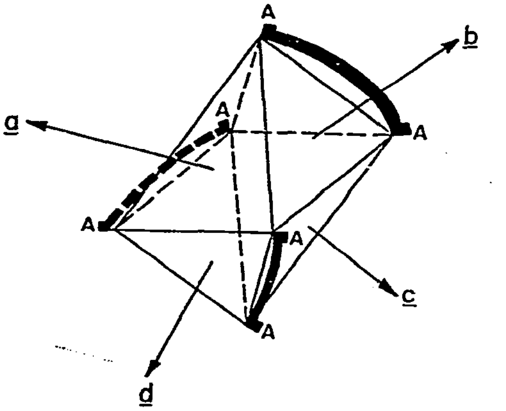


Fig. 7. The four octahedral face axes of a complex with three bidentate ligands. Axis *a* is the real or pseudo C_3 axis depending on the ligands involved while axes *b*, *c* and *d*, are imaginary C_3 axes.

mode of twisting a molecule about a real, pseudo, or imaginary C_3 axis, as depicted in Fig. 6. A real C_3 axis exists only for a tris complex with identical symmetric ligands or the *cis* isomer of a tris complex with identical unsymmetric ligands. A pseudo C_3 axis is defined[4] to exist if only the rings are considered while ignoring the substituents on the rings. For an octahedral complex with three β-diketonate ligands only one of the four octahedral face axes (axis as in Fig. 7) is a real or a pseudo C_3 axis. A twist about such an axis is pictured in Fig. 6(a) and is seen to involve a transition state that is a trigonal prism with the planes of all three ligands intersecting on a common line. This transition state is sometimes referred to as the trigonal prismatic intermediate. An imaginary C_3 axis has been defined[16] as any of the other octahedral face axes, excluding the real or pseudo C_3 axis, that would be of C_3 symmetry if all rings and differences of donor atoms are disregarded. The other three axes of Fig. 7 (*b*, *c* and *d*) are therefore imaginary C_3 axes and a twist about one of them, as pictured in Fig. 6(b), has a trigonal prismatic transition state with the plane of one ligand perpendicular to the planes of the other two ligands. This transition state is often referred to as a rhombic intermediate.

If an octahedral complex with two bidentate ligands and two *cis* monodentate ligands is considered, all four octahedral face axes are imaginary C_3 axes (see Fig. 8). Instead of leading to transition states of only two different symmetries, three possibilities exist and are shown in Fig. 9. Note that a twist like that in Fig. 9(b) results from both axes *b* and *c* of Fig. 8. The twist about *d* of Fig. 8, as depicted in Fig. 9(c) is unique in that no chelate ring spans the faces which are rotated. Thus twists after the first step are possible and in three twists in the same direction one returns to the starting point. Also notice that this twist axis (8*d*) is the only one which allows *cis–trans* interconversion.

For the tris chelate complexes the similarities between the three possible Ray and Dutt motions (Fig. 5) and the Bailar twists about the three imaginary C_3 axes (Fig. 6(b)) have been noted[16]. Bailar pictured the twist to occur with all DMD angles going to a minimum of 81°48′ in the transition state while Ray and Dutt pictured an intermediate

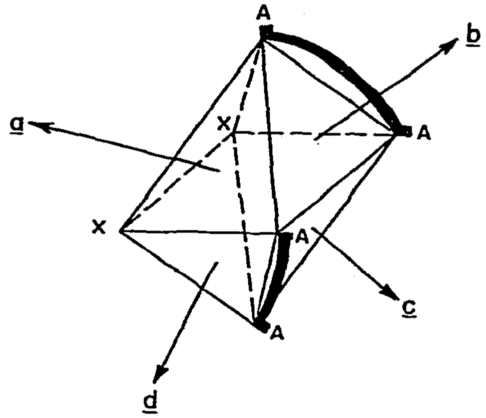


Fig. 8. The four octahedral faces axes of a complex with two bidentate ligands and two monodentate ligands. All four axes are imaginary C_3 axes.

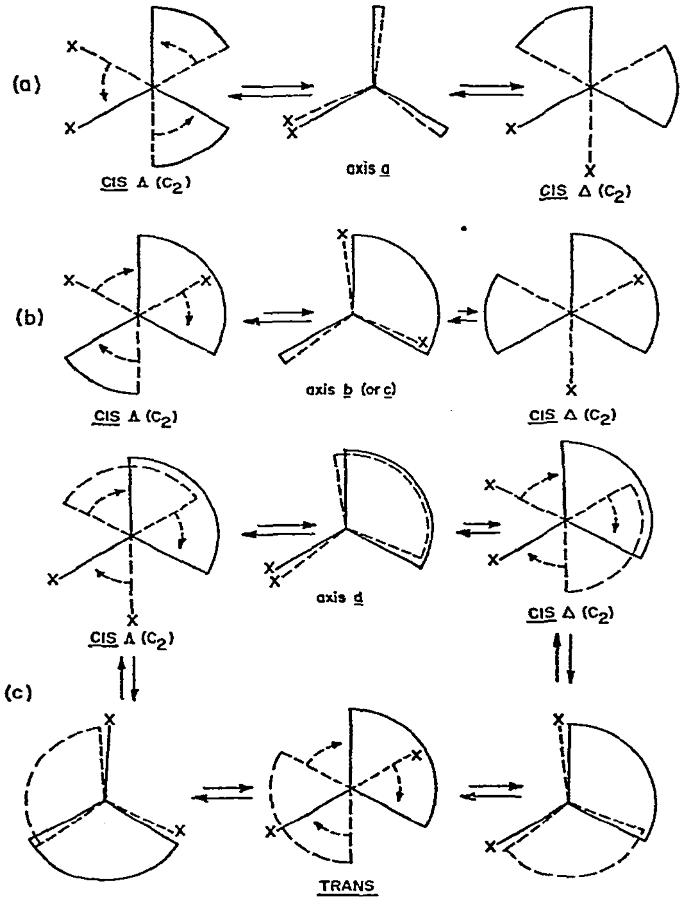


Fig. 9. Bailar twist mechanisms for intramolecular isomerization of complexes of two bidentate and two monodentate ligands. A twist about the imaginary C_3 axis *a* of Fig. 8 is given in (a); for two identical symmetrical bidentate ligands with two identical monodentate ligands the transition state has C_{2v} symmetry. A twist about imaginary C_3 axis *b* or *c* of Fig. 8 is depicted in (b); the transition states pictured would have C_s symmetry. A twist about the third imaginary C_3 axis (axis *d*) can be continued full cycle; with identical symmetric chelates and identical monodentate ligands the transition state between the two *cis* isomers would have C_{2v} symmetry while the intermediates between a *cis* isomer and a *trans* isomer would both have C_2 symmetry.

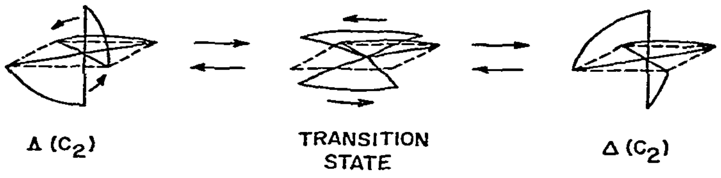


Fig. 10 The Springer mechanism which is the rigid ring equivalent to a Bailar twist about a real or pseudo C_3 axis. If all three ligands are symmetrical and identical the transition state has D_{3h} symmetry.

state with the DMD ring angles remaining at 90° while the DMD angles between rings would be reduced. The difference between the two motions is then merely a matter of whether the rings are fixed or flexed in the motion. The comparison is completed by picturing a rolling motion[16] of two rings with respect to the third while keeping all intra-ring DMD angles at 90° (see Fig. 10). This would be the rigid ring equivalent to the Bailar twist about the real or pseudo C_3 axis (Fig. 6(a)). It has been pointed out[16] that the Bailar twist can occur through either a trigonal prismatic or rhombic intermediate (see Fig. 6(a) and (b)). Twists about real or pseudo C_3 axes are sometimes referred to as trigonal twists[4] irregardless of whether they involve ring-flexing as in a Bailar twist or the analogous rigid ring mechanism. Likewise Rây and Dutt (rigid rings) twists or Bailar (flexing rings) twists about imaginary C_3 axes have been referred to as rhombic twists[4]. Models to illustrate differences in the mechanisms have been described[17]. It seems undesirable to call a trigonal prismatic transition state a Bailar type transition state and a rhombic transition state a Rây and Dutt type as very recently proposed[10,18], since a Bailar twist can occur through transition states of either symmetry. While a Bailar twist about an imaginary C_3 axis and a Rây and Dutt twist give equivalent final results there is a fundamental energetic difference in that the ring DMD bond angles are flexed during twisting in the former, whereas the ring DMD angles are fixed during the rigid translation of the latter. It is totally incorrect to state that they are "completely identical" and "equivalent at every point" in the motion[18]. The true mechanism for any given case may indeed be, and in fact most probably is, somewhere between the extremes of the fixed intra-ring DMD angles of some depictions and the substantial flexing of these angles of the Bailar proposal. Unfortunately there is no experimental method presently available to determine the degree of ring-flexing. However, the intra-ring DMD angles found for the trigonal prismatic (or rhombic) geometries in the solid state might hint as to which extreme is more nearly correct.

Twists about different axes can have different results in terms of geometrical isomerization but a twist about any of the four axes results in optical inversion. While one cannot totally exclude a certain twist on the basis that the one twist about only one of the four axes could not alone effect all the geometrical isomerization observed by NMR, it is valid in some cases[4] to rule out a twist about a real or pseudo C_3 axis as the lowest energy path. Recent discussions[19,20] have shown how twists about all the possible axes must be considered. Although twists about some axes may not be necessary and , indeed, cannot be used solely to explain certain results, one cannot argue that a twist about a given axis does not occur at all. A more fundamental question, however, is whether the intramolecular pathway for geometrical and/or optical inversion involves bond breaking or not. An experiment using NMR spin–spin coupling between the metal and ligand has recently been proposed[10] which might allow one to detect whether bond rupture occurs at a rate near or equal to the rate of isomerization

(c) General remarks on intramolecular mechanisms

For ease in considering the possible intramolecular pathways for structural rearrangements of octahedral complexes, topology has recently been applied[10,21,22] The octahedral species are considered as corners of a solid and the various transition states are the midpoints of lines connecting these points. Pathways for both twisting and bond rupture mechanisms with a trigonal bipyramid intermediate are depicted for tris(chelate) complexes involving either symmetric or unsymmetric ligands[21] Non-topological[23] and matrix[24] representations have also been discussed

Intramolecular processes for isomerization of pentacoordinate structures have been summarized in recent papers[25,26] Topological[21,26–29], non-topological[30] and matrix[31] representations of the rearrangements of pentacoordinate and other structures have been considered Topological representations for rearrangements of complexes of higher[21,28] and lower[28] coordination numbers have been presented.

(ii) Intermolecular processes

Only a brief description of some of the more probable possibilities will be given A number of works[32–34] give more detailed treatments

(a) Dissociation mechanisms

For chelate complexes which also contain monodentate ligands it might be expected that only the monodentate ligand is exchanged and the process will be much the same as that for a complex involving only monodentate ligands These ligands exchange processes can be accompanied by geometrical and/or optical isomerization depending, first, on whether the five-coordinate intermediate is symmetrical or undergoes any rearrangement and, secondly, on the point of attack of the incoming ligand Some possible S_N1 mechanisms for rearrangements of octahedral complexes of two symmetric chelate and two monodentate ligands are shown in Fig 11. Unsymmetric bidentate ligands would of course introduce the possibility of more isomers The five-coordinate (transition state) intermediate is most likely to have a trigonal-bipyramid or tetragonal-pyramid structure[35] if it is not solvated Species involving four monodentate and one bidentate ligands will not be considered since the number of isomers of such complexes is more closely related to the types of monodentate ligands than to the presence of a chelate.

If a bidentate ligand undergoes exchange, geometrical and/or optical isomerization may accompany the exchange Thomas[36] favored such a mechanism for exalato complexes but this mechanism was subsequently proven incorrect by Long[37]. The removal of a bidentate ligand leaves an intermediate (transition state) which could rearrange to either tetrahedral or square-planar geometry Such processes are depicted in Fig 12 for tris

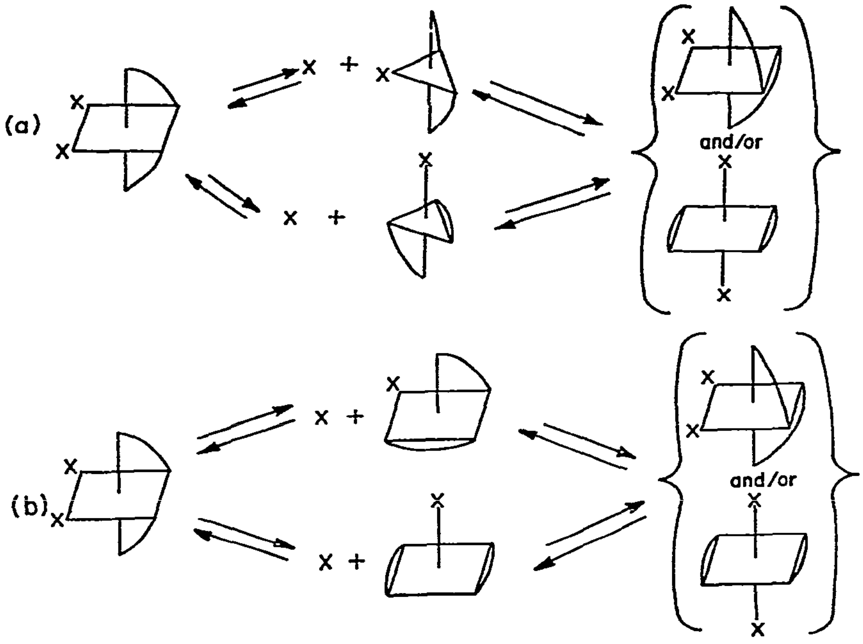


Fig. 11. Some possible intermolecular dissociation mechanisms for rearrangements of octahedral complexes of two bidentate and two monodentate ligands through (a) trigonal-bipyramidal transition states, and (b) tetragonal-pyramidal transition states

(chelate) complexes In many solvents the intermediate would be solvated, thus resulting in coordination numbers of five or six.

(b) Displacement mechanisms

In the exchange of either monodentate or bidentate groups of octahedral complexes through an S_N2 process, the incoming ligand can associate at either a site on the face adjacent to (*cis* attack) or at a site on a face opposite to (*trans* attack) that of the leaving ligand. Some exchange reactions are pictured in Fig. 13 for exchange of bidentate ligands of octahedral tris(chelate) complexes. If only symmetric bidentate ligands are considered, *cis* attack by a bidentate ligand will result in retention of optical configuration, while

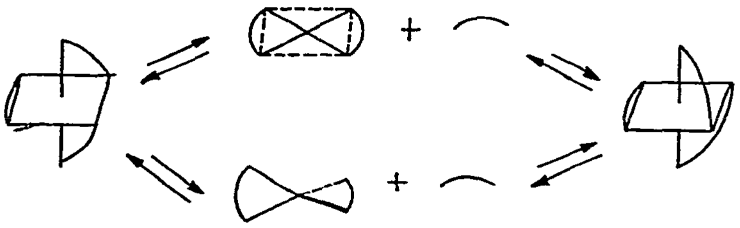
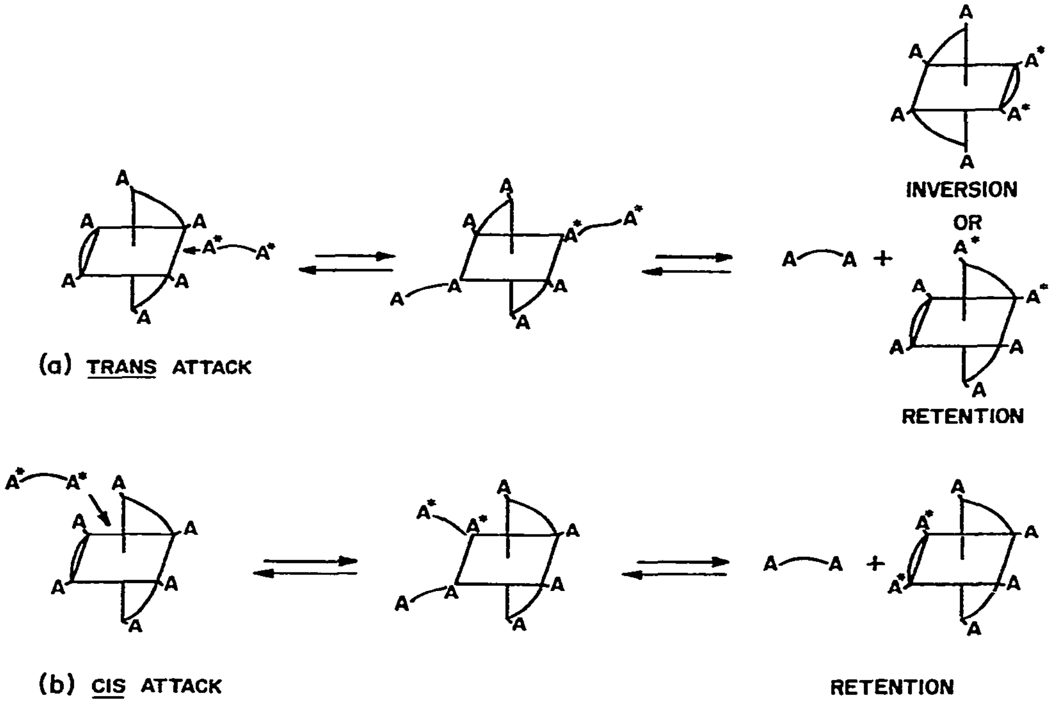


Fig. 12. Intermolecular dissociation mechanisms for rearrangements of octahedral complexes of three bidentate ligands involving either square planar or tetrahedral intermediates



(a) TRANS ATTACK

(b) CIS ATTACK

Fig 13. Intermolecular displacement mechanisms for rearrangements of octahedral complexes of three bidentate ligands The intermediates are of idealized geometry as the probable position of attack is an octahedral face

trans can cause inversion or retention If unsymmetric bidentate ligands are involved, both attacks can cause geometrical isomerization.

If a chelate complex involves monodentate ligands these may be involved in the exchange rather than the bidentate ligands, as illustrated in Fig 14 for complexes of two monodentate and two bidentate ligands. The structures of the intermediates are not meant to imply that exact geometry is involved, a more probable position of attack for the entering group is at an octahedral face[38], but the net stereochemical consequences are the same. Again *cis* attack to such a *cis* complex would result in retention of configuration while *trans* attack to the same complex would produce some optical inversion and some conversion to the *trans* isomer. A *cis* attack to a *trans* isomer would result in the *trans* isomer, while *trans* attack to the *trans* isomer would give a mixture of the two optical forms of the *cis* isomer. Both are depicted in Fig. 15.

A very improbable process for the exchange of a bidentate ligand would involve going through an eight-coordinate intermediate such as a dodecahedron or square antiprism formed by the simultaneous attachment of both ends of the incoming ligand One might also expect isomerization mechanisms through dimer or polymer intermediates to be less likely.

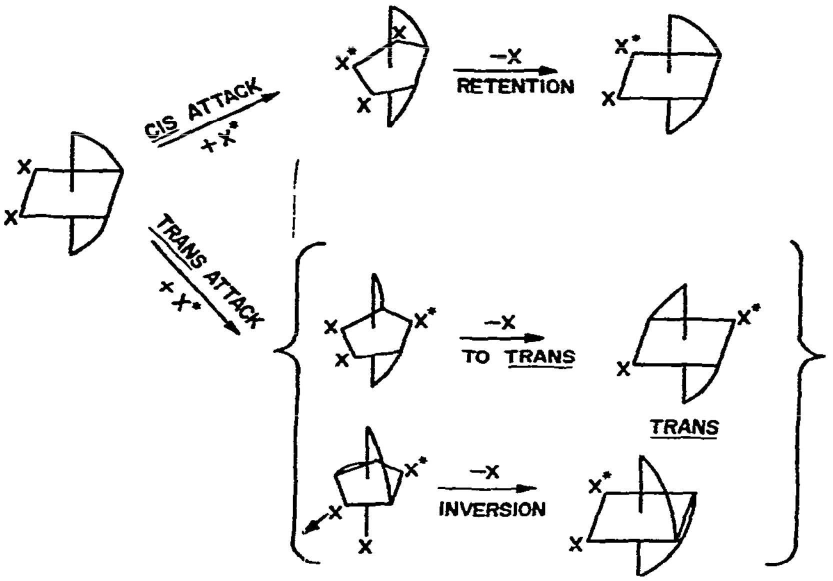


Fig 14. Some intermolecular displacement mechanisms for rearrangements of *cis* isomers of octahedral complexes of two bidentate and two monodentate ligands The intermediates are of idealized geometry

(iii) Summary

It can be readily seen that for any system in which ligand exchange is faster than or equal to stereoisomerization (geometrical and/or optical isomerization), the isomerization may be totally due to the intermolecular exchange On the other hand if rearrangement is faster than ligand exchange, an intermolecular mechanism cannot be the sole pathway.

Mechanisms of stereochemical rearrangements of octahedral complexes have been

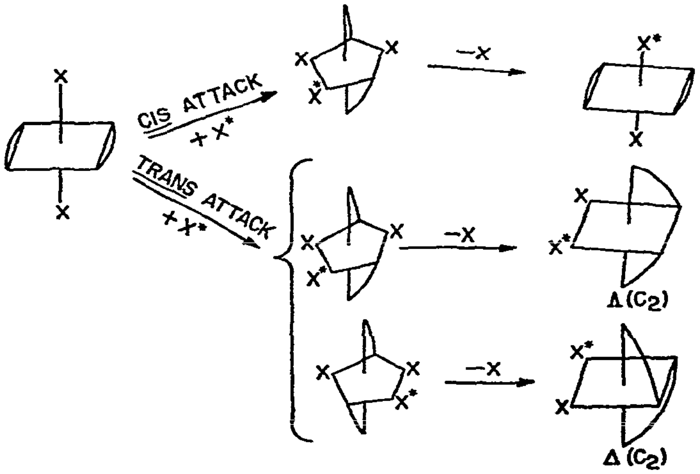


Fig 15. Some intermolecular displacement mechanisms for rearrangements of *trans* isomers of octahedral complexes of two bidentate and two monodentate ligands

substantiated to some degree or another for a few cases involving chelate ligands[39]. The intramolecular mechanism for stereoisomerization of any β-diketonate complex, however, has not yet been definitely shown to proceed via a bond rupture or twisting mechanism The mechanism problem may be summarized as follows.

(1) First, one must attempt to establish whether the process is predominately intermolecular or intramolecular. Although a number of researchers have found intramolecular isomerizations, as will be enumerated later, it must be kept in mind that other processes such as dissociation, association, solvation and ligand exchange, are occuring at some finite rates which may be only two orders of magnitude smaller[10] than the rate of the intramolecular rearrangement.

(2) If the reaction is intramolecular, try to obtain evidence to infer whether a bond rupture or a twisting mechanism is operative *(a)* If the reaction appears to proceed via a twisting mechanism, is one or more axes preferred over the others? *(b)* If a bond-rupture mechanism appears to be operative, what is the geometry of the transition state and are cartain bonds broken preferentially over others?

(3) If the reaction is intermolecular, establish whether a dissociative or associative process is the rate-determining step.

C EXPERIMENTAL STUDIES

(i) Symbolism

The types of β-diketonates studied thus far may be grouped by their ligand constituents. For the purposes of classifying and generalizing, the following shorthand notations will be used M represents a metal ion, AA^-, BB^- and CC^- represent symmetric β-diketonate ligands such as 2,4-pentanedionate (acetylacetonate), AB^-, AC^-, BC^-, CD^-, etc., represent unsymmetric β-diketonate ligands such as 1,1,1-trifluoro-2,4-pentanedionate; X^- and Y^- represent monodentate ligands, and xx^- and yy^- represent symmetric bidentate ligands other than β-diketones (e g ethylenediamine)

Abreviations used for specific β-diketonate ligands in this work are tabulated in Table 1.

(ii) Octahedral complexes involving only symmetric β-diketonate ligands: $M(AA)_3$, $M(AA)_2(BB)$ and $M(AA)(BB)(CC)$

Complexes of this type have only optical isomers and there are but a few reported classical studies of the rate of inversion of complexes of symmetric β-diketones There have been a number of partial resolutions of such complexes obtained by a variety of methods, and these are summarized in Table 2.

The earliest report on partially resolved $Co(acac)_3$ indicated that racemization of the sample was almost complete after 12 h in 20% aqueous alcohol[44]. More recent observations of partially resolved samples indicated that there was no detectable racemization in petroleum ether—benzene in two days[40] at ca. 25°C and chloroform solutions are stable towards racemization at room temperature for five weeks[41,42,52]. Some other so-

TABLE 1

Abbreviations for β-diketonate ligands

A. Symmetric ligands

acac⁻	2,4-pentanedionato (acetylacetonato)	dbm⁻	1,3-diphenyl-1,3-propanedionato (dibenzoylmethanato, bzbz⁻)
hfa⁻	1,1,1,5,5,5-hexafluoro-2,4-pentanedionato (hexafluoroacetylacetonato)	triac⁻	3-acetyl-2,4-pentanedionato
thd⁻	2,2,6,6-tetramethyl-3,5-heptanedionato (dipivaloylmethanato, dpm⁻)	dim⁻	2,6-dimethyl-3,5-heptandionato (diisobutyrylmethanato)

B Unsymmetric ligands

tfa⁻	1,1,1-trifluoro-2,4-pentanedionato (trifluoracetylacetonato)	fod⁻	1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato
bzac⁻	1-phenyl-1,3-butanedionato (benzoylacetonato)	macac⁻	1-methoxy-2,4-pentanedionato (methoxyacetylacetonato)
dhd⁻	2,2-dimethyl-3,5-hexanedionato (pivaloylacetonato, pvac⁻)	prac⁻	2,4-hexanedionato (propionoylacetonato)
		phd⁻	1-phenyl-1,3-hexanedionato

C Asymmetric ligands

d-hmc⁻	3-hydroxymethylene-*d*-camphorato
l-hmc⁻	3-hydroxymethylene-*l*-camphorato
d-atc⁻	3-acetyl-*d*-camphorato

TABLE 2

Partial resolution of octahedral complexes of symmetric β-diketones

Compound	*Technique*	*Reference*
(1) Co(acac)$_3$	(a) Column chromatography (with an optically active stationary phase)	40–43
	(b) Preferential crystallization (from a solution of an optically active salt)	44
	(c) Solvent extraction (with one phase optically active)	45
	(d) Zone melting (of a frozen solution also containing an optically active salt)	46
(2) Cr(acac)$_3$	(a) Column chromatography (as 1)	40, 42, 43
	(b) Preferential crystallization (as 1)	44
	(c) Solvent extraction (as 1)	45
(3) Cr(hfa)$_3$	Gas–solid chromatography (with an optically active stationary phase)	47, 48
(4) Gd(acac)$_3$	Column chromatography (as 1)	49

TABLE 2 (continued)

(5) $Rh(acac)_3$	(a) Solvent extraction (as 1)	45
	(b) Column chromatography (as 1)	41, 42
(6) $Si(acac)_3^+$	Precipitated as diastereoisomer	50, 51
(7) $Y(acac)_3$	Column chromatography (as 1)	49

lutions of this green chelate in chloroform decomposed[52] to form a pink solid after a few days but this decomposition was thought to involve solvent impurities, oxygen or sunlight Measurements in glacial acetic acid showed a 60% loss of optical activity in 5 weeks, but there was visual evidence of decomposition[52] The optical activity was not affected by exposure of the chelate in CCl_4 to activated charcoal for 12 h

It has been reported[41,42,52] that slow crystallization of partially resolved $Co(acac)_3$ leads to optically inactive crystals while evaporation of solvent with a stream of air results in a powder with little or no loss of optical activity[41,42,52] The racemization during crystallization was attributed to a surface reaction whereby the racemic crystal is preferentially formed and the benzene–hexane solution is enriched in the excess enantiomorph

Rate constants for optical inversion of partially resolved samples of $Co(acac)_3$, $Co(triac\text{-}d_3)_3$ and $Co(acac)_2(triac\text{-}d_3)$ in chlorobenzene solution at 90°C have recently been determined to be 0 4 $\times 10^{-4}$, 4 7 $\times 10^{-4}$ and 2.1×10^{-4} sec^{-1}, respectively[53] It should be noted that the rate of optical inversion is the rate of interconversion of optical isomers and is equal to half the rate of racemization which is defined as the rate of loss of optical activity The rate constants for linkage isomerization in which the free deuterated acetyl group replaces one of the acetyl groups bonded to the cobalt were found to be 3 0 $\times 10^{-5}$ and 2.5×10^{-5} sec^{-1} for the $Co(triac\text{-}d_3)$ and $Co(acac)_2(triac\text{-}d_3)$, respectively, under the same conditions Ligand exchange was found to be slow with respect to the rate of linkage isomerization It was argued that as the linkage isomerization requires a Co–O bond to rupture it is likely that a five-coordinate intermediate is formed Because optical inversion through a five-coordinate intermediate would not require the rotation about a C–C bond that the linkage isomerization does, the faster rate and lower activation energy report for the optical inversion could be accounted for by postulation of a five-coordinate intermediate.

Partially resolved $Cr(acac)_3$ in 20% aqueous alcohol was reported to be more stable than $Co(acac)_3$ while the optical forms of $Fe(acac)_3$ reportedly[44] "had a very fleeting life". Later work[40] indicated that racemization of partially resolved $Cr(acac)_3$ in *n*-hexane–benzene solution was 50% complete at ca. 25°C in ca. 8 days

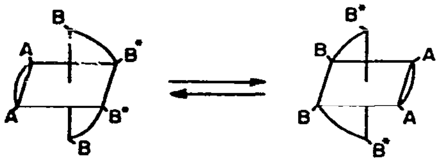
Optically active $Rh(acac)_3$ seems to be remarkably stable as it was not racemized with recrystallizations, chromatography on active alumina or treatment with aluminum chloride[41].

Collman and coworkers[42,52] subjected some partially resolved β-diketonate complexes of Co^{III}, Cr^{III} and Rh^{III} to electrophilic substitution reactions whereby the substituents on the central carbon of the chelate rings were replaced. In most instances the molar rotation of the products was found to be as large or larger than that of the starting material indicating that there was probably no racemization, although partial racemization could be occuring As substitution on a five-coordinate intermediate would almost certainly lead to racemization it was proposed that the substitution occurred without ring cleavage

Racemizations of partially resolved $Y(acac)_3$ and $Gd(acac)_3$ in benzene–petroleum ether have been reported to be slow and first-order[49]. The same work indicates that partially resolved $Y(acac)_3$ in chloroform racemizes rapidly In view of the lability of most yttrium and lanthanide complexes it is surprising that any resolution was achieved. Indeed, this is the only known report of the resolution of a lanthanide complex. Because of its obvious importance this interesting work should be experimentally confirmed.

The most thorough investigation by classical means of any β diketonate complex was performed on the optically active $Si(acac)_3^+$ ion in aqueous solution[40]. The k for racemization ranged from 1.2×10^{-4} sec^{-1} at 19 7° to 2.2×10^{-4} sec^{-1} at 24 65°C This loss of optical activity was shown to be caused by hydrolysis and not inversion, however, as the rates of hydrolysis were found to be equal to those of racemization The results have been independently confirmed[54] Additional studies in absolute methanol and methanol–water systems concur and it is proposed that the first step in the mechanims of hydrolysis probably involves a seven-coordinate intermediate[55]

The observed coalescence[56] of the NMR resonances of the terminal groups of some symmetric β-diketonate ligands in tris complexes with different ligands in a 2 1 ratio has led to studies of optical inversion of many complexes which racemize too quickly for partial resolution. By studying complexes of the form $Al(AA)(BB)_2$ it has been shown that NMR can be very useful in determining extremely fast rates of optical inversion[20]. These complexes with the symmetric ligands in a 2 1 or 1 2 ratio are particularly interesting in that the only stereoisomerization possible is optical inversion, furthermore, the terminal groups of the BB ligand in a complex of the form $Al(AA)(BB)_2$ exhibit two different NMR resonance frequencies due to their structural non-equivalence. One of the terminal groups of each of the BB ligands is opposite a terminal group of the other BB ligand, while the remaining BB terminal groups are each *trans* to a terminal group of the AA ligand A detailed study[20] of the spectra of the complexes $Al(acac)_2(thd)$, $Al(acac)(thd)_2$, $Al(hfa)(acac)_2$ and $Al(hfa)(thd)_2$ as a function of temperature showed that the two proton resonances of the terminal groups of the bis ligands coalesce as the temperature is raised. The coalescence of the t-butyl proton resonances of $Al(hfa)(thd)_2$ is shown in Fig 16. The coalescence is attributed to the averaging of the environments of the terminal groups of the bis ligands such as might accompany optical inversion



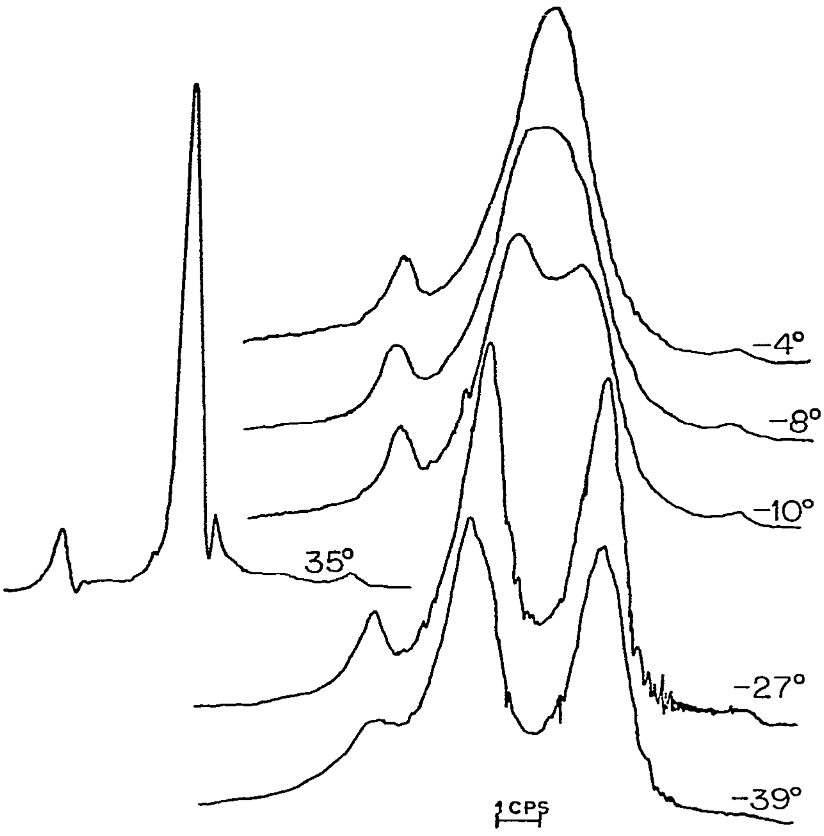


Fig. 16 The coalescence of the *t*-butyl proton resonances of Al(hfa)(thd)$_2$ in chlorobenzene The small peak downfield is due to Al(hfa)$_2$(thd) The spectrum at 35°C has been offset down-field sufficiently to allow full presentation

Because of the symmetry of the Al(AA)(BB)$_2$ complexes, each bidentate BB ligand has one terminal group in each magnetic environment; therefore, the two sites are equally populated Consequently, the rate of environmental averaging can be calculated for intramolecular processes at various temperatures in a range below the coalescence from the expression

$$k = \frac{1}{2\tau} = \frac{2\pi}{2\sqrt{2}} [\delta \nu_{se}^2 - \delta \nu_T^2]^{1/2}$$

as given by Gutowsky and Holm[57], where $\delta \nu_{se}$ is the frequency separation in the limit of slow environmental exchange and $\delta \nu_T$ is the frequency separation at temperature *T*, both expressed in Hertz. The coalescence temperatures and rate constants of environmental exchange at those temperatures in chlorobenzene were reported as follows[20]. Al(acac)$_2$(thd), 105°, 12 6 sec^{-1}; Al(acac)(thd)$_2$, 105°, 8 5 sec^{-1}, Al(hfa)(thd)$_2$ −8°, 6.9 sec^{-1}, and Al(hfa)(acac)$_2$, −18°, 5 3 sec^{-1} For the last three complexes extrapolation to 25°C gave rates of 0.79, 29 4 and 11.6, respectively. Rates were determined for other temperatures, allowing the calculation of frequency factors and energies and entropies of activation. It has been pointed out[58] that the somewhat unusual values of these thermodynamic functions (small E_a and large negative ΔS^*, may be due to the failure to correct for temperature-dependent solvent affects on the chemical shifts of the NMR resonances and thus their separations; such corrections have been applied in other studies [4,58]. It might be noted, however, that these corrections are large enough to reverse any mechanistic conclusions. If one assumes that the initial lessening of the frequency separation is due totally to solvent effects, it is surprising that for two such similar terminal groups the effect is either to increase the shielding on one and decrease it on the other, or to shield or deshield the two to greatly different extents Al(acac)(thd)$_2$ and Al(acac)$_2$ (thd) were also studied in carbon tetrachloride[20] and brief mention[56] was made of solutions of Al(hfa)(acac)$_2$ in CH_2Cl_2 exhibiting coalescence at about 7°C Fluorine NMR spectra of Al(hfa)$_2$(acac) and Al(hfa)$_2$(thd) indicate that the resonances coalesce in both cases[20].

Intermolecular ligand exchange was found to be very slow compared to the rates of environmental averaging[20]. The rates of environmental averaging were found to be independent of complex concentration indicating that the mechanism was first-order. Furthermore a free-ligand dissociation mechanism of the type proposed by Thomas was eliminated since uncomplexed ligand added to samples exhibited separate resonances well above the coalescence temperatures.

It was pointed out that the relationship of the rate of environmental to the rate of optical inversion will depend upon the mechanism by which the intramolecular rearrangements occur[20,59] The relationships are summarized in Table 3 While relationships were calculated for the trigonal bipyramidal intermediates both with and without the equatorial modes (Fig. 1(b)) which can cause coalescence without optical inversion, it seems more logical to consider both sets of operations together statistically, since the transition state in such a mechanism might well be of some intermediate form. The equatorial mode as sole mechanism of environmental averaging was eliminated The relationships were also calculated considering only the mono or bis ligands rupturing since it would seem to be a distinct possibility that the metal–oxygen bond of one type of ligand might be more susceptible to rupture than that of the other type

If very precise measurements of the rate of environmental averaging can be made for some complex by NMR and the rate of optical inversion can be carefully measured by another method, the comparison of rates may allow the assignment of a specific mechanism or at least elimination of some possibilities. Such an independent method might involve the use of the Pfeiffer effect. The chelates Al(acac)$_3$, Al(dbm)$_3$ and Al(hfa)$_3$ have already been observed to exhibit this effect[60] Another method[61] which might be useful for obtaining rates for comparison is circular polarization of luminescence emission (CPL)

The methyl resonances of the acac ligands of Ga(acac)$_2$(hfa) in dichloromethane solution were found[58] to coalesce at ca. −26.5°C and those of Ga(acac)$_2$(dbm) in benzene at ca. +81°C The environmental averaging was reported as due to an intramolecular mechanism. For Ga(acac)$_2$(hfa) in an equilibrium mixture with Ga(acac)$_3$, Ga(hfa)$_3$

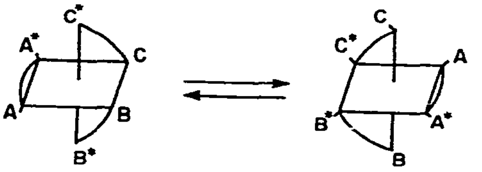
TABLE 3

Relationships of rates of optical inversion to rates of environmental averaging of NMR resonances of the terminal groups of the bis ligands of complexes of the form $M(AA)(BB)_2$

Mechanism	*Rate of optical inversion*
A Bond rupture mechanisms	
(1) Trigonal bipyramid intermediates (ignoring equatorial rupture modes)	
(a) All six ruptures possible	(3)r
(b) Mono ligand rupture only	(2)r
(c) Bis ligand rupture only	(4)r
(2) Trigonal bipyramid intermediates (including equatorial rupture modes)	
(a) All six ruptures possible	(3/2)r
(b) Mono ligand ruptures only	(2)r
(c) Bis ligand ruptures only	(4/3)r
(3) Square-based pyramid intermediates All, mono, only or bis only	(1)r
B. Twisting mechanisms	
(1) Bailar twist (all 4 axes considered)	(4/3)r
(2) Rây and Dutt modes only (the motions through rhombohedral transitions states)	(3/2)r
(3) Springer mode only (the one motion through a trigonal prismatic transition state)	(1)r

and $Ga(acac)(hfa)_2$ a line shape analysis was made using line widths observed for $Ga(acac)_3$ to estimate T_2. Rates were determined[58] over a range from −39.1 to −15 6°C and the value of the rate constant for methyl group environmental exchange to 25° was 9.8×10^2 sec^{-1} For $Ga(acac)_2(dbm)$ a similar analysis was not done due to the unfavorable overlap of the $Ga(acac)_3$ and $Ga(acac)(dbm)_2$ lines with those of $Ga(acac)_2(dbm)$. Rates were determined[58] using the simplified Gutowsky–Holm equation and the frequency separation using corrections for temperature dependent solvation effects found by extrapolation from temperatures of slow exchange. The corrections were justified on the basis of a constant ratio of the line widths of the methyl resonances of $Ga(acac)_2(dbm)$ to those of $Ga(acac)_3$ over the temperature range of slow environment exchange Kinetic data are given[58] between 62 5 and 78 0°C with the value extrapolated to 25°C found to be 8 8 $\times$ 10^{-2} sec^{-1}. The difference of four orders of magnitude found between rates at 25°C for $Ga(acac)_2(dbm)$ and $Ga(acac)_2(hfa)$ is indeed interesting. With the solvation correction the activation parameters were found to be in better agreement with those expected for a bond rupture process but, as the size of the corrections is very large, there may be some questions as to the degree of mechanistic significance of those parameters.

The studies of aluminum complexes have been extended to systems with three different symmetric β-diketonate ligands[62]. Solutions of Al(hfa)(acac)(thd) in chlorobenzene were studied at various temperatures by NMR. The two terminal groups of each of the three ligands in the complex exhibit different resonances due to their structural non-equivalence. The two peaks for each ligand were found to coalesce as the temperature was raised. The environmental averagings were attributed to optical inversion of the complex.



Experiments were cited which proved the process to be intramolecular, and the rates of environmental averaging for the terminal groups of each ligand were reported over a range of temperatures. The coalescence temperatures and rate constants of environmental averaging of the terminal groups of the ligands of Al(hfa)(acac)(tnd) are [62]: hfa, 57°C, 15.5 $\sec^{-1}$, acac, 17°, 19.5 $\sec^{-1}$, and thd, 8°, 8.7 $\sec^{-1}$. The three rate constants were found to be different at the same temperature with $k(-CH_3) > k[-C(CH_3)_3] \geq k(-CF_3)$. At 25°C the three rates were found by extrapolation to be: acac, 23.2 $\sec^{-1}$, thd, 12.3 $\sec^{-1}$, and hfa, 9.2 $\sec^{-1}$. These rates were uncorrected for solvent effects but application of corrections did not make all three rates equal. Thus some modes of rearrangements, such as the Bailar twist about only the pseudo-C_3 axes can be eliminated as the *sole* pathways. Various combinations of twists and/or bond ruptures are required to account for the different rates.

The relationships of the three rates of environmental averaging to the rate of optical inversion of a M(AA)(BB)(CC) complex were calculated for a general combination of twist mechanisms and for a general combination of bond ruptures through trigonal bipyramidal intermediates. Assuming only twisting modes to be operative the rate constant of optical inversion of [Al(hfa)(acac)(thd)] was shown to be less than or equal to $1/2[k(-CF_3) + k(-CH_3) + k(-C(CH_3)_3)]$ but greater than or equal to the combination of the fastest two, in this case $1/2[k(-CH_3) + k(-C(CH_3)_3)]$. Using the rates extrapolated to 25°C this would make k_{25} (optical inversion) be somewhere between 17.8 to 26.9 $\sec^{-1}$.

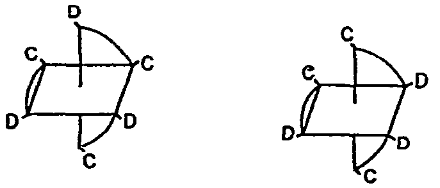
Considering only bond rupture modes going through trigonal bipyramidal intermediates (but a completely general case where any mode might contribute anywhere from everything to nothing to the rate) the rate constant for optical inversion must be less than or equal to $[k(-CF_3) + k(-CH_3) + k(-C(CH_3)_3)]$. At 25°C, therefore, the rate constant could range as high as 53.7 $\sec^{-1}$. These rates are calculated from rates of environmental averaging for which there was no attempt to correct for solvent effects.

The first unequivocal direct measurements by NMR coalescence techniques of the rate of inversion of a tris (β-diketonate) complex has been very recently completed[63]. The methyl doublet of the aluminum complex of diisobutyrylmethane, $Al(dim)_3$, is split into a quartet of four equal lines by the asymmetric center at the aluminum The quartet coalesces into a doublet with increasing temperature. This is undoubtedly caused by the increasing rate of inversion of the complex. Results of the detailed kinetic studies will be forthcoming[63].

(iii) Octahedral complexes involving unsymmetric β-diketonate ligands: $M(CD)_3$, $M(AA)(CD)_3$ and $M(AA)_2(CD)$

While the $M(CD)(AA)_2$ complexes possess only optical isomers, geometrical isomerization is possible for complexes of the form $M(CD)_3$ and $M(CD)_2(AA)$ The $M(DC)_3$ complexes have a *cis* isomer in which all three ligand terminal groups of the same type are at the same octahedral face of the complex, and a *trans* isomer in which two of the same terminal groups are across the metal from one another; each geometrical isomer has two optical forms due to the pitch of the chelate rings. It has also been proposed to call these geometrical forms facial (fac) and meridional (mer) isomers, respectively[64] These are shown in Fig 17. The fac isomer with the three like terminal groups on the same octahedral face, has a C_3 symmetry axis causing all three terminal groups to have equivalent environments The mer isomer, with each set of three like terminal groups around an octahedral meridan, has no symmetry save an identity element; therefore, each of the three like groups are in nonequivalent environments.

In Fig. 18 are depicted the three different geometrical forms possible with a $M(CD)_2(AA)$ complex The notation is based on the locations of the terminal groups of the unsymmetric ligand and follows that used for $M(tfa)_2(acac)$ [66] The first prefix refers to the relative orientation of the groups of the unsymmetric ligand which are most different from that of the symmetric ligand, and the second prefix to the relative orientation of the groups of the unsymmetrical ligand most like that of the symmetrical ligand. For example, the *trans–cis* isomer of $M(tfa)_2(acac)$ is that which has the trifluoroacetyl groups opposite (*trans*) one another and the acetyl groups of the trifluoroacetylacetonate ligands *cis* to one another Each of the three geometrical forms have optical isomers based on the pitch of the chelate rings The *cis–cis* isomer has no axis or plane of symmetry leading to non-equivalent environments for each A group, each C group and each D group. Both the *cis–trans* and *trans–cis* isomers have C_2 symmetry axes and



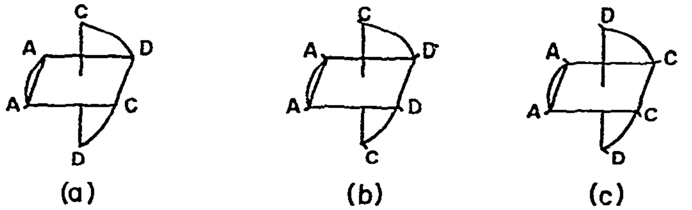
fac or cis

1 D resonance
1 C resonance

mer or trans

3 D resonances
3 C resonances

Fig. 17. The two geometrical isomers of an $M(CD)_3$ complex illustrating the number of different resonances possible for each terminal group



(a) cis—cis
2 D resonances
2 C resonances
2 A resonances

(b) cis— trans
1 D resonance
1 C resonance
1 A resonance

(c) trans—cis
1 D resonance
1 C resonance
1 A resonance

Fig 18 The three geometrical isomers of an $M(CD)_2(AA)$ complex illustrating the number of different resonances possible for each terminal group

there is only one environment apiece for A, C and D groups of each isomer.

Column chromatography using acid washed alumina allowed the separation of *cis* and *trans* isomers of the tris (benzoylacetonates)[7] of cobalt, chromium and rhodium and of tris (trifluoroacetylacetonates) of these same metals Attempts to separate the geometrical isomers of the tris (benzoylacetonates) of aluminum, manganese and iron were unsuccessful [7]. This was attributed to the greater "lability" (faster rearrangement) of the geometrical forms. The occurence of the *cis* isomers of the tris (benzoylacetonato) complexes in less than statistical amounts at room temperature equilibrium and the observation that *cis* to *trans* isomerization occurs at higher temperatures indicates that the *trans* isomers are more stable as might be predicted in terms of their lower dipole moments [7] Only the *trans* form of the tris (trifluoroacetylacetonates) of aluminum, gallium, indium, manganese and iron were found in the solid state [8].

$Co(tfa)_3$ in chloroform solutions was slow to establish *cis—trans* equilibrium while the Group IIIA metal complexes did so rapidly [8]. Heats of isomerization of $Al(tfa)_3$, $Ga(tfa)_3$ and $Co(tfa)_3$ were obtained from $\log K$ vs $1/T$ plots and free energies and entropies were calculated from the straight line plots [8].

Gas chromatography has been applied to the separation of the *cis* and *trans* isomers[48] of $Cr(tfa)_3$. The fac and mer isomers of $Co(dhd)_3$ were separated by thin layer chromatography[64] using Silica Gel D-5 and carbon tetrachloride as the solvent, the plates were developed using CH_2Cl_2

The NMR spectra of a *cis*-$M(tfa)_3$ isomer should exhibit only one fluorine resonance due to the equivalence of the three CF_3 groups while the *trans* isomer would be expected to have three distinct fluorine resonances in its ^{19}F NMR spectra barring any accidental degeneracy of the $-CF_3$ resonances or kinetic averaging of the environments of the three $-CF_3$ groups These differences have been observed [8] and have allowed the determination of the rate of geometrical isomerization of *cis*-$Co(tfa)_3$ in chloroform solution [4] at 66.1, 79.1, 90.4 and 99.2°C. The amount of *cis* and *trans* isomer observed after various lengths of time along with the equilibrium constant for that temperature allowed the calculation of the rate constants for the *cis* to *trans* and *trans* to *cis* rearrangements The isomerization

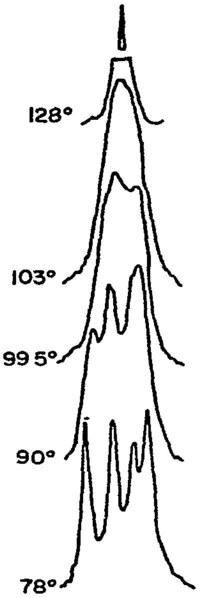


Fig 19. The coalescence of the fluorine resonances of Al(tfa)$_3$ (Ref 4, courtesy of Inorganic Chemistry)

follows first-order kinetics with $k(cis - trans)$ ranging^4 from 0.247 × 10^{-4} sec^{-1} at 66.1°C to 14.5 × 10^{-4} at 99.2°. The $k(trans - cis)$ was calculated^4 as 0.059 × 10^{-4} sec^{-1} at 66.1° to 3.7 × 10^{-4} at 99.2°. The energies and entropies of activation were reported^4.

cis-Cr(bzac)$_3$ was partially resolved by passing its solution in 1:1 benzene–hexane through a column of lactose powder^4. Attempts to resolve *cis*-Co(tfa)$_3$ were unsuccessful. In chloroform solutions, *cis*-Cr(bzac)$_3$ was found to be optically stable at temperatures below 51.4°C. In 1,1,2,2-tetrachloroethane the rate constant of optical inversion was measured^4 as 0.0023 min^{-1} at 95.5° and 0.009 min^{-1} at 105.0°C. At both of these temperatures racemization was found to be accompanied by *cis–trans* isomerization. Evaluation of relative amounts of the geometrical isomers by microscopic observation indicates that the rate of isomerization is approximately equal to the rate of racemization.

The three ^{19}F NMR resonances due to the *trans* form and the one ^{19}F resonance due to the *cis* form were found to coalesce at 103°C for Al(tfa)$_3$ and at 61.5°C for Ga(tfa)$_3$ in deuterochloroform. The ^{19}F spectra of Al(tfa)$_3$ at several temperatures near the coalescence region are shown in Fig. 19. After correction for solvent effects by extrapolation and averaging the splittings, the rate constants for environmental averaging were found to be 34 and 38 sec^{-1} for Al(tfa)$_3$ and Ga(tfa)$_3$ at their respective coalescence temperatures^4 by the method of Gutowsky and Holm^{57}. In(tfa)$_3$ exhibited only one ^{19}F magnetic resonance^4 even at −57°C indicating a k of greater than 36 sec^{-1} at that temperature. (The NMR spectrum of a mixture of *cis*- and *trans*-Co(tfa)$_3$ in chlorobenzene showed a strong temperature dependence^4 similar to that of aluminum and gallium compounds, but the resonance lines were very much broader, at 94°C the four lines had coalesced into a single broad peak but this peak did not sharpen even at 182°.) The rates measured may be considered as approximate measures of the rates of geometrical isomerization. A more exact treatment would involve the treatment of six exchange equilibria and six coalescences individually [59]. This rigor would be impractical [59] as it would require (*1*) assigning the four peaks to the four environments, (*2*) correction for temperature dependence not due to environmental averaging (solvent effects), and (*3*) the assumption of a mechanism. Furthermore there is considerable overlap of peaks and the method is an approximation in any case. From the rate constants, activation energies and free energies were calculated. The observation of *cis–trans* equilibrium allows the elimination of the twist about the real C_3 axis as the sole method of isomerization for *cis*-Cr(bzac)$_3$, and the tris (trifluoroacetylacetonates) of the Group IIIA elements [4]. It has been pointed out that combinations of twists about various axes cannot be eliminated, however [16].

The environmental averaging of the $-CF_3$ resonances of Al(tfa)$_3$ has been measured[4] in solvents with dielectric constants which vary from benzene to tetramethylene sulfone and the free energy of activation (at the coalescence temperature) for the exchange was shown to generally decrease with increasing dielectric constant of the solvent. This seems most compatible with a bond rupture mechanism. A bond rupture mechanism would also be in keeping with the activation parameters reported [4].

Both *cis*- and *trans*-Rh(tfa)$_3$ showed extreme stability with respect to isomerization and the rate constant for geometrical isomerization was estimated [4] as less than 9.2×10^{-7} sec^{-1} at 163°C.

Al(fod)$_3$ was examined in chlorobenzene solution and the *t*-butyl NMR resonances coalesced [59] at ~ 112°C. Using the average separation between peaks a rate constant for environmental averaging of either 14 or 6.3 sec^{-1} is obtained depending on whether a small peak at highest field is included or not. This peak may be due to the *cis* isomer or there may be an unresolved peak with the three more intense signals downfield. It is pointed out [59] that if isomerization is through a bond-rupture mechanism with a trigonal bipyramidal transition state and if all metal donor bonds are equally likely to rupture, the first-order rate constant of environmental averaging is 4/3 the value of the rate constant for optical inversion. The same relationship holds if all metal donor bonds at one end of the ligand are broken to the exclusion of those at the other end. If the mechanism is considered to be a twist with all possible twisting axes equally probable, then k is equal to the k of optical inversion. Springer [59] also points out that through use of an optically active solvent the chemical shifts of one optical form may be altered by prefered association with the solvent. Although many attempts to observe this phenomenon with these chelates have met with failure [65], if such a case could be found it might allow separate measurements of the rates of geometrical and optical isomerization and some conclusions as to the mechanism.

The separation of *trans–cis* Co(tfa)$_2$(acac) from the *cis–trans* and *cis–cis* isomers has been accomplished by column chromatography [66]. The four ^{19}F resonances due to the isomers of the Al(tfa)$_2$(acac) (two from the *cis–cis* and one each from the *trans–cis* and *cis–trans* isomers) were found to coalesce at 87°C and the rate of environmental averaging calculated [66] to be 43 sec^{-1} by the same method used for Al(tfa)$_3$. An intermolecular mechanism for environmental averaging was excluded, as the resonances for free trifluoroacetylacetone ligand as well as those for $Al(tfa)_3$ and $Al(tfa)(acac)_2$ were all distinct at the coalescence [66]. The coalescence of all four ^{19}F resonances of $Al(tfa)_2$ (acac) allows the exclusion of twisting about any one axis as a mechanism [66] but a combination of twists about various axes can account for the coalescence [16].

While the system does not involve β-diketonate ligands it is of interest that NMR studies [67] of tris (α-isopropyltropolonato)-aluminum(III) indicate that the methyl environments in the *cis* form and in the *trans* form are equilibrated before the *cis—trans* equilibrium is fast enough to average the resonances of the *cis* and *trans* isomers. This would make it appear that racemization is faster than *cis—trans* isomerization but the rates are too similar for meaningful mechanistic arguments.

β-Diketonate ligands which are asymmetric (optically active) as well as unsymmetric have provided the source of some interest [68-70] The tris complexes of 3-hydroxymethylene-*d*-camphorate (*d*-hmc, Fig. 20, R=H) with several metals, including Co^{III} (Refs 68, 70), Rh^{III} (Ref. 70),Cr^{III} (Ref. 70) and V^{III} (Ref. 68), have been investigated. Complexes with *l*-hmc have been reported for Co^{III} and V^{III} (Ref 68) The complexes of 3-acetyl-*d*-camphorate (*d*-atc, Fig. 20, $R=CH_3$) with Co^{III} (Refs 68, 69) and V^{III} (Ref 68) have also been studied. With one form of the ligand, only four diastereomeric species are possible; Λ-*trans*, Λ-*cis*, Δ-*trans* and Δ-*cis*. All four isomers have been isolated for the $Co(d\text{-atc})_3$ complex [69]. While the Λ isomers are somewhat more stable than the Δ isomers, the statistically expected 3 1, *trans—cis* ratios are found for both chiralities

As the chemical shift differences for nuclei in similar environments in chelate complexes have been found to be amplified in paramagnetic molecules [71], the NMR of the tris complexes of V^{III} with *d*-atc have been examined [68]. For each kind of proton in $V(d\text{-atc})_3$ one resonance is expected for the *cis* isomer and three for each *trans* isomer due to the lack of symmetry, but as diastereomers are possible with the asymmetric ligands, as many as eight signals may be observed for each kind of proton. Four intense acetyl methyl signals were found for the *cis* and *trans* forms of $\Lambda\text{-}V(d\text{-atc})_3$ with the *cis* and *trans* species in approximately statistical 1:3 distribution Three weaker signals are attributed to $\Delta\text{-}trans\text{-}V(d\text{-atc})_3$ but a fourth signal for the Δ-*cis* diastereomer could not be found, indicating that either this form is absent or the resonance lies under one of the stronger signals For the Λ-*trans* ⇌ Δ-*trans* equilibrium in chloroform at 29°C, *K* was found to be 0.31. Attempts to observe the temperature dependence of the equilibrium have failed thus far due to poor signal resolution at higher temperatures

The NMR spectra of $V(d\text{-hmc})_3$ and $V(l\text{-hmc})_3$ are identical [68], indicating that the solutions are enantiomeric. The spectrum of $V(d\text{-hmc})_3$ has overlapping of several signals but it appears that all four diastereomers are present.

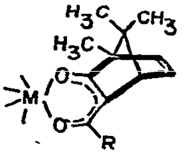


Fig 20 An illustration of asymmetric *d*-camphorato ligands· 3-hydroxymethylene-*d*-camphorato if R=H, 3-acetyl-*d*-camphorato if $R=CH_3$

Assuming a random distribution of ligands for V(dl-hmc)$_3$ prepared from racemic ligand, eight enantiomeric pairs of complexes are possible. Twenty resonance signals are possible for each kind of proton in a solution of all geometrical and optical isomers as only two pairs of these complexes could have C_3 symmetry axes. Although not analyzed because the chemical shift differences were too small, the spectrum of V(dl-hmc)$_3$ was identical [68] to that of a 1:1 mixture of V(d-hmc)$_3$ and V(l-hmc)$_3$ in chloroform, indicating that free exchange of ligands occurred before the spectrum could be recorded

While a $M(AA)_2(BB)$ complex should exhibit two NMR peaks for the –A groups and a $M(AA)_2(BC)$ complex should exhibit four –A group resonances, a $M(AA)_2(BC^*)$ complex should show eight –A group resonances since two dl pairs are possible. The ^{19}F NMR of Al(hfa)$_2$(d-atc) does show seven peaks [72], one of double degeneracy. As there are no geometrical isomers for complexes of this form, a direct means of showing that the cause of environmental averaging is optical inversion is possible if these peaks are found to coalesce at higher temperatures

Studies of the paramagnetic V(tfac)$_3$ complex have shown that the NMR resonances of the terminal groups of the ligands of the *cis* and *trans* isomers are considerably different by virtue of their greatly different contact shifts [71]. It is hoped that coalescence techniques may be extended to paramagnetic molecules of this type Indeed the greater difference in contact interactions may allow more accurate measurement due to increased separations of resonances.

(iv) Octahedral complexes involving other bidentate ligands in addition to β-diketonates: $M(dik)_2(xx)^n$ and $M(dik)(xx)_2^m$

The resolution of the optical isomers of $Co(acac)(en)_2{}^{2+}$ (en = ethylenediamine) has been achieved using (+)–arsenyl tartrate as a resolving agent[73] Proton NMR spectra of $[Co(acac)(en)_2]^{2+}$, $[Co(hfa)(en)_2]^{2+}$ and $[Co(tfa)(en)_2]^{2+}$, have been recorded [74]. There is only one possible environment for each different terminal group of a β-diketonate ligand in complexes of the form $M(dik)(xx)_2$ and, therefore, only one NMR resonance It is of interest to note, however, that the ethylenediamine $-CH_2-CH_2-$ protons show only a singlet for $[Co(acac)(en)_2]^{2+}$ while $[Co(hfa)(en)_2]^{2+}$ exhibits some fine structure[74] Confirmational interchange of these ethylenediamine protons can be rapid even while the compound maintains optical stability as these cobalt compounds are very stable with respect to optical inversion In other words the ethylenediamine rings are free to flex without the molecule twisting

Bis(acetylacetonato)oxalatocobalt(III) anions have been resolved [75]. Resolution of the optical isomers of $[Co(acac)_2en]I$ by formation of diastereoisomeric salts has been reported more recently [76]. Aqueous solutions of $(+)_{546}$ $[Co(acac)_2en]I$ were found to be optically stable at ~100°C for many hours [76] An initial report [77] indicated that $[Co(acac)_2(en)]^+$ in D_2O produced only one methyl peak even though there are two methyl groups which are non-equivalent by symmetry. This could not be caused by coalescence due to rapid optical inversion as the optically active compound is stable in solution for days at room temperature. Studies with more sensitive spectrometers [64] found a splitting of 0.003–0.010 ppm in D_2O and only slightly larger separations in

CH_3OD, CD_3OD and $(CD_3)_2SO$. Splitting of methyl resonances of bis(acetylacetonato) diaminecobalt(III) complexes (diamine = ethylenediamine, *N,N,N′, N′*-tetramethyl-ethylene-diamine, 2,2′-bipyridine, or 1,10-phenanthroline) were also reported in a variety of solvents [64]. The splitting increases in the order en < tmed < bipy < *o*-phen, indicative of a ring current diamagnetic anisotropy coupled with a smaller solvent and ion-pair effects From molecular models [64] it is predicted that the solvation and ion-pair differences of the methyl groups should be in the order tmed > *o*-phen ~ bipy > en. The order *o*-phen > bipy >> tmed ~ en would be expected due to the ring anisotropy effect [64] since the heterocyclic ligands would shield the acac methyl groups *trans* to one another and above the π cloud of the nitrogen heterocycle and deshield the other methyl groups lying in the plane of the diamine ligand The small variation in the separations [64] found for the same complex in different solvents suggests that solvent and ion-pair effects on both types of methyls are similar.

Chloroform solutions of $Co(acac)_2(aa)$, where aa represents a whole series of amino acids, show no racemization after seven weeks at room temperature in diffuse light, after refluxing for 5 h; or after passing through an alumina column [78] It is interesting to note that because of induced asymmetry at the cobalt metal from an asymmetric amino acid diastereoisomers will not rotate polarized light to the same extent and thus a racemic mixture has a resultant optical activity [78] Amino acids of the same configuration give rise to Cotton effects of the same sign [78].

The NMR spectra of $Ti(acac)_2(OCH_2CMe_2CH_2O)$ in CS_2 has been studied [79,80] and it was found that the two methyl resonances of the acac ligands were coalesced above –42.0°C. The α-proton of the neopentyl gycollate ligand also broadened at low temperatures and split into an AB pattern showing that a particular conformation of the titanium–neopentyl glycollate ring was stabilized [80]

The lower limit of the very rapid rate of optical inversion of (4,8-dimethyl-1,10-phenanthroline)bis(acetylacetonato)cobalt(II) has been found [81] by analysis of NMR line widths to have a $k \approx 5 \times 10^6$ at 25°C The spectrum of this paramagnetic cobalt ($S = 3/2$) complex exhibits one resonance peak for the acetylacetone methyls at room temperature but this splits into two equal peaks at lower temperature. The rate of signal collapse is concentration independent. The chemical shift difference between the two acac methyl groups is ~ 40 ppm at –33°C, which is about three orders of magnitude larger than separations for diamagnetic complexes, thus allowing the researchers to monitor the more rapid kinetic process

The complexes $[Co(macac)_2en]^+$ and $[Co(prac)_2en]^+$ can exist as any of three possible geometrical forms each having optical antipodes, just as the $M(AA)(CD)_2$ species (see Fig. 18). Two of these isomers would each have two sets of equivalent terminal groups while the third isomer has two sets of non-equivalent terminal groups The NMR could then show as many as four resonances for each terminal group in a mixture of isomers The NMR of $[Co(macac)_2en]^+$ exhibits two resonances each for the methyl, methoxy and methylene protons, each pair of lines having an intensity ratio [82] of approximately 3 2. The $[Co(prac)_2en]^+$ spectrum [82] has at least two superimposed ethyl patterns and three methyl resonances. It is proposed that the systems are mixtures of the three possible isomers [82]. It is noted that only a single unresolved methylene proton resonance occurs

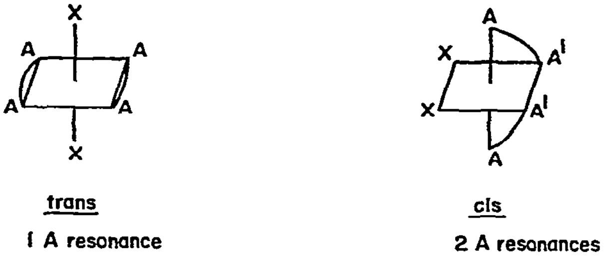


Fig. 21. The two geometrical isomers of an $M(AA)_2X_2$ complex illustrating the number of different resonances possible for the terminal groups of the AA ligands.

for the ethylenediamine suggesting that confirmational interchange of the ethylenediamine ring is rapid [82].

(v) Octahedral complexes involving symmetric β-diketonates and monodentate ligands· $M(AA)_2X_2$ and $M(AA)_2XY$

Complexes of the form $M(AA)_2X_2$ or $M(AA)_2XY$ can have both *cis* and *trans* forms (see Fig. 21) with the *cis* form having optical antipodes. The terminal groups of the symmetric β-diketonates in the *trans*-$M(AA)_2X_2$ complexes have only one environment and thus only one NMR resonance due to these groups. The *cis* form can exhibit two resonances due to non-equivalent environments for the terminal groups being *trans* to one another or *trans* to the monodentate ligands.

The *trans*-$M(AA)_2XY$ complexes will also show only one terminal group resonance but the *cis*-$M(AA)_2XY$ isomer has four non-equivalent environments for the terminal groups and, therefore may exhibit as many as four NMR resonances for these terminal groups. The complexes are pictured in Fig. 22. While the groups *trans* to the two different monodentate ligands are of course structurally different, the two terminal groups *trans* to one another are also in non-equivalent environments This can be easily seen if one considers what is *trans* to the other end of the ligand.

The NMR spectra of $M(AA)_2X_2$ complexes can often be used as a probe to determine whether the *cis* or *trans* configuration is obtained. For example the *cis* configuration has been found [79,80,83,84,93,104] for titanium(IV), germanium(IV) and tin (IV) complexes of the type $M(acac)_2Cl_2$. The existence of an equilibrium between the *cis* and *trans* forms for $Ge(acac)_2Cl_2$ and $Ge(thd)_2Cl_2$ has been noted more recently [85].

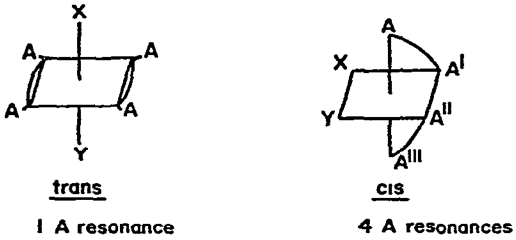


Fig. 22 The two geometrical isomers of an $M(AA)_2XY$ complex illustrating the number of different resonances possible for the terminal groups of the AA ligands

Since the frequency separations between groups in different environments may be too small for resolution, due to either small or counteracting structural and solvation effects, the assignment of a *trans* configuration on the basis of observing only one resonance will always be equivocal

Two terminal group resonances observed for $Sn(acac)_2X_2$, where X=Cl, Br or I, were first attributed [86] to a *trans* configuration with distorted acetylacetone ring structures "containing somewhat localized double bonds" It was observed, however, that these terminal group resonances for $Sn(acac)_2Cl_2$ coalesced to a single signal at higher temperatures which would indicate that either the postulated distorted *trans* form undergoes a rapid configurational interconversion or the two resonances are due to the *cis* configuration which undergoes optical inversion at a rate fast on the NMR time scale, thereby, averaging environments at the higher temperatures [87] Dipole moment studies [88,89] of $Sn(acac)_2Cl_2$ give strong evidence for a *cis* configuration with rapid optical inversion It is pointed out [87] that this rapid inversion could also account for difficulties found in attempts [90] to resolve optical antipodes of $[Sn(acac)_2(C_6H_5)_2]$ and $[Sn(dbm)_2(C_6H_5)_2]$ rather than indicating that they need be of the *trans* form Furthermore, $[Sn(acac)_2(C_6H_5)Cl]$ was reported [86] to have two CH signals and four CH_3 signals (expected for a *cis* arrangement) while a *trans* configuration would be expected to show only one CH and one CH_3 resonance for the acetylacetonato ligand In like fashion it has been pointed out [87] that optical inversion of the *cis* form of $[Sn(acac)_2(CH_3)Cl]$ fits better with the reported coalescence than does the initially proposed [91] *cis–trans* isomerization

Coalescence temperatures for the methyl resonances of $Sn(acac)_2Cl_2$ in six different solvents have been noted and frequency differences given [92] for bromoform solutions in the temperature range of 40 – 63°C This coalescence can also be explained by optical inversion of the *cis* form, rather than the proposed improbable "exchange between two distorted octahedrons" of the *trans* form

Considering all four possible twist axes [16] it should be noted that footnote 8 of Ref. 87 is not correct insofar as combinations of twists can average all four environments[93] The persistence of the tin coupling to the protons of the acetylacetonate ligands above the coalescence temperature [87] for $[Sn(acac)_2Cl_2]$ requires an intramolecular process for the environmental averaging

Since coalescence as well as accidental degeneracy can cause only one signal to be observed for the chelate terminal groups of the *cis* isomers, the absence of splitting cannot be used to argue conclusively for a *trans* configuration. With supporting evidence from IR and Raman spectroscopy some *trans* assignments have been suggested which are consistent with the NMR for such β-diketonate complexes as $[Cr(acac)_2(NO_2)_2]^-$ and $Co(acac)_2(NO_2)A$ where A represents NH_3, any of ten different substituted pyridines, quinoline, isoquinoline, imidazole and benzimidazole [94]

The Raman and IR spectra of $[Sn(acac)_2(CH_3)_2]$ [95,96], $[Sn(acac)_2(C_6H_5)_2]$ [95], and $[Pb(acac)_2(CH_3)_2]$ [95,96], have been used to support a *trans* configuration for these complexes, but the existence of non-zero dipole moments for the first two complexes [97] indicate a *cis* configuration It was further stated [97] that the IR and Raman data are not definitive in these cases and that the NMR spectra does not show two acac methyl resonances because of rapid intermolecular ligand exchanges or because of rapid inversion

A rapid intermolecular β-diketonate ligand exchange process is favored [97] in this case since the NMR spectra of a chloroform solution of a mixture of $(CH_3)_2Sn(acac)_2$ and $(CH_3)_2Sn(hfa)_2$ at 25°C shows only one Sn—CH_3 peak approximetaly midway between the resonances for Sn—CH_3 groups in the two starting complexes and methyl groups bound to tin do not exchange rapidly at 25°C.

Resolution of the *cis* and *trans* isomers of some complexes of the form $[M(AA)_2X_2]$ have been reported Thus *cis*-$[Co(acac)_2(NO_2)_2]^-$ has been prepared and separated from the *trans* form [98]. The same workers also separated *cis*- and *trans*-$[Co(acac)_2(NH_3)_2]^+$ by extraction [77]. The optical isomers of *cis*-$[Co(acac)_2(NH_3)_2]I$ have been resolved by formation of diastereoisomeric salts [76]. Aqueous solutions of the resolved complex lose optical activity with decomposition of the complex [76]. The isomerization of $Co(acac)_2NO_2$ (amine), the amine being pyridine or 4-*t*-butylpyridine, both from the *trans* form to an equilibrium mixture and from the *cis* form to an equilibrium mixture, is slow at room temperature, but at about 60°C the equilibrium was established in a few hours [99].

The coalescence temperatures of the acac methyl resonances of the complexes *cis*-$Ti(acac)_2X_2$ where X = OMe, OEt, OCH_2CF_3, O-*i*-Pr, O-*n*-Bu or Cl, have been reported [79,80]. Intermolecular exchange processes [80] were eliminated as possible mechanisms since addition of either monodentate or acetylacetonate ligand gave separate signals and had no effect on the spectra of the complexes. Furthermore, the lifetimes showed no concentration dependence, also indicating an intramolecular process Rates of intramolecular exchange were determined [80] at various temperatures using a peak height to peak minimum ratio method [100]. Results were found [80] to conform to Arrhenius plots from which activation parameters were deduced. The peak height to peak minimum method, using approximate line-shape functions and neglecting the natural line-width, may cause systematic errors [101] producing low values of activation energies and values of the entropies of activation which are too negative

The effect of increasing steric hindrance in $Ti(acac)_2(OR)_2$ for R = Me, Et, *i*-Pr, *t*-Bu, is to raise the coalescence temperature [80], indicating the rate of intramolecular rearrangement is "slowed down" if the splitting is assumed constant The trend towards increased activation energy with increase in size of the substituent is noted. Steric hindrance opposes intramolecular exchange and this does not support a partial dissociation mechanism in which relief of steric strain would occur in the five-coordinated transition state. It is suggested [80] that the activated complex in the optical inversion of $Ti(acac)_2X_2$ in the symmetrical trigonal prism which may be obtained by a twisting motion. The greater symmetry in the transition state than in the *cis* octahedral configuration of the ground state could explain in part the negative entropies of activation, which imply increased order in the transition state. Solvation effects may also be important in explaining these negative entropies It was also noted [80] that increased electronegativity of X causes faster rearrangement, which is just the opposite of what is expected if bond rupture of one end of an acac group is involved.

NMR spectra of *cis*-$Zr(acac)_2X_2$ and $Hf(acac)_2X_2$ (X = Cl or Br) indicated that the chelate rings undergo rapid stereochemical rearrangements because no splitting of the time-averaged acac methyl resonances was observed [102,103] even at temperatures as low as – 130°C.

A very thorough study of the environmental averaging of the acac methyl resonances of *cis*-Ti(acac)$_2$X$_2$ (X = F, Cl or Br) has been done [103,104] Rates were calculated by computer fitting of the spectra. First-order rate constants extrapolated to 25°C were found to be 1.6×10^4 sec^{-1} (X = F), 6.7×10^2 sec^{-1} (X = Cl) and 2.3×10^3 sec^{-1} (X = Br). Energies and entropies of activation were reported and kinetic data tabulated over the temperature ranges observed. The rates were found to be independent of complex concentration. Halide dissociation was eliminated as an attractive mechanism for environmental averaging as the activation energies were independent of the halogen, and rates of halide ligand exchange are slow compared to those of the methyl groups. Also complete dissociation of an acetylacetone ligand via the Thomas mechanism was eliminated because exchange with excess acetylacetonate ligands is not observed under the conditions of acac methyl averaging While the authors favor mechanisms going through a five-coordinate intermediate, twisting modes cannot be eliminated

It has been shown [93] that various twisting mechanisms or combinations thereof can account for the observed environmental averaging although the authors favor a bond-rupture Figure 23 shows twists about two of the four octahedral face C_3 axes Both twists interconvert the optical enantiomers while exchanging environments on the terminal groups. Note that the twist about the second C_3 axis can be carried through a full

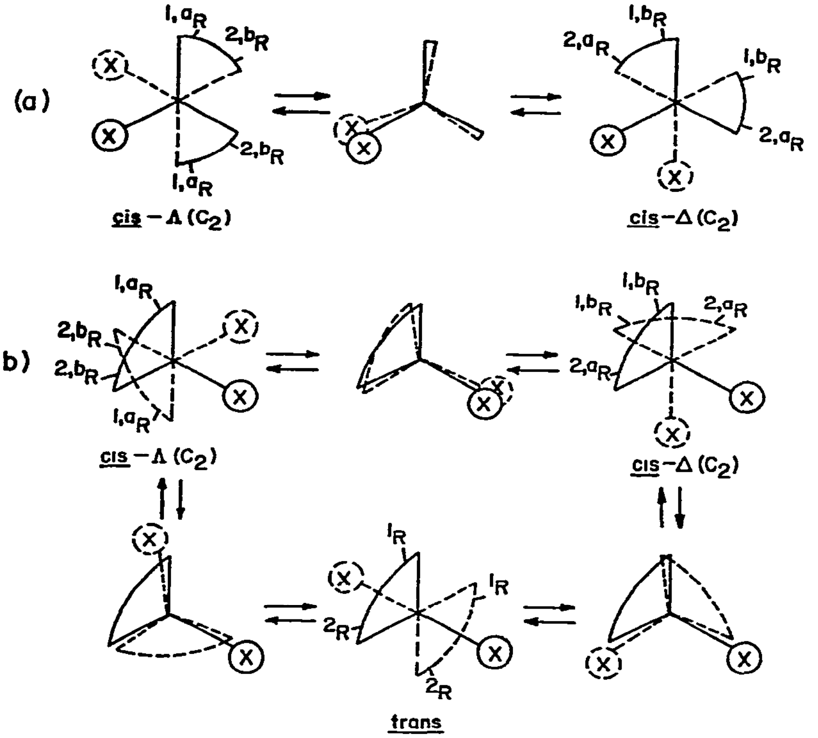


Fig. 23. Twist mechanisms for a *cis*-M(AA)$_2$X$_2$ complex. (a) Depicts a twist about imaginary C_3 axis *a* of Fig 8, (b) depicts twists about imaginary C_3 axis *d* of Fig 8 Numbers label terminal groups, letters label environments (Ref. 93, courtesy of Inorganic Chemistry).

rotation since there are no bidentate ligands spanning the twisted faces. This second twist also provides a path for *cis–trans* isomerization. The two twists both give transition states of C_{2v} symmetry but they differ in the orientation of the chelate rings about the trigonal prism

The *cis*-Ti(dbm)$_2$X$_2$ (X = F, Cl or Br) complexes have also been examined [93,103] by proton and fluorine NMR The spectrum of the phenyl protons exhibits too much spin–spin splitting to allow any precise measurements, but the line broadening observed is attributed to the exchange of phenyl groups between the two non-equivalent environments of the *cis* isomer.

The *cis*-Ge(acac)$_2$Cl$_2$ and *cis*-Sn(acac)$_2$X$_2$ (X = Cl, Br or I) complexes exhibit [84] non-equivalent methyl groups at room temperature indicating that these complexes undergo configurational changes more slowly than the corresponding complexes of titanium

Si(acac)$_2$(C$_2$H$_3$O$_2$)$_2$ in CHCl$_3$ and CH$_2$Cl$_2$ undergoes *cis–trans* isomerization [105] at a measurable rate Samples of the predominately *trans* solid form begin isomerization upon dissolution and equilibrium is reached at room temperature in approximately one half hour or less

Two NMR signals are discernable [106] for the acac methyl groups of Al(acac)$_2$(DMF)$_2^+$ in DMF solution (DMF = *N,N*-dimethylformamide) below 5°C. These were assigned [106] to the *cis* and *trans* isomers, but since there are two possible environments for the acac methyls of the *cis* isomer, these two resonances might better be assigned to the *cis* complex alone. From the separation of the acac methyl signals at –20°C a first-order rate constant for the configuration rearrangement (be it optical inversion of the *cis* form or *cis–trans* isomerization) at the coalescence temperature of 5° was estimated [106] to be 18 sec^{-1}. Using a computer line shape program and the known populations of the exchanging sites and the separations between the *N*-methyl resonances of the free and coordinated DMF, the rate constant for exchange of DMF with the Al(acac)$_2$(DMF)$_2^+$ complex was estimated to be 30 sec^{-1} at the coalescence temperature of the acac resonances, 5°C It was proposed that the rate-determining step for rearrangement of Al(acac)$_2$(DMF)$_2^+$ is the dissociation of DMF from the complex

Ga(acac)$_2$(DMF)$_2^+$ has been studied [107] in like fashion and below –20°C the methyl resonance due to acac$^-$ in this complex broadens and splits into two peaks of nearly equal intensity. Due to viscosity broadening, accurate signal widths and relative areas could not be obtained and rates of environmental averaging were not estimated. While the authors again favor [107] the assignment of the two peaks to *cis* and *trans* isomers the splitting can be more simply explained in terms of the *cis* isomer alone This *cis* assignment would also be more consistent with substantiated assignments for other M(acac)$_2$X$_2$ complexes quoted earlier in this section. The DMF resonances of Ga(acac)$_2$(DMF)$_2^+$ could not be detected at low temperatures due to the viscosity of the DMF solution.

Topological representations of rearrangements of complexes of the form M(AA)$_2$XY have been presented [10,22]

The complex (π-C$_5$H$_5$)Zr(acac)$_2$Cl has been found [108] to be sufficiently stereochemically rigid at room temperature in benzene solution to observe four non-equivalent environments for the methyl protons in its NMR spectrum. These resonances cannot be interpreted in terms of an equilibrium mixture of compounds of different stoichiometries as would arise from disproportionation. The existence of a single, sharp cyclopentadienyl resonance has been attributed to rapid rotation of the ring about the metal-ring axis [108]. The *cis* isomer of an octahedral structure could account for the four different methyl resonances but supporting evidence is quoted which favors an *eight-coordinate* dodocahedral arrangement with the cyclopentadienyl ring assumed to occupy a triangular face in forming three π bonds to zirconium [108]. A number of potentially detectable isomers are possible based on the higher coordination number but no isomerization was detected [108,109]. That the $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$ is sufficiently stereochemically rigid at room temperature to observe non-equivalence environments for the methyl protons is surprising in contrast to the single methyl resonances observed [102] for $Zr(acac)_2Cl_2$ and $Zr(acac)_3Cl$ at temperatures as low as $-130°C$ For $(\pi\text{-}C_5H_5)Zr(bzac)_2Cl$ at least four isomers were observed [108] but due to the unsymmetric ligands these could result from an octahedral geometry as well as a dodecahedral geometry.

The ^{19}F NMR spectrum of $(\pi\text{-}C_5H_5)Ti(hfa)_2Cl$ has been found [109] to exhibit two sets of four equal-intensity lines, with one set relatively weak Each set was assigned to a different isomer. The existence of isomers with each having all $-CF_3$ groups non-equivalent rules out octahedral coordination since a *trans* isomer would have all four $-CF_3$ groups equivalent. The above two species were nevertheless covered in this section due to their stoichiometry.

(vi) Octahedral complexes involving unsymmetrical β-diketonates and monodentate ligands : $M(AB)_2X_2$ and $M(AB)_2XY$

Complexes of the form $M(AB)_2X_2$ have five possible geometrical isomers (see Fig. 24) three with the two X ligands *cis* to one another, and two with the two X ligands *trans* to each other. The *cis*-X isomers each have optical antipodes but the *trans*-X isomers do not.

The NMR spectra of $Co(macac)_2NO_2py$ and $Co(prac)_2NO_2py$ in D_2O have been found consistent with those expected for a mixture of the *trans*-(X–Y)-*cis*(A)-*cis*(B) and *trans*-(X–Y)-*trans*(A)-*trans*(B) isomers [82] No geometrical isomerization is noted at room temperature

Variable temperature proton and fluorine spectra of $Ti(bzac)_2F_2$ in dichloromethane have been reported [93]. These spectra are shown in Figs 25 and 26 respectively Lines 1, 2, 5 and 6 of the fluorine spectra are assigned to an AB pattern due to the non-equivalent fluorines in the *cis*(F)-*cis*(bz)-*cis*(Me) isomer. Lines 3 and 4 were assigned to the other two isomers with *cis* fluorines on the basis that the $Ti(acac)_2X_2$ exists exclusively in the *cis* fluorine configuration in dichloromethane. The variable temperature proton NMR spectra at low temperatures exhibits four lines assigned to the four non-equivalent methyl groups of the three isomers which have fluorine atoms in *cis* positions The line broadening and coalescences are in both cases attributed [93] to isomerization among the three *cis*-(F) isomers which averages both the four non-equivalent fluorine sites and the four non-equivalent methyl environments Variable temperature proton spectra of $Ti(bzac)_2Cl_2$ and $Ti(bzac)_2Br_2$ can be interpreted [93] in the same manner as

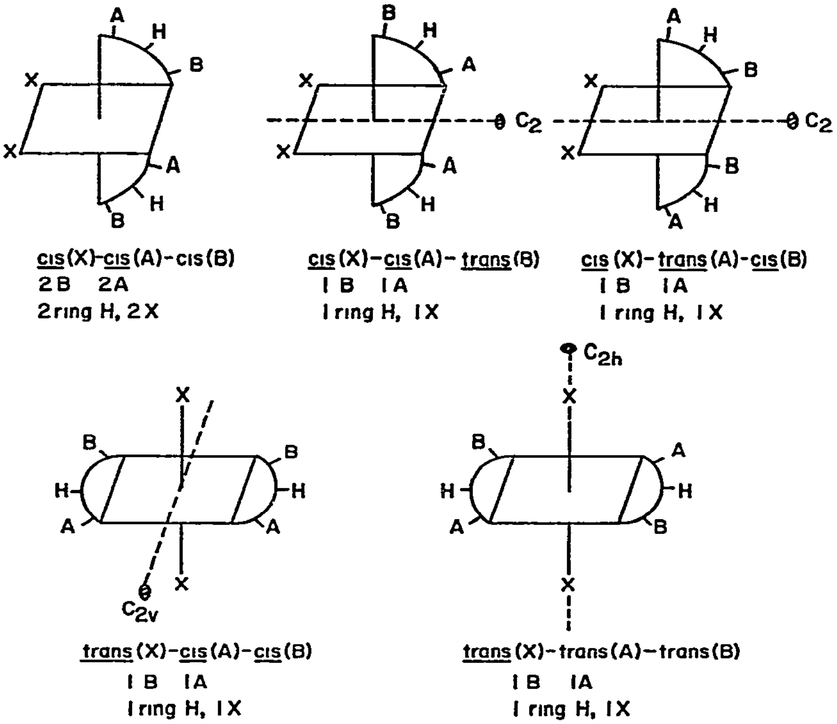


Fig 24 The five geometrical isomers of an $M(AB)_2X_2$ complex illustrating the number of different resonances possible for each terminal group of the AB ligands and for X.

the $Ti(bzac)_2F_2$. The implied simultaneous exchange of protons between all four environments of the three *cis*-dihalo isomers would demand six independent, first-order rate constants to describe the four-site exchange process The relaxation times of the methyl protons of the $Ti(bzac)_2X_2$ complexes also appear to be temperature dependent [93] Estimates of the rate constants of environmental averaging at the temperatures of coalescence were made [93] by approximating the four-site exchange process by a two site process using the frequency separation between the centers of gravity of the higher and lower field doublets of the proton spectra The coalescence temperatures and estimated first-order rate constants for the exchange of methyl groups in $Ti(bzac)_2F_2$, $Ti(bzac)_2Cl_2$ and $Ti(bzac)_2Br_2$ are [93], respectively, −37°C, 20 sec^{-1}, −24°C, 25 sec^{-1}; and −31.5°C, 30 sec^{-1}. By use of the activation energies of the corresponding $Ti(acac)_2X_2$ complexes, the rates were extrapolated to −31.5°C for comparison of the effect of the halogen on the rate, giving 35, 12 and 30 sec^{-1}, respectively.

While twists about any of the four axes reverse the chirality of the chelate rings, a twist about only one axis cannot exchange the methyl groups between all four environments. Twists about a single C_3 axis, therefore, cannot be used mechanistically to explain the coalescence of the four methyl resonances. Furthermore, this could not account for the collapse of all six lines in the fluorine spectra of $Ti(bzac)_2F_2$, which demand the exchange of fluorine between all four non-equivalent sites of the three *cis*-difluoro isomers.

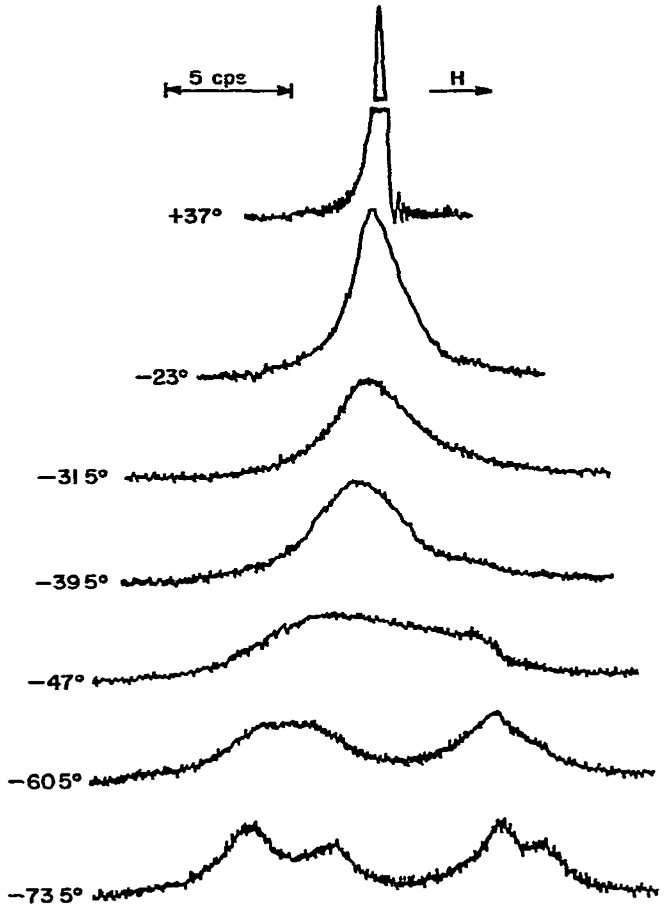


Fig 25. The coalescence of the methyl proton resonances of $Ti(bzac)_2F_2$ in dichloromethane (Ref 93, courtesy of Inorganic Chemistry)

The possibility of a combination of twists about different axes can account for the observed coalescences, however, and therefore, a definite choice between twisting mechanisms and intramolecular bond - rupture processes is impossible. Fig 27 shows a combination of twists about two of the four possible C_3 axes which can account for the observed results The 180° rigid rotations of the entire molecule are given to orient the two C_3 axes perpendicular to the plane of the paper before each step

The NMR spectrum of $Ge(Bzac)_2Cl_2$ shows non-equivalent methyl groups at room temperature [84] and has been interpreted in terms of a mixture of the three *cis*-dichloro isomers. The chelate rings of the germanium complex must, therefore, undergo configurational changes more slowly than those in the corresponding titanium complex The room temperature spectrum of $Ge(dhd)_2Cl_2$ exhibits resonances assignable to a mixture of the three *cis*-dichloro and two *trans*-dichloro isomers [85].

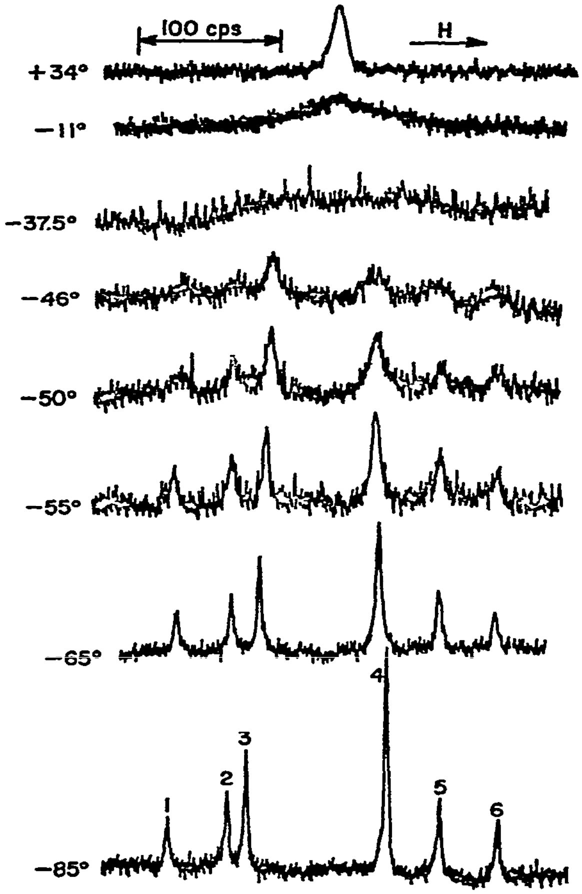


Fig. 26. The coalescence of the fluorine resonances of $Ti(bzac)_2F_2$ in dichloromethane (Ref 93, courtesy of Inorganic Chemistry).

(vii) Other coordination numbers

(a) Four-coordinate complexes

Complexes with four points of attachment to the central metal would be expected to assume either tetrahedral or square planar geometries Compounds of the form $M(AA)_2$, M(AA)(BB), M(AA)(BC), $M(AA)X_2$, M(AA)XY or $M(AB)X_2$, do not have any optical or geometrical isomers.

Tetrahedral complexes of the form $M(AB)_2$, $M(AB)(CD)_2$ and M(AB)XY will have optical antipodes but no geometrical isomers. Square planar complexes of these same structures have two geometrical isomers but neither geometrical form has optical activity.

Tetrahedral structures have been confirmed for such complexes as $Be(bzac)_2$ by partial resolution of diastereoisomers by preferential absorption on optically active

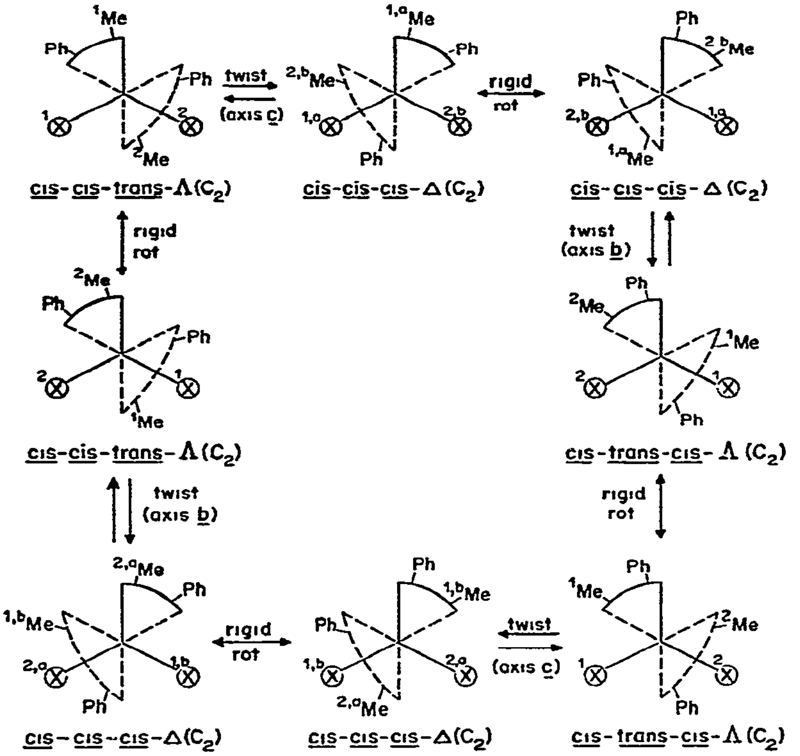


Fig 27. Combinations of twists about axes *b* and *c* of Fig 8 illustrating the exchange of nuclei between all non-equivalent environments for $Ti(bzac)_2X_2$ Numbers label methyl groups and halogen atoms, letters indicate non-equivalent environments (Ref 93, courtesy of Inorganic Chemistry)

quartz [110] or sodium chlorate crystals [111] Certain bis (β-diketonate) complexes as those of iron(II) [112] have been found to be polymeric, however While application of NMR to studies of rearrangements of tetrahedral complexes is not possible, it might be possible to observe *cis–trans* isomerization of coplanar square complexes of the form $M(AB)_2$ by NMR if a system was found that rearranged fast enough to average environments of the terminal groups or, if much slower, by following intensity changes of peaks assigned to different isomers over a period of time

(b) Five-coordinate complexes

The bis (β-diketonato)oxovanadium(IV) complexes have been shown [113] to have structures which are nearly square pyramidal in the crystalline state Complexes with symmetric chelate ligands cannot have geometrical or optical isomers but with unsymmetric ligands, complexes of the form $VO(AB)_2$ have both *cis* and *trans* forms with the *trans* form having optical antipodes. Attempts to resolve $VO(bzac)_2$ and $VO(tfa)_2$ have

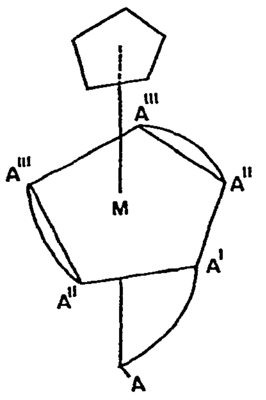


Fig. 28 The pentagonal-bipyramidal structure of a (π-C_5H_5)M(AA)$_3$ complex illustrating the four *different environments of the terminal groups of the chelate ligands*

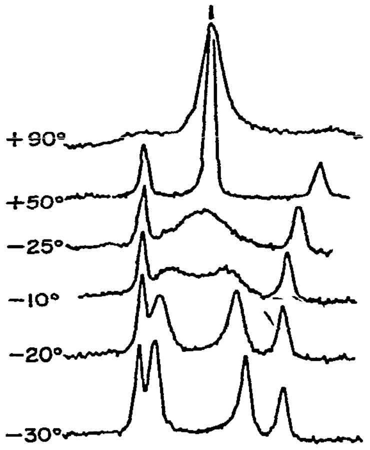


Fig. 29 The coalescence of the fluorine resonances of (π-C_5H_5)Zr(hfa)$_3$ in methylcyclohexane at 50 – 90°C and acetone at the lower temperatures The spectra of the complex have been aligned vertically although the chemical shifts differ appreciably in the two solvents (Ref 109, courtesy of the Journal of the American Chemical Society)

not been successful, however [114]. For some five-coordinate systems NMR may be of great use in identifying the *cis* and *trans* forms and in some cases it might allow estimation of rates.

(c) Seven-coordinate complexes

Zirconium(IV) and hafnium(IV) complexes of the form M(acac)$_3$X (X = Cl, Br, or when M = Zr, I) have been prepared and characterized [102] All reasonable seven-coordinate M(acac)$_3$X structures have two or more non-equivalent methyl groups, but only one time-averaged peak was observed even at temperatures as low as −130°C. This would indicate that the complexes undergo rapid configurational rearrangements of some type.

NMR and X-ray studies on (π-C_5H_5)Zr(hfa)$_3$ have led to formulation of pentagonal-bipyramidal geometry [109]. It is noted that while the π-cyclopentadienyl group may be considered tridentate, it is convenient to regard it in this case as occupying a single coordination position. The π-C_5H_5 group does occupy a larger share of the coordination sphere than typical ligands [109] as it is found to displace the equatorial ligands 10° below the plane of pentacoordination From pentagonal-bipyramidal geometry (see Fig 28) one can predict four lines of intensity ratio 2 2 1.1 in the fluorine spectra The two lines of double intensity would be due to the terminal groups indicated by double prime and triple prime in Fig. 28 and the single intensity lines to the fifth equatorial group (single prime) and the axial group The four lines with the proper intensities are observed [109] at −30°C in acetone. With increasing temperature the more intense pair due to totally equatorial ligands is averaged first (see Fig 29) Only above this coalescence temperature of +50°C does the less intense pair of bands become involved Those spectra at +50 and +90°C in Fig 29 are of the complex in methylcyclohexane with the spectra aligned vertically, although there is an appreciable chemical shift difference in the two solvents The apparently slower averaging of the fluorines on the chelate ring bridging the axial position is noteworthy

Both the proton and ^{19}F NMR spectra of (π-C_5H_5)Zr(tfa)$_3$ at room temperature show that two isomers are present [109] in a ratio of ca. 3 2 These isomers differ in the orientation of the tfa ligand bridging the axial and equatorial positions, i e , the $-CF_3$ can be equatorial or axial, leading to two ^{19}F resonances. The environmental averaging of both the methyls and the trifluomethyls of the totally equatorial ligands is rapid at room temperature i e , each isomer shows one ^{19}F resonance for the totally equatorial ligands with twice the intensity of the CF_3 resonance of the unique ligands. Each of the two isomers is thus characterized by two peaks in a 1 2 intensity ratio for both the CH_3 and CF_3 groups [109]

(d) Eight-coordinated complexes

For a square antiprismatic structure, a number of structural isomers can be imagined [115,116] Even for complexes with four identical, symmetrical, bidentate ligands there are three isomers as pictured in Fig 30. For the less symmetrical dodecahedron there would be twice as many stereoisomers [115]. With combinations of different ligands and unsymmetrical ligands many more possibilities exist. In the solid state there are examples of both square antiprismatic geometry, such as Zr(acac)$_4$ [117], and dodecahedrons, such as Cs[Y(hfa)$_4$] [118].

Fluorine NMR studies [119] of benzene solutions of eight-coordinate zirconium(IV), hafnium(IV), cerium(IV) and thorium(IV) β-diketonates which are equilibrium mixtures of M(tfa)$_x$(acac)$_{4-x}$ ($x = 0 - 4$) show only one ^{19}F resonance each for M(tfa)$_4$, M(tfa)$_3$ (acac), M(tfa)$_2$(acac)$_2$ and M(tfa)(acac)$_3$. If the eight-coordinate structures were stereochemically rigid, one would expect a larger number of lines due to geometrical isomers and non-equivalent $-CF_3$ environments for at least the first three of these stoichiometrically different complexes. Even at temperatures as low as −105°C in acetone, attempts

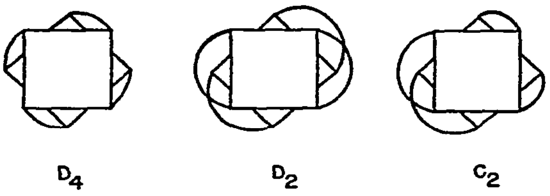


Fig 30 Structural isomers of an $M(AA)_4$ complex having a square antiprismatic structure

to detect geometrical isomers of $M(tfa)_4$ complexes by NMR have been unsuccessful. This would indicate that Group IVb β-diketonate complexes undergo very rapid intramolecular rearrangements. Accidental degeneracies of resonances or existence of only one isomer of each complex are not likely explanations. At higher temperatures the ^{19}F NMR lines due to the $Th(tfa)_x(acac)_{4-x}$ ($x = 1 - 4$) species coalesce due to intermolecular ligand exchange between the various stoichiometrically different species[119].

Proton NMR spectra[120] of benzene solutions of equilibrium concentrations of these same mixed ligand complexes (where M = Zr or Hf) exhibited only one acac methyl resonance and one tfa methyl resonance for each stoichiometrically different molecule containing those ligands. This also suggests rapid intramolecular rearrangements for each molecule. At higher temperatures all acac methyl peaks coalesce (see Fig 31) as do all tfa methyl resonances indicating rapid intermolecular ligand exchange The rates of exchange of tfa and acac were found to be of the same order of magnitude.

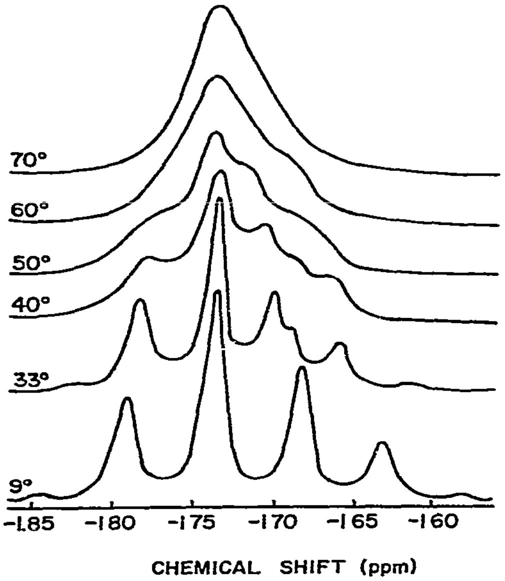


Fig 31. The coalescence of the methyl proton resonances for a $Zr(tfa)_x(acac)_{4-x}$ ($x = 0 - 4$) mixture in benzene. (Ref. 120, courtesy of Inorganic Chemistry).

The proton NMR spectra of $Th(dbm)_4$ and $U(dbm)_4$ in chloroform both indicate that either all of the phenyl rings are equivalent or undergo rapid environmental averaging [121]

$Y(hfa)_x(tfa)_{4-x}^-$ ions ($x = 0 - 4$) in equilibrium concentrations as formed from the parent tetrakis complexes in $CDCl_3$ were found [122] to exhibit eight methylene resonances at $-40°C$, one for the $-CH=$ proton(s) of hfa in each of the ions in which it occurs and one for the $-CH=$ proton(s) of acac in each of the ions in which it occurs. The presence of only eight absorptions, none of which show any splitting or assymmetry in shape, would indicate again that the rate if intramolecular interconversion of the isomers of each ion is fast enough to average the environments. With increasing temperature the resonances of the stoichiometrically different ions merge until at $+40°C$ only one hfa and one tfa methylene peak are observed. This again indicates a rapid intermolecular ligand exchange process Inasmuch as the methylene peaks appear to coalesce equally rapidly for both hfa and tfa, the two different ligands are apparently exchanging at approximately the same rate.

While twisting mechanisms can account for rapid intramolecular rearrangements, it seems more likely that bond rupture processes produce the rearrangements in view of the extreme lability of the bonds evidenced by the rapid intermolecular exchange. Since intramolecular isomerization is faster than intermolecular it is not possible definitely to eliminate twisting modes altogether as they could well contribute to the faster rearrangements.

D. SUMMARY

While kinetic studies of rapid geometrical and optical isomerization of octahedral complexes of β-diketonates by NMR have proven feasible, data thus obtained, combined with other rate information available, are only sufficient to indicate some very general trends. Comparisons are of necessity based on studies involving different conditions such as solvent and temperature

In terms of the effect of the β-diketonate ligands on the rate of intramolecular isomerization, systems involving the following ligands undergo isomerization in the decreasing order of rates : hfa > tfa > acac > thd > bzac > dbm One might expect dim and dhd to fall between acac and thd.

For octahedral systems having three bidentate ligands the rates of rearrangement decrease in the following order: $Co^{II} > In^{III} > Ga^{III} > Al^{III} > Co^{III} > Cr^{III} > Rh^{III}$ For octahedral systems which also involve monodentate ligands the rates decrease as follows $Zr^{IV} \approx Hf^{IV} >> Ti^{IV} > Sn^{IV} \approx Ge^{IV}$. Ligand exchange competing with the rearrangement may affect the order in some cases

The rates of rearrangement of complexes of β-diketones which also involve monodentate ligands have been found to be affected by the nature of the monodentate ligand The rate of rearrangement of complexes involving halides decreases in the order $F > Br > Cl$. Studies made on chelate complexes containing various organooxy ligands suggest that the rate of rearrangement decreases with increased size of the oxyanion and increases with increased electronegativity of these monodentate ligands.

As yet there has been no completely definitive experiments which completely rule out a bond rupture or twist mechanism for rearrangements of β-diketonates In all liklihood no single mode of either a twist or bond rupture mechanism is operative to the exclusion of all other modes in a given stereochemical rearrangement

There are certain to be future extentions of NMR methods discussed here to other than octahedral geometries. Paramagnetic systems are also expected to be more thoroughly examined. Magnetic resonance of the central metal atoms might also prove to be of mechanistic interest

It is hoped that this review will point out that the potential of NMR in dynamic studies of complexes may well be as vast as its structural applications have proven to be

ACKNOWLEDGEMENTS

The authors are indebted to Drs. T J Pinnavia and R.C. Fay for preprints and Dr. C.S. Springer, Jr. for many helpful suggestions and comments

ADDENDUM

In the time since this review was submitted a number of significant papers have appeared and a number of additional preprints have been received. In an attempt to make this review as current as possible the following are called to the reader's attention

R.C. Fay, A.Y. Girgis and U. Klabunde, Stereochemical rearrangements of metal tris-β-diketonates. I. Partial resolution and racemization of some tris-acetylacetonates, *J. Amer Chem Soc*, 92 (1970) 7056.

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R.B. VonDreele, J J Sterowski and R C Fay, The crystal and molecular structure of chlorotris(acetylacetonato)zirconium(IV), submitted for publication

The following related works were brought to our attention by the referees

H Weingarten, M G Miles and N K Edelmann, The structure and lability of some new titanium(IV) complexes, *Inorg Chem*, 7 (1968) 879

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