STEREOISOMERIZATION PROCESSES IN cis-OCTAHEDRAL-BIS-CHELATE COMPLEXES: ACTIVATION ENERGIES ASSOCIATED WITH THE DIFFERENT REARRANGEMENT MODES IN THE CASE OF PHENYLCHLOROBIS(BENZOYLACETATO)TIN

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Summary

The dynamic stereochemistry of phenylchlorobis(benzoylacetonato)tin has been investigated in solution with the aid of variable temperature ^{1}H NMR spectroscopy The results, analyzed in terms of permutational analysis and topological representations, reveal that in this complex at least two different rearrangement modes are necessary in order to give exchange of all the isomers and diastereotopic signals The free energies associated with each mode have been determined and have shown to be very similar to each other The residual isomerism is discussed in the light of the results

## Introduction

In a previous work on the static and dynamic stereochemistry of cis-octa-hedral bis-β-diketonato complexes [1] we investigated the dynamic aspects of the stereoisomerizations of these systems with the aid of permutational analysis and topological representations The major conclusion in this work was that when only twist mechanisms not involving bond rupture are considered, six rearrangement modes suffice to describe all the permutational consequences of the stereoisomerization processes in such systems, these modes were termed M_0, M_1, M_2, M_3, M_4 and M_5. Experimental evidence have indicated that among these modes only those which result in a net reversal of the helicity of the

structure need to be considered as feasible rearrangement pathways [1—3], and, within them, the mode M_4 was found to be the stereoisomerization pathway of lowest energy (threshold mechanism) in all systems of this type so far examined [1—3]

However, our analysis [1] indicated that in more complex derivatives a combination of different modes is necessary in order to interconvert all the stereoisomers In particular, for systems of general structure I if the monodentate

(I)
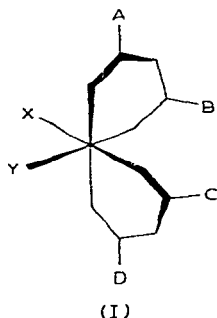
ligands are equal (X = Y) and the two β-diketonate rings are different and both lack a local C_2 axis coincident with the bond to the central metal atom, eight isomers (4 *dl* pairs) are possible The same situation arises in complexes in which the two monodentate ligands are different (X ≠ Y) and the two β-diketonato rings are equal (A = C, B = D) but still lack a local C_2 axis In these cases, our analysis reveals that even when interconversions among these eight forms by mode M_4 are rapid, two isomers (1 *dl* pair) still exist, and therefore such systems are suitable for detecting additional stereoisomerization pathways other than M_4 (vide infra).

In this paper we report kinetic NMR data on the stereoisomerization processes in the phenylchlorobis(benzoylacetonato)tin (II), which represents the first example of a bis-chelate system which needs at least two different stereoisomerization modes in order to permit coalescence of all its diastereotopic signals

Experimental

For the preparation of compound II 0 72 g (31 mmol) of Na was dissolved in 15 ml of methanol and 5 g (31 mmol) of benzoylacetone was added with stirring during 30 minutes, and the solvent was then removed under reduced pressure 4 33 g (26 mmol) of the salt obtained were added to a solution of $C_6H_5SnCl_3$ (3 g, 10 mmol) in 75 ml of dichloroethane and the mixture was refluxed for 4 h

The unreacted salt was filtered off and the desired product, which remained in solution, was then precipitated with petroleum ether

Recrystallization from benzene/petroleum ether gave white pure crystals, m p 155—157°C. Found C, 56 24, H, 4 23, Cl, 6 41, $C_{26}H_{23}ClO_4Sn$ calcd C, 56 46, H, 4 19, Cl, 6 33% [^1]H NMR spectra were recorded in a Perkin—Elmer R32 90 MHz spectrometer Temperatures are considered to be accurate to ±1°C

Saturation of the NMR signals was avoided NMR samples were ca 15% v/v solutions in $CDCl_3$ containing tetramethylsilane as internal reference

Results and discussions

As anticipated in the Introduction part, compound II can exist as eight stereoisomers (4 *dl* pairs), which are depicted in Fig 1 It can be easily seen that all four diastereomers are asymmetric, and therefore each methyl group within each isomer is magnetically non equivalent It follows that, when the interconversion among these four diastereomers is kinetically restricted, a mixture of these isomers should show four sets of signals in the methyl region of the NMR spectrum (in an achiral medium), each set consisting of two singlets of equal intensity, giving a total of eight methyl signals

The effect of the various rearrangement modes on the stereoisomers of II can be readily envisaged through the topological analysis given in Fig 2 Since previous results in these octahedral bis-chelate complexes [1—3] have indicated that the rearrangement processes are always accompanied by reversal of the helicity of the structure, our analysis is restricted to those modes which give rise to a helicity inversion, i e modes M_3, M_4 and M_5 [1]

Inspection of Fig 2 reveals that mode M_4 is able to interconvert four diastereomers at a time and even when all these interconversions are rapid on the time scale of observation two enantiomers [A, $\overline{B}$, $\overline{C}$, D], and [$\overline{A}$, B, C, $\overline{D}$] are still present, and cannot be averaged with each other by this mode

This is another manifestation of residual isomerism, a phenomenon already encountered with poly-aryl derivatives [4,5] In order to interconvert these residual enantiomers a pathway other than mode M_4 must be traversed this could be either mode M_5 or mode M_3, as can be easily inferred from Fig 2 Note that mode M_5 alone enantiomerizes B and $\overline{B}$, as well C and $\overline{C}$, but diasteromerizes A and $\overline{D}$ (as well $\overline{A}$ and D), leaving two residual achiral isomers ($B\overline{B}$ and $C\overline{C}$) and one *dl* pair ($A\overline{D}$ and $\overline{A}D$) A similar situation occurs with mode M_3 which give rise to two structures ($A\overline{A}$ and $D\overline{D}$) plus one *dl* pair ($B\overline{C}$ and $\overline{B}C$) A combination of modes M_3 and M_5 will yield two achiral diastereomers, i e. [A, $\overline{D}$, $\overline{A}$, D] and [B, $\overline{C}$, $\overline{B}$, C] Table 1 lists the environments of the methyl groups of the four diastereomers of II, which are exchanged by each of these modes Stereoisomerizations by mode M_4 will cause a coalescence of the eight methyl signals to two singlets of equal intensity, whereas either mode M_3 or M_5 will result in pairwise coalescence of the eight signals, giving rise to four singlets whose intensity is governed by the relative population of the resulting diastereomers A combination of modes M_3 plus M_5 will collapse the eight signals to two singlets of different intensity provided there is a difference in population of the two resulting diastereomers

Stereoisomerizations by mode M_4 followed by M_5 or by M_3, will coalesce all the methyl signals to a single peak Following this analysis, we can now discuss the experimental variable temperature ^1H NMR spectra of II When a $CDCl_3$ solution of II is cooled, at least six signals are present in the methyl region of the spectrum at $-25°C$ (Fig 3) Further cooling of the solution does not reveal additional signals Thus at this temperature the interconversion among the various possible stereoisomers is kinetically restricted on the NMR time scale
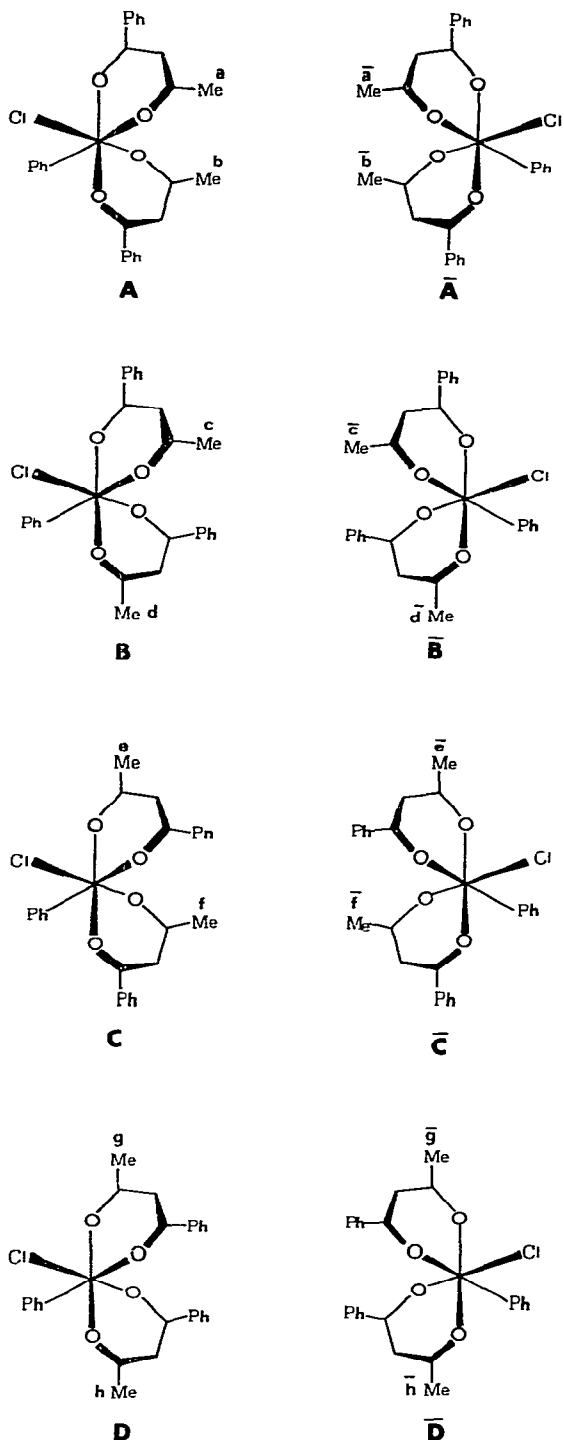
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Fig 1. The eight stereoisomers of II Capital letters indicate diastereomers, while lower case letters desig nate diastereotopic methyl signals Barred letters denote enantiomeric relationships
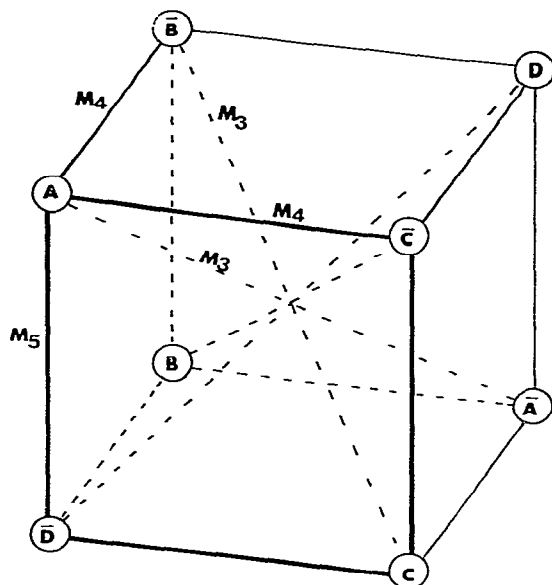
Fig 2 Topological representation of the effect of the various rearrangement modes in the eight stereoisomers of II See Fig 1 for identification of isomers

Unfortunately because of accidental isochronism it was not possible to observe all the eight expected methyl signals, but the results clearly indicate that more than one stereoisomer contributes to the NMR spectrum at this temperature. On increasing the sample temperature, the six signals coalesce gradually

TABLE 1

EFFECT OF STEREOISOMERIZATION PROCESSES ON THE ENVIRONMENTS OF THE METHYL GROUPS IN II [a]

Mode	Resulting isomerizations [b]	Resulting exchanges [b]
M_3	[A $\overline{A}$]	($\overline{ab}$) ($\overline{ba}$)
	[B $\overline{C}$]	($\overline{cf}$) ($\overline{de}$)
	[C $\overline{B}$]	($\overline{ed}$) ($\overline{fc}$)
	[D $\overline{D}$]	($\overline{gh}$) ($\overline{hg}$)
M_4	[A, $\overline{B}$ $\overline{C}$, D]	($\overline{adfg}$) ($\overline{bceh}$)
	[$\overline{A}$ B, C $\overline{D}$]	($\overline{adfg}$) ($\overline{bceh}$)
M_5	[A, $\overline{D}$]	($\overline{ah}$) ($\overline{bg}$)
	[B, $\overline{B}$]	($\overline{cd}$) ($\overline{dc}$)
	[C, $\overline{C}$]	($\overline{ef}$) ($\overline{fe}$)
	[D, $\overline{A}$]	($\overline{gb}$) ($\overline{ha}$)
$M_3 + M_5$	[A $\overline{D}$, $\overline{A}$, D]	($\overline{abgh}$) ($\overline{abgh}$)
	[B $\overline{B}$, C $\overline{C}$]	($\overline{cdef}$) ($\overline{cdef}$)
$M_4 + M_3$	[A $\overline{B}$ $\overline{C}$ D $\overline{A}$ B, C $\overline{D}$]	($\overline{abcdefgh}$) ($\overline{abcdefgh}$)
$M_4 + M_5$	[A $\overline{B}$, $\overline{C}$, D, $\overline{A}$, B C, $\overline{D}$]	($\overline{abcdefgh}$) ($\overline{abcdefgh}$)

[a] See Fig 1 for identification of isomers and methyl environments [b] Capital letters in brackets represent isomers which are interconverted by the mode in question, lower case letters in parentheses designate methyl groups whose environments are averaged by the mode indicated
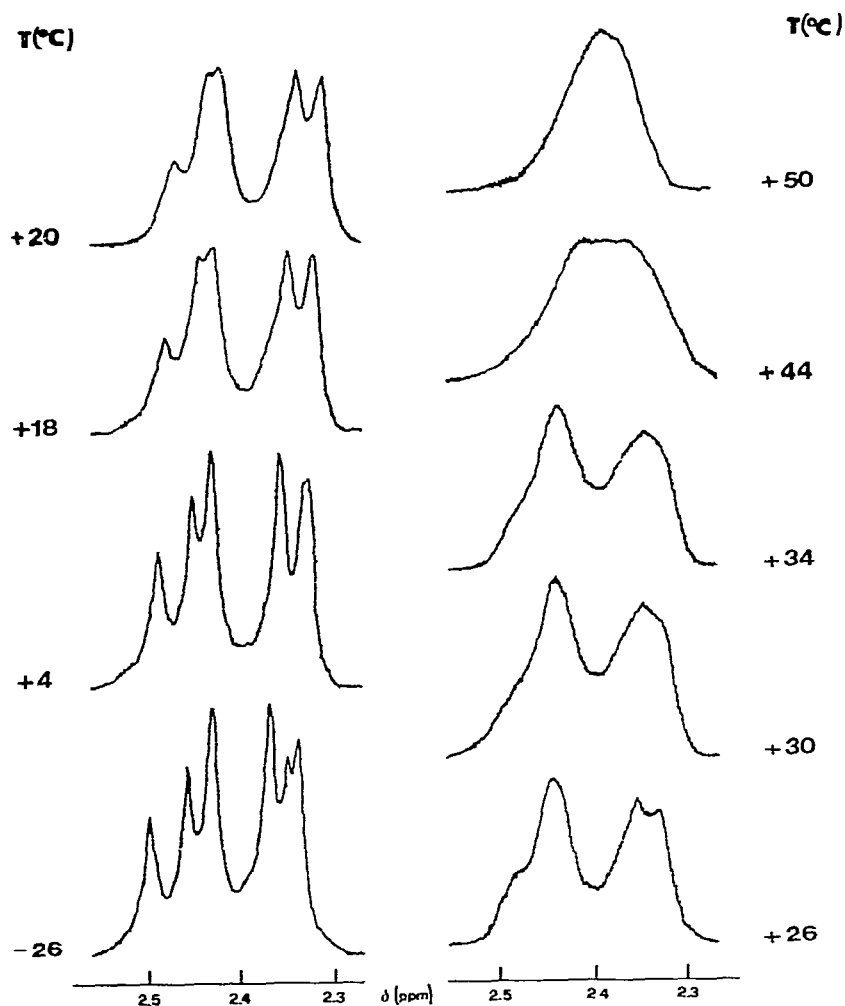
T(°C)   T(°C)

+20

+18

+4

−26

                                              +50

                                              +44

                                              +34

                                              +30

                                              +26

2.5   2.4   2.3   δ (ppm)   2.5   2.4   2.3

Fig 3 Temperature-dependent 90 MHz ^{1}H NMR spectra (methyl region) of II in CDCl₃ solution and tetramethylsilane as internal reference

into two singlets of equal intensity, which in turn coalesce to a single peak at 44° C

We come now to the energetics of the process and to the identification of the associated modes responsible for the coalescence behaviour Unfortunately, complete line-shape analysis of the variable temperature spectra was precluded because all the expected signals are not observed and because of the difficulties in constructing the exchange matrix for use in the Saunders [6] multi-exchange computer program For appropriate use of this matrix it is necessary to know the exact population ratio of the four diastereomers and the ratio of the rates of the eight diastereoisomerization processes (i e , A → $\overline{B}$, B → $\overline{D}$, C → $\overline{A}$, D → $\overline{C}$, plus the reverse processes), which have to be varied as necessary in order to obtain a reasonable fit to the experimental spectra. In spite of these difficulties a semi-quantitative approach of the problem is still of significance for our purposes

First of all, the six methyl signals are seen to coalesce into two singlets of equal intensity and this rules out all but mode M_4 (see Table 1) Therefore once again mode M_4 is found to be the threshold rearrangement pathway in these bis-chelate complexes [1—3]

A semiquantitative estimate of the energetics associated with the coalescence processes occurring through mode M_4 calculated by means of the Gutowsky— Holm approximation [7] in conjunction with the Eyring equation, reveals that the activation energies of such diastereoisomerization processes are in the range of 15.6—16.6 kcal/mol. (It should be noted that strictly speaking the Gutowsky—Holm approximation [7] is not applicable to such coalescence phenomena. However, it is well recognized that the energetics associated with any coalescence process depend primarily upon the coalescence temperature and are very little affected by the rate constants derived for the process in question, as can easily be verified by simple calculations)

This value is very close to that found for the racemization process of phenylchlorobis(2,4-pentanedionato)tin ($\Delta G_{25}^{\neq}$ 16 6 kcal/mol) [8], indicating, as found previously [1], that the nature of the β-diketone does not greatly affect the energy barrier for the relevant stereoisomerization in these bis-chelate complexes and that our computational procedure gives significant results

The ^{1}H NMR spectrum of II at 34°C (Fig 3) clearly shows that the methyl groups still residue in a diastereotopic environments, even though diastereoisomerization processes at that temperature are fast on the NMR time scale This is the first evidence in such complexes, of the manifestation of residual diastereotopism of the nuclei of the ring, a phenomenon widely encountered in polyaryl^1 derivatives [4,5]

As mentioned before, in order to exchange the sites of the residually diastereotopic β-diketonato methyl groups, a pathway different from mode M_4 is necessary and our analysis has shown that it could be either mode M_5 or M_3 (see Table 1) As shown in Fig 3 further increasing of the sample temperature causes the two methyl singlets to coalesce to a single peak at 44°C with an associated energy [7] of $\Delta G_{44}^{\neq}$ 16 7 kcal/mol, and so the energetics associated with the different rearrangement modes (i e mode M_4 and M_5 or M_3) in such bis-chelate complexes are very similar

This finding, which is greatly different from what was found with di- and poly-aryl derivatives, where the difference in energy between different rearrangement modes is considerable and permits the isolation of residual isomers [4,5], seems not to be uncommon in chelate complexes where the interconversions among the various stereoisomers occur through twist mechanism without bond rupture In fact, in tris(α-isopropenyl- and α-isopropyl-tropolonato)-aluminum, -cobalt and -gallium the free energies of activations associated with the threshold mechanism (i e , the trigonal twist) and the other pathways capable of interconverting the residual isomers or residual diastereotopic signals are all very close to each other in value [9,10], showing the differences in this respect between these systems and the stereochemically correspondent [11] triarylboranes It follows that even though bis-chelates and diaryl derivatives, as well as tris-chelate and triaryl boranes, are stereochemically correspondent [1,11] there is little possibility of isolating or observing residual isomers in these complexes, which is in contrast to the situation found with polyaryl derivatives [4].

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