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Configurational Rearrangements in *cis*-$M(AA)_2X_2$, *cis*-$M(AA)_2XY$, and *cis*-$M(AB)_2X_2$ Complexes
3. The *cis*-$M(AA)_2X_2$ System – Diastereotopic Probe on the Terminal AA Groups [1, 2]

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The series of complexes $Ti(dibm)_2X_2$ *[X = F, Cl, or Br; dibm = anion of diisobutyrylmethane],* $M(dibm)_2Cl_2$ *[M = Sn or Ge], and* $Ti(dpm)_2X_2$ *[X = F, Cl, or Br; dpm = anion of dipivaloylmethane] have been prepared and investigated by variable temperature nuclear magnetic resonance (NMR) spectroscopy. Except for* $Ti(dpm)_2F_2$ *and* $Ti(dpm)_2Cl_2$*, the above complexes have not been reported previously. NMR spectra indicate that these complexes possess the* cis-*diastereomeric configuration. Diastereotopic isopropyl methyl probes have been incorporated into the dibm ligand to follow the steric course of the configurational rearrangements taking place in these* C_2*-type complexes. The NMR spectra have been analyzed in terms of the permutational, and topological and mechanistic analyses reported earlier. It is shown that the rearrangements can be rationalized in terms of the* A_5 *averaging set, and it is argued that the likely sole reaction pathway is a twist process about the two opposite* $C_3(i')$ *and* $C_3(i''')$ *axes of the octahedral skeleton. Approximate rate constants for the configurational changes are reported; ligand labilization follows the order acac < dibm < dpm for the* $Ti(dik)_2Cl_2$ *complexes, and Cl < Br ~ F for the* $Ti(dibm)_2X_2$ *systems.*

1. Introduction

The ability to detect enantiomerization processes in non-rigid $M(AA)_3$ [3], $M(AB)_3$ [4–8], and $M(AA)_2(BB)$ [3, 9] chelate complexes has enabled significant progress in the elucidation of the mechanism(s) of rearrangement. Despite such progress, however, operation of a particular mechanism (trigonal twist) has only been demonstrated in a few cases: $M(\alpha\text{-}C_3H_5T)_3$ and $M(\alpha\text{-}C_3H_7T)_3$ where T is the tropolonate anion and M = Al(III), Co(III) [5], and Ga(III) [8], $[Fe(Me, Bz\text{-}dtc)_3]BF_4$ [10, 11], $Fe(Me, Bz\text{-}dtc)_3$ [11, 12], and $Ru(Me, Bz\text{-}dtc)_3$ [13] [dtc = dithiocarbamate anion]. Less definite but analogous results have been obtained for a series of $M(R,R'\text{-}dtc)_3$ complexes of V(III), Mn(III), Ga(III), In(III) and Cr(III) [14, 15].

Basically two techniques have been employed in the assignment of this particular mechanism: (1) complex coalescence patterns were computer-simulated for a variety of mechanisms, and visual comparison with experimental spectra suggested the most probable rearrangement pathway [5, 8], and (2) coalescence patterns of well separated resonances were observed and the rearrangment mechanism was determined directly from the observed permutation of nuclei [3, 10, 11, 13, 16–18].

While intensive efforts have focussed on tris chelate complexes, the important class of bis chelates containing two monodentate ligands appears to have been somewhat ignored [19, 20]. The more studied compounds in this class are the dihalobis(β-diketonato)-metal(IV) complexes [M = Ti, Zr, Hf, Ge, and Sn] [21–29], the corresponding dialkyoxy [30–32] derivatives, and the organometallic analogues RR′M-(β-diketonato) [33–35] where M is Si, Ge, and Sn. In spite of the significant synthetic and stereochemical studies reported on these chelates, there is a paucity of kinetic data surrounding intramolecular rearrangements occurring in the *cis*-diastereomers. Moreover, there is a scarcity of detailed knowledge as to the actual configurational changes taking place during the rearrangement process. An important question often raised in these types of studies deals with whether or not the rearrangement co-involves reversal of the helicity of the optically active *cis*-X_2 species. In this regard, Finocchiaro [36] and his co-workers [37] have recently suggested that in the octahedral complexes $Sn(dik)_2Cl_2$ [dik = acac, dpm, and bzac, anions of acetylacetone, dipivaloylmethane, and benzoylacetone, respectively] stereoisomerizations are accompanied by reversal of the helicity. Unfortunately, for these complexes (note no diastereotopic probes) the NMR experiment remains equivocal in this respect; indeed, no Δ–Λ interconversion is necessary to explain equilibration of terminal AA groups.

In the past several years, we have addressed ourselves to a systematic study of the bis chelate complexes. In particular, we have undertaken detailed theoretical analysis of the permutation of nuclei [1] during the NMR experiment, and of the topological and mechanistic aspects [2] of the intramolecular configurational changes occurring in the class of *cis*-$M(AA)_2X_2$, *cis*-$M(AA)_2XY$, and *cis*-$M(AB)_2X_2$ complexes. The present work reports our studies on the *cis*-$M(AA)_2X_2$ system [AA = dpm, and dibm = the anion of diisobutyrylmethane], in which a diastereotopic isopropyl group was incorporated into the terminal A group of the AA ligand (dibm) to obtain information about the steric course of the configurational changes. The resulting coalescence patterns have been related to the permutational analysis reported earlier [1] and a probable averaging set(s) (or rearrangement mode) is suggested.

Experimental

Reagents and Solvents

The following reagent grade chemicals were procured from commercial sources and were used without further purification: titanium(IV) fluoride and germanium(IV) chloride (Research Organic/Inorganic), titanium(IV) chloride, anhydrous tin(IV) chloride, and acetylacetone (Fisher), titanium(IV) bromide (Alpha Inorganics), diisobutyrylmethane and dipivaloylmethane (Eastman). Organic solvents (dichloromethane, hexane, and 1,1,2,2-tetrachloroethane) used in the syntheses, in the purification of compounds, and in the preparation of NMR samples were of reagent grade quality; these were dried by refluxing over calcium hydride chips for at least 12 hr and distilled therefrom immediately before use.

General Techniques and Syntheses

As most of the complexes reported here are subject to some degree of hydrolytic decomposition [23, 24], all syntheses and subsequent handling of the compounds were conducted under anhydrous conditions in a dry nitrogen atmosphere. Reactions and recrystallizations were carried out under nitrogen in glass-stoppered Erlenmeyer flasks equipped with a side-arm nitrogen inlet. Filtrations were performed using a modified fritted glass funnel similar to that described by Pinnavaia and Fay [38]. Melting points were measured with a Gallenkamp Melting Point Apparatus Model No. MF-370 in capillaries sealed with modeling clay, and are uncorrected. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn., USA. The complexes reported here were prepared in dichloromethane solvent by standard literature methods [23, 24] used in analogous complexes, and were purified by recrystallization (twice) from dichloromethane–hexane solutions. The pertinent data are reported in Table 1.

Nuclear Magnetic Resonance Spectra

Samples were prepared by weighing the compound directly into a 9-in precision nmr tube and then enough solvent was added to bring it to the desired concentration. The tube was flame-sealed *in vacuo* after several freeze–pump–thaw cycles to degass the solution.

Room-temperature and variable-temperature proton NMR spectra were recorded with a Varian A-60A spectrometer operating at 60.00 MHz and equipped with a variable temperature probe accessory, Model V-4343, and a temperature controller acces-

TABLE 1. Summary of Data from the Syntheses of Complexes.

Complex	Reflux Time, hr	% Yield	Mp, °C	Analysis							
				Calcd				Found			
				C	H	Ti	Cl	C	H	Ti	Cl
$Ti(dibm)_2F_2$	5.5	60	73–75d[a]	54.55	7.63	–	–	54.94	7.60	–	–
$Ti(dibm)_2Cl_2$	–	84	135–136d	50.37	7.05	11.16	16.52	50.73	7.01	11.41	16.75
$Ti(dibm)_2Br_2$	–	80	122–124d	41.73	5.84	–	–	41.85	5.81	–	–
$Sn(dibm)_2Cl_2$	3.5	80	129–131	43.24	6.05	–	–	43.39	5.95	–	–
$Ge(dibm)_2Cl_2$	12	65	116–118	47.63	6.66	–	–	47.93	6.57	–	–
$Ti(dpm)_2F_2$	6	84	139–141[b]	58.40	8.47	–	–	59.48[c]	7.90[c]	–	–
$Ti(dpm)_2Cl_2$	–	90	124–125d	54.44	7.89	9.87	14.61	54.60	7.82	9.62	14.88
$Ti(dpm)_2Br_2$	–	95	133–135d	46.02	6.67	–	–	46.26	6.59	–	–

[a] d = decomposition. [b] Lit., [27], 144–146 °C. [c] Product further purified by sublimation at *ca.* 95 °C and *ca.* 0.01 Torr; its purity was checked by proton nmr and infrared spectroscopy.

sory, Model V-6040. The spectrometer sweep widths (50, 100, and 250 Hz) were calibrated at room temperature using the standard audio frequency sideband technique. Temperatures below 37 °C were measured from the chemical shift differences between the CH_3 and OH proton resonances of CH_3OH; above room temperature, the chemical shifts of ethylene glycol were used. Temperatures were calculated using the appropriate Van Geet equations [39].

Variable-temperature, carbon-13 nmr spectra were recorded in dichloromethane on a Varian XL-100-15 spectrometer in the Pulse Fourier Mode with ^1H decoupling. Acetone-d_6 was employed as the internal ^2H lock. Chemical shifts are reported relative to tetramethylsilane (TMS) after calculating the shift from the internal $^{13}CH_2Cl_2$ which has a chemical shift of 54.0 ppm downfield from TMS [40].

Results

Proton nmr spectra of the isopropyl methyl groups of the $Ti(dibm)_2Cl_2$ complex at selected temperatures are reproduced in Figure 1. At room temperature the spectrum reveals a single spin-coupled doublet. Lowering the temperature causes this doublet to broaden until, at *ca.* – 23 °C, a broad, featureless resonance is observed, which on further cooling to *ca.* – 60 °C resharpens to form three doublets in a 2:1:1 intensity ratio. The isopropyl methine resonance appears as a septet at room temperature and on lowering the temperature, the fine structure of the multiplet is lost and a broad, featureless resonance is obtained. A single diketonate

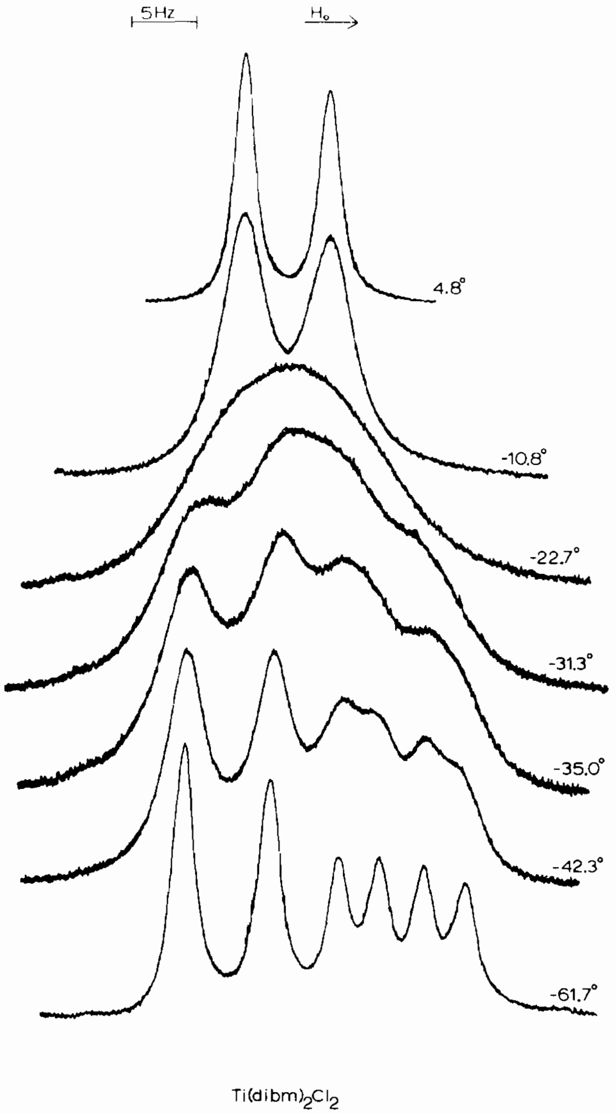

Fig. 1. Temperature dependence of the isopropyl methyl resonances in the proton nmr spectrum of $Ti(dibm)_2Cl_2$ in dichloromethane solution, 0.300 *M*.

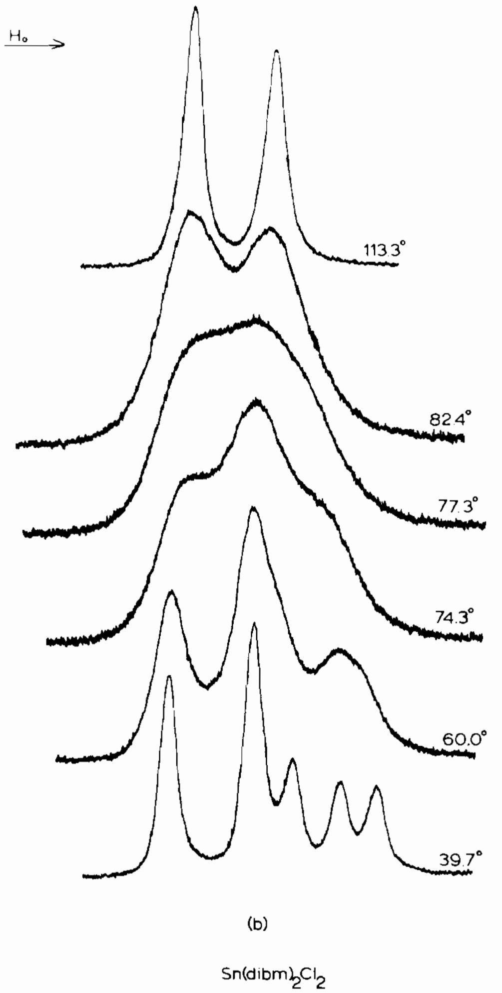

Fig. 2. Temperature dependence of the isopropyl methyl resonances in the proton nmr spectrum of $Sn(dibm)_2Cl_2$ in 1,1,2,2-tetrachloroethane solutions, 0.300 *M*.

–CH= signal is observed throughout the temperature range (see *e.g.* Figure 1) investigated. Analogous spectra were obtained for the Ti(dibm)$_2$F$_2$ and Ti(dibm)$_2$Br$_2$ complexes, with small changes in chemical shift separations at the lower temperatures.

The room-temperature spectrum of a 1,1,2,2-tetrachloroethane solution of Sn(dibm)$_2$Cl$_2$ reveals five resonances in the isopropyl methyl region (Figure 2) which may be resolved into three partially overlapping doublets with intensity ratios of 2:1:1. Raising the temperature causes these resonances to coalesce into a broad, featureless resonance signal which sharpens to a single time-averaged doublet above *ca.* 85 °C. No coupling between the tin nucleus and the isopropyl methyl protons was observed. The isopropyl methine protons appear as a septet at room temperature. As the temperature is raised, some fine structure is lost and then regained to reveal a septet at *ca.* 110 °C. The –CH= resonance is masked by the solvent absorption but appears as a single resonance in a dichloromethane solution. Solutions in dichloromethane were investigated down to – 60 °C; no further splitting of the isopropyl methyl resonance pattern was observed.

The Ge(dibm)$_2$Cl$_2$ complex possesses a room-temperature spectrum analogous to that of the tin(IV) complex with the exception of a shoulder on the lower field side of the most intense component of the isopropyl methyl resonance pattern. No change in the isopropyl methyl resonance pattern occurs on warming a 1,1,2,2-tetrachloroethane solution to *ca.* 100 °C. For example, $W_{1/2}$ for the lowest field component is 1.60 Hz at 39 °C and 1.68 Hz at 100 °C. The methine and –CH= proton resonances show the same temperature dependence as those noted above for the tin complex.

The carbon-13 chemical shifts for Ti(dibm)$_2$Cl$_2$ in dichloromethane solution and –80 °C are collected in Table II.

TABLE II. Carbon-13 Chemical Shifts[a] for Ti(dibm)$_2$Cl$_2$.

Carbon[b]	Chemical Shift
C, C″	–165.7, –161.6
C′	–105.6
$-\mathit{CH}(CH_3)_2$	–38.8, –37.7
$-CH(\mathit{CH}_3)_2$	–20.3, –19.6

[a] Dichloromethane solution; –80 °C; ppm (± 0.1) downfield from TMS. [b] $(CH_3)_2CH-COC'HC''O-CH(CH_3)_2$.

Discussion

Stereochemistry

In the case of diisobutyrylmethanate complexes, the isopropyl methyl proton NMR spectrum of the *cis* diastereomer should give rise to four spin-coupled doublets. This results from the gross terminal group nonequivalence together with the diastereotopic relationship of the methyl groups within each isopropyl moiety. Each nonequivalent isopropyl methyl group will appear as a doublet owing to the coupling with the geminal methine proton $-C\mathit{H}(CH_3)_2$. The *trans* diasteromer would give rise to a single spin-coupled doublet.

The revelation of more than a single doublet in the NMR spectra of the M(dibm)$_2$X$_2$ complexes indicates that these exist in solution in the *cis* diasteromeric configuration. Also, the resonance pattern for the Ge(dibm)$_2$Cl$_2$ complex suggests that no exchange processes occur at temperatures less than *ca.* 120 °C, not unexpected since the t-butyl methyl resonances in Ge(dpm)$_2$Cl$_2$ coalesce at *ca.* 200 °C [29]. NMR spectra further revealed no evidence for a *cis–trans* equilibrium.

As the proton NMR spectra of the M(dibm)$_2$X$_2$ complexes failed to reveal the expected four spin-coupled doublets for the isopropyl methyl groups, carbon-13 NMR spectra were recorded at –80 °C for Ti(dibm)$_2$Cl$_2$ (see Table II) and at room temperature for the Sn(dibm)$_2$Cl$_2$ complex in dichloromethane solutions. It was hoped that the expected four isopropyl methyl carbon resonances could be detected. Unfortunately the proton-decoupled carbon-13 spectra for both of these complexes show two isopropyl methyl carbon resonances in a 3:1 intensity ratio [41], in the slow exchange regions. For the titanium(IV) complex (Table II), two carbonyl carbon and two $-\mathit{CH}(CH_3)_2$ carbon resonances are observed, thus confirming the *cis* geometry. Apparently, the less dominant diamagnetic term for chemical shifts of carbon nuclei compared to proton chemical shifts, and the greater distance of the carbon nuclei from the chlorine atoms combine to generate less resolution in the carbon-13 spectra than in the proton spectra.

Observation of diastereotopic isopropyl methyl groups is attributed to the dissymmetry centred on the metal ion. However, it is possible – *though not probable* – that, owing to hindered rotation about the –C–CH(CH$_3$)$_2$ bond, the isopropyl methyl groups may be locked in, in a conformation which results in nonequivalent methyl groups. Rotation about this bond would then generate equivalent methyl groups. To decide between these sources, the analogous Ti(dpm)$_2$X$_2$ complexes were investigated. Hindered rotation should be more predominant in these dpm complexes as a result of the greater bulk of the t-butyl groups.

The NMR spectra of the Ti(dpm)$_2$X$_2$ [X = F, Cl, or Br] complexes reveal a single t-butyl methyl resonance at room temperature which broadens on cooling, and splits into two equally-intense resonances by –60 °C. This simply results from exchange of non-

TABLE III. Approximate Rate Constants[a] for Exchange of Isopropyl Groups in $Ti(dibm)_2X_2$ Complexes.

X	$\delta\nu$ (Hz)	T_c (°C)	k at T_c $Ti(dibm)_2X_2$	k at T_c $Ti(acac)_2X_2$[b]	k at T_c $Ti(dpm)_2Cl_2$[c]	k at –36 °C
F	11.5	–39	26	75	–	36
Cl	13.5	–23	30	18	89	8.7
Br	15.5	–36	34	14	–	34

[a] Sec^{-1}. [b] Calculated from the data of ref. 23. [c] Calculated from the data of ref. 42. [d] For $Ti(dibm)_2X_2$ at –36 °C, T_c when X = Br.

equivalent t-butyl groups within the *cis* diastereomers. This process has been observed and measured in several $Ti(dpm)_2X_2$ [X = Cl, NCO] [42], $Sn(dpm)_2X_2$ [X = F, Cl, Br, or I] [29], and $Ge(dpm)_2X_2$ [X = Cl, Br, or I] [29, 43] complexes. If hindered rotation were a viable process, additional methyl proton resonances should appear. Also, in the proton spectrum of 1,3,5-trimethyl-2-isopropylbenzene, in which rotation of the isopropyl group about the sp^3–sp^2 bond is restricted, no splitting of the isopropyl methyl doublet was observed even at –60 °C [44]. This has been used to argue [3] in favour of the plausible source for the splitting observed in complexes related to $M(dibm)_2X_2$ to be the dissymmetry centred on the metal ion.

Kinetics of Exchange

No complex lineshape analyses of the temperature-dependent NMR spectra of the $M(dibm)_2X_2$ complexes were attempted. Inasmuch as these complexes present a four-site exchange problem, six first-order rate constants are necessary to completely describe the exchange process. In addition, coupling to the methine protons must also be considered, and to make matters worse, the relaxation times T_2 appear to be temperature dependent. It is possible, however, using a method reported earlier [24, 45], to make estimates of approximate rate constants at the temperatures of coalescence of the isopropyl methyl resonances. Such estimates provide useful indications of the relative labilities of analogous $M(dik)_2X_2$ complexes and of the dependence of lability on the nature of the halogen.

It is instructive to classify the four nonequivalent methyl groups (Figure 1 and 2) into two sets: a set of two forming the low field doublet (which may be assigned to the equatorial groups *trans* to the X groups) [33] and a set of two which form the two doublets at higher field. In order to estimate rate constants, the four-site exchange problem has been approximated by a two-site exchange process, the chemical shift between the two sites, $\delta\nu$ (in Hz), being the chemical shift between the centers of gravity of the downfield doublet and the upfield quartet in the low temperature spectra of $Ti(dibm)_2X_2$. Inasmuch as the two sites are equally populated, the first-order rate constant k_{T_c}, at the coalescence temperature T_c, for exchange of isopropyl methyl groups between the two sites is given by $\pi\delta\nu/\sqrt{2}$ [46].

Approximate rate constants obtained by this procedure for the $Ti(dibm)_2X_2$ complexes are listed in Table III, along with values of $\delta\nu$ and T_c. The fifth column of Table III gives rate constants for exchange of methyl groups in $Ti(acac)_2X_2$ complexes [23] at temperatures corresponding to T_c for the related $Ti(dibm)_2X_2$ complex. Column six gives the rate constant for exchange of t-butyl groups in the $Ti(dpm)_2Cl_2$ complex at T_c for the $Ti(dibm)_2Cl_2$ complex. In the last column of Table III are listed the values of k for $Ti(dibm)_2X_2$ extrapolated to a common temperature, –36 °C, T_c for $Ti(dibm)_2Br_2$. These values were calculated assuming that the activation energies for the $Ti(dibm)_2X_2$ complexes are the same as those found for the corresponding acetylacetones [11.6 kcal/mol (X = F); 11.2 kcal/mol (X = Cl)] [23]. Comparison of the fourth and fifth columns indicates that the lability of the $Ti(dibm)_2X_2$ and $Ti(acac)_2X_2$ complexes is quite comparable, at least for X = Cl and Br; $Ti(dibm)_2F_2$ appears to be less labile than the corresponding acetylacetonate, a feature noted previously concerning the $Ti(bzac)_2F_2$ complex [45]. Moreover, comparison of columns four, five and six for X = Cl suggests that the exchange rates increase in the order acac < dibm < dpm. The last column shows lability to increase in the order Cl < Br ~ F. For the acetylacetonates, exchange rates were found to increase in the order Cl < Br < F [23], while for the $Ti(bzac)_2X_2$ complexes the halogen dependence [45] was reported to be similar to that noted above for the $Ti(dibm)_2X_2$ complexes.

Approximate rate constants obtained by the above procedure for the $Sn(dibm)_2Cl_2$ complex are presented in Table IV. A calculation of the exchange rate for the $Sn(acac)_2Cl_2$ and $Sn(dpm)_2Cl_2$ complexes at the T_c for the $Sn(dibm)_2Cl_2$ complex indicates that bidentate ligand labilization increases also in the order acac < dibm < dpm.

Permutational and Mechanistic Considerations

Permutational and mechanistic analyses of allowed rearrangements within the *cis*-$M(AA)_2X_2$ system have been presented earlier [1, 2]. Consulting Table IV of

TABLE IV. Approximate Rate Constants for Exchange in $Sn(dik)_2Cl_2$ Complexes.

Complex	$\delta\nu$ (Hz)	T_c (°C)	k (sec^{-1}) at T_c for $Sn(dibm)_2Cl_2$
$Sn(acac)_2Cl_2$[a]	5.41	82	10
$Sn(dibm)_2Cl_2$	8.5	79	19
$Sn(dpm)_2Cl_2$[b]	8.82	65	54

[a] Calculated from data of ref. 28. [b] Calculated from data of ref. 29.

ref. 1 which lists the expected changes in signal multiplicities for the various averaging sets, it may be noted that no averaging set will predict the collapse of the diastereotopic terminal groups of the AA ligand to a *single* doublet. The minimum number of doublets predicted is two, generated by sets A_2, A_3, A_4, A_5, and A_6. It is quite reasonable to expect the collapse of the low temperature spectra (which already encompasses groups with degenerate shifts) for these $M(dibm)_2X_2$ complexes to a single doublet in the fast exchange region to be the result of an accidental chemical shift degeneracy of the expected two doublets. It is then necessary to distinguish between the five averaging sets: A_2, A_3, A_4, A_5, and A_6.

The following arguments may lead to the elimination of some of these averaging sets. Inasmuch as exchange of nonequivalent methyl and t-butyl groups occur in the $Ti(dik)_2X_2$ and $Sn(dik)_2X_2$ complexes [dik = acac, dpm; X = halogen] [23, 28, 29, 42], it is not unreasonable to suppose that exchange of axially and equatorially nonequivalent isopropyl groups occur in the rearrangement of $M(dibm)_2X_2$ complexes; A_4 may then be eliminated. Also, since diastereotopic splitting was observed in the slow exchange region and is removed upon warming, and since the Pfeiffer effect has been observed for related $Ti(acac)_2X_2$ and $Sn(acac)_2X_2$ complexes [47, 48], reversal of the helicity probably occurs during the rearrangement. On the basis of this evidence, averaging sets A_2 and A_3 may be eliminated as they do not provide a path for optical inversion. *It should be noted*, however, that the $M(dibm)_2X_2$ spectra can be rationalized using averaging set A_2 or A_3 without invoking enantiomerization processes; but attachment of diastereotopic isopropyl probes in other chelate systems has demonstrated that these systems rearrange *via* a process which involves inversion of the molecular configuration [3, 5, 6, 8, 49]. Thus, exclusion of averaging sets A_2 and A_3 is not unreasonable.

This leaves us to distinguish between averaging sets A_5 and A_6. The most obvious difference between these two possible averaging sets is that they predict different ratios of rate of enantiomerization to rate of terminal group exchange. A_6 predicts a ratio of unity; A_5 predicts a ratio of 2:1. Figures 1 and 2 indicate that the diastereotopic splitting observed in the slow exchange region for the $M(dibm)_2X_2$ complexes is removed first, and then complete collapse to a single doublet occurs. This may simply be a result of the smaller diastereotopic splitting (*ca.* 3–6 Hz) *versus* overall group nonequivalence (*ca.* 9–16 Hz) causing the diastereotopic splitting to possess a lower coalescence temperature with the operation of the A_6 averaging set. On the other hand, it may reflect a greater rate of enantiomerization than of terminal group exchange, as A_5 would necessitate. A detailed total lineshape computer simulation could possibly distinguish between these two alternatives; however, owing to the difficulties mentioned earlier, namely the six first-order rate constants and the temperature dependence of T_2's, a detailed kinetic analysis of the problem was not attempted.

Some evidence does exist for support of A_5 as the averaging set responsible for the observed permutation of nuclei in the $M(dibm)_2X_2$ complexes. The averaging set A'_{13} appears to rationalize the rearrangement processes in the $Ti(dibm)_2Cl(OCH_3)$ complex [50]. Using the correlation listed in Table XII of ref. 1 and with the tacit assumption of similar physical mechanisms operating in the rearrangements, A'_{13} correlates with A_5 on going from the *cis*-$M(AA)_2XY$ to the *cis*-$M(AA)_2X_2$ system. A recent study [37] on the rearrangement modes in the tin complexes, $Sn(dik)_2Cl_2$ [dik = acac, dpm, bzac], has identified mode M_4 (permutationally equivalent to A_5 in the present system) as the threshold rearrangement mode which interconverts all three diastereomers in *cis*-$Sn(bzac)_2Cl_2$, and also in the C_2-type complexes. Interestingly enough, M_4 permutationally corresponds also to the lowest energy rearrangement mode in diaryl derivatives of the type Ar_2ZX [37]. Hence, on the basis of the above arguments, set A_5 is favoured over the A_6 averaging set.

Conclusions

Considering the A'_{13}–A_5 relationship (Table XII of ref. 1) and referring to Table I of ref. 2 it is suggested that configurational rearrangements in the species discussed in this work occur – though not unequivocally – by the following pathways (when taken as sole reaction paths): (1) twist processes about either or both of the corresponding $C_3(i')$ and $C_3(i''')$; and (2) bond rupture processes *via* square pyramidal axial intermediates by breaking any one of the four M–O bonds. The latter pathway is not considered too likely owing to the discriminatory manner in which the axial dangling ligand end would have to attack one particular basal position of the square pyramidal intermediate [51].

In order to obtain a more direct measure of the relative rates of enantiomerization and terminal group exchange in these C_2-type *cis* complexes, the isopropyl probe was positioned in the 3-position of the acetylacetonate ring and is the subject of another report [52].

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