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Configurational Rearrangements in *cis*-$M(AA)_2X_2$, *cis*-$M(AA)_2XY$ and *cis*-$M(AB)_2X_2$ Complexes.
9. The *cis*-$M(AB)_2X_2$ System – Diastereotopic Probe on AB

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The complexes $Ti(tibm)_2Cl_2$, $Sn(tibm)_2Cl_2$ and $Ti(tdh)_2Cl_2$ have been prepared and their variable-temperature nuclear magnetic resonance spectra characterized in dichloromethane and 1,1,2,2-tetrachloroethane solutions. These are complexes of the $M(AB)_2X_2$-type in which AB represents an unsymmetrical 1,3-ketoenolate bidentate ligand and contains a diastereotopic group on the tibm ligand (anion of 1,1,1-trifluoro-5-methyl-2,4-hexanedione). It is shown that these complexes, which can exist in five diastereomeric forms (two have trans-X_2 *groups and three have* cis-X_2 *groups) adopt the three* cis-X_2 *diastereomeric configurations. Terminal group exchange in the AB chelate ligand occurs in parallel with inversion of the molecular configuration. Such rearrangements can be described by the A_6'' averaging set which scrambles the terminal groups and the –CH = proton amongst all the possible nonequivalent sites of the* cis-X_2 *diastereomers, and in addition leads to Λ–Δ interconversion. It is suggested that the rearrangements proceed* via *twist processes.*

Introduction

Complexes of the type $M(AB)_2X_2$, where AB and X represent an unsymmetrical bidentate and monodentate ligands, respectively, may exist in five possible diastereomeric forms; these are illustrated in Fig. 1. Diastereomers possessing *cis*-X_2 groups are enantiomeric and the expected nuclear magnetic resonance (NMR) signal multiplicities are indicated with each diastereomer.

The most detailed study of $M(AB)_2X_2$-type complexes has been reported for the $Ti(bzac)_2X_2$ complexes (bzac = anion of benzoylacetone, X = F, Cl, Br) [1]. These complexes have been shown to possess the three diastereomeric forms having *cis*-X_2 groups. A rapid rearrangement process was found to interconvert these three diastereomers [1]. Similar observations have also been reported for $Sn(bzac)_2Cl_2$ [2, 3]. The $Ge(dhd)_2Cl_2$ (dhd = 2,2-dimethyl-3,5-hexanedionate anion) complex exists in all five isomeric geometries [4]; no information on the possible exchange processes has been reported.

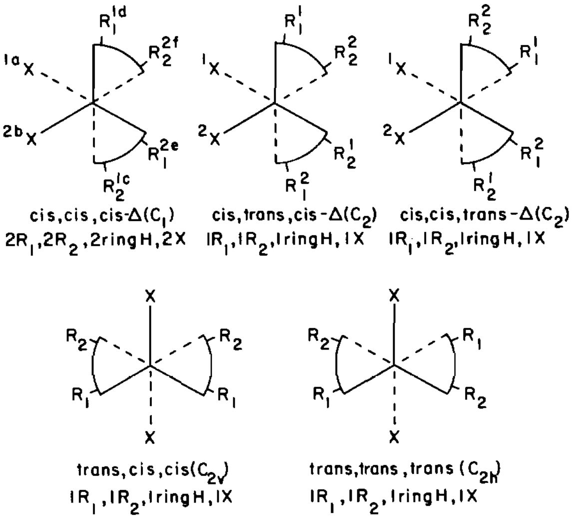

Fig. 1. Possible isomers for an $M(AB)_2X_2$ complex. Numerical superscripts label nonequivalent groups; letter superscripts label the different environments. Numerical subscripts label the different types of terminal groups on the AB ligand. The stereochemistry is described by three *cis* or *trans* prefixes which denote the relative orientation of the X, R_1, and R_2 groups in that order.

To the extent that $M(AB)_2X_2$ complexes investigated thus far adopt the *cis*-X_2 geometry, it appears very likely that $Ti(dik)_2X_2$ complexes (dik = unsymmetrical β-diketonate; X = alkoxy or phenoxy groups) will also adopt the *cis*-X_2 geometries. Owing to the enantiomeric nature of the *cis*-X_2 diastereomers, placement of a diastereotopic probe on the chelate ring presents an opportunity to explore enantiomerization processes during the interconversions of these *cis*-X_2 isomers. The present work presents our results on this expectation as part of our systematic studies on configurational rearrangement phenomena [5].

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Experimental

All organic solvents used in the preparation and purification of the compounds were reagent grade and were dried by refluxing over CaH_2 chips for at least 12 h and distilled therefrom immediately prior to use. The β-diketones were obtained from commercial suppliers (Eastman, Aldrich, K & K Laboratories) and were employed without further purification. Titanium(IV) and tin(IV) halides were also used as received. Chemicals and reactions were handled under a dry nitrogen atmosphere in a glove bag. Analyses were carried out by Galbraith Laboratories of Knoxville, Tenn., USA. Melting points are not corrected.

Dichlorobis(1,1,1-trifluoro-5-methyl-2,4-hexanedionato)titanium(IV), Ti(tibm)₂Cl₂

To a solution of 5.40 g (29.7 mmol) of 1,1,1-trifluoro-5-methyl-2,4-hexanedione in 50 ml of benzene was added, dropwise, 1.50 ml (2.58 g, 13.7 mmol) of $TiCl_4$. A red-orange solution immediately formed with concomitant evolution of hydrogen chloride. The solution was N_2-purged for ~30 min, followed by evaporation of some benzene. Addition of hexane resulted in the formation of a yellow-green solid, which was collected, washed with hexane, and dried *in vacuo;* yield 6.50 g (78%). Two recrystallizations from CH_2Cl_2–hexane solutions yielded a bright yellow-green solid; mp 90–92 °C (dec.). *Anal.*, Calcd. for $TiC_{14}H_{16}O_4F_6Cl_2$: C, 34.95; H, 3.35; Ti, 9.96; F, 23.70; Cl, 14.56%. Found: C, 34.99; H, 3.59; Ti, 10.03; F, 23.54; Cl, 14.56%.

Dichlorobis(1,1,1-trifluoro-5-methyl-2,4-hexanedionato)tin(IV), Sn(tibm)₂Cl₂

A mixture of 1.10 ml (2.46 g, 9.42 mmol) of anhydrous $SnCl_4$ and 5.30 g (29.1 mmol) of 1,1,1-trifluoro-5-methyl-2,4-hexanedione in 50 ml of CH_2Cl_2 was refluxed for 3.5 h. The resulting pale yellow solution was filtered and the solvent was removed with a nitrogen sweep to yield an off-white solid, which was slurried in hexane at –78 °C, filtered, and dried *in vacuo*; yield 4.2 g (80%). Recrystallizations from CH_2Cl_2–hexane solutions gave a bright white solid; mp 72–74 °C. The purity of this complex was verified by infrared and NMR spectroscopy.

Dichlorobis(1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedionato)titanium(IV), Ti(tdh)₂Cl₂

To a solution of 5.00 g (25.5 mmol) of 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione in 50 ml CH_2Cl_2 was added, dropwise, 1.30 ml (2.25 g, 11.3 mmol) of $TiCl_4$. An orange solution formed and hydrogen chloride was evolved. The solution was N_2-purged for ~30 min and the solution subsequently concentrated to ~10 ml. Addition of excess hexane produced an orange solid. Two recrystallizations from CH_2Cl_2–hexane gave a bright orange solid; mp 119–121 °C (dec.). The purity of this product was verified also by infrared and NMR spectroscopy.

The ^1H NMR spectral techniques used to record the variable-temperature NMR spectra have been described in detail earlier [6].

Results and Discussion

Figure 2 illustrates the low temperature dependence of the isopropyl methyl resonance of the $Ti(tibm)_2Cl_2$ complex in dichloromethane solution. At ambient temperature, a single doublet is observed. Upon cooling the solution, the doublet broadens into a broad, featureless resonance. Further cooling results in the emergence of three doublets in a 1:2:2 intensity ratio by ~ –55 °C. At low temperature the ring proton (–CH=) resonance is broadened ($W_{1/2}$ values are approximately doubled on going from 25 °C to ~ –60 °C) but no splitting is observed. The temperature dependence of the ^{19}F NMR was not investigated.

In order to determine whether the observed exchange of isopropyl methyl groups in the $Ti(tibm)_2Cl_2$ complex is a result of configurational rearrangement of the chelate rings or hindered rotation of the isopropyl moiety, the analogous derivative containing t-butyl groups was examined.

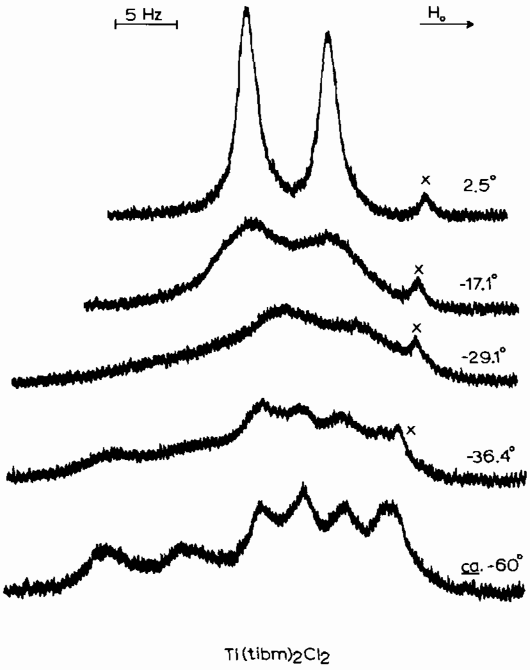

Fig. 2. Temperature dependence of the isopropyl methyl resonance of the $Ti(tibm)_2Cl_2$ complex in dichloromethane solution, 0.300 *M*. The resonance marked x arises from an impurity.

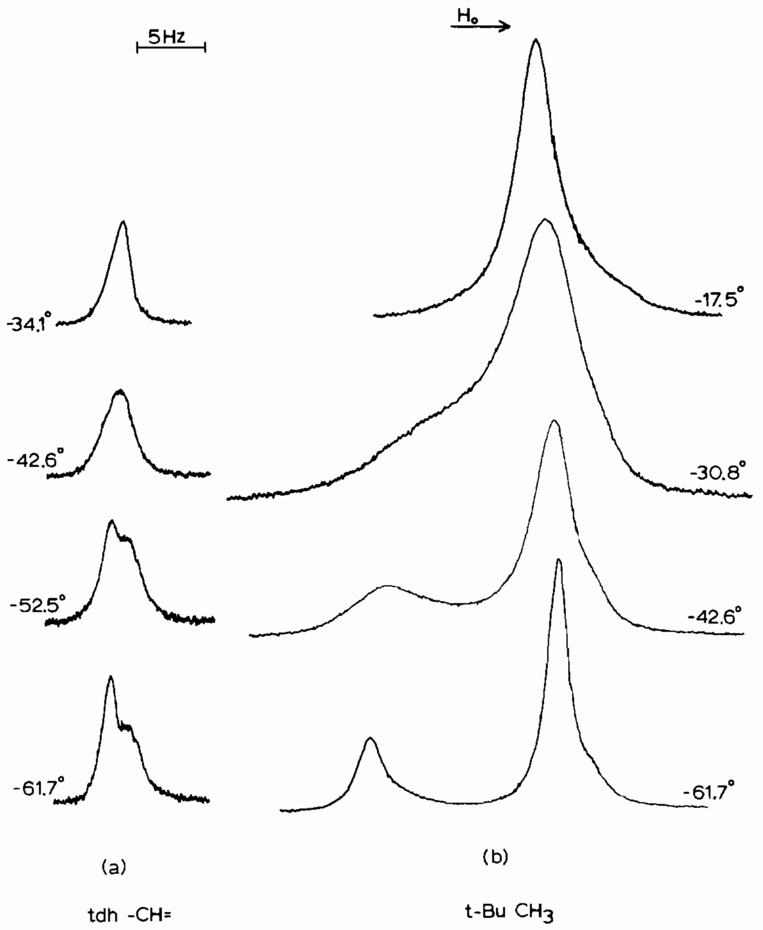

Fig. 3. Temperature dependence of the (a) tdh ring proton (–CH=) and (b) the t-butyl methyl resonance of the Ti(tdh)$_2$Cl$_2$ complex in dichloromethane solution, 0.300 *M*.

Figure 3 shows the temperature dependence of the ring proton (–CH=) and t-butyl methyl resonance of the Ti(tdh)$_2$Cl$_2$ complex. The t-butyl methyl resonance region reveals a similar lineshape behaviour to that of the isopropyl methyl resonance of the Ti(tibm)$_2$Cl$_2$ complex. Considerable broadening of the t-butyl methyl resonance signal occurs upon cooling with the emergence of a resonance at lower field, with relative intensities of 1:3. The ring proton resonance also undergoes exchange broadening and two resonance signals can be observed by ~–50 °C.

These above results are in accord with the Ti(tibm)$_2$Cl$_2$ and Ti(tdh)$_2$Cl$_2$ complexes existing as a mixture of *cis*-Cl$_2$ diastereomers, based on the expected similarity with the Ti(bzac)$_2$X$_2$ (X = halogen) complexes [1]. Although the Ti(tdh)$_2$Cl$_2$ spectra can also be rationalized as a mixture of *trans*-Cl$_2$ isomers, the observed spectra for the corresponding tibm complex necessitates the population of at least one *cis*-Cl$_2$ diastereomeric form, as the two *trans* isomers would result in only two isopropyl methyl doublets. Inasmuch as the related Ti(dik)$_2$Cl$_2$ complexes (dik = acac, acetylacetonate; hfac, hexafluoroacetylacetonate; dibm, diisobutyrylmethanate; dpm, dipivaloylmethanate) adopt the *cis*-Cl$_2$ configuration [7–9], the simplest rationalization for the NMR spectra of Ti(tibm)$_2$Cl$_2$ and Ti(tdh)$_2$Cl$_2$ complexes is that they adopt all three *cis*-X$_2$ diastereomeric configurations. The isopropyl methyl pattern at ~–60 °C for the Ti(tibm)$_2$Cl$_2$ complex thus appears to result from chemical shift differences between non-equivalent isopropyl groups rather than between the methyl groups of a particular isopropyl moiety. Enantiomerization must then either occur rapidly, even at ~–60 °C, or the diastereotopic splitting of the isopropyl methyl groups is too small to be resolved.

The well documented [10] rate-accelerating influence of CF$_3$ groups has led us to investigate a system less labile than Ti(tibm)$_2$Cl$_2$. Figure 4 depicts the temperature dependence of the isopropyl methyl resonance of Sn(tibm)$_2$Cl$_2$ in 1,1,2,2-tetrachloroethane solution. In the fast exchange region (> ~ 80 °C) a single isopropyl methyl doublet is observed, which broadens into a single featureless resonance as the temperature is lowered. From this broad, featureless resonance, fine structure begins to emerge as the

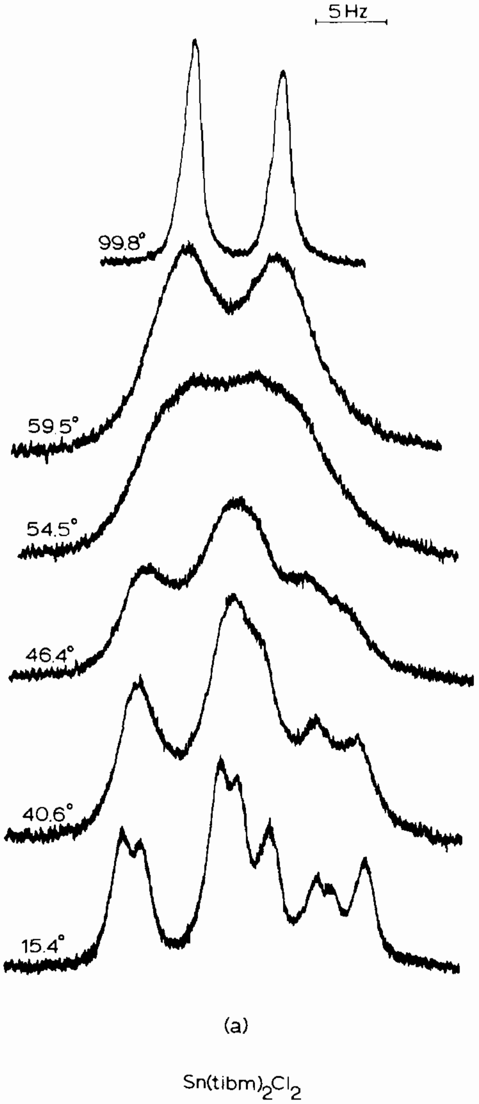

Fig. 4. Temperature dependence of the isopropyl methyl resonances in the ^1H NMR spectrum of $Sn(tibm)_2Cl_2$ in 1,1,2,2-tetrachloroethane solutions, 0.300 *M*.

temperature is lowered further until the complex pattern at 15 °C is observed. No further splitting is observed down to −2.2 °C, at which point viscosity broadening occurs and results in poorer resolution. Solvent interference prevents the reliable identification of the ring proton resonance in tetrachloroethane; a single −CH= resonance signal is found in the room-temperature NMR spectra of dichloromethane and chloroform solutions. The coupling of methyl groups with the isopropyl methine proton is complex; fine structure is evident near the slow- and fast-exchange regions.

The rate enhancement from the presence of CF_3 groups is noticeable on comparing coalescence temperatures for the $Sn(tibm)_2Cl_2$ and $Sn(dibm)_2Cl_2$ [6] complexes. The former possesses a coalescence temperature ~25 °C lower than that for the $Sn(dibm)_2Cl_2$ complex.

The isopropyl methyl resonance pattern observed at 15 °C for $Sn(tibm)_2Cl_2$ may be resolved into five partially overlapping doublets of unequal relative intensities. Assuming that this complex populates only the *cis*-Cl_2 diastereomers, then if terminal group exchange were slow and inversion fast, four doublets are expected. But if terminal group exchange and inversion are both slow processes, eight doublets would be expected. Hence, the observation of five doublets necessitates that terminal group exchange and inversion be slow at 15 °C in the $Sn(tibm)_2Cl_2$ complex.

Perusal of Table IX of ref. 11, which lists the expected changes in signal multiplicities for the various averaging sets for a *cis*-$M(AB)_2X_2$ system, indicates that no averaging set will predict the collapse of the diastereotopic terminal groups of the AB ligand to a single doublet. It is reasonable to expect the collapse of the low temperature spectra (which already encompass groups with degenerate shifts) of the $Sn(tibm)_2Cl_2$ complex to a single doublet to be the result of an accidental chemical shift degeneracy of the expected doublets. Averaging sets A_i'' ($=A_i'''$ in this case as Cl does not function as a NMR probe) predict that the number of doublets is a multiple of two, and it is unlikely that four (or more) doublets would overlap in the fast exchange region. It is then necessary to distinguish between averaging sets A_4'' and A_9'' (which correspond to A_3''' and A_6''' of Table XI of ref. 11).

On the basis of changes in signal multiplicities, no distinctions between A_3''' and A_6''' can be made for any combination of diastereotopic and/or non-diastereotopic groups. Differences between A_3''' and A_6''' are such that the former does not lead to enantiomerization while the latter does result in inversion of the molecular configuration. Now since slow inversion is detected for the $Sn(tibm)_2Cl_2$ complex, and following the arguments presented earlier for the analogous complexes $M(dibm)_2Cl_2$ [6] and $M(dibm)_2XY$ [12] for which we have argued that these complexes undergo configurational rearrangements with inversion and that such rearrangements could be rationalized in terms of the A_5 and A_{13}' averaging sets, respectively, it is probable that inversion does occur also in these *cis*-$M(AB)_2X_2$ complexes during the rearrangement, thus favouring averaging set A_6'''. Some additional support for the A_6''' set is derived from its correlation with the A_{13}' averaging set suggested for the rearrangement of *cis*-$Ti(dibm)_2Cl(OCH)_3)$ (*cf.* Table XII of ref. 11).

A consideration of Tables II, III, and IV of ref. 13, with the equivalency $A_6''' = A_9''$, reveals that this A_6'' set may be accommodated by a twist mechanism and a bond rupture mechanism via TBP-axial and SP-axial intermediates. The SP-axial pathway is less attractive as A_6''' results only from selective attack of the dangling ligand end in the basal plane. Such discrimination is not expected *a priori* because of the difference in donor atoms (O *vs.* Cl) in the basal plane. The twist mechanism about the $C_3(i')$ and/or $C_3(i''')$ axes of the cotahedron [14] and a bond rupture mechanism via TBP-axial intermediates are equally probable, and no choice between the two is possible on the basis of presently available data.

Some support for the twist mechanism is afforded by the correlation of averaging sets and physical processes for the *cis*-Ti(dibm)$_2$Cl(OCH$_3$) [12] and *cis*-Sn(tibm)$_2$Cl$_2$ complexes. This argument, however, involves the tacit assumption that differences in metal ion and donor ligands do not impose different physical pathways for the rearrangement reactions. Also, the above discussion is based on the premise that these M(AB)$_2$X$_2$ complexes adopt only the geometries possessing *cis*-X$_2$ groups and that the rearrangement process is the result of a single physical pathway.

To extend the complexity of the system as a means of characterizing the rearrangement process in more detail, M(AB)$_2$X$_2$ complexes in which the X group may function as a NMR probe have been investigated. These studies will be reported in a forthcoming publication.

Acknowledgements

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