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Configurational Rearrangements in *cis*-$M(AA)_2X_2$, *cis*-$M(AA)_2XY$, and *cis*-$M(AB)_2X_2$ Complexes.

10. The *cis*-$M(AB)_2X_2$ System – Diastereotopic Probe on the X Ligands

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Diastereotopic probes have been incorporated on the X ligands of $M(AB)_2X_2$, where AB is an unsymmetrical bidentate ligand. The complexes $Ti(bzac)_2(O^iC_3H_7)_2$ and $Ti(bzac)_2(2,6\text{-}^iPr_2C_6H_3O)_2$ have been prepared (bzac = anion of benzoylacetone) and their stereochemistry characterized by nuclear magnetic resonance spectroscopy. The complexes adopt the cis-X_2 *geometry. These C_1-type complexes undergo terminal group exchange (and probably) in parallel with inversion of configuration. The latter, however, was not confirmed because of unresolved diastereotopic splittings. The averaging set for the rearrangement phenomena is identified as A_9'' and the rearrangements are discussed in terms of twist motions about the C_3 axes of the octahedral framework and bond rupture.*

Introduction

In our last paper of this series [1], we remarked that $M(AB)_2X_2$ complexes (AB = an unsymmetrical bidentate ligand; X = a monodentate ligand) may exist in five diastereomeric forms: three have *cis*-X_2 groups and two have *trans*-X_2 groups. Results thus far obtained demonstrate that complexes of the type $M(AA)_2X_2$, $M(AA)_2XY$, and $M(AB)_2X_2$ possess the *cis*-X_2 or *cis*-XY stereochemistry. Positioning the diastereotopic group on the AB ligand in $M(AB)_2X_2$ indicates that AB terminal group exchange occurs in parallel with inversion of the molecular configuration. We also inferred from the nuclear magnetic resonance data that rearrangements probably proceed via twist processes.

Where the complexes are *cis*-$M(AA)_2X_2$ and *cis*-$M(AA)_2XY$ (AA = a symmetrical bidentate ligand), placement of diastereotopic probes on the X ligands in the former complex (X = various isopropyl-substituted phenoxy groups) [2] and on Y in the latter complex (Y = isopropoxide and 2,6-diisopropylphenoxide) [3] has revealed the steric course of the configurational rearrangements in these dissymmetric species. Two complexes in particular, $Ti(acac)_2(2\text{-}^iPrC_6H_4O)_2$ and $Ti(acac)_2(2,6\text{-}^iPr_2C_6H_3O)_2$ where acac is acetylacetonate, afforded conclusive evidence [3] that these rearrangements occur with inversion of configuration. Arguments were presented to suggest that the probable mechanism(s) involve predominantly twist motions; some contributions from a bond rupture pathway through square-pyramidal axial and/or trigonal-bipyramidal equatorial intermediates could not be precluded with the available data.

An interesting set of complexes has provided contrasting expectations [4]. The series of bis(chelate)bis(2,6-diisopropylphenoxy)titanium(IV) complexes (chelate = acetylacetonate (acac), 8-hydroxyquinolinate (ox), and 8-hydroxyquinaldinate (quin)) showed some significant differences in the kinetic parameters for the inversion process from which we inferred that the ox and quin complexes possess a different rearrangement route than that for the acac analog. Isopropyl methyl group exchange (inversion) results from the process *cis*(phenoxy), *cis*(N)-, *trans*(O)-$\Lambda(\Delta) \rightleftharpoons$ *cis*(phenoxy), *cis*(N), *trans*-(O)-$\Delta(\Lambda)$. Such a stereochemical rearrangement can only be generated by a Ti–N bond rupture occurring via a trigonal-bipyramidal axial intermediate.

Although some $Ti(bzac)_2(alkoxy)_2$ complexes have been reported [5], their stereochemistry was not investigated. This paper reports our recent results of a study on the stereochemical nature of, and rearrangement processes in the $Ti(bzac)_2(O^iC_3H_7)_2$ and $Ti(bzac)_2(2,6\text{-}^iPr_2C_6H_3O)_2$ complexes in which diastereotopic probes have been incorporated on the monodentate ligands. The latter complex is also important insofar as it provides evidence that the $Ti(quin)_2(2,6\text{-}^iPr_2C_6H_3O)_2$ species exists as the single diastereomer *cis*(phenoxy), *cis*(N), *trans*(O) in solution [4].

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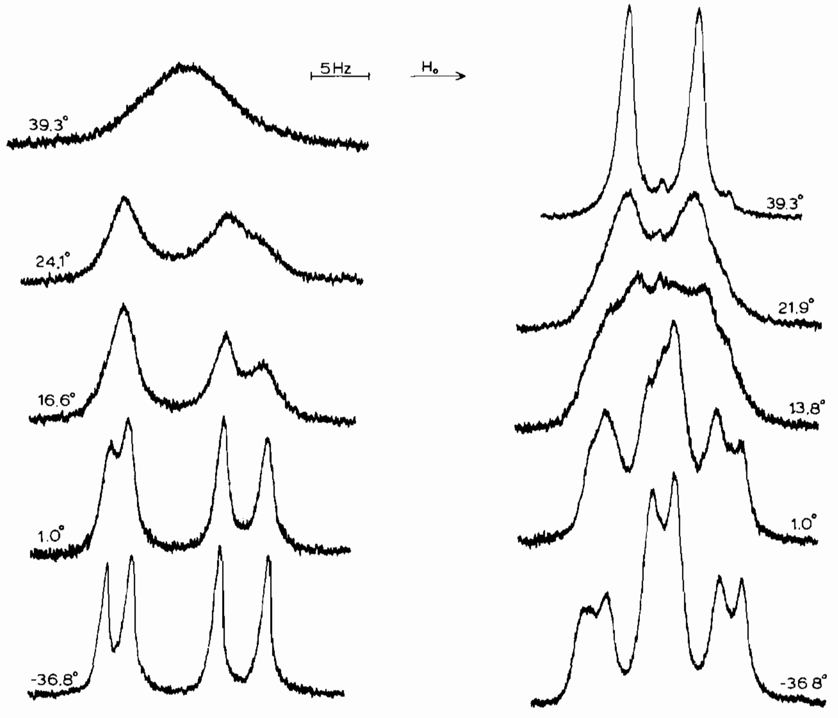


(a) bzac CH_3

(b) i-Pr CH_3

Fig. 1. Temperature dependence of the (a) benzoylacetonate methyl resonance and the (b) isopropyl methyl resonance of the $Ti(bzac)_2(O^iC_3H_7)_2$ complex in methylene chloride solution.

Experimental

Titanium(IV) isopropoxide (Research Organic/Inorganic), benzoylacetone (Aldrich), and 2,6-diisopropylphenol (Aldrich) were used as received without further purification. All organic solvents used in the syntheses were of reagent grade quality and were dried by refluxing over CaH_2 chips and distilled therefrom just prior to use. Chemicals and reactions were handled under a dry nitrogen atmosphere in a glove bag. Melting points are not corrected.

The proton NMR spectral techniques employed to obtain the variable temperature NMR spectral data have been described in detail elsewhere [6].

Bis(isopropoxy)bis(benzoylacetonato)titanium(IV), $Ti(bzac)_2(O^iC_3H_7)_2$

A solution of 6.35 g (39.2 mmol) of benzoylacetone in 50 ml of methylene chloride was added to a solution of 5.46 g (19.2 mmol) of pure titanium(IV) isopropoxide. The pale-yellow solution was stirred overnight at ambient temperature. Concentrating the solution to *ca.* 20 ml and adding 50 ml of hexane yielded a cream-colored solid which was collected, washed with hexane, and dried *in vacuo*; yield 8.0 g (85% theoretical). The crude product was recrystallized from a methylene chloride–hexane solution; m.p. 102–104 °C. The purity of the product was further verified by infrared and NMR spectroscopy.

If this product is left exposed to light for several days, it appears to undergo a photochemical decomposition to a greenish-blue solid. Hence, the product was stored in the dark when not needed. Similar observations have been reported for $Ti(acac)_2(OC_2H_5)_2$ and $Ti(bzbz)_2(OC_2H_5)_2$ (bzbz = anion of dibenzoylmethane) [5].

Bis(2,6-diisopropylphenoxy)bis(benzoylacetonate)titanium(IV), $Ti(bzac)_2(2,6\text{-}^iPr_2C_6H_3O)_2$

To a solution of 3.21 g (6.57 mmol) if $Ti(bzac)_2(O^iC_3H_7)_2$ in 20 ml of benzene was added 2.93 g (16.4 mmol) of 2,6-diisopropylphenol. The resulting dark red mixture was stirred overnight at ambient temperature. Concentrating the solution under reduced pressure gave a viscous red liquid, that was dissolved in a minimum amount of methylene chloride. After addition of hexane, the solution was frozen in liquid nitrogen. Upon warming to ambient temperature, a red-orange solid was recovered, washed with hexane, and dried *in vacuo*; yield 3.5 g (*ca.* 75% theoretical). The product was recrys-

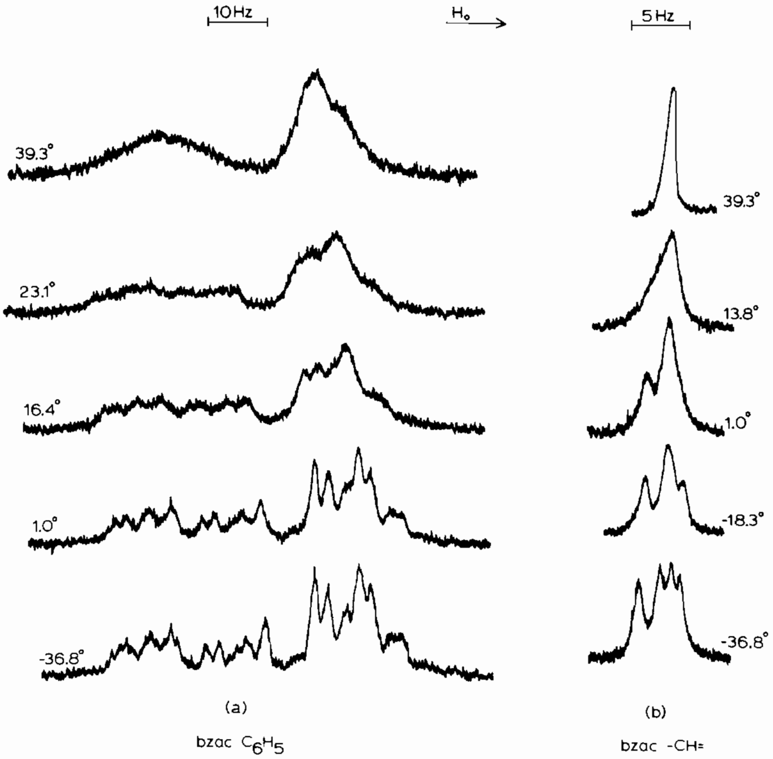


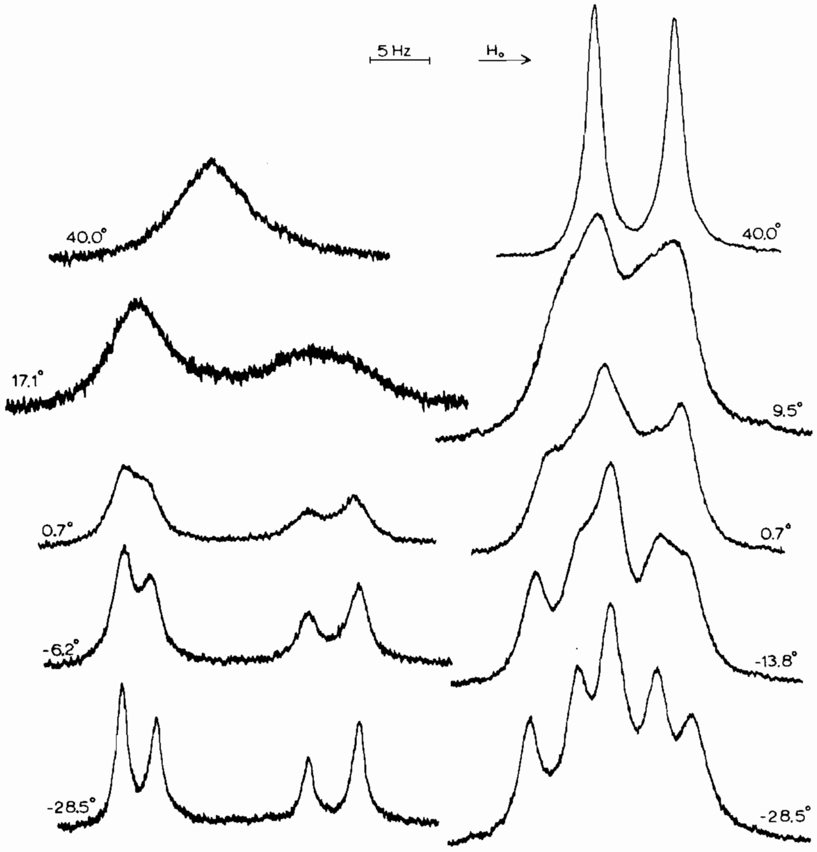
Fig. 2. Temperature dependence of the (a) benzoylacetonate phenyl resonance and the (b) benzoylacetonate ring proton (–CH=) resonance of the $Ti(bzac)_2(O^iC_3H_7)_2$ complex in methylene chloride solution.

tallyzed from methylene chloride–hexane solution. m.p. 89–92 °C (dec.).

Results and Discussion

The temperature dependence of the various NMR resonances of the $Ti(bzac)_2(O^iC_3H_7)_2$ complex is illustrated in Figs. 1 and 2. Figure 1(a) shows that the benzoylacetonate methyl resonance is very broad at room temperature, and upon cooling splits into four resonances of equal intensity. The temperature dependence of the isopropyl methyl resonance signal is complex, as Fig. 1(b) reveals. The –36.8 °C isopropyl methyl pattern may be resolved into four partially overlapping doublets of equal intensity. Further cooling reveals no additional splitting and the pattern is noticeably broadened at *ca.* –65 °C, probably a result of viscosity broadening or a more complex unresolved pattern. The benzoylacetonate phenyl region of the proton NMR spectrum is also temperature dependent. Figure 2(a) shows that these phenyl groups appear as two broad lines at ambient temperature. On cooling to –36.8 °C, fine structure caused by complicated coupling patterns of nonequivalent phenyl groups is observed. The resonance pattern at ambient temperature is reminiscent of the patterns observed for the phenyl region of the $Ti(bzac)X_2$ (X = F, Cl, Br) complexes at intermediate exchange rates [7]. It is expected that the resonances in Fig. 2(a) would sharpen further and reveal fine structure again at the fast exchange limit. No experiments were conducted above ambient temperature. Figure 2(b) indicates that the single benzoylacetonate ring proton (–CH=) resonance line at room temperature broadens with decreasing temperature until four resonances, of almost equal intensity, are observed at –36.8 °C. This represents the first $Ti(bzac)_2X_2$ complex for which more than one –CH= resonance is observed in the slow exchange region; the $Ti(bzac)_2X_2$ (X = F, Cl, Br) species reveal a single –CH= resonance signal even at *ca.* –65 °C [7], although considerably broadened.

Spectra for the $Ti(bzac)_2(2,6\text{-}^iPr_2C_6H_3O)_2$ complex are similar to those for the isopropoxy complex. Figures 3 and 4 illustrate that the benzoylacetonate methyl, phenyl, and –CH= groups are involved in exchange processes, as well as the isopropyl methyl groups. Four bzac methyl resonances are observed at low temperature and, unlike the isopropoxy complex, possess unequal relative intensities. The isopropyl methyl pattern at –28.5 °C (Fig. 3(b)) may be resolved into three overlapping doublets with relative intensities of 1:2:1. No further



(a)

bzac CH_3

(b)

i-Pr CH_3

Fig. 3. Temperature dependence of the (a) benzoylacetonate methyl resonance and the (b) isopropyl methyl resonance of the $Ti(bzac)_2(2,6\text{-}^iPr_2C_6H_3O)_2$ complex in methylene chloride solution.

splitting is observed even at lower temperatures. Figure 4(a) reveals that the temperature dependence of the benzoylacetonate phenyl region is similar to that for the isopropoxy complex. The bzac ring protons (–CH=) appear as a single resonance at ambient temperature, but broadens with decreasing temperature until three lines in a 1:2:1 intensity ratio are observed by –28.5 °C (Fig. 4(b)).

By analogy with the $Ti(bzac)_2(halogen)_2$ complexes [7], we rationalize the above observations as resulting from a rapidly interconverting mixture of the three diastereomers possessing *cis*-X_2 groups [1]. To the extent that the analogous $Ti(acac)_2(O^iC_3H_7)_2$ [8–10] and $Ti(acac)_2(2,6\text{-}^iPr_2C_6H_3O)_2$ [9, 10] adopt *cis*-X_2 geometries, it is not unreasonable to expect their bzac analogs to adopt similar configurations. With reference to Fig. 1 of ref. [1], a mixture of the *cis*-X_2 diastereomers will generate four bzac methyl, four bzac phenyl, four bzac –CH=, and four X (isopropyl methyl doublets) resonances in the absence of exchange processes. Spectra for the $Ti(bzac)_2(O^iC_3H_7)_2$ and $Ti(bzac)_2(2,6\text{-}^iPr_2C_6H_3O)_2$ complexes (Figs. 1 through 4) are consistent with such a mixture present at low temperature. A rapid exchange process interconverts all nonequivalent groups amongst the three *cis*-X_2 diastereomers. From previous experience [2], the diastereotopic splitting of isopropyl methyl group resonances is expected to be relatively small. For the three *cis*-X_2 isomers, each of which is enantiomeric, a total of eight isopropyl methyl doublets are expected in the slow exchange limit. Four and three doublets may be resolved for the isopropoxy and diisopropylphenoxy complexes, respectively, and are probably a result of the gross molecular nonequivalence of the X groups rather than from the dissymmetry centred on the titanium in each isomer. The isopropyl methyl patterns tend to broaden and are less resolved at temperatures below *ca.* –30 °C. This probably results from the severe overlapping of the expected eight doublets at lower temperatures, as the smaller diastereotopic splittings require lower

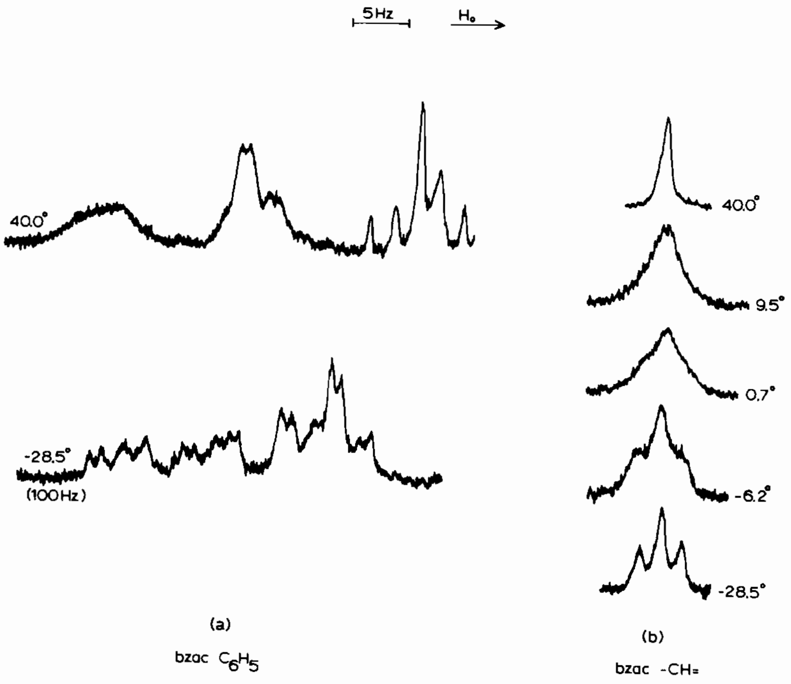


Fig. 4. Temperature dependence of the (a) benzoylacetonate phenyl resonance and the (b) benzoylacetonate ring proton (–CH=) resonance of the Ti(bzac)$_2$(2,6-^{i}Pr$_2$C$_6$H$_3$O)$_2$ complex in methylene chloride solution.

temperatures to be observed than the larger separation of environments resulting from overall symmetry nonequivalence.

The relative equilibrium concentrations of the three *cis*-X$_2$ isomers deserve some comment. If a statistical distribution of diastereomers obtains, the relative concentrations will be in the ratio *cis, cis, cis: cis, trans, cis* (or *cis, cis, trans*): *cis, cis, trans* (or *cis, trans, cis*) = 2:1:1 and four equally intense terminal group resonances are expected. The Ti(bzac)$_2$F$_2$ complex closely approaches a statistical distribution of diastereomers [7]. The Ti(bzac)$_2$(O^{i}C$_3$H$_7$)$_2$ complex also exists as a near statistical mixture since the four bzac methyl resonances are of similar intensity. However, a distribution of intensities obtained for the Ti(bzac)$_2$(2,6-^{i}Pr$_2$C$_6$H$_3$O)$_2$ complex indicates departures from a statistical mixture of diastereomers. It might be expected that the isomer possessing *trans* phenyl groups may experience some added steric strains with the more bulky 2,6-diisopropylphenoxy ligands than with isopropoxy ligands; thus the least intense resonance in Fig. 3(a) may be assigned to this diastereomer. Since the *cis, cis, cis* isomer should generate two equally intense bzac methyl resonances, the two signals of medium intensity in Fig. 3(a) are assigned to this diastereomer. Finally, the resonance at lowest field may be assigned to the isomer containing *trans* bzac methyl groups. The relative concentrations are not known with sufficient accuracy to allow determination of isomerization enthalpies from the temperature dependence of the concentrations. However, enthalpies are expected to be small [5].

The observation of a mixture of *cis*-X$_2$ isomers for the Ti(bzac)$_2$(2,6-^{i}Pr$_2$C$_6$H$_3$O)$_2$ complex supports the suggestion made earlier [4] that the Ti(quin)$_2$(2,6-^{i}Pr$_2$C$_6$H$_3$O)$_2$ and Ti(ox)$_2$(2,6-^{i}Pr$_2$C$_6$H$_3$O)$_2$ complexes exist as a single diastereomer in solution possessing a *cis*(N), *trans*(O) arrangement of quin and ox donor atoms.

Assignment of an averaging set responsible for the rearrangements in the Ti(bzac)$_2$(O^{i}C$_3$H$_7$)$_2$ and Ti(bzac)$_2$(2,6-^{i}Pr$_2$C$_6$H$_3$O)$_2$ complexes is difficult as both A_4'' and A_9'' of Table IV of ref. [11] predict identical changes in signal multiplicities. When X contains a diastereotopic isopropyl group, no averaging set predicts a single isopropyl methyl doublet in the fast exchange region. It is assumed that the single doublet observed is a result of the chemical shift degeneracy of the expected two doublets; it is not likely that four (or more) doublets would possess degenerate chemical shifts. As was the case earlier [1], a distinction between averaging set A_4'' and A_9'' is necessary; however, in this case, no information on whether the rearrangement occurs with or without enantiomerization is available as no diastereotopic splittings are observed for the isopropyl methyl groups. But to the extent that the related Ti(acac)$_2$(O^{i}C$_3$H$_7$)$_2$ [8] and Ti(acac)$_2$(2,6-^{i}Pr$_2$C$_6$H$_3$O)$_2$ [2] complexes exhibit diastereotopic splitting for their isopropyl methyl resonances and hence indicative of inversion, it is not inconceivable that the bzac analogs also undergo enantiomerization reactions. This would identify the averaging set as A_9''.

Reference to Tables II and III of ref. [12] indicates that the A_9'' set is accomodated by twist motions about the nearly equivalent $C_3(i')$ and $C_3(i''')$ axes of the octahedral framework [13] for all three *cis*-X_2 diastereomers; A_9'' can also be accommodated by a bond rupture pathway proceeding via trigonal-bipyramidal axial and/or square-pyramidal axial intermediates. It is difficult to distinguish between the twist modes *vs.* the bond rupture modes for the rearrangement processes. But we note that for the latter, square-pyramidal axial intermediates may be excluded to the extent that they would be required to discriminate attack by the dangling ligand end unto the basal plane sites. Previously [1], we have argued in favour of twist modes on the basis that averaging sets (A_9'' in the present case) correlate with A'_{13} for *cis*-Ti(dibm)$_2$Cl(OCH$_3$) [14] (dibm = anion of diisobutyrylmethane) and A_6''' of *cis*-Sn(tibm)$_2$Cl$_2$ (1) complexes (tibm = trifluoro analog of dibm). In all of these, we have made the tacit assumption from the outset that differences in metal ion and donor ligands *do not* impose diffferent physical pathways for the rearrangement reactions; and in favouring twist modes, we made the further assumption that the rearrangement process(es) is the result of a single pathway. Complete delineation between twist motions and bond rupture pathways, unfortunately, continues to elude attempts in these *cis*-M(AA)$_2$X$_2$, *cis*-M(AA)$_2$XY, and *cis*-M(AB)$_2$X$_2$ complexes.

Acknowledgements

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