

$s^{-1}$ , in accord with the fact that the exchanging electron is located in the  $\pi$  system of the aromatic ligand. The Cr(III) quenchers span a wide range of electrode potential and can be expected to be useful in other quenching studies, especially if the excited-state reduction potential is quite negative. The quenching results for the Cr(III) series are somewhat complicated because parallel energy-transfer and electron-transfer quenching occurs. Fortunately, because (exergonic) electron-transfer quenching enjoys a considerable kinetic advantage and because the rate constant for energy-transfer quenching is nearly constant across the series, the analysis of the rate data is straightforward. Apparently, low-spin Cr(II) products are formed when electron-transfer

quenching occurs, minimizing the overall activation energy of the process.

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**Registry No.** Cu(dpp) $_2^+$ , 85626-37-5; Cr(hFac) $_3$ , 14592-80-4; Cr(hFac)(tFbzac) $_2$ , 94620-39-0; Cr(tFbzac) $_3$ , 28096-65-3; Cr(tta) $_3$ , 15488-08-1; Cr(tFac) $_3$ , 14592-89-3; Cr(dbm) $_3$ , 21679-35-6; Cr(pdo) $_3$ , 15636-02-9; *cis*-Cr(bzac) $_3$ , 64726-51-8; *trans*-Cr(bzac) $_3$ , 64726-50-7; Cr(acac) $_3$ , 21679-31-2; *p*-dinitrobenzene, 100-25-4; *m*-dinitrobenzene, 99-65-0; 4,4-dinitrobiphenyl, 1528-74-1; 1-chloro-4-nitrobenzene, 100-00-5; nitrobenzene, 98-95-3.

## Modes of Rearrangements in *cis*-M(AB) $_2$ XY Six-Coordinate Bis Chelate Complexes. 1. A Theoretical Study of the Possibilities of 1D and 2D NMR

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**Abstract:** This work presents a detailed permutational analysis of isomerism and rearrangements of *cis* bis chelate complexes of the type M(AB) $_2$ XY. This analysis establishes the full correlation between the modes of rearrangements of M(AB) $_2$ XY systems and those of the M(AA) $_2$ X $_2$ , M(AB) $_2$ X $_2$ , and M(AA) $_2$ XY systems previously described, through the concept of mode splitting. The low symmetry of M(AB) $_2$ XY systems results in a larger number of modes, allowing one to distinguish all rearrangements, provided signal assignments are possible. It is demonstrated that even in the absence of signal assignment use of 2D NMR spectroscopy gives the number of modes of rearrangements and the type of exchange pattern responsible for observed isomerizations in the M(AB) $_2$ XY systems, types of stereochemical information hard to deduce from the traditional analysis of residual diastereotopism in the fast exchange region of 1D spectra. The merits of both 1D and 2D NMR spectroscopy are discussed in light of the dynamic stereochemistry of M(AB) $_2$ XY systems.

Twenty years of intensive research have been performed on the dynamic stereochemistry of six-coordinate bis chelate complexes.<sup>3</sup> Several theoretical descriptions have been given for the rearrangements of systems of the types *cis*-M(AA) $_2$ X $_2$ , *cis*-M(AB) $_2$ X $_2$ , and *cis*-M(AA) $_2$ XY in which X and Y represent monodentate ligands and AA represents symmetric and AB dissymmetric bidentate ligands.<sup>4</sup> In contrast, M(AB) $_2$ XY systems were described

only shortly.<sup>4e,f</sup> It is the first aim of this paper to give a unifying description of the four systems based on the concept of modes of rearrangements, and especially, of mode splitting. Special emphasis will be put on the permutational analysis of the dynamic stereochemistry of M(AB) $_2$ XY systems. Systems with two different chelates do not need to be discussed since they do not provide additional dynamic stereochemical information, the number of observable modes being already maximum for M(AB) $_2$ XY.

Residual diastereotopism<sup>6,7</sup> in the fast exchange region of a 1D (one-dimensional) NMR spectrum only seldom gives direct information on the number of modes of rearrangements which determine this stereochemical conversion: when only low, and,

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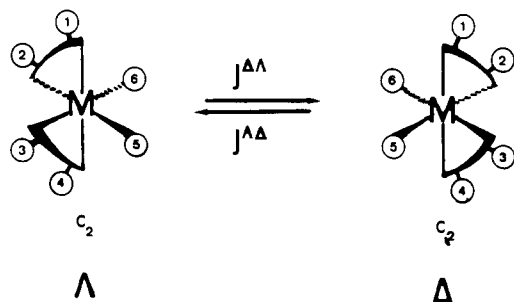


Figure 1. Skeleton labeling and inversion operator in M(diketonate)<sub>2</sub>XY complexes (X = Y or X ≠ Y).

a fortiori, no residual diastereotopism results from a dynamic process in the fast exchange 1D spectrum, it is often impossible to distinguish single modes from combinations of modes. Moreover, line shapes in the coalescence region are difficult to simulate for mixtures of modes, especially when the system is complicated by the presence of several diastereomers.<sup>46,5</sup> Therefore the assumption has very often been made that the dynamic stereochemistry of M(AA)<sub>2</sub>X<sub>2</sub>, M(AA)<sub>2</sub>XY, and M(AB)<sub>2</sub>X<sub>2</sub> can be understood in terms of one single pathway<sup>3e,4a,5</sup> (mode of rearrangements is meant here), or at most in terms of the smallest number of them (see, however, ref 3d,f for a specific example of elucidation of mixture of modes in Ti(AA)<sub>2</sub>(OR)<sub>2</sub> systems). It is therefore the second aim of this paper to show that slow exchange 2D (two-dimensional) NMR spectra<sup>8-11</sup> allows the direct determination of the number of modes involved in the rearrangements of M(AB)<sub>2</sub>XY systems and a partial insight into the nature of these combinations of modes, even in situations where signal assignment cannot be achieved.

In the next paper of this issue,<sup>12</sup> we present experimental 1D and 2D NMR data on (C<sub>6</sub>H<sub>5</sub>)ClSn(bzac)<sub>2</sub> (bzac<sup>-</sup> = benzoylacetate). Since the use of slow exchange 2D NMR leads to a new approach to dynamic stereochemistry, the interpretation of these data required the subsequent mathematical mode analysis.

### Permutational Analysis and Modes of Rearrangements

**Scope.** Permutational aspects of the dynamic stereochemistry of *cis*-M(AA)<sub>2</sub>X<sub>2</sub>, *cis*-M(AA)<sub>2</sub>XY, and *cis*-M(AB)<sub>2</sub>X<sub>2</sub> complexes have been studied very extensively by Bickley and Serpone,<sup>4a-c</sup> but this was not based on the concept of mode of rearrangements. They made a systematic study of all the possible exchange patterns, which they called averaging sets, and the resulting residual diastereotopism<sup>7</sup> for bis chelate complexes, according to the number and the position of diastereotopic probes, allowing the observation of inversion of chirality.<sup>4a-c</sup> This was based on a similar study of tris chelate complexes by Eaton and Eaton<sup>13</sup> inspired by the Longuet-Higgins approach to nonrigid molecules.<sup>14</sup> No analogous description of M(AB)<sub>2</sub>XY systems was given. The dynamic stereochemistry of these systems was first described by Finocchiaro and others<sup>4e</sup> for (C<sub>6</sub>H<sub>5</sub>)ClSn(bzac)<sub>2</sub> in terms of the modes of rearrangements of the more symmetric M(AA)<sub>2</sub>X<sub>2</sub> system.

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Recently, an explicit analysis in terms of modes of rearrangements of M(AB)<sub>2</sub>XY was given by Gielen,<sup>4f</sup> who pointed out that the former approach considers together within the same mode, rearrangements which are potentially distinguishable because of the lower symmetry of M(AB)<sub>2</sub>XY with respect to M(AA)<sub>2</sub>X<sub>2</sub>. For all these reasons we give here a *complete and homogeneous* description of the modes of rearrangements of *all four* systems, including their mutual correlation<sup>6,17</sup> through the concept of mode splitting.<sup>16j,22,24</sup>

**Group of Allowed Permutations and Static Stereochemistry.** We restrict ourselves here to the case where diastereotopic probes are absent from the molecular skeleton, which is actually the case for (C<sub>6</sub>H<sub>5</sub>)ClSn(bzac)<sub>2</sub> described in the next paper of this issue.<sup>12</sup> Figure 1 shows the skeleton numbering adopted. Circled labels refer to skeleton labelling, while uncircled ones to ligand labels.<sup>16d</sup> The restricted group of allowed permutations and permutation-inversions for this skeleton is<sup>16e,17f,g,18</sup>

$$S = \{[I,(12)] \otimes [I,(34)] \wedge [I,(14)(23)] \otimes [I,J] \quad (1)$$

where *I* represents the identity; the permutations (12) and (34) represent transpositions of bridgeheads within a single bridge while (14)(23) represents an exchange of bridges; the operator *J*, defined by Figure 1, represents inversion of chirality;  $\wedge$  and  $\otimes$  represent, respectively, semidirect and direct products. The permutation (56) of identical monodentate ligands does not need to be included in (1) (see footnote 19).

Figure 2 gives a comparative overview of the static stereochemistry of the four systems mentioned above: all the possible isomers are drawn for each system. Such isomers are represented by all the permutations contained in each double cosets of the type *AxB*, in which *A* is the permutational representation of the subgroup of rotational symmetry operations of the molecular skeleton<sup>16</sup> (see Figure 1), *B* represents the subgroup of permutations of identical ligands, and *x* is a representative permutation or permutation-inversion generating the isomer considered. The

(15) In this work, we call configuration, a set of distributions of labeled ligands on labeled molecular sites which can be mapped onto each other by a permutation belonging to the permutational representation of the group of rotational symmetry operations of the molecular skeleton; for more details see ref 16a.

(16) Reference 6: (a) pp 45-47, 195-198. (b) pp 51-53, 226-229. (c) pp 137, 596. (d) Chapter 6. (e) Chapter 7. (f) pp 181-185. (g) pp 255-257. (h) pp 248-249. (i) Chapter 10. (j) pp 258-263, 315-322. (k) Section 12-7. (m) pp 596-597. (n) pp 399-400, 503-507.

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(18)  $\otimes$  and  $\wedge$  represent the symbols for direct and semidirect products, respectively; permutation (1423), for instance, means ligand in site 1 moves to site 4, ligand in site 4 moves to site 2, ligand in site 2 moves to site 3, ligand in site 3 moves to site 1, whatever the labels of these ligands may be.<sup>16d</sup> *J* defines the enantiomerization of the chiral skeleton (Figure 1).

(19) In the analysis of Fe(diphosphine)<sub>2</sub>H<sub>2</sub> complexes<sup>20</sup> and of M(AA)<sub>2</sub>X<sub>2</sub> and M(AB)<sub>2</sub>X<sub>2</sub> systems,<sup>4a-c</sup> an additional permutation (56) representing transposition of identical monodentate ligands is introduced. Even if the hydride ligands are here observable NMR probes, the use of (56) is not necessary in general, because it is easy to show that with each permutation involving the transposition (56) is associated a permutation which does not contain (56) having the same stereochemical result, up to a rotation in space of the molecule. Note on the other hand that the use of the set of all permutamers,<sup>4b</sup> of order 384 is not necessary for reasons discussed previously.<sup>16b,m</sup>

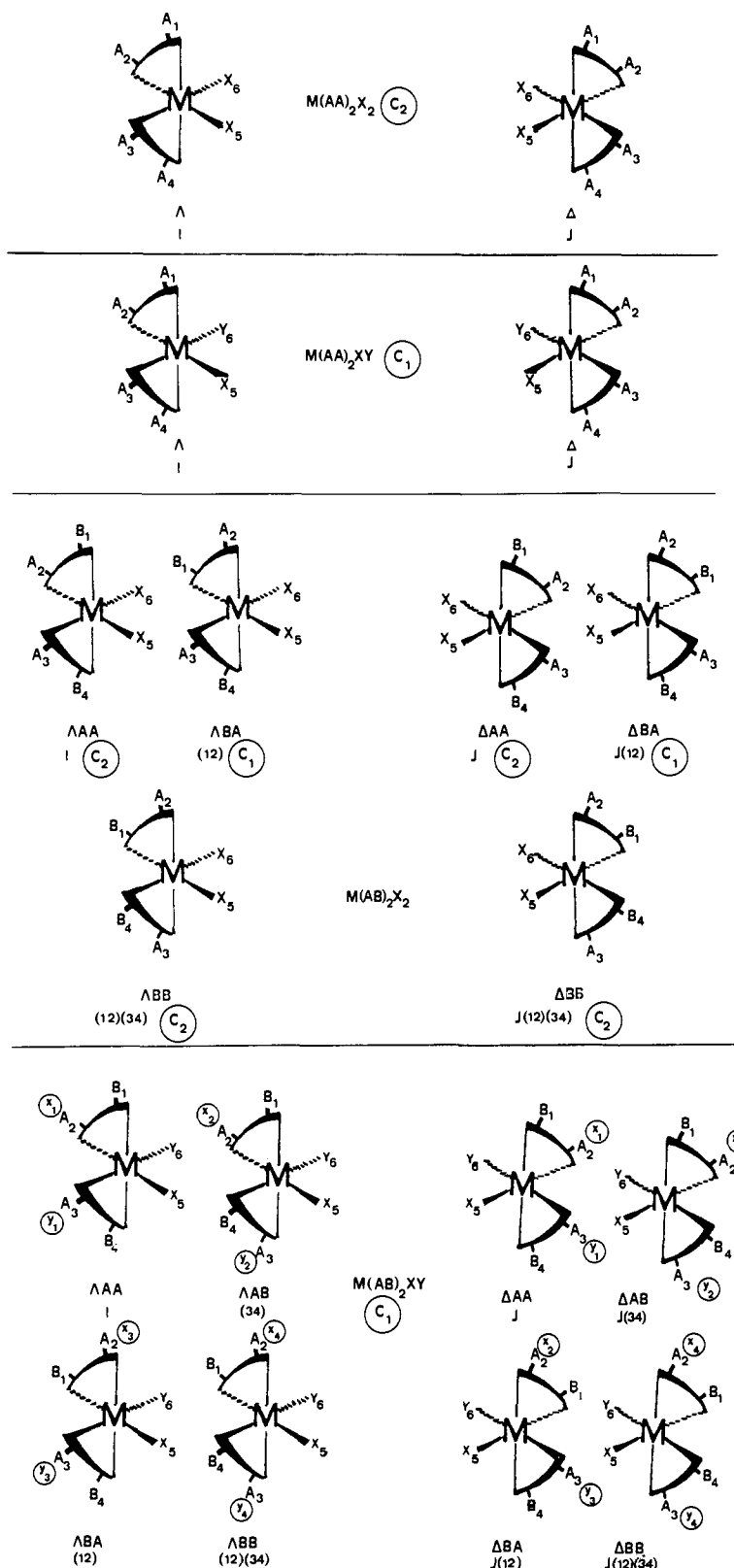
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**Figure 2.** Stereoisomers in  $M(AA)_2X_2$ ,  $M(AA)_2XY$ ,  $M(AB)_2X_2$ , and  $M(AB)_2XY$  systems. For each isomer, the isomer symbol, double coset representative, and symmetry point group are indicated. In the case of the  $M(AB)_2XY$  system, all the isomers have  $C_1$  symmetry. The circled symbols  $x_i$  and  $y_i$  refer to the diastereotopic methyl sites of the benzoylacetate ligand necessary for the analysis of the magnetic site exchange patterns due to the rearrangements; see text.

subgroup  $\hat{A}$  is  $[I,(14)(23)]$  for  $M(AA)_2X_2$  and  $M(AB)_2X_2$  systems, because of the  $C_2$  axis of the skeleton, and reduces to the identity in  $M(AA)_2XY$  and  $M(AB)_2XY$  because this  $C_2$  axis is lost. The subgroup  $B$ , which reflects that both chelates are identical and accounts for their symmetry or dissymmetry, is  $B = \{[I,(12)] \otimes [I,(34)]\} \Delta [I,(14)(23)]$  for  $M(AA)_2X_2$  and  $M(AA)_2XY$ , and  $B$

$= [I,(14)(23)]$  for  $M(AB)_2X_2$  and  $M(AB)_2XY$ . In Figure 2 each isomer is given with the representative  $x$  of the double coset  $\hat{A}xB$ , together with a simple and mnemotechnic symbol to characterize it. Each isomer is characterized by its configuration  $\Lambda$  or  $\Delta$ . The isomers of  $M(AB)_2X_2$  and  $M(AB)_2XY$  systems must be characterized by an additional symbol, indicating the chelate moiety

situated in trans position to the sites 5 and 6 in that order, i.e., in trans position to X and Y, respectively, for M(AB)<sub>2</sub>XY. The permutational representation of the actual rotational symmetry group  $A_W$  must contain all those symmetry operators of  $\hat{A}$  (the skeleton) which also permute identical ligands. This has been shown<sup>16f</sup> to be  $A_W = \hat{A} \cap x_W B x_W^{-1}$  for the isomer W represented by  $\hat{A} x_W B$ . Therefore  $\hat{A} = \hat{A}_W$  for the isomers of M(AA)<sub>2</sub>X<sub>2</sub> and M(AA)<sub>2</sub>XY. For the M(AB)<sub>2</sub>X<sub>2</sub> system, two pairs of enantiomers have C<sub>2</sub> symmetry (AA and BB) and one pair C<sub>1</sub> symmetry<sup>4d</sup> (BA). For M(AB)<sub>2</sub>XY four C<sub>1</sub> pairs result.

For studies of exchange patterns of magnetic sites under modes of rearrangements it is necessary that the chelate bears at least one NMR probe so that there is a one-to-one correspondence between one molecular site, on one hand, and a unique NMR signal (e.g., methyl, *tert*-butyl) or a unique set of signals arising from first-order coupling splittings (e.g., isopropyl groups), on the other hand. In the case of M(AB)<sub>2</sub>XY each probe gives rise to eight diastereotopic sites, two for each of the four diastereomeric pairs of  $\Delta\Lambda$  enantiomers. We characterize each site by a symbol  $x_i$  or  $y_i$ ;  $x$  represents the symbol of a probe (e.g., methyl) situated in the chelate of which one moiety is trans to X, while  $y$  represents the probe of a chelate trans to Y; the index  $i$  varies from 1 to 4 and represents the pairs of diastereomers, 1 = AA, 2 = AB, 3 = BA, 4 = BB, in alphabetical order. No distinction is made between the sites which are enantiotopic by external comparison<sup>21</sup> since they give rise to identical signals in achiral environment. These symbols are indicated in Figure 2 and characterize mnemonically the isomer and the chelate in which the probe is situated.

#### Dynamic Stereochemistry: Mode Splitting

For a chiral skeleton, when the chelate bridges are symmetric, only one pair of enantiomers is present as in M(AA)<sub>2</sub>X<sub>2</sub> and M(AA)<sub>2</sub>XY systems, so that a permutational mode corresponds to a double coset<sup>16g,17g</sup>

$$M(x) = \hat{A}x\hat{A} \quad (2)$$

in  $S$ . Modes which represent mutually reverse rearrangements,  $M(x) = \hat{A}x\hat{A}$  and  $M(x^{-1}) = \hat{A}x^{-1}\hat{A}$  have to be considered together because, if  $M(x)$  proceeds with a given rate constant, microreversibility requires that  $M(x^{-1})$  proceeds with the same rate constant.<sup>16h,17k,22</sup> The sets  $M(x)$  and  $M(x^{-1})$  are either identical or disjoint.<sup>11,23</sup> In the former case  $M(x)$  is said to be self-inverse (SI), in the latter it is non-self-inverse (NSI).<sup>11,23</sup> In the particular case we consider here, in which inversion of chirality cannot be observed, the modes  $M(x) = \hat{A}x\hat{A}$  and  $M(xJ) = \hat{A}xJ\hat{A}$  cannot be distinguished experimentally. When the chelate bridges are nonsymmetric, more than one pair of enantiomers is present, as in the systems M(AB)<sub>2</sub>X<sub>2</sub> and M(AB)<sub>2</sub>XY, and the rearrangements have to be considered in terms of pairs of mutually reverse polytopal modes of rearrangements<sup>16i</sup> of the type  $M^{VW}(y)$  and  $M^{VW}(y^{-1})$ . Indeed microreversibility requires that  $y$  and  $y^{-1}$  proceed with comparable rate constants when V and W have comparable energies. In the formalism used here and explained elsewhere<sup>16j</sup> the set  $M^{VW}(y)$  is given by

$$M^{VW}(y) = \hat{A}yA_W \quad (3)$$

where  $A_W$  represents the rotational symmetry group of the isomer W. This way to construct the modes is valid when *all* the isomers can be derived from a common skeleton and *all* are observed experimentally.<sup>16j,22,24</sup> In a first step, the permutations of the modes  $\hat{A}x\hat{A}$  of the more symmetric systems M(AA)<sub>2</sub>X<sub>2</sub> are applied to *all* the isomers of the less symmetric M(AA)<sub>2</sub>XY, M(AB)<sub>2</sub>X<sub>2</sub>, and M(AB)<sub>2</sub>XY systems. In a second step, each mode  $\hat{A}x\hat{A}$  of the more symmetric system is partitioned into sets  $\hat{A}yA_W$ , in order to account for the eventual symmetry lowering. In this way the modes of the more symmetric systems (*idealized* modes) are split into those of the less symmetric ones (*split* modes).<sup>16j,22,24</sup> This splitting establishes naturally, in a mathematically founded way, the correlation between the modes of rearrangements of all four systems. It should be stressed that the way in which a given idealized mode splits depends on the symmetry of the isomer to

which this mode is applied. When a split mode  $M^{VW}(y) = \hat{A}yA_W$ , converts an isomer W to an isomer V, then, the reverse mode converting V to W, which is the reverse of  $M^{VW}(y)$ , can be represented by

$$M^{VW}(y^{-1}) = \hat{A}y^{-1}A_V \quad (4)$$

provided  $M^{VW}(y^{-1})$  is applied to that configuration<sup>15</sup> of V which is generated by application to W of the permutation  $y$ .

In general, the modes  $M^{VW}(y) = \hat{A}yA_V$  and  $M^{VW}(y^{-1}) = \hat{A}y^{-1}A_W$  do not contain the same number of permutations, but  $M^{VW}(y)$  and  $M^{VW}(y^{-1})$  are certainly mutually inverse sets when  $\hat{A} = A_V = A_W$ .

Table I gives a complete survey of the modes of the systems M(AA)<sub>2</sub>X<sub>2</sub>, M(AB)<sub>2</sub>X<sub>2</sub>, M(AA)<sub>2</sub>XY, and M(AB)<sub>2</sub>XY, together with the mode splitting scheme when going from the most symmetric to the less symmetric system.

Table II gives the relation between the mode symbols of Table I and those of several previous references.

In Table I, each permutation  $x$  and its corresponding permutation inversion  $xJ$  appear on the same row in the condensed form  $x(J)$ . The modes to which  $x$  or  $xJ$  belong appear as  $\bar{M}_k$  with which  $M_k$  is meant for  $x$  and  $\bar{M}_k$  for  $xJ$ . Note that  $\bar{M}_k = JM_k$  and  $M_k = J\bar{M}_k$ . Our symbolism establishes the natural correlation existing between a permutation and its permutation-inversion; in ref 4a an analogous symbolism was used for the M(AA)<sub>2</sub>XY system (see Table II). The operations  $x$  and  $xJ$  are further treated together because they are indistinguishable within the present NMR context (no diastereotopic probes present).

The distinction between  $M_k$  and  $\bar{M}_k$  is nevertheless justified in view of mechanistic considerations (see next paper in this issue<sup>12</sup>). It appears from Table I that the  $2 \times 8$  elements of  $S$  are partitioned into three pairs of modes  $\bar{M}_0$ ,  $\bar{M}_1$ , and  $\bar{M}_2$  for M(AA)<sub>2</sub>X<sub>2</sub>. The subscript of these modes indicates whether no, single, or double axial-equatorial exchange does occur. Note that  $\bar{M}_1$  contains four elements,  $\bar{M}_0$  and  $\bar{M}_2$  only two. In the third part of Table I, for M(AB)<sub>2</sub>X<sub>2</sub>, each column represents an isomer conversion, either a single step or a pair of mutually reverse steps. The  $\Delta$  or  $\Lambda$  configuration of the isomers is not indicated since the modes  $M_k$  and  $\bar{M}_k$  are treated together. An empty entry in Table I indicates that the isomer conversion at the top of the column cannot be performed with the permutation of the considered row. When an entry is not empty, it is filled with the symbol of the mode which performs the considered isomer conversion. When a given mode symbol appears in the entry of a pair of mutually reverse steps, this means that the same permutation describes the considered isomer conversion in both senses. If the mode remains unsplit for the considered isomer conversion, as is the case for  $\bar{M}_0$  and  $\bar{M}_2$  in M(AB)<sub>2</sub>X<sub>2</sub>, the mode symbol remains the same since exactly the same permutations are performed. In contrast, when splitting does occur, the mode is characterized by two symbols, the first one indicates the mode of M(AA)<sub>2</sub>X<sub>2</sub> which has been split, and the second accounts for the symmetry lowering and describes the effect of the performed permutation. It appears for M(AB)<sub>2</sub>X<sub>2</sub> that while the mode  $\bar{M}_1$  remains unsplit when applied to AA and BB, it is split into  $\bar{M}_{1'}$  and  $\bar{M}_{1''}$  when applied to the configuration of BA represented in Figure 2. The split modes  $\bar{M}_{1'} = \{(12), (1324)\}(J)$  and  $\bar{M}_{1''} = \{(34), (1423)\}(J)$  generate the isomers AA and BB, respectively, and are the reverse of  $\bar{M}_1$  applied to AA and BB, respectively.

It should be stressed that  $\bar{M}_{1'}$  and  $\bar{M}_{1''}$  are NMR distinguishable modes since they convert the isomer BA into different isomers; literature data show, however, that they proceed with comparable rate constants, i.e., that they are observed in the same coalescence region for all the M(AB)<sub>2</sub>X<sub>2</sub> systems studied up to now.<sup>3e,4d,5f,g,25</sup> Therefore they were considered together and assigned a common symbol in previous work, but strictly speaking they should be treated separately (see Table II).

As shown in the fourth part of Table I, the splitting of the modes is complete for M(AA)<sub>2</sub>XY systems because the symmetry of the

(25) (a) Serpone, N.; Fay, R. C. *Inorg. Chem.* **1967**, *6*, 1835. (b) Pinnaiva, T. J.; Matienzo, L. J.; Peters, Y. A. *Inorg. Chem.* **1970**, *9*, 993.

Table I. Modes of Rearrangements in Cis Bis Chelate Systems of the Type  $M(AA)_2X_2$ ,  $M(AA)_2XY$ ,  $M(AB)_2X_2$ ,  $M(AB)_2XY$ , and  $M(AA)_2X_2$  to Split Modes in  $M(AA)_2X_2$ ,  $M(AA)_2XY$ ,  $M(AB)_2X_2$ ,  $M(AB)_2XY$ , and  $M(AB)_2XY$  Systems<sup>a</sup>

permutations or permutation-inversions	modes					
	$M(AA)_2X_2$			$M(AB)_2XY$		
$I(U)$	$AA \updownarrow AA$	$AA \updownarrow AA$	$AA \updownarrow AA$	$AA \updownarrow AA$	$AA \updownarrow AA$	$AA \updownarrow AA$
$(14)(23)(U)$	$BA \updownarrow BA$	$BA \updownarrow BA$	$BA \updownarrow BA$	$BA \updownarrow BA$	$BA \updownarrow BA$	$BA \updownarrow BA$
$(12)(U)$	$BB \updownarrow BB$	$BB \updownarrow BB$	$BB \updownarrow BB$	$BB \updownarrow BB$	$BB \updownarrow BB$	$BB \updownarrow BB$
$(1324)(U)$	$AA \updownarrow BA$	$BA \updownarrow AA$	$AA \updownarrow BA$	$BA \updownarrow AA$	$AA \updownarrow BA$	$BA \updownarrow AA$
$(1423)(U)$	$BA \updownarrow AA$	$AA \updownarrow BA$	$BA \updownarrow AA$	$AA \updownarrow BA$	$BA \updownarrow AA$	$AA \updownarrow BA$
$(34)(U)$	$AA \updownarrow BA$	$BA \updownarrow AA$	$AA \updownarrow BA$	$BA \updownarrow AA$	$AA \updownarrow BA$	$BA \updownarrow AA$
$(13)(24)(U)$	$AA \updownarrow BA$	$BA \updownarrow AA$	$AA \updownarrow BA$	$BA \updownarrow AA$	$AA \updownarrow BA$	$BA \updownarrow AA$
$(12)(34)(U)$	$AA \updownarrow BA$	$BA \updownarrow AA$	$AA \updownarrow BA$	$BA \updownarrow AA$	$AA \updownarrow BA$	$BA \updownarrow AA$
	$M(AA)_2X_2$	$M(AA)_2XY$	$M(AB)_2X_2$	$M(AB)_2XY$	$M(AB)_2X_2$	$M(AB)_2XY$
	$\tilde{M}_0$	$\tilde{M}_{on}$ $\tilde{M}_{ob}$	$\tilde{M}_0$	$\tilde{M}_{on}$ $\tilde{M}_{ob}$	$\tilde{M}_0$	$\tilde{M}_{on}$ $\tilde{M}_{ob}$
	$\tilde{M}_1$	$\tilde{M}_{ix}$ $\tilde{M}_{ib}$ $\tilde{M}_{ib}^{-1}$	$\tilde{M}_1$	$\tilde{M}_{ix}$ $\tilde{M}_{ib}$ $\tilde{M}_{ib}^{-1}$	$\tilde{M}_1$	$\tilde{M}_{ix}$ $\tilde{M}_{ib}$ $\tilde{M}_{ib}^{-1}$
	$\tilde{M}_2$	$\tilde{M}_{iy}$ $\tilde{M}_{ib}$ $\tilde{M}_{2n}$	$\tilde{M}_2$	$\tilde{M}_{iy}$ $\tilde{M}_{ib}$ $\tilde{M}_{2n}$	$\tilde{M}_2$	$\tilde{M}_{ib}$ $\tilde{M}_{2n}$

<sup>a</sup> The arrows at the modes  $\tilde{M}_{ib}$  and  $\tilde{M}_{ib}^{-1}$  indicate to which sense of the isomer conversion they refer, since these modes are not self-inverse.

Table II. Symbols of Rearrangements throughout Literature Data for Cis Bis Chelate Complexes

system	this work	ref 4a	ref 4b	ref 4d and 4e	ref 4f
$M(AA)_2X_2$	$M_0/\bar{M}_0$ $M_1/\bar{M}_1$ $M_2/\bar{M}_2$		$A_1/A_4$ $A_2/A_5$ $A_3/A_6$	$M_0/M_3$ $M_1/M_4$ $M_2/M_5$	$M_0/M_3$ $M_1/M_4$ $M_2/M_5$
$M(AB)_2X_2$	$M_0/\bar{M}_0$ $M_1/\bar{M}_1$ $M_1'/\bar{M}_1'$ $M_1''/\bar{M}_1''$ $M_2/\bar{M}_2$		$A_1'''/A_4'''$ $A_3'''/A_6'''$ $A_2'''/A_5'''$	$M_0/M_3$ $M_1/M_4$ $M_2/M_5$	$\hat{M}_0/\hat{M}_3$ $\hat{M}_1/\hat{M}_4$ $\hat{M}_2/\hat{M}_5$
$M(AA)_2XY$	$M_{on}/\bar{M}_{on}$ $M_{ob}/\bar{M}_{ob}$ $M_{ix}/\bar{M}_{ix}$ $M_{ib}/\bar{M}_{ib}$ $M_{ib}^{-1}/\bar{M}_{ib}^{-1}$ $M_{iy}/\bar{M}_{iy}$ $M_{2b}/\bar{M}_{2b}$ $M_{2n}/\bar{M}_{2n}$	$A_1/A_1'$ $A_4/A_4'$ $A_3/A_3'$ $A_6/A_6'$ $A_2/A_2'$ $A_7/A_7'$ $A_5/A_5'$	$A_1'/A_8'$ $A_4'/A_{11}'$ $A_3'/A_{10}'$ $A_6'/A_{13}'$ $A_2'/A_9'$ $A_7'/A_{14}'$ $A_5'/A_{12}'$		
$M(AB)_2XY$	$M_{on}/\bar{M}_{on}$ $M_{ob}/\bar{M}_{ob}$ $M_{ix}/\bar{M}_{ix}$ $M_{ib}/\bar{M}_{ib}$ $M_{ib}^{-1}/\bar{M}_{ib}^{-1}$ $M_{iy}/\bar{M}_{iy}$ $M_{2b}/\bar{M}_{2b}$ $M_{2n}/\bar{M}_{2n}$			$M_0/M_3$ $M_1/M_4$ $M_2/M_5$	$M_{01}/M_{31}$ $M_{02}/M_{32}$ $M_{11}/M_{41}$ $M_{12}/M_{42}$ $M_{13}/M_{43}$ $M_{14}/M_{44}$ $M_{21}/M_{51}$ $M_{22}/M_{52}$

molecule is lowered from  $C_2$  for  $M(AA)_2X_2$  to  $C_1$  for  $M(AA)_2XY$ ; i.e., each permutation or permutation-inversion is a mode by its own.

Indeed,  $\tilde{M}_0$  splits into  $\tilde{M}_{on}$  (split identity mode or inversion mode) and  $\tilde{M}_{ob}$  (detectable exchange of bridges). The labels b and n indicate, respectively, whether there is exchange of bridges as a whole or not.

$\tilde{M}_1$  is split into four modes  $\tilde{M}_{ix}$ ,  $\tilde{M}_{iy}$ ,  $\tilde{M}_{ib}$ , and  $\tilde{M}_{ib}^{-1}$ .  $\tilde{M}_{ix}$  and  $\tilde{M}_{iy}$  correspond to single axial-equatorial exchanges, without bridge exchange, within the chelate bridges trans to the X and Y ligands, respectively. They are SI modes.<sup>11,23</sup>  $\tilde{M}_{ib}$  and  $\tilde{M}_{ib}^{-1}$  combine  $\tilde{M}_{ix}$  and  $\tilde{M}_{iy}$ , respectively, with exchange of bridges, as again indicated by the label b. It is important to stress here that they are mutually reverse NSI modes. They must therefore be considered together since only their mean effect can be observed.

Finally, the mode  $\tilde{M}_2$  splits into  $\tilde{M}_{2b}$  (double axial-equatorial exchange with exchange of bridges) and  $\tilde{M}_{2n}$  (double axial-equatorial exchange, but no bridge exchange).

Because  $M(AA)_2XY$  already has the minimum  $C_1$  symmetry, no further splitting occurs when going to  $M(AB)_2XY$  systems. The only difference lies in the isomerism of  $M(AB)_2XY$ . Therefore, the modes of  $M(AA)_2XY$  all have to be applied to each possible isomer (more precisely to a fixed configuration of each one) of the  $M(AB)_2XY$  system. This results in the right part of Table I. In this case, each isomer conversion, and within this, each mode can be observed separately, provided experimental signal assignment is possible. In general, this cannot be achieved in systems of this type. On the other hand, the isomers have generally comparable energies.<sup>12</sup> The chemical significance of this is that the substituents on the bidentate ligands have only a minor influence on the energy of the isomers. Consequently, the assumption can safely be made that a given mode of  $M(AA)_2XY$  applied to all the isomers, results in chemical pathways proceeding with rate constants of the same order of magnitude, so that they are all observed within the same coalescence region. It is therefore usual to consider these pathways together in an experimental

Table III. Magnetic Site Exchange Patterns of the Modes of a M(AB)<sub>2</sub>XY System<sup>a</sup>

modes	M(AB) <sub>2</sub> XY (equilibria)										NRS	NPCP	
	AA ‡ AB	AB ‡ BB	BB ‡ BA	BA ‡ AA	AA ‡ AA	BB ‡ BB	AB ‡ AB	BA ‡ BA	AB ‡ BA	AA ‡ BB			
$\tilde{M}_{0n}$					none	none	none	none				8	0
$\tilde{M}_{0b}$					[x <sub>1</sub> , y <sub>1</sub> ]	[x <sub>4</sub> , y <sub>4</sub> ]				[x <sub>2</sub> , y <sub>3</sub> ] [x <sub>3</sub> , y <sub>2</sub> ]		1 + 1 + 2 = 4	4
$\tilde{M}_{1x}$		[x <sub>2</sub> , x <sub>4</sub> ] [y <sub>2</sub> , y <sub>4</sub> ]		[x <sub>1</sub> , x <sub>3</sub> ] [y <sub>1</sub> , y <sub>3</sub> ]								2 + 2 = 4	4
$\tilde{M}_{1b}$ } $\tilde{M}_{1b}^{-1}$ }	[x <sub>1</sub> , y <sub>2</sub> ] [y <sub>1</sub> , x <sub>2</sub> ]	[y <sub>2</sub> , x <sub>4</sub> ] [x <sub>2</sub> , y <sub>4</sub> ]	[x <sub>4</sub> , y <sub>3</sub> ] [y <sub>4</sub> , x <sub>3</sub> ]	[y <sub>3</sub> , x <sub>1</sub> ] [x <sub>3</sub> , y <sub>1</sub> ]								1 + 1 = 2	8
$\tilde{M}_{1y}$	[x <sub>1</sub> , x <sub>2</sub> ] [y <sub>1</sub> , y <sub>2</sub> ]		[x <sub>3</sub> , x <sub>4</sub> ] [y <sub>3</sub> , y <sub>4</sub> ]									2 + 2 = 4	4
$\tilde{M}_{2b}$							[x <sub>2</sub> , y <sub>2</sub> ]	[x <sub>3</sub> , y <sub>3</sub> ]		[x <sub>1</sub> , y <sub>4</sub> ] [x <sub>4</sub> , y <sub>1</sub> ]		1 + 1 + 2 = 4	4
$\tilde{M}_{2n}$										[x <sub>2</sub> , x <sub>3</sub> ] [y <sub>2</sub> , y <sub>3</sub> ]	[x <sub>1</sub> , x <sub>4</sub> ] [y <sub>1</sub> , y <sub>4</sub> ]	2 + 2 = 4	4

<sup>a</sup> In order to avoid heavy symbolism, the isomers are indicated with numerical labels in such a way that natural arithmetic order corresponds to the alphabetical order of isomers symbols: 1 = AA; 2 = AB; 3 = BA; 4 = BB. The symbol NRS means number of residual signals in the fast exchange 1D spectrum; NPCP means number of pairs of cross peaks in the slow exchange 2D spectrum; see text for further comments hereon.

stereochemical analysis. This assumption has been called "noninterdigitation" of modes<sup>7,26</sup> and has been used implicitly in previous works on M(AB)<sub>2</sub>X<sub>2</sub><sup>3e,4d,e,5f,g</sup> systems and also on internal rotations of organic polyaryl compounds.<sup>7,26</sup>

Since the isomers are quasi-isoenergetic, the mode  $\tilde{M}_{1b}$  and its microreversible  $\tilde{M}_{1b}^{-1}$  do proceed with rate constants of the same order of magnitude and are considered therefore pairwise.

As seen from Table II, this work is the first attempt to present a homogeneous symbolism for and a complete description of the dynamic stereochemistry of six-coordinate bis chelate complexes from M(AA)<sub>2</sub>X<sub>2</sub> to M(AB)<sub>2</sub>XY. Note that in some cases, especially for M(AB)<sub>2</sub>XY systems,<sup>4d,e</sup> but also partially for M(AB)<sub>2</sub>X<sub>2</sub><sup>4b,d,e,f</sup> descriptions were provided which consider together rearrangements which are in principle distinguishable. To show the experimental value of this approach we present, in the next section, a permutational NMR analysis—emphasized on 2D NMR—of the modes of M(AB)<sub>2</sub>XY systems, that will be applied to (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CISn(bzac)<sub>2</sub> in the next paper of this issue.<sup>12</sup>

#### NMR Analysis of the Modes of M(AB)<sub>2</sub>XY. A Comparison of 1D and 2D Spectroscopy

Table III shows how the magnetic sites are exchanged under each mode of M(AB)<sub>2</sub>XY; the mutually inverse modes  $\tilde{M}_{1b} + \tilde{M}_{1b}^{-1}$  form one single entry since only their mean effect can be observed. The symbol [x<sub>i</sub>, y<sub>j</sub>] indicates that the magnetizations associated with the magnetic sites x<sub>i</sub> and y<sub>j</sub> (see Figure 1) are transferred to one another. For a 1D spectrum this results in the coalescence of the signals associated with the magnetic sites x<sub>i</sub> and y<sub>j</sub>. Hence, there is a one-to-one correspondence between the set of mutually exchanging sites and one residual signal<sup>16n</sup> in the fast exchange region.<sup>7,16n</sup> In a slow exchange 2D spectrum the mutual magnetization transfer between x<sub>i</sub> and y<sub>j</sub> gives rise to a pair of nondiagonal contour signals, a pair of cross peaks,<sup>8</sup> at row x<sub>i</sub> and column y<sub>j</sub> and at row y<sub>j</sub> and column x<sub>i</sub>. Therefore the symbol [x<sub>i</sub>, y<sub>j</sub>] represents such a pair of cross peaks in a slow exchange 2D spectrum.

Table III shows that each mode, and, consequently, each combination of modes, has a unique pattern of cross peaks, which can be established experimentally, provided assignment of signals to magnetic sites is possible. Unfortunately such an assignment can seldom be realized in systems with different isomers having identical symmetries. In that case the only stereochemically useful information resulting from 1D spectroscopy is the number of

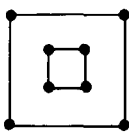
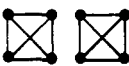

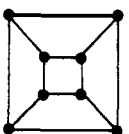
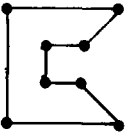
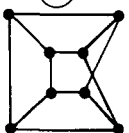
residual signals (NRS) in the fast exchange region. Tables III and IV show that NRS = 4, which is unambiguously characteristic of a single SI mode,<sup>11,23</sup> but no choice between them is possible. On the other hand, NRS = 2 indicates the pair of mutually inverse NSI modes<sup>11,23</sup>  $\tilde{M}_{1b} + \tilde{M}_{1b}^{-1}$  or some combinations of two SI modes, or even some combinations of three modes.

The remaining combinations of two or three modes and all combinations of four or more modes give rise to a unique residual signal (NRS = 1). It is clear that even for the low symmetry M(AB)<sub>2</sub>XY systems, the NRS is not correlated with the number of modes of which the combined effect is observed. For M(AA)<sub>2</sub>X<sub>2</sub>, M(AB)<sub>2</sub>X<sub>2</sub>, and M(AA)<sub>2</sub>XY systems, the situation is even worse since it is not possible to deduce whether the presence of a unique residual signal in the fast exchange 1D spectrum is due to some *unique* SI mode or pair of mutually inverse NSI modes or to a combination of modes proceeding *together*. This has implicitly been recognized as a limitation in the stereochemical analysis of these bis chelate systems by Bickley and Serpone,<sup>3e,4a-c,5a,b,g</sup> who systematically assumed that they observed the effects of a unique mode; this was the simplest assumption compatible with their results. In contradistinction, Table III shows that for M(AB)<sub>2</sub>XY systems the presence of a unique residual signal must be due to a combination of modes.

This property is the only advantage of M(AB)<sub>2</sub>XY systems with respect to the other ones, as far as 1D fast exchange NMR is concerned. Table III shows that the number of pairs of cross peaks (NPCP) in a slow exchange 2D spectrum is four for each SI mode and eight for the pair of NSI modes  $\tilde{M}_{1b} + \tilde{M}_{1b}^{-1}$ . This illustrates the statement of Nourse<sup>10</sup> that the NPCP is twice as large for NSI pairs of modes as for a SI mode. It should be stressed that no further choice between SI modes can be made without signal assignment. Therefore, even from the point of view of 2D spectroscopy, M(AB)<sub>2</sub>XY systems do not give additional stereochemical information with respect to 1D fast exchange NMR as long as only single SI modes or single pairs of NSI modes are concerned. This is, however, no longer the case for combinations of modes. Combinations of modes proceeding together result in a NPCP equal to four times the number of combined modes, as shown by Table IV. This number is a type of stereochemical information hard to deduce without 2D spectroscopy, certainly from the NRS of fast exchange 1D spectra. Moreover, for M(AB)<sub>2</sub>XY systems 2D slow exchange NMR gives more than only the number of mode combinations. Indeed, from the positions of the cross peaks in the slow exchange 2D spectrum, the graph associated with the magnetic site exchange pattern can be constructed. This is a consequence of the fact that the slow exchange 2D spectrum is a faithful graphical representation of the Kubo-Sack matrix<sup>8</sup> associated with the considered rearrangement.

(26) (a) Willem, R.; Pepermans, H.; Hoogzand, C.; Hallenga, K.; Gielen, M. *J. Am. Chem. Soc.* **1981**, *103*, 2297. (b) Willem, R.; Pepermans, H.; Hallenga, K.; Gielen, M.; Dams, R.; Geise, H. *J. Org. Chem.* **1983**, *48*, 1890. (c) Pepermans, H.; Gielen, M.; Hoogzand, C.; Willem, R. *Bull. Soc. Chim. Belg.* **1983**, *92*, 465 and references cited therein.

Table IV. NMR Characteristics of All the Possible Combinations of Two and Three Modes of  $M(AB)_2XY$  Systems<sup>a</sup>

two modes NPCP = 8	NRS	type of exchange pattern	three modes NPCP = 12	NRS	type of exchange pattern
$\tilde{M}_{1b} + \tilde{M}_{1b}^{-1}$	2	(2A) 	$\tilde{M}_{1b} + \tilde{M}_{1b}^{-1} + \tilde{M}_{2n}$	2	(3A) 
$\tilde{M}_{0b} + \tilde{M}_{2b} + \tilde{M}_{2n}$ $\tilde{M}_{1x} + \tilde{M}_{1y} + \tilde{M}_{2n}$ $\tilde{M}_{1y} + \tilde{M}_{2n}$ $\tilde{M}_{2b} + \tilde{M}_{2n}$		III 	$\tilde{M}_{0b} + \tilde{M}_{2b} + \tilde{M}_{2n}$ $\tilde{M}_{1x} + \tilde{M}_{1y} + \tilde{M}_{2n}$		(3B) 
$\tilde{M}_{0b} + \tilde{M}_{1x} + \tilde{M}_{1y}$ $\tilde{M}_{1x} + \tilde{M}_{2b}$ $\tilde{M}_{1y} + \tilde{M}_{2b}$	1	(2B) 	$\tilde{M}_{0b} + \tilde{M}_{1x} + \tilde{M}_{1y} + \tilde{M}_{2b}$ $\tilde{M}_{1y} + \tilde{M}_{2b}$ $\tilde{M}_{1x} + \tilde{M}_{1y} + \tilde{M}_{2b}$	1	(3C) 
			$\tilde{M}_{0b} + \tilde{M}_{1x} + \tilde{M}_{2n}$ $\tilde{M}_{1y} + \tilde{M}_{2n}$ $\tilde{M}_{1x} + \tilde{M}_{2b} + \tilde{M}_{2n}$ $\tilde{M}_{1y} + \tilde{M}_{2b} + \tilde{M}_{2n}$	1	

<sup>a</sup> Number of residual signals, NRS, in a fast exchange 1D spectrum; number of pairs of cross peaks, NPCP, in a slow exchange 2D spectrum; types of exchange patterns represented by graphs in which dots represent magnetic sites.

Therefore a slow exchange 2D spectrum is formally a square matrix with zero and nonzero nondiagonal elements. The vertices of the graph associated with this Kubo-Sack matrix represent the magnetic sites (the row and column indices of the matrix), while the edges represent the nonzero nondiagonal elements and correspond to magnetic site transfers. For any single SI mode, this graph consists of four disjoint edges representing magnetization transfers between pairs of magnetic sites, confirming that no distinction between single SI modes is possible. For combinations of two modes (Table IV) two types of graphs result: two disconnected squares (type 2A) or an octagon (type 2B). For combinations of three modes three types of graphs result: one with two disconnected subgraphs (type 3A) and two completely connected graphs (types 3B and 3C). Note that mode  $\tilde{M}_{2n}$  is not represented in exchange patterns of type 3B and that the pair of modes  $\tilde{M}_{1b} + \tilde{M}_{1b}^{-1}$  is not represented in patterns of type 3C. Important to note is that this graph contains implicitly the information deduced from the fast exchange 1D spectrum: the NRS is merely the number of disconnected subgraphs in an exchange pattern.

Finally, 2D spectroscopy reduces in general the detrimental consequences of accidental isochrony of signals on the stereochemical analysis. Accidental isochrony of two signals in the slow exchange region reduces the NPCP per mode eventually from 4 to 3, which does not give serious problems to count the modes. In 1D spectroscopy, the identification of the proceeding modes can be completely erroneous because of accidental isochrony of residual signals (see, for example, ref 26a) in the fast exchange

region, a problem which is completely irrelevant in the 2D approach of stereochemical elucidation.

### Conclusion

A detailed permutational analysis of the stereochemistry of *cis*- $M(AB)_2XY$  complexes correlates its modes with those of *cis*- $M(AA)_2X_2$ , *cis*- $M(AA)_2XY$ , and *cis*- $M(AB)_2X_2$  systems, using the concept of mode splitting.<sup>16j,22,24</sup> Only the use of  $M(AB)_2XY$  systems allows us to deduce from the 1D fast exchange NMR spectrum whether only single modes or combinations of modes are proceeding.

Counting modes in such combinations is cumbersome from fast exchange 1D NMR but straightforward from slow exchange 2D NMR. The latter allows us in addition to get an insight into the topology of the exchange pattern. Our work shows therefore that fast exchange 1D information is contained in the slow exchange 2D spectrum, but that the reverse statement is not true.

In the next paper of this issue,<sup>12</sup> we use this theoretical study to analyze experimental 1D and 2D data we obtained for  $(C_6H_5)ClSn(bzac)_2$  and to illustrate the wider possibilities offered by 2D spectroscopy. This leads to more precise mechanistic information about the stereochemistry of such bis chelate complexes than is usually available from fast exchange 1D spectra alone.

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