

Research Notes on the Topological Effect on  
Molecular Orbitals (TEMO); 4.\*

A Topological Model for some  
Dinuclear Metal Complexes

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A new topological model applicable to dinuclear complexes of certain tetradentate ligands is presented. The appearance of inversions within the union of the MO spectra of a pair of topologically related isomers constructed by means of this model cannot be excluded.

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\* Part 3: Match, this issue.

1. General Remarks:

A brief description of the TEMO theorem and the role which it plays in molecular physics have been given recently [1]. Also the display of TEMO within the MO pattern obtained by SCF ab initio calculation has been investigated by means of some examples [2-4]. The relation of TEMO to the general problem of molecular topology is discussed elsewhere [5].

The essence of TEMO is briefly as follows: Certain pairs of isomers may be considered as being constructed from pairwise isomorphic subunits which are connected in a different manner in the respective isomers. Such pairs of isomers are termed *topologically related isomers*; they are usually denoted by S and T. The modes of construction of topologically related isomers are called *topological models*; some models have been described elsewhere [1, 6-11]. Let x denote the (continuous) variable of the MO eigenvalues,  $\{x_j^S\}$  and  $\{x_j^T\}$ , of the topologically related isomers S and T, respectively, which are labelled by the index  $j=1,2,3,\dots$  in the order of their increasing values, i.e.:  $x_1^S \leq x_2^S, x_1^T \leq x_2^T$ , etc.; further, let  $S(x)$  and  $T(x)$  denote the characteristic polynomials associated with the S and the T isomers, respectively; then, in the range of the variable x within which one has  $T(x) \geq S(x)$ , the following inequality holds:

$$\dots \leq x_{2k-1}^S \leq x_{2k-1}^T \leq x_{2k}^T \leq x_{2k}^S \leq \dots \quad (1)$$

In those ranges of  $x$  within  $T(x) < S(x)$ , the sequence (1) is inverted; this means:

$$\dots < x_1^I < \dots < x_{2k}^S < x_{2k}^T < x_{2k+1}^T < x_{2k+1}^S < \dots < x_{1+1}^I < \dots$$

The values of  $x$  at which such inversions take place,  $\{x_1^I\}$ , are given by the real roots of odd degeneracy [10] of the difference polynomial  $\Delta(x)$  which is defined by

$$\Delta(x) = T(x) - S(x) \quad (2)$$

It is evident that TEMO without inversions results if  $\Delta(x) \geq 0$  holds in the complete range of the variable,  $x \in (-\infty, +\infty)$ . This is guaranteed when  $\Delta(x)$  may be represented by a square of a polynomial or by a sum of such squares. Otherwise it is rather difficult to conclude that no inversions appear. But it should be noted that even  $\Delta(x) < 0$  indicates only the possibility but not the necessity of the appearance of some inversions while, in contrast to this, the appearance of inversions is strictly excluded by  $\Delta(x) \geq 0$ .



Of the several topological models established hitherto [1,6-11] none may be applied to the pair of topologically related isomers I and II. Therefore, such a model is presented here. As is shown in the case of this model, the appearance of inversions within the union of the MO eigenvalue spectra of the S and the T isomer cannot be excluded.

### 3. The Topological Model

The inspection of the constitutional formulae I and II shows that these two complexes differ only with respect to the connections to one of the RNCO moieties. Hence, this moiety is chosen as a construction subunit, A. A has three non-equivalent sites of valence, k, l, and m, which correspond to the atoms O, C, and N, respectively. I and II consist of two such subunits and two bivalent  $\text{Me}_2\text{Ga}$  moieties in which the Ga atom is the site of both valencies. A topological model consistent with the constitutional formulae I and II is shown in Figure 1. Evidently, this model is more general than necessary for the pair I, II, because in this pair the subunits A and B as well as C and D are isomorphic. But for the sake of generality we ignore these isomorphisms at the beginning and we shall take them into account only just for the final specification of the general result obtained.

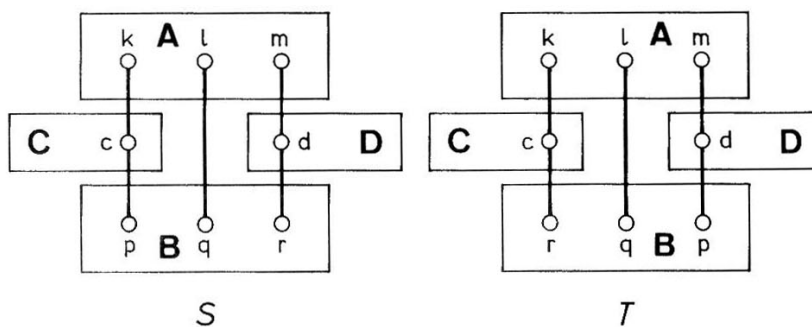


Figure 1: Scheme of the S and T isomer constructed by means of the model treated here.

4. Derivation of the Difference Polynomial and Conclusion  
about Inversions

The subunits A, B, C, and D are connected by five edges. Removing these edges from S and T, respectively, one obtains for the characteristic polynomial of the S isomer

$$\begin{aligned}
 S(x) = & ABCD - AB^pC^cD + AB^{pr}C^cD^d - A^lB^{pqr}C^cD^d \\
 & - AB^rCD^d + A^kB^rC^cD^d - A^{kl}B^{qr}C^cD^d \\
 & - A^kBC^cD + A^lB^{pq}C^cD - A^{lm}B^{pq}C^cD^d \\
 & - A^lB^qCD + A^lB^{qr}CD^d - A^{klm}B^qC^cD^d \\
 & - A^mBCD^d + A^mB^pC^cD^d \\
 & + A^{kl}B^qC^cD \\
 & + A^{km}BC^cD^d \\
 & + A^{lm}B^qCD^d
 \end{aligned}$$

$$\begin{aligned}
 & -2tA_{kl}B^{pq}C^cD - 2tA_{km}B^{pr}C^cD^d - 2tA_{lm}B^{qr}CD^d \\
 & +2tA_{kl}B^{r}C^cD^d + 2tA_{km}B^{q}C^cD^d + 2tA_{lm}B^{p}C^cD^d \\
 & +2tA_{kl}B^{m}C^cD^d + 2tA_{lm}B^{k}C^cD^d .
 \end{aligned}$$

In the case of the T isomer the characteristic polynomial is obtained as follows:

$$\begin{aligned}
 T(x) = & ABCD - AB^pCD^d + AB^{pr}C^dD^d - A^1B^{pq}rC^dD^d \\
 & - AB^rC^dD^d + A^kB^pC^dD^d - A^{kl}B^{pq}C^dD^d \\
 & - A^kBC^dD^d + A^1B^{pq}CD^d - A^{lm}B^{qr}C^dD^d \\
 & - A^1B^qCD^d + A^1B^{qr}C^dD^d - A^{klm}B^qC^dD^d \\
 & - A^mBCD^d + A^mB^rC^dD^d \\
 & + A^{kl}B^qC^dD^d \\
 & + A^{km}BC^dD^d \\
 & + A^{lm}B^qCD^d \\
 \\
 & - 2tA_{kl}B_{qr}C^dD^d - 2tA_{km}B_{pr}C^dD^d - 2tA_{lm}B_{pq}CD^d \\
 & + 2tA_{kl}B_{qr}^pC^dD^d + 2tA_{km}^1B_{pr}^qC^dD^d + 2tA_{lm}^rB_{pq}C^dD^d \\
 & + 2tA_{kl}^mB_{qr}C^dD^d + 2tA_{lm}^kB_{pq}C^dD^d.
 \end{aligned}$$

Here the same notation is used as in [11]; its meaning may be exemplified by

$$A^{kl} = \mu(A-k-1)$$

$$A_{lm}^k = \sum_{(P_{lm})} \mu(A-k-P_{lm})$$

where  $\mu(G)$  denotes either the characteristic ( $t=1$ ) or the acyclic ( $t=0$ ) polynomial of the graph  $G$ [15] and  $P_{lm}$  denotes a path which connects the vertices  $l$  and  $m$  in  $G$ .



From these expressions the difference polynomial,  $\Delta(x)$ , is formed according to eq. (2); it results in

$$\begin{aligned}
 \Delta(x) = & \\
 & A(B^p - B^r)(C^c D - CD^d) + \\
 & + (A^k - A^m)(B^p - B^r)C^c D^d - \\
 & - A^l(B^{pq} - B^{qr})(C^c D - CD^d) \\
 & - (A^{kl} - A^{lm})(B^{pq} - B^{qr})C^c D^d \quad (3) \\
 & + 2t[A_{kl}C^c D - A_{lm}CD^d](B_{pq} - B_{qr}) \\
 & - 2t(A_{kl} - A_{lm})(B_{pq}^r - B_{qr}^p)C^c D^d \\
 & - 2t(A_{kl}^m - A_{lm}^k)(B_{pq} - B_{qr})C^c D^d.
 \end{aligned}$$

Obviously, eq. (3) may be simplified when C and D are assumed to be isomorphic subunits such that in a bijective mapping of C onto D the vertex c is mapped onto d and vice versa. Then the following identities hold for their polynomials

$$C = D, \quad C^c = D^d.$$

After insertion of these, the first and the third term of eq. (3) cancel and one obtains

$$\begin{aligned}
 \Delta(x) = & \\
 & (A^k - A^m)(B^p - B^r)(C^c)^2 - \\
 & - (A^{kl} - A^{lm})(B^{pq} - B^{qr})(C^c)^2 + \\
 & + 2t(A_{kl} - A_{lm})(B_{pq} - B_{qr})CC^c - \quad (4) \\
 & - 2t(A_{kl} - A_{lm})(B_{pq}^r - B_{qr}^p)(C^c)^2 - \\
 & - 2t(A_{kl}^m - A_{lm}^k)(B_{pq} - B_{qr})(C^c)^2.
 \end{aligned}$$

In the case that A and B are isomorphic such that the bijections  $k \leftrightarrow p$ ,  $l \leftrightarrow q$ , and  $m \leftrightarrow r$  are part of a bijective mapping of A onto B or vice versa, eq. (4) finally takes the form

$$\begin{aligned} \Delta(x) = & [(A_{kl}^k - A_{lm}^m)C^C]^2 - \\ & - [(A_{kl}^{k1} - A_{lm}^{1m})C^C]^2 + \\ & + 2t(A_{kl} - A_{lm})^2 C^C - \\ & - 4t(A_{kl} - A_{lm})(A_{kl}^m - A_{lm}^k)(C^C)^2 . \end{aligned} \quad (5)$$

From this expression one cannot conclude that  $\Delta(x) \geq 0$  must hold in the complete range of  $x$ . Hence, no conclusion can be drawn concerning the non-appearance of inversions in the union of the MO eigenvalue patterns of the topologically related isomers S and T.

The model described here may be applied to a series of dinuclear-metal complexes of tetradentate ligands when the ligand consists of two moieties which are linked by only one bond and at least a pair of valence sites in the ligand are non-equivalent.

##### 5. Acknowledgment

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6. References

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[14] See for example "model 2" in [1], scheme 5 in [9], "model 2.1" in [10], or "model 2, l=2" in [11].

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