a manyfold excess of acetylene initially present) to produce a product ratio of 7.5:1.0:0.24:0.19:0.02 of *nido*-2,3-$C_2B_4H_8$, 3-CH_3-*nido*-2-CB_5H_8, 4-CH_3-*nido*-2-CB_5H_8, 2-CH_3-*nido* 2-CB_5H_8, and 1-CH_3-*nido*-2-CB_5H_8, respectively. This assessment is made after heating the sample at 225 °C and after ca. 15% of the initial quantity of pentaborane is still remaining. It is pertinent to note that the 3-CH_3-*nido*-2-CB_5H_8/4-CH_3-*nido*-2-CB_5H_8 ratio is 3.9 at the end of the last heating period. This ratio is 0.84 at the end of an earlier 215 °C heating period and a value of 1.6 at the end of a 220 °C intermediate heating period. (A very small amount of yellow-brown solid material is also produced during the reaction, and it is difficult to know whether or not some of this is a result of some product decomposition; see elsewhere in this paper). In a related study (see Introduction), flash thermolysis (355 °C) of 2-ethenyl-*nido*-B_5H_8 gives 2-CH_3-*nido*-2-CB_5H_8 (15%), 3-CH_3-*nido*-2-CB_5H_8 (23%), and 4-CH_3-*nido*-2-CB_5H_8 (13%).[22] Again, the 3-CH_3-*nido*-2-CB_5H_8 isomer predominates.

In this regard it is of some interest to note that MP2/6-31G*//3-21G+ZPE(3-21G) calculations (Table III) on all of the CH_3-*nido*-2-CB_5H_8 isomers indicate that the order of stabilities to be 3-CH_3-*nido*-2-CB_5H_8 > 4-CH_3-*nido*-2-CB_5H_8 > 1-CH_3-*nido*-2-CB_5H_8 > 2-CH_3-*nido*-2-CB_5H_8. In additional experiments carried out in the present study we discovered that 4-CH_3-*nido*-2-CB_5H_8 will slowly convert to 3-CH_3-*nido*-2-CB_5H_8 under the thermal conditions of its formation. Also, it appears that the 3-CH_3-*nido*-2-CB_5H_8 isomer can convert to 4-CH_3-*nido*-2-CB_5H_8 under the same conditions, but because slow *B*-CH_3-*nido*-2-CB_5H_8 decomposition is occuring simultaneously, it is not possible to achieve true equilibrium quantities. But by examination of the results from both rearrangement reactions, it seems suggestive that the equilibrium ratio at the rearrangement temperature of 225 °C is somewhere between 2:1 and 3.3:1.0 for the 3-CH_3-*nido*-2-CB_5H_8/4-CH_3-*nido*-2-CB_5H_8 ratio. The ratio suggested by MP2/6-31G*//3-21G+ZPE(3-21G) results is 1.9:1. When the calculations are carried out at the MP2/6-31G*//6-31-G+ZPE(6-31G) level, the ratio climbs slightly to 2.2:1. Everything considered, the agreement between the experimentally obtained and calculational approaches is rather good. There is no experimental evidence to suggest that either 1- or 2-CH_3-*nido*-2-CB_5H_8 enter into the equilibrium mixture pot. It does appear, though, that the 2-CH_3-*nido*-2-CB_5H_8 isomer, once produced, is more thermally stable toward further reaction than the *B*-CH_3-*nido*-2-CB_5H_8 isomers.

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A Topological Method for the Enumeration of Bridging Modes and Connectivity Patterns of the Clusters $M_mQ_nL_l$ with Four-Coordinate Metal Sites and $Q_{\mu_{2,3,4}}$ Bridging Atoms

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For the extensive family of metal clusters $M_mQ_nL_l$ containing four-coordinate metal (M) sites, n_a bridging atoms Q_{μ_a} (a = 2–4), and unidentate terminal ligands (L), a topological procedure for isomer enumeration using a matrix method has been developed. The method calculates all possible bridging modalities $[n_2,n_3,n_4]$ for a given formula, which are utilized to generate atom connectivity matrices that uniquely define structures. Because of the very large number of possible structures for $m \geq 4$, other constraints may be applied in order to afford sets of the more probable structures. The structures of 14 Fe_mQ_n clusters (Q = S, Se) taken as a data base indicate certain structural features of frequent occurrence which define these constraints: M_2Q_2 rhomb-only structures, uniterminal ligation, and rational stereochemistry (usually tetrahedral) at the M sites. The method is outlined and is tested and applied, under the various constraints, to clusters of assorted nuclearities. Bridging modalities are calculated for known and unknown structures with nuclearities m = 2–9 ($l \neq 0$) and for certain cyclic clusters (l = 0) of nuclearities m = 18 and 20. The constraints may be altered to include M sites of higher coordination number. The method rationalizes known structures, provides an organizational framework for all structures within its purview, and offers a basis for predicting potentially accessible new clusters. Among the latter are uncharacterized protein-bound iron–sulfur clusters and the cofactors of nitrogenase.

Introduction

An extensive family of metal clusters exists in which the constituent metal atoms are four-coordinate and are bridged by chalcogenide atoms to generate a core unit, M_mQ_n. The best known and most highly developed group within this family is composed of iron–sulfur or –selenium clusters, many of which have been studied extensively in this laboratory.[1–13] These clusters, which span the nuclearity range 2–20, present a diversity of geometric motifs that illustrate important structural principles.

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Table I. Possible Bridging Modalities[a] and Numbers of M_2Q_2 Rhombs in the Clusters $M_mQ_nL_l$ and Structurally Proven Examples (Q = S, Se, Te)

formula	$[n_2,n_3,n_4]$[a]	n_r[b]	examples[c]	n_r(obs)	ref
$M_nQ_{2n-2}L_4$	[2*n*–2,0,0]	*n* – 1	$[Fe_nQ_{2n-2}L_2]^{2-}$, *n* = 2 (**1**), 3 (**2**), 4 (**3**)	*n* – 1	1, 3, 12, 16
$M_3Q_4L_3$	[3,1,0]	3	$[Fe_3S_4(SR)_3]^{2-}$ (**4**)	3	17–19
$M_4Q_3L_7$	[0,3,0]	3, 4	$[Fe_4S_3(NO)_7]^-$ (**5**)	3	20
	[1,1,1]	3, 4			
$M_4Q_4L_4$	[0,4,0]	4–6	$[Fe_4Q_4L_4]^{1-,2-,3-}$ (**6**)	6	1, 6, 12, 21, 22
	[1,2,1]	4, 5			
	[2,0,2]	4, 5			
$M_6Q_6L_6$	[0,6,0]	6–9	$[Fe_6S_6L_6]^{2-,3-}$ (**7**)	6	23
	[1,4,1]	6–8	$Fe_6Q_6(PR_3)_4L_2$[d] (**8**)	6	5, 7
			$[Fe_6S_6(PEt_3)_6]^{+}$[d]		7c
	[2,2,2]	6–8			
	[3,0,3]	6, 7			
$M_6Q_9L_2$	[5,4,0]	7, 8			
	[6,2,1]	7, 8	$[Fe_6Q_9(SR)_2]^{4-}$ (**9**)	8	2, 24
	[7,0,2]	7			
$M_7Q_6L_7$	[0,3,3]	8–10	$Fe_7S_6(PEt_3)_4Cl_3$ (**10**)	9	4
	[1,1,4]	8–10			
$M_8Q_6L_8$	[0,0,6]	9–12	$[Fe_8S_6I_8]^{3-}$ (**11**)	12	25
$M_{18}Q_{30}$	[18,12,0]	21–27	$[\beta\text{-}Na_2Fe_{18}S_{30}]^{8-}$[d] (**12**)	24	13
	[19,10,1]	21–26			
	[20,8,2]	21–26	$[\alpha\text{-}Na_2Fe_{18}S_{30}]^{8-}$ (**13**)	22	8
	[21,6,3]	21–25			
	[22,4,4]	21–25			
	[23,2,5]	21–24			
	[24,0,6]	21–24			
$M_{20}Q_{38}$	[34,4,0]	21–23			
	[35,2,1]	21, 22			
	[36,0,2]	21, 22	$[Na_9Fe_{20}Se_{38}]^{9-}$ (**14**)	21	11, 13

[a] From eqs 1 and 2, with all M atoms four-coordinate and Q atoms μ_2, μ_3, or μ_4 bridging ligands. [b] From eq 3, for structures constructed entirely of M_2Q_2 rhombs. [c] Q = S and Se for all cases except **6**, for which Q = S, Se, and Te examples are known; L = RS^-, ArO^-, or halide. [d] Not a rhomb-only structure.

They range in structural complexity from the simple binuclear species $[Fe_2Q_2L_4]^{2-}$ (Q = S, Se; L = RS^-, ArO^-, halide),[1] to the *mono*cyclic cluster $[Na_2Fe_{18}S_{30}]^{8-}$,[8,13] and finally to *bi*cyclic $[Na_9Fe_{20}Se_{38}]^{9-}$.[11,13] The Fe_mQ_n cluster set is composed of 14 members of different structures that, however, are unified by several common features: (i) metal atoms exhibit (distorted) tetrahedral coordination; (ii) ligand bridge atoms occur in one or more of the multiplicities μ_2, μ_3, and μ_4; (iii) core structures are built up largely or exclusively from edge- and/or vertex-shared Fe_2Q_2 rhombs; (iv) except for the terminal metal atoms in $[Fe_nQ_{2n-2}L_4]^{n-}$, metal atoms form three or four Fe–Q core bonds and, in the presence of three such bonds, no more than one Fe–L terminal ligand bond with anionic unidentate ligands; and (v) metal–metal bonding is weak.

Feature i is a reflection of the tetrahedral stereochemical preference of four-coordinate Fe(II,III). Concerning feature iii, 12 of the 14 structural types are composed *entirely* of rhombs; elsewhere we have introduced the useful concept of cluster buildup by different patterns of rhomb fusion.[8] The four-coordination of feature iv, which includes uniterminal ligation, is set by the size and charge of anionic Q and L ligands; coordination numbers exceeding four have been achieved only with chelating,[9,14] cyclopentadienyl,[15] or small neutral ligands.[10] Feature v results in antiferromagnetic spin coupling of metal centers, but the Fe–Fe separations (≥2.7 Å), as well as the local open-shell electron configurations at the metal sites, are not consistent with strong metal–metal bonding. Consequently, iron atoms are not included in coordination numbers.

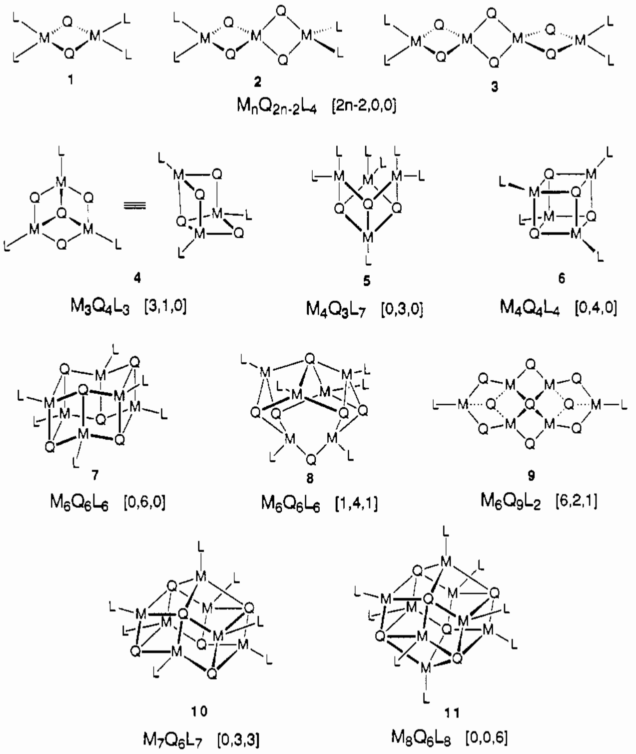

Figure 1. Structurally established $M_mQ_nL_l$ clusters **1–11** with nuclearity *m* ranging from 2 to 8. All structures are built up entirely of M_2Q_2 rhombs except **8**; examples are given in Table I.

The structural diversity of the Fe_mQ_n cluster group is apparent from depictions of all structurally characterized members **1–14** in Figures 1 and 2. Specific examples are provided in Table I.[1-9,11-13,16-25] These species are presented in terms of the gen-

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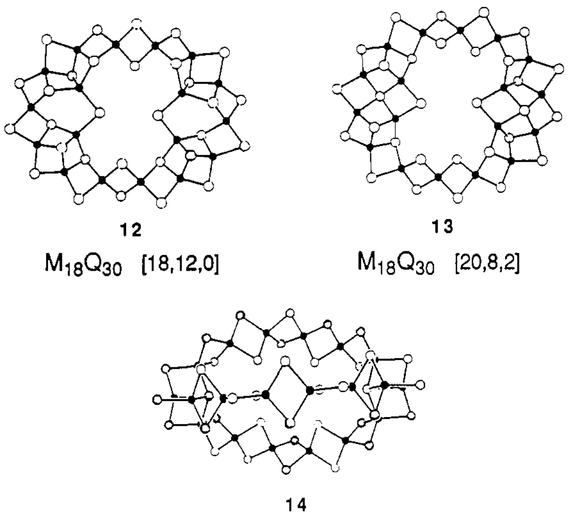

12 $M_{18}Q_{30}$ [18,12,0]

13 $M_{18}Q_{30}$ [20,8,2]

14 $M_{20}Q_{38}$ [36,0,2]

Figure 2. Structurally established $M_mQ_nL_l$ cyclic clusters ($l = 0$) with nuclearities 18 (**12**, **13**) and 20 (**14**).

eralized formula $M_mQ_nL_l$ inasmuch as the considerations that follow are not necessarily limited to these specific compounds. Note that two topological isomers of the formula $[Fe_6S_6L_6]^z$ have been prepared (although not in the same core oxidation state), the prismane[23] (**6**) and basket[7] (**7**) clusters. Further, $[Na_2Fe_{18}S_{30}]^{8-}$ has recently been demonstrated to occur as (at least) two isomers: the α-form (**13**) with 22 Fe_2S_2 rhombs and the bridging pattern $20\mu_2$-S + $8\mu_3$-S + $2\mu_4$-S[8] and the β-form (**12**) with 24 rhombs and the pattern $18\mu_2$-S + $12\mu_3$-S.[13] The uniqueness of the bridging mode combination of initially characterized $[\alpha\text{-}Na_2Fe_{18}S_{30}]^{8-}$ called for further examination of the reaction system affording this isomer and led to the discovery of a second isomer. The wide range of core structures and the occurrence of structural isomers raise the unsolved problem of enumeration of all possible structures for a given formula, $M_mQ_nL_l$. Structural features i–v reduce to a manageably narrow range the possible connectivity patterns of m metal sites bridged by n ligand atoms if the nuclearity m is not too large.

We introduce here a matrix method for enumerating all possible isomers of the clusters $M_mQ_nL_l$ under the conditions specified below. While our principal interest in species of this sort lies in the Fe_mQ_n cluster field, and examples from that field will be frequently employed, the topological principles involved in the method can be easily generalized to many other systems. The method generates skeletal connectivity patterns. It is not concerned with the correlation of structure with skeletal electron counts; consequently metal oxidation states and cluster charge need not be considered.

Topological Method

Definitions and Bridging Modality. Consider the clusters $M_mQ_nL_l$ in which metal atoms M are four-coordinate, M–M bonding is weak, bridging atoms Q have the μ_a bridging modes $a = 2$–4, n_a is the number of Q atoms with the mode μ_a, and L is a monodentate terminal ligand. Further, n_r is the number of Fe_2Q_2 rhombs, $[n_2,n_3,n_4]$ is the *bridging modality* of the structure, and Q–Q bonds are absent. For clusters that are not supported by strong metal–metal bonding, molecular topological closure requires that all bonds originating at the M atom terminate at either a bridging or terminal ligand atom. Thus, all possible connectivity patterns must meet the requirements of eqs 1 and 2. With the requirement that n_a values are integers, these

$$1 + 2n_2 + 3n_3 + 4n_4 = 4m \qquad (1)$$

$$n_2 + n_3 + n_4 = n \qquad (2)$$

equations provide a limited number of solutions and define the bridging modalities for a given formula.[26] Note that the parity (evenness, oddness) of n_a values is implied when rearranged forms of eqs 1 and 2 are examined: $n_3 + l = 2(2m - n - n_4)$ and $n_4 - n_2 = 2(2m - n) - (n + l)$, respectively. The first implies that n_3 and l should have the same parity; the second implies that n_2 and n_4 should have the same parity when $n + l$ is even and opposite parity when $n + l$ is odd. Collected in Table I are solutions of these equations as applied to selected formulas that correspond to Fe_mQ_n clusters of known structure.

For certain formulas, there is a unique bridging modality. Thus, it is $[2n-2,0,0]$ for $M_nQ_{2n-2}L_4$ (**1**–**3**), [3,1,0] for the site-voided cubane $M_3Q_4L_3$ (**4**), and [0,0,6] for stellated octahedral $M_8Q_6L_8$ (**11**). However, multiple solutions of eqs 1 and 2 are nearly always encountered and therefore indicate the possibility of structural isomers. In the case of $M_6Q_6L_6$, for instance, there are four bridging modalities. As already noted, two of these [0,6,0] and [1,4,1], have been realized in the form of prismane (**7**) and basket (**8**) clusters, respectively. These species have isomeric Fe_6S_6 cores. Clusters with the [2,2,2] and [3,0,3] modalities are unknown.

The number of bridging modalities is not necessarily equal to the number of isomers inasmuch as a given modality in general corresponds to more than one structure. Up to this point, the only constraints on structures are those of eqs 1 and 2. However, because the bond connectivity patterns that represent these structures frequently do not correspond to either structural precedent or stereochemical rationality at M sites or for the overall structure, we adopt from structural features i–v certain constraints on probable structures: (A) rhomb-only structures, (B) uniterminal ligation, and (C) rational stereochemistry. In the considerations that follow, some or all of these constraints may be applied to the cases examined.

Rhomb-Only Structures and the Number of M_2Q_2 Rhombs. The only exceptions to rhomb-only structures in Figure 1 are **8** and **13**, which contain two fused and two separate M_3Q_3 rings, respectively. Numerous other plausible structures can be anticipated from different rhomb-shared configurations.[8] It is, therefore, instructive as part of the topological structure description to determine the number of rhombs present in *rhomb-only* structures. This can be accomplished by analyzing the possible connectivity properties of Q atoms in a given bridging mode.

There is only one connectivity pattern for a Q_{μ_2} atom; each such atom contributes to a half-rhomb in **15**. For a Q_{μ_3} atom two connectivities, **16** and **17**, have been observed. The former occurs in the prismanes **7** and the latter in the cubanes **6** and other clusters. In **16** the Q_{μ_3} atom contributes to two half-rhombs and in **17** to three half-rhombs. For a Q_{μ_4} atom the two connectivities

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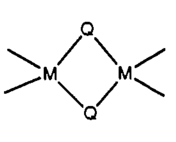
(26) These equations were solved using a computer program that searched through all possible combinations of allowed n_a values. As long as M–M bonds are not counted in the four bonds at each,M atom, the equations are valid for clusters with such bonds. Similarly, they apply to clusters with nonmonodentate ligands so long as l implies the number of monodentate ligand equivalents (e.g., 2 for a bidentate chelate) at a four-coordinate M atom.



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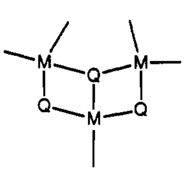

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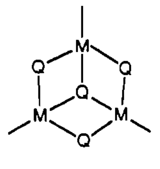

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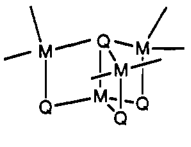

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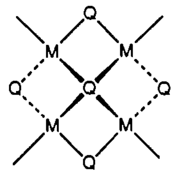

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18 and **19** have been established, in clusters **14** and **9**, respectively. This atom contributes to three half-rhombs in **18** and four half-rhombs in **19**. For a given structure, the total number of M_2Q_2 rhombs follows from the contributions of all Q atoms to rhomb-sharing. Thus, for a given bridging modality, the possible number of rhombs n_r will fall in a range whose minimum value is set by all Q_{μ_3} and Q_{μ_4} atoms assuming connectivities with the least contributions, and whose maximum value arises from the inverse situation. The result is expressed by eq 3, where the truncation function Int and the additive term 0.5 are entered to ensure integer results in consideration of the fact that a rhomb-only structure must contain an integral number of rhombs.[27]

$$\mathrm{Int}(0.5n_2 + n_3 + 1.5n_4 + 0.5) \le n_r \le \mathrm{Int}(0.5n_2 + 1.5n_3 + 2n_4) \quad (3)$$

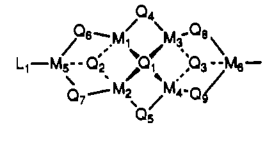
When the inequality is applied to the formulas in Table I, the observed value n_r(obs) for known structures is the calculated value or is included in the range of calculated values. Bridge modalities and rhomb numbers for other cluster formulas are presented in Tables II and III; rhomb numbers do not necessarily imply stereochemically rational structures. With eqs 1–3, a rhomb-only structure for a given formula is uniquely determined in favorable cases. For example, the unique bridging modality $[2n-2,0,0]$ and value $n_r = n - 1$ require the M-vertex-shared linear structures **1**–**3**, ... for $M_mQ_{n-1}L_n$ (n = 2–4, ...). For other cases, a comprehensive method is required to derive all possible structures.

Connectivity Matrices and Their Topological Validity Conditions. Each unique structure has an associated topological bond connectivity pattern. A structure is described by a connectivity matrix C of dimension $m \times (n + l)$ with its elements $C_{ij} = 1$ when M_i is bonded to Q_j or L_j, and zero otherwise. For example, the connectivity matrix in (4) for $M_6Q_9L_2$ with bridging modality [6,2,1] is readily formulated. The concept of a connectivity matrix is parallel to that of an adjacency matrix in graph theory[28] except that C is a block submatrix of the latter and therefore is generally not square. Topological closure imposes the conditions of eq 5, every M atom is four-coordinate, and of eq 6, every Q atom forms a number of M–Q bonds equal to its bridging multiplicity.

Table II. Possible Bridging Modalities and Numbers of M_2Q_2 Rhombs in the Clusters $M_6Q_{5-8}L_{4-10}$

formula[a]	$[n_2,n_3,n_4]$, n_r[b]
$M_6Q_5L_4$	[0,0,5], 8–10
$M_6Q_5L_5$	[0,1,4], 7–9
$M_6Q_5L_6$	[0,2,3], 7–9; [1,0,4], 7, 8
$M_6Q_5L_7$	[0,3,2], 6–8; [1,1,3], 6–8
$M_6Q_5L_8$	[0,4,1], 6–8; [1,2,2], 6, 7; [2,0,3], 6, 7
$M_6Q_5L_9$	[0,5,0], 5–7; [1,3,1], 5–7; [2,1,2], 5, 6
$M_6Q_5L_{10}$	[1,4,0], 5, 6; [2,2,1], 5, 6; [3,0,2], 5
$M_6Q_6L_4$	[0,4,2], 7–10; [1,2,3], 7–9; [2,0,4], 7–9
$M_6Q_6L_5$	[0,5,1], 7–9; [1,3,2], 7–9; [2,1,3], 7, 8
$M_6Q_6L_7$	[1,5,0], 6–8; [2,3,1], 6, 7; [3,1,2], 6, 7
$M_6Q_6L_8$	[2,4,0], 5–7; [3,2,1], 5, 6; [4,0,2], 5, 6
$M_6Q_6L_9$	[3,3,0], 5, 6; [4,1,1], 5
$M_6Q_6L_{10}$	[4,2,0], 4, 5; [5,0,1], 4
$M_6Q_7L_4$	[1,6,0], 7–9; [2,4,1], 7–9; [3,2,2], 7, 8; [4,0,3], 7, 8
$M_6Q_7L_5$	[2,5,0], 6–8; [3,3,1], 6–8; [4,1,2], 6, 7
$M_6Q_7L_6$	[3,4,0], 6, 7; [4,2,1], 6, 7; [5,0,2], 6
$M_6Q_7L_7$	[4,3,0], 5, 6; [5,1,1], 5, 6
$M_6Q_7L_8$	[5,2,0], 5; [6,0,1], 5
$M_6Q_7L_9$	[6,1,0], 4
$M_6Q_7L_{10}$	[7,0,0][c]
$M_6Q_8L_4$	[4,4,0], 6–8; [5,2,1], 6, 7; [6,0,2], 6, 7
$M_6Q_8L_5$	[5,3,0], 6, 7; [6,1,1], 6
$M_6Q_8L_6$	[6,2,0], 5, 6; [7,0,1], 5
$M_6Q_8L_7$	[7,1,0], 5
$M_6Q_8L_8$	[8,0,0], 4
$M_6Q_8L_9$	none
$M_6Q_8L_{10}$	none

[a] Formula $M_6Q_nL_l$ is equivalent to $M'M_5Q_nL_{l+2}$ when one four-coordinate M is replaced by six-coordinate M′. [b] Note the restrictions in ref 27 on the calculated values of n_r. [c] No possible rhomb-only structure.



9

$$\begin{array}{cc|cccccc|cc}
 & & M_1 & M_2 & M_3 & M_4 & M_5 & M_6 & & \text{sum} \\
\mu_4 & Q_1 & 1 & 1 & 1 & 1 & 0 & 0 & \rightarrow & 4 \\
\hline
\mu_3 & Q_2 & 1 & 1 & 0 & 0 & 1 & 0 & \rightarrow & 3 \\
 & Q_3 & 0 & 0 & 1 & 1 & 0 & 1 & & \\
\hline
\mu_2 & Q_4 & 1 & 0 & 1 & 0 & 0 & 0 & \rightarrow & 2 \\
 & Q_5 & 0 & 1 & 0 & 1 & 0 & 0 & & \\
 & Q_6 & 1 & 0 & 0 & 0 & 1 & 0 & & \\
 & Q_7 & 0 & 1 & 0 & 0 & 1 & 0 & & \\
 & Q_8 & 0 & 0 & 1 & 0 & 0 & 1 & & \\
 & Q_9 & 0 & 0 & 0 & 1 & 0 & 1 & & \\
\hline
L(\mu_1) & L_1 & 0 & 0 & 0 & 0 & 1 & 0 & \rightarrow & 1 \\
 & L_2 & 0 & 0 & 0 & 0 & 0 & 1 & & \\
\hline
\text{sum} & & \multicolumn{6}{c|}{\downarrow\ 4} & &
\end{array} \quad (4)$$

$$\sum_{j=1}^{n+l} C_{ij} = 4 \qquad i = 1, 2, ..., m \quad (5)$$

$$\sum_{i=1}^{m} C_{ij} = a \quad (6)$$

$$j = 1, 2, ..., n, n + 1, ..., n + l;$$
$$a = 2\text{–}4 \text{ for } Q_{\mu_a} \text{ and } 1 \text{ for L}$$

Derivation of a complete set of valid connectivity matrices will exhaust all possible structures for a given bridging modality of a particular formula. However, permutated matrices that correspond to a given structure but differ in the atom numbering scheme must be eliminated in order to obtain a nonredundant set of structures. For example, exchanges of sequence numbers for atoms M_1 and M_2, or Q_1 and Q_2, or a combination of these operations will result in three matrices different from the original, but representing an identical structure. These matters are considered next.

Reduced Connectivity Matrix. In formulating C matrices, Q atoms are arranged, and atom numbers increase, in descending rows in the order μ_4, μ_3, μ_2, and μ_1(L), as in matrix 4. Permutation of Q atoms can only be performed within the same *class* of Q's, viz., those with a given multiplicity. If a C matrix is divided into submatrices according the μ_a values and the elements C_{ij} of each

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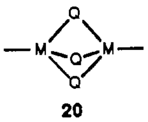
(27) The Q atom connectivity patterns considered here are limited to those that actually occur in Fe_mQ_n clusters, and do *not* include all possible situations. For example, the pattern **20** is conceivable; while unknown



20

in chalcogenide clusters, it is of some occurrence in bridged halide compounds (Q = halide). Further, when Q_{μ_2} is part of *two* rhombs with Q_{μ_3} and/or Q_{μ_4} atoms, a feasible but unknown structural situation, eq 3 may not predict the entire range of rhomb numbers. Examples include **23**–**25** in Figure 3 which have 6 rhombs vs n_r = 4 and 5 from eq 3. This equation can be recast to include structurally unproven bridging situations such as these, but the range of n_r expands and becomes less useful.

(28) (a) Randić, M. *J. Phys. Chem.* **1974**, *60*, 3920. (b) Mackay, A. L. *J. Phys. Chem.* **1975**, *62*, 308.

Table III. Possible Bridging Modalities and Numbers of M_2Q_2 Rhombs in the Clusters $M_{7-9}Q_{8-10}L_{4-7}$

formula[a]	$[n_2,n_3,n_4]$, n_r[b]
$M_7Q_8L_4$	[0,8,0], 8–12; [1,6,1]; 8–11; [2,4,2], 8–11; [3,2,3], 8–10; [4,0,4], 8–10
$M_7Q_8L_5$	[1,7,0], 8–11; [2,5,1]; 8–10; [3,3,2], 8–10; [4,1,3], 8, 9
$M_7Q_8L_6$	[2,6,0], 7–10; [3,4,1]; 7–9; [4,2,2], 7–9; [5,0,3], 7, 8
$M_7Q_8L_7$	[3,5,0], 7–9; [4,3,1]; 7, 8; [5,1,2], 7, 8
$M_7Q_9L_4$	[3,6,0], 8–10; [4,4,1]; 8–10; [5,2,2], 8, 9; [6,0,3], 8, 9
$M_7Q_9L_5$	[4,5,0], 7–9; [5,3,1]; 7–9; [6,1,2], 7, 8
$M_7Q_9L_6$	[5,4,0], 7, 8; [6,2,1]; 7, 8; [7,0,2], 7
$M_7Q_9L_7$	[6,3,0], 6, 7; [7,1,1]; 6, 7
$M_7Q_{10}L_4$	[6,4,0], 7–9; [7,2,1]; 7, 8; [8,0,2], 7, 8
$M_7Q_{10}L_5$	[7,3,0], 7, 8; [8,1,1], 7
$M_7Q_{10}L_6$	[8,2,0], 6, 7; [9,0,1], 6
$M_7Q_{10}L_7$	[9,1,0], 6
$M_8Q_8L_4$	[0,4,4], 10–14; [1,2,5], 10–13; [2,0,6], 10–13
$M_8Q_8L_5$	[0,5,3], 10–13; [1,3,4], 10–13; [2,1,5], 10–12
$M_8Q_8L_6$	[0,6,2], 9–13; [1,4,3], 9–12; [2,2,4], 9–12; [3,0,5], 9–11
$M_8Q_8L_7$	[0,7,1], 9–12; [1,5,2], 9–12; [2,3,3], 9–11; [3,1,4], 9–11
$M_8Q_9L_4$	[0,8,1], 10–14; [1,6,2], 10–13; [2,4,3], 10–13; [3,2,4], 10–12; [4,0,5], 10–12
$M_8Q_9L_5$	[0,9,0], 9–13; [1,7,1], 9–13; [2,5,2], 9–12; [3,3,3], 9–12; [4,1,4], 9–11
$M_8Q_9L_6$	[1,8,0], 9–12; [2,6,1], 9–12; [3,4,2], 9–11; [4,2,3], 9–11; [5,0,4], 9, 10
$M_8Q_9L_7$	[2,7,0], 8–11; [3,5,1], 8–11; [4,3,2], 8–10; [5,1,3], 8–10
$M_8Q_{10}L_4$	[2,8,0], 9–13; [3,6,1], 9–12; [4,4,2], 9–12; [5,2,3], 9–11; [6,0,4], 9–11
$M_8Q_{10}L_5$	[3,7,0], 9–12; [4,5,1], 9–11; [5,3,2], 9–11; [6,1,3], 9–10
$M_8Q_{10}L_6$	[4,6,0], 8–11; [5,4,1], 8–10; [6,2,2], 8–10; [7,0,3], 8, 9
$M_8Q_{10}L_7$	[5,5,0], 8–10; [6,3,1], 8, 9; [7,1,2], 8, 9
$M_9Q_8L_4$	[0,0,8], 12–16
$M_9Q_8L_5$	[0,1,7], 12–15
$M_9Q_8L_6$	[0,2,6], 11–15; [1,0,7], 11–14
$M_9Q_8L_7$	[0,3,5], 11–14; [1,1,6], 11–14
$M_9Q_9L_4$	[0,4,5], 12–16; [1,2,6], 12–15; [2,0,7], 12–15
$M_9Q_9L_5$	[0,5,4], 11–15; [1,3,5], 11–15; [2,1,6], 11–14
$M_9Q_9L_6$	[0,6,3], 11–15; [1,4,4], 11–14; [2,2,5], 11–14; [3,0,6], 11–13
$M_9Q_9L_7$	[0,7,2], 10–14; [1,5,3], 10–14; [2,3,4], 10–13; [3,1,5], 10–13
$M_9Q_{10}L_4$	[0,8,2], 10–16; [1,6,3], 11–15; [2,4,4], 11–15; [3,2,5], 11–14; [4,0,6], 11–14
$M_9Q_{10}L_5$	[0,9,1], 11–15; [1,7,2], 11–15; [2,5,3], 11–14; [3,3,4], 11–14; [4,1,5], 11–13
$M_9Q_{10}L_6$	[0,10,0], 10–15; [1,8,1], 10–14; [2,6,2], 10–14; [3,4,3], 10–13; [4,2,4], 10–13; [5,0,5], 10–12
$M_9Q_{10}L_7$	[1,9,0], 11–14; [2,7,1], 10–13; [3,5,2], 10–13; [4,3,3], 10–12; [5,1,4], 10–12

[a] Formula $M_6Q_nL_l$ is equivalent to $M'M_5Q_nL_{l+2}$ when one four-coordinate M is replaced by six-coordinate M′. [b] Note the restrictions in ref 27 on the calculated values of n_r.

submatrix are summed along each column, a quantity independent of the permutation of Q and L atoms is obtained. This quantity **R**, the *reduced connectivity matrix*, is defined by eq 7, where the

$$R_{i,5-a} = \sum_{j}^{n_a} C_{ij} \qquad a = 1\text{–}4 \tag{7}$$

subscript 5 – *a* denotes that the first row of **R** is for Q_{μ_4}, etc., and the summation is over each class of Q or over L. For [6,2,1]-$M_6Q_9L_2$, the **R** matrix (8) expresses the number of Q_{μ_a} and L atoms bound to M_{1-6}.

$$\begin{pmatrix} 1 & 1 & 1 & 1 & 0 & 0 \\ 1 & 1 & 1 & 1 & 1 & 1 \\ 2 & 2 & 2 & 2 & 2 & 2 \\ 0 & 0 & 0 & 0 & 1 & 1 \end{pmatrix} \tag{8}$$

With recognition of the concept of a reduced connectivity matrix, the task of deriving connectivity matrices **C** for all possible configurations is reduced to two steps: obtain all possible **R** matrices for a particular bridging modality and expand **R** matrices into **C** matrices.

The introduction of **R** matrices eliminates all possible permutations along the Q/L rows. We next eliminate column-permuted **R** matrices by setting a descending order rule following the idea of Randic's method.[28] If we read down each column of **R** as a four-digit number and term that number e_i, a valid **R** matrix must conform to eq 9. Any matrix violating this condition will be

$$e_1 \geq e_2 \geq \ldots \geq e_m \tag{9}$$

transformable by permutation of columns into a unique matrix satisfying eq 9. To derive all possible valid **R** matrices, it is necessary to specify validity or *boundary* conditions, restricting **R**'s for a given bridging modality. A valid **R** matrix meets the conditions of eqs 10 and 11, which specify the sum of each column and row, respectively. The possible minimum and maximum (the lesser of 4 or n_{μ_a}) of any element is $0 \leq R_{i,5-a} \leq \min(4,n_a)$. A matrix **B** is introduced to represent the boundary conditions; such a matrix (eq 12) defines a complete set of **R** matrices for a given bridging modality.

$$\sum_{a=4}^{1} R_{i,5-a} = 4 \qquad i = 1, 2, \ldots, m \tag{10}$$

$$\sum_{i=1}^{m} R_{i,5-a} = an_a \qquad a = 1\text{–}4 \tag{11}$$

$$\mathbf{B} = \begin{bmatrix} \min(4,n_4), & 4 \times n_4 \\ \min(4,n_3), & 3 \times n_3 \\ \min(4,n_2), & 2 \times n_2 \\ \min(4,l), & l \end{bmatrix} \tag{12}$$

With the permutation problem solved and the validity conditions for **R** matrices specified, a procedure can be established to obtain all possible valid **R**'s for a given bridging modality of a particular formula. It starts with the first row for Q_{μ_4} and then subsequent rows for Q_{μ_3}, Q_{μ_2}, and L and derives all possible patterns of four rows that meet the descending order rule and the boundary conditions. A detailed description of the procedure is given in the Appendix. Here we provide a brief illustration in Scheme I using one of the three bridging modalities, [1,2,1], of $M_4Q_4L_4$. In this case, five valid **R** matrices are found. We note that one necessary condition for a structure to be constructed entirely of M_2Q_2 rhombs (rhomb-only structure) is that the element $R_{i4} \leq 2$ (i = 1, 2, ..., m); i.e., no M site may have more than two terminal ligands. The requirement for one such ligand is $R_{i4} \leq 1$. Matrix $\mathbf{R}_1$ contains the element $R_{44} = 3$, meaning that it corresponds to a structure not completely built of rhombs, and so it is considered

Scheme I. **R** and **C** Matrices for $[M_4Q_4L_4]^{Z-}$

Bridging Modality: [1,2,1]

$$\text{Boundary Conditions: } \mathbf{B} = \begin{bmatrix} 1,4 \\ 2,6 \\ 1,2 \\ 4,4 \end{bmatrix}$$

R matrices:

$$\underset{\substack{\mathbf{R}_1 \\ \text{(non-rhomb-} \\ \text{only)}}}{\begin{pmatrix} 1&1&1&1 \\ 2&2&2&0 \\ 1&1&0&0 \\ 0&0&1&3 \end{pmatrix}} \quad \underset{\mathbf{R}_2}{\begin{pmatrix} 1&1&1&1 \\ 2&2&2&0 \\ 1&0&0&1 \\ 0&1&1&2 \end{pmatrix}} \quad \underset{\mathbf{R}_3}{\begin{pmatrix} 1&1&1&1 \\ 2&2&1&1 \\ 1&1&0&0 \\ 0&0&2&2 \end{pmatrix}} \quad \underset{\mathbf{R}_4}{\begin{pmatrix} 1&1&1&1 \\ 2&2&1&1 \\ 1&0&1&0 \\ 0&1&1&2 \end{pmatrix}} \quad \underset{\mathbf{R}_5}{\begin{pmatrix} 1&1&1&1 \\ 2&2&1&1 \\ 0&0&1&1 \\ 1&1&1&1 \end{pmatrix}}$$

$$\downarrow \qquad \downarrow \qquad \downarrow \qquad \downarrow$$

C matrices:

$$\underset{\substack{\mathbf{C}_1 \\ \mathbf{26}}}{\begin{vmatrix} 1&1&1&1 \\ 1&1&1&0 \\ 1&1&1&0 \\ 1&0&0&1 \\ 0&1&0&0 \\ 0&0&1&0 \\ 0&0&0&1 \\ 0&0&0&1 \end{vmatrix}} \quad \underset{\substack{\mathbf{C}_2 \\ \mathbf{27}}}{\begin{vmatrix} 1&1&1&1 \\ 1&1&1&0 \\ 1&1&0&1 \\ 1&1&0&0 \\ 0&0&1&0 \\ 0&0&1&0 \\ 0&0&0&1 \\ 0&0&0&1 \end{vmatrix}} \quad \underset{\substack{\mathbf{C}_3 \\ \mathbf{28}}}{\begin{vmatrix} 1&1&1&1 \\ 1&1&1&0 \\ 1&1&0&1 \\ 1&0&1&0 \\ 0&1&0&0 \\ 0&0&1&0 \\ 0&0&0&1 \\ 0&0&0&1 \end{vmatrix}} \quad \underset{\substack{\mathbf{C}_4 \\ \mathbf{29}}}{\begin{vmatrix} 1&1&1&1 \\ 1&1&1&0 \\ 1&1&0&1 \\ 0&0&1&1 \\ 1&0&0&0 \\ 0&1&0&0 \\ 0&0&1&0 \\ 0&0&0&1 \end{vmatrix}}$$

$$\swarrow \qquad \searrow$$

$$\underset{\mathbf{S}^{\mathbf{M}}_1}{\begin{pmatrix} 4&3&3&2 \\ 3&3&3&1 \\ 3&3&3&1 \\ 2&1&1&2 \end{pmatrix}} \quad \underset{\mathbf{S}^{\mathbf{Q}}_1}{\begin{pmatrix} 4&3&3&2 \\ 3&3&3&1 \\ 3&3&3&1 \\ 2&1&1&2 \end{pmatrix}} \quad \underset{\mathbf{S}^{\mathbf{M}}_2}{\begin{pmatrix} 4&4&2&2 \\ 4&4&2&2 \\ 2&2&2&1 \\ 2&2&1&2 \end{pmatrix}} \quad \underset{\mathbf{S}^{\mathbf{Q}}_2}{\begin{pmatrix} 4&3&3&2 \\ 3&3&2&2 \\ 3&2&3&2 \\ 2&2&2&2 \end{pmatrix}}$$

less likely to correspond to a real structure than the other four. These rhomb-only structures are illustrated in Figure 3 as **26–29**, together with rhomb-only structures **6** and **21–25** for the two other bridging modalities of $M_4Q_4L_4$. Note that two of the structures (**27**, **29**) can be immediately identified from the fourth (n_1) row of the **R** matrices.

With a complete set of **R** matrices and the two conditions on R_{i4}, it is not unusual that a few definite structures, and even a unique structure, can be determined by the procedures up to this point. For example, $M_8Q_6L_8$ has only one bridging modality, for which there is only one valid **R** matrix, (13), under constraint B.

$$\begin{pmatrix} 3&3&3&3&3&3&3&3 \\ 0&0&0&0&0&0&0&0 \\ 0&0&0&0&0&0&0&0 \\ 1&1&1&1&1&1&1&1 \end{pmatrix} \tag{13}$$

Consequently, each M atom must be bound to three Q_{μ_4} atoms and one terminal ligand. It is not difficult to recognize that the stellated octahedron **11** is the only possible structure that meets the connectivity requirement and is stereochemically rational.

For clarity in the exposition of the topological method, **C** matrices were introduced first and then compressed to **R** matrices, which follow from the boundary condition matrix **B**. However, in applications of the method the process is reversed, as in Scheme I. The **B** matrix is readily written down from the bridging modality, and the **R** matrices developed thereafter. In expanding the latter to **C** matrices, which in the general case are required for structure recognition because they convey atom connectivities, the permutation problem arises again. The method for expansion of **R** to **C** matrices is described in the Appendix.

Criterion for Rhomb-Only Structures. Consider two square matrices, S^M with dimensions $m \times m$ and S^Q with dimensions $n \times n$, termed *sharing* matrices for M and Q atoms, respectively. These are defined as the left and right product of the M–Q part of a **C** matrix and its transpose, eqs 14 and 15, respectively. These

$$S^M_{ij} = \sum_{k=1}^{n} C_{ik}C_{jk} \quad i, j = 1, 2, ..., m \tag{14}$$

$$S^Q_{ij} = \sum_{k=1}^{m} C_{ki}C_{kj} \quad i, j = 1, 2, ..., n \tag{15}$$

matrices are diagonally symmetric; the structural meaning of S^M is the number of Q atoms shared by M_i and M_j, and of S^Q the number of M atoms shared by Q_i and Q_j. The necessary and sufficient condition for a rhomb-only structure is that the S^M and S^Q matrices corresponding to a given C matrix must contain one nondiagonal element no less than 2 in every column or row. In other words, every M atom must share no less than two Q atoms with another M atom, and conversely. In Scheme I, S^M and S^Q matrices for the two connectivity matrices corresponding to structures **26** and **27** are provided as examples.

The topological method is capable of specifying bridge modalities and, in principle, all possible structures for $M_mQ_nL_l$ under the constraints of eqs 1 and 2 and conditions for valid connectivity matrices. The number of such structures becomes enormously large as m increases, and the method becomes impractical, particularly if all connectivity patterns are required. However, under the constraints A–C, the number of possible structures reduces to a manageable number for at least some formulas of current interest. In the following section, the procedure is used to examine the structural chemistry of known and unknown Fe_mQ_n and related clusters.

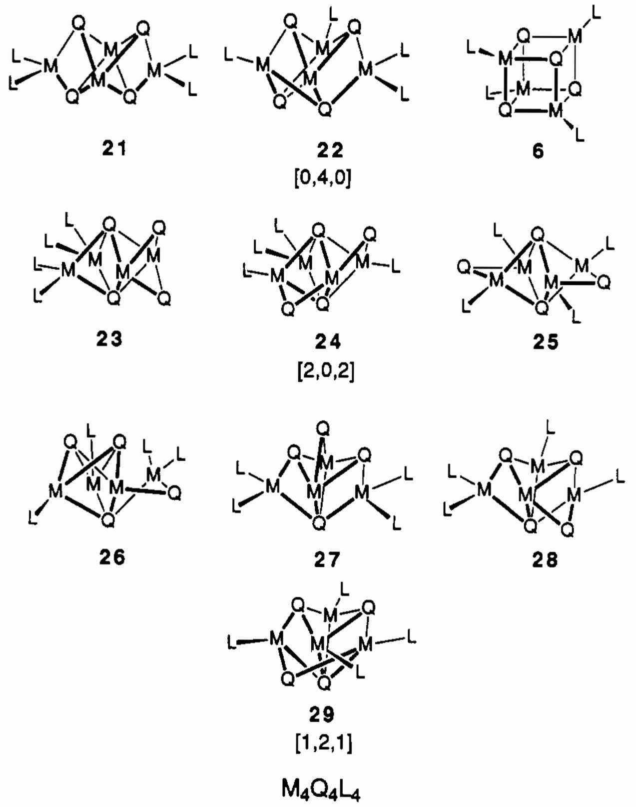


Figure 3. The rhomb-only structures **6** and **21–29** for the three bridging modalities of $M_4Q_4L_4$; only structures **6** and **25** have been prepared.

Applications

Selected cases are considered with the aid of Tables I–III, which contain bridging modalities and rhomb numbers,[27] Figures 1 and 2, which summarize known structures, and Figures 3–6, which depict structures deduced from the topological method. In view of our interest in Fe_mQ_n clusters, the majority of cases involve tetrahedral M sites. The structures considered for each case are constrained to the rhomb-only type unless noted otherwise. Many of these could not be constructed with one or more planar M sites. As will be seen, the experimental structure is without exception included in the possible set of structures generated by the method.

1. $\mathbf{M_nQ_{2n-2}L_4}$. For a given n value, the bridging modality $[2n-2,0,0]$ and rhomb number $n_r = n - 1$ are unique and uniterminal ligation is not possible. Structures are formed by M-vertex sharing; homo- and/or heteronuclear clusters with $n = 2$–6 have been prepared. All known compounds with this general formula are rhomb-only and manifest these structural features.

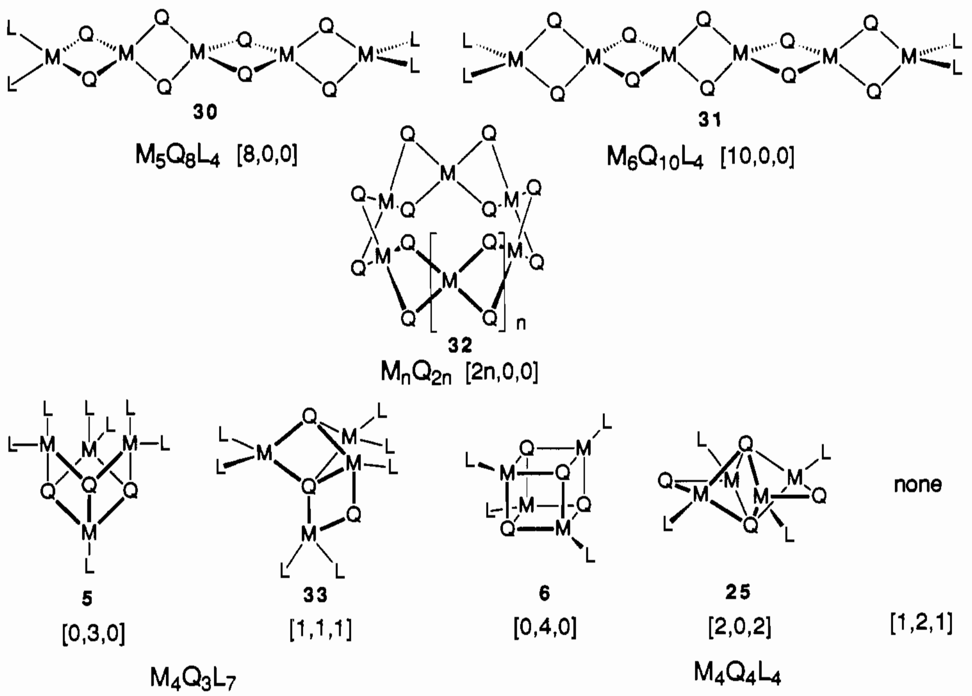


Figure 4. All possible rational rhomb-only structures for $M_5Q_8L_4$ (**30**), $M_6Q_{10}L_4$ (**31**), M_nQ_{2n} (**32**), $M_4Q_3L_7$ (**5**, **33**), and $M_4Q_4L_4$ (**6**, **25**); bridging modalities are indicated.

The most widely observed examples are those with $n = 2$ (**1**) such as $[Fe_2Q_2L_4]^{2-}$ [1,12] and $[S_2MS_2FeL_2]^{2-}$ (M = Mo, W),[29] in which both metal centers are tetrahedral. The structures of numerous examples of linear clusters with nuclearities $n \geq 2$ have been summarized;[30,31] some of these are presented below.

a. $M_3Q_4L_4$ (2). Over 50 structural examples of linear trinuclear clusters have been reported. Examples include $[Fe_3Q_4L_4]^{3-}$,[3,12] $[Cl_2FeS_2VS_2FeCl_2]^{3-}$,[32] $[S_2MS_2FeS_2MS_2]^{3-}$,[33] and $Cl_2HgCl_2MCl_2HgCl_2$ in which the M = Pd and Pt sites are planar.[34] Bridging atoms in any structure may also be part of a chelate ring, as found in this group for $[Ni_3(SR)_8]^{2-}$ complexes with Ni-vertex-shaped rhombs and planar coordination.[35]

b. $M_4Q_6L_4$ (3). Linear tetranuclear clusters of this formula include $[Fe_4S_6(SR)_4]^{4-}$ [16] and $[Fe_2S_2(WS_4)_2]^{4-}$,[36] with tetrahedral metal sites, and planar $[Cu_4X_{10}]^{2-}$ ($X = Cl^-$, Br^-).[37]

c. $M_5Q_8L_4$ (30). The linear four-rhomb structure is uncommon, one of the few examples being planar $Cu_5Cl_{10}(PrOH)_2$.[38]

d. $M_6Q_{10}L_4$ (31). The linear five-rhomb structure is rare. The ion $[Ge_6Se_{14}]^{10-}$, which has been isolated as its Cs^+ salt from a high-temperature reaction, possesses a linear arrangement of the six germanium atoms in a structure in which selenide atoms act as bridging and terminal ligands.[39] The complex $[Ni_6(S_2C_3H_6)_7]^{2-}$ contains two terminal and five bridging propane-1,3-dithiolate ligands.[35] Because of nonzero dihedral angles between planar NiS_4 units, the nickel atoms are not linearly disposed but rather occur in a severely bent one-dimensional chain.

2. M_nQ_{2n}. For these generalized species the bridging modality [2*n*,0,0] and $n_r = n$ are unique. Structures are necessarily rhomb-only and cyclic, as illustrated with **32** (Figure 4), and appear to be possible only with $n \geq 4$. A set of $Ni_n(SR)_{2n}$ species with $n = 4$–6 and 8 and planar rhombs is known.[40]

3. $M_3Q_4L_3$. This formula corresponds to one bridging modality, [3,1,0], and one structure, the M-voided cuboidal entity **4**. While this M_3Q_4 core structure is of considerable occurrence in compounds of six-coordinate M(IV),[41] it is known only in the form of $[M_3Q(SR)_6]^{2-}$ (M = Fe, Co)[42] and the protein-bound clusters $Fe_3S_4(S(Cys))_3$ for four-coordinate metal atoms.

4. $M_4Q_3L_7$. Only two bridging modalities are possible, [0,3,0] and [1,1,1]. The former is compatible only with the Q-voided cuboidal structure **5**, which is found with $[Fe_4S_3(NO)_7]^-$ and $Fe_4S_3(NO)_4(PPh_3)_3$.[43] The latter modality uniquely corresponds to structure **33** (Figure 4), which has not been synthesized.

5. $M_4Q_4L_4$. Collected in Figure 3 are the 10 possible structures for the three bridging modalities. Among them, only **6** and **25** meet the condition that all M atom sites in a given structure have a rational stereochemistry.[44] The cubane structure **6** has been

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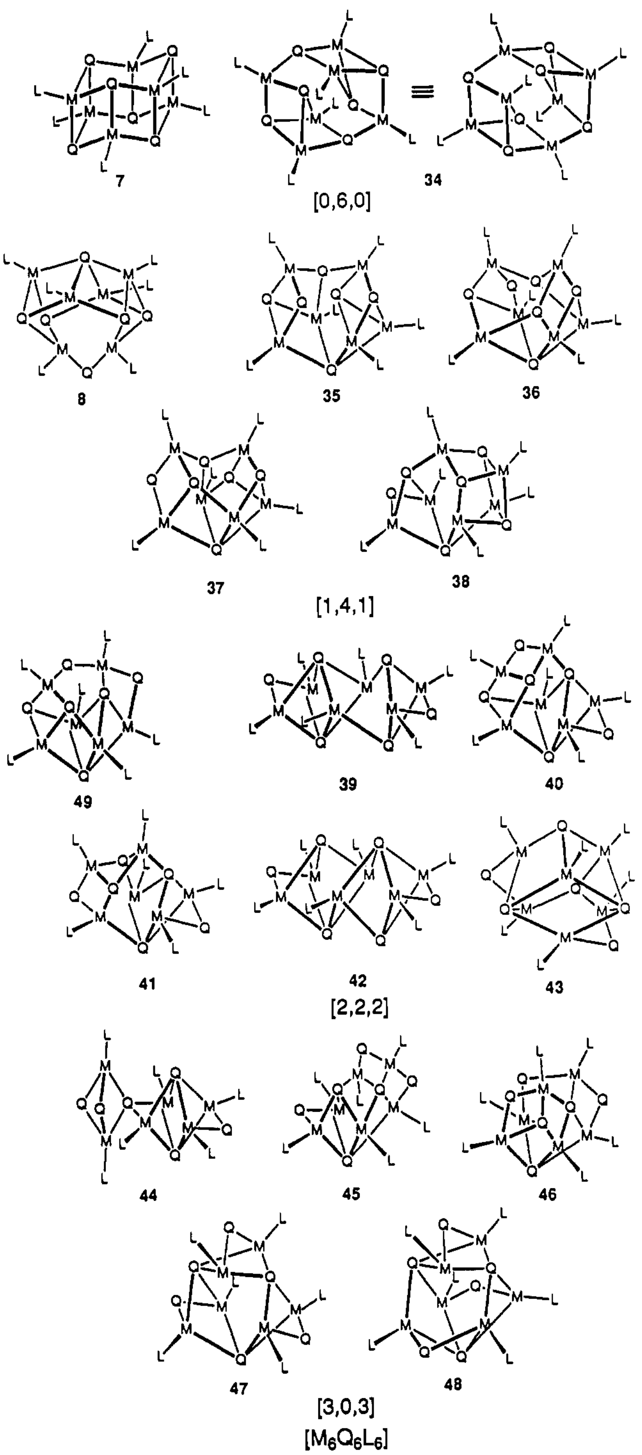

Figure 5. All possible rational structures with uniterminal ligation for the four bridging modalities of $M_6Q_6L_6$. The set includes rhomb-only (**34**–**48**) and non-rhomb-only (**8**, **49**) structures; only the prismane structure **7** and the basket structure **8** have been prepared.

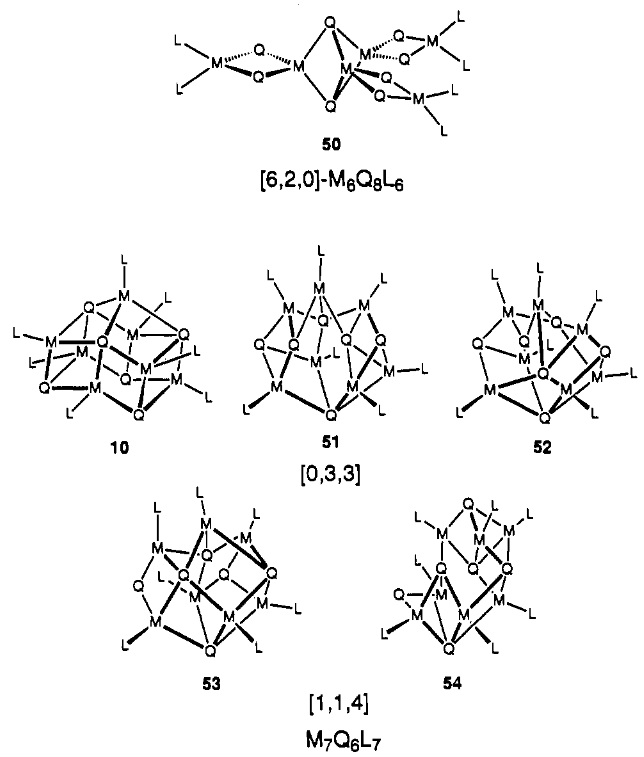

Figure 6. A rational rhomb-only structure for [6,2,0]-$M_6Q_8L_6$ (**50**) and all possible rational rhomb-only structures with uniterminal ligation for the two bridging modalities of $M_6Q_6L_7$ (**10**, **51**–**54**). Trigonal cluster **50** and the monocapped prismane **10** have been prepared.

established in over 100 cases, ranging from the homonuclear chalcogenide-bridged examples in Table I to such compounds as halide-bridged $M_4Br_4(PEt_3)_4$ (M = Cu, Ag),[45] methoxide-bridged $Zn_4(OMe)_4Me_4$,[46] and heteronuclear $MCu_3S_4Cl(PPh_3)_3$.[47] The bicapped planar structure **25** of idealized D_{2h} symmetry has thus far been demonstrated only for $Ag_4Br_4(MeN(PPh_2)_2)_2$,[48] which contains distorted tetrahedral Ag(I). There is a proven isomer of the ubiquitous cubane core, viz., "stepped" $M_4(Q_{\mu_3})_2(Q_{\mu_2})_2$ as found in compounds such as $Cu_4X_4(PPh_3)_4$ ($X = Br^-, I^-$).[49] These compounds contain tetrahedral and trigonal-planar Cu(I) and thus do not conform to eq 1. One of the forms of [2,2,0]-$M_4Q_4L_6$ contains the isomeric stepped core and is stereochemically rational but has not been prepared.

6. $M_6Q_6L_6$. Four bridging modalities are possible, from which the 16 rhomb-only structures **7** and **34**–**48** in Figure 5 can be derived with the imposition of constraints B and C, the latter with tetrahedral M site stereochemistry. For [0,6,0], two isomers are possible. The prismane structure **7** of D_{3h} symmetry has been stabilized in $[Fe_6S_6L_6]^{2-,3-}$ and in $M_4(WS_3Q)_2(PPh_3)_4$ (M = Cu, Ag; Q = O, S).[50] Structure **34** has not been detected. For [1,4,1], there are four structures, **35**–**38**, none of which has been found. There are five isomers, **39**–**48**, of the [3,0,3] modality, all experimentally unknown. If the rhomb-only condition is relaxed, the basket structure **8** in [1,4,1] and the isomer **49** in [2,2,2] emerge. These fail the rhomb-only condition because of one Q_{μ_2} atom not incorporated into a rhomb. The compact basket structure of C_{2v} symmetry has been proven for the examples in Table I and for $[Fe_6S_5(SPh)(PR_3)_4L_2]^+$.[51]

The set of structures in Figure 5 serves to demonstrate the considerable number of possibilities for a cluster formula of

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(44) This term implies a close approach to or achievement of planar or tetrahedral stereochemistry. In the representations of the connectivity matrices for this (Figure 3) and other formulas, careful attempts have been made to provide the stereochemically most reasonable renditions of the structures. While these renderings have a subjective component, they cannot disguise the most improbable M atom stereochemistries, such as the pyramidal-type MQ_4 fragments present in **23** and **27**, among others.

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relatively low nuclearity even with all constraints, A–C, imposed. The method generates the two known structures (when the rhomb-only constraint is omitted). These have the highest symmetries among the possible isomers, the rest of which are of C_i, C_s, or C_1 symmetry.

7. $M_6Q_8L_6$. There are two possible bridging modalities, [6,2,0] and [7,0,1]. One rhomb-only [6,2,0] structure is **50** in Figure 6, and has been synthesized as $[Fe_3S_2(WS_4)_3]^{4-}$.[52] There are no known examples of the other modality. It might be noted that the clusters $[M_6S_8(PR_3)_6]^z$, while of this formula type, contain five-coordinate M = Fe or Co sites[53] and thus do not conform to eq 1.

8. $M_7Q_6L_7$. Two bridging modalities are possible: [0,3,3] and [1,1,4]. While possible structures may be derived by the method of Scheme I, another procedure may also be utilized in which $M_7Q_6L_7$ is treated as an adduct of $M_6Q_6L_6$ and an M–L unit. Because any $M_6Q_6L_6$ portion of a valid cluster must itself be an independently valid structure, one may consider the addition of an M–L unit to the structures in Figure 5. In this way, the five possible structures **10** and **51–54**, shown in Figure 6, under constraints B and C were obtained. All except **10** lack symmetry and have not been observed. $Fe_7S_6(PEt_3)_4Cl_3$ exhibits the monocapped prismane structure of idealized C_{3v} symmetry.

9. $M_8Q_6L_8$. As noted earlier, this formula has the unique bridging modality [0,0,6]. Similar to the preceding case, the structure corresponding to this modality can be derived by the addition of an M–L unit to the valid structures for $M_7Q_6L_8$. Only one result compatible with the bridging modality is possible, the stellated octahedron **11**. In addition to $[Fe_8S_6I_8]^{3-}$, the structure has been demonstrated for $[Fe_3Ni_5S_6I_8]^{4-}$,[25] $[Co_8S_6(SPh)_8]^{4-,5-}$,[54] and $Ni_8(PPh)_6(CO)_8$[55] and related Ni clusters.[56] The latter illustrate cases with strong metal–metal bonding to which the method may be applied.[26]

10. $M_9Q_6L_9$. No rational structure can be derived by the addition of an M–L unit to the stellated octahedron. This exemplifies the case of a formula for which no rational structure can be constructed; indeed, no bridging modalities are compatible with this formula.

11. Cyclic Clusters. In contrast to the M_nQ_{2n} case, for which structure **32** is unique, the other known cyclic clusters $M_{18}Q_{30}$ (**12**, **13**) and $M_{20}Q_{38}$ (**14**) present a very large number of possible structures. The clusters isolated are specified in Table I. As discussed elsewhere,[8,13] the sodium contents are undoubtedly indispensable to cluster stability. They are not included in the structural depictions in Figure 2 in order to emphasize the Fe–Q topology. The $M_{18}Q_{30}$ case involves seven bridge modalities, each with many isomers. Similarly, the $M_{20}Q_{38}$ case has three modalities, also with many possibilities. Development of the isomeric structures for these cases is a herculean task. The method is nonetheless quite useful in providing a structural circumscription of these complex cases in the form of allowed bridging modalities. The latter serve to emphasize a potentially enormous structural diversity in chalcogenometalates of these and other large nuclearities.

12. Iron–Sulfur Protein Clusters of Unknown Structure. Recently, several structurally uncharacterized protein-bound clusters have been detected. Firm analytical data for the iron and sulfur contents of these clusters are lacking. However, given the precedents in this field,[1,17–19,57] it is probable that the clusters have Fe_mQ_n cores, and we proceed on this basis. The cluster in a protein from *Desulfovibrio vulgaris* (Hildenborough) has EPR characteristics similar to those of $[Fe_6S_6L_6]^{3-}$ and is thought to have the prismane structure **7**.[58] A similar cluster may occur in a protein recently isolated from *Desulfovibrio desulfuricans* together with another probable 6-Fe cluster with $S = {}^9/_2$.[59] A cluster with this spin state has also been detected in the dissimilatory sulfite reductase from *D. vulgaris* (Hildenborough).[60] Also, 6-Fe clusters ("H-clusters") have been suggested to be present in certain hydrogenases.[61] While this is not a complete list of uncharacterized Fe–S protein clusters, it is sufficient to indicate that these putative 6-Fe clusters, if not of the prismane type, pose structural questions that could be pursued with the topological method. Bridging modalities and rhomb numbers for selected clusters in the composition range $M_6Q_{5-8}L_{4-10}$ are set out in Table II.

Other uncharacterized biological Fe–S clusters include the FeMo and FeV cofactors of nitrogenase.[62] The more thoroughly investigated FeMo cofactor has the apparent composition range $MoFe_{6-8}S_{8-10}L_l$. On the basis of extended X-ray absorption fine structure (EXAFS) analyses of the cofactors[62] and structures of the heterometal cubane-type $MoFe_3S_4$ and VFe_3S_4 clusters,[30,63,64] the molybdenum and vanadium sites are six-coordinate. The overall structures of the cofactors are unknown and represent a major problem in advancing the understanding of the enzymes. Bridging modalities and rhomb numbers are listed in Table III for selected clusters in the compositional range $M_{7-9}Q_{8-10}L_{4-7}$. While appropriate to homonuclear clusters of these nuclearities, the information also applies to clusters containing one six-coordinate heterometal (M′) site because of the relationship $M_mQ_nL_l \equiv M'M_{m-1}Q_nL_{l+2}$. A similar relationship applies to the data in Table II. The information in these tables provides a starting point for the development of feasible structures under the constraints of the topological method. Numerous cofactor structures have been proposed.[30,54a,65,66] All are encompassed by the topological treatment with the allowance of five- or six-coordinate M′ sites. For example, our early proposed model $[MoFe_7S_6L_{10}]^z$ [54a] is rhomb-only [0,0,6]-$M_8Q_6L_8$ = $M'M_7Q_6L_{10}$ with structure **11**.

Other Cluster Types. Equation 1 can be modified to eq 16 to describe clusters containing six-coordinate metal sites in the clusters $M_mQ_nL_l$. For heterometal clusters with four-coordinate M sites, eq 1 applies without change. However, for the formula $M'_{m'}M_mQ_nL_l$, eq 17 must be used. These equations in combination with eq 2 provide the algorithms for determination of the possible bridging modalities in these cluster types.

$$l + 2n_2 + 3n_3 + 4n_4 = 6m \tag{16}$$

$$l + 2n_2 + 3n_3 + 4n_4 = 6m' + 4m \tag{17}$$

Summary. The topological method introduced here is, to our knowledge, the first comprehensive treatment of cluster molecules $M_mQ_nL_l$ in which the intent is to rationalize existing structures, provide an organizational framework for all structures within its purview, and offer a basis for predicting potentially accessible new structures. The method imposes the conditions of four-coordinate M atoms and three bridging modes, Q_{μ_a} (a = 2–4), which with the algorithm of eqs 1 and 2 define the possible bridging modalities $[n_2,n_3,n_4]$. These provide the organizational framework. For each modality, the boundary condition matrix **B** is obtained, reduced connectivity matrices **R** are constructed, and connectivity matrices C are generated by expansion of **R** matrices. The latter define

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all possible structures. On the basis of the structural data base represented by Figure 1, one or more of the additional constraints of rhomb-only structures, uniterminal ligation, and rational M site stereochemistry serve to identify further the more probable structures for a given formula.

When implemented by further programming, the topological method will provide an even more powerful tool for identifying all possible rational structures for a given formula. At present, solutions to eqs 1 and 2 and derivation of **B** and **R** matrices have been programmed. Further elaboration would involve inclusion of different coordination numbers, generation of unique **C** matrices, and analysis of M site stereochemical rationality in terms of spatial restrictions on allowable bond angles and distances. Achievement of these goals would provide a method of analysis of all possible molecular structures for clusters with the same and mixed coordination numbers at M sites, and sufficiently low nuclearities to render the approach practicable.

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Appendix

Derivation of R Matrices for a Given Bridging Modality. The Randic descending order rule[28a] for **R** matrices can be described alternatively as follows: (1) elements in the first nonzero row should be in a descending order, namely, $R_{ij} \geq R_{i'j}$ if $i < i'$; (2) elements in any two columns in rows under the first nonzero row should also be in a descending order unless the elements in these two columns and in rows above the row in question are not all equivalent. The descending order rule implies assigning a smaller sequencing number to metal atoms connected to Q atoms with higher bridging mode.

The procedure for deriving the complete set of **R**'s for a given bridging modality follows a treelike strategy. It starts with the first row for Q_{μ_4} which is initialized so that it, if read as an m-digit number, is the largest possible number satisfying the boundary condition set by **B**. This is a valid first-row pattern. Using it as a source pattern and starting at $R_{l,m-1}$ as the source element, $R_{1,i}$ ($i = m - 1 + 1, ..., m$) are chosen progressively as the target element, reducing the source element by 1 and adding 1 to the target element to generate new patterns. Next, $R_{1,m-2}$, $R_{1,m-3}$, ..., $R_{1,1}$ are assigned progressively as the source elements, and the procedure is continued to generate further patterns. Those violating the boundary conditions or the descending order rule or any duplicates are eliminated from the newly generated patterns to give a unique set of new first-row patterns. The procedure is repeated by assigning each member of this new set as the source pattern and working accordingly until no new patterns can be generated (when all source patterns are reduced to the smallest possible number satisfying the descending order rule). The collection of all new patterns is a complete and nonredundant set of all possible patterns satisfying the boundary conditions and the descending order rule.

For each member of the complete set for the first row, a complete set of patterns for the second row for Q_{μ_3} is generated by an analogous procedure. Note that (a) the boundary conditions set by **B** should be observed and (b) the descending order rule for rows below the first row allows nondescending sequences if the elements in the upper rows in the two columns in question are not all equivalent. The procedure is then applied to each member of the second-row patterns for a given first-row pattern to achieve the complete set of patterns for the third row for Q_{μ_2}. This, when combined with the given first- and second-row patterns and the complementary fourth row for L uniquely determined by eq 10, offers the complete set of **R**'s for a given modality.

The preceding version is intended to be descriptive. The program implemented uses a more efficient variation of this procedure.

Expansion of R to C Matrices. By defining an **R** matrix, we have actually assigned the distribution of the unit elements along the metal atom axis in a corresponding **C** matrix. To define fully a connectivity pattern, we need to complete the assignment of unit elements along the Q axis, that is, to expand **R** to its set of **C** matrices. The general strategy is to expand each of the four rows of **R** into the corresponding four submatrices by progressively assigning unit elements into all possible unique positions of these submatrices. All possible combinations of the submatrices minus their permutation equivalents are the complete set of **C** matrices.

A sequence rule similar to that for **R** is required for elimination of the permutation-equivalent **C**'s when **R** is expanded to **C**. We term the number ${e^a}_i$ given by reading down the ith column of the submatrix for Q_{μ_a} as the name of the column for the submatrix, and require that

$$ {e^a}_i \geq {e^a}_{i+1} \qquad i = 1, 2, ..., m - 1; a = 2\text{–}4 $$

for submatrices whose original **R** has the condition that $R_{i,5-a} = R_{i+1,5-a}$, unless the names for these two columns in submatrices above the submatrix in question are not all equivalent. In this case, ${e^{a'}}_i \neq {e^{a'}}_{i+1}$ ($4 \geq a' \geq a$), where a and a' denote the bridging modes. Equivalently, the descending order rule should hold for any given two columns in the submatrix in question when they are expanded from **R** elements of equal values unless the two columns in the higher submatrices are not identical. The descending order rule should also hold for the L submatrix. This rule will eliminate most of the permutation-equivalent **C**'s except for certain cases with high symmetry, which usually can be identified readily if the structures are not too complicated.

The procedure for expansion of an **R** matrix begins by expanding the first row of **R** into the submatrix for Q_{μ_4}. The first column of the submatrix is always set to be the largest possible name. In assigning the following unit elements, it is necessary first to introduce the concept of a unique position in order to eliminate the potential row permutations. An unoccupied element position C_{ij} is considered nonunique if there is an unoccupied element $C_{ij'}$ with $j' \leq j$ such that $C_{i'j} = C_{i'j'}$ for $i' = 1, 2, ..., i - 1$, viz., if there is a row of smaller sequencing numbers whose first $i - 1$ elements are equivalent to the first $i - 1$ elements of the row in question. Starting from the first unit element of the second column, a treelike procedure somewhat similar to that for deriving **R**'s is employed to generate all possible **C**'s. Unit elements are assigned to all possible unique positions; those that violate the descending order rule or the topological conditions set by eqs 5 and 6 or that are permutation equivalents are eliminated.

Similar procedures, except with disregard of the descending order rule, are then applied to derive the submatrices for Q_{μ_3} and Q_{μ_2}. All possible combinations of the three classes of submatrices are made. Those combinations which violate the descending order rule, are permutation equivalents, or correspond to structures consisting of discrete fragments are eliminated. Note that the descending order rule does not require the names for columns of Q_{μ_3} and Q_{μ_2} submatrices to be in descending order when the neighboring two columns in the upper submatrices are not totally identical. Also note that, unlike the situation for the first three rows of a given **R** for which more than one **C** matrix is usually obtained from the expansion, there is only one uniquely determined terminal ligand L submatrix for each given **R**. This submatrix is added to resultant combinations to complete the expansion.