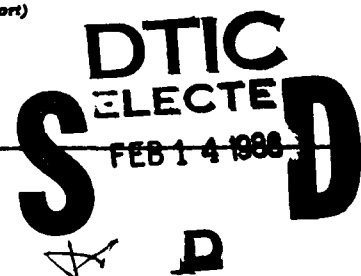


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d orbitals of each of the platinum atoms in the top and bottom triangles of the stack. The more complicated tetraanion $Pt_{19}(CO)_{22}^{4-}$ can be regarded structurally as a threaded tube in which a Pt_{15} stack of three pentagons is the tube and a Pt_4 chain is the thread. Edge-localized bonding is then seen to occur within both the Pt_{15} stack (25 edges) and the Pt_4 thread (3 edges) with additional delocalized bonding within the pentagonal pyramidal chambers at each end of the stack. These seemingly rather exotic topological bonding models are consistent with the general principles of metal cluster bonding and reproduce exactly the observed electron counts for the stacked platinum carbonyl clusters.

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by

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Abstract

Previously discussed topological models of metal cluster bonding are now extended to the treatment of stacked platinum carbonyl clusters, whose structure and bonding exhibit a variety of new features. The stacked triangle cluster dianions $Pt_{3k}(CO)_{6k}^{2-}$ ($k=2,3,4,5$) are best regarded as built from edge-localized bonds with additional Möbius delocalization on both the top and bottom triangles of the stack. These stacked triangles thus appear to be the first examples of stable chemical species having planar rings of atoms exhibiting twisted Möbius rather than untwisted Hückel delocalization. Such Möbius delocalization can naturally arise from the phase changes of appropriate d orbitals of each of the platinum atoms in the top and bottom triangles of the stack. The more complicated tetraanion $Pt_{19}(CO)_{22}^{4-}$ can be regarded structurally as a threaded tube in which a Pt_{15} stack of three pentagons is the tube and a Pt_4 chain is the thread. Edge-localized bonding is then seen to occur within both the Pt_{15} stack (25 edges) and the Pt_4 thread (3 edges) with additional delocalized bonding within the pentagonal pyramidal chambers at each end of the stack. These seemingly rather exotic topological bonding models are consistent with the general principles of metal cluster bonding and reproduce exactly the observed electron counts for the stacked platinum carbonyl clusters.



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1. Introduction

Previous papers in this series discuss the bonding topologies of osmium² and gold¹ clusters. This paper presents an analogous treatment of stacked platinum carbonyl clusters.^{3,4} Such clusters are of particular interest since they have rather different structures from clusters of other transition metals. Thus whereas other transition metal clusters have structures derived from deltahedra, the stacked platinum carbonyl clusters are constructed by stacking planar rings of odd numbers of platinum atoms. Despite successes in understanding other types of metal clusters,^{5,6,7,8,9,10,11,12} no satisfactory electron counting theory has been developed for the platinum carbonyl clusters owing at least to the following two difficulties:

(1) Uncertainties regarding the bonding orbital manifolds¹ of the vertex platinum atoms since cylindrical spd^5 7-orbital manifolds, toroidal sp^2d^5 8-orbital manifolds, and spherical sp^3d^5 manifolds are all possible for platinum relating to the stabilities of 14-, 16-, and 18-electron configurations, respectively.

(2) Uncertainties regarding the number of internal orbitals^{9,10} contributed by each vertex platinum atom to the skeletal bonding of the stacked cluster polyhedron.

These two difficulties increase the "degrees of freedom" in developing electron counting schemes for platinum clusters. However, the platinum frameworks of these clusters also have symmetry properties that restrict the allocations of electrons and orbitals thereby compensating for the above added degrees of freedom of the vertex atoms. This paper develops for the first time this symmetry approach to cluster bonding

for which the well-characterized platinum carbonyl clusters provide one of the most interesting illustrations of its applicability. An intriguing result from this work is that such symmetry considerations require stacked platinum carbonyl clusters of the type $\text{Pt}_{3k}(\text{CO})_{6k}^{2-}$ to be the first examples of systems in which planar polygons of atoms exhibit Möbius rather than Hückel delocalization.

2. Background

The well-characterized large platinum carbonyl clusters fall into the following two categories (Figure 1):

(1) Stacked $Pt_3(CO)_6$ triangles leading to the dianions $Pt_{3k}(CO)_{6k}^{2-}$ ($k=2,3,4,5$).³

(2) Three stacked Pt_5 pentagons (BDB in Figure 1) having a Pt_4 chain (ACCA in Figure 1) inside the stack thereby leading to the $Pt_{19}(CO)_{22}^{4-}$ cluster.⁴

A common feature of both of these types of systems is the stacking of Pt_n polygons leading to a system containing a principal C_n axis on which none of the platinum atoms of the polygons are located. A rotation axis of this type will be called a non-fixing axis since rotation around such an axis leaves no atoms fixed. This is the symmetry feature that will be used for the development of the bonding topology models for these systems. If the Pt_n polygons are pentagons rather than triangles, there is space for a platinum chain inside the pentagonal stack; this platinum chain is collinear with the C_5 axis of the pentagonal stack.

In view of these geometrical features of the platinum carbonyl clusters, it is important to consider the properties of polyhedra of identical vertex atoms having a non-fixing C_n rotation axis. In such systems the number of electrons arising from the vertex metal atoms must be a multiple of n , or using standard mathematical notation¹³:

$$e_m \equiv -z \pmod{n} \quad (1)$$

In equation 1 e_m is the number of electrons arising from the metal atom vertices and z is the charge on the species. Furthermore the number of skeletal bonding molecular orbitals in such systems divided by n must give a remainder r which corresponds to the number of skeletal bonding molecular orbitals unchanged by the C_n symmetry operation of the non-fixing axis, i.e.

$$s^+ \equiv r(\text{mod } n) \quad (2)$$

In equation 2 s^+ is the number of skeletal bonding molecular orbitals. Application of these rules to the platinum carbonyl cluster compounds allows us to make some interesting observations concerning their bonding.

Before discussing the platinum carbonyl clusters, let us illustrate these symmetry rules by their application to borane clusters which have been well-studied by other methods.^{5,6,14,15} Table 1 illustrates these rules for the deltahedral borane dianions $B_nH_n^{2-}$ having a non-fixing C_3 axis (i.e., $n \equiv 0 \pmod{3}$). These systems are required by equation 1 to have $2 \pmod{3}$ skeletal electrons where the 2 arises from the -2 charge on the dianion. Since each skeletal bonding orbital is occupied by an electron pair, this corresponds to a system having $1 \pmod{3}$ skeletal bonding orbitals. This implies a unique bonding orbital located on the C_3 axis. This unique bonding orbital is located at the core of the deltahedron and arises from the n -center bond of the unique internal orbitals of the vertex atoms.^{9,10} Thus these symmetry requirements on the number of bonding orbitals in deltahedral systems having a non-fixing C_3 axis are consistent with earlier metal cluster bonding models.^{9,10}

TABLE 1

SYMMETRY RESTRICTIONS ON THE NUMBER OF SKELETAL ORBITALS
FOR HOMOMETALLIC POLYHEDRAL CLUSTERS HAVING A NON-FIXING AXIS

<u>Vertex Atoms</u>	<u>Polyhedron</u>	<u>Non-fixing Axis</u>	<u>Skeletal bonding Orbitals for a Dianion</u>	<u>Example</u>
6	Octahedron	C ₃	1 (mod 3)	B ₆ H ₆ ²⁻
9	Tricapped trigonal prism	C ₃	1 (mod 3)	B ₉ H ₉ ²⁻
12	Icosahedron	C ₃	1 (mod 3)	B ₁₂ H ₁₂ ²⁻
3k	Stacked triangles	C ₃	1 (mod 3)	Pt _{3k} (CO) _{6k} ²⁻
		C ₂	0 (mod 2)	Pt _{3k} (CO) _{6k} ²⁻ (k even)

3. Stacked Triangle Platinum Carbonyl Clusters

The rotational subgroup of the symmetry group of the stacked triangle $\text{Pt}_{3k}(\text{CO})_{6k}^{2-}$ clusters ($k=2,3,4,5$) is D_3 implying a C_3 axis and three C_2 axes in a plane perpendicular to the C_3 axis. The C_2 axes suggest that the skeletal molecular orbitals are the same at both the top and the bottom of the platinum triangle stack. Equation 1 indicates that the C_3 axis requires $2 \pmod{3}$ bonding electrons from the vertex atoms.

In view of these considerations a possible bonding model for the $\text{Pt}_{3k}(\text{CO})_{6k}^{2-}$ clusters is a globally delocalized bonding model similar to that well-established^{8,9} for the deltahedral $\text{B}_n\text{H}_n^{2-}$ anions. In such a model each $\text{Pt}(\text{CO})_2$ vertex uses three internal orbitals thereby acting as a donor of two skeletal electrons provided that the platinum atom uses a spherical sp^3d^5 bonding orbital manifold.¹ Thus the $\text{Pt}_{3k}(\text{CO})_{6k}^{2-}$ clusters are $2n + 2$ (or $6k + 2 \equiv 2 \pmod{6} \equiv 2 \pmod{3}$) skeletal electron systems like the $\text{B}_n\text{H}_n^{2-}$ anions.

If such a bonding model is valid for the $\text{Pt}_{3k}(\text{CO})_{6k}^{2-}$ clusters, then why are such clusters not deltahedra rather than stacked triangles? Overlap of the $3k$ unique internal orbitals of the $3k$ platinum vertices at the center of a Pt_{3k} deltahedron would give the required $3k$ -center bond for a non-fixing C_3 axis system having $2 \pmod{3}$ skeletal bonding electrons. However, in a stacked triangle $\text{Pt}_{3k}(\text{CO})_{6k}^{2-}$ globally delocalized system the unique internal orbitals of platinum atoms three or more layers apart would be too far away to overlap significantly thereby preventing the multicenter core bond required for globally delocalized bonding. Since platinum triangle stacks as high as five

layers are well characterized³ (and even higher stacks may exist), a valid bonding model for these systems cannot depend upon overlap between orbitals on platinum atoms several layers apart. The bonding in these systems must therefore be localized into specific regions of the platinum network.

Such considerations make much more plausible an alternative edge-localized bonding model for the $\text{Pt}_{3k}(\text{CO})_{6k}^{2-}$ clusters. A $\text{Pt}_{3k}(\text{CO})_{6k}^{2-}$ system of stacked triangles has $3 + 6(k-1) = 6k - 3$ edges which require $12k - 6$ skeletal electrons for edge-localized bonding. Let us now consider the $\text{Pt}_{3k}(\text{CO})_{6k}^{2-}$ clusters as being built from $\text{Pt}(\text{CO})_2$ vertices using four internal orbitals noting that the distribution of carbonyl groups between terminal and bridging carbonyl groups does not affect the formal electron counting.² Such a $\text{Pt}(\text{CO})_2$ vertex has five (i.e., $9 - 4$) external orbitals which will formally use the ten electrons from Pt^0 thereby making a $\text{Pt}(\text{CO})_2$ vertex using four internal orbitals a donor of four skeletal electrons with these electrons formally coming from the two carbonyl groups. The available skeletal electrons for the $\text{Pt}_{3k}(\text{CO})_{6k}^{2-}$ stacked triangle clusters can then be counted as follows:

(a) $3k \text{ Pt}(\text{CO})_2$ vertices (4 internal orbitals, 4 skeletal electrons each): $(3k)(4) =$	12k electrons
(b) -2 charge on dianion	<u>2 electrons</u>
Total skeletal electrons	12k + 2 electrons

In connection with this electron counting scheme, note the following:

(1) The vertices of interior triangles in the $\text{Pt}_{3k}(\text{CO})_{6k}^{2-}$ stack (Figure

1) have degree four (i.e., four edges meet at each of these vertices) so that the proposed four internal orbitals from these $\text{Pt}(\text{CO})_2$ vertices match the corresponding vertex degrees in accord with expectations for edge-localized bonding.¹⁰

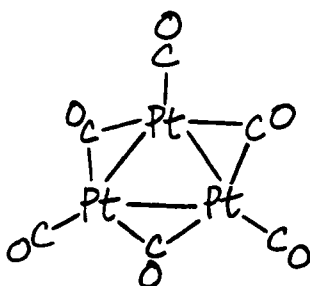
(2) The vertices of the two exterior triangles in the $\text{Pt}_{3k}(\text{CO})_{6k}^{2-}$ stack have degree three. After using three internal orbitals of these $\text{Pt}(\text{CO})_2$ vertices for edge-localized bonding, there remains one internal orbital from each of the six platinum atoms of the two exterior triangles for further skeletal bonding. For reasons that will become apparent below, let us call this "extra" internal orbital on each vertex atom of the exterior triangles the Möbius orbital. A $\text{Pt}_{3k}(\text{CO})_{6k}^{2-}$ cluster therefore has six Möbius orbitals as long as k is at least 2.

(3) Edge-localized bonding in each of the $6k - 3$ edges of the $\text{Pt}_{3k}(\text{CO})_{6k}^{2-}$ stack requires $12k - 6$ skeletal electrons. Since there are a total of $12k + 2$ skeletal electrons, this leaves eight skeletal electrons for the molecular orbitals generated from overlap of the two groups of three Möbius orbitals at the top and bottom of the triangle stack. Let us call these eight electrons the Möbius electrons. The symmetry of the C_2 axes of the D_{3h} $\text{Pt}_{3k}(\text{CO})_{6k}^{2-}$ systems force equal allocation of these eight Möbius electrons to the top and bottom of the $\text{Pt}_{3k}(\text{CO})_{6k}^{2-}$ stack. This means that at both ends of the $\text{Pt}_{3k}(\text{CO})_{6k}^{2-}$ stack we have four Möbius electrons for the molecular orbitals formed by the three triangularly situated Möbius orbitals (Figure 2). This electron counting situation suggests $4m$ electron (m an integer) Möbius overlap involving a twisted ring of the Möbius orbitals rather than the $4m + 2$ electron Hückel overlap found in planar aromatic hydrocarbons such as benzene.¹⁶ If the Möbius orbitals are d orbitals, then this

twisted overlap is possible for an odd number of metal atoms (e.g., a triangle or pentagon but not a quadrilateral) since d orbitals change phase (i.e. "twist") at each metal center.

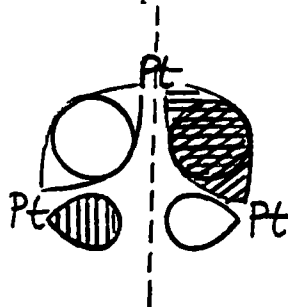
This bonding model for the $\text{Pt}_{3k}(\text{CO})_{6k}^{2-}$ stacked clusters suggests edge-localized bonding along the $6k - 3$ edges of the stack coupled with three-center delocalized Möbius bonding at both the top and the bottom of the stack. Thus the edge-localized bonding in the $\text{Pt}_{3k}(\text{CO})_{6k}^{2-}$ clusters corresponds to the edge-localized carbon-carbon σ -bonding in benzene whereas the Möbius bonding at the top and the bottom of the $\text{Pt}_{3k}(\text{CO})_{6k}^{2-}$ stack corresponds to the Hückel π -bonding in benzene.

Let us now consider the specific platinum orbitals involved in this bonding model of the $\text{Pt}_{3k}(\text{CO})_{6k}^{2-}$ clusters. An individual $\text{Pt}_3(\text{CO})_6$ triangle of the stack can be depicted as follows:



Each platinum atom forms five bonds in the plane of the triangle: two to other platinum atoms, two to bridging carbonyl groups, and one to a terminal carbonyl group. In addition to forming these five equatorial bonds the platinum atoms of the interior triangles in a $\text{Pt}_{3k}(\text{CO})_{6k}^{2-}$ stack form axial bonds to the corresponding platinum atoms in the triangles above and below the interior triangle in question. These

platinum atoms are therefore seven-coordinate having approximate pentagonal bipyramidal hybridization necessarily using s , x , y , z , x^2-y^2 , xz , and z^2 orbitals with the z axes taken as orthogonal to the plane of the triangle. Similarly the platinum atoms of the two exterior triangles in a $\text{Pt}_3\text{k}(\text{CO})_6\text{k}^{2-}$ stack may be regarded as six-coordinate with approximate pentagonal pyramidal hybridization, which can be taken to use s , x , y , z , x^2-y^2 , and xy orbitals in order to keep the platinum hybridizations of the interior and exterior triangles as similar as possible. This leaves the xz and yz orbitals of the platinum atoms of the two exterior triangles to hybridize to generate two additional hybrids for these platinum atoms. One of these hybrids is directed to maximize in phase overlap with the Möbius orbital(s) of adjacent platinum atom(s) in the same exterior triangle. The other hybrid becomes an external orbital which contains a non-bonding electron pair already accounted for in the electron counting scheme above. The phase of the overlaps of the internal hybrids (i.e., the Möbius orbitals) in an exterior triangle can be depicted as follows:



Note the change in phase at each metal center and the single node (i.e., twist) required for Möbius rather than Hückel overlap.

This analysis shows that the platinum atoms in the $\text{Pt}_3\text{k}(\text{CO})_6\text{k}^{2-}$ have appropriate orbitals in their spherical sp^3d^5 manifolds for the bonding scheme outlined above.

4. The Threaded Tubular Cluster $Pt_{19}(CO)_{22}^{4-}$

The structure of the threaded stacked pentagonal cluster⁴ $Pt_{19}(CO)_{22}^{4-}$ (Figure 1) can be built as follows:

(1) Three Pt_5 pentagons (BDB in Figure 1) are stacked on top of each other forming two pentagonal prismatic chambers sharing a pentagonal face. This pentagonal stack is called the Pt_{15} tube.

(2) A linear Pt_4 chain (ACCA in Figure 1) is placed collinear to the C_5 axis of the stacked pentagons so that the two end members of the Pt_4 chain are the apices of pentagonal pyramids at the top and the bottom of the pentagonal stack and the two central members of the Pt_4 chain are located in the centers of the two pentagonal prismatic chambers noted above. This Pt_4 chain is called the Pt_4 thread.

This structure of $Pt_{19}(CO)_{22}^{4-}$ has the following consequences:

(1) The Pt_4 thread in $Pt_{19}(CO)_{22}^{4-}$ can be regarded formally as a stack of four one-vertex polygons. Using this formalism stacks of the first three types of odd-vertex polygons are found in platinum carbonyl clusters with the one- and five-vertex polygon stacks in $Pt_{19}(CO)_{22}^{4-}$ and the three-vertex polygon (i.e., triangle) stacks in the clusters $Pt_{3k}(CO)_{6k}^{2-}$.

(2) Stacks of platinum triangles and platinum pentagons may be regarded topologically as tubes. The internal volume of a tube from stacked triangles is not large enough to contain a platinum thread. However, the internal volume of a tube from stacked pentagons is large enough to contain a platinum thread as shown by the structure of $Pt_{19}(CO)_{22}^{4-}$. In fact the Pt_4 thread inside the Pt_{15} stack of three pentagons is probably necessary to prevent collapse of the pentagonal Pt_{15} stack

into a Pt₁₅ stack of five triangles. A Pt₁₅ stack of three pentagons has 25 edges whereas a Pt₁₅ stack of five triangles has 27 edges thereby making the latter more stable for systems which can have an appropriate number of electrons.

(3) In Pt₁₉(CO)₂₂⁴⁻ the center platinum atoms of the Pt₄ thread located in the centers of the two pentagonal prismatic chambers have only internal orbitals. Therefore all of the electrons of these two platinum atoms are skeletal electrons. For this reason fewer carbonyl groups per platinum (i.e., CO/Pt = 1.16) are needed in Pt₁₉(CO)₂₂⁴⁻ relative to Pt_{3k}(CO)_{6k}²⁻ (CO/Pt=2.00) in order for the system to have the necessary number of skeletal electrons.

The proposed bonding model for Pt₁₉(CO)₂₂⁴⁻ has the following general features:

(1) Edge-localized bonding along the 25 edges of the Pt₁₅ stack of three pentagons having the two pentagonal prismatic chambers. This requires 50 skeletal electrons.

(2) Edge-localized bonding along the three edges of the Pt₄ thread inside the pentagonal stack. This requires 6 skeletal electrons.

(3) Delocalized bonding within the pentagonal pyramidal chambers at the top and the bottom of the pentagonal stack. These chambers can be viewed as nido systems¹⁴ analogous to B₆H₁₀, which require 16 skeletal electrons (= 2n + 4 for n = 6). However, for each of the two pentagonal pyramidal chambers 10 of the required 16 skeletal electrons can come from delocalization of the five edge-localized bonds in the pentagonal face being capped to form the pentagonal pyramidal chamber. Thus the incremental number of skeletal electrons for each pentagonal pyramidal chamber is 6 (= 16 - 10).

The 19 platinum atoms in $\text{Pt}_{19}(\text{CO})_{22}^{4-}$ may be divided into 17 peripheral platinum atoms and two interstitial platinum atoms (C in Figure 1). All nine sp^3d^5 orbitals of the spherical bonding manifold¹ of the interstitial platinum atoms are internal orbitals and overlap with orbitals of the platinum atoms of the Pt_{15} triple pentagonal stack by making some of the two-center edge-localized bonds in the Pt_{15} stack into three-center bonds involving an orbital of an interstitial platinum atom. The 17 peripheral platinum atoms each have four internal and five external orbitals. The internal orbitals of the peripheral platinum atoms are used as follows (see Figure 1 for the significance of the letters A, B, and D):

(A) End platinum atoms of the Pt_4 thread (2 platinum atoms): three internal orbitals for a delocalized pentagonal pyramid^{9,10} and the fourth internal orbital for a localized bond to the nearest interstitial platinum atom also in the Pt_4 thread.

(B) Platinum atoms of the top and bottom Pt_5 pentagons of the Pt_{15} tube (10 platinum atoms): three internal orbitals for a delocalized pentagonal pyramid^{9,10} and the fourth internal orbital for a localized bond to the nearest platinum atom of the middle Pt_5 pentagon.

(D) Platinum atoms of the middle Pt_5 pentagon of the Pt_{15} tube (5 platinum atoms): all four internal orbitals are used for edge-localized bonds to neighboring platinum atoms. Note that these platinum vertices of the Pt_{15} tube have degree 4 (ignoring any interaction of the Pt_{15} tube with the Pt_4 thread).

The electrons in $\text{Pt}_{19}(\text{CO})_{22}^{4-}$ can now be counted as follows:

(1) Source of skeletal electrons:

17 PtCO vertices using 4 internal orbitals: $(17)(2)=$	34 electrons
5 "extra" CO groups	10 electrons
2 interstitial platinum atoms: $(2)(10)=$	20 electrons
-4 negative charge on anion	<u>4 electrons</u>
Total available skeletal electrons	68 electrons

(2) Use of skeletal electrons:

Edge-localized bonding in the Pt_{15} tube: 25 edges	50 electrons
Edge-localized bonding in the Pt_4 thread: 3 edges	6 electrons
<u>Incremental</u> electrons for each of the two delocalized pentagonal pyramidal chambers: $(2)(6)=$	<u>12 electrons</u>
Total skeletal electrons required	68 electrons

This indicates that the anion $\text{Pt}_{19}(\text{CO})_{22}^{4-}$ has exactly the number of electrons required for the above bonding model.

The anion $\text{Pt}_{19}(\text{CO})_{22}^{4-}$ is isoelectronic with a hypothetical neutral molecule $\text{Pt}_{19}(\text{CO})_{24}$ which would be one member (i.e., $n=3$) of a predicted series of threaded tubular clusters having the general formula $\text{Pt}_{6n+1}(\text{CO})_{6n+6}$. The Pt_{5n} tubes in this series of clusters consist of a stack of n Pt_5 pentagons. These tubes contain a thread of $n+1$ platinum atoms. These clusters thus have $5n+2$ peripheral platinum atoms and $n-1$ interstitial platinum atoms. The general electron counting of the threaded tubular $\text{Pt}_{6n+1}(\text{CO})_{6n+6}$ goes as follows:

(1) Source of skeletal electrons:

5n+2 PtCO vertices using 4 internal orbitals apiece	
2(5n+2)=	10n + 4 electrons
n+4 "extra" CO groups	2n + 8 electrons
n-1 interstitial platinum atoms: 10(n-1)=	<u>10n - 10 electrons</u>
Total available skeletal electrons	22n + 2 electrons

(2) Use of skeletal electrons:

Edge-localized bonding in the Pt_{5n} tube:

10n - 5 edges	20n - 10 electrons
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Edge-localized bonding in the Pt_{n+1} thread:

n edges	2n electrons
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Incremental electrons for each of the two

delocalized pentagonal pyramidal chambers:

(2)(6)=	<u>12 electrons</u>
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Total skeletal electrons required	22n + 2 electrons
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Analogy with Pt₁₉(CO)₂₂⁴⁻ suggests that these threaded tubular clusters may be found as the tetraanions Pt_{6n+1}(CO)_{6n+4}⁴⁻ rather than as the neutral molecules Pt_{6n+1}(CO)_{6n+6}.

5. Summary

This paper presents the first detailed electron-precise bonding models of the previously enigmatic platinum carbonyl clusters Pt_{3k}(CO)_{6k}²⁻ (k ≥ 2) and Pt₁₉(CO)₂₂⁴⁻. These systems are seen to consist of stacks of platinum atoms, platinum triangles, and/or platinum pentagons having edge-localized bonding within the stacks. The tops

and bottoms of the platinum stacks in these clusters contain interesting additional features, namely Möbius triangles in the cases of the triangular stacks $Pt_{3k}(CO)_{6k}^{2-}$ and delocalized pentagonal pyramids in the case of the pentagonal stack $Pt_{19}(CO)_{22}^{4-}$. The $Pt_{3k}(CO)_{6k}^{2-}$ systems are significant in representing the first series of stable chemical species in which orbitals from a planar group of atoms appear to overlap in a twisted Möbius manner rather than in an untwisted Hückel manner; symmetry considerations require this unusual model made feasible by the properties of appropriate platinum d orbitals. The $Pt_{19}(CO)_{22}^{4-}$ cluster appears to be the first known example of a threaded tubular cluster derived from a neutral species $Pt_{6n+1}(CO)_{6n+6}$ having a tube consisting of a Pt_{5n} pentagonal stack threaded by a Pt_{n+1} chain. The synthesis of other threaded tubular clusters of this series represents an interesting challenge.

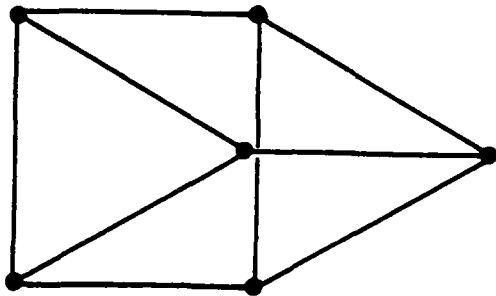
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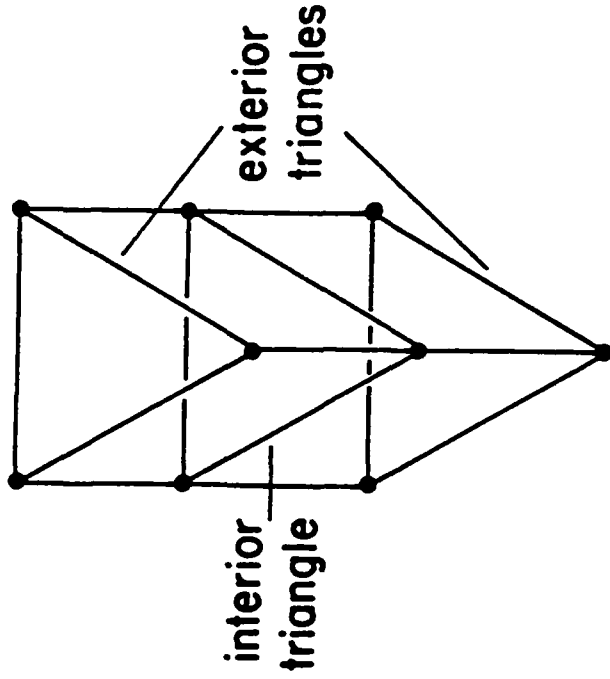
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Figure 1: Schematic diagrams of the stacked triangle platinum carbonyl anion clusters $\text{Pt}_{3k}(\text{CO})_{6k}^{2-}$ and the threaded tubular cluster $\text{Pt}_{19}(\text{CO})_{22}^{4-}$.

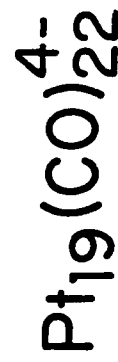
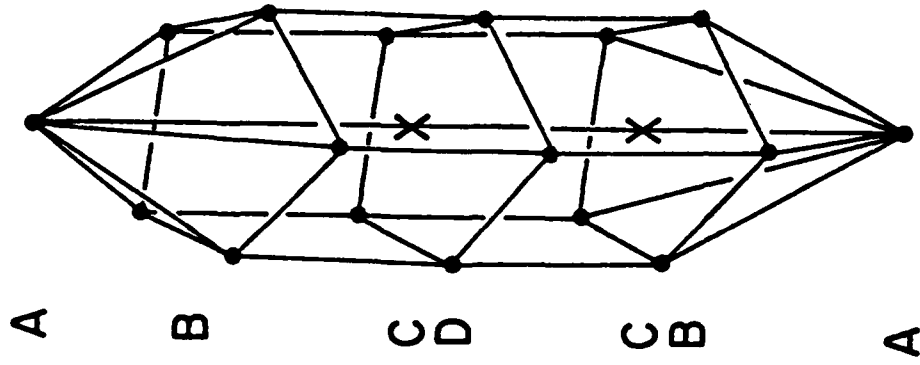
Figure 2: A comparison of the energy levels in Hückel and Möbius triangles.

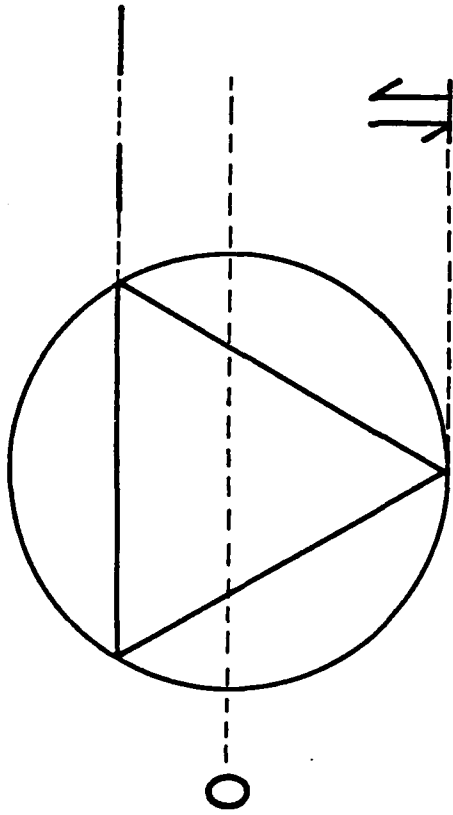


$k=2$



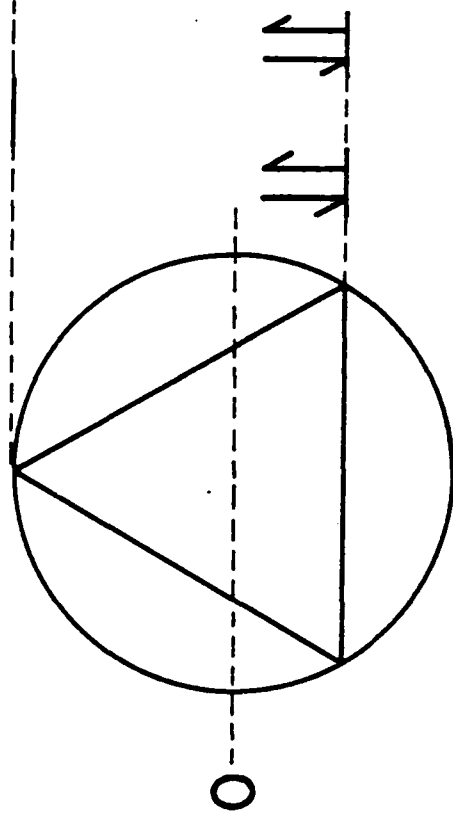
$k=3$





Hückel Overlap

(no phase change)



Möbius Overlap

(odd number of phase changes)

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