currents. The gold plate was extensively corroded and gold particles were recovered at the end of the experiment. A study of the scan rate dependence of the electrode process revealed a positive shift of the anodic peak with increasing scan rate similar to that observed in ammonia.[4] The $E°$ value for the Au^-/Au^0 redox couple is −1.95 V (vs. Ag wire).

Use of (18-crown-6)potassium triflate as a supporting electrolyte and Na-K alloy + cryptand [2.2.2][5] produced a rapid dissolution of gold, and identical voltammograms were obtained as before except that larger peak currents due to higher concentrations of Au^- in solution were observed. However, solvent decomposition was equally rapid and extensive under these conditions. Disappearance of the blue solution was followed by Au^- decomposition to gold as seen by the slow disappearance of the cyclic voltammetric peaks and a return to the initial current-voltage curve obtained in the presence of supporting electrolyte alone.

Attempts to generate large concentrations of solvated electrons coulometrically to react with metallic gold were unsuccessful in our hands. The solvent decomposition was rapid, and a sufficient steady-state concentration of electrons could not be established to dissolve the gold samples.

The $\Delta G°$ for the reaction of solid gold with solvated electrons to produce Au^- in ethylenediamine can be estimated from the $E°$ for the reaction $Au + e^- \rightarrow Au^-$ (vs. the electron electrode): $\Delta G°$ is −14.9 kcal/mol at 30 °C. Conclusive evidence confirming the presence of Au^- was obtained by observing the characteristic charge-transfer-to-solvent (CTTS) band of metal anions. In a typical spectroscopic experiment ethylenediamine (3 mL) was distilled into a reservoir and reacted with a potassium mirror; a medium to deep blue solution was produced. Reaction of this solution with gold foil (0.0015 g) was followed by filtering the solution into an attached quartz optical cell (0.1 mm); a new broad band at 278 nm was present in the spectrum. The blue color faded rapidly. A spectrum obtained after considerable reaction time had elapsed (1 h) showed an Au^- band off-scale and an additional peak at about 340 nm. Blank experiments allow us to assign the 340-nm band to a product from solvent decomposition (amide band?). In the presence of 18-crown-6 and cryptand [2.2.2], the reaction of gold was rapid and the decomposition of the solutions was equally rapid.

Preliminary electrochemical experiments in methylamine with the same supporting electrolyte revealed a different behavior. Coulometric generation of electrons and reaction with gold metal was feasible at about −20 °C in this solvent. At room temperature the decomposition of solvated electrons was rapid. A cyclic current-voltage curve obtained at −20 °C revealed cathodic and anodic peaks for Au^- at −2.40 and −1.95 V vs. a Ag wire. Warming the cell to room temperature results in rapid disappearance of solvated electrons, followed by a dark violet coloration throughout the cell. With time, we observe the agglomeration of the gold colloid and precipitation of black particles of gold metal. Cooling to −20 °C and regeneration of solvated electrons result in instantaneous dissolution of the freshly precipitated gold. Cooling this solution further (−40 °C) results in disappearance of Au^- peaks in the cyclic current-voltage curve, suggesting the precipitation of a Au^--containing salt at the lower temperatures. The absorption spectral data in methylamine at 25 °C indicate the presence of a Au^- peak at 274 nm that shifts to 280 nm in the presence of 18-crown-6. Effects due to ion pairing seem to be more pronounced in this low dielectric constant solvent compared to those in ammonia where the absorption band appears at 289 nm in the presence and absence of 18-crown-6 or the cryptand [2.2.2].

The foregoing results suggest that Au^- is the only metal anion that has been detected in both liquid ammonia and amines. Further research to observe and stabilize Au^- in other solvents is continuing in our laboratories. It appears that Au^- may be a useful probe, both electrochemically and spectroscopically, to study the nature of anion-solvent interactions.

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Registry No. Au^-, 19498-55-6; Au, 7440-57-5; ethylenediamine, 107-15-3; Na-K alloy (1:1), 12675-23-9.

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(5) The IUPAC name for 18-crown-6 is 1,4,7,10,13,16-hexaoxacyclooctadecane, and for cryptand [2.2.2] it is 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane.

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Interrelationships between the Topological Electron-Counting Theory and the Polyhedral Skeletal Electron Pair Theory

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Teo et al.[1,2] have published papers in this journal describing the "new topological electron-counting theory" based on Euler's theorem for polyhedra and the effective atomic number (EAN) rule. It has been claimed that this approach represents a more widely applicable alternative to the *polyhedral skeletal electron pair theory* (PSEPT)[3] and provides new insights into the electronic requirements of various polyhedral cluster structures and their interrelationships.[1] This new approach is based on the fundamental formula

$$\mathrm{CVMO} = 8V - F + 2 + X \qquad (1)$$

which relates the number of cluster valence molecular orbitals (CVMO) to the number of vertices (V) and faces (F) of the polyhedron. Each polyhedron is characterized by a parameter X, which is defined as the number of "extra" electron pairs in excess of the EAN rule. The parameter X has been defined by Teo in terms of a set of rules. Some theoretical justification for these rules has been provided,[1] and Teo and his co-workers[2] have demonstrated its applicability in a well-documented and thorough review.[2]

The PSEPT is also based implicitly on the EAN rule and incorporates the topological features of the cluster by designating specific classes of polyhedra, e.g. deltahedra, electron-precise three-valent polyhedra, etc. Given that the two approaches are based on the same fundamental assumptions, they must share many of the same advantages and deficiencies.[4] It is the purpose of this paper to demonstrate that the rules described by Teo for deriving X in formula 1 are consistent with the basic assumptions of the PSEPT and indeed can be derived from them by using simple algebraic manipulations.

Table I summarizes in an economical fashion the CVMO characteristics for the important classes of polyhedra adopted by metal carbonyl clusters as set out in the PSEPT.[5] In order to make a connection with Teo's work, the number of faces for these polyhedra is also specified. The derivation of the rules is made by substituting these values into the PSEPT expressions for the CVMO's.

Rule 1: For All Three Connected Polyhedra $X = 0$. In the PSEPT, three connected polyhedra are described as either elec-

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Table I

Summary of the CVMO's Derived from the Polyhedral Skeletal Electron Pair Approach[3,5]

polyhedral type	CVMO's[a,b]	relationship between F and V	examples
electron-precise or cubic polyhedra	$15V/2$ $(V \geqslant 4)$	$V = 2F - 4$	$Ir_4(CO)_{12}$, $Ni_8(PPh)_6(CO)_8$
closo deltahedra	$7V + 1$ $(V \geqslant 5)$	$F = 2V - 4$	$Os_5(CO)_{15}^{2-}$
nido deltahedra	$7V + 2$ $(V \geqslant 4)$	$F = V$ (pyramids)	$Os_5C(CO)_{15}$
arachno deltahedra	$7V + 2$ $(V \geqslant 4)$		$Fe_4H(CO)_{13}^-$–butterfly geometry

Condensed Polyhedra Derived from Components with V_1, $(CVMO)_1$, and V_2, $(CVMO)_2$, Vertices and Cluster Valence Molecular Orbitals[9]

vertex sharing:	edge sharing:	triangular face sharing:
$(CVMO)_1 + (CVMO)_2 - 9$	$(CVMO)_1 + (CVMO)_2 - 17$	$(CVMO)_1 + (CVMO)_2 - 24$

[a] V = number of vertices; F = number of faces; CVMO = number of bonding cluster valence molecular orbitals.[7] [b] The number of skeletal electron pairs (N) is related to CVMO by $N = \text{CVMO} - 6V$; e.g., for electron-precise polyhedra $N = 15V/2 - 6V = 3V/2$, for closo deltahedra $N = 7V + 1 - 6V = V + 1$, etc.

tron-precise polyhedra or cubic polyhedra and are characterized by $15V/2$ CVMO's. Since for these polyhedra $V = 2F - 4$, then

$$\begin{aligned} \text{CVMO} &= 15V/2 = 8V - V/2 \\ &= 8V - F + 2 \end{aligned}$$

I.e., X in eq 1 must equal 0.

Rule 2: Capping an N-gonal Face of a Polyhedron Leads to an Increase of X by $N - 3$. In the PSEPT, the capping principle has been widely used[6] and states that the CVMO increases by 6 on capping a face with a single atom. Since this process increases V by 1 and F by $N - 1$, it then follows that X must increase by $N - 3$.

Rule 3: $X = 0$ for All Pyramids. In the PSEPT, pyramids are examples of nido clusters[3] that are characterized (Table I) by $7V + 2$ CVMO's. Since for pyramids $F = V$, the following is true:

$$\begin{aligned} \text{CVMO} = 7V + 2 &= 8V - V + 2 \\ &= 8V - F + 2 \end{aligned}$$

I.e., X must equal 0.

Rule 4: For Bipyramids $X = 0$ (or 2) for Trigonal, $X = 1$ (or 3) for Tetragonal, and $X = 3$ for Pentagonal. In the PSEPT, bipyramids are examples of closo clusters with $7V + 1$ CVMO, and for these (and all deltahedra) $F = 2V - 4$; therefore

$$\begin{aligned} \text{CVMO} = 7V + 1 &= 8V - V + 1 \\ &= 8V - F - 2 \end{aligned}$$

I.e., $X = (F - 6)/2$. In this manner $X = 0$ for a trigonal bipyramid ($F = 6$), $X = 1$ for a tetragonal bipyramid ($F = 8$), etc. The possibility pointed out by Lauher[7] that some of these bipyramids may distort to accommodate $7V + 3$ CVMO's leads to the alternative values of X given in parentheses above.

Rule 5: $X = 1$ for a Trigonal Antiprism, $X = 1$ or 3 for a Square Antiprism, and $X = 3$ for a Pentagonal Antiprism. Therefore, the values of X in this rule reflect the designation of a trigonal antiprism (octahedron) as closo and a pentagonal antiprism as arachno and the ambiguous designation of a square antiprism either as closo derived from a dodecahedron by minor distortions[8] or as an arachno bicapped square antiprism.

Rule 6: $X = S$ for Vertex or Edge-Sharing (Connected) Polyhedra, Where S Is the Number of Shared Vertices or Edges, Respectively. Recently, the PSEPT approach has been extended to condensed polyhedral clusters.[9] For a pair of cubic polyhedra sharing a common vertex, it can be demonstrated[9] that CVMO $= 15(V + 1)/2 - 9$. For such polyhedra $V = 2F - 9$; therefore

$$\begin{aligned} \text{CVMO} &= \tfrac{1}{2}(16V - V - 3) \\ &\quad \tfrac{1}{2}(16V - 2F + 6) \\ &= 8V - F + 3 \end{aligned}$$

I.e., $X = 1$, the number of shared vertices. A similar analysis leads to $X = 1$ for edge-sharing cubic polyhedra.

Given that nearly all polyhedral carbonyl clusters have electron counts between $14V - 4$ and $15V$, then only a limited number of topological variables must suffice for rationalizing the observed skeletal geometries. The PSEPT defines these topological variables in terms of the classes of polyhedra given in Table I. The "new topological electron-counting theory" utilizes many of the same classes of polyhedra, e.g. three connected polyhedra, capped polyhedra, and condensed polyhedra, but replaces the deltahedral class by bipyramids, pyramids, and antiprisms. Since the latter can generally also be described as closo, nido, and aracho deltahedra, this does not introduce a major new topological variable. The two approaches share common assumptions, have rules that are interconvertible, and lead to identical conclusions for the great majority of carbonyl cluster compounds.

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TEC and SEP Electron-Counting Rules for Polyhedral Cluster Systems: Similarities and Differences, Strengths and Weaknesses

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In the preceding paper, it is shown by Mingos that the newly developed topological electron counting[1-3] (TEC) approach is related, via Euler's theorem for polyhedra, to the widely used polyhedral skeletal electron pair theory[4-8] (PSEPT). In this paper,

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