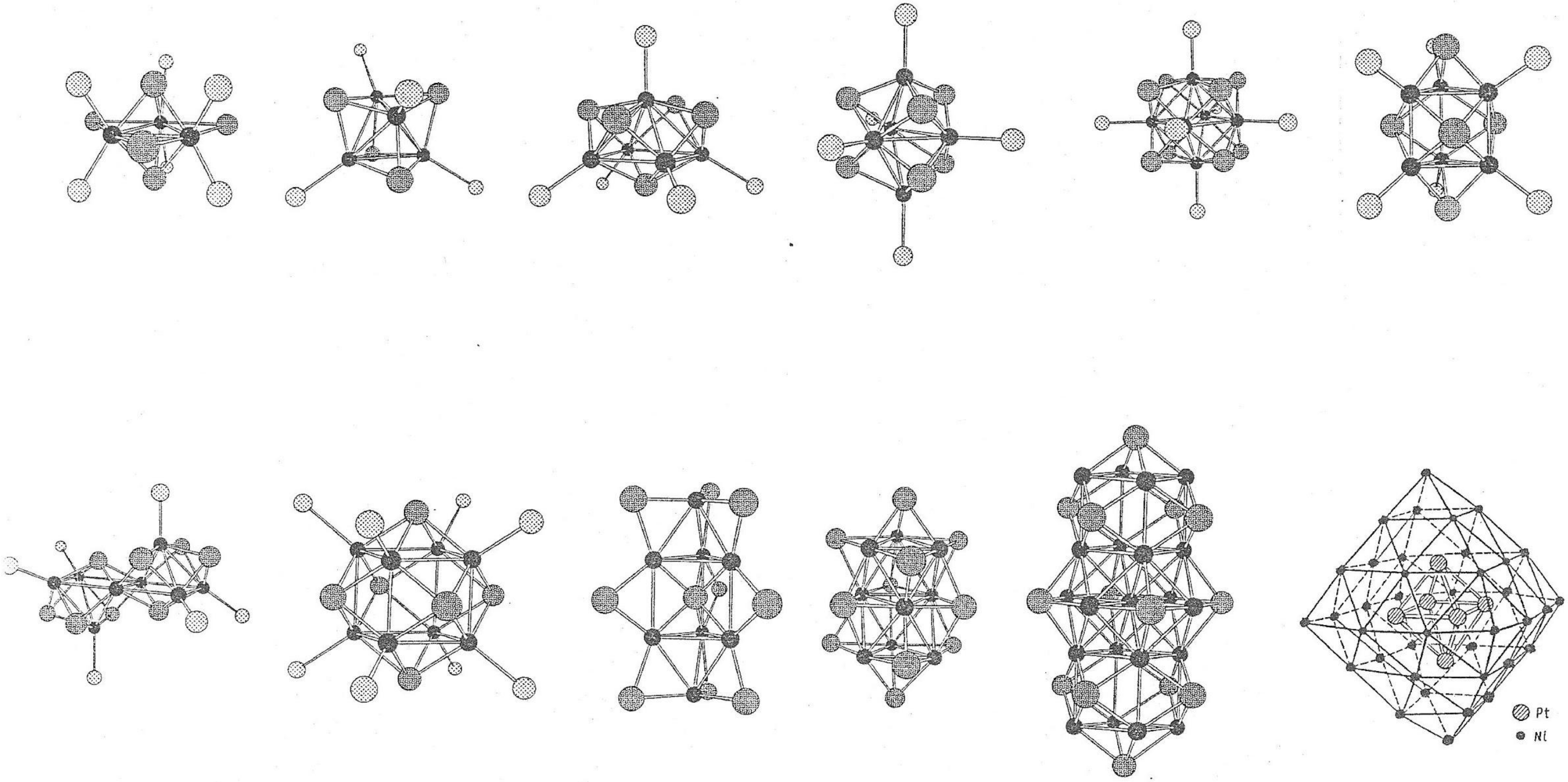
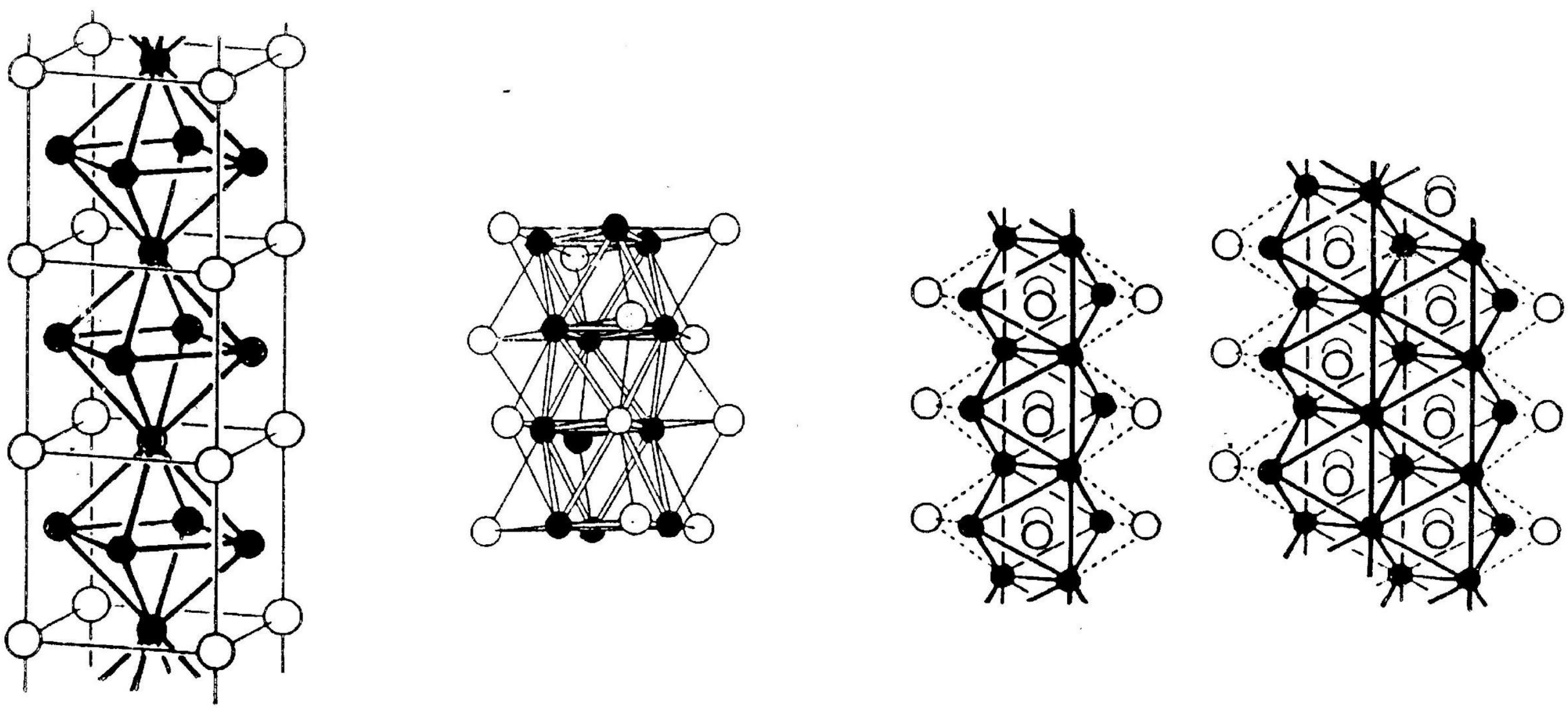
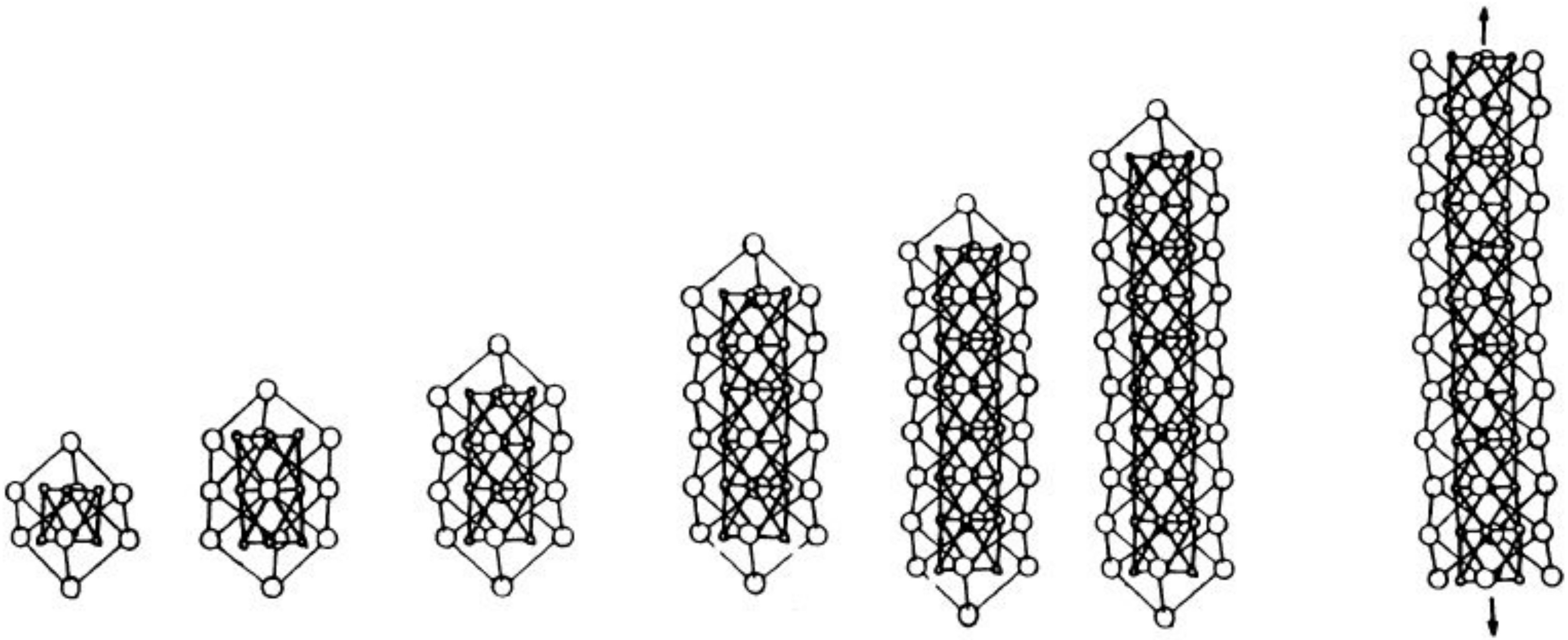
ГИГАНТСКИЕ КЛАСТЕРЫ


Pt
Ni

Примеры одномерной конденсации октаэдрических металлокластеров



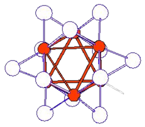
Прогрессивная одномерная конденсация октаэдрических кластеров молибдена



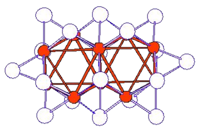
$[Mo_6X_8]$ $[Mo_9X_{11}]$ $[Mo_{12}X_{14}]$ $[Mo_{18}X_{20}]$ $[Mo_{24}X_{26}]$ $[Mo_{30}X_{32}]$ ${}^{1}_{\infty}[Mo_3X_3]$

Oxomolybdates

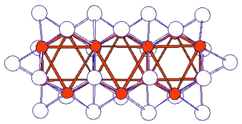
Cluster



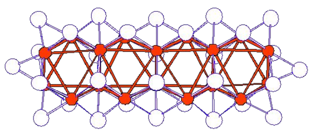
Mo_6O_{12}



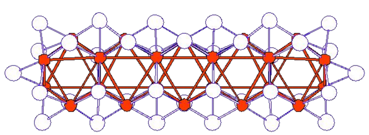
$Mo_{10}O_{18}$



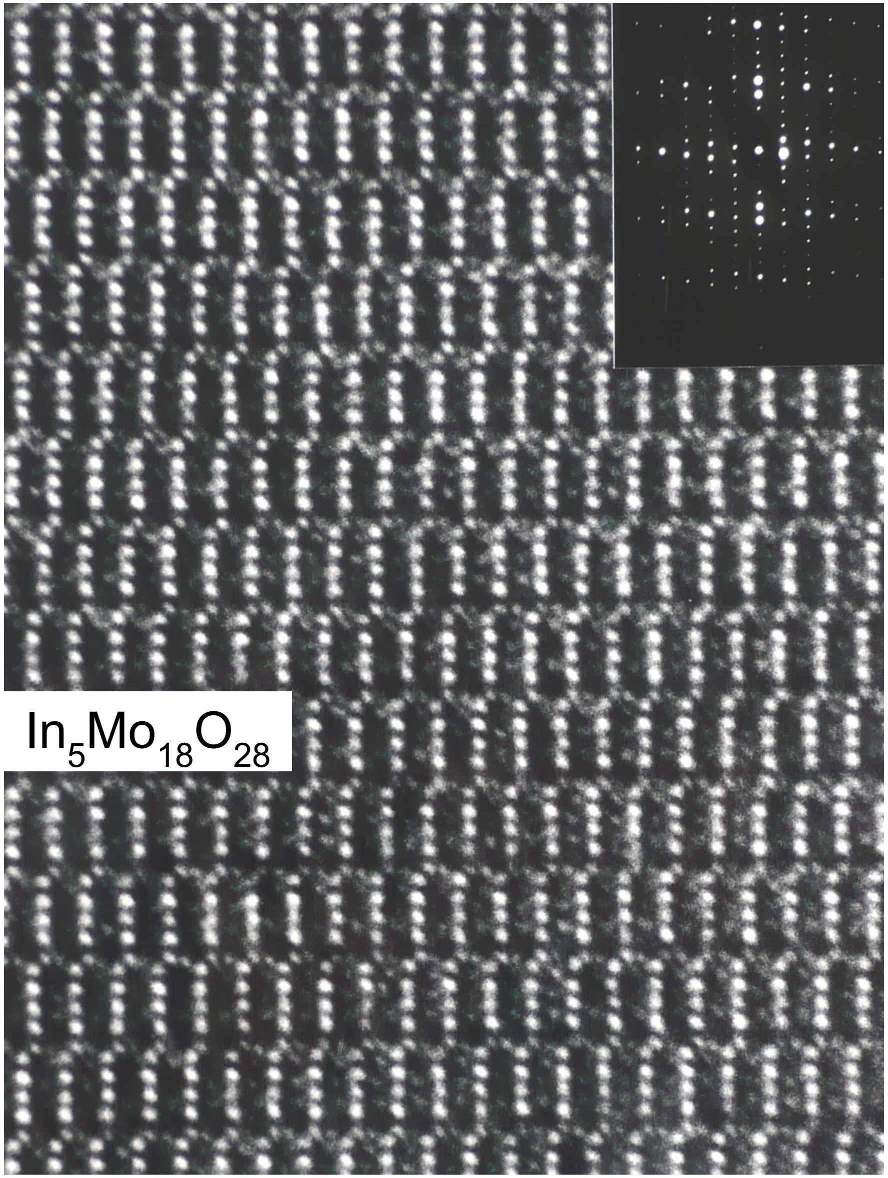
$Mo_{14}O_{24}$



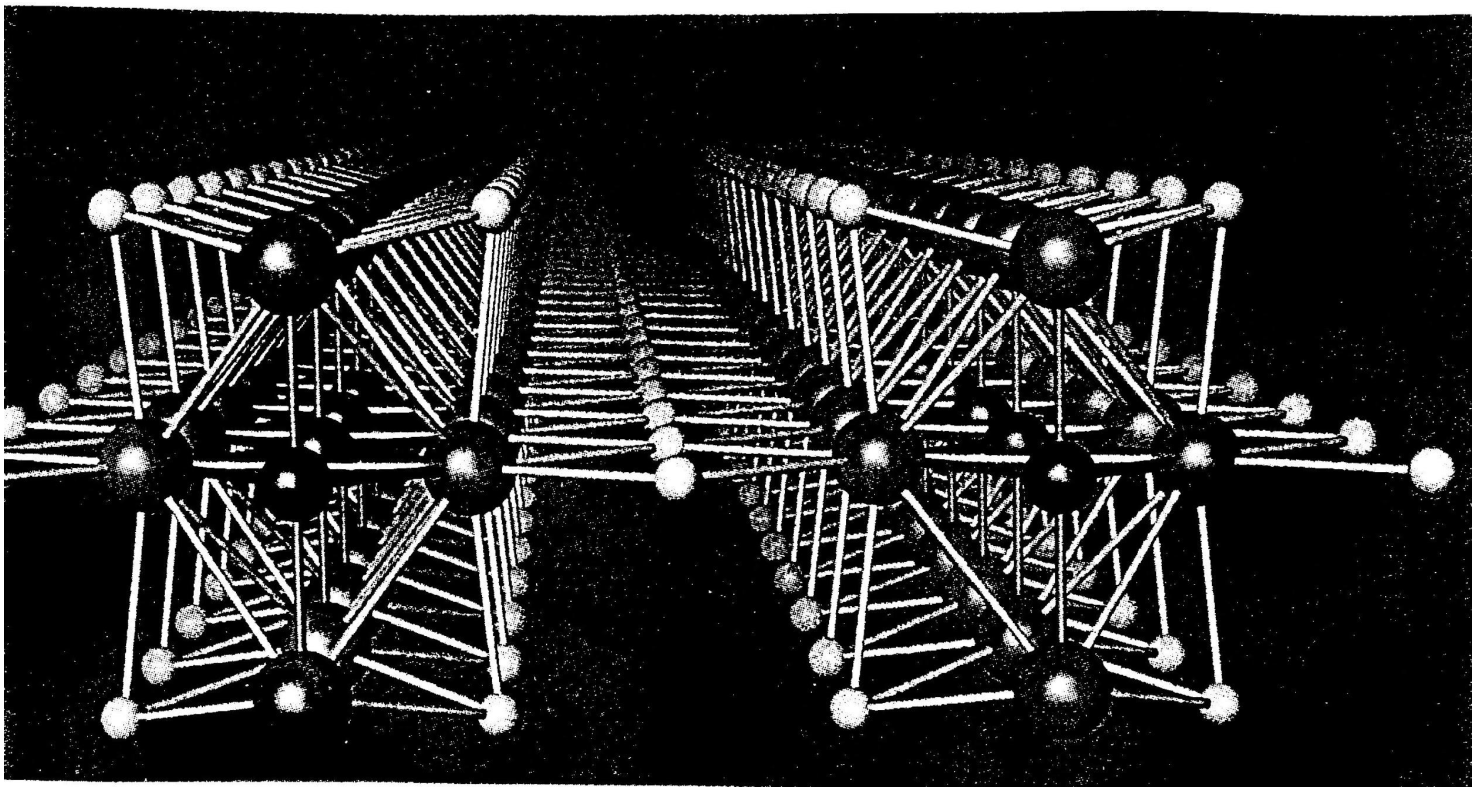
$Mo_{18}O_{30}$



$Mo_{22}O_{36}$

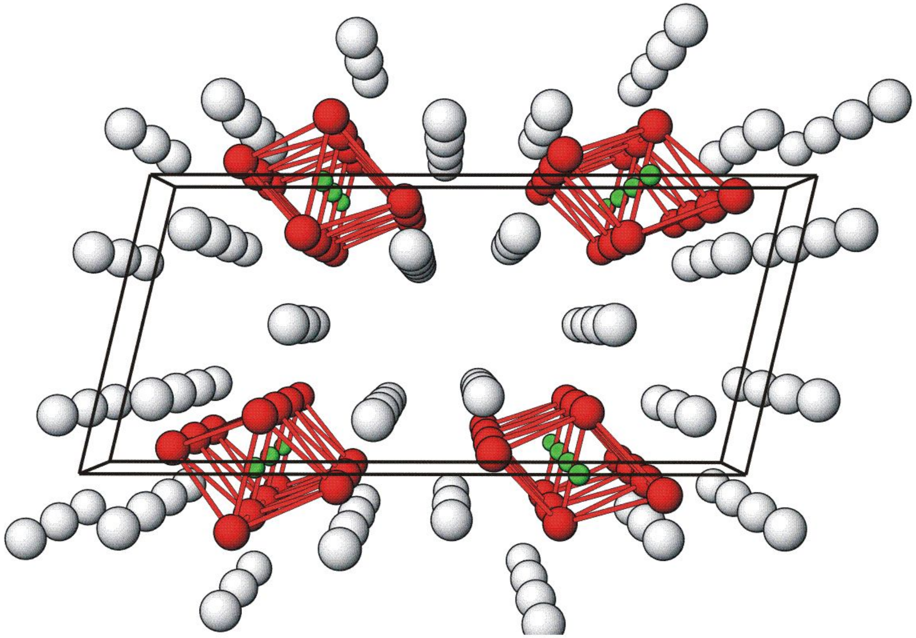


$Pr_4(Ru)I_5$



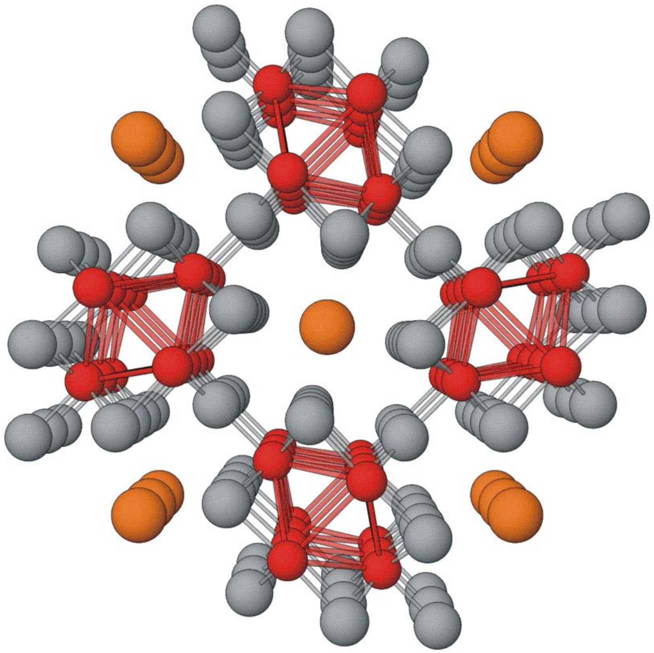
Связывание металлокластерных цепочек в слой через *транс*-мостиковые атомы иода

Chains

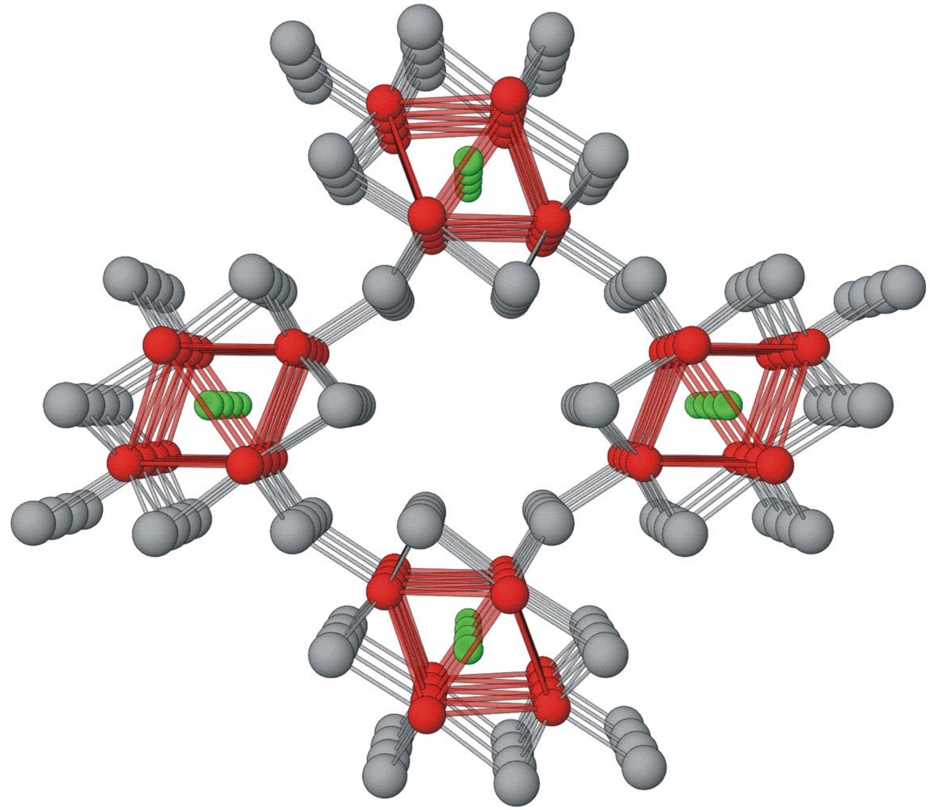


Gd_4I_5C

Chains of Octahedra



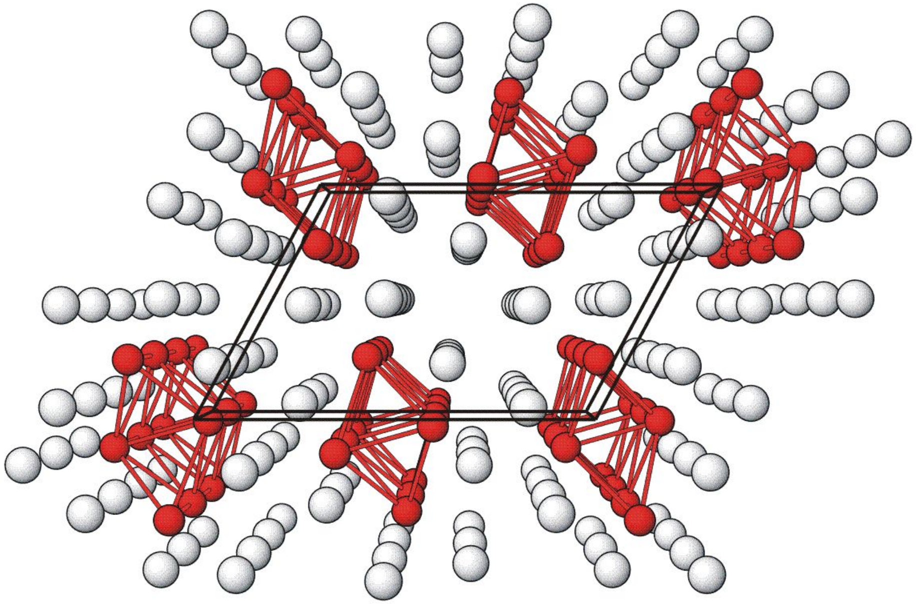
$NaMo_4O_6$



Gd_4Br_6Si

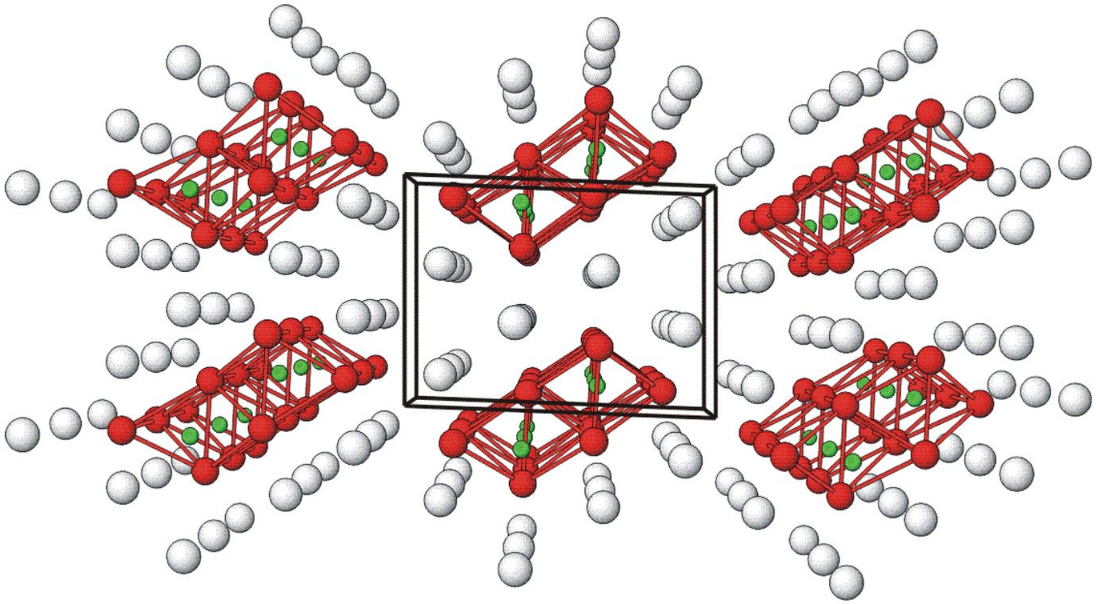
Связывание металлокластерных цепочек через *цис*-мостиковые лиганды

Chains



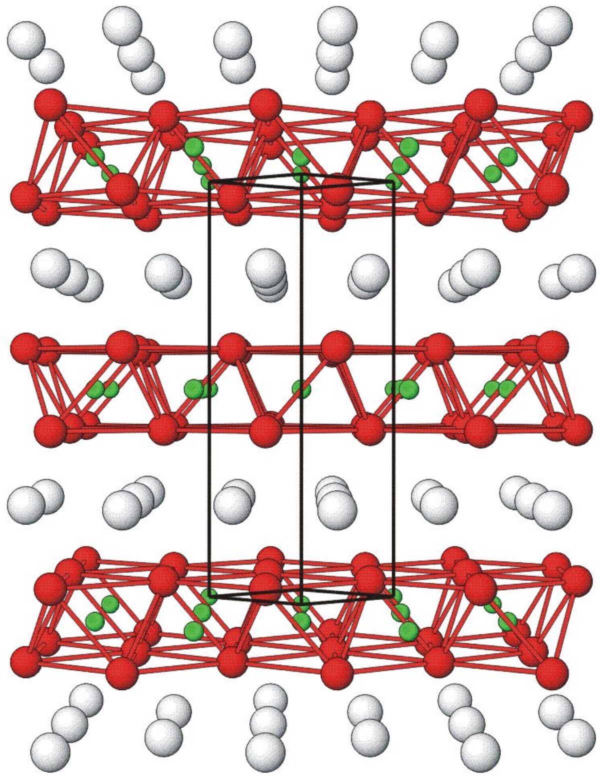
Gd_2Cl_3

Twin-Chains



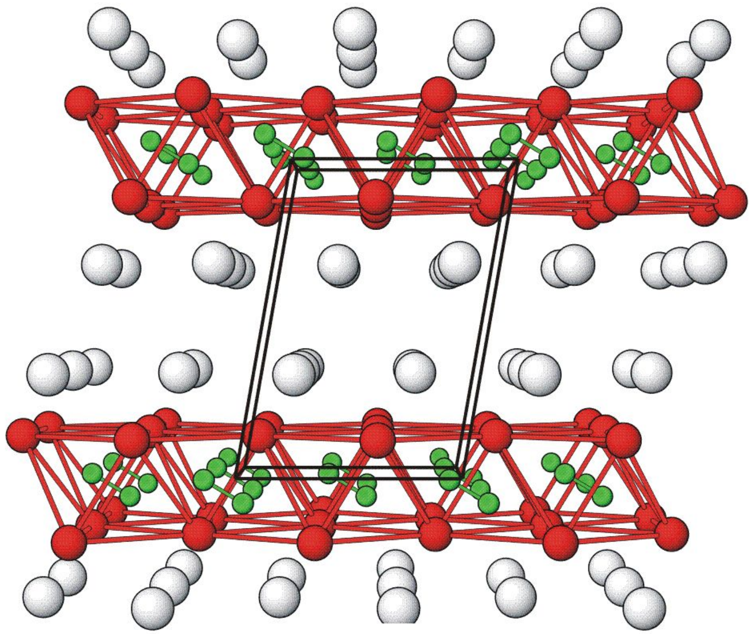
Gd_3I_3C

Layers



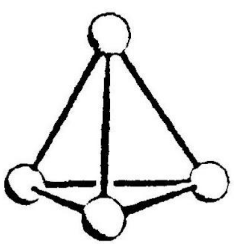
Gd_2IC

Layers

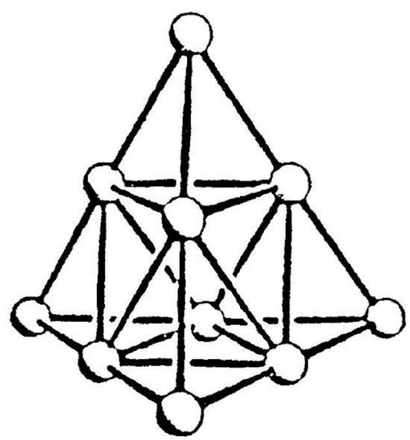


$Gd_2Cl_2C_2$

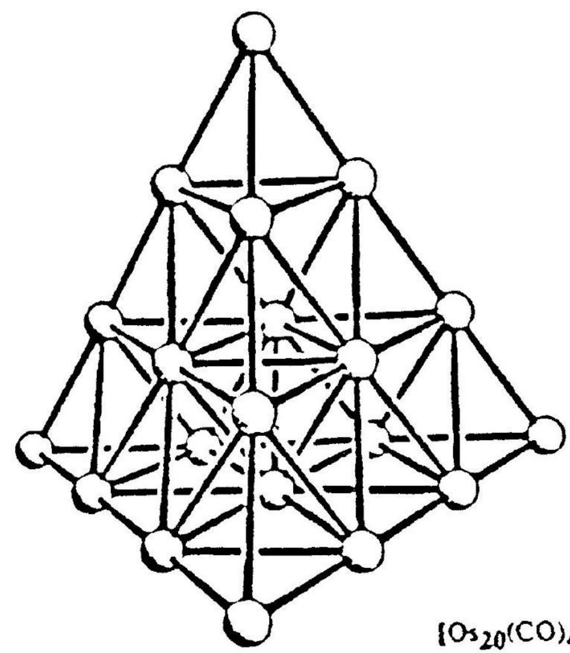
Конденсация тетраэдрических металлокластеров



$[H_2Os_4(CO)_{12}]^{2-}$



$[Os_{10}C(CO)_{24}]^{2-}$

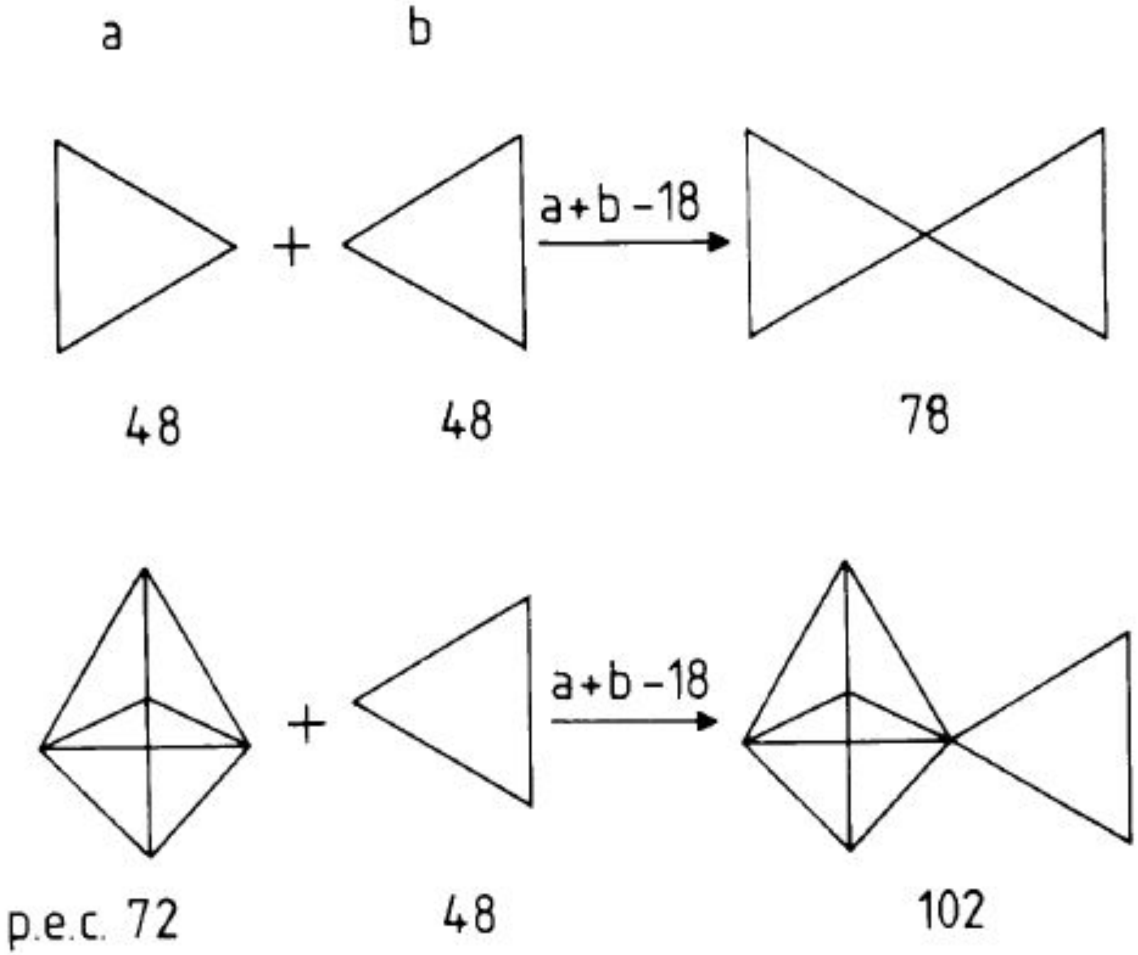


$[Os_{20}(CO)_{40}]^{2-}$

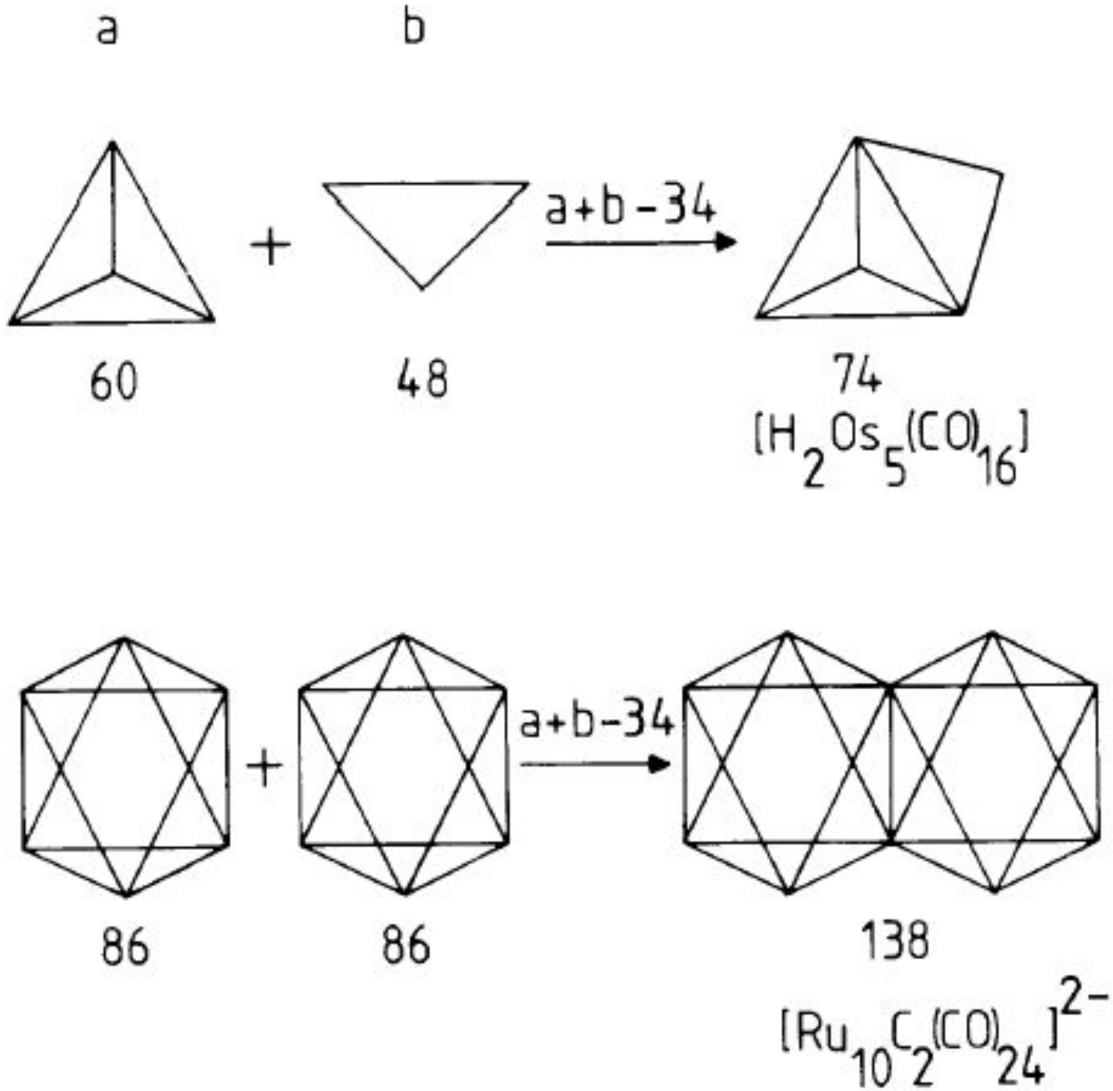
Правило подсчета числа электронов для конденсированных кластеров:

число кластерных валентных электронов (КВЭ) конденсированных кластеров равно сумме КВЭ исходных полиэдров минус число электронов атома, лежащего в общей вершине (18e), пары атомов в общем ребре (34e) или граневых атомов, общих для обоих полэдров (48e для общего треугольника, 62 для общего квадрата)

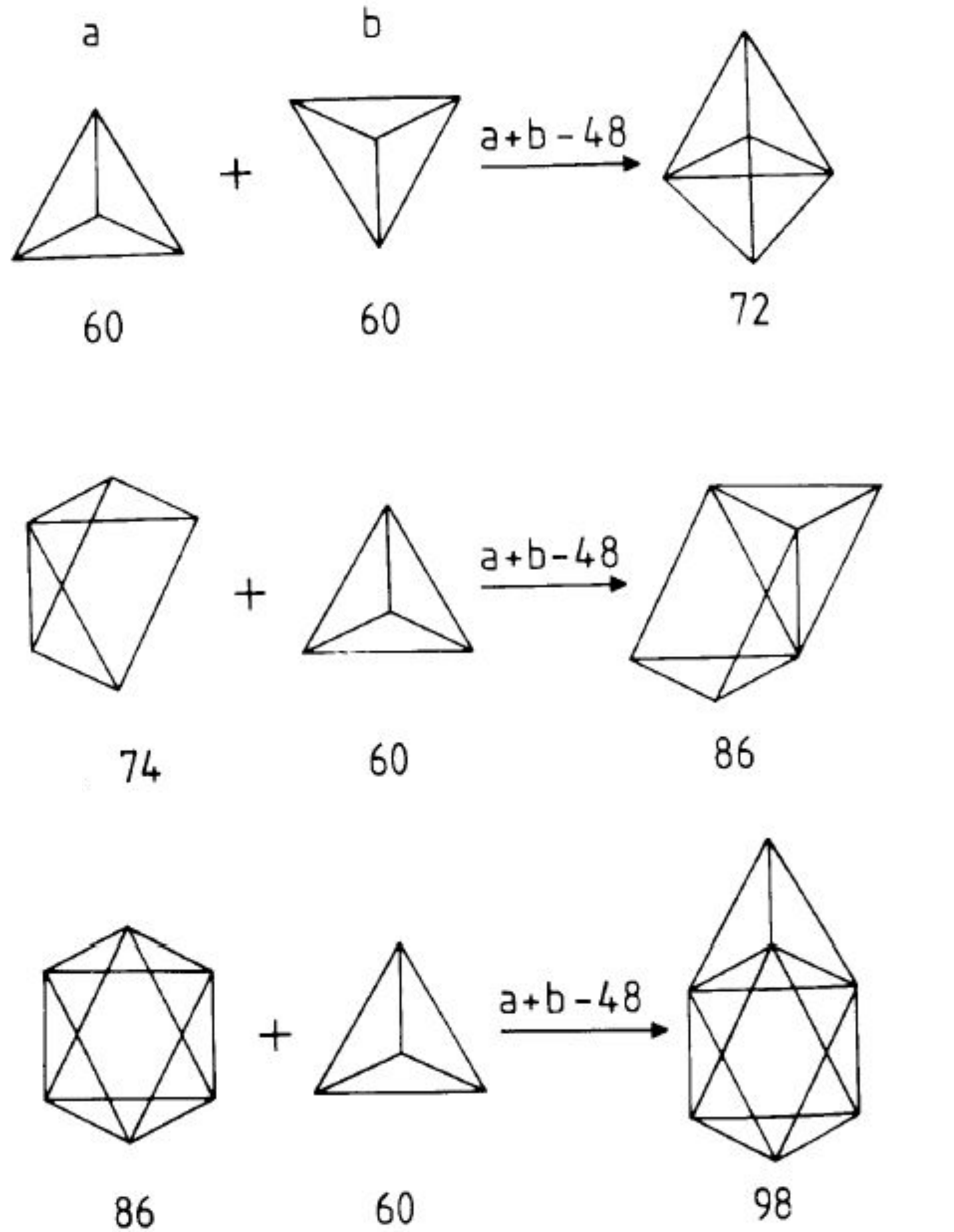
Конденсация металлокластеров через общую вершину

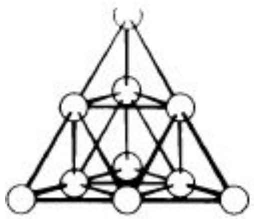


Конденсация металлокластеров через общее ребро



Конденсация металлокластеров через общую треугольную грань

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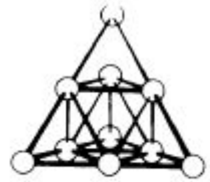
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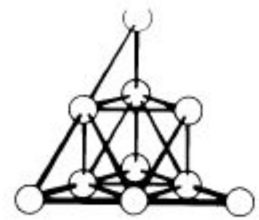
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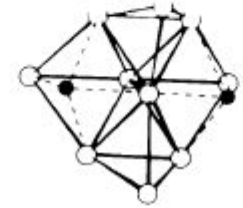
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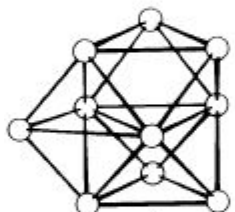
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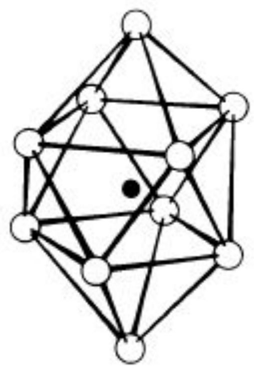
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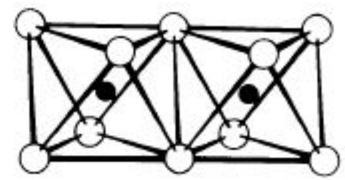
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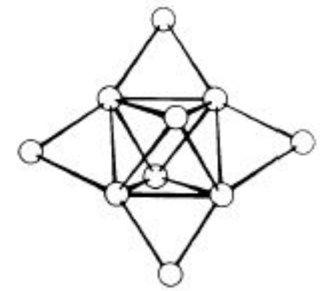
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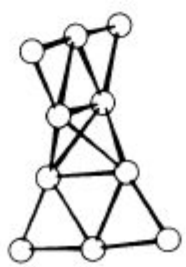
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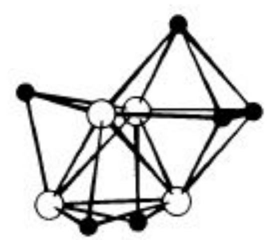
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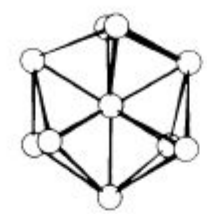

11

10-ядерные металлокластеры

$[H_4Os_{10}(CO)_{24}]^{2-}$
$[Os_{10}C(CO)_{24}]^{2-}$
$[HOs_{10}C(CO)_{24}]^{-}$
$Os_{10}C(CO)_{23}(POMe)_3)I_2$
$Os_{10}C(CO)_{21}(P(OMe)_3)_4$
$[Os_{10}C(CO)_{23}(NO)]$
$[Os_{10}C(CO)_{22}(NO)I]^{2-}$
$[Cu_6Fe_4(CO)_{16}]^{2-}$
$Hg_6Rh_4(PMe_3)_{12}$
$[Os_{10}C(CO)_{24}(NO)]^{-}$
$[Os_{10}C(CO)_{22}I]^{-}$
$Os_{10}C(CO)_{24}I_2$
$Os_{10}S_2(CO)_{23}$
$[Rh_{10}(CO)_{21}]^{2-}$
$[Rh_{10}S(CO)_{22}]^{2-}$
$[Rh_{10}P(CO)_{22}]^{-}$
$[Rh_{10}As(CO)_{22}]^{2-}$
$[Ru_{10}C_2(CO)_{24}]^{2-}$
$Au_2Os_8(CO)_{22}(PPh_3)_2$
$[Co_3Ni_7C_2(CO)_{15}]^{3-}$
$[Ni_{10}C_2(CO)_{16}]^{2-}$
$Pd_{10}(CO)_{14}(PBu_3)_4$
$Pd_{10}(CO)_{12}(PBu_3)_6$
$[Fe_4Pt_6(CO)_{22}]^{2-}$
$Au_2Ir_8(CO)_{20}(PhPPPh)(PEt_3)_2$
$Co_4As_6(PPh_3)_4$
$[Au_{10}(PPh(C_6H_5)_2)_6Cl_3]^{+}$

14 atoms

$[Rh_{14}(CO)_{26}]^{2-}$

$[Rh_{14}(CO)_{25}]^{4-}$

$[HRh_{14}(CO)_{25}]^{3-}$

$[Rh_{14}C_2(CO)_{33}]^{2-}$

15 atoms

$[Rh_{15}(CO)_{27}]^{3-}$

$[Rh_{15}(CO)_{30}]^{2-}$

$[Rh_{15}C_2(CO)_{28}]^{-}$

$[Pt_{15}(CO)_{30}]^{2-}$

16 atoms

$[Ni_{16}(C_2)_2(CO)_{23}]^{4-}$

$Fe_{10}Tl_6(CO)_{36}]^{6-}$

17 atoms

$[Rh_{17}(CO)_{30}]^{3-}$

$[Rh_{17}S_2(CO)_{32}]^{3-}$

19 atoms

$[Pt_{19}(CO)_{22}]^{4-}$

21 atoms

$[AuOs_{20}C_2(CO)_{48}]^{2-}$

$[HgOs_{20}C_2(CO)_{48}]^{2-}$

22 atoms

$[Rh_{22}(CO)_{37}]^{4-}$

$[Rh_{22}(CO)_{35}H_x]^{5-}$

$[Rh_{22}(CO)_{35}H_{x+1}]^{4-}$

23 atoms

$[Pd_{23}(CO)_{22}(PEt_3)_{10}]$

$[Pd_{23}(CO)_{20}(PEt_3)_8]$

24 atoms

$[Pt_{24}(CO)_{30}]^{2-}$

25 atoms

$[Ag_{12}Au_{13}Cl_6(PPh_3)_{12}]^{m+}$

26 atoms

$[Pt_{26}(CO)_{32}]^{2-}$

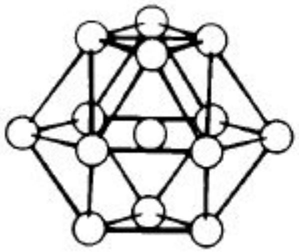
$[Pt_{26}(CO)_{30}]^{2-}$

34 atoms

$[HNi_{34}C_4(CO)_{38}]^{5-}$

35 atoms

$[Ni_{35}C_4(CO)_{39}]^{6-}$



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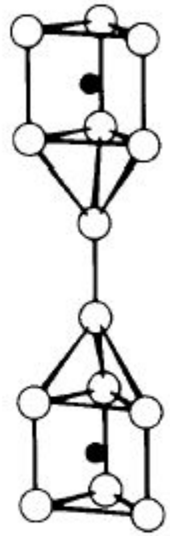
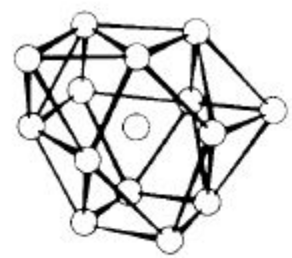


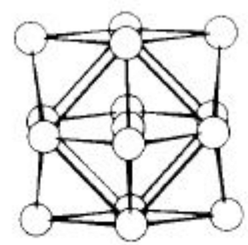
2

Rh_{14}

M_{15}



1



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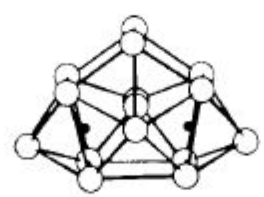

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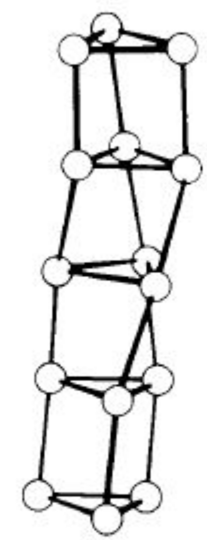

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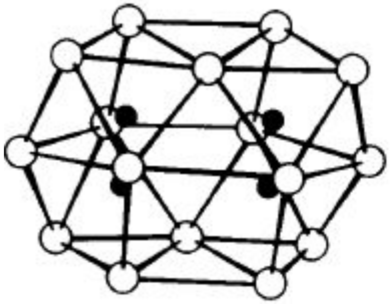

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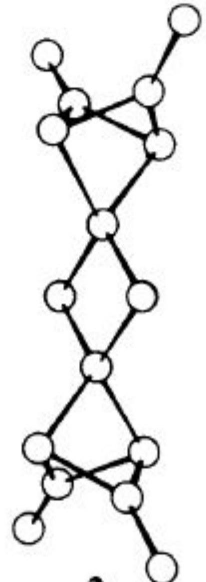
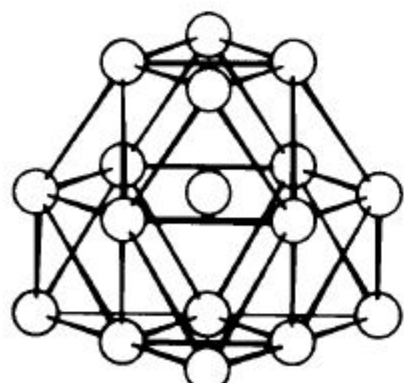


2

M_{16}

Rh_{17}



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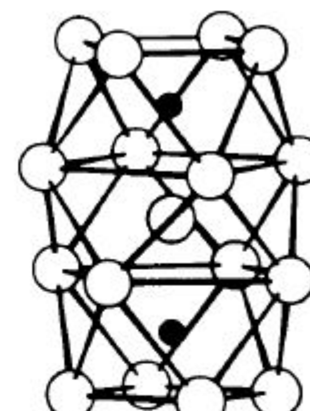

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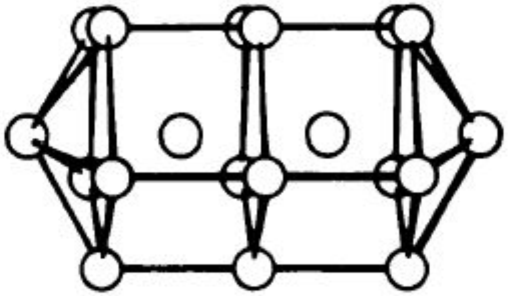
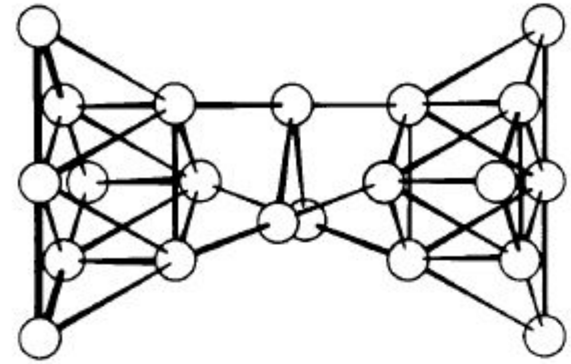
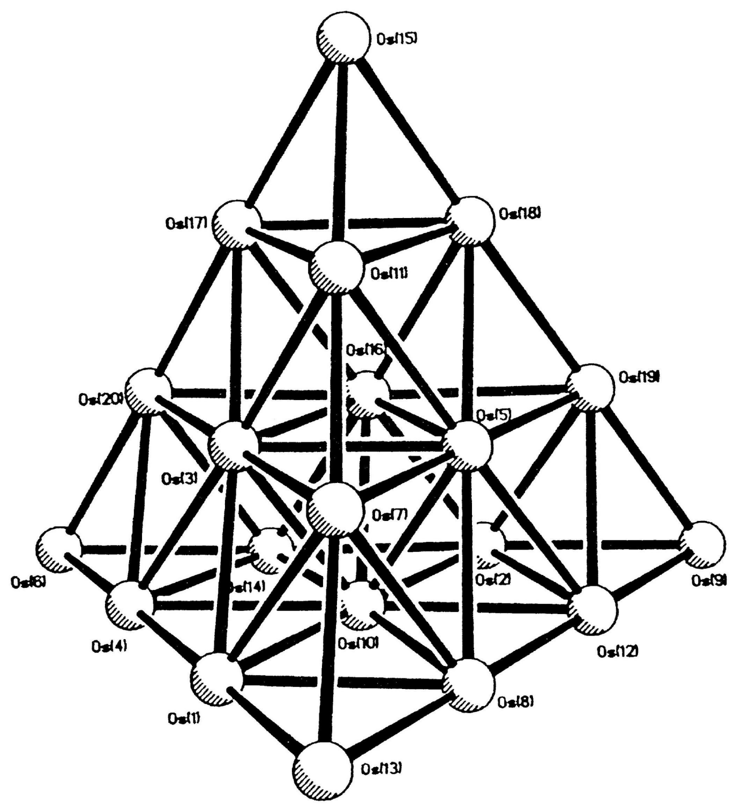


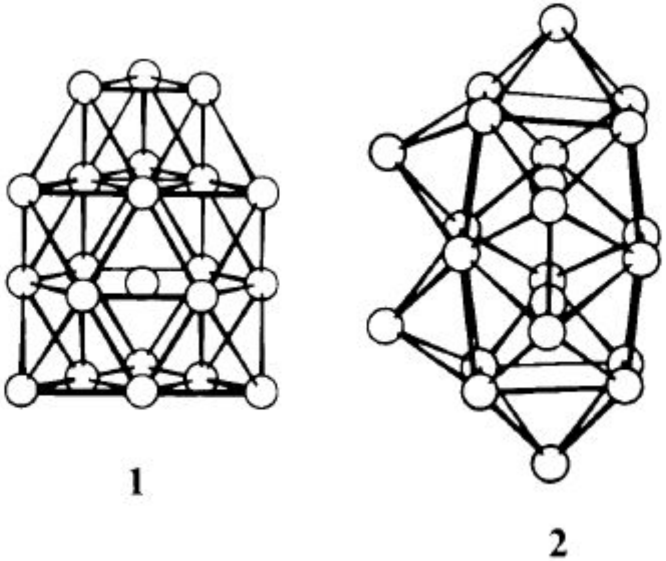
Pt_{19}



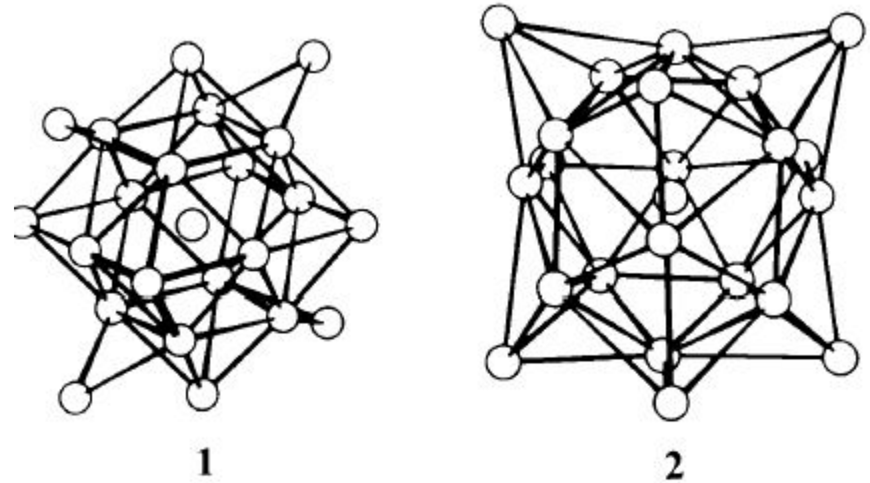
$Os_{20}M$ (M=Au, Hg)



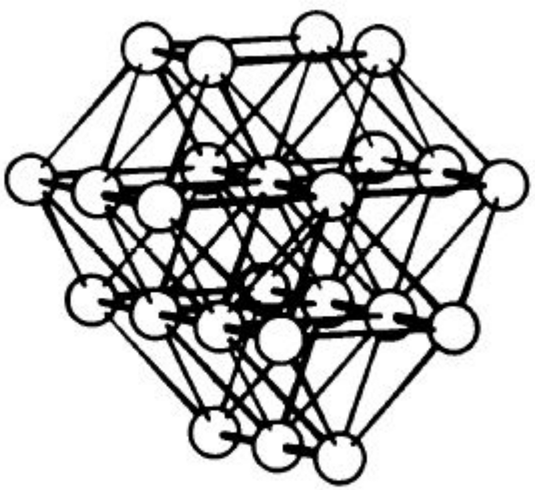
$[Os_{20}(CO)_{40}]^{2-}$



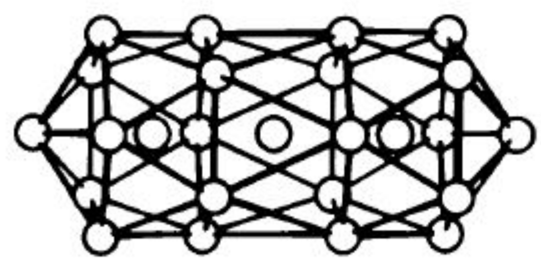
Rh_{22}



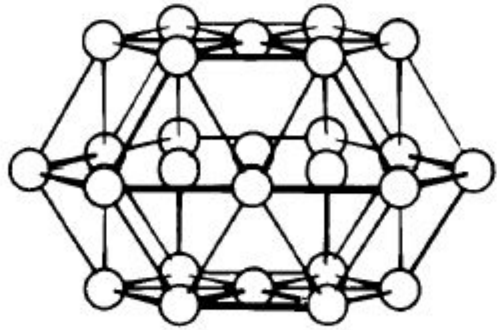
Pd_{23}



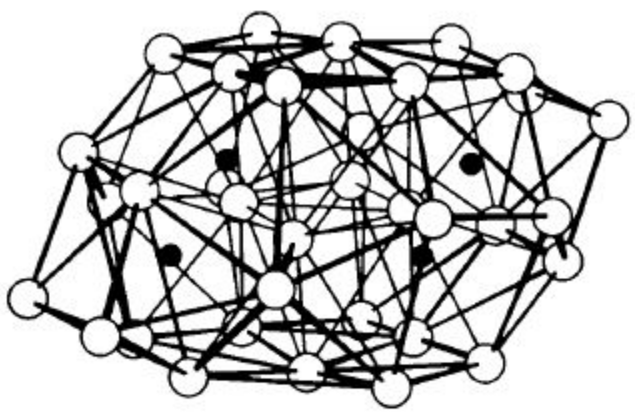
Pt_{24}



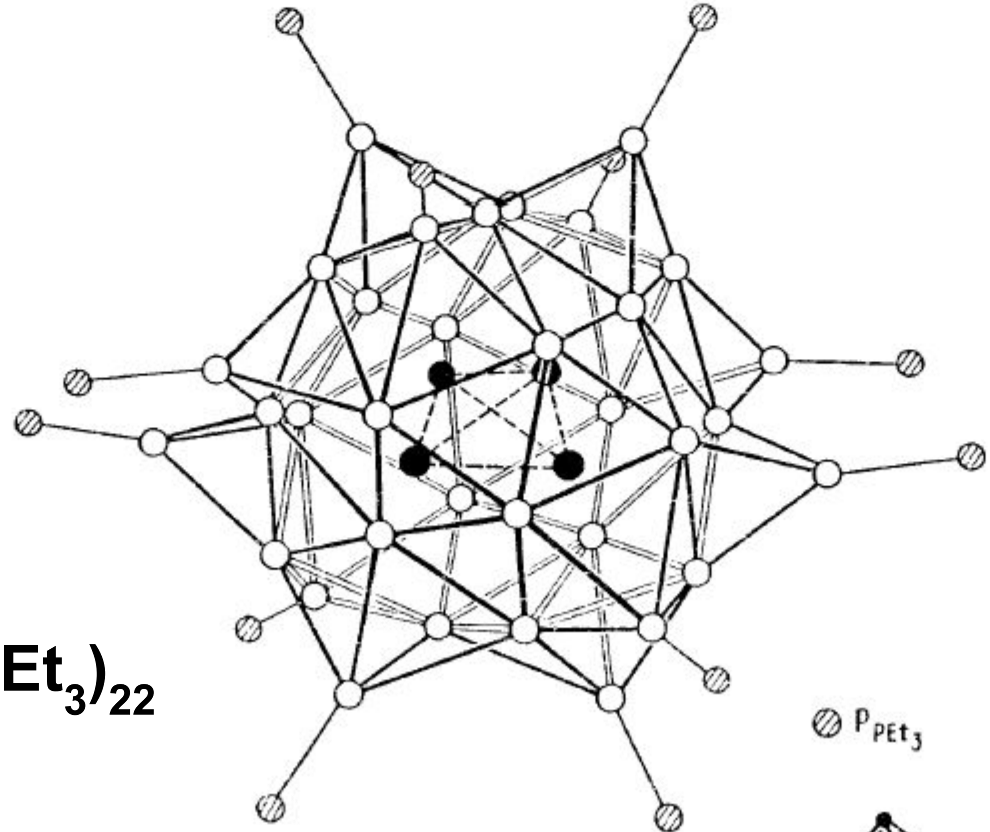
$Ag_{12}Au_{13}$



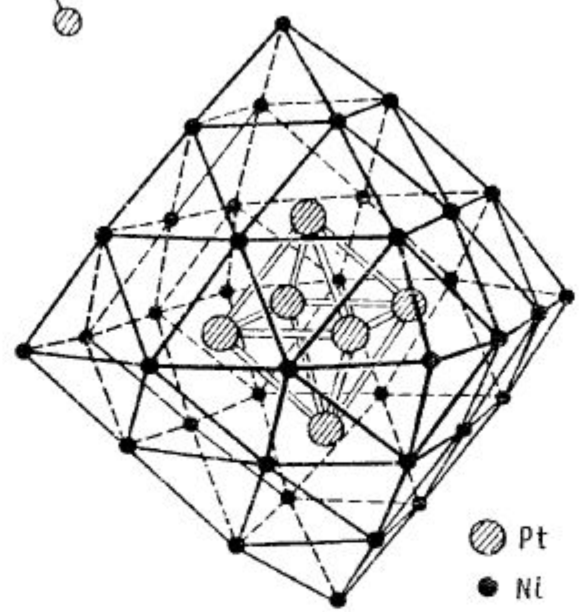
$[Pt_{26}(CO)_{32}]^{2-}$



$Ni_{34}C_4(CO)_{38}]^{5-}$



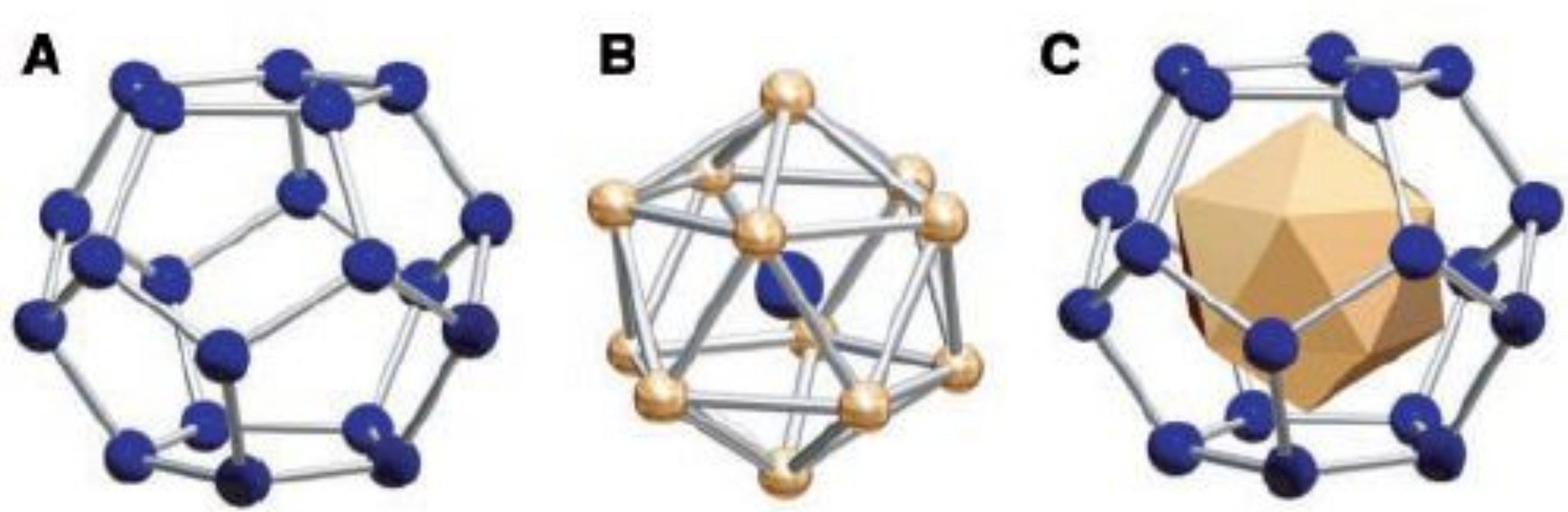
$Pd_{38}(CO)_{30}(PEt_3)_{22}$



$[Ni_{38}Pt_6(CO)_{48}H_2]^{4-}$

M.J. Moses, J.C. Fettinger, B.W. Eichhorn,
Interpenetrating As_{20} Fullerene and Ni_{12} Icosahedra in the Onion-Skin
$[As@Ni_{12}@As_{20}]^{3-}$ Ion,
SCIENCE VOL 300 2 MAY 2003

As_{20} **$[Ni_{12}\text{-}(\mu_{12}\text{-}As)]^{3-}$** **$[As@Ni_{12}@As_{20}]^{3-}$**



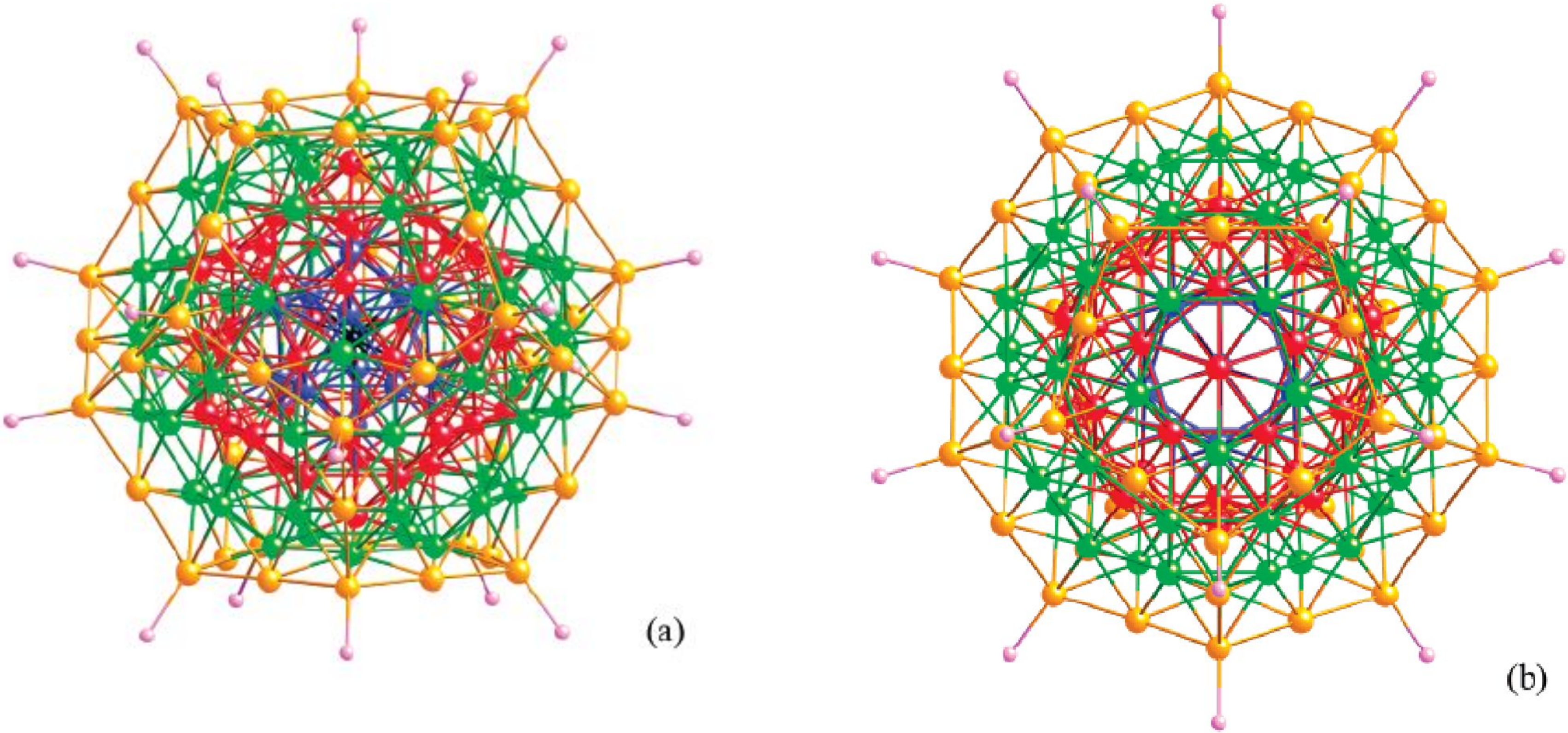
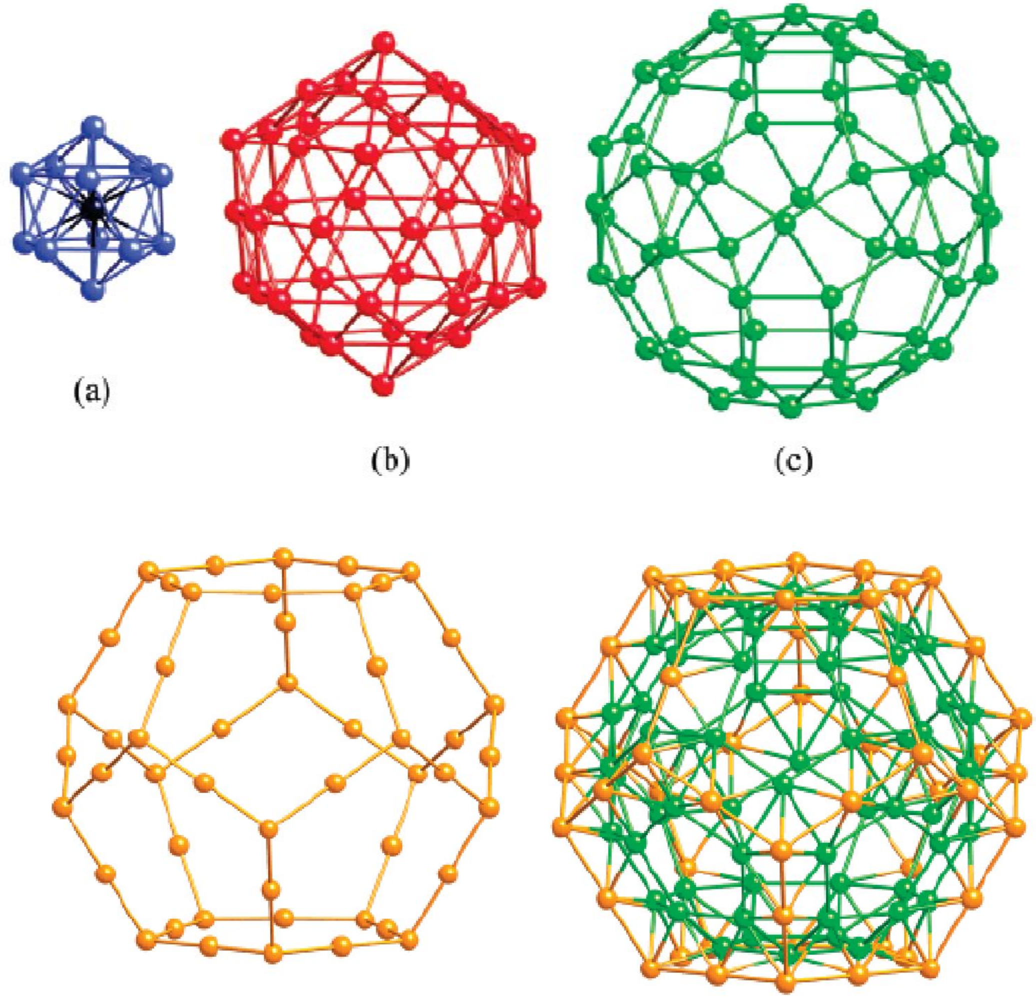


Figure 1. Side/top views of $(\mu_{12}\text{-Pt})\mathrm{Pd}_{164-x}\mathrm{Pt}_x(\mathrm{CO})_{72}\mathrm{P}_{20}$ fragment in Pt-centered four-shell 165-atom Pd−Pt cluster, $(\mu_{12}\text{-Pt})\mathrm{Pd}_{164-x}\mathrm{Pt}_x(\mathrm{CO})_{72}(\mathrm{PPh}_3)_{20}$ ($x \approx 7$), of pseudo icosahedral I_h ($2/m\bar{3}\bar{5}$) and cubic crystallographic T_h

$$\mathrm{Pd}_{10}(\mathrm{CO})_{12}(\mathrm{PPh}_3)_6\ (\mathbf{3}) + \mathrm{Pt}(\mathrm{CO})_2(\mathrm{PPh}_3)_2\ (\mathbf{4}) \rightarrow \mathrm{Pd}_{157}\mathrm{Pt}_8(\mathrm{CO})_{72}(\mathrm{PPh}_3)_{20}\ (\mathbf{1}) + \ldots \quad (1)$$

Evgueni G. Mednikov,[*,†] Matthew C. Jewell,[‡] and Lawrence F. Dahl[*,†]


(a)
(b)
(c)

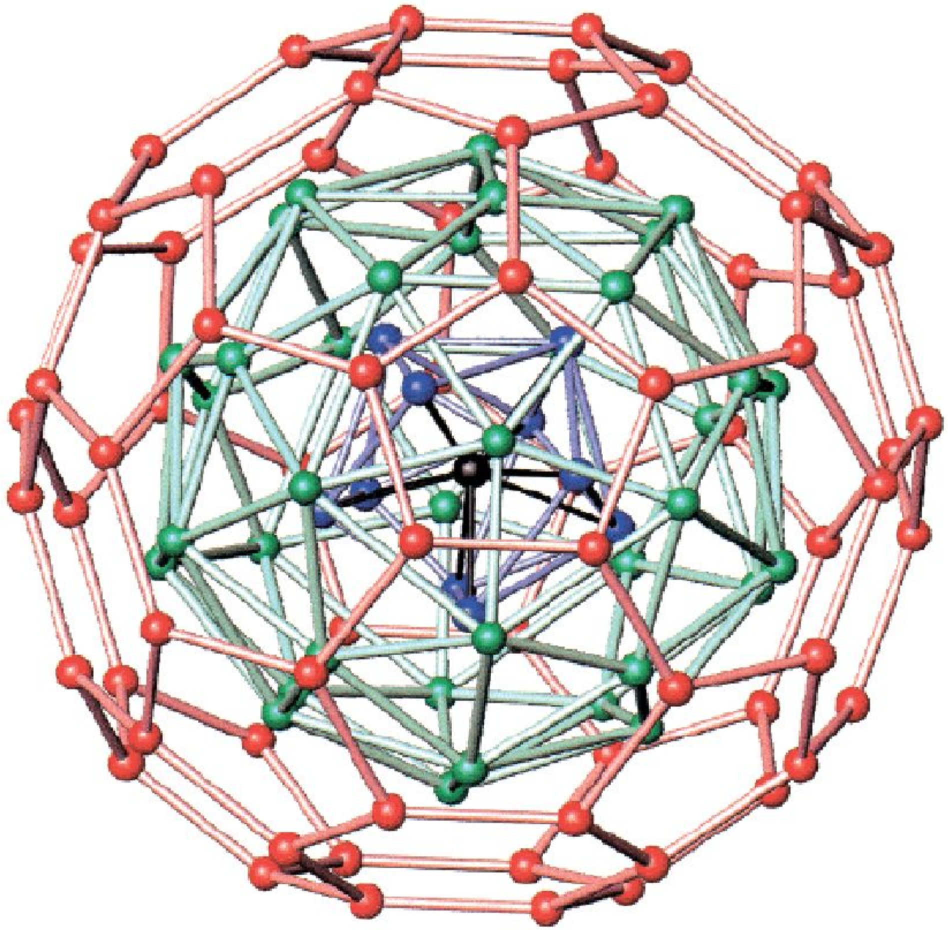
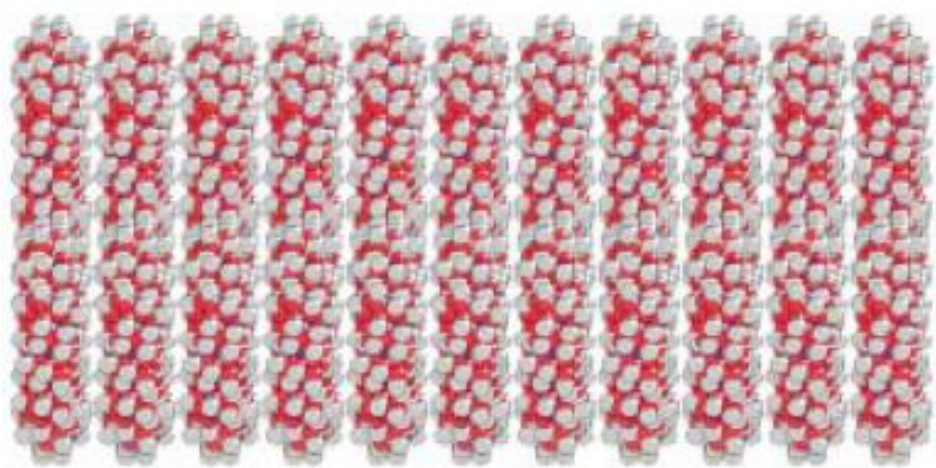
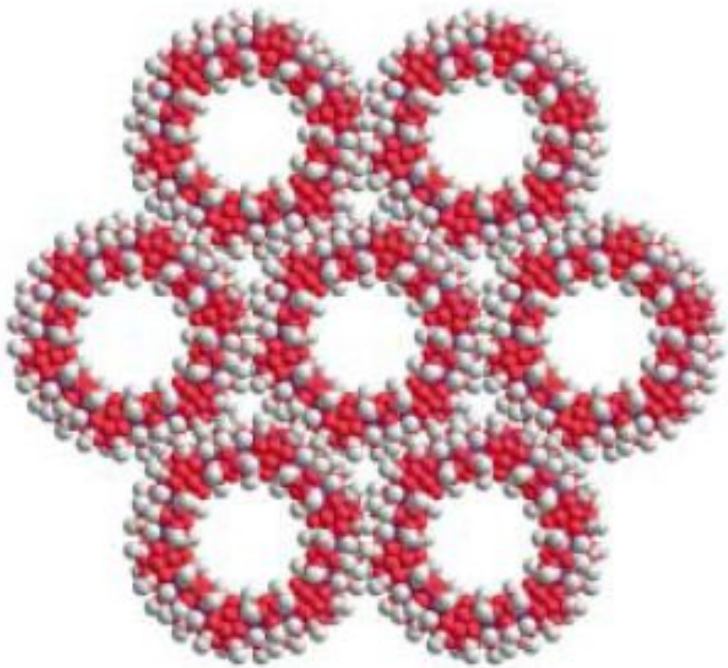


Figure 14. The multiply-endohedral $Ni@In_{10}@Ni_{37}@In_{70}$ cluster extracted from the structure of $Na_{172}In_{197}Ni_2$ with atoms in this sequence colored black, blue, green, and red, respectively. Each Na lies below the center of each pentagonal or hexagonal face of the In_{70} fullerane, but interconnections within the green Na_{37} polyhedron are meant only to guide the eye.

$[Mn_{84}O_{72}(O_2CMe)_{78}(OMe)_{24}(MeOH)_{12}(H_2O)_{42}(OH)_6]\cdot xH_2O\cdot yCHCl_3$

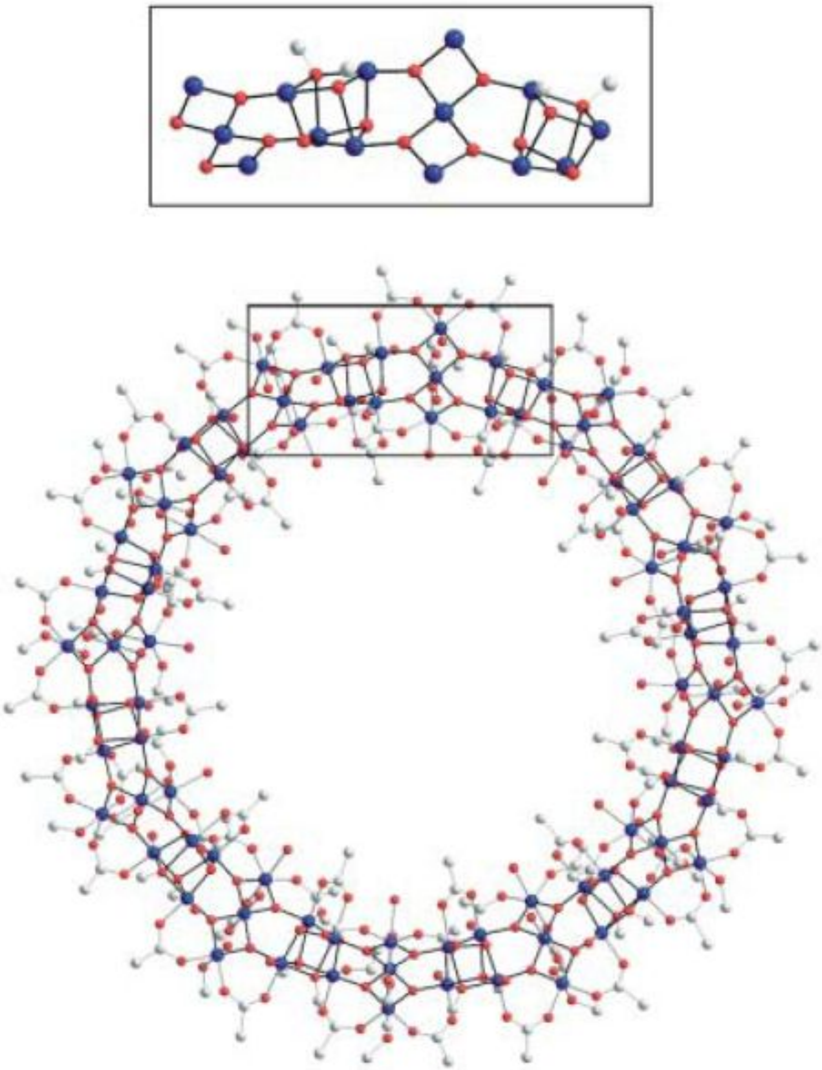


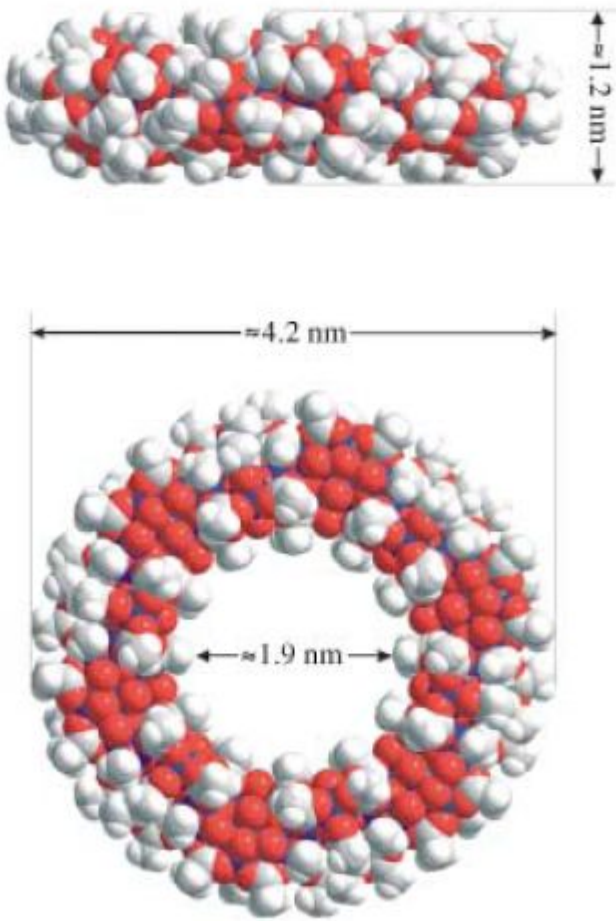


A.J. Tasiopoulos, A. Vinslava, W. Wernsdorfer, K.A. Abboud, G. Christou, Giant Single-Molecule Magnets: A $\{Mn_{84}\}$ Torus and Its Supramolecular Nanotubes, *Angew. Chem. Int. Ed.* 2004, 43, 2117 –2121

Near-linear $[Mn_3O_4]$ and cubic $[Mn_4O_2(OMe)_2]$ subunits

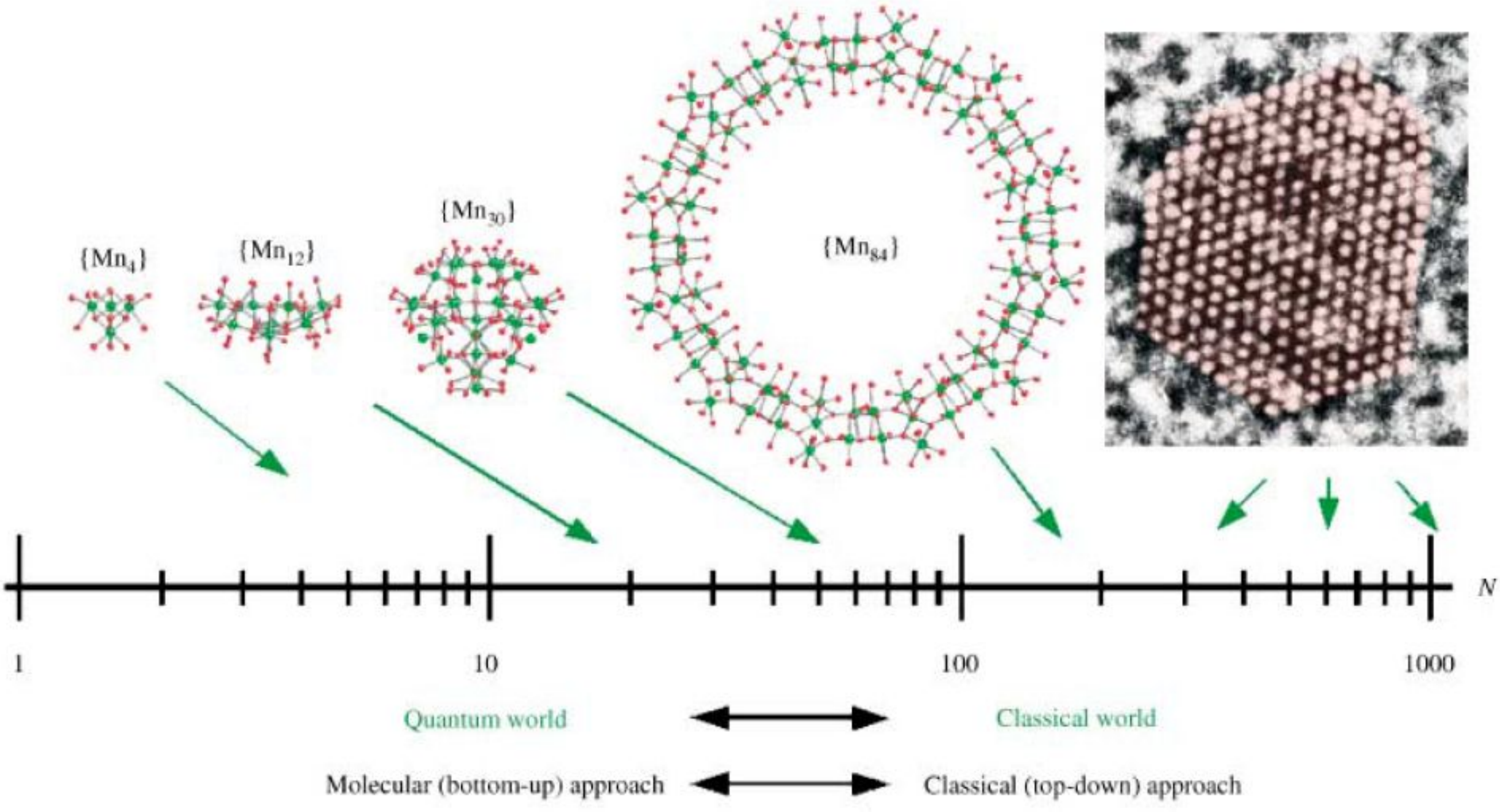
Single-molecule magnets (SMMs)

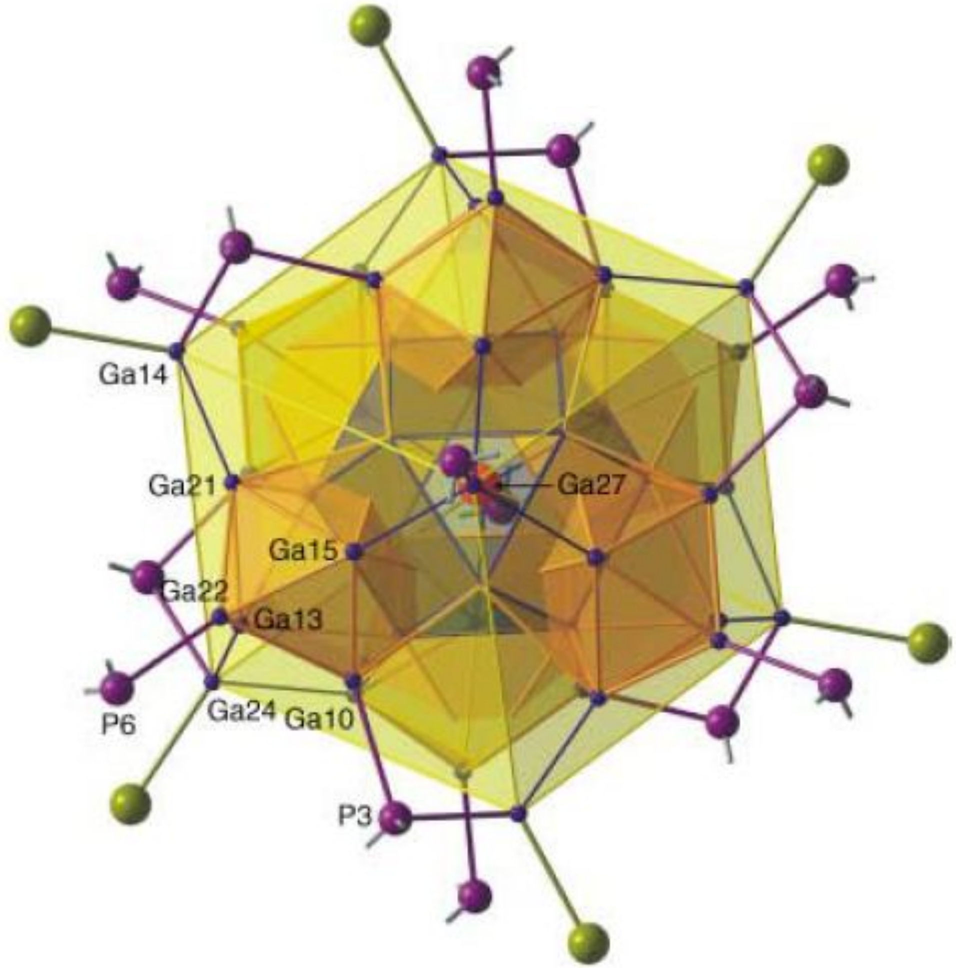




$[Mn_{84}O_{72}(O_2CMe)_{78}(OMe)_{24}(MeOH)_{12}(H_2O)_{42}(OH)_6]\cdot xH_2O\cdot yCHCl_3$

A.J. Tasiopoulos, A. Vinslava, W. Wernsdorfer, K.A. Abboud, G. Christou, Giant Single-Molecule Magnets: A $\{Mn_{84}\}$ Torus and Its Supramolecular Nanotubes, *Angew. Chem. Int. Ed.* 2004, 43, 2117 –2121





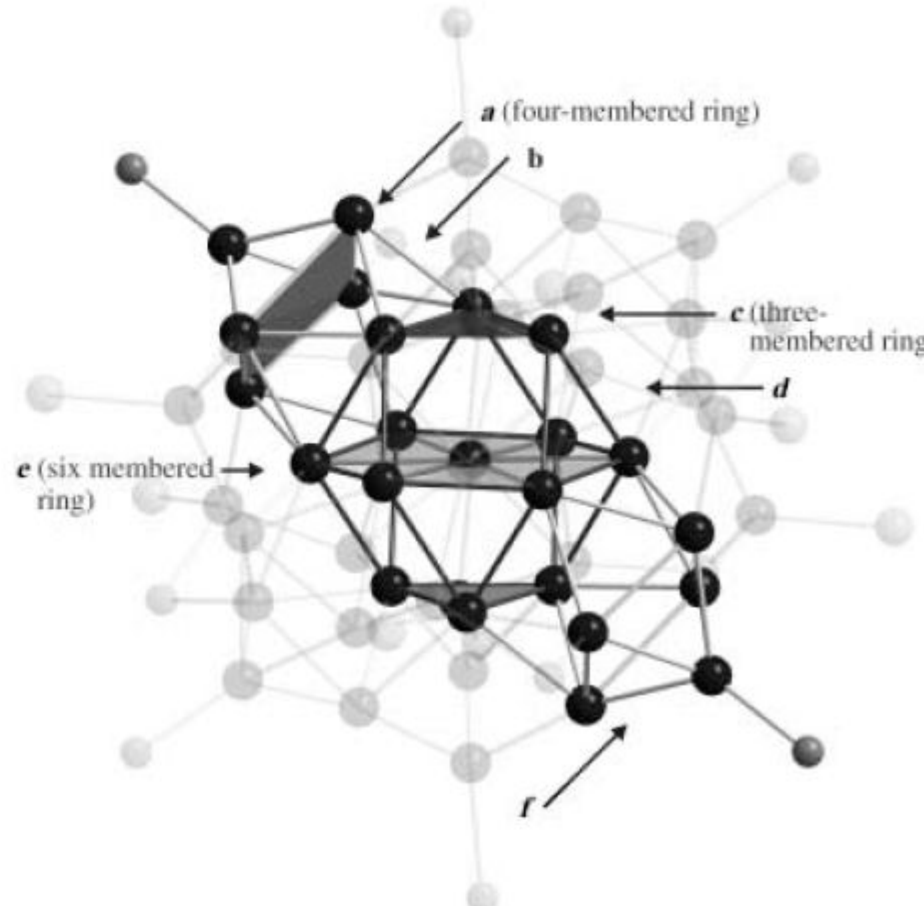


Figure 2. To illustrate the variance of the Ga–Ga distances, a cross-section of **1 a** is highlighted (see text). The following distances [pm] are observed: *a* 259.5–295.8, *b* 258.9–278.4, *c* 284.8–286.2, *d* 279.3–295.3, *e* 275.8–278.8, *f* 245.5–268.1.

J. Steiner, G. Stößer, H. Schnöckel,
$[Ga_{51}(P\textit{t}Bu_2)_{14}Br_6]^{3-}$: An Elementoid Gallium Cluster with Metalloid and Nonmetalloid Structural Elements,
***Angew. Chem. Int. Ed.* 2004, 43, 302 –305**

N.T. Tran, D.R. Powell, L.F. Dahl,

Nanosized $Pd_{145}(CO)_x(PEt_3)_{30}$ Containing a Capped Three-Shell 145-Atom Metal-Core Geometry of Pseudo Icosahedral Symmetry

***Angew. Chem. Int. Ed.* 2000, 39, 4121–4125**

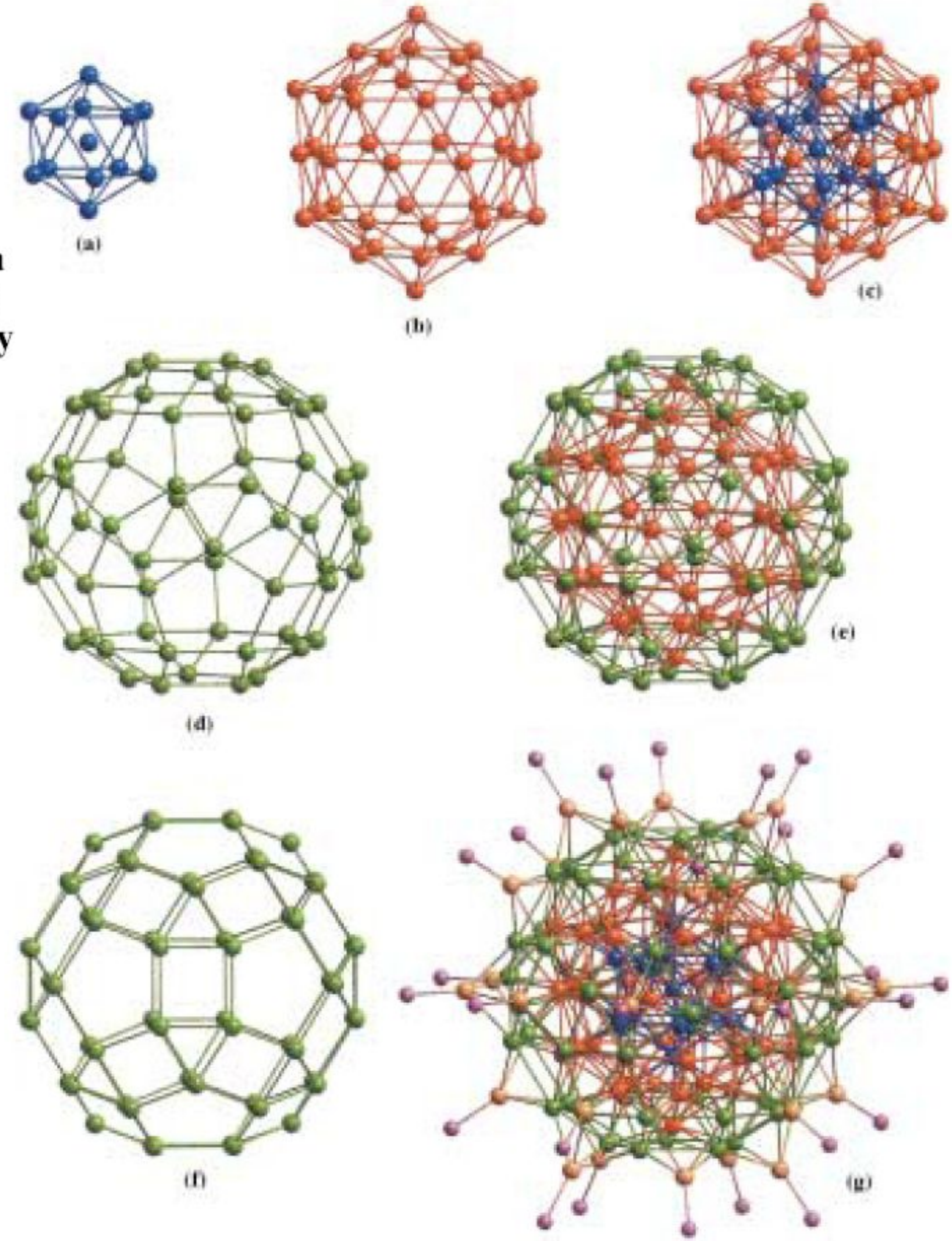
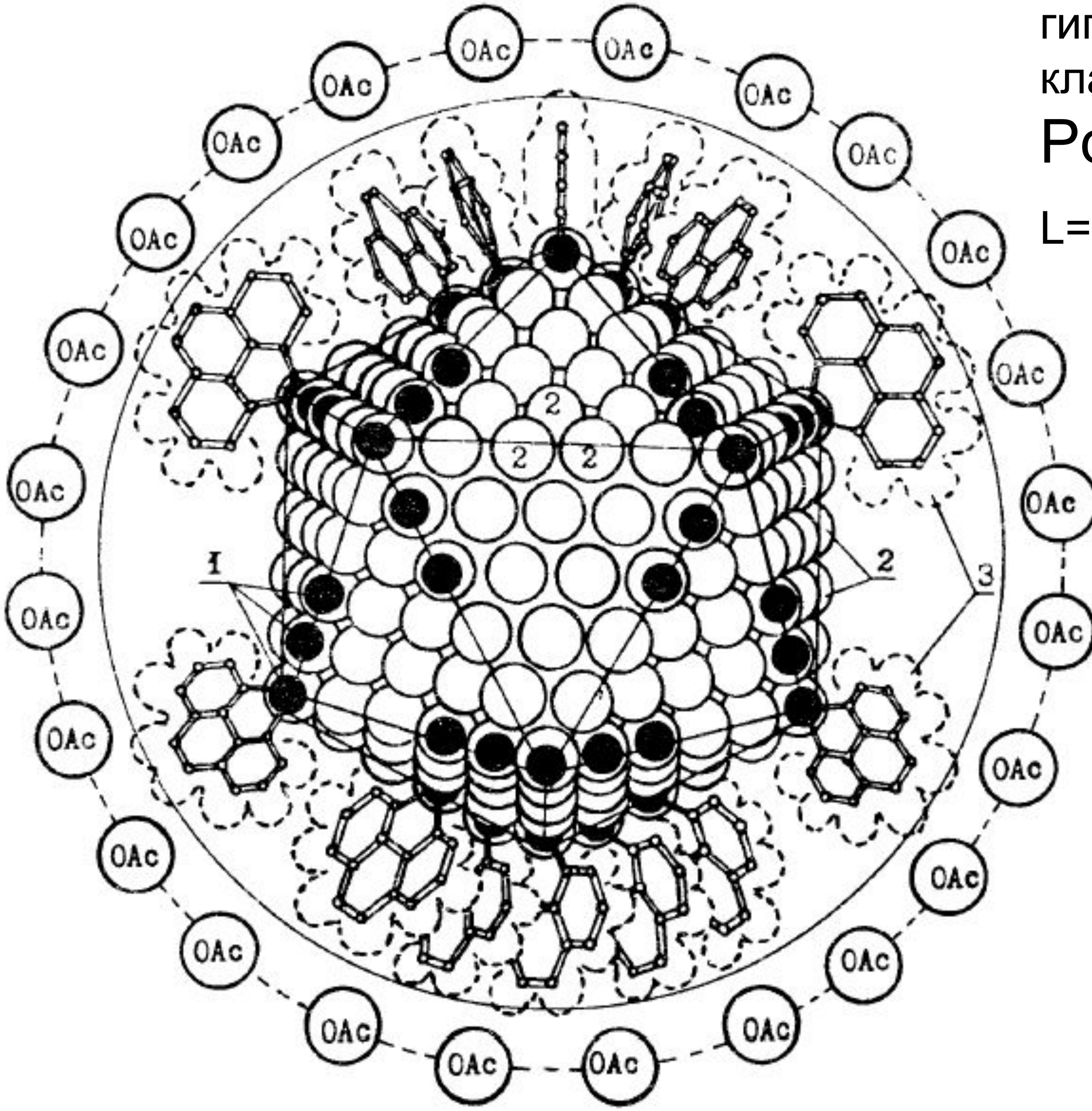


Figure 1. Formal concentric construction of the capped three-shell nanosized Pd_{145} core of pseudo I_h symmetry in $Pd_{145}(CO)_x(PEt_3)_{30}$: a) 12-atom ν_1 icosahedron surrounding the central atom (ν_n denotes $(n+1)$ equally spaced atoms along each edge). This centrosymmetrically centered icosahedron, one of the five regular Platonic solids (with equivalent vertices and identical faces composed of only one polygon), comprises: (1) six five-fold axes through opposite pairs of 12 vertices; (2) 10 three-fold axes through midpoints of opposite pairs of 20 triangular faces; and (3) 15 two-fold axes through midpoints of opposite pairs of 30 edges. b) 42-atom ν_2 icosahedron (shell 2) generated by the addition of an atom to the midpoint of each of the 30 edges of the 12-atom ν_1 icosahedron. c) Shell 2 encapsulating the Pd-centered shell 1 to give a 55-atom Mackay icosahedron. d) 60-atom polyhedron (shell 3), mathematically named a rhombicosidodecahedron (3.4.5.4). The numbers N (in parentheses) designate the Schläfli symbol which represents in cyclic order the polygons (N-gons) meeting at each equivalent vertex. e) Shell 3 encapsulating shell 2. f) Another orientation of the outermost third-shell polyhedron that more clearly shows the 60 equivalent vertices along with the 62 faces (namely, the 12 pentagons, 20 equilateral triangles, and 30 squares). This Archimedean polyhedron, a semi-regular one in that all 60 vertices are identical but there are three different polygons, has pseudo I_h symmetry. g) Entire 3-shell Pd_{145} core including 30 exopolyhedral Pd atoms (with attached triethylphosphane P atoms (purple)) that form square pyramids by capping of the 30 square polygons of the third shell.

Длины связей Pd-Pd в икосаэдрической структуре $Pd_{145}(CO)_x(PEt_3)_{30}$

Connectivity[b]	N[c]	Mean [Å][a]	Range [Å]
Pd(A)-Pd(B)	12	2.63 (2.63)	2.629(3) – 2.633(3)
Pd(B)-Pd(B)	30	2.77 (2.77)	2.757(4) – 2.778(5)
Pd(B)-Pd(C)	12	2.74 (2.73)	2.734(4) – 2.737(4)
Pd(B)-Pd(D)	60	2.70 (2.70)	2.696(4) – 2.709(4)
Pd(C)-Pd(D)	60	2.82 (2.82)	2.811(6) – 2.836(6)
Pd(D)-Pd(D)	60	2.82 (2.82)	2.810(5) – 2.825(6)
Pd(C)-Pd(E)	60	2.73 (2.73)	2.714(7) – 2.749(7)
Pd(D)-Pd(E)	120	2.74 (2.73)	2.724(6) – 2.756(6)
Pd(E)-Pd(E) (triangle/square shared edge)	60	2.82 (2.82)	2.795(8)-2.844(9)
Pd(E)-Pd(E) (pentagon/square shared edge)	60	3.09 (3.09)	3.070(8) – 3.112(9)
Pd(E)-Pd(F)	120	2.84 (2.84)	2.809(9)-2.874(9)

N **– число эквивалентных по симметрии связей (при икосаэдрической I_h симметрии)**



Предполагаемое строение гигантского палладиевого кластерного комплекса

$Pd_{561}L_{60}(O_2)_{150}(OAc)_{150}$

L= bipy, phen