Abstract: This review classifies and analyzes over thirty heterooligonuclear platinum clusters with a wide variety of metal frameworks, from twelve to forty-four. There are thirteen heterometals (Ge, Sn, Hg, W, Mo, Ru, Rh, Pd, Os, Ni, Cu, Ag, Au) which are the partners of platinum. The clusters mostly crystallize in monoclinic (36.4%) and triclinic (30.3%) crystal classes. Their structures are complex, with platinum most commonly preferring interstitial sites, such as the centroids of icosahedrons. There are examples of distortion isomerism. The most common ligands are CO and PPh₃, and it is interesting that the mean Pt-CO and M-CO bond distances are identical at 1.84 Å. In contrast, the mean Pt-µCO and M-µCO are of values of 2.02 and 1.97 Å, respectively, while the Pt-PPh₃ and M-PPh₃ bond distances are 2.30 and 2.28 Å, respectively. The shortest Pt-Pt, Pt-M (non-transition) and Pt-M (transition) bond distances are 2.559(2) Å, 2.412(2) Å (M = Ge) and 2.510(2) Å (M = Ni).

Keywords: structure, heterooligonuclear, platinum, distortion, isomerism

1 Introduction

The chemistry of heterometallic clusters has attracted much attention in the last few decades because of their significance in catalytic and biological functions. These compounds may serve as model systems in providing a better understanding of the underlying mechanisms of action and the development of new techniques in these fields. Among such derivatives, attention has been paid to the platinum clusters that have a variable number of metal atoms in their inner core, and which possess certain interesting properties. A considerable number of structural determinations have been carried out, which have helped to shed light on catalytic and other activity of heteronuclear platinum clusters. Because of the large number of structures involved, this review is the ninth part of a comprehensive structural overview. The earlier articles cover heterobi- [1,2], heterotri- [3], heterotetra-[4], heteropenta- [5], heterohexa- [6], heterohepta- and heteroocta- [7], and heteronona- and heterodecanuclear [8] platinum clusters. In this review undecanuclear and oligonuclear heterometallic clusters involving platinum have been classified according to the total number of metal atoms present in the unit. The heterometal atoms include both non-transition and transition metals, with the latter being more frequent. The primary source of information has been the Cambridge Crystallographic Data base up to the end of 2000.

2 Heteroundecanuclear Pt clusters

There are fifteen coloured heteroundecanuclear Pt clusters of metal combinations: Pt₅Os₆ (1 example), Pt₂M₉ (3 examples), Pt₆W₃Mo₂ (1 example), Pt₃Ru₆Au₂ (1 example), PtₙAuₘ (5 examples), and PtₙCuₙ (2 examples). Their crystallographic data are gathered in Table 1, indicating the complexity of their structures. For example, the core of triclinic [Pr₅Os₅(Cl)₁₈(CH₂Cl)₂]₉ [9] can be viewed as two trigonal bipyramidal groups, Pt₁(1)Pt(2)Pt(3)Os(2)Os(3) and Pt(1)Pt(4)Pt(5)Os(4)Os(5) that share “butterfly” tetrahedral groups, Pt₁(1)Pt(4)Os(4)Os(5) and Pt(1)Pt(2)Os(2)Os(3) with fused square pyramids.
In addition, there are Os(CO)$_4$ moieties bridging two of the Pt-Pt bonds, Pt(2)-Pt(5) and Pt(3)-Pt(4). The Pt-Pt bond lengths range from 2.642(2) to 2.698(2) Å (ave 2.649 Å). The Pt-Os bond lengths range from 2.669(2) to 2.871(2) Å (ave 2.749 Å).

Dark red [K(crypt)][(PPh$_3$)$_2$Pt$_2$Sn$_9$] derivative crystallizes as two different triclinic solvates, one with an ethylenediamine solvate molecule and one with a toluene solvate molecule in the crystal lattice [10]. Otherwise, their structures are identical. The [(PPh$_3$)$_2$Pt$_2$Sn$_9$]$^-$ anion has virtual C$_{3v}$ point symmetry defined by an elongated tricapped trigonal prismatic Sn$_9$ cluster with a linear Pt-Pt-PPh$_3$ rod inserted into the top triangular face. The Sn-Sn distances range from 3.002(3) to 3.136(3) Å. The Pt(2) atom resides in the center of the tricapped trigonal prismatic Sn$_9$ cluster with nine Pt-Sn bonds in a narrow range of 2.675(2)–2.793(2) Å. The Pt(1) atom caps the top of the triangular face of the cluster with three mean Pt-Sn bonds of 2.690(4) Å. The Pt-Pt bond length is 2.6965(4) Å.

The structure of monoclinic Pt$_2$Rh$_9$ cluster [11] consists of well separated NEt$_4^+$ cations and a [Pt$_2$Rh$_9$(μ-CO)$_{11}$]$_3^-$ anion. The metal skeleton of the anion, which has ideal D$_{3h}$ symmetry, consists of three face-to-face condensed octahedra with a common edge, Pt(1)-Pt(2), coincident with the ideal three-fold axis. The Pt-Pt bond is 2.812(2) Å, and the mean Pt-Rh and Rh-Rh bond distances are 2.707 and 2.852 Å, respectively.

The structure of [PtRh$_{10}$(μ$_5$-N)(μ-CO)$_{10}$]$_2^-$ [12] is shown in Fig. 1. The anion lies on a two-fold crystallographic axis passing through the Pt atom and the interstitial nitrogen atom. The overall idealized symmetry of the anion is C$_3v$. The metal atom cluster inhibits a geometry, which can be described as a two-layer arrangement, i.e. a folded hexagon of rhodium atoms {Rh(1,2,3,1',2',3')} centered by the platinum atom, superimposed along the C$_3$ axis direction on a folded square of rhodium atoms {Rh(4,5,4',5')}. Of the 21 carbonyls, 11 are bound terminally, one per metal atom, and 10 are double-bridging on the Rh-Rh edges of the folded hexagon and square layers. The platinum forms six Pt-Rh bonds at a mean distance of 2.711 Å with the rhodium atoms of the folded hexagon. On the other hand, of four more Pt-Rh contacts, two {with Rh(4) and Rh(4')} are significantly longer (3.180(2) Å and the remaining two, {with Rh(5) and Rh(5')}) at (3.492(2) Å), are too long be considered bonded. The Rh-Rh bond lengths range from 2.728(2) to 3.088(2) Å, the longer ones being the interlayer connections between the folded hexagon and the folded square. The interstitial nitrogen atom occupies an unusual type of cavity in which it is connected to five metal atoms, Pt-N 1.92(2) Å, Rh(4,4')-N 2.05(1) Å and Rh(5,5')-N 2.12(1) Å.

A triclinic orange PtAu$_{10}$ cluster [13] contains a well-separated [PtAu$_{10}$(η$_2$-dppe)$_{10}$]$^{4-}$ cation, NO$_3^-$ anions and solvate CH$_2$Cl$_2$ molecules. The PtAu$_{10}$ framework in the complex cation has icosahedral geometry. The platinum atom is positioned at the vertex of three distorted square faces given by the four-atom sets: Au(3)Au(4)Au(9)Au(10); Au(4)Au(5)Au(6)Au(10); and Au(6)Au(8)Au(9)Au(10). The mean radial bond distance from the platinum to the ten peripheral gold atoms is 2.661 Å. The mean bond distances between gold atoms that are bridged by a diphosphine ligand are somewhat shorter (2.900 Å) than those that are directly bonded with no diphosphine bridge (2.946 Å).

The structure of monoclinic brown [Pt$_6$W$_3$Mo$_2$(μ$_3$-CMe)$_2$($\eta_5$-C$_6$H$_4$Me-4)(CO)$_{10}$]$_2$(PMe$_2$Ph)$_4$(η$_5$-cp)$_5$ [14] is shown in Fig. 2. The molecule consists of five μ$_3$-CMo$_2$ (M = Mo or W) groups linked together, with four of the platinum atoms sharing vertices. Of the six platinum atoms present, all except Pt(1) and Pt(6) are approximately tetrahedrally coordinated by alkylidyne-metal fragments. The other two, Pt(1) and Pt(6), have essentially square planar geometries, being ligated by one alkylidyne tungsten fragment and two PMe$_2$Ph groups. The mean dimensions of the μ$_3$-CMo$_2$ fragments are: Pt-W 2.751 Å, Pt-Mo 2.744 Å, Pt-Pt 3.040 Å, μ$_3$C-Pt 2.05 Å, μ$_3$C-W 2.04 Å and μ$_3$C-Mo 1.98 Å.

The structure of monoclinic dark brown [Pt$_3$Ru$_6$(AuPEt$_3$)$_2$(μ$_3$-H)(CO)$_{21}$] cluster [15] consists of a stacked arrangement of the six ruthenium and three platinum atoms, with the three platinum atoms as a triangle sandwiched between two Ru$_3$ triangles. Two AuPEt$_3$ groups occupy triple-bridging sites in PtRu$_2$.
triangles on opposite sides of the Pt\textsubscript{t} triangle. The mean metal-metal bond distance elongates in the order: 2.655 Å (Pt-Pt) < 2.810 Å (Pt-Ru) < 2.832 Å (Au-Ru) < 2.898 Å (Pt-Au) < 3.008 Å (Ru-Ru).

For red orthorhombic \([\text{Hg}_2\text{Pt(AuPPh}_3)_8]\)(NO\textsubscript{3})\textsubscript{2}, only unit cell dimensions are given [16]. The structure of tetragonal red PtHg\textsubscript{2}Au\textsubscript{8} cluster [17] contains a well-separated \([\text{Hg}_2\text{Pt(AuPPh}_3)_8]\)^{4+} cation, NO\textsubscript{3}\textsuperscript{-} anions and solvate CH\textsubscript{2}Cl\textsubscript{2} molecules. In the complex cation, the PtAu\textsubscript{8}Hg\textsubscript{2} skeleton, with a crystallographic four-fold rotation axis, is a centered square antiprism capped on the square faces by mercury atoms, with approximately D\textsubscript{4h} symmetry. The mean metal-metal distance increases in the following order: 2.632 Å (Pt-Au) < 2.917 Å (Au-Au, between the two squares) < 2.987 Å (Pt-Hg) < 3.004 Å (Au-Hg) < 3.280 Å (Au-Au). One could propose a similar structure of the orthorhombic cluster [16].

There are three triclinic red PtAu\textsubscript{8}M\textsubscript{2} clusters, \([(\text{H})\text{Pt(CuCl)}_2(\text{AgPPh}_3)_8]\)NO\textsubscript{3} [18] and two isomers of \([(\text{H})\text{Pt(AgNO}_3)_2(\text{AuPPh}_3)_8]\)NO\textsubscript{3} [19]. All three have a central platinum atom surrounded by eight silver and two copper [18], or eight gold and two silver [19] atoms. The silver and gold atoms are attached to PPh\textsubscript{3} ligands; the copper atoms are coordinated to chlorine and the silver atoms to nitrate via an oxygen atom. In these clusters, the hydride ligand is located “trans” to the copper atoms [18] or to the silver atoms [19]. The mean metal-metal distance in the PtAu\textsubscript{8}Cu\textsubscript{2} cluster [18] increases in the following order: 2.632 Å (Pt-Au) < 2.917 Å (Au-Au, between the two squares) < 2.987 Å (Pt-Hg) < 3.004 Å (Au-Hg) < 3.280 Å (Au-Au). One possible explanation is the difference in the covalent radii of M, 1.38 Å (Cu) compared to 1.53 Å (Au).

Inspection of the data in Table 1 reveals that there are seven categories of metal composition: Pt\textsubscript{5}Os\textsubscript{6} (x1), Pt\textsubscript{2}M\textsubscript{9} (x3), PtM\textsubscript{10} (x2), Pt\textsubscript{6}W\textsubscript{3}Mo\textsubscript{2} (x1), Pt\textsubscript{3}Ru\textsubscript{6}Au\textsubscript{2} (x1), PtAu\textsubscript{8}M\textsubscript{2} (x5) and PtAu\textsubscript{6}Cu\textsubscript{4} (x2). The clusters crystallize in four crystal classes: orthorhombic and tetragonal each (x1); monoclinic (x5) and triclinic (x8). Their structures are complex, and a summary of the metal-metal bond distances are given in Table 2. As can be seen, there are ten metal atoms, including transition (Cu, Ag, Au, W, Mo, Ru, Rh, Os) and nontransition (Sn, Hg) metals, that form bonds with platinum. The shortest Pt-M bond distances in the orthorhombic cluster are 3.352 Å (Cu-Cu), 3.523 Å (Cu-Au), and 3.572 Å (Cu-Au). The cluster of composition \([(\text{H})\text{Pt(AgNO}_3)_2(\text{AuPPh}_3)_8]\)NO\textsubscript{3} exists in two isomeric forms [19]. Their structures differ mostly by degree of distortion and are examples of distortion isomerism [21]. There are several examples of...
### Table 1: Crystallographic and structural data for heteroudecanuclear platinum clusters.

| COMPOUND (colour) | Crys.cl Sp.Grp | a [Å]  | b [Å]  | c [Å]  | α [°]  | β [°]  | γ [°]  | Chromophore | M-L [Å]  | M-M [Å]  | M-L-M [°] | L-M-L [°] | Ref |
|-------------------|----------------|--------|--------|--------|--------|--------|--------|-------------|----------|-----------|----------|-----------|-----|
| [Pt₅Os₆(CO)₂₅]. CH₂Cl₂ (brown) | tr PI 2 | 12.250(1) | 17.476(4) | 11.889(2) | 109.87(1) | 112.66(1) | 83.05(2) | PtCO₅Pt₄ | 2.184(4) | 2.878(2) | 2.671(2) | not given | 9 |
| [Pt₅Os₆(CO)₂₅]. CH₂Cl₂ (brown) | tr PI 2 | 13.170(6) | 13.312(6) | 24.323(10) | 79.445(1) | 76.067(1) | 83.726(1) | PtSn₉Pt | 2.184(4) | 2.878(2) | 2.671(2) | not given | 10 |
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## Table 1: Crystallographic and structural data for heteroudecanuclear platinum clusters

| COMPOUND | Crys.cl | Sp.Grp | a [Å] | b [Å] | c [Å] | α [°] | β [°] | γ [°] | Chromophore | M-L | M-M [Å] | M-L-M [°] | L-M-L [°] | Ref |
|----------|---------|--------|-------|-------|-------|-------|-------|-------|--------------|------|---------|-----------|-----------|-----|
| Pt₃Ru₆(AuPEt₃)₂.₉₂(µ₃-H)₂(CO)₂₁ | m | P₂₁/c | 11.740(2) | 17.351(4) | 25.542(6) | 90.89(2) | | | | OC 1.83(3,7) | | | | Ru₂Au.64.7(1,4) | 15 |
| | | 4 | | | | | | | | | | | | |
| Ru₆Au₈(µ₃-H).₉₂(µ₃-H)₂(CO)₂₁ | P₄/n | 17.8002(6) | 23.049(1) | | | | | | Au₂.6307-2.6324(4) | | | | Au₂.6307-2.6324(4) | 16 |
| | | 2 | | | | | | | | | | | | |
| AuPRu₄Pt₃ | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |
| AuPP₄Hg₄ | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |
| Au₄PP₄Hg₄ | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |
| HgAu₄Pt | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |
| AuPP₄Hg₄ | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |
| Au₄PP₄Hg₄ | | | | | | | | | | | | | | |
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| HgAu₄Pt | | | | | | | | | | | | | | |
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| Au₄PP₄Hg₄ | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |
| HgAu₄Pt | | | | | | | | | | | | | | |
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| AuPP₄Hg₄ | | | | | | | | | | | | | | |
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| Au₄PP₄Hg₄ | | | | | | | | | | | | | | |
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| HgAu₄Pt | | | | | | | | | | | | | | |
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| AuPP₄Hg₄ | | | | | | | | | | | | | | |
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| Au₄PP₄Hg₄ | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |
| HgAu₄Pt | | | | | | | | | | | | | | |
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| AuPP₄Hg₄ | | | | | | | | | | | | | | |
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| Au₄PP₄Hg₄ | | | | | | | | | | | | | | |
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| HgAu₄Pt | | | | | | | | | | | | | | |
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| AuPP₄Hg₄ | | | | | | | | | | | | | | |
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| Au₄PP₄Hg₄ | | | | | | | | | | | | | | |
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| HgAu₄Pt | | | | | | | | | | | | | | |
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| AuPP₄Hg₄ | | | | | | | | | | | | | | |
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| Au₄PP₄Hg₄ | | | | | | | | | | | | | | |
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| HgAu₄Pt | | | | | | | | | | | | | | |
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| AuPP₄Hg₄ | | | | | | | | | | | | | | |
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| Au₄PP₄Hg₄ | | | | | | | | | | | | | | |
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| HgAu₄Pt | | | | | | | | | | | | | | |
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| AuPP₄Hg₄ | | | | | | | | | | | | | | |
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| Au₄PP₄Hg₄ | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |
| HgAu₄Pt | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |
Pt-M and M-M distances which are over 3.0 Å, with Pt-M separations ranging from 3.045 to 3.180 Å and M-M from 3.001 to 3.492 Å.

3 Heterododeca and Heterooligonuclear Pt Clusters

There are nineteen such clusters for which structural parameters are available, with metal compositions: Pt8M4 (2 examples), Pt4Cu8, Pt3Ni9, Pt7Os6, Pt2Rh11, PtRh12, PtAg12, Pt4Cu12, Pt2Rh18, Pt10Ni14, Pt2Au10Ag13, PtAuAg12, PtAuAg12, Pt6Ni38 and Pt13Pd28. Their structures are complex and are summarized in Table 3.

The structure of the tetragonal Pt8M4 clusters \([22]\) contains well-separated PPh\(_4^+\) cations and a \([\text{Pt}_8(\text{MCl}_2)_4(\mu-\text{CO})_2(\text{CO})_8]^2-\) anion (M = Ge or Sn). The complex anions have similar structures, with overall D\(_{2d}\) crystallographic symmetry of the anions. The structure of \([\text{Pt}_8(\text{SnCl}_2)_4(\mu-\text{CO})_2(\text{CO})_8]^2-\) is shown in Fig. 3. The Pt Metal core consists of three stacked, edge-sharing, tetrahedra of platinum atoms which generate four concave butterfly surfaces, each coordinated by one MCl\(_2\) group. The whole Pt8M4 metal framework can be thought of as derived from the

Footnotes: a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean. b. The chemical identity of the coordinated atom or ligand is specified in these columns.
Layering of two outer, symmetry-related Pt(1)-Pt(1’)
edges and two inner, symmetry-related Pt(2)-Sn-Pt(2’)-Sn
planar rhombuses. The chlorine atoms are essentially
coplanar with the Pt3Sn3 rhombuses. Of the ten CO ligands,
eight are terminally bonded to the eight platinum atoms,
and two are double-bridging the outer Pt(1)-Pt(1) edges.
The surface metal atoms are also observed to be staggered,
with a torsion angle Pt(3)-C(17)-Pt(4)-C(25) of 40.8°. The
{Pt3Ni3(µ-CO)6(CO)3} unit. The metal-metal bond
distances are: Pt-Pt 2.845(2) Å (mean), Pt-Ni 2.541(4)–
2.922(4) Å, Ni-Ni 2.451(1)–2.950(4) Å.

The structure of tetragonal red [Pt2Cu3(µ-η2-CPh)4]2+
[23] consists of two distorted octahedral arrays of Pt2Cu3
metal cores linked together by an unsupported Pt...Pt
interaction (Pt(2)...Pt(3) 3.116(2) Å). Each octahedron
consists of two platinum metal centers in a mutually trans
disposition, with four copper atoms in an equatorial plane
bonded by the alkynyl ligands in a π-coordination mode.
The Pt-Cu distances of 2.931(2)–3.021(2) Å are suggestive
of some very weak metal-metal bonding, but the Cu...Cu
separations (3.084(3)–4.361(4) Å) exclude metal-metal
bonding. The two square planar [Pt(C≡CPh)2] fragments
on the upper octahedron are found to be almost eclipsed,
with a torsion angle Pt(1)-C(1)-Pt(2)-C(9) of 78° between
adjacent fragments. The other two [Pt(C≡CPh)2] fragments
on the lower octahedron are found to be staggered
with a torsion angle Pt(3)-C(17)-Pt(4)-C(25) of 40.8°. The
{Pt(C≡CPh)2} fragments containing Pt(2) and Pt(3)
atoms are observed to be staggered, with a torsion
angle of 44.6°.

A monoclinic black Pt3Ni9 cluster [24] contains well
separated NEt4+ cations and a [(H)Pt3Ni3(µ-CO)12(CO)12]3+
anion. In the complex anion the platinum atoms occupy
the inner triangle of the central Ni, Pt planar triangulated
array. Two [Ni3(µ-CO)(CO)3] fragments “sandwiched” the
central [Pt3Ni3(µ-CO)(CO)3]3+ unit. The metal-metal bond
distances are: Pt-Pt 2.845(2) Å (mean), Pt-Ni 2.541(4)–
2.922(4) Å, Ni-Ni 2.451(1)–2.950(4) Å.

The structure of monoclinic brown [(η5-cod)2
Pt2Os2(CO)12(CH2Cl)2] [25] consists of layers of metal atoms
(Fig. 4). A Pt(cod)-capped Os3 triangle, on the far right
sits next to a planar Pt5 layer, which in turn lies next to
a planar five-atom Os5Pt5 layer on the far left of Fig. 4.
The latter contains another Pt(cod) moiety bonded to
four other metal atoms. The mean Os-Os bond distance of
2.86 Å is somewhat longer than the mean Pt-Pt bond
distance, 2.79 Å. The Pt(2)-Pt(5) distance of 3.008(2) Å is
the longest bonding distance in this cluster, involving the
unique μ4-Pt(cod) bridging group Pt(2).

The D3h idealized symmetry metal atoms cluster in the
[PtRh6(µ-CO)12(CO)12]4– [26] consists of a “twinned”
cuboocathedral array of rhodium atoms with a central
platinum atom. The [PtRh6(µ-CO)12(CO)12]4– anion [26]
consists of the same cluster with one platinum atom at
the center and the second platinum atom disordered on
the surface. In both PtRh13+n (n = 1,2) clusters, the CO
geometries imply that each surface metal atom bears
one terminal CO ligand and is connected to two edge-
bridging CO ligands. The following bond parameters are
for the tetra-anion, those of the tri-anion being of poorer
quality owing to disorder. The Pt-Rh bond distances are
in the range 2.743(4)–2.812(6) Å, with a mean value of
2.776 Å. The twenty-four Rh-Rh bond distances range from
2.743(4)–2.812(6) Å, with a mean value of
2.776 Å. The twenty-four Rh-Rh bond distances range from
2.743(4)–2.812(6) Å, with a mean value of
2.776 Å. The twenty-four Rh-Rh bond distances range from

| Pt-M | Mean (Å) | Shortest [ref] | Longest [ref] |
|------|---------|---------------|--------------|
| Pt–Cu | 2.636 | 2.532(5) [18] | 2.712(8) [20] |
| Pt–Sn | 2.687 | 2.675(3) [10] | 2.714(3) [10] |
| Pt–Au | 2.692 | 2.640(1) [13] | 2.907(2) [15] |
| Pt–Rh | 2.724 | 2.774(2) [11] | 2.965(5) [15] |
| Pt–Mo | 2.744 | 2.777(2) [11] | 2.965(5) [14] |
| Pt–Os | 2.749 | 2.669(2) [9] | 2.871(2) [9] |
| Pt–W | 2.751 | 2.723(2) [14] | 2.797(4) [14] |
| Pt–Ru | 2.810 | 2.744(3) [15] | 2.921(3) [15] |
| Pt–Ag | 2.839 | 2.784(4) [19] | 2.906(8) [19] |
| Pt–Hg | 2.928(4) [17] | 2.928(2) [17] | 2.928(2) [17] |
| Cu–Cu | 2.656 | 2.562(3) [20] | 2.72(2) [17] |
| Pt–Pt | 2.710 | 2.642(2) [9] | 2.965(5) [14] |
| Rh–Rh | 2.839 | 2.721(2) [14] | 2.997(4) [14] |
| Au–Au | 2.907 | 2.814(2) [20] | 2.964(5) [19] |
| Os–Os | 2.958 | 2.947(2) [9] | 2.970(2) [9] |
| Ru–Ru | 2.971 | 2.953(4) [15] | 2.986(4) [15] |
| Au–Cu | 2.741 | 2.632(3) [20] | 2.854(9) [20] |
| Au–Ru | 2.832 | 2.818(3) [15] | 2.847(3) [15] |
| Au–Hg | 2.839 | 2.784(4) [19] | 2.998(6) [19] |

The structure of triclinic dark brown
[PPPh3]2Au4Ag2Pt(Ag(µ-I)3)2(thf)2 [27] can be described
as a complete, platinum centered, Au4Ag2icosahedral
cluster capped with two other Ag atoms (Ag(7) and Ag(8)).
The six surface gold atoms form a cyclohexane style
“chair” configuration, capped on top and below by two
silver triangles (Fig. 5a). Each of the six PPh3 ligands is
coordinated to the six individual gold atoms in a radial
Table 3: Crystallographic and structural data for heterododeca- and heterooligonuclear platinum clustersa.

| COMPOUND (colour)                                                                 | Crys.cl Sp.Grp | a [Å]  | b [Å]  | c [Å]  | α [°]  | β [°]  | γ [°]  | Chromophore | M-L [Å] | M-M [Å] | M-L-M [°] | L-M-L [°] | Ref |
|---------------------------------------------------------------------------------|---------------|--------|--------|--------|--------|--------|--------|-------------|---------|---------|-----------|-----------|-----|
| (PPh₄)₂[Pt₄(µ-CO)₄(CO)₈]                                                     | tg            | I42m   | 14.417(4) | 17.972(4) | PtcGe₄Pt₄ (x4) | OC not given | μOC not given | Ge 2.412-2.918(2) | Pt 2.690-2.840(1) | not given | 22   |
| (PPh₄)₂[Pt₄(SnCl₂)₄] (µ-CO)₂(CO)₈                                            | tg            | I42m   | 14.550(3) | 18.220(4) | PtcSn₄Pt₃ (x4) | OC not given | μOC not given | Sn 2.595-2.950(1) | Pt 2.656-2.977(1) | not given | 22   |
| [Pt₂Cu₄(µ-η⁴-C≡CPh)₈][(NEt₄)₃]                                               | m             | P₄/n   | 15.937(2) | 21.982(5) | Ptc₄Cu₂ | C 2.14(1,2) | μC 2.01(1,4) | Cu 2.931-3.021(2) | C 94.6(6,2.6) | Pt 3.116-3.934(2) | C,C not given | 23   |
| [(η⁴-cod)₂Pt₇Os₆(CO)₂₁]CH₂Cl₂ (brown)                                          | m             | P₂₁/n  | 21.061(6) | 12.086(3) | Ptc₄Os₃ | OC not given | μOC 1.922 | Ni 2.541-2.912(4) | Pt 2.845(3) | Ni 2.451-2.950(4) | not given | 24   |
| Cs₄[PtRh₁₂(CO)₁₂] (brown)                                                   | or            | P₂₁cn  | 11.889(5) | 12.379(5) | Ptc₁₂   | OC not given | μOC 1.896 | Os 2.598-2.911(2) | Pt 2.658-3.008(2) | Os 2.705-2.986(2) | Os,Os 60.0(1,1.5) | 25   |
| [(PPh₃)₆Au₆Ag₆]Pt{Ag(µ-I)₃}₂(thf)₂ (dark brown)                              | tr            | 17.590 | 71.05   | 23.917  | 60.52  | PtAu₆Ag₆ | Au 2.728 | not given | Ag 2.744 | PAg₁Pt₁62.1 | not given | 27   |
Continued Table 3: Crystallographic and structural data for heterododeca- and heterooligonuclear platinum clusters.

| COMPOUND (colour) | Crys.cl | Sp.Grp | \(a\) [Å] | \(b\) [Å] | \(c\) [Å] | Chromophore | M-L | M-M [Å] | L-M-L [°] | Ref |
|-------------------|---------|--------|----------|----------|----------|-------------|-----|--------|----------|-----|
| \([\text{Pt}_2\text{Cu}_4(\mu-\eta^1\text{-C≡CPh})_8]\)_{3} (violet-green) | tg | P4/ncc | 16.143(2) | 32.538(3) | PtC_4 | Cu 1.994(8) | 2.012(7) | Cu 2.918(1) | 3.020(1) | 3.027(1) | Pt 2.995(1) | C,Pt 91.1(2,2.3) | 28 |
| \((\text{NEt}_4)_4[\text{Pt}_4\text{Rh}_{18.} (\mu-\text{CO})_2(\text{CO})_{14}]\cdot \text{Me}_2\text{CO}\) (brown) | or | P2_1,2,4 | 12.914(9) | 27.196(15) | PtRh_9Pt_3 | Rh 2.633-3.356(3) | Pt 2.559-2.827(2) | not given | not given |
| \((\text{NBu}_4)_4[\text{Pt}_{10}\text{Ni}_{14.} (\mu-\text{CO})_{18}(\text{CO})_{12}]\cdot \text{Me}_2\text{CO}\) (black) | m | P2_1/n | 26.716(1) | 15.276(1) | NiC_7PtNi_9 | Ni 2.673-2.854(2) | Pt 2.612-2.817(1) | not given | not given |
| \([\text{Pt}_2(\text{AuPPh}_3)_{10.} \text{Ag}_{13}(\mu-\text{Cl})_5(\text{Cl})_2]\cdot 10\text{Et}_2\text{O}\) (dark red) | m | P2_1/m | 17.154(2) | 25.256(2) | Ph_2PtAgAu_5Ag_7 | Au 2.679-2.689(5) | Ag 2.789-2.839(8) | not given | P,Pt 177.6(8,1.1) |
| \([\text{Pt}_2\text{Au}_{11}(\text{PPh}_3)_{10.} \text{Ag}_{12}(\mu-\text{Cl})_5(\text{Cl})_2]\cdot 22\text{EtOH}\) (dark red) | m | P2_1/n | 16.553(4) | 25.130(7) | AuPPlAg_4 | Au 2.674-2.829(3) | Ag 2.780-2.821(6) | not given | not given |
| \([\text{Pt}_2\text{Ag}_{11}(\text{PPh}_3)_{10.} \text{Au}_{12}(\mu-\text{Cl})_5(\text{Cl})_2]\cdot 22\text{EtOH}\) (dark red) | m | P2_1/n | 16.553(4) | 25.130(7) | AuPPlAg_4 | Au 2.674-2.829(3) | Ag 2.780-2.821(6) | not given | not given |
**Table 3:** Crystallographic and structural data for heterododeca- and heterooligonuclear platinum clusters.

| COMPOUND (colour) | Crys.cl Sp.Grp | a [Å] | b [Å] | c [Å] | α [°] | β [°] | γ [°] | Chromophore | M-L [Å] | M-M [Å] | M-L-M [°] | L-M-L [°] | Ref |
|------------------|----------------|-------|-------|-------|-------|-------|-------|--------------|---------|---------|-----------|-----------|-----|
| [Pt₂Au₁₂(PPh₃)₁₀. Ag₁₂(µ-Cl)₅(Cl)₂]Cl. 17EtOH (dark brown) | m    | 16.534(3) | 24.360(4) | 29.819(6) | 103.25(3) | PtAuAg₆ | 117.3(2,5.5) | AuAu 65.0(1,1) | 33 |
| AuPPIAg₆Au₆ (x10) | Ph₃P 2.29(3,3) | Au 2.804-3.018(0) | Au 2.870-2.904(0) | Cl 73(1,3) | AuAu 59.2(2,2.0) | 105.3(2,3.5) |
| AuPPIAg₆Au₆ (x2) | Cl 2.39(3) | µCl 2.50(3,5) | Cl 73(1,3) | AuAu 59.2(2,2.0) | 105.3(2,3.5) |
| AgClPtAu₂. Ag₅ (x10) | AgClPtAu₅ (x2) | Ni 2.536-2.776(2) | Pt 2.709-2.733(1) | Ni 2.421-2.782(2) | not given | 35 |
| AgClPtAu₅ (x2) | Pt 2.725-2.878(2) | Pt 2.725-2.878(2) | Pt 2.725-2.878(2) | not given | 35 |
| AgClPtAu₅ (x2) | Ni 2.534-2.861(2) | µOC 1.99(2) | µOC 1.99(2) | Ni 2.534-2.861(2) | not given | 35 |
| AgClPtAu₅ (x2) | PtNi₉Pt₃ | Ni 2.524-2.783(3) | Ni 2.524-2.783(3) | Ni 2.524-2.783(3) | not given | 35 |
| AgClPtAu₅ (x2) | PtNi₉Pt₃ | Ni 2.524-2.783(3) | Ni 2.524-2.783(3) | Ni 2.524-2.783(3) | not given | 35 |
| AgClPtAu₅ (x2) | PtNi₉Pt₃ | Ni 2.524-2.783(3) | Ni 2.524-2.783(3) | Ni 2.524-2.783(3) | not given | 35 |
| AgClPtAu₅ (x2) | PtNi₉Pt₃ | Ni 2.524-2.783(3) | Ni 2.524-2.783(3) | Ni 2.524-2.783(3) | not given | 35 |
| AgClPtAu₅ (x2) | PtNi₉Pt₃ | Ni 2.524-2.783(3) | Ni 2.524-2.783(3) | Ni 2.524-2.783(3) | not given | 35 |
| AgClPtAu₅ (x2) | PtNi₉Pt₃ | Ni 2.524-2.783(3) | Ni 2.524-2.783(3) | Ni 2.524-2.783(3) | not given | 35 |
| AgClPtAu₅ (x2) | PtNi₉Pt₃ | Ni 2.524-2.783(3) | Ni 2.524-2.783(3) | Ni 2.524-2.783(3) | not given | 35 |
| AgClPtAu₅ (x2) | PtNi₉Pt₃ | Ni 2.524-2.783(3) | Ni 2.524-2.783(3) | Ni 2.524-2.783(3) | not given | 35 |
| AgClPtAu₅ (x2) | PtNi₉Pt₃ | Ni 2.524-2.783(3) | Ni 2.524-2.783(3) | Ni 2.524-2.783(3) | not given | 35 |
| AgClPtAu₅ (x2) | PtNi₉Pt₃ | Ni 2.524-2.783(3) | Ni 2.524-2.783(3) | Ni 2.524-2.783(3) | not given | 35 |
| AgClPtAu₅ (x2) | PtNi₉Pt₃ | Ni 2.524-2.783(3) | Ni 2.524-2.783(3) | Ni 2.524-2.783(3) | not given | 35 |

Footnotes: a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean. b. The chemical identity of the coordinated atom or ligand is specified in these columns. c. There are two crystallographically independent clusters.
In terms of the cyclohexane style “chair” analogy, they are occupying the “equatorial” position (Fig. 5b). All metal-metal distances, including the capping silver atoms, are within bonding distances and follow the trend of Pt-Au (2.728 Å) < Pt-Ag (2.774 Å) < Au-Au (2.890 Å) ~ Ag-Ag (2.890 Å) < Au-Ag (2.908 Å) < Ag-Ag (capping) (2.996 Å).

Tetragonal dark violet-green crystals of Pt₆Cu₁₂ cluster [28] are formed of discrete trimers of a hexanuclear octahedral cluster unit {[Pt₂Cu₄(µ-η3-C≡CPh)₈]}₃, stabilized by two unsupported Pt-Pt interactions, 2.995(1) Å. The trimer has exact crystallographic D₄ symmetry as does the central {Pt₂Cu₄(C≡CPh)₈} unit, while the outer {Pt₂Cu₄(C≡CPh)₈} units have C₄ symmetry. The formal oxidation states are +2 for the Pt atoms and +1 for the Cu atoms. The Pt-Cu distances are for central {Pt₂Cu₄}, 2.918(1) Å, and for external {Pt₂Cu₄}, 3.027(1) and 3.020(1) Å. The Cu-Cu distances are 3.031(2) and 3.301(2) Å, respectively.

An orthorhombic brown Pt₄Rh₁₈ cluster [29] contains well-separated NEt₄⁺ cations, a [Pt₄Rh₁₈(µ-CO)₂₁(CO)₁₄]⁴⁻ anion and solvate acetone molecule. The overall idealized symmetry of the complex anion is Cᵥ with the two-fold axis passing through the mid-points of the Pt(3)-Pt(4) and Rh(2)-Rh(5) edges and through the C(16)-O(16) carbonyl. The inner part of the metallic frame is a distorted tetrahedron of platinum atoms, with bonding distances in the range 2.559(1)–2.827(2) Å (mean 2.698 Å). Eighteen rhodium atoms surround the platinum tetrahedron. The metallic structure can be described as a slightly distorted body-centered cubic framework. The Pt-Rh distances range from 2.663(3)–3.356(3) Å and Rh-Rh distances range from 2.660(3)–3.167(4) Å.

The structure of monoclinic black Pt₁₀Ni₁₄ cluster [30] contains well-separated NBu₄⁺ cation, a complex [Pt₁₀Ni₁₄(µCO)₁₁(CO)₁₂]₄⁻ – anion and solvate acetone

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### Table 4: Summary of the metal-metal bond distances (< 3.0 Å) in heterododeca-and heterooligonuclear platinum clusters.

| Pt-M | Mean  | Shortest [ref] | Longest [ref] |
|------|-------|----------------|---------------|
| Pt—Ge | 2.592 | 2.412(2) [22] | 2.918(2) [22] |
| Pt—Au | 2.701 | 2.672(5) [33] | 2.829(3) [32] |
| Pt—Ni | 2.709 | 2.510(2) [36] | 2.944(4) [24] |
| Pt—Sn | 2.719 | 2.595(1) [22] | 2.959(0) [22] |
| Pt—Rh | 2.745 | 2.629(3) [26] | 2.867(3) [29] |
| Pt—Pd | 2.750 | 2.680(1) [37] | 2.83(1) [37] |
| Pt—Os | 2.752 | 2.598(1) [25] | 2.911(2) [25] |
| Pt—Ag | 2.796 | 2.767(8) [33] | 2.839(8) [31] |
| Pt—Cu | 2.930 | 2.918(1) [28] | 2.942(1) [23] |
| Ni—Ni | 2.647 | 2.393(2) [36] | 2.815(3) [30] |
| Pd—Pd | 2.73 | 2.65 [37] | 2.80 [37] |
| Rh—Rh | 2.765 | 2.580(4) [36] | 2.977(3) [29] |
| Pt—Pt | 2.782 | 2.559(2) [29] | 2.993(1) [28] |
| Os—Os | 2.860 | 2.705(2) [26] | 2.986(2) [26] |
| Au—Au | 2.883 | 2.839(4) [32] | 2.904(4) [33] |
| Ag—Ag | 2.910 | 2.830(8) [33] | 2.996(1) [27] |
| Au—Ag | 2.887 | 2.804(9) [33] | 2.999(7) [32] |

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**Figure 3:** Structure of [Pt₆(SnCl₂)₄(µ-CO)₂(CO)₈]²⁻ [22].

**Figure 4:** Structure of [[(η⁴-cod)₂Pt₇Os₆(CO)₂₁] [25].
molecule. The metal frame in the complex anion is based on an unprecedented hcp sequence of M$_7$, M$_{10}$ and M$_7$ layers. The metal sites (relative number of metal atoms in parentheses) of the tetraanion display quite a spread of metallic coordination: 4(4Ni), 5(2Ni/Pt), 6(1Pt/4Ni/Pt), 7(6Ni/4Pt), 8(1Pt) and 12(2Pt). The Ni/Pt substitution disorder is limited to the two middle-layer sites with metal connectivity of 5, and their adjacent atoms belonging to the top- and bottom-layer and displaying a metal connectivity of 6. The metal-metal bond distances range as follows: 2.612–2.817(1) Å (Pt-Pt); 2.673–2.854(2) Å (Pt-Ni) and 2.466–2.815(3) Å (Ni-Ni).

A monoclinic dark red [Pt$_2$(AuPPh$_3$)$_{10}$Ag$_{13}$(µ-Cl)$_5$(Cl)$_2$] [31] is shown in Fig. 6. The structure consists of two identical icosahedral Pt-centered sub-units sharing a single common vertex occupied by a silver atom. Each of the gold atoms is bonded to a phosphine ligand. Atoms Ag(7) and Ag(7') are bonded to chlorine terminally, whereas the two silver pentagons are interconnected through five bridging chlorine atoms situated in the mirror plane perpendicular to the C$_5$ axis. The radial Pt-Au bond distances, ranging from 2.679 to 2.689 Å, are shorter than the radial Pt-Ag bond distances of 2.789 to 2.839 Å. The peripheral Au-Au bond distances range from 2.876 to 2.886 Å. The peripheral intraicosahedral Au-Ag distances range from 2.807 to 3.045 Å, whereas the intericosahedral Ag-Ag distances ranges from 2.84 to 3.07 Å. The Pt-Ag(7)-Cl(6) bond angle (178.6°) deviates slightly from linearity.

The metal core in monoclinic dark red [Pt$_2$(Au)$_{11}$(PPh$_3$)$_{10}$Ag$_{12}$(µ-Cl)$_5$(Cl)$_2$] [32] can be described as a two-centered Au$_6$Ag$_6$ icosahedron sharing a common gold atom. The four metal pentagons adopt the staggered-eclipsed-staggered (ses) configuration. The ten PPh$_3$ ligands coordinate to the ten peripheral (surface) gold atoms in a radial fashion. There are five double-bridging chlorine atoms connecting two Ag$_6$ pentagons, and two more chlorine atoms coordinating terminally to two apical silver atoms. The mean metal-metal bond distances
increase in the following sequence: 2.706 Å (Pt-Au) < 2.796 Å (Pt-Ag) < 2.874 Å (Au-Au) < 2.900 Å (Au-Ag) < 2.928 Å (Ag-Ag).

The structure of monoclinic dark brown [PtAu₁₂(PPh₃)₁₀Ag₁₂(µ-Cl)(Cl)]Cl [33] is similar to Pt₂Au₁₀Ag₁₃ [31] and Pt₂Au₉Ag₁₁ [32]. The structures of these clusters [31-33] satisfy the site preference rules established for mixed-metal vertex-sharing polyicosahedral nanoclusters. The determined structures of these mixed-groups ten metal clusters shows that the site preference is a manifestation of the various and often competing bonding effects. The platinum prefers interstitial sites such as the centroids of icosahedra due to its higher cohesive energy (Pt > Au > Ag). Gold prefers the interstitial sites such as centres of icosahedra, or the shared vertices, due to its higher cohesive energy and high electronegativity (Au > Ag). The more electronegative gold prefers phosphine coordination while the more electropositive silver prefers halide coordination or halide bridging. The mean metal-metal bond distances in these clusters follow the trend of Pt-Au (2.692 Å) < Pt-Ag (2.804 Å) < Au-Au (2.881 Å) < Au-Ag (2.897 Å) < Ag-Ag (2.921 Å), which correlates (in reverse order) with the corresponding trend of the bond energies (in kJ/mol): Pt-Au (77.83) > Pt-Ag (70.88) > Au-Au (61.37) > Au-Ag (54.43) > Ag-Ag (47.48) [34].

An asymmetric unit of the co-crystallized mixture of \([\text{NH}_3(\text{CH}_2\text{Ph})]_6 [\text{Pt}_4\text{Ni}_36(\text{CO})_{45}]_0.5\) and \([\text{NMe}_3(\text{CH}_2\text{Ph})]_6[\text{Pt}_4\text{Ni}_37(\text{CO})_{46}]_0.5\) [35] consists of one anion located on a crystallographic C₃ axis with an average occupancy factor of 0.5, two \([\text{NMe}_3(\text{CH}_2\text{Ph})]^{+}\) cations in general positions, and a disordered isopropanol molecule located on a crystallographic C₃ axis. The metal core of the \([\text{Pt}_4\text{Ni}_{36}(\text{CO})_{45}]^{-}\) anion (Fig. 7) consists of a Pt₄ tetrahedron fully encapsulated in a shell of 36 Ni atoms belonging to a very distorted and incomplete v₅ tetrahedron. The \([\text{Pt}_4\text{Ni}_{37}(\text{CO})_{46}]^{-}\) hexaanion derives from the former by capping the unique triangular face of the metal polyhedron with an additional Ni(CO) fragment. The Pt-Pt bond distances range from 2.709(1) to 2.733(1) Å, whereas a wider range of Pt-Ni bond distance, 2.536(2)–2.776(2) Å and Ni-Ni 2.421(2)–2.782(2) Å, clearly shows deformation of the metal framework. The carbonyl groups from the coordination point of view are arranged into the three sets, compressing, from 9 CO groups terminally coordinated, 24 CO groups edge bridging and 12 CO groups face bridging, respectively.

The structure of monoclinic black Pt₆Ni₃₈ cluster [36] contains well-separated \{AsPh₄\}⁺ and \{NBU₄\}⁺ cations and a \([\text{Pt}_6\text{Ni}_{38}(\text{CO})_{48}]^{-}\) anion. There are two crystallographically independent anion molecules, differing mostly by degree of distortion. The Pt₆Ni₃₈ framework consists of an inner octahedron of six platinum atoms fully encapsulated in a v₉ octahedron of 38 nickel atoms. The twelve Pt-Pt bond distances have a mean value of 2.719 Å. The 48 Ni-Pt bond distances connecting the inner Pt₉ octahedron to the outer Ni₃₈ octahedron are between 2.510 and 2.764 Å (ave 2.630 Å). The 108 surface Ni-Ni bonds vary in lengths, 2.393–2.762 Å (mean 2.580 Å). The metal framework provides a molecular model of bimetallic “cherry” crystallite. In both the independent molecules, the O₉ idealized symmetry of the framework is reduced to a Dₙₙ idealized symmetry by the presence of the 48 carbonyls (18 terminal, 12 edge-bridging and 18 face-bridging), as a result, of the two opposite v₉ triangular faces differ from the other six.

The molecular geometry of triclinic dark brown \([(\text{PtPPh}_3)_{12}(\text{PtPMe}_3)\text{Pd}_{28}(\text{H})_{12}(\text{CO})_{27}]^{-}\) [37], which closely
Conforms to pseudo-C3\textsubscript{3} symmetry, is composed of a four-layer hcp Pd\textsubscript{28}Pt core (viz. Pd\textsubscript{3}, Pd\textsubscript{7}, Pd\textsubscript{7}, Pd\textsubscript{12} and PtPd\textsubscript{6} layers) that contains four tetrahedrally-linked interior Pd(i) atoms, each with a localized hcp environment (Fig. 8). The pseudo-3-fold axis passes through one Pd(1), the bottom-layer centered Pt and its attached PMe\textsubscript{3} ligand. The Pd\textsubscript{28}Pt core has 12 highly distorted square pyramidal Pd\textsubscript{5} cavities each capped by an external Pt(PPh\textsubscript{3}) fragment. The 27 carbonyl ligands consist of 18 double-bridging and 9 triple-bridging ligands. The proposed location of the 12 hydride atoms is in the 12 square-pyramidal Pd\textsubscript{5} cavities capped by the 12 Pt(PPh\textsubscript{3}) fragments. The Pt-Pd bond distances range from 2.68–2.83 Å and Pd-Pd from 2.65–3.19 Å.

Inspection of the data in Table 3 reveals mixed-metal clusters with a wide variability of metal frameworks: twelve (Pt\textsubscript{8}Ge\textsubscript{4}, Pt\textsubscript{8}Sn\textsubscript{4}, Pt\textsubscript{4}Cu\textsubscript{8}, Pt\textsubscript{3}Ni\textsubscript{9}); thirteen (Pt\textsubscript{7}Os\textsubscript{6}, Pt\textsubscript{2}Rh\textsubscript{11}, PtRh\textsubscript{12}); fifteen (PtAg\textsubscript{8}Au\textsubscript{6}); eighteen (Pt\textsubscript{6}Cu\textsubscript{12}); twenty-two (Pt\textsubscript{4}Rh\textsubscript{18}); twenty-four (Pt\textsubscript{10}Ni\textsubscript{14}); twenty-five (Pt\textsubscript{2}Ag\textsubscript{13}Au\textsubscript{10}, Pt\textsubscript{2}Ag\textsubscript{12}Au\textsubscript{11}, PtAg\textsubscript{12}Au\textsubscript{12}); twenty-eight (Pt\textsubscript{4}Ni\textsubscript{24}), forty + forty-one (Pt\textsubscript{4}Ni\textsubscript{36} + Pt\textsubscript{4}Ni\textsubscript{37}); forty-one (Pt\textsubscript{3}Pd\textsubscript{38}) and forty-four (Pt\textsubscript{6}Ni\textsubscript{38}). The clusters crystallize in five crystal classes: hexagonal (1 example), triclinic (2 examples), orthorhombic (3 examples), tetragonal (5 examples) and monoclinic (7 examples). Their structures are complex, with more frequent examples in which the platinum sits as the centroid of an icosahedron.

The most common ligands are CO and PPh\textsubscript{3}. The mean Pt-CO and M-CO bond distances are each 1.84 Å. However, the mean Pt-µCO and M-µCO differ, with the values of 2.02 and 1.97 Å. The mean PtPPh\textsubscript{3} and M-PPh\textsubscript{3} bond distances are 2.30 and 2.28 Å. A summary of the metal-metal bond distances are gathered in Table 4 where it is seen that although platinum is classified as a soft or class B metal atom, it is found bonded to a variety of other metal atoms of both soft and hard (class A). The shortest Pt-M (non-transition) and Pt-M (transition) bond distances are 2.412(2) Å (M = Ge) and 2.510(2) Å (M = Ni), respectively. The Ni-Ni bond distance of 2.393(2) Å is the shortest for homo-metals, and the Ag-Au bond distance of 2.804(9) Å for hetero-metals. The shortest Pt-Pt bond distance is 2.559(2) Å. There are also metal-metal distances over 3.0 Å, ranges from 3.00 to 4.36 Å (Table 3).

4 Conclusions

This review classifies and analyzes over thirty heterooligonuclear platinum clusters contain from twelve to forty-four metal atoms per unit. The clusters crystallize in five crystal classes: hexagonal (3%) < orthorhombic (12.1%) < tetragonal (18.2%) < triclinic (30.0%) < monoclinic (36.4%). The clusters are for the most part red, brown and black, some due to the metal partners of platinum, to ligand absorption or to charge-transfer bands. For example, when Ni is partner of platinum, the clusters are only of black color.

A cluster of triclinic red [(H)Pt(AgNO\textsubscript{3})\textsubscript{2}(AuPPh\textsubscript{3})\textsubscript{8}]NO\textsubscript{3} [19] exists in two isomeric forms, and [(H)Pt(Ni\textsubscript{3})(CO)\textsubscript{8}]\textsubscript{36} contains two crystallographically independent molecules within the same crystal. These isomers as well as independent molecules differ mostly by degree of distortion and all are classical examples of distortion isomerism [1]. This type of isomerism is very prevalent even in the chemistry of platinum [21].

This review together with its precursors [1-8] represents the first comprehensive overview of about 1400 heterometallic platinum clusters, illustrating a rich diversity in the chemistry of platinum. It is hoped that this overview on structural parameters will help to focus attention on areas of platinum chemistry that could be enhanced by further study and assist in predicting the properties of the platinum atom in a variety of important biological and catalytic activities. In gathering the data, it became evident that some of it is buried in the literature and effectively invisible to automated data retrieval searches for a variety of reasons. In other cases, incorrect information had been promulgated in the literature. This review hopes to organise and correct, where necessary, the information and provide a base upon which new information can grow. A similar review on heteronuclear polymeric platinum complexes is in progress.

Abbreviations

| Abbreviation | Description |
|--------------|-------------|
| AsPh\textsubscript{4} | tetraphenylarsenium |
| cod | cycloocta-1,5-diene |
| cp | cyclopentadienyl |
| crypt | cryptate |
| dppp | 1,3-bis(diphenylphosphine)propane |
| Et | ethyl |
| hx | hexagonal |
| m | monoclinic |
| NBu\textsubscript{4} | tetrabutylammonium |
| NEt\textsubscript{4} | tetraethylammonium |
| or | orthorhombic |
| PET\textsubscript{3} | triethylphosphine |
| PMe\textsubscript{3} | trimethylphosphine |
PPh₃  triphenylphosphine
PPh₄  tetraphenylphosphonium
tg  tetragonal
thf  tetrahydrofuran
tr  triclinic

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