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**Review**

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# Structural characterization of heterometallic platinum complexes with non-transition metals. Part V: Heterooligo- and heteropolynuclear complexes

**Abstract:** This review classifies and analyzes heterooligo- and heteropolynuclear Pt complexes in the presence of non-transition metals as partners. There is a wide variability of metal combinations: $Pt_6M$, $Pt_2M_5$, $Pt_3Hg_2Ru_2$; $Pt_6M_2$, $Pt_4Zn_4$, $Pt_2Hg_6$, $PtHgAu_6$, $PtHg_2Au_5$; $Pt_6Hg_4$, $Pt_3HgRu_6$, $PtHgAu_8$; $Pt_2Sn_9$, $PtHg_2Au_8$; $Pt_8Ge_4$, $Pt_8Sn_4$ and $\{PtM\}_n$. The complexes crystallized in the following crystal classes: trigonal, orthorhombic (each 1 example)<tetragonal (6 examples)<triclinic (15 examples)<monoclinic (19 examples). The mean Pt-Pt bond length is 2.770 Å. The mean Pt-M bond length increased in the order 2.430 Å (M=Ga)<2.685 Å (Ge)<2.770 Å (Zn)<2.822 Å (Sn)<2.834 Å (Hg)<2.932 Å (Tl). This review together with the previous parts gives a comprehensive view on heterometallic Pt complexes with non-transition metals.

**Keywords:** crystal structures; heterooligo- and heteropolynuclear complexes; non-transition metals; platinum.

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**Abbreviations:** acac, acetylacetonate; bpe, 1,2-bis(4-pyridyl)ethylene; bpy, 2,2′-bipyridine; Bu, butyl; 5,5′-$Bu^t_2$bpy, 5,5′-di-tertbutyl-bpy; $C_5H_8(PPh_2)_2$, cyclopentane-1,2-diyl-bis(diphenylphosphane); $C_6F_5$, pentaflurohexyl; CNxyl, xylylcyanide; cp, cyclopentadienyl; cp*, pentamethylcyclopentadienyl; crypt, 2,2,2-cryptand; dcpe, bis(cyclohexylphosphino) ethane; dpph, 1,6-bis(diphenylphosphino)hexane; dppm, bis(diphenylphosphino)methane; dppp, 1,3-bis(diphenylphosphino)propene; en, ethylenediamine; mec, 1-methylcytosinate; memal, 2-methylmalonate; $NBu_4$, tetrabutylammonium; ox, oxalate; $P_2$-crown, $(Ph_2PCH_2)_2$diaza-18-crown-6; piv, pivalate; $PPh_3$, triphenylphosphine; $PPh_4$, tetraphenylphosphonium; $PPhcy_2$, di(cyclohexyl)phenylphosphine; $PPr^i_2Ph$, di(isopropyl)phenylphosphine; ur, uracilate.

## Introduction

Heterometallic complexes have attracted much attention because of their significance in catalysis and biological science. Part of the attention has been shown to the platinum complexes that have a variable number of metal atoms in their inner core and that possess certain interesting behaviors. A considerable number of structural determinations that have helped to shed light on the catalytic and other activity of heteronuclear platinum complexes have been done. Because of the large number of structures being reported, this review is the fifth part of a series of comprehensive structural overviews. More than 90 heterodinuclear (Melník and Mikuš, 2012), more than 100 heterotrinuclear (Melník and Mikuš, 2013a), more than 35 heterotetranuclear (Melník and Mikuš, 2013b), and almost 40 heteropenta- and heterohexanuclear (Melník and Mikuš, 2013c) complexes were classified and analyzed. The aim of this review is to classify and analyze heterooligo- and heteropolynuclear complexes. There are more than 40 such examples. The structural parameters of all series of non-transition metals as partners are summarized and discussed.

## Heterooligonuclear complexes

There are 20 heterooligonuclear complexes of the composition $Pt_6M$ (2 examples), $Pt_2Ga_5$, $Pt_3Hg_2Ru_2$, $Pt_6Me$ (4 examples), $Pt_4Zn_4$, $Pt_2Hg_6$, $PtAu_6Hg$, $PtAu_5Hg_2$, $Pt_6Hg_4$, $Pt_4Hg_6$, $Pt_3Ru_6Hg$, $PtAu_8Hg$, $Pt_2Sn_9$, $PtAu_8Hg_2$, $Pt_8Ge_4$, and $Pt_8Sn_4$, for which structural parameters are available.

## Heteroheptanuclear complexes

The structure of a monoclinic black $Pt_6Tl$ complex (Hao et al., 1996a,b) consists of well-separated $[(\eta^2\text{-dppp})_3(\mu\text{-CO})_6Pt_6Tl]^+$ [dppp=1,3-bis(diphenylphosphino)propene] cation and $BPh_4^-$ anion. In the complex cation, the six Pt atoms have a geometry that is intermediate between the trigonal prism and antiprism. [The dihedral angles typified by P(1)Pt(1)Pt(5)P(5) and P(1)Pt(1)Pt(4)P(4) fall in the ranges 32.4–34.4° and -79.0 to -86.8°; ideal values would be 0 and -120° for the trigonal prism and 60° and -60° for the trigonal antiprism.] The Pt-Pt bond distances within each Pt triangle fall in the range between 2.658(3) and 2.682(3) Å (average, 2.670 Å), but the intertriangle Pt...Pt separations are greater than 5 Å. The Tl(I) atom is bonded in sandwich fashion to all six Pt atoms with Pt-Tl bond distances in the range 2.860(3)–2.992(3) Å (average, 2.932 Å).

In the monoclinic green complex $[\{(CNxyl)_3(\mu\text{-CNxyl})_3Pt_3\}_2Hg]$ (CNxyl=xylylcyanide) (Figure 1) (Yamamoto et al., 1982), the six Pt atoms define a trigonal prism; the edges of the Pt triangles are associated with the six bridging and six terminal xylylisocyanide ligands. The Hg atom occupies the pseudocenter of the prism. The molecule shows a small rotational distortion of the two triangular $Pt_3$ fragments from an eclipsed $D_{8h}$ configuration by ca. 11° [torsion angles: Pt(1)HgPt(4)C(40), 11.9(19)°; Pt(4)HgPt(1)C(10), 10.9(17)°]. The intertriangular Pt...Pt separations occur between the Pt(1)...Pt(4) of 4.854(3) Å (the closest) and the Pt(3)...Pt(5) of 5.928(3) Å (the longest), suggesting the absence of a bond. The dihedral angle between two triangles is 7.41(8)°. The Pt-Pt bond lengths within each triangle are in the range of 2.633(3)–2.664(3) Å (average, 2.643 Å). The Hg atom is nearly equidistant (2.51 Å) from each of the two $Pt_3$ planes. The Hg-Pt distances are between 2.900(2) and 3.010(3) Å.

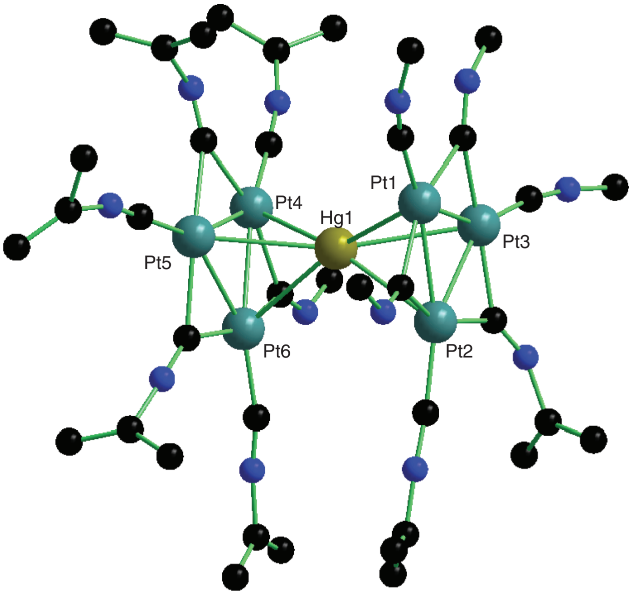

**Figure 1** Simplified view of the molecular structure (diamond) of $[\{(CNxyl)_3(\mu\text{-CNxyl})_3Pt_3\}_2Hg]$ (Yamamoto et al., 1982).

The molecular structure of monoclinic ruby red cluster $Pt_2Ga_5(cp^*)_5$ (cp*=pentamethylcyclopentadienyl) (Weiss et al., 2000) consists of a central unit of two Pt atoms with Pt(1)-Pt(2) bond length of 2.582(1) Å. The $Pt_2$ unit is surrounded by Ga(Cp*) groups [Ga(1) and Ga(2)] and three bridging Ga(Cp*) groups [Ga(3)...Ga(5)]. All Cp* moieties are bound to the Ga centers in a nearly ideal $\eta^5$ mode. The coordination pattern of the five Ga(Cp*) units at the central Pt(1)-Pt(2) core results in a diplatinum centered trigonal-bipyramidal structure with an essentially linear (Cp*)Ga-Pt-Pt-Ga(Cp*) arrangement. The terminal Pt-Ga bonds of 2.329 Å (average) are shorter than the bridging Pt-Ga bonds (average. 2.464 Å).

The structure of triclinic dark purple $Pt_3Hg_2Ru_2$ complex (King and Lukehart, 1998) contains well-separated $[(\eta^2\text{-dppm})_3Pt_3\{(\mu_4\text{-Hg})Ru(CO)_2(cp)\}_2]^{2+}$ [dppm=bis(diphenylphosphino)methane; cp=cyclopentadienyl] cation and $PF_6^-$ anions. The cation is composed of a triangular array of Pt atoms with dppm-P,P′ ligands bridging each Pt-Pt edge. The Pt-Pt bonds within the triangle are 2.648 Å (average). The $Pt_3$ triangle is capped above and below by Hg atoms, which are also bound to the Ru atoms of the $(cp)Ru(CO)_2$ units. The mean Pt-Hg bond distance is 2.795(3) Å, and the mean Hg-Ru bond distance is 2.609(4) Å.

## Heterooctanuclear complexes

The structure of the monoclinic blue violet octanuclear cluster $[(\mu\text{-}\eta^2\text{-dppm})_3(\mu\text{-CO})_6Pt_6(SnBr_3)_2]$ (Figure 2) (Spivak et al., 1996) has approximately $D_{3h}$ symmetry, and the metal core can be described as a trigonal prism of Pt atoms with each triangular face capped by a $SnBr_3$ group. The Pt-Pt bond distances within each $Pt_3$ triangle are 2.668 Å (average), whereas the distances between the triangles are 2.937 Å (average). The Pt-Sn bond distances range from 2.745(3) to 2.950(3) Å. The eclipsed conformations of the two $Pt_3$ triangles and $SnBr_3$ groups are indicated by the dihedral angles P(1)-Pt(1)-Pt(4)P(4) and Br(1)-Sn(1)-Sn(2)-Br(2), which fall in the ranges of 1.5–6.1° and 7.2–10.7°, respectively. The structure of the monoclinic red octanuclear cluster $[(\mu\text{-}\eta^2\text{-dppm})_3(\mu\text{-CO})_6Pt_6(HgI)_2]$ (Hao et al., 1997) is similar to that of the tin-containing $Pt_6Sn_2$ cluster (Spivak et al., 1996). The intertriangle Pt-Pt distances

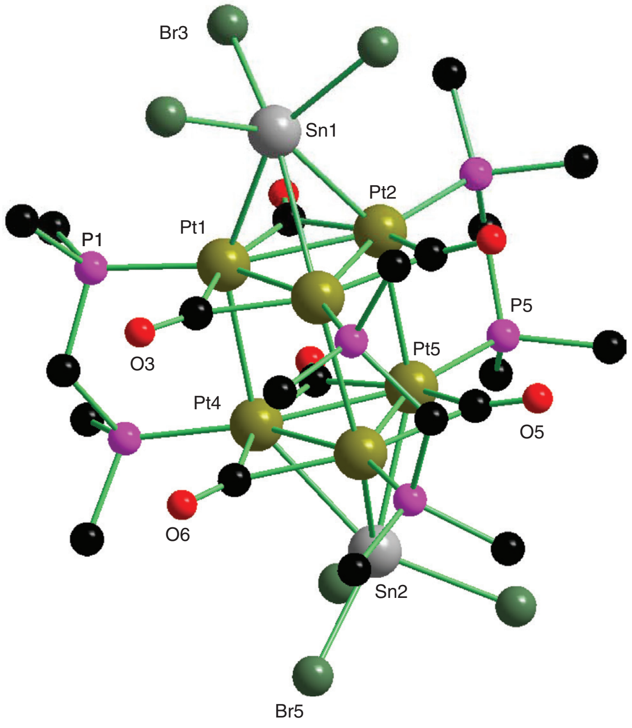

**Figure 2** Simplified view of the molecular structure (diamond) of $[(\mu\text{-}\eta_2\text{-dppm})_3(\mu\text{-CO})_6Pt_6(SnBr_3)_2]$ (Spivak et al., 1996).

[2.910(1)–2.948(1) Å] are longer than the Pt-Pt distances within the $Pt_3$ triangle [2.634(1)–2.687(1) Å]. The Pt-Hg bonds range from 2.770(1) to 2.867(1) Å.

The structure of the monoclinic green mercury-containing cluster $[Hg_2Pt_6(\mu\text{-}\eta^2\text{-dpph})_3(\mu\text{-NCxyl})_6]$ [dpph=1,6-bis(diphenylphosphino)hexane] (Tanase et al., 1992) consists of two triangular $Pt_3$ units, which are connected by three dpph-P,P′ ligands. The Pt and Hg atoms created an antitrigonal prismatic cage. The Hg-Hg bond is 2.872(7) Å. The Pt-Pt bond distances range from 2.656(4) to 2.672(4) Å, and the Pt-Hg distances from 2.878(6) to 2.993(6) Å. The structure of the triclinic violet cluster $\{Pt_3(\mu\text{-CO})_6(\ PPr^i_2Ph\ )_6\ Hg\}_2$ [ $PPr^i_2Ph$ =di(isopropyl)phenylphosphine] (Albinati et al., 1982) consists of two triangular moieties each capped by a Hg atom. These two fragments are linked through the mercury atoms at a distance of 3.225(1) Å. Each Hg atom lies above a $Pt_3$ triangle, with Pt-Hg distances ranging from 2.932(1) to 3.084(1) Å. The mean Pt-Pt bond within the $Pt_3$ triangles is 2.658(1) Å.

The structure of the triclinic colorless cluster $[\{(\eta^2\text{-en})Pt(\mu\text{-}\eta^4\text{-ur})Zn(H_2O)_3\}_4](SO_4)_4$ (en=ethylenediamine; ur=uracilate) (Navarro et al., 2000) consists of well-separated $[\{(\eta^2\text{-en})Pt(\mu\text{-}\eta^4\text{-ur})Zn(H_2O)_3\}_4]^{8+}$ cation and $SO_4^{2-}$ anions. In the complex cation, the cyclic $\{(en)Pt(ur)_4\}^{4+}$ framework with the uracil N1 and N3 donor sites is platinated with 1,3-alternate arrangement of the uracil. The mean separation between the Pt centers, which define the sites of the box, is ca. 5.8 Å, whereas the diagonal is 8.2 Å. In addition to the four Pt centers, four $\{Zn(H_2O)_3\}^{2+}$ entities are strongly bound to pairs of exocyclic O3 and O4 donor atoms of uracil. The Pt-Zn bond distances range from 2.743(1) to 2.789(1) Å.

The structure of another triclinic colorless $Pt_2Hg_6$ octanuclear complex (Rauter et al., 1997) contains well-separated $[\{(MeNH_2)_2Pt(\mu\text{-}\eta^3\text{-mec})_2Hg_3(\mu\text{-OH})(\mu\text{-ONO}_2)\}_2]^{+4}$ (mec=1-methylcytosinate) cation (Figure 3) and $NO_3^-$ anions. The basic form of the centrosymmetric cation is that of a compressed hexagon (sides 7.0 and 5.5 Å) with four Hg(II) and two Pt(II) atoms at the edges and four nucleobases and two OH groups representing the corners. Two additional Hg(II) atoms, which bridge pairs of deprotonated exocyclic NH groups to the cytosine bases, are located along the Pt-Pt vector. All metal atoms and OH groups are almost coplanar. The Pt-Hg(4) bond is 2.727(1) Å and Pt...Pt separation is 9.6 Å. The Hg...Hg separations range from 3.540(3) to 5.244(3) Å.

The structures of the monoclinic orange cluster $[(PPh_3)Pt(AuPPh_3)_6(HgNO_3)]NO_3$ ($PPh_3$=triphenylphosphine) (Gould and Pignolet, 1994) and the triclinic red cluster $[(PPh_3)Pt(AuPPh_3)_5(HgNO_3)_2]NO_3$ (Ito et al., 1991) can be described as icosahedral with a Pt center. The peripheral $M_3$ units form approximate equilateral triangles, and the peripheral metal atoms are close to the vertex positions of a centered icosahedron. In the former cation, the peripheral M-M distances [Hg···Au(2), 3.636 Å; Au(2)···Au(4), 3.244 Å; Au(5)···Au(7), 3.258 Å] are significantly elongated

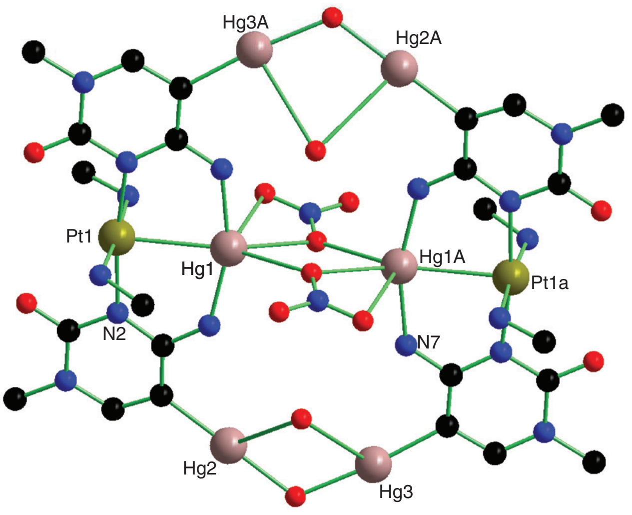

**Figure 3** Simplified view of the molecular structure (diamond) of $[\{(MeNH_2)_2Pt(\mu\text{-}\eta_3\text{mec})_2Hg_3(\mu\text{-OH})(\mu\text{-ONO}_2)\}_2]^{4+}$ (Rauter et al., 1997).

compared with the remaining one (average, 2.893 Å; range, 2.770–3.070 Å), giving distorted nonplanar square faces. The mean nearest peripheral M-M distances in the latter icosahedron is 2.931 Å (range, 2.775–3.072 Å).

## Heterodecanuclear complexes

The structure of the trigonal deep red cluster $[(HgBr)_2\{Pt_3(\mu\text{-}CO)_3(PPhcy_2)_3\}_2(\mu\text{-}HgBr)_2]$ [$PPhcy_2$=di(cyclohexyl)phenylphosphine] (Albinati et al., 1992) consists of two $Hg_2Pt_3$ trigonal bipyramids (one of these is shown in Figure 4). Each of the trigonal bipyramids is bonded to a bromine atom on one side and two bridging bromine atoms on the other side. The central part of the cluster core consists of a square planar arrangement of two Hg(II) atoms and two bridging bromine atoms. In addition, each of these Hg atoms is bonded to the triangular $Pt_3$ unit of the $\{Pt_3(\mu\text{-}CO)_3(PPhcy_2)_3\}$ cluster, the latter being capped by a HgBr fragment. The mean Pt-Pt bond of 2.656(1) Å is shorter than the mean Pt-Hg bond, which is 2.843(1) Å.

The monoclinic black $[Hg_6\{Pt(diph)\}_4]$ cluster (Wurst and Strähle, 1991) has the symmetry $C_2$. The central unit is a $Hg_6$ octahedron of which four faces are occupied by $Pt(\eta^1\text{-}diph)$ groups. The mean of eight Pt-Hg bonds can be divided into the two groups, two center bonds of lengths 2.676 Å, which are about 0.204 Å shorter than the two (Pt-Hg-Pt) three center bond distances with the Pt-Hg mean value of 2.880 Å. The Hg···Hg separations range from 3.080 to 3.275 Å.

The structure of monoclinic red $(NBu_4)[Pt_3Ru_6(\mu_3\text{-}HgI)(\mu_3\text{-}H)_2(CO)_2]$ (Bu=butyl; $NBu_4$=tetrabutylammonium) (Figure 5) (Adams et al., 1996) contains layer-segregated arrangements of the $Pt_3Ru_6$ core with the $Pt_3$ triangle sandwiched between the two $Ru_3$ triangles in a staggered orientation. The Hg atom is attached to the $Pt_3Ru_6$ cluster as a triple-bridging (HgI) group across one of the six $PtRu_2$ triangles. Both hydrid ligands occupy triple-bridging positions across the $Ru_3$ triangles. The metal-metal bonds elongated in the order 2.757(2) Å (Hg-Ru)<2.799(2) Å (average Pt-Ru)<2.893 Å (Pt-Hg)<3.010(3) Å (Ru-Ru).

Another monoclinic red $PtAu_8Hg$ cluster (Gould et al., 1995) contains well-separated $[HgPt(AuPPh_3)_8]^{2+}$ cation and $NO_3^-$ anions. The structure of the complex cation (Figure 6) is a Pt-centered square antiprism monocapped by a Hg atom. The mean metal-metal distance elongated in the order 2.628 Å (Pt-Au)<2.810 Å (Pt-Hg)<3.017 Å (Hg-Au)<3.122 Å (Au-Au).

## Heteroundecanuclear complexes

The triclinic dark red $[K(crypt)_6]_2[(PPh_3)Pt_2Sn_9]$ (crypt=2,2,2-cryptand) salt crystallized as two different solvates, one with an ethylenediamine solvate molecule

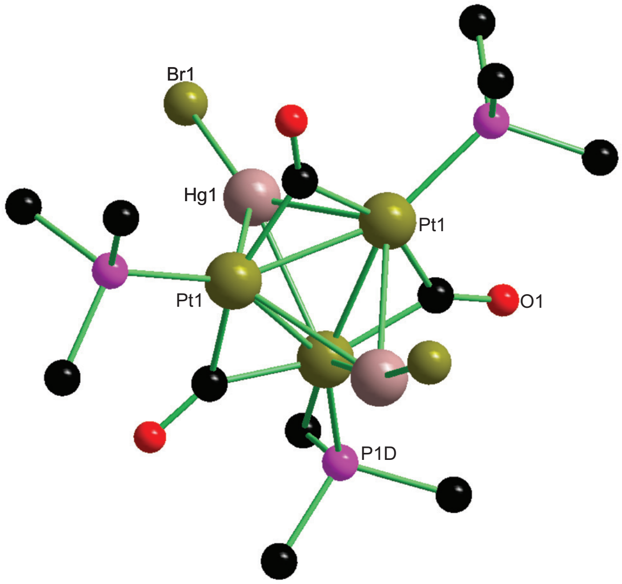

**Figure 4** Simplified view of the molecular structure (diamond) of $[Pt_3(\mu\text{-}CO)_3(PPhcy_2)_3(\mu\text{-}HgBr)_2]$ (Albinati et al., 1992).

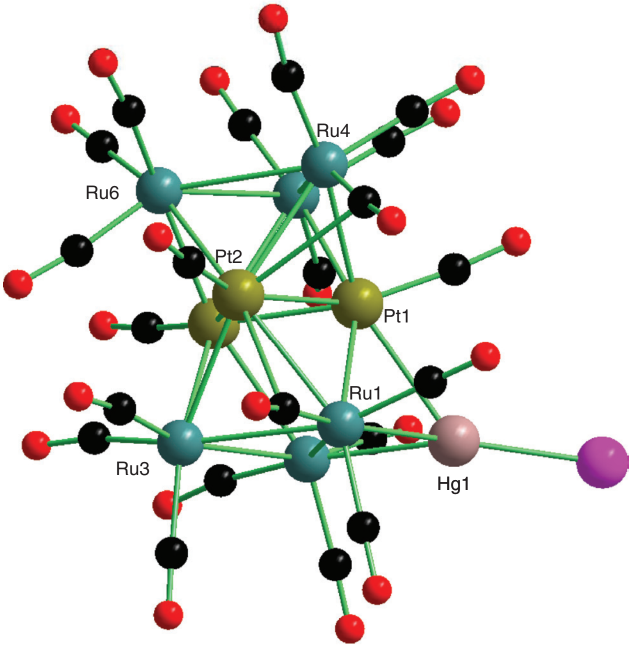

**Figure 5** Simplified view of the molecular structure (diamond) of $[Pt_3Ru_6(\mu_3\text{-}HgI)(\mu_3\text{-}H)_2(CO)_2]^-$ (Adams et al., 1996).

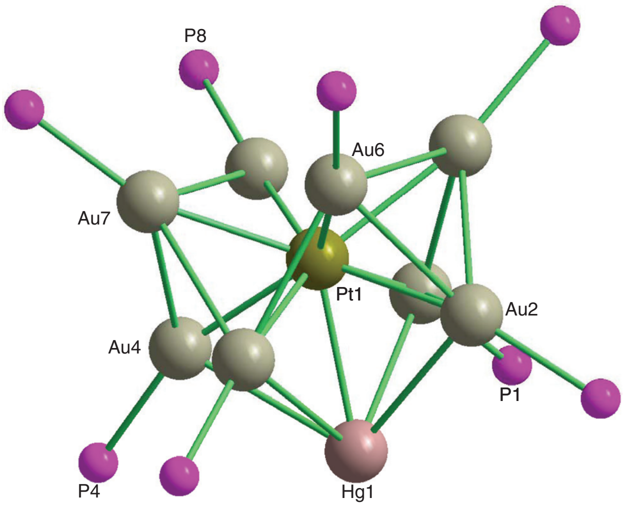

**Figure 6** Simplified view of the molecular structure (diamond) of $[HgPt(AuPPh_3)_8]^{2+}$ (Gould et al., 1995).

and one with a toluene solvate molecule in the crystal lattice (Kesanli et al., 2002). The structures are identical. The $[(PPh_3)Pt_2Sn_9]^{2-}$ anion (Figure 7) 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) caps the top of the triangular face of the cluster with three Pt-Sn bonds [average length, 2.692(2) Å]. The Pt-Pt bond distance is 2.6965(4) Å.

The structure of tetragonal red $[Hg_2Pt(AuPPh_3)_8](NO_3)_4$ (Bour et al., 1990) shows that the $PtAu_8Hg_2$ skeleton, with a crystallographic fourfold rotation axis, is a centered square antiprism capped on the square faces by Hg atoms, with approximately $D_{4h}$ symmetry. The mean metal-metal distance increases in the 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 in the squares).

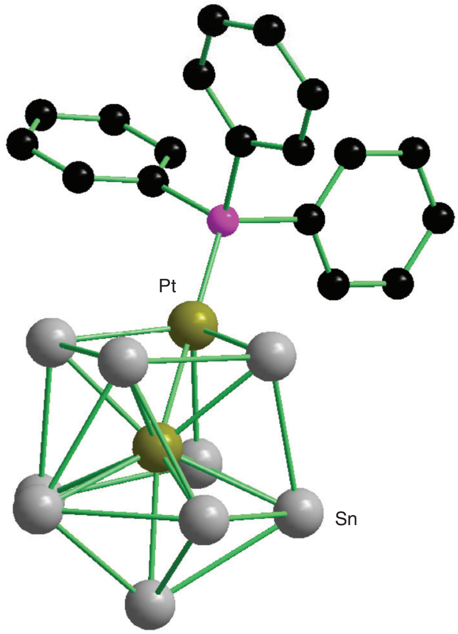

**Figure 7** Simplified view of the molecular structure (diamond) of $[(PPh_3)Pt_2Sn_9]^{2-}$ (Kesanli et al., 2002).

## Heterododecanuclear complexes

The structures of the tetragonal clusters $(PPh_4)_2[Pt_8(MCl_2)_4(\mu\text{-}CO)_2(CO)_8]$ ($PPh_4$=tetraphenylphosphonium; M=Ge or Sn) (Brivio et al., 1995) are very similar (Figure 8). The $Pt_8$ metal core consists of three stacked edge-sharing tetrahedra of Pt atoms that generate four concave butterfly surfaces, each of which is coordinated by one $MCl_2$ group. The whole $Pt_8M_4$ framework can be thought of as deriving from the layering of two outer symmetry-related Pt(2)-M-Pt(2)-M planar rhombuses. The chlorine atoms are essentially coplanar with the $Pt_2M_2$ rhombuses. Of the 10 CO ligands, eight are terminally bonded to the eight Pt atoms, and the remaining two are double-bridging the outer Pt(1)-Pt(1) edges. The Pt tetrahedra are significantly elongated along the $T_1$ axis, with the mean Pt-Pt bond distances being 2.665 Å (intralayer) and 2.925 Å (interlayer). The intralayer Pt-M bonds [Pt-Ge, 2.918(2) Å, and Pt-Sn, 2.950(1) Å]

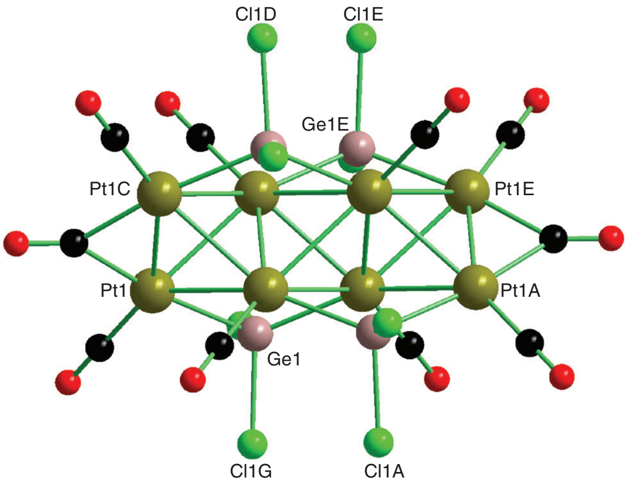

**Figure 8** Simplified view of the molecular structure (diamond) of $[Pt_8(GeCl_2)_4(\mu\text{-}CO)_2(CO)_8]$ (Brivio et al., 1995).

are somewhat longer than the mean interlayer distances (M=Ge, 2.839 Å, and M=Sn, 2.925 Å).

The mean Pt-M bond distance in the series of heterooligonuclear complexes increases in the order 2.430 Å (M=Ga)<2.638 Å (Pt)<2.685 Å (Ge)<2.770 Å (Zn)<2.822 Å (Sn)<2.834 Å (Hg)<2.932 Å (Tl). The inner coordination spheres about the Pt atoms are four- (square planar), five- (trigonal bipyramid), and six- (pseudo octahedral) coordinated, and those about the M atoms are two- (Hg); four- (Sn, Hg); five- (Hg); six- (Ga, Tl, Ge, Sn, Zn, Hg) and even seven- (Ga) coordinated. The complexes crystallized in the following crystal classes: trigonal (1×)<tetragonal (2×)<triclinic (7×)<monoclinic (1×).

## Heteropolynuclear complexes

There are more than 20 heteropolynuclear $(PtM)_n$ (M=non-transition metals) complexes for which structural parameters are available. In triclinic 'copper-colored' $Rb_{1.67}Pt(ox)_2\cdot 1.5H_2O$ (ox=oxalate) (Kobayashi et al., 1978, 1979), the planar $\{Pt(ox)_2\}^{2-}$ anions stack parallel to the *b* axis of the crystal. The Pt(2.33) atoms form a sixfold distorted chain along the *b* axis. Three independent Pt-Pt distances are 2.715(2), 2.832(2), and 3.014(2) Å. The Pt-Pt-Pt angles are 177.93(12)° and 174.34(7)°. The oxalate ligands are bidentate and are staggered (46°, 56°, 80°) with respect to the ligands directly above and below them along the chain, whereas alternate ligands are eclipsed or staggered (~90°). There are four independent anions based on the assumption of $D_{2h}$ symmetry. The structure contains five independent Rb atoms. Three Rb atoms are seven-coordinated ($RbO_7$), and the remaining two are eight- coordinated ($RbO_8$). The neighboring Pt chains are linked by coordination of the terminal O atoms to the Rb atoms. In another triclinic $Rb_{1.6}Pt(ox)_2\cdot 1.2H_2O$ (Kobayashi et al., 1977), the $\{Pt(ox)_2\}$ groups are stacked face to face along the *b* axis to form a linear chain. There are two independent Pt-Pt bonds, 2.837 and 2.868 Å, and Pt(1)-Pt(3)-Pt(2) angle of 175°. The bidentate oxalate ligands are staggered (~45°) with respect to the ligand directly above and below it in the chain. The monoclinic cluster $K_2Pt(ox)_2\cdot 2H_2O$ (Mattes and Krogmann, 1964) shows a one-dimensional polynuclear structure. The structures of the monoclinic yellow cluster $Mg_{0.82}Pt(ox)_2\cdot 5.3H_2O$ (Krogmann, 1968b) and the triclinic red cluster $CaPt(ox)_2\cdot 3.5H_2O$ (Krogmann, 1968a) are similar. The mean Pt-Pt bond distance is 2.85 Å.

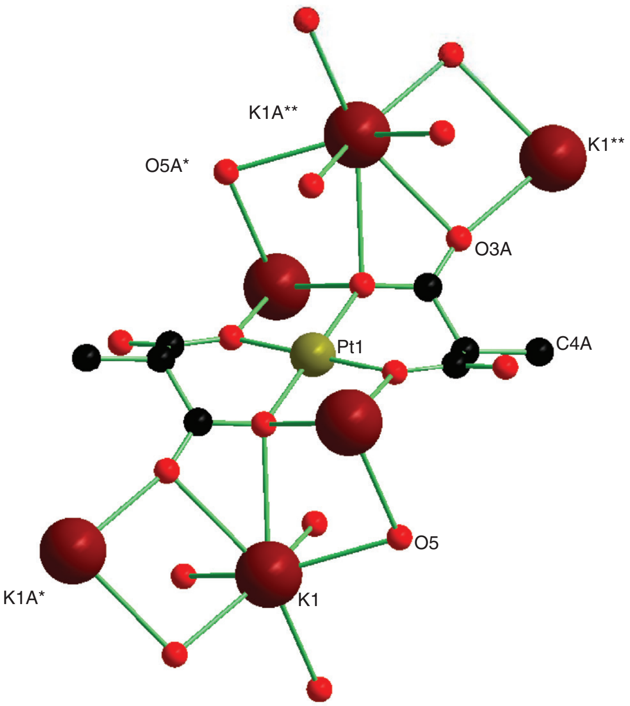

**Figure 9** Simplified view of the molecular structure (diamond) of $K_2Pt(memal)_2\cdot 2H_2O$ (Dunham et al., 1991).

In the triclinic red cluster $K_2Pt(memal)_2\cdot 2H_2O$ (memal=2-methylmalonate) (Figure 9) (Dunham et al., 1991), the 2-methylmalonate ligand is in a boat conformation and the anionic units stack as a column chain along the crystallographic *a* axis, with a Pt···Pt separation of 4.059(2) Å. Hydrogen bonding interaction between pairs of lattice water molecules and the O(4) atoms of neighboring anionic units link neighboring 'columns' of anionic units of chains that run along the unit cell *a*, *c* diagonal. The K(I) is seven-coordinated ($KO_7$) and the Pt(II) is four-coordinated ($PtO_4$).

The structure of the monoclinic brown $\{PtK\}_n$ complex (Cherkashima et al., 2002) is built from the $\{Pt(piv)_4\}^{2-}$ (piv=pivalate) anion, $K^+$ cations, and solvate THF molecules, which are held by the ionic and van der Waals interactions and C-H···O bonds. The Pt(II) has a square planar environment ($PtO_4$) and K(I) is six-coordinated ($KO_6$). The triclinic yellow cluster $Tl_2Pt(C_6F_5)_2(C{\equiv}CBu^t)_2$ ($C_6F_5$=pentaflurohexyl) (Figure 10) (Ara et al., 1997) has a very unusual one-dimensional chain extending along the crystallographic *c* axis of the lattice. The polynuclear complex can be regarded as composed of trimeric octahedral fragments, *trans*, *trans*, *trans*-$\{PtTl_2(C_6F_5)_2(C{\equiv}CBu^t)_2\}$ linked via alkynyl-thallium interactions. Both Pt-Tl distances within the octahedral unit are 3.135(1) Å. The Pt···Tl [3.785(1) Å) and Tl···Tl (3.982(1) Å) separations between the units are close to the sum of the van der Waals radii of the corresponding atoms, indicating no bonding.

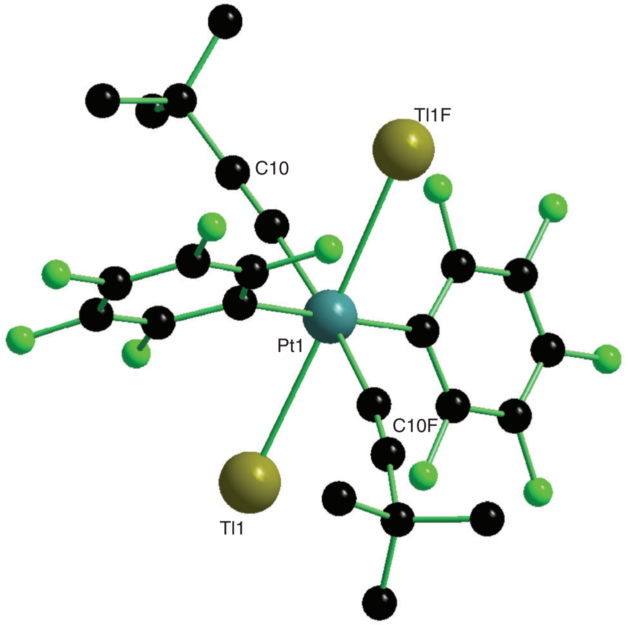

**Figure 10** Simplified view of the molecular structure (diamond) of $Tl_2Pt(C_6F_5)_2(C{\equiv}C\text{-}t\text{-}Bu)_2$ (Ara et al., 1997).

There are four yellow cyanide complexes of platinum, two of the formula $K_2Pt(CN)_4X_{0.3}nH_2O$ (X=Cl, $n$=6; X=Br, $n$=2.3) (Krogmann and Hausen, 1968), crystallizing tetragonal, and two of the formula $K_2Pt(CN)_4{\cdot}nH_2O$ ($n$=1.5, triclinic; $n$=3, orthorhombic) (Reis and Peterson, 1978), in which square planar $\{Pt(CN)_4\}$ groups are stacked in columns whose axis is occupied by $Pt^{2+}$ and $K^+$ cations in one-dimensional polymeric chains. In general, the $CN^-$ anions serve as Pt-C-N-K bridges. The Pt-Pt distances are 2.88(1), 2.887(1) Å (Krogmann and Hausen, 1968) and 2.972(1) Å (Reis and Peterson, 1978). Another three yellow, monoclinic $K_2M\{Pt(CN)_4\}_2{\cdot}6H_2O$ (M=Pb, Balch et al., 1993) or Sr (Krogmann and Stephan, 1968) and triclinic $[\{Me_3Sn(\mu\text{-}OH)(bpe)\}Pt(CN)_4SnMe_3]$ (bpe=1,2-bis(4-pyridyl)ethylene) (Chen et al., 2002) also contain {Pt-C-N-M} bridges, which created one-dimensional polymeric chains. The Pt···Pt separations are 3.27 Å, a distance that is below twice of the van der Waals radius of Pt (3.40–3.60 Å).

The structure of the triclinic orange $\{K_2Pt\}_n$ complex (Li et al., 2000a) shows that the complex displays a quasi one-dimensional infinite chain of two $\{K(db\text{-}18\text{-}C_6)\}^+$ cations and a $\{Pt(SCN)_4\}^{2-}$ anion bridged by $K^+...\pi$ interactions between the units. The principal interactions of the $K^+$ cation involve the six O atoms of the crown ether and one N atom from the $SCN^-$ anion. In another monoclinic orange $\{K_2Pt\}_n$ complex (Liu et al., 2000) the $\{K(18\text{-crown-}6)\}^+$ cations and $\{Pt(SCN)_4\}^{2-}$ anions are bridged by water molecules and form a one-dimensional infinite chain. The Pt(II) is located on the twofold axis ($PtS_4$), and the $K^+$ cation lies almost symmetrically within the crown ether and one N atom from the $SCN^-$ anion is also bound to $K^+$.

In the polymeric chain of the monoclinic orange $\{KPt\}_n$ complex (Spevak et al., 1999) two $\{Pt(mso)Cl_3\}^-$ anions differ mostly by the degree of distortion. Each Pt(II) has a square planar environment ($PtCl_3S$). The K(1) atoms are also different. K(I) is five-coordinated ($KCl_4O$), whereas K(2) is seven-coordinated ($KCl_6O$). The structure of the triclinic red compound $K_2Pt(ox)Cl_2{\cdot}H_2O$ (Dunham et al., 1991) is characterized by a zigzag chain. The Pt(II) has a square planar environment ($PtO_2Cl_2$) and K(1) and K(2) are eight- and seven-coordinated, respectively. The Pt···Pt separations are 3.799(2) Å in the same unit cell and 3.815(2) Å in adjacent unit cells. In monoclinic yellow salt $CsPt(NH_3)(Meu)I_2{\cdot}4H_2O$ (Figure 11) (Freisinger et al., 2000), each Pt(II) atom has a square planar arrangement ($PtN_2I_2$). The $Cs^+$ cations are connected to the complex units via two water molecules as well as via the iodine atoms. The polymeric network of the complex can be dissected into two interconnected chains running along the $y$ and $x$ axis, respectively. In the first one, $Cs^+$ cations are arranged in a zigzag fashion (Cs···Cs, 7.005(2) Å). When viewed along the $x$ axis, the $Cs^+$ cations are arranged in a collinear fashion, bridging pairs of Pt-containing anions [Cs···Cs, 7.167(1) Å].

In a monoclinic red $\{KPt\}_n$-type complex (Mason et al., 1969), the $\{Pt(acac)_2Cl\}^-$ (acac=acetylacetonate) anions are linked via electrostatic interactions with the $K^+$ cations in such a way as to form pseudo-polymeric chains parallel to the crystallographic $b$ axis. Each unit cell contains

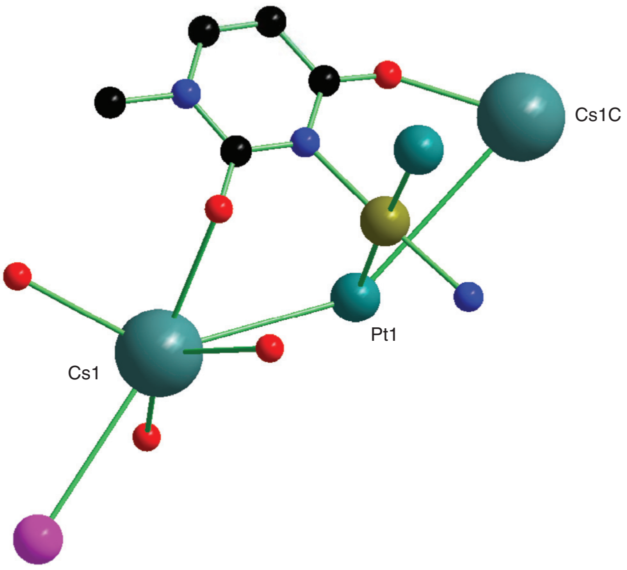

**Figure 11** Simplified view of the molecular structure (diamond) of $CsPt(NH_3)(Meu)I_2{\cdot}4H_2O$ (Freisinger et al., 2000).

two such chains separated by van der Waals interactions. The tetragonal red complex $\mathrm{K_2Pt(CN)_5{\cdot}3H_2O}$ (Piccinin and Toussaint, 1967) contains both Pt(II) and Pt(IV). The chain consists of anionic square planar $\{\mathrm{Pt(CN)_4}\}^{2-}$ and octahedral $\{\mathrm{Pt(CN)_6}\}^{2-}$ units linked via CN groups. Unfortunately, the data for coordination about K(I) are not available. One can expect that the atoms are also involved in this polymeric chain.

The heteropolymeric complexes crystallized in four crystal classes: orthorhombic (1×)<tetragonal (3×)<triclinic (8×)<monoclinic (9×). There are seven different non-transition metals, K, Rb, Cs, Mg, Ca, Tl and Sn, which are partners to Pt atoms. The most frequent among these is the K atom. In 20 examples the Pt atoms are in the oxidation state +2 and all are square planar coordinated with the following inner coordination spheres: $\mathrm{PtX_4}$ (X=O, C, or S), $\mathrm{PtCl_3S}$, $\mathrm{PtO_2Cl_2}$, $\mathrm{PtN_2I_2}$, and $\mathrm{PtO_2CCl}$. The M atoms are four- (Tl), five- (K, Sn), six- (K, Cs), seven- (K, Rb), and eight- (K, Rb) coordinated. The mean Pt-Pt bond distances are 2.87 and 3.53 Å, respectively.

## Conclusions

This review together with its previous parts (Melník and Mikuš, 2012, 2013a,b,c) gives a comprehensive view on heterometallic platinum complexes in which the metal partners are non-transition elements. There are more than 300 such complexes, which cover a wide variability of heterodi-, tri-, tetra-, penta-, hexa-, hepta-, octa-, deca-, undeca-, dodeca-, and polymers. The complexes crystallized in the following crystal classes: cubic, rhombohedral, (each 0.35%)<trigonal (1.3%)<tetragonal (2%)<orthorhombic (7.8%)<triclinic (32.7%)<monoclinic (55.5%). There is a wide variability of the metal partners as well: Li, Na, K, Rb, Mg, Ca, Al, Ga, In, Tl, Ge, Sn, Pb, Sb, Bi, Zn, Cd, and Hg. The soft Pt(II) as well as Pt(IV) atoms form Pt-M bonds with a wide variability of non-transition metals: hard, borderline, and soft. The mean Pt-M bond length increases in the sequence 2.326 Å (M=Al)<2.390 Å (Ga)<2.486 Å (Ge)<2.534 Å (In)<2.550 Å (Sb)<2.677 Å (Sn)<2.683 Å (Li)<2.722 Å (Pt)<2.736 Å (Zn)<2.747 Å (Pb)~2.747 Å (Hg)<2.792 Å (Cd)<2.818 Å (Tl)<2.960 Å (Ca).

An analysis of the crystallographic and structural data of almost 300 heterometallic platinum complexes with non-transition elements shows that about 5% of them exist in isomeric forms. There are several examples: $\mathrm{[Bu^t{}_2bpy)(Me)_2(I)Pt(SnMe_3)][SnMe_3I]}$ (bpy=2,2′-bipyridine; $\mathrm{Bu^t{}_2bpy}$=5,5′-di-tertbutyl-bpy) (Levy et al., 1996), $\mathrm{[\{C_5H_8(PPh_2)_2\}ClPt(SnCl_3)]}$ [$\mathrm{C_5H_8(PPh_2)2}$=cyclopentane-1,2-diyl-bis(diphenylphosphane)] (Dahlenburg and Mertel, 2001), $\mathrm{[(dppe)(I)Pt(SnCl_3]}$ (Farkas et al., 1996), $\mathrm{[Me_2Pt(P_2\text{-}crown)Tl]NO_3}$ [$\mathrm{P_2}$-crown=$\mathrm{(Ph_2PCH_2)_2}$diaza-18-crown-6] (Balch and Rowley, 1990), $\mathrm{[\{(dppm)(Cl)Pt\}_2HgCl_2]}$ (Sharp, 1986), $\mathrm{[Me_2(dppm)_2(\mu\text{-}I)Pt_2Hg]}$ (Toronto and Balch, 1994), $\mathrm{[(PPh_3)_4Pt_2(\mu_3\text{-}S)_2Zn(bpy)Cl]PF_6}$ (Li et al., 2000b), $\mathrm{[(dcpe)Pt\{Ga(cp^*)\}_2]}$ (dcpe=bis(cyclohexylphosphino)ethane) (Sharma et al., 2000), $\mathrm{[(pp3)PtHgMn(CO)_5]}$ (Schuh et al., 2001), $\mathrm{(NBu_4)[\{(C_6F_5)_2(\mu\text{-}Cl)Pt\}_3Sn]}$ (Usón et al., 1990), and $\mathrm{[Cl_2Pt\{Sb(Ph_3\}_2]}$ (Wendt et al., 1998), which contain two crystallographically independent molecules within the same crystal. There is also one example, $\mathrm{[Rb_{1.37}Pt(\mu\text{-}ox)_2{\cdot}1.5H_2O]_{\mathit{n}}}$ (Kobayashi et al., 1978, 1979), which contains even four such molecules. These crystallographic independent molecules present within the same crystal of the respective examples are different from each other by the degree of distortion that reflects on the discrepancies between the Pt-M, Pt-L, and M-L bond distances as well as the rich variability of the angles. All these complexes are classic examples of distortion isomerism (Melník, 1982; Melník and Holloway, 2006).

Platinum and non-transition metals as well as their complexes are important both from a chemical and a biological point of view, and structural information is also important for better understanding of their role in both areas. It is hoped that such a review will serve to draw together common structural trends and stimulate activity in areas of particular interest in the field of heterometallic complexes.

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