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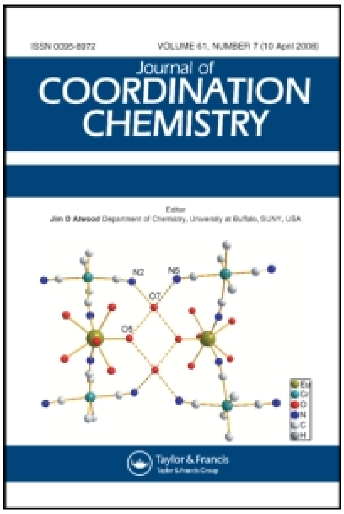

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
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Stereochemistry of heterometallic platinum clusters

M. Melnik[a]; J. Garaj[a]; C. E. Holloway[b]
[a] Institute of Natural and Social Sciences, Alexander Dubcek University Trencin, Studentska 1, 911 50 Trencin, Slovakia [b] Department of Chemistry, York University, North York, Ontario, Canada

To cite this Article Melnik, M. , Garaj, J. and Holloway, C. E.(2008) 'Stereochemistry of heterometallic platinum clusters', Journal of Coordination Chemistry, 61: 19, 3021 — 3065
To link to this Article: DOI: 10.1080/00958970802010591
URL: http://dx.doi.org/10.1080/00958970802010591

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Journal of Coordination Chemistry
Vol. 61, No. 19, 10 October 2008, 3021–3065

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Review Article

Stereochemistry of heterometallic platinum clusters

M. MELNIK*†, J. GARAJ† and C.E. HOLLOWAY‡

†Institute of Natural and Social Sciences, Alexander Dubcek University Trencin,
Studentska 1, 911 50 Trencin, Slovakia
‡Department of Chemistry, York University, 4700 Keele St., North York, M3J 1P3,
Ontario, Canada

(*Received 13 November 2007; in final form 10 January 2008*)

Heterometallic platinum complexes cover a huge field, as shown by a recent survey covering the crystallographic and structural data of almost 1500 examples. About 5% of those complexes exists as isomers and are summarized in this review; except one *cis-trans* example, the remainder are distortion isomers. These are discussed in terms of the coordination about the platinum atom, and correlations are drawn between donor atom, bond lengths and interbond angles, with attention to *trans* effect and metal-metal bonds. Distortion isomers, differing only by degree of distortion in Pt–L and Pt–M distances and L–M–L bond angles, spread over a wide range of oxidation states of platinum: zero, +1, +2 (most common) and +4. The mean Pt–Pt bond distance elongate with increase in oxidation state of platinum: 2.705 Å (Pt(0)–Pt(0)) < 2.720 Å (Pt(I)–Pt(I)) < 2.773 Å (Pt(II)–Pt(II)). The shortest mean Pt–M bond distances are: Pt(0)–Ga = 2.37 Å; Pt(I) = Au 2.697 Å, Pt(II)–Fe = 2.625 Å and Pt(IV)–Sn, 2.580 Å.

Keywords: Stereochemistry; Isomers; Heterometallic; Platinum

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1. Introduction

In chemistry, sustainability deals with how syntheses can be performed safely with minimum input of energy and other resources and at the same time reducing waste and byproducts. Stereoselectivity in coordination compounds is often related to important stereospecificity of biological systems, catalysis and stereochemical effects in technical processes. Preparative chemists must be aware of the diversity of isomers which may be produced. Isomerism can be broadly classed into structural and stereoisomers. The former can be divided into ionization, hydrate, coordination, linkage and polymerization sub-categories. The latter can be divided into geometric (*cis-trans*, *fac-mer*), optical, ligand and distortion isomerism.

Platinum exists in oxidation states from zero to +6, including non-integral Pt(2.87), Pt(3.25) and Pt(3.5); +2 and +4 are the most common. Platinum coordination chemistry has been surveyed [1] with over 200 isomeric examples noted. These isomers

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*Corresponding author. Email: milan.melnik@stuba.sk

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970802010591

were analyzed and classified [2]. There are four types of isomerism, including distortion (65%) *cis*-*trans* (30%), mixed isomers (*cis*-*trans* + distortion) and ligand isomerism.

The heterometallic platinum clusters also cover a huge field, as shown by a recent survey covering the crystallographic and structural data of almost 1500 examples [3]. About 5% of these clusters exist as isomers and are summarized in this review. These examples are classified to show that stereoisomers are more common than structural isomers, and surprisingly, that except for one example, all are distortion isomers.

The aim of this presentation is to discuss the factors which could lead to a better understanding of stereochemical interaction within the coordination sphere of heterometallic platinum clusters, bond lengths, as well as metal-metal bond and interbond angles, with attention to *trans* effect.

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2. Distortion isomerism

The coexistence of two or more species differing only by degree of distortion of M–L bond distances and L–M–L bond angles is typical of the general class of distortion isomers [4]. There are over 80 such examples in the chemistry of heterometallic platinum compounds, which can be divided into several subgroups.

2.1. *Pairs of isomeric forms*

There are two pairs of heterotrinuclear [5, 6], four pairs of heterotetranuclear [7–10] and one pair of heterohexanuclear [11,12] clusters; their crystallographic and structural data are gathered in table 1. Orange $[(PPh_3)_4Pt_2(\mu_3\text{-}S)_2Ag(PPh_3)]PF_6$, orthorhombic and triclinic [5] have similar structures, both show a sulfide-bicapped $[AgPt_2]$ triangle, but some of their bonding parameters, especially the $M \cdots M$ separation, are significantly different (table 1). The two Pt–Ag distances are essentially identical in orthorhombic isomer (3.061(1) *versus* 3.066(1) Å) but significantly different in triclinic isomer (2.962(1) *versus* 3.240(1) Å). The $Pt \cdots Pt$ separations are 3.351(2) and 3.375(2) Å, respectively. The coordination about each Ag(I) atom has Y-shaped AgS_2P. Each Pt(II) is square planar (PtS_2P_2).

Both isomeric forms, yellow and orange of another trimer $[\{(Br)(dmso)Pt\}_2(\mu\text{-}dmat)_2Fe]$ [6] belong to the homo-monoclinic crystal class. Their structures are shown in figure 1. In each trimer two {Pt(dmso)Br}fragments are bridged by the ferrocenylamine ligand. Each has Pt(II) in distorted square-planar environments (PtCNSBr). In the yellow isomer (figure 1a) the Fe of the ferrocenylamine ligand is situated on a crystallographic center of symmetry, in such a way that the Pt atoms are located at opposite sides of the staggered ferrocene ring. In the orange isomer an approximately eclipsed coordination is observed.

Four pairs of isomers are tetranuclear. In one [7] both crystal classes are homo-monoclinic. The remaining examples differ from each other not only by degree of distortion but also by crystal class. In three of these, one isomer is monoclinic and the

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Table 1. Crystallographic and structural data for heterometallic platinum compounds – pairs of distortion isomers.[a]

Compound (color)	Cryst.cl. Space gr. z	a[Å] b[Å] c[Å]	α[°] β[°] γ[°]	Chromo- phore	M–L [Å]	M – M [Å] M–L–M [°]	L–M–L [°]	Ref.
A: Trinuclear								
[(PPh$_3$)$_4$Pt$_2$(μ_3-S)$_2$ · Ag(PPh$_3$)]PF$_6$ (orange)	or *P*2$_1$2$_1$2$_1$ 4	14.229(1) 18.674(1) 30.127(1)		Pt^{II}S$_2$P$_2$	μ_3S^b 2.359(1,12) Ph$_3$P 2.284(1,1) 2.301(1,7)	Ag 3.063(1,3) S 77.5(1,1.3) Pt 3.351(2) S 90.5(1,1)	S,S^b 82.8(1,1) P,P 101.2(1,2.2) S,P 88.1(1,1.5) 170.8(1,1.2)	[5]
				Ag^{I}S$_2$P	μ_3S 2.479(1) 2.585(1) Ph$_3$P 2.327(1)		S,S 76.04(3) S,P 141.7(1,1.5)	
[(PPh$_3$)$_4$Pt$_2$(μ_3-S)$_2$ · Ag(PPh$_3$)]PF$_6$ (orange)	tr *P*$\bar{1}$ 2	14.934(1) 15.039(1) 19.744(1)	74.55(1) 88.01(1) 79.88(1)	Pt^{II}S$_2$P$_2$	μ_3S^b 2.358(2,15) Ph$_3$P 2.288(2,10)	Ag 2.962(1) 3.240(1) S 78.3(1,5.3) Pt 3.375(2) S 91.3(1,1)	S,S 89.4(1,4) P,P 103.9(8,3.1) S,P 87.4(1,1.4) 168.3(1,5)	[5]
				Ag^{I}S$_2$P	μ_3S 2.502(2) 2.607(2) Ph$_3$P 2.343(2)		S,S 74.33(7) S,P 142.8(1,7.4)	
[{Br(dmso)Pt}$_2$(μ-η^2: η^5-dmat)$_2$Fe] (yellow)	m *P*2$_1$/*c* 2	14.277(5) 8.974(3) 10.951(2)	 105.77(2)	PtCNSBr	$\mu\eta^2\mu$C 1.998(9) $\mu\eta^s\eta$N 2.143(8) DmsoS 2.194(3) Br 2.537(1)		C,N 81.5(4)^c S,Br 91.2(1) C,S 94.9(3) N,S 175.9(2) C,Br 172.4(2)	[6]
				FeC$_{10}$	η^5not given		not given	
[{Br(dmso)Pt}$_2$(μ-η^2: η^5-dmat)$_2$Fe] (orange)	m *P*2$_1$/*c* 4	9.984(3) 10.335(2) 25.929(7)	 92.28(2)	PtCNSBr	$\mu\eta^2\mu$C 1.97(2) $\mu\eta^2\mu$N 2.14(2) DmsoS 2.202(5) Br 2.523(2)	Pt 4.327(1)	C,N 80.8(6)^c S,Br 90.6(1) C,S 95.5(5) N,S 175.2(4) C,Br 173.8(4)	[6]
B: Tetranuclear								
(PEt$_3$)$_2$Pt$_2$(μ_3-CO) (μ-CO)$_2$W$_2$(CO)$_3$ (cp)$_2$ (brown)	m *P*2$_1$/*n* 2	8.768(7) 14.147(2) 13.580(6)	 77.96(5)	Pt^{0}PW$_2$Pt	μOC 2.29(1,4) μ_3OC 2.56(1,19) Et$_3$P 2.281(3)	W 2.805(1,31) C 82.3(5,2.5) C (8, 2.4) Pt 2.662(1) C 61.9(8)	P,Pt 171.8(2) W,W 123.3(2) W,Pt 61.7(1,1.1)	[7]

(*continued*)

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Table 1. Continued.

Compound (color)	Cryst.cl. Space gr. z	a[Å] b[Å] c[Å]	α[°] β[°] γ[°]	Chromophore	M–L [Å]	M – M [Å] M–L–M [°]	L–M–L [°]	Ref.
				$W^0C_{10}Pt_2$	OC not given μOC 1.95(1,2) μ_3OC 2.06(1) η^5cpC 2.32		Pt,Pt 56.63(2)	
$(PEt_3)_2Pt_2(\mu_3\text{-}CO)$ $(\mu\text{-}CO)_2W_2(CO)_3$ $(cp)_2$ (brown)	m $P2_1/n$ 2	11.920(3) 12.930(6) 12.166(3)	61.72(2)	Pt^0PW_2Pt	μOC 2.38(4,36) μ_3OC 2.76(4,20) Et_3P 2.28(1)	W 2.810(2,23) C 85(2,1) μ_3C 69(3,4) Pt 2.675(3) μ_3C 69(3,4)	P,Pt 170.5(3) W,W 123.16(4) W,Pt 61.6(1,9)	[7]
				$W^0C_{10}Pt_2$	OC not given μOC 1.95(7,2) μ_3OC 2.04(4) η^5cpC 2.30		Pt,Pt 56.85(4)	
$[\{(PPh_3)_2Pt(\mu\text{-}\eta^2\text{-}S_2C{=}$ $C\{C(O)Me\}_2Ag\}_2]\cdot$ $(ClO_4)_2\cdot 2Et_2O$ (white) (at 173 K)	m $P2_1/n$ 2	11.0089(2) 29.4225(5) 14.0317(3)	100.84(1)	$Pt^{II}S_2P_2$	μS 2.366(1,4) Ph_3P 2.295(1,4)	Ag 3.1204(5)	S,S 74.98(4) P,P 100.92(4) S,P 92.56(4,3.8)	[8]
				Ag^IS_2	μS 2.443(4,16)	Ag 3.163(8)	Pt,Ag 71.32(1) S,S 168.32(4)	
$[\{(PPh_3)_2Pt(\mu\text{-}\eta^2\text{-}S_2C{=}$ $C\{C(O)Me\}_2Ag\}_2]\cdot$ $(ClO_4)_2\cdot 2Me_2O$ (yellow) (at 173 K)	tr $P\bar{1}$ 1	10.6869(10) 12.574(2) 16.482(2)	80.422(10) 73.741(10) 87.582(10)	$Pt^{II}S_2P_2$	μS 2.358(1,0) Ph_3P 2.303(1,3)	Ag 3.2387(3)	S,S 74.97(3) P,P 99.79(3) S,P 92.05(3,1.8)	[8]
				Ag^IS_2	μS 2.423(1,11)	Ag 3.0588(6)	Pt,Ag 65.82(1) S,S 174.0(3)	
$[\{(PPh_3)_2Pt)\mu\text{-}\eta^2\text{-}S_2C{=}$ $C\{C(O)Me\}_2Au\}_2]\cdot$ (white) (at 163 K)	m $P2_1/c$ 2	12.058(2) 19.540(3) 22.863(4)	92.96(1)	$Pt^{II}S_2P_2$	μS 2.376(1,5) Ph_3P 2.287(1,9)	Au 3.2235(5)	S,S 75.43(4) P,P 98.95(4) S,P 93.0(1,1.7) 166.9(1,2.6)	[9]
				Au^IS_2	μS			
$[\{(PPh_3)_2Pt)\mu\text{-}\eta^2\text{-}S_2C{=}C$ $\{C(O)Me\}_2Au\}_2]\cdot$ $(ClO_4)_2\cdot 2Me_2CO$ (white) (at 143 K)	tr $P\bar{1}$ 1	12.1896(10) 12.3262(12) 15.5870(12)	78.878(3) 77.180(3) 74.962(3)	$Pt^{II}S_2P_2$	μS 2.3562(8) 2.3704(9) Ph_3P 2.288(1,1)	Au 3.334(3) P,P 100.17(3) S,P 92.3(1,3.2)	S,S 75.63(3) 165.1(1,5.6)	[9]
				Au^IS_2	μS 2.318(1,2)	Au 3.0347(3)	S,S 175.20(3)	
$(Pcy_3)(CO)PtOs_3(\mu\text{-}H)\cdot$ $(\mu\text{-}CH_2)(CO)_9$	tr $P\bar{1}$	12.244(5) 9.533(4)	77.00(3) 72.79(3)	$PtCPOs_3$	OC 1.858(11) cy_3P 2.380(3)	Os 2.730(1) 2.820(1,6)	C,P 92.6(4) Os,Os 60.1(1)	[10]

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(orange yellow) (at 220 K)	2	16.239(7)	75.84(3)				64.1(1,3)	
				$OsC_3H_2PtOs_2$	OC 1.91(13,23) μH 1,85(12,14)	Os 2.826(1) 2.947(1,7) H 110(7,6)	Pt,Os 59.4(1,2) Os,Os 57.3(1)	
				OsC_4HPtOs_2 (×2)	OC 1.921(13,23) μH_2C 2.130(8,13) μH 1.731(6,6)	C 83.1(3)	Pt,Os 58.2(1,1.9) Os,Os 61.3(1,3)	
$[(Pcy_3)(CO)PtOs_3 \cdot (\mu\text{-}H)_2(\mu\text{-}CH_2)(CO_9)^d$ (red) (at 220 K)	m $P2_1/c$ 8	18.708(4) 16.664(3) 22.875(5)	101.82(2)	$PtCPOs_3$	OC 1.816(19) 2.3 cy_3P 47(4)	Os 2.789(1) 2.861(1,8)	C,P 96.7(6) Os,Os 61.0(1,1.6)	[10]
				$OsC_3H_2PtOs_2$	OC 1.917(19,18) μH not given	Os 2.834(1,32) 2.973(1)	Pt,Os 58.6(1,3) Os,Os 59.4(1)	
				OsC_4HPtOs_2 (×2)	OC 1.903(19,49) μC 2.142(19,19)	C 81.9(6)	Pt,Os 60.0(1,1.8) Os,Os 60.3(1,3.0)	
				$PtCPOs_3$	OC 1.847(15) cy_3P 2.341(4)	Os 2.675(1) 2.860(1,5)	C,C 97.9(5) Os,Os 62.2(1,2.3)	
				$OsC_3H_2PtOs_2$	OC 1.902(19,35) μH not given	Os 2.839(1,26) 2.976(1)	Pt,Os 58.4(1) Os,Os 59.3(1)	
				OsC_4HPtOs_2 (×2)	OC 1.908(20,52) μC 2.142(20,53)	C 84.0(6)	Pt,Os 59.8(1,2.0) Os,Os 60.4(1,2.8)	
C: HEXANUCLEAR								
$(CO)_2Pt_2Ru_4(CO)_{16}$ (purple black)	or $Pna2_1$ 4	12.542(8) 15.350(4) 15.252(3)	105.32(3)	Pt^0Ru_3Pt	OC 1.827(8)	Ru 2.6456(8) 2.8160(8) 2.8730(8) Pt 2.6656(8)	Ru,Ru 62.77(20 109.2 170.41(2) Ru,Pt 62.06(2,1.1) 109.55(2)	[11]
				$Ru^0C_4Pt_2Ru$ (×2)	OC 1.93(1,3)	Ru 2.8480(9)	Pt,Pt 55.87(2) Pt,Ru 55.69(2) 98.64(2)	
				Ru^0C_4PtRu (×2)	OC 1.93(1,2)		Pt,Ru 61.54(2)	
$(CO)_2Pt_2Ru_4(CO)_{16}$ (purple black)	or $Pna2_1$ 4	17.738(3) 15.596(2) 10.357(1)		Pt^0CRu_3Pt	OC 1.80(2)	Ru 2.650(2,2) 2.822(2,9) 2.878(2,17) Pt 2.665(1)	Ru,Ru 63.03(6,40) 108.96(5,75) 171.38(6,29) Ru,Pt 62.13(4,2.1) 112.60(5,1.2)	[12]
				Ru^0C_4PtRu (×2)	OC 1.94(3)	Ru 2.864(3,11)	Pt,Pt 55.74(4,26) Pt,Ru 55.55(6,7) 100.72(2,19)	
				Ru^0C_4PtRu (×2)	OC 1.94(3)		Ru,Ru 61.06(4,4)	

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[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] Five-membered metallocyclic ring.

[d] There are two crystallographically independent molecules·

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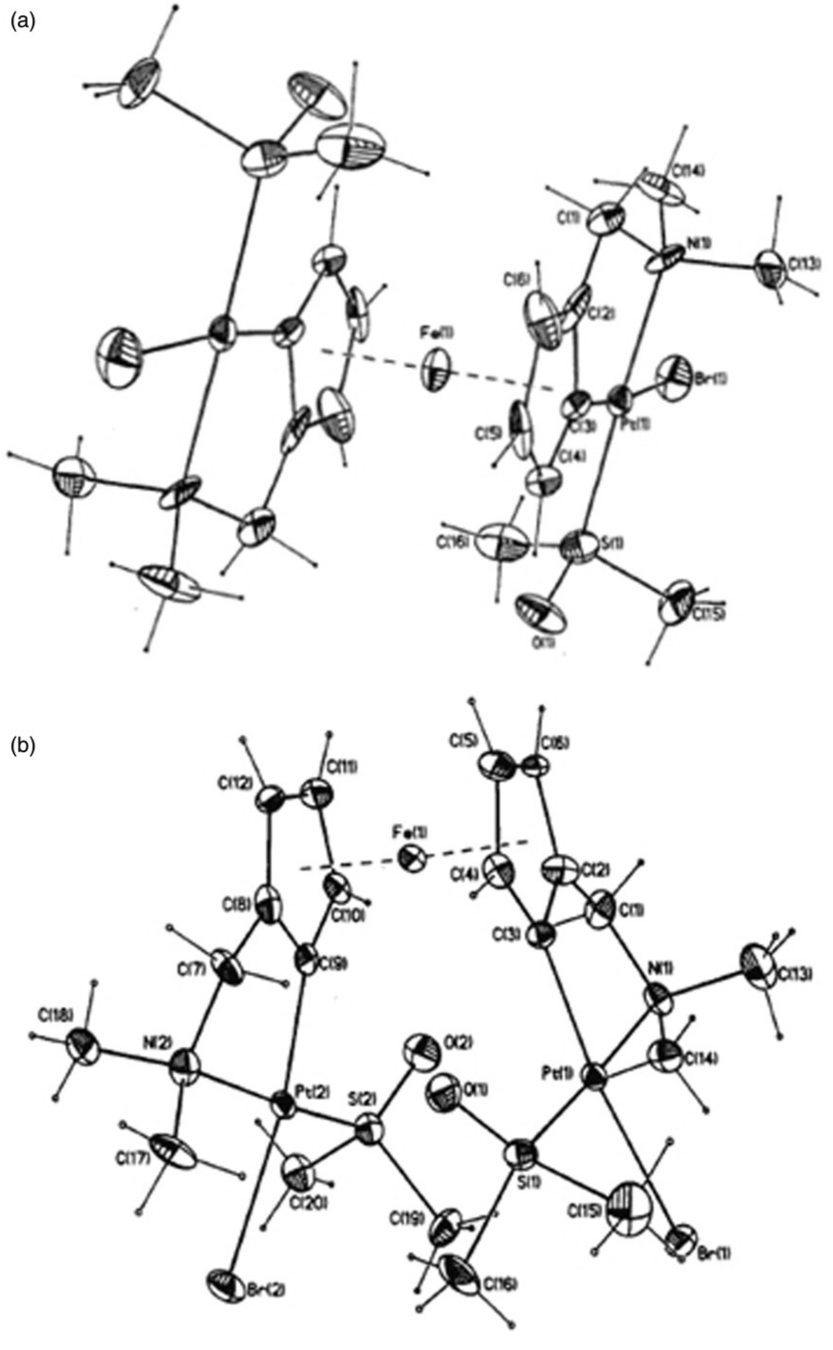

Figure 1. (a) Structure of [{(Br)(dmso)Pt}$_2$(μ-dmat)$_2$Fe] yellow isomer [6]; (b) Structure of [{(Br)(dmso)Pt}$_2$(μ-dmat)$_2$Fe] orange isomer [6].

other is triclinic [8–10]. In addition, a monoclinic example [10] contains two crystallographically independent molecules within the same crystal.

The four metals (Pt_2W_2) in [$(PEt_3)_2Pt_2\,\mu_3$-CO)(μ-CO)$_2W_2(CO)_6cp_2$] [7] form a parallelogram with the center of symmetry in the middle of the Pt–Pt bond (2.662(1) and 2.675(3) Å). Each PEt_3 is bonded to a Pt (*trans*). Each cp ligand is η^2-bonded to W and the CO ligands of each $W(CO)_3$ tripod occupy asymmetric bridging positions, with two μ-CO ligands between W and Pt or Pt′, respectively, and one μ_3-CO between W, Pt and Pt′. The Pt–Pt and mean Pt–W bond distances are 2.662(1) and 2.805(1) Å (molecule 1) and 2.675(3) and 2.810(2) Å (molecule 2).

There are two pairs of clusters, $[\{(PPh_3)_2Pt(\mu\text{-}S_2C{=}C\}\{C(O)Me\}_2M]^{2+}$ cations M=Ag (monoclinic and triclinic) [8], Au (monoclinic and triclinic) [9] and all exhibit a crystallographic inversion symmetry. Each 1,1-ethylenedithiolate serves as bridge building a distorted eight-membered central ring $\{$–Pt–S–M–S–$\}_2$. Each Pt(II) has a square-planar arrangement (PtS_2P_2) with different degree of distortion. Each M(I) atom is in a distorted linear environment (MS_2).

Crystal structures of $(Pcy_3)(CO)PtOs_3(\mu\text{-}H)(\mu\text{-}CH_2)(CO)_9$ isomers (yellow-orange and red) [10] are shown in figure 2. Both species have a closo distorted tetrahedral geometry for the metal atoms, with the methylene group bridging an Os–Os edge cisoid to the Pcy_3 ligand on the platinum in the orange-yellow isomer (figure 2a) and transoid to the phosphine group in the red isomer (figure 2b). The mean Pt–Pt and Pt′–Os bond distances are 2.790 and 2.907 Å (orange-yellow isomer), 2.837 and 2.880 Å (red isomer, molecule 1) and 2.828 and 2.885 Å (red isomer, molecule 2).

Purple black $(CO)_2Pt_2Ru_4(CO)_{16}$ is the only example of a hexanuclear species which exists in two isomeric forms differing not only by degree of distortion but also by crystal class. One isomer is monoclinic [11] and the other orthorhombic [12]. Each isomer contains an open, but folded, array of six metal atoms. Two mutually bonded ruthenium atoms (2.848 Å [11] and 2.854(1) Å) [12] are joined to the mutually bonded platinum atoms (2.665 Å in both isomers), which are bonded to a second pair of mutually bonded ruthenium atoms (2.848 Å in the former and 2.875 Å in the latter). The mean Pt–Ru bond distances are 2.778 and 2.797 Å, respectively. The intermolecular interactions are presumably stronger in the monoclinic isomer, as suggested by its smaller size.

2.2. *Independent molecules*

2.2.1. Binuclear complexes. There are 16 heterobinuclear species containing two crystallographically independent molecules [13–27] and one example, $Cl_2Pt(totpp)_2Fe$ [28] containing eight such molecules (table 2). The platinum oxidation states are +4 [13] or +2.

In yellow [η^2-Bu^t_2bpy)$(Me)_2(I)PtSnMe_3)]_2Sn(Me)_3I$ [13] each Pt(IV) has a distorted tetragonal bipyramidal coordination $(4+1+1)$. The plane is built up by two N atoms of bidentate Bu_2^+bpy ligand and two Me groups. One axial position is occupied by iodide (Pt–I, 2.881(4) Å (molecule 1) and 2.959(4) Å (molecule 2), respectively, and the other by $SnMe_3$ (Pt–Sn 2.547(5) and 2.567(4) Å).

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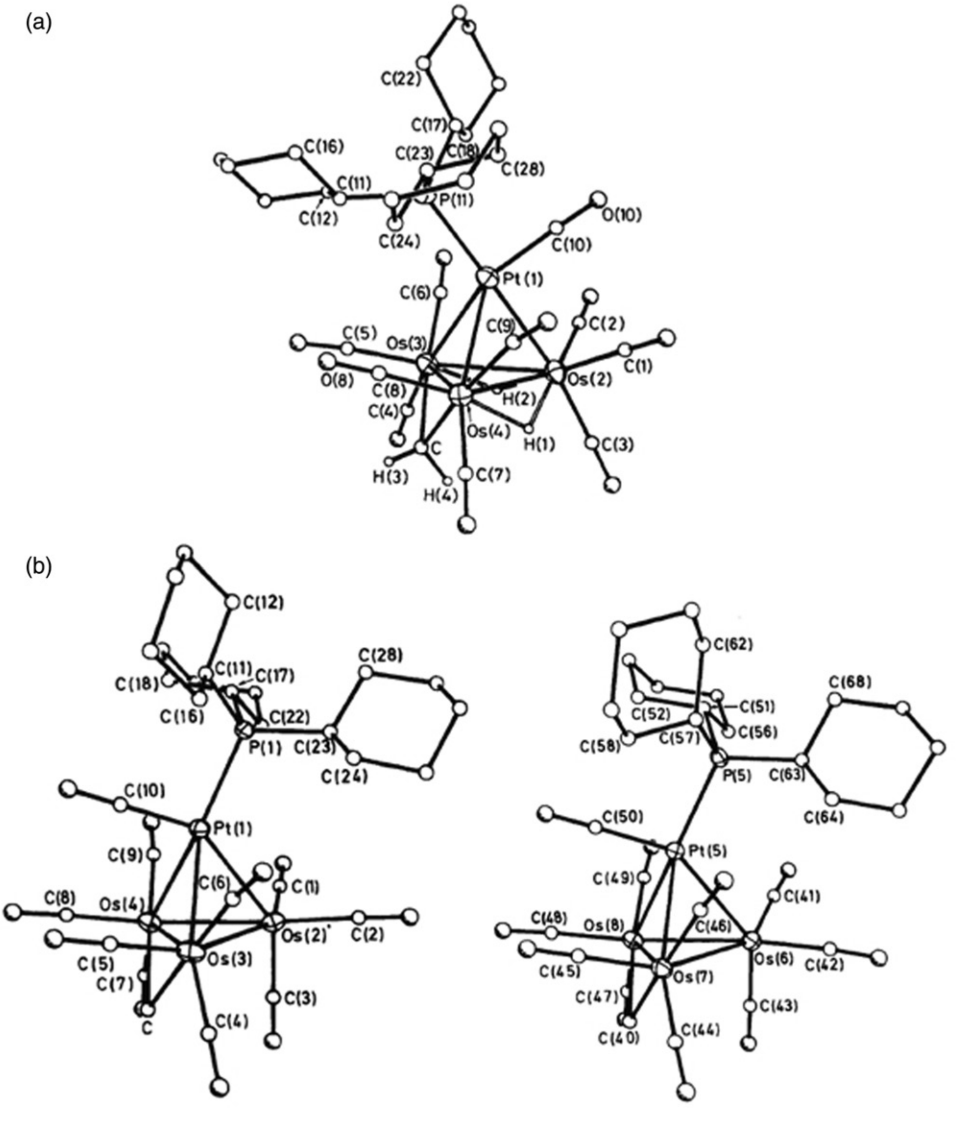

Figure 2. (a) Structure of [(Pcy$_3$)(CO)PtOs$_3$(μ-H)(μ-CH$_2$)(CO)$_9$] yellow-orange [10]; (b) Structure of [(Pcy$_3$)(CO)PtOs$_3$(μ-H)(μ-CH$_2$)(CO)$_9$] [10] red (molecule 1 and molecule 2).

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Another two yellow PtSn species [14, 15] contain a chiral chelating diphosphine ({$C_5H_8(PPh_2)_2$} [14], and dppe [15] and SnX_3 (X = Cl [14], I [15] ligands. Each Pt(II) is square planar (PtP$_2X$Sn) with different degree of distortion. The Pt–Sn bond distances of 2.562(1) and 2.572(1) Å [14] are shorter than those found in [15] (2.6113(13) and 2.6154(14) Å. The bond angles at the Pt(II) are also sensitive to the conformation of the chirality of chelating diphosphine which links Pt atoms.

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Table 2. Crystallographic and structural data for heterobinuclear platinum compounds – crystallographically independent molecules.[a]

Compound (color)	Cryst.cl. Space gr. z	a[Å] b[Å] c[Å]	α[°] β[°] γ[°]	Chromo-phore	M–L [Å]	M – M [Å] M–L–M [°]	L–M–L [°]	Ref.
$[(\eta^2\text{-Bu}^t_2\text{bpy}))(\text{Me})_2(\text{I})\cdot\text{Pt}(\text{SnMe}_3)]_2\text{Sn}(\text{Me})_3\text{I}$ (yellow)	m $P2_1/m$ 2	11.204(2) 13.926(2) 22.485(3)	96.40(1)	$\text{Pt}^{IV}\text{N}_2\text{C}_2\text{ISn}$	η^2N[b] 2.140(18) MeC 2.063(26) I 2.881(4)	Sn 2.547(5)	N,N[b] 77.0(10)[c] C,C 88.1(14) I,Sn 179.6(1) N,C 97.5(9,0) 174.5(9)	[13]
				$\text{Sn}^{II}\text{C}_3\text{Pt}$	MeC 2.184(47,16)		Cl,Cl 107.9(13,2) Cl,Pt 108.0(10,0) 116.8(17)	
				$\text{Pt}^{IV}\text{N}_2\text{C}_2\text{ISn}$	η^2N 2.115(21) MeC 2.048(24) I 2.959(4)	Sn 2.567(4)	N,N 74.7(11)[c] C,C 93.6(14) I,Sn 176.9(1) N,C 95.8(9,0)	
				$\text{Sn}^{II}\text{C}_3\text{Pt}$	MeC 2.128(31) 2.289(50)		Cl,Cl 110.5(11,1.2) Cl,Pt 108.5(15,7)	
$[\eta^2\{\text{C}_5\text{H}_8(\text{PPh}_2)_2\}(\text{Cl})\cdot\text{Pt}(\text{SnCl}_3)]$ (yellow)	m $P2_1/c$ 8	22.019(1) 14.794(1) 22.210(1)	119.366(5)	$\text{Pt}^{II}\text{P}_2\text{ClSn}$	η^2P 2.278(5,3) Cl 2.283(9)	Sn 2.572(1)	P,P 87.0(2)[c] Cl,Sn 85.2(3) P,Cl 90.6(3) 176.9(3)	[14]
				$\text{Sn}^{II}\text{Cl}_3\text{Pt}$	Cl 2.349(8,23)		Cl,Cl 96.7(3,3.4) Cl,Pt 120.3(2,2.8)	
				$\text{Pt}^{II}\text{P}_2\text{ClSn}$	η^2P 2.284(5,2) Cl 2.289(9)	Sn 2.562(1)	P,P 86.9(2)[c] Cl,Sn 85.0(2) P,Cl 90.9(3) 177.2(3)	
				$\text{Sn}^{II}\text{Cl}_3\text{Pt}$	Cl 2.37(2,3)		Cl,Cl 94(2,4) Cl,Pt 118.7(2,3.9)	
$[(\eta^2\text{-dpppe})(\text{I})\text{Pt}(\text{SnCl}_3)]\cdot\text{CHCl}_3$ (yellow)	m $P2_1$ 4	15.488(0) 14.999(2) 16.303(2)	98.67(1)	$\text{Pt}^{II}\text{P}_2\text{ISn}$	η^2P 2.275(5,28) I 2.6565(13)	Sn 2.6113(13)	P,P 95.7(2)[d] I,Sn 82.96(4) P,I 90.71(13) 172.48(13)	[15]
				$\text{Sn}^{II}\text{Cl}_3\text{Pt}$	Cl not given		not given	
				$\text{Pt}^{II}\text{P}_2\text{ISn}$	η^2P 2.275(4,22) I 2.6415(13)	Sn 2.6154(14)	P,P 91.0(2)[d] 86.73(4) 91.00(11) 170.84(14)	
				$\text{Sn}^{II}\text{Cl}_3\text{Pt}$	Cl not given		not given	

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Table 2. Continued.

Compound (color)	Cryst.cl. Space gr. z	a[Å] b[Å] c[Å]	α[°] β[°] γ[°]	Chromo-phore	M–L [Å]	M – M [Å] M–L–M [°]	L–M–L [°]	Ref.
$[(NC)_2Pt(\mu\text{-}\eta^2:\eta^6\text{-}P_2\text{-}crown)\,Tl]NO_3\cdot 1.5H_2O\cdot 0.5CH_2Cl_2$ (colorless) (at 130K)	m $P2_1/c$ 8	21.476(7) 14.274(4) 32.660(9)	104.36(2)	$Pt^{II}C_2P_2$	NC not given η^2P 2.338(8,5)	Tl 2.911(2)	P,P 171.0(3) P,C 90.0(7,5.0) P,Tl 94.5(2,1.7)	[16]
				$Tl^{I}O_4N_2Pt$	η^6O 2.76(3,2) η^6N 3.07(2,8)		not given	
				$Pt^{II}C_2P_2$	NC not given η^2P 2.322(11,12)	Tl 2.958(2)	P,P 172.0(3) P,C 90.0(2,10.0) P,Tl 94.0(2,1.6)	
				$Tl^{I}O_4N_2Pt$	η^6O 2.83(2,8) η^6N 3.01(2,4)		not given	
$Cl_2Pt(\mu\text{-}dpep)Cu$ (purple)	tr $P\bar{1}$ 4	19.333(2) 23.74(1) 12.984(5)	103.28(4) 108.29(3) 76.47(3)	$Pt^{II}N_2Cl_2$	η^2N 1.99(3,3) Cl 2.265(10,25)		N,N 179(1) Cl,Cl 174.2(4) N,Cl 90.0(8,3.5)	[17]
				$Cu^{II}N_4$	η^4N 1.99(3,3) 2.01(2,1)		N,N 90(1,5)^d 176(1,1)	
				$Pt^{II}N_2Cl_2$	η^4N 1.98(3,2) Cl 2.28(1,1)		N,N 177(1) Cl,Cl 174.1(4) N,Cl 90(1,3)	
				$Cu^{II}N_4$	η^4N 1.96(3,1) 2.01(2,1)		N,N 90(1,2)^d 177(1,1)	
$(PPh_3)_2ClPt(\mu\text{-}\eta^2\text{-}3,5Ph_2pz)AgCl$	m $P2_1/c$ 8	21.948(4) 11.946(3) 36.733(5)	96.76(1)	$Pt^{II}P_2NCl$	Ph_3P 2.258(5) 2.288(6) N 2.073(15) Cl 2.353(5)	Ag 3.317(2)	P,P 100.2(2) N,Cl 83.7(4) P,N 90.1(4) P,Cl 85.3(2) 174.1(2)	[18]
				$Ag^{I}NCl$	N 2.076(18) Cl 2.308(7)		N,Cl 176.9(5)	
				$Pt^{II}P_2NCl$	Ph_3P 2.257(6) 2.293(6) N 2.064(17) Cl 2.336(7)	Ag 3.368(2)	P,P 97.7(2) N,Cl 85.5(5) P,N 90.7(5) P,Cl 86.3(2) 174.1(2)	
				$Ag^{I}NCl$	N 2.157(19)		N,Cl 173.5(5)	

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					Cl 2.312(8)			
$[Cl_2(dmso)Pt(\mu\text{-}\eta^2\text{-}$	m	6.958(2)		Pt^ICl_2NS	Cl 2.297(7,0)		Cl,Cl 175.6(3)	[19]
$NC_6H_4O\text{-}2)$	Cc	18.047(3)	92.04(2)		$\mu\eta^2$N 2.03(2)		N,S 177.2(5)	
$Ti(Cl)(cp)_2]$ (yellow)	4	33.216(5)			dmsoS 2.225(6)		Cl,N 88.6(5,2.5)	
							Cl,S 91.6(2,3.3)	
				TiOCl	η^5cpC 2.36(2,5)		O,Cl 94.1(6)	
					$\mu\eta^2$O 1.93(2)			
					Cl 2.332(7)			
				Pt^ICl_2NS	Cl 2.301(8,11)		Cl,Cl 176.5(3)	
					$\mu\eta^2$N 2.04(2)		N,S 177.7(5)	
					dmsoS 2.219(6)		Cl,N 89.1(6,2.0)	
							Cl,S 91.0(2,3.2)	
				TiOCl	η^5cpC 2.38(3,4)		O,Cl 94.3(2)	
					$\mu\eta^2$O 1.90(2)			
					Cl 2.364(7)			
$[(PEt_3)_2(Ph)Pt(\mu\text{-}H)W(H)$	tr	11.150(3)	88.1(1)	$Pt^{II}P_2HC$	Et_3P 2.330(5,2)	W 3.440(1)	P,P 171.6(4)	[20]
$(cp)]Bph^4$(red brown)	$P\bar{1}$	19.842(2)	88.2(1)		H not given	H not given	P,C 86.6(5,2.0)	
	4	22.322(4)	76.4(1)		PhC 2.04(1)			
				$W^VC_5H_2$	η^5cpC not given		not given	
					μH not given			
					H not given			
				$Pt^{II}P_2HC$	Et_3P 2.335(5,3)		P,P 170.6(4)	
					PhC 2.03(1)		P,C 86.3(5,1.3)	
				$W^VC_5H_2$	not given		not given	
$(\eta^1\text{-}3,5Me_2pz)_2$	tr	12.085(2)	79.82(3)	$Pt^{II}N_2P_2$	pzN 2.02(3,1)		N,N 86.4(12)	[21]
$Pt(\mu\text{-}\eta^2\text{-}dppf)$ (orange)	$P\bar{1}$	15.935(2)	77.34(3)		$\mu\eta^2$P 2.272(9,2)		P,P 101.4(2)	
	4	21.785(4)	88.58(3)					
				FeC_{10}	η^5C not given		not given	
				$Pt^{II}N_2P_2$	pzN 2.05(3,2)		N,N 88.1(10)	
					$\mu\eta^2$P 2.280(9,13)		P,P 97.6(3)	
				FeC_{10}	η^5P not given		not given	
$Cl_2Pt(\mu\text{-}\eta^2\text{-}dmppf)$ (yellow)	or	14.0951(5)		$Pt^{II}Cl_2P_2$	Cl 2.348(3,6)	Fe 4.288(2)	Cl,Cl 87.4(1)	[22]
	$P2_12_12_1$	16.8149(6)			$\mu\eta^2$P 2.254(3,0)		P,P 102.0(1)	
	4	29.3881(11)					Cl,P 85.7(1,1.3)	
							169.8(1,2)	
				FeC_{10}	η^5C not given		not given	
				$Pt^{II}Cl_2P_2$	Cl 2.339(3,5)	Fe 4.240(2)	Cl,Cl 85.9(1)	
					$\mu\eta^2$P 2.267(3,1)		P,P 99.6(1)	
							Cl,P 87.4(1,1.8)	
							172.5(1,2.4)	
				FeC_{10}	η^5C not given		not given	

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Table 2. Continued.

Compound (color)	Cryst.cl. Space gr. z	a[Å] b[Å] c[Å]	α[°] β[°] γ[°]	Chromophore	M–L [Å]	M – M [Å] M–L–M [°]	L–M–L [°]	Ref.
$[(\eta^2\text{-dmit})Pt(\mu\text{-}\eta^2\text{-dppf})]\cdot 1.5CHCl_3$ (yellow)	tr $P\bar{1}$ 4	15.3323(8) 17.361(1) 19.1005(11)	69.337(1) 69.017(1) 66.334(1)	$Pt^{II}S_2P_2$	η^2S 2.327(2,4) $\mu\eta^2$P 2.295(2,11)		S,S 89.59(7)^c P,P 95.96(7) S,P 87.4(1,2) 174.7(1,5)	[23]
				FeC_{10}	η^5C not given		not given	
				$Pt^{II}S_2P_2$	η^5S 2.326(2,4) $\mu\eta^2$P 2.297(2,16)		S,S 89.59(7)^c P,P 95.96(7) S,P 87.4(1,2) 174.7(1,5)	
				FeC_{10}	η^5C not given		not given	
$[(Ph_3P)_2(Br)Pt(\mu\text{-}\eta^1:\eta^4\text{-dppo})Co]\cdot 0.5CH_2Cl_2$ (dark purple)	m $P2_1/c$ 4	13.344(2) 29.730(6) 14.451(2)	91.10(1)	$Pt^{II}P_2CBr$	Ph_3P 2.268(4) 2.367(4) $\mu\eta^1$C 1.95(1) Br 2.527(1)		P,P 177.5(2) C,Br 178.1(5) P,C 90.2(5,2) P,Br 89.8(1,5)	[24]
				$Co^{II}N_4$	$\mu\eta^4$N 1.96(1)		N,N not given	
				$Pt^{II}P_2CBr$	Ph_3P 2.248(4) 2.374(4) $\mu\eta^1$C 2.06(2) Br 2.501(2)		P,P 178.1(2) C,Br 175.9(4) P,C 89.2(4,3.5) P,Br 90.8(1,0)	
				$Co^{II}N_4$	$\mu\eta^4$N 1.95(1,2)		N,N not given	
$[ClPt(\mu\text{-}\eta^1:\eta^2\text{-}C{\equiv}CMe).(\mu\text{-}\eta^2\text{-dppm})_2Rh(CO)]PF_6$(orange)	or $Pn2_1a$ 8	43.93(1) 25.178(9) 10.164(6)		$Pt^{II}P_2CCl$	$\mu\eta^2$P not given μC 1.95(2) Cl not given	Rh 3.066(2)	not given	[25]
				$Rh^IC_3P_2$	μC 2.34(2,12) OC not given $\mu\eta^2$P not given		not given	
				$Pt^{II}P_2CCl$	μC 1.94(2)	Rh 3.086(2)	not given	
				$Rh^IC_3P_2$	μC 2.38(2,9)		not given	
$[(\eta^2\text{-bpy})Pt(\mu\text{-aet})_2Rh\cdot(\eta^2\text{-aet})]Br_2\cdot 5.5H_2O$ (orange)	m $P2_1/c$ 4	14.595(2) 14.149(3) 28.769(3)	99.74(1)	$Pt^{II}N_2S_2$	η^2N 2.048(8,8) μS 2.309(2,9)	Rh 3.3066(8) S 91.8(1,4)	N,N 80.2(3)^c S,S 81.00(8) N,S 99.7(2,2.2) 174.3(2,1)	[26]
				$Rh^{III}N_3S_3$	η^2N 2.101(8) η^2S 2.336(3) $\mu\eta^2$N 2.123(8,23)		N,N 94.9(3,2.6) S,S 88.9(1,7.9) N,S 85.4(2,1.7)^c	

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					$\mu\eta^2$S 2.308(3,7|			
				Pt^{II}N$_2$S$_2$	η^2N 2.042(8,5)		N,N 80.1(3)^c	
					μS 2.310(3,15)	S 91.2(1,4)	S,S 80.67(3)	
							N,S 99.7(2,3.3)	
							176.5(2,1.2)	
				Rh^{III}N$_3$S$_3$	η^2N 2.094(8)		N,N 94.7(3,4.2)	
					η^2S 2.343(3)		S,S 88.6(1,7.8)	
					$\mu\eta^2$N 2.118(8,12)		N,S 85.6(2,1.1)^c	
					$\mu\eta^2$S 2.306(2,1)			
[(Ph$_3$P)(Br)Pt($\eta^2:\eta^4$-dppo)	m	13.333(6)		Pt^{II}P$_2$CBr	Ph$_3$P 2.232(7)		P,P 177.4(2)	[24]
Ni] · 0.5CH$_2$Cl$_2$ (purple)	*P*2$_1$	29.719(9)	91.14(4)		2.389(7)		C,Br 176.6(7)	
	4	14.441(7)			$\mu\eta^1$C 2.02(2)		P,C 88.8(7,1.9)	
					Br 2.504(3)		P,Br 91.2(2,1.5)	
				Ni^{II}N$_4$	$\mu\eta^4$N 1.94(2,3)		N,N not given	
				Pt^{II}P$_2$CBr	Ph$_3$P 2.264(7)		P,P 178.3(2)	
					2.375(7)		C,Br 177.5(7)	
					$\mu\eta^1$C 1.97(2)		P,C 90.7(7,1.7)	
					Br 2.535(3)		P,Br 89.3(2,0)	
				Ni^{II}N$_4$	$\mu\eta^4$N 1.95(2,4)		N,N not given	
[(η^2-Et$_4$en)Pt(μ-$\eta^2:\eta^4$-	tr	13.160(12)	113.80(4)	Pt^{II}N$_2$S$_2$	η^2N 2.06	Ni 7.12	N,N 84.7(6)^c	
norpc)Ni] · 0.5CHCl$_3$	$P\bar{1}$	16.526(10)	92.93(6)		$\mu\eta^2$S 2.269(5,4)		S,S 91.2(2)^c	
(violet)	4	20.374(11)	98.34(6)					
				Ni^{II}N$_4$	$\mu\eta^4$N 1.89(1,2)		N,N 89.9(6)	
							177.1(5)	
				Pt^{II}N$_2$S$_2$	η^2N 2.06	Ni 7.10	N,N 84.1(5)^c	
					$\mu\eta^2$S 2.259(5,4)		S,S 91.7(2)^c	
				Ni^{II}N$_4$	$\mu\eta^4$N 1.87(1,1)		N,N 89.9(6)	
							177.1(5)	
Cl$_2$Pt(μ-$\eta^1:\eta^5$-totpp)$_2$	tr	21.990(4)	101.72(3)	Pt^{II}Cl$_2$P$_2$	Cl 2.355(10,5)	Fe 9.25(1)	Cl,Cl 88.0(3)	
Fe^e (yellow)	$P\bar{1}$	29.865(6)	108.68(3)		$\mu\eta^4$N 2.25(1,1)		P,P 98.8(2)	
	16	29.877(6)	108.66(3)				Cl,P 87.6(2,1.1)	
				FeC$_{10}$	η^5C not given		not given	

---

[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. The chemical identity of the coordinated atom or ligand is specified in these columns.

[b] Five-membered metallocyclic ring.

[c] Six-membered metallocyclic ring.

[d] There are eight crystallographically independent molecules.

Structure of $[(NC)_2Pt(\mu\text{-}P_2\ \text{crown})Tl]^+$ cation [16] consists of a planar $P_2Pt(CN)_2$ unit that is capped by the diaza-crown portion with the Tl(1) atom sitting within TlO_4N_2. The Pt–Tl bond distances in the two independent cations in the crystals are 2.911(2) and 2.958(2) Å and the mean Tl–Pt–P five membered (–Tl–Pt–C–N–) bite angles are 94.5(2) and 94.0(2)°.

In the remaining Pt–M species, where M is a transition metal, Cu [17], Ag [18], Ti [19], W [20], Fe [21–23, 28], Co [24], Rh [25, 27] and Ni [24, 27], Pt(II) is square-planar with different degree of distortion in a wide variety of chromophores without any "real" Pt–M bond (table 2). Their structures are complex.

Three crystal classes were found in these heterobinuclear derivatives: monoclinic (×9), triclinic (×6) and orthorhombic (×2).

The purple $[Cl_2Pt(\mu\text{-dpep})Cu]$ [17] is shown in figure 3 with the porphyrinato core distorted from planarity to approximately S_4 symmetry. The average dihedral angle between the mean plane of adjacent pyrole rings in molecule 1 is 14.4(9)° and 10.4° in molecule 2. In both molecules the Cu(II) is essentially in the mean plane defined by the four pyrole nitrogens with an out of plane displacement of less

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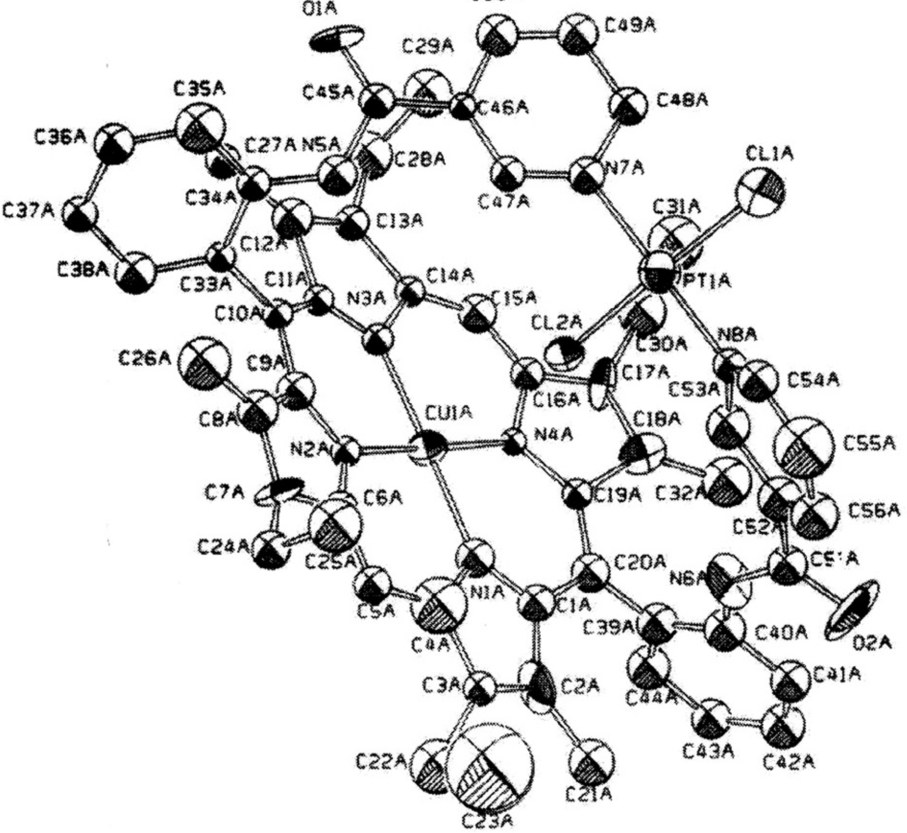

Figure 3. Structure of $[Cl_2Pt(\mu\text{-dpep})Cu]$ [17].

than 0.01 Å. The Pt(II) has a typical square-planar coordination (PtN_2Cl_2). A structure feature of the binuclear PtCu complexes is the nearly perpendicular orientation of the PtN_2Cl_2 and CuN_4 planes. In molecule 1, the dihedral angle formed by these two planes is 75°. The corresponding dihedral angle in molecule 2 is 83°.

2.2.2. Trinuclear complexes. Crystallographic and structural data for heterotrinuclear compounds are gathered in table 3. There are eighteen species which contain two crystallographically independent molecules [29–45] and $(PPh_3)_2Pt(\mu_3\text{-}S)_2Fe_2(CO)_6$ [41] with four such molecules: The platinum oxidation states are zero [35, 36, 40], +1 [29, 30, 38] and +2 in all remaining species. There are three types of trimers, the first Pt_2M (M = Hg [29, 30], Zn [31], Cd [31], Mn [32], Ag [33], Pd [34]); the second PtM_2 (M = Ga [35], Co [36], Ru [37], Mo [38], W [39], Fe [40–42]), and the third with PtMnM (M = Fe [43], Hg [44]) and PtFeOs [45]. There are two crystal classes, triclinic (×11) and monoclinic (×8).

Heterotrinuclear structures are very complex. For example, in $[\{\eta^2\text{-dppm})(Cl)Pt\}_2HgCl_2]\cdot 0.5CH_2Cl_2$ [29] two nearly identical molecules in the asymmetric unit have "A-frame" structures with $HgCl_2$ at the apex bridging the two Pt(I) atoms. The Pt–Pt and mean Pt–Hg bond distances are 2.7119(8) and 2.712 Å (molecule 1) and 2.7361(9) and 2.704 Å (molecule 2).

In another yellow complex $[(NC)_2(\mu\text{-}\eta^2\text{-dppm})_2(\mu\text{-I})Pt_2HgI]$ [30] each molecule consists of a doubly-bridged "A-frame" with $\{HgI\}^+$ and I^- fragments at the bridging sites. The Pt–Pt and mean Pt–Hg bond distances (2.819(2) and 2.713 Å (molecule 1) and 2.823(2) and 2.715 Å (molecule 2)) are somewhat longer than those previously reported [29].

Two yellow $[(PPh_3)_4Pt_2(\mu\text{-}S)_2M(\eta^2\text{-bpy})Cl]PF_6$ [31] (M = Zn or Cd) complexes are isostructural. In each complex cation a sulfide bicaps the heterometallic $\{Pt_2M\}$ triangle with phosphines on Pt(II) and the other ligands on M(II). Each Pt(II) is square planar (PtS_2P_2) and each M(II) is trigonal bipyramidal (MN_2S_2Cl).

In a pale yellow $\{Pt_2Mn\}$ complex [32] the Pt(II) atoms are linked to the central Mn(II) atom through four $NHCOBu^+$ ligands (syn-syn arrangement) and also by Pt–Mn interactions. The coordination sphere of the Pt(II) is completed by two NH_3 and two amidate ligands in *cis* position to each other (PtN_4). The central Mn(II) is coordinated by four oxygen atoms of the four amidate ligands. The Pt–Mn–Pt angle in one molecule is linear (180.00°) and Mn(II) is square planar (MnO_4). The Pt–Mn–Pt angle in the other molecule is only 114.12(6)° and Mn(II) is tetrahedral (table 3).

In $[\{C_6F_5)_3Pt(\mu\text{-tht})\}_2Ag]^-$ [33] each $\{Pt(C_6F_5)_3(\mu\text{-tht})\}$ fragment is connected to the Ag(I) center through Pt–Ag and (tht)μS–Ag bonds. The mean Pt–Ag bond distances are 2.783(1) Å (molecule 1) and 2.862(1) Å (molecule 2).

In *cis*-$[(NH_3)_2Pt(meu)_2Pd(meu)_2Pt(NH_3)_2]^{2+}$ cations [34] the Pt(II)'s are linked to the central Pd(II) through 1-methyluracylate ligands and also by Pt–Pd interactions. The Pt(II) coordination in both molecules is through N_3 of the meu ligand and Pd(II) coordination through the exocyclic O_4. The mean Pt–Pd bond distances are 2.837(1) and 2.839(1) Å, respectively.

In a yellow $\{PtGa_2\}$ complex [35] the three metal atoms form a "V-shape" with Pt(0) between two Ga(0) atoms with mean Pt–Ga bond distances of 2.361(2) Å (molecule 1)

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Table 3. Crystallographic and structural data for heterotrinuclear platinum compounds – crystallographically independent molecules.[a]

Compound (color)	Cryst.cl. Space gr. z	a[Å] b[Å] c[Å]	α[°] β[°] γ[°]	Chromophore	M–L [Å]	M – M [Å] M–L–M [°]	L–M–L [°]	Ref.
[{(η^2-dppm)(Cl)Pt}$_2$	tr	11.578(3)	65.53(2)	$Pt^{I}P_2$ ClHgPt	η^2P^b 2.300(4,11)	Hg 2.6991(8)	P,P^b 174.3(1,1)	[29]
-$HgCl_2$]·CH_2Cl_2	$P\bar{1}$	22.156(5)	76.53(2)		Cl 2.343(4,7)	2.7097(8)	P,Cl 87.4(1,1.7)	
(orange)	4	23.036(5)	84.30(2)			Pt 2.7361(9)	Hg,Pt 59.7(1,3)	
				$Hg^{II}Cl_2Pt_2$	Cl 2.447(5,2)		Cl,Cl 103.3(1)	
							Pt,Pt 60.78(1)	
				$Pt^{I}P_2$ClHgPt	η^2P 2.301(4,10)	Hg 2.7122(8)	P,P 175.2(1,8)	
					Cl 2.334(4,4)	2.7153(7)	P,Cl 88.6(1,2.4)	
						Pt 2.7119(8)	Hg,Pt 60.02(2,6)	
				$Hg^{II}Cl_2Pt_2$	Cl 2.429(4,12)		Cl,Cl 106.0(1)	
							Pt,Pt 59.96(2)	
[(NC)$_2$(μ-η^2-dppm)$_2$(μ-I)-	tr	15.311(3)	82.99(2)	$Pt^{I}P_2$CIHgPt	$\mu\eta^2$P 2.308(8,6)	Hg 2.700(2)	P,P 172.2(3,1)	[30]
$Pt_2Hg(I)$]·CH_2Cl_2·1.5H_2-	$P\bar{1}$	16.132(5)	81.02(2)		NC 1.95(4,5)	2.725(2)	C,I 121.3(8,3.2)	
O (orange) (at 130 K)								
	4	24.911(6)	89.80(2)		μI 2.913(3,3)	Pt 2.819(2)	I,Hg 119.8(1,4)	
						I not given	I,Pt 61.2(1,0)	
							Hg,Pt 58.7(1,4)	
				$Hg^{II}IPt_2$	I 2.655(2)		I,Pt 148.61	
							Pt,Pt 62.6(1)	
				$Pt^{I}P_2$CIHgPt	$\mu\eta^2$P 2.310(7,13)	Hg 2.700(2)	P,P 171.9(3,1)	
					NC 2.00(3,2)	2.725(2)	C,I 119.2(9,2.8)	
					μI 2.916(3,9)	Pt 2.819(2)	I,Hg 119.7(1,8)	
						I not given	I,Pt 61.0(1,4)	
							Hg,Pt 58.7(1,5)	
				$Hg^{II}IPt_2$	I 2.656(3)		I,Pt 148.6(1,1.5)	
							Pt,Pt 62.7(1)	
[$(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2Zn$	tr	14.5319(2)	83.434(1)	$Pt^{II}S_2P_2$	μ_3S 2.364(2,14)	Zn 3.205(1,56)	S,S 80.2(1,1)	[31]
(η^2-bpy)Cl]PF_6	$P\bar{1}$	20.0832(2)	88.522(1)		Ph_3P 2.293(2,6)	S not given	P,P 100.5(1,26)	
(yellow) (at 183 K)	4	29.2213(3)	88.281(1)		2.314(2,2)	Pt 3.252(2)	S,P 89.7(1,4.9)	
						S not given	169.3(1,5.2)	
				$Zn^{II}N_2S_2Cl$	η^2N 2.190(7,19)		N,N 74.1(3)^c	
					μ_3S 2.491(2,41)		S,S 75.35(7)	
					Cl 2.299(2)		N,Cl 99.5(2,3.9)	
							S,Cl 113.6(1,7.9)	
				$Pt^{II}S_2P_2$	S 2.363(2,14)	Zn 3.202(1,64)	S,S 80.4(1,1)	

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					Ph_3P 2.2942,12) 2.311(2,0)	S not given Pt 3.249(2) S not given	P,P 99.8(1,6) S,P 89.9(1,3.5) 169.9(1,3.4)	
				$Zn^{II}N_2S_2Cl$	η^2N 2.169(7,25) μ^3S 2.495(2,70) Cl 2.283(2)		N,N 75.6(3)^c S,S 75.32(6) N,Cl 99.6(2,3.8) S,Cl 115.4(1,5.4)	
$[(PPh_3)_4Pt_2(\mu_3\text{-}S)_2Cd$ $(\eta^2\text{-bpy})Cl]PF_6$ (yellow) (at 183 K)	tr $P\bar{1}$ 4	14.5256(5) 20.1188(7) 29.3002(11)	83.110(1) 88.390(1) 82.842(1)	$Pt^{II}S_2P_2$	μ^3S 2.359(2,14) Ph_3P 2.287(2,5) 2.301(2,7)	Cd 3.270(1,44) S not given Pt 3.274(3) S not given	S,S 81.7(1,1) P,P 100.6(1,2.2) S,P 88.9(1,4.7) 170.1(1,5.1)	[31]
				$Cd^{II}N_2S_2Cl$	η^2N 2.374(6,0) μ_3S 2.626(2,1) Cl 2.468(2)		N,N 68.5(2)^c S,S 72.05(5) N,Cl 99.6(1,4.7) S,Cl 115.6(1,6.3)	
				$Pt^{II}S_2P_2$	μ_3S 2.360(2,13) Ph_3P 2.283(2,12) 2.301(2,4)	Cd 3.270(1,4) S not given Pt 3.257(3)3 S not given	S,S 82.0(1,4) P,P 99.9(1,5) S,P 89.0(1,3.7) 170.6(1,3.7)	
				$Cd^{II}N_2S_2Cl$	η^3N 2.366(6,24) μ_3S 2.621(2,35 Cl 2.444(2)		N,N 69.6(2)^c S,S 72.40(5) N,Cl 99.3(1,4.7) S,Cl 119.7(1,3.7)	
$[\{(NH_3)_2Pt(\mu\text{-}\eta^2\text{-}NHCO\text{-}$ $Bu^t)_2\}_2Mn](ClO_4)_2\cdot$ $4H_2O$ (pale yellow)	m $P2_1/n$ 6	11.4228(17) 34.480(5) 16.128(3)	 91.48(1)	$Pt^{II}N_4Mn$	H_3N 2.048(13,23) $\mu\eta^2N$ 2.013(11,6)	Mn 2.6644(5,0)	N,N 90.0(5,2.8)	[32]
				$Mn^{II}O_4Pt_2$	$\mu\eta^2O$ 2.092(10,18)		O,O 90.0(5,1.0) Pt,Pt 180	
				$Pt^{II}N_4Mn$	H_3N 2.031(16,25) $\mu\eta^2N$ 1.993(12,4) 2.031(12)	Mn 2.8807(18) 2.9995(18)	N,N 90.0(6,5.0)	
				$Mn^{II}O_4Pt_2$	$\mu\eta^2O$ 2.044(8)		O,O 99.6(4,10.0) 145.4(4) Pt,Pt 114.12(6)	

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Table 3. Continued.

Compound (color)	Cryst.cl. Space gr. z	a[Å] b[Å] c[Å]	α[°] β[°] γ[°]	Chromo-phore	M–L [Å]	M – M [Å] M–L–M [°]	L–M–L [°]	Ref.
$(NBu_4)[\{(C_6F_5)_3Pt(\mu\text{-tht})\}_2Ag]$ (white) (at 293(1) K)	tr $P\bar{1}$ 2	13.486(3) 14.697(4) 17.333(4)	106.01(2) 90.50(2) 98.03(3)	$Pt^{II}C_3SAg$	C 2.022(6) 2.076(9,4) μS 2.326(2)	Ag 2.783(1,0) S 65.4(1)	C,C 88.7(3,2) 174.6(3) C,S 91.4(2,3.7) 175.3(2)	[33]
				$Ag^{I}S_2Pt_2$	μS 2.778(2,0)		S,Ag 65.2(1) S,Pt 49.4(1) Pt,Pt 180	
				$Pt^{II}C_3SAg$	C 2.025(1,0) 2.075(8,4) μS 2.294(2)	Ag 2.862(1,0) S 72.3(1)	C,C 89.0(3,9) 174.9(3) C,S 91.4(2,3) 170.3(2)	
				$Ag^{I}S_2Pt_2$	μS 2.548(2,0)		S,Ag 58.0(1) S,Pt 49.8(1) Pt,Pt 180	
$[\{(NH_3)_2Pt(\mu\text{-}\eta^2\text{-meu})_2\}_2\text{-}Pd](ClO_4)_2 \cdot 2.25H_2O$ (golden tan)	tr $P\bar{1}$ 2	12.064(2) 12.524(1) 13.730(1)	80.05(1) 106.72(1) 108.62(1)	$Pt^{II}N_4Pd$	H_3N 2.059(10,1) $\mu\eta^2N$ 2.033(8,1)	Pd 2.837(1,0)	N,N 90.0(3,1.1) 178.9(3,3)	[34]
				$Pd^{II}O_4Pt_2$	$\mu\eta^2O$ 2.015(8,2)		O,O 90.0(3,1.0) Pt,Pt 180	
				$Pt^{II}N_4Pd$	H_3N 2.064(10,4) $\mu\eta^2N$ 2.038(10,3)	Pd 2.839(1,0)	N,N 90.0(4,3.0) 178.0(3,4)	
				$Pd^{II}O_4Pt_2$	$\mu\eta^2O$ 2.033(9,13)		O,O 90.0(3,1.4) Pt,Pt 180	
$[(\eta^2\text{-dcpe})Pt\{Ga(cp^*)\}_2]$ (yellow) (at 193 K)	m $P2_1/c$ 8	12.260(3) 18.970(5) 40.507(11)	93.81(1)	$Pt^{0}P_2Ga_2$	η^2P 2.253(5,3)	Ga 2.355(2) 2.367(2)	P,P 90.7(2)^{d} Ga,Ga 97.07(7)	[35]
				$Ga^{0}C_5Pt$	η^5cp^* C 2.36(2,8)	Ga 3.538	not given	
				$Pt^{0}P_2Ga_2$	η^2P 2.265(5,1)	Ga 2.371(2) 2.382(2)	P,P 92.3(2)^{d} Ga,Ga 96.21(7)	
				$Ga^{0}C_5Pt$	η^5cp^*C 2.39(2,3)	Ga 3.510	not given	
$(CO)\ PtCo_2(\mu\text{-}\eta^2\text{-dppe})\text{-}(\mu\text{-}CO)(CO)_4$ (red brown)	tr $P\bar{1}$ 4	10.9719(2) 13.9234(2) 21.804(2)	87.249(1) 83.265(1) 74.873(1)	$Pt^{0}CPCo_2$	OC 1.85(2) $\mu\eta^2P$ 2.259(3)	Co 2.507(2) 2.531(2)	C,P 101.6(4) C,Co 105.5(4) 165.7(4)	[36]

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							P,Co 92.68(7)	
							Co,Co 62.30(3)	
				Co^0C_3PPtCo	OC 1.78(2,2)	Co 2.531(2)	100.4(1)	
						C 81.6(5)	69.0(4)	
							P,Pt 94.8(1)	
							Pt,Co 60.30(6)	
				Co^0C_4PtCo	OC 1.78(2,3)		47.7(4)	
					μOC 1.98(1)		Pt,Co 59.40(5)	
$(Ph_3P)_2Pt(\mu\text{-}S)_2Ru_2$	tr	22.471(4)	93.77(1)	$Pt^{II}S_2P_2$	μS 2.324(7,12)	Ru 4.15(-,2)	not given	[37]
$(\mu\text{-}SPr^i)_2(cp^*)_2$ (dark red)	$P\bar{1}$	24.353(5)	97.48(1)		Ph_3P not given	S not given		
	4	11.890(1)	70.88(1)					
				$Ru^{III}C_5S_3Ru$	η^5cp^*C not given	Ru 2.767(2)	not given	
						S not given		
				$Pt^{II}S_2P_2$	μS 2.332(7,8)	Ru 4.15(−2)	not given	
				$Ru^{III}C_5S_3Ru$	μS 2.318(7,27)	Ru 2.779(3)	not given	
$(Et_3P)_2Pt_2\{\mu\text{-}PHPh)$	m	20.027(9)		Pt^IP_4	Et_3P 2.340(6,0)	Mo 4.504(5)	P,P 89.5)2,2.2)	[38]
Mo- $(CO)_5\}_2$ (yellow)	$P2_1/a$	10.465(4)	103.00(3)		μP 2.407(5,10)	P 126.1(2)		
	4	20.774(9)						
				Mo_0C_5P	OC 1.981(23)		not given	
					2.052(24,25)			
					μP 2.644(5)			
				Pt^IP_4	Et_3P 2.333(6,0)	Mo 4.573(2)	P,P 90.0(2,2.6)	
					μP 2.397(4,0)	P 130.0(2)		
				Mo_0C_5P	OC 1.968(20)		not given	
					2.067(25,27)			
					μP 2.648(5)			
$[(Et_3P)_2Pt\{\mu\text{-}\eta^2\text{-}C{\equiv}CC{\equiv}\ C)$	m	17.925(2)		$Pt^{II}C_2P_2$	$\mu\eta^2C$ 2.00(1,1)		C,C 86.4(4)	[39]
$W(CO)_3(cp)\}_2]CHCl_3$	$P2_1/c$	21.652(3)	101.663(2)		Et_3P 2.309(3,6)		P,P 100.3(1)	
	8	22.686(3)					C,P 86.8(3,4.3)	
				WC_9	not given		not given	

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Table 3. Continued.

Compound (color)	Cryst.cl. Space gr. z	a[Å] b[Å] c[Å]	α[°] β[°] γ[°]	Chromo-phore	M–L [Å]	M – M [Å] M–L–M [°]	L–M–L [°]	Ref.
[(dmso)Pt(μ-η^1:η^5-C≡C-C_5H_4)(μ-η^2 : η^5-dmat)-{Fe(cp)}$_2$] (orange red)	m $C2/c$ 8	29.924(10) 10.132(3) 19.366(6)	112.810(7)	Pt^{II}C$_2$NS	$\mu\eta^2$N 2.141(4) μC 2.023(5) $\mu\eta^1$C 2.059(6) dmsoS 2.191(1)		C,C 172.4(2) 82.7(18)^c C,N 90.03(19) C,S 90.47(6) S 96.68(14) N,S 177.3(1)	[40]
				FeC$_{10}$	η^5C not given		not given	
[(η^2-dppe)Pt(μ-η^2 : η^{10}-docp){Fe(cp)}$_2$ (orange) (at 173 K)	tr $P\bar{1}$ 2	11.0890(7) 12.7052(9) 15.1559(10)	? ? ?	Pt^{II}O$_2$P$_2$	$\mu\eta^2$O 2.038(3,0) η^2P 2.2332(10)		O,O 83.9(10 P,P 86.14(4)^c	[41]
				FeC$_{10}$	η^5C not given		not given	
[Cl$_2$Pt{(μ-η^1 : η^5-dppcp)-Fe(η^5-C$_5$H$_4$CO$_2$)}$_2$] (orange)	tr $P\bar{1}$ 3	11.041(2) 17.126(3) 18.961(3)	101.40(1) 105.64(1) 103.11(1)	Pt^{II}Cl$_2$P$_2$	Cl 2.299(1) $\mu\eta^1$P 2.328(1)		Cl,P 90.0(1,3.7)	[42]
				FeC$_{10}$	η^5C not given		not given	
				Pt^{II}Cl$_2$P$_2$	Cl 2.282(1,13) $\mu\eta^1$P 2.323(1,4)		Cl,P 90.0(1,3.7)	
[(η^1-bdphmo)(CO)Pt(μ_3-C≡CHPh)Fe(CO)$_3$Mn(CO)$_2$(cp)] · 0.5C$_5$H$_{12}$ (dark green)	tr $P\bar{1}$ 4	13.646(9) 18.496(8) 19.099(9)	76.55(3) 70.96(3) 73.33(3)	Pt^{II}C$_3$PFe	OC not given μ_3C 2.24(1) 2.24(1)	Fe 2.617(3) Mn 3.512(3)	not given	[43]
				FeC$_4$PtMn	OC not given μ_3C 1.88(1)	Mn 2.676(3) C 88.5(5)	Pt,Mn 83.14(9)	
				MnC$_8$Fe	OC not given η^5cpC not given μ_3C 1.95(1)		not given	
				Pt^{II}C$_3$PFe	C 2.18(1)	Fe 2.632(2)	not given	

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				FeC_4PtMn	μ_3C 2.23(1) μ_2C 1.84(1)	Mn 3.718(3) Mn 2.692(3) C 90.2(5)	Pt,Mn 88.57(9)	
				MnC_8Fe	μ_3C 1.96(1)		not given	
$[(\eta^4\text{-pp3})PtHgMn(CO)_5]$- otf,$1.5CH_2Cl_2$ (yellow) (at 218(2) K)	m $P2_1/c$ 8	19.437(4) 32.201(6) 17.411(4)	94.44(2)	Pt^0P_4Hg	η^4P 2.271(7,23) 2.315(7,10)	Hg 2.590(2)	P,Hg 93.3(2,4.2) 175.1(2)	[44]
				Hg^0PtMn Mn^0C_5Hg	OC not given	Mn 2.618(4)	Pt,Mn 176.1(1) C,Hg 82.8(11,3.3) 178.2(1)	
				Pt^0P_4Hg	η^4P 2.276(7,40) 2.334(7,1)	Hg 2.605(2)	P,Hg 93.3(2,1.7) 177.7(2)	
				Hg^0PtMn Mn^0C_5Hg	OC not given	Mn 2.647(5)	Pt,Mn 178.9(1) C.Hg 84(2) 176.4(11)	
$[(dppf)Pt(Cl)(\mu\text{-}N)OsO_3]$ (red)	m $P2_1/c$ 8	20.058(2) 14.899(1) 23.949(2)	114.57(2)	$Pt^{II}P_2NCl$	η^1P 2.267(5,2) μN 2.05(1) Cl 2.317(5)	N 160.4(9)	P,P 99.6(2) P,N 91.9(4) 168.1(4) P,Cl 85.0(2) 175.4(2) N,Cl 83.5(4)	[45]
				FeC_{10} OsO_3N	η^5C not given O 1.72(2,5) μN 1.66(1)		not given O,O 110.7(9,2.0) O,N 108.0(9,1.6)	
				$Pt^{II}P_2NCl$	η^1P 2.268(5,19) μN 2.06(1) Cl 2.354(6)		P,P 97.7(2) P,N 90.4(5) 171.8(5) P,Cl 87.7(2) 174.6(2)	
				FeC_{10} OsO_3N	η^5C not given O 1.62(2,9) μN 1.65(2)		not given O,O 111(1,5) O,N 107(1,4)	

(*continued*)

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Table 3. Continued.

Compound (color)	Cryst.cl. Space gr. z	a[Å] b[Å] c[Å]	α[°] β[°] γ[°]	Chromo- phore	M–L [Å]	M – M [Å] M–L–M [°]	L–M–L [°]	Ref.
$(PPh_3)_2Pt(\mu_3\text{-}S)_2\cdot$	m	24.885(9)		$Pt^{II}S_2P_2$	μ_3S 2.317(10,3)	Fe 3.30	S,S 75.5(5)	[46]
$Fe_2(CO)_6$[e] (red)	$P2_1/c$	19.770(8)	90.55(1)		Ph_3P 2.288(9,14)	S 93.8(4,2.0)	P,P 92.5(3)	
	16	34.085(12)					S,P 93.5(3,2.2)	
							169.0(3.2.2)	
				$Fe^{I}C_3S_2Fe$	OC not given	Fe 2.484(7)	S,S 76.6(4,2)	
					μ_3S 2.29(1,1)	S 65.7(3,1)	S,Fe 57.1(3,4)	
				$Pt^{II}S_2P_2$	μ_3S 2.350(9,24)		S,S 76.7(3)	
					Ph_3P 2.266(9,16)	S 92.1(4,5.2)	P,P 97.1(4)	
							S,P 93.1(3,1.1)	
							169.7(4,1.1)	
				$Fe^{I}C_3S_2Fe$	μ_3S 2.30(1,3)	Fe 2.494(7)	S,S 78.8(4,3)	
						S 65.8(3,3)	S,Fe 57.1(3,6)	
				$Pt^{II}S_2P_2$	μ_3S 2.34(1,3)		S,S 75.5(3)	
					Ph_3P 2.315(9,8)	S 92.6(4,1.5)	P,P 98.6(3)	
							S,P 92.9(3,1.0)	
							168.4(3,1.1)	
				$Fe^{I}C_3S_2Fe$	μ_3S 2.27(1,3)	Fe 2.499(8)	S,S 78.3(4,5)	
						S 66.6(3,4)	S,Fe 56.7(3,9)	
				$Pt^{II}S_2P_2$	μ_3S 2.32(1,0)		S,S 75.1(3)	
					Ph_3P 2.29(1,3)	S 94.4(4,8)	P,P 99.3(4)	
							S,P 92.7(3,2.1)	
							167.4(4,1.6)	
				$Fe^{I}C_3S_2Fe$	μ_3S 2.29(1,3)	Fe 2.506(8)	S,S 75.9(4,3)	
						S 66.2(3,6)	S,Fe 56.9(3,7)	

[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] Five-membered metallocyclic ring.

[d] Six-membered metallocyclic ring.

[e] There are four crystallographically independent molecules.

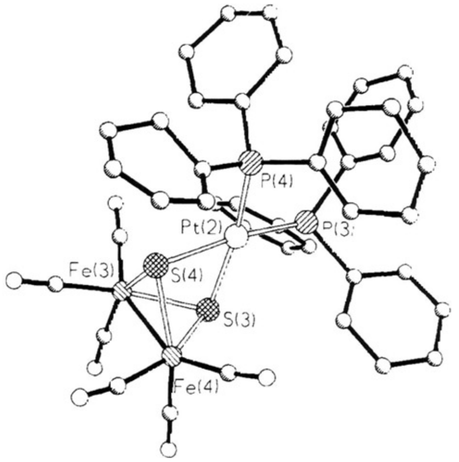

Figure 4. Structure of [$(PPh_3)_2Pt(\mu_3\text{-}S)_2Fe_2(CO)_6$] [46].

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and 2.376(2) Å (molecule 2) and Ga–Pt–Ga bond angles of 97.07 and 96.21(7)°, respectively.

In a red brown complex [36] $PtCo_2$ forms a triangle with mean Pt–Co and Co–Co bond distances of 2.520(2) and 2.531(2) Å. Unfortunately only for one molecule are data available.

Dark green {PtFeMn} [43] possesses a trimetallic chain core with Pt–Fe bond distances of 2.617(3) Å (molecule 1) and 2.632(21) Å (molecule 2). The Pt $\cdots$ Mn separations are 3.512(3) and 3.718(21) Å, respectively, and Fe–Mn bond distances of 2.676(3) and 2.692(3) Å are supported by μ_3-C=CHPh.

Yellow (PtHgMn) derivative [44] also contains a trimetallic chain with Pt–Hg and Hg–Mn bond distances of 2.590(2) and 2.618(4) Å (molecule 1) and 2.605(2) and 2.647(5) Å (molecule 2).

Red $(PPh_3)_2Pt(\mu_3\text{-}S)_2Fe_2(CO)_6$ [46] contains four crystallographically independent molecules; the structure of one is shown in figure 4. While Pt $\cdots$ Fe separations are over 3.3 Å and evidently nonbonding, the Fe–Fe bonds are 2.484(7), 2.494(7), 2.499(8) and 2.506(8) Å.

In the series of derivatives (table 3) the inner coordination spheres about Pt(0) are PtP_2Ga_2 [35], $PtCPCo_2$ [34] and PtP_4Hg [45]; the Pt(I) atoms: PtP_2XHg ($X=$ Cl [29], I[30] and PtP_4 [38]. The Pt(II) atoms with a square-planar environment have a vide variety of donor atoms.

2.2.3. Tetranuclear clusters.

There are seven tetranuclear clusters, Pt_3Sn [47], Pt_2Mo_2 [7, 48], $PtOs_3$ [49, 50] and $PtRu_3$ [51, 52], which contain two crystallographically independent molecules, and their crystallographic and structural data are given in table 4. Four have triclinic crystal class, two monoclinic and one orthorhombic.

The Pt_3Sn cluster [47] can be described as a $\{Pt_3(\mu\text{-}Cl)_3(C_6F_5)_4\}^{3-}$ unit with a six-membered, puckered Pt_3Cl_3 ring in which the Pt(II)'s are interconnected by chloride bridges and linked to the Sn(II) by Pt–Sn bonds. The mean Pt–Sn bond distances are 2.726 Å (molecule 1) and 2.723 Å (molecule 2). Each Pt(II) is square pyramidal with an apical Sn atom (PtC_2Cl_2Sn).

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Table 4. Crystallographic and structural data for heterotetranuclear platinum clusters – crystallographically independent molecules.[a]

Compound (color)	Cryst.cl. Space gr. z	a[Å] b[Å] c[Å]	α[°] β[°] γ[°]	Chromo-phore	M–L [Å]	M – M [Å] M–L–M [°]	L–M–L [°]	Ref.
$(NBu_4)[(\eta^1\text{-}C_6F_5)_2$ $(\mu\text{-Cl})Pt\}_3Sn\}$ (pale yellow)	m Cc 8	19.3965(12) 15.882(9) 41.4803(25)	 93.799(5) 	$Pt^{II}C_2Cl_2Sn$	η^1C^b 1.964(24,21) 2.042(24,26) μCl 2.372(7,1)	Sn 2.704(2) 2.737(2,5)	C,C^b not given	[47]
				$Sn^{II}Pt_3$			Pt,Pt 87.7(3)	
				$Pt^{II}C_2Cl_2Sn$	η^1C 1.967(25,22) 2.027(23,21) νCl 2.391(7,6) 2.420(7,19)	Sn 2.703(2) 2.733(2,1)	not given	
				$Sn^{II}Pt_3$			Pt,Pt 88.1(9)	
$[(PEt_3)_2Pt_2(\mu_3\text{-}CO)\text{-}Mo_2$ $(CO)_3(cp)_2]$ (violet)	tr $P\bar{1}$ 2	10.026(2) 11.155(4) 15.126(4)	85.17(2) 75.44(2) 84.33(2)	$Pt^0C_2PMo_2Pt$	νOC 2.29(2,10) η^3OC 2.56(3,18) Et_3P 2.284(5)	Mo 2.806(2,29) C 83.1(7,2.6) μ_3C 74.1(8,3.1) Pt 2.677(1) μ_3C 72.6(6)	Pt,Pt 173.3(1) Mo,Mo 123.01(4) Mo,Pt 61.50(4,4.1)	[7]
				$Mo_0C_{10}Pt_2$	OC not given μOC 1.97(2,0) $\mu\eta^3$OC 2.04(2) η^5cpC 2.34		Pt,Pt 56.99(4)	
				$Pt^0C_2PMo_2Pt$	μOC 2.40(2,12) μ^3OC 2.45(2,20) Et_3P 2.289(5)	Mo 2.819(1,27) C 80.7(7,2.4) μ_3C 74.1(8,3.1) Pt 2.646(1) μ_3C 64.6(5)	Pt,Pt 169.7(1) Mo,Mo 124.05(3) Mo,Pt 62.02(4,1.0)	
				$Mo^0C_{10}Pt_2$	μOC 1.98(2,0) μ_3OC 2.10(2) η^5cpC 2.33		Pt,Pt 55.95(4)	
$[\{(cp)(CO)_2Mo$ $(\mu\text{-}PPh_2)Pt(H)\}_2]$ (red)	m $P2_1/n$ 4	25.434(2) 13.209(5) 17.027(7)	 93.34(4) 	$Pt^{II}P_3HMo$	μP 2.254(4) 2.30194,8) μH not given	Mo 2.957(3) P 78.2(1) Pt 3.597(4)	P,P 77.1(2) 107.0(2) P,Mo 53.5(1) 122.4(1)	[48]
				MoC_7PPt	OC 1.962(15,18) η^5cpC not given μP 2.429(4)		P,Pt 48.2(1)	
				$Pt^{II}P_3HMo$	μP 2.247(4) 2.304(4,6)	Mo 2.974(3) P 78.5(1) Pt 3.580(4)	P,P 78.0(2) 105.0(2) P,Mo 53.1(1) 123.8(1)	
				MoC_7PPt	OC 1.962(16,18) μP 2.424(8)		P,Pt 47.9(1)	

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$[(Pcy_3)(CO)Pt(\mu\text{-}H)_2Os_3$	or	20.848(1)		$Pt^{II}H_2CPOs_3$	μH not given	Os 2.723(4)	H,H 107.0(1)	[10, 49]
$(\mu\text{-}H)_2(CO)_9]$	Pccn	36.254(26)			OC 1.788(46)	2.930(4)	Os,Os 57.7(1)	
(yellow) (at 210 K)	16	18.350(9)			cy_3P 2.386(1)	3.015(4)		
						H 109.3(−2)		
				$OsP_3H_2PtOs_2$	OC 1.87(4,2)	Os 2.871(3)	H,H 102.0(-,5.7)	
					1.93(4,3)	2.988(4,15)	Pt,Os 59.3(1,4.4)	
					μH not given	H 111.6(-,2)	Os,Os 60.0(1,2.6)	
				$Pt^{II}H_2CPOs_3$	μH not given	Os 2.710(4)	H,H 105.4	
					OC 1.802(43)	2.939(4)	Os,Os 57.6(1)	
					cy_3P 2.360(10)	3.003(4)	63.2(1,3)	
						H 113.4(−4)		
				$OsP_3H_2PtOs_2$	OC 1.88(4,3)	Os 2.862(3)	H,H 101.3(-,10.3)	
					1.94(4,2)	2.959(4,22)	Pt,Os 59.3(1,4.8)	
							Os,Os 60.1(1,2.8)	
$(PMe_2Ph)\ _2Pt(\mu_3\text{-}S)\cdot$	tr	10.404(4)	85.23(5)	$Pt^{II}P_2SOs_2$	P 2.264(5,15)	Os 2.782(1)	P,S 97.7(1)	[50]
$Os_3(CO)_9(PMe_2Ph)$ (red)	$P\bar{1}$	13.746(7)	88.43(4)		μ_3S 2.354(4)	2.807(1)	161.33(17)	
	4	29.332(16)	74.25(4)			S 72.0(1,2)	S,Os 54.7(1)	
							P,Os 110.2(1,6)	
							134.4(1,2.5)	
							Os,Os 62.73(2)	
				OsC_3SPtOs_2	OC 1.85(2,6)	Os 2.877(1,7)	Pt,Os 58.6(1,4)	
				(×2)	μ_3S 2.397(5,6)	2.907(1)	118.2(1,6)	
						S 74.6(1)	Os,Os 59.7(2,2)	
				OsC_3Pos_2	OC 1.83(2,2)		Os,Os 60.68(2)	
					P 2.335(5)			
				$Pt^{II}P_2SOs_2$	P 2.266(5,2)	Os 2.789(1)	P,S 99.1(1)	
					μ_3S 2.339(4)	2.835(1)	160.70(6)	
						S 72.7(1,7)	S,Os 54.9(1,5)	
							P,Os 109.5(1,1.7)	
							136.5(1,1)	
							Os,Os 60.49(1)	
				OsC_3SPtOs_2	OC 1.84(1,10)	Os 2.833(1)	Pt,Os 59.7(1,8)	
				(×2)	μ_3S 2.405(4,1)	2.889(1,2)	120.2(1,8)	
						S 72.15(12)	Os,Os 60.6(1,1)	
				OsC_3Pos_2	OC 1.88(1,1)		Os,Os 58.71(2)	
					P 2.332(4)			

(*continued*)

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Table 4. Continued.

Compound (color)	Cryst.cl. Space gr. z	a[Å] b[Å] c[Å]	α[°] β[°] γ[°]	Chromo-phore	M–L [Å]	M – M [Å] M–L–M [°]	L–M–L [°]	Ref.
$(Pcy_3)(CO)Pt(\mu\text{-}H)Ru_3\text{-}(\mu\text{-}CO)_2(\mu\text{-}\eta^2\text{-}C_8H_{13})(CO)_7$ (dark red)	tr $P\bar{1}$ 4	10.192(1) 12.121(7) 21.235(6)	118.83(3) 96.67(2) 95.56(2)	$PtHCPRu_3$	μH not given OC not given cy_3P 2.370(3)	Ru 2.798(1) 2.859(1,10)	not given	[51]
				RuC_5PtRu_3 (×2)	OC not given μH not given	Ru 2.683(1,22) 2.809(1)	not given	
				RuC_5HPtRu_2	μ_2C 2.226(13,11)		not given	
				$PtHCPtRu_3$	Cy_3P 2.374(3)	Ru 2.817(1) 2.862(1,16)	not given	
				RuC_5PtRu_3 (×2)		Ru 2.674(2,16) 2.868(2)	not given	
$[(CO)Pt(\mu\text{-}H)_2Re_2(\mu\text{-}H)(CO)_8\{Re(CO)_5\}]$ (yellow)	tr $P\bar{1}$ 4	11.764(1) 13.737(4) 15.787(3)	64.83(2) 83.86(1) 89.19(2)	PtH_2CRe_3	μH not given OC 1.83(2)	Re 2.769(1) 2.938(1) 3.050(1)	Re,Re 66.80(2) 120.39(2) 157.42(3)	[52]
				$ReC_4H_2PtRe_2$ (×2)	OC 1.97(2,8) μH not given	Re 3.145(1)	Pt,Re 58.8(2) 54.0(2)	
				ReC_5Pt	OC 2.01(2,4)			
				PtH_2CRe_3	μH not given OC 1.88(2)	Re 2.776(1) 2.934(1) 3.067(1)	Re,Re 69.94(2) 116.88(3) 158.01(3)	
				ReC_4H_2PtRe (×2)	OC 1.96(2,6)	Re 3.152(1)	Pt,Re 58.9(2) 54.4(2)	
				ReC_5Pt	OC 1.99(2,7)			

[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.

The violet Pt_2Mo_2 cluster [7] contains a planar, triangulated parallelogram of metal atoms. The center of symmetry of these molecules is at the Pt(I)–Pt(1)′ bond; Pt–Pt bond distances are 2.677(1) and 2.646(1) Å, respectively. The mean Pt–Mo bond distances are 2.806(2) and 2.819(2) Å, respectively.

In red $[\{(cp)(CO)_2Mo(\mu\text{-}PPh_2)Pt(H)\}_2(\mu\text{-}PPh_2)_2]$ [48] two centrosymmetric independent but practically identical heteronuclear clusters are present. In bent chain Mo–Pt–Pt–Mo, each Pt(II) is bonded to one Mo atom at 2.95(2) Å (molecule 1) and 2.974(3) Å (molecule 2), whereas the two Pt atoms are at non-bonding distances of 3.597(4) and 3.580(4) Å, respectively. The two Pt atoms are nearly symmetrically bridged by two PPh_2 ligands, and the Mo–Pt bonds asymmetrically bridged by a PPh_2 (table 4).

In yellow $PtOs_3$ [10, 49] the metal is closo, and hydrido-ligands bridge two Pt–Os and two Os–Os bonds. The Pt–Os and Os–Os distances range from 2.723(4)–3.015(4) Å (av. 2.889 Å) and 2.871(3) – 3.003(4) Å (av. 2.945 Å) (molecule 1) and 2.710(4)–3.003(4) Å (av. 2.884 Å) and 2.862(3)–2.993(4) Å (av. 2.945 Å) (molecule 2).

Structure of $(PMe_2Ph)_2Pt(\mu_3\text{-}S)Os_3(CO)_9(PMe_2Ph)$ [50] is an approximately planar cluster of $PtOs_3$. There are five metal-metal bonds and triply bridged sulfide on the $PtOs_2$ triangular face. The mean Pt–Os bond distances are 2.794(1) Å (molecule 1) and 2.812(1) Å (molecule 2), shorter than the mean values of three Os–Os bonds, 2.887(1) Å and 2.870(1) Å, respectively.

In the dark green $PtRu_3$ cluster [51] the metal atoms are tetrahedral with a cyclo –C_8H_{13} ligand bridging two Ru atoms in a three-electron donor μ-allyl mode, while the other two Ru–Ru edges are bridged by carbonyl ligands. The mean (three of each) Pt–Ru and Ru–Ru bond distances are 2.839(1) and 2.752(1) Å (molecule 1) and 2.847(1) and 2.742(1) Å (molecule 2).

The structure of yellow $[(CO)Pt(\mu\text{-}H)_2Re_2(\mu\text{-}H)(CO)_8\{Re(CO)_5\}]$ [52] consists of a $PtRe_2$ triangle plus a Re atom, which belongs to $HRe(CO)_5$, bound to the platinum. In the triangular moiety one hydride lies in a bridging position on the Re–Re edge, and a second bridges the longer Pt–Re bond. The mean Pt–Re and Re–Re distances are 2.926(1) and 3.152(1) Å (molecule 1) and 2.919(1) and 3.154(1) Å (molecule 2).

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2.2.4. Oligonuclear clusters. There are 21 clusters with 19 [53–63, 65–71] containing two crystallographic independent molecules, one [64] contains three such molecules and another one [72] four (table 5). Three are heteropentanuclear Pt_3Re_2 [53], Pt_2Os_3 [54] and Pt_3AgAu [55] clusters (table 5A). Deep red Pt_3Re_2 [53] has approximately a trigonal bipyramidal metal core. Each $PtPPh_3$ fragment is connected to the Re–Re bridge (which elongates upon successive edge-capping) by two Re-Re bonds bridged by two equatorial, formally, terminal CO ligands. The mean Pt–Re and Pt–Pt distances are 2.750(2) and 2.982(2) Å (molecule 1) and 2.742(2) and 3.017(2) Å (molecule 2). The Re–Re distances are longer, 3.237(2) and 3.258(2) Å, respectively.

Both molecules of emerald green $(CO)_2Pt_2Os_3(CO)_{12}$ [54] consist of a triangulated planar cluster of five metal atoms. The Pt–Pt and the mean Pt–Os bond distances are 2.670(3) and 2.691(3) Å (molecule 1) and 2.684(3) and 2.693(3) Å (molecule 2), respectively. The Os–Os distances are 2.891(3) and 2.895(3) Å, respectively.

Red Pt_3AgAu cluster [55] is constructed of well-separated $[Pt_3(\mu_3\text{-}S)(AuPPh_3)(\mu_3\text{-}AgCl)(\mu\text{-}\eta^2\text{-}dppm)_2]^+$ cations and PF_6^- anions. The structure of each cation is based on approximately isosceles triangle of platinum atoms. Only Pt(1) and Pt(2) are directly bonded to one another (2.615(3) Å, molecule 1 and 2.619(3) Å, molecule 2).

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Table 5. Crystallographic and structural data for heteropenta- and heterooligonuclear platinum clusters – crystallographically independent molecules.[a]

Compound (color)	Cryst.cl. Space gr. z	a[Å] b[Å] c[Å]	α[°] β[°] γ[°]	Chromo- phore	M–L [Å]	M – M [Å] M–L–M [°]	L–M–L [°]	Ref.
A: Pentanuclear								
$(PPh_3)_3Pt_3Re_2(\mu\text{-}CO)_6(CO)_4$ (deep red)	or $P2_1cn$ 8	19.714(3) 13.195(3) 46.486(7)		$Pt^0C_3PRe_2$	OC^b 1.853 μOc 2.03 Ph_3P not given	Re 2.750(2,31) Pt 2.982(2,27)	C,C^b not given	[53]
				$Ru^0C_5Pt_3$	OC 1.936 μOC 2.18	Re 3.237(2)	not given	
				$Pt^0C_3PRe_2$	not given	Re 2.742(2,12) Pt 3.017(2,56)	not given	
				$Ru^0C_5Pt_3$	not given	Re 3.258(2)	not given	
$(OC)_2Pt_2Os_3(CO)_{12}$ (emerald green)	m $P2_1/c$ 8	14.895(3) 12.060(2) 25.615(3)	 92.84(1)	Pt^0COs_3Pt	OC 1.78(4)	Os 2.710(3,10) Pt 2.670(3)	Os,Os 64.23(7) 118.14 177.52(8) 59.8(2,6.3) Os,Pt 123.91(8)	[54]
				Pt^0COs_2Pt	OC 1.81(6)	Os 2.626(3) 2.681(3)	Os,Os 122.5(1) Os,Pt 61.24(7,3)	
				$Os^0P_4Pt_2$	OC 1.90(5,3) 1.96(5,4)	Os 2.891(3)	Pt,Pt 59.7(1,3) Pt,Os 57.9(1,8) 117.36(8)	
				Pt^0COs_3Pt	OC 1.85(4)	Os 2.718(3,2) Pt 2.684(3)	Os,Os 64.34(6) 117.75 117.45(8) Os,Pt 58.8(1,7)	
				Pt^0COs_2Pt	OC 1.79(4)	Os 2.625(3) 2.685(3)	Os,Os 122.4(1) Os,Pt 61.2(1,3)	
				$Os^0P_4Pt_2$	OC 1.87(7,4)	Os 2.895(3)	Pt,Pt 59.8(1,2) Pt,Os 57.8(1,5) 117.29(8)	
$[(\mu\text{-}\eta^2\text{-dppm})_3(\mu_3\text{-}S)\text{-}Pt_3$ $(AgCl)(AuPPh_3)]PF_6$ (red)	tr $P\bar{1}$ 4	17.639(5) 18.651(5) 28.328(6)	94.83(2) 98.88(2) 90.33(3)	PtP_2SAgPt (×2)	η^2P 2.242(12,10) 2.284(10) μ_3S 2.267(11,11)	Ag 2.834(4,27) Pt 2.615(3) S 70.4(3)	P,P 110.2(4,1.2) P,S 100.0(4,5) 149.3(4,5) Ag,Pt 62.5(1,1.1)	[55]
				PtP_2SAgAu	η^2P 2.287(11,7) μ_3S 2.383(9)	Ag 2.780(4) Au 2.577(3) Pt 3.658(2,16) S 103.7(4,3)	P,P 160.0(4) P,S 97.9(4,1.0) Ag,Au 110.9(1)	
				$AgClPt_3$	Cl 2.413(1)	Au 4.414(3)	Pt,Pt 54.9(1)	

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							81.3(1,9)	
				AuPPt	Ph_3P 2.287(11)		P,Pt 174.4(3)	
				PtP_2SAgPt	η^2P 2.255(10,6)	Ag 2.837(4,6)	P,P 110.5(1,8)	
				(×2)	2.300(12,2)	Pt 2.619(3)	P,S 99.5(4,1)	
					μ_3S 2.276(9,2)	S 70.3(3)	119.8(4,8)	
							Ag,Pt 62.5(1,2)	
				PtP_2SAgAu	η^2P 2.263(12,4)	Ag 2.768(4)	P,P 159,1(4)	
					μ_3S 2.394(9)	Au 2 575(3)	P,S 97.5(4,1.8)	
						Pt 3.678(2,48)	Ag,Au 109.4(1)	
						S 103.9(4,1.9)		
				$AgClPt_3$	Cl 2.388(10)	Au 4.361(3)	Pt,Pt 55.0(1)	
							82.1(1,1.2)	
				AuPPt	Ph_3P 2.267(11)		P,Pt 174.1(3)	
B: Hexanuclear								
$Pt_3Ir_3(\mu\text{-}CO)_3(CO)_3$	m	41.811(34)		$Pt^0C_2Ir_2Pt_2$	μOc 1.89(6,17)	Ir 2.664(3,39)	Ir,Ir 170.1(1,5.7)	[56]
$(cp^*)_3$ (dark brawn)	$P2_1/n$	9.183(6)	90.99(6)			C 84.0(1,7.0)	Ir,Pt 59.3(1,1.1)	
	8	21.892(14)				Pt 2.707(3,7)	119.2(1,1.5)	
							Pt,Pt 60.0(1,2)	
				$Ir^0C_8Pt_2$	OC 1.77(4,1)		Pt,Pt 61.0(1,1)	
					μOC 2.06(4,2)			
					η^5cp^*C not given			
				$Pt^0C_2Ir_2Pt_2$	μOC 1.90(5,15)	Ir 2.670(3,31)	Ir,Ir 175.3(1,1.4)	
						C 77.0(1,9.0)	Ir,Pt 59.7(1,1.1)	
						Pt 2.700(3,9)	118.4(1,1.3)	
							Pt,Pt 60.0(1,3)	
				$Ir^0C_8Pt_2$	OC 1.79(4,1)		Pt,Pt 60.8(1,1)	
					μOC 2.07(4,6)			
$[Pt_2(\mu\text{-}C{\equiv}CBu^t)_8Ag_4]$	m	37.062(7)		$Pt^{II}C_4$	μC 1.970(25,8)	Ag 3.062(2,28)	Ag,Ag 62.0(1,1.1)	[57]
(yellow) (at 273 K)	C_2	13.022(1)	107.48		2.034(24,29)	3.149(2,25)	93.1(1,4)	
	6	20.459(3)				C 93.8(1,2.4)		
				Ag^IC_4	C 2.38(2,15)	Ag 3.199(2,30)	Pt,Pt 86.5(1,3)	
							Pt,Ag 59.0(1,1.8)	
							Ag,Ag 90.0(1,9)	
				$Pt^{II}C_4$	μC 1.958(21,8)	Ag 3.148(2,4)	Ag,Ag 60.5(1,4.0)	
					2.033(2,28)	C 91.4(1,6.5)	91.5(1,7.6)	
				Ag^IC_4	C 2.33(2,0)	Ag 3.273(4,40)	Pt,Pt 87.2(1)	
					μC 2.34(2,11)		Pt,Ag 58.5(1,2.0)	
							Ag,Ag 90.0(1,2.0)	

(continued)

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Table 5. Continued.

Compound (color)	Cryst.cl. Space gr. z	a[Å] b[Å] c[Å]	α[°] β[°] γ[°]	Chromo-phore	M–L [Å]	M – M [Å] M–L–M [°]	L–M–L [°]	Ref.
$[\{(MeNH_2)_2Pt(\mu\text{-}\eta^2\text{-}ampy)_2Pd_2(\eta^1\text{-}ONO_2)_2(H_2O)\}_2](NO_3)_2 \cdot 3.5H_2O$ (dark red)	m C2/c 4	21.722(2) 22.013(5) 23.909(4)	100.57	$Pt^{II}N_4$	N not given μN 2.00(2,2)	Pt 6.949(1) 6.990(1)	N,N 173.5(7,1.6)	[58]
				$Pd^{II}N_2O_2Pd$	2.05(1,3) O not given	Pd 2.877(2) 2.855(2) N 89.0(6,1)	N,N 76.4(5,1)	
$(CO)PtRu_5(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{14}$ (red)	m $P2_1/n$ 8	9.341(2) 14.957(3) 36.80(1)	90.38(2)	PtC_3Ru_4	OC 1.87(2) μOC 2.13(1) μ_6OC 2.04(1)	Ru 2.777(1)–3.045(2) C 90.6(5,5.8)	Ru,Ru 89.3(1,2.6)	[59]
				RuC_5PtRu_3 RuC_4PtRu_3 RuC_4PtRu_2 (x2) RuC_4Ru_4	OC 1.91(2,10) μOC 1.99(2,1) μ_6C 2.05(2,3)	Ru 2.826(2)–2.951(2)	Pt,Ru 89.7(1,1.2) Ru,Ru 89.8(1,4.3)	
				PtC_3Ru_4	OC 1.89(1) μOC 2.14(1) μ_6C 2.05(1)	Ru 2.779(1–3.046(1)	Ru,Ru 89.7(1,2.0)	
				RuC_5PtRu_3 RuC_4PtRu_3 RuC_4PtRu2 (x2) RuC_4Ru_4	OC 1.90(2,4) μOC 1.99(2,1) μ_6C 2.05(1,3)	Ru 2.824(2–2.865(2)	Pt,Ru 89.6(1,1.8) Ru,Ru 90.2(1,3.5)	
$(\eta^4\text{-}cod)PtRu_5(\mu_6\text{-}C)(\mu\text{-}CO)_4(CO)_{10}$ (red orange)	tg $P4_12_12$ 16	17.302(4) 38.128(5)		PtC_5Ru_4	η^4C 2.21(3,1) 2.27(3,3) μ_6C 2.04(2)	Ru 2.848(2,5) 2.962(2) 3.072(2)	Ru,Ru 59.2(1,3)	[60]
				RuC_xPtRu_3 RuC_xRu_4	OC not given μOC not given μ_6C 2.06(7)	Ru 2.826(3)–2.944(3)	not given	
				PtC_5Ru_4	η^4C 2.22(3,2) 2.28(3,0)	Ru 2.860(2,2) 2.954(2) 3.074(2)	Ru,Ru 59.1(1,8)	
				RuC_xPtRu_3 RuC_xRu_4	2.05(2)	Ru 2.822(3) 2.967(4)	not given	
$(PMe_2Ph)PtRu_5(\mu_6\text{-}C)$	or	44.897(5)		PtC_2Ru_4	P 2.26(4)	μOCnot given	not given	[61]

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(μ-CO)$(CO)_{14}$ (red)	*Pna*2_1	14.590(2)						
	?	10.208(2)		PtC_2PRu_4	P 2.27(1)	not given	not given	
$(PBu^t_3)PtRu_5(\mu_5\text{-}C)(\mu\text{-}CO)_2(CO)_{13}$ (red) (at 190 K)	m	12.4684(10)		PtC_2PRu_2	not given	Ru 2.7894(5)	not given	[62]
	P$2_1/n$	17.9669(15)	107.613(2)		P not given	2.8018(5)		
	4	17.3412(14)				3.3076(5)		
				RuC_xPtRu_3	not given	not given	not given	
				RuC_xRu_3				
				RuC_xRu_4				
				PtC_2PtRu_2	not given	Ru 2.8213(5)	not given	
						2.8282(5)		
						3.1603		
$(CO)PtRu_5$	m	19.586(5)		PtC_4Ru_3	OC not given	Ru 2.741(4)	not given	[63]
$(\mu_5\text{-}C)(\mu_3\text{-}PhC{\equiv}CPh)$	*P*$2_1/n$	12.073(2)	97.26(2)		μC 2.16(1,10)	2.900(1,30)		
$(\mu\text{-}PhC{\equiv}CPh)$ $(CO)_{12}$ (red)	8	36.467(6)						
				RuP_3PtRu_3	μC 2.16(1,8)	Ru 2.684(2)–3.023(2)	Ru,Ru 90.0(1,3.6)	
				RuC_2PtRu_3	μ_5C 2.01(1,11)		Pt,Ru 110.6(1,1.0)	
				$RuCRu_3$	2.09(1,3)		118.7(1,3)	
				PtC_4Ru_3	OC not given	Ru 2.745(1)	not given	
					μC 2.17(1,12)	2.908(1,53)		
				RuP_3PtRu_3	2.15(1,8)	Ru 2.673(2)–3.090(2)	Ru,Ru 90.0(1,4.1)	
				RuC_2PtRu_3	μ_5C 1.98(1)		Pt,Ru 111.5(1)	
				$RuCRu_3$	2.06(1,3)		119.5(1,2.1)	
$PtOs_5(\mu_3\text{-}S)(\mu\text{-}H)_6$	tr	19.541(6)	94.69(1)	$PtSOs_5$	μ_3S 2.38(1,11)	Os 2.667(2)–2.901(2)	Os,Os 64.5(1,4.2)	[64]
$(CO)_{15}{}^c$(red)	*P*$\bar{1}$	23.071(3)	100.81(2)			S 74.5(2,1.2	113.7(1,1.9)	
	6	9.771(2)	98.90(2)				131.6(1,1)	
							163.6(1.1)	
				OsC_3SPt	OC 1.95(4,16)	Os 2.890(2)–2.950(2)	Os,Os 60.0(5,5)	
				OsC_3Pt	μ_3S 2.413(7,22)	S 75.3(2,6)	Pt,Os 57.9(1,1.8)	
				$PtSOs_5$		Os 2.669(2)–2.905(2)		
				$PtSOs_5$		Os 2.673(2)–2.897(2)		
C: Oligonuclear								
$[(\eta^4\text{-}cod)_3Pt_3Os_4(CO)_{11}]\cdot$	m	12.198(4)		PtC_4Os_3	η^4C not given	Os 2.610-2.933(2)	Os,Os 61.4(1,2.3)	[65]
C_6H_6 (red)	*P*$2_1/c$	21.284(3)	107.18(2)	(x2)				
	8	24.802(7)						
				PtC_5Os_2	η^4C not given			

(*continued*)

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Table 5. Continued.

Compound (color)	Cryst.cl. Space gr. z	a[Å] b[Å] c[Å]	α[°] β[°] γ[°]	Chromo-phore	M–L [Å]	M – M [Å] M–L–M [°]	L–M–L [°]	Ref.
				$OsC_3Pt_2Os_3$	μ_3C 2.30(4) OC 1.90(4,9)	Os 2.775–2.886(2)	Pt,Pt 114.16(8) 124.63(6,7) Pt,Os 64.5(1,9.0) 109.8(1,8.0) Os,Os 60.0(1,4.0)	
				PtC_4Os_3(×2)		Os 2.639–2.910(2)	Os,Os 61.4(1,2.7)	
				PtC_5Os_2				
				$OsC_3Pt_2Os_3$		Os 2.701–2.868(1)	Pt,Pt 114.88(7) 126.8(1,1.8) Pt,Os 65.1(1,2.5) 109.3(1,6.4) Os,Os 60.0(1,3.5)	
$[(\mu\text{-}\eta^2\text{-dppm})_3(\mu\text{-CO})_6Pt_6(AuPPr^i_3)_2](PF_6)_2$ (dark red)	tr $P\bar{1}$ 2	15.505(4) 26.544(5) 30.690(6)	91.46(1) 96.21(1) 103.72(1)	PtC_2PAuPt_2	μOC not given P not given	Au 2.729–2.918(2) Pt 2.687–3.106(2)	not given	[66]
				$AuPPt_3$	P not given		not given	
				PtC_2PAuPt_2	μOC not given P not given	Au 2.786–2.944(3) Pt 2.670–3.059(2)	not given	
				$AuPPt_3$	P not given		not given	
$(\eta^4\text{-cod})_2Pt_2Ru_6(\mu_6\text{-C})(\mu\text{-CO})(CO)_{12}$ (red)	m $P2_1/c$ 8	12.983(5) 35.475(8) 18.366(7)	 92.63(4)	PtC_4Ru_2	η^4C 2.13(4,9) 2.37(4,15)	Ru 2.769–2.996(4)	Ru,Ru 64.4(1,1.4)	[60]
				RuC_4Pt_2 RuC_4Pt (×2) RuC_4 (×3)	not given	Ru 2.766–3.120(5)	not given	
				PtC_4Ru_2	η^4C 2.14(4,6) 2.31(4,11)	Ru 2.751–2.990(4)	Ru,Ru 64.5(1,7)	
				RuC_4Pt_2 RuC_4Pt (×2) RuC_4 (×3)	not given	Ru 2.761–3.114(5)	not given	
$Pt_3Ru_6(\mu_3\text{-H})_2(\mu\text{-CO})$	m	21.314(4)		$PtCRu_4Pt_2$	OC 1.87(3)	Ru 2.726–2.937(2)	Ru,Ru 109.0(1,5.0)	[67]

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$(CO)_{21}$ (brown red)	$P2_1/n$	16.544(4)	116.89(1)	$PtHCRu_4Pt_2$	μ_3H 2.0(2)		151.0(1,1.3)	
	8	22.318(4)					R,Pt 92.7(1,3.9)	
				$RuC_3H_2Pt_2Ru_2$	OC 1.91(3)	Ru 2.870–3.025(2)	Ru,Ru 87.2(1,2.4)	
				$RuC_3HPt_2Ru_2$	μ_3H 1.9(3,2)	Pt 2.645 – 2.714(1)		
				$RuC_4Pt_2Ru_2$				
$[Pt_2Ru_8(\mu_4\text{-}EtC_2Et)$	m	12.759(2)		PtC_2Ru_6	μOC 2.17(2,2)	Ru 2.684 – 2.800(2)	Ru,Ru 62.3(1,3.2)	[68]
$(\mu_3\text{-}Et\text{-}C_2Et)_2(CO)_{18}]\cdot$	$P2_1$	18.438(2)	91.99(1)		μC 2.07(2,2)	Pt 3.259(1)	83.6(1,3) 105.8(1,9)	
$0.5CH_2Cl_2$ (brown red)	4	20.197(3)					122.4(1,1.9)	
							174.9(1,1.3)	
				RuC_2PtRu_3	OC 1.87(2,1)	Ru 2.737 – 3.084(4)	Pt,Pt 73.3(1,1.8)	
				RuC_2PtRu_2	μ_3C 2.14(2,22)	C 75.1(7,6)	Pt,Ru 59.1(1,2.6)	
				$RuC_3Pt_2Ru_4$	μ_4 2.02(2,5)	127(1)	95.8(1,1.4)	
				$RuCPt_2Ru_4$			Ru,Ru 61.4(1,4.7)	
				$RuCPt_2Ru_2$			88.3(1,7.8)	
							117.8(1,2.3)	
				PtC_2Ru_6	μOC 2.18(2,2)	Ru 2.691 – 2.800(2)	Ru,Ru 62.2(1,5.4)	
					μC 2.06(2,2)	Pt 3.301(1)	82.7(1,1)	
							105.1(1,7)	
							122.0(1,2.3)	
							175.3(1,1)	
				RuC_2PtRu_3	OC not given	Ru 2.751 – 3.084(2)	Pt,Pt 74.0(1,1.6)	
				RuC_2PtRu_2	μ_3C 2.16(2,20)	C not given	Pt,Ru 59.5(1,2.7)	
				$RuC_3Pt_2Ru_4$	μ_4C 2.03(2,4)		95.6(1,1.3)	
				$RuCPt_2Ru_4$			Ru,Ru 61.2(1,5.0)	
				$RuCPt_2Ru_2$			87.7(1,9.8)	
							118.3(1,2.5)	
$[(H)Pt(AuPPh_3)_9](NO_3)_2$	tr	17.0451(1)	89.891(1)	$PtAu_9$		Au 2.660 – 2.726(1)	not given	[69]
(orange) (at 173(2) K)	$P\bar{1}$	17.4045(2)	85.287(1)					
	4	55.2353(1)	75.173(1)					
				$AuPPtAu_3$	P 2.308(6,29)	Au 2.883 – 3.766(1)	P,Pt 163.4(2,4.5)	
							174.6(2,4.3)	
				$PtAu_9$		Au 2.645 – 2.783(1)	not given	
				$AuPPtAu_3$	P 2.315(6,21)	Au 2.902 – 3.988(1)	163.2(2,6)	
							173.6(2,5.3)	

(*continued*)

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Table 5. Continued.

Compound (color)	Cryst.cl. Space gr. z	a[Å] b[Å] c[Å]	α[°] β[°] γ[°]	Chromo-phore	M–L [Å]	M – M [Å] M–L–M [°]	L–M–L [°]	Ref.
$[(CO)Pt(AuCl_3)_3\text{-}(AuPPh_3)_6]\cdot$ 1.5toluene (red) (at 223 K)	tr $P\bar{1}$ 4	21.393(4) 24.671(4) 25.619(1)	79.74(9) 80.06(6) 66.05(5)	$PtCAu_9$	OC 1.92(4)	Au 2.675 – 2.738(2)	not given	[70]
				$AuClPtAu_3$ $AuPPtAu_3$	Cl 2.342(9,5) P 2.261(9,14)	Au 2.796 – 3.004(2)	not given	
				$PtCAu_9$	OC 1.89(3)	Au 2.673 – 2.739(2)	not given	
				$AuClPtAu_3$ $AuPPtAu_3$	Cl 2.348(9,16) P 2.265(9,19)	Au 2.824 – 2.990(2)	not given	
$(AsPh_4)_2(NBu_4)_3[(H)Pt_6Ni_{38}$ $(\mu_3\text{-}CO)_{18}(\mu\text{-}CO)_{12}(CO)_{18}]$ (black)	m $P2_1/c$ 4	30.927(5) 31.881(7) 19.045(3)	91.9(2)	$PtNi_8Pt_2$		Ni 2.510 – 2.764 Pt 2.719(av)	not given	[71]
				$NiC_nPt_nNi_n$	not given	Ni 2.393 – 2.762	not given	
$\{Rb_{1.67}Pt(\mu\text{-}ox)_2\cdot 1.5H_2O\}_n{}^d$ (coper colored)	tr $P\bar{1}$ 6	12.690(10) 17.108(14) 11.367(3)	102.0(4) 115.17(3) 43.58(4)	PtO_4	oxO 2.01(2,4)	Pt 2.717(3) 2.830(3) 3.015(3)	O,O 83.7(8,2.9) Pt,Pt 176.1(1,1.8)	[72]
				RbO_7	oxO 3.09(5,20) H_2O 2.98(6,9)			
				RbO_8	oxO 3.03(5,24) H_2O 3.07(5,16)			

[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 three crystallographically independent molecules.

[d] There are four crystallographically independent molecules.

Each edge of the triangle is bridged by a μ-η^2-dppm ligand, and opposite faces capped by μ_3-bridging AgCl and S groups. The cluster is completed by a terminal $AuPPh_3$ (fragment attached to Pt(3)). The Pt–Au and mean of three Pt–Ag bond distances are 2.577(3) and 2.819(4) Å (molecule 1) and 2.575(3) and 2.814(4) Å (molecule 2).

There are eight heterohexanuclear Pt_3Ir_3 [56], Pt_2M_4 (M = Ag [57], Pd [58], PtM_5 (M = Ru [59–63] clusters which contain two crystallographically independent molecules and one example, $PtOs_5$ [64], contains three such molecules. The main feature of dark brown Pt_3Ir_3 [56] is a near-planar array of metals with a central triangle of platinums [Pt–Pt (mean) 2.704 Å (molecule 1) and 2.703 Å (molecule 2)], each edge-bridged by an iridium [Ir–Pt (mean) 2.675 and 2.655 Å)] (table 5B).

In yellow $[Pt_2(\mu\text{-}C{\equiv}CBu^t)_8Ag_4]$ [57] the six metal atoms are arranged in a slightly irregular octahedron with the platinum(II)'s mutually *trans* and the silver(I)'s in the equatorial plane, with Pt–Ag and Ag–Ag distances longer than 3.0 Å. Each Pt(II) is in an almost square-planar environment formed by four $C{\equiv}CBut^t$ ligands (table 3B).

In dark red $[\{(MeNH_2)_2Pt(\mu_3\text{-}\eta^2\text{-ampy})_2Pd_2(ONO_2)_2(H_2O)\}_2](NO_3)_2 \cdot 3.5H_2O$ [58] the two complex cations have a crystallographic C_2 axis, which passes through the two Pt centers in molecule 1, and is perpendicular to the Pt–Pt vector in molecule 2. Each *trans*-$\{Pt(MeNH_2)_2\}$ unit carries two coplanar aminopyridinate rings that are bound to Pt(II) through the endocyclic ring N atoms, adopting a head-to-head orientation. The two Pd_2 units each bridge four deprotonated exocyclic amide nitrogens to give a μ_3-η^2-coordination pattern for the ampy ligands. The resulting Pd_2N_2 rings are folded along the N–N vectors leading to Pd–Pd bonds (2.8772(2) and 2.855(2) Å). The Pt···Pt separations are 6.949(1) Å (molecule 1) and 6.990(1) Å (molecule 2).

In $(CO)PtRu_5(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{14}$ [59] the six metal atoms are an octahedron with the carbide located in the center. The Pt(1)-Ru(3) bond distance 2.777(1) Å (molecule 1) and 2.779(1) Å (molecule 2) is the shortest and is bridged by a carbonyl. The remaining Pt–Ru distances range from 2.882(1)–3.095(2) Å (molecule 1) and 2.902(1)–3.046(1) Å (molecule 2). The mean values of eight Ru–Ru bond distances are 2.892 and 2.895 Å, respectively.

The structure of red orange $PtRu_5$ [60] is similar to red $PtRu_5$ [59] with Pt–Ru distances ranging from 2.844(2)–3.072(2) Å (molecule 1) and 2.858(2)–3.074(2) (molecule 2). The mean Ru–Ru distances are 2.884 and 2.883 Å, respectively. Another $PtRu_5$ cluster [61] has similar structure to those reported [57, 60].

Red $(PBu^t_3)PtRu_5(\mu_5\text{-}C)(\mu\text{-}CO)_2(CO)_{13}$ [62] consists of a square-pyramidal cluster of five rutheniums with one platinum atom spanning an edge of the square base. The platinum is primarily bonded to two rutheniums with mean Pt–Ru bond distances 2.795 Å (molecule 1) and 2.825 Å (molecule 2). A carbido ligand lies inside the base of the square pyramid.

The structure of one independent molecule of red $(CO)PtRu_5(\mu_5\text{-}C)(\mu_3\text{-}PhC{\equiv}CPh)(\mu\text{-}PhC{\equiv}CPh)(CO)_{12}$ [63] is shown in figure 5. The molecule consists of square pyramid of five ruthenium atoms with the Pt(CO) capping a triangular triruthenium, Ru(1)–Ru(2)–Ru(5). The carbide ligand occupies an interstitial position in the base of the square pyramid. A triply-bridging PhC_2Ph ligand occupies the Pt(1)–Ru(1)–Ru(2) triangle and an edge-bridging PhC_2Ph bridges the Pt(1)–Ru(5) bond between the platinum and the apex of the square pyramid. The latter has the commonly observed perpendicular bridging, while the former exhibits μ_3-II coordination. The mean Pt–Ru bond distances are equal in both molecules (2.847 Å), while Ru–Ru distances range from 2.684(2)–3.107(2) Å (molecule 1) and 2.637(2)–3.090(2) Å (molecule 2).

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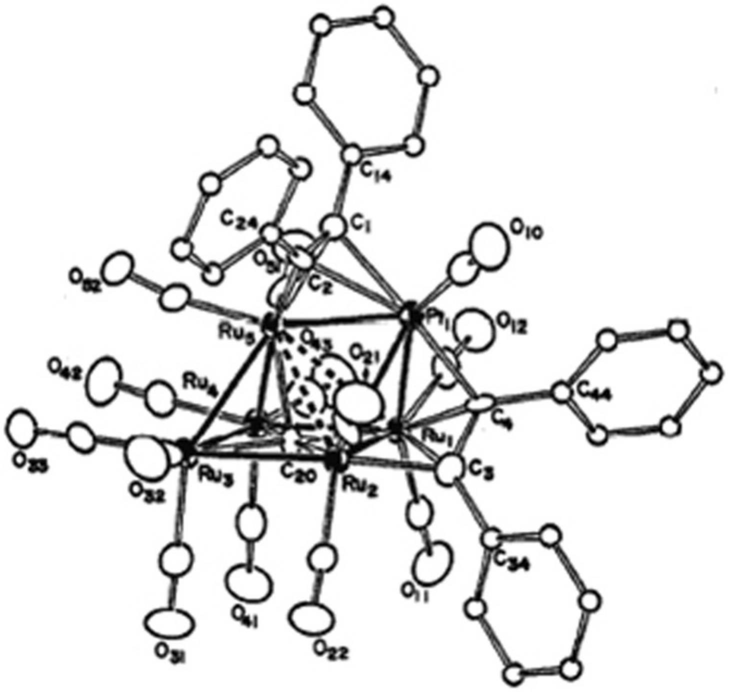

Figure 5. Structure of [(CO)PtRu$_5$(μ_5-C)(μ_3-PhC≡CPh)(μ-PhC≡CPh)(CO)$_{12}$] [63].

Red PtOs$_5$(μ_3-S)(μ-H)$_6$(CO)$_{15}$ [64] contains three crystallographically independent molecules. The cluster can be viewed as a combination of a tetrahedral PtOs$_3$ cluster joined to a triangular PtOs$_2$ cluster by a common platinum. A triply-bridging sulfido ligand bridges the PtOs$_2$ triangular group. The Pt–Os bond distances range from 2.667(2)–2.901(2) Å (av. 2.766 Å, molecule 1), 2.669(2)–2.905(2) Å (av. 2.770 Å, molecule 2) and 2.673(2)–2.897(2) Å, (av. 2.766 Å, molecule 3). The Os–Os bond distances range from 2.890(2)–2.950(2) Å (av. 2921 Å).

Red [(cod)$_3$Pt$_3$Os$_4$(CO)$_{11}$]C$_6$H$_6$ [65] is the only example of heteroheptanuclear cluster which contains two crystallographically independent molecules. Both molecules consist of Os$_4$ tetrahedra that are capped on three adjacent triangular faces by Pt(cod). The Pt–Os and Os–Os bond distances range from 2.610(2)–2.933(2) Å (av. 2.755 Å) and 2.775(2)–2.886(2) Å (av. 2.838 Å) (molecule 1) and 2.639(2)–2.910(2) Å (av. 2.755 Å) and 2.701(1)–2.868(1) Å (av. 2816 Å) (molecule 2) (table 5C).

There are two heterooctanuclear, Pt$_6$Au$_2$ [66] and Pt$_2$Ru$_6$ [60], clusters which contain two independent molecules (table 5C). Pt$_6$Au$_2$ [66] has approximately D$_{3h}$ symmetry with a distorted trigonal prismatic Pt$_6$ core in which a triply-bridging AuPPri$_3$ group caps each triangular face. The μ-CO ligands bridge each edge of the Pt$_3$ triangles and the μ-η^2-dppm ligands bridge between pairs of platinum atoms on adjacent Pt$_3$ triangles. The mean values of intratriangle Pt–Pt bond distances are 2.706 Å (molecule 1) and 2.705 Å (molecule 2). The mean values of intertriangle Pt–Pt distances are 3.071 and 3.037 Å, respectively. The mean Pt–Au bond distances are 2.819 and 2.822 Å, respectively.

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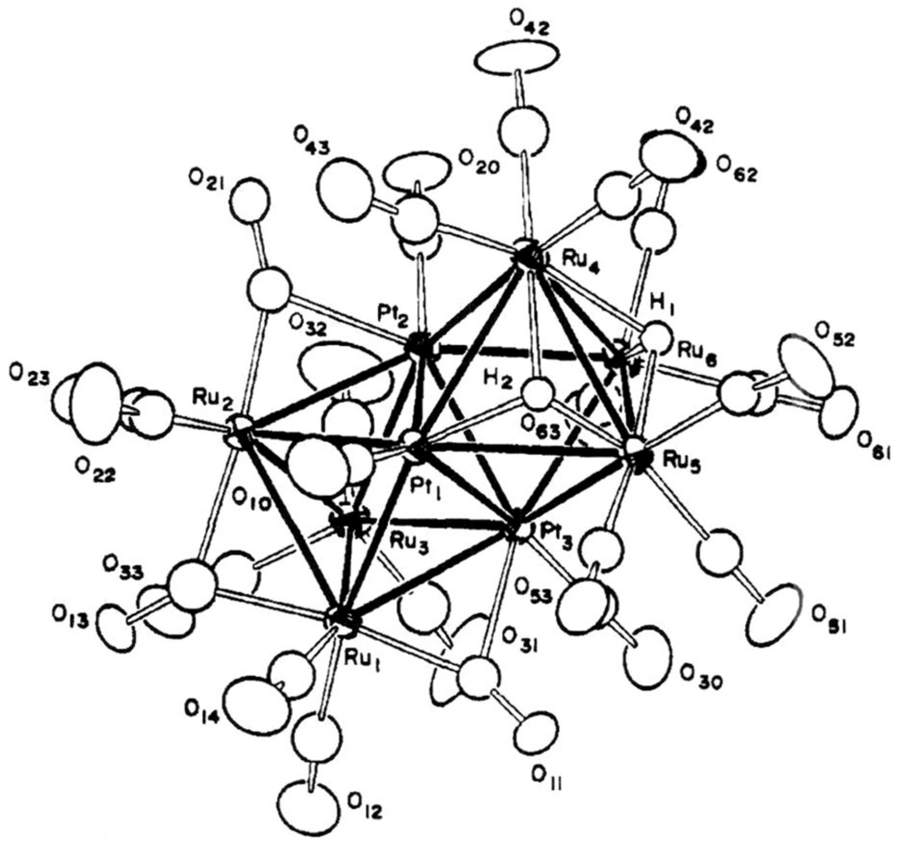

Figure 6. Structure of $[Pt_3Ru_6(\mu_3\text{-}H)_2(\mu\text{-}CO)(CO)_{21}]$ [67].

The structure of $Pt_3Ru_6(\mu_3\text{-}H)_2(\mu\text{-}CO)(CO)_{21}$ [67] is shown in figure 6. The molecule consists of two edge-fused bioctahedra sharing a Pt_3 face. There is a symmetrical bridging CO ligand across the Ru(1)–Ru(2) bond. Each molecule has two triply-bridging hydride ligands, H(1) across a Ru_3 triangle and H(2) bridging a $PtRu_2$ triangle. The M–M bonds associated with bridging hydride ligands are longer than the others, as expected. The mean Pt–Pt and Pt–Ru bond distances are 2.669(1) and 2.844(2) Å, respectively. Unfortunately, the data are only available for one molecule.

Brown red Pt_2Ru_8 [68] is shown in figure 7. Eight of the metal atoms (Pt_2Ru_6) are a dodecahedron. The two remaining ruthenium atoms, Ru(2) and Ru(3), cap adjacent triangular faces of this dodecahedron. All of the metal–metal distances lie in the range 2.684(2) to 3.084(2) Å. The longest ruthenium-ruthenium distance is between the atoms Ru(5) and Ru(7), 3.084(2) Å in molecule 1 and 3.078(1) Å in molecule 2. The Pt–Pt distance across the cluster is 3.269(1) Å in molecule 1 and 3.301(1) Å in molecule 2. The compound contains three EtC_2Et ligands. Two of these are triply-bridging ligands spanning the Pt(1)–Ru(1)–Ru(6) and Pt(2)–Ru(4)–Ru(6) triangular faces. The third is bonded to four ruthenium atoms Ru(2), Ru(3), Ru(5) and Ru(7).

The orange $PtAu_9$ cluster [69] contains well separated $[(H)Pt(AuPPh_3)_9]^{2+}$ cations and NO_3^- anions. The molecule is platinum-centered with the nine $AuPPh_3$ groups

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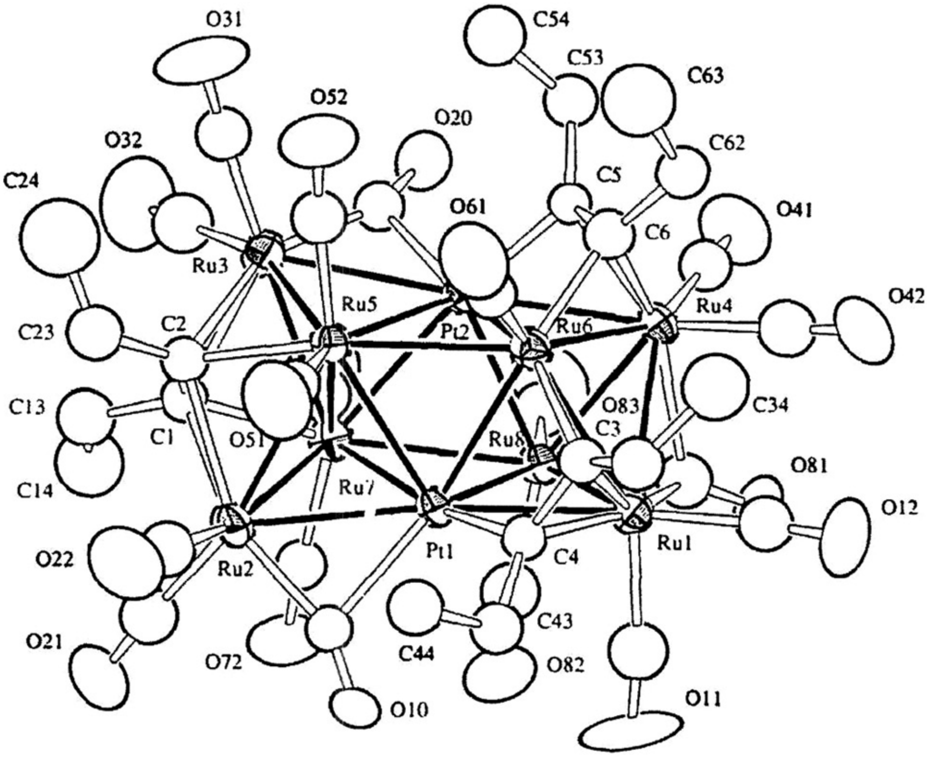

Figure 7. Structure of $[Pt_2Ru_8(\mu\text{-}EtC_2Et)(\mu_3\text{-}EtC_2Et)(CO)_{18}]$ [68].

positioned around Pt in a distorted icosahedral arrangement. The Pt–Au bond distances lie in the range 2.660(1) to 2.726(1) Å (av. 2.684 Å) in molecule 1 and from 2.654(1) to 2.738(1) Å (av. 2.687 Å) in molecule 2.

The red $PtAu_9$ cluster [70] is similar to the orange $PtAu_9$ [69]. The nine gold atoms form a fragment of an icosahedron with the platinum atom in its center. The mean Pt–Au bond distances of 2.703 Å (molecule 1) and 2.710 Å (molecule 2) are somewhat longer than those in [69].

Structure of black (mega)-cluster Pt_6Ni_{38} [71] consists of well separated $AsPh_4^+$, NBu_4^+ cations and $[(H)Pt_6Ni_{38}(\mu\text{-}CO)_{18}(\mu\text{-}CO)_{12(}(CO)_{18}]^{5-}$ anions. The Pt_6Ni_{38} framework in both molecules consists of an inner octahedron of six platinum atoms fully encapsulated in a ν_3 octahedron of 38 nickel atoms (figure 8). The twelve Pt–Pt bond distances have a mean value of 2.719 Å; the 48 Ni–Pt bonds connecting the inner Pt_6 to the outer Ni_{38} octahedron are between 2.510 and 2.764 Å (mean value 2.630 Å). The 108 surface Ni–Ni bonds also vary in length (2.393 – 2.762 Å, mean value of 2.580 Å). The metal framework of both molecules provides a molecular model of bimetallic "cherry" crystallites.

In both the independent molecules in the crystal, the O_h idealized symmetry of the metal framework is reduced to a D_{3d} idealized symmetry by the presence of 48 carbonyl ligands (18 terminal, 12 edge-bridging, and 18 face-bridging); as a result, the two opposite ν_3 triangular faces differ from the other six.

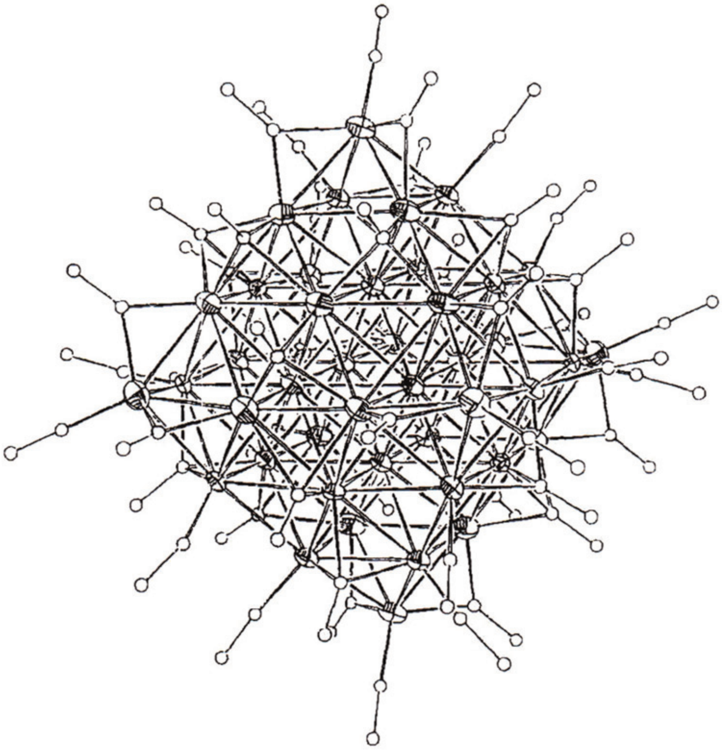

Figure 8. Structure of $[(H)Pt_6Ni_{38}(\mu\text{-}CO)_{18}(\mu\text{-}CO)_{12}(CO)_{18}]^{5-}$ [71].

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There is a polymeric $\{Rb_{1,67}Pt(ox)_2 \cdot 1.5H_2O\}$ [72] which contains four crystallographically independent molecules (table 5C).

3. *Cis-trans* isomerism

There is only one example, $[(NH_3)_2Pt(\mu\text{-}NHCOMe)_2Ag]NO_3 \cdot 4H_2O$ [73], which exists as *cis-* and *trans-*isomers (table 6). These two isomers differ by the crystal class, the *cis-*isomer belongs to tetragonal, the *trans-*isomer to triclinic.

The *cis-*cation is built up of infinite chains of alternating Pt and Ag atoms bridged by amidate ligands. The metal-metal distances in the chain are 2.879(1) (Pt–Ag) and 2.903(1) Å (Pt–Ag(a)). The angles Ag–Pt–Ag(a) and Pt–Ag–Pt(a) are 176.1(3) and 165.7(1)°. The acetamide is assumed to coordinate to Ag through the amide oxygen and to Pt through the deprotonated amide nitrogen. The mean planes through the ligands are nearly perpendicular to each other (84.9(2)°).

The *trans-*polymeric cations are built up by two crystallographically independent Pt atoms sitting on inversion centers (1/2, 0, 0 and 12, 0, 1/2) separated from Ag by 2.925(2) and 2.919(2) Å. The Pt–Ag–Pt unit is significantly bent [Pt(1)–Ag–Pt(2) 162.6(1)°] and torsion angle [Pt(1)–Ag–Pt(2)–Ag(a)] is 78.6°. The dihedral angle between the amidate planes is 13.6°. In both isomers, each Pt(II) has square-planar geometry (PtN_4) (table 6).

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Table 6. Crystallographic and structural data for *cis-trans* isomers.[a]

Compound (color)	Cryst.cl. Space gr. z	a[Å] b[Å] c[Å]	α[°] β[°] γ[°]	Chromo- phore	M–L [Å]	M – M [Å] M–L–M [°]	L–M–L [°]	Ref.
cis-[$(NH_3)_2$Pt(μ-η^2-NH-COMe)$_2$Ag]	tg	15.874(2)		PtN_4	H_3N^b 2.090(5,28)	Ag 2.897(1)	N,N[b] 90.0(2,3.6)	[73]
$NO_3 \cdot 4H_2O$ (colorless)	$I4_1/a$				μLN 2.000(4,20)	2.903(1)	177.8(2,1)	
	16	22.918(5)					N,Ag 90.1(1,8.1) Ag,Ag 176.1(3)	
				AgO_2	μLO 2.229(4,7)		O,O 172.5(2) Pt,Pt 165.7(1)	
trans-[$(NH_3)_2$Pt(μ-η^2-NH-COMe)$_2$Ag]	tr	7.143(3)	78.61(4)	PtN_4	H_3N 2.03(1,2)	Ag 2.919(1,2)	N,N 90.0(5,1.2)	[73]
$NO_3 \cdot 1.5H_2O$ (colorless)	$P\bar{1}$	8.416(5)	89.67(4)		μLN 2.02(1,1)	2.925(2)	N,Ag 84.8(4,3.8)	
	2	11.544(6)	83.79(4)					
				AgO_2	μLO 2.21(1,2)		O,O 161.9(4) Pt,Pt 162.0(1)	

[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.

4. Conclusions

An analysis of almost 1500 heterometallic platinum complexes (clusters) show that some 5% of them exist in isomeric forms [3]. Except one example [73], which exists as *cis*- and *trans*-isomers, all others are distortion isomers. While the *cis-trans* isomers are classical examples of Pt(II), the distortion isomers differ only by degree of distortion in M–L bond distances and L–M–L angles, and spread over a range of oxidation states of platinum (zero, +1, +2 (most common) and +4).

Seven derivatives exist in two separate distortion isomeric forms with homo- as well as hetero-crystal classes. In three derivatives both forms belong to the homo-monoclinic [6, 7] and orthorhombic [11, 12]. The remaining four examples [5, 8–10] differ from each other not only by degree of distortion but also by crystal class; one isomer is orthorhombic and the other triclinic [5], or one isomer is monoclinic and the other triclinic [8–10]. There are 60 examples [7, 13, 27, 29–45, 47–51, 53–63, 65–71] which contain two crystallographically independent distortion isomers within the same crystal. In one case there are three such isomers [64], in another two there are four such isomers [41, 72] and in one [28], eight such isomers are present.

It seems that distortion isomers prefer two crystal classes, monoclinic (×31) and triclinic (×27), with only five examples of orthorhombic and one of tetragonal.

"Soft" platinum is found in a wide variety of uni-, bi-, ter-, tetra-, hexa- and even heptadentate ligands forming two-, three-, and four-coordination about Pt(0) and Pt(I) atoms, a square-planar geometry about Pt(II) and octahedral geometry about Pt(IV), with varying degrees of distortion. Although platinum preferentially bonds to "soft" ligands such as C, PR_3 and S-donor groups, it can also be found bonded to "borderline" (e.g. bromide, RNH_2) and hard donor atoms (commonly N-donor ligands and chloride).

The mean Pt(0)–L bond distance elongated in the order: 1.815 Å (CO) < 2.24 Å (tetradentate CL) < 2.26 Å (bi-PL) < 2.285 Å (PEt_3) < 2.300 Å (tetra-PL). The mean Pt(1)–L bond distance elongated in the order: 1.96 Å (CN) < 2.305 Å (bi-PL) < 2.338 Å (Cl) < 2.345 Å (PEt_3) < 2.400 Å (μ-PPh_2) < 2.915 Å (μ-I).

The mean Pt(II)–C bond distance elongated in the order: 1.83 Å (CO) < 2.025 Å (η-C_6F_5) < 2.035 Å (η-Ph); Pt(II)–P: 2.265 Å (PMe_2Ph) < 2.270 Å (bi-PL) < 2.285 Å (PPh_3) < 2.310 Å (Pcy_3) < 2.332 Å (PEt_3); and Pt(II)–X: 2.285 Å ($X = \mathrm{Cl}$) < 2.520 Å (Br) < 2.650 Å (I). In the series of bridging ligands the mean Pt(II)–L bond distance elongated in the sequence: 2.055 Å (μ-N) < 2.2755 Å (μ-PPh_2) < 2.310 Å (μ-SL) < 2.328 Å (μ-S, *trans* to C) < 2.365 Å (μ-bi-SL, *trans* to P) < 2.383 Å (μ_3-S, *trans* to PR_3) < 2.400 Å (μ-Cl, *trans* to CO).

The *trans* effect of H on Pt(II)–P bond distance elongated the length: 2.285 Å (PPh_3, mutually *trans*) *versus* 2.375 Å (*trans* to H); 2.310 Å (Pcy_3, mutually *trans*) *versus* 2.365 Å (*trans* to H). The *trans* effect of PR_3 on Pt(II)–Cl bond distances also elongated: 2.285 Å (Cl, mutually *trans*) *versus* 2.342 Å (*trans* to PR_3).

The mean Pt(IV)–L bond distance elongated in the order: 2.06 Å (CL) < 2.13 Å (bidentate NL) < 2.920 Å (I).

There is a wide variety of homo- as well as heterodentate ligands. The homobidentate ligands include N, C, S and P donors; heterobidentate include O + N and N + S; tridentate are homo-C and hetero-2O + N; homotetradentate C and P; hexadentate homo-N, and hetero-5C + P and 4N + 2S; and heteroheptadentate with 5C + 2P donor sites.

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Noticeably, in the series of heterobidentate ligands, the platinum prefers to bond soft donors. Correspondingly, there is a wide variety of metallocyclic rings, and the effect of both steric and electronic factors can be seen from the values of the L–Pt–L bond angles. The five-membered metallocyclic rings are most common and open in the order: 75.8° ($-NC_2N^-$, unsaturated) < 82.3° ($-NC_2N^-$, saturated) < 82.7° ($-NC_2C^-$) < 85.5° ($-NC_2S^-$) < 87.6° ($-PC_2P^-$) < 90.5° ($-SC_2S^-$) < 94.3° ($-PCNTl^-$). The six-membered chelate ring is 92.3° ($-PC_3P^-$).

The data presented here illustrated the heterometallic isomeric derivatives with two to 44 metal atoms per unit, which exist in a variety of heterobi- to polymeric forms, with a range of ligand donor atoms. Metals include in the order of M: Rb, Ga, Ti, Mn, Rh, Ir, Re, Cu, Zn, Cd (a′×1) < Tl, Co, Pd (a′×4) < Au (×5) < Ag (×6) < Ru,Os (a′×8) < Fe (×11).

The mean values of Pt–Pt as well as Pt–M bond distances (values over 3.0 Å were excluded) elongated in the orders: 2.705 Å (Pt(0)–Pt(0)) < 2.720 Å Pt(1)–Pt(1)) < 2.773 Å (Pt(II)–Pt(II)); Pt(0)–M: 2.374 Å (M = Ga) < 2.520 Å (Co) < 2.597 Å (Hg) < 2.630 Å (Ni) < 2.667 Å (Ir) < 2.744 Å (Re) < 2.750 Å (Os); Pt(I)–M: 2.697 Å (M=Au) < 2.713 Å (Hg) < 2.815 Å (Ag); Pt(II)–M: 2.625 Å (M=Fe) < 2.638 Å (Pd) < 2.723 Å (Sn) < 2.797 Å (Mn) < 2.843 Å (Ru) < 2.854 Å (Re) < 2.862 Å (Os) < 2.869 Å (Ag) < 2.934 Å (Tl) < 2.964 Å (Mo); and Pt(IV)–Sn: 2.580 Å.

This overview, together with its precursors [1–3], has surveyed almost 400 stereoisomers of platinum chemistry. There are four types of stereoisomers: distortion (by far most common), *cis-trans*, mixed isomerism (*cis-trans* plus distortion) and ligand isomerism. In the series of distortion isomers oxidation states of platinum spread over a wide range (zero, +1, +2 (most common), +3, +4) than *cis-trans* isomers (+2 and +4), mixed-valence (+2 only) and ligand isomerism (+2 only).

It is hoped that this overview proved that even in platinum chemistry distortion isomerism is common. Such a dominance of this form of isomerism is also seen in the chemistry of copper [4]. It is also hoped that such an overview will help to focus attention on areas of platinum chemistry that could be enhanced by further study, and assist in allowing comparative behavior of the platinum.

Acknowledgements

The authors wish to thank those who gave permission for reproduction of original figures, the Ministry of Education of Slovak Republic, APVT-20-005504 and VEGA 1/2452/05 for financial support.

Abreviations

aet	2-aminoethanethiolate
ampy	2-aminopyridinate
bpy	2,2′-bipyridine
Bu	butyl

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Bu^t	t-butyl
Bu_2bpy	5,5′-dibutyl-2,2′-bipyridine
$C_5H_8PPh_2$	cyclopentane-1,2-diyl-*bis*(diphenylphosphane)
C_6F_5	pentafluorohexyl
C_8H_{13}	cyclo-2,4-octenyl
cod	cycloocta-1,5-diene
cp	cyclopentadienyl
cp*	pentamethylcyclopentadienyl
dbphmo	$Ph_2PCH_2P(=O)Ph_2$
depe	*bis*(cyclohexylphosphino)ethane
dmat	$Me_2NCH_2C_5H_4$
dmit	1,3-dithiole-2-thione-4,5-dithiolate
dmso	dimethylsulphoxide
dnppf	1,1′-*bis*(naphtylphenylphosphine)ferrocene
docp	$C_{12}H_8O_2$
dpep	2,2-5,15-*bis*(2-(nicotinoylamino)phenyl)-2,2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin
dppe	1,2-*bis*(diphenylphosphino)ethane
dppep	1,1′-*bis*(diphenylphosphino)cyclopentadienyl
dppf	1,1′-*bis*(diphenylphosphino)ferrocene
dppm	1,2-*bis*(diphenylphosphino)methane
dppo	5,15-diphenylphorphirinate(2-)
dpppe	2,4-*bis*(diphenylphosphino)pentane
Et_4en	N,N,N′N′-tetraethylethylenediamine
m	monoclinic
Me	methyl
3,5-Me_2pz	3,5-dimethylpyrazolate
meu	1-methyluracylate
NBu_4	tetrabutylammonium
norpe	norphtalocyanine-2,3-dithiolate
or	orthorhombic
otf	CF_3SO_3
ox	oxalate
P_2 crown	$(Ph_2PCH_2)_2$ diaza-18-crown-6
Pcy_3	tricyclohexylphosphine
PEt_3	triethylphosphine
Ph	phenyl
$PhC\equiv CPh$	1,2-diphenylacetylene
3,5-Ph_2pz	3,5-diphenylpyrazolate
PMe_2Ph	dimethylphenylphosphine
PPh_2	diphenylphosphide
PPh_3	triphenylphosphine
Pr^i	iso-propyl
tg	tetragonal
tht	tetrahydrothiophene
totpp	2,5,13,16-tetraoxa-8,8,10,10-tetraphenyl-8,10-diphosphacyclopentadienyl
tr	triclinic

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